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

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Abstract. In this analysis a 3.5 years data set of aerosol and precipitation chemistry, obtained in a remote site in Central Amazonia (Balbina, (1°55′ S, 59°29′ W, 174 m a.s.l.), about 200 km north of Manaus) is discussed. Aerosols were sampled using stacked filter units (SFU), which separate fine ($d < 2.5\,\mu m$) and coarse mode ($2.5\,\mu m < d < 10.0\,\mu m$) aerosol particles. Filters were analyzed for particulate mass (PM), Equivalent Black Carbon (BC_E) 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). Natural sources dominated the aerosol mass during the wet season, when it was predominantly of natural biogenic origin mostly in the coarse mode, which comprised up to 81 % of PM_{10}. Biogenic aerosol from both primary emissions and secondary organic aerosol dominates the fine mode in the wet season, with very low concentrations (average $2.2\,\mu g\,m^{-3}$). Soil dust was responsible for a minor fraction of the aerosol mass (less than 17 %). Sudden increases in the concentration of elements as Al, Ti and Fe were also observed, both in fine and coarse mode (mostly during the April-may months), which we attribute to episodes of Saharan dust transport. During the dry periods, a significant contribution to the fine aerosols loading was observed, due to the large-scale transport of smoke from biomass burning in other portions of the Amazon basin. This contribution is associated with the enhancement of the concentration of S, K, Zn and BC_E. Chlorine, which is commonly associated to sea salt and also to biomass burning emissions, presented higher concentration not only during the dry season but also for the April–June months, due to the establishment of more favorable meteorological conditions to the transport of Atlantic air masses to Central Amazonia. The chemical composition of rainwater was similar to those ones observed in other remote sites in tropical forests. The volume-weighted mean (VWM) pH was 4.90. The most important contribution to acidity was from 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. Wet deposition rates for major species did not differ significantly between dry and wet season, except for NH_4^+, citrate and acetate, which had smaller deposition rates during dry season. While biomass burning emissions were clearly identified in the aerosol component, it did not present a clear signature in rainwater. The biogenic component and the long-range transport of sea salt were observed both in aerosols and rainwater composition. The results shown here indicate that in Central Amazonia it is still possible to observe quite pristine atmospheric conditions, relatively free of anthropogenic influences.

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; Martin et al., 2010a,b). Large areas of the

tropics are covered with rain forests that act as source regions of biogenic particles and trace gases to the global atmosphere (Andreae, 2007; Jaenicke, 2005, Schneider et al., 2011). The properties of atmospheric biological particles have been studied in only a few studies with measurements of their physical and chemical properties (Artaxo and Hansson, 1995; Artaxo et al., 1988; Guyon et al., 2003, Pöschl et al., 2010). Baseline knowledge of the source strengths, properties and processes of natural biogenic aerosols is necessary to correctly assess present-day burdens, direct radiative forcing and nutrient cycling in tropical regions (Martin et al., 2010a, b; Jaenicke, 2005).

Tropical rainforests depend on efficient nutrient recycling to maintain its primary production levels (Davidson and Artaxo, 2004). Usually residing over poor soils (Vitousek and Sanford, 1986), the tropical rainforest environment has become adapted to this condition along its own evolutionary history, developing a system that provides a stable equilibrium to the rainforest ecosystem (Salati and Vose, 1984). Atmosphere-biosphere interactions are an important component of tropical nutrient cycling. 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 (Davidson et al., 2012; Mahowald et al., 2005).

In spite of the high deforestation rates in Southeastern Amazonia in the last 3 decades most of the forested area is still preserved (~83 % of the original forest area). Deforestation is not spread over the entire Amazon basin but concentrated in the so-called "deforestation arc" region mostly in the Southeast/Southwest portion of the Amazon Basin. This region is subject to intense biomass-burning emissions every year during the dry season (Artaxo et al., 2002; Silva-Dias et al., 2002). The intensity of these emissions is a complex function of socioeconomic pressures for new agricultural areas, climatic effects and governance policies (Bowman et al., 2009, 2011; Morton et al., 2008; Koren et al., 2007).

The central and western portions of the Amazon rainforest are mostly well preserved with small rates of deforestation. The state of Amazonas, the largest in Brazil comprising about 1.6 million km^2 with a population of 3 484 000 inhabitants, where this work was conducted, has only 2 % of deforested area. Under such pristine conditions, natural sources and sinks of gases and aerosols play the most important roles in controlling atmospheric composition, especially during the wet season (Davidson et al., 2012).

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; Martin et al., 2010a,b; Pöschl et al., 2010). Natural biogenic aerosol comprises up to 80 % of PM$_{10}$ aerosol mass, with most of the mass (approx. 70 %) in the coarse mode fraction (Echalar et al., 1998; Gerab et al., 1998; Gilardoni et al., 2011). Biogenic particles consist of particles primarily emitted by the vegetation (e.g. bacteria, fungi,

spores, and plant and insects debris), mainly in coarse mode ($d_p > 2.5$ μm) (Artaxo and Hansson, 1995; Jaenicke, 2005), and sub-micron particles as a product of gas-to-particle conversion of biogenic trace gases emitted naturally by the vegetation (Pöschl et al., 2010; Martin et al., 2010a, b; Chen et al., 2009; Hoffmann et al, 1997, 1998; Claeys et al., 2004). Soil dust observed at Central Amazonia is a combination of local emission and the long range transport of Saharan dust, which takes place mostly between February and May (Ansmann et al., 2009; Talbot et al., 1990; Swap et al., 1992, 1996; Formenti et al., 2001).

The fine mode fraction is strongly associated with the production of Secondary Organic Aerosols (SOA) that comprises about 80 % of PM$_{1.0}$ (Martin et al., 2010a, b; Pöschl et al., 2010). Most of these are produced from oxidation of volatile organic compounds (VOCs) (Chen et al., 2009).

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 gas 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. 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 only in aqueous media (Scott and Laulainen, 1979; Hegg et al., 1984; Hegg and Hobbs, 1988), and biotransformation by microorganisms (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. The final result of rainwater chemistry is the combination of these two processes named rainout (*in-cloud*) and washout (*below-cloud*)

Previous studies of rainwater composition in Central Amazonia (Stallard and Edmond 1981; Andreae et al., 1990; Williams et al., 1997; Forti et al., 2000) reported small or even no anthropogenic influence in rainwater composition. These studies have 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
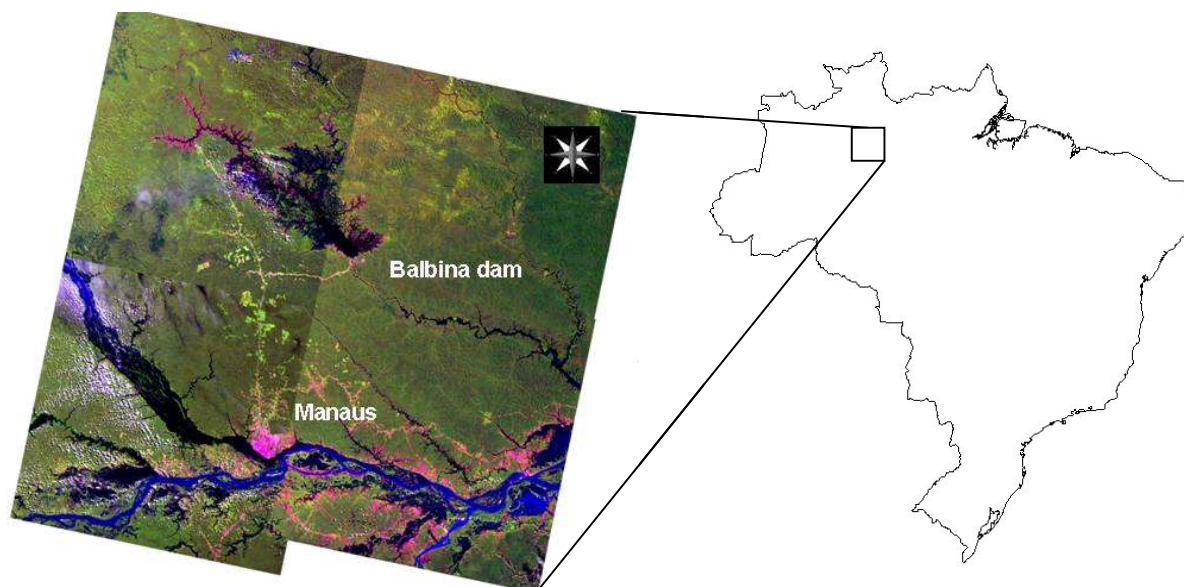
Fig. 1. Landsat image of the sampling site area. The city of Manaus (population 1 700 000) is shown in the low central portion of the figure. Balbina is located about 200 km North from Manaus in a preserved area free of deforestation and under influence of natural emissions of gases and aerosols.
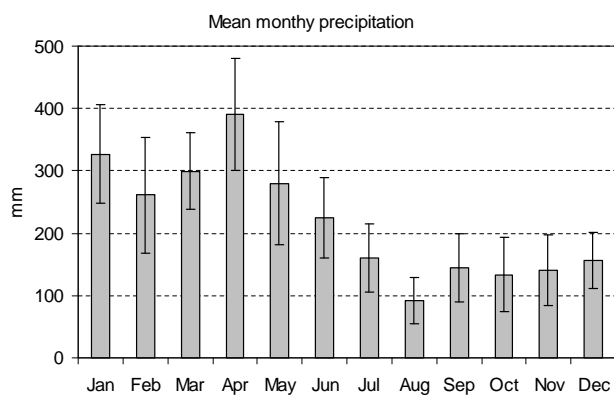

Fig. 2. Average monthly precipitation in the Balbina region during the period 1998–2001. Data were obtained from four hydrological stations operated by the Brazilian National Water Agency (http://hidroweb.ana.gov.br). Error bars correspond to standard deviation of data.

burning emissions during the dry season, depending on the distance from sources.

In this study we carried out a 3.5 years measurement of aerosol and precipitation chemistry in a remote site in Central Amazonia. The main objective was to investigate the aerosol – precipitation chemistry linkage under pristine conditions, with the aim of understanding how important the influence of aerosol composition is on rainwater chemistry in remote continental areas. It is important to emphasize that this study does not deal with aerosol composition in areas heavily im-

pacted by biomass burning such as Rondonia, Alta Floresta or Southeast Amazonia. Biomass burning effects on aerosol and rainwater composition were characterized in detail during the LBA/SMOCC campaign (Fuzzi et al., 2007; Trebs et al., 2005).

1.1 Sampling location

1.2 Description of the sampling site

Balbina, the sampling site (1°55′ S, 59°29′ W, 174 m a.s.l.), is a small village located about 200 km North of Manaus (see Fig. 1). The population density of the region is only 0.49 inhabitant km^{-2} 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 large hydroelectric plant, a lake which covers approximately 240 000 ha.

1.3 Precipitation climatology and site characterization

Figure 2 shows the annual cycle of monthly accumulated precipitation for the region around the sampling site between 1998–2001 (data available at http://hidroweb.ana.gov.br). From the figure it is possible to observe large monthly variability in precipitation and that Central Amazonia wet season takes place from January to May, and dry season from August to November. June, July and December are transition months. Total annual precipitation was 2530 ± 330 mm for this period. Variability in inter-annual 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 (Marengo et al., 2001). The South Atlantic Convergence Zone also plays a role in some precipitation events (Carvalho et al., 2004).

Balbina is mostly influenced by eastern air masses associated to the trade winds circulation. From the tropical Atlantic ocean, air masses travel more than 1000 km over pristine primary tropical rainforest before reaching the site. It makes this region an excellent choice to observe natural background chemical conditions for aerosol and precipitation, in particular during the wet season when there are no biomass burning reaching the site. Several previous works dealing with the natural component of aerosols were published based on data collected at Balbina (e.g. Zhou et al., 2002; Graham et al., 2003a, b; Rissler et al., 2004). During the dry season (August–November) the site is subject to the large-scale transport of biomass-burning aerosols that typically occurs in other portions of the basin. This signal, which has significant influences in the fine mode concentration during the drier months, was detected and quantified in our analysis, and is described in detail latter.

2 Experimental

2.1 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 PM_{10} inlet. The SFU collects particles on 47 mm diameter polycarbonate membrane filters. An 8 µm pore size filter collects coarse particles ($2.5 < d_p < 10$ µm) while a 0.4 µm pore size filter collects fine particles ($d_p < 2.5$ µm). 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 (Gerab et al., 1998). 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 (Gerab et al., 1998).

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 ^{210}Po radioactive sources. Detection limit for the aerosol mass concentration is 0.3 µg m^{-3}. Precision is estimated at about 10 %. Equivalent black carbon (BC_E) concentration on the fine and coarse fraction of the SFU filters was obtained by a light reflectance technique. The optical absorption of the polycarbonate filters was analyzed by a smoke stain reflectometer that measures light attenuation by the aerosol particles. The instrument was calibrated using standard Monarch "soot" carbon deposited in gravimetrically analyzed Nuclepore filters (Martins et al., 1998a, 1998b). The term "equivalent" black carbon is used in this work following suggestions from several studies indicating the mixed presence of several types of absorbing aerosols, as well as the so-called "brown carbon", a light absorbing aerosol that is not elemental carbon (Andreae and Gelencsér, 2006).

2.2 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 rainwater collectors, in high-density polyethylene bottles, which had been previously rinsed with miliQ water. Immediately 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 WMO recommendations (WMO, 2004).

The pH of each sample was measured twice: immediately after sampling (Cole Parmer portable pH meter model CON 10) and later in the laboratory (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 4.00 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 0.01µM l^{-1}. It was possible to determine concentrations of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, F^-, acetate (CH_3COO^-), formate

(HCOO$^-$), NO$_2^-$, Br$^-$, oxalate (C$_2$O$_4^{2-}$), citrate (C$_6$H$_5$O$_7^{3-}$), PO$_4^{3-}$, and Dissolved Inorganic Carbon (DIC).

2.3 Data analysis

Data analysis procedures have to deal with the fact that the concentration of ionic species in rainwater is dependent not only on the amount of the component, but also 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

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

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 identify and remove the possible influence of marine contribution, the non-seasalt (nss) component for some selected compounds was 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)

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

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 estimate the portion of the different aerosol components (using elemental composition) and precipitation composition (using ionic deposition rates) (Hopke, 1985; Switlicki et al., 1996). 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 to 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
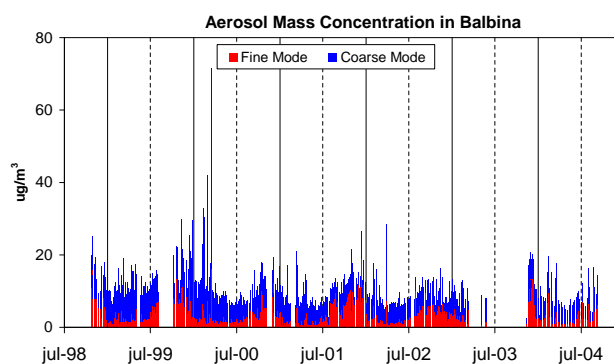

Fig. 3. The aerosol mass concentration time series at Balbina from October 1998 to September 2004. Concentrations are shown separately for Fine Particulate Mass (FPM, $d_p < 2.5 \,\mu\text{m}$) and Coarse Particulate Mass (CPM, $2.5 \,\mu\text{m} < d_p < 10 \,\mu\text{m}$).

Analysis (FA) after VARIMAX rotation. The result of the linear regression allows for determining quantitatively the absolute contribution of each extracted component for each chemical compound (Switlicki et al., 1996).

3 Results

3.1 Aerosol measurements

The time series of fine and coarse mode aerosol mass concentrations is shown in Fig. 3. The fine mode mass concentration (PM$_{2.5}$) is shown in red, while the coarse mode fraction is shown in blue. The sum of both components is the PM$_{10}$ aerosol mass concentration. The observed average aerosol mass concentration was very low, amongst the lowest values observed in remote continental areas. PM$_{2.5}$ concentrations in the wet season were as low as 2.2 µg m^{-3}. During the dry season, it was possible to observe some influence of long range biomass burning plumes that increased PM$_{2.5}$ to 6.2 µg m^{-3}. The typical annual mean of PM$_{10}$ concentration of 11 µg m^{-3} experienced an increase during the dry season due to an enhancement of the concentration in the fine mode. The coarse mode concentration mostly associated with primary biogenic particles is rather constant along the year at about 7 µg m^{-3}. It is also possible to observe in Fig. 3 some significant episodic enhancements in the coarse particle mass. These episodes were associated with dust transport from the Sahara desert, documented in several studies (Formenti et al., 2001; Swap et al., 1992, 1996; Koren et al., 2006; Ansmann et al., 2009; Baars et al., 2011; Ben-Ami et al., 2010).

Time series of fine and coarse mode BC$_E$ concentration are shown in Fig. 4. The annual average fine mode BC$_E$ concentrations were 170 ng m^{-3}, which is a low value for a continental region. The fine mode BC$_E$ concentration (Fig. 4a) had a similar seasonal variability as the PM$_{2.5}$ concentrations and

is a combination of two components: the natural optical absorption of fine mode primary aerosol particles and the optical absorption by the biomass burning component. The BC_E concentration in the coarse mode aerosols, with an average of 50 ng m^{-3}, is shown in the Fig. 4b. This component represents absorbing aerosols in the primary biogenic particles in the coarse mode fraction and is essentially constant throughout the sampling period. This suggests that the coarse mode natural biogenic absorbing component is not affected significantly during the dry season. This is in agreement with other studies that point to a natural biogenic contribution to absorbing aerosols (Guyon et al., 2003; Andreae and Gelencsér, 2006; Rizzo et al., 2011).

Two large aerosol studies with intensive sampling campaigns were carried out in Balbina as part of LBA-CLAIRE (Cooperative LBA Airborne Regional Experiment) (Andreae et al., 2002). The first CLAIRE 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 wet season 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 only 9 hotspots for the whole Amazonas state, which is evidence that local/regional contribution was very small or negligible, and that pollution plumes from distant sources were probably responsible for such an enhancement in particle number concentration. Figure 5 shows the spatial distribution of fire hotspots observed from July to November in 2001 in Brazil. In July the Amazonas state was almost free of fire spots. However, from August to November many hotspots were observed along the Amazonas River (southeast of Balbina). As such, some regional 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. 8 for 25 September 2001, at the peak of the biomass-burning season. Back trajectories were calculated using the Hysplit model. The trajectories show that for a variety of air mass levels reaching Balbina (100, 1000 and 2000 m a.g.l.) all of the trajectories passed over the Amazonas river path, where fire hotspots were observed, and that probably the biomass-burning influence detected in Balbina is due to the transport of plumes originated in this region during the biomass burning season.

A summary of average elemental concentrations measured in aerosols at Balbina is shown in Table 1, for fine and coarse mode aerosols. Averages were separated as annual, first and second semester means. In spite that separation by semester is affected by the transition months (as described in Sect. 2), the first and the second semester are representative of wet and dry season regimes, respectively. Aerosol mass is dominated
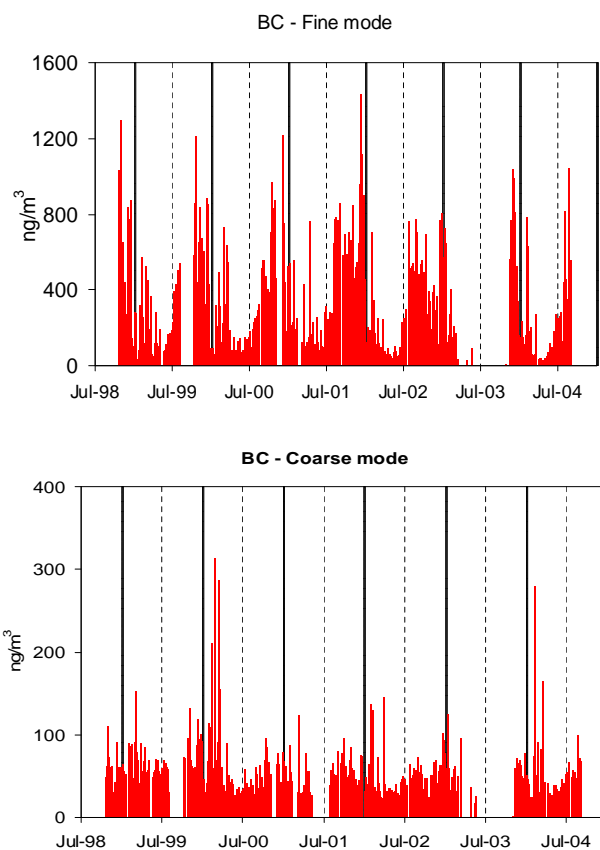

Fig. 4. The equivalent black carbon (BC_E) concentration observed in Balbina for **(a)** fine mode (top) and **(b)** coarse mode (bottom) during the same period presented in Fig. 2. Mean concentrations were 170 ± 180 ng m^{-3} for the fine mode and 50 ± 40 ng m^{-3} for the coarse mode. Note the increase 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.

by the coarse mode component over fine particles. BC_E concentration was predominantly in the fine mode, with higher values during the 2nd semester, corresponding to the dry season. The elements S, K and Zn also experienced higher concentrations during the dry season. Sulfur concentrations, on the order of 100–300 ng m^{-3}, are low in Central Amazonia. Monthly means of particulate mass, BC_E and elemental concentrations are shown in Fig. 6. Plots are separated in coarse mode in the left and fine in the right side, and the analysis of these data allows characterizing the typical annual cycle of each measured component, as well as the CPM, FPM and BC_E.

Coarse and fine particulate mass

The variation of monthly means of CPM was quite small, and a minimum concentration was observed in August
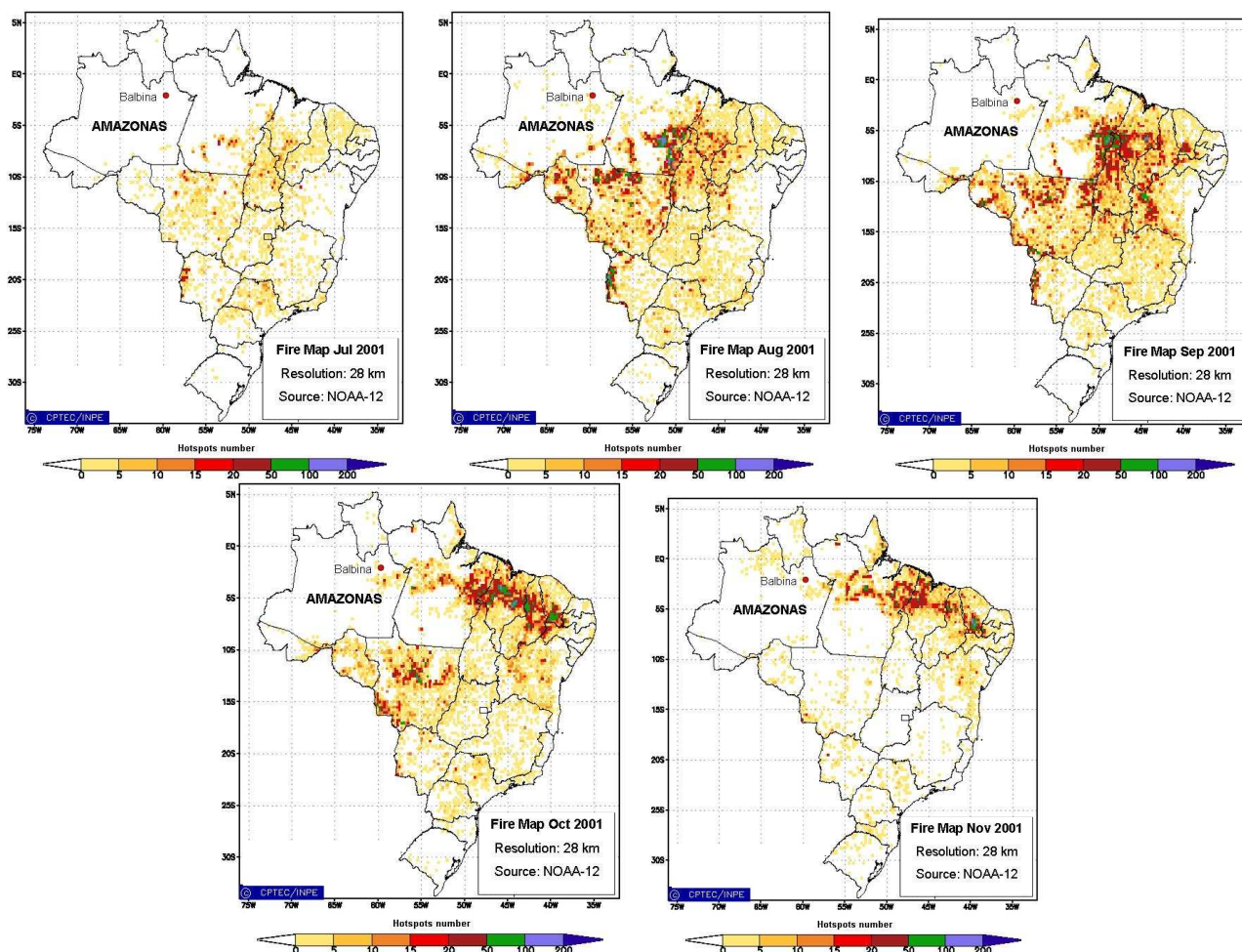
Fig. 5. Spatial distribution of fire hotspots in Brazil for Jul–Nov in 2001. The Amazonas state had not an important contribution of biomass-burning emissions, in spite of an increase (mainly southeast from Balbina) of hotspots after August. Source: CPTEC/INPE (at http://www.cptec.inpe.br/products/queimadas/queimamensaltotal.html#).

($4000 \, \text{ng m}^{-3}$). In fact, for the remaining months it varied within 6000–$8000 \, \text{ng m}^{-3}$, which is a rather small range. This is a completely different behavior of FPM, which presented a clear seasonal variation. FPM presented a significant increase in its concentration for the period July–November, a slight reduction in December and a steep reduction in January. This pattern is compatible with the annual cycle of precipitation, shown in Fig. 2.

BC$_E$, K, S and Zn

In the coarse mode, two patterns of annual cycles were observed. Zn and K presented an almost constant level throughout the year, whereas BC$_E$ and S presented some seasonality. BC$_E$ and S typically increased their concentration after July, with a reduction in December. When comparing the difference of average BC$_E$ concentrations of the wet sea-

son ($48 \pm 8 \, \text{ng m}^{-3}$) with the dry season ($53 \pm 5 \, \text{ng m}^{-3}$) it is possible to see that it is not statistically significant ($p < 0.01$). Moreover, it is possible to see that (except for October) all the monthly means of the dry season were smaller than the concentrations of January and February. Thus, it is likely that the annual cycle of BC$_E$ in the coarse mode is more related to natural processes (e.g. absorption component of biogenic aerosols, see Rizzo et al., 2011) than biomass-burning influences.

BC$_E$ variations in the fine mode followed the FPM pattern. During the wet season, when natural sources of particles dominate the concentration, it represents the absorbing component of biogenic of aerosols (Pöschl et al., 2010; Martin et al., 2010a, b; Andreae and Galencsér, 2006). During the dry season the increase in BC$_E$ concentration is due to the influence of the large scale transport of biomass burning plumes

from other regions in the Amazon Basin (Soto-Garcia et al., 2011).

Ti, Fe, Al, Si and Ca

These elements are usually employed as tracers for soil dust aerosols. Monthly means of these elements presented a similar behavior both in fine and coarse modes. Typically, the monthly means of these elements was consistently larger in Jan/Feb/Mar/Apr, followed by a reduction in May/Jun and then a moderate increase until December. However, as shown in the discussion of the Principal Component Analysis, it was in April and May that we observed bursts of this elements. We attribute it to the transport of Saharan dust, which has been shown to be more likely to happen during these months (Baars et al., 2011).

Cl

Most of Cl content was present in the coarse mode fraction, as can be seen in Fig. 6 (note the different vertical scales for each size fraction). Concentration in the coarse mode was about 15 times greater than the fine mode. The monthly means presented a quite broad variation, presenting two maxima throughout the year. During the rainy months Cl concentrations reached the highest value. With respect to the dry season, when fine and coarse modes varied the concentration of Cl varied quite similarly, with maximum in October. Potential sources of Cl in Balbina are the marine contribution (seasalt aerosols advected from the Atlantic as NaCl) and biomass burning (generally as KCl) during the dry season. Thus, a possible explanation for this behavior could be that the transport of seasalt aerosols during the wet season was the most important source for Cl, and that during the dry season a combination of both sources was responsible by the Cl budget in the atmosphere. Nevertheless, in spite that biomass-burning was clearly detected during the dry season in this study, it is possible that at least for Cl it was not important at Balbina. In fact, Cl presented low concentrations during the dry season. Further, in the factor analysis, it was not possible to observe a component connecting K and Cl, as shown in the upcoming analysis. Thus, we state that Cl budget is predominantly associated with the strength of the marine contribution, and that other contributions are minor.

Factor analysis

Factor analysis was used to identify common variability between the different trace elements in the data set. With the goal of a better separation of dry and wet seasons influences, the whole data set was analyzed separately for the 1st and 2nd semester. Fine mode VARIMAX rotated factor-loading matrices are shown in Table 2, while in Table 3 the results for the coarse mode are shown. It is also possible to observe in these tables the component and cumulative explained variance, and the communalities for each element included in the analysis.

In the 1st semester, the first factor in the fine mode (shown in Table 2) have high loadings for Al, Fe, Si, Ca, FPM and K, representing soil dust aerosol mostly from long range transported Sahara dust. The second factor has high loadings for BC_E, K, S and FPM, and represents the natural biogenic aerosols. The third factor is related to P, Zn, S and FPM, and represents a second natural biogenic aerosol component. These two different components for natural biogenic aerosols were already observed in previous studies in the same area during the wet season (Artaxo and Hansson, 1995). It is normally observed that K and P have very different variability patterns, and the reason for this behavior is unknown. 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.

Four components were extracted for the 2nd semester. The first (BC_E, K, FPM and S) is related to the large scale transport of biomass burning plumes, as discussed in previous sections. The second and third factors are the soil dust and natural biogenic aerosols already also observed in the first semester. The additional fourth component is associated with the transport of seasalt aerosols (Cl was not included in the fine mode wet season analysis due to insufficient number of samples above detection limit). This 4-factors solution explained 90 % of the data variability in the second semester.

Factor analysis results for the coarse mode are shown in Table 3. Soil dust and biogenic components were also observed in both semesters, with a similar signature to the observed in the fine mode. The 3rd component observed for the 1st semester, associated with Cl, is the seasalt transport. In the 2nd semester a 4th component with absorbing aerosol (BC_E) 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 but natural biogenic absorbing aerosols, as pointed out in the previous section.

For the coarse mode aerosols, 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_E loadings were 0.68 and 0.48 for the 1st semester analysis, in comparison to the 0.94 loading of the BC_E component in the 2nd semester. It means that the 3 extracted components for the wet season were not really sufficient to explain BC_E variance satisfactorily. In fact, the lowest communality observed among all analyzed elements was for BC_E. This BC_E component in coarse mode is likely associated with optically active coarse mode natural biogenic particles. There is no evidence that biomass burning caused any increase in coarse mode BC_E and no seasonal difference was observed in the concentration pattern, and instead coarse mode biogenic aerosols provide an alternative explanation.

Table 1. First and second semester mean aerosol elemental composition in fine and coarse mode in Balbina, Central Amazonia.

	Coarse mode		Fine Mode	
	1st semester	2nd semester	1st semester	2nd semester
PM*	6600 ± 2900 (163)	7200 ± 2100 (142)	2200 ± 1300 (154)	6200 ± 3100 (148)
BC_E	53 ± 16 (163)	48 ± 19 (142)	161 ± 129 (154)	490 ± 260 (148)
Mg	24 ± 16 (105)	32 ± 19 (114)	20 ± 20 (81)	25 ± 14 (64)
Al	48 ± 71 (163)	55 ± 50 (142)	61 ± 84 (154)	32 ± 32 (148)
Si	110 ± 170 (163)	88 ± 82 (142)	130 ± 190 (154)	58 ± 72 (148)
P	35 ± 11 (163)	25 ± 13 (142)	4.2 ± 2.2 (154)	6 ± 3 (148)
S	37 ± 17 (163)	54 ± 22 (142)	100 ± 63 (154)	310 ± 180 (148)
Cl	73 ± 77 (163)	75 ± 73 (142)	10 ± 13 (103)	10 ± 8 (123)
K	93 ± 27 (163)	77 ± 29 (142)	40 ± 35 (154)	140 ± 88 (148)
Ca	26 ± 28 (163)	26 ± 16 (142)	15 ± 17 (154)	13 ± 9 (148)
Ti	5.3 ± 6.8 (123)	5.6 ± 5.7 (142)	5.3 ± 6.7 (124)	3.4 ± 3.2 (111)
V	0.51 ± 0.34 (5)	0.80 ± 0.63 (3)	0.82 ± 0.38 (16)	1.4 ± 0.9 (5)
Cr	2.1 ± 1.7 (57)	2.3 ± 1.9 (18)	1.3 ± 0.8 (76)	1.6 ± 1.6 (29)
Mn	1.0 ± 0.9 (130)	0.85 ± 0.61 (108)	0.91 ± 0.95 (100)	0.59 ± 0.49 (77)
Fe	34 ± 50 (163)	40 ± 30 (142)	36 ± 50 (154)	20 ± 19 (148)
Ni	0.38 ± 0.55 (17)	0.33 ± 0.36 (20)	0.77 ± 0.74 (101)	1.1 ± 1.0 (31)
Cu	0.34 ± 0.49 (103)	0.30 ± 0.32 (72)	0.55 ± 0.60 (113)	0.44 ± 0.53 (75)
Zn	0.95 ± 0.42 (163)	0.92 ± 0.48 (142)	0.70 ± 0.63 (154)	1.5 ± 1.1 (148)
Br	0.39 ± 0.28 (17)	0.38 ± 0.12 (11)	2.7 ± 1.6 (73)	2.5 ± 2.4 (98)
Pb	0.19 ± 0.12 (14)	0.30 ± 0.13 (18)	0.24 ± 0.16 (24)	0.36 ± 0.20 (60)

All values are expressed in $ng\,m^{-3}$ and the variability represents standard deviation of measurements. The number between brackets represents the number of samples that presented concentrations above the detection limit.
*PM is the Particulate Matter concentration

Table 2. Component loadings from the application of Principal Component Analysis for fine mode aerosol concentration data*. Results are shown separately for the 1st and 2nd semester. In the last line, it is shown the explained and cumulative (between brackets) variance for each extracted component. Chlorine was not included in the wet season analysis due to insufficient samples above detection limits to perform component analysis.

	1st semester				2nd semester				
	Saharan absorbing	Biogenic dust	Biogenic non absorbing	COM[b] Burning	Biomass dust	Saharan absorbing	Biogenic non	Seasalt	COM[b]
BC_E	0.31	**0.92**	–	0.95	**0.94**	–	–	–	0.93
K	**0.64**	**0.71**	–	0.94	**0.91**	–	–	–	0.97
FPM[a]	**0.66**	**0.56**	0.37	0.89	**0.91**	–	0.32	–	0.94
S	–	**0.71**	**0.54**	**0.88**	**0.74**	–	0.36	0.41	0.85
Al	**0.95**	–	–	0.99	–	**0.98**	–	–	0.97
Fe	**0.95**	–	–	0.99	–	**0.97**	–	–	0.96
Si	**0.96**	–	–	0.99	–	**0.97**	–	–	0.95
Ca	**0.89**	0.30	–	0.90	0.36	**0.78**	–	0.34	0.85
Zn	–	0.38	**0.71**	**0.70**	0.39	–	**0.80**	–	0.83
P	–	–	**0.95**	0.91	0.40	–	**0.64**	0.40	0.74
Cl	–	–	–	–	–	–	–	**0.90**	**0.94**
Cumulative Variance (%)	46	26 (72)	19 (91)		33	32 (65)	13 (78)	12 (90)	

*Loadings smaller than 0.20 were omitted.
[a]FPM is Fine Particulate Mass concentration
[b]COM is the communality correspondent to the chemical compound

CPM - Monthly means

FPM - Monthly means

BC - Coarse - Monthly means

BC - Fine - Monthly means

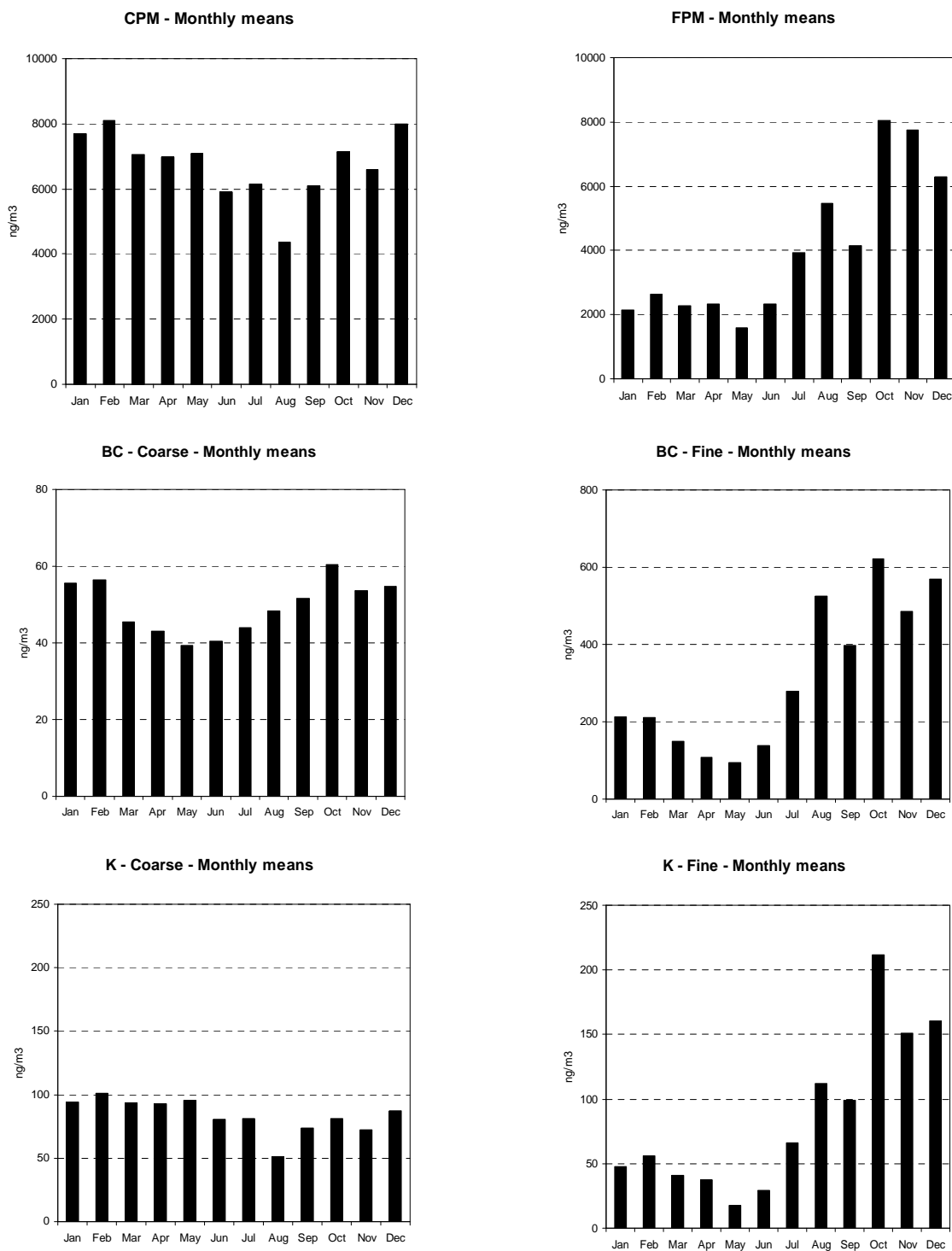**K - Coarse - Monthly means**

K - Fine - Monthly means

Fig. 6. Monthly means of coarse mode (left) and fine (right) particulate, black carbon equivalent and elemental mass concentration.

S - Coarse - Monthly means

S - Fine - Monthly means

Zn - Coarse - Monthly means

Zn - Fine - Monthly means

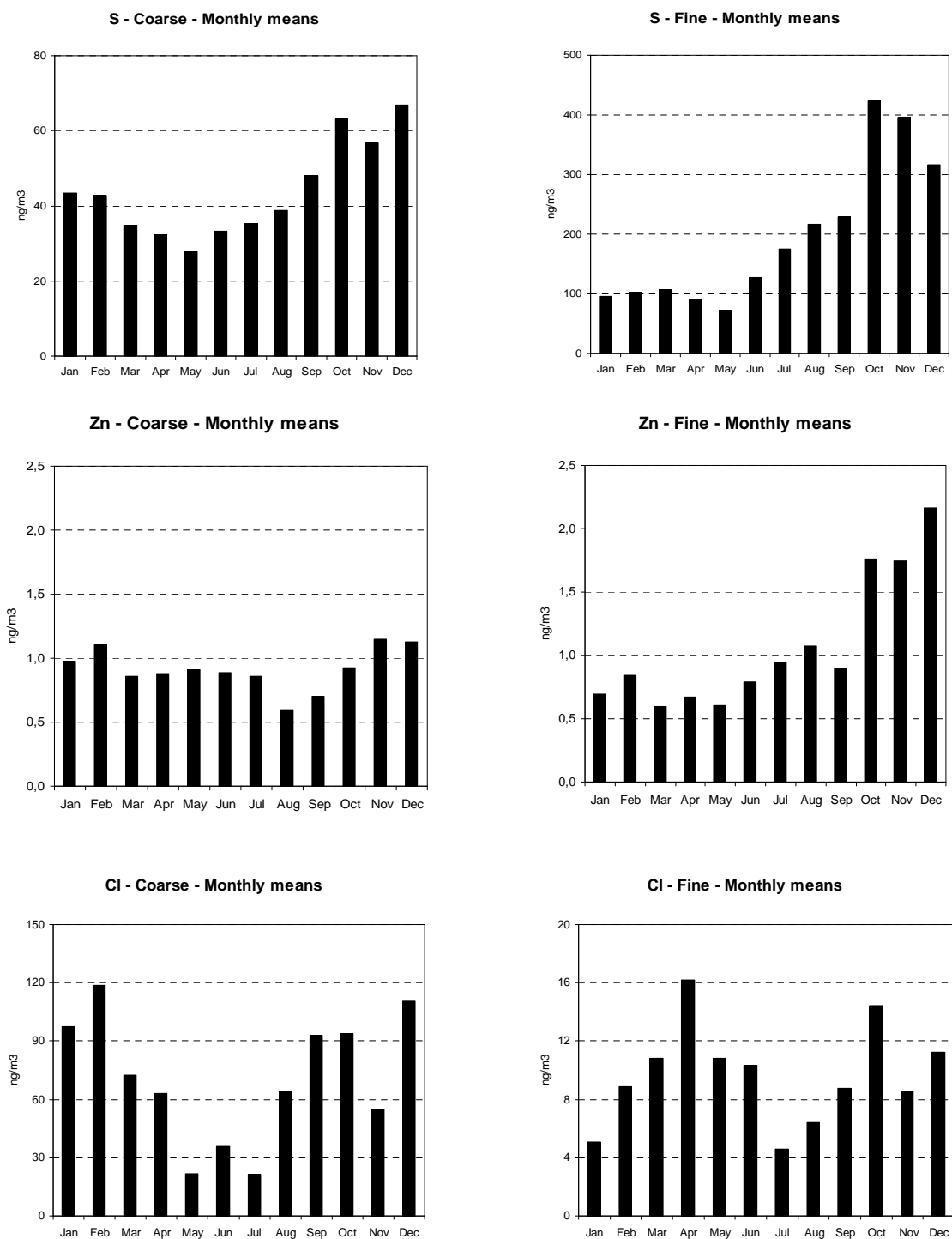**Cl - Coarse - Monthly means**

Cl - Fine - Monthly means

Fig. 6. Continued.

In fact, when we visually inspect the coarse mode filters after 3–4 days collection in the wet season, they are actually gray in color. On the other hand, fine mode BC_E is clearly associated with biomass burning emissions during the dry season, given the clear seasonality of measurements, with a somewhat constant component due to absorption by fine mode biogenic aerosol, often called "brown carbon", during the wet season.

The absolute apportionment of trace element concentrations was obtained through the application of the APFA
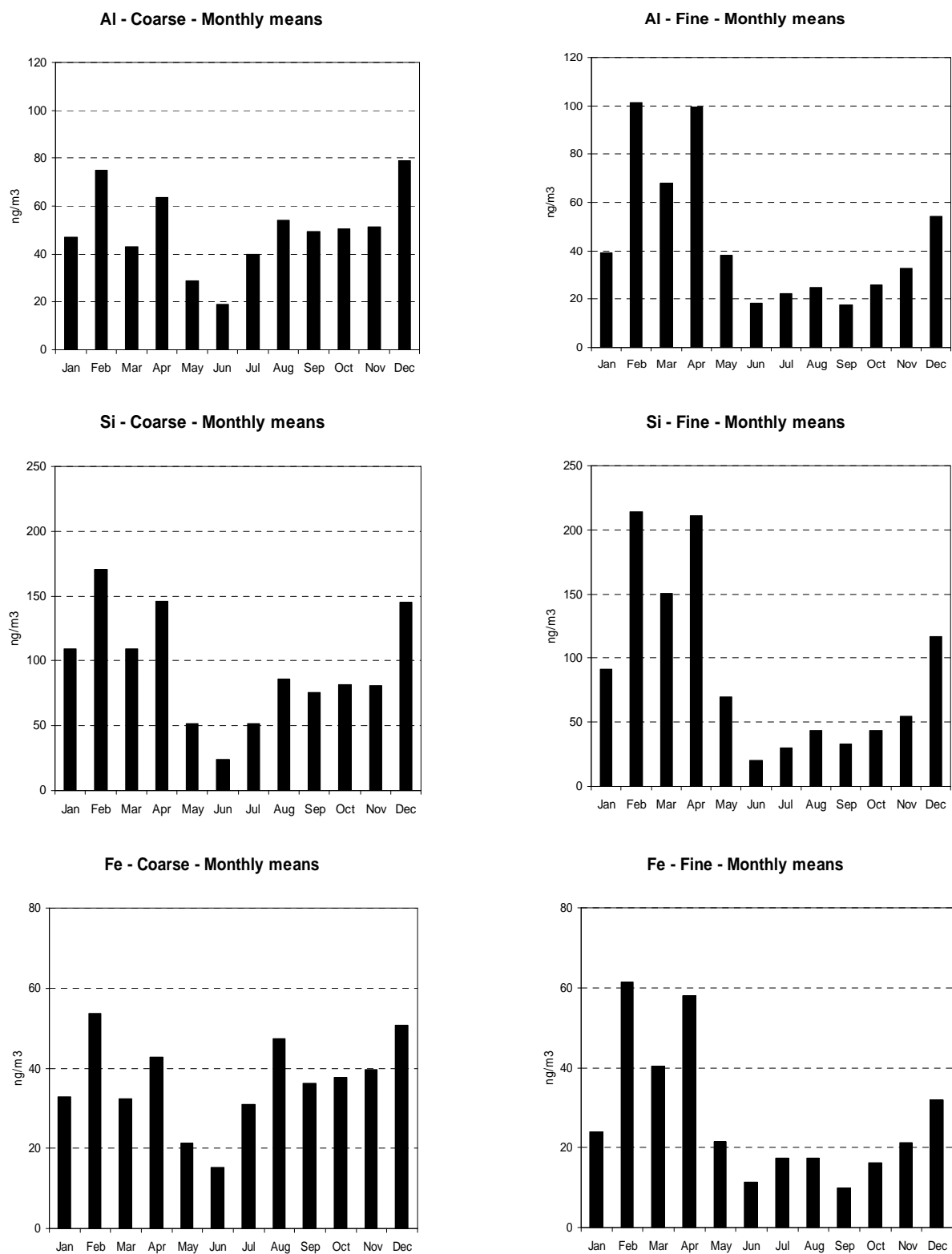
Al - Coarse - Monthly means

Al - Fine - Monthly means

Si - Coarse - Monthly means

Si - Fine - Monthly means

Fe - Coarse - Monthly means

Fe - Fine - Monthly means

Fig. 6. Continued.

Ti - Coarse - Monthly means

Ti - Fine - Monthly means

Ca - Coarse - Monthly means
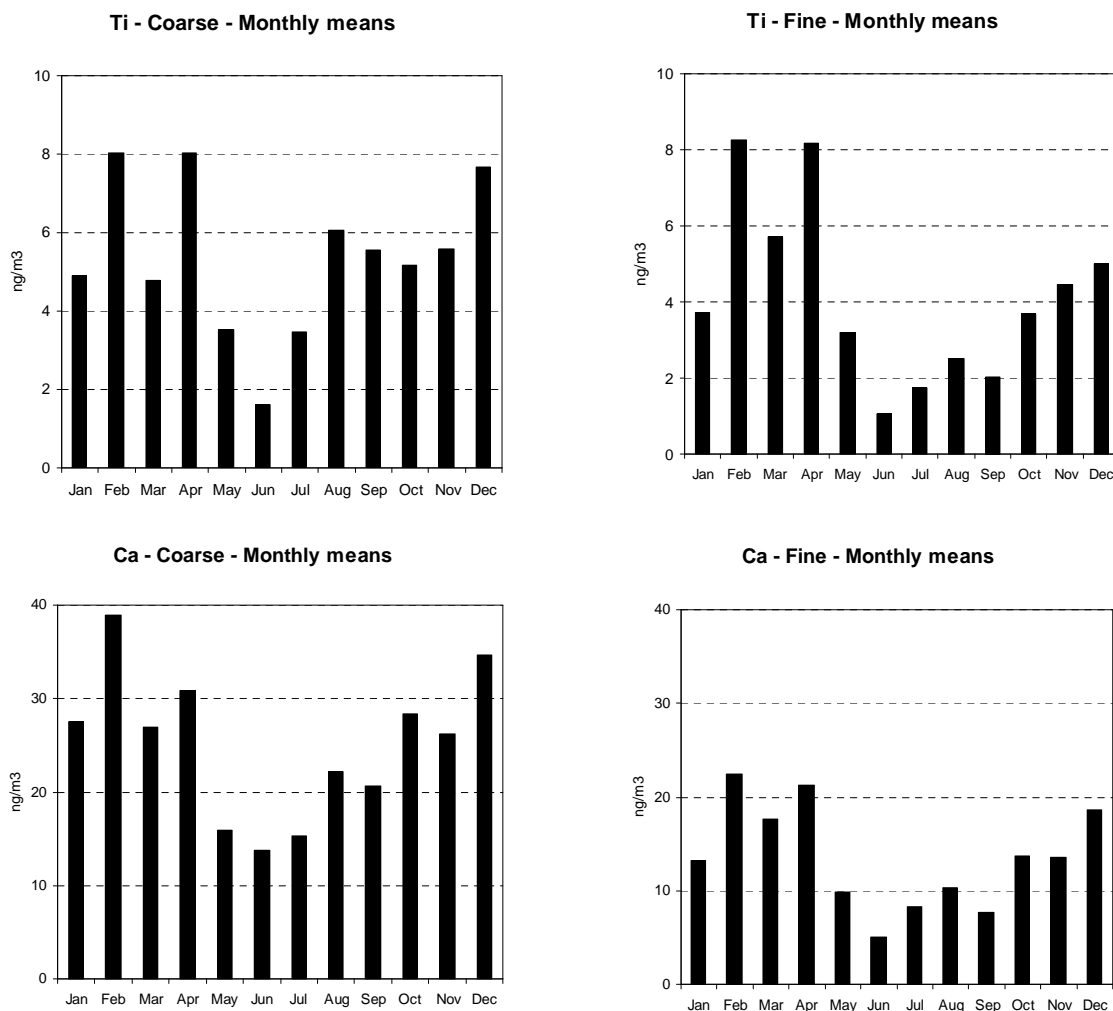
Ca - Fine - Monthly means

Fig. 6. Continued.

procedure. The mean 1st and 2nd semester results are presented in Figs. 9 and 10, respectively. In the 1st semester natural biogenic particles dominate the aerosol mass, with 90 % of the coarse mode and 83 % of the fine mode aerosol, followed by soil dust with 5 % and 17 % of coarse and fine modes, respectively. The small contribution of soil dust in the coarse mode is due to the combination of the soil being covered permanently with a thick forest litter and very high humidity, which suppresses the emission of dust particles.

With respect to the 2nd semester APFA analysis (Fig. 10), the non absorbing biogenic aerosol contribution was also predominant in the coarse mode (83 % of the aerosol mass), followed by soil dust (7 %), absorbing biogenic aerosols (5 %) and seasalt (5 %). In the fine mode, biomass burning contribution dominates the picture with 77 % of fine aerosol mass, followed by biogenic aerosols (13 %), soil dust (6 %) and seasalt (4 %)

In Figs. 11 and 12 these results are shown as time series throughout the entire sampled period. The biogenic contribu-

tion is displayed in Figs. 11a (fine mode) and 12a (coarse). The absorbing and non-absorbing components are shown separately. In fine mode they have the same order of magnitude, while in the coarse mode the non-absorbing component domains the picture, with concentration 20 times greater than the absorbing component whose average concentration of $300 \, \text{ng m}^{-3}$ represents approximately 5 % of the CPM.

Surprisingly, a decrease in the concentration of the nonabsorbing biogenic component was observed both in fine and coarse modes. This result is unexpected. The rainforest environment surrounding the site area has been well preserved during the sampling period, and no significant changes (e.g. deforestation) have taken place within hundreds of kilometers from the sampling area. We could not provide any plausible explanation for the behavior of this biogenic component.

Soil dust time series in fine and coarse modes is shown in Figs. 11b and 12b. It is possible to observe that the typical behavior of this component is a rather small background concentration with extreme peaks. A possible explanation

for this behavior is the occurrence of burst events related to weather changes (e.g. squall lines) that favor the transport of soil dust originated from Sahara, especially in April and May when the Amazon Basin is subject to large-scale transport of these particles (Swap et al., 1992, 1996; Formenti et al., 2001).

Biomass-burning component (only 2nd semester data), is shown in Fig. 11c. As expected from a very seasonal source, it presents the largest amplitude among the extracted components, with concentrations up to $12\,000\,\mathrm{ng\,m^{-3}}$. It also presents important inter-annual differences, which are controlled by basin-wide climatological issues.

In Fig. 12c the contribution of coarse mode seasalt can be observed. It also had important inter-annual variability, since year to year precipitation patterns vary significantly as well as the long range transport from the tropical Atlantic Ocean to Amazonia.

3.2 Rainwater chemistry measurements

3.2.1 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 similar to the observed in other tropical remote regions around the world, when little biomass burning impact is observed. The mean observed acidity was $<\mathrm{pH}> = 4.90$, 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 African Savanna site. The explanation for the discrepancy is the high buffering capacity for this site, as one can see by its higher concentration of NH_4^+ and Ca^{2+} in the Sahelian savanna site than observed in other measurements.

Buffering capacity in our site was low compared to other remote sites. VWM for NH_4^+ was similar to the observed in the previous work conducted in central Amazonia by Williams et al. (1997). Furthermore, NH_4^+ was remarkably lower than the observed concentration in Zoétélé (Sigha-Nkandjou et al., 2003), a similar ecosystem site in the African rainforest, and for the South African semi-arid site (Mphepya et al., 2004). The authors reported that this enhanced concentration of NH_4^+ (and also of K^+ and Cl^-) in African sites was due to the influence of biomass burning during the dry season, which is not the case for Balbina. For the Sahelian Savanna site (Galy-Lacaux and Modi, 1998), the authors attributed the origin of the 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 smaller concentration of formate in comparison with acetate, which are anions directly associated with the presence of formic and acetic acids. This is an unexpected result because in remote areas of the world the most typical result is a predominance of formic (F) over acetic (A) 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 lower than the reported values of other sites subject to marine influence (e.g. Costa Rica $VWM_{Na^+} = 27.2\,\mu\mathrm{eq\,l^{-1}}$) (Elklund et al., 1997). However, 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 of $4.0\,\mu\mathrm{eq\,l^{-1}}$ (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 component along the 1200 km distance from the Atlantic is responsible for the observed Na^+ concentrations. Considering that the altitude difference between Manaus and its estuary is about 80 m, 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.

3.2.2 Analysis of Balbina rainwater chemistry measurements

VWM concentrations and wet deposition rates are shown in Table 5. As for aerosols, averages are shown as annual, 1st and 2nd semester means and subject to the same bias due to the transition months, but also keeping its representativity with respect to the wet and dry seasons.

With respect to 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 2nd than in the 1st semester. 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 pronounced differences in the corresponding deposition fluxes for most ions due to the inversely

Table 3. The same as Table 2, but for the coarse mode aerosols*. Ti in the 1st semester was not included due to insufficient samples above detection limits to perform component analysis.

	1st semester				2nd semester				
	Saharan dust	Biogenic (total)	Sea salt salt	COM[b]	Saharan dust	Biogenic non absorbing	Sea	Biogenic absorbing	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_E	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*
Cumulative Variance (%)	40	35 (75)	17 (92)		35	29 (64)	17 (81)	10 (91)	

* Loadings smaller than 0.30 were omitted.
[a] CPM is Coarse Particulate Mass concentration
[b] COM is the communality correspondent to the chemical compound

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 $\mu eq\,l^{-1}$, except for DIC expressed in $\mu m\,l^{-1}$.

	This work	Africa Sahelian Savanna[1]	Africa Forest (Zoetele)[2]	South Africa Semi arid[3]	Torres del Paine	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: [1] Galy-Lacaux and Modi (1998); [2] Sigha-Nkamdjou et al. (2003); [3] Mphepya et al. (2004); [4] Galloway et al. (1996); [5] Sanhueza et al. (1992); [6] Likens et al (1987); [7] Elklund et al. (1997); [8] Williams et al. (1997); [9] Andreae et al. (1990).
[a] DIC is *Dissolved Inorganic Carbon*, which is expressed in $\mu m\,l^{-1}$.
[b] DEF is ionic deficit, defined as (Σ cations-Σ anions) and expressed in $\mu eq\,l^{-1}$.

Table 5. Volume Weighted Mean (VWM) concentrations and deposition rates observed in rainwater at Balbina. Results area 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 μeq l^{-1} (except for DIC expressed in μm l^{-1}), and deposition rates in μeq m^{-2} (μM 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
nss-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
nss-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
nss-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
nss-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
nss-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 μeq l^{-1}.
nss is the non-seasalt fraction

proportional rain volume. 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. Further, the higher concentrations in the 2nd semester are likely connected to the less frequent removal of atmospheric particles.

The non-sea salt (nss) fraction for some selected ions is also shown in Table 5. From these results we conclude 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 86 % for SO_4^{2-}, 93 % for K^+, 91 % for Ca^{2+} and 55 % for Mg^{2+}. This is in agreement with the aerosol analysis by APFA, which pointed that K, S, Ca levels are predominantly subject to the combination of biogenic, soil dust and biomass-burning sources (Mg was not included in aerosol APFA). The exception to this pattern was Cl^-, with a 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) and is also in agreement with aerosol analysis of the previous section.

The concentration of oxalate was quite below the concentration of acetate and formate, which is an expected result in a remote site like Balbina. Oxalic acid is usually the most abundant among the dicarboxylic acids in the atmosphere (Kawamura et al., 1996), and in polluted circumstances (which are not our case) it can have concentration levels even higher than the sum of formic and acetic acid (Kawamura et al., 2001). The presence of oxalic acid in Balbina is likely associated to 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., 2005). Oxalic acid is also an end product of several photochemical oxidation reactions (Chebbi and Carlier, 1996) 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 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.

3.2.3 Monthly analysis of rainwater chemistry

In Fig. 7 it is displayed the monthly evolution of VWM and wet deposition fluxes for most of the measured ions. Plots are separated in VWM concentrations on the left and wet deposition fluxes in the right side. As for aerosols, these plots improve the analysis of the annual cycle of the measured ions.

The acidity profile

Except for November that presented a pronounced difference compared to the other monthly means ($25.0\,\mu eq\,l^{-1}$), VWM of H^+ did not vary broadly, ranging between $8.0\,\mu eq\,l^{-1}$ (April) and $15.5\,\mu eq\,l^{-1}$ (January). These rather constant level of H^+ throughout the year resulted in a larger H^+ flux during the wet season months of Jan–May in comparison to the dry season (Aug–Oct) (except for November). This is an important result because, given the clear signature of biomass burning in aerosols, an increase in acidity during the dry season associated to the biomass-burning source was expected.

In the same figure it is shown the annual cycle of SO_4^{2+}, NO_3^-, Acetate (Ac^-) and Formate (Fo^-). It is possible to observe that the VWM of the mineral acidity anions SO_4^{2+}, NO_3^- enhanced their concentrations in dry season, which is an evidence of biomass burning influence. However, this enhancement was not observed in deposition rates, as can be seen in the corresponding plots in the right side of the figure. For example, average monthly deposition for Jan–May was $690 \pm 250\,\mu eq\,m^{-2}$, which is statistically compatible with the observed average for Aug–Oct of $660 \pm 290\,\mu eq\,m^{-2}$. This seasonal difference was not observed in VWM of the organic anions Ac^- and Fo^-, resulting in smaller deposition fluxes of these anions during the dry season.

Sea salt contribution

Na^+ is the most important signature for the seasalt contribution. Clearly, VWM of this ion was higher during dry season, as well as for Cl^-. Nevertheless, deposition rates for Na^+ and Cl^- did not vary broadly during the year, similarly to most of ions. It is also shown in Fig. 7 the monthly mean Cl/Na ratio. It ranged between 1.3–2.1, which is quite close to the Cl/Na ratio in seawater (= 1.17). It corroborates with the assumption stated in the previous section that elemental Cl observed in aerosol is predominantly from marine contribution.

Biomass-burning contribution

With respect to the annual cycle of ions commonly associated to biomass-burning (K^+, SO_4^{2-} and NH_4^+), it is possible to observe that K^+ and SO_4^{2-} presented higher VWM concentrations in the 2nd semester, but did not for deposition rates. For NH_4^+, even a seasonal difference in VWM was not observed. These results make it difficult to conclude something with respect to the actual influence of biomass burning. It seems that the degree of disturbance in the atmospheric budget of aerosols was enough to result in an elevation of the seasonal VWM concentration of ions but not in deposition, which is the case in urban polluted areas where fluxes are quite higher. Previous studies in Amazonia observed a similar pattern. Forti et al. (2000) performed measurements in the Amapá state, in Northern Amazonia. The authors stated that biomass-burning influenced the composition of precipitation based on the seasonal differences in the VWM of K^+, SO_4^{2-}, and Zn^+. However, similarly to this study, they did not observe differences in seasonal deposition rates.

Thus, we state that the measurements were not conclusive with respect to the influence of biomass burning in precipitation chemistry. A clear signal of biomass-burning should appear both in VWM and deposition. It seems that Balbina is a limit case, influenced by distant sources, whose biomass-burning plumes were subject to several physical and chemical processes during its transport. If one considers the VWM as the parameter for decision, there are clear and significant differences comparing K^+, SO_4^{2+} and Cl^-. On the other hand, if deposition be considered as the key parameter it is not conclusive.

Ca^+

In aerosols, Ca was mainly associated to soil dust. Due to the lack of other soil dust tracers in our analysis of rainwater, it was not straightforward to connect Ca^+ to a specific source. As shown below, it was not possible to extract a soil component in the Principal Component Analysis, and Ca^+ appears in the biogenic and organic acidity components. Nevertheless, comparing the annual cycle of Ca in aerosols and in rainwater it is possible to observe that

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.

	Biogenic +sea-salt	Organic acidity	Ammonium oxalate	Phosphate	Citrate	COM*
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	

*COM is the communality correspondent to the related ionic species.

monthly means variation was smoother in rainwater VWM than in the aerosol concentration, and that deposition rates were smaller during the dry season due to the reduced precipitation volume.

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 loading values for Na^+ (0.89) and Cl^- (0.87), while the high loading for K^+ (0.83) 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 could be associated to marine contribution. However, the mean observed proportion of K^+/Na^+ 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, the loading values for SO_4^{2-} (0.85), Ca^{2+} (0.76) and Mg^{2+} (0.79) are also observed, an indication that biogenic processes also play an important role on the deposition of these ions. Their correlations with K^+ were significant ($r = 0.86$, $r = 0.79$ and $r = 0.85$, all with $p < 0.0005$, 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).

The rainwater chemistry second component corresponds to processes related to acidity in rainwater, in particular the organic fraction. The loading values observed for H^+, (0.76) NO_3^- (0.56), acetate (0.84) and oxalate (0.52), indicate 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 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 (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
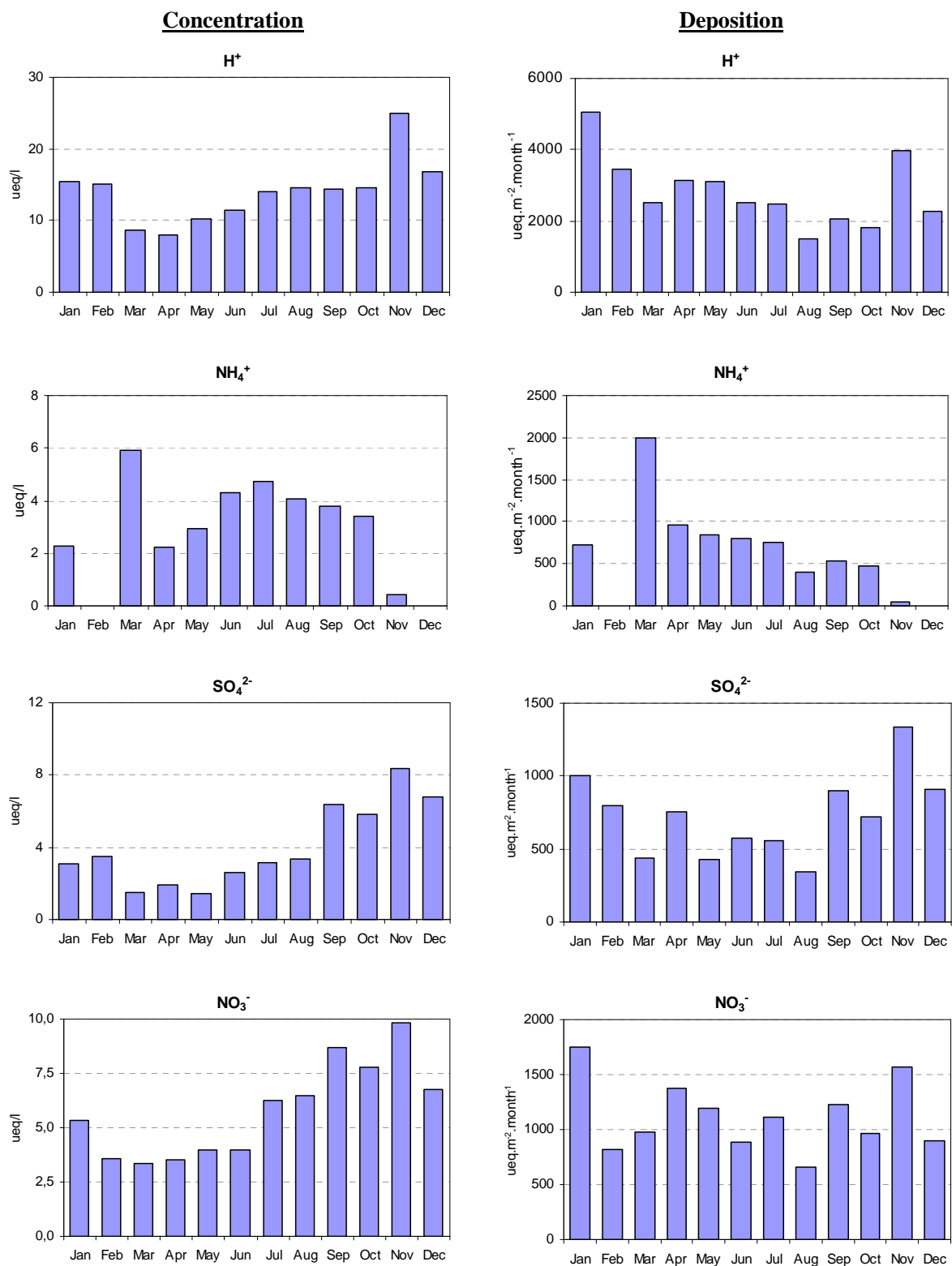
Concentration

Deposition

Fig. 7. Monthly means of observed ionic VWM concentration (left) and deposition (right) in rainwater.

Concentration

Ac⁻

Fo⁻

K⁺

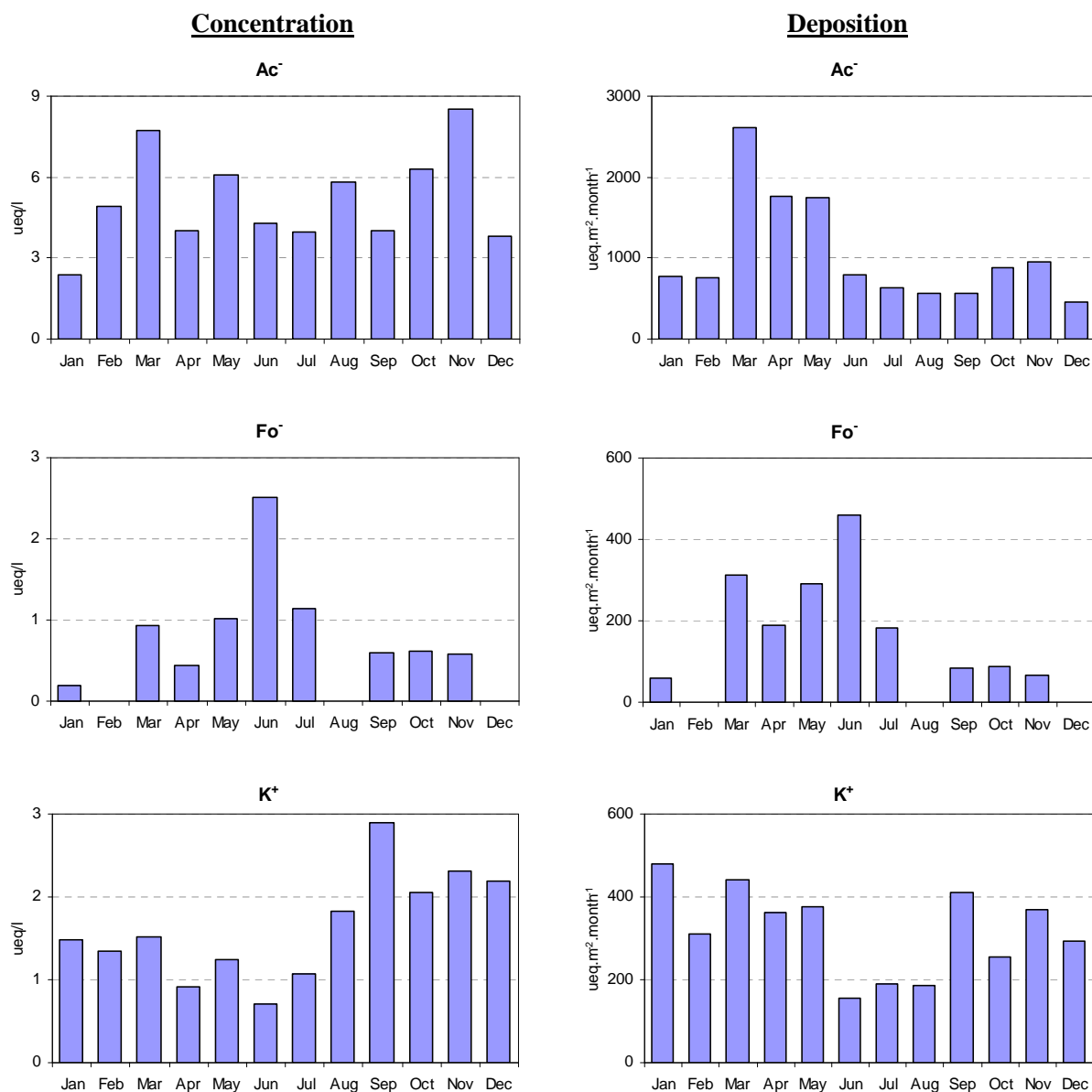## Deposition

Ac⁻

Fo⁻

K⁺

Fig. 7. Continued.

a common feature observed in pristine tropical areas (Sanhueza et al., 1991).

The third component loadings of NH_4^+ (0.91) and oxalate (0.52) indicate 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 PO_4^{3-} and citrate, respectively. 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 previously 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

Concentration

Deposition

Ca²⁺

Ca²⁺

Cl⁻

Cl⁻

Na⁺

Na⁺
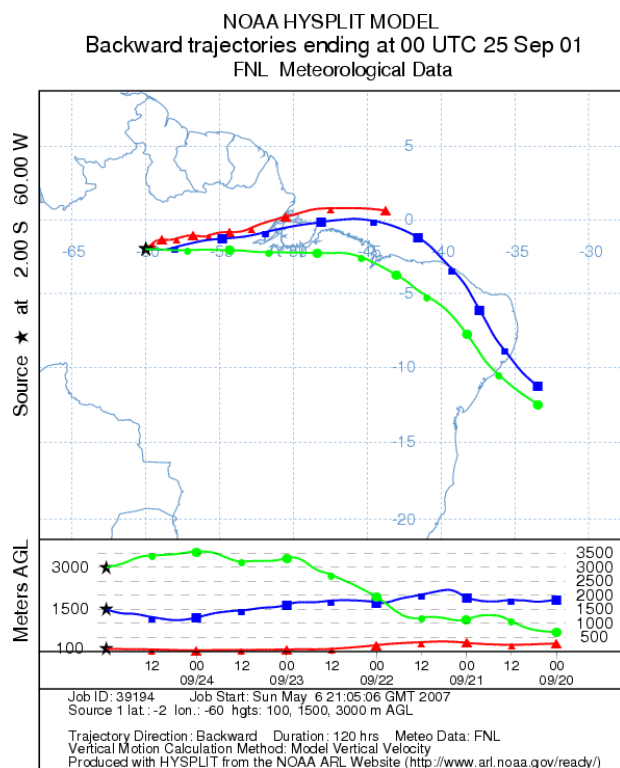
Cl-/Na+
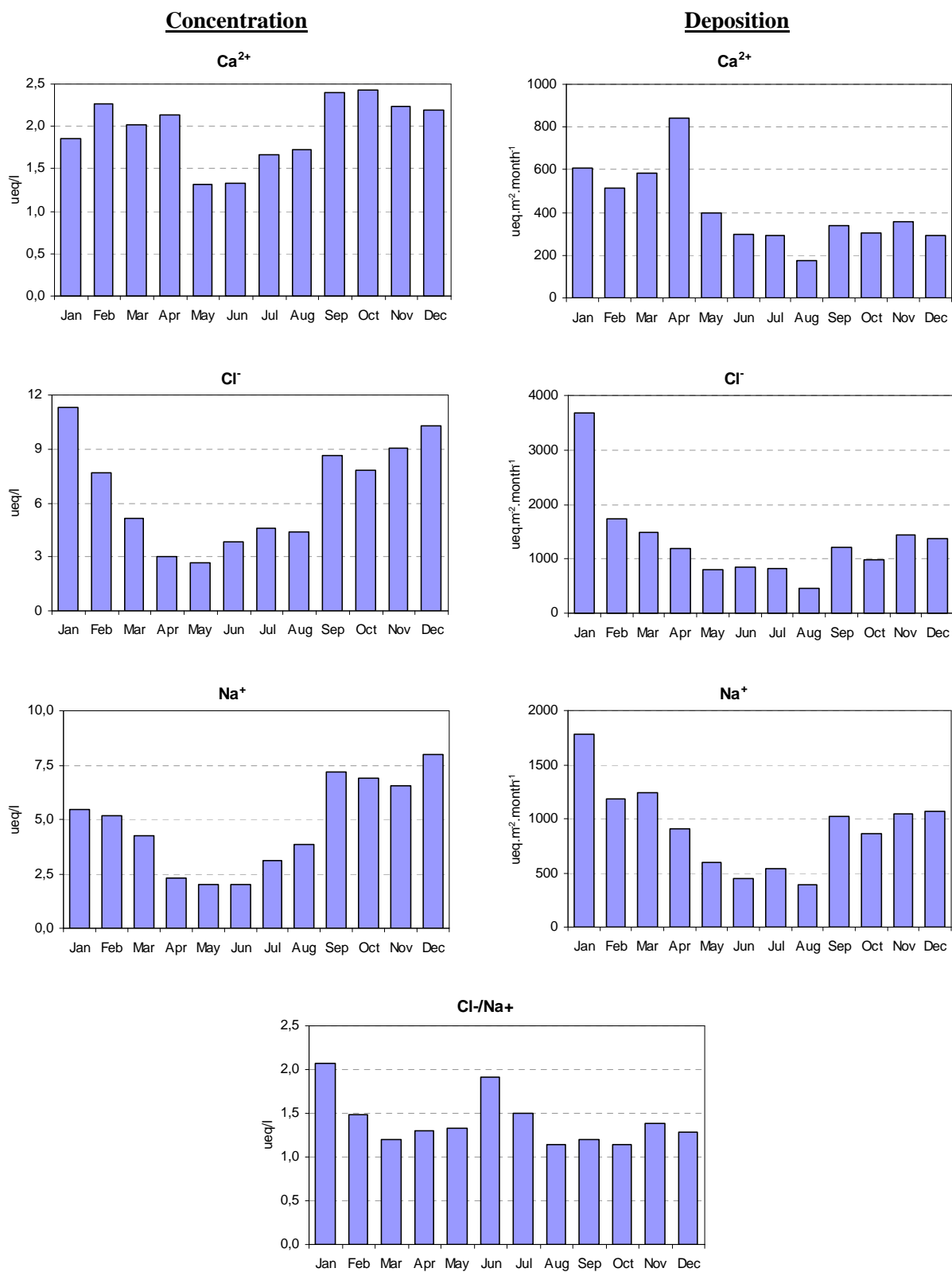
Fig. 7. Continued.

Fig. 8. Hysplit backward trajectories of air masses reaching Balbina at 25 September 2001, when hotspots where observed along the Amazonas river. The resulted wind streamlines are favorable to the transport of biomass-burning plumes to the sampling site.

absence of such measurements of any compound similar to citrate in aerosols.

4 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 during the wet season is predominantly of natural biogenic origin, comprising 90 % of coarse mode and 83 % of fine mode aerosol mass.

Biomass burning emission was the second most important contribution to aerosol mass, acting only during the dry season. This influence was mainly due to the large-scale transport of plumes originated in distant locations that spread over 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. In fact, even during the dry season the average PM_{10} concentration of $8.5\,\mu g\,m^{-3}$, which is a pretty low concentration when compared to other heavily impacted areas of Southern Amazonia. This is because plumes of biomass burning typi-

cally 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 pattern 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 a clear signature of biomass burning in the wet deposition fluxes, thought the VWM of SO_4^{2-}, NO_3^- and K^+, were higher in the dry season. However, the enhancement of these concentrations was not conclusive with respect to the signal of biomass burning because even ions not related to biomass burning also presented higher VWM during the dry season months (e.g. Na^+).

Further, factor analysis applied on rainwater data was unable to extract any component related to biomass burning. A linear relationship between Cl^- and K was observed 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 biogenic processes.

The chemical composition of precipitation and deposition rates in Balbina is typical of the background composition in remote 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 we attributed to marine contribution.

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. It is explained by the absence of a clear soil dust tracer in rainwater as in aerosols (e.g. Al, Fe, Ti, and 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 to biogenic and sea salt and not to 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 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
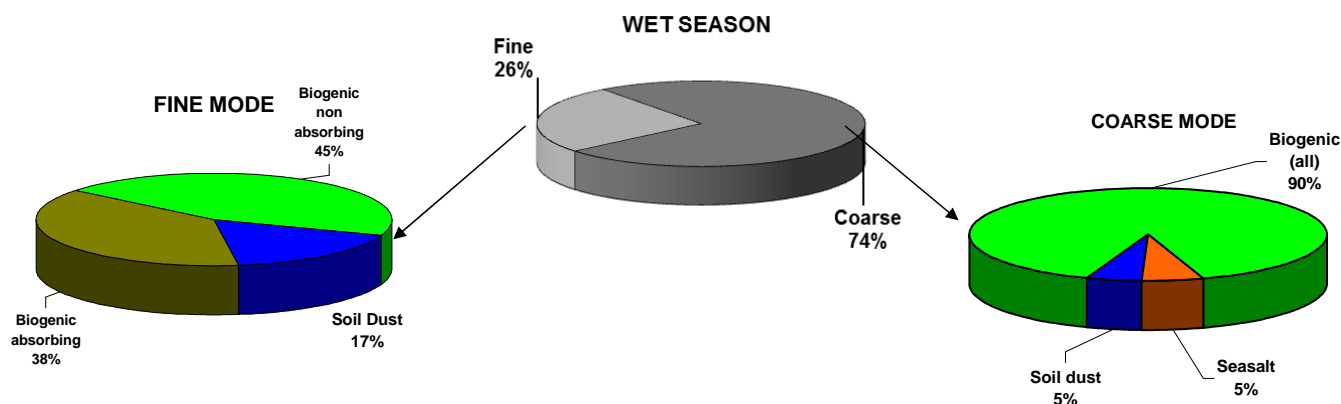
WET SEASON

FINE MODE

Fine
26%

Coarse
74%

Biogenic non absorbing
45%

Soil Dust
17%

Biogenic absorbing
38%

COARSE MODE

Biogenic (all)
90%

Soil dust
5%

Seasalt
5%

Fig. 9. Final result of Absolute Principal Component Analysis: fine/coarse mode partitioning of aerosol concentration during the 1st semester, and the individual contribution for each extracted principal component. The mean concentrations were $6.6 \pm 2.9\,\mu g\,m^{-3}$ for the coarse mode and $2.2 \pm 1.3\,\mu g\,m^{-3}$ for the fine mode.

DRY SEASON

FINE MODE

Fine
48%

Coarse
52%

Biomass burning
77%

Biogenic non absorbing
13%

Seasalt
4%

Soil dust
6%

COARSE MODE

Biogenic non absorbing
83%

Soil dust
7%

Biogenic absorbing
5%

Seasalt
5%
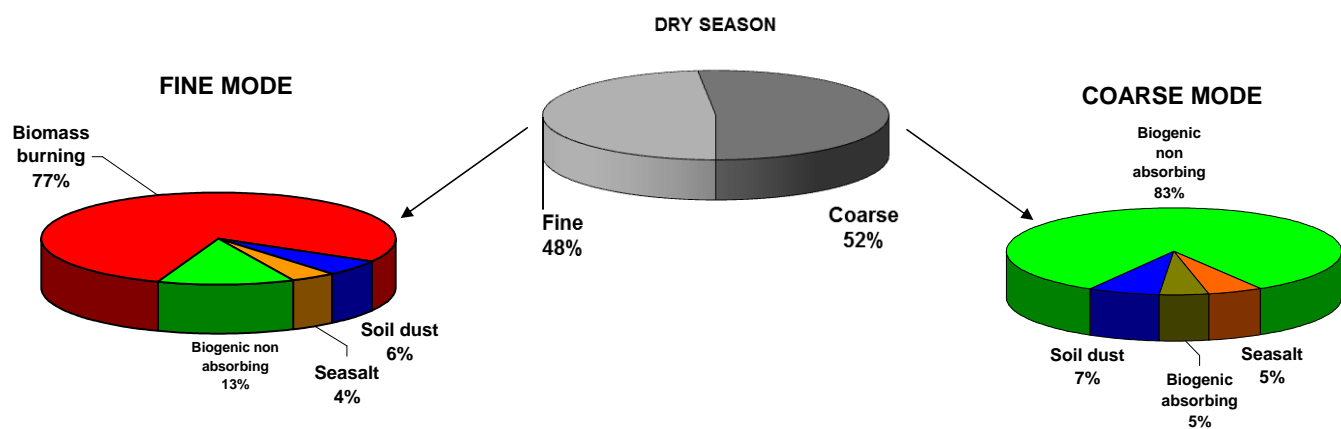
Fig. 10. The same as the previous figure but for the 2nd semester. The mean concentrations were $7.2 \pm 2.1\,\mu g\,m^{-3}$ for the coarse mode and $6.2 \pm 3.1\,\mu g\,m^{-3}$ for the fine mode.

same argument is valid for the 5th rainwater component, associated with citrate.

This study 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 was shown that during the wet season both aerosols and rainwater chemistry are dominated by the biogenic emissions. Biomass-burning plumes advected from other regions of the Amazon starts to have an impact after July. This perturbation extends until December, when the whole basin is in the wet period and biomass-burning emissions are negligible in Amazonia. Coarse mode aerosols did not present any significant influence of biomass-burning, and its profile could be attributed only to natural biogenic sources. Minimum concentrations of particulate matter and concentrations of non-crustal elemental were typically observed in May. On the other hand, the soil tracers Ti, Fe, Al and Si clearly presented higher concentrations during the wet

season months of Jan–Apr in the fine mode. This pattern was attributed to the long range transport of Saharan dust to the Amazon Basin, which is a phenomenon largely documented.

Rainwater presented a similar profile, with no influence of anthropogenic sources in the wet season. Even the influence of biomass-burning during the dry season was not evident, and could be observed only through the enhancement in the ionic concentration of K^+ and SO_4^{2-} but not in the corresponding deposition rates. PCA detected at least three processes (the three last components) that are mutually independent and associated with natural processes that deserve further research. With respect to acidity, it was mostly dominated by weak organic acids, especially acetic and formic acids. The proportion acetic:formate was the contrary of the most commonly reported for other remote sites around the world.

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 were
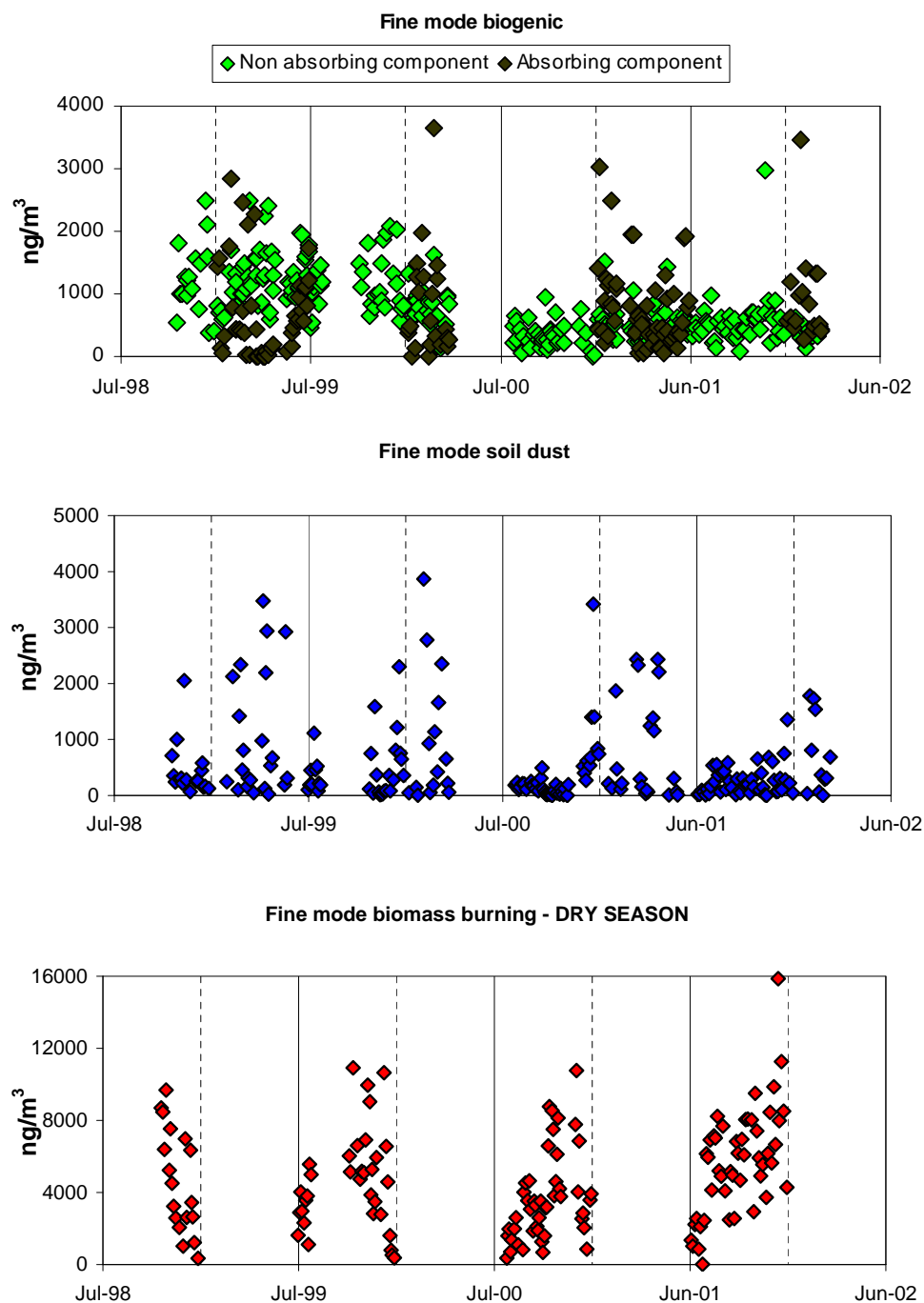
Fig. 11. Absolute concentration of aerosols in the fine mode for each sample, obtained by the APCA technique. Each plot in the figure represents the absolute mass contribution of the identified sources of aerosols: **(a)** Biogenic contribution, separated in absorbing and non-absorbing components, **(b)** Soil dust and **(c)** Biomass burning (Jul–Dec only).

we still can observe quite pristine atmospheric composition, especially in the tropics.
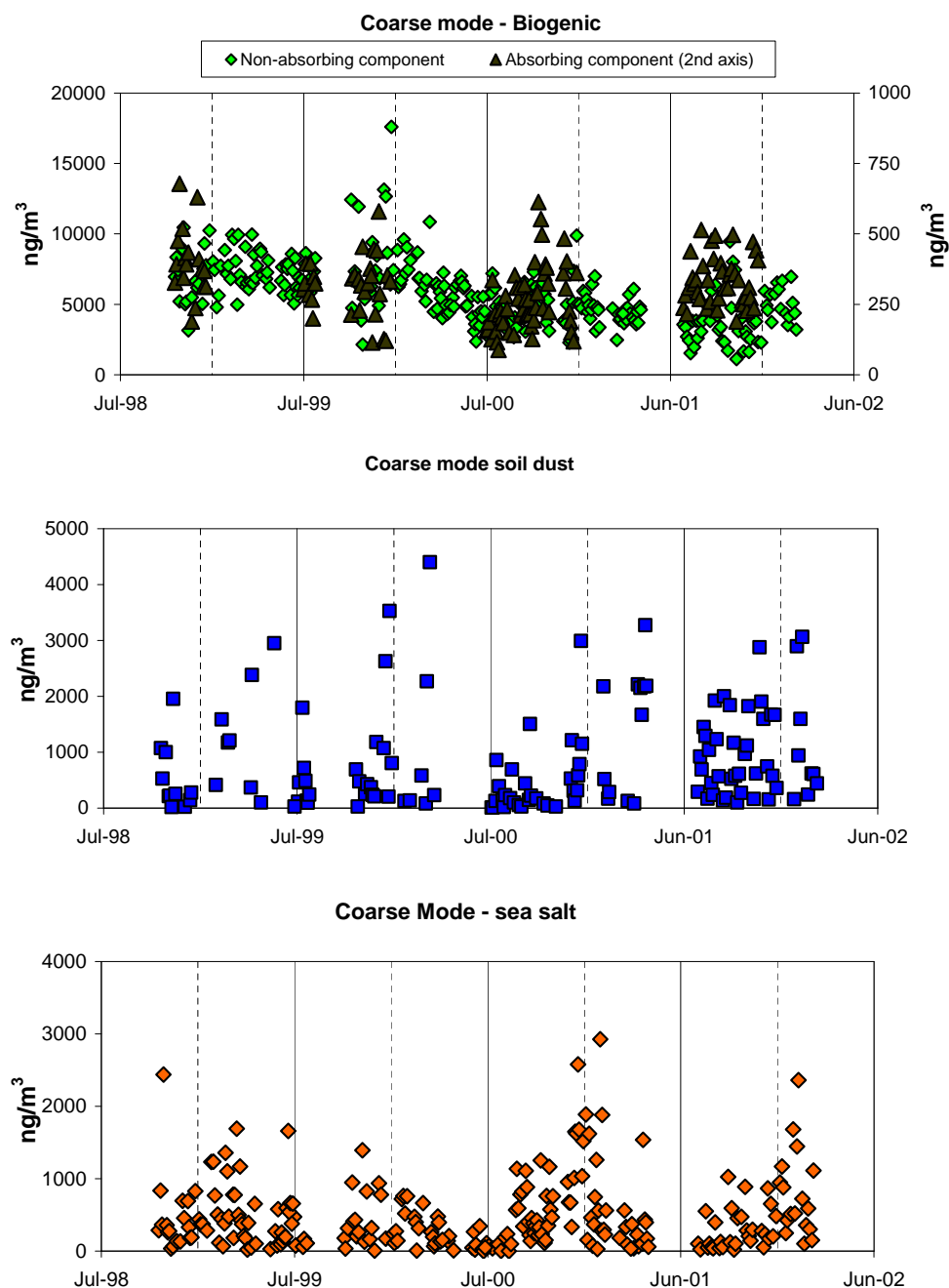
Fig. 12. The same of Fig. 11, but for coarse mode: **(a)** Biogenic contribution, separated in absorbing and non-absorbing components, **(b)** Soil dust and **(c)** Seasalt .

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