

Long Term Monitoring of Atmospheric Aerosol Particles in the Antarctic Peninsula

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ABSTRACT

Atmospheric aerosols were sampled continuously from December 1985 to December 1993 at the Brazilian Antarctic Station "Comandante Ferraz" (62°05'S; 58°23.5'W). Stacked filter units fitted with 10 µm inlets were used to collect a total of 301 samples in the fine and coarse particle-size modes. The concentrations of 23 elements with atomic number greater than 10 were measured by Particle-Induced-X-ray Emission analysis. Average aerosol mass concentrations during summertime were 3.78 µg m⁻³ and 6.52 µg m⁻³, fine and coarse particle-size modes respectively, whereas during wintertime they were 2.92 µg m⁻³ and 5.04 µg m⁻³, fine and coarse particle-size modes. The non-sea-salt sulfur concentration in the fine particle-size mode showed clear seasonality. Non-sea-salt sulfate concentration averages on 440 ng m⁻³ during summer and 157 ng m⁻³ during wintertime. Principal factor analyses identified four different types of antarctic aerosols: sea-salt in the coarse and fine particle-size modes, soil dust and sulfates. The concentration of some trace elements like Ni, Pb and others appeared too high, indicating the existence of sources of regional or long-range transported pollution in the Antarctic Peninsula.

Key words: Antarctic, aerosol particles, atmospheric monitoring, global change.

INTRODUCTION

The importance of atmospheric aerosols concerning global climate changes, radiation budget and biogeochemical cycles have been recognized recently. They can exert direct effects on climate due to their properties on absorbing or scattering the sunlight radiation. The aerosol particles can also affect the atmospheric radiation balance acting as cloud condensation nuclei, modifying cloud radiative properties and cloud lifetimes (Charlson *et al.*, 1992).

The Antarctic continent is situated far from important sources of anthropogenic pollution and so it is an ideal site to assess the trends of the concentration of several trace elements, both regionally and globally, by the means of long term studies. There have been several previous works on atmospheric aerosol particles in Antarctic or sub-Antarctic regions (Artaxo *et al.*, 1990; Bodhaine *et al.*, 1986; Maenhaut *et al.*, 1979; Tuncel *et al.*, 1989; Wagenbach *et al.*, 1988; Zoller *et al.*, 1974). Several of these studies were carried out at the geographic South Pole. It is important to collect atmospheric aerosol data over sites at the edge of the Antarctic continent, as they are needed to sum up with previous results in order to improve the un-

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derstanding of the overall processes which take place in the Antarctic atmosphere. The Antarctic Peninsula is an adequate site to study the properties of marine aerosol particles, due to the surrounding ocean and to its very low soil dust load (Mészáros & Vissy, 1974; Fitzgerald, 1991).

There are several mechanisms responsible for the production of marine aerosols (Andreae *et al.*, 1986). Of special concern is the sulfur cycle (Toon *et al.*, 1987) and the significant excess sulfate observed over marine regions, due to optical properties which can influence the radiation budget and also to the possibility of these particles to act as cloud condensation nuclei (Schwartz, 1988; Savoie *et al.*, 1989). Sulfur-bearing particles consist in the vast majority of sulfates. They are produced by several mechanisms of heterogeneous sulfur conversion, including oxidation of DMS (dimethyl sulfide) produced by biogenic processes.

Part of the excess sulfur observed over remote ocean areas can also be explained by heterogeneous sulfur conversion in sea-salt particles and within cloud droplets (Sievering *et al.*, 1991), whereas in-cloud processes could be responsible for the production mechanisms of CaSO₄ particles (Andreae *et al.*, 1986).

Harvie *et al.* (1980) report on a hydrologic model about the expected sequence of mineral compounds to be formed on the evaporation of sea-water. This affords a pathway for mineral crystals to be released to the atmosphere during the evaporation of sea-water droplets formed from the bubble bursting process. In addition, many studies report the enrichment of heavy metals at the air-sea interface (Weisel *et al.*, 1984; Arimoto *et al.*, 1990; Zhou *et al.*, 1990). Besides to long-range transport of anthropogenic aerosols, biogenic agents may be responsible for part of these enrichments. Among the suggested processes are low-temperature volatilization processes such as biological methylation, emissions from plants (Cattell & Scott, 1978) and metabolization of heavy metals at the sea-air interface by bacteria, phytoplankton and zooplankton (Duce *et al.*, 1972).

This work reports on measurements made in the fine ($d_p < 2.0 \mu\text{m}$, where d_p is the aerodynamic

diameter of the particle) and coarse ($2.0 \mu\text{m} < d_p < 10 \mu\text{m}$) particle-size modes of atmospheric aerosol particles collected continuously from December 1985 to December 1993 at the Antarctic Peninsula. There were clear seasonal variabilities for several elements. The elemental concentrations were measured by Particle-Induced X-Ray Emission (PIXE) and the data sets obtained were examined by stepwise multiple regression, non-hierarchical cluster analysis and principal factor analysis (PFA).

EXPERIMENTAL PROCEDURE

SAMPLING SITE AND PROCEDURES

The sampling station is located at the Brazilian Antarctic Station "Comandante Ferraz" ($62^\circ 05'S$; $58^\circ 23.5'W$), in the King George Island, on the Admiral Bay, Antarctic Peninsula. The sampling site is upwind from local sources, at about 1 km from the main station, and it is located at about 300m from the sea coast. The station was operated continuously from December 1985 to December 1993, including during the winter season.

Aerosol particles were collected with stacked filter units (Parker *et al.*, 1977) making a total of 301 samples in the fine and coarse particle-size modes. Particles in the coarse particle-size mode ($2.0 \mu\text{m} < d_p < 10 \mu\text{m}$) were sampled on a 47-mm-diameter, 8 μm pore-size apiezon-coated filter, while a 0.4 μm pore-size filter collected the particles in the fine particle-size mode ($d_p < 2.0 \mu\text{m}$). The flow rate was 10 to 161 min^{-1} which resulted in 50% cut-off diameter between fine and coarse particle-size fractions of about 2.0 μm . The stacked filter units were fitted with a specially designed inlet which provided a 50% cut-off diameter of 10 μm . Air volumes were measured with calibrated gas meters with a precision of about 5%. The stacked filter units were loaded with the filters in our São Paulo clean room laboratory, transported in a sealed container, and hand-carried after the sampling. Blank filters received the same handling as exposed filters before and after sampling. The

collection time per stacked filter unit sample varied between 5 to 8 days.

GRAVIMETRIC ANALYSIS

The fine and coarse particle-size fractions of aerosol mass concentrations were obtained by gravimetric analysis of the filters, which were weighed before and after sampling in an electronic microbalance with 1 μg sensitivity. Before weighing, the filters were equilibrated for 24 hours at 50% relative humidity and 20°C. Electrostatic charges were controlled by means of ²¹⁰Po radioactive sources. The detection limit for the aerosol mass concentration is typically 0.3 $\mu\text{g m}^{-3}$ and the precision is estimated at about 15%. The coarse particle-size mode aerosol mass concentration is named CPM, whereas the fine particle-size mode aerosol mass concentration is named FPM.

ELEMENTAL CONCENTRATION MEASUREMENT

The elemental concentrations were measured by PIXE (Johansson & Campbell, 1988). The samples were irradiated by a 2.4 MeV proton beam, supplied by the isochronous cyclotron of the University of Gent (Maenhaut *et al.*, 1981, 1987; Maenhaut & Raemdonck, 1984). The following 23 elements were detected in the samples: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb. The detection limit was typically 5 ng m^{-3} for elements with $Z < 20$, and 0.1 ng m^{-3} for $21 < Z < 30$. The precision of the PIXE analysis was better than 3% for the major elements and about 10% for elements with concentrations near the detection limit.

STATISTICAL PROCEDURES

STEPWISE MULTIPLE REGRESSION

The data sets of the elemental concentrations measured by PIXE were validated by screening the data for outliers with the method of stepwise multiple regression. In this approach the variability of the dependent variable, which is the concentration of a given element in all the samples measured, is

regressed against the variability of all the other variables (*i.e.* the concentrations of the remaining elements in all samples measured). Only the independent variables which are statistically significant at a confidence level of 95% are considered for these regressions. If a specific sample shows differences greater than 3σ between the measured and predicted concentrations this sample will be double-checked for contamination or analytical problems.

After the check for outliers some variables had their missing values estimated. For these calculations variables with less than 8% of missing values were considered, but only one variable in this range presented more than 5% of missing values, out of a total of 21 variables. This variable was Sr in the fine particle-size mode, which presented near 8% of missing values.

PRINCIPAL FACTOR ANALYSIS (PFA)

The use of receptor models for the determination of the elemental composition of particulate matter sources is a technique widely employed (Gordon, 1988; Artaxo & Orsini, 1987). With the principal factor analysis procedure (Harman, 1976) it is possible to build a qualitative source profile using the measured elemental concentrations.

To avoid scalling effects the original concentration data are normalised so that each variable (element) presents a concentration mean value of 0 and a standard deviation of 1. A model of the variability of the trace element concentration is constructed so that the set of intercorrelated variables is transformed into a set of independent, uncorrelated variables. This is done by finding the eigenvalues and eigenvectors of the correlation matrix. The most prominent eigenvectors (factors) are retained and orthogonally rotated by a VARIMAX rotation. The resulting "factor-loading" matrix represents the correlations between the trace elements and each orthogonal factor. Also "factor scores" are calculated and they indicate the relative importance of each factor for the individual samples. The set of elements which better correlate with each factor in the rotated factor loading matrix help to identify the factors.

NON-HIERARCHICAL CLUSTER ANALYSIS

In non-hierarchical cluster analysis the samples are grouped on the basis of their similarities concerning the elemental concentrations (Hopke, 1991). The more they are likely to be composed of particles from the same source. This analysis provides an alternative way to assess qualitatively the sources of the aerosol. It is a procedure independent of the PFA, based entirely on geometrical considerations and in general the agreement between the two techniques on the identified aerosol sources is expected to be satisfactory.

Each sample in the database can be viewed as a point in the space spanned by the n variables whose concentrations are determined. Therefore two "near" points in that n -fold space correspond to two samples with similar concentrations of the measured elements. The two nearest points are grouped in one single cluster and the analysis is repeated again to the remaining $n-1$ objects. The distance is calculated as the quadratic Euclidean distance between the points and the Ward's error sum method is used for the calculation of the distances between newly formed groups and the remaining samples or clusters (Massart & Kaufman, 1983). Alternatively it is also possible to group the variables (*i.e.* the elemental concentrations) in the space spanned by the N samples (Hopke, 1991).

RESULTS

Table I shows the average elemental concentrations for all the samples which were above the detection limit for the fine particle-size mode. The non-sea-salt sulfur concentration (NSS S) is calculated by subtracting the sea-salt sulfur from the total sulfur concentration, taking Cl as sea-salt reference element, according with sea-water composition data from Riley & Chester (1971). The first column shows the average concentration measured on all samples, while the second and third ones show the average on the samples collected during austral summertime and wintertime, respectively. In the definition of the period of time which comprises summer and wintertime it was used the following criterion: summertime runs

from October 1st (274th Julian day) to March 31st (90th Julian day), whereas wintertime is comprised between April 1st and September 30th.

There is a strong dominance of sea-salt elements in the fine particle-size mode aerosol. Most of the elements usually associated with soil dust particles show very low concentrations. The concentrations of some trace elements which could be associated with anthropogenic activities (*e.g.* Cr, Ni, Cu and Pb) appear low and are affected by regional contributions, since in the region there are transport vehicles and equipments, like diesel generators, that contribute with high emission rates for these elements (Boutron & Wolff, 1989).

Table II shows the average elemental concentrations in the coarse particle-size mode. Similarly to the fine particle-size fraction, the sea-salt elements present concentrations that prevail upon the remaining ones. In both the fine and coarse particle-size modes there is a seasonality of the average concentrations, with most of the summertime averages greater than the wintertime ones.

There are relatively few works reporting elemental concentrations in aerosols collected on coastal sites in Antarctica. The comparisons are not easy to perform, since the measurements are made with different techniques and sampling equipments. In the work of Lawson & Winchester (1978, 1979) the sulfur concentration in the fine particle-size mode on the southern tip of South America was measured in the range of 52 to 98 ng m^{-3} . The yearly average of 79.5 ng m^{-3} in this work falls within this range, with wintertime average of 51.9 ng m^{-3} near the lower limit and the summertime average of 125 ng m^{-3} somewhat above the higher limit. In Samoa (14°S; 170.5°W) the same authors report 60 ng m^{-3} for the sulfur in the fine particle-size mode and 87 ng m^{-3} in the coarse particle-size mode. The measured wintertime fine and coarse particle-size modes averages are near these values. Savoie & Prospero (1989) report concentrations of non-sea-salt sulfate ranging from 220 to 400 ng m^{-3} at various remote sites on South Pacific. The results in this work are near that range: assuming all sulfur to be in the form of sulfates, the yearly average concentration of non-sea-salt sulfate was estimated at 263 ng m^{-3} , with

TABLE I
Average elemental concentrations for fine mode antarctic aerosol.¹

Element	All samples		Summertime ⁽²⁾		Wintertime ⁽²⁾	
	Concentration (ng m^{-3})	N	Concentration (ng m^{-3})	N	Concentration (ng m^{-3})	N
Na	242	301	283	113	216	188
Mg	35.5	301	41.5	113	32.0	188
Al	4.85	100	3.34	32	5.56	68
Si	32.6	72	19.2	28	41.2	44
S	79.5	301	125	113	51.9	188
Cl	609	301	670	113	573	188
K	16.4	301	19.1	113	14.7	188
Ca	18.2	301	21.2	113	16.4	188
Ti	0.65	45	0.31	17	0.86	28
Cr	1.06	37	1.38	10	0.95	27
Mn	0.13	90	0.14	26	0.12	64
Fe	1.11	240	1.04	96	1.16	144
Ni	0.088	18	0.17	5	0.056	13
Cu	0.23	123	0.24	47	0.22	76
Zn	1.07	287	0.88	104	1.17	183
Pb	0.25	32	0.29	18	0.21	14
Se	0.059	85	0.064	51	0.051	34
Br	3.48	301	2.76	113	3.92	188
Rb	0.20	9	0.12	2	0.22	7
Sr	0.32	301	0.37	113	0.28	188
NSS S ⁽³⁾	51.3	301	94.1	113	25.5	188
FPM ⁽⁴⁾	3.24	301	3.78	113	2.92	188

⁽¹⁾Only the concentrations above the detection limits were used in calculating the averages.

⁽²⁾Summertime: averages of concentrations on samplers collected between October 1st and March 31st. Wintertime: averages of concentrations on samples collected between April 1st and September 30th. N is the number of samples that presented concentrations above the detection limit for each element.

⁽³⁾NSS S: non-sea-salt sulfur concentration calculated by subtracting the sea-salt sulfur concentration from the total sulfur concentration using Cl as the reference for sea-salt aerosol, according with data by Riley & Chester (1971).

⁽⁴⁾FPM: fine particle mass concentration, presented in $\mu\text{g m}^{-3}$.

averages of 440 ng m^{-3} during summertime and 157 ng m^{-3} during wintertime.

Enrichment factors (EF) were calculated using Cl as sea-salt reference element, according with the following expression:

$$EF(X) = \frac{[C(X)/C(Cl)]_{\text{aerosol}}}{[C(X)/C(Cl)]_{\text{sea-water}}}$$

where $C(X)$ is the concentration of the element X in the aerosol or in the reference sea-water. The

composition of bulk sea-water was obtained from Riley & Chester (1971). Cl was used as the reference element instead of Na due to much higher accuracy in measuring Cl by the PIXE method. Figure 1 shows the calculated enrichment factors for the samples collected during summertime and wintertime in both fine and coarse particle-size modes. The elements with EF values near 1 (Na, Mg, K, Ca, Br, Sr and S) have probably a marine origin. Some elements which usually are associ-

TABLE II
Average elemental concentrations for coarse mode antarctic aerosol.¹

Element	All samples		Summertime ⁽²⁾		Wintertime ⁽²⁾	
	Concentration (ng m ⁻³)	N	Concentration (ng m ⁻³)	N	Concentration (ng m ⁻³)	N
Na	384	301	442	113	350	188
Mg	81.3	301	94.5	113	73.3	188
Al	15.4	233	10.3	92	18.7	141
Si	48.9	214	23.2	92	68.4	122
S	99.7	301	124	113	84.8	188
Cl	1356	301	1539	113	1245	188
K	38.5	301	42.3	113	36.3	188
Ca	45.2	301	49.8	113	42.9	188
Ti	2.32	167	1.31	71	3.07	96
Cr	0.64	98	0.62	32	0.65	66
Mn	0.54	134	0.35	51	0.66	83
Fe	10.8	301	9.70	113	11.4	188
Ni	0.18	41	0.18	13	0.18	28
Cu	2.78	223	3.21	84	2.52	139
Zn	3.43	296	4.11	111	3.03	185
Pb	0.81	132	0.91	41	0.76	91
Br	5.18	301	5.20	113	5.17	188
Rb	0.72	5	0.69	2	0.73	3
Sr	0.78	301	0.88	113	0.73	188
NSS S ⁽³⁾	36.5	301	52.6	113	26.8	188
CPM ⁽⁴⁾	5.59	301	6.52	113	5.04	188

⁽¹⁾Only the concentrations above the detection limits were used in calculating the averages.

⁽²⁾Summertime: averages of concentrations on samplers collected between October 1st and March 31st.

Wintertime: averages of concentrations on samples collected between April 1st and September 30th. N is the number of samples that presented concentrations above the detection limit for each element.

⁽³⁾NSS S: non-sea-salt sulfur concentration calculated by subtracting the sea-salt sulfur concentration from the total sulfur concentration using Cl as the reference for sea-salt aerosol, according with data by Riley & Chester (1971).

⁽⁴⁾CPM: coarse particle mass concentration, presented in $\mu\text{g m}^{-3}$.

ated with soil dust aerosol (Si, Mn, Ti, Fe and Al) are significantly enriched. Some of the remaining elements show high EF values, similarly to the presented in other work at the South Pole (Tuncel *et al.*, 1989). In addition to the local contribution, another possible explanation for the presence of these enriched heavy elements is long-range transport from polluted areas to Antarctica. Also, sea-water droplets are enriched with heavy metals like Zn, Cu (Cattell & Scott, 1978) and others, by frac-

tionation mechanisms occurring at the sea-atmosphere interface (Harvie *et al.*, 1980).

Figure 2 shows the temporal series of fine and coarse particle-size modes of the aerosol mass concentration. There is an overall little seasonality pattern, although the FPM series seems to bear more resemblance with the changing of the seasons than the CPM series does. Typically the FPM concentration is about 3.78 ng m^{-3} during summertime and 2.92 ng m^{-3} during wintertime, whereas the

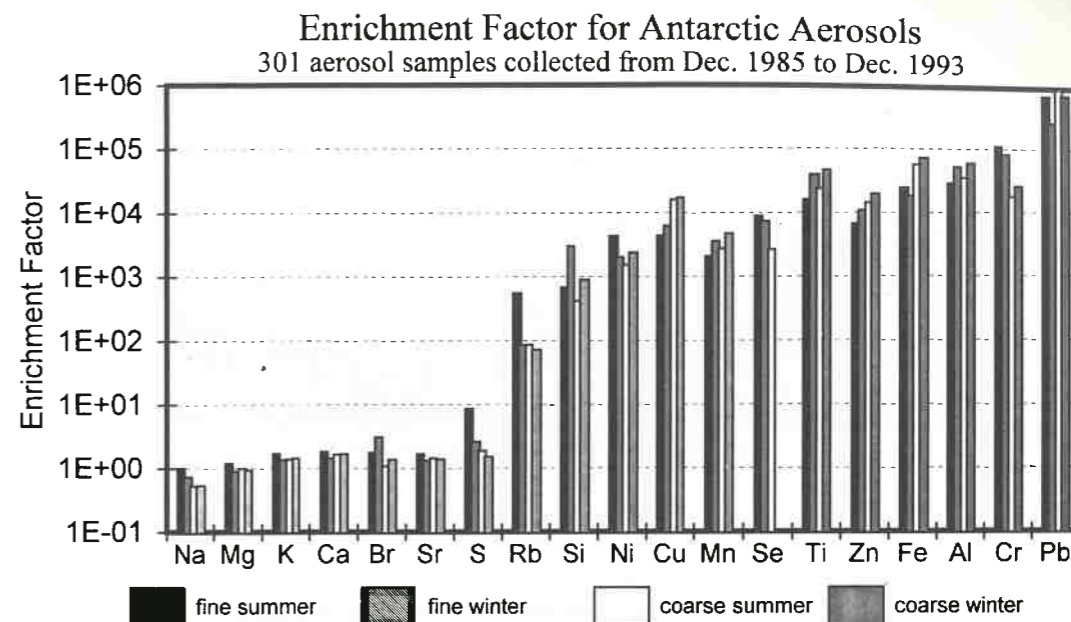


Fig. 1 — Enrichment factors for 301 aerosol samples collected from December 1985 to December 1993 in the Antarctic Peninsula, during summertime and wintertime in both fine and coarse models. Cl in bulk sea-water was used as the reference element according with composition data from Riley & Chester (1971).

CPM presents nearly a summertime concentration of 6.52 ng m^{-3} and 5.04 ng m^{-3} during wintertime.

Figure 3 shows the temporal series of the non-sea-salt sulfur in both particle-size fractions. The fine particle-size mode presents a clear seasonality, in accordance with other studies (Prospero *et al.*, 1991; Wagenbach *et al.*, 1988), while in the coarse particle-size mode this seasonality is not as clear. Typically the non-sea-salt sulfur concentration in the fine particle-size mode is about 94.1 ng m^{-3} in the summer and 25.5 ng m^{-3} during winter. For the coarse particle-size mode the typical concentration values are nearly 52.6 ng m^{-3} during summer and 26.8 ng m^{-3} in the winter.

The mass fraction of non-sea-salt sulfur on the total measured sulfur was computed for both particle-size modes. In the fine particle-size mode the mass fraction averages on 75% during summertime and on 49% during wintertime. For the coarse particle-size mode the non-sea-salt sulfur accounts for an average of 42% of the total sulfur during summertime and for an average of 32% at wintertime. The non-sea-salt sulfur in the fine particle-size mode has a biogenic origin, whereas part of the coarse particle-size mode can be explained by

reactions of gaseous sulfur on already existing coarse particle-size mode aerosol particles (one of the pathways for heterogeneous sulfur conversion).

Three principal factor analyses of the elemental concentrations measured were performed: the first considering all the samples collected, the second with only the samples collected during summertime and the third with the samples collected during wintertime. In these three analyses, concentrations of fine and coarse particle-size modes were included. Elements which could be associated with local pollution sources, such as Pb and Cu, were not used in the analyses. In all three cases, four factors were retained, and they explained near 86% to 89% of the data variability.

Table III shows the factor loading matrix after the VARIMAX rotation for the analysis of all the samples, whereas Tables IV and V show the VARIMAX rotated factor loading matrices for the samples collected during only summer and wintertime, respectively.

In Table III, the first factor was identified with the sea-salt aerosol in the coarse particle-size mode due to its high loadings for the elemental concentrations of Cl, Mg, S, K, Sr, Ca, Na and Br (all in

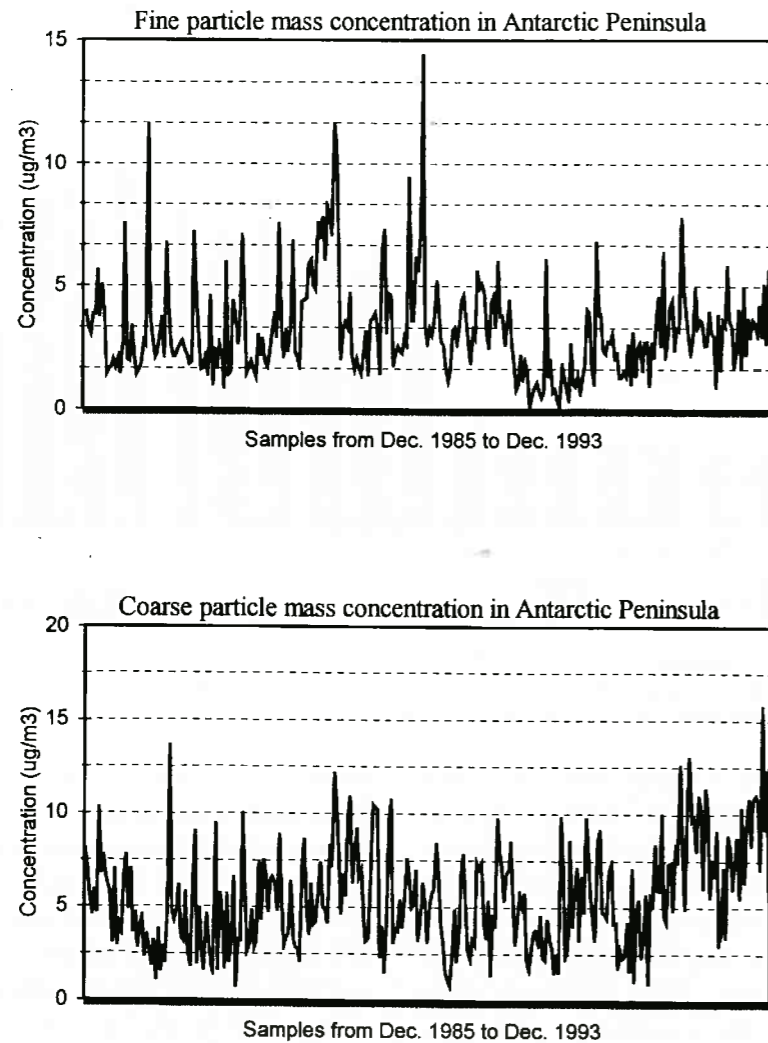


Fig. 2 — Temporal series of the fine (above) and coarse (below) particle mass concentrations in $\mu\text{g m}^{-3}$ for all aerosol samples collected in the Antarctic Peninsula.

the coarse particle-size mode), and also for the CPM. The second factor presented high factor loadings for the concentrations of Ca, K, Cl, Mg, Sr, Na and Zn (all in the fine particle-size mode), and also for the FPM, and so it represents the sea-salt aerosol in the fine particle-size mode. The third factor represents soil dust aerosol, for the only significant factor loadings were the ones corresponding to the Fe concentration in both particle-size fractions. The other elements which could be used as tracers for the aerosol provenient from soil dust, such as Al, Ti and Si, could not be measured in all samples, and thus these data were not used in

the calculations. The last factor had significant loadings only for the concentration of sulfur in the fine particle-size mode and, to a lesser extent, for the FPM, showing that for this yearly average PFA the variability of sulfur is independent of the variability of the sea-salt aerosol, considering the fine particle-size mode. Although this factor has a relatively high loading of 0.52 for the FPM, the highest loading of 0.64 for this variable corresponds to the second factor which is the one associated with sea-salt aerosol in the fine particle-size mode. The greatest contribution for the FPM variability comes from the sea-salt aerosol concentration variability

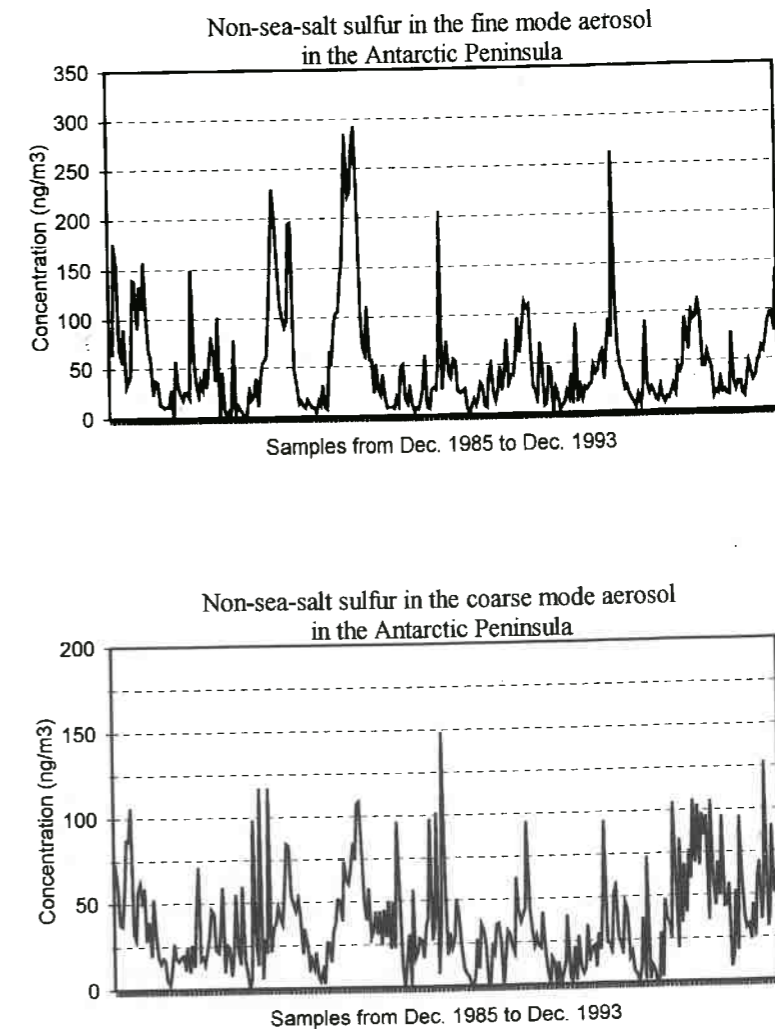


Fig. 3 — Temporal series of the fine (above) and coarse (below) modes of the non-sea-salt sulfur concentrations in ng m^{-3} for all samples collected in the Antarctic Peninsula.

in the fine particle-size mode, followed by the sulfur concentration variability.

In Tables IV and V, principal factor analysis was performed separately for summer and wintertime samples. For both analyses the first factor was identified with sea-salt aerosol in the coarse particle-size mode and the elemental concentrations with high loadings coincide with the ones from the first factor of Table III. In both these tables it is possible to observe a factor corresponding to sea-salt aerosol in the fine particle-size mode and also a factor due to soil dust aerosol. The important results are the modifications that occur in the PFA

when all the samples are analyzed together, compared to the summer and wintertime samples analyzed separately: during summertime the sulfur concentration variability has a greater importance for the FPM variability than the sea-salt aerosol concentration does, regarding the fine particle-size mode. As we have observed, the non-sea-salt sulfur has an average mass fraction of 75% on the summertime fine particle-size mode sulfur concentration. This implies that in the fine particle-size fraction during summertime, the concentration of non-sea-salt sulfur has a variability that rules on the FPM variability, being of secondary impor-

TABLE III
VARIMAX rotated factor loading matrix for the concentrations of elements present in samples of atmospheric aerosol from the Antarctic Peninsula collected during both summer⁽¹⁾ and wintertime⁽¹⁾.

Element	Sea-Salt (Coarse)	Sea-Salt (Fine)	Soil Dust	Sulfate
ClC	0.93	0.10	-0.11	0.11
MgC	0.91	0.30	-0.05	0.06
SC	0.90	0.21	-0.06	0.24
CPM	0.87	0.22	0.13	0.17
KC	0.87	0.26	0.31	0.002
SrC	0.84	0.21	0.35	0.02
CaC	0.82	0.22	0.39	-0.007
NaC	0.78	-0.02	-0.07	0.29
BrC	0.73	0.39	-0.15	-0.19
CaF	0.13	0.94	0.13	0.11
KF	0.26	0.92	0.10	0.12
ClF	0.30	0.92	-0.09	0.01
MgF	0.36	0.88	-0.07	0.14
SrF	0.28	0.88	0.07	0.14
NaF	0.36	0.86	-0.04	0.20
FPM	0.16	0.64	-0.08	0.52
ZnF	-0.34	0.60	0.18	-0.04
FeC	0.06	0.05	0.94	-0.03
FeF	0.08	-0.005	0.92	0.02
SF	0.22	0.34	0.03	0.82

⁽¹⁾Summertime is comprised between October 1st and March 31st, whereas wintertime runs from April 1st to September 30th.

⁽²⁾The names of the elements are followed by a letter "C" or "F" to indicate the coarse and fine particle modes concentrations, respectively. CPM stands for coarse particle mass concentration, whereas FPM is the fine particle mass concentration.

tance the variability of the sea-salt aerosol concentration.

During wintertime (Tab. V) and in the fine particle-size mode, the variability of both the FPM and the sulfur concentration (and so also the non-sea-salt sulfur concentration) are greatly associated with the variability of the concentrations of elements assigned to sea-salt aerosol: the separation observed in Tables III and IV can not be further distinguished. This kind of seasonality is in accordance with the conjectured biogenic origin of the fine particle-size fraction of the non-sea-salt sulfur: during summertime the biogenic activity is maximum, the non-sea-salt sulfur concentration in the fine particle-size mode gets on its highest val-

ues and this could afford for its variability to be independent from the sea-salt concentration variability in the same particle-size mode. During wintertime the biogenic activity is minimum and, in the fine particle-size mode, the average concentration of the non-sea-salt sulfur is low in such a way that its variability could be greatly influenced by some other factors which rule over the sea-salt concentration variability. For the PFA of the winter samples it was not possible to use Fe concentration in the fine particle-size mode, because this variable presented too many missing values. In Table V it is shown also that the variability of the Zn concentration in the fine particle-size mode is independent of the variability of the other elements, although it

TABLE IV
VARIMAX rotated factor loading matrix for the concentrations of the elements present in samples of atmospheric aerosol from the Antarctic Peninsula collected during summertime⁽¹⁾.

Element ⁽²⁾	Sea-Salt (Coarse)	Sea-Salt (Fine)	Soil Dust	Sulfate
KC	0.92	0.27	0.01	-0.03
ClC	0.91	0.08	-0.31	0.06
SC	0.90	0.18	-0.07	0.25
CPM	0.87	0.22	0.14	0.16
MgC	0.86	0.36	-0.17	0.06
CaC	0.86	0.26	0.20	-0.03
SrC	0.85	0.28	0.17	0.01
NaC	0.74	-0.09	-0.07	0.20
BrC	0.65	0.44	-0.25	-0.004
CaF	0.15	0.94	0.16	0.14
KF	0.23	0.93	0.13	0.14
ClF	0.32	0.91	-0.13	0.04
SrF	0.24	0.90	-0.01	0.18
NaF	0.32	0.87	-0.01	0.19
MgF	0.37	0.87	-0.12	0.16
ZnF	-0.21	0.62	0.41	0.01
FeC	0.02	0.10	0.92	-0.10
FeF	0.01	-0.03	0.90	0.04
SF	0.13	0.17	0.004	0.87
FPM	0.16	0.49	-0.09	0.72

⁽¹⁾Summertime is comprised between October 1st and March 31st.

⁽²⁾The names of the elements are followed by a letter "C" or "F" to indicate the coarse and fine particle modes concentrations, respectively. CPM stands for coarse particle mass concentration, whereas FPM is the fine particle mass concentration.

has a moderate loading corresponding to the sea-salt aerosol factor in the fine particle-size mode. The results of the PFA agree in general with a previous work where a similar data set collected until 1988 was analyzed (Artaxo *et al.*, 1992).

Three non-hierarchical cluster analyses were performed, the first considering all the samples collected, while the second and third ones considering separately the summertime and the wintertime samples, respectively. Figure 4 shows the dendrogram of the non-hierarchical cluster analysis including all the samples collected. In this case it can be observed that there is a general agreement with the identified sources by the PFA for the same data set. In the coarse particle-size mode, the elemental concentrations of Na, Cl, Ca, Sr, K, Mg, S, Br and also the CPM were grouped in one single

cluster, corresponding to the coarse particle-size mode sea-salt aerosol source early identified by the PFA as the first factor shown in Table III. The same is valid for the third factor of this table, corresponding to soil dust aerosol: the elemental concentrations of Fe both in the fine and coarse particle-size modes were clustered in one separate group. In the fine particle-size mode sea-salt component the elemental concentrations of Cl, Mg, Na, K, Ca, and Sr were clustered together. The FPM, Zn and S concentrations were also clustered with the other fine particle-size mode sea-salt elements, but they are somewhat distant. This is in accordance with the relatively low loadings of these variables in the fine particle-size mode sea-salt factor calculated in the PFA. The clustering shows also a certain proximity between the S concentration and

TABLE V
VARIMAX rotated factor loading matrix for the concentrations of the elements present in samples of atmospheric aerosol from the Antarctic Peninsula collected during wintertime⁽¹⁾.

Element ⁽²⁾	Sea-Salt (Coarse)	Sea-Salt (Fine)	Soil Dust	Zinc
ClC	0.93	0.16	-0.09	-0.14
SC	0.92	0.27	-0.05	-0.07
MgC	0.92	0.28	-0.02	-0.07
CPM	0.89	0.23	0.15	-0.03
SrC	0.83	0.16	0.42	-0.02
KC	0.82	0.28	0.41	-0.02
CaC	0.81	0.18	0.47	0.05
BrC	0.80	0.29	-0.13	0.25
NaC	0.77	0.15	-0.08	-0.33
KF	0.24	0.93	0.11	0.10
MgF	0.28	0.93	-0.02	0.008
CaF	0.09	0.93	0.14	0.22
ClF	0.25	0.92	-0.06	0.14
NaF	0.32	0.91	-0.05	-0.01
SrF	0.25	0.90	0.13	0.01
SF	0.20	0.80	0.08	-0.11
FPM	0.16	0.76	-0.11	0.23
FeC	0.08	0.002	0.96	0.07
ZnF	-0.28	0.45	0.12	0.74

⁽¹⁾Wintertime is comprised between April 1st and September 30th.

⁽²⁾The names of the elements are followed by a letter "C" or "F" to indicate the coarse and fine particle modes concentrations, respectively. CPM stands for coarse particle mass concentration, whereas FPM is the fine particle mass concentration.

the FPM, which is confirmed in the PFA by the high loading of this variable in the sulfate factor.

When only the summertime samples are analyzed the dendrogram obtained by the non-hierarchical cluster analysis is that shown in the upper part of figure 5. In this case there is a better agreement between the two analyses: all the coarse particle-size mode sea-salt related elements identified by the PFA shown in Table IV were grouped together in the cluster analysis, the same occurring for the soil dust and the sulfate factors. In the fine particle-size mode sea-salt cluster it can be seen that the Zn concentration is relatively distant from the others, which is in accordance with the PFA since this is the variable with the smallest loading among the ones related to the fine particle-size mode sea-salt factor.

In the lower part of figure 5 it is shown the dendrogram obtained by the non-hierarchical cluster analysis of the wintertime samples. Again the results coincide with the PFA classification. All the elements which were identified with the coarse particle-size mode sea-salt aerosol source by the PFA in Table V were also grouped together in the cluster analysis. The same occurred for the factors identified with fine particle-size mode sea-salt, soil dust and for the factor associated with Zn. In the cluster analysis the fine particle-size mode Fe concentration was included for illustrative purposes, and it appears clustered together with the coarse particle-size mode Fe concentration as it did in all the other circumstances. This indicates consistency in the separation of the sources of soil dust and sea-salt aerosol. In the fine particle-size mode, the Zn concentration appears near the variables related

Non-hierarchical cluster analysis of all samples collected

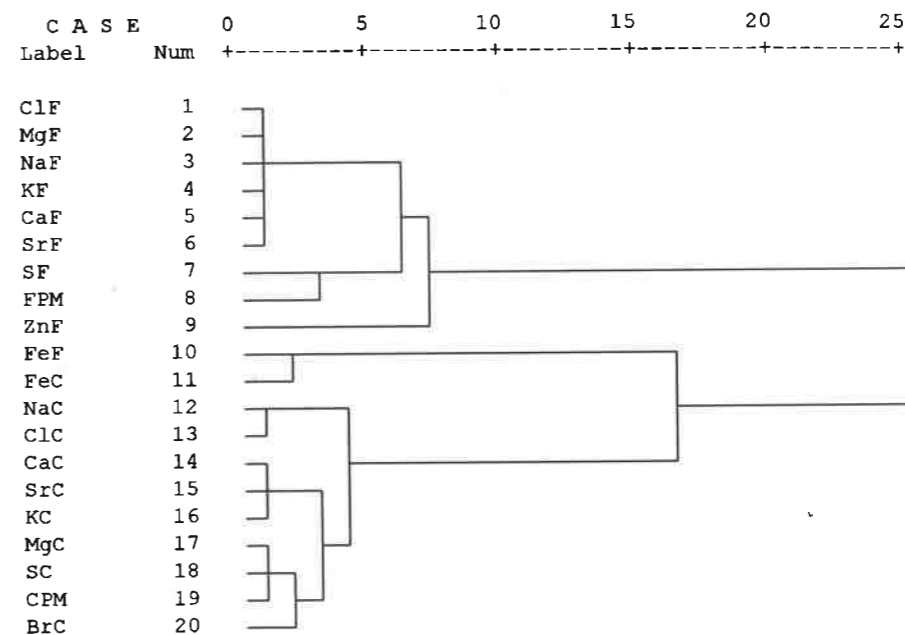


Fig. 4 — Dendrogram of the non-hierarchical cluster analysis for all the samples collected. The names of the elements are followed by a letter "F" or "C" to indicate the fine or coarse modes. FPM stands for fine particle mass concentration, whereas CPM is the coarse particle mass concentration.

to sea-salt, bearing some resemblance with the PFA where the Zn concentration appears with a considerable loading in the fine particle-size mode sea-salt factor.

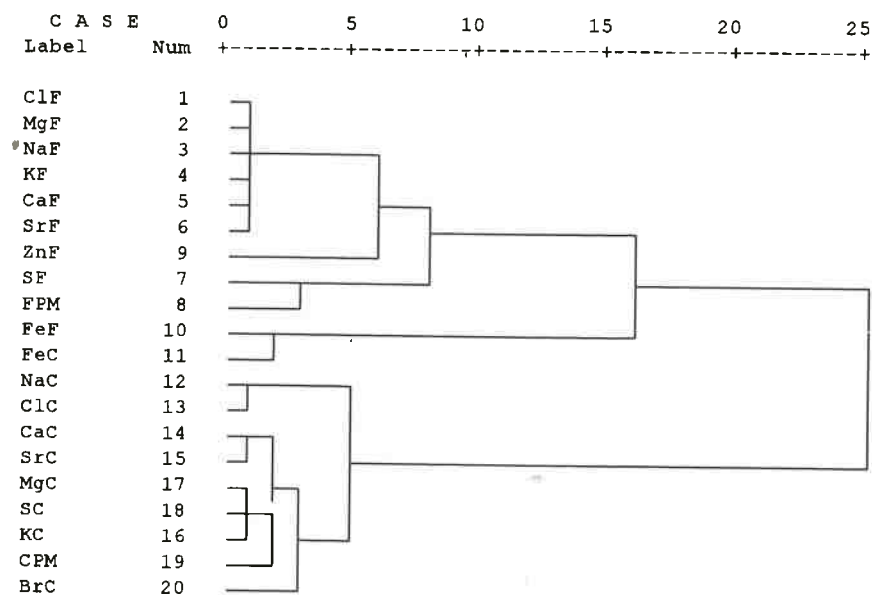
Although the Zn concentration can easily be affected by contamination, presenting an enrichment factor near 10^4 , in all three cluster analyses performed this variable showed some proximity of the elements related to fine particle-size mode sea-salt aerosol, indicating that a fraction of the measured Zn can have a marine origin.

One of the main advantages of the cluster analysis is the qualitative visual information it can provide compared to the PFA, where a group of variables is assigned to just one factor and there is little information about the relations of different variables. In cluster analysis, instead, it is possible to compare visually the differences between variables within a given group or to assess the behavior of a variable which could possibly be associated with more than one cluster.

CONCLUSIONS

There is a strong dominance of the sea-salt elements in the Antarctic Peninsula aerosol particles. The sulfur concentrations and also the non-sea-salt sulfates measured in this work are similar to the presented by other authors. The non-sea-salt sulfur showed a clear seasonal pattern in the fine particle-size mode, probably due to biogenic activities, and its average mass fraction in the total sulfur measured is 75% during summertime and 49% during winter. The variability in the concentration of non-sea-salt sulfur in the coarse particle-size mode is partly explained by heterogeneous sulfur conversion on the surface of existing coarse particle-size mode aerosol particles. In this particle-size fraction the non-sea-salt sulfur contributes with an average of 42% of the total sulfur in the summer and with 32% during winter. Relatively high concentrations were observed for some heavy metals (Pb, Ni and others) that are the result of regional or long-range-transported anthropogenic air pollution.

Non-hierarchical cluster analysis of samples collected during summertime



Non-hierarchical cluster analysis of samples collected during wintertime

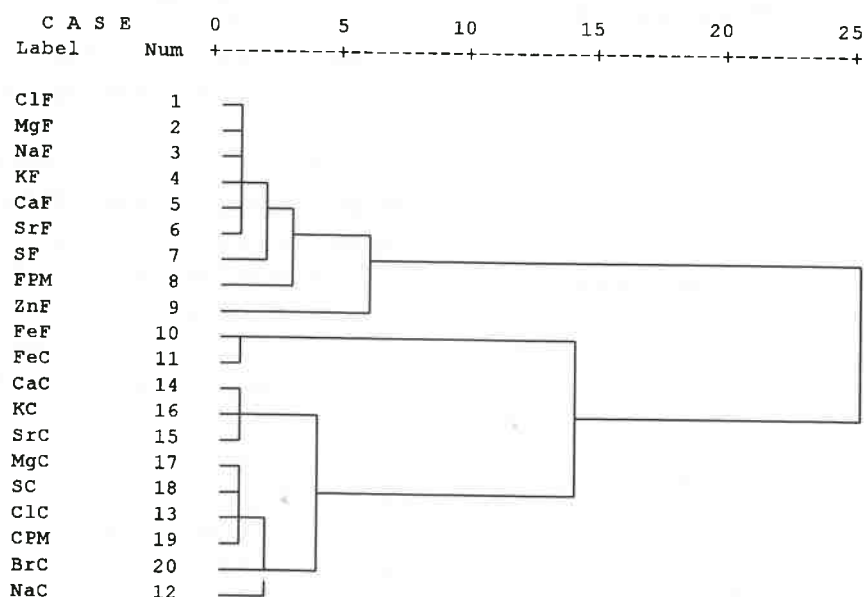


Fig. 5 — Dendrogram of the non-hierarchical cluster analysis for the samples collected during summertime (above) and wintertime (below). The names of the elements are followed by a letter "F" or "C" to indicate the fine or coarse modes. FPM stands for fine particle mass concentration, whereas CPM is the coarse particle mass concentration.

Principal factor analyses were carried out and the factors retained explained near 87% of the total variability of the data. Considering the summertime samples the four factors retained correspond to sea-salt aerosol in the coarse and fine particle-size modes, soil dust and sulfates. In this case the FPM variability was associated with the sulfur concentration variability in the fine particle-size mode, showing the importance of the sulfur compared to the sea-salt elements concentration variability in this particle-size fraction. This is of special relevance since the sulfur aerosol particles have a well recognized important role in processes related to global change concern, mainly in the fine particle-size mode range. During wintertime the four factors retained correspond to sea-salt aerosol in the coarse and fine particle-size modes, soil dust and zinc. In the fine particle-size mode, the variabilities of the sulfur and the mass concentrations could not be distinguished from the variabilities of the concentrations of the sea-salt-related elements. This can be due to the seasonality of the biogenic activities, which are low during winter and could not explain a significant fraction of the variability of the FPM as they did during summertime. Cluster analyses were performed and they confirmed the principal factor analyses done, also affording a visual approach where the dissimilarities of the variables within each cluster or factor can be directly assessed.

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