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Elemental composition of aerosol particles from two atmospheric monitoring stations in the Amazon Basin

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One key region for the study of processes that are changing the composition of the global atmosphere is the Amazon Basin tropical rain forest. The high rate of deforestation and biomass burning is emitting large amounts of gases and fine-mode aerosol particles to the global atmosphere. Two background monitoring stations are operating continuously measuring aerosol composition, at Cuiabá, and Serra do Navio. Fine- and coarse-mode aerosol particles are being collected using stacked filter units. Particle induced X-ray emission (PIXE) was used to measure concentrations of up to 21 elements: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, and Pb. The elemental composition was measured at the new PIXE facility from the University of São Paulo, using a dedicated 5SDH tandem Pelletron nuclear accelerator. Absolute principal factor analysis (APFA) has derived absolute elemental source profiles.

At the Serra do Navio sampling site a very clean background aerosol is being observed. Biogenic aerosol dominates the fine-mode mass concentration, with the presence of K, P, S, Cl, Zn, Br, and FPM. Three components dominate the aerosol composition: soil dust particles, the natural biogenic release by the forest, and a marine aerosol component. At the Cuiabá site, during the dry season, a strong component of biomass burning is observed. An aerosol mass concentration up to 120 $\mu g/m^3$ was measured. APFA showed three components: soil dust (Al, Ca, Ti, Mn, Fe), biomass burning (soot, FPM, K, Cl) and natural biogenic particles (K, S, Ca, Mn, Zn). The fine-mode biogenic component of both sites shows remarkable similarities, although the two sampling sites are 3000 km apart. Several essential plant nutrients like P, K, S, Ca, Ni and others are transported in the atmosphere as a result of biomass burning processes.

1. The emission of aerosol particles by the tropical rain forest

The Earth's atmosphere is a vital natural resource that until recently appeared unaffected by human activities, except on urban or regional scales [1]. However, it has become clear that the worldwide anthropogenic activities have an impact on the global atmosphere. In order 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.

Biomass burning of tropical rain forests is a major source of particulate matter and gaseous emissions into the atmosphere. The aerosol particles emitted in tropical biomass burning are active as cloud condensation nuclei and exert a strong influence on the concentrations and sizes of cloud droplets. Measurements of Artaxo et al. [2] show enrichment of particulate phase water soluble components such as SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, K^+ in biomass burning plumes. Elemental carbon associated with potassium was identified as tracer for biomass burning plumes in remote oceanic areas [3]. A major component of the particles is elemental carbon (also called graphitic carbon, black carbon or soot carbon) that has strong radiative absorption properties [4]. Estimates of total biomass consumed on a global basis range from 2 to 10 Pg (1 petagram = 10^{15} g) per year [1]. In terms of total particulate matter (TPM), emissions are around 104 Tg (1 teragram = 10^{12} g) per year. For particulate matter in the fine mode (FPM), emissions are estimated as 49 Tg per year, accounting for about 7% of the global emission rate. For elemental carbon, the emission of 19 Tg/yr accounts for a very high 86% of the total anthropogenic emissions.

2. Experimental methods

Aerosol particles were sampled using stacked filter units (SFU). The SFU was fitted with a specially designed inlet, which provided a 50% cutoff diameter of 15 μm. The SFU collects coarse mode particles ($2.0 < d_p < 15$ μm) on a 47-mm-diameter, 8 μm pore-size

Nuclepore filter while a 0.4 μm pore-size Nuclepore filter collects the fine mode particles ($d_p < 2.0$ μm).

Two monitoring stations are being operated continuously. 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 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.

Particle-induced X-ray emission (PIXE) [5] was used to measure concentrations of up to 21 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Se, Rb, Sr, Zr, and Pb). A new dedicated 5SDH tandem Pelletron accelerator facility at the University of São Paulo was used for PIXE analysis. 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 10%, with 30% for elements with concentration near the detection limit. Gravimetric analysis was performed to obtain the fine and coarse aerosol mass concentration. Soot carbon concentration was determined by a reflectance technique. The large data base collected in these experiments was analyzed using receptor modeling. Absolute principal factor analysis [6,7] was used to extract quantitative source profiles from the variability of the elemental concentrations.

3. Results of background aerosol monitoring in the Amazon Basin

A large number of samples were collected at the Cuiabá sampling station, from which results from 106 fine-mode aerosol samples are presented in this paper. For Serra do Navio, 28 fine-mode samples were analyzed. Fig. 1 presents the time series of the fine, coarse and inhalable particulate matter concentration for the 106 SFU samples collected at the Cuiabá sampling site. There is very clearly a large increase in aerosol loading in the atmosphere during the biomass burning season. From an inhalable particulate matter (IPM) concentration of 20 μg/m^3 during the wet season, the concentration goes as high as 120 μg/m^3 during the biomass burning season. Aircraft measurements over large areas of the Amazon Basin show very high IPM concentrations up to 300 μg/m^3. These high concentrations are observed in areas as large as two millions square kilometers, using aircraft and remote sensing measurements. Soot carbon concentrations are also high. Table 1 presents the average elemental concentrations for the fine mode aerosol from both sampling sites. FPM represents the fine-mode aerosol mass concentration in μg/m^3. Sulfur at Cuiabá, with an average concentration of 426 ± 365 ng/m^3 appears higher than in other studies of aerosol composition in the Amazon Basin

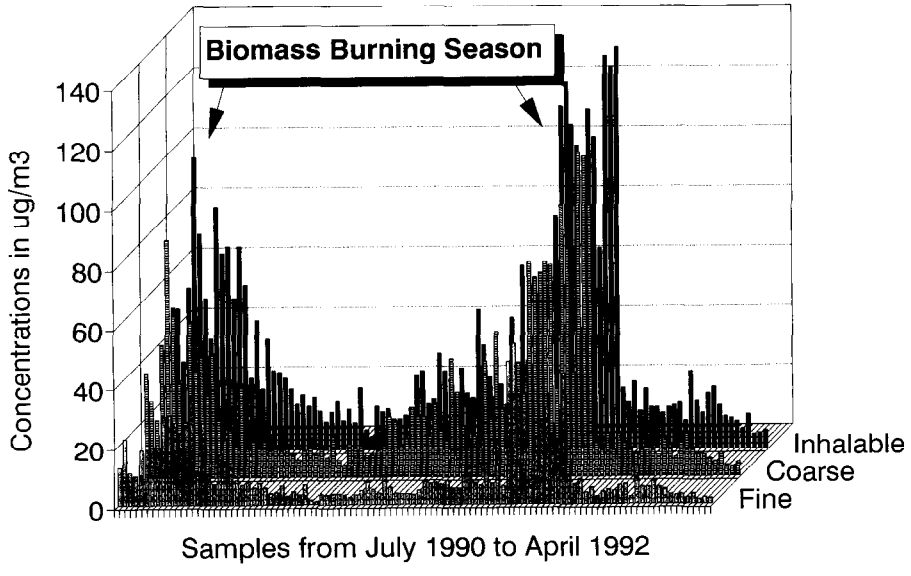

Fig. 1. Time series of the fine, coarse and inhalable particulate matter concentration for the 106 stacked filter unit samples collected at the Cuiabá sampling site. There is clearly a large increase in aerosol loading in the atmosphere during the biomass burning season.

Table 1
Average elemental concentration in ng/m^3 and standard deviation (σ) for fine-mode aerosol collected at two background sampling stations in the Amazon Basin. The station at Cuiabá is situated in a region with influence of regional biomass burning. The Serra do Navio sampling site is in a primary forest location far away from biomass burning regions. n is the number of samples with elemental concentration above the detection limits

Element	Cuiabá	n	Serra do Navio	n
Al	104 ±107	106	209 ±232	28
Si	148 ±146	79	479 ±558	28
P	10.6 ± 7.5	67	15.1 ± 10.9	19
S	426 ±365	106	726 ±411	28
Cl	11.9 ± 12.9	106	15.5 ± 8.2	28
K	369 ±379	106	375 ±182	28
Ca	32.4 ± 25.8	106	62.0 ± 39.5	28
Ti	7.68± 8.07	106	15.9 ± 17.7	28
V	–	–	1.20± 0.22	5
Cr	3.79± 2.97	55	2.51± 0.92	13
Mn	4.00± 3.29	106	4.13± 2.04	28
Fe	199 ±183	106	140 ±127	28
Ni	0.57± 0.57	1	0.17± 0.17	1
Cu	1.53± 1.14	44	1.32± 0.81	9
Zn	6.39± 5.09	106	3.69± 1.59	28
Se	0.35± 0.23	5	5.26± 3.15	1
Br	5.62± 5.89	86	5.26± 3.15	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± 0.91	5	1.39± 0.59	23
Pb	1.68± 1.35	87	0.82± 0.21	16
FPM [a]	10.9 ± 10.7	106	14.2 ± 6.9	28
Soot [b]	2.10± 1.79	106	–	–

[a] FPM is the fine-mode aerosol mass concentration in μg/m^3
[b] Soot carbon concentration is expressed in μg/m^3.

Table 2
Factor analysis results for the fine-mode Cuiabá aerosol samples. VARIMAX rotated factor loading matrix. Three factors were statistically significant

Variable	Factor 1 soil dust	Factor 2 biomass burning	Factor 3 biogenic particles	Communality
Al	*0.87*	0.36	0.29	0.97
S	0.41	0.36	*0.78*	0.91
Cl	0.14	*0.90*	0.19	0.88
K	0.45	*0.59*	*0.61*	0.93
Ca	*0.73*	0.18	*0.58*	0.91
Ti	*0.93*	0.24	0.24	0.99
Mn	*0.71*	0.39	*0.53*	0.94
Fe	*0.91*	0.23	0.31	0.97
Zn	*0.58*	0.40	*0.63*	0.89
FPM	0.25	*0.91*	0.25	0.96
Soot	0.39	*0.85*	0.26	0.95

[8,9], due to the high influence of biomass burning emissions. At the Serra do Navio site, the fine mode sulfur concentration (726 ± 411 ng/m^3) is partially a result of marine air masses entering the Amazon basin region. The average concentrations of heavy metals like Zn, Cu, Ni, Sr, Zr, Rb, Pb, etc. are very low, showing the absence of atmospheric anthropogenic emissions at the sites, with the exception of biomass burning.

The variability of the elemental concentrations was analyzed using the Absolute Principal Factor Analysis (APFA) technique. For the fine-mode Cuiabá aerosol samples, only three factors account for most of the

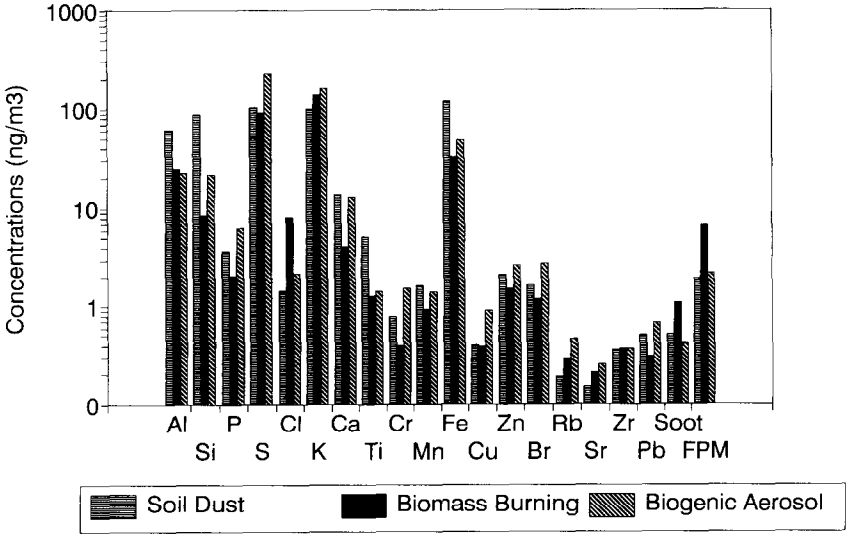

Fig. 2. Elemental source profiles for the Cuiabá Absolute Principal Factor Analysis calculations.

tracc elemcnt variability. Table 2 presents the VARIMAX rotated factor loading matrix. The first factor with high loadings for Al, Ca, Ti, Mn, Fe and Zn represents soil dust aerosol particles. The second factor with high loadings for Soot, FPM, K and Cl represents biomass burning aerosol. The third factor with high loadings for S, K, Ca, Zn and Mn represents biogenic aerosol particles. The communality for each element is shown in the last column, and is very high for all variables. Table 3 shows the VARIMAX rotated factor loading matrix for the Serra do Navio sampling site. Three factors were statistically significant. The first factor has high loadings for Al, Si, Ca, Ti, Mn, and Fe, clearly representing soil dust aerosol particles. The second factor has high loadings for K, S, Zn, Br, FPM, and Cl, representing biogenic aerosol particles. The third factor has significant loadings only for chlorine, representing marine aerosol particles. The Serra do Navio sampling site is about 500 km away from the ocean, and the prevailing wind direction is from the sea coast to the sampling site. Communality for all elements in table 3 is very high.

The APFA procedure allows obtaining absolute source profiles in units of ng/m^3. Fig. 2 shows the elemental source profiles for the APFA Cuiabá data set. Potassium has high elemental concentrations for the three factors, because it has contribution from soil dust, biomass burning and biogenic aerosol emissions. Fine-mode chlorine is emitted mainly by biomass burning. Rubidium and strontium were shown to be emitted by biogenic and biomass burning processes. Pb and Cr are present mainly in the biogenic and soil dust components. Zr is similarly distributed along the three components.

Table 3
Factor analysis results for the fine-mode Serra do Navio aerosol samples. VARIMAX rotated factor loading matrix. Three factors were statistically significant

Element	Factor 1 soil dust	Factor 2 biogenic aerosol	Factor 3 marine aerosol	Communality
Al	*0.96*	−0.14	−0.19	0.99
Si	*0.97*	−0.14	−0.16	0.99
S	−0.28	*0.94*	0.01	0.96
Cl	−0.24	*0.64*	*0.70*	0.97
K	0.00	*0.99*	0.03	0.98
Ca	*0.94*	0.03	0.02	0.88
Ti	*0.97*	−0.17	−0.14	0.99
Mn	*0.91*	−0.14	0.28	0.93
Fe	*0.99*	−0.11	−0.09	0.99
Zn	−0.05	*0.97*	0.17	0.96
Br	−0.08	*0.88*	0.16	0.80
FPM	−0.14	*0.96*	0.02	0.93

Fig. 3 shows the elemental composition of the biogenic component for the two sampling sites. P, Ca, Cr, Zn, Br, Rb, Sr, Zr and Pb show similar concentrations for both sampling sites, despite the three thousand kilometers distance between the two sampling stations. S, Cl, K and FPM show higher concentrations for the Serra do Navio sampling site. In Cuiabá, due to the high soil dust load in the atmosphere, it is possible to observe Al, Si, Ti and Fe in the biogenic elemental profile. The biogenic elemental source profile is similar to the one observed near Manaus during the ABLE-2B experiment [2,6,8,10], and in other forested regions of Brazil [11]. This agreement is surprising because the

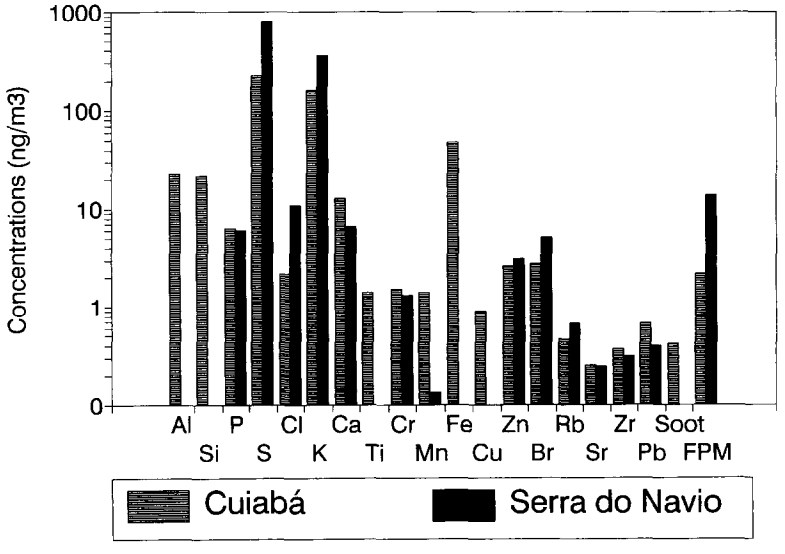

Fig. 3. Elemental composition of the biogenic component for the two background aerosol sampling sites. P, Ca, Cr, Zn, Br, Rb, Sr, Zr and Pb show similar concentrations for both sampling sites, despite the 3000 km distance.

large differences in ecosystems and plant species in the Amazon Basin. Individual particle analysis using scanning electron microprobe [12] and nuclear microprobe analysis [13] shows similar results, with the morphology of biogenic aerosol particles indicating that most of them are algae, fungus, plant debris and other particles difficult to identify.

4. Conclusions

Fine-mode aerosol particles in the Amazon basin are mainly classified in four groups: naturally released biogenic particles, biomass burning emitted particles, soil dust particles and marine aerosol particles. From a background concentration of about 20 $\mu g/m^3$ for inhalable particulate matter, the mass concentration goes as high as 150 $\mu g/m^3$ during the biomass burning season at the Cuiabá sampling station. 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, 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 elemental profiles in several sampling sites in the Amazon Basin, despite the large differences in ecossistems, pluviometric regimes and biodiversity. The high measured concentrations indicates the global importance of fine-mode biomass burning emissions.

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