

## TRACE ELEMENTS AND RECEPTOR MODELLING OF AEROSOLS IN THE ANTARCTIC PENINSULA

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Atmospheric aerosols were sampled continuously since December 1985 at the Brazilian Antarctic Station “Comandante Ferraz”, (62.1°S; 58.4°W) in the King George Island, Antarctic Peninsula. Stacked filter units (SFU) were used to collect fine ( $d_p < 2.0 \mu\text{m}$ ) and coarse ( $2.0 \mu\text{m} < d_p < 15 \mu\text{m}$ ) particles on Nuclepore filters. The concentrations of elements with  $Z > 10$  were measured by particle-induced X-ray emission (PIXE) analysis. The X-ray spectra were fitted for 23 elements: 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 fine and coarse mass concentrations were determined by gravimetric analysis. Absolute principal factor analysis (APFA) was used to obtain the aerosol source profiles. For the coarse mode, two factors explained 95% of the data variability. The first factor had significant loadings for Na, Mg, Cl, S, Sr, K, Ca, and the coarse particle mass concentration (representing sea-salt aerosol), and the second factor had significant loadings for Al, Si, Fe, Ti, and Ca (soil dust aerosol). In the fine mode, three factors explained 94% of the data variability, and they represented sea-salt aerosol, soil dust and sulfates. The communalities for the fine and coarse mode aerosol were very high for all variables. The source profiles obtained by APFA for both fine and coarse mode aerosol were extracted for each retained factor. The sea-salt source profile agreed with the average sea-water elemental composition to within 20% for the elements Na, Mg, S, Cl, K, Ca and Br. For the soil dust component, the elements Mg, Al, Si, K, Ca, Ti, Mn, and Fe were predicted by APFA within 40% of the average bulk elemental composition for the earth crust. The source apportionment for the coarse particle mass concentration (CPM) showed that 76% of the CPM is accounted for by the sea-salt aerosol component, 4.5% by soil dust and 20% of the CPM could not be apportioned. For the fine particle mass concentration (FPM), sea-salt aerosol accounted for 80%; sulfates for 16%, soil dust for 1.1%, and 3.5% of the FPM could not be apportioned. No anthropogenic components could be distinguished.

### 1. Introduction

Since several years extensive experiments are carried to investigate the characteristics of atmospheric aerosols in remote areas. In most of these experiments the aerosol composition is measured by nondestructive, multi-element analytical techniques such as particle-induced X-ray emission (PIXE). However, only a few of these studies have taken advantage of powerful techniques for aerosol source recognition and apportionment. Multivariate data analysis methods like absolute principal factor analysis [1], stepwise multiple regression [2] and cluster analysis [3] have recently been applied in background aerosol characterization studies in order to assist in the interpretation of trace element concentration data.

Antarctica is supposed to suffer minimally from anthropogenic pollution, although the concentrations of several trace gases are known to be increasing over this continent. The recent interest in the Antarctic atmosphere, due to the “Antarctic ozone hole”, had resulted

in a recognition of the need for long term background aerosol characterization studies. Furthermore, it is important to follow the concentrations of heavy metals in the atmosphere in order to detect trends in global anthropogenic pollution. As the Antarctic continent is very far from important anthropogenic sources, it is an ideal site to follow the trends in regional (and global) concentrations of heavy metals in the atmosphere. Some studies of the Antarctic aerosol have been carried out already [4–9], but most of these were done at the geographic South Pole, and very few have collected aerosol with size-segregated samplers. Data from various sites at the edge of the continent are required in order to improve our understanding of the overall Antarctic aerosol chemistry. In this paper, we report on measurements carried out in the Antarctica Peninsula. Aerosol collections were performed in separate coarse and fine size fractions, the samples were analyzed by PIXE, and the multielement data sets obtained were examined by absolute principal factor analysis.

## 2. Experimental methods

### 2.1. Sampling site and sampling procedures

The sampling station is located at the Brazilian Antarctic Station, "Comandante Ferraz" (62.1°S; 58.4°W), in the King George Island, on the Admiral Bay, Antarctic Peninsula. The sampling site is located upwind from local sources, at about 1 km from the main station, and it is at about 300 m from the sea coast. The station is operated continuously since December 1985, including during the winter season.

Aerosol particles were collected with stacked filter units (SFU) [10,11]. Coarse particles ( $2.0 \mu\text{m} < d_p < 15 \mu\text{m}$ ) were collected on a Nuclepore 8.0  $\mu\text{m}$  pore size 47 mm diameter filter, and the fine particles ( $d_p < 2.0 \mu\text{m}$ ) were sampled on a 0.3  $\mu\text{m}$  high density pore filter. The flow rate was 10 to 22 liters per minute, and at the face velocity used, the 50% cutoff diameter of the coarse filter is about 2.0  $\mu\text{m}$  [12]. A special inlet was fitted to sample only inhalable particles with a 50% cutoff diameter of 15  $\mu\text{m}$  [11]. Air volumes were measured with calibrated gas meters with a precision of about 3%. The SFU were loaded with the Nuclepore 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 the actual filter samples before and after sampling. The collection time per SFU sample varied between 3 and 7 days.

### 2.2. Elemental and mass concentration measurements

The aerosol elemental concentrations were measured by particle-induced X-ray emission (PIXE) analysis [13]. The samples were irradiated by a 2.4 MeV proton beam, supplied by the cyclotron of the University of Gent. The X-ray spectra were fitted by the AXIL program, and concentration data were obtained for 23 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb. However, because of its soft X-ray energy, the data for Na should be considered as semi-quantitative only. The detection limit was typically 5 ng/m<sup>3</sup> for elements with  $Z < 20$ , and down to 0.1 ng/m<sup>3</sup> for elements with  $Z > 21$ . 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. Full details about the PIXE experimental setup, analytical procedures, calibration, and uncertainties are given elsewhere [14–16].

The fine and coarse aerosol mass concentrations were obtained by gravimetric analysis. The filters were weighed before and after sampling in a Mettler M3 electronic microbalance with 1  $\mu\text{g}$  sensitivity. Before weighing, the filters were equilibrated for 24 hours at 50% relative humidity and 20 °C. Electrostatic charges

were controlled by <sup>210</sup>Po radioactive sources. Detection limit for fine and coarse mode aerosol mass concentrations is typically 0.1  $\mu\text{g}/\text{m}^3$  and precision is better than 15%.

## 3. Receptor models

In receptor modelling [17] concentrations of various airborne species (elements) are measured at the ambient sampling site, (the "receptor"), and using the data set obtained, it is then attempted to identify the number of major particle sources, to determine the source profiles, and to obtain the total mass source apportionment [18]. In the present study absolute principal factor analysis (APFA) was employed.

In principal factor analysis, the variability in the trace element concentrations is used as a basis for transforming the intercorrelated variables into a set of independent, uncorrelated variables. This is done by determining the eigenvalues and associated eigenvectors of the correlation matrix of elemental concentrations [19]. The most prominent factors (eigenvectors) are retained and orthogonally rotated by a VARIMAX rotation. The final results are a "factor loading" matrix which represents the correlations between the trace elements and each factor, and the so-called "factor scores" which indicate the importance of each factor for the individual cases [20,21].

In absolute principal factor analysis (APFA) [22], the absolute principal factor scores (APFS) for each sample are calculated. The elemental concentrations in each sample are subsequently regressed on the APFS to obtain the concentrations of the elements for each source. These source profiles can then be compared with literature values or used in a quantitative source apportionment of the aerosol mass and atmospheric trace element concentrations [23].

## 4. Results and discussion

The PIXE analysis was performed on samples collected in 1985, 1986, and 1987, making a total of 46 fine mode and 47 coarse mode Antarctic aerosol samples. The average elemental concentrations are presented in Table 1. The strong dominance of sea-salt elements is evident. The concentrations of elements associated with soil dust are very low. The sulphur concentration in the fine mode is 77 ng/m<sup>3</sup>, and in the coarse mode, where sulphur is mainly related to sea-salt spray, its concentration is 81 ng/m<sup>3</sup>. The aerosol mass concentration was 2.3  $\mu\text{g}/\text{m}^3$  in the fine mode and 4.6  $\mu\text{g}/\text{m}^3$  in the coarse mode. The concentrations of trace elements that could be associated with anthropogenic sources, like Cr, Ni, Cu and Pb are very small. It is difficult to compare

Table 1

Average elemental concentrations in  $\text{ng}/\text{m}^3$  for the fine and coarse mode Antarctic aerosol. Summer and winter time samples collected in 1985, 1986 and 1987 <sup>a)</sup>

Element	Fine particles ( $d_p < 2.0 \mu\text{m}$ )		Coarse particles ( $2.0 \mu\text{m} < d_p < 15 \mu\text{m}$ )	
Na	57.4 ± 98.2	(46)	320 ± 248	(47)
Mg	22.9 ± 15.5	(46)	56.4 ± 33.7	(47)
Al	3.37 ± 2.81	(18)	9.94 ± 8.07	(47)
Si	83.7 ± 45.3	(10)	20.1 ± 19.8	(47)
P	–		3.82 ± 1.63	(5)
S	77.1 ± 45.3	(46)	81.0 ± 44.9	(47)
Cl	386 ± 291	(46)	1036 ± 631	(47)
K	11.6 ± 7.19	(46)	28.5 ± 15.3	(47)
Ca	14.1 ± 10.9	(46)	36.5 ± 20.4	(47)
Ti	0.28 ± 0.24	(4)	1.09 ± 1.03	(47)
Cr	0.46 ± 0.29	(12)	0.48 ± 0.31	(23)
Mn	0.15 ± 0.09	(4)	0.40 ± 0.40	(28)
Fe	1.25 ± 1.80	(46)	12.9 ± 13.4	(47)
Ni	0.09 ± 0.09	(3)	0.18 ± 0.13	(24)
Cu	0.13 ± 0.09	(23)	0.62 ± 0.57	(40)
Zn	3.09 ± 1.13	(46)	10.7 ± 13.8	(47)
Se	0.06 ± 0.03	(18)	–	
Br	2.74 ± 1.99	(46)	–	
Rb	0.18 ± 0.05	(5)	0.51 ± 0.41	(4)
Sr	0.24 ± 0.16	(46)	0.67 ± 0.43	(47)
Pb	0.17 ± 0.11	(14)	0.63 ± 0.59	(35)
Mass	2344 ± 1198	(46)	4550 ± 2230	(47)

<sup>a)</sup> The number of samples for which the element was measured above the detection limit is indicated in parentheses. Mass is the fine or coarse aerosol mass concentration.

aerosol concentrations measured with different samplers and during different periods where seasonal variations are large, but for sulphur our results are about 30% higher than those measured at the German Antarctic station (located in the Antarctic coastal region at 70°S, 8°W) where a high volume sampler operated continuously from 1983 to 1985 [8]. Cuong et al. [24] measured values in the range of 400–1000  $\text{ng}/\text{m}^3$  for  $\text{SO}_4$  in the Antarctic Ocean. Lawson and Winchester [25] report fine mode sulphur concentrations in the range of 52 to 98  $\text{ng}/\text{m}^3$  for several remote sites in the South American continent. They also reports 60  $\text{ng}/\text{m}^3$  fine mode and 87  $\text{ng}/\text{m}^3$  coarse mode sulphur measured in Samoa (14°S, 170.5°W), values very similar to the ones observed in this work. Savoie and Prospero [26] measured non-sea-salt sulphate values of 220 to 400  $\text{ng}/\text{m}^3$  for several remote sites in the South Pacific. Our results are within this range, with a non-sea-salt sulphate average of 275  $\text{ng}/\text{m}^3$  (calculated assuming a S/Cl ratio of 0.0468 and sulphate equals three times sulphur concentration).

The factor analysis for the Antarctic coarse mode samples was performed on a data set with concentrations of 12 variables that were measured in all samples,

Table 2

VARIMAX rotated factor loading matrix and communalities for the coarse mode aerosol collected in the Antarctic Peninsula <sup>a)</sup>

Variable	Factor 1 (sea-salt aerosol)	Factor 2 (soil dust)	Communalities
Na	0.95	0.03	0.90
Mg	0.98	0.07	0.96
S	0.96	0.15	0.95
Cl	0.99	0.03	0.98
K	0.97	0.20	0.97
Sr	0.88	0.37	0.91
CPM	0.95	0.09	0.90
Al	0.19	0.96	0.97
Si	0.06	0.97	0.95
Fe	0.10	0.98	0.97
Ti	0.13	0.98	0.98
Ca	0.77	0.60	0.95

<sup>a)</sup> CPM is the coarse particle mass concentration.

so that problems with estimation of missing values were avoided. The unrotated eigenvalue analysis indicated that only two factors were statistically significant, and these explained 94.9% of the data variance. As the combined error of sampling plus analysis is about 10%, the two retained factors thus explain all data variability that has to be accounted for. Table 2 gives the VARIMAX rotated factor loadings and the communalities for the coarse mode aerosol. The first factor that accounts for 66.2% of the data variability is related to Na, Mg, S, Cl, K, Sr, Ca, and CPM (coarse particle mass concentration). It clearly represent sea-salt aerosol. The second factor is related with Al, Si, Ti, Fe and Ca, representing the soil dust aerosol. The communalities for all variables are very high, indicating the adequacy of the factor model for this data set. In the factor analysis for the fine mode aerosol, we used a data set

Table 3

VARIMAX rotated factor loading matrix and communalities for the fine mode aerosol collected in the Antarctic Peninsula <sup>a)</sup>

Variable	Factor 1 (sea-salt aerosol)	Factor 2 (sulfates)	Factor 3 (soil dust)	Communalities
Na	0.89	0.40	–0.05	0.96
Mg	0.94	0.28	–0.11	0.97
Cl	0.96	0.17	–0.11	0.97
K	0.94	0.27	0.09	0.95
Ca	0.94	0.25	0.07	0.95
Br	0.90	–0.06	–0.21	0.86
Sr	0.85	0.37	0.01	0.86
FPM	0.88	0.10	–0.30	0.88
S	0.25	0.95	0.13	0.98
Fe	–0.10	0.11	0.98	0.97

<sup>a)</sup> FPM is the fine mode gravimetric mass concentration.

with the concentrations of 10 variables that were measured in all samples. Only three factors were statistically significant, and they explained 93.8% of the data variability. The VARIMAX rotated factor loading matrix is presented in Table 3. The first factor clearly represents sea-salt aerosol, sulphur is the only element which is significantly correlated with the second factor which obviously represents sulfates, and the third factor is the soil dust component. The soil dust component in the fine mode is very weak and explains only 6.2% of the data variability.

The airborne elemental concentrations were regressed on the factor scores, and the source profiles were extracted according to the absolute principal factor analysis method. Fig. 1 shows the source profiles for the two factors that were identified in the coarse mode aerosol. In the upper part of fig. 1, the elemental concentrations in the sea-salt component, as observed by APFA, are indicated by the left bars, whereas the right bars represent the concentrations in global average sea-water as given by Riley and Chester [27]. The concentrations in sea-water were normalized so that the Cl

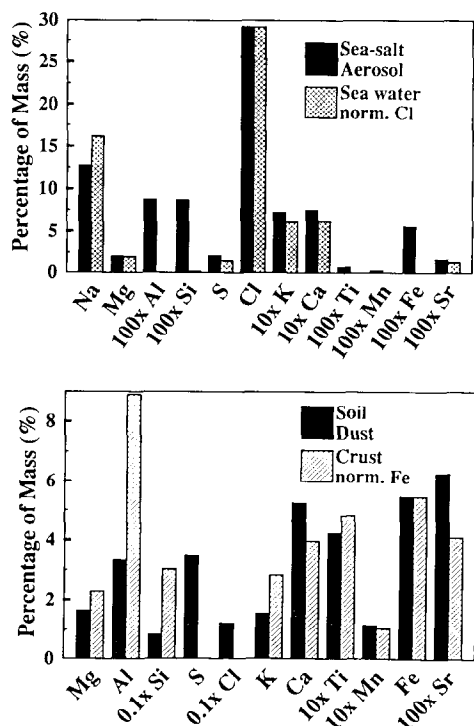


Fig. 1. Elemental source profiles for the sea-salt and soil dust components in the coarse mode Antarctic aerosol. The elemental concentrations in the source profiles obtained by APFA are indicated by the left bars. The right bars indicate the concentrations in average sea-water (from Riley and Chester [27]) and in average crustal rock (from Mason [28]). The concentrations in these literature profiles were scaled (see text).

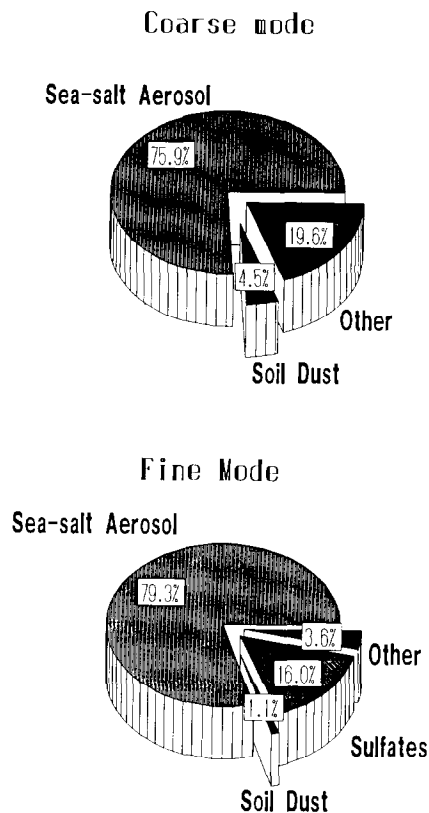


Fig. 2. Source apportionment for Antarctic coarse and fine mode aerosol mass concentration.

content equals that in the sea-salt component. The sea-salt source profile agrees very well with average sea-water composition for Na, Mg, S, K, Ca, and Sr. There is a small presence of soil-dust related elements (Al, Si, Ti, Mn and Fe) in the sea-salt aerosol component (note the  $100 \times$  factor for these elements in the plot). The lower part of Fig. 1 shows the coarse mode soil dust elemental profile (indicated by the left bars) and the average crustal composition given by Mason [28] (right bars). The elemental concentrations of the average crustal rock composition were normalized, so that the Fe content equals that in the soil profile. The agreement between the soil dust source profile and the average crust is very good for Mg, K, Ca, Ti, Mn and Sr. For Al and Si, lower concentrations were observed, probably because of different mineral participation in Antarctic soil than in the global crustal average.

The fine and coarse aerosol mass concentrations were regressed on the absolute factor scores, in order to obtain the fine and coarse aerosol mass source apportionment. Fig. 2 presents the results of this calculation. In the coarse mode (upper part of fig. 2), 75.9% of the aerosol mass is associated with sea-salt aerosol, soil dust accounts for 4.5%, and 19.6% of the measured gravimet-

ric mass concentration is not apportioned. This fraction can be organic aerosol or water which are both not related to the measured airborne elements. The lower part of Fig. 2 presents the mass source apportionment for the fine mode aerosol. Sea-salt aerosol accounts for 79.3%, sulfates for 16.0%, and soil dust for only 1.1% of the aerosol mass. Despite this very low contribution, the APFA method was able to discriminate this very small fine mode soil component.

## 5. Conclusions

Through the use of PIXE and multivariate statistical procedures it was possible to discriminate the components and sources of fine and coarse mode Antarctic aerosol. PIXE has the advantages of low detection limits and good accuracy for thin aerosol samples, and also allows the study of a large number of samples. The aerosol in the Antarctic Peninsula is dominated in the fine and coarse modes by the sea-salt component, but there is also a small soil dust contribution. In the fine mode, a sulfate component was also observed. It was not possible to distinguish any anthropogenic contribution from this data set. The aerosol sampling is continuing, and we hope that in few years we will have a good time series of major and trace element concentrations so that trends and seasonal differences in aerosol compositions and sources may be investigated.

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