

The Chemistry of Atmospheric Aerosol Particles in the Amazon Basin

Paulo Artaxo, Fábio Gerab, Márcia A. Yamasoe, and José V. Martins

Instituto de Física, Universidade de São Paulo, Caixa Postal 20516,
CEP 01452-990, São Paulo, SP, Brazil

Amazon Basin tropical rainforest is a key region to study the processes that are responsible for global atmospheric changes. There are large emissions of primary biogenic aerosol particles released naturally by the vegetation, and also large amounts of fine mode aerosol particles emitted during biomass burning. Fine and coarse mode aerosol particles were collected at three sites using Stacked Filter Units. Particle induced X-ray emission (PIXE) measured 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.

Biogenic and biomass burning aerosol particles dominate the fine mode mass concentration, with the presence of K, P, S, Cl, Zn, Br, and FPM (Fine mode mass concentration). During the dry season, at two sites, a strong component of biomass burning is observed. Inhalable particulate matter ($d_p < 10 \mu\text{m}$) mass concentration up to $700 \mu\text{g}/\text{m}^3$ was measured. Absolute Principal Factor Analysis (APFA) showed four components: soil dust (Al, Ca, Ti, Mn, Fe), biomass burning (Black carbon, FPM, K, Cl), natural biogenic particles (K, S, Ca, Mn, Zn), and marine aerosol (Cl). Samples collected directly over biomass burning fires in cerrado and primary forest show large amounts of organic acids, in addition to K, Cl, P, black carbon and other species.

Biogenic and Biomass Burning Aerosol Particles in Tropical Rainforest Regions

Tropical rainforest vegetation formations are characterized by intense sources of biogenic gases and aerosols. The Amazon Basin has the world's largest rainforest, and is a region with intense convective activity (*I*), resulting in 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 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. It also is necessary to obtain a better understanding of the alterations in the atmospheric composition due to changes in land use in tropical rainforests. The tropical rainforests of the world are in a delicate nutrient-limited environment (2). Due to nutrient poor oxisols and ultisols in these regions the deposition of airborne aerosol particles is needed to achieve a nutrient balance (2, 3). Several elements, like phosphorus, are a critical airborne element that could limit annual net primary production of the Amazon basin tropical rainforest (4).

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 (5, 6). Only few studies involving natural released biogenic aerosols have been conducted in tropical rainforests (7-16). 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. A significant fraction also comprises secondary aerosol particles formed by gas-to-particle conversion of organic and sulfur-related biogenic gases. These biogenic particles can be sub-micrometric in size. Bacteria in forested areas were found in the size range of 0.5 to 2.5 μm in size. Biological particles exhibit cloud influencing and can act as cloud condensation nuclei, potentially affecting the cloud formation mechanisms.

The rapid deforestation now occurring 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 (17). 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 cerrado in Africa and deforestation in the Amazon Basin (18). Estimates of total biomass consumed on a global basis range from 2 to 10Pg (1 Petagram= 10^{15}g) per year (17). In terms of total particulate matter (TPM), emissions are around 104 Tg (1 Teragram = 10^{12}g) per year (19). 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 particle emission rate. For elemental carbon, the emission of 19 Tg/year could account for a very high (86% of the total) anthropogenic emissions (19).

Experimental Methods

Fine and coarse aerosol particles were sampled using stacked filter units (SFU) (20). The SFU was fitted with a specially designed inlet, which provided a 50% cutoff diameter of 10 μm (21). 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 ($d_p < 2.0 \mu\text{m}$) (22). The flow rate was typically 16 liters per minute, and sampling 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 vegetation formations. Figure 1 shows a map of South America with the location of the three background sampling stations. The first aerosol sampling station is situated in Cuiabá, at the Brazilian cerrado, south of the Amazon basin rainforest. The Cuiabá sampling station allows the analyses of regional effects of biomass burning emissions due to the location of the station. The site is heavily affected by regional cerrado biomass burning. A second aerosol sampling station was installed 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 rainforest. The Serra do Navio sampling site is relatively free from regional biomass burning emissions, and there are no industrial activities for at least a thousand kilometers around the sampling site. The third sampling site is in the region of "Alta Floresta", near the border of Mato Grosso and Amazonas states. The Amazon basin dry season starts in March, extending until late September. Biomass burning occurs mainly in the end of the dry season, in August and September.

Direct biomass burning emissions were measured directly over the fires in two different vegetation formations. Fires in primary forest were measured in the state of Rondônia, near the village of Ariquemes. Fires in the cerrado vegetation formation were measured at the Brasília Ecological Station, administrated by IBGE (Instituto Brasileiro de Geografia e Estatística). Fine and coarse mode aerosols were collected using Stacked Filter Units with battery operated vacuum pumps. Sampling time varied from 2 to 10 minutes, since samples were collected a few meters over the fires. A $10 \mu\text{m}$ inlet was used to collect only inhalable particles.

The elemental concentrations were measured with the Particle-Induced X-ray emission (PIXE) (23) 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 analyses. Detection limits are typically 5 ng/m^3 for elements in the range $13 < Z < 22$ and 0.4 ng/m^3 for elements with $Z > 23$. 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 analyses of the Nuclepore filters. 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.

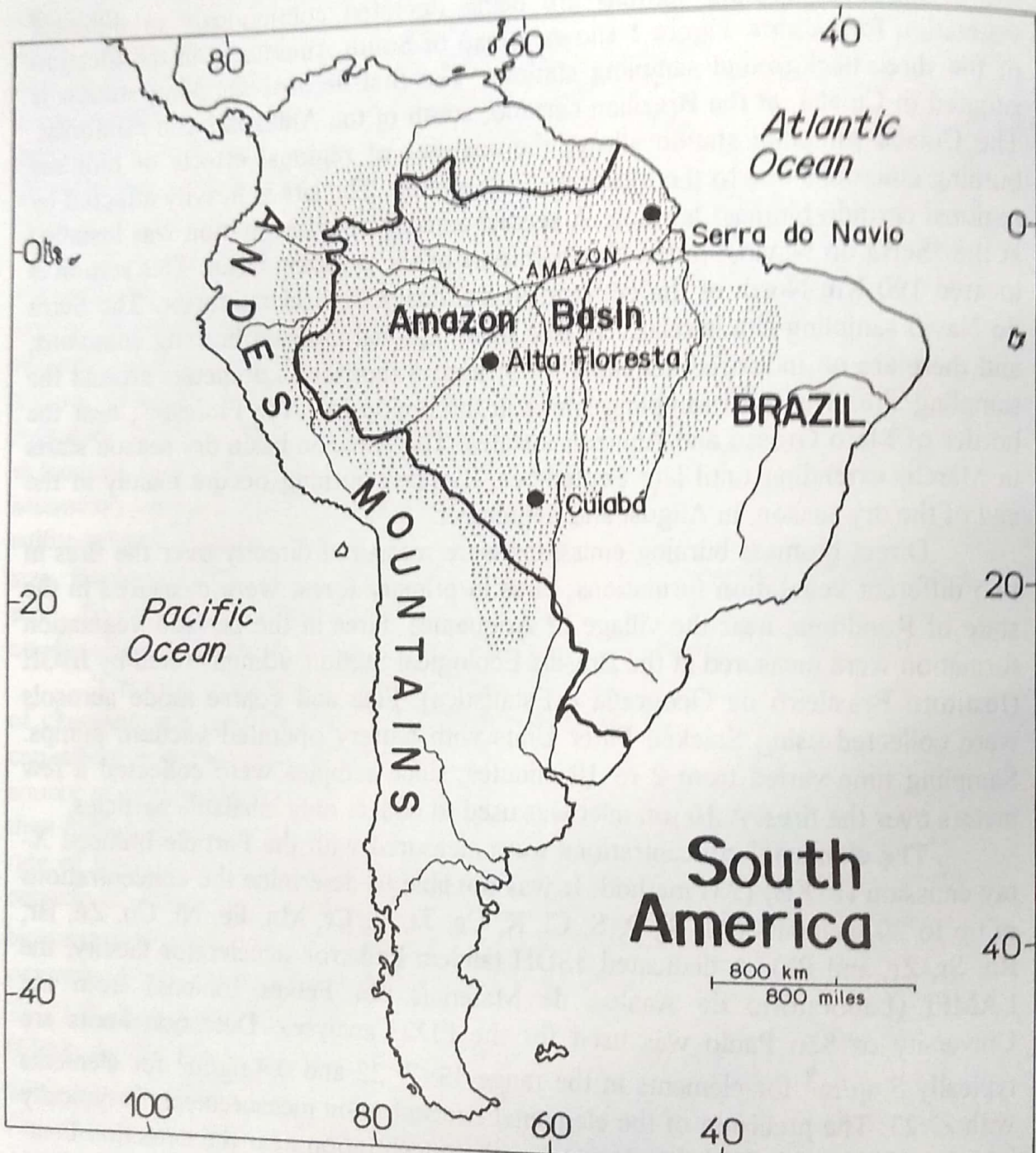


Figure 1. Map of South America with the location of three background monitoring stations in the Amazon Basin: Cuiabá, Alta Floresta and Serra do Navio.

Absolute Principal Factor Analyses

To separate the different components of natural biogenic aerosols using the elemental composition, absolute principal factor analyses (APFA) was used (24, 25). 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 analyses. In principal factor analyses 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 (12, 13). The elemental concentrations are subsequently regressed on the APFS to obtain the contribution of each element for each component. The measured aerosol mass concentration can also be regressed on the APFS to obtain the aerosol total mass source apportionment.

Background Aerosol Monitoring - 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. The aerosol mass concentration for the fine, coarse and inhalable particulate matter, and the fine fraction ($dp < 2\mu\text{m}$) elemental data obtained from the fine mode SFU filters collected at the three sampling stations will be discussed in this paper.

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 to $150\ \mu\text{g}/\text{m}^3$ during the biomass burning season. Aircraft measurements over large areas of the Amazon Basin show very high IPM concentrations up to $300\ \mu\text{g}/\text{m}^3$ (16). These high concentrations are observed in areas as large as 2 million square kilometers, using aircraft and remote sensing measurements, and they generally last for about two months, August and September. For the Alta Floresta site, concentrations higher than $600\ \mu\text{g}/\text{m}^3$ were observed. 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. Only in December and January, with heavy rains, aerosol concentrations dropped below $20\ \mu\text{g}/\text{m}^3$. In

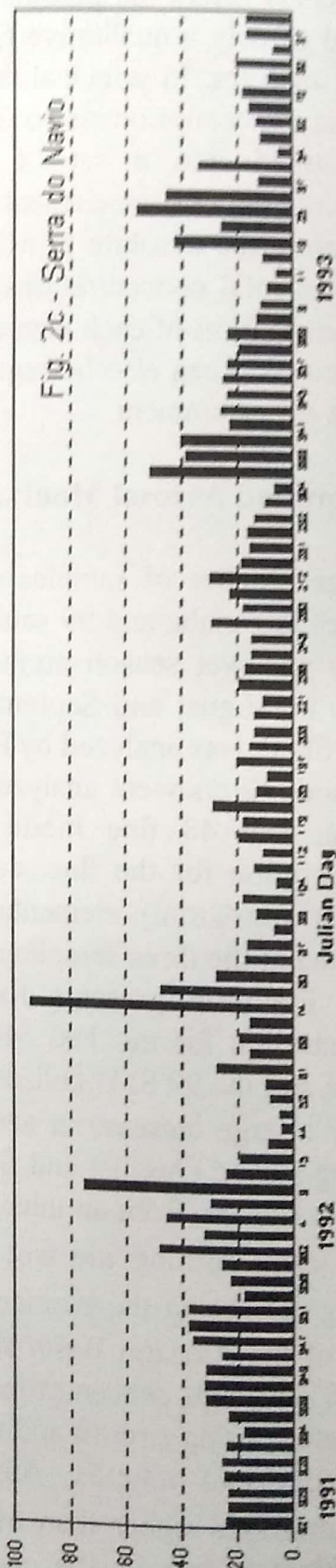
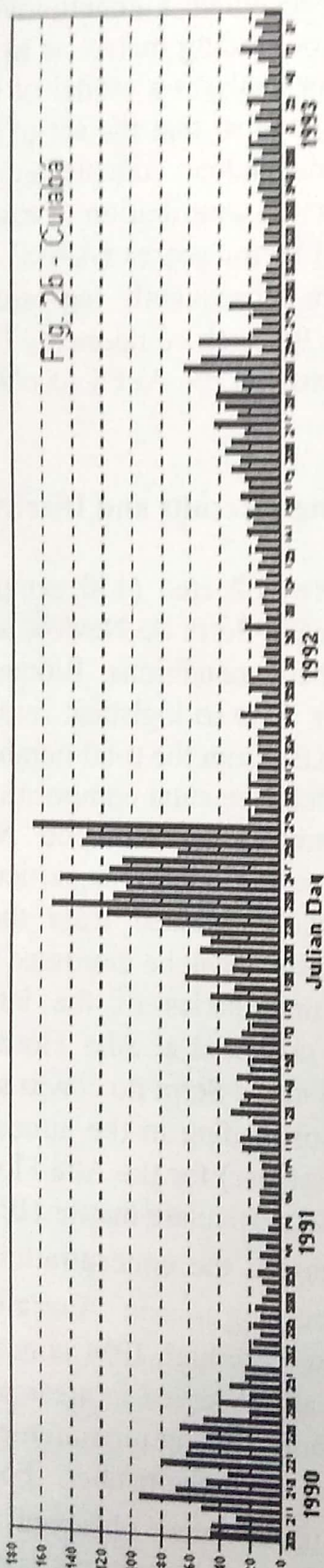
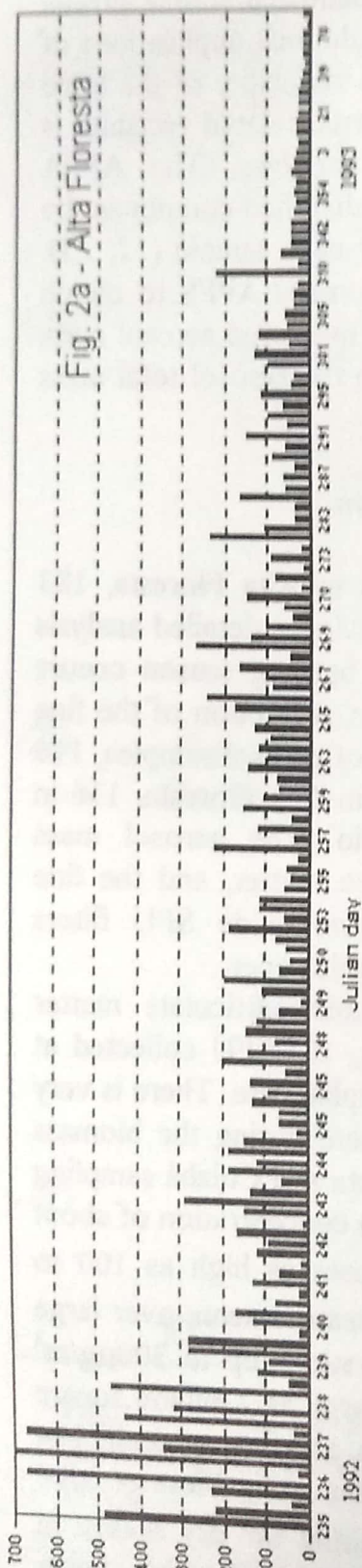


Figure 2. Amazon Basin inhalable aerosol mass concentrations in $\mu\text{g}/\text{m}^3$ for three atmospheric monitoring stations.

Serra do Navio, much lower inhalable particulate mass concentration was observed. A background value of 10-20 $\mu\text{g}/\text{m}^3$ is observed. Higher concentrations (40 to 80 $\mu\text{g}/\text{m}^3$) were observed in January and February, possibly an effect of the long range transport of Saharan dust. 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. Some increase during the biomass burning season can be seen in Serra do Navio time series of fine mass concentration, 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 ITCZ (Intertropical Convergence Zone) allows the intrusion of Sahara dust into the Amazon basin, as discussed in detail in Prospero et al. (4,26).

The fine mode aerosol samples were analyzed by the PIXE method to obtain the elemental composition of the airborne particles. Table I presents the average elemental concentration in ng/m^3 for the fine mode aerosol at the three sampling sites. FPM represents the fine mode aerosol mass concentration in $\mu\text{g}/\text{m}^3$. 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. The higher soil dust concentrations in Alta Floresta can also be deduced from the high concentration of Al, Si, 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 $5\text{ng}/\text{m}^3$. This fact 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 II presents the VARIMAX rotated factor loading matrix for the three sampling sites. For 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 black carbon concentrations for the Alta Floresta fine fraction samples, not allowing the discrimination between the biomass burning component and the natural released biogenic particles. 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, black 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 analyses results. Black carbon is essentially emitted by biomass burning, as well as sulfur and potassium were observed as naturally emitted by the vegetation in background areas not affected by biomass burning in the Amazon basin (11, 13).

Table I. Average Elemental Concentration in ng/m^3 for Fine Mode Aerosol Particle ($d_p < 2\mu\text{m}$) in three Remote Atmospheric Monitoring Stations in the Amazon Basin (*).

	<i>Alta Floresta</i>		<i>Cuiabá</i>		<i>Serra do Navio</i>	
	Average	Std. Dev. (n)	Average	Std. Dev. (n)	Average	Std. Dev. (n)
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 (48)
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)
Black	-	-	2051	1922 (136)	-	-
FPM(*)	49.9	54.8 (116)	10.5	10.7 (136)	9.87	7.47 (48)

(*) Average and standard deviation (Std.Dev.) 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. Black is the black carbon concentration. FPM is the fine particle gravimetric mass concentration expressed in $\mu\text{g/m}^3$.

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

	<i>Alta Floresta</i>		<i>Cuiabá</i>			<i>Serra do Navio</i>		
	<i>Soil</i>	<i>Biog./B.</i>	<i>Soil</i>	<i>Burning</i>	<i>Biog.</i>	<i>Soil</i>	<i>Biog.</i>	<i>Marine</i>
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
Black	-	-	0.29	0.90	0.26	-	-	-
λ	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 bold represents the statistically significant factor loadings. λ is the eigenvalue for each retained factor; Var. represents the percentage of the variance explained by each factor.

At the Serra do Navio sampling site, three factors were obtained. The first one with high loading 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 that these particles are Sahara desert dust particles being injected into the Amazon Basin (4,27). The second factor at Serra do Navio with high loadings for K, FPM, S, Br, and Zn represents 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 is explained by the factor analyses model. This indicates the adequacy of the factor model, and the number of factors retained in each analyses.

The APFA procedure allows obtaining absolute source profiles in units of ng/m^3 . Figure 3 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 % (28). 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, Cuiabá and Serra do Navio sampling sites, whereas Zn in plants appears at an average of 0.02% (28), a value very close to the ones obtained in this work. The elemental profiles for the three sites agree relatively well for several elements such as P, Cl, K, Ca, Cr, Zn and Br. Black carbon 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 (29, 30). The remaining 70 to 80% of the aerosol mass is organic carbon. Most of the sulfur concentration is of biogenic origin as there are no large power plants or industries in the Amazon basin. The absolute elemental source profile for the soil dust component is presented in Figure 4. The absolute concentration in ng/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 show similar concentrations for Al, Si, Ti and Cu.

These results shows that 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 $10 \mu\text{g/m}^3$ for inhalable particulate matter, the mass concentration goes as high as $150 \mu\text{g/m}^3$ during the biomass burning season at the Cuiabá sampling station, and more than $600 \mu\text{g/m}^3$ 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

Amazon Basin Fine Mode Aerosol

Biogenic + Burning Source Profile

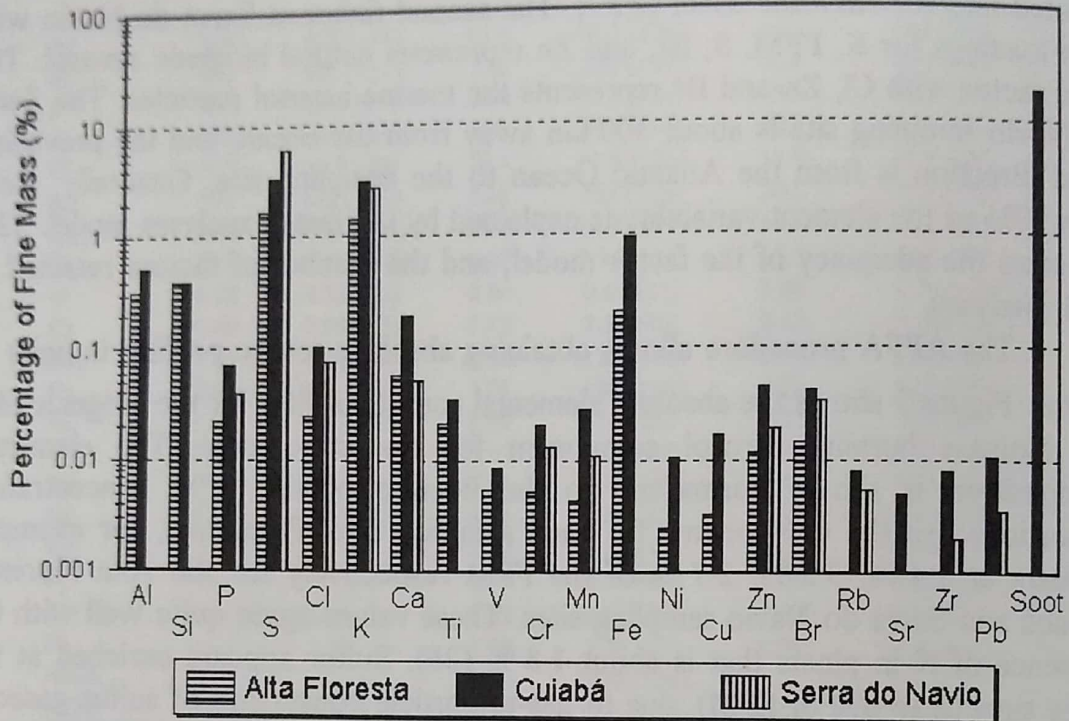


Figure 3. Biogenic and biomass burning elemental profile for the three sites.

Amazon Basin Soil Dust Aerosol

Fine Mode Soil Dust Component

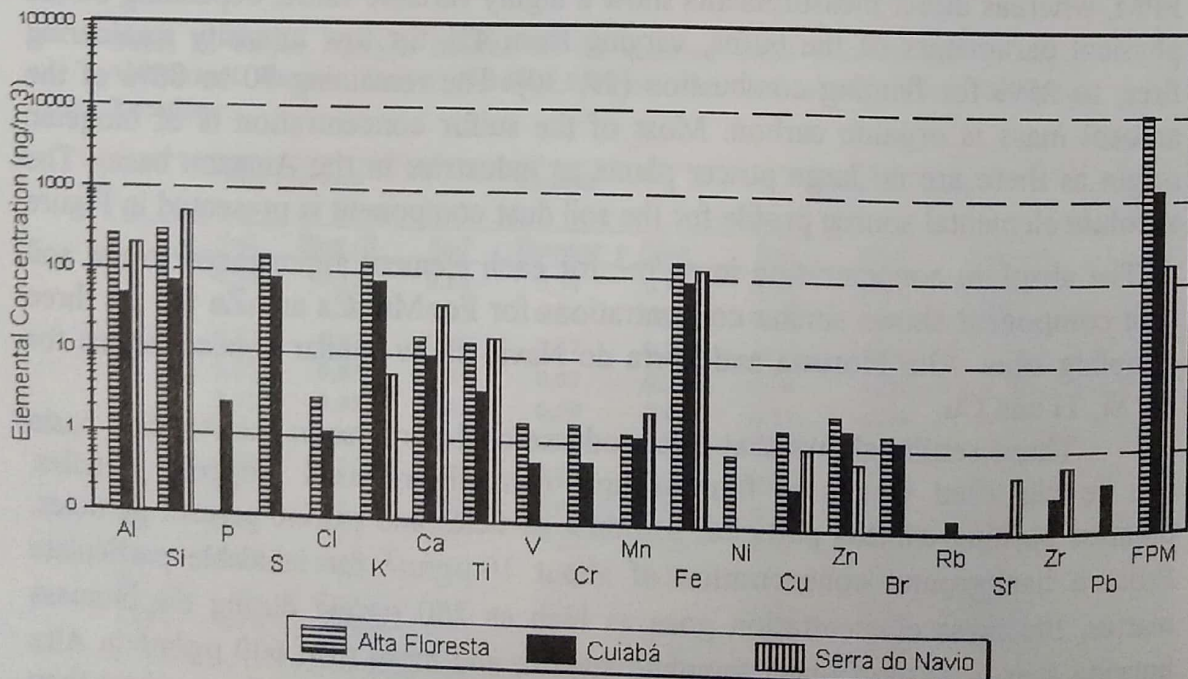


Figure 4. Source profile of the fine mode soil dust component for the three sites.

dominated by organic and black carbon, with the presence of K, Cl, S, Ca, Mn, Zn, and other elements. The natural biogenic component emitted by the Amazon tropical rainforest 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 between the sampling areas and pluviometric regimes. The high concentrations measured indicate the possibility of regional and global importance of fine mode biomass burning emissions.

Aerosol Measurements Directly over Fires in the Amazon Basin

In two different vegetation formations - cerrado and primary forest, aerosol samples were collected directly over the fires. For the cerrado fires, sampling occurred in the Brasília ecological reserve of IBGE (Instituto Brasileiro de Geografia e Estatística). They were planned prescribed fires. For the primary tropical forest emissions, sampling was done in the state of Rondônia, near the village of Ariquemes. Stacked Filter Units were used for sampling, and normal PIXE and Ion Chromatography (IC) was used to measure the elemental and ionic component. Table III shows the fine mode average concentration for the measured species separated for ecosystem and fire type. In order to be able to compare concentrations with large spatial variability, the elemental and ionic concentration were normalized to the total fine mode mass concentration. Figure 4 shows the average elemental composition for each fire phase and each type of ecosystem. For some elements like phosphorus, the concentrations are very similar for all four situations, whereas for Zn the emissions factors differ significantly. Emissions of nitrates and chlorine are much higher in the cerrado ecosystem than in the tropical forest. It is difficult to know if these differences are due to changes in the biomass composition or distinct processes regulating the emissions.

The comparison of our measurements with similar data collected by other authors is shown in Table IV. The emission factor for Cl, SO₄ and Ca is normalized to potassium emissions. It is possible to observe that emissions for sulfates, reported by several authors, varies by a factor of 8. Crutzen et al. (31) and Bingemer et al. (32) have studied the sulfur cycle over the tropical forest ecosystem and found large emissions of organic sulfur compounds in both natural release and biomass burning emissions. The results from Ward and Hardy (33) are similar to ours. Gaudichet et al. (Gaudichet, A.; Echalar, F.; Chatenet, B.; Quisefit, J.P.; Malingre, G.; Cachier, H.; Buat Menard, P.; Artaxo, P.; Maenhaut, W. J. *Atmos. Chem.*, in press.) have also compared emissions from Africa and Amazonia, observing similar differences in the emissions as those observed in this work. Table V shows the factor analyses calculations for the elements and ionic species measured over the fires in the tropical cerrado and forest. Potassium and Chlorine are always closely associated with Zn. Magnesium and calcium are closely related for both cerrado and forest fires emissions. The organic acids (formic and acetic) are not directly associated with any other element or ion. Some factors are similar

Table III. Amazon Basin Biomass Burning Aerosol Direct Emissions: Ionic and Elemental Composition. Samples from Savanna and Tropical Forest for Different Fire Combustion. Values Expressed as Ratios to Fine Particle Mass in Percentage

	<i>Savanna</i> (% of fine mass)		<i>Tropical Forest</i> (% of fine mass)	
	<i>Phase flaming</i>	<i>Phase smoldering</i>	<i>Phase flaming</i>	<i>Phase smoldering</i>
Ac ⁻	0.28 ± 0.11 (56)	0.25 ± 0.11 (32)	0.23 ± 0.10 (21)	0.27 ± 0.08 (39)
Fo ⁻	0.024 ± 0.012 (55)	0.023 ± 0.013 (32)	0.019 ± 0.008 (13)	0.025 ± 0.014 (29)
NO ₃ ⁻	0.61 ± 0.36 (54)	0.36 ± 0.32 (31)	0.11 ± 0.08 (15)	0.12 ± 0.07 (25)
SO ₄ ²⁻	0.74 ± 0.36 (56)	0.35 ± 0.33 (32)	0.87 ± 0.64 (21)	0.36 ± 0.31 (39)
C ₂ O ₄ ²⁻	0.08 ± 0.05 (56)	0.06 ± 0.05 (30)	0.06 ± 0.06 (19)	0.04 ± 0.04 (34)
Na ⁺	0.022 ± 0.016 (39)	0.024 ± 0.020 (20)	0.016 ± 0.11 (17)	0.020 ± 0.037 (25)
NH ₄ ⁺	0.10 ± 0.08 (28)	0.047 ± 0.037 (11)	0.09 ± 0.06 (14)	0.046 ± 0.039 (23)
K ⁺	2.9 ± 2.0 (56)	1.3 ± 1.7 (32)	0.7 ± 0.6 (21)	0.43 ± 0.25 (39)
Mg ²⁺	0.035 ± 0.024 (36)	0.032 ± 0.019 (20)	0.024 ± 0.021 (18)	0.026 ± 0.028 (20)
Ca ²⁺	0.10 ± 0.09 (42)	0.09 ± 0.09 (24)	0.08 ± 0.03 (20)	0.06 ± 0.04 (37)
Al	2.3 ± 6.0 (14)	0.7 ± 1.2 (11)	0.4 ± 0.4 (8)	0.5 ± 0.5 (18)
Si	4.2 ± 1.6 (17)	2.3 ± 1.3 (10)	---	---
P	0.049 ± 0.019 (9)	0.043 ± 0.012 (16)	0.048 ± 0.011 (11)	0.033 ± 0.010 (20)
Cl	1.5 ± 1.4 (53)	0.7 ± 1.0 (27)	0.12 ± 0.14 (8)	0.08 ± 0.05 (16)
Fe	0.15 ± 0.26 (13)	0.09 ± 0.15 (12)	0.031 (1)	0.048 ± 0.027 (8)
Cu	0.006 ± 0.004 (54)	0.004 ± 0.002 (26)	0.004 ± 0.001 (20)	0.003 ± 0.002 (36)
Zn	0.019 ± 0.015 (54)	0.012 ± 0.015 (12)	0.006 ± 0.004 (20)	0.004 ± 0.002 (25)
Br	0.06 ± 0.04 (35)	0.04 ± 0.02 (8)	0.05 ± 0.02 (8)	0.05 ± 0.06 (9)
Black	13 ± 7 (56)	8 ± 7 (32)	8 ± 7 (21)	4.4 ± 2.6 (39)

For each element or ion, averages, standard deviation and number of samples in which the element or ion was measured above analytical detection limits are presented. Averages were calculated using only values above the detection limit.

Table IV. Ratios for Potassium of the Average Values for Emissions of Cl, SO₄ and Ca Observed in Direct Emissions of Biomass Burning Plumes. Samples from Savanna and Tropical Forest (Values Observed by Other Authors Are Also Shown)

Type of Vegetation	Cl	SO ₄ ⁻	Ca
Savanna (Brasília) ("flaming") ^a	0.52	0.26	0.03
Savanna (Brasília) ("smoldering") ^a	0.54	0.27	0.07
Tropical Forest (Rondônia) ("flaming") ^a	0.17	1.24	0.11
Tropical Forest (Rondônia) ("smoldering") ^a	0.19	0.84	0.14
Savanna (Brasília) ("flaming") ^b	0.33	0.1	0.1
Tropical Forest (Rondônia) ("flaming") ^b	0.48	0.54	0.16
Tropical Forest (Rondônia) ("smoldering") ^b	0.25	0.38	0.21
Savanna ^c	0.17	0.95	0.05
Savanna ^d	0.59	0.18	0.18

Data from: a) This work; b) Ref. 33 (BASE-B-Brasília, Marabá); c) Ref. 14 (Brushfire/80-Brasília); d) Ref. 30 (DECAFE/FOS - Ivory Coast, Africa).

Table Va. Principal Factor Analysis Results for Biomass Burning Direct Emissions in the Amazon Basin Savanna - Brasilia

Var.	Fac. 1	Fac. 2	Fac. 3	Fac. 4	Fac. 5	Fac. 6	Fac. 7	Comm.
K	0.97	-	-	-	-	-	-	0.96
Cl	0.93	-	-	-	-	-	-	0.90
Zn	0.55	-0.30	0.26	-0.25	-	0.23	0.42	0.75
Cu	-	-	-	0.23	-	-	0.87	0.87
Mg	-	-	-	-	0.82	-	-	0.73
Br	-	-	0.24	-	-	0.71	-	0.65
Ca	-	-	-0.20	-	0.79	-	-	0.71
Black C	-	-	-	0.85	-	-	0.29	0.84
FPM	-0.50	0.74	-	-0.25	-	-	0.25	0.93
Ac ⁻	-	0.94	-	-	-	-	-	0.92
Fo ⁻	-	-	0.86	-	-	-	-	0.78
NO ₃ ⁻	0.53	-0.21	0.44	-	-0.21	-	0.24	0.65
SO ₄ ⁻	0.78	-	-	-	-	-	0.24	0.71
C ₂ O ₄ ²⁻	0.62	0.55	-	0.35	-	-0.25	-	0.90
Na ⁺	-0.25	-	-0.55	-0.58	-	-	-	0.78
NH ₄ ⁺	-	-	-	-	-	0.83	-	0.75

Table Vb. Factor Analysis Results for Biomass Burning Direct Emissions in Tropical Rainforest - Rondônia

Var.	Fac. 1	Fac. 2	Fac. 3	Fac. 4	Fac. 5	Fac. 6	Fac. 7	Comm.
K	0.83	-0.31	-	-	-	-	-	0.87
Cl	0.75	-	-	-	-0.20	0.21	-	0.72
Zn	0.79	-0.80	-	-0.25	0.20	-	0.25	0.82
Cu	-	-	-	-	-	-	0.87	0.80
Mg	-	0.27	0.80	-0.26	-	-	-0.24	0.91
Br	0.85	-	0.35	0.21	-	-	-	0.92
Ca	-	-	0.91	0.21	-	-	-	0.92
Black C	0.36	-0.56	-0.35	-	0.30	0.30	-	0.76
FPM	-	0.86	-	-	-	-	-	0.86
Ac ⁻	-	0.86	-	0.26	-	-	-	0.87
Fo ⁻	-	0.27	-	0.92	-	-	-	0.94
NO ₃ ⁻	-	-	-	-	-	0.70	0.49	0.76
SO ₄ ⁻	-	-0.69	-	-	0.58	-	-	0.89
C ₂ O ₄ ²⁻	0.21	0.21	0.24	0.30	0.70	-0.20	-	0.79
Na ⁺	-	-	-	-	-	-0.82	-	0.71
NH ₄ ⁺	-0.44	-	0.21	-0.47	0.58	-	-	0.81

Only eigenvalues larger than 0.20 are shown. The last column shows the communalities.

for cerrado and forest, like the FPM (fine particle mass) and acetate, indicating the high organic influence in the FPM.

Acknowledgments

We would like to acknowledge Paulo Roberto Neme do Amorim, José Roberto Chagas, Saturnino José da Silva Filho, INPE and ICOMI for support during the sampling program in the Amazon basin. We thank Alcides Camargo Ribeiro, Ana Lúcia Loureiro, Francisco Echalar, Társis Germano and Márcio Sacconi for assistance during sampling and PIXE analyses. This work was financed through grant 90/2950-2 from "FAPESP-Fundação de Amparo à Pesquisa do Estado de São Paulo", and contract number CII*-CT92-0082 from the Commission of the European Communities.

Literature Cited

1. Garstang, M.; Scala, J.; Greco, S.; Harriss, R.; Beck, S.; Browell, E.; Sachse, G.; Gregory, G.; Hill, G.; Simpson, J.; Tao, W.K.; Torres, A. *J. Geophys. Res.* **1988**, *93*, 1528-1550.
2. Vitousek, P.M.; Sanford, R.L. *Ann. Rev. Ecol. Syst.* **1986**, *17*, 137-167..
3. Salati, E.; Vose, P.B. *Science* **1984**, *225*, 129-138.
4. Swap, R.; Garstang, M.; Greco, S.; Talbot, R.; Kallberg, P. *Tellus* **1992**, *44B*, 133-149.
5. Cachier, H.; Buat-Menard, P.; Fontugne, M.; Rancher, J. *J. Atmos. Chem.* **1985**, *3*, 469-489.
6. Crozat, G.; Domergue, J.L.; Baudet, J.; Bogui, V. *Atmos. Environ.* **1978**, *12*, 1917-1920.
7. Lawson, D.R.; Winchester, J.W. *Science* **1979**, *205*, 1267-1269.
8. Orsini, C.; Artaxo, P.; Tabacnicks, M. *Atmos. Environ.* **1982**, *16*, 2177-2181.
9. Artaxo, P.; Orsini, C. In *Aerosols: Formation and Reactivity*; Israel, G., Ed.; Pergamon Journals, Great Britain, 1986; pp 148-151.
10. Artaxo, P.; Orsini, C. *Nucl. Instrum. Meth. in Physics Res.*, *B22*, 1987; pp 259-263.
11. Artaxo, P.; Maenhaut, W. *Nucl. Instrum. and Meth. in Physics Res.*, *B49*; 1990, 366-371.
12. Artaxo, P.; Storms, H.; Bruynseels, F.; Van Grieken, R.; Maenhaut, W. *J. Geophys. Res.* **1988**, *93*, 1605-1615.
13. Artaxo, P.; Maenhaut, W.; Storms, H.; Van Grieken, R. *J. Geophys. Res.* **1990**, *95*, *D10*, 16971-16985.
14. Artaxo, P.; Yamasoe, M.; Martins, J.V.; Kocinas, S.; Carvalho, S.; Maenhaut, W. In *Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*; Crutzen, P.J.; Goldammer, J-G., Eds.; Dahlem Konferenzen ES13, Chichester: John Wiley & Sons, 1993; pp. 139-158.

15. Artaxo, P.; Rabello, F. Watt, M.L.C.; Grime, G.; Swietlicki, E. *Nucl. Instrum. and Meth. in Physics Res.*, B75 1993, pp. 521-525.
16. Artaxo, P.; Gerab, F.; Rabello, M.L.C. *Nucl. Instrum. and Meth. in Physics Res.*, B75 1993, pp. 277-281.
17. Crutzen, P.; Andreae, M. O. *Science* 1990, 250, 1669-1678.
18. Setzer, A.W.; Pereira, M.C. *Ambio* 1991, Vol. 20, 19-22.
19. Levine, J., *EOS* 1990, vol. 71(37), 1075-1077.
20. Parker, R.D.; Buzzard, G.H.; Dzubay, T.G.; Bell, J.P. *Atmos. Environ.* 1977, 11, 617-621.
21. Cahill, T.A.; Eldred, R.A.; Barone, J.; Ashbaugh, L. *Report Federal Highway Administration FHWA-RD-78-178*; ., Air Quality Group, University of California: Davis, USA, 1979; 78 pp.
22. John, W.; Hering, S.; Reischl, G.; Sasaki, G. *Atmos. Environ.* 1983, 17, 373-382.
23. Johansson, S.A.E.; Campbell, J.L. *PIXE - A Novel Technique for Elemental Analysis*; John Wiley & Sons: New York, 1988.
24. Thurston, G.C.; Spengler, J.D. *Atmos. Environ.* 1985, 19, 9-25.
25. Hopke, P.K. *Receptor Modeling in Environment Chemistry*; John Wiley: New York, 1985.
26. Prospero, J.M.; Glaccum, R.A.; Nees, R.T. *Nature* 1981, 289, 570-572.
27. Talbot, R.W.; Andreae, M.O.; Berresheim, H.; Artaxo, P.; Garstang, M.; Harriss, R.C.; Beecher, K.M.; Li, S.M. *J. Geophys. Res.* 1990, 95, 16955-16970.
28. Bowen, H.J.M. *Environmental Chemistry of the Elements*; Academic Press, N.Y., 1979.
29. Lobert, J.M.; Warnatz, J In *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*; Crutzen, P.J.; Goldammer, J.-G., Eds.; Dahlem Konferenzen, ES13., Chichester: John Wiley & Sons. 1993; pp 15-37.
30. Lacaux, J.-P; Cachier, H.; Delmas, R. In *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*; Crutzen, P.J.; Goldammer, J.-G., Eds.; Dahlem Konferenzen, ES13., Chichester: John Wiley & Sons. 1993; pp 159-191.
31. Crutzen, P.J.; Heidt, L.E.; Krasnec, J.P.; Pollock, W.H.; Seiler, W. *Nature* 1979, 282, 253-256,.
32. Bingemer, H.G.; Andreae, M.O.; Andreae, T.W.; Artaxo, P.; Helas, G.; Jacob, D.J.; Mihalopoulos, N.; Nguyen, B.C. *J. Geophys. Res.* 1992, 97, D6, 6207-6217.
33. Ward, D.E.; Hardy, C.C. *International* 1991, 17, 117-134.

RECEIVED November 28, 1994