Composition and diurnal variability of the natural Amazonian aerosol

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[1]   As part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment (CLAIRE) 2001 campaign, separate day and nighttime aerosol samples were collected in July 2001 at a ground-based site in Amazonia, Brazil, in order to examine the composition and temporal variability of the natural "background" aerosol. A combination of analytical techniques was used to characterize the elemental and ionic composition of the aerosol. Major particle types larger than $\sim$0.5 μm were identified by electron and light microscopy. Both the coarse and fine aerosol were found to consist primarily of organic matter ($\sim$70 and 80% by mass, respectively), with the coarse fraction containing small amounts of soil dust and sea-salt particles and the fine fraction containing some non-sea-salt sulfate. Coarse particulate mass concentrations (CPM $\approx$ PM$_{10}$ $-$ PM$_2$) were found to be highest at night (average = 3.9 $\pm$ 1.4 μg m^{-3}, mean night-to-day ratio = 1.9 $\pm$ 0.4), while fine particulate mass concentrations (FPM $\approx$ PM$_2$) increased during the daytime (average = 2.6 $\pm$ 0.8 μg m^{-3}, mean night-to-day ratio = 0.7 $\pm$ 0.1). The nocturnal increase in CPM coincided with an increase in primary biological particles in this size range (predominantly yeasts and other fungal spores), resulting from the trapping of surface-derived forest aerosol under a shallow nocturnal boundary layer and a lake-land breeze effect at the site, although active nocturnal sporulation may have also contributed. Associated with this, we observed elevated nighttime concentrations of biogenic elements and ions (P, S, K, Cu, Zn, NH$_4^+$) in the CPM fraction. For the FPM fraction a persistently higher daytime concentration of organic carbon was found, which indicates that photochemical production of secondary organic aerosol from biogenic volatile organic compounds may have made a significant contribution to the fine aerosol. Dust and sea-salt-associated elements/ions in the CPM fraction, and non-sea-salt sulfate in the FPM fraction, showed higher daytime concentrations, most likely due to enhanced convective downward mixing of long-range transported aerosol.   INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); KEYWORDS: biogenic aerosol, spores, elemental composition, Amazon, bioaerosol, organic aerosol

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1. Introduction

[2] Both from a regional and global perspective, the Amazon Basin represents an interesting and important region for the study of atmospheric aerosols. The vast tracts of tropical rainforest ($\sim 5 \times 10^6$ km^2) provide a year-round release of natural biogenic aerosol, comprised of both primary biological particles, such as microorganisms, pollen and vegetation detritus [*Artaxo et al.*, 1988; *Artaxo and Maenhaut*, 1990; *Artaxo and Hansson*, 1995], as well as secondary particles, formed by gas-to-particle conversion of organic and nitrogen- and sulfur-containing gases emitted by the forest [*Andreae et al.*, 1990a; *Artaxo and Hansson*, 1995]. During the dry season months, this "background" aerosol is often overwhelmed by smoke aerosol produced by extensive deforestation and pasture-clearing fires [*Andreae et al.*, 2002]. The intense convective activity associated with the tropics may lead to rapid uplifting and transport of both aerosol types to higher latitudes, creating the potential for far-reaching impacts on atmospheric chemistry, climate and the biogeochemical cycling of nutrients [*Greco et al.*, 1990; *Pickering et al.*, 1996; *Andreae et al.*, 2001; *Staudt et al.*, 2001]. Conversely, the Amazon Basin itself receives seasonally variable inputs of natural aerosol from distant regions, including marine aerosol from the Atlantic Ocean and mineral dust from the Sahara [*Talbot et al.*, 1990; *Formenti et al.*, 2001], which may be important sources of nutrients for the rainforest [*Reicholf*, 1986].

[3] In July 2001, the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment (CLAIRE) 2001 campaign was carried out near Balbina, a small town located in central Amazonia. Although the experiment took place toward the beginning of the dry season, the effects of biomass burning are generally not as pronounced in this area compared to other parts of Amazonia (P. Artaxo, unpublished data, 2002), and there was relatively little influence of anthropogenic emissions on the atmospheric composition. Here we report on efforts to characterize the composition of the CLAIRE 2001 aerosol using a multianalytical technique approach. A combination of particle-induced X-ray emission (PIXE), instrumental neutron activation analysis (INAA), and ion chromatography (IC) was used to analyze the elemental and ionic components of the aerosol, while thermooptical transmission analysis was used to characterize the carbonaceous component. Light microscopy, environmental scanning electron microscopy (ESEM), and electron probe X-ray microanalysis (EPXMA) were used to identify the major aerosol particle types larger than ~ 0.5 μm in diameter. One of the major features of the study was the adoption of a day-night sampling regime. This enabled us to examine diurnal variations in the concentration and composition of the aerosol, and to further investigate an interesting phenomenon that has recently been reported in the literature of enhanced nighttime concentrations of "coarse" aerosol and biogenic-associated elements within tropical forested areas [*Artaxo and Maenhaut*, 1990; *Roberts et al.*, 2001; *Artaxo et al.*, 2002; *Guyon et al.*, 2003a].

2. Sampling and Analytical Methods

2.1. Site Description

[4] Ground-based measurements were performed as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment 2001 (CLAIRE 2001) in July 2001 at Balbina, Amazonia (1°55′S, 59°24′W, 174 m above sea level). This site (Figure 1) is located approximately 100 km north of Manaus, on the southern periphery of the Balbina hydroelectric reservoir, and faces more than 1000 km of pristine rainforest to the east.

2.2. Aerosol Sampling

[5] A two-stage "Gent" PM$_{10}$ stacked filter unit (SFU) sampler (~ 4 m above ground level) was used to collect aerosol particles on Nuclepore polycarbonate filters in "coarse" (~ 2–10 μm aerodynamic diameter (AD)) and "fine" (less than ~ 2 μm AD) size fractions [*Maenhaut et al.*, 1994; *Hopke et al.*, 1997]. A series of PM$_{10}$ samples were also collected using a second SFU sampler fitted with a single Nuclepore filter (0.4 μm pore size). Filters were stored in sterilized Petri dishes in a refrigerator after sampling. A dichotomous high-volume (HiVol) sampler (~ 4 m above ground level) was used to collect samples in two size fractions (particles smaller and larger than ~ 2.5 μm AD) [*Solomon et al.*, 1983] on Pall Gelman quartz fiber filters (prebaked for 15 hours at 550°C), as described by *Graham et al.* [2002]. Although the latter sampler did not have an upper cut off, fine wire mesh was placed over the inlet to prevent the entry of insects. Loaded filters were stored in the dark in clean glass jars in a freezer at −18°C until the time of analysis.

[6] For both the SFU and HiVol samplers, separate daytime and nighttime samples were collected. To ensure sufficient loadings of aerosol particles for analysis, aerosol was sampled for three consecutive days or nights using each filter set. Filters were changed at ~ 0800 and 1800 LT. Between samplings, the filters (still housed in their holders) were wrapped in clean aluminum foil, placed in sealed vessels, and stored in the freezer. A total of four pairs of day-night Nuclepore filter sets (FPM, CPM, PM$_{10}$) were collected between 16 July and 28 July, while three pairs of quartz filter sets were collected between 19 July and 28 July.

[7] An additional set of samples was collected for microscopic examination of particles with AD > 4 μm using a rotating impactor and an isokinetic jet impactor [*Matthias-Maser and Jaenicke*, 1994]. The impaction substrates used were glass slides coated with an adhesive glycerin jelly containing a Coomassie Blue dye [*Matthias*, 1987]. Any protein-containing biological particles were stained a bluish color and could be distinguished from the nondyed particles by light microscopy. Sampling with the rotating and jet impactors was carried out intermittently between 20 and 26 July (at a height of 2 m above ground level), for periods generally ranging from 30 to 60 min. Most samples were collected during the day because high-humidity conditions (mist) often led to condensation of water on the slides at night. One nighttime sample suitable for microscopic examination was obtained on the night of 22 July. All samples were refrigerated postcollection.
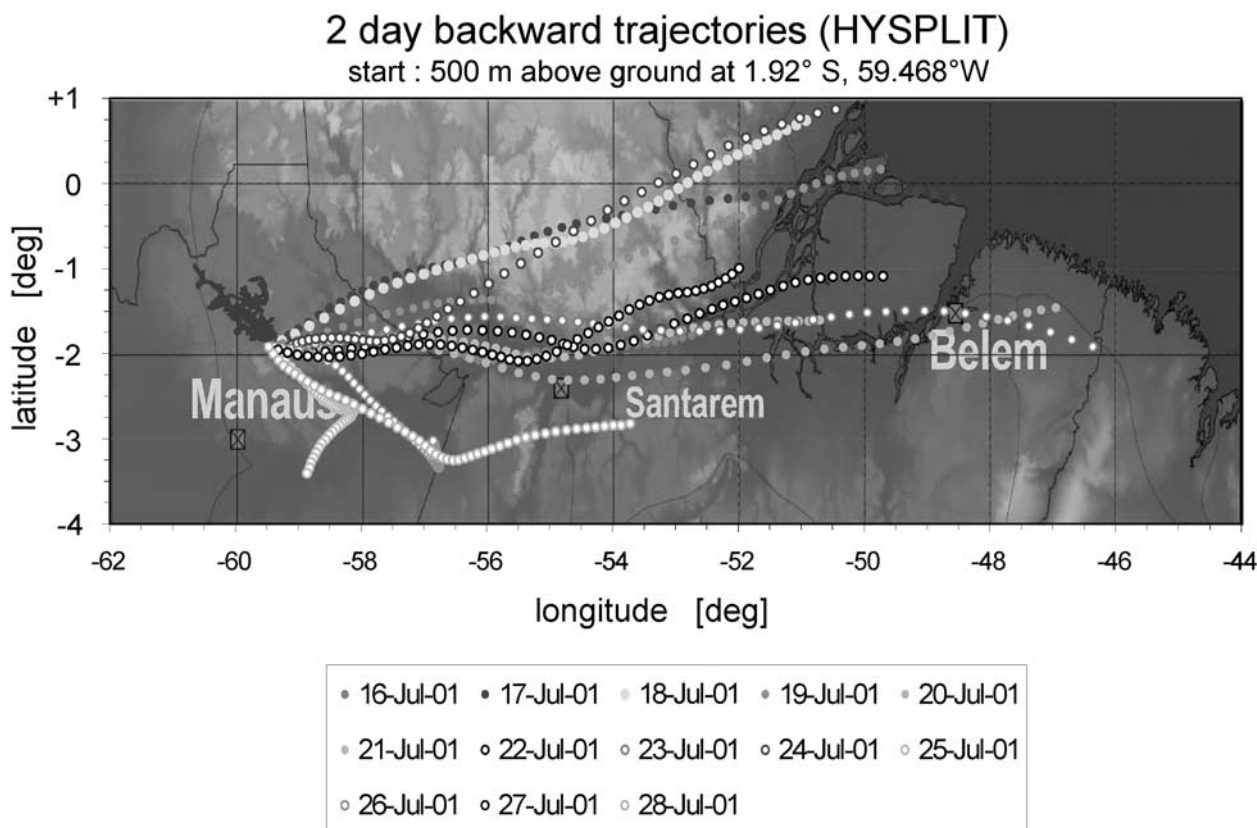
2 day backward trajectories (HYSPLIT)
start : 500 m above ground at 1.92° S, 59.468°W

Figure 1. Map showing the position of the Balbina sampling site (1°55′S, 59°24′W), relative to the Balbina hydroelectric reservoir, and the Brazilian cities of Manaus, Santarem, and Belem. Representative 2-day backward trajectories for the period 16–28 July 2001 are also shown for a starting altitude of 500 m. See color version of this figure at back of this issue.

[8] All aerosol samples were collected at ambient relative humidity (RH) and temperature. Daytime RH ranged between 60 and 100%, while nighttime RH was almost always close to 100%.

2.3. Aerosol Analysis

[9] Coarse and fine particulate mass concentrations (CPM and FPM, respectively) were determined by weighing the coarse and fine fraction SFU filters (allowing at least a 24 hour preequilibrium period at 20°C and 50% RH) before and after sampling using a Mettler MT5 electronic balance with 1 μg sensitivity, and an accuracy of ±5 μg. The filters were then analyzed for elements between Na and Pb using a combination of PIXE and INAA [*Maenhaut and Zoller*, 1977; *Maenhaut et al.*, 1981; *Maenhaut and Raemdonck*, 1984]. Detection limits were typically 5 ng m^{-3} for elements in the range $13 < Z < 22$, and 0.4 ng m^{-3} for elements with $Z > 23$. Portions of the filters were also analyzed for major water-soluble ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$ oxalate, K$^+$, Na$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}) by IC, and black carbon (BC) by a light reflectance technique [*Andreae*, 1983; *Andreae et al.*, 1984]. Concentrations of the latter are referred to as "black carbon equivalent" (BC$_e$) because the light reflectance technique determines the equivalent amount of soot giving the same absorption signal as the sample, which can be influenced by light-absorbing species other than soot, and

because of the uncertainties related to the absorption cross section of BC in ambient aerosols [*Fuller et al.*, 1999].

[10] A thermooptical transmission method, based on the technique of *Birch and Cary* [1996], was used to measure the total carbon (TC), organic carbon (OC), and apparent elemental carbon (EC$_a$) contents of the HiVol quartz filter samples [*Schmid et al.*, 2001].

[11] Individual particle analysis was performed on the PM$_{10}$ Nuclepore filter samples using EPXMA [*Van Dyck et al.*, 1984; *Artaxo et al.*, 1988]. The filters were coated with a thin carbon film and analyzed in a JEOL JSM6300 Scanning Microscope (JEOL, Tokyo, Japan) equipped with a PGT energy dispersive X-ray detector (Princeton Gamma Tech, Princeton, USA). An accelerating voltage of 20 kV and a beam current of 1nA were used, with an X-ray spectrum acquisition time of 60 s live time and magnification of 1000. A total of 200 particles were analyzed per sample. Hierarchical cluster analysis was used to classify the particles into groups according to their elemental composition, using the Ward's error sum technique [*Massart and Kaufman*, 1983]. For this purpose, the Integrated Data Analysis System (IDAS) software package was used [*Bondarenko et al.*, 1996]. Only those variables (elements) which were detected in more than 1% of the analyzed particles were retained.

[12] Light microscopic examination of the glass slide samples was performed using a Zeiss Axiophot microscope.
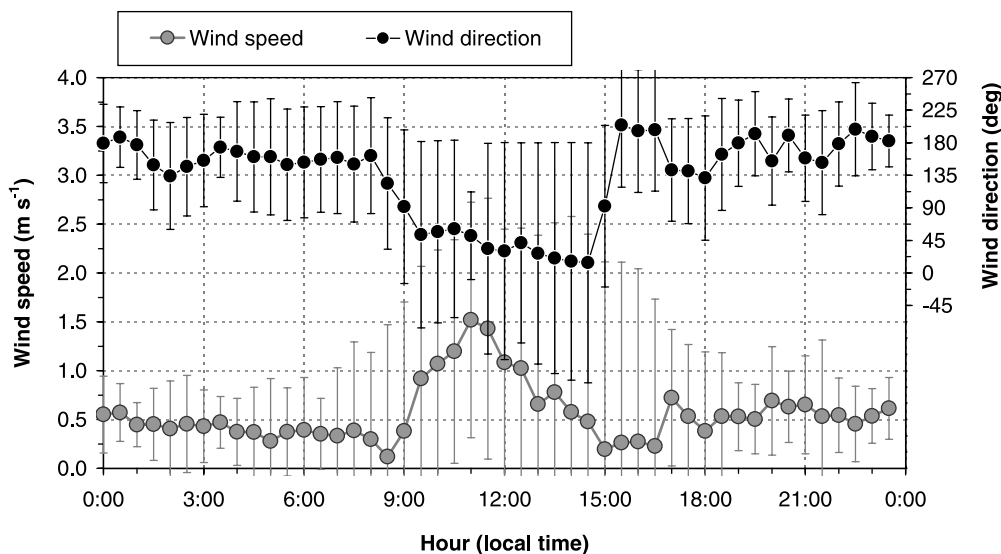
Figure 2. Average daily variations in wind speed and direction at Balbina, Amazonia, for 16–28 July 2001.

Further details are provided by P. E. Taylor et al. (manuscript in preparation, 2003). Individual particle analysis was also carried out on selected glass slide samples, together with some of the PM_{10} Nuclepore filter samples, by ESEM. A detailed description of the technique is provided by *Ebert et al.* [2003]. One major advantage of ESEM over traditional SEM is that the analysis of samples may be performed at pressures up to 30 hPa and relative humidities up to 102%, avoiding the deterioration of biological particles that often occurs under the high-vacuum conditions required for SEM.

3. Results and Discussion

3.1. Meteorological Conditions

[13] The CLAIRE 2001 campaign was held in July, which lies at the beginning of Brazil's dry season. During this month, the Inter Tropical Convergence Zone (ITCZ) was located at ∼6°N (INPE/CPTEC/MCT, available at http://www.cptec.inpe.br/cgi-bin/climalis.cgi?mes=07&ano=01), and airflow over the lowest 5 km of the atmosphere was dominated by an easterly trade wind flow, which transported humid oceanic air masses from the Atlantic over the forests of the Amazon Basin [*Silva Dias et al.*, 2002]. Two-day back trajectories calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (http://www.arl.noaa.gov/ready/hysplit4.html) indicate that air flow toward Balbina was persistently from the easterly sector for the period 16–28 July (Figure 1).

[14] Figure 2 shows the average daily variations in wind speed and direction measured at the Balbina site between 16 and 28 July. During the night, wind speeds were generally very low (∼0.5 m s^{-1} on average) and the prevailing wind
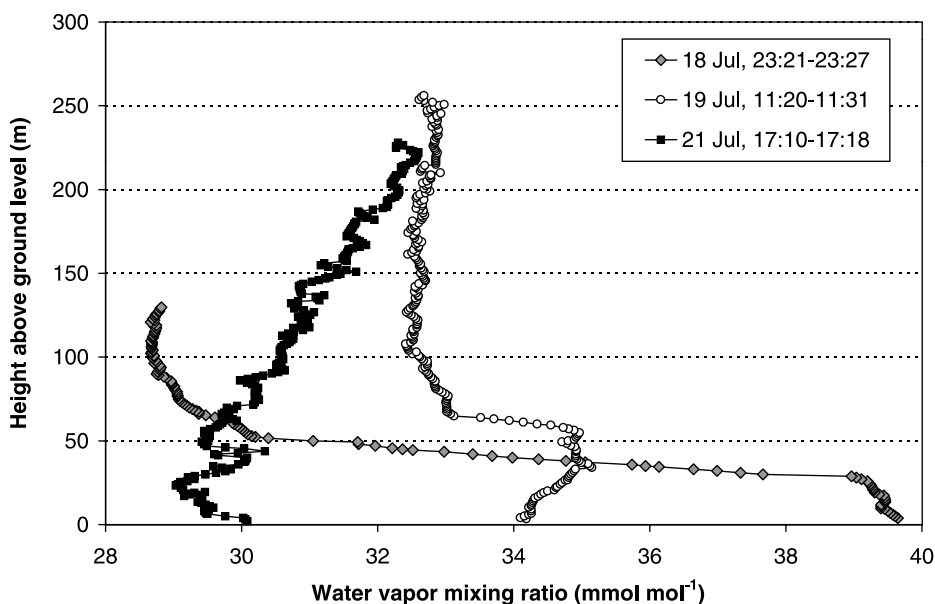

Figure 3. Vertical profiles of the water vapor mixing ratio measured above Balbina, Amazonia, with a tethered balloon between 18 and 21 July 2001. The times shown are local.

direction was from the south. Wind speeds increased moderately during the daytime to values of around 1 m s^{-1}, with air flowing predominantly from the NE sector. This distinctive diurnal wind pattern, superimposed on the synoptic easterly airflow, reflects the fact that Balbina is located on the southern edge of a 2,360 km^2 hydroelectric dam (Figure 1). During the day, the forest canopy heats up more quickly, and to a greater extent, than the lake. The air in contact with the forest warms and rises, causing a lake breeze circulation in which cool air flows from the lake to the forest at the surface, while a compensatory flow of air from the forest to the lake occurs aloft. At night, when the forest canopy cools more quickly and to a greater extent than the lake, a land breeze circulation is set up, so that the site is more under the influence of air derived from forested areas directly to the south.

[15] Previous measurements in the Amazon Basin, including at Balbina itself [*Garstang et al.*, 1988], have shown that radiative cooling results in the formation at dusk of a shallow, decoupled nocturnal boundary layer over the forest, while heating of the surface in the morning causes a deepening, convectively mixed layer to develop at a vertical growth rate of 1–10 m min^{-1}. During the CLAIRE 2001 campaign, water vapor mixing ratio profiles measured with a tethered balloon between 18 and 21 July also showed the presence of a decoupled nighttime surface layer (Figure 3), with a profile measured near 0000 LT on 18 July indicating a surface layer with a roughly constant mixing ratio of ~40 mmol mol^{-1}, capped by a strong decrease starting at about 30 m above ground level. In contrast, a profile measured the next day before noontime revealed a far less stratified vertical profile, with only a slight decrease in mixing ratio occurring at a height of ~60 m, likely attributable to the lake's internal boundary layer. A late afternoon profile measured on 21 July revealed a thoroughly mixed boundary layer, greater than 250 m in depth (maximum height of balloon ascent). Given the presence of a deep, well-mixed layer during the daytime, coupled with the synoptic easterly airflow and vast expanses of pristine forest situated to the east, the daytime aerosol sampled at Balbina can be expected to have been representative of the natural background aerosol.

[16] The combined effects of the diurnal boundary layer height development and lake breeze were found to exert a major influence on the concentration and composition of the surface aerosol measured at the Balbina site, as detailed in the following sections.

3.2. Aerosol Mass Concentrations

[17] The average atmospheric concentrations of FPM and CPM that we measured during the CLAIRE 2001 campaign were 2.6 ± 0.8 and 3.9 ± 1.4 μg m^{-3}, respectively. These values are quite similar to those reported by *Guyon et al.* [2003a] for wet season aerosol sampled at a remote primary rainforest site located on the SW periphery of the Amazon Basin (2.2 ± 1.4 and 3.8 ± 1.3, respectively). Moreover, they compare favorably with those reported by *Formenti et al.* [2001] for Balbina during the CLAIRE 98 wet season campaign (1.6 and 5.8 μg m^{-3} for FPM and CPM, respectively), and by *Artaxo et al.* [1990] for two further Amazonian sites located near Manaus (2.1 ± 0.7 and 6.1 ± 1.8 μg m^{-3} for FPM and CPM, respectively). Thus the
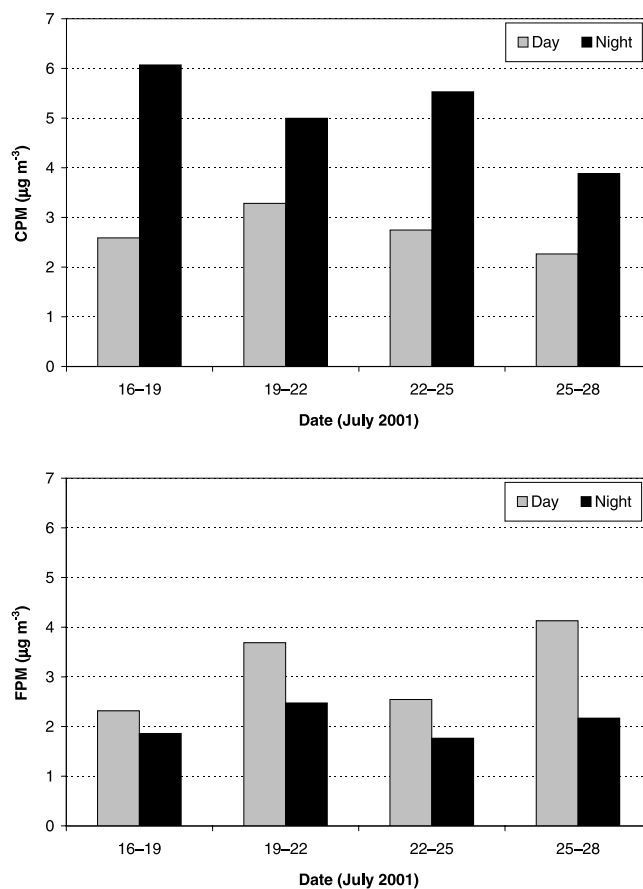

Figure 4. Temporal variation in (top) CPM and (bottom) FPM determined by gravimetric analysis of atmospheric aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16–28 July 2001).

sampled aerosol appears to have been fairly representative of the natural "background" aerosol found over Amazonia, despite the fact that sampling took place at only a semi-remote site and was carried out at the beginning of the dry season. As noted earlier, long-term measurements at Balbina have shown that the effects of biomass burning are generally not as pronounced in this area compared to other parts of the Amazon Basin (P. Artaxo, unpublished data, 2002).

[18] Figure 4 shows the time series of CPM and FPM concentrations measured over the course of the CLAIRE 2001 campaign. CPM values were found to be consistently higher at night (mean night/day ratio = 1.9 ± 0.4), while FPM levels were higher during the day (mean night/day ratio = 0.7 ± 0.1). This phenomenon has also been reported for other tropical forest locations, both within the Brazilian Amazon [*Artaxo et al.*, 2002; *Guyon et al.*, 2003a] as well as the African Congo [*Roberts et al.*, 2001], and thus appears to be a quite general one. *Roberts et al.* [2001] ascribed it to the trapping of surface-derived forest aerosol under a shallow nocturnal boundary layer, coupled with efficient downward mixing of long-range transported fine aerosol during the day due to enhanced thermal convective activity. This explanation is consistent with the meteorological observations made at Balbina (section 3.1). In the present case, however, it seems likely that the measured

Table 1. Concentration of Major Primary Biogenic Aerosol Particle Types Identified in Aerosol Samples by Light Microscopy[a]

	Nighttime Sample (2355–0105 LT)	Daytime Sample (0910–0948 LT)
Pollen	103	1700
Fern spores	0	1100
Fungi	233,000	23,500
Algae	0	<20
Insect fragments	0	209

[a]Concentrations are in m^{-3}. Samples were collected on 22 July during the CLAIRE 2001 campaign. Times shown are local.

diurnal variation in CPM may have been reinforced (at least to some degree) by the lake breeze effect observed at the site, since the air above the lake was most probably depleted of coarse aerosol relative to the forest air.

3.3. Microscopic Identification of Coarse Particle Types

[19] Microscopic analyses of the glass slide and PM_{10} Nuclepore filter samples verified the nighttime increase in coarse biological particles, many with AD < 10 μm. A sample collected on the night of 22 July showed very high concentrations of fungal particles (Table 1), especially yeasts (2–10 μm in diameter), which accounted for 87% of the total fungal spore number. Thus our observations provide direct evidence that the nighttime increase in CPM is predominantly associated with biogenic aerosol (previous studies have inferred such an association from elemental measurements only). Many of these fungi were smaller than 2.5 μm and would have, therefore, contributed to the fine aerosol samples.

[20] While the increase of biogenic particles at night was predominantly a "passive" consequence of the shallow nocturnal boundary layer and lake breeze effect, it is worth noting that many fungi are known to be nocturnal sporulators [*Van Arsdel*, 1967; *De Groot*, 1968; *Paulitz*, 1996]. It is, therefore, possible that the observed nighttime increase in fungal spore numbers and CPM was partially associated with an active release of spores during the night. The mechanism of release of yeast aerosols has not been investigated, but might involve rain splash, wind disturbance, or active release. It is widely believed that the preferential nighttime release of some fungal spore types occurs in response to a rise in RH during the evening hours [*Van Arsdel*, 1967; *De Groot*, 1968; *Paulitz*, 1996]. Although RH is persistently high in the Amazon Basin, it frequently reaches 100% during the night, leading to the formation of mists. This fact may be significant given the recent hypothesis of *Fuzzi et al.* [1997] that fog may act as a culture medium for airborne biological particles. These researchers found that the concentration of airborne bacteria and yeasts in the Po Valley, Italy, was enriched by up to two orders of magnitude under foggy conditions compared to clear air conditions. The nocturnal release of spores in tropical locations may have the added selective advantage that spores are more likely to be dispersed horizontally, following paths around relatively small, stratified thermal cells [*Van Arsdel*, 1967], rather than swept up to high altitudes by large-scale convective currents during the day, where they may be exposed to harsh radiation levels and have less chance of remaining viable. The

distribution of yeasts and small fungal spore aerosols remains to be investigated, however they are not efficiently scrubbed from the air by rainfall. Heavy rainfall can lead to higher levels of these organisms in the air.

[21] While there is insufficient data to establish the degree to which nocturnal yeast and fungal spore release may have contributed to the observed diurnal variation, some indication for such an effect is that the fungal population varied between day and nighttime samples (P. E. Taylor et al., manuscript in preparation, 2003). The daytime coarse fraction also consisted of pollen grains (7–26 μm diameter), fern spores (15–50 μm) and some algae (8 μm). There was a large release of epiphytic *Polypodium* fern spores each morning (20–40 μm). Occasionally, fern sporangia and leaf hairs were found in the daytime samples, although the latter were quite rare. The release of these "giant" particles into the air is most likely driven by lowered relative humidity and enhanced wind speeds/thermal convective activity during daylight hours, with the mechanisms of entrainment

Table 2. Mean Concentrations and Associated Standard Deviations of Elements in the Fine and Coarse Size Fractions of Atmospheric Aerosol Samples Collected With an SFU Sampler During the CLAIRE 2001 Campaign (16–28 July 2001)[a]

	Fine Size Fraction		Coarse Size Fraction	
Species	Mean ± SD	N[b]	Mean ± SD	N[b]
	CLAIRE 2001			
Na	45.7 ± 48.0	8	78.7 ± 90.6	8
Mg	43.3 ± 35.5	2	26.3 ± 0.5	2
Al	15.9 ± 11.7	8	19.4 ± 14.7	8
Si	24.9 ± 16.8	8	32.6 ± 23.2	8
P	4.5 ± 1.2	6	23.3 ± 15.2	8
S	108.8 ± 48.4	8	26.1 ± 9.8	8
Cl			64.9 ± 85.7	4
K	34.8 ± 16.0	8	57.5 ± 30.1	8
Ca	9.2 ± 6.0	6	11.2 ± 9.0	8
Ti	1.2 ± 0.5	5	1.4 ± 1.1	7
V	0.11 ± 0.07	8	0.07 ± 0.03	4
Mn	0.19 ± 0.10	8	0.32 ± 0.10	8
Fe	8.9 ± 7.5	8	11.2 ± 8.9	8
Cu	2.1 ± 1.0	8	0.93 ± 0.40	8
Zn	0.93 ± 0.83	8	0.48 ± 0.19	8
Br	1.7 ± 0.5	7	1.5 ± 0.5	8
I	0.27 ± 0.13	8	0.16 ± 0.06	8
	LBA-EUSTACH 1			
Na				
Mg			29.0 ± 23.2	23
Al	34.5 ± 30.9	24	52.5 ± 50.8	24
Si	42.5 ± 37.9	28	52.0 ± 59.8	25
P	5.6 ± 1.9	28	23.4 ± 9.3	28
S	87.7 ± 87.2	28	23.5 ± 14.8	28
Cl	6.1 ± 7.9	11	8.9 ± 5.4	28
K	26.8 ± 26.5	28	48.2 ± 14.9	28
Ca	8.4 ± 6.1	28	12.2 ± 7.5	28
Ti	3.8 ± 4.1	14	6.5 ± 7.3	14
V				
Mn	0.56 ± 0.36	28	0.87 ± 0.57	28
Fe	21.6 ± 29.7	26	34.2 ± 46.8	26
Cu	0.42 ± 0.44	27	0.32 ± 0.2	28
Zn	0.68 ± 0.72	23	0.72 ± 0.39	28
Br	1.05	1		
I				

[a]Mean concentrations are in ng m^{-3}. Data from the LBA-EUSTACH 1 wet season campaign at a primary rainforest site in Rondônia, Brazil, are shown for comparison [*Guyon et al.*, 2003a].
[b]N is the number of samples in which the element was observed above its detection limit.
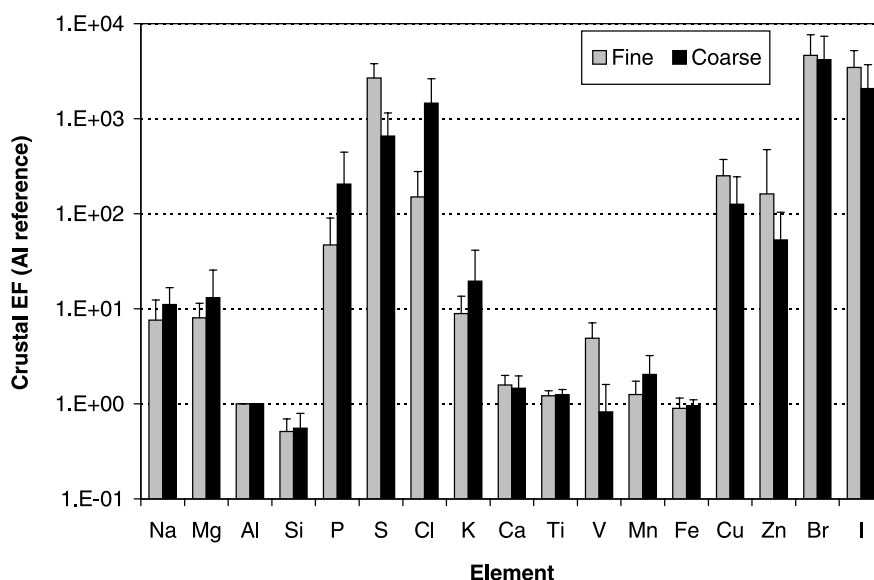
Figure 5. Mean elemental enrichment factors (EFs) for the fine and coarse size fractions of atmospheric aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16–28 July 2001). The EFs were calculated relative to the global average crustal rock composition of *Mason and Moore* [1982], using Al as the reference element. The error bars represent one standard deviation.

including direct wind action and indirect, abrasive dislodgement, as well as thermal convection and/or thermal or photophoresis [*Wickmen*, 1994]. Some plant and ferns have built-in "catapult" systems to aid in pollen/spore release [*Gregory*, 1973]. Such large particles would be expected to sediment fairly quickly at night in response to the cessation of convective activity, reduction in wind speeds, and increased relative humidity (section 3.1). Insect activity also appeared to be more intense during the day, with whole or fragmented insects observed in a number of the daytime samples. Further details regarding the microscopic analysis of the samples are provided by P. E. Taylor et al. (manuscript in preparation, 2003).

3.4. Elemental Composition

[22] Table 2 reports the average atmospheric concentrations of elemental species measured by PIXE and INAA for the FPM and CPM aerosol samples collected with the SFU sampler (day and nighttime samples combined). For comparison, Table 2 also shows average elemental concentrations recently reported by *Guyon et al.* [2003a] for aerosol collected above a primary rainforest in Rondônia, Brazil, during the LBA-EUSTACH 1 wet season campaign (April–May 1999). When all elements other than Na, Cl, Br and I were assumed to be present in the state of their most common oxide [*Mason and Moore*, 1982], the PIXE/INAA data could account for an average of 20% and 14% of the FPM and CPM concentrations, respectively, with the remaining aerosol mass being attributable to organic matter, elemental carbon (EC), and elements lighter than Na.

[23] In general, the individual elemental concentrations we obtained are quite comparable to the values reported by *Guyon et al.* [2003a], as well as those of *Artaxo et al.* [1990] and *Formenti et al.* [2001] for wet season background aerosol, although some differences were found in the levels of soil dust elements (Al, Si, Ti, Mn, and Fe) and Cl

between the sites. This further demonstrates that our data are fairly representative of the aerosol present over the Amazon Basin in its "natural" state, and that there was relatively little influence of anthropogenic emissions on atmospheric composition during the period of the campaign.

[24] Figure 5 presents the mean crustal enrichment factors (EFs) for the elements detected in the fine and coarse aerosol fractions. These were calculated relative to the global average crustal rock composition of *Mason and Moore* [1982] using Al as the reference element:

$$EF(X) = \frac{[C(X)/C(Al)]_{\text{aerosol}}}{[C(X)/C(Al)]_{\text{soil dust}}}, \tag{1}$$

where $C(X)$ is the concentration of element X for the aerosol or the reference crustal rock. In both size fractions, the elements commonly associated with mineral dust (Al, Si, Ca, Ti, Mn, Fe) showed EF values close to unity, indicating soil dust dispersal as the major source (the depletion of Si in the aerosol relative to crustal rock is a commonly observed phenomenon and is attributed to crust-to-air fractionation [*Rahn*, 1976]). The very low concentrations of these species (Table 2) are not surprising, given that wind erosion is fairly minimal in the Amazon Basin due to the dense vegetative cover. Indeed, a major fraction of the dust over the Amazon is thought to derive from long-range transport of Saharan mineral dust rather than local sources [*Talbot et al.*, 1990]. Evidence for such a distant source is provided by the fact that the concentrations of the dust-associated elements are comparable for the fine and coarse size fractions (Table 2). Dust measured near its source has a predominantly coarse mode distribution, however the relative contribution of fine particles would be expected to increase with increasing distance from the source, due to the higher settling velocity of the coarse particles. The lower values we observed compared
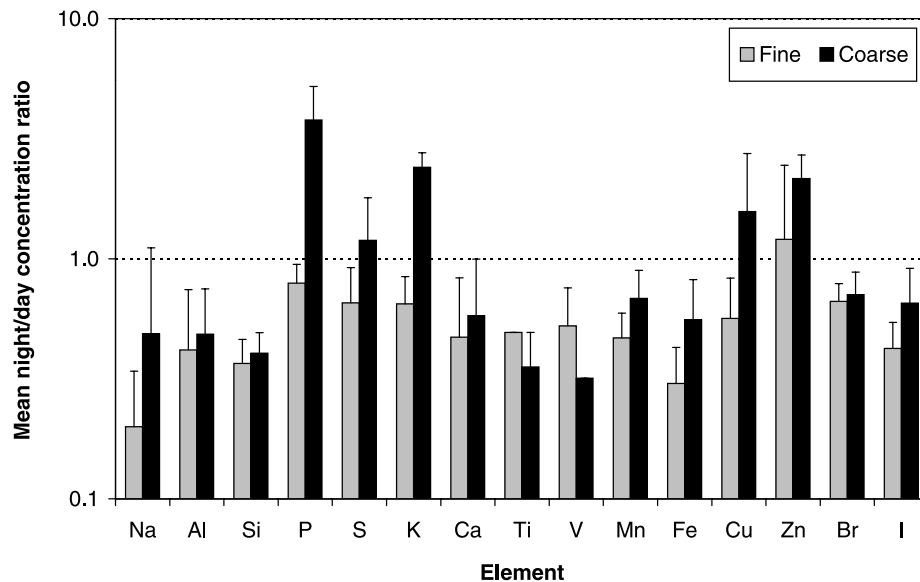
Figure 6. Mean ratios of nighttime-to-daytime elemental concentrations (log scale) for the fine and coarse atmospheric aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16–28 July 2001). The error bars represent one standard deviation.

to concentrations measured during campaigns held in April–May (ABLE-2A [*Artaxo et al.*, 1990], CLAIRE 98 [*Formenti et al.*, 2001], and LBA-EUSTACH 1 [*Guyon et al.*, 2003a]) are consistent with the observation of *Artaxo et al.* [1990] that dust concentrations tend to be higher during the wet season because large-scale atmospheric circulation patterns are more conducive to trans-Atlantic air flow from the Sahara region during this period.

[25] The higher EFs for coarse P, S, K, Cu and Zn are consistent with previous observations from tropical forest sites [*Artaxo et al.*, 1990; *Formenti et al.*, 2001; *Roberts et al.*, 2001; *Guyon et al.*, 2003a], and it is generally agreed that these elements are associated with primary biogenic emissions [*Mamane and Noll*, 1985; *Xhoffer et al.*, 1992; *Matthias-Maser and Jaenicke*, 1994]. Evidence for such a biogenic origin has been derived from profile measurements made within forest stands, which have shown that below-canopy concentrations of these elements in the coarse fraction tend to be higher than above-canopy ones [*Artaxo and Hansson*, 1995; *Roberts et al.*, 2001; *Guyon et al.*, 2003a]. P and K were significantly enriched in the coarse aerosol (Table 2), and exhibited their highest EFs in this fraction, which provides further evidence for an association with the primary biological aerosol. In contrast, Cu, Zn and S were mostly present in the fine aerosol fraction (Table 2) and exhibited even higher EFs in this fraction than the coarse one (Figure 5). The principally fine-fraction distribution of S is indicative of gas-to-particle production of sulfate from reduced atmospheric sulfur gases (IC measurements showed that the fine S was almost exclusively present in the form of SO_4^{2-}; see section 3.5 below). Previous studies have concluded that background levels of sulfate over the Amazon Basin can be partly attributed to forest emissions of several sulfur-containing gases (dimethylsulfide (DMS), H_2S, CS_2), but that the main background source is probably oxidation of marine DMS derived from the Atlantic Ocean [*Andreae et al.*, 1990a]. The very low

levels of EC_a recorded in the samples (see section 3.6 below) suggest that anthropogenic pollution did not make a significant contribution to the observed levels of S.

[26] It is unclear what the exact origin of the fine Cu and Zn in our samples was; however, we note that Cu is often considered to be a biogenic component [*Beauford et al.*, 1975, 1977; *Guyon et al.*, 2003b], despite the fact that its spatial and temporal variation can sometimes be quite different from those of other biogenic elements. *Artaxo et al.* [1988], *Artaxo and Hansson* [1995], and *Echalar et al.* [1998] all identified a distinct component loaded with Zn and S in fine wet season aerosol and ascribed this a biogenic origin (in addition to a separate biogenic coarse component loaded with P and K), although slightly higher concentrations above the forest canopy [*Artaxo and Hansson*, 1995] suggest a source external to the forest. This component has also been associated with biomass burning [*Guyon et al.*, 2003b]; however, as noted above, this seems unlikely to have been a major source in the present study.

[27] The high EFs for Na and Cl (Figure 5), coupled with the higher concentrations of these elements in the coarse aerosol (Table 2), are consistent with a marine source for these elements. There is clear evidence that this sea-salt component derives from the long-range transport of Atlantic marine aerosol into the interior of the Amazon Basin [*Talbot et al.*, 1988, 1990; *Andreae et al.*, 1990b; *Greco et al.*, 1990; *Artaxo and Hansson*, 1995; *Formenti et al.*, 2001]. It should be noted, however, that Cl is also emitted during plant transpiration [*Nemeruyk*, 1970] and may therefore also have an additional forest source. Indeed, *Artaxo and Hansson* [1995] were able to show, using principal component analysis, that some Cl within the coarse aerosol is associated with the coarse P-containing and K-containing biogenic aerosol component. The average coarse Cl-to-Na mass ratio that we determined (0.4) is substantially lower than of seawater (1.8) and indicates that the marine aerosol became heavily depleted of Cl during its transport across the rain-
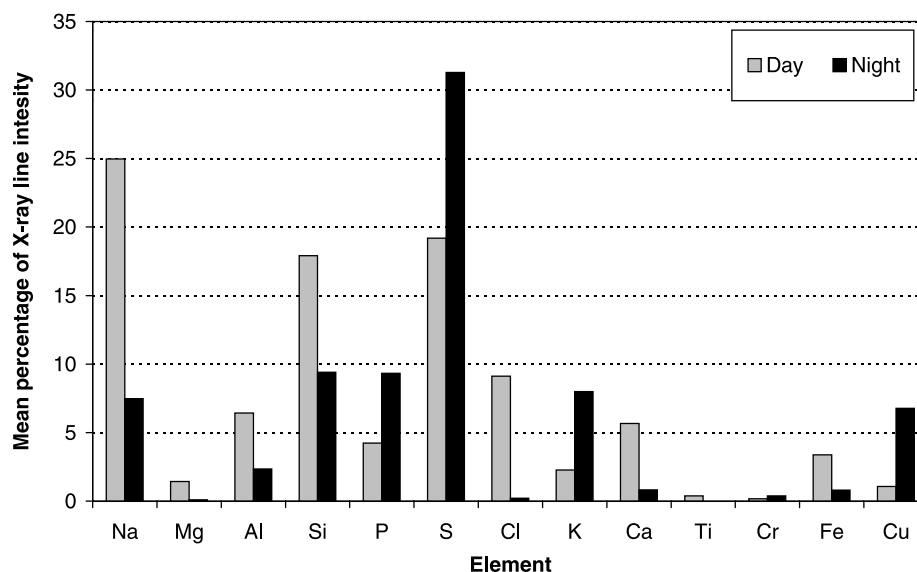
Figure 7. Mean abundance of EPXMA-detected elements (expressed as percentages of total X-ray line intensity) for two daytime and two nighttime PM_{10} aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16–28 July 2001).

forest, most likely as a result of reaction with acidic organic and S-containing gases emitted by the vegetation. This is consistent with the earlier observations of *Talbot et al.* [1988, 1990].

[28] Other elements which exhibited high EFs were Mg, I and Br, in both the fine and coarse fractions, and V in the fine fraction. The sources for Mg, I and Br include marine aerosol, biogenic matter and pyrogenic emissions [*Artaxo et al.*, 1988, 1990; *Kleeman et al.*, 1999; *Maenhaut et al.*, 2002; *Guyon et al.*, 2003b]. Fine-fraction V, a tracer for oil burning [*Chow*, 1995], most likely derived from anthropogenic emissions; however, its concentrations were either very low or below detection limit in all samples, as were those of other elements typically associated with such emissions (Ni, Cr, Pb) [*Chow*, 1995], indicating a very minimal contribution of anthropogenic air pollution to the total aerosol loading.

[29] The majority of elements exhibited distinct diurnal variations in concentration, as indicated by the average night-to-day concentration ratios shown in Figure 6 (note: ratios could not be determined for some elements because of too few data above detection limit). In general, elements associated with aerosol components originating from sources external to the forest were elevated during the daytime, while those associated with primary biogenic aerosol were enriched at night. The fine aerosol fraction showed consistently higher concentrations of almost all elements during the day (ratios below unity), coinciding with enhanced convective downward mixing of air from the planetary boundary layer to the surface during the day, and suggesting that long-range transported aerosol and aerosol formed aloft were the dominant sources for much of the fine aerosol. Likewise, coarse-fraction elements associated with soil dust (Al, Si, Ca, Ti, V, Mn, Fe) and sea salt (Na, Cl, Br, I) exhibited higher daytime concentrations, with the formation of the shallow, decoupled nocturnal boundary layer leading to depletion during the night by dry deposition. On the other hand, coarse-fraction P, S, K, Cu and Zn were significantly

enriched at night (by factors between 1.2 and 3.8), due to reduced atmospheric dispersion of the surface-derived forest aerosol. Similar observations have been reported previously by *Artaxo and Maenhaut* [1990], *Roberts et al.* [2001], *Artaxo et al.* [2002], and *Guyon et al.* [2003a] for a number of tropical forest sites.

[30] The results from the PIXE-INAA analyses of the bulk aerosol were corroborated by single-particle elemental analyses made on several of the PM_{10} Nuclepore filter samples using EPXMA. The analysis was performed only on particles larger than 0.5 μm diameter, due to the resolution of the instrument and the carbon coating of the particles required for X-ray microanalysis. Figure 7 shows the mean abundance of EPXMA-detected elements for the day and nighttime aerosol (as percentages of the total X-ray line intensity), based on the results for two daytime and two nighttime samples. In agreement with the PIXE-INAA data, elements associated with biogenic matter, P, K, S, and Cu, were more prominent at night, while those linked to suspended soil dust or marine aerosol were more prevalent during the daytime.

[31] Table 3 presents the results of cluster analyses performed on the EPXMA data for the day and nighttime samples. For each group of particles, the percentages of the total X-ray line intensity are used as a rough indication of the elemental composition. Also, the average particle diameter for each group is given. The content of light elements (C and O) was often quite large, as deduced from the relative intensities of the Bremsstrahlung background. However, the concentration of the light elements could not be determined by EPXMA.

[32] For the daytime samples, two distinct clusters (numbers 1 and 6) were identified that could be associated with soil dust by virtue of their high Al and Si contents. Together, these accounted for a total of 22.5% of the EPXMA-detected particles. Cluster 4 (5.5%) may represent an additional soil component, comprised of quartz particles (SiO_2). Cluster 2 (21.5%), and possibly cluster 5 (5.5%),

Table 3. Hierarchical Cluster Analysis of the EPXMA Data for Two Daytime and Two Nighttime PM$_{10}$ Aerosol Samples Collected With an SFU Sampler During the CLAIRE 2001 Campaign (16−28 July 2001)[a]

	Daytime Clusters								Nighttime Clusters							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
% of total	12.7	21.5	19.0	5.5	5.5	9.8	20.0	6.0	6.0	4.8	11.0	43.5	6.3	19.8	4.3	4.5
Na	3.7	46.0	33.5	3.4	19.0	10.2	29.3	2.3	17.7	0.0	8.7	1.3	0.3	14.9	0.0	42.9
Mg	2.4	1.3	0.1	0.0	0.0	2.8	2.7	0.0	0.0	0.0	0.0	0.0	0.5	0.4	0.0	0.0
Al	33.2	0.0	0.5	2.6	0.3	16.1	0.2	5.6	0.9	0.0	0.0	0.2	35.5	0.0	0.0	0.0
Si	50.6	4.0	13.5	82.9	5.0	27.4	2.3	0.8	29.3	0.0	0.3	2.0	52.2	7.3	48.6	0.0
P	0.0	0.0	0.5	0.3	0.0	0.6	20.4	0.0	0.0	43.8	0.0	3.4	0.2	29.1	0.0	0.0
S	2.0	23.4	36.4	7.1	22.9	7.0	22.4	2.9	37.3	56.2	48.6	20.6	2.6	36.9	47.9	57.1
Cl	0.2	20.2	4.5	0.3	1.2	2.3	16.1	6.1								
K	2.8	2.9	1.1	0.8	0.2	1.5	4.2	0.6	14.8	0.0	31.3	3.5	3.4	9.7	0.0	0.0
Ca	0.8	1.4	9.1	0.4	51.3	3.3	1.5	0.8	0.0	0.0	5.6	0.4	0.4	0.0	0.0	0.0
Ti	0.3	0.0	0.0	0.0	0.0	1.2	0.0	3.8								
Cr	0.1	0.2	0.1	0.0	0.2	0.0	0.4	0.0	0.0	0.0	0.0	0.2	0.0	0.5	1.1	0.0
Fe	3.8	0.0	0.3	2.1	0.0	27.5	0.2	0.3	0.0	0.0	0.4	1.2	4.1	0.0	0.0	0.0
Cu	0.1	0.3	0.3	0.0	0.0	0.1	0.3	14.4	0.0	0.0	4.6	13.8	0.7	0.9	0.9	0.0
Mean diameter, μm	1.74	1.83	1.38	1.50	0.94	1.40	2.00	1.00	2.00	1.80	1.70	1.70	1.30	2.20	1.20	1.80

[a]Data for 400 particles (200 per sample) were used in each cluster analysis.

appear to represent aged sea-salt particles, as indicated by the presence of high relative amounts Na and S, together with a depletion of Cl. Similarly, Cluster 3 (19%), with relatively high amounts of Na, S and Si, may be attributable to a mixture of internally mixed aged sea salt and quartz particles. Cluster 7 (20%), with a high loading of the biogenic-related elements P and S, is likely associated with biological particles derived from the forest, but also contains high relative amounts of Na and Cl. The identity of cluster 8 (6%) is less clear, but it may also be associated with Cu-containing biogenic particles.

[33] In comparison to the daytime samples, the major clusters identified for the nighttime samples appear to be associated with biogenic particles, as indicated by high loadings of the biogenic elements P, S, K and Cu; cluster 2 (4.8%) contains largely P and S, cluster 3 (11%) S and K, cluster 4 (43.5%) S and Cu, and cluster 6 (19.8%) predominantly P, S and K. Cluster 1 (6%), with high relative amounts of Na, Si, S and K, may also be associated with

biogenic matter, but could also be due to internally mixed aged sea salt and quartz. Cluster 5, the only cluster distinctly attributable to soil dust, accounted for only 6.3% of the identified particles, much less than the total found for the daytime samples (total of 28% for clusters 1, 4 and 6). The remaining minor clusters may also be associated with nonbiogenic particles, cluster 7 (4.3%) possibly representing sulfate-coated quartz particles, and cluster 8 (4.5%) aged sea salt. Nevertheless, it is clear that the nighttime samples contained relatively fewer particles of marine or soil origin, in agreement with the PIXE-INAA data reported above, and the IC results described in section 3.5.

[34] While our EPXMA analyses did not include an attempt to calculate actual atmospheric concentrations of particles, it is interesting to compare the relative size distributions determined for the day and nighttime samples. Figure 8, which shows the percentage abundance of detected particles as a function of size, indicates that the nighttime samples contained a relatively higher fraction of
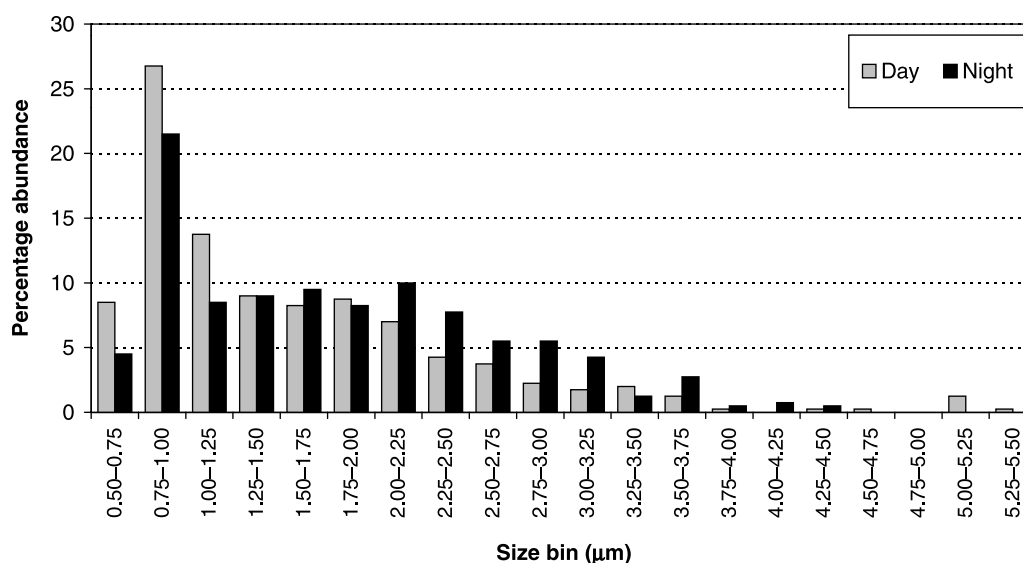

Figure 8. Relative size distributions of EPXMA-detected particles for two daytime and two nighttime PM$_{10}$ aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16−28 July 2001).

Table 4. Mean Concentrations and Associated Standard Deviations of Water-Soluble Ions in the Fine and Coarse Size Fractions of Atmospheric Aerosol Samples Collected With an SFU Sampler During the CLAIRE 2001 Campaign (16−28 July 2001)[a]

	Fine Size Fraction		Coarse Size Fraction	
Species	Mean ± SD	N[b]	Mean ± SD	N[b]
NO_3^-	23.1 ± 36.1	5	112.7 ± 129.1	7
SO_4^{2-}	324.4 ± 152.2	8	51.4 ± 36.0	8
Oxalate	48.7 ± 48.6	8	40.0 ± 33.0	6
Cl^-	4.8 ± 5.7	3	59.1 ± 83.2	8
Na^+	48.3 ± 56.9	8	99.9 ± 123.1	8
NH_4^+	49.5 ± 25.1	8	26.6 ± 19.9	5
K^+	29.2 ± 14.1	8	52.6 ± 28.5	8
Mg^{2+}	4.3 ± 4.8	8	13.3 ± 12.1	8
Ca^{2+}	8.3 ± 3.5	8	9.5 ± 7.7	8

[a]Mean concentrations are in ng m^{-3}.
[b]N is the number of samples in which the element was observed above its detection limit.

particles between ∼2 and 4.5 μm in diameter, while the daytime samples contained a larger proportion of particles between ∼0.5 and 1.25 μm. These results are in broad agreement with the gravimetric data presented in section 3.2. The larger number of particles in the 2−4 μm size range is consistent with the increased numbers of yeasts and small fungal spores present in this size range at night (section 3.3; Table 1; see also P. E. Taylor et al. (manuscript in preparation, 2003)). The detection of greater numbers of particles larger than 4.5 μm in the daytime samples by EPXMA is also consistent with our light microscopic observations of enhanced concentrations of "giant" bioaerosol particles during the day (section 3.3; Table 1).

3.5. Ionic Components

[35] Table 4 reports the average concentrations of water-soluble ions determined by IC for both the fine and coarse aerosol fractions (day and nighttime samples combined),

while Figure 9 shows the average night-to-day concentration ratios determined for each of the ions. The ions accounted for, on average, 19 and 14% of FPM and CPM, respectively, while the combined IC and PIXE/INAA data could account for an average of 24 and 19% of the respective fractions. Consistent with the PIXE/INAA results (Table 2), SO_4^{2-} was confined predominantly to the FPM fraction, while Na^+, K^+, and Cl^- were more concentrated in the CPM fraction. Nitrate was also most prevalent in the coarse aerosol, as first noted by *Artaxo et al.* [1988], who measured average fine and coarse concentrations similar to ours at a forest site near Manaus during the wet season (13.5 and 111 ng m^{-3}, respectively), and *Talbot et al.* [1988], who measured significantly higher average fine and coarse concentrations in the boundary layer during the dry season (68 and 205 ng m^{-3}, respectively). Ammonium was more concentrated in the fine fraction, where it was likely present in the form of ammonium sulfate/bisulfate. Emissions of N-containing gases (e.g., NO and NH_3) from the rainforest could be expected to have contributed to the formation of the aerosol NO_3^- and NH_4^+ in the atmosphere. The measured oxalate may also have been largely of secondary origin, deriving from the photooxidation of volatile organic forest emissions, with the relatively high coarse fraction concentrations of both NO_3^- and oxalate attributable to condensation of these species onto large, preexisting aerosol particles. It is possible, however, that much of the coarse fraction oxalate may have been a constituent of primary biogenic aerosol particles.

[36] Most of the quantified ions showed higher daytime concentrations for both the FPM and CPM fractions (Figure 9). The exceptions were coarse NH_4^+ and K^+, which were likely associated with the primary biogenic aerosol that was more concentrated at ground level during the night. The higher daytime concentrations of the sea-salt-associated and soil-dust-associated ions are largely consistent with the PIXE/INAA data (Figure 6) and the proposed long-range
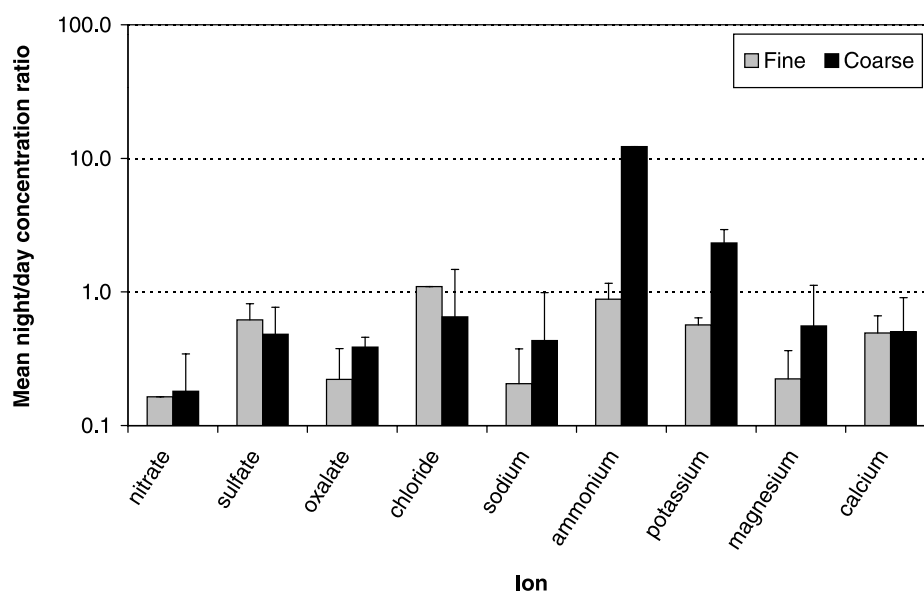

Figure 9. Mean ratios of nighttime-to-daytime concentrations (log scale) of water-soluble ions for the fine and coarse atmospheric aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16−28 July 2001). The error bars represent one standard deviation.
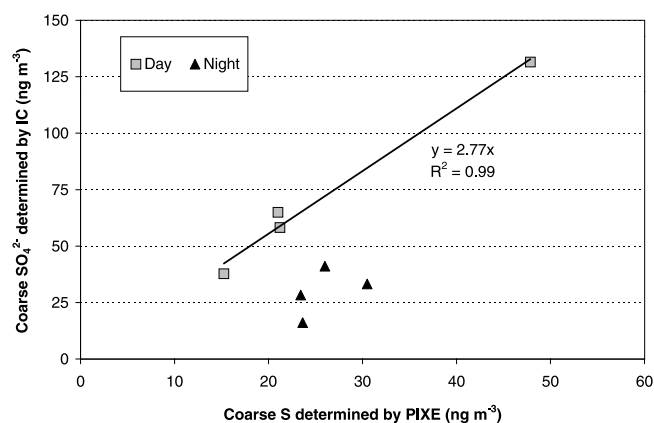
Figure 10. Concentrations of SO_4^{2-} (determined by IC) versus S (by PIXE) for the coarse atmospheric aerosol samples collected with an SFU sampler during the CLAIRE 2001 campaign (16–28 July 2001). The regression line shown (forced through zero) refers to the daytime data only.

sources described above, while the higher concentrations of oxalate and NO_3^- observed during the daytime may have also been partly attributable to enhanced photochemical production.

[37] The IC-determined SO_4^{2-} and PIXE-determined S concentrations were found to be strongly correlated for the fine aerosol fraction ($R^2 = 0.97$, day and night samples combined), with regression analysis yielding a fine SO_4^{2-}-to-S ratio of 3.00, the value expected if all fine S was present as SO_4^{2-}. A similar analysis for the coarse aerosol fraction indicated that the major fraction of coarse S present during the day was also in the form of SO_4^{2-} (regression slope = 2.77, $R^2 = 0.99$); however, for the nighttime samples, the amount of S was found to be significantly higher than that predicted from the IC measurements (Figure 10). This suggests that other S species may have been present in the aerosol, most likely associated with the primary biogenic particles. It may also have been the case that much of the SO_4^{2-} was present inside intact biological cells, and thus not accessible via the mild aqueous extraction procedure used to dissolve the ions from the SFU filters.

[38] For the fine aerosol fraction, a reasonably good ion balance was achieved for both the day and nighttime samples, with average percentage ion balance differences (PDI = ($\Sigma C_{anions} - \Sigma C_{cations})/(\Sigma C_{anions} + \Sigma C_{cations}) \times$ 100%) of 10 and 16% for the day and nighttime samples, respectively. The "missing" cation fraction was probably composed largely of H^+ ions. For the coarse aerosol fraction, anion deficits were observed for all samples, particularly the nighttime ones, with average day and nighttime PDI values of −7 and −55%, respectively. We are unsure as to the identity of the missing anion component, but it may have included phosphate (as suggested by the high nighttime coarse P levels), carbonate, organic acids other than oxalic acid, and humic substances [*Andreae and Crutzen*, 1997; *Havers et al.*, 1998; *Gelencsér et al.*, 2002].

3.6. Carbonaceous and Light-Absorbing Components

[39] Table 5 reports the average OC and EC_a contents of the HiVol quartz filter aerosol samples for both the fine (<2.5 μm) and coarse (>2.5 μm) aerosol fractions, as well as

the BC_e content of the FPM and CPM samples collected with the SFU sampler (day and nighttime samples combined). The values compare favorably with the limited data available on the carbonaceous content of wet season aerosols. *Formenti et al.* [2001] found average OC concentrations of 0.59 and 2.50 μg m^{-3} for the FPM and CPM fractions, respectively, and less than 0.01 μg m^{-3} of EC_a in the FPM fraction, during the CLAIRE 98 campaign held in Balbina (background conditions only). *Guyon et al.* [2003a] reported average OC, EC_a, and BC_e concentrations of 0.82, 0.08 and 0.28 μg m^{-3}, respectively, for the fine aerosol sampled above a rainforest canopy during the LBA-EUSTACH 1 campaign.

[40] OC concentrations were found to be about twice as high in the coarse fraction compared to the fine fraction, consistent with the large contribution of primary biological particles to the total aerosol loading. However, in contrast to the elevated nighttime CPM values associated with the trapping of the forest aerosol under the nocturnal boundary layer (section 3.2), concentrations of OC in the coarse HiVol filter samples were found to be slightly higher during the day (Figure 11). The likely reason for this is that the HiVol sampler did not have an upper cut-off stage, and would therefore have also collected some of the "giant" bioaerosol particles present during the daytime (Table 1). In particular, the fern spores and pollen grains observed in the daytime samples by light microscopy (section 3.3) would be expected to have contributed to the OC content of the HiVol coarse filters, but not the measured CPM levels.

[41] For the fine fraction, OC concentrations were also observed to be somewhat higher during the day than the night. This trend most likely reflects a combination of convective downward mixing of fine organic aerosol from aloft during the day, as well as enhanced secondary organic aerosol (SOA) production via photochemical gas-to-particle conversion of volatile organic compounds (VOCs) emitted by the forest vegetation. Further evidence for the latter process was obtained from the results of gas chromatography-mass spectrometry analyses made on extracts of the aerosol samples, described by *Graham et al.* [2003] and M. Claeys et al. (Formation of secondary organic aerosols through photooxidation of isoprene, submitted to *Science*, 2003, hereinafter referred to as Claeys et al., submitted manuscript, 2003).

[42] EC_a concentrations were consistently very low, averaging only 4 and 1% of the total carbon in the fine

Table 5. Mean Concentrations and Associated Standard Deviations of OC, EC_a, and BC_e in the Fine and Coarse Size Fractions of Atmospheric Aerosol Samples Collected During the CLAIRE 2001 Campaign (16–28 July 2001)[a]

Species	Fine Size Fraction		Coarse Size Fraction	
	Mean ± SD	N[b]	Mean ± SD	N[b]
OC	1.13 ± 0.36	6	2.26 ± 0.38	6
EC_a	0.05 ± 0.02	6	0.02 ± 0.01	6
BC_e	0.29 ± 0.14	8	0.07 ± 0.04	8

[a]Mean concentrations are in ng m^{-3}. OC and EC_a values were measured on fine (<2.5 μm) and coarse (>2.5 μm) aerosol samples collected with the HiVol sampler, while BC_e values were measured on CPM and FPM samples collected with the SFU sampler.
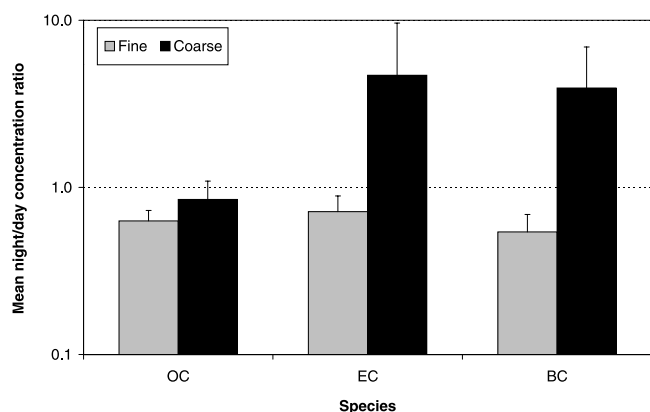[b]N is the number of samples in which the element was observed above its detection limit.

Figure 11. Mean ratios of nighttime-to-daytime concentrations (log scale) of OC, EC_a, and BC_e for the fine and coarse atmospheric aerosol samples collected during the CLAIRE 2001 campaign (16–28 July 2001). OC and EC_a values were measured on fine (<2.5 μm) and coarse (>2.5 μm) aerosol samples collected with a HiVol sampler, while BC_e values were measured on CPM and FPM samples collected with the SFU sampler. The error bars represent one standard deviation.

and coarse fractions, respectively. Even though the HiVol sampler sampled slightly different size fractions to the SFU sampler, this indicates that essentially all of the FPM and CPM unaccounted for by PIXE and IC was composed of organic matter. The concentrations of EC_a were higher in the fine fraction and highest during the day for this fraction, suggesting that much of it may have derived from long-range transported smoke aerosol. It should be noted, however, that smoke may have also originated from local or regional sources, since fire is widely used in Brazil throughout the year for domestic purposes, charcoal production, and in various factories (e.g., brick making) [*Andreae*, 1991; *Echalar et al.*, 1998]. ESEM analyses of the PM_{10} Nuclepore filter samples confirmed the presence of soot particles in the sampled aerosol.

[43] EC is usually assumed to be the only light-absorbing matter in aerosols (with the exception of metal oxides, which are normally present in negligible quantities). However, the BC_e values we measured were found to be much higher than the EC_a values (by average factors of 7 and 4 for the fine and coarse aerosol fractions, respectively), indicating that other nonsoot components likely contributed to absorption. *Guyon et al.* [2003b] also observed a large discrepancy between BC_e and EC_a for fine aerosol collected above the Amazon forest canopy during the wet season, and were able to show, using statistical techniques, that biogenic aerosol was responsible for up to ~50% of aerosol light absorption during the wet season. Further evidence for such a biogenic contribution is provided by the fact that a substantial amount of BC_e was present in the CPM fraction (with average coarse-to-fine BC_e ratios of 0.11 and 0.54 for the day and nighttime samples, respectively), and that the coarse BC_e values were higher (on average) during the night (Figure 11), coinciding with the nighttime increase in primary biogenic aerosol in the CPM fraction (section 3.3). The data, therefore, appear to bear out the suggestion of

Andreae and Crutzen [1997] that much of the BC_e in the wet season may have a biogenic origin. Biogenic light-absorbing components could potentially include pigments present in primary biogenic aerosol particles, as well as naturally occurring humic and fulvic acids present in the soil and decaying plant litter [*Havers et al.*, 1998; *Gelencsér et al.*, 2002]. It has also recently been speculated that light-absorbing humic-like substances may be generated through in situ atmospheric polymerization reactions involving VOCs emitted from the soil and vegetation [*Gelencsér et al.*, 2002, 2003].

3.7. Chemical Mass Apportionment

[44] Together, the chemical analysis data for the Nuclepore and quartz filter samples were used to perform a chemical mass apportionment (CMA) of the FPM and CPM aerosol fractions, the results of which are shown graphically in Figure 12. The apportionment is somewhat approximate, due in part to the different fine-coarse cut points of the SFU and HiVol samplers (~2 μm versus 2.5 μm), and the fact that the cut off for the SFU is not very sharp, but is adequate to demonstrate the dominant contribution of organic matter to both the fine and coarse size fractions of the background aerosol.

[45] For both fractions, soil dust concentrations were estimated from the measured Al concentrations using the average crustal rock composition of *Mason and Moore* [1982], while sea salt was calculated from the Na concentrations [*Riley and Chester*, 1971] after first accounting for the Na present in silicate dust [*Mason and Moore*, 1982]. For the fine fraction, sulfate was treated as $(NH_4)HSO_4$, based on the measured approximately 1:1 ammonium-to-sulfate molar ratio for the samples; for the coarse fraction, the contributions of sulfate (and nitrate) were minimal. Together, these various components could account for an average of $25 \pm 9\%$ and $18 \pm 17\%$ of the gravimetrically determined FPM and CPM values, respectively. The contributions were generally higher during the day (Figure 12), which was likely due to downward mixing of long-range transported aerosol from aloft and enhanced mobilization of dust during the day.

[46] The contribution of anthropogenic air pollution to the total aerosol loading during CLAIRE 2001 appears to have been very minimal, as indicated by the fact that the concentrations of elements typically associated with such emissions (V, Ni, Cr, Pb) [*Chow*, 1995] were either very low or below detection limit in all samples. In addition, the thermooptical transmission analysis data for the HiVol filter samples indicates that EC_a made only a minimal contribution to the fine and coarse aerosol ($1.7 \pm 0.7\%$ and $0.6 \pm 0.5\%$, respectively), thus the remaining mass in both aerosol fractions was most likely comprised of particulate organic matter (POM). Assuming the remainder of FPM ($73 \pm 9\%$) to be POM leads to an average predicted POM/OC ratio of 1.81 ± 0.28 (based on the measured OC content of the fine HiVol filters), which lies near the midrange of POM/OC values (1.2–2.2) published in the literature [*Russell*, 2003]. Even assuming a POM/OC ratio at the lower end of the scale leads to an estimated minimum contribution of POM to FPM of $49 \pm 4\%$.

[47] For the coarse fraction, the amount of OC detected on the coarse HiVol filters is actually greater than the fraction of
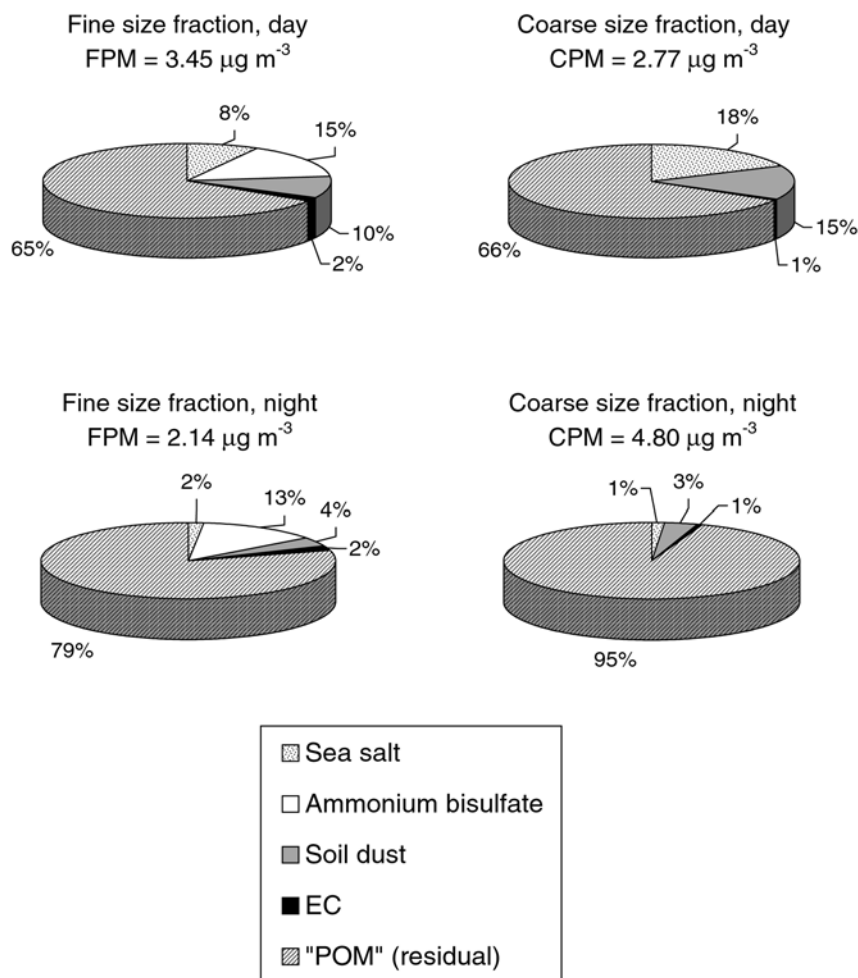
Fine size fraction, day
FPM = 3.45 µg m^{-3}

8% | 15%
65% | 10% | 2%

Coarse size fraction, day
CPM = 2.77 µg m^{-3}

18%
66% | 15% | 1%

Fine size fraction, night
FPM = 2.14 µg m^{-3}

2% | 13% | 4%
79% | 2%

Coarse size fraction, night
CPM = 4.80 µg m^{-3}

1% | 3% | 1%
95%

☒ Sea salt
☐ Ammonium bisulfate
▨ Soil dust
■ EC
▨ "POM" (residual)

Figure 12. Mean chemical mass apportionment (CMA) of the fine and coarse atmospheric aerosol samples collected during the CLAIRE 2001 campaign (16–28 July 2001). The CMA is based on the combined chemical analysis data for the SFU and HiVol filter samples.

CPM unaccounted for by the inorganic components on the coarse SFU filters. This reflects the fact that the HiVol sampler did not have a well-defined upper cut off, and would have also collected some of the "giant" biogenic aerosol particles (AD > 10 µm) present in the air, i.e., fern spores, pollen grains, leaf debris and insect fragments. The adsorption of organic vapors to the quartz filters (positive artefact) may have also partly contributed to the high OC content of the HiVol samples. Nonetheless, the HiVol data, together with the results of our light microscopic analyses (section 3.3) (P. E. Taylor et al., manuscript in preparation, 2003), indicate that it is likely that POM, primary biogenic aerosol particles in particular, accounted for the bulk of CPM (81 ± 17%). The fraction of CPM believed to represent POM was noticeably higher for the nighttime samples (Figure 12), which is consistent with our microscopic observations of a large increase in fungal spores numbers in the 2–10 µm size range at night (section 3.3).

[48] The results of our CMA are consistent with the findings of *Formenti et al.* [2001], who estimated that ∼70% of PM$_{10}$ was comprised of POM during the CLAIRE 98 campaign in Balbina (under background conditions), with mineral dust accounting for ∼20% of PM$_{10}$, and

sulfate and sea salt, together, only ∼10%. The CMA results are also in broad agreement with source contribution estimates derived from absolute principal component/factor analysis of wet season Amazonian aerosol data sets [*Artaxo et al.*, 1990; *Echalar et al.*, 1998; *Maenhaut et al.*, 2002; *Guyon et al.*, 2003b]. For example, *Artaxo et al.* [1990] found that only two components, biogenic aerosol and soil dust, could explain ∼90% of the variance in their data for fine and coarse aerosol collected a forest site near Manaus, with biogenic aerosol accounting for 55–92% of the fine mass, and 65–95% of the course mass. Similarly, *Echalar et al.* [1998] reported that biogenic emissions were responsible for 65 and 70% of FPM and CPM, respectively, for aerosol sampled at the Amazonian site of Alta Floresta during the wet season, with soil dust accounting for only 7 and 11% of the respective mass fractions.

4. Summary and Conclusions

[49] In this study, the diurnal variability of the natural Amazonian aerosol was examined by analyzing a series of day-night segregated samples collected during the CLAIRE 2001 campaign. Despite the fact that the site was subject to

a distinct lake breeze effect, the composition and temporal variability of the aerosol were found to be representative of the "background" aerosol present over the rainforest. The coarse aerosol fraction was comprised predominantly of primary biological particles, but included minor contributions from soil dust and sea salt. As observed in previous studies, CPM concentrations were found to increase at night, which microscopic analyses confirmed was due to an increase in primary biogenic aerosol, mainly yeasts and small fungal spores, from the forest. Concentrations of "giant" bioaerosol particles with >20 μm AD (pollen, fern spores, large fungal spores and some leaf fragments), however, increased during the day, as did coarse soil dust and sea-salt concentrations. These diurnal variations appear to be closely related to the meteorological conditions (shallow nocturnal boundary layer; decreased relative humidity, enhanced wind speeds and convective activity during the day), but additional factors, such as a preferential nighttime release of yeasts and small fungal spores, could also play a role. The temporal variability of the coarse biogenic aerosol could be traced via a number of inorganic elements/ions. The fine aerosol fraction also consisted largely of organic matter, but included contributions from sulfate, soil dust, and sea-salt aerosol. All of these components exhibited higher concentrations during the day, which indicates that the much of the fine surface aerosol was derived from aloft and/or preferentially produced during the daytime. This aerosol likely included long-range-transported material, as well as secondary aerosol produced by the oxidation of volatile emissions from the forest (reduced S, N, and organic species). Further data pertaining to the composition and diurnal variability of the aerosol sampled during the CLAIRE 2001 campaign are described in a number of other papers [*Graham et al.*, 2003; Claeys et al., submitted manuscript, 2003; P. E. Taylor et al., manuscript in preparation, 2003].

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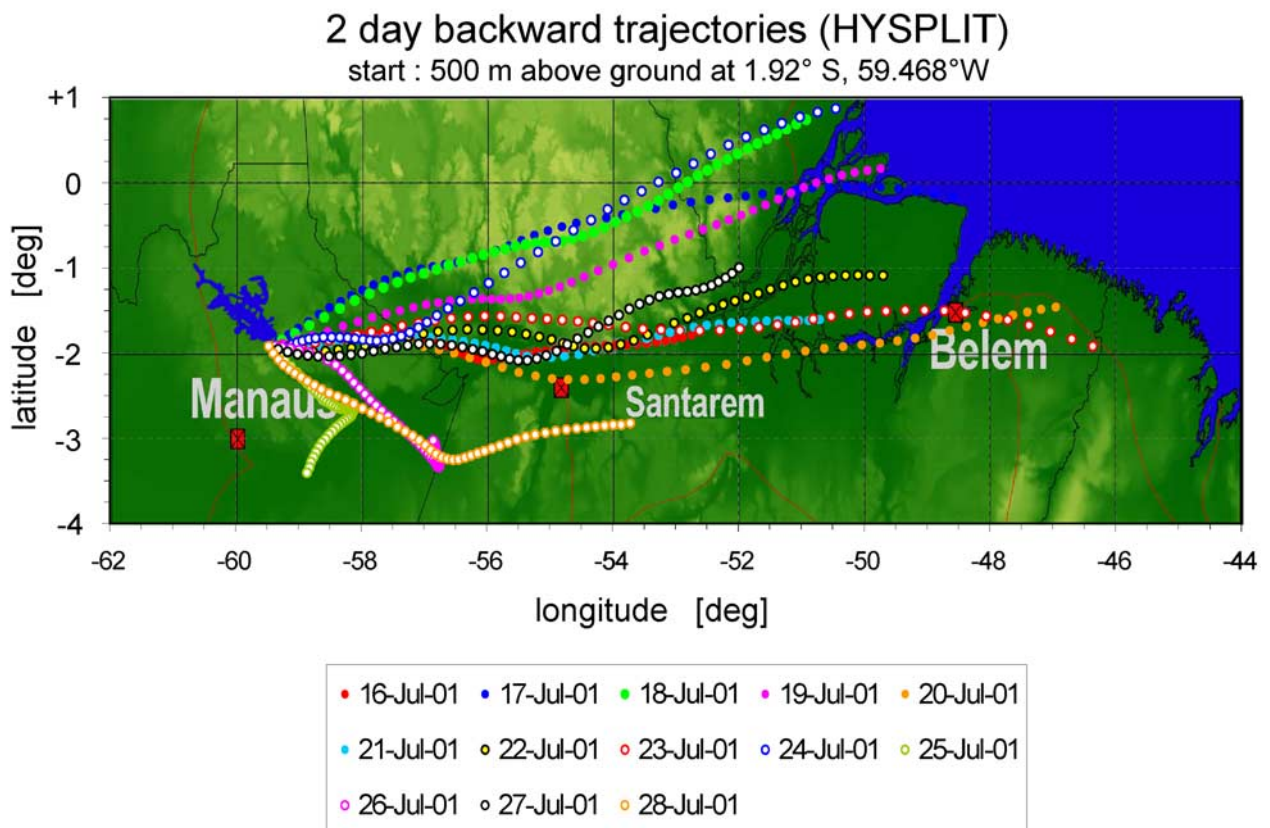
Figure 1. Map showing the position of the Balbina sampling site (1°55′S, 59°24′W), relative to the Balbina hydroelectric reservoir, and the Brazilian cities of Manaus, Santarem, and Belem. Representative 2-day backward trajectories for the period 16–28 July 2001 are also shown for a starting altitude of 500 m.