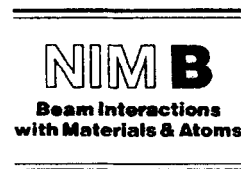




ELSEVIER

Nuclear Instruments and Methods in Physics Research B 136–138 (1998) 955–960



# PIXE, PIGE and ion chromatography of aerosol particles from northeast Amazon Basin

Fábio Gerab <sup>a,\*</sup>, Paulo Artaxo <sup>b</sup>, R. Gillett <sup>c</sup>, G. Ayers <sup>c</sup>

<sup>a</sup> Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Caixa Postal 11049, 05422-970, São Paulo, Brazil

<sup>b</sup> Instituto de Física da Universidade de São Paulo – IFUSP, Caixa Postal 66318, 05315-970, São Paulo, Brazil

<sup>c</sup> Commonwealth Scientific and Industrial Research Organization – CSIRO, Private Bag No. 1, Mordialloc, Victoria 3195, Australia

---

## Abstract

Characterization of atmospheric aerosols collected in the northeast part of the Amazon Basin is presented. The main aerosol source in that region is the forest natural biogenic emission. The aerosol samples were collected using stacked filter units, and were analyzed applying several analytical techniques: Particle Induced X-ray Emission (PIXE) for the quantitative analysis of trace elements with  $Z > 11$ ; Particle Induced Gamma-ray Emission (PIGE) for the quantitative analysis of Na; Ion Chromatography (IC) was used to quantify ionic contents of aerosols from the fine mode particulate samples. A reflectance technique was used in order to measure black carbon concentrations; Gravimetric analysis was used in order to determine the total atmospheric aerosol mass concentration. The comparison from PIXE and IC concentration measurements for S, K and Ca techniques were in an excellent agreement. A good agreement was also obtained for Na concentrations measured by PIGE and IC techniques. Multivariate statistical analysis was used in order to identify and characterize the sources of the atmospheric aerosol present in the sampled region. The Serra do Navio aerosol is characterized by biogenic emissions, responsible for the majority of the total fine mass concentration. A strong marine influence was also noted. Soil dust is also an important aerosol source in that region. © 1998 Elsevier Science B.V.

---

## 1. Introduction

Tropical rainforests are characterized by an intense release of biogenic trace gases and aerosols. The Amazon Basin has the world's largest rainforest. It is a region with intense convective activity [1] resulting in a rapid vertical mixing of biogenic gases and aerosols to high altitudes where they can be transported over long distances and have

an impact on the global atmospheric chemistry. The tropical rainforests of the world are in a delicate nutrient-limited environment [2,3]. Several nutrients, like phosphorus and nitrogen, are critical in these ecosystems and could limit their annual primary productivity [4]. It is necessary to extend our knowledge of the chemical processes that determine the background composition of the atmosphere in these areas, and to understand the biosphere–atmosphere interactions. It is also important to obtain a better understanding of the effects of changes in land use in tropical forests

---

\* Corresponding author.

on the atmospheric composition. Vegetation plays a fundamental role in the control and composition of the atmosphere in tropical forest regions. It is an important source of sulfur gases, such as COS, DMS (dimethyl sulfide), DMDS (dimethyl disulfide), SO<sub>2</sub>, H<sub>2</sub>S and CS<sub>2</sub>. The tropical forest is also a major source of atmospheric organic particles [5,6]. The emitted biogenic aerosol is composed of different kinds of primary particles, and an important fraction of them is secondary aerosol, originating from gas to particle conversion processes.

The Amazon rainforest, with around 4 million km<sup>2</sup>, is the greatest tropical forest. It is responsible for a large fraction of the world's biogenic aerosol production. Biogenic aerosols can act as cloud condensation nuclei (CCN) [7–10], potentially affecting the cloud formation processes. The increased number of CCN can generate brighter clouds, with a bigger reflectivity of solar radiation back to space. Some important nutrients, like S, P, K and Ca, are also emitted during the process. The rapid deforestation now occurring in tropical regions has the potential of changing the atmospheric composition with a regional climatic impact near the equator. Biomass burning is one of the most important anthropogenic sources of particulate matter and gaseous emission into the atmosphere [11]. Aircraft measurements during the burning season show high concentrations of aerosols and black carbon in large areas of the Amazon Basin [12]. This is confirmed by aerosol analysis using remote sensing techniques [13].

In order to investigate the major aerosol sources in Amazon, an aerosol monitoring network has been operating at different locations of the Amazon since 1991 [14,15]. The collected samples were analyzed using different analytical techniques (nuclear-related techniques and chemical analysis) to characterize the atmospheric aerosol. This work presents a comparison among the results obtained by Particle Induced X-ray Emission (PIXE), Particle Induced Gamma-ray Emission (PIGE) and Ion Chromatography (IC) analysis of samples collected in Serra do Navio (0° 54' N, 52° 0' W), in the northeast part of the Amazon Basin. This site is located 190 km north of Equator in a primary tropical rainforest. The Serra do Navio sampling site is

relatively free from anthropogenic aerosol emissions: there is no industry activity for at least 1000 km around, and it has no severe contributions from regional biomass burning emissions. The aerosol source apportionment obtained at the Serra do Navio is also discussed.

## 2. Experimental methods

PM<sub>10</sub> aerosol particles, with an aerodynamic diameter ( $d_p$ ) smaller than 10 μm, were sampled using Stacked Filter Units (SFU) [16]. The SFU can separate the PM<sub>10</sub> aerosol in two fractions: coarse particulate matter (CPM), with  $2.0 < d_p < 10$  μm, collected on a 47-mm diameter, 8 μm pore-size Nuclepore filter, and the fine particulate matter (FPM), with  $d_p < 2.0$  μm, collected on a 47-mm diameter, 0.4 μm pore-size Nuclepore filter. The flow rate is typically 15 l per minute. The SFUs are fitted with a specially designed PM<sub>10</sub>, so that only inhalable particles are sampled. SFUs are loaded with Nuclepore filters in a clean room at the University of São Paulo, transported in a sealed container, and hand-carried after the sampling.

The mass concentration of both CPM and FPM were obtained by gravimetric analysis. The filters were weighed before and after sampling by a Mettler M3 electronic microbalance with 1 μg sensitivity. Filters were equilibrated for 24 h at 50% relative humidity and 20°C before the weighing. Electrostatic charging was avoided by means of <sup>210</sup>Po radioactive sources. The detection limit for aerosol mass concentration is 0.3 μg/m<sup>3</sup>. Black carbon concentrations were determined using a variation of the reflectance technique [17]. The black carbon concentration is proportional to the absorption of light originated from a source illuminating the sample. The equipment is calibrated by means of filters loaded with known amounts of black carbon originated from the combustion of acetylene. The precision of this method is around 20%, and the detection limit for black carbon for sample volumes and filter areas used is about 50 ng/m<sup>3</sup>. PIXE [18] was used to measure concentrations of up to 28 elements (Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni

Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Au, Hg, Pb). The samples were irradiated by a 2.4 MeV proton beam, supplied by a dedicated NEC (National Electrostatics Corporation) 5SDH tandem Pelletron accelerator facility, at the LAMFI (Laboratório de Análise de Materiais por Feixes Iônicos) from University of São Paulo. Detection limits are typically  $3 \text{ ng/m}^3$  for elements in the range  $13 < Z < 23$  and  $0.1 \text{ ng/m}^3$  for elements with  $Z > 22$ . These detection limits were calculated based on a sampling flow rate of 15 l per minute, sampling time of 72 h 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 detection limit. The Na concentration was measured using PIGE [19]. The PIGE detection limit for Na quantification was  $25 \text{ ng/m}^3$  for a 2.4 MeV proton beam and when the 440 keV gamma line (from the  $^{23}\text{Na}(p,\gamma)^{23}\text{Na}$  reaction) is measured. IC was used to determine the water-soluble concentrations of acetate, acetic acid, formate, formic acid, methyl sulfonic acid,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , in the Serra do Navio aerosol fine fraction. The IC measurements were made in CSIRO, Australia. Principal Factor Analysis (PFA) was applied to the measured elemental compositions in order to separate the different aerosol sources at Serra do Navio [20,21].

### 3. Results and discussion

The time series of FPM and CPM concentrations measured at Serra do Navio show a background value of about  $15 \text{ } \mu\text{g/m}^3$  for the  $\text{PM}_{10}$  aerosol concentration. Serra do Navio presents a different rain pattern when compared with other regions of Amazon basin. The most rainy period in Serra do Navio occurs between March and June with an average precipitation of approximately 2700 mm/month. During the driest period, September and October, the monthly precipitation in Serra do Navio is still high, 80 mm/month. Therefore, there is not a well defined dry season in Serra do Navio, as there is in the central Amazon. Furthermore, the Serra do Navio sampling site is not strongly affected by biomass burning, in contrast

to other regions of Amazon Basin. A large aerosol emission from biomass burning occurs at the eastern and the southern Amazon during the end of the dry season (July–September) [14,15]. Thus, a much smaller concentration of inhalable particulates was expected in Serra do Navio than in the central Amazon. Some increase in the FPM concentration during the biomass burning season can be detected in Serra do Navio, but far less intense than in other regions of the Amazon Basin, where biomass burning is the strongest source [14,15].

Although an almost constant aerosol mass concentration at Serra do Navio was observed during the year, some clear episodes of higher coarse mode aerosol concentrations ( $40\text{--}60 \text{ } \mu\text{g/m}^3$ ) were identified. These episodes during December and February are possibly caused by long range transport of Saharan dust [22]. During this time of the year, the position of Intertropical Convergence Zone (ITCZ) allows the intrusion of Saharan dust into the Amazon Basin. This phenomenon has been reported and broadly discussed in the literature [4,22,23].

As samples are being regularly collected, only results from the fraction of the filters already analyzed by PIXE and the other complementary analytical techniques are presented (18 November 1991 to 21 June 1994). Up to 15 October 93 IC results allowed a comparison with PIXE and PIGE. Fig. 1 shows the correlation between the sodium concentration from PIGE and IC measurements. The results are in good agreement. The linear regression between PIGE and IC results is presented

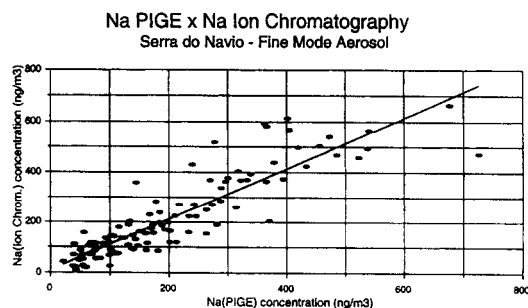


Fig. 1. Sodium quantification in fine mode aerosol samples using PIGE and IC.

Table 1  
PIXE, PIGE, and IC linear regression results for Na, S, K and Ca

Element	Linear regression	R <sup>2</sup>
Na	IC concentration = (1.058 ± 0.043) PIGE + (4.0 ± 10.0) concentration	0.83
S	IC concentration = (0.922 ± 0.021) PIXE + (11.7 ± 9.3) concentration	0.94
K	IC concentration = (0.946 ± 0.018) PIXE + (-16.4 ± 4.3) concentration	0.96
Ca	IC concentration = (0.614 ± 0.019) PIXE + (4.17 ± 0.97) concentration	0.90

in Table 1. The adjusted linear coefficient is very close to one, showing an excellent agreement, in terms of absolute scale, between the two data sets. Also, no scale shift was detected, since the adjusted constant term is compatible with zero. The linear regression results for PIXE versus IC are also shown in Table 1. Ion chromatography sulfur concentrations were obtained by stoichiometric analysis of  $\text{SO}_4^{2-}$ . Also good agreement between PIXE and IC results were obtained for S and K. IC concentration measurements for Ca are 61% of the PIXE ones. One possible explanation for this fact is the different nature of PIXE and IC analysis. PIXE measures the total elemental concentrations and IC measures only its soluble fraction.

Table 2 presents the average concentration for all elements and compounds measured in the fine and the coarse mode aerosol. The CPM concentration is more than twice the FPM concentration. Much larger concentrations of coarse Na and Cl in the Serra do Navio aerosol indicate the strong influence of sea salt aerosol characterized by large crystals of NaCl. The concentration of soil dust characteristic elements, such as Si, Al, Ca, Ti and Fe are around three times greater in the coarse mode than in the fine mode aerosol. On the other hand, S is twice more concentrated in the fine mode. An important fraction of the sulfur present in the aerosol appears as fine sulfate particles, formed by gas-to-particle conversion of the  $\text{SO}_2$  emitted by the vegetation and the sea.

PFA [20] applied to the Serra do Navio concentration time series identified four factors in the fine mode aerosol and three factors in the coarse mode. In case of the PFA, the variability in trace element concentrations is used as a basis for transforming the intercorrelated variables to a set of independent, uncorrelated variables. The first fine mode factor is associated with a natural biogenic aerosol

source. This source has strong contributions from the ionic compounds, K, S, and FPM. Black carbon and Zn associated with this factor can be explained as a small influence of biomass burning plus the natural biogenic release of these compounds. The elemental compositions of biomass burning and natural biogenic aerosol are similar, making their separation by PFA technique difficult. The second and third factors are clearly associated with soil dust (Al, Si, Ca, Ti, Fe and Co) and sea salt (Na, Cl and Mg) aerosol particles, respectively. The fourth factor, associated only with Mn, represents the local contribution from Mn mining activities in Serra do Navio, which has the biggest Brazilian manganese mine.

The first coarse mode has significant component loadings for Si, Al, Sr, Ti, Ca, K, CPM, Sc, Fe and Co. This factor has a clear association with soil dust particles, but the K component loading (0.88) for this factor is an indication of an interference of natural biogenic emission. The second factor is clearly related to sea salt aerosol, with high component loadings for Cl, Na, S and Mg. The third factor is again associated with Mn from mines in Serra do Navio.

#### 4. Conclusions

PIXE, PIGE and IC analysis of aerosol samples present consistent results, demonstrating the utility of the application of these complementary analytical techniques in aerosol research. Serra do Navio has smaller concentrations of FPM and CPM than other sampling sites in the Amazon Basin affected by biomass burning aerosol emissions. Natural biogenic emissions is well correlated with the fine particulate mass concentration. Biogenic aerosol also responds by the majority of  $\text{SO}_4^{2-}$  and carbon

Table 2

Average concentrations, in  $\text{ng}/\text{m}^3$ , for the aerosol particles collected in Serra do Navio. Mean, mean standard deviation, and number of samples, in which the concentrations of the element was above the detection limit are shown

	Serra do Navio fine fraction			Serra do Navio coarse fraction		
	Mean	Mean std. dev.	Number of samples	Mean	Mean std. dev.	Number of samples
Na	194	13	(125)	2060	110	(142)
Mg	109.0	5.8	(125)	269	12	(142)
Al	129	14	(125)	404	42	(142)
Si	298	33	(125)	770	91	(142)
P	1.870	0.069	(6)	7.6	1.2	(38)
S	348	26	(125)	137.0	6.3	(142)
Cl	13.7	3.3	(9)	1059	51	(142)
K	176	14	(125)	135	10	(142)
Ca	37.0	3.2	(125)	161	17	(142)
Sc	1.220	0.067	(125)	3.19	0.25	(142)
Ti	10.8	1.2	(125)	46.2	4.2	(142)
V	0.46	0.11	(19)	2.36	0.25	(99)
Cr	1.72	0.58	(5)	1.59	0.14	(54)
Mn	3.63	0.33	(125)	59.20	0.62	(142)
Fe	81.9	8.3	(125)	472	42	(142)
Co	0.560	0.050	(125)	1.50	1.31	(142)
Ni	0.170	0.026	(13)	0.820	0.075	(88)
Cu	15.8	–	(1)	10.3	3.7	(142)
Zn	1.80	0.12	(125)	7.4	2.2	(142)
Ga	0.130	0.014	(54)	0.673	0.077	(36)
Ge	0.098	0.011	(45)	0.504	0.072	(17)
As	0.373	0.034	(80)	1.46	0.14	(89)
Se	0.255	0.018	(125)	0.459	0.027	(76)
Br	3.79	0.33	(125)	1.721	0.098	(77)
Rb	0.78	0.10	(44)	1.54	0.28	(34)
Sr	0.548	0.055	(125)	2.22	0.17	(142)
Au	0.185	0.022	(51)	0.680	0.080	(24)
Hg	0.321	0.036	(54)	1.49	0.23	(14)
Pb	0.739	0.050	(125)	2.83	0.56	(55)
H <sup>+</sup>	1.96	0.23	(125)	–	–	–
Na <sup>+</sup>	210	15	(125)	–	–	–
NH <sub>4</sub> <sup>+</sup>	138	16	(125)	–	–	–
K <sup>+</sup>	150	14	(125)	–	–	–
Mg <sup>2+</sup>	22.6	1.3	(125)	–	–	–
Ca <sup>2+</sup>	27.1	2.1	(125)	–	–	–
Cl <sup>-</sup>	6.09	0.65	(125)	–	–	–
NO <sub>3</sub> <sup>-</sup>	20.6	3.1	(85)	–	–	–
SO <sub>4</sub> <sup>2-</sup>	996	73	(125)	–	–	–
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	79.6	5.5	(125)	–	–	–
PO <sub>4</sub> <sup>3-</sup>	6.50	0.65	(35)	–	–	–
Acetate	6.56	0.72	(56)	–	–	–
Acetic ac.	12.9	1.6	(62)	–	–	–
Formate	5.84	0.71	(125)	–	–	–
Formic ac.	6.44	0.79	(125)	–	–	–
MSA	8.02	0.53	(125)	–	–	–
BC <sup>*</sup>	746	60	(125)	–	–	–
FPM <sup>*</sup>	6.82	0.57	(125)	–	–	–
CPM <sup>*</sup>				14.62	0.93	(142)

\* BC, FPM and CPM are black carbon, fine particulate mass and coarse particulate mass concentrations, respectively. FPM and CPM are expressed in  $\mu\text{g}/\text{m}^3$ .

particles. These compounds act as cloud condensation nuclei and can have a role in Amazon atmospheric albedo. The coarse fraction of the aerosol shows a significant influence of sea spray. The second main source of coarse aerosol has contributions both from biogenic natural aerosol release and soil dust particulate.

## References

- [1] M. Garstang, J. Scala, S. Greco, R. Harriss, S. Beck, E. Browell, G. Sachse, G. Gregory, G. Hill, J. Simpson, W.K. Tao, A. Torres, *J. Geophys. Res.* 93 (1988) 1528.
- [2] P.M. Vitousek, R.L. Sanford, *Annu. Rev. Ecol. Syst.* 17 (1986) 137.
- [3] E. Salati, P.B. Vose, *Science* 225 (1984) 129.
- [4] R. Swap, M. Garstang, S. Greco, R. Talbot, P. Kallberg, *Tellus* 44B (1992) 133.
- [5] H. Cachier, P. Buat-Menard, M. Funtugne, R. Chesselet, *J. Atmos. Chem.* 3 (1985) 469.
- [6] G. Crozat, J.L. Domergue, J. Baubet, V. Bogui, *Atmos. Environ.* 12 (1978) 1917.
- [7] L.R. Maki, K.J. Willoughby, *J. Appl. Meteorology* 17 (1978) 1049.
- [8] R.C. Schnell, *Tellus* 34 (1982) 92.
- [9] G. Vali, M. Christensen, R.W. Fresh, E.L. Galyvan, R.R. Maki, R.C. Schnell, *J. Atmos. Sci.* 33 (1976) 1565.
- [10] A.M. Dingle, *J. Rech. Atmos.* 2 (1966) 231.
- [11] P.J. Crutzen, M.O. Andreae, *Science* 250 (1990) 1669.
- [12] E.B. Pereira, A.W. Setzer, F. Gerab, P.E. Artaxo, M.C. Pereira, G. Monroe, *J. Geophys. Res.* 101 (1996) 23983.
- [13] M.E. Prins, W.P. Menzel, D.E. Ward, in: V.W.J.H. Kirchhoff (Ed.), *SCAR-B Proceedings*, Transtec Editorial, S.J. Campos, Brazil, 1997, p. 153.
- [14] P. Artaxo, F. Gerab, M.L.C. Rabello, *Nucl. Instr. and Meth. B* 75 (1993) 277.
- [15] P. Artaxo, F. Gerab, M.A. Yamasoe, J.V. Martins, *J. Geophys. Res.* 99D (1994) 22857.
- [16] R.D. Parker, G.H. Buzzard, T.G. Dzubay, J.P. Bell, *Atmos. Environ.* 11 (1977) 617.
- [17] M.O. Andreae, T.W. Andreae, R.J. Ferec, H. Raemdonck, *Sci. Total Environ.* 36 (1984) 73.
- [18] S.A.E. Johansson, J.L. Campbell, *PIXE: A Novel Technique for Elemental Analysis*, Wiley, Chichester, 1988.
- [19] L. Asking, E. Swietlicki, M.L. Garg, *Nucl. Instr. and Meth. B* 22 (1987) 368.
- [20] S.R. Thurston, J.D. Spengler, *Atmos. Environ.* 19 (1985) 9.
- [21] P.K. Hopke, *Receptor Modeling for Air Quality Management*, Elsevier, Amsterdam, 1991.
- [22] R. Swap, S. Ulanski, M. Cobbett, M. Garstang, *J. Geophys. Res.* 101 (1996) 4205.
- [23] J.M. Prospero, R.A. Glaccum, R.T. Nees, *Nature* 289 (1981) 570.