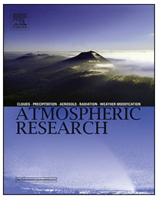
Atmospheric Research 215 (2019) 75–84

Contents lists available at ScienceDirect

Atmospheric Research

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



Carbonaceous components and major ions in PM_{10} from the Amazonian Basin

Danilo Custodio[a,b,c,*], Célia Alves[b], Yendry Jomolca[a], Pérola de Castro Vasconcellos[a]

[a] *Institute of Chemistry, University of São Paulo, São Paulo 05508-000, Brazil*
[b] *Centre for Environmental and Marine Studies, Department of Environment, University of Aveiro, Aveiro 3810-193, Portugal*
[c] *Helmholtz-Zentrum Geesthacht (HZG), Institute of Coastal Research, Geesthacht, Germany*

ARTICLE INFO

Keywords:
Amazon air pollution
Amazonia aerosol
Aerosol composition
Air quality
Atmospheric chemistry

ABSTRACT

Air pollution mainly resulting from deforestation and agricultural activities has become one of the major concerns in the Amazonian Basin. A detailed analysis of the PM_{10} chemical composition is critical for devising pollution control measures and improving climate models. In this study, daily 24-h filter samples were collected and analyzed in different sites of the Amazon Basin between 2008 and 2016 (over 200 samples). The six sampling sites were classified into two groups, one in South Amazonia, a region with strong influence of land occupation, and another in a remote forest region to the North. The high mean concentrations of PM_{10} and the occurrences of extreme events at the Southern site denote air pollution episodes. High correlations between the temporal trends of PM_{10} and primary species linked to soil re-suspension and biomass burning highlight the contribution of these sources of air pollution in the region. Significant differences between PM_{10} in the South and North regions were observed, for which levels of $72.6 \pm 66.5\,\mu g\,m^{-3}$ and $8.9 \pm 4.2\,\mu g\,m^{-3}$, respectively. The average concentrations of organic carbon (OC) and elemental carbon (EC) in the aerosol were $5.81 \pm 4.18\,\mu g\,m^{-3}$, $2.43 \pm 1.65\,\mu g\,m^{-3}$ and $5.17 \pm 5.54\,\mu g\,m^{-3}$, $0.51 \pm 0.41\,\mu g\,m^{-3}$, respectively, for the Southern and Northern Amazonia sampling sites. The aerosol was largely composed of inorganic species in Southern Amazonia, whose carbonaceous matter accounted for 16% of the gravimetrically measured PM_{10}. However, in the forest region, the contribution of carbonaceous species, mainly OC, accounted for > 90% and remained more constant throughout the seasons. Na^+ was the dominant water soluble ion in samples from the Southern region, followed by $SO_4{}^{-2}$, $NO_3{}^-$, Ca^{2+} and K^+. High levels of carbonate (CC) were also observed for these samples. For the Northern region, $SO_4{}^{-2}$ was the dominant soluble ion, followed by K^+ and $NH_4{}^+$. Some of these species exhibited a clear seasonal trend during the study period. This study provides a better understanding of the current state of air pollution in diversified Amazon basin sites.

1. Introduction

The Brazilian Amazon is one of vastest and richest biomes of the planet, covering 5.1 million km^2, which corresponds to 60% of the area of the country. However, approximately $2 \times 10^4\,km^2$ of this area is deforested annually, influencing air quality by degrading visibility, affecting human health and ongoing global climate equilibrium (Scot et al. 2010, Barregard et al., 2006; Pope III and Dockery, 2006; Schwartz et al., 2002; Watson, 2002; Reinhardt et al., 2001). The agricultural expansion and climate variability have become important agents of disturbance of the atmosphere of the Amazon basin (Davidson et al., 2012). Fires have been recurrently used as a clearing tool, being a major source of particulate matter (PM) in the dry season (Artaxo et al., 2013; Ten Hoeve et al., 2012) with a concomitant and significant increase in the occurrence of respiratory diseases during this period (Jacobson et al., 2014; Carmo et al., 2010).

Among all air pollutants, particles are of great interest to the scientific community and policy makers because of their potential to result in health risks, as well as their influence on air quality and global climate (Oliveira Alves et al., 2017; Kumar et al., 2010).

The Amazonian aerosol particles present considerable variations in space and time and many studies have been conducted to assess sources, physical properties and chemical composition (Alves et al., 2015; Scot et al. 2010; and reference therein). However, as these studies focused more on forest areas on the North of the Amazon basin, little or no field information is available for the Southern part of the basin. This lack of information is of particular concern given the current knowledge about the aerosol spatial distribution in Amazonia. Exceedances of the

---

[*] Corresponding author at: Institute of Chemistry, University of São Paulo, São Paulo 05508-000, Brazil.
E-mail address: danilocustod@gmail.com (D. Custodio).

https://doi.org/10.1016/j.atmosres.2018.08.011
Received 8 April 2018; Received in revised form 13 August 2018; Accepted 17 August 2018

World Health Organization daily limit for PM_{10} are common during the dry season due to mineral dust re-suspension and intense biomass burning events, which are largely dependent on human development in the region (Martin et al., 2010). Furthermore, Amazonia has been subject to an intensive process of land use and human activities' change, even in some of these most remote areas. Baseline knowledge of composition, source strengths, properties and atmospheric processes of aerosols is necessary to correctly assess present-day burdens and judge the effects of human activities. Moreover, research on chemical composition of particles remain key priorities since the mass and ratios of different components may trace back to the various sources and formation mechanisms. It is crucial to develop detailed chemical databases of particles to precisely conduct source apportionment and evaluate environmental impacts. Further, analysis of chemical signatures of particulate matter may be a strong support for model validation and emission control strategies.

This paper reports a quantitative description of particulate matter concentrations, providing comprehensive information about the seasonal variation of PM_{10} and associated carbonaceous fractions (OC and EC), carbonate and inorganic soluble ions in six different sites in Amazonia. The objective of this study was to: (1) assess exposure to particulate matter in remote forest and transition region forest / savannah; (2) investigate the relationships between PM_{10} concentrations and the main constituents of aerosol; and (3) describe the relevant sources of particulate matter and their seasonality, which can drive further a better understanding of the origin of aerosol particles and therefore support the adoption of measures and new strategies to ensure better air quality.

2. Methodology

2.1. Sampling sites

One hundred and seventy six samples (87% of total samples) were collected in five different places in Mato Grosso State in the South of Amazonia (Cuiaba, Campo Novo dos Parecis, Nobres, Jacira and Nova Mutum), whereas other twenty six samples were collected in a pristine area in the remote Amazon forest (Cuieiras ZF2 natural reserve), between 2008 and 2016 (Fig. 1). South Amazonian samples were collected in a transition zone between the three most characteristic Brazilian ecosystems: Amazon, Savannah and Pantanal. The climate is tropical and humid, precipitation is concentrated from September to May, while the mass of dry air over the centre of Brazil inhibiting the rain formation occurs from June to August. The cold fronts dissipate the heat associated with the smoke produced by fires lit during the dry season. The relative humidity drops to very low levels, sometimes below 15%. The mean annual rainfall is 1351 mm, with maximum intensity from December to March. The mean maximum temperature reaches 34 °C, but the absolute maximum can attain 40 °C in hotter months. However, it is muffled on rainy days, when the maximum temperature is typically only 28 °C. In July, the coldest month, the mean temperature is 16.6 °C with wind chill of 10 °C (INMET, 2017). The vegetation is characterized by extensive savannah formations crossed by gallery forests and stream valleys (INPE, 2017). Samples from the Northern of Amazonia were collected equally distributed among rainy and dry season in a remote area in the rainforest, located about 150 km northeast of the city of Manaus, for South of Amazonia samples, 64% were collected during dry season. An overview of the atmospheric, geographic and ecological conditions for this site were reported by Andreae et al. (2015).

2.2. Sampling and analytical method

Particulate matter samples were collected for a period of 24 h, with high-volume air samplers (Hi-Vol), operating at a flow rate of $1.13\,m^3\,min^{-1}$, with 10 µm size selective inlets (Thermo Andersen, USA). Prior to sampling, quartz fiber filters (20 cm × 25 cm, Millipore, USA) were baked for 6 h at 550 °C to remove organic contaminants. Mass concentrations were obtained by gravimetry with an analytical microbalance (MettlerToledo AG285). The filters were wrapped in aluminum foil and frozen until chemical analyses were performed. Following the analytical procedure described in Custódio et al. (2016), ten major water soluble inorganic species (Li^+, Na^+, K^+, Mg^{2+}, Ca^{+2}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) were analyzed by ion-chromatograph (DIONEX, ICS-2500/2000). For these analyses, four 9 mm punches taken from the filters were subjected to extraction with 5 mL of Milli-Q ultrapure water under ultra-sonication for 15 min at room temperature. The liquid extracts were then filtered with a 0.45 µm pore PTFE syringe filter to remove insoluble particles. The cations Li^+, NH^4 $^+$, Na^+, K^+, Ca^{2+} Mg^{2+} were determined using an IonPac CG12A guard column and a CS12Aanalytical column with 10 mM H_2SO_4 as the eluent. The anions Cl^-, NO_3^-, SO_4^{2-} were measured with an IonPac AG4A guard column and an AS4A analytical column with a Na_2CO_3/NaHCO3 (1.8 and 1.7 mM, respectively) buffer solution as the eluent. The analytical uncertainty based on triplicate measurements of standards was below 5%. The method presents detection limits ranging from 0.1 to 1 ng m^{-3}.

Organic carbon (OC) and elemental carbon (EC) in samples were analyzed by a thermal-optical transmittance technique described in detail by Pio et al. (2011) and Custódio et al. (2014). The uncertainty for this method based on triplicate analysis of sample filters was below 5% and the detection limits were 30 ng m^{-3} for OC and 3 ng m^{-3} for EC. Carbonate carbon (CC) was analyzed through the release of CO_2, and measured by the same non dispersive infrared analyser coupled to

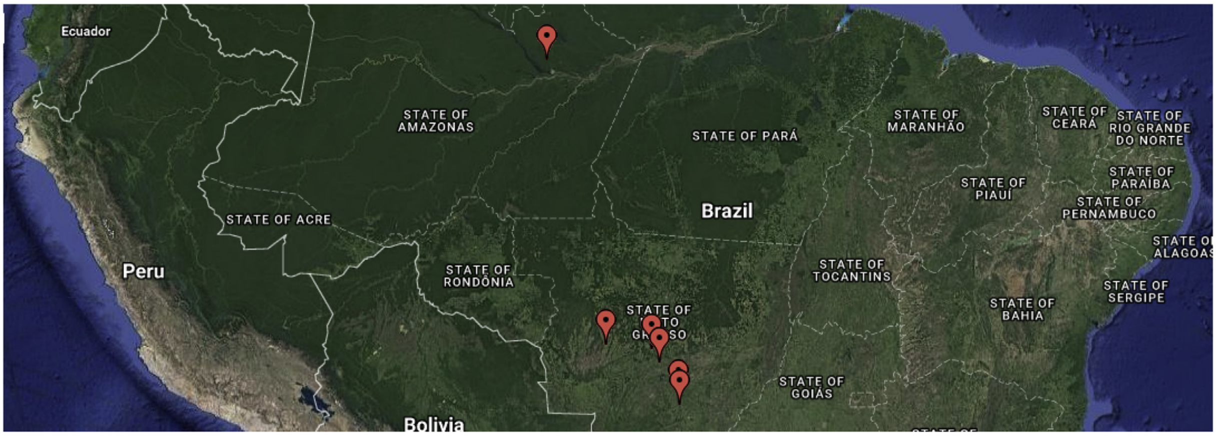


Fig. 1. Map of the Amazon Basin, North of Brazil, with the sampling sites marked.