

## Fine mode aerosol composition at three long-term atmospheric monitoring sites in the Amazon Basin

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**Abstract.** The Amazon Basin tropical rain forest is a key region to study processes that are changing the composition of the global atmosphere, including the large amount of fine mode aerosol particles emitted during biomass burning that might influence the global atmosphere. Three background monitoring stations, Alta Floresta, Cuiabá, and Serra do Navio, are operating continuously measuring aerosol composition. Fine ( $dp < 2.0 \mu\text{m}$ ) and coarse ( $2.0 < dp < 10 \mu\text{m}$ ) mode aerosol particles were collected using stacked filter units. Particle-induced X-ray emission was used to measure concentrations of up to 20 elements in the fine mode: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, and Pb. Soot carbon and gravimetric mass analysis were also performed. Absolute Principal Factor Analysis (APFA) has derived absolute elemental source profiles. APFA showed four aerosol particle components: soil dust (Al, Ca, Ti, Mn, Fe), biomass burning (soot, fine mode mass concentration, K, Cl), natural primary biogenic particles with gas-to-particle component (K, S, Ca, Mn, Zn), and marine aerosol (Cl). Biogenic and biomass burning aerosol particles dominate the fine mode mass concentration, with the presence of K, P, S, Cl, Zn, Br, and fine mode mass concentration (FPM). At the Alta Floresta and Cuiabá sites, during the dry season, a strong component of biomass burning is observed. Inhalable particulate matter ( $dp < 10 \mu\text{m}$ ) mass concentration up to  $700 \mu\text{g}/\text{m}^3$  was measured. Fine particle mass concentration alone can go as high as  $400 \mu\text{g}/\text{m}^3$  for large regions. The fine mode biogenic and biomass burning components show remarkable similarities in the elemental composition, even though the sampling sites are more than 3000 km apart. Fine mode sulfur concentration is entirely associated with the primary biogenic aerosol particles, with gas-to-particle conversion and the biomass burning component. Large amounts of essential plant nutrients like P are mobilized into the atmosphere and possibly lost from the Amazon Basin ecosystem by long-range transport.

### 1. Introduction

The Earth's atmosphere is a vital natural resource that until recently appeared unaffected by human activities, except on urban or regional scales [Galbally, 1989]. However, it has become clear that the worldwide anthropogenic activities have an impact on the global atmosphere. To assess the role of the tropical atmosphere in global atmospheric changes it is necessary to identify and quantify important physical and chemical processes in the generation, transformation and deposition of aerosol particles in tropical areas. The tropical rain forest is a globally important ecosystem, with large emissions of biogenic gases and particles. The Amazon Basin, with about 4 million square kilometers, plays an important role in emissions of water vapor, gases and aerosol particles to the global atmosphere [Harriss *et al.*, 1990].

Tropical rain forest ecosystem is characterized by intense sources of biogenic gases and aerosols. The Amazon Basin has the world's largest rain forest and is a region with intense convective activity [Garstang *et al.*, 1988], resulting in rapid verti-

cal mixing of biogenic gases and aerosols to high altitudes where they can be transported over long distances and have an impact on the global tropospheric chemistry. It is becoming clear that it is necessary to increase our knowledge of the chemical processes that determine the composition of the atmosphere in background areas and to understand biosphere-atmosphere interactions. Also it is necessary to obtain a better understanding of the alterations in the atmospheric composition due to changes in land use in tropical rain forests. The tropical rain forests of the world are in a delicate nutrient-limited environment [Vitousek and Sanford, 1986]. Due to nutrient poor oxisols and ultisols in these regions the deposition of airborne aerosol particles is needed to achieve a nutrient balance [Salati and Vose, 1984; Vitousek and Sanford, 1986]. Several elements, like phosphorus, are a critical airborne element that could limit annual net primary production of the Amazon Basin tropical rain forest [Swap *et al.*, 1992].

### 2. Biogenic and Biomass Burning Aerosol Particles in Tropical Rain Forest Regions

In a tropical forest atmosphere, vegetation plays a major role in controlling the airborne particle concentration. The forest vegetation is the principal global source of atmospheric organic particles [Cachier *et al.*, 1985; Crozat *et al.*, 1978]. Only few

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studies involving natural released biogenic aerosols have been conducted in tropical rain forests [Lawson and Winchester, 1979; Orsini et al., 1982; Artaxo and Orsini, 1986, 1987; Artaxo and Maenhaut, 1990; Artaxo et al., 1988, 1990, 1992, 1993c].

The natural biogenic aerosol particles consist of many different types of particles, including pollen, spores, bacteria, algae, protozoa, fungi, fragments of leaves, excrement and fragments of insects. Also a significant fraction comprises secondary aerosol particles formed by gas-to-particle conversion of organic and sulfur-related biogenic gases. These biogenic particles can be submicrometer in size. Bacteria in forested areas were found in the size range of 0.5 to 2.5  $\mu\text{m}$  in size [Jaenicke and Mathias-Maser, 1992]. Biological particles exhibit cloud influencing properties [Maki and Willoughby, 1978; Schnell, 1982; Vali et al., 1976; Dingle, 1966] and can act as cloud condensation nuclei, potentially affecting the cloud formation mechanisms. Biogenic aerosol particles, even in urban areas, can be as much as 50% of the aerosol mass, suggesting that sources of natural biogenic aerosol particles have been underestimated in the past [Jaenicke and Mathias-Maser, 1992].

The continuous natural release of aerosols by plants was studied by some investigations. Crozat [1979] hypothesized that forest is a major natural global source of aerosols. Fish [1972] suggested that haze observed in forested areas could be due to submicrometer particles from electrical generation of biogenic aerosol by leaves. Decaying vegetation generate small particles that can act as cloud nuclei. Beauford et al. [1977] have discussed the wind action on plant leaves that result in mechanical abrasion, generating large biogenic particles with the presence of heavy metals. Biological activity of microorganisms on leaf surfaces and forest litter results in airborne particles, and wind-blown pollen grains certainly contribute to coarse fraction particles in forested areas. Particulate material containing Zn, Pb and Cu was observed to be produced by higher plants [Beauford et al., 1975, 1977]. The transpiration of plants can lead to migration of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  to the atmosphere [Ferry and Ward, 1959]. The biogenic related elements (e.g., K, P, S, Zn, Rb) are essential elements in superior plants and are present in the fluids circulating in the plant and are released from the leaves to the atmosphere during guttation and transpiration [Nemeryk, 1970].

The emission of sulfur gases from terrestrial plants is well established. Vegetation is known to emit a large number of sulfur containing gases like COS (carbonyl sulfide), DMS (dimethylsulfide), DMDS (dimethyldisulfide),  $\text{SO}_2$  (sulfur dioxide),  $\text{H}_2\text{S}$  (hydrogen sulfide),  $\text{CS}_2$  (carbon disulfide), MeSH (methylmercaptan) and others. The emission of DMS from trees was observed by Lovelock [1974]. Generally, the emission rate for sulfur gases increases with temperature [Fall et al., 1988]. Vegetation is believed as the major worldwide sink for COS [Brown and Bell, 1986]. Measurements of the sulfur cycle compounds in the African rain forest by Bingemer et al. [1992] showed similar concentration to those measured in Amazonia [Andreae et al., 1990]. Many of these sulfur compounds are rapidly oxidized to sulfate in the very humid and hot atmosphere of the Amazon forest. As sulfur is also present in the fluids of the vegetation together with P, K, Ca and other biogenic elements, it is also emitted during the natural processes of transpiration and guttation. It is important to notice that there is no large power plants or industries in the Amazon Basin. Most of the sulfur concentration is of biogenic origin.

The fast deforestation occurring now in tropical regions has

the potential of changing the atmospheric composition and has a regional climatic impact that can affect a large portion of the equatorial region. Biomass burning is a major source of particulate matter and gaseous emissions into the atmosphere [Crutzen and Andreae, 1990]. More than 80% of the emissions from biomass burning originate in the tropics. The high rate of tropical biomass burning in the last decade is mainly a result of burning of savanna in Africa and deforestation in the Amazon Basin [Setzer and Pereira, 1991]. Estimates of total biomass consumed on a global basis range from 2 to 10 Pg (1 petagram= $10^{15}$  g) per year [Crutzen and Andreae, 1990]. In terms of total particulate matter (TPM), emissions are around 104 Tg (1 teragram =  $10^{12}$  g) per year [Levine, 1990]. For particulate matter in the fine mode (FPM,  $d_p < 2.0 \mu\text{m}$ ), emissions are estimated as 49 Tg of fine particles per year, accounting for about 7% of the global fine mode aerosol particles emission rate. For elemental carbon, the emission of 19 Tg/yr. could account for a very high 86% of the total anthropogenic emissions [Levine, 1990].

The emissions of gases during biomass burning are affecting the global concentrations of gases like  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{N}_2\text{O}$ , COS and others [Crutzen et al., 1979]. Much less studied is the composition of aerosol particle emissions. The composition and size distribution of aerosol particles were measured in forest fires in Rondonia, Brazil, with large emissions of potassium, sulfur, silicon, zinc and organic matter [Artaxo et al., 1993a]. Elemental carbon associated with potassium was identified as tracer for biomass burning plumes in remote oceanic areas [Andreae, 1983]. Ward and Hardy [1991] give a detailed description of the processes that generate aerosol particles in the different phases of biomass burning. Emission factors for particulate matter vary from 5 to 40 g/kg as the combustion efficiency goes from 98% to 60%, with high emissions of Na, K, Cl, Ca, S and other elements.

Aerosol particles emitted in tropical biomass burning are active cloud condensation nuclei (CCN) and can exert strong influence on the concentration and size of cloud droplets [Rogers et al., 1992]. Warner and Twomey [1967] observed elevated concentrations of CCN in the plumes of sugar cane fires in Australia. Desalmand et al. [1985] observed significant amounts of CCN in brushfire events in the Ivory Coast region of West Africa. There is a possibility of changing the precipitation pattern and composition, due to the changes in CCN characteristics. These aerosol particles have also the possibility of directly cooling the climate, reflecting solar radiation to space [Coakley et al., 1983; Robock, 1988]. A major component of the particles is elemental carbon (also called graphitic carbon or black carbon) that has strong radiative absorption properties. This indicates that the tropical biomass burning particle flux is mostly composed of particles that can act as CCN. These particles could have a global effect since they can travel long distances in the atmosphere.

### 3. Experimental Methods

Fine and coarse aerosol particles were sampled using stacked filter units (SFU) [Parker et al., 1977]. The SFU was fitted with a specially designed inlet, which provided a 50% cutoff diameter of 10  $\mu\text{m}$  [Cahill et al., 1979]. The SFU collects coarse mode particles ( $2.0 < d_p < 10 \mu\text{m}$ ) on a 47-mm-diameter, 8- $\mu\text{m}$  pore size Nuclepore filter while a 0.4- $\mu\text{m}$  pore size Nuclepore filter collects the fine mode particles ( $d_p < 2.0 \mu\text{m}$ ) [John et al., 1983]. The flow rate was typically 16 l per minute, and sam-



Figure 1. Map of South America, showing the location of the three sampling sites where continuous monitoring of aerosol particles is being carried out.

pling time varied from 24 to 72 hours. Particle bounce is not a problem in the Amazon Basin due to the high relative humidity (70 to 95 %).

Three monitoring stations are being operated continuously in different ecosystems. Figure 1 shows a map of South America with the location of the three background sampling stations. The first sampling station is situated in Cuiabá, at the Brazilian savanna, south of the Amazon Basin rain forest. The Cuiabá sampling station allows the analysis of regional effects of biomass burning emissions due to the location of the station. The site is heavily affected by regional savanna biomass burning. A second aerosol sampling station was installed in November 1991 at the "Serra do Navio," in the northern part of the Amazon Basin. This station is located 190 km north of the equator, in a primary tropical rain forest. The Serra do Navio sampling site is relatively free from regional biomass burning emissions, and there are no industrial activities for at least 1000 km around the sampling site. The third sampling site is in the region of "Alta Floresta," near the border of Mato Grosso and Amazonas states. Alta Floresta is in the middle of a primary forest region, with land clearing some kilometers around the sampling site, affecting the aerosol concentration during the dry season (August-September). The nearest major urban area is more than 500 km away from Alta Floresta. The Amazon Basin dry season

starts in March, extending until late September. Biomass burning occurs mainly in the end of the dry season, August and September.

The elemental concentrations were measured with the particle-induced X ray emission (PIXE) [Johansson and Campbell, 1988] 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. Detection limits are typically  $5 \text{ ng/m}^3$  for elements in the range  $13 < Z < 22$  and  $0.4 \text{ ng/m}^3$  for elements with  $Z > 23$ . These detection limits were calculated based on a sampling flow rate of 16 l per minute sampling time of 48 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  $1 \mu\text{g}$  sensitivity. Before weighing, the filters are equilibrated for 24 hours at 50% relative humidity and  $20^\circ\text{C}$  temperature. Electrostatic charges are controlled by means of  $^{210}\text{Po}$  radioactive sources. Detection limit for the aero-

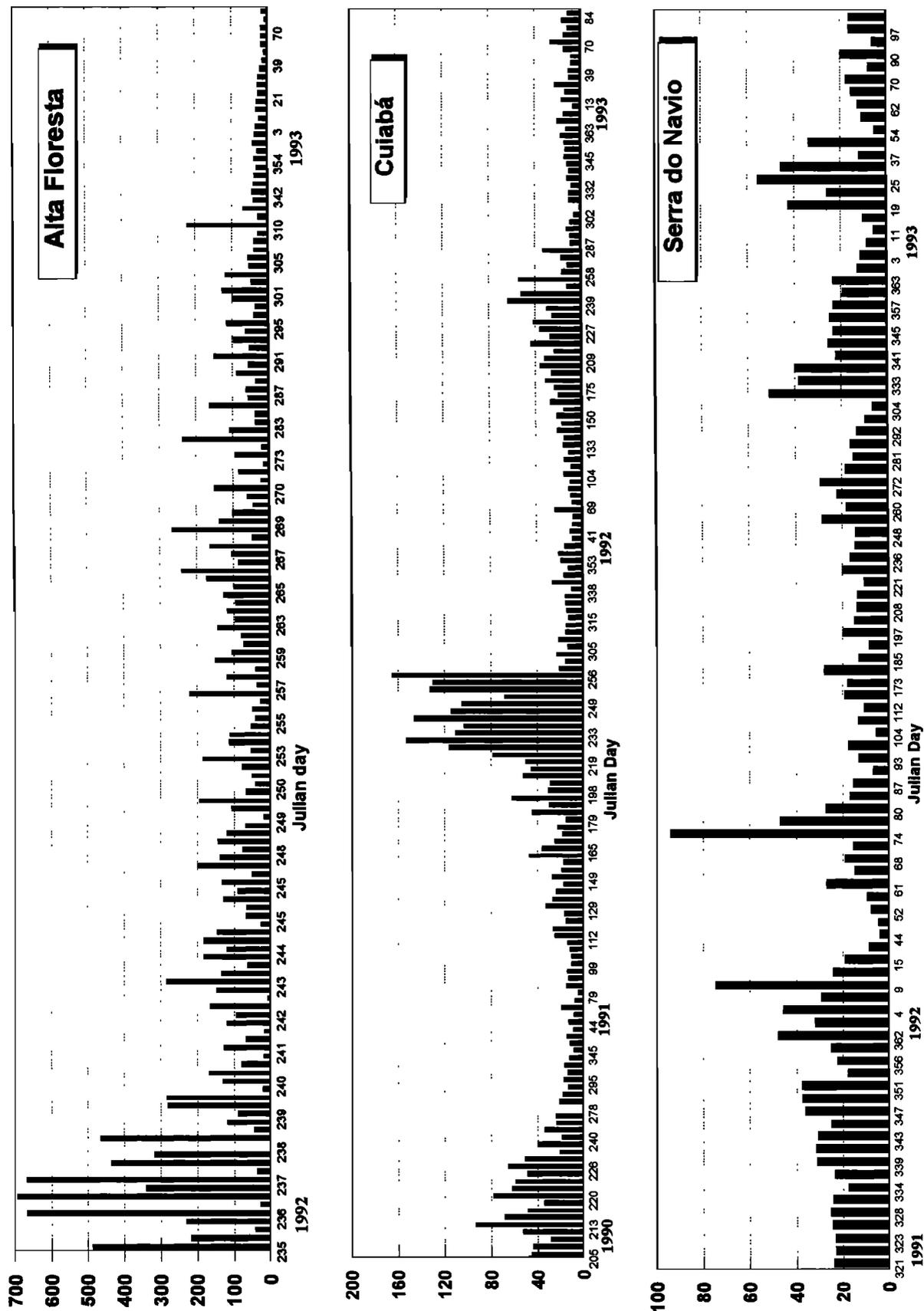


Figure 2. Time series of the inhalable ( $dp < 10 \mu\text{m}$ ) particulate matter concentration in  $\mu\text{g}/\text{m}^3$  for the 150 SFU collected at Alta Floresta, 183 SFU collected at Cuiabá and the 99 SFU collected in the Serra do Navio sampling site. Note that timing of the sampling is different for the three sampling stations.

sol mass concentration is  $0.3 \mu\text{g m}^{-3}$ . Precision is estimated at about 15%. Soot carbon concentration was measured using a reflectance technique using a photometer.

#### 4. Absolute Principal Factor Analysis

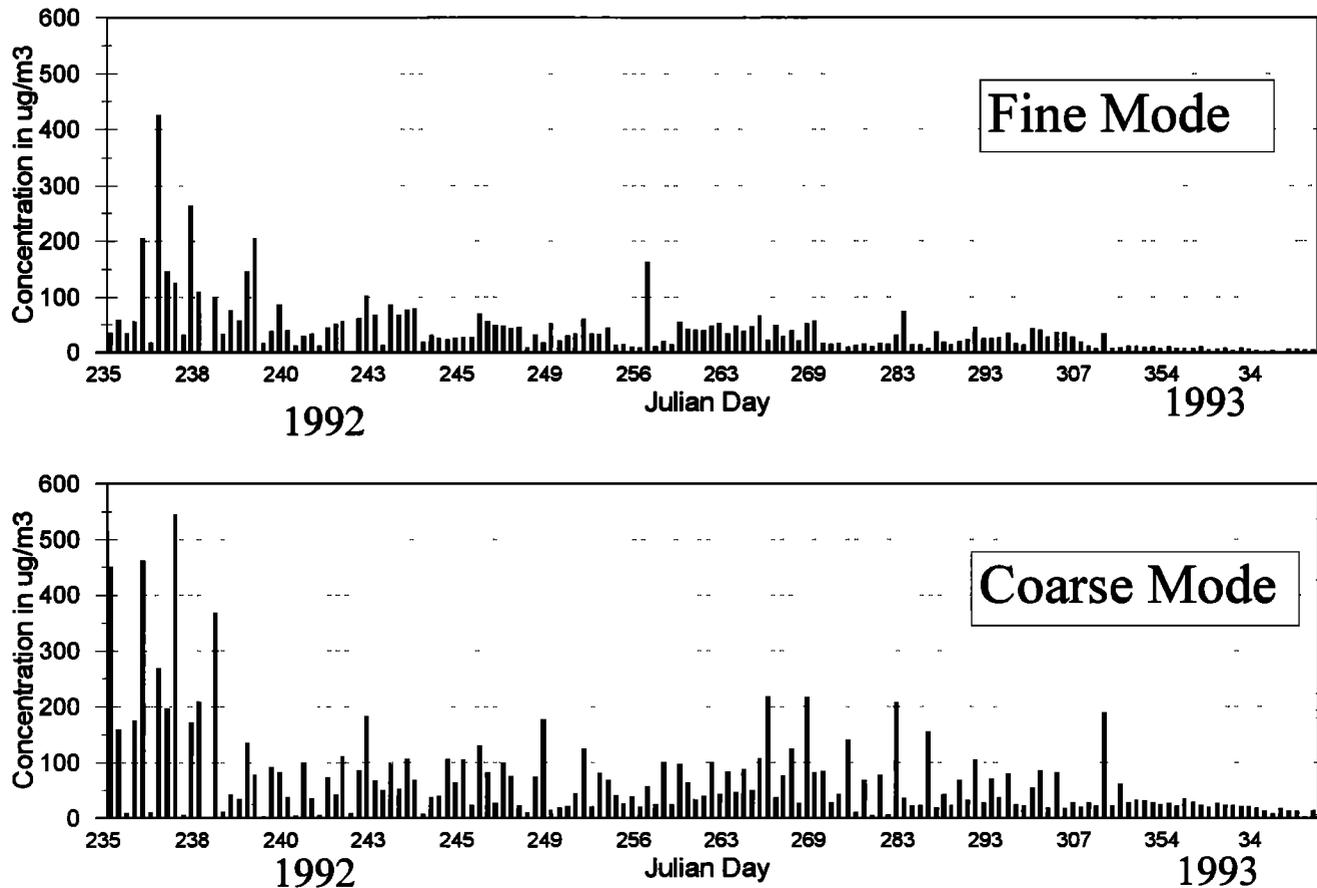
To separate the different components of natural biogenic aerosols using the elemental composition, absolute principal factor analysis (APFA) was used [Thurston and Spengler, 1985; Hopke, 1985]. APFA offers the possibility to obtain a quantitative elemental source profile instead of only a qualitative 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. [Hopke, 1985]. The measured aerosol mass concentration can also be regressed on the APFS to obtain the aerosol total mass source apportionment.

#### 5. Results and Discussion

A large number of samples were collected (150 samples in Alta Floresta, 183 samples in Cuiabá and 99 samples in Serra do Navio), allowing a detailed analysis of dry and wet season atmospheric conditions. Biomass burning season occurs mainly in August and September. Due to logistical reasons, a fraction of the fine mode filters was analyzed by PIXE. From the total number of aerosol samples, 116 fine mode filters were analyzed for elemental composition in Alta Floresta, 136 in Cuiabá, and 48 fine mode samples in Serra do Navio. It will be discussed in this paper the aerosol mass concentration for the fine, coarse and inhalable particulate matter, and the fine mode fraction ( $d_p < 2 \mu\text{m}$ ) elemental data obtained from the fine mode SFU

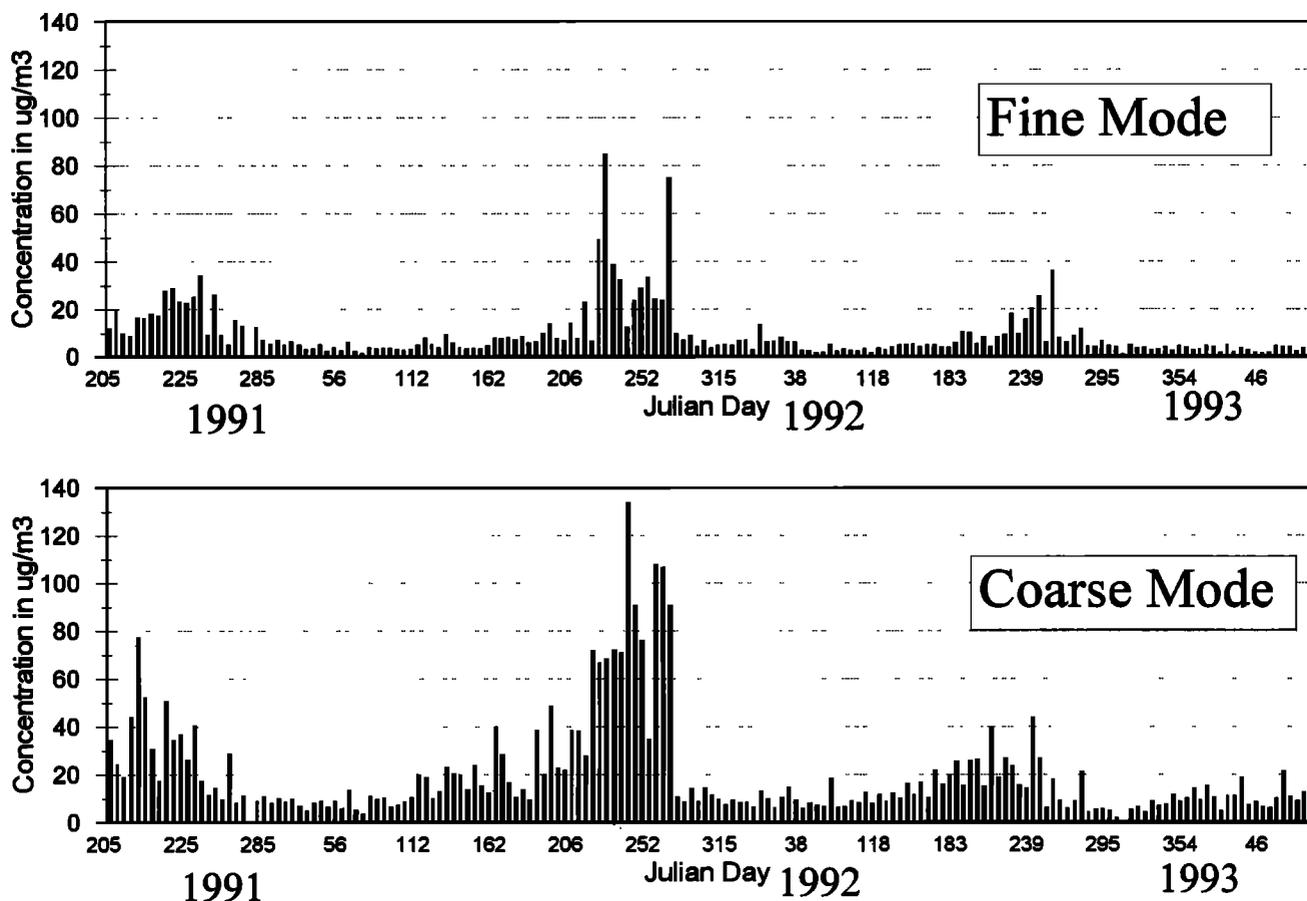
## Alta Floresta Aerosol Mass Concentration



**Figure 3.** Fine ( $d_p < 2.0 \mu\text{m}$ ) and coarse ( $2.0 < d_p < 10 \mu\text{m}$ ) aerosol mass concentration in Alta Floresta, from August 1992 to March 1993. Higher concentrations in the fine mode are indicative of biomass burning impact, whereas high concentrations in the coarse mode indicate impact by soil dust aerosol particles.

# Cuiabá

## Aerosol Mass Concentration



**Figure 4.** Time series of the fine and coarse mass concentration for the Cuiabá sampling site, from July 1990 to March 1993. Three biomass burning seasons can be observed, with very high concentrations for the 1992 biomass burning season.

filters collected at the three sampling stations.

Figure 2 presents the time series of the inhalable particulate matter concentration for the 150 SFU collected at Alta Floresta, 183 SFU collected at Cuiabá and the 99 SFU collected in the Serra do Navio sampling site. There is very clearly a large increase in aerosol loading in the atmosphere during the biomass burning season (August and September) for the Alta Floresta and Cuiabá sampling sites. In Cuiabá, from an inhalable particulate matter (IPM) concentration of about  $10\text{--}20\ \mu\text{g}/\text{m}^3$  during the wet season, the concentration goes as high as  $100\text{--}150\ \mu\text{g}/\text{m}^3$  during the biomass burning season. Aircraft measurements over large areas of the Amazon Basin show very high IPM concentrations up to  $300\ \mu\text{g}/\text{m}^3$  [Artaxo *et al.*, 1993a]. These high concentrations are observed in areas as large as 2 million square kilometers, using aircraft and remote sensing measurements, and generally they last for about 2 months, August and September. For the Alta Floresta site, IPM concentrations higher than  $600\ \mu\text{g}/\text{m}^3$  were observed. In Serra do Navio, much lower IPM concentration was observed. A background value of  $10\text{--}20\ \mu\text{g}/\text{m}^3$  is observed. Higher concentrations ( $40\text{--}80\ \mu\text{g}/\text{m}^3$ ) were observed in January and February, possibly an effect of the long

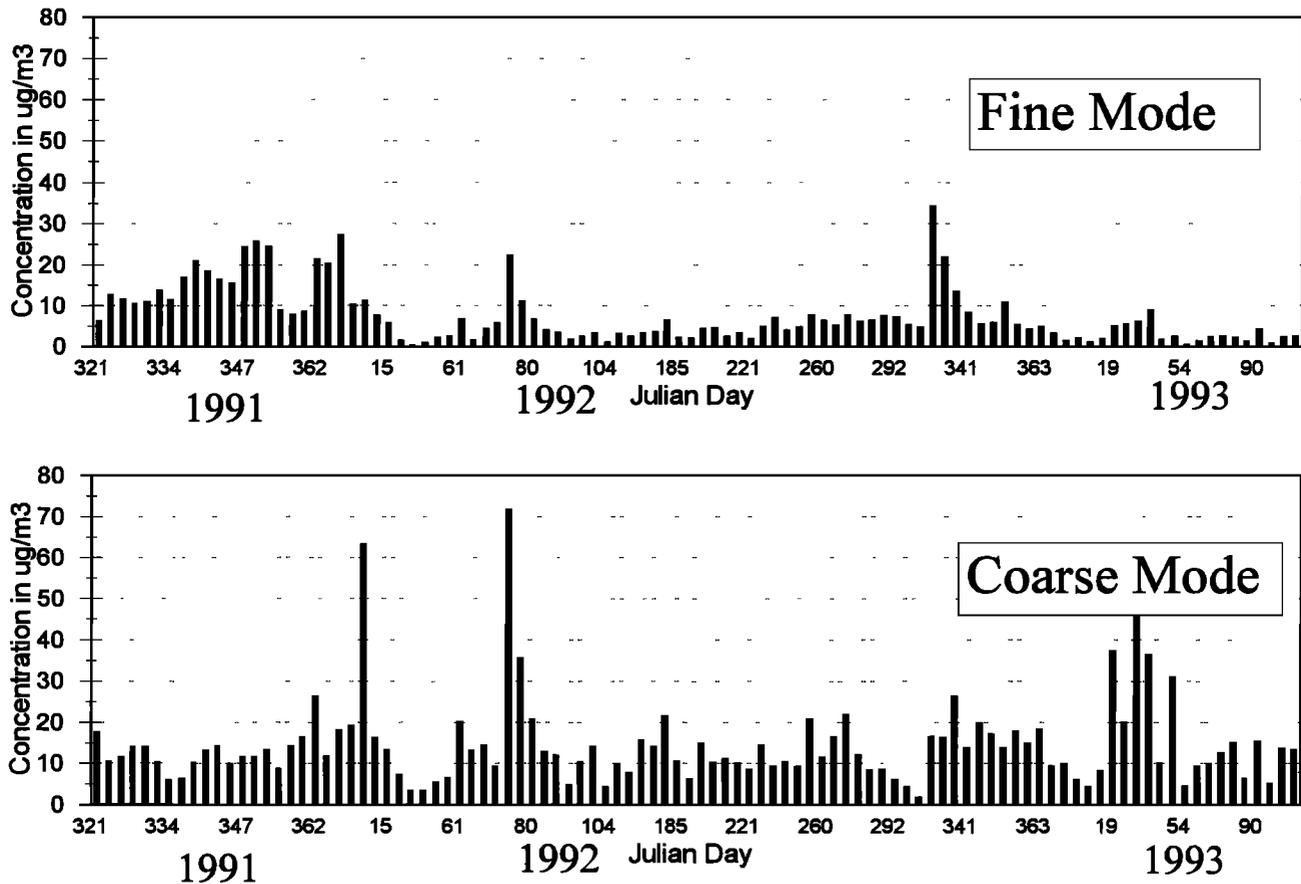
range transport of Saharan dust, as will be discussed later.

Figure 3 shows the fine and coarse aerosol mass concentration in Alta Floresta, from August 1992 to March 1993. Higher concentrations in the fine mode are indicative of biomass burning impact, whereas high concentration in the coarse mode indicates impact by soil dust aerosol particles. During the dry season in Alta Floresta and Cuiabá, soil dust concentrations can be relatively high, being suppressed when the heavy rains arrive, generally in October. In Alta Floresta during the months of August and September, both biomass burning and soil dust, are enhanced, producing very high concentrations of airborne particulate matter. Fine particle mass concentration alone can go as high as  $400\ \mu\text{g}/\text{m}^3$ . It is possible to observe that even during the rainy season (October to March), sporadically it was observed coarse particle concentrations of about  $200\ \mu\text{g}/\text{m}^3$ . Only in December and January, with heavy rains, concentrations really dropped below  $20\ \mu\text{g}/\text{m}^3$ .

Figure 4 shows the long time series of fine and coarse mass concentration for the Cuiabá sampling site, from July 1990 to March 1993. Three biomass burning seasons can be observed in Figure 4, with very high concentrations for the 1992 biomass

# Serra do Navio

## Aerosol Mass Concentration



**Figure 5.** Time series of the fine and coarse particulate matter for the 99 SFU samples collected at the Serra do Navio sampling site. The geographical location in the north of the Amazon Basin of the Serra do Navio sampling site makes it less influenced by regional biomass burning.

burning season. One interesting peculiarity in Cuiabá is that the increase in coarse particles precedes the increase in fine particles for 1 or 2 months. The reason for that is that biomass burning only occurs in the end of the dry season, whereas soil dust particles increase in concentration as soon as the weather dries. In 1992, the dry season had an unusual weather pattern, with unexpected rains occurring at the last week of August, right when the ranchers were preparing to burn the cleared land. Many farmers were left with the forest clearing without burning and had to wait for the 1993 biomass burning season to complete the clearing of their land.

Figure 5 shows the time series of the fine and coarse particulate matter for the 99 SFU samples collected at the Serra do Navio sampling site. The geographical location in the north of the Amazon Basin of the Serra do Navio sampling site makes it less influenced by regional biomass burning. Typically, the biomass burning season in the north of the Amazon Basin occurs in December to February. It can be seen in Serra do Navio time series of fine mass concentration some increase during the biomass burning season, but not so pronounced as in Cuiabá

and Alta Floresta. The coarse particle mass concentration shows some clear episodes of high concentration during January and February. During this time of the year, the position of the Inter-tropical Convergence Zone allows the intrusion of Sahara dust into the Amazon Basin [Reichholf, 1986], as discussed in detail by Prospero *et al.* [1981] and Swap *et al.* [1992]. As will be observed later with the elemental concentrations, the increase in this coarse mode particle concentration is due to airborne mineral dust.

The fine mode samples were analyzed by the PIXE method to obtain the elemental composition of the airborne particles. Table 1 presents the average elemental concentration in  $\text{ng}/\text{m}^3$  for the fine mode aerosol at the three sampling sites. FPM represents the fine mode aerosol mass concentration in  $\mu\text{g}/\text{m}^3$ . Generally, the concentrations are similar among the three sampling stations, with some remarks. It is possible to observe the higher effect of biomass burning at the Alta Floresta site, with the higher concentrations for K, S, Zn, FPM and other elements. Also the higher soil dust concentrations in Alta Floresta can be deduced from the high concentration of Al, Si,

**Table 1.** Average Concentration for Fine Mode Aerosol ( $d_p < 2 \mu\text{m}$ ) in Three Remote Atmospheric Monitoring Stations in the Amazon Basin

	Concentration, $\text{ng/m}^3$		
	Alta Floresta	Cuiabá	Serra do Navio
Al	398±468 (116)	91.5±98.1 (136)	170±201 (48)
Si	485±508 (116)	134±129 (109)	414±496 (48)
P	16.0±18.6 (12)	10.0±7.6 (72)	15.5±10.8 (20)
S	948±741 (116)	389±339 (136)	526±397 (48)
Cl	12.9±10.0 (70)	10.4±11.9 (136)	13.2±10.4 (38)
K	701±728 (116)	326±353 (136)	251±205 (48)
Ca	43.6±37.3 (116)	29.1±24.2 (136)	54.1±40.9 (48)
Ti	23.6±26.0 (116)	6.92±7.36 (136)	14.2±15.9 (48)
V	4.28±4.53 (86)	0.86±0.61 (25)	1.68±1.79 (17)
Cr	5.09±3.98 (67)	3.42±2.89 (66)	2.23±0.98 (17)
Mn	3.53±3.20 (46)	3.60±3.26 (136)	3.78±1.98 (48)
Fe	249±269 (116)	175±170 (136)	120±119 (48)
Ni	1.98±1.52 (12)	1.09±0.67 (8)	0.21±0.06 (2)
Cu	3.22±3.12 (53)	1.55±1.19 (69)	1.65±1.78 (25)
Zn	8.21±6.91 (116)	5.81±4.84 (136)	3.08±1.85 (48)
Br	5.86±3.27 (4)	5.61±5.86 (87)	5.26±3.14 (28)
Rb	-	1.32±1.02 (41)	1.07±0.54 (19)
Sr	-	0.70±0.59 (49)	1.06±0.56 (20)
Zr	-	1.22±0.92 (95)	1.40±0.59 (23)
Pb	-	1.68±1.35 (87)	0.82±0.21 (16)
Soot	-	2051±1922 (136)	-
FPM	49.9±54.8 (116)	10.5±10.7 (136)	9.87±7.47 (48)

Average and standard deviation are shown. Numbers in parentheses are the number of samples in which the concentrations of the element was above the detection limit. Only samples with values above the detection limit were used in calculating the average. FPM is the fine particle gravimetric mass concentration expressed in  $\mu\text{g/m}^3$ .

Ti, and Fe. The concentration of some elements like P, Cl, Ca, Mn, and Br are very similar for the three sites. The average concentration of heavy metals indicative of industrial contributions as Cr, Ni, Cu, Pb, is very low, generally below  $5 \text{ ng/m}^3$ , indicates the absence of industrial or other anthropogenic emissions at the sites, with the exception of biomass burning.

The variability of the elemental concentrations at the three sampling sites was analyzed using the Absolute Principal Factor

Analysis (APFA) technique. Table 2 presents the VARIMAX rotated factor loading matrix for the three sampling sites. For the Alta Floresta samples, only two factors explain most of the data variability. The first factor clearly represents soil dust aerosol, with high loadings for Al, Si, Ca, Ti, and Fe. The second factor representing natural biogenic aerosol mixed with biomass burning aerosol particles has high loadings for K, FPM, S, Cl, Ca, and Zn. Unfortunately, it was not possible to measure

**Table 2.** Factor Analysis Results for the Amazon Basin Fine Aerosol Fraction: VARIMAX Rotated Factor Loading Matrices for Each of the Three Sampling Locations

	Alta Floresta		Cuiabá			Serra do Navio		
	Soil	Biog./Bur.	Soil	Burning	Biogenic	Soil	Biogenic	Manne
Al	0.94	(0.32)	0.86	(0.34)	(0.32)	0.99	(0.01)	(-0.06)
Si	0.94	(0.32)	0.93	(0.14)	(0.26)	0.98	(-0.05)	(0.02)
S	(0.32)	0.87	(0.40)	(0.37)	0.77	(-0.13)	0.97	(0.08)
Cl	(0.25)	0.85	(0.17)	0.87	(0.23)	(0.04)	0.51	0.79
K	(0.35)	0.92	(0.42)	0.59	0.64	(0.11)	0.98	(0.13)
Ca	0.74	0.62	0.68	(0.20)	0.64	0.91	(0.08)	(0.30)
Ti	0.92	(0.37)	0.91	(0.25)	(0.29)	0.99	(-0.08)	(0.02)
Mn	--	--	0.63	(0.41)	0.63	0.79	(0.06)	(-0.08)
Fe	0.94	(0.33)	0.89	(0.23)	(0.36)	0.99	(-0.01)	(0.09)
Zn	(0.53)	0.67	(0.54)	(0.42)	0.66	(0.25)	0.68	0.64
Br	--	--	--	--	--	(-0.23)	0.79	0.47
FPM	(0.35)	0.90	(0.18)	0.93	(0.22)	(0.07)	0.95	(0.22)
Soot	--	--	(0.29)	0.90	(0.26)	--	--	--
$\lambda$	4.7	4.4	4.9	3.6	2.8	5.5	4.2	1.4
Var, %	47	44	41	30	23	46	35	12

Values in parentheses represent factor loadings with smaller significance,  $\lambda$  is the eigenvalue for each retained factor; var represents the percentage of the variance explained by each factor.

soot carbon concentrations for the Alta Floresta fine fraction samples, not allowing the discrimination between the biomass burning component and the natural released biogenic particles. Also the time series is not long enough to allow separation of the components based on the seasonal variability. For the Cuiabá sampling site, three factors explain most of the data variability. The first factor has high loadings for Si, Ti, Fe, Al, Ca and Mn, representing soil dust particles. The second factor has high loadings for FPM, soot carbon, Cl and K, representing biomass burning particles. The third factor with S, Zn, K, Ca and Mn represents the naturally released biogenic particles. There are several arguments that support this interpretation for the Cuiabá factor analysis results. Soot carbon is essentially emitted by biomass burning, as well as chlorine and organic material responsible for the FPM concentrations [Artaxo *et al.*, 1993a]. Zinc, sulfur and potassium were observed as naturally emitted by the vegetation in background areas not affected by biomass burning in the Amazon Basin [Artaxo *et al.*, 1990]. At the Serra do Navio sampling site, three factors were obtained. The first one with high loadings for Al, Fe, Ti, Si, Ca and Mn represents soil dust particles. Studies of long range transport of aerosol particles in the Amazon Basin have indicated the possibility of these particles be Sahara desert dust particles being injected in the Amazon Basin [Talbot *et al.*, 1990; Swap *et al.*, 1992]. The temporal variability of the factor scores for the second factor at Serra do Navio indicates higher scores for the months of January to April, where the long range transport of Sahara Desert dust is possible [Swap *et al.*, 1992]. The second factor at Serra do Navio with high loadings for K, FPM, S, Br, and Zn represent natural biogenic aerosol. The third factor with Cl, Zn and Br represents the marine aerosol particles. The Serra do Navio sampling site is about 300 km away from the ocean,

and the prevailing wind direction is from the Atlantic Ocean to the sampling site. Generally, more than 90% of the element variability were explained by the factor analysis model. This indicates the adequacy of the factor model, and the number of factors retained in each analysis.

The APFA procedure allows obtaining absolute source profiles in units of  $\text{ng/m}^3$ . The interesting point in this approach is that it makes possible to source apportion elements that were not detected in all the samples. Manganese in Alta Floresta, for example, was detected in 46 of the 116 samples, making it impossible to include Mn in the factor analysis calculations. However, it is possible to perform multiple linear regression (MLR) among these 46 manganese elemental concentrations and the absolute factor scores for each of the discriminated aerosol sources. The resulting coefficients and standard deviation of the MLR are statistically checked through F tests to be sure that the regression coefficients are statistically significant at the 95% confidence level. In the case of Mn in Alta Floresta, it was statistically significant for both soil dust and biogenic aerosol components, making it possible to quantitatively apportion the Mn concentration for the two factors. Figure 6 shows the absolute elemental source profiles for the biogenic plus the biomass burning aerosol component for the three sites. The elemental composition is shown normalized to the fraction of the FPM concentration apportioned to the components for each sampling site. Potassium, for example, appears at 1.4 %, 3.2 %, 2.7 % of the FPM, respectively, for the Alta Floresta, Cuiabá and Serra do Navio sampling sites. These values agree quite well with the presence of K in plants that is about 1.8 % [Bowen, 1979]. Sulfur appears enriched at the three sites (2 to 6% of FPM), due to gas-to-particle conversion of sulfur gaseous compounds. Zinc appears at 0.01, 0.05, 0.02%, respectively, for the Alta Floresta,

### Amazon Basin Fine Mode Aerosol Biogenic + Burning Source Profile

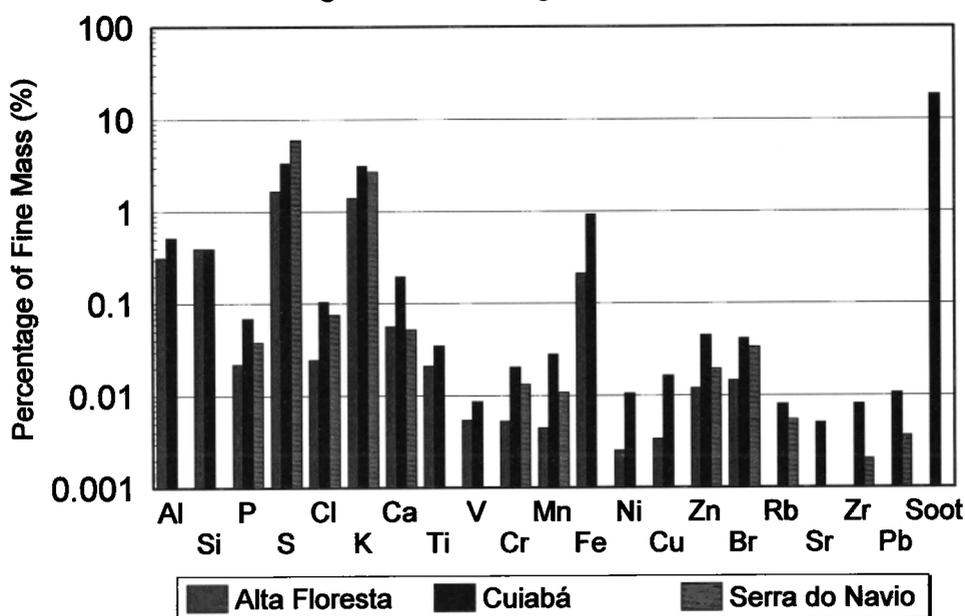


Figure 6. Absolute elemental source profiles for the biogenic aerosol component for the three sampling sites. The APFA procedure allows obtaining absolute source profiles in units of  $\text{ng/m}^3$ . The elemental composition is showed normalized to the fraction of the fine particle mass concentration (FPM) apportioned to the biogenic component for each sampling site.

## Amazon Basin Soil Dust Aerosol

Fine Mode Soil Dust Component

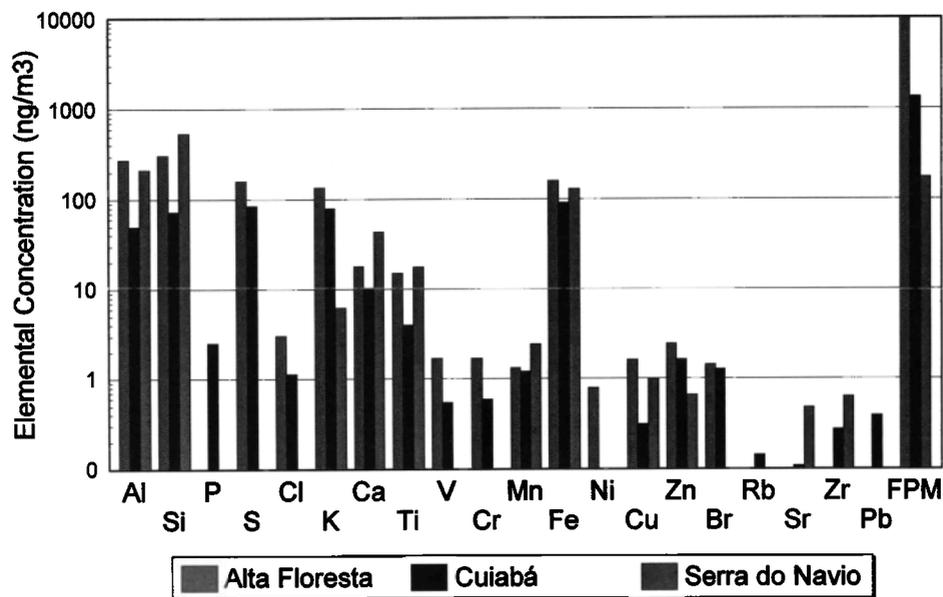


Figure 7. Absolute elemental source profiles in  $\text{ng}/\text{m}^3$  for the soil dust aerosol component for the three sampling sites.

Cuiabá and Serra do Navio sampling sites, whereas Zn in plants appears at an average of 0.02% [Bowen, 1979], a value very near to the ones obtained in this work. The elemental profiles for the three sites agree relatively well for several elements like P, Cl, K, Ca, Cr, Zn and Br. Soot at Cuiabá appears at 19% of the FPM, whereas direct measurements show a highly variable value, depending on the physical parameters of the burns, varying from 4% for low intensity smoldering fires, to 25% for flaming combustion [Lobert and Warnatz, 1993; Lacaux et al., 1993]. The remaining 70 to 80% of the aerosol mass is organic carbon. Most of the sulfur concentration is of biogenic origin as there is no large power plants or industries in the Amazon Basin. Individual particle analysis using scanning electron microprobe [Artaxo et al., 1988, 1990] and nuclear microprobe analysis [Artaxo and Hansson, 1990; Artaxo et al., 1993b] shows similar elemental profiles than the bulk analysis.

The absolute elemental source profile for the soil dust component is presented in Figure 7. The absolute concentration in  $\text{ng}/\text{m}^3$  for each element apportioned to the soil dust component shows similar concentrations for Fe, Mn, Ca and Zn for the three sampling sites. Alta Floresta and Serra do Navio shows similar concentrations for Al, Si, Ti and Cu. Enrichment factor calculation shows values near unity for most of the characteristic elements for soil dust particles.

### 6. Conclusion

Fine mode aerosol particles in the Amazon Basin can be classified mainly in four groups: naturally released biogenic particles, biomass burning emitted particles, soil dust particles and marine aerosol particles. From a background concentration of about  $10 \mu\text{g}/\text{m}^3$  for inhalable particulate matter, the mass concentration goes as high as  $150 \mu\text{g}/\text{m}^3$  during the biomass burning season at the Cuiabá sampling station, and more than  $600 \mu\text{g}/\text{m}^3$  in Alta Floresta. Large amounts of fine particles are

injected in the atmosphere, where they can travel for long distances. The composition of these biomass burning particles is dominated by organic and soot carbon, with the presence of K, Cl, S, Ca, Mn, Zn, and other elements. The natural biogenic component emitted by the Amazon tropical rain forest is rich in K, P, Zn, Mn, S, Cl, Ca and organic components. There are close similarities between the biogenic and biomass burning elemental profiles in the three sampling sites in the Amazon Basin, despite the large differences in ecosystems and pluviometric regimes. The high measured concentrations indicates the possibility of regional and global importance of fine mode biomass burning emissions.

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