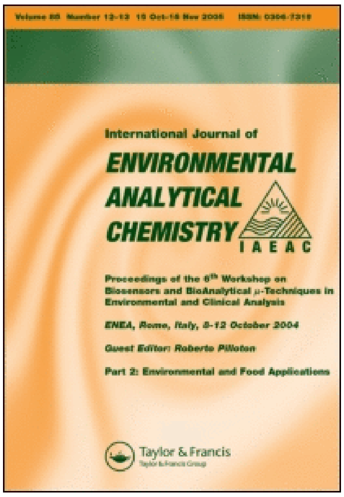

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A PRELIMINARY CHARACTERIZATION OF THE ELEMENTAL COMPOSITION OF THE AEROSOL COARSE FRACTION AT TERRA NOVA BAY (ANTARCTICA) DURING THE 1990–91 AUSTRAL SUMMER

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Aerosol sampling was performed at Campo Icaro, in the vicinity of the Italian Base at Terra Nova Bay, in the period between November 1990 and February 1991. The duration of the sampling intervals was approximately 12 hrs and a special aerosol sampler was used, with separation of the coarse fraction from the fine ($\phi_{aer} < 2.3$ μm) fraction. We will present the aims and methods of the experiment as well as the results of the PIXE analysis of 51 samples of the coarse fraction, collected on Nuclepore filters.

Mean values and standard deviations of volume concentrations (ng/m^3) are given for the following elements: Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br.

KEY WORDS: Aerosol, Antarctica, multielemental composition, troposphere.

INTRODUCTION

Relatively little is known about the atmospheric aerosol in the Antarctic region, even though this region is in fact an essential part of the global earth system. Being far removed from anthropogenic sources, the Antarctic region is an ideal place for the observation of natural aerosols and for understanding their roles on a local, regional and global scale. On the other hand, since relatively little aerosol is produced locally, studies performed in Antarctica should allow the observation—essentially in the "fine" fraction—of aerosols produced elsewhere[1], a fact which could also be interesting in connection with problems of "global monitoring". However, some difficulties exist concerning the determination of the origin of the air masses, due to specific aspects of the Antarctic atmospheric circulation.

A succinct review of the main roles of the Antarctic aerosols and of the main research problems in this field has been recently published[2]. Here we will present those aspects of direct interest for our research.

The major components observed[1] in Antarctic aerosol are: "natural sulfate" aerosol, "sea salt" aerosol, "crustal" aerosol, meteoritic aerosol[1]. The annual cycles of the C.N.'s (condensation nuclei) observed at the South Pole, and the evidence that the C.N.'s are correlated to sulfate containing aerosol[3] may suggest a possible connection between such a cycle and the cycle of solar radiation[3,1]. On the other hand, the sulfate concentration seems too high to be explained by volcanic emissions only. The above arguments indicate that the Antarctic region may be an interesting place for the study of the natural sulphur cycle, in relation to the possible marine origin of the gaseous precursors of the sulfates, (as produced by marine biota) and also in view of possible feedback mechanisms in the climatic system. Most of the non-sea-salt sulfate containing aerosols should be associated with the fine fraction ($\phi_{aer} \leq 2$ μm).

The above picture is also supported by the data on non-sea-salt sulfates (n.s.s.s.) obtained at the German Antarctic Research Station[4] in a coastal site. These data display strong seasonal dependence, with striking summer maxima of n.s.s.s. concentration. Seasonal effects were also observed in n.s.s.s. (fine fraction) in the Antarctic Peninsula[5], well inside the Ocean.

The sea salt component associated with marine spray, as observed at the South Pole, appears mostly during limited time episodes ("sodium storms")[1,3]. On the other hand, in a peripheral region, i.e. the Antarctic Peninsula, sea salt aerosol is the dominating aerosol component[5,6]. Most of the sea salt aerosol there is associated with the coarse fraction, even though the sea salt component is quite significant in the fine fraction. As concerns the specific site of Terra Nova Bay, an individual particle analysis has been published[7] which concerns a few hundred particles with $\phi \geq 1.0$ μm. The data display a significant presence of Na and/or Cl, which can be considered to be tracers of marine salt. Crustal particles were also observed.

At the German station, a maximum concentration of sea salt aerosol during the austral autumn is reported, while no clear spring minimum is reported[4]. The same authors also suggest that a rather uniform distribution of the mineral aerosol component may be expected in the upper troposphere over Antarctica.

The components of direct or indirect marine origin (n.s.s.s. and sea salt) are both essential components of the Antarctic aerosol system and it is important to investigate their properties and behavior in connection with the biogeochemical cycles and with the climatic system, as well as with transport problems at various scales. Furthermore, as remarked by Artaxo[5], data from various sites at the edge of the Antarctic continent are required in order to improve our understanding of the overall continental Antarctic aerosol chemistry.

Terra Nova Bay, situated in the Ross Sea region, where the Italian base is located, appears to be an interesting place for effecting a study of both aerosol components.

Within the above outlined framework, it is interesting to perform experiments which allow the determination of the elemental composition of the aerosol, and to try to establish its correlation with the meteorological parameters. A knowledge of the elemental composition may allow the statistical determination of the "principal components" of the aerosol, allowing one to connect the intensity and properties of such components with the origins of the air masses.

A further element of interest in the study of the Antarctic aerosol is connected to the problem of the interpretation of the ice records of the past: the aerosol particles initially deposited in the snow, and subsequently included in the ice, carry some significant information on the atmospheric composition, and thus on the climate, at the time of the deposition. From this point of view, once again, it may be interesting to investigate the relationship between composition of the aerosol and origin of the air masses.

The above mentioned points are at the origin of an experiment performed in the austral summer months (November to February) during the 1990–91 campaign, at the "Campo Icaro" site, near the Italian base. The principal aims were the following:

(1) to perform separate sampling of "fine" ($\phi_{\text{aerodyn}} \leq 2.3$ μm) and "coarse" aerosol fractions;

(2) to perform relatively short (~12 h) sampling in continuous time sequence. This feature should allow evaluation of correlations between the multielemental structure of the aerosol and air mass origin and properties;

(3) to determine the elemental composition (in particular, by means of PIXE analysis) of the aerosol samples. Absolute elemental concentrations (ng/m^3) vs. time and thus ratios of elemental concentrations vs. time, and correlations of elemental concentrations should be obtained for both aerosol fractions;

(4) to describe with a model atmospheric circulation by using both meteorological data from three sets of stations ("IFA", "ENEA", "American stations"), on different space scales, and orographic data. This feature should help to isolate homogeneous meteorological episodes, as well as to determine the possible influence of local contamination sources and, in a later phase, also help to determine air mass properties and possibly (at least to some extent) air mass trajectories;

(5) to try to perform a multivariate analysis of the elemental data (principal component analysis, factor analysis) in order to try to separate the contributions of different aerosol populations and sources; to perform comparisons of concentration ratios with relatively "known" elemental source profiles, in particular from geochemical data (sulfates as "signed" by sulphur; sea-salt component; crustal component; others). Attention should also be devoted to the possible presence of local contamination;

(6) if one, or several, components (in particular sulfates) are separated, to then try to determine their origin, at different space and time scales (by using the data obtained from point (4)) and to get an indication on production and/or interaction, as well as transport properties.

We want to stress here that the basic difficulties in an experiment of this type arise from the very low level of aerosol concentration, and thus from the low level of the mass of the available samples (with short sampling times) for chemical analysis. We tried to partially confront this problem by using a special aerosol sampler.

In a previous article[8], we presented the preliminary results concerning only the fine fraction of the aerosol. In what follows, we present corresponding and complementary results concerning the "coarse" aerosol fraction. A multivariate analysis of the elemental data in terms of "principal components", as well as connections with atmospheric circulation, will be presented at a later date.

EXPERIMENTAL

Sampling site and sampling procedures

Campo Icaro (lat. 74° 42′ 43″ S, long. 164° 06′ 58″ E)—the best solution available to us in 1990/91—is relatively far from the main base, (~3 km south) and not much contamination is expected from the base. The distance of the sampler from a local power generator was 150 m and the sampler was installed upwind with respect to the prevailing wind directions. Local contamination cannot be completely excluded a priori. However, important information on possible contamination can be obtained by means of measured concentration levels (or upper limits) of elemental tracers (e.g. element V) by means of published and/or measured contamination source profiles (e.g. "Residual oil"[9]), and with the help of local circulation data.

A chemical laboratory, with a laminar flow hood, was installed and used near the aerosol sampler.

Aerosol sampler

A special sampling device[10] was designed and built for the present experiment with the following features:

(a) relatively high air flow: (~14 m^3/h);

(b) three basic parts of the sampler, namely the inlet stage, the impaction stage and the final filtering stage, are all located inside a horizontal rigid component, which is free to rotate following the wind direction.

(c) a special fluidodynamic design of the inlet stage, the direct connection of this stage with the impaction stage and the above mentioned freedom of rotation, ensure a good representation of aerosol diameter spectrum up to high wind speeds and large aerosol diameters.

(d) an impaction stage for the collection of the "coarse" ($\phi_{aer} \geq 2.3$ μm) aerosol fraction. Both the inlet stage and the impaction stage have a rectangular cross section, 90 mm high, thus a rectangular deposit of aerosol particles is obtained by impaction, with an area of ~90 × 2 mm^2. The aerosol deposit is collected on a vertical rectangular Nuclepore membrane (8 μm porosity), with an oleic acid solution coating, to avoid particle rebouncing[11].

(e) The "fine" fraction is collected on a circular ($\phi \approx 12$ cm) Nuclepore membrane with 0.45 μm porosity. The large membrane dimensions allow internal consistency checks and various possible types of analyses, by using different pieces of the membrane.

(f) The above mentioned rigid component (see b), with the inlet stage and the two membrane holders (d, e), can be removed from the main body of the apparatus, closed and taken to the laboratory for membrane exchange. This feature avoids contamination on the field.

(g) The dimensional separation properties of the instruments are expressed by the collection efficiency curve of the impaction stage versus the aerosol aerodynamic diameter, ϕ_{aer}. An experimental curve has been obtained[12] for liquid aerosols impacting on dry Nuclepore membranes. From the curve, one can particularly determine the 50% cutoff diameter, which is about 2.3 μm, at the present flux value, and the asymptotic value of the collection efficiency, which is about 100%. Also, the shape of the curve corresponds well to the one computed via a fluidodynamic model.

(h) The above mentioned use of liquid aerosols (in the determination of the collection efficiency curve) should minimize possible losses due to particle rebouncing on the impaction surface. Therefore, the experimental results express the separation properties of the instrument from a fluidodynamic point of view. However, in the case of solid aerosols—which more realistically corresponds to our situation on the field—a reduction of efficiency is expected, due to rebouncing effects.

Considerable improvements can be obtained for solid aerosols[11], if a porous impaction surface is covered with an adequate liquid solution. In the present experiment we followed a procedure similar to the published ones[11] and used 8 μm porosity Nuclepore membranes (vs. the quoted 10 μm porosity), covered with a 20% solution of ultrapure oleic acid in hexane, with an areal density of 4.5 μl/cm^2. Also, the average velocity of the air in the jet through the impaction stage, and thus the kinetic energy of the aerosol particles, were comparable to those used in the measurements[11] by Turner *et al.* Furthermore, it should be noted that the effective areal density of the aerosol deposit is so low that only a small fraction of the total surface, potentially available for deposit, is covered by aerosol particles.

For the above reasons, we are presently using the published value (ref. 15, Figure 6) for the sticking efficiency, about 0.9, as obtained for monodisperse 1.45 μm particles. However, a direct measurement of the overall collection efficiency in the actual conditions of our device is being planned.

Handling of the Nuclepore membranes

Each rectangular membrane was cut out of a standard rectangular membrane (8″ × 10″) in our laboratory in Legnaro; it was put in a dedicated rectangular box; its extremities were fastened therein and the box was sealed.

In Antarctica, the membranes were extracted from the above mentioned boxes, they were covered with the oleic acid solution and were installed in the appropriate holder of the sampling device. At the end of the sampling operation, the "exposed" membrane was again put in its own box, its extremities were fastened therein and the box was sealed. Before PIXE measurement, each rectangular membrane was extracted from its box, cut into three pieces, and each piece was installed in one of our standard frames. All the above operations were performed (both in Legnaro and in Antarctica) under a filtered air, laminar flux hood. The sealed boxes were kept at a temperature of −30°C within larger containers in Antarctica, during the journey and in laboratory. Both in Legnaro and in Antarctica, a set of blank membranes was submitted to the same cutting, installation, removal and oil coverage procedures performed for the sampling membranes. In Antarctica, the operations on such blank membranes were performed at regular time intervals, during the sampling period.

PIXE multielemental analysis of the "coarse" fraction

An absolute measurement of the elemental areal densities (ng/cm^2) of the aerosol deposited over Nuclepore membranes was performed with the "Fisamb" PIXE set-up[13] at the AN 2000 accelerator in the "Laboratori Nazionali di Legnaro" of the INFN Padova, Italy. Proton energy was 1.8 MeV, and the use of an X-ray, *mylar* "funny" filter, 50 μm thick, allowed the simultaneous measurement of all the elements in the X-ray spectrum.

For measurement and analysis of coarse fraction samples, the three pieces obtained from each original membrane were measured separately by PIXE, using a 20 μC total proton charge. The counting rate was <1000 s^{-1}

The corresponding PIXE spectra were subsequently added together and the resulting spectrum was used to get the basic elemental data. One piece (over three) of each original membrane was also remeasured by using a 100 μm thick *mylar* filter, to evaluate possible "pile-up" effects.

The spatially homogeneous proton beam was the same used previously for measuring the fine fraction samples; its cross section at the target plane was a circle, 15 mm in diameter, and the aerosol deposit was aligned with a diameter. In this way, by using three pieces of each membrane, an overall length of 45 mm of the aerosol deposit (i.e. one half of its total original length) was explored.

Good consistency among the *PIXE* data concerning the three different pieces corresponding to the same original membrane was observed.

Due to the focusing effect of the impaction stage, in this case the areal density of the aerosol deposit is much larger with respect to a homogeneous collection on a filtering membrane and thus with respect to the fine fraction samples as well. The signal to background ratio is correspondingly improved for most elements and better detectability of the elements is expected. It should also be mentioned that the beam diameter is larger than the membrane width (10 mm), and thus slightly decreases the level of the background spectrum.

Elements detected and minimum detection limit

(a) No peak was observed for Na and Mg by direct inspection of the PIXE aerosol spectra. This fact is quite compatible with the low sensitivity of our set-up at low X-ray energies and we must consider these elements undetectable in the present experimental conditions.

(b) The X-ray spectra obtained from blanks and aerosol samples were fitted by the *SESAMX* program[14,15] for 17 elements: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br. Due to the low areal densities of the deposits, the problem of the correct representation of the continuous background *bremsstrahlung* spectrum under the elemental peaks was quite critical. The best results were obtained by using the experimental shape

Table 1 Columns A and B: areal densities (ng/cm^2) on the blanks (see also text); M: average value; σ: standard deviation. Column C: M.D.L. (ng/m^3) as obtained by multiplying 3·σ by the area of the membrane and dividing by the standard volume of 180 m^3. The asterisk means that the element was not present in the blank, and therefore the M.D.L. was obtained by the spectra fitting program *PIXAN.*

	PROPERTIES OF THE BLANKS		*MDL*
ELEMENT	*(A)* *M* *ng/cm^2*	*(B)* σ *ng/cm^2*	*(C)* *ng/m^3*
Al (*)			0.9
Si	62.	16.	3.
P (*)			0.5
S	10.0	1.8	0.3
Cl	43.4	5.1	0.9
K	4.47	0.65	0.1
Ca	4.	1.6	0.3
Ti	1.32	0.28	0.05
V (*)			0.05
Cr	2.51	0.67	0.1
Mn (*)			0.04
Fe	9.	11.	2.
Co (*)			0.04
Ni (*)			0.1
Cu	1.11	0.19	0.03
Zn (*)			0.1
Br	14.1	1.1	0.2

of the spectrum, as determined by averaging the results from several "clean" blanks (i. e. blanks not submitted to the above outlined field and laboratory routine handling), after cancellation of the elemental peaks corresponding to impurities, rather than by representing that shape by means of mathematical treatment (as in the normal *SESAMX* procedure).

(c) No detectable amount was observed in our reference blanks for the elements Al, P, V, Mn, Co, Ni, Zn and the M.D.L. (minimum detection limit) value (ng/cm^2) was obtained for these elements by using the X-ray fitting program *PIXAN*[16,17].

(d) For the remaining elements (Si, S, Cl, K, Ca, Ti, Cr, Fe, Cu, Br) considered in the present analysis, peaks due to impurities or contaminations were observed in the reference blanks. The corresponding areal densities (ng/cm^2) were determined by means of the program *SESAMX*. We used the mean values, M, of the areal densities of these elements for the set of reference blanks for background subtraction purposes, and the corresponding standard deviations, σ, for defining the aerosol elemental detection thresholds. Table 1 displays the values of M and σ.

(e) We define the areal density, A, of an element in a given aerosol sample, as the areal density, *P*, corresponding to its peak (as measured in the spectrum), minus the mean value *M*, introduced above

$$A = P - M$$

and we consider that an element is detected if $A > 3\sigma$. Correspondingly, the M.D.L. value is defined, for the elements listed above in point c), by putting:

$$\text{M.D.L.} = 3\sigma.$$

A negligible contamination of background events is expected to survive this cut, at least if we assume that our limited set of reference blanks is fully representative of the background and that the distributions are gaussian.

(f) For each element and each sample, aerosol density (ng/cm^2), as obtained in d), and the M.D.L. value (ng/cm^2), as obtained in b) or d), were respectively converted to concentration (ng/m^3) and volume M.D.L. value (ng/m^3) by using total air sampling volume (m^3), beam cross section and ratio of total length of deposit to beam diameter. The value was corrected for a factor 1/0.9, taking into account the sticking efficiency, as described in point h of the section "Aerosol sampler".

(g) Peaks with energies and widths compatible with the $K\alpha$ line of the element Vanadium were observed in 49 samples. A different interpretation, however, was also compatible with the same data, i.e. a pile-up effect of the characteristic photons of the elements S and Cl. As a check of the second hypothesis we remeasured one piece (over three) of each of the original membranes by using a *mylar* X-ray filter (100 μm thick) in front of the detector, in order to absorb 80% of the S photons, most of the Cl photons but only a small fraction of the V photons. Under these conditions, the reduction of the S peak was accompanied by the disappearance of the V peak. We conclude, therefore, that the counts in the "V" peaks must be entirely attributed to a pile-up effect, so that element V is not observed in our samples.

(h) In the experimental conditions described above in point g), in addition to the complete removal of the "V" counts, we also noticed a reduction (22 % on average) of counts in the $K\alpha$ "Ti" peak. The reduction was again attributed to the removal of a pile-up effect. It was thus possible to obtain a correction factor, sample by sample, of the areal density of Ti, thus allowing the elimination of the pile-up effect and resulting in the effective areal density of this element.

RESULTS AND DISCUSSION

"Coarse" fraction aerosol samples

Sampling period and sampling conditions were exactly the same as previously described[8] for the "fine" fraction. The sampling period extended from November 15th, 1990, to February 8th, 1991. Sampling was interrupted on a few occasions, either because of technical difficulties or bad weather, but the general approach was to sample and measure as much as possible, and to possibly cut some data after careful analysis of the meteorological or environmental data (e.g. danger of local pollution). In this way, a priori, systematic cuts were minimized. 89 coarse fraction aerosol samples were obtained. Unfortunately, 38 samples, corresponding to the initial period (until December 13th), were damaged in a transport accident. Therefore, only 51 samples, corresponding to the period from December 13th, 1990, to February 8th, 1991, were available for analysis. For the same reason, the number of available blanks was reduced to 6. The blanks were submitted to the previously outlined procedures, at regular time intervals, during the entire sampling period. 38 aerosol samples correspond to approximately sampling intervals of 12 hours and 13 samples to 24 hour intervals. The set of 51 samples and 6 blanks is the basic set for measurement and analysis of the "coarse" fraction. We would like to remark however, that we have not taken into account, at the present state of the analysis, the meteorological data (and the derived data on the atmospheric circulation) which need further work. Such data would be necessary for a better definition of the set of samples to be used in a careful analysis and, later, in the search for possible correlations. For the above reasons, the results concerning the "coarse" fraction samples, presented below, are necessarily preliminary in nature.

Elemental concentrations

The values of the average concentrations (ng/m^3) and their standard deviations for 15 elements (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br) are presented in Table 2. Column A displays the number of samples in which each element was detected. Due to the fact that certain elements were not detected in all samples, and that we wish to obtain average values relative to the whole set of 51 samples, these values were computed under two extreme hypotheses. In the first case (Column C), we assumed that the value of its concentration was equal to zero in all samples in which an element was undetected. In the second case (Column D), we assumed that its concentration was equal to the corresponding M.D.L. value.

At this stage, it would be useful to make several comparisons with the corresponding data previously obtained on the fine fraction of the aerosol[8]. A comparison between the data displayed in the two corresponding tables of the two papers (Table 2, Column A, in both cases), shows that in the present case most elements under consideration are observed in a much larger fraction of samples and that one element (Al) was not observed at all in the fine fraction.

Since the average values of the atmospheric concentrations (ng/m^3) are similar or smaller (Columns C and D) in the present case, the above mentioned fact is explained by the increased sensitivity due to the focalizing effect of the impaction stage. As a significant consequence of the fact that the major elements are present in most coarse fraction samples, a principal component analysis turns out to be possible and is currently being carried out.

Concerning the roles of some particular elements, it is worth noting a considerable reduction (one order of magnitude) in the average level of S, which was widely dominating in the fine fraction. On the other hand, Cl appears to be the dominating element in the coarse fraction, and is observed in about 90% of samples (to be compared with less than 20% in the fine fraction). The fact that the level of V (a possible tracer of contamination sources) is under the detection threshold is significant in itself, as well as in view of the use of elemental profiles of possible contamination sources.

Since Co, Cu and Br are detected only in a relatively small fraction of samples, and since their detection depends critically on the M.D.L. values, the results concerning these elements should be considered to be marginal.

Table 2 Elemental concentrations (ng/m^3). A correction factor of 1.11 was applied, taking into account particle sticking efficiency; also, data for Ti are corrected in order to eliminate pile-up effects (see also text).

(A) Number of samples in which the element was detected (see text).

(B) Maximum detected concentration.

(C) Average concentration (ng/m^3) and standard deviation for the whole set of 51 samples. Whenever an element was not detected in a sample, its concentration was set equal to zero (see also text).

(D) Average concentration (ng/m^3) and standard deviation for the whole set of 51 samples. Whenever an element was not detected in a sample, its concentration was set equal to the M.D.L. (see also text).

ELEMENT	*(A)*	*(B)* ng/m^3	*(C)* ng/m^3	*(D)* ng/m^3
Al	30	27.9	4.6 ± 6.0	5.3 ± 5.7
Si	35	49.8	8. ± 10.	9.2 ± 9.2
S	50	39.4	12.0 ± 9.6	12.0 ± 9.6
Cl	45	452.	90. ± 100.	90. ± 100.
K	49	12.8	3.3 ± 3.0	3.3 ± 3.0
Ca	51	27.0	9.3 ± 6.7	9.3 ± 6.7
Ti	50	5.3	0.72 ± 0.80	0.72 ± 0.80
Cr	48	2.3	0.76 ± 0.53	0.77 ± 0.52
Mn	48	0.84	0.19 ± 0.15	0.19 ± 0.15
Fe	46	36.0	8.0 ± 7.1	8.3 ± 6.8
Co	5	0.200	0.009 ± 0.034	0.053 ± 0.030
Ni	40	1.87	0.25 ± 0.36	0.26 ± 0.35
Cu	16	4.08	0.17 ± 0.64	0.19 ± 0.63
Zn	38	2.58	0.23 ± 0.42	0.25 ± 0.41
Br	19	1.13	0.15 ± 0.25	0.30 ± 0.19

CONCLUDING REMARKS AND PERSPECTIVES

An aerosol sampling device, allowing the separate collection of fine and coarse fractions, was operated during relatively long and continuous time sequences, mostly in 12 hour sampling intervals. The coarse fraction samples were collected by impaction. PIXE multi-elemental analysis of the samples allowed the detection of ten major elements in most samples, despite the low concentration levels.

At the present preliminary state of the analysis, we observe a very different situation with respect to our corresponding and previously published fine fraction data. In particular, the fine fraction Sulphur dominance has disappeared and Chlorine now appears to be somewhat the dominating element.

We anticipate here that the availability of data concerning several elements will allow a multivariate statistical analysis, which will be published at a later date. This analysis will concern identification of principal components, as well as determination of elemental profiles and of time dependence of each individual component. Further work is in progress on meteorological and derived atmospheric circulation data.

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References

1. G. E. Shaw, *Rev. Geophys.*, **26**, 1, 89–112 (1988).
2. B. A. Bodhaine, L. A. Barrie, R. C. Schnell, G. E. Shaw, and J. K. McKie, *Tellus*, **44B**, 250–251 (1992)
3. B. A. Bodhaine, J. J. Deluisi, J. M. Harris, P. Houmere, and S. Bauman, *Nucl. Instr. and Meth.*, **B22**, 241–247 (1987).
4. D. Wagenbach, U. Görlach, K. Moser, and K. O. Münnich, *Tellus*, **40B**, 426–436 (1988).
5. P. Artaxo, M. L. C. Rabello, W. Maenhaut, and R. Van Grieken, *Tellus*, **44B**, 318–334 (1992).
6. P. Artaxo, F. Andrade, and W. Maenhaut, *Nucl. Instr. and Meth.*, **B49**, 383–387 (1990).
7. G. Santachiara, F. Prodi, and M. Tagliazucca, *SIF: Conference Proceedings Vol.* **20**: *Italian Research on Antarctic Atmosphere* (M. Colacino, G. Giovanelli, and L. Stefanutti eds., Bologna, 1989).
8. P. Mittner, D. Ceccato, S. Del Maschio, R. Cini, and U. Giostra, *Ann. Chim.* (Roma), **81**, 605–613 (1991).
9. W. Maenhaut *et al.*, *Atm. Env.*, 24B, **3**, 419–435 (1990).
10. V. Prodi, F. Belosi, G. Bettazzi, and S. Agostini, *Set-up and manufacture* by "Lavoro e Ambiente", Bologna, Italy. Unpublished (1988).
11. J. R. Turner and S. V. Hering, *J. Aerosol Sci.*, **18**, 2, pp. 215–224 (1987).
12. Lavoro e Ambiente, s. c. r. l., *Report on impactor calibration*. Bologna, Italy. Unpublished (1992).
13. G. Calvelli, D. Ceccato, P. Mittner, E. Schiavuta, V. Bisceglie, and P. Giaretta, in: "*Physics in Environmental and Biomedical Research*" (S. Onori and E. T. Tabet, eds., World Scientific Publishing Co., 1986) pp. 87–90.
14. E. Bombelka, W. Koenig, F. W. Richter, and U. Wätjen, *Nucl. Instr and Meth.*, **B22**, 21–28 (1987).
15. U. Wätjen, *Nucl. Instr. and Meth.*, **B22**, 29–33 (1987).
16. J. L. Campbell, W. Maenhaut, E. Bombelka, E. Clayton, K. Malmquist, J. A. Maxwell, J. Pallon, and J. Van Den Haute, *Nucl. Instr and Meth.*, **B14**, (1986).
17. E. Clayton, *Nucl. Instr. and Meth.*, **218**, 221–224 (1983).