PIXE AND RECEPTOR MODELS APPLIED TO REMOTE AEROSOL SOURCE APPORTIONMENT IN BRAZIL

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We have used PIXE together with receptor modeling for quantiative source apportionment of remote aerosols. The Sao Paulo PIXE system uses an 8 MeV alpha particle beam, and it can detect elements with $Z > 11$ with a detection limit between 1 and 30 ng m^{-3}. We sampled atmospheric aerosols in six remote sites: Amazon Basin, Atlantic Forest, Arembepe, Fernando de Noronha, Firminopolis and Itaberai. Sampling was performed using stacked filter units, cascade impactors with 6 or 10 stages and linear streakers.

Source apportionment of the coarse mode aerosols was done using three receptor models: chemical mass balance, principal factor analysis and stepwise multiple regression analysis. Three sources of aerosols were quantiatively distinguished: marine aerosols, soil dust and aerosols released by plants. The emission of aerosols by vegetation is very clear for all sampling sites and with all three receptor models. In the Amazon Basin and Atlantic Forest the aerosol released by plants is the major source and accounts for 60–80% of airborne concentrations.

1. Introduction

During the last years extensive experiments have been done to investigate the characteristics of atmospheric aerosols in remote areas. Several of these experiments have used PIXE for elemental analysis in forested areas [1], and in marine and continental sites. Just a few of these studies take into account powerful techniques for source recognition and apportionment. Receptor models [2] have been developed basically for urban aerosol source apportionment to help with control strategies, but they are also very good for remote aerosol studies. Principal factor analysis (PFA) has been applied to remote aerosols [3], and the factors structure is much easier to interpret than in urban studies.

2. Sampling

We sampled in several airsheds with different source structures, aiming to check the efficiency of receptor models to make a correct source apportionment of remote environments. Sampling was performed using 6 or 10 stage cascade impactors (CI) of Battele design. The CI stages can be grouped into fine ($d_p < 2$ μm) and coarse (2 μm $< d_p < 15$ μm) particulate matter. Nucleopore stacked filter units (SFU) were used to obtain the gravimetric mass and elemental concentrations for fine and coarse modes. Linear streakers give trace element concentrations every 2 h.

In the Amazon Basin, we sampled in two sites, both near Manaus – Ducke Reserve and Bacia Modelo – where sampling was done inside the jungle, on a tower about 40 m high with battery operated equipment. In the Atlantic Forest we sampled continuously for two years in a location sited in the jungle at about 800 m from the ocean, with battery operated pumps, and the sampling devices were mounted at 1.80 m from the ground. Two other sites on the northeast of Brazil, with a predominant marine influence, were selected as sampling sites: Fernando de Noronha and Arembepe. Samples were also collected at Firminopolis and Itaberai, two inland areas in the Brazilian savannah. A full description of the sampling sites, sampling schedule, analytical methods, and results can be found elsewhere [4,5].

3. Analytical procedures

The elemental concentrations for elements with $Z > 11$ were measured by the PIXE method. Some analyses were made using the FSU PIXE system [6], but the greater part of the analyses were made using the Sao Paulo PIXE system. Each sample was irradiated using an 8 MeV alpha particle beam from the Pelletron accelerator of the University of Sao Paulo [7]. The X-ray spectrum produced by each sample was analysed by the HEX-B program. Detection limits for different ranges of elements are 30 ng m^{-3} for $11 < Z < 16$, 1 ng m^{-3} for $17 < Z < 30$ and 10 ng m^{-3} for $31 < Z < 40$. Accuracy of the analysis ranges from 10% for medium Z elements to 30% for light and

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heavy elements. The sodium concentrations should be interpreted as semiquantative because of the X-ray absorption corrections. The filters are very light loaded (around 30 $\mu g/cm^2$) but particle size effects can be important for sodium concentrations.

Gravimetric mass analyses were performed for Atlantic Forest samples using a Mettler M3 electronic microbalance with 1 μg sensitivity. Humidity, temperature and electrostatic charges were controlled for this analysis [8].

4. Receptor models

Aiming to identify the sources of remote aerosols we used three receptor models [9]: principal factor analysis (PFA), chemical mass balance (CMB), and stepwise multiple regression analysis (SMRA). In PFA the variability of the trace element concentrations is used to obtain information about the sources. Due to the different magnitudes of elemental concentrations for each element, we normalized them taking zero as mean value and unity as standard deviation. From this set of normalized concentrations we extracted the eigenvalues and eigenvectors of the correlation matrix. The result is a principal component analysis that is truncated to a few factors (generally 3 or 4 in remote aerosols). A varimax rotation is applied to the factor loading matrix, and the final factors should be related with the sources.

CMB is based on a simple mass conservation argument. We calculate an effective variance least squares fitting between the measured elemental concentrations

and a set of source "fingerprints" or source profiles [9]. We have used basically four source profiles: marine aerosols, soil emission, sulfate and aerosols emitted by plants. For marine and soil aerosols we have corrected for the observed fractionation between the interfaces soil–atmosphere and sea–atmosphere with data from the literature. For the fingerprint of plant emission we simply used the bulk elemental composition of plant material, because we have no information about the fractionation between plant and atmosphere and about the mechanisms for plant emission of aerosols.

In SMRA a multiple regression of the gravimetric mass against the concentrations of selected tracer elements is done. The tracers must be carefully chosen if reliable results are desired [10]. SMRA gives us two important results: the participation of the particular tracer in the source it represents and the total concentration of the source. Thus, we can check the source profile with SMRA. The CMB and SMRA results can be directly compared and they must agree within experimental error.

5. Results

Table 1 shows the results of PFA for the coarse mode aerosol from the Atlantic Forest. The first factor has high loadings for P, S, K, Ca, Mn and the coarse mode aerosol gravimetric concentration (CP). This factor can be interpreted as aerosols released by the forest. Others results will support this identification. Factor 2 is clearly a soil related aerosol and factor 3 is

Table 1
Factor loading matrix (varimax rotated) for principal factor analysis of two years SFU data in the Atlantic Forest coarse mode aerosols.

Varible	Communalities	Factor 1	Factor 2	Factor 3
Na	0.91	0.33	−0.66	0.89
Mg	0.90	0.15	0.04	0.93
Al	1.00	0.03	1.00	−0.07
Si	0.86	0.01	0.91	−0.17
P	0.63	0.56	−0.27	0.50
S	0.73	0.78	0.03	0.34
Cl	0.79	0.37	−0.13	0.80
K	0.88	0.90	0.03	0.25
Ca	0.88	0.90	0.10	0.21
Ti	0.86	0.04	0.90	0.19
Mn	0.80	0.83	0.32	0.04
Fe	0.90	0.40	0.83	−0.19
CP mass	0.85	0.84	0.10	0.35
Eigenvalues		5.89	3.76	1.39
Percent of variance		45.4	29.0	10.7
Identification		plant	soil	marine

a marine related aerosol. The communalities for all the elements are high, indicating the adequacy of the model. We have explained 85% of the total variance.

Table 2 shows us the SMRA results for the coarse mode of Atlantic Forest aerosol. For each source we ran it with several possible tracers (e.g. for soil aerosols we have four possible tracers: Fe Al, Si and Ti), and we can see that the SMRA results for soil and marine aerosol are generally very close to the average of the reference compositions. For plant emission, the K and Ca participations in this source are within 40% of the bulk plant elemental composition. For each source the SMRA results for the total aerosol concentration agree within 3% of the CMB calculations. The

Table 2
Stepwise multiple regression analysis results for Atlantic Forest coarse mode aerosols[a].

Tracer element	Participation (percent of mass)	Reference average (%)
Marine aerosols		
Na	18.6 ± 1.7	28.3 ± 10.7
Mg	2.97 ± 1.49	3.45 ± 1.51
Cl	41.2 ± 7.7	42.3 ± 16.9
S	3.19 ± 1.24	3.00 ± 0.35
Soil dust		
Al	3.93 ± 0.32	7.76 ± 0.56
Si	26.0 ± 6.50	26.4 ± 4.35
Ti	0.31 ± 0.11	0.52 ± 0.18
Fe	4.39 ± 3.74	4.48 ± 0.96
Plant emission		
K	1.04 ± 0.40	1.31 ± 0.49
Ca	1.61 ± 0.68	1.15 ± 0.75

[a] Participation of tracer elements in each source as percent of total source mass. Reference averages were calculated based on bulk composition data and/or source fingerprints.

Table 3
Chemical mass balance results for atlantic forest coarse mode aerosols[a].

Element	In?	Marine	Soil	Plant	Sulfate	Sum	Measured + S.D.
LE	No	443.1	396.9	3803.9	223.2	4867.1	–
Na	Yes	376.1	15.8	6.0	–	397.9	559 ± 386
Mg	Yes	49.4	12.0	7.7	–	69.0	102 ± 35
Al	No	33.5	55.4	2.1	–	91.1	55 ± 39
Si	Yes	21.0	134.8	0.9	–	156.6	94 + 66
P	No	–	0.6	9.8	–	10.4	42 ± 16
S	Yes	59.0	0.2	14.5	185.0	185.0	185 ± 76
Cl	Yes	713.5	0.2	8.5	–	722.2	711 ± 71
K	Yes	14.9	6.0	59.6	–	80.5	77 ± 33
Ca	Yes	25.1	12.3	27.7	–	65.1	66 ± 42
Ti	No	0.6	3.4	–	–	4.0	6.1 ± 4.6
Mn	No	–	0.6	2.7	–	3.3	2.4 ± 1.9
Fe	Yes	4.1	29.9	0.6	–	34.6	47 ± 15
Ni	No	–	–	–	–	0.1	1.5 ± 0.9
Cu	No	–	0.1	0.1	–	0.2	3.8 ± 4.2
Zn	No	–	0.1	0.4	–	0.5	19 ± 25
Br	No	2.5	–	0.1	–	2.6	15.9 ± 6.3
Mass		1743	668	3944	335	6691	13580
σ		172	235	2045	231	2078	4326
Fraction		26.1%	10.0%	58.9%	5.0%	100%	

[a] Concentrations in ng m^{-3}. The column "In?" indicates whether the element is in or out of the fit, and LE indicates light elements not detected by PIXE. Contributions of marine, soil, plant, and sulfate components are summed for comparison with measured concentrations and standard deviations.

Table 4

Chemical mass balance results for Amazon Basin coarse mode aerosols sampled at Bacia Modelo tower[a].

Element	In?	Soil	Plant	Sulfate	Sum	Measured + S.D.
LE	No	247.5	2309.3	62.5	2619.3	–
Al	Yes	34.5	1.0	–	35.5	38.7 ± 5.2
Si	Yes	84.0	0.9	–	84.9	65.1 ± 10.6
P	Yes	0.4	9.6	–	10.0	10.4 ± 1.4
S	Yes	0.1	8.1	31.2	39.4	39.4 ± 4.1
Cl	No	0.1	10.3	–	10.4	52.6 ± 5.4
K	Yes	3.7	39.0	–	42.7	47.3 ± 4.2
Ca	Yes	7.7	16.8	–	24.4	19.2 ± 2.7
Ti	No	2.1	–	–	2.1	4.1 ± 0.5
Mn	No	0.4	1.9	–	2.3	0.3 ± 0.2
Fe	Yes	18.7	0.6	–	19.3	29.0 ± 3.5
Ni	No	–	–	–	–	0.4 ± 0.2
Cu	No	–	0.1	–	0.1	0.3 ± 0.2
Zn	No	0.1	0.3	–	0.4	2.7 ± 1.1
Mass		400	2398	94	2891	–
σ		34	186	12	190	–
Fraction		13.8%	83.0%	3.3%	100%	

[a] See footnote to table 3.

most important source is the aerosols emitted by plants ((59 ± 31)%) followed by marine aerosols ((26 ± 31)%) and soil emission ((10.0 ± 3.5)%).

Table 3 shows the CMB calculations for Atlantic Forest coarse mode aerosols. Comparing the measured and calcuated sum columns we can see that almost all elements were predicted within experimental errors. Especially K and Ca were well predicted despite the fact that the three sources give a significant contribution to the amount of K and Ca present. About 80% of the manganese concentrations originated from plant emission, and these CMB results agree with the PFA results from table 1, which confirms that manganese is related with the plant emission factor. Ni, Cu and Zn were not well predicted in any of our CMB fits in the fine and coarse modes. These elements are known to be anomalously enriched in almost all remote aerosol studies, and it was similar for all our sites or fits.

CMB can be run for each sample, and we have done numerous CMB fits for Amazon Basin aerosol. Table 4 shows one of these fits for coarse mode aerosols from the Bacia Modelo tower. P, S, K and Ca were well fitted, showing that the aerosols released by plants in the coarse mode is similar to the plant bulk elemental composition. The soil accounted for only 13.8% in the total airborne concentrations. The sulfate probably originated from gas-to-particle conversion and is responsible for only 3.3% of the total mass (some of the fine particles are collected on the coarse filter of the SFU). CMB fits from other sites, for the coarse mode, show that plant aerosols accounted for

70–90% and soil aerosols contributed 10–30% of the aerosol concentrations. In the fine mode fits we saw a very strong enrichment of potassium compared with P, S, Cl and Ca. This K enrichment for fine mode aerosols was observed for all the sites and ranges from 5 to 20 times the plant bulk elemental composition. The reason for this strong fine K enrichment has been investigated using single particle analysis with laser microprobe mass analysis (LAMMA) and automated scanning electron microprobe. These analyses show that we can find about eight different groups of particles with different elemental compositions. All these groups contain K, Ca, S, P, and some minor elements together with organic material [11].

6. Conclusions

PIXE is a very good analytical tool for the study of remote aerosols because it permits simultaneous detection of elements with $Z > 11$ with low detection limits and good accuracy.

Receptor models have been shown to be useful for remote aerosol studies as well as for urban aerosol source apportionment. PFA has made a good separation of the sources in the coarse mode, and normally soil, marine and plant-derived aerosols are represented by orthogonal factors. It is more difficult to resolve the sources of fine mode aerosols by PFA, perhaps because of the possibility of long range transport, long residence time in the atmosphere, and gas to particle conversion processes, which results in some mixing

between factors. Besides these problems for the fine mode, the same three sources contributing to the coarse mode can also be recognized in the fine mode. For the coarse mode the SMRA results for the Atlantic Forest aerosols are identical to CMB fits in terms of quantitative source apportionment. The source profiles obtained by SMRA are very close to the expected participation of the tracer element in the source it represents. SMRA results for potassium and calcium show that for the coarse mode their concentration in the aerosols released by plants is close to the plant bulk elemental composition. This fact was confirmed by the CMB analysis.

CMB fits were in good agreement with the measured trace element concentrations. In forested areas plant emission accounts for 70–90% of the airborne particulate concentrations in fine and coarse modes. Nearly 97% of the source profile for plant emission consisted of elements with $Z < 11$ (mainly carbon and oxygen). For areas where marine aerosols are the most abundant components in the coarse mode, the concentrations of the elements Na, Mg, S and Cl were generally well accounted for in the CMB calculations. Soil dust was present in all the sites and its importance ranges between 10 and 70%. Al, Si, Ti, and Fe concentrations were generally well predicted by the CMB fits.

The average ratio (measured/predicted by CMB) for all sites and for all elements is 1.09 ± 0.18 for the coarse mode aerosols and 1.04 ± 0.10 for the fine mode aerosols. As the accuracy and precision of the PIXE method are between 10 and 20% we can conclude that CMB can predict the measured concentrations for fine and coarse mode remote aerosols.

Acknowledgements

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