Atmospheric Environment 44 (2010) 503–511

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Aerosol properties, in-canopy gradients, turbulent fluxes and VOC concentrations at a pristine forest site in Amazonia

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ARTICLE INFO

Article history:
Received 8 May 2009
Received in revised form
27 October 2009
Accepted 2 November 2009

Keywords:
Biogenic aerosols
VOC
Turbulent fluxes
Amazon

ABSTRACT

Aerosol physical and chemical properties were measured in a forest site in central Amazonia (Cuieiras reservation, 2.61S; 60.21W) during the dry season of 2004 (Aug–Oct). Aerosol light scattering and absorption, mass concentration, elemental composition and size distributions were measured at three tower levels (Ground: 2 m; Canopy: 28 m, and Top: 40 m). For the first time, simultaneous eddy covariance fluxes of fine mode particles and volatile organic compounds (VOC) were measured above the Amazonian forest canopy. Aerosol fluxes were measured by eddy covariance using a Condensation Particle Counter (CPC) and a sonic anemometer. VOC fluxes were measured by disjunct eddy covariance using a Proton Transfer Reaction Mass Spectrometer (PTR-MS). At nighttime, a strong vertical gradient of phosphorus and potassium in the aerosol coarse mode was observed, with higher concentrations at Ground level. This suggests a source of primary biogenic particles below the canopy. Equivalent black carbon measurements indicate the presence of light-absorbing aerosols from biogenic origin. Aerosol number size distributions typically consisted of superimposed Aitken (76 nm) and accumulation modes (144 nm), without clear events of new particle formation. Isoprene and monoterpene fluxes reached respectively 7.4 and 0.82 mg m^{-2} s^{-1} around noon. An average fine particle flux of 0.05 ± 0.10 10^6 m^{-2} s^{-1} was calculated, denoting an equilibrium between emission and deposition fluxes of fine mode particles at daytime. No significant correlations were found between VOC and fine mode aerosol concentrations or fluxes.

1. Introduction

The Amazon tropical forest constitutes a complex ecosystem, in which biosphere and atmosphere are linked via vertical fluxes of momentum, heat, water vapor, aerosols and trace gases. The forest, with its natural metabolism, emits a large amount of biogenic particles and gases to the atmosphere, affecting the global atmosphere as a consequence of convective activity (Andreae et al., 2001). Under natural conditions, Amazonian aerosols come mostly from biogenic sources (Graham et al., 2003), with a small component of soil dust. Average PM_{10} aerosol mass concentrations range between 10 and 15 $\mu g\ m^{-3}$, with 70–80% of mass on coarse mode (diameter $> 2.0\ \mu m$) (Martin et al., in press). Number concentrations range between 300 and 500 particles cm^{-3}. These concentrations are comparable to values reported for other remote continental sites in the world, making Amazonia one of the few continental regions where there are still pristine atmospheric conditions in terms of aerosols (Andreae, 2007).

By scattering and absorbing light, particles have a strong influence on regional radiation budgets (Satheesh and Moorthy, 2005), photochemical reactions (Martin et al., 2003) and atmospheric stability (Menon et al., 2002). In Amazonia it was shown that aerosol particles from biomass burning strongly influence photosynthetic rates, affecting the regional carbon balance (Oliveira et al., 2007). Understanding these effects requires detailed information on aerosol sources and sinks, and on processes that regulate aerosol emissions and transformations. The study of aerosol exchanges between biosphere and atmosphere in natural environments can provide a better understanding on feedbacks and equilibrium processes, and clarify how ecosystems deal with complex aerosol effects. This work reports the first measurements of eddy covariance particle fluxes in a remote tropical forest.

Concerning to natural emissions of trace gases, the Amazon forest is a major source of natural volatile organic compounds (VOC) to the global atmosphere (Guenther et al., 1995), emitting hydrocarbons such as isoprene and monoterpenes, as well as oxygenated compounds (Kesselmeier et al., 2000, 2002). Isoprene and monoterpenes are directly emitted by vegetation, while oxygenated compounds like acetone and acetaldehyde are mostly produced as

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doi:10.1016/j.atmosenv.2009.11.002

oxidation products of other VOC species, and can also originate from biomass burning (Karl et al., 2007; Salisbury et al., 2003). Some VOC species may act as gaseous precursors in the process of new particle formation and growth (Zhang et al., 2004). VOC compounds also affect oxidant concentrations of species including hydroxyl radical and ozone. This work reports measurements of aerosol and VOC concentrations and fluxes in parallel, aiming at a better understanding of secondary organic aerosol formation in Amazon.

2. Experimental

2.1. Site description and instrumentation

Intensive field measurements were made during the dry season of 2004 (Aug–Oct) at the reservation of Cuieiras, C14 tower (2.61S; 60.21W; 140 m asl), situated 60 km northwest of Manaus in central Amazonia. This field study was conducted prior to AMAZE-08 Experiment (Amazonian Aerosol Characterization Experiment) (Martin et al., in press) at the same forest reserve, but at a tower site located 20 km away from that of the AMAZE-08. Our experiment is at another season and adds new and relevant information for the central Amazon Basin. The site is undisturbed, as prevailing trade winds blow over vast areas of intact tropical forest before reaching the measurement tower. Canopy height is about 30 m and leaf area index is 5–6 (for detailed information, refer to Araujo et al., 2002). At this site, CO_2 fluxes have been continuously measured since 1995 by INPA (Instituto Nacional de Pesquisas da Amazonia). Aerosol and VOC fluxes, as well as particle physical–chemical properties, were measured under the scope of the LBA Experiment (Large scale Biosphere-atmosphere experiment in Amazonia) (Davidson and Artaxo, 2004).

Aerosol measurements were taken at four tower heights, referred hereafter as: Ground (2 m), Canopy (28 m), Top (40 m) and Anemometer level (54 m) (Fig. 1). On the first three levels, simultaneous measurements of aerosol mass and number concentration, elemental composition, scattering coefficient, size distribution and equivalent black carbon concentration (BCe) were performed. Measurements of aerosol turbulent fluxes were performed at Anemometer level between September 18th and October 2nd, while VOC fluxes were measured from September 23rd to 27th at the same height.

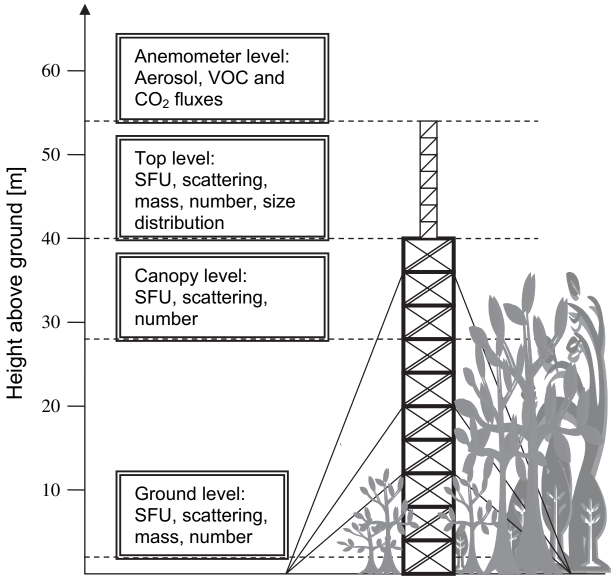

Fig. 1. Diagram of the C14 tower at the Cuieiras forest site. The figure describes the properties measured in four levels of the tower, nominated as Ground (2 m), Canopy (28 m), Top (40 m) and Anemometer (54 m).

Two-stage stacked filter units (SFU) were used to collect coarse particle mode (CPM with aerodynamic diameter $2.0 < Dp < 10$ μm) and fine particle mode (FPM, with $D_p < 2.0$ μm) aerosols. From August 25th to September 19th, daytime (7am–5pm LT) and nighttime (5 pm–7am LT) samples were differentiated, with typical sampling times of 24 h. The flow rate was typically 16 lpm. Polycarbonate filters were analyzed for particulate mass, BCe and elemental composition (Maenhaut et al., 2002). PIXE analysis (Particle Induced X-Ray Emission) were made at University of São Paulo LAMFI (*Laboratório de Análise de Materiais por Feixes Iônicos*) to determine the concentration of 22 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb) (Artaxo and Orsini, 1987). BCe concentrations were obtained using a light reflectance technique. Particulate PM_{10} ($D_p < 10$ μm) concentration was also measured in real time using two TEOM monitors. A TSI-SMPS-3936 (Scanning Mobility Particle Sizer) was used along with a TSI-CPC-3010 (Condensational Particle Counter) to measure particle size distributions at the range of 10–350 nm.

A proton transfer reaction mass spectrometer (PTR-MS) was used for concentration measurements of isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), acetone (CH_3COCH_3), acetaldehyde (CH_3CHO), methanol (CH_3OH) and acetonitrile (CH_3CN) (Karl et al., 2004, 2007).

2.2. Flux measurements

Aerosol turbulent fluxes were measured by an eddy covariance (EC) system consisting of a sonic anemometer (RM-Young-Campbell) and a particle counter (TSI-CPC-3010). The anemometer was mounted 54 m above the forest floor, with horizontal distance of 1.5 m from the mast, aligned with local prevailing trade winds. A 5 m copper tube (inner diameter 4 mm) was used to sample air into the CPC, with 1 lpm flux. The CPC lower particle diameter was 10 nm, and its analog output was used to get particle counts recorded at 10 Hz frequency using a Campbell datalogger. Wind and concentration high frequency data were stored in 30 min packages. Simultaneous high response CO_2 and water vapor concentration were measured by INPA using an IR-absorption gas analyzer (Licor-6262), and its final data was available for analysis and comparisons.

The EC method assumes that the vertical flux of a scalar within the turbulent boundary layer is given by the covariance between vertical wind speed and concentration. Concentration data was pre-filtered to exclude periods with strong instability from the calculations (criterion: >100% concentration variation concentration in less than 30 min). Slow trends in wind and concentration signals were removed using a recursive digital filter with time constant of 50 s. The delay due to the travel time of particles in the sampling tube was calculated in each loop as the lag corresponding to the maximum absolute of cross-correlation function between vertical wind speed and concentration time series (Massman, 2000). The delay time depends on wind velocity and direction, making it necessary to calculate it for each loop instead of using the average travel time of particles through the sampling tube. Triple coordinate rotation of wind speed components was executed to minimize advection (Wilczak et al., 2001). For particle fluxes observed under optimal atmospheric conditions (as will be discussed on Section 3.4), the flux underestimation due to limited frequency response of instruments was 3% in average, estimated according to Massman (2000). Another error is related to the uncertainty in EC flux measurement (Buzorius et al., 2003), comprising the uncertainty in vertical wind speed measurements (1%) and the uncertainty due to discrete particle counting (5%). This gives us a total flux uncertainty in the order of 5%. There is also a variability of calculated flux values depending on the methods chosen for data processing. Sensitivity tests were made to choose an adequate integration time (30 min), and recursive digital filter's time constant (50 s) for data detrend. Power and co-spectra were calculated to check for applicability of Kolmogorov's similarity theory.

Isoprene and monoterpene fluxes were measured using the disjunct eddy covariance (DEC) technique with a PTR-MS (Karl et al., 2004). The DEC method is a variant of EC method, in which air samples are taken almost instantaneously (~0.1 s) and separated by a longer time interval (~1–5 s) (Rinne et al., 2001). Therefore, a subset of a continuous high frequency time series is created. This is a direct flux measurement technique that allows the use of an analyzer which cycles over multiple compounds, without relying on empirical parameterizations.

2.3. *RH corrections for aerosol size distributions*

Due to complex field conditions and limited infrastructure available during the experiment, particles were not dried prior to sampling. The ambient relative humidity (RH) above the canopy was in the range of 88–100% for 50% of the time. Considering that Amazonian particles have relatively small hygroscopic growth factors, this is not believed to have a large influence on measurements of aerosol mass and number concentrations. However, it does influence size distribution and scattering measurements.

Aerosol hygroscopicity measurements in Balbina, a forest site located 125 km northeast of Manaus (1.93S; 59.42W), report the occurrence of two groups of particles in Amazonia: hydrophobic, with growth rates at 90% RH ranging from 1.02 to 1.15, and less-hygroscopic, with growth rates around 1.17 for particles with a dry diameter of 50 nm (Rissler et al., 2004; Zhou et al., 2002). Hänel (1976) proposed a parameterization describing aerosol growth factor as a function of relative humidity (*RH*), expressed as:

$$\frac{r}{r_{\mathrm{dry}}} \approx \left[1 + \frac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{water}}} \mu \frac{RH}{1 - RH}\right]^{1/3}, \qquad (1)$$

where r/r_{dry} represents the aerosol growth factor, ρ_{dry} and ρ_{water} are the densities of dry particle and pure water respectively, and μ is defined as the linear mass increase coefficient which depends on aerosol composition. Similar parameterizations have been used elsewhere to account for humidity effects on aerosol physical properties (Eichler et al., 2008). Using Hänel parameterization, it was possible to calculate aerosol dry diameters for each SMPS size distribution (10 min averaged), as a function of RH and measured wet diameter. However, above 90% RH this parameterization is not reasonable, due to great uncertainties related to the measurement of high RH values. Therefore, only diurnal size distributions fulfilling the RH $<$ 90% condition will be presented and discussed in this paper. Ambient RH levels were used for these calculations, since no humidity measurements were available inside the SMPS. A low limit was estimated for the SMPS-RH based on RH measurements inside a nephelometer that was running in parallel. Using ambient RH instead of the unknown RH inside the SMPS results in overestimated particle growth factors, with maximum uncertainties ranging from 3% (35 nm particles) to 7% (265 nm particles).

3. Results and discussion

3.1. *Aerosol properties at ground, canopy and top levels*

Throughout the experiment, the forest site was affected by regional transportation of biomass burning pollution in 41% of the days. Most of biomass burning transport events occurred between August 15th and September 15th, comprising the majority of aerosol filter measurements. The aerosol and VOC flux measurement period was cleaner, although weaker biomass burning influence was detected occasionally. This was demonstrated by Hysplit back-trajectories calculations (www.arl.noaa.gov/HYSPLIT.php) and NOAA12–AVHRR satellite images (www.cptec.inpe.be/queimadas). Intermediate BCe and PM_{10} concentrations were observed at Top level all through the experiment, averaging 730 ng m^{-3} and 13 μg m^{-3} respectively. Number concentration averaged 1400 particles cm^{-3}. Those values are above the Amazonian background concentrations (Andreae, 2007), revealing the influence of regional pollution over this pristine forest site.

Table 1 presents average particulate mass, BCe and trace element concentrations for fine and coarse mode aerosols for the three sampling heights. When assumed to be in the state of their most common oxides, soil dust particles are characterized by Al_2O_3, SiO_2, K_2O, $CaCO_3$, TiO, Fe_2O_3, MnO_2 and VO (Maenhaut et al., 2002), and these compounds comprise 6% of FPM and 10% of CPM on average. Due to the high $NH4^+/SO_4^{2-}$ ratios, typically observed in tropical regions (Trebs et al., 2005), sulfate (SO_4^2) is considered to be neutralized by ammonia (NH^{4+}), comprising 17% of FPM and 3% of CPM on average. BCe concentrations corresponded to 9% of FPM and 1% of CPM. The remaining mass (70% of FPM and 85% of CPM) is attributed to organic matter, inorganic matter from biogenic origin, interstitial water and, to a minor extent, nitrates. This result is in accordance with several studies conducted at undisturbed regions in Amazonia, which report aerosol organic fractions ranging between 60 and 70% of FPM and 70–85% of CPM (Artaxo et al., 2004; Fuzzi et al., 2007; Martin et al., in press).

PM_{10} concentrations, measured with two different techniques (TEOM and filter weighting), were similar at the three measurement levels. Analyzing fine and coarse modes individually from the SFU dataset, a predominance of fine particles (FPM $D_p < 2$ μm) was observed at Top and Canopy levels (Fig. 2) for both daytime and nighttime samples. It suggests the existence of a source of fine particles above the canopy, also demonstrated by the observed downward fine aerosol fluxes in 69% of the cases (Section 3.4). Fig. 3a shows the ratio between fine mode Si concentrations and total FPM concentrations for the three measurement levels at daytime and nighttime. On Top level, daytime Si share in the fine mode is 50% higher in comparison to the nighttime Si percentage in FPM. Similar diurnal enrichments and vertical gradients were also observed for Ca, Fe (typically related to soil dust), and S, Cl, K (related to biomass burning aerosols, Artaxo et al., 1998).This means that there is a source of soil dust and biomass burning particles during daytime that is not as strong during nighttime. Soil dust particles are not expected to be produced in significant amounts below the canopy, since the in-canopy wind velocity is low and the forest soil is covered by dead leaves. Therefore, the major source of these particles is related to regional transport of air masses. According to Rummel et al. (2002), the levels above and below the canopy are nearly decoupled in a closed-canopy forest with high leaf area index. Our results agree with that, indicating that a significant fraction of fine aerosols coming from aloft deposit in the upper canopy.

Fine mode BCe concentrations showed a more uniform vertical distribution, with a smaller vertical gradient. Guyon et al. (2003) observed a similar behavior for BCe concentrations measured at three levels in another forest tower in Amazonia (Jaru Reserve, 10.08S,61.93W). In recent studies, there has been evidence that some type of biogenic particles could have significant light absorption coefficients (Andreae and Gelencsér, 2006; Guyon et al., 2003). Hence, part of what was accounted as BCe through reflectance analysis may be in fact light-absorbing biogenic aerosols. A source of light-absorbing biogenic aerosols below canopy may explain the less steep vertical gradient of BCe observed at two distinct forest sites in Amazonia.

Coarse mode particles showed large differences between daytime and nighttime (Fig. 2). During the day, higher CPM concentrations were observed at Top level. Coarse mode Si vertical profile was

Table 1

Average atmospheric concentrations (avg), standard deviations (std) and number of valid samples (n) of fine and coarse particulate mass, black carbon (BCe) and trace elements for aerosol samples collected on three levels of the C14 tower at the Cuieiras Reserve, Amazonas, Brazil (August 25th to September 19th 2004). Mass concentrations are in μg m^{-3}; black carbon and trace elements concentrations are in ng m^{-3}.

	Ground (2 m)						Canopy (28 m)						Top (40 m)					
	Fine Mode			Coarse Mode			Fine Mode			Coarse Mode			Fine Mode			Coarse Mode		
	avg	std	n	avg	std	n	avg	std	n	avg	std	n	avg	std	n	avg	std	n
Mass	6.7	1.5	15	6.3	2.3	15	8.7	2.4	15	5.5	1.9	15	8.1	1.8	15	5.2	1.1	15
BCe	635	174	15	79	25	15	715	228	15	53	39	15	691	172	15	60	33	15
Mg	–	–	–	60	33	2	–	–	–	92	45	11	–	–	–	64	46	5
Al	46	–	1	99	71	12	34	–	1	150	77	11	38	–	8	99	38	13
Si	37	21	15	72	40	15	52	25	15	123	64	15	58	34	15	146	65	15
P	7.1	2.4	5	23	11	12	9.8	2.3	13	15	6	11	5.5	4.3	3	12	5	5
S	359	90	15	63	17	15	429	136	15	69	22	15	430	93	15	66	19	15
Cl	7.7	3.8	11	69	61	15	8.7	4.3	13	97	83	15	9.1	2.5	13	96	87	15
K	151	40	15	66	27	15	177	64	15	48	12	15	179	47	15	50	12	15
Ca	10	4	15	29	16	15	15	7	15	41	17	15	18	9	15	50	23	15
Ti	3.5	3.3	12	6.4	4.7	12	3.1	1.3	12	11	9	14	3.1	1.6	13	11	5	14
V	–	–	–	0.9	–	1	–	–	–	1.0	0.8	5	0.3	–	1	1.2	0.6	9
Cr	3.0	–	1	0.9	0.8	4	1.1	–	1	1.1	0.7	6	9.8	–	3	1.0	0.4	5
Mn	0.6	0.4	15	1.2	0.5	15	0.9	0.4	15	1.4	0.5	15	1.0	0.6	15	1.4	0.4	15
Fe	14	8	14	34	19	15	20	10	15	59	21	15	23	11	15	71	22	15
Ni	0.5	0.2	14	0.6	0.3	15	0.3	0.1	14	0.8	0.7	15	0.4	0.3	13	1.0	1.5	15
Cu	0.4	0.2	10	0.3	0.1	9	0.2	0.2	10	0.3	0.1	7	0.4	0.4	11	0.3	0.1	12
Zn	2.1	1.5	15	1.1	0.6	15	1.8	0.5	15	0.8	0.3	15	2.0	0.4	15	1.7	1.8	15
Se	0.2	0.1	8	0.2	0.2	2	0.2	0.1	6	0.4	0.3	7	0.2	0.1	13	0.3	0.2	9
Br	1.0	0.6	9	–	–	–	2.1	0.7	8	1.2	0.4	5	2.4	0.6	11	0.7	0.1	2
Rb	0.7	0.5	14	0.4	0.2	9	0.9	0.4	13	0.3	0.2	6	1.2	0.8	15	0.5	0.1	2
Sr	0.3	0.2	9	0.5	0.2	12	0.3	0.1	11	0.5	0.3	13	0.3	0.1	12	0.6	0.3	12
Zr	0.4	0.2	5	0.3	0.2	4	0.5	0.2	5	0.3	0.2	2	0.3	0.1	5	0.8	0.3	5
Pb	1.0	0.7	9	2.4	3.6	10	0.9	0.4	11	2.1	3.4	7	1.1	0.5	13	6.8	5.0	8

similar to that of fine mode Si, with higher concentrations at Top level. A similar behavior was observed for other elements related to soil dust: coarse mode Al, Ca and Fe, corroborating the existence of a source related to regional transport of air masses. At night, however, there was a clear reversal of the vertical gradient, with CPM concentrations 44% smaller at Top level in comparison to Ground level (Fig. 2), suggesting a nocturnal source of coarse mode particles inside the canopy. Strong vertical gradients of P were observed from Ground to Top, both during daytime and nighttime (Fig. 3b). Particle phase phosphorus is emitted mostly from biogenic processes, and is a critical nutrient to the Amazonian ecosystem, being a limiting factor for primary productivity (Mahowald et al., 2005). An analogous vertical profile was observed for coarse mode K, also typically related to biogenic emissions (Artaxo et al., 1998). This clear enrichment of P and K at Ground level compared to Top level indicates that biogenic particles are produced below the canopy, with an increased production at night. The mechanisms are still unknown.

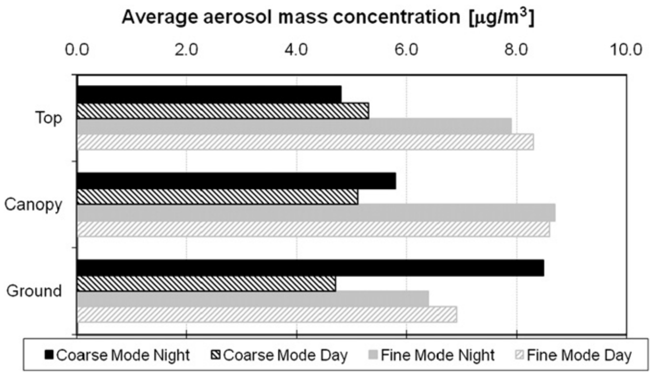

Fig. 2. Average mass concentration of fine and coarse mode aerosols at three measurement levels: Ground (2 m), Canopy (28 m) and Top (40 m). Measurements were categorized into nocturnal and diurnal samples.

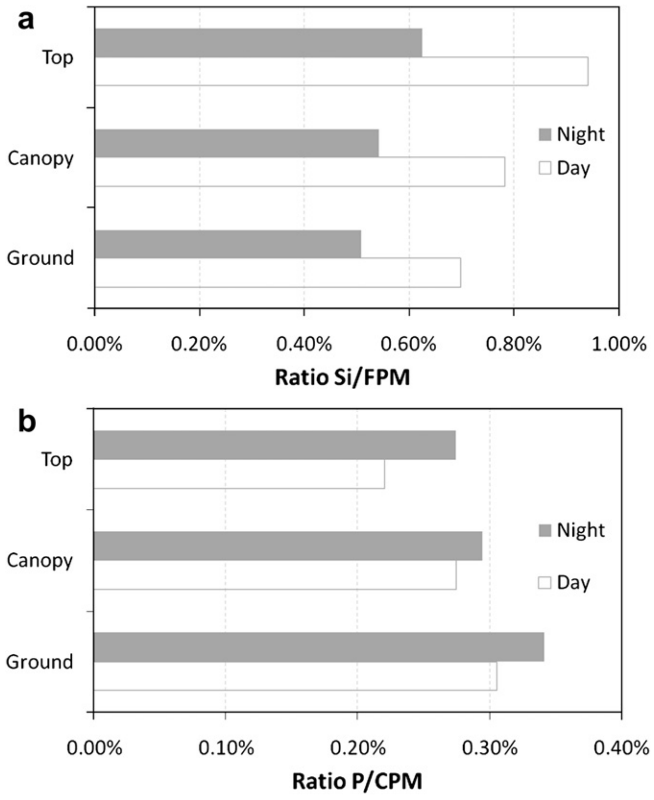

Fig. 3. a) Average ratio between fine mode Si and fine particle mass (FPM) for diurnal and nocturnal samples collected at three heights: Ground (2 m), Canopy (28 m) and Top (40 m). b) Average ratio between coarse mode P and coarse particle mass (CPM) mass for diurnal and nocturnal samples collected at the same three heights.

A similar vertical gradient of biogenic particles was observed at Jaru forest site (Artaxo et al., 2004). While Cuieiras Reserve is surrounded by hundreds of kilometers of untouched forest, Jaru Reserve is a forest adjacent to a degraded pasture area. Hence, the observation of alike vertical gradients at both sites denote a recurrent pattern of below-canopy biogenic particle emission in the Amazon. Limited turbulent activity below the canopy combined with proximity to the source, where concentrations are highest, explain the observed vertical gradient. An unknown biological process could be responsible for this emission. This emission mechanism may be a proficient way to cycle P and K only locally, keeping those key nutrients inside the ecosystem, close to where they were emitted.

3.2. *Sub-micrometer aerosol number size distributions*

Aerosol size distributions were continuously measured at Top level, with particle diameters ranging from 10 to 350 nm. Diurnal size distributions measured at ambient RH $< 90\%$ were corrected according to the procedure described in Section 2.3. Fig. 4 shows the average aerosol dry size distribution for the whole experiment, considering 1002 spectra measured at ambient RH $< 90\%$. The error bars represent one standard deviation.

Lognormal modes were fitted to 271 half-hour averaged dry size distributions using the least square method. Table 2 shows statistics of fitting parameters, as well as a comparison to previous measurements at Balbina forest site during the experiments CLAIRE-1998 and 2001. The distributions were bimodal in 81% of observations, consisting of Aitken and accumulation modes, often overlapped. Number concentrations averaged 926 ± 643 and 986 ± 416 cm^{-3}, respectively for Aitken and accumulation modes. The standard deviations denote a high variability of particle number concentrations corresponding to various meteorological conditions. Comparing our values to previous measurements in Balbina during the wet season, higher number concentrations were found at the Cuieiras forest site. This was expected, since the Cuieiras field campaign was conducted during the dry season, being somewhat affected by regional transport of biomass burning emissions. The geometric mean diameters and geometric standard deviations are comparable with average values calculated for the Amazonian wet season (Martin et al., in press).

Nucleation mode was present in 19% of observed size distributions. New particle formation (NPF) events were not clearly observed. The absence of nucleation events is in accordance with previous observations in Amazonia (Zhou et al., 2002; Rissler et al., 2004). As a matter of comparison, in boreal forests nucleation events are observed on ~50 days $year^{-1}$, mostly during spring time (Kulmala et al., 2004). Long-term measurements are required to identify seasonal variations in Amazonia, and to improve knowledge on the formation of secondary biogenic particles in tropical remote areas.

3.3. *VOC fluxes and concentrations*

When available, concentration measurements of isoprene, monoterpenes, acetone, acetaldehyde, methanol and acetonitrile were carried out in parallel with aerosol measurements. Average diurnal cycles are presented on Fig. 5. Error bars represent one standard deviation. Isoprene and monoterpenes show a clear diurnal cycle with concentrations peaking in the early afternoon, reaching 7.8 and 0.29 ppb respectively. As vegetation emissions decrease at night, mixing ratios of 2.0 and 0.1 ppb were observed correspondingly. Those values are in accordance to previous measurements conducted in different forest sites in Amazonia during the wet season (Kesselmeier et al., 2000, 2002; Greenberg et al., 2004; Kuhn et al., 2007). Acetaldehyde mixing ratios were below 1.5 ppb without a clear diurnal cycle. Methanol ranged between 2 and 5 ppb. Similar concentrations were detected by Kesselmeier et al., 2002 at another forest site in Amazonia. Acetone ranged between 1.0 and 2.5 ppb, in accordance to measurements performed in a forest site in Costa Rica (Karl et al., 2004). Acetonitrile, a tracer for biomass burning emissions (Holzinger et al., 1999), ranged between background values around 0.2 ppb (Scheeren et al., 2003) and higher mixing ratios up to 0.8 ppb. It reflects the episodic influence of biomass burning regional transport throughout the VOC measurement period.

Fluxes of isoprene and monoterpenes were close to zero during nighttime (18:00–6:00 local time). With sunrise and establishment of forest biogenic activities, the fluxes began to rise, reaching its maximum at noon: 7.4 mgC m^{-2} h^{-1} for isoprene and 0.82 mgC m^{-2} h^{-1} for monoterpenes. A compilation of measurements of isoprene and monoterpene fluxes in Amazonia is shown at Table 3. The maximum diurnal isoprene emission (around noon) ranges between 2.2 mgC m^{-2} h^{-1} at Tapajós forest reserve (Oriental Amazon) and 9.8 mgC m^{-2} h^{-1} at Jaru forest reserve (Central Amazonia). Monoterpenes fluxes correspond typically to 10% of isoprene emissions. Some variation of VOC fluxes is expected, since their emission patterns depend on tree species, temperature, humidity, light, stage of plant development and stress level. It is known that the Amazon forest has a high biodiversity and heterogeneity that is associated with spatial and temporal variability in VOC fluxes and concentrations (Harley et al., 2004).

In spite of the substantial concentrations and fluxes of isoprene and monoterpenes observed in Amazonia, no clear nucleation

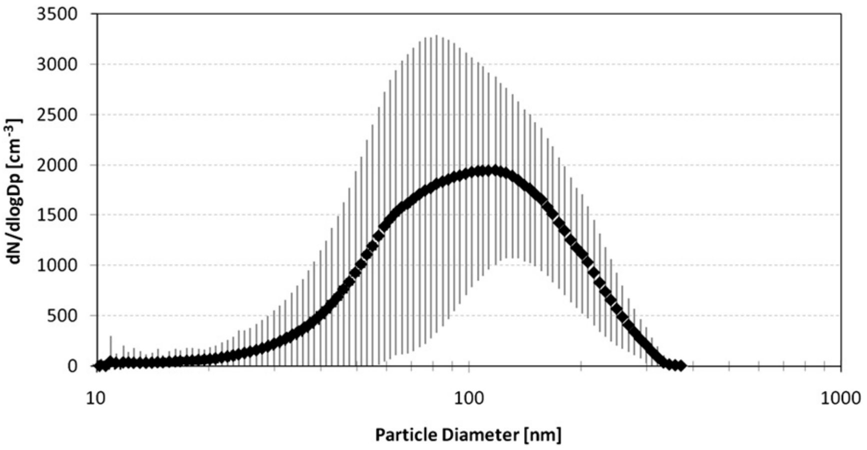

Fig. 4. Average aerosol dry size distribution $dN/dlogD_p$ considering 1002 spectra measured at ambient RH $< 90\%$. The error bars represent one standard deviation.

Table 2

Statistics of particle number size distributions at Cuieiras Reserve, during the dry season of 2004. Size distributions measured at ambient RH lower than 90% were corrected to dry particle sizes, using typical growth rates of Amazonian aerosols. A total of 271 thirty-minute spectra were fitted with two or three lognormal distributions. Also shown are the statistics of previous measurements in another forest site (Balbina, Amazonas state, Brazil).

	Mode	Frequency of Occurence [%]	Number Concentration [cm-3]			Geometric Mean Diameter [nm]	Geometric Standard Deviation
			Mean	Geometric Mean	Median		
This work: Cuieiras Reserve 2004 Aug–Oct Dry Season (RH < 90%)	Ultrafine	19	6.6 ± 3.4	5.6	6.2	33 ± 16	1.72 ± 0.51
	Aitken	100	926 ± 643	720	774	76 ± 15	1.49 ± 0.17
	Accumulation	100	986 ± 416	898	994	144 ± 18	1.45 ± 0.08
Rissler et al., 2004 Balbina, CLAIRE 2001 Jun–Jul Wet-to-Dry Season	Ultrafine	55	276 ± 290	163	185	15 ± 9	1.29 ± 0.22
	Aitken	100	304 ± 184	244	250	68 ± 9	1.32 ± 0.14
	Accumulation	100	736 ± 159	641	760	139 ± 7	1.45 ± 0.04
Zhou et al., 2002 Balbina, CLAIRE 1998 Mar–Apr Wet Season	Ultrafine	18	92 ± 99	55	24	24 ± 10	1.31 ± 0.15
	Aitken	100	239 ± 154	137	68	68 ± 12	1.40 ± 0.14
	Accumulation	100	177 ± 115	200	151	151 ± 22	1.40 ± 0.10

events were detected (Section 3.2). Neither significant correlations between VOC and aerosol concentration and flux were observed. Correlations between VOC and aerosol time series were calculated to account for the delay time from the formation of a new particle to its detection at 10 nm diameter. The relatively low correlation coefficients obtained (<0.40, $p = 0.05$) indicate a poor linear relationship between VOC and fine mode particles. In fact, the processes of new particle formation and growth are non linear, and depend on several physical, chemical, biological and climatic parameters. A non-significant correlation between NPF events and concentration of possible organic precursors in the gas phase was also observed in boreal forest areas (Buzorius et al., 2001). The exact mechanisms of VOC emissions and the influence on secondary organic aerosol formation still remain unclear (Boy et al., 2004).

Several reasons could explain the lack of observation of NPF in Amazonia. Observations in boreal forests have shown a relationship between nucleation rates and ambient sulphuric acid concentrations (Riipinen et al., 2007). In the Amazon, low SO_2 concentrations (Andreae et al., 1990) may restrain the occurrence of sulfate nucleation. Also, the high humidity levels in Amazonia may restrict NPF. Several chamber studies report lower aerosol yields in humid conditions in comparison to experiments conducted under dry conditions (Na et al., 2007). Finally, it is still under debate the quantitative role of isoprene on secondary organic aerosol formation (Clayes et al., 2004; Paulot et al., 2009; Kiendler-Scharr et al., 2009). However, it is important to point out that the lack of observations of NPF in Amazonia does not mean that gas-to-particle conversion does not occur in Amazonia. It is possible that low-vapor

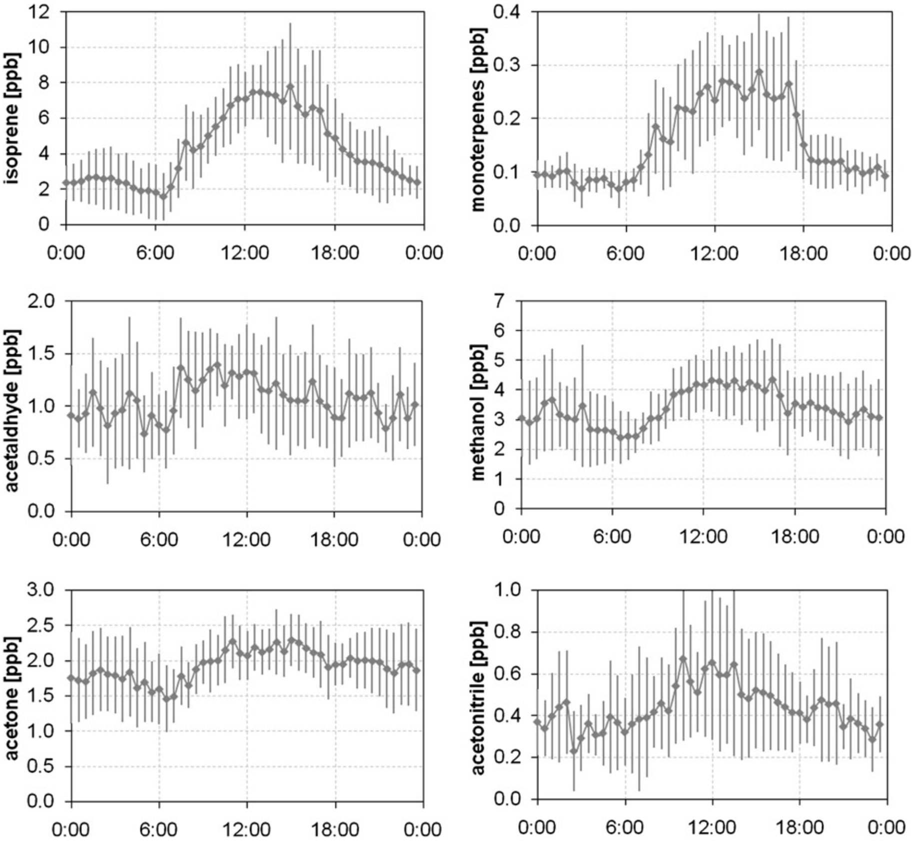

Fig. 5. Average diurnal cycles of isoprene, monoterpenes, acetaldehyde, acetone, methanol and acetonitrile. Concentrations were measured between 20 and 27 September 2004. The error bars represent one standard deviation.

Table 3
Compilation of maximum diurnal fluxes of isoprene and monoterpenes measured in different forest sites in Amazonia.

	Isoprene maximum diurnal emission [mgC m^{-2} h^{-1}]	Monoterpenes maximum diurnal emission [mgC m^{-2} h^{-1}]
Balbina, Apr 1998, wet season[a]	5.3	0.35
Jaru Reserve, Feb 1999, wet season[a]	9.8	0.79
FLONA Tapajós Reserve, Feb 2000, wet season[a]	2.2	0.27
FLONA Tapajós Reserve, Jul 2000, dry season[b]	2.4	0.29
Cuieiras Reserve Jul 2001, dry season[c]	5.4	1.70
Cuieiras Reserve Sep 2004, dry season (this work)	7.4	0.82

[a] Greenberg et al., 2004.
[b] Rinne et al., 2002.
[c] Kuhn et al., 2007.

pressure oxidation products from the plentiful observed VOC concentrations condense over pre-existing particles, instead of forming new ones. Or else, it could be that NPF occurs somewhere above the canopy (Kulmala et al., 2004, Kazil et al., 2007). The observed Aitken mode of aerosol size distributions very likely contains secondary aerosols, which may have grown from ultrafine aerosols nucleated somewhere within the boundary layer or in the free troposphere.

3.4. *Aerosol flux measurements*

Fluxes of aerosol particles with diameters greater than 10 nm were measured between September 19th and October 2nd 2004. Upward fluxes, characterizing emission from forest to atmosphere, are defined as positive by convention. The average number flux of particles was 0.05 ± 0.10 10^6 particles m^{-2} s^{-1}, and the median was 0.02 10^6 particles m^{-2} s^{-1}. These values were obtained considering only optimal measurement periods, characterized by: i) unstable stratification conditions ($z/L < 0$); ii) friction velocity (u^*) greater than 0.2 m s^{-1}; iii) wind direction non coincident to the one that carries urban plumes from Manaus ($\neq 135°–195°$). Therefore, the flux observations reported here comprise mostly diurnal measurements, which in general satisfied the stability criteria described above. The histogram of 193 selected particle flux observations, as well as its cumulative function, is shown at Fig. 6. A great variability of positive and negative aerosol fluxes was observed (ranging between −4.5 and +6.4 10^6 particles m^{-2} s^{-1}), but small magnitude aerosol fluxes predominated. This range of particle fluxes is similar to the range observed by Ahlm et al. (2009) at the same forest reservation, but in another tower (K34), during the wet and dry season of 2008. Fig. 6 shows that observed fluxes were negative in 69% of the observed cases, indicating fine particle deposition. This is consistent with the downward vertical gradient observed for fine particles related to soil dust and biomass burning (Section 3.1). The predominance of particle deposition during daytime was also observed by Ahlm et al. (2009).

The calculated average fine particle flux close to zero indicates that there is equilibrium between emission and deposition fluxes, at least during daytime for accumulation mode particles. One should keep in mind that the number flux of coarse mode particles could not be measured. Coarse mode particles in Amazonia are characterized by significant mass concentrations (7–12 µg m^{-3}) and low number concentrations (<1 cm^{-3}), which does not provide a statistically appropriate counting at the high frequencies required for the EC method. It is also important to highlight that this mean flux value does not include nighttime measurements, since they did not satisfy the established criteria for optimal atmospheric conditions.

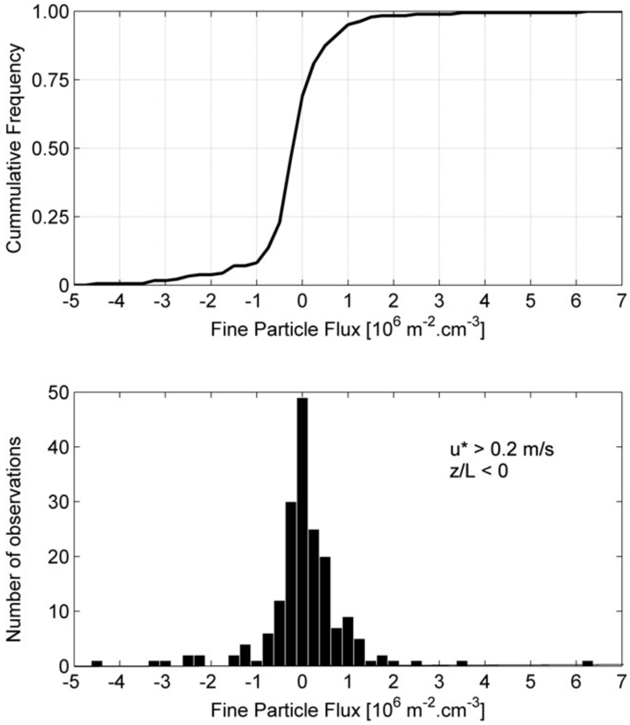

Fig. 6. Particle flux cumulative function (a) and histogram (b). Only measurements performed under optimal atmospheric conditions were accounted for, comprising 193 data points. The selection of samples followed the criteria: i) unstable stratification conditions ($z/L < 0$); ii) friction velocity u^* greater than 0.2 m s^{-1}; iii) wind direction not coincident to the one that carries urban plumes ($\neq 135°–195°$). Therefore, the flux values reported here refer generally to diurnal observations.

For sake of comparison, boreal forest fine particle fluxes ($7 < Dp < \approx 1000$ nm) have magnitudes about 10 times higher than the ones observed in this experiment. However, the average flux value, considering similar atmospheric stability conditions, is also close to zero (Buzorius et al., 2001). Ruuskanen et al. (2007) suggest that, in absence of new particle formation events, there is a balance between emission and deposition fluxes of fine particles at a boreal forest site. That could be a consequence of an established equilibrium between biosphere and atmosphere, in terms of fine particle exchange. Or, alternatively, it could be an indication that particle exchanges happen mostly in the coarse mode, which was not measured in this work. Also, the relatively low aerosol deposition rates make particle flux measurements over a tropical forest a difficult experimental task, comprising uncertainties and large data scatter.

Right after the sunrise, a positive flux together with an increase in particle concentration was observed recurrently (11 out of 14 sampling days). Four years later, Ahlm et al. (2009) have also observed these morning upward particle fluxes at the same forest reserve, which shows that this is a recurrent and reliable event. This could be explained by a combination of early mixing layer development plus the existence of a nocturnal source of particles below the canopy. Due to the usually high stratification of nocturnal boundary layer, biogenic particles eventually emitted at night would accumulate close to its in-canopy source. After the turbulent activity is initiated in early morning, those biogenic emitted particles could reach upper levels, leading to the observed higher concentration and positive flux enhancement above the canopy.

4. Summary and conclusions

Several aerosol physical properties were measured at three heights in a remote forest site in central Amazonia. Analysis of filter samples have shown a predominance of FPM aerosols above the canopy, consisting mostly of soil dust and biomass burning particles brought by regional transportation of air masses. In accordance to that, EC fluxes of fine particles were downward in 69% of daytime samples. Coarse mode particles, on the other hand, were more plentiful at Ground level, where higher concentrations of phosphorus and potassium, key nutrients for the Amazonian ecosystem, were observed at night. This vertical gradient of P and K was observed in previous measurements, suggesting that emission of biogenic particles below-canopy may be a widespread behavior in Amazonia. Despite the number of observed evidences of biogenic particle emissions, its exact mechanisms, concerning physical, chemical and biological processes still remain unknown.

Turbulent fluxes of aerosols and VOC were simultaneously measured for the first time in a forest site in Amazonia. Fine particle fluxes ranged between −4.5 (deposition) and +6.4 (emission) 10^6 particles m^{-2} s^{-1}. The average diurnal flux of fine particles was 0.05 ± 0.10 10^6 particles m^{-2} s^{-1}, indicating a balance between upward and downward fine particles fluxes. It is important to highlight that reported flux values exclude coarse mode particles and nighttime measurements.

Observed isoprene and monoterpene fluxes were compatible with previous measurements. Even though these VOC species may have a role on secondary organic aerosol formation, no significant correlations were found between VOC and particle time series. Aerosol size distributions did not show any clear nucleation events as well. The low-vapor pressure oxidation products from VOC may condense over pre-existent particles instead of forming new ones. Alternatively, it is possible that nucleation occurs somewhere else in boundary layer or even in free troposphere.

It should be emphasized that some of the results obtained in the course of this work, cannot, in principle, be extrapolated to other forest sites in Amazonia. This is due to the heterogeneity of the Amazonian rain forest. Therefore, biophysical processes that govern particle and VOC emission and deposition, as well as gas-to-particle conversion processes, may vary significantly from site to site. Long-term measurements at different sites in Amazonia are needed to account for local and seasonal variations, and particle flux measurements should ideally include coarse mode particles.

Acknowledgments

This work was carried out under the scope of LBA experiment. It was financially supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico (Instituto do Milênio, Milênio-LBA2). The National Center for Atmospheric Research (NCAR) is sponsored by the National Science Foundation (USA). We thank all members of LBA science teams for their support during the field campaign, especially Alcides Ribeiro, Ana Lucia Loureiro, Julio Tota, Társis Germano and Theotonio Pauliquevis. We also acknowledge LAMFI staff for helping with PIXE analysis.

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