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Nuclear microprobe analysis and source apportionment of individual atmospheric aerosol particles

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In atmospheric aerosol research, one key issue is to determine the sources of the airborne particles. Bulk PIXE analysis coupled with receptor modeling provides a useful, but limited view of the aerosol sources influencing one particular site or sample. The scanning nuclear microprobe (SNM) technique is a microanalytical technique that gives unique information on individual aerosol particles. In the SNM analyses a 1.0 μm size 2.4 MeV proton beam from the Oxford SNM was used. The trace elements with $Z > 11$ were measured by the particle induced X-ray emission (PIXE) method with detection limits in the 1–10 ppm range. Carbon, nitrogen and oxygen are measured simultaneously using Rutherford backscattering spectrometry (RBS). Atmospheric aerosol particles were collected at the Brazilian Antarctic Station and at biomass burning sites in the Amazon basin tropical rain forest in Brazil.

In the Antarctic samples, the sea-salt aerosol particles were clearly predominating, with NaCl and $CaSO_4$ as major compounds with several trace elements as Al, Si, P, K, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb. Factor analysis of the elemental data showed the presence of four components: 1) soil dust particles; 2) NaCl particles; 3) $CaSO_4$ with Sr; and 4) Br and Mg. Strontium, observed at 20–100 ppm levels, was always present in the $CaSO_4$ particles. The hierarchical cluster procedure gave results similar to the ones obtained through factor analysis. For the tropical rain forest biomass burning aerosol emissions, biogenic particles with a high organic content dominate the particle population, while K, P, Ca, Mg, Zn, and Si are the dominant elements. Zinc at 10–200 ppm is present in biogenic particles rich in P and K. The quantitative aspects and excellent detection limits make SNM analysis of individual aerosol particles a very powerful analytical tool.

1. Introduction

Most of the studies of the elemental composition of aerosol particles and source apportionment were performed with bulk analytical methods like PIXE (particle induced X-ray emission), XRF (X-ray fluorescence), INAA (instrumental neutron activation analysis) and other techniques. The microanalysis of individual aerosol particles provides a very different and powerful view. For individual aerosol particle analysis, two techniques have proven to provide useful information: EPMA (automated electron probe X-ray microanalysis) and LAMMA (laser microprobe mass analysis) [1]. The development of the SNM (scanning nuclear microprobe) technique has opened new possibilities for aerosol particle analysis. SNM is a novel technique that can provide detection limits of 2–20 ppm, for particles larger than 1 μm for most of the elements with $Z > 10$. The SNM technique also allows the measurement of carbon, nitrogen and oxygen by the rutherford backscattering spectrometry (RBS) technique. Quantification for SNM analysis is straightforward, and an accuracy better than 20% can easily be obtained [2]. In this work samples collected in the Amazon Basin and Antarctica were analyzed, in order to investigate the background aerosol composition in these two different environments. One of the objectives is to do a better characterization of biogenic [3–5] and marine aerosol particles [6].

2. Scanning nuclear microprobe (SNM)

In SNM analysis, a well-focused beam of high energy protons is scanned over the sample. One of the major advantages of this technique is the excellent detection limit, of the order of 2–20 ppm, depending

on the SNM design [7]. The proton beam with an energy of about 2.5 MeV is focused to a diameter of 0.5–2 μm, with beam currents of 50–100 pA. There are several processes occurring in the interaction of the proton beam with the sample. X-rays are generated by PIXE, allowing concentration measurements for elements heavier than sodium. Backscattered particles contain information on light elements like carbon, nitrogen and oxygen through the RBS technique. Normally PIXE and RBS analysis are done simultaneously, allowing the determination of carbon, nitrogen and oxygen together with 15–22 trace elements heavier than sodium [7,8].

The SNM analyses were performed at the Oxford SNM system [7], with an 1.0 μm size beam with a current of 50–100 pA. The aerosol particles were collected on polycarbonate filters and coated with a thin carbon layer to make the particles conductive. Multivariate statistical analysis (factor and cluster analysis) was used to help in the data interpretation. Qualitative analyses of several particles from Antarctica were also performed with the new Lund SNM [8]. The elemental maps revealed many particles and particle agglomerates with complex and inhomogeneous elemental composition.

3. Results and discussion

3.1. SNM results for biomass burning aerosol particles

A coarse mode (10 μm > d_p > 2 μm) Nuclepore filter (sample CUI16G) was analyzed for 52 individual aerosol particles. This sample was collected in a background sampling station (Cuiabá) during the biomass burning season in the Amazon Basin. Absolute concentrations as low as 4 ppm were measured for Ni, Cu, Zn and others. A total of 21 elements were measured by PIXE in the particles (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Zr, and Pb), in addition to carbon, nitrogen and oxygen measured by RBS. Some elements (Na, Mn, Ni, Br, Rb, Sr, Zr and Pb) appeared in a very limited number of particles, not allowing an understanding of their sources. For the 13 remaining elements, factor analysis was used to study the relationship between the elemental concentrations. Table 1 shows the VARIMAX rotated factor matrix for the five statistical significant factors. The high communalities on the last column of table 1 show the adequacy of the five factor model. The first factor has high loading for P, Mg, Zn and Cl. These elements have shown in previous works to be biogenic related elements or emitted during the biomass burning process [1,3,4]. The second factor has high loading for K, Al and Si, indicating soil dust aerosol particles. The third factor represents $CaSO_4$ with Cl. The fourth factor represents Fe and As (maybe a soil dust component). The fifth factor has high loading for Cu, Ti and Al, representing a third soil dust component. The bulk PIXE and factor analysis of many samples from the same site revealed only two components, identified as biogenic and soil dust. It is interesting to note that the enrichment factor for the soil dust related elements are near unity for the bulk analysis, whereas when individual particle analysis is performed, three different components for soil dust are discriminated, with different elemental composition. Iron was shown to have a weak correlation with Al and Si when individual particles are analyzed, probably because of the presence of different minerals in different particles. The reason for the

Table 1
Amazon basin biomass burning aerosol – scanning nuclear microprobe analysis of 52 individual aerosol particles. VARIMAX rotated factor matrix

Element	Factor 1 Biogenic	Factor 2 Soil 1	Factor 3 $CaSO_4$	Factor 4 Fe + As	Factor 5 Soil 2	Communality
Mg	0.85	−0.14	0.12	−0.09	0.14	0.79
Al	−0.14	0.81	0.01	0.15	0.43	0.89
Si	−0.16	0.81	−0.06	0.02	0.18	0.73
P	0.93	0.02	0.13	−0.04	−0.01	0.90
S	0.29	0.01	0.85	−0.08	−0.12	0.83
Cl	0.54	0.17	0.63	−0.03	−0.23	0.78
K	0.34	0.85	0.08	0.11	−0.11	0.87
Ca	0.08	−0.08	0.88	−0.01	0.23	0.85
Ti	−0.10	0.26	−0.00	0.09	0.77	0.68
Fe	−0.08	0.17	−0.10	0.90	0.18	0.90
Cu	0.33	0.05	0.03	0.04	0.80	0.76
Zn	0.83	0.05	0.31	−0.01	0.09	0.80
As	−0.03	0.03	0.01	0.95	−0.02	0.91

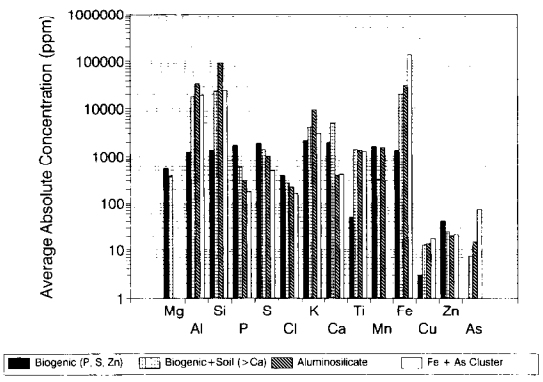

Fig. 1. Average elemental composition of the first four groups of biomass burning aerosol particles analyzed through SNM and cluster analysis.

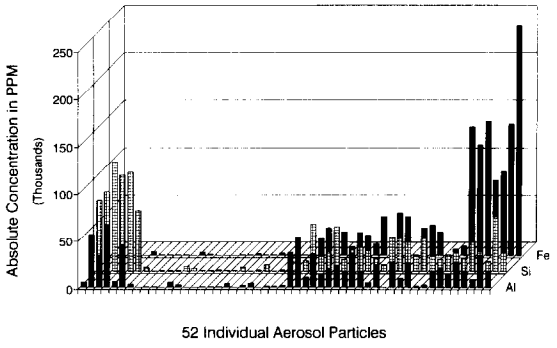

Fig. 2. Concentrations of Fe, Si and Al in individual particles emitted in biomass burning. Note the differences between the ratios of Si to Fe for the various aerosol particles.

relationship between Fe and As is unclear.

Hierarchical cluster analyses were performed and four clusters were analyzed. The first one with 38% of the number of the particles consists of biogenic aerosol particles, with high P and S concentrations. This cluster 1 corresponds to the factor 1, and has a very homogeneous composition. The second cluster with 37% of the number of particles is a soil dust group, with Al, Si, and Fe, and also rich in calcium. This cluster 2 represents a mixture of factor 2 (soil 1) and factor 3 ($CaSO_4$). Cluster 3 with 12% of the number of particles is an aluminosilicate group with high Al and Si and low Fe, and is associated with factor 2. Cluster 4 (12%) is a group with high Fe and As, similar to factor 4. Fig. 1 shows the average composition of the four groups analyzed through cluster analysis. Note the elevated concentrations of Mg, P, S, Cl, Mn, and Zn in the biogenic particle group. In biomass burning emissions, most of the particles are not pure compounds, but internal and external mixtures of different particle types.

Fig. 2 shows the concentration of Fe, Si and Al in individual particles emitted in biomass burning. The large differences between the ratios of Si to Fe for the various particles are very clear. This can be compared with the fact that the bulk PIXE analysis shows an enrichment factor near unity for these elements. Zinc, with a concentration of 8–301 ppm is present in the biogenic particle group associated with P and S.

3.2. SNM results for Antarctic aerosol particles

Two coarse mode samples collected during summertime in the Antarctic Brazilian station in the Antarctic peninsula were analyzed for a total of 55 particles. Table 2 presents the VARIMAX rotated factor matrix for the 11 elements and the four factor solution. The first factor has high loading for Si, Fe, Al and K, indicating soil dust aerosol particles. Factor 2 is a $CaSO_4$ factor with the presence of Sr. Factor 3 represents NaCl particles from sea-salt. Factor 4 has a high loading for Br and Mg, and a moderate loading for K. The joint presence of Ca and Sr is very strong. K is

Table 2
Antarctic aerosol – scanning nuclear microprobe analysis of individual particles. VARIMAX rotated factor matrix of 55 particles

Element	Factor 1 Soil dust	Factor 2 $CaSO_4$ + Sr	Factor 3 NaCl	Factor 4 Br + Mg + K	Communality
Na	−0.07	−0.25	0.93	0.04	0.95
Mg	−0.04	−0.11	0.19	0.86	0.79
Al	0.95	−0.06	−0.09	0.03	0.91
Si	0.99	−0.03	−0.06	0.02	0.98
S	−0.04	0.94	−0.19	−0.02	0.94
Cl	−0.09	−0.24	0.93	0.07	0.95
K	0.40	−0.04	−0.41	0.38	0.48
Ca	−0.04	0.97	−0.12	−0.10	0.97
Fe	0.97	−0.02	−0.05	0.00	0.95
Br	0.05	−0.01	−0.08	0.89	0.81
Sr	−0.04	0.95	−0.18	−0.04	0.95

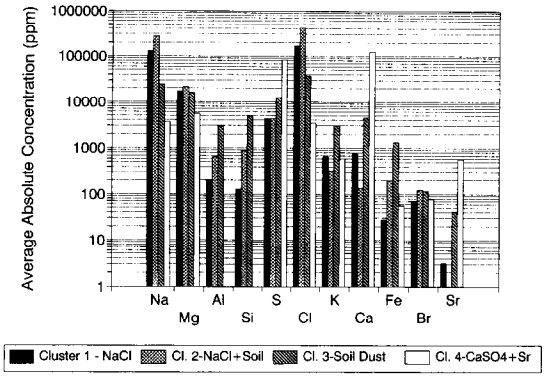

Fig. 3. Average elemental composition of four groups obtained through SNM and hierarchical cluster analysis for Antarctic aerosol particles.

present in three different factors, because this source can be either soil dust or sea-salt.

Hierarchical cluster analysis shows the presence of four particle groups. The first cluster, responsible for 45% of the number of particles represents sea-salt aerosol with predominance of NaCl, and corresponds to factor 3. The second cluster (with 11% of the number of particles) is also sea-salt, but richer in Br and soil dust related elements. Group number 4 responsible for 11% of the number of particles is $CaSO_4$ with Sr, and cluster number 3 is soil dust aerosol, rich in Al, Si and Fe, and responsible for 33% of the number of particles. Fig. 3 shows the average elemental composition of the four clusters. It is interesting to analyze the Cl to Na ratios in these groups. The two sea-salt clusters have average Cl/Na ratio of 1.33 and 1.55, that compares quite well with the expected value (the molar ratio of NaCl is 1.54). For the $CaSO_4$ cluster, the Cl to Na ratio is 0.94, a low value probably because of the presence of sulfur that releases chlorine

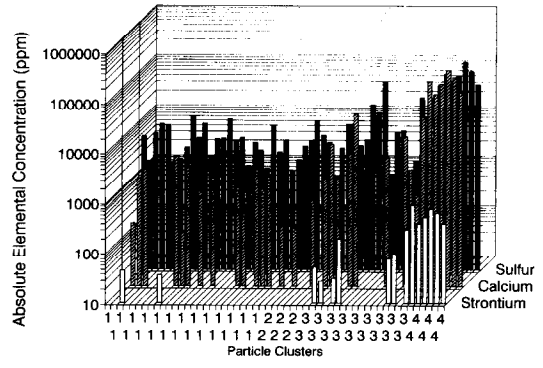

Fig. 4. Elemental concentrations for S, Ca and Sr for the 55 individual aerosol particles from the Antarctic. Note the presence of Sr at low concentrations of about 200 ppm for particles clustered in group number 4.

in the gas phase, leaving an enrichment of sodium in the particle. Fig. 4 shows the S, Ca and Sr elemental concentration for the 55 particles from Antarctic. Sr is present in group 4 at concentrations of about 200 ppm. It is also possible to observe that sulfur was measured in all particles, even in soil dust aerosol particles. Possibly this is due to the fact that these particles have been transported for long distances and coated with sulfur species originating from oceanic biogenic sulfur.

Both multivariate statistical techniques gave similar results in the interpretation of SNM individual particle analysis. The bulk PIXE and receptor modeling calculations of a large number of aerosol samples provide only two components, a strong sea-salt and a soil dust component. Electron microprobe analysis of the same type of samples shows several particle types, but without the quantitative aspects and excellent detection limits that makes the SNM analysis a very powerful analytical tool.

4. Conclusions

It was possible to observe a better aerosol source apportionment using SNM analysis than with traditional bulk PIXE coupled with receptor modeling. SNM analysis was able to discriminate different particle types and to clarify atmospheric processes in a unique way. This was clear for the Amazon basin samples, where the biogenic aerosol component was shown to consist of different particle types. For Antarctic aerosol particles the sea-salt component was split up in three particle types, revealing reactions of sulphur gases with NaCl particles and $CaSO_4$ particles, in addition to soil dust aerosol particles.

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