Titulo: Elemental Composition of aerosols in the Antarctic Peninsula

ABSTRACT

Aerosols collected during 1986/87 in Ferraz station (62°S, 58°W), Antarctic Peninsula were analysed by NAA techniques. Sodium and clorine derived from sea spray were the predominant component in the aerosols. Soil dust components Al and Mn were about 30 times larger than at the South Pole due probably to a combination of the proximity to the S. America and to local sources. A marked decrease in concentration followed by the same change in the atmospheric radon and wind velocity from 1986 to 1987 were also observed. Zn and Sb presented a clear minimum concentration during winter while Br and V displayed a steadily decrease with time. Fe, Ca, Au, La, and Sc did not presented any clear trend during the year.

INTRODUCTION

The study of trace-elements in antarctic aerosols establishes an important tool for the understanding of the geochemical cycles in the troposphere. Major concern nowadays is devoted to the aerosol data acquisition in the antarctic continental plateau due to its remoteness. Nevertheless, coastal stations do provide crucial informations on the exchange of these particulates at the continental boundary.

The trace element composition of aerosols collected in coastal stations suffers a direct influence not only of the surrounding oceans (Wagenbach et al., 1988) but also of the ice stripped continental masses further ...th, as inferred by radon data (Polian et al., 1986; Pereira, 1989). Furthermore, since some of the coastal stations are located over rock basement, the effect of local aerosol production cannot be oversighted, notably during the summer season.

The Brazil's Ferraz Antarctic Station is located on King George island, in the South Shetland Islands of the Antarctic Peninsula (62°05'S, 58°23.5'W). In 1986 a routine base aerosol survey was added to an on going program of gaseous trace elements study. The preliminary result of the first two year of operation is reported in this work.

EXPERIMENTAL SET-UP

The aerosols were sampled from a small laboratory designed to host several low background, high sensitivity experiments on atmospheric trace-elements. It is located at about 300 meters upwind from the main station at 31 meters above the mean sea level. The station was erected in the Keller peninsula of King George island, over a beach area composed mainly by coarse Mezosoic volcanic debris. The island is heavily glaciate and ice cliffs form much of its coastline. The dome of this ice cap reaches an elevation of about 500 m above the sea. Heavy melting occurs during summer creating an ice free area around the station which reaches its maximum during late summer to early fall season.

The aerosols were collected on 0.45 μm MILLIPORE membrane filters. Flow rate was maintained at about 5 liters per minute by a membrane pump. Due to this relatively low flow rate the sampling time was set to one week, providing a total air sample volume of about 40 m^3. The filters were placed on plexiglass frames protected against snow and rain by an specially designed plastic shield.

After conclusion of the sampling period the filters were carefully sealed on plastic bags and documented for latter analysis in Brazil. Blank filters from the same allotment were analyzed for background corrections.

Neutron Activation Analysis (NAA) was employed in the trace elements determinations due to the relatively low total air volume sampled by the membrane pumps. This technique provides very low limits of detection for most trace elements and is well documented in the scientific literature (Amiel, 1981). Nevertheless, it is a very expensive method due to the need of a nuclear reactor for the nuclear activation process. The flux of neutrons available in the employed nuclear reactor was limited to 10^{12} $cm^{-2}s^{-1}$ in order to prevent the complete destruction of the polyethylene capsules containing the filters.

A total of 14 trace-elements were analyzed by choosing two different irradiation times and several measuring times, according to the half-live of each radioisotope corresponding to each trace-element. Detection limits and analytical precision were distinct for each trace-element and are given in Table 1. The detailed description of all the experimental procedures, including the preparation of the spikes, is given in Loureiro (1989).

EXPERIMENTAL RESULTS

For practical purposes data acquisition in Ferraz were divided into two periods. The "winter" period be...

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by March 16 and ended by November 11 when the wintering group was replaced by the new summer crew. The 1986/1987 "summer" period comprised the months from December 12 to March 13. During the summer period the personnel at Ferraz more than duplicate. Furthermore, most of the outdoor working activities of maintenance and repair of the station is performed, some of them involving motorized operations. The presence of the Brazilian support ship Barão de Teffé as well as of other foreign ships in the Admiralty Bay is not uncommon during this period. Thus samples collected during winter period at Ferraz probably constitute a more reliable set of data for trace elements study than those collected during the busier summer period.

Table 2 shows the averages and the corresponding standard deviations of the sea salt derived Na and Cl, and the soil dust derived Al and Mn obtained for the winter period operations of 1986 and 1987. The average results of the remaining trace-elements are shown in Table 3. With the exception of V all trace-elements in Table 3 were determined using the 24 hour irradiation time procedure. The long irradiation time was only available for the year of 1986 due to time and budget restrictions for the use of the nuclear reactor. The concentrations of V were measured for both 1986 and 1987 but the entire year of 1987 presented results below the detection levels for this technique.

Certain trace-elements suffered the effects of interfering peaks in some samples during the NAA procedure. These results were, of course, not used in this study. The potassium, for example, suffered a strong interference of ^{24}Na which prevented the determination of K in most of the samples. For this reason the time series of K is not reported here, and the remaining reliable K determinations were used only for averaging comparisons.

For the sake of comparison Table 2 also shows the results of local atmospheric radon, atmospheric temperature, and wind speed. Radon data were obtained for the same period at Ferraz and appear to be a good tracer for air masses which have performed part of its trajectory over the S. American continent (Pereira, 1989).

The time series of these determinations are shown in Figures 1 through 5. Figures 1 and 2 are for the two years of observations. Vertical scales are logarithmic whenever large changes of more than a decade were observed in data points. Figures were drawn by simply connecting the observation points by straight lines, with exceptions of Figure 2 for Rn, wind, and temperature. In these cases, a running mean average of 7 days were taken before plotting the curve. This was made in order to eliminate the very short period fluctuations of these data. These rapid fluctuations cannot be registered by the aerosol data due to the long sampling time, thus they are useless for comparison purposes between the time series.

DISCUSSIONS

Winter period averages for the terrigenous elements Al and Mn decreased by more than 60% in 1987 with respect to 1986 as shown in Table 2. The V also decreased to values below the detection limits of the method in all 1987 samples. The same discrepancy was also observed for surface wind intensity and atmospheric radon. Averages for sea-salt components Na and Cl, on the other hand were subjected to a smaller 22% decrease from one year to another. Mean surface air temperatures were virtually the same in these two periods.

With the exception of Al a broad relative maximum is observed during summer. The aluminum had probably its maximum masked by the high concentrations observed for the entire year of 1986.

Compared to aerosols collected in other antarctic stations, the two year averages of the terrigenous elements (Al = 17.7 ng m^{-3} and Mn = 0.33 ng m^{-3}) were about 30 times higher than values found by Zoller (1974) for the South Pole (Al = 0.57 ng m^{-3} and Mn = 0.010 ng m^{-3}) and by Wagenbach et al. (1988) for the Georg von Neumayer Station, in the Ekström ice shelf at 70°S ice shelf (Mn = 0.011 ng m^{-3}).

In addition to the direct influences of the aerosols from the major continental mass of South America, which is located only about 800 km NW of Ferraz, it is difficult not to consider the possibility of an effective local supply of soil dust aerosols at Ferraz. Notably, there are major differences in the terrain where these stations are located. Ferraz was erected over rock basement while the two other stations lay directly over ice. Nevertheless, bare rocks and soils at King George island are restricted to only part of the coastline and comprises less than 1% of the total area of the island during summer, which imposes some doubts on this issue. During the winter to late spring months even these coastal zones are covered by layers of ice and snow of variable thickness. A few rock formations with steep slopes (volcanic necks and "nunataks") are permanently swept clear of snow by winds but they constitute only a minor part of the area. These exposed rock surfaces, however, may have contributed with small amounts of terrigenous aerosols due to the abrasive effects of the ice particles on the rock surfaces during events of very high winds. Otherwise, most of the

terrigenous aerosols observed during the winter months were most likely transported via troposphere from distant sources. The primary source of terrigenous aerosols and atmospheric radon are the continental masses further north. Thus, the association of a large amount of these trace elements and high radon concentrations in 1986 as compared to that of 1987 suggests that the direct tropospheric transport by air masses that have performed part of its trajectories in the S.American continent was more effective during 1986.

The Na and Cl time series of Figure 1 showed a much definite change in concentrations from summer to winter periods, notably during the year of 1987. Our results show a broad minimum concentration of sea spray derived Na and Cl around June and August, in agreement with Wagenbach et al. (1988) for sea-salt derived aerosols data collected at the coastal station Neumayer. Nevertheless, the maxima observed at Ferraz extended from January to April while Wagenbach's data showed a much sharper maximum occurring earlier in November to December. Wagenbach's data also display a much larger difference in concentration between summer and winter.

Most often the sea salt derived Na and Cl in coastal antarctic stations are primarily associated to locally produced sea spray as indicated by the Na to Cl ratios very close to that of sea water. Nevertheless, the sea ice in the King George Island area does not develop permanently until early August and does it in a relatively short period of time compared to the observed slow change in the time series of Figure 1. There are, of course, brief formations of transitory sea ice during very calm days, but this ordinarily occurs inside protected seas and bays of the island and disappears as fast as they are formed. Thus, the sea spray observed at Ferraz must have an effective contribution from a much larger area that includes also the sea further to the south, where permanent sea ice starts earlier in the year, in order to explain the relatively slow change of these constituents.

Although the major inorganic components Na and Cl in the aerosols had the same relative concentrations of the sea waters, the other sea spray inorganic components were subjected to several degrees of fractionation. Table 4 presents the enrichment factors of the measured elements with respect to the sea water. With the noteworthy exception of Br all others sea spray derived elements were enriched in the aerosols by factors proportional to their atomic weights. This effect has been described by other authors in several coastal stations, including in the Antarctica (Kombayasi, 1962). The reason for the discrepant behavior of Br is not known.

The other trace-elements measured in Ferraz were divided into three major groups, based on the general tendency of their concentration time series. The metals Sb and Zn (Figure 3) exhibit the same general behavior of the elements in Figure 1, with minimum concentrations during winter and maximum during summer. Potassium could perhaps be included in this group but due to the analytical problems already pointed out in this report there is a lack of sufficient reliable data to support this assumption.

These metals are primarily associated to the anthropogenetic industrial activities. Local contaminations of these elements by the activities of the Station are doubtful since they cannot explain the minimum concentrations during winter. Furthermore, it is not evident whether the observed isolated high concentration events could be attributed to the incineration of the waste of the Station or not. Waste incinerated in Ferraz includes only food remains and paper products scraps. Plastic, metal wastes, and all other materials are packed and returned by ship to Brazil. Moreover, this burning was systematically made every week and only when winds were such as to prevent the smoke residuals to reach the Atmospheric Science Laboratory, otherwise pumps were turned off during the entire burning routine.

The presence in the same King George island of 9 other scientific stations and military bases, however, does not preclude the possibility of local trace metals contaminations since we do not know the precautions taken by these other stations with respect to their waste disposal.

A second group of trace elements exhibited a general tendency of decreasing concentrations during the year (Figure 4). This class includes Br and V. Although the most probable source of Br in the Antarctica is the sea-spray, its behavior seems to disagree with this assumption for two reasons: it is depleted in the aerosols with respect to the sea water (enrichment factor = 0.65 in Table 4), and its concentration decreases with time during the year instead of presenting a minimum during winter time like Na and Cl. Vanadium was also measured *in the samples* collected during 1987 but showed concentrations that were below the detection method in all cases. An explanation for these two discrepancies is not known.

The third and last group of elements is represent by those elements that did not presented a definite trend, showing a more or less constant level throughout the year or a doubtful trend. This is the case of Ca and Fe, and perhaps Au, La and Sc (not shown) although these last

three elements showed a discrete tendency for a minimum during winter.

CONCLUSIONS

The average soil dust trace elements Al and Mn in the aerosols collected at Ferraz during 1986 were considerably higher than for the same period in 1987. The time series for these elements displayed a tendency to a minimum during winter months. However, the concentrations of Al in 1986 were systematically high somewhat masking this minimum trend. A potential source for this presumed anomaly was the abrasion of suspended ice particles and wind on the bare rock surfaces of the nunatacks and volcanic necks of the island. Frequent episodes of high winds registered during this first year of observations corroborate this assumption.

The sea spray components Na and Cl had about the same ratio of sea waters. An enrichment in proportion to the respective atomic weight was observed in the aerosol with respect to sea water for these two elements and also for K and Ca. Unlike the soil dust derived Al and Mn, the Na and Cl did not reveal a marked decrease in concentration between 1986 and 1987, whereas the tendency for a minimum during winter was present in both years.

High mean values of atmospheric radon in 1986 compared to 1987 are in agreement with the mean results for the soil dust derived Al and Mn. The time series of radon, however, did not exhibit any tendency for minimum concentrations during winter months.

The other measured trace elements were classified according to the nature of their time series. Antimonium and Zn displayed the same minimum trend during winter as the soil dust and the sea spray aerosol components. Anthropogenetic activities are generally attributed to these elements but apparently not from the station's activities. In addition, the natural minimum trend during winter could not be explained in terms of local sources.

Bromine and V exhibited a clear tendency of decreasing concentration during the year. Bromine, in addition, was significantly depleted in the aerosols with respect to the sea water source.

The remaining measured trace elements, Ca, Fe, Au, La, and Sc did not display any clear trend during the year.

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Trace Elements	Detection Limit (ng)	Analytical Precision (%)
La (7)	500 x 10-3	10.6
Sb (19)	200 x 10-3	13.1 - 24.8
Au (8)	10 x 10-3	31.2
V (2)	2	2.7
Mn (10)	2	1.6 - 5.1
Br (12)	2	4.8
Zn (9)	10	4.9
Sc (8)	20	4.1
Al (4)	40	5.3
Na (11)	200	3.8 - 5.8
Fe (22)	200	5.7 - 8.2
Cl (8)	700	6.2
K (12)	1000	6.6
Ca (10)	2000	5.8

TABLE 1 - Limits of detection and analytical precision of the employed NAA method. The figures were calculated by using two international reference standard samples (Loureiro, 1989).

	1986	1987
Na	1111 + -486(34)	866 + -537(33)
Cl	2048 + -902(34)	1614 + -980(33)
Al	26.0 + -12.7(34)	9.5 + -5.6(33)
Mn	0.41 + -0.44(34)	0.15 + -0.07(26)
V	0.30 + -0.14(34)	< 0.15
Rn	0.026 + -0.018	0.014 + -0.008
Wind	7.2 + -6.0	5.0 + -4.1
Temp.	-5.0 + -6.0	-4.7 + -5.9

TABLE 2 - Averages of soil dust and sea spray in the aerosols of 1986 and 1987. Results for mean atmospheric radon (Bq m^{-3}), wind velocity (m s^{-1}), and temperature (^{o}C) are also shown for comparison.

Trace-Element	Concentration (ng m^{-3})
Ca	224.5 + - 174.4 (31)
K	116.9 + - 151.6 (17)
Fe	24.81 + - 7.36 (34)
Zn	5.17 + - 7.22 (34)
Br	4.07 + - 2.20 (34)
La	(30.01 + - 18.67) x 10-3 (27)
Sb	(15.79 + - 14.57) x 10-3 (33)
Au	(3.44 + - 2.75) x 10-3 (34)
Sc	(3.39 + - 1.32) x 10^{-3} (33)

TABLE 3 - Averages of trace elements measured in the 1986 aerosols. The V was also measured in 1987 and showed concentrations below the limit of detection of 0.65 ng m^{-3}.

Element	Enrichment Factor
Na	1.00
Cl	1.02
K	3.87
Ca	6.00
Br	0.65

TABLE 4 - Enrichment factors of sea spray derived elements in the aerosols with respect to the sea water composition. The Na was used as the reference ion in the calculations.

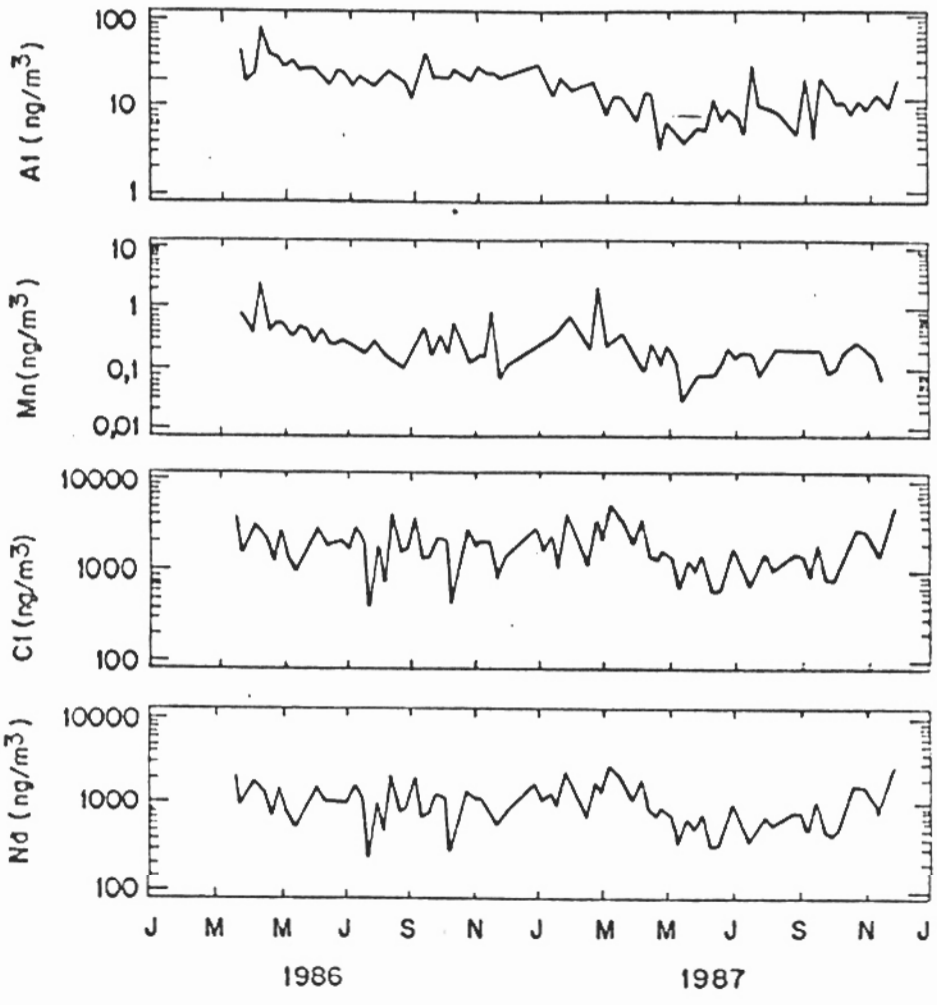

FIGURE 1 - Time series of soil dust components Al and Mn, and sea spray components Cl and Na for the two years of data acquisition.

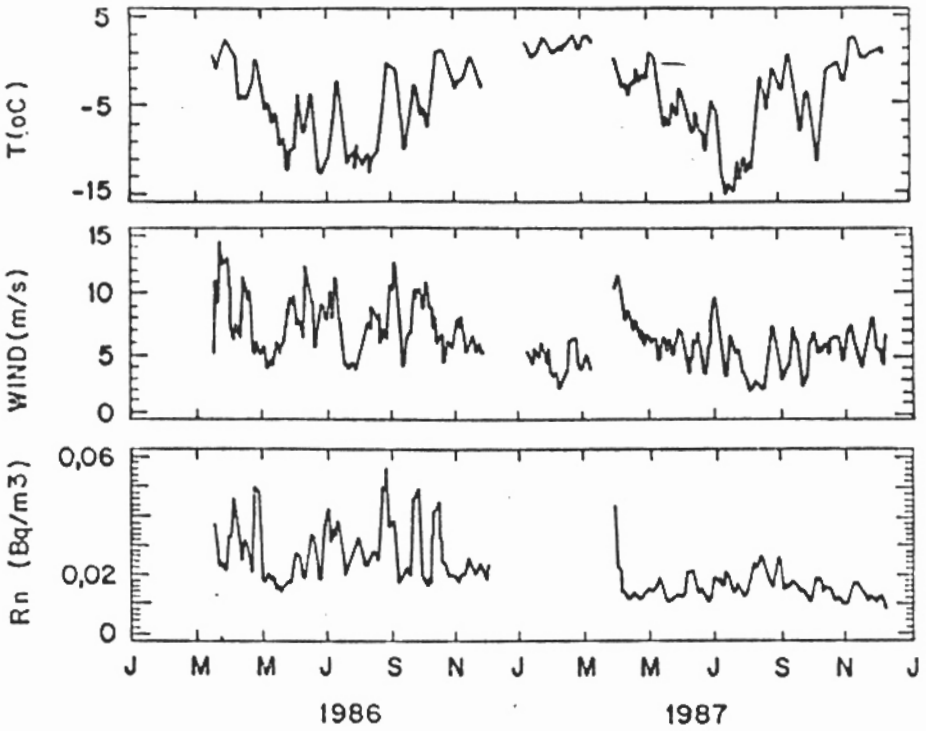

FIGURE 2 - Time series of the 7 point moving averages of atmospheric radon, wind velocity, and temperature.

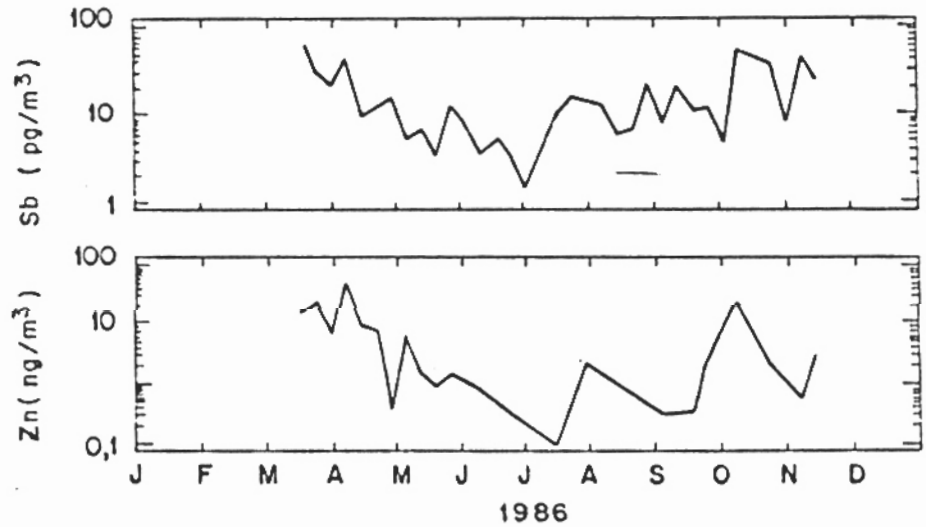

FIGURE 3 - Time series of trace metals Sb, Zn from filters collected in 1986. These trace-elements exhibited a tendency of minimum concentration during winter.