



Appendix 5

RECEPTOR MODELLING OF ATMOSPHERIC AEROSOLS IN THE URBAN AREA OF SÃO PAULO

P. ARTAXO, W. E. DE CASTRO, JR., M. DE FREITAS, K. M. LONGO

Grupo de Estudos de Poluição do Ar, Departamento de Física Aplicada, Instituto de Física Universidade de São Paulo, USP, Caixa Postal 66318, CEP 05389-970, São Paulo, SP, Brazil.

1. INTRODUCTION

The city of São Paulo (latitude $23^{\circ}37'S$, longitude $46^{\circ}39'W$) is one of the largest urban areas in the world. It has a population of about 18.4 million inhabitants in 1990 that is expected to be about 24 million in year 2000. It is one of the five largest urban areas in the world. With an altitude of 800 meters, an annual precipitation of 1930 mm, and a temperature range of $15-22^{\circ}C$, it has an unfavorable meteorology for dispersion of pollutants during the winter months (June to August).

There are two main air pollution sources in the metropolitan area: industrial emissions and transportation. In terms of industry, the state of São Paulo is responsible for 50% of the Brazil national gross product of US\$ 300 billion. Most of the industries operate in the urban and suburban areas of the greater São Paulo. On the positive side, the energy sector has a negligible component in terms of direct emission of atmospheric pollutants, due to the fact that 95% of the electricity in Brazil are hydroelectric. In the urban area of São Paulo, there is about 4 million vehicles. A large part of the fleet is alcohol-fueled, with about 1.2 million automobiles using mainly ethanol. There are 2.2 million gasoline vehicles, and 300,000 diesel powered buses and trucks.

During the winter months, a strong inversion layer at low altitude makes it difficult the dispersion of air pollutants in the urban area. Low wind speed and low precipitation rate help to obtain high levels of air pollution in winter. The main pollutants in the urban area are: particulate matter, SO_2 , ozone and carbon monoxide. There is no lead in the gasoline used in São Paulo, because there is a mixture of about 25% ethanol in the gasoline to reduce automobile emissions.

2. SAMPLING CAMPAIGN

Aerosols were collected at a site located downtown, at the Medicine Department of the University of São Paulo. The site is affected by heavy traffic nearby, and the site is relatively far from industrial emissions. The aerosol sampler was located at the roof of the 4-floor Medicine Department building, of about 20 meters to minimize re-suspended soil dust from the nearby streets. There is no unpaved roads in the vicinity of the sampling site.

Sampling was performed during June and August 1994, with a 12-hour sampling time, from 8:00 am to 8:00 pm daily. The sampler was the "Gent" Stacked Filter Unit [2,7], fitted with a specially designed inlet that provided a 50% cut-off diameter of $10 \mu m$. The inlet was designed with an impactor, to collect only particles smaller than $10 \mu m$. Fine and coarse aerosol particles were sampled with the SFU using Nuclepore filters. The SFU collects

coarse mode particles ($2.0 < d_p < 10 \mu\text{m}$) on a 47-mm-diameter, 8- μm pore size Nuclepore filter while a 0.4 μm pore size Nuclepore filter collects the fine mode particles ($d_p < 2.0 \mu\text{m}$) [5]. The flow rate was typically 17 liters per minute. Particle bounce was minimized by the use of Apiezon coated coarse mode filters, and also by the fact that high relative humidity was observed during the sampling period. The volume was obtained with volume integrators, calibrated with Hastings Precision Mass Flowmeters.

3. ANALYTICAL METHODOLOGY

The elemental concentrations were measured with the particle-induced X ray emission (PIXE) [4] method. It was possible to determine the concentrations of up to 20 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, and Pb). A dedicated 5SDH tandem Pelletron accelerator facility, the LAMFI (Laboratório de Análise de Materiais por Feixes Iônicos) from the University of São Paulo was used for the PIXE analysis. A proton beam with an energy of 2.4 MeV was used, with a beam current of 30-50 nA. Irradiation times were 600 seconds. The São Paulo PIXE system was calibrated with a large number of MicroMatter standards [6]. The fitting of the X-ray spectra was performed using the AXIL-PC software [1].

Detection limits are typically 5 ng/m³ for elements in the range $13 < Z < 22$ and 0.4 ng/m³ for elements with $Z > 23$. These detection limits were calculated based on a sampling flow rate of 17 l per minute sampling time of 12 hours and irradiation time of 600 s. The precision of the elemental concentration measurements is typically less than 10%, with 20% for elements with concentration near the detection limit. The fine and coarse fraction aerosol mass concentrations are obtained through gravimetric analysis of the Nuclepore filters. The filters were weighed before and after sampling in an electronic microbalance with 1 μg sensitivity. Before weighing, the filters are equilibrated for 24 hours at 50% relative humidity and 20°C temperature. Electrostatic charges are controlled by means of ²¹⁰Po radioactive sources. Detection limit for the aerosol mass concentration is 0.3 $\mu\text{g m}^{-3}$. Precision is estimated at about 15%. Black carbon concentration was measured using a reflectance technique using a photometer calibrated with artificial black carbon standards.

4. RECEPTOR MODELING

To separate the different components present in the samples using the elemental composition, absolute principal factor analysis (APFA) was used [3,8]. APFA offers the possibility to obtain a quantitative elemental source profile instead of only a qualitative factor loading matrix as in traditional applications of factor analysis. The absolute elemental source profiles help in the identification of the factors and can be used to quantitatively compare the factor composition with the assumed aerosol sources. In principal factor analysis a model of the variability of the trace element concentrations is constructed so that the set of intercorrelated variables is transformed into a set of independent, uncorrelated variables. The APFA procedure obtains the elemental mass contribution of each identified component by calculating the absolute principal factor scores (APFS) for each sample [Artaxo et al., 1988, 1990]. The elemental concentrations are subsequently regressed on the APFS to obtain the contribution of each element for each component. These source profiles thus obtained can be compared with values from the literature to gain information on enrichment and atmospheric chemistry processes [3]. The measured aerosol mass concentration can also be regressed on the APFS to obtain the aerosol total mass source apportionment

Cluster analysis was used to measure the distances in the elemental space between the samples and the variables. Ward's error sum strategy was used to classify the samples, and the squared Euclidean distance was used to measure the distances. SPSS for Windows version 6.0 and Statgraphics version 6.0 were used in the receptor Modeling calculations.

5. RESULTS AND DISCUSSION

Figure 1 shows the fine, coarse and inhalable aerosol mass concentration for the samples collected during this experiment. It is possible to observe the high inhalable particulate mass concentration, with 6 events exceeding $150\mu\text{g}/\text{m}^3$ that is the maximum allowed daily concentration for the Brazilian air pollution legislation. There is high daily variability, with concentrations varying from 20 to $170\mu\text{g}/\text{m}^3$.

During the sampling period a beta gauge aerosol monitoring instrument was operated by the state air pollution control agency (CETESB) nearby our sampling site. Figure 2 shows the measurements for the two instruments (the beta gauge and the SFU) taken during the sampling period. The beta gauge instruments give hourly values that were integrated for the SFU sampling time. It is possible to observe in Figure 2 the excellent agreement between the SFU measurements and the beta gauge results from CETESB for PM10. This parallel sampling can be used to validate the SFU PM10 inlet against the Beta gauge instrument. Also the accuracy and precision of the two completely independent methods are relatively low, otherwise this agreement could never be obtained.

Figure 3 shows the regression curve between the measurements from the two instruments. The regression equation is: $\text{PM10Beta} = \text{PM10SFU} \cdot 0.992 - 2.214$. The R^2 value for the regression was 0.86.

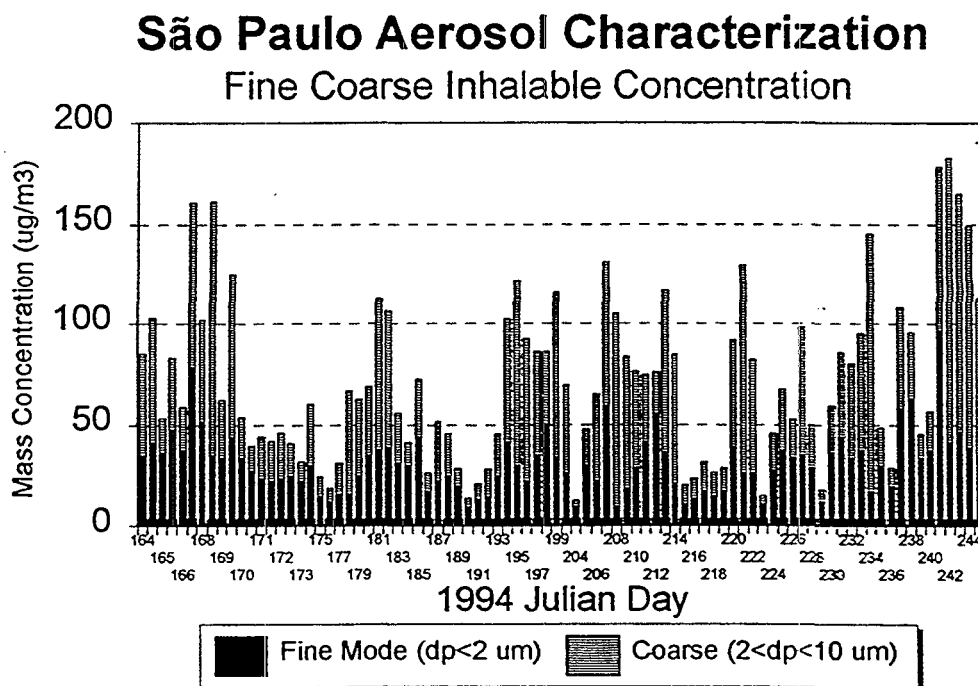


Figure 1 - Fine, coarse and inhalable aerosol mass concentration.

São Paulo Aerosol Characterization

PM10 Mass Concentration 1994

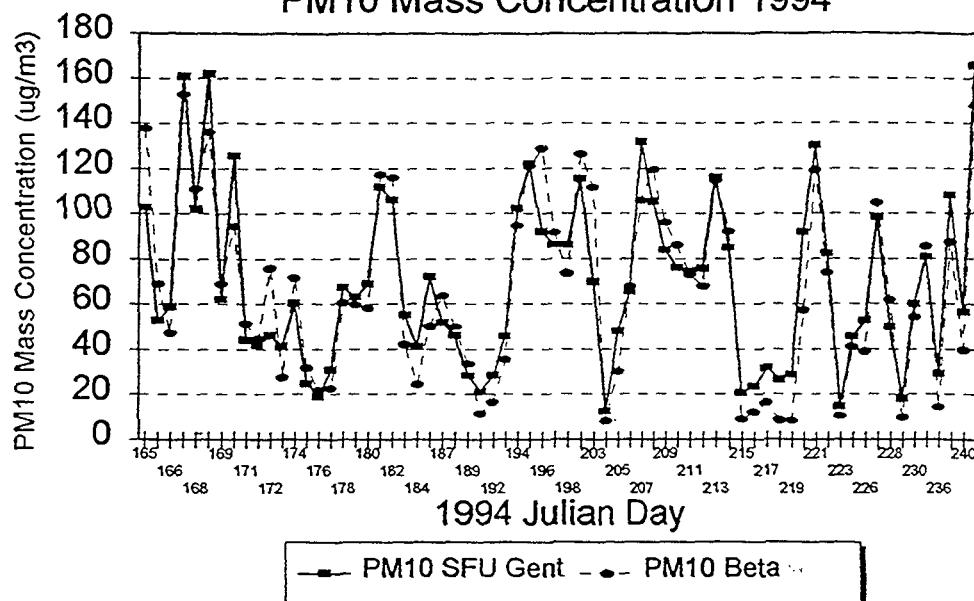


Figure 2 - Inhalable aerosol mass concentration (PM10) provided by the beta gauge aerosol monitoring instrument operated by the state air pollution control agency nearby our sampling site and the SFU equipped with an PM10 inlet.

The volume integrator was calibrated against a precision Hastings mass flowmeter, giving a ratio of 0.817 for the volume measured by the Volume integrator and the Hastings MFM. The final volume used in calculating concentrations were the values provided by the volume integrator, corrected for the calibration with the Hastings Mass flowmeter. Figure 4 shows the curve obtained with the calibration of the volume integrator and the Hastings precision mass flowmeter. One of the main sources of errors in aerosol sampling could be the integration of the air volume.

Black carbon concentration was measured for all fine mode samples. Figure 5 shows the time series of the black carbon concentration. Peak values of up to $15\mu\text{g}/\text{m}^3$ were observed. The ratio of Black carbon to fine mode aerosol mass concentration can be observed in figure 6. It is remarkably constant the BC/FPM ratio, with the exception of two samples. This could mean a unique source for the BC that could contribute significantly to the fine mode aerosol mass concentration. This source possibly represents the diesel emissions from buses in the urban area of São Paulo. This BC/FPM ratio is a relatively high 26.1 ± 9.7 , excluding the two high BC/FPM events.

A total of 82 samples was analyzed by PIXE in the fine fraction, providing elemental concentrations for 19 elements, black carbon and the gravimetric fine mass concentration. Table 1 shows the average elemental concentrations. It is possible to observe the relatively low sulfur concentration ($1527\text{ ng}/\text{m}^3$), compared to the fine mode mass concentration ($\text{FPM} = 30.9\mu\text{g}/\text{m}^3$). Black carbon has a high value of $7.97\mu\text{g}/\text{m}^3$, showing the relatively high diesel emissions impact in the São Paulo atmosphere.

São Paulo Aerosol Characterization 94
PM10 - Beta Gauge versus Gent SFU

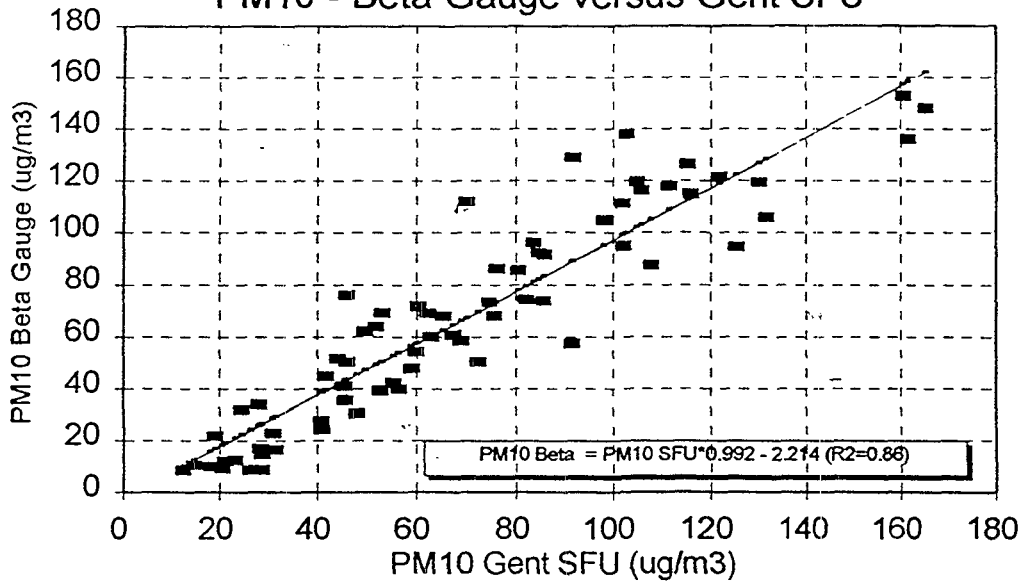


Figure 3 - Regression curve between the measurements from the two instruments (Beta gauge and SFU) for PM10.

Volume Integrator Calibration

Hastings Precision Mass Flowmeter

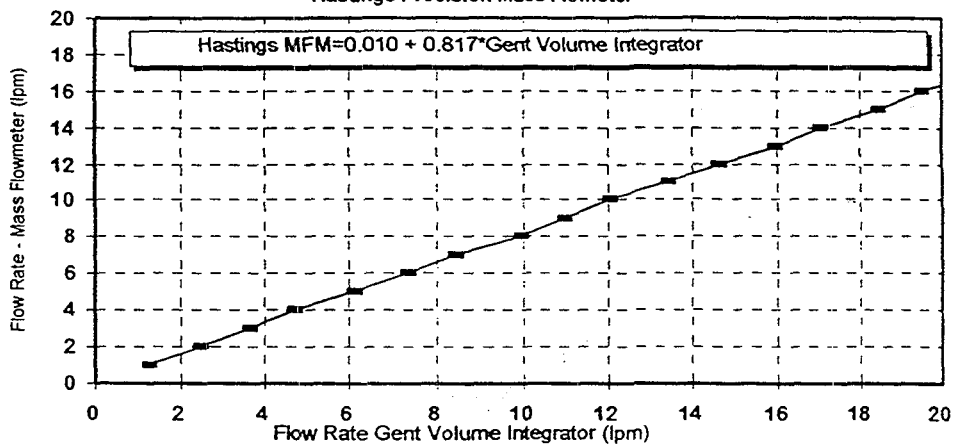


Figure 4 - Calibration of the volume integrator with the Hastings precision mass flowmeter

São Paulo Aerosol Characterization

Black Carbon Concentration

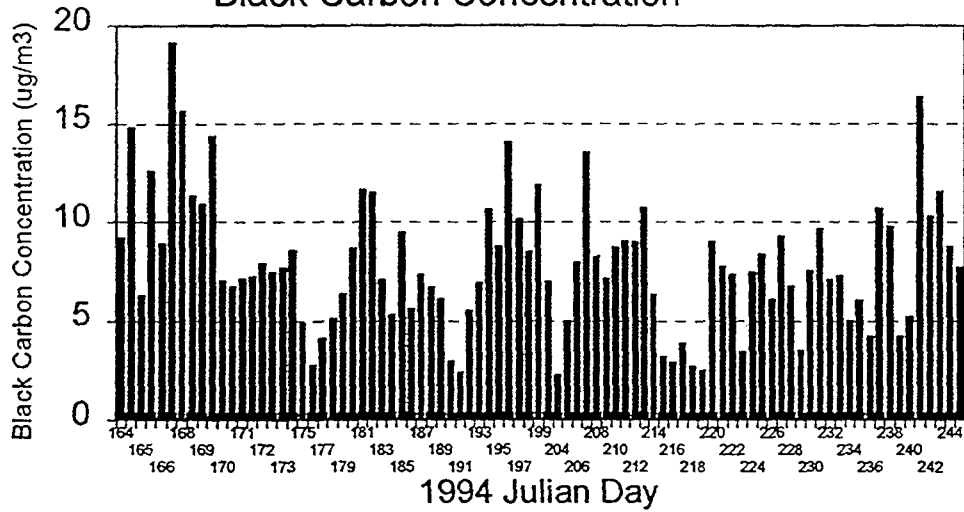


Figure 5 - Black carbon concentration in $\mu\text{g}/\text{m}^3$ in the fine mode.

São Paulo Aerosol Characterization 94

Ratio of Black Carbon to Fine Mass

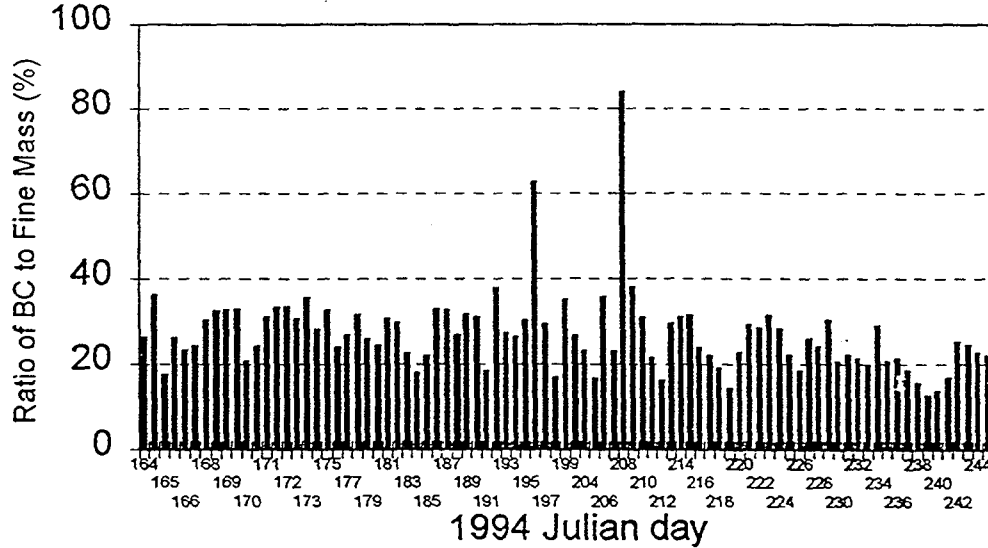


Figure 6 - Ratio of black carbon to fine mode aerosol mass concentration.

A total of 82 samples was analyzed by PIXE in the fine fraction, providing

Table 1 - São Paulo Aerosol Characterization Study - 1994 - Fine Mode Elemental Concentrations in ng/m³

Variable	Mean	Std. Dev.	Min.	Max.	N
Al	115	69.5	4.48	253	67
Si	175	50.1	104	236	16
S	1527	1039	94.9	5294	82
Cl	35.9	27.0	3.26	132	74
K	530	268	36.3	1357	82
Ca	91.5	39.4	18.2	217	82
Ti	15.1	8.34	0.93	36.8	82
V	7.25	4.21	0.73	19.2	82
Cr	5.43	3.91	0.25	18.1	68
Mn	21.9	14.7	0.34	68.8	82
Fe	346	159	46.9	887	82
Ni	6.28	4.04	0.33	16.7	82
Cu	15.3	9.96	2.12	52.6	82
Zn	127	104	5.24	530	82
Br	7.77	4.24	1.25	17.4	82
Rb	2.34	1.09	0.76	5.33	34
Sr	1.43	0.47	1.06	2.12	6
Zr	4.84	2.86	1.98	9.37	8
Pb	44.4	35.6	3.16	178	82
FPM(*)	30.9	14.9	3.64	79.8	82
BC(*)	7.97	3.49	1.62	19.3	82

(*) FPM is the aerosol fine mode mass concentration in $\mu\text{g}/\text{m}^3$. BC is the Black Carbon concentration in $\mu\text{g}/\text{m}^3$. N is the number of samples in which the variable appears above the analytical detection limit. Only values above detection limit were used in calculating average and standard deviation.

Factor analysis with VARIMAX rotation was performed in the elemental data set, including only variables that were measured in all samples. Four factors were statistically

significant, and the communalities for most of the variables were typically 85%. Table 2 shows the VARIMAX rotated factor matrix, with the communalities. Factor 1 has high loadings for Zn, Pb, Cu, BC, Mn and the FPM. This could represent contributions from the transportation sector, with diesel, gasoline and alcohol emissions. Factor 2 represents soil dust with contributions from Ti, K, Ca, FPM, but also with a component of resuspended soil dust by traffic, because of the BC, Cu, and Mn components. The fine mode sulfur is also high in this component. The third component with V, Ni, S and Fe could represent the oil combustion component. The fourth factor is loaded mainly with Br, and it is not clear to us the source associated with this component.

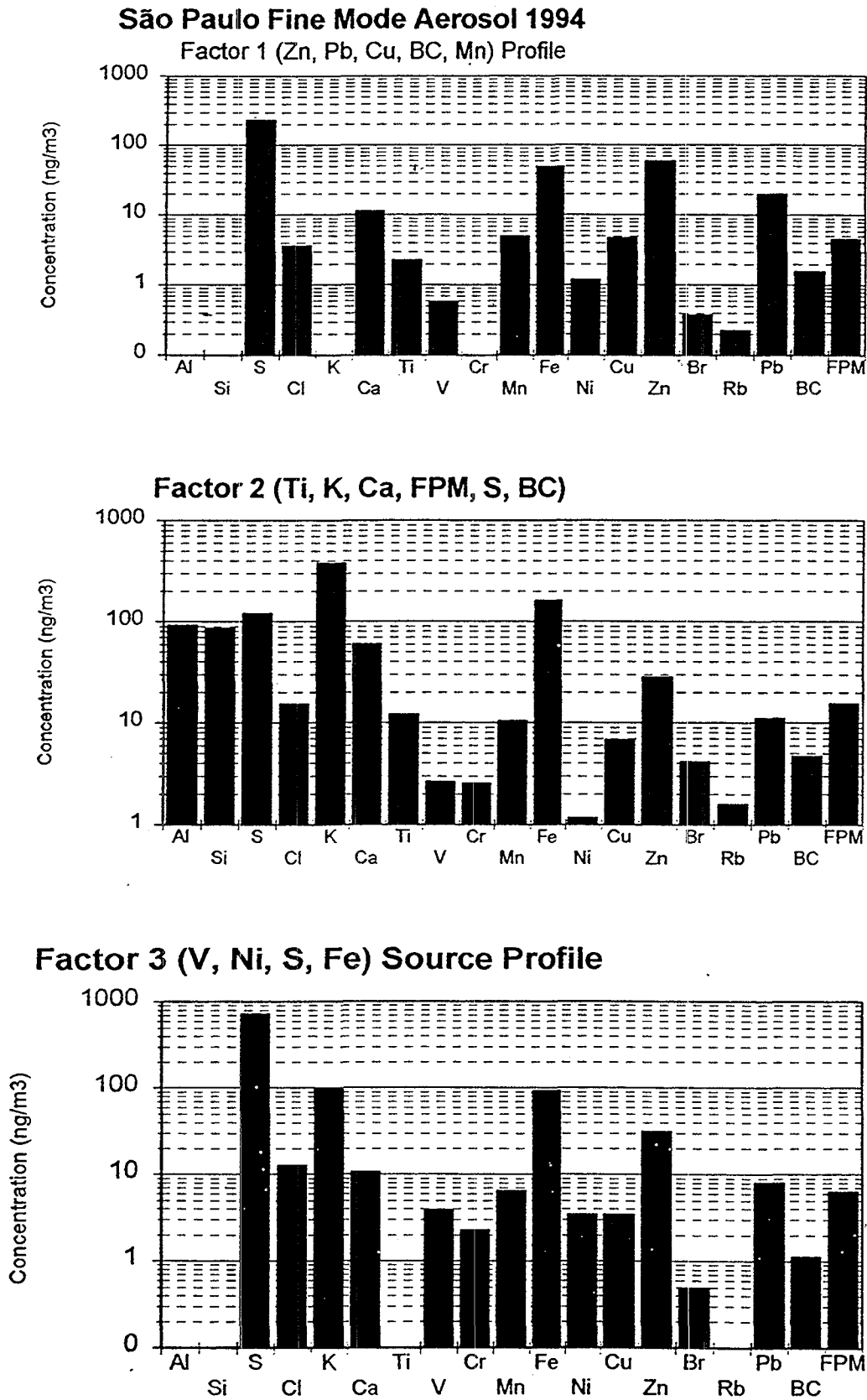
Table 2 - São Paulo Aerosol Characterization Study - 1994 - VARIMAX Rotated Factor Matrix for the Fine Mode Aerosol

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
Zn	0.89	-	0.29	-	0.91
Pb	0.88	-	-	-	0.90
Cu	0.73	0.35	0.33	-	0.79
BC	0.65	0.58	-	-	0.83
Mn	0.55	0.46	0.47	-	0.75
Ti	0.44	0.82	-	-	0.90
K	-	0.77	0.36	0.37	0.87
Ca	0.42	0.69	-	-	0.75
FPM	0.48	0.56	0.41	0.43	0.90
V	-	0.28	0.88	-	0.90
Ni	0.44	-	0.82	-	0.91
S	0.34	0.67	0.55	-	0.89
Fe	0.46	0.49	0.54	0.31	0.86
Br	-	0.46	-	0.81	0.90*

*Only factor loadings above 0.25 are shown. The last column shows the communalities for each variable.

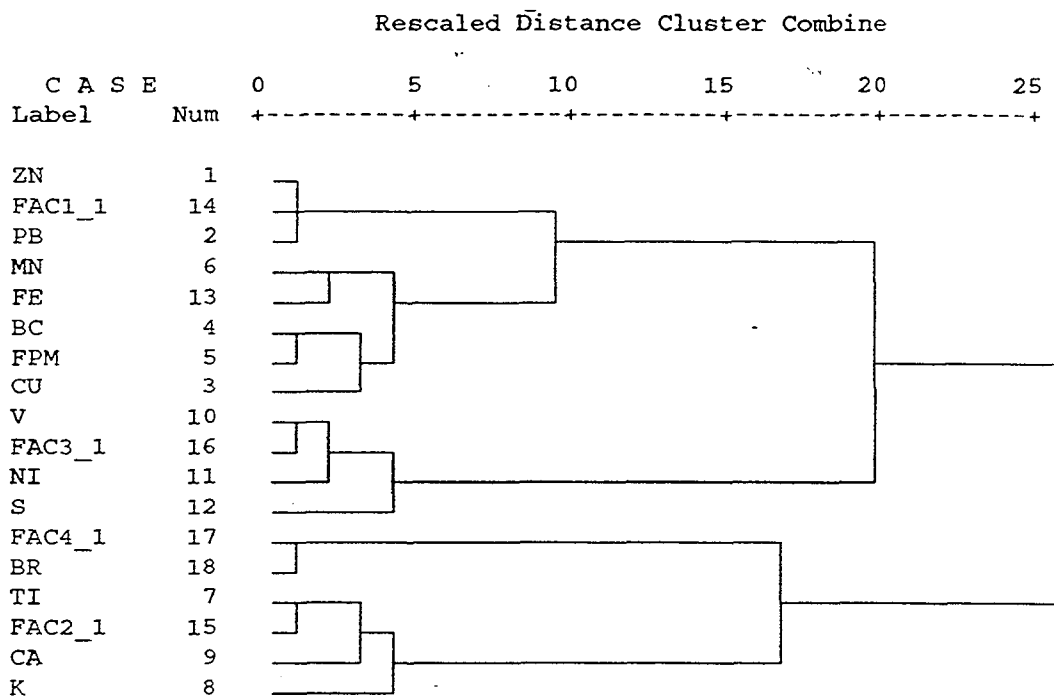
The Absolute Principal Factor Analysis model produced the absolute source profiles showed in Figure 7. It is difficult to make a complete interpretation of the source profiles, but they should represent the absolute elemental concentration associated with each factor. We observe the large S component in the oil combustion profile. Al and Si are significant only for the resuspended soil dust component.

Figure 7 - Absolute elemental profiles obtained for the fine mode São Paulo aerosol using Absolute Principal Factor Analysis.



Cluster analysis was performed to further investigate the relationship between the elemental concentrations. The factor scores for each of the retained 4 factors were also included in the cluster analysis to facilitate the interpretation of the cluster structure. Figure 8 shows the results for the cluster analysis. It is remarkably similar to the factor analysis results. It is important to emphasize that the two analyses are two completely independent techniques.

Figure 8 - Fine Mode São Paulo Aerosol 1994 - Cluster Analysis -Ward's Error - Quadratic Euclidean Distance - Z-scores.



(*) FACX_Y are the factor scores for the 4-factor solution factor analysis.

CONCLUSIONS

The urban area of São Paulo has shown high concentrations of inhalable particulate matter, indicating air pollution problems. Back carbon concentration represents $26.1 \pm 9.7\%$ of the fine mode aerosol mass, indicating the importance of diesel emission. Factor analysis was able to separate four factors, with a transportation-related component, a resuspended soil dust and an oil combustion component. A fourth factor mainly with Br was also observed. An independent multivariate analysis technique using Cluster analysis showed very similar elemental

relationships. The results indicate that the transportation sector gives an important contribution to fine mode aerosol concentration.

Acknowledgments. We would like to acknowledge Alcides C. Ribeiro, Ana L. Loureiro and Tarsis Germano for assistance during sampling and PIXE analysis. We also acknowledge the staff from the Medicine Department from USP for support during sampling. We acknowledge financial support through a "Thematic project" grant from FAPESP-Fundação de Amparo à Pesquisa do Estado de São Paulo

REFERENCES

- Artaxo, P., and C. Orsini, PIXE and receptor models applied to remote aerosol source apportionment in Brazil, *Nucl. Instrum. Methods Phys. Res.*, B22, 259-263, 1987.
- Cahill, T.A., R.A. Eldred, J. Barone, and L. Ashbaugh, Ambient aerosol sampling with stacked filter units, *Rep. Fed. Highway Adminis. FHW-RD-78-178*, 78 pp., Air Qual. Group, Univ. of Calif., Davis, 1979.
- Hopke, P.K., *Receptor Modeling in Environmental Chemistry*, John Wiley, New York, 1985.
- Johansson, S.A.E., and J.L. Campbell, *PIXE - A Novel Technique for Elemental Analysis*, John Wiley, New York, 1988.
- John, W., S. Hering, G. Reischl, and G. Sasaki, Characteristics of Nuclepore filters with large pore size, II, Filtration properties, *Atmos. Environ.*, 17, 373-382, 1983.
- Orsini, C.; Tabacniks, M.; Artaxo, P.; Andrade, F.; Kerr, A., "Characteristics of fine and coarse particles of natural and urban aerosols of Brazil", *Atmospheric Environment*, Vol. 20, no. 11, pg. 2259-2269, 1986
- Parker, R.D., G.H. Buzzard, T.G. Dzubay, and J.P. Bell, A two stage respirable aerosol sampler using Nuclepore filters in series, *Atmos. Environ.*, 11, 617-621, 1977.
- Thurston, G.C., and J.D. Spengler, A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston, *Atmos. Environ.*, 19, 9-25, 1985.