



Chemical characterisation of total suspended particulate matter from a remote area in Amazonia



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ABSTRACT

This research had as study object the total suspended particulate matter collected in the Alenquer region, a remote area in the Pará state. The main objectives were the characterisation of the inorganic and organic chemical composition of the aerosol, looking for seasonal patterns and the identification of probable emission sources and formation processes. A set of 30 samples were collected in the rainy (April–May) and dry season (August–September) of 2014. The analytical methods included gravimetric analysis, water-soluble ions analysis by ion chromatography (IC), elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) equipped with collision cell technology, carbonaceous content determination with a thermal-optical system and organic speciation by gas chromatography–mass spectrometry (GC-MS). The average concentrations of particulate matter ranged from $14 \pm 1.3 \mu\text{g}\cdot\text{m}^{-3}$ to $31 \pm 7.8 \mu\text{g}\cdot\text{m}^{-3}$, in the rainy and dry season, respectively. The carbonaceous content represented, on average, approximately 27% and 21% of the particulate matter in the rainy and dry season, respectively. Na^+ , Cl^- , SO_4^{2-} , and NO_3^- yield the highest concentrations in both seasons. Na was the dominant element, reflecting the transport of air masses from the Atlantic. An increase in concentrations between the rainy and dry seasons was especially noted for the terrigenous elements such Mn, Fe and Al. The chromatographically resolved organics included *n*-alkanes, *n*-alkenes, PAHs, *n*-alkanoic acids, *n*-di-acids, resin acids and some phenolic compounds. The primary inputs of organic constituents to the aerosols of Alenquer based on the homologous compound series and biomarkers were: (i) natural emissions from terrestrial higher plants waxes, particularly in dry season; (ii) anthropogenic emissions from diesel fuel combustion and biomass combustion, predominating during the dry season. The chemical characterisation along with the backward trajectory cluster analysis suggests a great influence from natural sources such as marine aerosol, mainly in the rainy season. In the dry season, the region is also affected by soil dust re-suspension and some biomass burning.

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1. Introduction

Amazonia is simultaneously a natural and anthropogenic source of aerosols. Its tropical location, the flora and fauna variety and the intense metabolism of all living beings, make the Amazonia a natural source of aerosols. It is also a source of anthropogenic particles, especially during the dry season, due to forest fires (in pasture areas and primary forest), dust resuspension as a result of agricultural, deforestation and urban activities (Andreae and Crutzen, 1997). All the chemical compounds arising from such processes can reach high altitudes and be carried to long distances. Consequently, Amazonia can be recognised as one of the major direct sources of aerosol particles (mainly organic aerosols)

to the global atmosphere (Andreae et al., 2002; Crozat, 1979). The Amazonia region is also affected by aerosol particles resulting from long-distance transport, such as mineral dust and biomass burning particles from North Africa, and marine particles with Atlantic origin (Artaxo et al., 2002; Chen et al., 2009; Guyon et al., 2003; Swap et al., 1992). Atmospheric processes are major drivers of climate variability and interact with diverse components and functions of ecosystems at various scales. Aerosols affect the Earth's climate both directly (by scattering and absorbing radiation) and indirectly (by serving as nuclei for cloud formation). They provide sites for surface chemistry and condensed-phase chemistry to take place in the atmosphere. Aerosol particles also exert a fundamental role in the biogeochemistry of ecosystems and nutrient cycles (Artaxo et al., 2002). In remote areas of Amazonia, the two main sources of natural aerosol particles are the direct emission of biogenic particles, and the oxidation of volatile

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organic compounds (VOC) emitted by the vegetation which are subject to chemical and photochemical processes giving rise to new aerosol particles. Despite the relatively vast area of tropical forests, throughout the years, only a few studies involving the chemical characterisation of natural aerosol particles in remote areas of Amazonia rain forest have been undertaken. Most studies have focused on the inorganic composition, encompassing elements and ions (Artaxo et al., 1990; Artaxo and Hansson, 1995; Gonçalves and Figueiredo, 2015; Echalar et al., 1998; Graham et al., 2003a). Studies focused on the organic components of aerosol particles are even more limited (Claeys et al., 2004; Graham et al., 2003b; Kesselmeier et al., 2000; Simoneit et al., 1990; Vasconcellos et al., 1998). Furthermore, Amazonia has been subject to an intensive process of land use and human activities change, even in some of these more remote areas. Baseline knowledge of the source strengths, properties and processes of aerosols is necessary to correctly assess present-day burdens and contribute with new data for the maintenance and preservation of this territory in the future.

The city of Alenquer was chosen to carry out this study because of its remote location and low anthropogenic influence, which makes it a suitable place to understand the natural characteristics of the region. It may be considered a natural laboratory for understanding the effects of anthropogenic pollution on the aerosol life cycle in the tropics. The main objectives were to accomplish a detailed chemical characterisation of the total suspended particulate matter (TSP), to look for seasonal patterns and to identify potential emission sources and formation processes.

2. Methodology

2.1. Studied area and sampling details

The sampling station was located near the Uruxi lake (01°57'49" S, 54°41'41"W), 7 km from Alenquer and about 12 m above sea level

(Fig. 1). Alenquer is located in the Lower Amazon mesoregion of the Para state and has 54,353 inhabitants (IBGE, 2015). The Amazon River and Uruxi lake are in the southwest and east of the study area, respectively. Alenquer's economy is based in activities such as services, agriculture and cattle raising, industry (dairy cooperative, timber extraction and ice production) and traditional fishing (Silva Junior and Szlafsztein, 2013). A meteorological station was installed for the characterisation of meteorological parameters such as temperature, relative humidity and precipitation. All meteorological parameters were continuously measured using a Campbell Scientific data logger CR1000 model, a multi-parameter sensor Vaisala WX520 and a Campbell solar panel 10 W. In Northern Brazil the seasons are differentiated according to the monthly distribution of rainfall: the rainy season occurs between November and May, being March and April the wettest months; the dry season occurs between June and October, being August the month with the lowest rainfall (Arana and Artaxo, 2014; Falesi, 1971). Taking this into account, two sampling campaigns were carried out: the first campaign took place between April 20 and May 5 of 2014, coinciding with the rainy season; the second campaign was conducted between August 18 and September 2 of 2014, coinciding with the dry season. A total of 30 samples were obtained. The particulate material was collected on quartz fibre filters (Whatman) with a high volume sampler for TSP (flow rate: $\sim 1.5 \text{ m}^3 \text{ min}^{-1}$) for 24 h periods. Following the sample collection, filters were stored in a freezer (at $-14 \text{ }^\circ\text{C}$) prior to analysis. To better understand the influence of atmospheric transport on aerosol properties, backward trajectory cluster analysis was carried out using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model developed by NOAA's Air Resources Laboratory (Draxler and Hess, 1997, 1998) with meteorological data from GDAS (Global Data Analysis System). Ten days (240 h) backward trajectories ending at the sampling place were calculated.

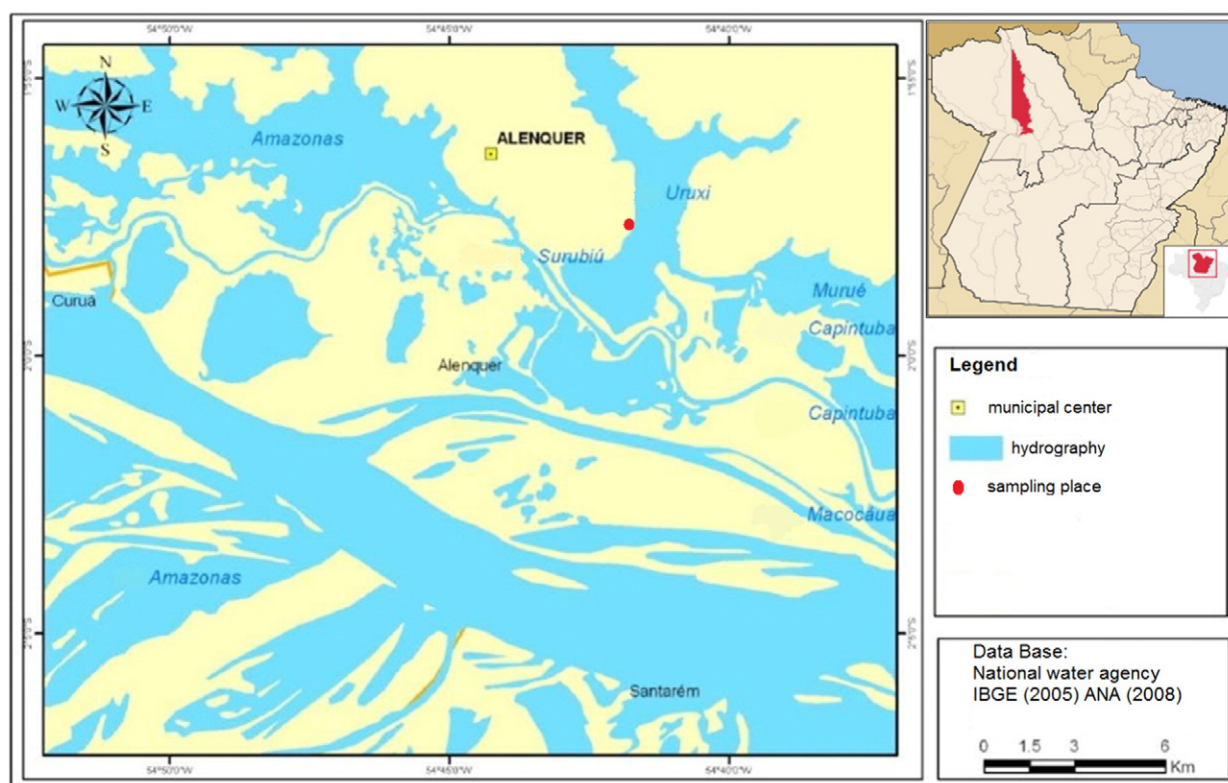


Fig. 1. Sampling place and Alenquer city location map. (adapted from Silva Junior and Szlafsztein, 2013)

2.2. Analytical methods

Gravimetric analysis was performed with a microbalance (Sartorius CP225D) after 24 h equilibration in a room with controlled temperature and relative humidity (20 ± 2 °C; 50 ± 5 %). Quartz fibre filters used in this study were placed in an oven at 500 °C for 6 h, to remove organic contamination, before use. Filter weight before and after sampling was obtained as the average of several measurements, when observed variations were <5%.

After sampling, the filters were subjected to different types of analyses that allowed the inorganic and organic characterisation of total suspended particulate matter.

The determination of water soluble ions was carried out by ion chromatography (IC). The solution obtained after extraction with 20 mL of ultra-pure deionised water was filtered with PTFE syringe filter with a pore size of 0.45 μm (VertiClean™) and subsequently analysed in a Thermo Scientific Dionex™ ICS-5000 Ion Chromatography. The filter extracts were analysed for Cl^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . For anions, the following components were used: IonPac AS19 Capillary Column (0.4 \times 250 mm) in combination with the AG19 Guard Column (0.4 \times 50 mm), Anion Capillary Electrolytic Suppressor (ACES™ 300) and Eluent Generator Cartridges (EGC) for the generation of potassium hydroxide (KOH) with concentrations between 2 and 50 $\text{mmol}\cdot\text{L}^{-1}$. The runs lasted 30 min with a flow of 0.010 $\text{mL}\cdot\text{min}^{-1}$ and the following concentrations' slope: 0–10 min (2–10 $\text{mmol}\cdot\text{L}^{-1}$); 10–20 min (10–45 $\text{mmol}\cdot\text{L}^{-1}$); 20–21 min (45–50 $\text{mmol}\cdot\text{L}^{-1}$); 21–21.1 min (50–2 $\text{mmol}\cdot\text{L}^{-1}$) and 21.1–30 min (2–2 $\text{mmol}\cdot\text{L}^{-1}$). For cations, the components were as follows: IonPac CS12A Capillary Column (2 \times 250 mm) in combination with the CG12A Guard Column (2 \times 50 mm), Cations Capillary Electrolytic Suppressor (CCES™ 300) and Eluent Generator Cartridges (EGC) for the generation of methanesulfonic acid (MSA) at a concentration of 20 $\text{mmol}\cdot\text{L}^{-1}$ and a flow of 0.25 $\text{mL}\cdot\text{min}^{-1}$ throughout the 17 min run. For both determinations, the injection was made by the Automatic Sampling System (Dionex AS-AP) with a high performance conductivity detector. Data were treated with the Chromeleon 6.8 software. For the equipment calibration, analytical curves were constructed for each of the ionic species, obtaining for each curve 7 concentration points (in triplicate) at the following concentrations: 0.2; 0.4; 0.6; 0.8; 1.0; 2.0 e 3.0 $\text{mg}\cdot\text{L}^{-1}$. The detection limits (of the mass of 8 blank filters) were estimated to be 0.17 $\mu\text{g}\cdot\text{mL}^{-1}$ for Na^+ , 0.01 $\mu\text{g}\cdot\text{mL}^{-1}$ for NH_4^+ , 0.17 $\mu\text{g}\cdot\text{mL}^{-1}$ for K^+ , 0.01 $\mu\text{g}\cdot\text{mL}^{-1}$ for Mg^{2+} , 0.07 $\mu\text{g}\cdot\text{mL}^{-1}$ for Ca^{2+} , 0.003 $\mu\text{g}\cdot\text{mL}^{-1}$ for Cl^- , 0.03 $\mu\text{g}\cdot\text{mL}^{-1}$ for NO_3^- , 0.33 $\mu\text{g}\cdot\text{mL}^{-1}$ for PO_4^{3-} , 0.11 $\mu\text{g}\cdot\text{mL}^{-1}$ for SO_4^{2-} and 0.13 $\mu\text{g}\cdot\text{mL}^{-1}$ for $\text{C}_2\text{O}_4^{2-}$.

Approximately 1/8 of the filter was extracted to analyse elements by inductively coupled plasma mass spectrometry (ICP-MS) equipped with collision cell technology (CCT) (Xseries II-Thermo Scientific). The filters were extracted with a diluted acid solution (HNO_3 , 1%), remaining for 5 h in a mechanical shaker (115 rpm) at room temperature, for a better removal of elements to the solution. Before ICP-MS analysis, the samples were filtered with PTFE syringe filters with a pore size of 0.45 μm (VertiClean™). This analytical technique allowed the determination of 57 different elements, but only 13 elements were quantified in this study. The detection limits (of the mass of 8 blank filters) were estimated to be 0.4 $\text{ng}\cdot\text{mL}^{-1}$ for Al, 9.0 $\text{ng}\cdot\text{mL}^{-1}$ for Ca, 0.05 $\text{ng}\cdot\text{mL}^{-1}$ for Cu, 29 $\text{ng}\cdot\text{mL}^{-1}$ for Fe, 47 $\text{ng}\cdot\text{mL}^{-1}$ for K, 0.2 $\text{ng}\cdot\text{mL}^{-1}$ for Mg, 0.03 $\text{ng}\cdot\text{mL}^{-1}$ for Mn, 2.0 $\text{ng}\cdot\text{mL}^{-1}$ for Na, 0.002 $\text{ng}\cdot\text{mL}^{-1}$ for Pb, 0.01 $\text{ng}\cdot\text{mL}^{-1}$ for Rb, 0.009 $\text{ng}\cdot\text{mL}^{-1}$ for Sr, 0.08 $\text{ng}\cdot\text{mL}^{-1}$ for Ti and 0.004 $\text{ng}\cdot\text{mL}^{-1}$ for Zn. The same analytical method has been previously applied to quartz filters for the determination of elements (Puxbaum et al., 2004; Vasconcellos et al., 2007). For quality control, all analyses were performed in triplicate (IC) and duplicate (ICP-MS). The blank values for ions and elements were subtracted from the sample results. For ions the uncertainties were in the range of 0.1–4.1%. For elements the uncertainties were in the range of 0.5–4.9%.

For the determination of the carbonaceous content, small discs with 9 mm diameter were punched out of the quartz fibre filters. The carbonaceous content (organic carbon (OC), elemental carbon (EC)) of particulate matter was measured with a homemade thermal-optical system, based on the thermal desorption/oxidation of particulate carbon to CO_2 , which is subsequently analysed by non-dispersive infrared (NDIR) CO_2 analyser. Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilization at $T < 200$ °C of lower molecular weight organics (OC_1). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 200 to 600 °C (OC_2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2 . This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance (Alves et al., 2011; Pio et al., 2011; Vicente et al., 2013).

TSP composite samples were subjected to detailed organic analysis by gas chromatography–mass spectrometry (GC–MS). Based on the determined OC content of collected samples, 3 to 4 consecutive filters were pooled, resulting in 4 sets of samples for each period studied (ALH1 to ALH4 - rainy season; ALS1 to ALS4 - dry season). The combined portions of the filters were consecutively extracted with dichloromethane and methanol (Fisher Scientific) and the total organic extract was separated into five different organic fractions by flash chromatography with activated silica gel and different solvents of increasing polarity. After elution, the obtained extracts were vacuum concentrated and evaporated to approximately 1 mL using a rotary evaporator and then dried under a gentle ultra-pure nitrogen flow. The description of the methodology for the organic compounds extraction can be found in Alves et al. (2011). The fractionated extracts were analysed with a Gas Chromatography model 6890, quadrupole Mass Spectrometry Detector 5973 from Hewlett Packard and with a Shimadzu QP5050A gas chromatography–mass spectrometer (GC–MS) with automatic injection. Before injection, the compounds with hydroxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). The GC–MS calibration was performed with injection of about 110 standards in different concentration ranges and relative response factors calculated for each compound and for each organic class. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds with similar chemical structure and retention time. Standards and samples were both co-injected with one internal standard: Tetracosane- d_{50} (Sigma Aldrich). Compounds identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns. The quantitative analysis was performed by both single ion monitoring (SIM) and total ion chromatogram (TIC) methods, in two separate GC runs. The blank filters were analysed in the same way as for the samples and the data obtained were subtracted from the samples in order to obtain blank-corrected results. To test the recoveries, blank filters previously spiked with five different known concentration ranges of representative organic standards were extracted and analysed. For the whole procedure (extraction and analysis), reproducible results of $95 \pm 3.9\%$ and $96 \pm 5.8\%$ were obtained for polar and non-polar compounds, respectively. In the case of levoglucosan, the extraction and fractionation procedure enabled a recovery of $91 \pm 11\%$. The overall inaccuracy of the calibration procedure did not

exceed 14% for the aliphatic fraction, 15% for polycyclic aromatic compounds, 15% for acids and 12% for sugars.

3. Results and discussion

3.1. Meteorological conditions and air mass trajectories

The Alenquer region, due to its location, has equatorial climate, which is characterised as hot and humid, characteristic of Tropical Forests, not subject to significant changes in temperature. The temperature, relative humidity and precipitation mean values obtained during the rainy season campaign were 26.8 °C, 80% and 12 mm, respectively. The rainiest days were 25 and 27 April with 44 mm and 35 mm, respectively. During the dry season campaign the mean values obtained for temperature, relative humidity and precipitation were 27.4 °C, 69% and 2 mm, respectively. The rainiest day was 30 August with 15 mm. Two tables with complete data for meteorological parameters are attached as supplementary material (Tables 1S and 2S). The sampling place shows low anthropogenic influence coming from Alenquer, because the prevailing wind, SE-E, reaches the sampling site before reaching the city. Backward trajectory cluster analysis was carried out by using the HYSPLIT model. The 10 days (240 h) backward trajectories were clustered after calculation. Each cluster is formed by similar trajectories and represents a possible pattern of air-mass behaviour over the studied area. The details of the programme are given in Draxler (1999). Fig. 2 shows the average trajectories of the four clusters retained for the two studied seasons. During the rainy season, the Alenquer region was mostly affected by air masses with Atlantic origin (96% of backward trajectories) that develop along the Amazon River (Fig. 2a). According to Fig. 2b, during the dry season the situation was quite different, with most of the backward trajectories passing through several northern states of Brazil, before arriving at the study site.

3.2. Total suspended particulate matter and carbonaceous content

TSP concentrations varied between 12 and 17 $\mu\text{g}\cdot\text{m}^{-3}$ and between 16 and 43 $\mu\text{g}\cdot\text{m}^{-3}$, in the rainy and dry season, respectively. A substantially higher mean concentration ($31 \pm 7.8 \mu\text{g}\cdot\text{m}^{-3}$) was obtained for

the dry season in comparison with the wet season ($14 \pm 1.3 \mu\text{g}\cdot\text{m}^{-3}$) (Fig. 3).

The carbonaceous content (TC = OC + EC) represented, on average, approximately 27% and 21% of the particulate matter in the rainy and dry season, respectively (Fig. 3). In the rainy season, the OC concentrations varied between 2.2 and 4.7 $\mu\text{g}\cdot\text{m}^{-3}$, with an average of $3.3 \pm 0.63 \mu\text{g}\cdot\text{m}^{-3}$, whilst EC presented values between 0.21 and 0.58 $\mu\text{g}\cdot\text{m}^{-3}$, averaging $0.37 \pm 0.10 \mu\text{g}\cdot\text{m}^{-3}$. In the dry season, the OC concentrations varied between 3.5 and 10 $\mu\text{g}\cdot\text{m}^{-3}$, with an average of $5.5 \pm 2.2 \mu\text{g}\cdot\text{m}^{-3}$. EC varied between 0.40 and 2.03 $\mu\text{g}\cdot\text{m}^{-3}$, averaging $0.96 \pm 0.50 \mu\text{g}\cdot\text{m}^{-3}$. The origin of carbonaceous particles can be assigned on the basis of the relation between OC and EC. Since EC is predominately emitted from primary combustion sources, it has often been used as a tracer to estimate primary OC (Cao et al., 2004). High OC–EC correlations ($R^2 = 0.89$) (Fig. 1Sb)) in dry season indicates that the relative rates of EC and OC emission would be proportional to each other and common sources and transport processes for both carbonaceous species. The very weak correlation between OC and EC ($R^2 = 0.07$) (Fig. 1Sa)) in the rainy season, suggests that OC and EC fractions were not contributed by a single primary source rather could be related to multiple sources, and a dissimilar influence of meteorological factors on the two carbonaceous constituents (Kumar and Yadav, 2016). OC/EC ratios exceeding 2.0 have been used to identify secondary organic aerosol (SOA) formation by chemical reactions in the atmosphere (Alves et al., 2007). During the rainy season, OC/EC ratios ranged from 6 to 15, with an overall average of 9. In the dry season, OC/EC ratios ranged between 4 and 9, averaging 6.

TSP, OC and EC average concentrations from this study are compared in Table 3S (table with more complete data attached as supplementary material) with those from other studies made in the Amazon basin. It is necessary to note that in addition to variations in the concentration values from place to place; different sampling techniques and analytical methods can lead to some disparities.

The TSP levels are comparable to those described by Martin et al. (2010), for the Santarem region, mean values between 2 and 10 $\mu\text{g}\cdot\text{m}^{-3}$ for the fine and coarse fractions and between 25 and 40 $\mu\text{g}\cdot\text{m}^{-3}$ for the fine and coarse fractions, for rainy and dry season,

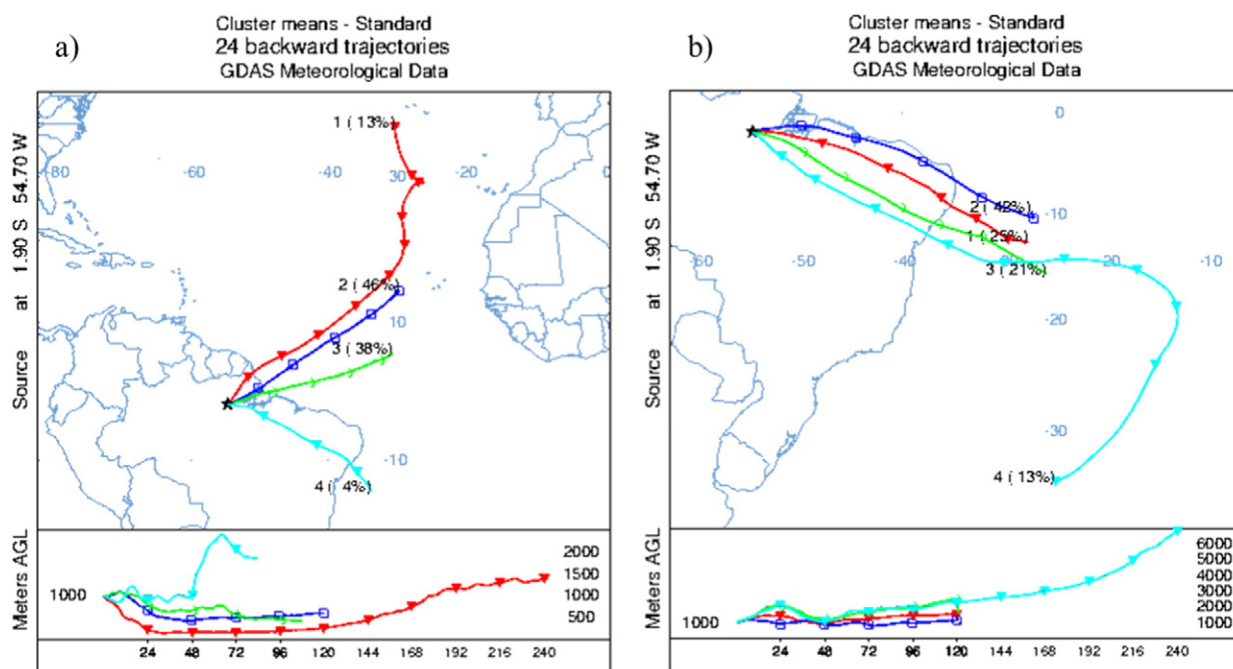


Fig. 2. HYSPLIT model backward trajectories arriving at Alenquer area in two different periods, rainy season (Fig. 2a) and dry season (Fig. 2b).

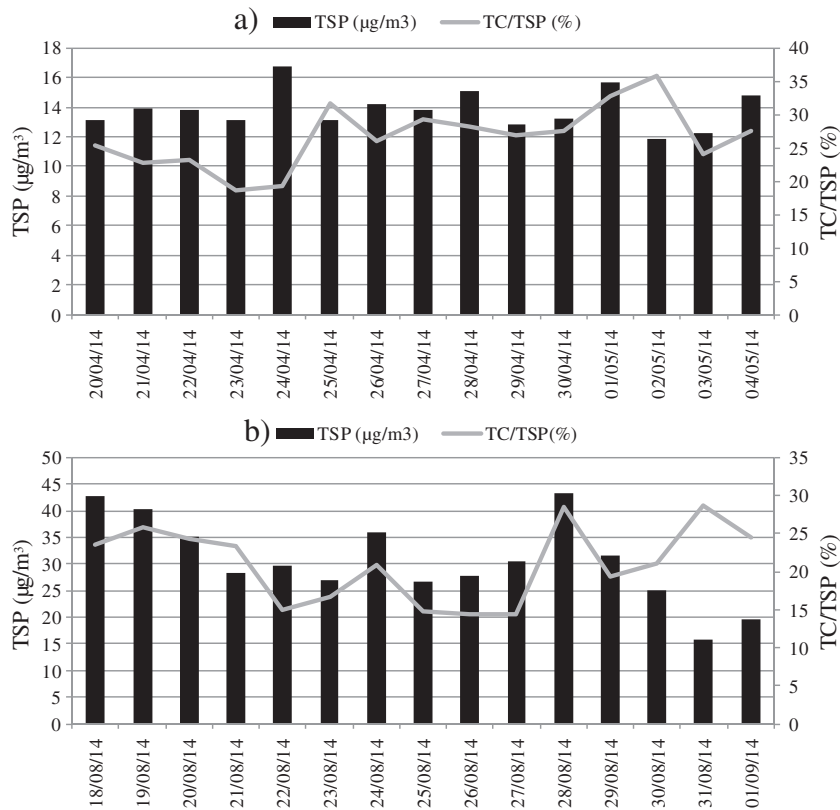


Fig. 3. Variation of aerosol mass and percentage of total carbon in TSP, rainy season (Fig. 3a) and dry season (Fig. 3b).

respectively (Table 3S). The TSP values are also in accordance with the data described by Formenti et al. (2001) for Balbina region during the so-called “dusty period”. During the rainy season (December–April), the Intertropical Convergence Zone (ITCZ) (i.e., the confluence between the northeastern and southeastern trade winds extending from West Africa to South America) has an important influence in the northern and central Amazonia. Mineral dust and biomass burning particles from Africa reach the northern coast of South America when the ITCZ is located to the south of the equator between December and April (Formenti et al., 2001; Swap et al., 1992). During those periods, in Balbina, mean values between 8.4 and 18 $\mu\text{g}\cdot\text{m}^{-3}$ for the fine and coarse particle fractions were, respectively, were registered (Formenti et al., 2001).

The carbonaceous content in the Alenquer particulate matter is higher than values observed in central Amazonia (Balbina), regardless of the season, and also than values observed in southern Amazonia (Fazenda Nossa Senhora Aparecida and Reserva Biológica Jarú) during the rainy season (Table 3S). These facts may be related with the long-distance transport and with the burning episodes which affect the study area.

3.3. Inorganic speciation of total particulate matter

The average concentrations of water-soluble ions for rainy and dry season are presented in Table 1. Tables with complete data are attached as supplementary material (Tables 4S and 5S). The ionic balance was calculated to assess the quality of the data. In both campaigns 70% of the samples showed satisfactory values. Satisfactory values correspond to a variation within $\pm 10\%$ range (Feitosa and Manoel Filho, 1997). In analytical terms, this indicates that the data are reliable. The water-soluble ions accounted for about 3 to 14% of the concentration of TSP, with an average of 7%, during the rainy season. In the dry season they represent about 7 to 32% of TSP, averaging 18%. In the rainy season the

dominant ions were SO_4^{2-} , Na^+ , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ and Cl^- . In the dry season, there was an average concentrations increase of all ions, but especially the Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} (Table 1).

In the rainy season, the Na^+ , Cl^- and Mg^{2+} were strongly correlated ($R^2 > 0.90$) indicating the same emission source. The average ratio Na^+/Cl^- of 1.3 is within the typical range (0.5–1.5) (Chesselet et al., 1972) associated with a marine source. In the dry season, the Na^+ and Cl^- remain well correlated ($R^2 = 0.91$), but the average ratio $\text{Na}^+/\text{Cl}^- = 3$ is out of this range, indicating an enrichment of Na^+ , probably from soil. In the rainy season, secondary species, such as SO_4^{2-} and NO_3^- resulting from the oxidation of SO_2 and NO emissions, exhibit a good correlation ($R^2 = 0.83$). In the dry season, the NO_3^- and SO_4^{2-} have lower correlation with each other ($R^2 = 0.74$), which may indicate different origins other than the marine. The K^+ average concentration increased from 120 $\text{ng}\cdot\text{m}^{-3}$ in the rainy season to 340 $\text{ng}\cdot\text{m}^{-3}$ in the dry season. Since the studied region is strongly affected by marine aerosol, especially in the rainy season, and the sea salts are one of the main contributors to ionic species, the input from other sources excluding marine aerosol can be estimated, using the concentrations of non-sea-salt-potassium

Table 1

Average concentration and standard deviations for water-soluble ions by season.

Water-soluble ions ($\text{ng}\cdot\text{m}^{-3}$)	Rainy season ($n = 15$)	Dry season ($n = 15$)
Na^+	142 \pm 126	1267 \pm 822
NH_4^+	n.d.	63 \pm 45
K^+	120 \pm 26	340 \pm 115
Mg^{2+}	24 \pm 14	222 \pm 68
Ca^{2+}	45 \pm 41	161 \pm 92
Cl^-	127 \pm 135	954 \pm 1020
NO_3^-	139 \pm 81	1004 \pm 437
SO_4^{2-}	173 \pm 105	1256 \pm 422
$\text{C}_2\text{O}_4^{2-}$	139 \pm 13	n.d.
PO_4^{3-}	43 \pm 37	256 \pm 165

n.d. – not detected.

(nss-K⁺) and non-sea-salt-sulphate (nss-SO₄²⁻) as expressed by the following formulas: $C_{\text{nss-K}}^+ = C_K^+ - 0.0355 * C_{\text{Na}}^+$ and $C_{\text{nss-SO}_4}^{2-} = C_{\text{SO}_4}^{2-} - 0.2455 * C_{\text{Na}}^+$ (Lai et al., 2007). High ratios of nss-SO₄²⁻ to SO₄²⁻ (82% - rainy season; 76% - dry season) suggest that sea salt was not the main carrier of particulate sulphate in both seasons. Furthermore, the very high ratios of nss-K⁺/K⁺ (96% - rainy season; 85% - dry season) are likely associated with other emissions, such as biomass burning, instead of sea salt contribution. This hypothesis is supported by the reasonable correlation observed between nss-K⁺ and OC (R² = 0.44 - rainy season; R² = 0.47 - dry season) (Fig. 2Sa) and b)) indicating that a substantial part of OC is from biomass burning. The average K⁺/OC ratios in Alenquer varied from 0.04 to 0.06 in the rainy and dry seasons, respectively. These ratios are comparable to those calculated from emission factors reported by Andreae and Merlet (2001) for tropical forest (average 0.06).

Although in the wet season large wildfire events are not expected, small scale burnings are likely to occur. In the dry season, the sulphate mean concentration is higher due to much less wet scavenging, as well as to the biomass burning particles from nearly 4474 forest fires in the Pará state and in the other large states (Maranhão, Tocantins, Bahia, Piauí and Ceará), whose plumes may have somehow reached the Alenquer sampling site (INPE, 2015) (Fig. 2b).

NH₄⁺ / (NO₃⁻ + SO₄²⁻) lower than 0.5 in both seasons indicate that HNO₃ and H₂SO₄ cannot be fully neutralised by ammonia. Neutralisation is mainly performed by mineral aerosols coming from soil. In the dry season, Ca²⁺ and Mg²⁺ do not correlate, probably due to the fact that Mg²⁺ is in part coming from sea salt and not entirely from soil. This assumption is corroborated by the reasonable correlation between Mg²⁺ and Cl⁻ (R² = 0.58) (Fig. 3Sa)). Although Ca²⁺ may be partially associated with marine aerosols, the lack of correlation with both Na⁺ and Cl⁻ suggest a major origin in soil.

The average concentrations of principal elements for rainy and dry season are presented in Table 2. Tables with complete data are attached as supplementary material (Tables 6S and 7S).

With regard to the mean concentrations of elements, Na, Ca and K were predominant, in the rainy season. Except for Cu and Zn, in the dry season, in general, increased concentrations of all elements were observed, especially for Mn, Fe and Mg. The Ca (rainy season: 229 ng·m⁻³; dry season: 209 ng·m⁻³) and Cu (rainy season: 96 ng·m⁻³; dry season: 89 ng·m⁻³) mean concentrations do not show any seasonal trend. Regarding Ca, it could not be established correlations with any other element to explain its origin. Its constant presence in the two seasons may be justified because it is a natural element from the soil. Copper was detected at appreciable amounts. Although it has been pointed out as a good tracer in urban environments for non-exhaust vehicle emissions (Alves et al., 2015; Calvo et al., 2013), Cu has been identified as biogenic aerosol in Amazonia (Guyon et al., 2003). In this study, the Cu high concentrations observed in can be justified with the use of soil correction products. As observed

for the corresponding water soluble ions, Na and Mg were strongly correlated in rainy (R² = 0.95) and dry (R² = 0.98) season (Fig. 4Sa) and b)). In general, the individual elemental concentrations obtained in this study are quite comparable to the values reported by Artaxo et al. (1988, 1990), as well as those from Formenti et al. (2001) for dry and rainy season background aerosol in the north area of the Amazon basin, although some differences were found in the levels of Ca, K, Na. The soil observed in the study region is the varzea type. According to Konhauser et al. (1994) the only nutrient-rich soils in Amazonia. Compared to other Amazonia regions, these soils show the highest cation to silica ratios, with the concentration of Ti, Mn, Mg, Ca, K, P and Na most closely approaching crustal abundance (Konhauser et al., 1994). Based on this information and in the enrichment factors calculation (not shown in the article) it is noticed that there will be other sources for certain elements.

3.4. Organic speciation of total particulate matter

The organic fraction of the carbonaceous aerosol is formed by a complex mixture of compounds, which can be grouped into classes such as *n*-alkanes, *n*-alkenes, polycyclic aromatic hydrocarbons (PAH), *n*-alkanols, *n*-alkanals, hydroxyl compounds, *n*-alkanoic acids, sugars and other non-linear compounds. In this study, attention was focused on *n*-alkanes, *n*-alkenes, PAH, *n*-alkanoic acids and *n*-alkenoic acids. The identification and quantification of some of these species associated with the application of diagnostic parameters, such as carbon preference index (CPI), average chain length (ACL) and chain-length ratios, supply data that can help to assign sources or atmospheric processes. For *n*-alkanes, the CPI is expressed as a sum of the odd carbon number homologs, over a range, divided by a sum of even carbon homologs, over the same range. For *n*-alkanoic acids, CPI is calculated inverting the ratio to have even-to-odd homologs. Splitting the CPI range, the microbial contributions (C₁₀ to C₂₄) can be distinguished from the higher plant wax inputs (C₂₂ to C₃₄), for example. The ACL is calculated as an average number of carbon atoms per molecule based on the abundance of the odd or even high homologs (Alves, 2008). Table with complete organic classes data is attached as supplementary material (Table 8S).

The *n*-alkane total concentrations varied from 7 to 12 ng·m⁻³, with an average of 9 ng·m⁻³ and from 5 to 35 ng·m⁻³, with an average of 15 ng·m⁻³, in the rainy and dry seasons, respectively (Fig. 4).

These levels are lower than those measured, during the dry season, in the Alta Floresta (South area of the Amazon basin) (12–238 ng·m⁻³; average = 68 ng·m⁻³) by Vasconcellos et al. (1998), and in the Ducke Forest Reserve (North area of the Amazon basin) (260–810 ng·m⁻³; average = 422 ng·m⁻³) by Simoneit et al. (1990). This comparison is also temporal once the latter study was made over 20 years ago. The *n*-alkane series comprised the homologues from C₁₁ to C₃₈, with an odd carbon number predominance and maximising for the homologues ≥ C₂₃ (Fig. 4), in both seasons studied. Long chain *n*-alkanes (C₂₁–C₃₇), are synthesised as part of the epicuticular leaf wax of terrestrial plants and are among the most recognisable and widely used plant biomarkers. Plants typically produce a range of *n*-alkanes, commonly with a strong odd-over-even predominance and one or two dominant chain lengths (Abas and Simoneit, 1996, 1997; Alves, 2008; Bush and McInerney, 2013). In this study, the two dominant *n*-alkanes (C_{max}) were C₂₉ and C₃₁, in both seasons. The ratio between these two homologues remained approximately constant over the observation period (Table 3), suggesting a constancy in the typology of wax *n*-alkane emissions along the two studied seasons. The ACL values of *n*-alkanes also presented a regular behaviour along the two seasons.

The CPI average for the whole range of *n*-alkanes varied from 1.4 in the rainy season and 3 in the dry season (Fig. 4). CPI values near unity, as observed in the rainy season, have been pointed out as indicative of anthropogenic inputs, such as emissions from incomplete combustion of fossil fuels (Alves, 2008). On the other hand, values near or >3, as

Table 2
Average concentration and standard deviations for principal elements by season.

Elements (ng·m ⁻³)	Rainy season (n = 15)	Dry season (n = 15)
Al	18 ± 8.6	34 ± 13
Ca	229 ± 77	209 ± 66
Cu	96 ± 30	89 ± 32
Fe	7.0 ± 4.0	32 ± 15
K	111 ± 20	289 ± 85
Mg	43 ± 15	133 ± 63
Mn	1.2 ± 0.55	6.4 ± 3.6
Na	387 ± 129	1040 ± 648
Pb	0.21 ± 0.05	0.51 ± 0.15
Rb	0.27 ± 0.04	0.72 ± 0.29
Sr	0.55 ± 0.19	1.2 ± 0.42
Ti	n.d.	0.25 ± 0.07
Zn	3.8 ± 1.7	n.d.

n.d. - not detected.

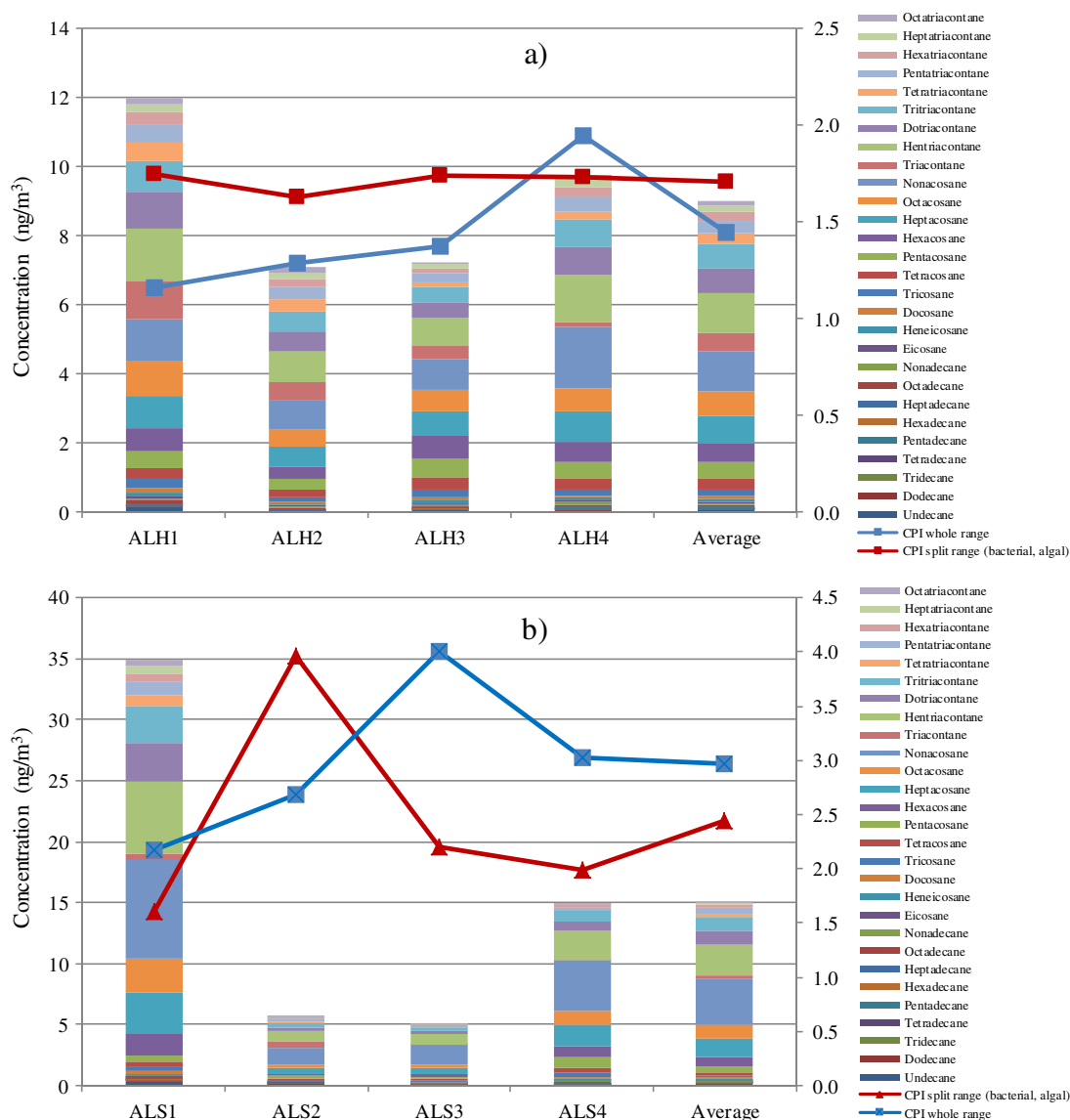


Fig. 4. Seasonal variation of *n*-alkanes concentration and CPI indexes in the rainy season (Fig. 4a) and dry season (Fig. 4b). ALH1 – 20 to 23/04/14; ALH2 – 24 to 27/04/14; ALH3 – 28/04 to 01/05/14; ALH4 – 02 to 04/05/14; ALS1 – 18 to 21/08/14; ALS2 – 22 to 25/08/14; ALS3 – 26 to 29/08/14; and ALS4 – 30/08 to 01/09/14.

verified in the dry season, indicate that the *n*-alkanes are predominantly from terrestrial higher plant waxes.

Due to the permanent wet scavenging processes, the *n*-alkanes concentration along the rainy season is much more constant than in the dry season. In the dry season, one set of samples (ALS1) is noteworthy for

having concentrations substantially higher than the others. This peak is likely of local anthropogenic origin, since they correspond to the minimum values of the global CPI. Even in the dry season, the CPI for microbial contributions shows a peak for the ALS2 set, suggesting that during those days there was a greater contribution of this nature.

The aliphatic fraction also contains *n*-alkenes. The *n*-alkene total concentrations varied from 0.15 to 0.90 ng·m⁻³, with an average of 0.47 ng·m⁻³ and from 0.42 to 2.5 ng·m⁻³, with an average of 1.1 ng·m⁻³, in the rainy and dry seasons, respectively. The *n*-alkenes series comprised homologues from C₁₂ to C₂₈, with an even carbon number predominance along the two studied seasons. The two dominant *n*-alkenes (C_{max}) were C₂₁ and C₂₅, in the rainy and dry seasons respectively. *n*-Alkenes are constituents of gasoline fuels, motor vehicle exhaust emissions and biomass fuel. The presence of these compounds in atmospheric particulate may be related to the way energy is produced in the region. The electric power is generated by diesel fuel combustion in thermoelectric powerplant.

PAH are one of the organic compound classes most studied due to its carcinogenic and mutagenic characteristics. PAH are generated from fossil fuels and from primary products of incomplete combustion of organic materials (Rogge et al., 1993a; Schauer et al., 1996). The total

Table 3
Ratios and other parameters calculated with homologous compound series of organic compounds.

Ratios	Range		Average	
	Rainy season	Dry season	Rainy season	Dry season
<i>n</i> -Alkane C _{max}	C ₂₉ , C ₃₁	C ₂₉ , C ₃₁		
<i>n</i> -Alkene C _{max}	C ₂₁	C ₂₅		
<i>n</i> -Alkane C ₃₁ / (C ₃₁ + C ₂₉)	0.44–0.56	0.33–0.42	0.49	0.38
<i>n</i> -Alkane CPI (whole range)	1.2–1.9	2.2–4.0	1.4	3.0
<i>n</i> -Alkanoic acids C _{max}	C ₁₀	C ₁₆		
<i>n</i> -Alkanoic acid > C ₂₂ / <i>n</i> -Alkanoic acid < C ₂₀	...–0.013	0.015–0.028	0.007	0.021
<i>n</i> -Alkanoic acid CPI (whole range)	1.2–2.6	8.6–13	1.8	10
ACL <i>n</i> -alkanes	28.9–29.8	29.1–29.8	29.5	29.5
ACL <i>n</i> -alkanoic acid	22.4–22.5	22.7–23.5	22.5	23.3

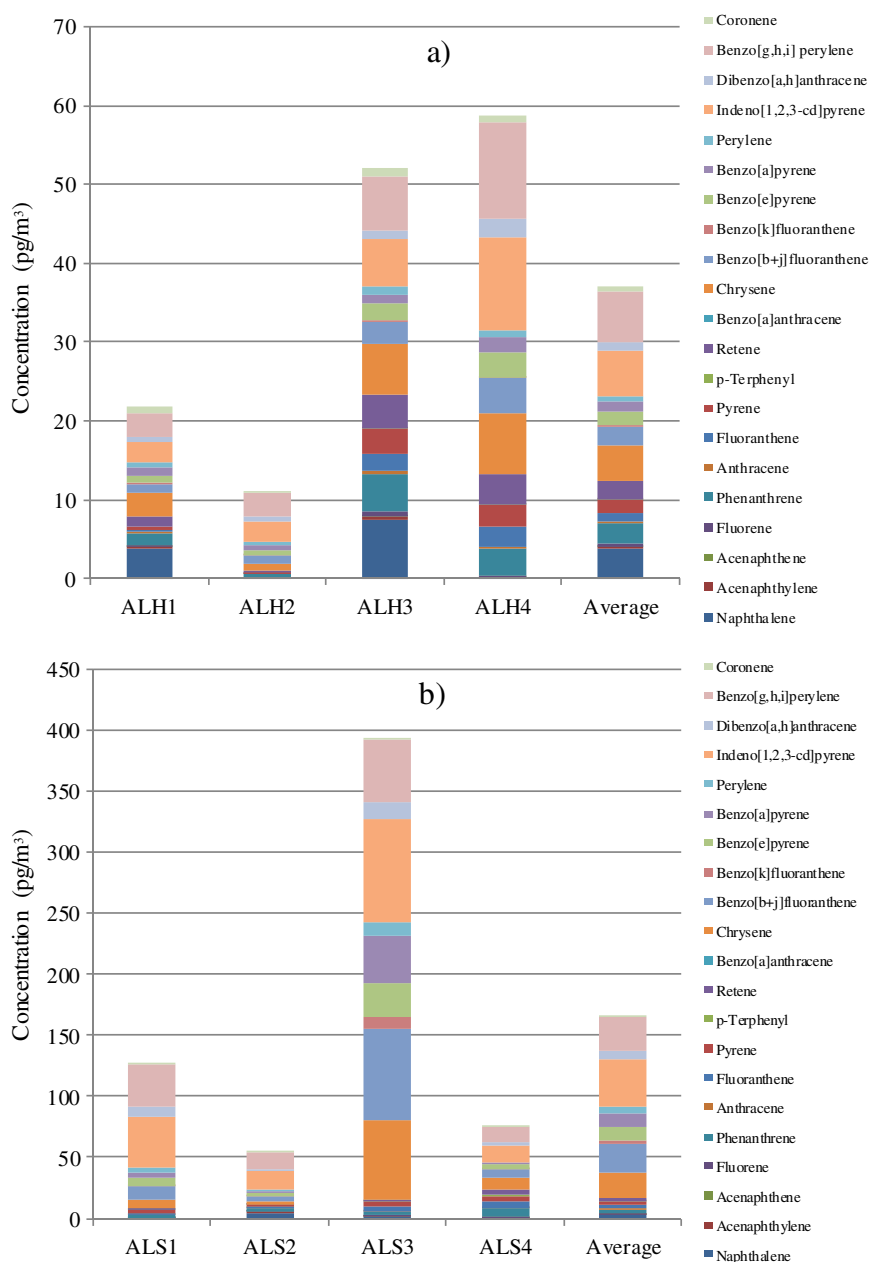


Fig. 5. Seasonal variation of PAH concentration in the rainy season (Fig. 5a) and dry season (Fig. 5b).

concentrations varied from 11 to $59 \text{ pg}\cdot\text{m}^{-3}$, with an average of $36 \text{ pg}\cdot\text{m}^{-3}$ and from 54 to $393 \text{ pg}\cdot\text{m}^{-3}$, with an average of $162 \text{ pg}\cdot\text{m}^{-3}$, in the rainy and dry seasons, respectively (Fig. 5). The four most abundant PAH detected in both studied seasons were benzo[g,h,i]perylene (rainy season - $25 \text{ pg}\cdot\text{m}^{-3}$; dry season - $113 \text{ pg}\cdot\text{m}^{-3}$), indeno[1,2,3-cd]pyrene (rainy season - $23 \text{ pg}\cdot\text{m}^{-3}$; dry season - $153 \text{ pg}\cdot\text{m}^{-3}$), chrysene (rainy season - $18 \text{ pg}\cdot\text{m}^{-3}$; dry season - $85 \text{ pg}\cdot\text{m}^{-3}$) and benzo[b + j]fluoranthene (rainy season - $9.5 \text{ pg}\cdot\text{m}^{-3}$; dry season - $96 \text{ pg}\cdot\text{m}^{-3}$). It is observed that in the dry season the concentrations of those PAH were significantly higher. Typically, the background concentrations of PAH reported for remote locations have 1–2 times smaller magnitude compared to urban areas (Halsall et al., 1997). In Alenquer, PAH were found in all samples, but at low concentrations, typical of remote locations.

Comparing remote site samples with urban samples, the ratio benzo[e]pyrene/benzo[a]pyrene is important. The ratio is close to unity from gasoline, diesel fuel and burning oil emissions. In the

particulate matter collected in this study, these ratios were 1.3 and 2.4 in the rainy and dry seasons, respectively. It can be assumed that these reasons in the dry season are high due to biomass burning.

These levels are lower than those measured, during the dry season, in Alta Floresta (South area of the Amazon basin) ($13\text{--}9866 \text{ pg}\cdot\text{m}^{-3}$; average = $3334 \text{ pg}\cdot\text{m}^{-3}$) by Vasconcellos et al. (1998). The six most abundant PAH detected in Alta Floresta were benzo[b + j + k]fluoranthene, benzo[e]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, chrysene and benzo[a]pyrene. They are also lower than the values described by Krauss et al. (2005), for the Manaus secondary forest region, during the dry season. On the other hand, Simoneit et al. (1990), in the studies developed in the Duck Forest Reserve region, during the dry season (North area of the Amazon basin) found PAH only at trace levels.

n-Alkanolic acids constitute another group of solvent-extractable compounds present in the Alenquer aerosol samples. The *n*-alkanoic acids distribution ($\text{C}_8\text{--}\text{C}_{26}$) is characterised by an even carbon number

preference, in both seasons. The *n*-alkanoic acids total concentrations varied from 0.46 to 2.6 $\text{ng}\cdot\text{m}^{-3}$, with an average of 1.8 $\text{ng}\cdot\text{m}^{-3}$ and from 8.2 to 20 $\text{ng}\cdot\text{m}^{-3}$, with an average of 12 $\text{ng}\cdot\text{m}^{-3}$, in the rainy and dry seasons, respectively (Fig. 6). These levels are lower than those measured during the dry season in the Ducke Forest Reserve (North area of the Amazon basin) (200–620 $\text{ng}\cdot\text{m}^{-3}$; average = 427 $\text{ng}\cdot\text{m}^{-3}$) by Simoneit et al. (1990), but are of the same order of magnitude of those described by Graham et al. (2003b) (fine fraction = 13 $\text{ng}\cdot\text{m}^{-3}$; coarse fraction = 23 $\text{ng}\cdot\text{m}^{-3}$), during the dry season, in the Balbina region (North area of the Amazon basin).

The ratio $>C_{22}/<C_{20}$ *n*-alkanoic acids under 1 (Table 3) and C_{max} at C_{10} in the rainy season and C_{16} in the dry season reflects microbial and phytoplankton contributions. The link between the clear dominance of *n*-alkanoic acids $<C_{20}$ and the microbial or oceanic source of the organic aerosol has been described by Graham et al. (2003b), Kawamura et al. (2003) and Simoneit et al. (1990). The probability of being derived from phytoplankton from Amazon river and its tributaries or from Atlantic phytoplankton is not negligible taking into account the influence that the sampling site undergoes. The ACL values of *n*-alkanoic acids do not show variations along the two seasons (Table 3). During the rainy season, CPI (whole range) values showed a constant distribution with values always between 1.2 and 2.6. In the dry season values are much higher, ranging from 8.6 to 13. These distributions are quite variable but it is according to that described by Simoneit et al. (1990). These values are strongly indicative of incorporation of biological constituents into the aerosol sample, especially in the dry season. In the dry season, it is observed that the presence of hexadecanoic ($C_{16:0}$) and octadecanoic ($C_{18:0}$) acid in large average

concentrations, 5.1 $\text{ng}\cdot\text{m}^{-3}$ and 3.1 $\text{ng}\cdot\text{m}^{-3}$, respectively, indicating biological input.

In addition to the *n*-alkanoic acids, *n*-alkenoic acids, such as oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids, were also detected in the Alenquer aerosol samples, mainly in the rainy season. Unsaturated *n*-fatty acids may also be issued to the atmosphere by biomass and coal burning, fossil fuel combustion, cooking, plants of terrestrial biosphere and also associated with sea salt aerosol, phytoplankton and marine bacteria (Oros and Simoneit, 2000, 2001; Rogge et al., 1993b; Schauer et al., 1999; Simoneit et al., 1988; Tervahattu et al., 2002). These acids are prone to oxidative processes and conversion to shorter chain species, which may explain the lower concentration observed in the dry season.

The *n*-alkanedioic acids are also present in these samples. The series ranged from C_3 to C_{10} , maximising at C_4 , in both seasons. The total concentration varied from 2.0 to 11 $\text{ng}\cdot\text{m}^{-3}$, with an average of 6.8 $\text{ng}\cdot\text{m}^{-3}$, in the rainy season and from 24 to 55 $\text{ng}\cdot\text{m}^{-3}$, with an average of 42 $\text{ng}\cdot\text{m}^{-3}$, in the dry season. This type of acid is frequently present in atmospheric aerosols samples because it may have very different sources (Wu et al., 2015). Dicarboxylic acids $<C_{10}$ may have origin in combustion engines, meat cooking, pyrolysis of soil or plant constituents, or atmospheric oxidative processes. As example, the C_8 and C_9 compounds are formed by photo-oxidation of unsaturated *n*-alkenoic acids, such as oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids (Gogou et al., 1996). Pereira et al. (1982) identified *n*-alkanedioic acids ranging from C_4 to C_9 in airborne ash resulting from pyrolysis of organic soil constituents, plants and trees.

A range of “other acids” were also identified and quantified. This group includes some resin acids, such isopimaric (rainy season -

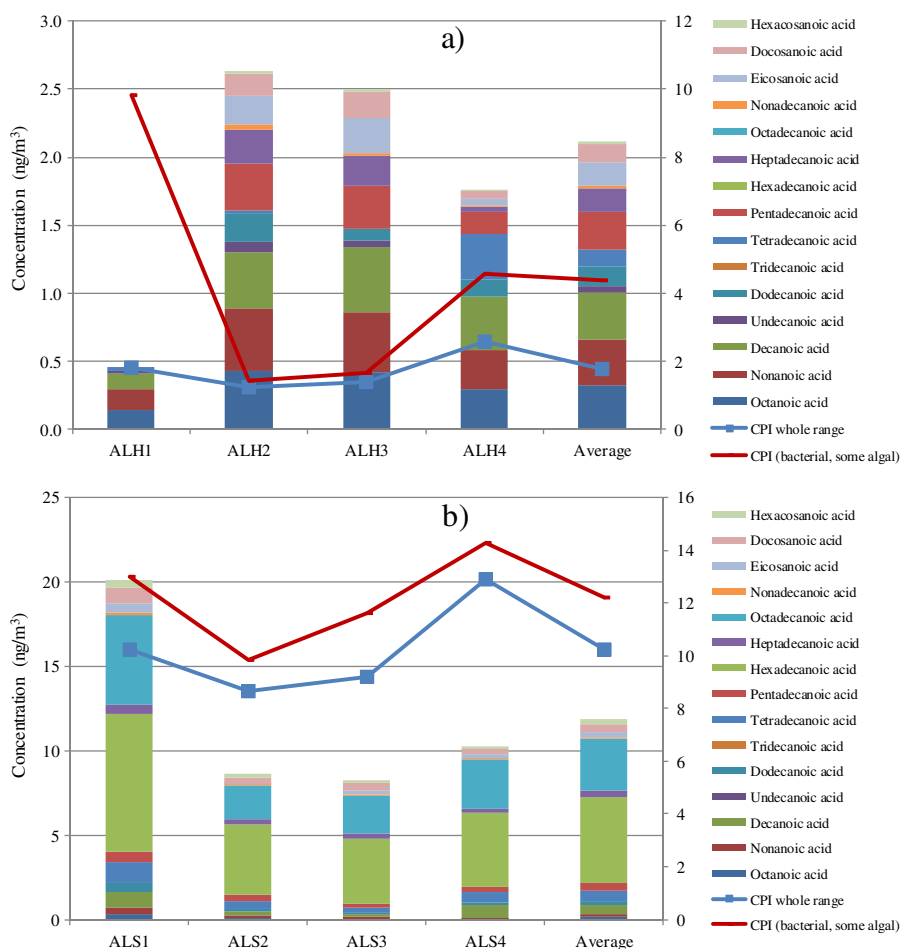


Fig. 6. Seasonal variation of concentration of *n*-alkanoic acids and CPI indexes in the rainy season (Fig. 6a) and dry season (Fig. 6b).

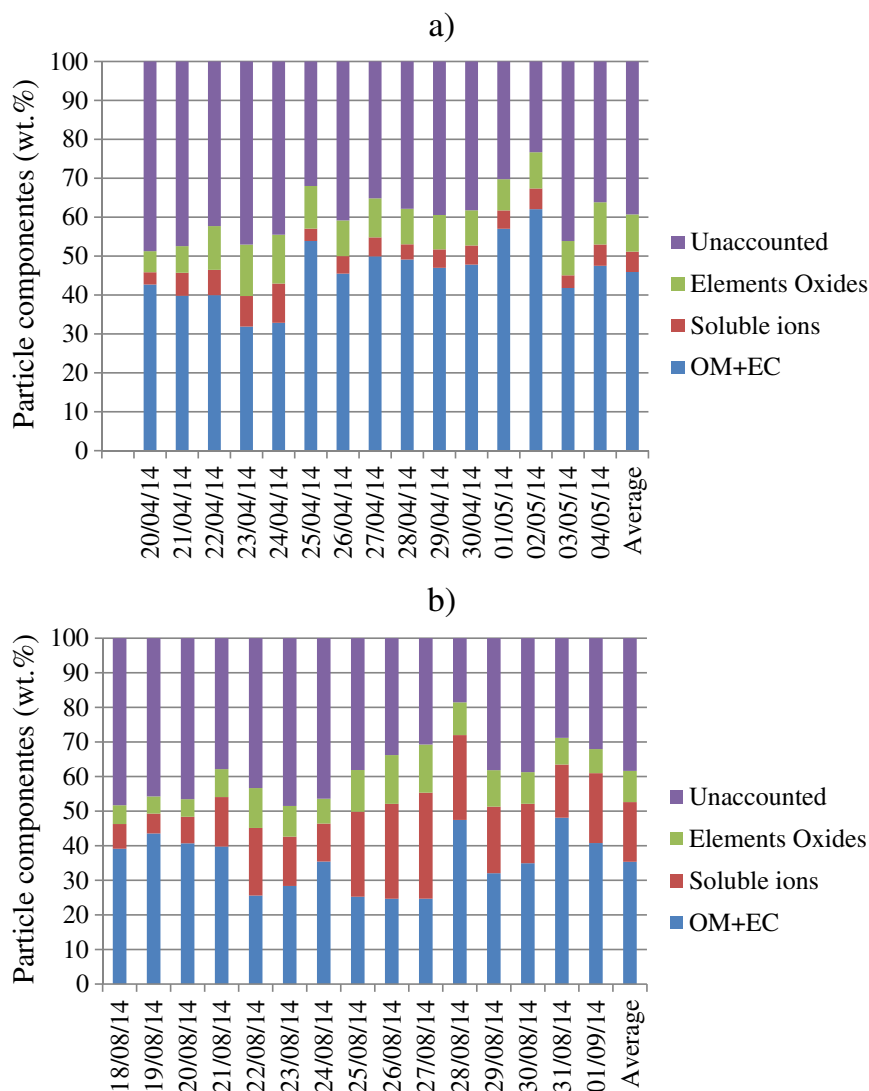


Fig. 7. Reconstructed TSP mass for the rainy season (Fig. 7a) and dry season (Fig. 7b).

$0.225 \text{ ng} \cdot \text{m}^{-3}$; dry season - $0.049 \text{ ng} \cdot \text{m}^{-3}$), dehydroabietic (rainy season - $0.184 \text{ ng} \cdot \text{m}^{-3}$; dry season - $0.187 \text{ ng} \cdot \text{m}^{-3}$) and abietic (rainy season - $0.009 \text{ ng} \cdot \text{m}^{-3}$; dry season - $0.041 \text{ ng} \cdot \text{m}^{-3}$). Other biomass burning tracers were also identified, such as syringic acid (rainy season - $0.036 \text{ ng} \cdot \text{m}^{-3}$; dry season - $0.748 \text{ ng} \cdot \text{m}^{-3}$) and vanillic acid (rainy season - $0.015 \text{ ng} \cdot \text{m}^{-3}$; dry season - $0.187 \text{ ng} \cdot \text{m}^{-3}$). These data contradict those described by Simoneit et al. (1988) who stated that these compounds were not detectable in aerosols from Amazonia, consistent with the absence of coniferous vegetation in this region. According to Souza (2010), the Brazilian phyto-geographical domain with the highest number of species of gymnosperms is Amazonia, with 16 species.

3.5. Mass balance

Taking into account the gravimetric data and all identified aerosol species, it is possible to perform a mass balance (chemically analysed mass vs. gravimetrically determined mass). For this, it is necessary to determine the organic matter (OM) from OC measurements. OM is estimated by using a factor (f) that accounts for the oxygen, hydrogen, nitrogen, and sulfur present in the organic material (McMeeking et al., 2009). The organic mass to organic carbon ratio (OM/OC) takes values between 1.3 and 2.2 (Chazette and Liousse, 2001; Hegg et al., 1997;

Pöschl, 2005; Reid et al., 2005; Turpin and Lim, 2001), depending on the aerosol origin, its composition and the aerosol aging level (Puxbaum and Tenze-Kunit, 2003; Stelson and Seinfeld, 1981). The f value used in this study was 1.8 (Temesi et al., 2001). Thus, the equation used to reconstruct the TSP mass was as follows (Chow et al., 2015):

$$\text{TSP} = \sum \text{Soluble ions} + \sum \text{Element oxides} + \text{EC} + \text{OC} \times f$$

Elements were assumed to exist in their common oxide forms (e.g. Al_2O_3 , CaO , K_2O , Fe_2O_3 , etc.). The calculated sum of analysed aerosol constituents corresponds, on average, to 61% and 62% of the TSP weighted, in rainy and dry seasons, respectively (Fig. 7). The unknown mass may be due to some components not determined and absorption of water by the aerosol (Temesi et al., 2001), since sampling was carried out under at very high relative humidity conditions.

4. Conclusions

In this study, a detailed chemical characterisation of the total suspended particulate matter (TSP) from an Amazonia remote region was performed, to look for seasonal patterns and to identify potential emission sources and formation processes. Analyses included water-soluble ions, principal elements, carbonaceous content (OC, EC and

TC), and the identification and quantification of approximately 115 organic compounds.

Throughout the study it was observed that during the rainy season, the Alenquer region was mostly affected by air masses with Atlantic origin that develop along the Amazon river. By contrast, during the dry season most of the air masses went through different northern states bringing a continental influence, before arriving to the study site. With respect to TSP, a higher mean concentration ($31 \pm 7.8 \mu\text{g} \cdot \text{m}^{-3}$) was obtained for the dry season in comparison with the rainy season ($14 \pm 1.3 \mu\text{g} \cdot \text{m}^{-3}$). The water-soluble ions accounted, on average, for 7% and 18% during the rainy and dry seasons, respectively, of the concentration of TSP. In the rainy season the dominant ions were SO_4^{2-} , Na^+ , NO_3^- and Cl^- . In the dry season, in general, an increase of concentrations of all ions was registered, especially for Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} . In the rainy season, the Na^+ , Cl^- and Mg^{2+} were strongly associated with a marine source, whereas in the dry season an enrichment of Na^+ , probably from soil, was observed. In the dry season, the SO_4^{2-} , NO_3^- and K^+ mean concentrations were higher due to much less wet scavenging, as well as to the biomass burning plumes from forest fires in Pará state and in other states, which are transported with the air masses and reach the sampling site. In the rainy season, the principal elements were Na, Ca and K. In the dry season, increased concentrations were observed, especially for Mn, Fe and Mg. As observed for the corresponding water soluble ions, the enrichment observed for Na and Mg, especially in the rainy season, is explained by the influence of the marine aerosol. The individual elemental concentrations obtained in this study are quite comparable to the values reported for rainy and dry season background aerosol in the north area of the Amazon basin.

The carbonaceous content of the Alenquer particulate matter is higher than values observed in central Amazonia, regardless of the season, and also than values observed in southern Amazonia during the rainy season. The primary inputs of organic constituents to the aerosols of Alenquer based on the homologous compound series and biomarkers were: (i) natural emissions from terrestrial higher plant waxes, particularly in dry season, which is expressed, for example, by the *n*-alkane series with an odd carbon number predominance; (ii) anthropogenic emissions from diesel fuel combustion and biomass combustion, predominating during the dry season given, for example, by the presence of *n*-alkene with an even carbon number predominance; and by the *n*-alkanoic acids distribution characterised by an even carbon number preference and together with the CPI values of 10, strongly indicative of incorporation of biological constituents into the aerosol sample. In Alenquer, PAH were found in all samples, but at low concentrations. Contrary to what would be expected some resin acids (isopimaric acid, dehydroabietic acid and abietic acid) and other biomass burning tracers such syringic acid and vanillic acid were identified. The inorganic and organic compounds found in particulate matter could be conducive to source apportionment studies and will contribute to the improvement of emission inventories in the Amazonia remote region.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2016.07.027>.

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