

Aerosol and precipitation chemistry in a remote site in Central Amazonia: the role of biogenic contribution

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A long-term (2–3 years) measurement of aerosol and precipitation chemistry was carried out in a remote site in Central Amazonia, Balbina, (1°55′ S, 59°29′ W, 174 m above sea level), about 200 km north of Manaus city. Aerosols were sampled using stacked filter units (SFU), which separate fine ($d < 2.5 \mu\text{m}$) and coarse mode ($2.5 \mu\text{m} < d < 10.0 \mu\text{m}$). Filters were analyzed for particulate mass (PM), black carbon (BC) and elemental composition by Particle Induced X-Ray Emission (PIXE). Rainwater samples were collected using a wet-only sampler and samples were analyzed for pH and ionic composition, which was determined using ionic chromatography (IC). Aerosol mass was predominantly of biogenic origin and concentrated in coarse mode, comprising up to 81% of PM_{10} concentration during the wet season. Natural biogenic aerosol also dominates the fine mode in the wet season, with very low concentrations (average $2.2 \mu\text{g}/\text{m}^3$). Large-scale transport of smoke from biomass burning was the second most important contribution, reaching 77% of fine mode particulate mass during the dry season. Soil dust was responsible by a minor fraction of the aerosol mass (less than 17%). Rainwater chemistry was controlled by biogenic emissions. The volume-weighted mean (VWM) pH was 4.90. The most important contribution to acidity was weak organic acids. The organic acidity was predominantly associated with the presence of acetic acid, instead of formic acid which is more often observed in pristine tropical areas. Deposition rates for major species did not differ significantly between dry and wet season, except for NH_4^+ and acetate, which had smaller deposition rates during dry season. While biomass burning emissions were clearly identified in the aerosol component, it was not possible to discern any presence of biomass burning emissions in rainwater chemistry. The long-range transport of sea salt and biogenic particles was observed both in aerosols and rainwater composition. The results showed here indicate that in Amazonia it is still possible to observe pristine atmospheric conditions, relatively free of anthropogenic influences.

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1 Introduction

Tropical biogenic atmospheric aerosols play important roles in climate and atmospheric chemistry: they scatter sunlight, provide condensation nuclei for cloud droplets (Roberts et al., 2001, 2002), and participate in heterogeneous chemical reactions (Andreae and Crutzen, 1997, Artaxo et al., 1998, Andreae, 2007). Large areas of the deep tropics are covered with forests that act as source regions of biogenic particles and trace gases to the global atmosphere (Andreae, 2007; Jaenicke, 2005). It seems that atmospheric biological particles in its majority have been overlooked in the past, with few studies emphasizing their physical and chemical properties (Artaxo and Hansson, 1995; Artaxo et al., 1988; Guyon et al., 2003). Studies of aerosols in the 30° N to 60° N “conveyor belt” of the United States, Europe, China, Russia, and Japan have provided much insight into aerosol processes, yet interpretations are typically complicated by the uncertain mixing of anthropogenic and natural aerosols, especially with regard to organic aerosols. Baseline knowledge of the source strengths and processes of natural aerosols is necessary to correctly assess present-day burdens, direct radiative forcing and nutrient cycling in tropical regions (Jaenicke, 2005).

Tropical rainforests depend on efficient nutrient recycling to maintain its primary production levels. Usually residing over poor soils (Vitousek and Sanford, 1986), the rainforest forest environment has become adapted to this condition along its own evolutionary history, developing a system of mechanisms that provides a stable equilibrium to the rainforest ecosystem (Salati and Vose, 1984). Atmosphere-biosphere interactions are an important component of tropical nutrient cycling. Thus, the correct understanding of processes that modulate atmospheric composition and the deposition of trace elements and nutrients is important to infer the role of atmospheric processes in nutrient cycling (e.g., Mahowald et al., 2005).

In spite of the high deforestation rates that some parts of the Amazon Basin have been subject to in the recent decades, most of the forested area is still preserved (~84% of the original forest area). Contrary to popular perceptions, deforestation is

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not wide spread over the entire basin but concentrated in the “deforestation arc” region mostly in the east/south/southwest portion of the Amazon Basin. This region is subject to biomass-burning every year during the dry season (Artaxo et al., 2002). On the other hand, the central and western portions of the Amazon rainforest have suffered few and insignificant land-use changes in recent times and has been very well preserved. The state of Amazonas (the largest in Brazil comprising about 1.6 million km² with a population of 3 200 000) where this work was conducted has only 2% of deforested area. Under such preserved condition, natural sources and sinks of gases and aerosols play the most important roles in determining the atmospheric composition. Previous studies indicate that vegetation is the most important source of natural biogenic particles in pristine areas in the Amazon Basin (Artaxo et al., 1988, 1990, 1998; Graham et al., 2003a, b). Natural biogenic aerosol comprises up to 80% of PM₁₀ aerosol mass, with most of the mass (aprox. 70%) in the coarse mode fraction (Echalar et al., 1998; Gerab et al., 1998). The mechanisms of generation of these coarse mode biogenic particles is not completely understood (Jaenicke, 2005), but probably include mechanical abrasion by wind, biological activity of microorganisms on plant surfaces and forest litter, and plant physiological processes such as transpiration and guttation (Artaxo, 2001; Artaxo and Hansson, 1995). In the fine mode fraction a significant fraction of particles is comprised of secondary aerosols formed by gas-to-particle conversion of organic and sulfur-related natural biogenic gases (Artaxo, 2001).

Precipitation is among the most important sink pathways for atmospheric compounds. It acts as an external input of nutrients to the forest environment, and is also an important pathway in nutrient recycling in tropical areas. Due to this linkage, rainwater composition is influenced by airborne aerosol particles and trace gases chemistry. Rainwater composition is influenced by atmospheric chemistry in two ways. The first one is on the formation of cloud drops, when scavenged aerosol particles act as cloud condensation nuclei (CCN), contributing to the composition of the initial drop (Hobbs, 1993). The aqueous environment of the drop is also adequate for the absorption of soluble trace gases, working as a catalytic factor to many chemical reactions possible

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only in aqueous media (Scott and Laulainen, 1979; Hegg et al., 1984; Hegg and Hobbs, 1988), and biotransformation by micro-organisms (Amato et al., 2007). The second removal process takes place when precipitation begins. Falling raindrops collide with airborne aerosols below cloud base, collecting these particles and adding matter to raindrops (Pruppacher and Klett, 1997). This mechanism of aerosol removal is one of the major processes by which the atmosphere is cleansed (Hobbs, 1993). The final result of rainwater chemistry is the combination of these two processes named rainout (*in-cloud*) and washout (*below-cloud*) (Seinfeld e Pandis, 1998).

Previous studies of rainwater composition in Central Amazonia (Stallard and Edmond 1981; Andreae et al., 1990; Williams et al., 1997) reported few or even no anthropogenic influence in rainwater composition, and characterized the composition of (natural) rainfall by its low ionic concentration of major species, low acidity (pH ranging from 4.7 to 5.3) and an important contribution of organic acids (mainly acetic and formic acid) to the acidity profile of precipitation, a common feature in remote sites (Andreae et al., 1988; Keene et al., 1983; Sanhueza et al., 1991; Khare et al., 1999). In the aerosol phase, previous studies of aerosol composition in remote sites in Amazonia (Artaxo et al., 1988, 1990, 1998), showed that natural biogenic emissions are predominant in the aerosol mass during the wet season, and subject to some influence of biomass burning emissions during the dry season, depending on the distance from sources. Biogenic particles consist of particles primarily emitted by the vegetation (e.g.: bacteria, fungi, spores, and plant and insects debris), mainly in coarse mode ($d_p > 2.5 \mu\text{m}$) (Artaxo and Hansson, 1995), and sub-micron particles as a product of gas-to-particle conversion (GPC) of biogenic trace gases emitted naturally by the vegetation (e.g.: oxidation of terpenes, Hoffmann et al., 1997, 1998, and isoprene, Claeys et al., 2004). Minor but important contributions were also observed by long-range dust transport from Sahara, which add a very low concentration of local soil dust (Talbot et al., 1990; Swap et al., 1992, 1996; Formenti et al., 2001).

In this study we carried out a long-term measurement of aerosol and precipitation chemistry in a remote site in Central Amazonia. The main objective was to inves-

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5 tigate the aerosol – precipitation chemistry linkage under pristine (free of significant anthropogenic influences) conditions, with the aim of understanding how important the influence of aerosol composition is on rainwater chemistry. It is important to emphasize that this paper do not deal with aerosol composition in areas heavily impacted by biomass burning such as Rondonia. Biomass burning effects on aerosol composition were characterized in detail during the SMOCC campaign (Dias et al., 2002, Fuzzi et al., 2007).

2 Study area

10 Balbina, the sampling site (1°55' S, 59°29' W, 174 m above sea level), is a small village located about 200 km north of Manaus (see Fig. 1). The population density of the region is low (0.49 hab/km²) and there is no significant agricultural activity in its surroundings, with almost no local biomass burning activity. It is close to the lake of the Balbina hydroelectric plant (constructed in 1989), a lake which covers approximately 240 000 ha. The air masses reaching Balbina are predominantly from east, crossing more than 1000 km of preserved areas of primary tropical rainforest and experiencing essentially only natural sources of aerosol emissions. It makes this region an excellent choice to observe natural background chemical conditions for aerosol and precipitation, despite some occasional influence of long range transported biomass burning emissions.

20 The climate in Central Amazonia is characterized by a wet period, from January to June, and a dry period, from July to December. Typical annual precipitation totals for the wet season is 1560±290 mm and for the dry season 760±160 mm based on records for the period 1992–2001. Inter-annual differences in seasonal precipitation characteristics are mainly correlated with equatorial Pacific and Atlantic sea surface temperature (SST), which strongly modulate the intensity and the onset of the wet season in Central Amazon (Fisch et al., 1996; Marengo et al., 2001). The South Atlantic Convergence Zone also plays an intermediate role in some precipitation events

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3 Experimental

3.1 Aerosol sampling and analysis

Aerosol sampling at Balbina was operated continuously from October 1998 to March 2002. Fine and coarse mode aerosol particles were collected using stacked filter units (SFU) (Hopke et al., 1997) fitted with a PM₁₀ inlet. The SFU collect particles on 47 mm diameter polycarbonate membrane filters. An 8 μm pore size filter collects coarse particles ($2.5 < d_p < 10 \mu\text{m}$) while a 0.4 μm pore size filter collects fine particles ($d_p < 2.5 \mu\text{m}$). The flow rate was typically 16 liters per minute, and sampling time varied from 2 to 5 days.

Elemental concentrations for the SFU filters samples were obtained by Particle-Induced X-Ray Emission (PIXE) analysis (Artaxo and Orsini, 1987). It was possible to determine the concentrations of up to 18 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb). A dedicated 5SDH tandem Pelletron accelerator facility at the University of Sao Paulo LAMFI (Laboratório de Análise de Materiais por Feixes Iônicos) was used for the PIXE analyses. 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 $Z > 22$, Z being the atomic number. Precision of elemental concentration measurements is typically better than 7%, reaching up to 20% for elements with concentrations near the detection limit.

Mass concentrations were obtained through gravimetric analysis. Both fine and coarse filters from the SFU were weighed before and after sampling in a Mettler M3 electronic microbalance with 1 μg sensitivity. Before weighing, filters were kept for 24 h at 50% relative humidity and 20°C. Electrostatic charges were controlled by means of ²¹⁰Po radioactive sources. Detection limit for the aerosol mass concentration is 0.3 $\mu\text{g m}^{-3}$. Precision is estimated at about 10%. Black carbon (BC) concentration

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on the fine and coarse fraction of the SFU filters was obtained by a light reflectance technique (Martins et al., 1998a, 1998b).

3.2 Rainwater sampling and analysis

The precipitation sampling was operated from April 1998 to December 2001, with interruptions between June 1999–February 2000 and February–June 2001. A set of 87 samples was collected, representing 52% of the total precipitation (5673 mm) for the sampling period. Samples were collected using automated wet only collectors, in high-density polyethylene bottles, which had been previously rinsed with milliQ water. After its collection in the field, Thymol was added to preserve samples from microbial growth and the resulting deterioration of organic acids and nitrogen species (Gillett and Ayers, 1991). In order to check the quality of the data set, Ionic Balance (IB) was used as the key parameter to identify outliers, in agreement with the ICP Forests recommendations (ICP Forests, 1999).

The pH of each sample was measured twice: immediately after sampling (Cole Parmer portable pH meter model CON 10) and later in laboratory analysis (Orion pH meter model EA940 with a glass electrode) using low ionic strength buffer solutions (Orion application solution). For calibration, two standard solutions with pH 4.01 and 7.00 were used. The resolution of the measurement was 0.01 pH units. Anions and cations concentrations were determined at the Isotopic Ecology Laboratory, CENA – USP (Center for Nuclear Energy in Agriculture of University of São Paulo – Brazil), with a DIONEX DX600 ion chromatograph (IC). The system used a gradient pump (GP40), with electrochemical (ED40) and conductivity detectors (CD20) for anions and cations, respectively, and a DIONEX IonPac AS-11 and CS-12 with pre-columns DIONEX AG-11 and CG-12. The eluents were NaOH and MSA for anions and cations, respectively. Ionic standards (Ultra-Science) were used for IC calibration. Detection limits were 0.05 μM , the precision was within an interval of 3% and the accuracy was 0.01 $\mu\text{M/l}$. It was possible to determine concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- ,

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SO_4^{2-} , F^- , acetate (CH_3COO^-), formate (HCOO^-), NO_2^- , Br^- , oxalate ($\text{C}_2\text{O}_4^{2-}$), citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), PO_4^{3-} , and Dissolved Inorganic Carbon (DIC).

3.3 Data analysis

The concentration of ionic species in rainwater is dependent on storm size. Larger storms tend to dilute ionic concentrations while smaller storms tend to be more concentrated. To avoid this effect, the results for precipitation are presented in the form of Volume Weighted Mean (VWM). The VWM concentration of the j -th ionic species is defined as

$$(\text{VWM})_j = \frac{\sum_{i=1}^N C_{i,j} v_i}{\sum_{i=1}^N v_i} \quad (1)$$

where v_i is the storm size in the i -th sample, $C_{i,j}$ is the concentration of the j -th ionic species in the i -th sample, and N is the total number of samples. The numerator can be understood as the total deposition for the j -th ion during the sampling period.

In order to remove the possible influence of marine contribution, the non-seasalt (nss) component for some selected compounds were calculated. The determination of this value was calculated considering the ionic proportion to Na^+ in seawater (Riley, 1975), and assuming that Na^+ concentration is exclusively due to marine emissions. Thus, the nss contribution for the species X was determined using Eq. (2)

$$[X]_{nss} = [X]_{\text{rainwater}} - \left[\frac{X}{\text{Na}} \right]_{\text{seawater}} \times [\text{Na}]_{\text{rainwater}} \quad (2)$$

In order to separate the different aerosol and rainwater components, Absolute Principal Factor Analysis (APFA) was applied to the measurements database analyzing data variability. The APFA procedure was used to apportion the different aerosol compo-

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nents (using elemental composition) and precipitation composition (using ionic deposition rates) (Thurston and Spengler, 1985; Hopke, 1985). APFA offers the possibility of obtaining a quantitative component profile instead of only a qualitative factor loading matrix as in traditional applications of factor analysis, and has been successfully applied in aerosol studies in the Amazon Basin (e.g.: Echalar et al., 1998; Maenhaut et al., 2002) . The absolute source profile helps in the identification of the factors and can be used to compare the factor composition with the presumed source composition. The absolute profile is determined by calculating a linear regression between each measured concentration (for each chemical compound) and the normalized contribution of each component for each sample (the “so-called factor scores”), a result provided by traditional Factor Analysis (FA) after VARIMAX rotation. The result of the linear regression allows for determining quantitatively the absolute contribution of each extracted compound for each chemical compound.

4 Results

4.1 Aerosol measurements

The long time series of aerosol mass concentration is shown in Fig. 2. The fine mode mass concentration is shown in red, while the coarse mode fraction is shown in blue. The sum of both components is the PM₁₀ aerosol mass concentration. The observed typical aerosol mass concentration was very low, close to values reported for other remote sites in the world (e.g.: Heymsfield e McFarquhar, 2001), a consequence of the pristine condition of the sampling area. However, in spite of this relative isolation, it was possible to observe some influence of anthropogenic emissions during the dry season. The typical observed PM₁₀ aerosol concentration, about 11 μg m⁻³, experienced a slight increase during the dry season due to an increase of the concentration in the fine mode due to long range biomass burning emission. It is also possible to observe in Fig. 2 some significant peaks in the coarse particle mass due to episodic

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transport of dust from the Sahara desert (Swap et al., 1992). Time series for fine and coarse mode BC concentration are shown in Fig. 3. The fine mode BC concentration (Fig. 3a) was synchronous with the seasonal pattern of PM₁₀ concentration, which is clear evidence of biomass burning emissions influencing the aerosol loading in Central Amazonia. The average fine mode BC concentrations was 170 ng/m³, a very low value for a continental region. The BC concentration in the coarse mode is shown in the Fig. 3b, with an average of 50 ng/m³. This component represents absorbing aerosols in the coarse mode fraction and is essentially constant along the sampling period, suggesting that the natural biogenic absorbing component in the coarse mode particles is not affected significantly during the dry season.

Considering the pristine character of the sampling site, it is assumed that fine mode increase in BC concentration during the dry season is not due to local sources. Instead, it is assumed to be related to the large-scale transport of biomass burning plumes originated hundreds of kilometers far from the sampling site. Actually, there is evidence for contribution from both regional and distant sources. Two large aerosol studies with intensive sampling campaigns were carried out in Balbina as part of the LBA-CLAIRE Experiment (Andreae et al., 2002). The first intensive sampling campaign was carried out in March–April 1998 (mid-wet season), and the second in July 2001 (wet-to-dry season transition). A significant difference in mean particle number concentration was observed. Zhou et al. (2002) reported mean concentration of 590±440 #/cm⁻³ for the 1998 experiment, a significantly lower value than Rissler et al. (2004) reported for the July 2001 sampling campaign, 1140±690 #/cm⁻³. Nevertheless, the number of fire hotspots during July 2001 was very low (9 hotspots for the whole of Amazonas state), an evidence that local/regional contribution was negligible, and that pollution plumes from distant sources were probably responsible for such an enhancement in particle number concentration. Figure 4 shows the spatial distribution of hotspots observed from July to November in 2001. In July the Amazonas state was almost free of biomass burning. However, from August to November many hotspots were observed along the Amazonas River (southeast of Balbina). As such, some re-

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gional contribution is expected to reach Balbina, influencing the aerosol composition during the most intense periods of biomass burning activity. To test this hypothesis, backward air masses trajectories reaching Balbina were calculated for a representative day. This result is shown in Fig. 5 for 25 September 2001, in the core of the biomass-burning season (see Fig. 4). Backtrajectories were calculated using the Hysplit model (<http://www.arl.noaa.gov/ready/hysplit4.html>). The trajectories show that for a variety of air masses levels reaching Balbina (100, 1000 and 2000 m a.g.l.) all of the trajectories passed over the Amazonas river path, where hotspots were observed, and that probably the biomass-burning influence detected in Balbina is due to the transport of plumes originated in this region.

A summary of average elemental concentrations measured in aerosols at Balbina is shown in Table 1 for the fine and coarse mode and dry and wet seasons. Aerosol mass dominates in the coarse mode over fine particles. Absorbing aerosols (BC) concentration was predominantly in fine mode, with higher values during the dry season. The elements S, K and Zn, commonly used as a signature for biomass burning, experienced higher concentrations during the dry season in agreement with the analysis discussed above. Sulfur concentrations, on the order of 100–300 ng/m³, are very low in Central Amazonia..

4.1.1 Factor analysis of aerosol measurements

Factor analysis was used to identify joint variability between trace elements in aerosols in Balbina. In order to possibly observe different aerosol structure for dry and wet seasons, we have performed factor analysis on two subsets of the data, according to season. Fine mode VARIMAX rotated factor-loading matrices are shown in Table 2, while in Table 3 the factor analysis results for the coarse mode is shown. It is also possible to observe in these tables the component explained variance and the communalities for each element included in the analysis.

For the fine mode factor analysis, the extracted components were essentially the same for wet and dry seasons. The first factor in the wet season fine mode aerosol

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(shown in Table 2) have high loadings for Al, Fe, Si, Ca, FPM and K, representing soil dust aerosol. The second factor has high loadings for BC, K, S and FPM, with a lower loading for Zn. This composition is an indication that it is related to biomass burning (Artaxo et al., 1998). The third factor is related to P, Zn, S and FPM, being associated with natural biogenic aerosol (Artaxo and Hansson, 1995). These 3 factors explained 91% of the data variability, with most of the communalities around 90%, showing the adequacy of the 3 component factor model. The dry season analysis in the fine mode aerosol show a similar picture, with an additional weak chlorine component. For the dry season, the 4 factor solution explained 90% of the data variability. Cl was not included in the fine mode wet season analysis due to insufficient number of samples above detection limit. Basically, the factor analysis of the fine mode aerosol shows 3 components: soil dust, natural biogenic aerosol and biomass burning, with an additional chlorine factor in the dry season that could be indicative of the impact of sea salt particles, or a natural biogenic chlorine component.

The factor analysis calculations for the coarse mode aerosol is shown in Table 3. Soil dust and biogenic components were also observed for wet and dry seasons, with similar tracers. A 3rd component, associated with Cl was also identified and, for the dry season, a 4th component associated with absorbing aerosol (BC) variability was identified. No influence of biomass burning was observed in the coarse mode, in spite of the observation of this 4th coarse mode absorbing component that we do not consider as evidence of biomass burning, as pointed out in the previous section.

Some important features of this factor analysis should be highlighted. Sampling time was usually longer during wet season than the dry. This is due to the necessity for allowing collection of sufficient mass for gravimetric and PIXE analysis with accuracy. Thus, it is reasonable to regard component separation as more efficient during dry periods. This seems to be the case. For the coarse mode, it is possible that the 3rd component observed during the wet season was separated in the 3rd and 4th component of the dry period. In fact, one can see that BC loadings were not high for the wet season analysis, in opposition to dry season. It means that the 3 extracted

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components for the wet season were insufficient to explain BC variance satisfactorily due to the poor separation of events caused by longer sampling times. In fact, the lowest communality observed among all analyzed elements was for BC.

The origin of the component having mostly Cl as the tracer element has two possible explanations: natural biogenic and sea-salt aerosols. The sea-salt alternative is corroborated by the identification of a sea-salt component in rainwater (see next section), with an observed linear relationship between Na and Cl ($r^2=0.85$, $p<0.01$) in precipitation. As the predominant wind direction reaching Balbina is from the east (trade winds), it is reasonable that air masses from the Atlantic Ocean containing sea-salt aerosols may reach Central Amazonia eventually. This long range transport of sea-salt over 2000 km over primary forests with high loading of natural biogenic aerosol explains the presence of chlorine in association with natural biogenic aerosol, as observed in the 4th component in the fine mode dry season aerosol. Thus, this component represents the large-scale transport of aerosols containing both biogenic and sea-salt particles.

The BC component in coarse mode is possibly associated with optically active coarse mode natural biogenic particles. There is no evidence that biomass burning caused any increase in coarse mode BC and no seasonal difference was observed in the concentration pattern. Since the measurement technique is related to the absorption of light on the nuclepore filter before and after sampling, coarse mode biogenic aerosols provide an alternative explanation. When we visually inspect the coarse mode filters after 3-4 days collection in the wet season, it is actually gray in color. On the other hand, fine mode BC is strictly associated with biomass burning emissions given the clear seasonality of measurements.

The absolute apportionment of trace element concentrations was obtained through the application of APFA. The wet season results are presented in Fig. 6, while Fig. 7 shows the dry season analysis. In the wet season, natural biogenic particles dominates the aerosol mass, with 94% of the coarse mode and 45% of the fine mode aerosol. Biomass burning contributed with 38% of fine mode aerosol mass, while 17% was attributed to soil dust. Soil dust shows a very small contribution in the coarse mode

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fraction. It is because the forest floor is covered with forest litter, and very high humidity in the wet season suppress the emission of coarse mode soil dust particles in the forest.

With respect to the dry season APFA analysis (Fig. 7), the biogenic aerosol contribution was predominant in the coarse mode (83% of the aerosol mass). In the fine mode, the biomass burning contribution dominates the picture, with 77% of fine aerosol mass. Soil dust is responsible for a very small 6.9% portion of the aerosol mass in the coarse mode and 6% in the fine mode.

The absolute contribution for each component in each sample is shown in Fig. 8. Top plots (Figs. 8a, b and c) represent the absolute concentration for each observed component in fine mode, while the 3 plots at the bottom (Figs. 8d, e and f) show the results for the coarse mode fraction. In Fig. 8a the time series for biomass burning contribution is shown, where it is possible to observe the typical seasonal behavior that characterizes biomass burning emissions. Biomass burning concentration levels were higher at the beginning (1999 and 2000) and at the end (for 1999 and 2001) of the wet seasons. This was due to inter-annual differences in the onset of the wet and dry season, which are controlled by large scale precipitation systems and in some years may be favorable to farmers advance or extend biomass burning activities. Coarse CI and BC (only dry season) components are shown in Fig. 8d. These components showed a remarkably constant behavior along the sampled period, with a slight increase during the 2000 dry season.

The behavior of concentration for the biogenic components concentrations is shown in the mid column plots (Figs. 8b and e). For dry season (fine mode), biogenic contribution was considered as the sum of both biogenic and CI contribution, in agreement with the analysis that during wet season the statistical approach was incapable of separating them. In fact, the sum of average concentrations of each component (biogenic and CI) is statistically compatible with the average concentration of wet season biogenic component. Surprisingly, a constant decrease in its absolute contribution for the biogenic component for both fine and coarse mode was observed. This result is totally unexpected. The rainforest environment surrounding the site area has been well

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preserved during the sampling period, and no significant changes (e.g., deforestation) have taken place within hundreds of kilometers of from the sampling area. We could not provide any plausible explanation for that behavior of biogenic contribution.

Soil dust contribution is shown in the right column plots (Figs. 8c and f). One can see that the typical behavior of this component is a very low background concentration between extreme peaks. As discussed below, the variance of such behavior is high and it is the reason for the clear identification of this component throughout the sampled period. A possible explanation for this behavior is the occurrence of burst events related to weather changes (e.g., squall lines). Furthermore, in April and May the Amazon Basin is subject to large-scale transport of soil dust originated from Sahara (Swap et al., 1992, 1996; Formenti et al., 2001), a phenomenon that can explain partially the peak events at least for these months.

4.2 Rainwater chemistry measurements

4.2.1 Comparison of rainwater chemistry in Central Amazonia to other remote sites around the world

The annual VWM concentrations are compared to results from other remote sites around the world in Table 4. The observed ionic concentrations were low, similar to the observed in other tropical remote regions around the world, when little biomass burning impact is observed. The mean observed acidity was $\langle \text{pH} \rangle = 4.90$, within the range 4.4–5.5. This pH value is in agreement with typical acidity observed in the other remote sites except for the Sahelian Savanna site. The explanation for the discrepancy is the high buffering capacity for this site, as one can see by its high concentration of NH_4^+ and Ca^{2+} in comparison with other measurements.

Buffering capacity in our site was low compared to other remote places. VWM for NH_4^+ was low, similar to the observed in the previous work conducted in Central Amazonia by Williams et al. (1997). On the other hand, it was remarkably lower than the observed concentration in Zoétélé (Sigha-Nkandjou et al., 2003), a similar ecosystem

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site in the African rainforest, and for the South African semi-arid site (Mphepya et al., 2004). The authors reported that this high concentration for NH_4^+ (and also for K^+ and Cl^-) in African sites was due to the influence of biomass burning during the dry season, which apparently is not the case for Balbina. For the Sahelian Savanna site (Galy-Lacaux and Modi, 1998), the authors attributed the origin of the high levels of NH_4^+ in rainwater to the high density of domestic animals in the region and its related production of ammonia, as a result of hydrolysis of urea deposited in pasture-grazing areas. This is also an absent influence in Central Amazonia.

A remarkable difference between Balbina and the other remote sites was the very low concentration for formate and the high concentration for acetate, directly associated with formic and acetic acids. This is a totally unexpected result because in remote areas of the world the most typical result is a predominance of formic over acetic acid (Keene et al., 1983; Sanhueza et al., 1991, 1992; Chebbi and Carlier, 1996). The observed mean F:A ratio in this work was 0.23. Williams et al. (1997) in a site relatively near our measurement site also observed this predominance of acetate over formate in Central Amazonia (F:A = 0.31), which indicates that our result is not an artifact or due to analytical issues. However, we could not provide any explanation for this divergent result from other remote places. Andreae et al. (1990) collected rain samples during a short period during the wet season (6 weeks) and obtained F:A = 1.5, but in this study it was not possible to observe such result even for the similar period in the year.

VWM for Na^+ was low compared to sites subject to marine influence (e.g.: Costa Rica $\text{VWM}_{\text{Na}^+} = 27.2 \mu\text{eq l}^{-1}$) (Elklund et al., 1997), but it was not so small if one has in mind that Balbina is about 1200 km from the Atlantic coastline. For comparison, the Zoétélé site is relatively close to the coastline (about 200 km) and presented a similar Na^+ VWM concentration (Sigha-Nkandjou et al., 2003). This could be due to the presence of a mountain range between Zoétélé and the coastline, which is an important local driver for the generation of orographic rains for air masses coming from the ocean. Thus, most of Na^+ is scavenged before it can reach Zoétélé. In Central Amazonia, the very large precipitation rate and efficient removal of possible sea-salt

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component along the 1200 km distance from the Atlantic is responsible for the low Na^+ concentrations. The altitude difference between Manaus and its estuary is about 80 m, for a horizontal distance of about 1200 km. It is reasonable that, under adequate weather conditions, oceanic air masses could be advected to Central Amazonia and carry with them sea-salt aerosols that would be gradually scavenged by wet deposition along its path.

4.2.2 Analysis of Balbina rainwater chemistry measurements

Seasonal and annual VWM concentrations and wet deposition rates are shown in Table 5. In the annual mean, the most abundant ion was H^+ , followed in decreasing order of importance by NO_3^- , Acetate, Cl^- , Na^+ , NH_4^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ , F^- , Formate, Oxalate, NO_2^- , Br^- , Citrate and PO_4^{3-} . In a general way, many ions showed a larger concentration in the dry season than in wet season. It is the case for the major ions H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_3^- , SO_4^{2-} and (to a lesser extent) DIC (Dissolved Inorganic Carbon). However, it was not possible to observe significant differences in seasonal wet deposition of the above-cited ions in spite of their larger concentrations. Considering that wet deposition is directly related to the loading of chemical species in the atmosphere, a possible explanation for this result is that the strength of the mechanism which releases these ions to the atmosphere is rather constant throughout the year. However, the opposite effect was observed for NH_4^+ , acetate and formate. These ions did not show a significant seasonal difference in VWM concentration, but the deposition in dry season for these species was quite lower. This means that the atmospheric loading for these ions is smaller in the dry season than during the wet season, an indication that for our site, biomass burning emissions do not influence significantly the deposition rates. In fact, the most commonly observed signals of biomass burning influence on rainwater chemistry were not observed. The deposition rate of H^+ was smaller in dry season even with a smaller buffering capacity (see the dry season deposition rates for NH_4^+ and Ca^{2+}). Beyond that, no one among the other common tracers

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for biomass burning (e.g.: SO_4^{2-} , K^+ , Cl^- , acetate and formate) demonstrated higher deposition rates during the dry season. Furthermore, Principal Component Analysis applied to rainwater chemistry (see the next subsection) did not identify any component that could be associated with biomass burning emissions.

5 The non sea salt (*nss*) fraction for some selected ions is also shown in Table 5. From these results, it is possible to realize that there are other important processes than marine emissions contributing to the observed amount of K^+ , Ca^{2+} , SO_4^{2-} and Mg^{2+} in rainwater. Indeed, the *nss* fraction for these ions was high: 86% for SO_4^{2-} , 93% for K^+ , 91% for Ca^{2+} and 55% for Mg^{2+} . The exception to this pattern was Cl^- , with a
10 small *nss* fraction. It suggests the absence of any alternative process to explain Cl^- in rainwater than marine emission. A linear relationship between Cl^- and Na^+ was observed ($r^2=0.85$, $p<0.01$) indicating the presence of NaCl in rainwater, a result that was already reported in previous works on rainwater chemistry in Central Amazonia (Andreae et al., 1990; Williams et al., 1997).

15 The concentration of oxalate was quite below the acetate and formate concentrations. Oxalic acid is usually the most abundant among the dicarboxylic acids in the atmosphere (Sempere and Kawamura, 1996; Kawamura et al., 1996), and in polluted circumstances (which is not our case) it can have concentration levels even higher than the sum of formic and acetic acid (Kawamura and Kaplan, 1987; Kawamura et al., 2001). The very low concentration observed for oxalate is a consequence of the
20 remote character of our sampling site.

The presence of oxalic acid, in our case, is likely associated with natural emissions from vegetation. Isoprene is the major volatile organic compound emitted by plants. It has been shown that pyruvic acid and methylglyoxal formed by the oxidation of isoprene act in the pathway of the *in-cloud* formation of oxalic acid (Ervens et al., 2004; Lim et al.,
25 2005). Oxalic acid is also an end product of several photochemical oxidation reactions (Chebbi and Carlier, 1996; Kawamura and Ikushima, 1993) and can accumulate in the atmosphere. Once formed, it is expected to be quite stable and to be present as fine mode particulate. Hence, the most important removal mechanism for oxalic acid is

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expected to be wet deposition.

Due to the association of oxalic acid with photochemical reactions, it is believed that the hydroxyl radical (OH^-) is the primary agent in the formation of oxalic acid in the atmosphere. However, the formation of HNO_3 is also linked to OH^- levels because it participates in the conversion mechanism of NO_2 to HNO_3 . Thus, oxalic and nitric acid can be formed in parallel pathways, with the production rate of one well correlated with that of the other. In fact, a linear relationship was observed between oxalate and nitrate ($r^2=0.82$, $p<0.01$), and we suggest that this similar dependence with OH^- is the reason for this correlation.

4.2.3 Factor Analysis of rainwater measurements

The results of principal component analysis (PCA) applied to rainwater measurements are shown in Table 6. Five principal components were extracted, explaining 93% of the original data variability. All components have a biogenic character, and in some cases, the combination of biogenic with other natural processes. The first component in Table 6 represents the biogenic emissions coupled with the large-scale transport of marine aerosol. The marine contribution was identified by the high loading values for Na^+ and Cl^- , while the high loading for K^+ was the signature for biogenic (Artaxo et al., 1988, 1990, 1994). A linear relationship between Na^+ and K^+ ($r=0.84$, $p<0.0005$) was also observed, which could suggest that K^+ deposition would be associated with marine contribution. However, the mean proportion K^+/Na^+ observed in rainwater ($=0.36$) was 16 times greater than the seawater ratio ($=0.022$), indicating that only marine emissions do not explain the K^+ apportionment and that there are other processes acting, in this case biogenic processes. In this same component, high loading values for SO_4^{2-} , Ca^{2+} e Mg^{2+} are also observed, an indication that biogenic processes also play an important role on the deposition of these ions. Their correlations with K^+ were high ($r=0.86$, $r=0.79$ e $r=0.85$, all $p<0.0005$, respectively), corroborating this analysis. Some of the mineral acidity was also related to this component due to the significant loadings observed for H^+ (0.52), NO_3^- (0.69) and SO_4^{2-} (0.85).

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The rainwater chemistry second component corresponds to processes related to acidity in rainwater, in particular the organic fraction. High loading values were observed for H^+ , NO_3^- , acetate and oxalate, indicating the presence of nitric, acetic and oxalic acid. These compounds are final products of photochemical and aqueous phase reactions (Khare et al., 1999; Sanhueza et al., 1991; Chebbi e Carlier, 1996). In particular the presence of NO_3^- and oxalate together in the same component is evidence of the parallel formation pathways related to oxidation processes dependent on OH^- levels to which both acids are subject. One should expect that any eventual influence of biomass burning emissions (as observed in fine mode aerosols) would be reflected in this component. However, it is not possible to find any clear evidence of such an effect. If this had happened, a significant correlation between NH_4^+ and SO_4^{2-} , which are abundantly emitted by biomass burning, should be observed, and this is not the case. Beyond that, the concentrations of acetate and oxalate were comparable to the observed values in remote areas and smaller than typical values observed both in urban (Fornaro, 2003; Kawamura et al., 2001) and biomass burning influenced areas (Yoboué et al., 2005).

Most of H^+ explained variance is associated with the two first factors. In terms of total deposition, they were responsible for 75% of H^+ deposition (calculated via APFA). The second component was responsible by 52% of the whole H^+ deposition, while the first factor accounts for 25% of the H^+ deposition, which helps to characterize the acidity in Balbina as organic. This domain of organic over mineral acidity is a common feature observed in pristine tropical areas (Sanhueza et al., 1991).

The third component demonstrated high loading values only for NH_4^+ and oxalate, indicating that some fraction of the observed concentration of oxalate was possibly in the form of ammonium oxalate. Another possible explanation is the recombination of NH_4^+ and oxalate after the dissociation of oxalic acid, a buffering effect. Both explanations reside on the availability of NH_4^+ in rainwater, which is an indication of the existence of local mechanisms acting in the production and/or emission of NH_4^+ .

Factors four and five had high loadings only for, respectively, PO_4^{3-} and citrate. The

identification of components with a single chemical compound is not straightforward because it is not possible to associate them with other more common tracers, as we did in the previous analyzed components. For the fourth component it is possible to do a parallel analysis with aerosol data, where P (predominantly in the coarse mode) is associated with biogenic emissions from the vegetation. The same conclusion can be drawn for rainwater; i.e., the presence of PO_4^{3-} is related to biogenic origin, possibly by the scavenging of biogenic aerosols. However, such an approach could not be done for the fifth component due to the absence of such measurements of any compound similar to citrate in aerosols.

5 Discussion and conclusions

The results and analyses examined in previous sections allow us to comment on several aspects of aerosol and rainwater composition in pristine tropical rainforest areas. The first one is that the composition of aerosols in Central Amazonia is predominantly of natural biogenic origin. The biogenic components (in the fine and coarse modes) were responsible for 81% of the total aerosol concentration during the wet season and, even during the dry season when some biomass burning influence was observed, natural biogenic aerosol accounts for 49% of aerosol concentration.

Biomass burning emission was the second most important contribution to aerosol mass. This influence was mainly due to the large-scale transport of plumes originated in distant locations that spread for huge areas in South America (Andreae et al., 2001; Freitas et al., 2000, 2005). In spite of this effect, Central and Western Amazonia are regions subject to a minor influence of smoke. This is because plumes of biomass burning typically follow a pathway in agreement with the dominant atmospheric circulation in the period from August to November, the peak of the biomass burning activity. During this period, a counterclockwise atmospheric circulation is established in Central Brazil (Satyamurty et al., 1998), which results in the formation of a preferential corridor where smoke flows to south/southeast of South America. This circulation pat-

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tern keeps Western and Central Amazonia relatively free of a significant influence of biomass burning emissions.

Apparently, this relative small impact of biomass burning made it impossible to detect any possible effect of biomass burning emissions on rainwater chemistry in Central Amazonia. Factor analysis applied on rainwater data was unable to extract any component related to biomass burning. It was observed a linear relationship between Cl^- and K that could be indicative of biomass burning impacts. However, the presence of this relationship also in the wet season makes the identification of most of Cl^- and K^+ as originated from natural sources.

The chemical composition of precipitation and deposition rates in Balbina are typical of the background composition in tropical areas. The majority of components extracted by PCA were associated with natural biogenic emissions. The only exception was the sea-salt contribution (in combination with biogenic) identified as part of the first principal component. PCA analysis for aerosols also extracted a biogenic component during the wet periods that could be separated in two components during the dry season. This separation resulted in a biogenic and in a Cl^- associated component, which is suspected to be of marine origin. The greater discrimination of components during dry season was possible due to the smaller sampling time needed, which allowed for a better separation of these distinct effects.

A linkage between aerosol and rainwater was harder to establish for the remaining components. The main difficulty is that the different analytical methods utilized for aerosols and rainwater resulted in a lack of similar chemical compounds in each analysis. For example, soil dust contribution was not observed in rainwater. A possible explanation for it is the absence of a clear soil dust tracer in rainwater as it is in aerosols (e.g.: Al, Fe, Ti, Si). Ca^{2+} is crustal but it also has biogenic contributions (Artaxo et al., 1988, 1990). Beyond that, Ca^{2+} in rainwater appeared in the first component, which is related with biogenic and sea salt and not with soil dust contribution. The main similarity observed in aerosol and rainwater was the marine contribution, which appeared in both analyses. Although it is not significant in terms of the PM_{10} aerosol mass or

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deposition rates, it was a clear signal in PCA analysis.

The remaining rainwater components could not be associated with aerosols due to the different nature of the assumed processes they represent. For example, the second and third rainwater components, which were associated with acidity and buffering effects, have no parallel effect in aerosols. The same argument is valid for the 5th rainwater component, associated with citrate.

This manuscript describes 2–3 years of continuous measurements of aerosols and rainwater chemistry, showing that the continental Amazonia could be one of the regions where the least anthropogenic influence could be observed in the tropics and temperate regions. It is hard to find sites in Asia and Africa that have little anthropogenic influences, due to the high population density of these continents. Perhaps Amazonia is the last region where we still can observe quite pristine atmospheric composition.

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Table 1. Dry and wet season fine and coarse mode average aerosol elemental composition in Balbina.

	Coarse mode		Fine mode	
	Dry season	Wet season	Dry season	Wet season
PM ^a	7200±2100 (142)	6600±2900 (163)	6200±3100 (148)	2200±1300 (154)
BC	48±19 (142)	53±16 (163)	490±260 (148)	161±129 (154)
Mg	32±19 (114)	24±16 (105)	25±14 (64)	20±20 (81)
Al	55±50 (142)	48±71 (163)	32±32 (148)	61±84 (154)
Si	88±82 (142)	110±170 (163)	58±72 (148)	130±190 (154)
P	25±13 (142)	35±11 (163)	6±3 (148)	4.2±2.2 (154)
S	54±22 (142)	37±17 (163)	310±180 (148)	100±63 (154)
Cl	75±73 (142)	73±77 (163)	10±8 (123)	10±13 (103)
K	77±29 (142)	93±27 (163)	140±88 (148)	40±35 (154)
Ca	26±16 (142)	26±28 (163)	13±9 (148)	15±17 (154)
Ti	5.6±5.7 (142)	5.3±6.8 (123)	3.4±3.2 (111)	5.3±6.7 (124)
V	0.80±0.63 (3)	0.51±0.34 (5)	1.4±0.9 (5)	0.82±0.38 (16)
Cr	2.3±1.9 (18)	2.1±1.7 (57)	1.6±1.6 (29)	1.3±0.8 (76)
Mn	0.85±0.61 (108)	1.0±0.9 (130)	0.59±0.49 (77)	0.91±0.95 (100)
Fe	40±30 (142)	34±50 (163)	20±19 (148)	36±50 (154)
Ni	0.33±0.36 (20)	0.38±0.55 (17)	1.1±1.0 (31)	0.77±0.74 (101)
Cu	0.30±0.32 (72)	0.34±0.49 (103)	0.44±0.53 (75)	0.55±0.60 (113)
Zn	0.92±0.48 (142)	0.95±0.42 (163)	1.5±1.1 (148)	0.70±0.63 (154)
Br	0.38±0.12 (11)	0.39±0.28 (17)	2.5±2.4 (98)	2.7±1.6 (73)
Pb	0.30±0.13 (18)	0.19±0.12 (14)	0.36±0.20 (60)	0.24±0.16 (24)

All values are expressed in ng/m³ and the variability represents standard deviation of measurements. The number between brackets represents the number of samples that presented concentrations above the detection limit.

^a PM is Particulate Matter

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Table 2. Component loadings from the application of Principal Component Analysis for fine mode aerosol concentration data*. Results are shown separately for wet and dry seasons. In the last line, it is shown the cumulative explained variance of the analysis. Chlorine was not included in the wet season analysis due to insufficient samples above detection limits, which is not the case for dry season.

	Wet season				Dry season				
	<i>Soil dust</i>	<i>Biomass Burning</i>	<i>Biogenic</i>	<i>COM^b</i>	<i>Biomass Burning</i>	<i>Soil dust</i>	<i>Biogenic</i>	<i>Chlorine</i>	<i>COM^b</i>
BC	0.31	0.92	0.95		0.94				<i>0.93</i>
K	0.64	0.71		0.94	0.91				<i>0.97</i>
FPM ^a	0.66	0.56	0.37	0.89	0.91		0.32		<i>0.94</i>
S		0.71	0.54	0.88	0.74		0.36	0.41	<i>0.85</i>
Al	0.95			0.99		0.98			<i>0.97</i>
Fe	0.95			0.99		0.97			<i>0.96</i>
Si	0.96			0.99		0.97			<i>0.95</i>
Ca	0.89	0.30		0.90	0.36	0.78		0.34	<i>0.85</i>
Zn		0.38	0.71	0.70	0.39		0.80		<i>0.83</i>
P			0.95	0.91	0.40		0.64	0.40	<i>0.74</i>
Cl								0.90	0.94
Cummulative Variance (%)	46	72	91		33	65	78	90	

* Loadings smaller than 0.20 were omitted.

^a FPM is Fine Particulate Mass.

^b COM is the communality correspondent to the chemical compound.

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Table 3. The same as Table 2, but for the coarse mode aerosols*.

	Wet season				Dry season				
	Soil	Biogenic and soil	Chlorine	COM ^b	Soil	Biogenic	Chlorine	BC	COM ^b
Si	0.95	–	–	0.99	0.90	–	0.39	–	0.97
Al	0.94	–	–	0.98	0.96	–	–	–	0.98
Fe	0.94	–	–	0.99	0.95	–	–	–	0.96
Ti					0.97	–	–	–	0.96
Ca	0.86	–	0.39	0.92	0.52	–	0.72	–	0.85
P	–	0.94	–	0.94	–	0.95	–	–	0.96
Zn	–	0.86	–	0.79	–	0.78	–	–	0.72
K	0.43	0.86	–	0.94	–	0.93	–	–	0.92
CPM ^a	0.44	0.81	–	0.92	–	0.89	–	–	0.89
BC	0.37	0.68	0.48	0.81	–	–	–	0.94	0.95
S	0.47	0.61	0.58	0.91	–	0.49	0.62	0.41	0.87
Cl	0.54	–	0.80	0.92	–	–	0.92	–	0.92
Cummulative Variance (%)	40	75	92		35	64	81	91	

* Loadings smaller than 0.30 were omitted. ^a CPM is Fine Particulate Mass. ^b COM is the communitary correspondent to the chemical compound.

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Table 4. Comparison of the rainwater chemistry results obtained in this study with other data from remote sites around the world. Values represent annual Volume Weighted Means expressed in $\mu\text{eq l}^{-1}$, except for DIC expressed in $\mu\text{M l}^{-1}$.

	This work	Africa Sahelian Savanna ¹	Africa Forest (Zoetele) ²	South Africa Semi arid ³	Torres del Paine ⁴	Venezuela (Savanna) ⁵	Austrália ⁶	Costa Rica ⁷	Amazonia ⁸	Amazonia (wet season) ⁹
pH	4.90	5.7				4.6–5.4			4.77	
H ⁺	12.6	2.1	12.0	12.2	10.9	4.3–23.6	16.3	4.6	17	5.6
Na ⁺	3.8	7.7	4.0	9.3	13.2	3.5–8.1	3.3	27.2	2.4	3.5
NH ₄ ⁺	3.7	12.9	10.5	9.7	0.6	<1.9–13.4	2.8	6.0	3.0	1.9
K ⁺	1.5	4.7	5.0	3.8	0.4	0.26–7.2	0.8	1.8	0.8	1.6
nss-K ⁺	1.39					0.23–7.1		1.2	0.75	
Mg ²⁺	1.93	5.6	2.4	4.1	3.2	0.48–4.0	1.0	7.4	0.90	0.71
nss-Mg ²⁺	1.06					0.11–2.2		1.3	0.36	
Ca ²⁺	1.81	31.2	8.9	12.0	1.1	0.94–14.6	1.5	6.8	2.40	1.2
nss-Ca ²⁺	1.64					0.88–14.2		5.6	2.29	
F ⁻	0.76									
Acetate	5.2	2.7	3.2	4.3	0.5	2.1–5.9	2.1		9.3	2.3
Formate	0.45	4.5	8.2	11.5	4.9	5.9–8.4	9.6		2.9	3.2
Cl ⁻	5.2	7.4	4.3	10.0	17.0	3.5–11.8	6.1	33.0	4.6	3.9
nss-Cl ⁻	0.7					1.9–4.1		1.5	1.8	
NO ₂ ⁻	0.054									
Br ⁻	0.029									
NO ₃ ⁻	5.4	12.3	6.9	8.0	0.5	2.3–4.6	3.6	4.1	4.2	1.09
SO ₄ ²⁻	3.4	8.6	5.1	14.5	2.8	2.7–5.6	3.0	14.8	2.00	0.9
nss-SO ₄ ²⁻	3.0					2.1–4.6		11.5	1.71	
Oxalate	0.25	1.0								0.13
PO ₄ ³⁻	0.0085				0.06				0.03	
Citrate	0.022									
DIC ^a	23.4									
DEF ^b	5.5									

References: ¹Galy-Lacaux and Modi, 1998; ²Sigha-Nkamdjou et al., 2003; ³Mphepya et al., 2004; ⁴Galloway et al., 1996; ⁵Sanhueza et al., 1992; ⁶Likens et al., 1987; ⁷Elklund et al., 1997; ⁸Williams et al., 1997; ⁹Andreae et al., 1990.

^a DIC is *Dissolved Inorganic Carbon*, which is expressed in $\mu\text{M l}^{-1}$.

^b DEF is ionic deficit, defined as $(\Sigma \text{ cations} - \Sigma \text{ anions})$ and expressed in $\mu\text{eq l}^{-1}$.

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Table 5. Volume Weighted Mean (VWM) concentrations and deposition rates observed in rainwater at Balbina. Results are shown separately for wet and dry seasons and annual mean. The range column refers to minimum and maximum observed concentration observed in the collected samples. Concentrations are expressed in $\mu\text{eq l}^{-1}$ (except for DIC expressed in $\mu\text{M l}^{-1}$), and deposition rates in $\mu\text{eq m}^{-2}$ ($\mu\text{M m}^{-2}$).

	Concentration				Deposition		
	Wet	Dry	Annual	Range	Wet	Dry	Annual
pH	5.01	4.80	4.90	4.4–5.5			
H ⁺	9.7	16.0	12.6	1.7–38	17.2	14.0	33.4
Na ⁺	2.4	5.6	3.8	0.62–25	4.3	4.9	10.1
NH ₄ ⁺	3.4	3.9	3.7	0.27–19	6.0	3.4	9.8
K ⁺	1.1	1.9	1.5	0.033–21	2.0	1.7	4.0
<i>nss</i> -K ⁺	1.1	1.8	1.4		1.9	1.6	3.7
Mg ²⁺	1.5	2.5	1.9	0.70–14	2.6	2.1	5.1
<i>nss</i> -Mg ²⁺	0.95	1.20	1.1		1.7	1.0	2.8
Ca ²⁺	1.6	2.1	1.8	0.30–20	2.8	1.8	4.8
<i>nss</i> -Ca ²⁺	1.5	1.9	1.6		2.6	1.6	4.3
F ⁻	0.6	1.3	0.76	0.53–2.6	1.1	1.1	2.0
Acetate	5.2	5.2	5.2	0.086–19	9.2	4.5	13.8
Formate	0.51	0.41	0.45	0.58–4.9	0.91	0.36	1.2
Cl ⁻	3.3	7.4	5.2	0.70–29	5.9	6.5	13.8
<i>nss</i> -Cl ⁻	0.5	0.9	0.7		0.89	0.79	1.9
NO ₂ ⁻	0.049	0.058	0.054	0.0043–1.0	0.087	0.051	0.14
Br ⁻	0.030	0.025	0.029	0.0025–0.12	0.053	0.022	0.077
NO ₃ ⁻	3.7	7.5	5.4	0.40–26.9	6.6	6.5	14.3
SO ₄ ²⁻	2.0	5.1	3.4	0.40–27.4	3.5	4.5	9.1
<i>nss</i> -SO ₄ ²⁻	1.7	4.5	3.0		3.0	3.9	7.8
Oxalate	0.21	0.28	0.25	0.0091–0.83	0.37	0.24	0.66
PO ₄ ³⁻	0.0061	0.010	0.0085	0.0020–0.29	0.011	0.009	0.023
Citrate	0.031	0.016	0.022	0.0047–0.13	0.055	0.014	0.058
DIC	21.2	24.8	23.4	9.6–105	37.7	21.7	62.0
DEF	5.4	5.7	5.5	-24 to 35	9.6	5.0	14.6

^a DIC is *Dissolved Inorganic Carbon*.

^b DEF is ionic deficit, defined as (Σ cations – Σ anions) and expressed in $\mu\text{eq l}^{-1}$.

nss is the non-seasalt fraction.

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Table 6. Component loadings resulted from the application of Principal Component Analysis application on the rainwater chemistry data. Loading values smaller than 0.30 were omitted. In the last line, it is shown the cumulative explained variance of the analysis.

	<i>Biogenic + sea-salt</i>	<i>Organic acidity</i>	<i>Ammonium oxalate</i>	<i>Phosphate</i>	<i>Citrate</i>	<i>COM</i>
Na ⁺	0.89	–	–	–	–	0.97
Cl [–]	0.87	0.35	–	–	–	0.92
SO ₄ ^{2–}	0.85	0.34	–	–	–	0.95
K ⁺	0.83	–	0.38	–	–	0.90
Mg ²⁺	0.79	0.48	–	–	–	0.98
Ca ²⁺	0.76	0.48	–	–	–	0.92
NO ₃ [–]	0.69	0.56	–	–	–	0.94
Acetate	0.37	0.84	–	–	–	0.89
H ⁺	0.57	0.76	–	–	–	0.94
Oxalate	0.34	0.52	0.52	0.35	–	0.80
NH ₄ ⁺	0.30	–	0.91	–	–	0.94
PO ₃ ^{4–}	–	–	–	0.94	–	0.98
Citrate	–	–	–	–	0.97	1.00
Cumulative variance (%)	41	62	74	84	93	

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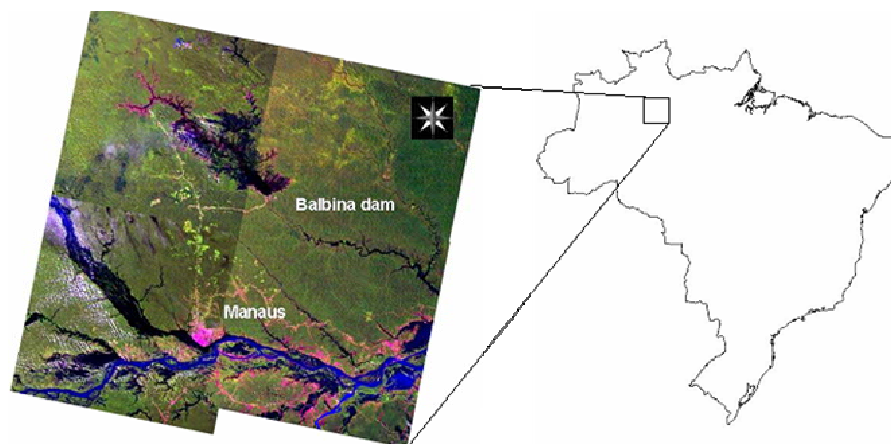


Fig. 1. Landsat image of the sampling site area. The city of Manaus (population 1 700 000) is shown in the low central portion of the portrait. Balbina is located about 200 km north far from Manaus in a preserved area free of deforestation and under influence of natural emissions of gases and aerosols.

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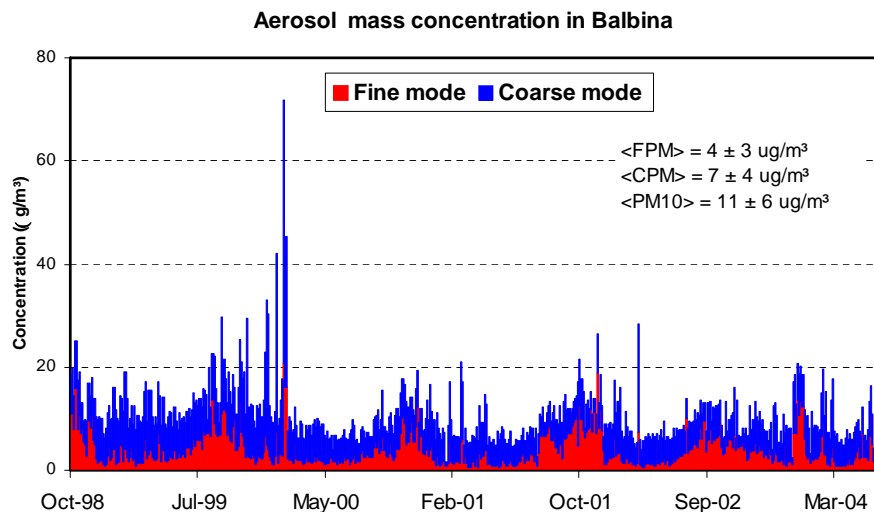


Fig. 2. The aerosol mass concentration time series at Balbina from October 1998 to September 2004. Concentrations are shown separately for Fine Particulate Mass (FPM, $d < 2.5 \mu\text{m}$) and Coarse Particulate Mass (CPM, $2.5 \mu\text{m} < d < 10 \mu\text{m}$).

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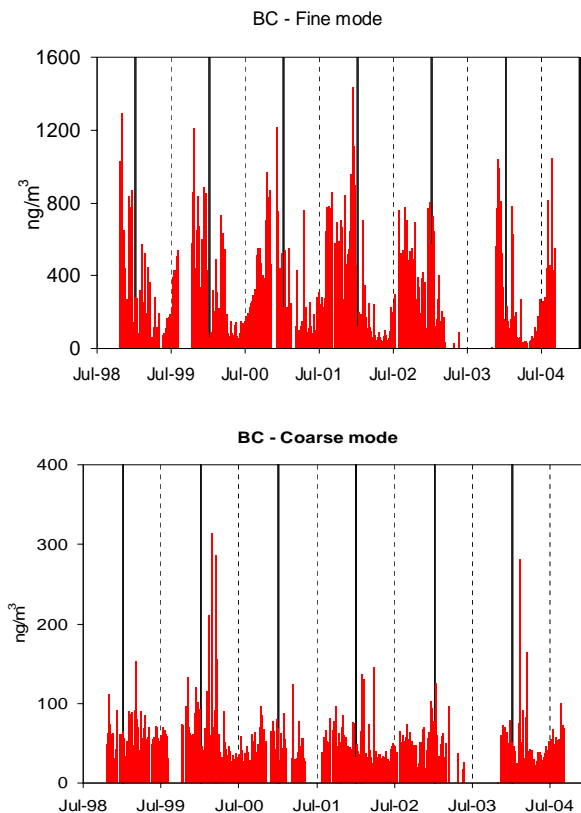


Fig. 3. The black carbon (BC) concentration observed in Balbina for **(a)** fine mode (top) and **(b)** coarse mode (bottom) during the same period presented in Fig. 2. Mean concentrations were $170 \pm 180 \text{ ng m}^{-3}$ for fine mode and $50 \pm 40 \text{ ng m}^{-3}$ for coarse mode. Note the increase in fine mode concentration during dry periods synchronized with the increase in fine particulate mass. This behavior is not observed in coarse mode, which is not influenced by the biomass-burning emissions.

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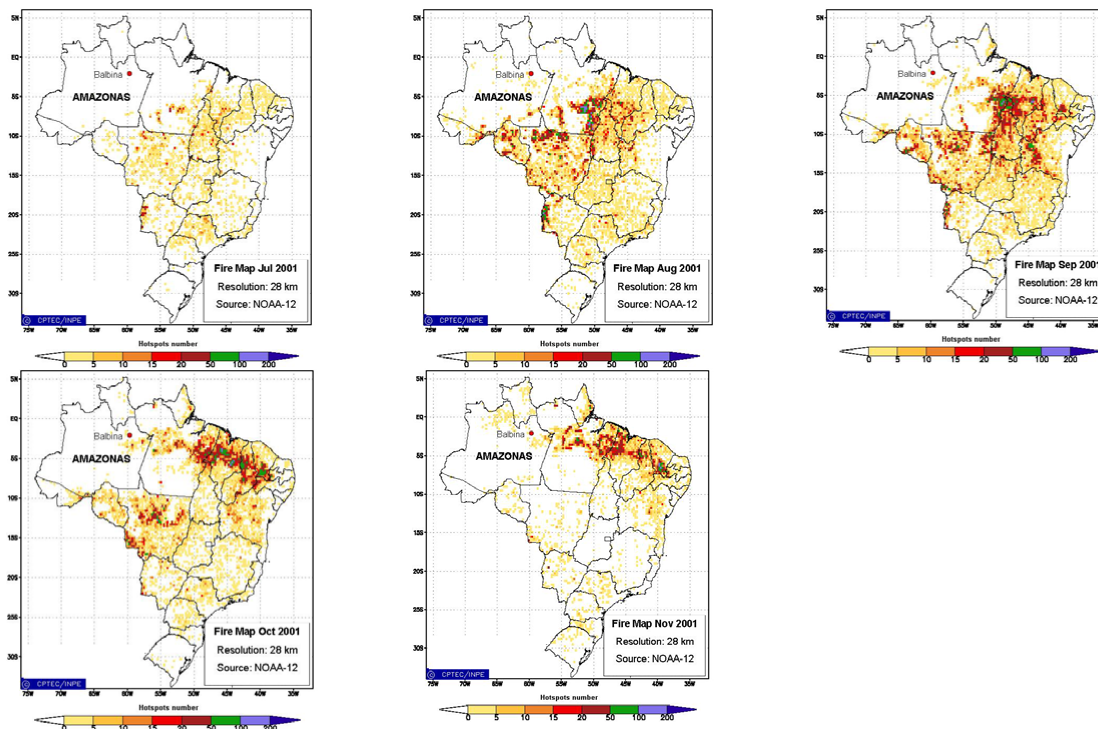


Fig. 4. Spatial distribution of hotspots in Brazil for July–November in 2001. The Amazonas state had not an important contribution of biomass-burning emissions, in spite of an increase (mainly southeast from Balbina) of hotspots number after August. Source: CPTEC/INPE (at <http://www.cptec.inpe.br/products/queimadas/queimamensaltotal.html#>).

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NOAA HYSPLIT MODEL
 Backward trajectories ending at 00 UTC 25 Sep 01
 FNL Meteorological Data

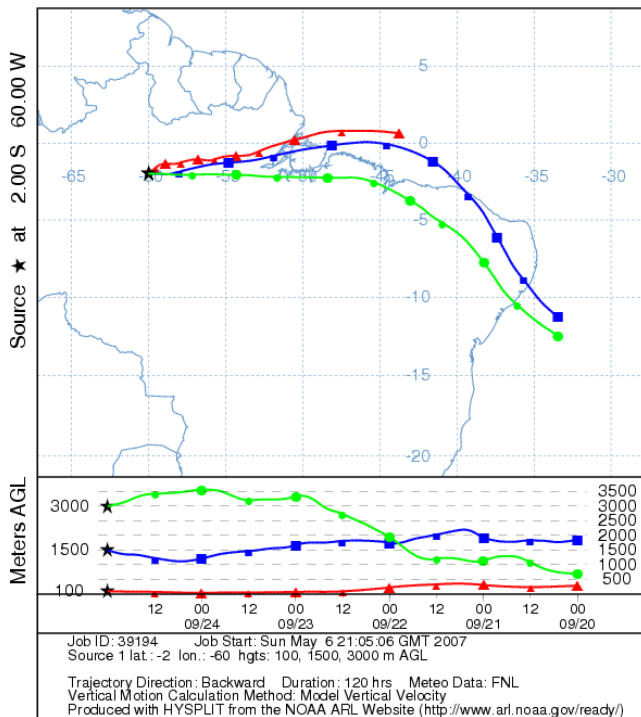


Fig. 5. Hysplit derived backward trajectories of air masses reaching Balbina at 25 September 2001, when hotspots were observed along the Amazonas river. The resulted wind streamlines are favorable to the transport of biomass-burning plumes to the sampling site.

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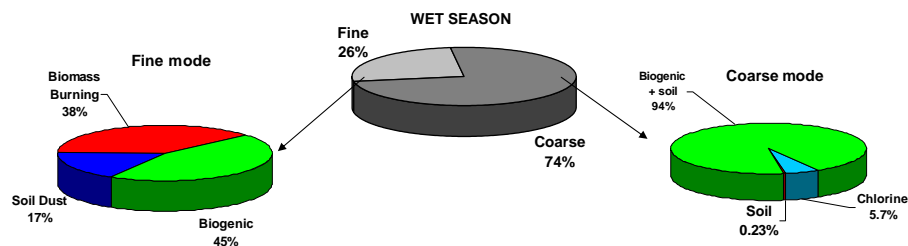


Fig. 6. Final result of Absolute Principal Component Analysis: fine/coarse mode partitioning of aerosol concentration during wet season and the individual contribution for each extracted principal component. The mean wet season concentrations were $7.3 \pm 4.5 \mu\text{g}/\text{m}^3$ for the coarse mode and $2.5 \pm 2.3 \mu\text{g}/\text{m}^3$ for the fine mode.

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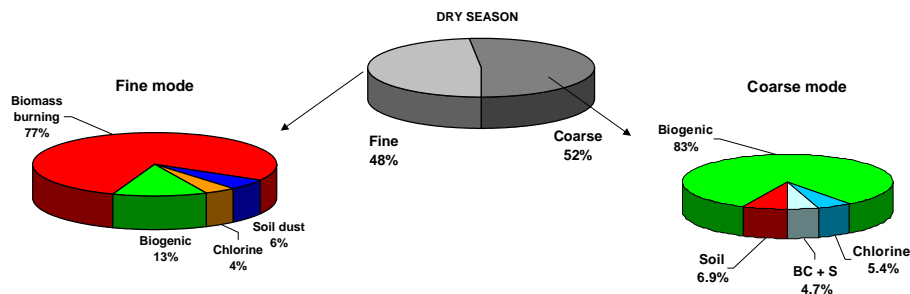


Fig. 7. The same as the previous figure but for dry season. The mean dry season concentrations were $6.3 \pm 2.8 \mu\text{g}/\text{m}^3$ for the coarse mode and $5.9 \pm 3.1 \mu\text{g}/\text{m}^3$ for the fine mode.

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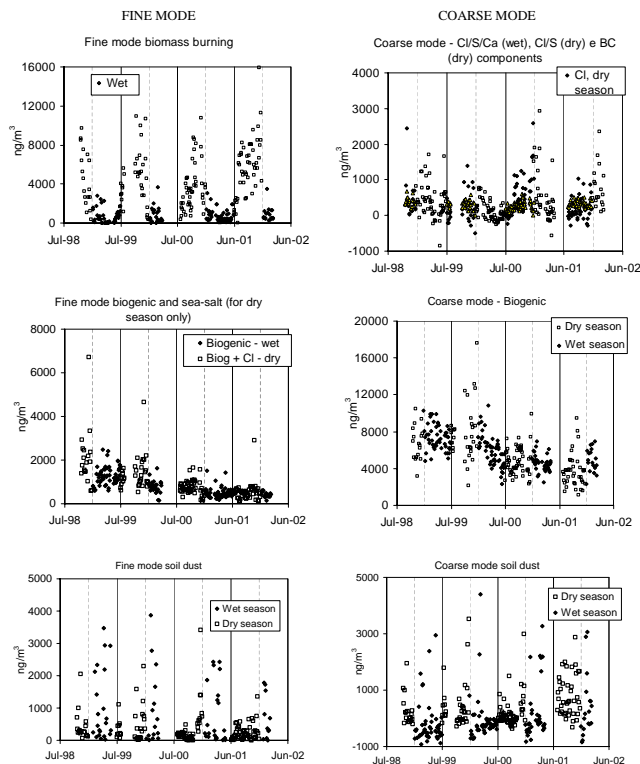


Fig. 8. Absolute concentration of aerosols in Balbina obtained by Absolute Principal Component Analysis. Each plot in the figure represents the absolute mass contribution of identified sources of aerosols, which are shown separately. In the 1st column it is shown the fine mode contribution (from top to the bottom) **(a)** biomass-burning, **(b)** biogenic, and **(c)** soil dust. In the 2nd column, the coarse mode contribution is shown: **(d)** chlorine and black carbon components, **(e)** biogenic, and **(f)** soil dust. In the case of the fine mode biogenic contribution during the dry season it was considered the sum of biogenic and chlorine components (Fig. b).

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