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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 $14 \pm 1.3\ \mu g \cdot m^{-3}$ to $31 \pm 7.8\ \mu g \cdot m^{-3}$, 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.

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: ~1.5 m^3 min^{-1}) for 24 h periods. Following the sample collection, filters were stored in a freezer (at −14 °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 (HYSPLIT) 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.

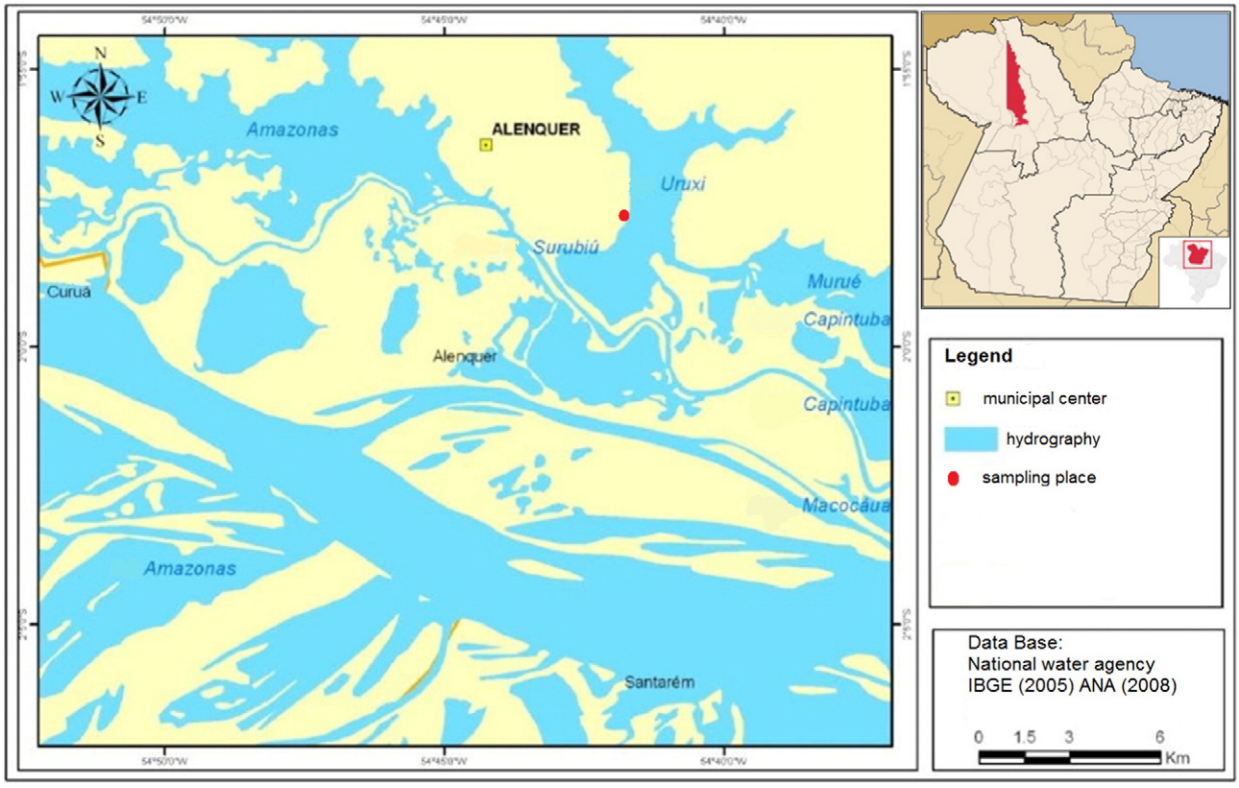

Fig. 1. Sampling place and Alenquer city location map.
(adapted from Silva Junior and Szlafsztein, 2013)