



Structural signatures of water-soluble organic aerosols in contrasting environments in South America and Western Europe[☆]



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ABSTRACT

This study describes and compares the key structural units present in water-soluble organic carbon (WSOC) fraction of atmospheric aerosols collected in different South American (Colombia – Medellín and Bogotá, Peru – Lima, Argentina – Buenos Aires, and Brazil – Rio de Janeiro, São Paulo, and Porto Velho, during moderate (MBB) and intense (IBB) biomass burning) and Western European (Portugal – Aveiro and Lisbon) locations. Proton nuclear magnetic resonance (¹H NMR) spectroscopy was employed to assess the relative distribution of non-exchangeable proton functional groups in aerosol WSOC of diverse origin, for the first time to the authors' knowledge in South America. The relative contribution of the proton functional groups was in the order H-C > H-C-C= > H-C-O > Ar-H, except in Porto Velho during MBB, Medellín, Bogotá, and Buenos Aires, for which the relative contribution of H-C-O was higher than that of H-C-C=. The ¹H NMR source attribution confirmed differences in aging processes or regional sources between the two geographic regions, allowing the differentiation between urban combustion-related aerosol and biological particles. The aerosol WSOC in Aveiro, Lisbon, and Rio de Janeiro during summer are more oxidized than those from the remaining locations, indicating the predominance of secondary organic aerosols. Fresh emissions, namely of smoke particles, becomes important during winter in Aveiro and São Paulo, and in Porto Velho during IBB. The biosphere is an important source altering the chemical composition of aerosol WSOC in South America locations. The source attribution in Medellín, Bogotá, Buenos Aires, and Lima confirmed the mixed contributions of biological material, secondary formation, as well as urban and biomass burning emissions. Overall, the information and knowledge acquired in this study provide important diagnostic tools for future studies aiming at understanding the water-soluble organic aerosol problem, their sources and impact at a wider geographic scale.

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1. Introduction

Nowadays, it is firmly established that atmospheric organic

aerosols (OA) are inexorably linked to both climate change and adverse health outcomes (e.g., Kanakidou et al., 2005; Heal et al., 2012; Booth et al., 2012; Laskin et al., 2015). OA have been shown to be ubiquitous in urban, rural, and remote locations, representing an important component of air particulate matter (PM) (Jimenez et al., 2009; references therein; Putaud et al., 2010). The OA are highly dynamic, with a myriad of sources and formation

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mechanisms contributing significantly to the OA burden in the atmosphere. OA can be directly emitted into the atmosphere (from both natural and anthropogenic sources) or formed *in situ* from chemical reactions (i.e., secondary formation). Once in the atmosphere, OA can also undergo a wide variety of oxidation processes that modify their physico-chemical properties (Hallquist et al., 2009). One of the most important attributes of atmospheric OA for both climate and health impacts is their chemical composition. It has been shown that most OA mass at urban and anthropogenically influenced rural/remote areas is dominated by oxygenated species (e.g., Zhang et al., 2007; Duarte et al., 2007, 2015; Crilley et al., 2014; Lopes et al., 2015), and it contains both water-soluble and water-insoluble organic components. The water-soluble organic carbon (WSOC) fraction is usually below 70% of the organic carbon (OC) present in the air particulate matter (e.g., Duarte et al., 2007; Wozniak et al., 2012; Zhang et al., 2014; Lopes et al., 2015). The enrichment of air particles in WSOC and its mixing state with the inorganic counterpart plays an important role in several atmospheric processes. The WSOC might potentially affect the properties that determine the aerosols' ability to act as cloud condensation nuclei (Dinar et al., 2006; Padró et al., 2010). It has been also suggested that the WSOC might contribute to the absorption of solar radiation, and thus atmospheric heating and global climate change (Dinar et al., 2008; Mladenov et al., 2010). Furthermore, the wet deposition fluxes of atmospheric water-soluble organic matter (WSOM) indicate that it may be an important temporal source of OC to surface waters and, thus, playing an important role in the global carbon cycle (Jurado et al., 2008). From the public health perspective, there are evidences on the association between aerosol OC and adverse health effects (Cassee et al., 2013), with the secondary OC component (more water-soluble) being suggested as a valuable air quality metric. Despite its significance, the multitude of molecular forms, sources, and atmospheric reactivity makes a complete characterization of aerosol WSOC extremely difficult. Nevertheless, determining its structural composition is needed to explore its dynamics as well as its sources and formation mechanisms. Furthermore, targeting the chemical composition of aerosol WSOC is also essential for climatic and epidemiological studies, whose results are critical to support and evaluate informed policies on atmospheric pollution reduction at regional and global levels (Cassee et al., 2013; Saffari et al., 2014; Atkinson et al., 2015).

In the quest for untangle the complex molecular composition of the water-soluble component of OA, it has been shown that the WSOC consists of a highly diverse suite of oxygenated compounds, including dicarboxylic acids, keto-carboxylic acids, aliphatic aldehydes and alcohols, saccharides, saccharide anhydrides, aromatic acids, phenols, but also amines, amino acids, organic nitrates, and organic sulfates (e.g., Duarte et al., 2007, 2008, 2015; Timonen et al., 2013; Ng et al., 2010; Cleveland et al., 2012; Shakya et al., 2012; Pietrogrande et al., 2013; Chalbot et al., 2014; Paglione et al., 2014; Lopes et al., 2015; Chalbot et al., 2016). A common ground of the available compositional datasets on aerosol WSOC is that they refer to studies carried out in urban, rural, and remote locations predominantly at North America and Europe, besides a few urban sites in Asia. On the other hand, comprehensive structural identification within the complex aerosol WSOC mixture has been rarely reported for Southern Hemisphere locations. Most field studies within this region have included measurements of ambient concentrations of OC, elemental carbon (EC), and WSOC, specific organic markers (e.g., *n*-alkanes, PAHs, and levoglucosan), or the amount of hydrocarbon-like and oxygenated OA components [e.g., in Brisbane (Australia), Tanzania (rural background site), São Paulo (Brazil), Rondônia (Amazon Basin, Brazil), Buenos Aires (Argentina), Bogotá (Colombia), and Santiago (Chile)] (Graham et al., 2002;

Mayol-Bracero et al., 2002; Tagliavini et al., 2006; Vasconcellos et al., 2010, 2011; Mkoma and Kawamura, 2013; Crilley et al., 2014; Souza et al., 2014; De Oliveira Alves et al., 2015; Villalobos et al., 2015). Although these studies have provided a glimpse into the bulk chemical makeup of OA, the current understanding of the role of aerosol WSOC in global climate change still is incomplete. In order to draw a meaningful picture of the climate and health-related properties of atmospheric WSOC, one first needs to understand its chemical composition at a wider geographic scale. It becomes, therefore, crucial to lengthen the observational records by improving the current knowledge on the structural composition of aerosol WSOC and, simultaneously, glean additional information on how these compositional features change across different environments and ambient conditions.

The objective of this study was to investigate and compare the structural characteristics of WSOC in atmospheric aerosols collected in different locations (urban, suburban, and forest) at South America (Colombia – Medellín and Bogotá, Peru – Lima, Argentina – Buenos Aires, and Brazil – Rio de Janeiro, São Paulo and Porto Velho) and Western Europe (Portugal – Aveiro and Lisbon). The approach chosen to fulfill this objective encompasses functional group analysis using proton nuclear magnetic resonance (^1H NMR) spectroscopy. This strategy has been successfully applied to different aerosol WSOC samples, namely from biomass burning aerosols, marine organic aerosols, secondary organic aerosols (SOA), urban aerosols, rural aerosols, and size-fractionated atmospheric aerosols (Graham et al., 2002; Tagliavini et al., 2006; Decesari et al., 2007; Chalbot et al., 2014, 2016; Lopes et al., 2015). In this study, the acquired ^1H NMR datasets were further used to build fingerprints for source contribution analysis, following the method of Decesari et al. (2007). With this study it is expected to get a deeper insight into the yet unsolved structural composition of aerosol WSOC at different Southern Hemisphere locations, and to understand possible composition variations in WSOC due changes in their sources at contrasting environments.

2. Materials and methods

2.1. Aerosol samples collection

Aerosol samples were collected at nine different locations, extending from Aveiro and Lisbon (Portugal) located at the West European Coast, to Medellín and Bogotá (Colombia), Lima (Peru), Porto Velho, Rio de Janeiro and São Paulo (Brazil), and Buenos Aires (Argentina), located in South America (Fig. 1). Table 1 summarizes relevant information about the studied locations, including the particle size, sampling period, season, sampling duration, and air mass transport features during the aerosol sampling campaigns. The meteorological data, including air temperature, accumulated rainfall, relative humidity, solar radiation, maximum wind velocity, and air masses origin, across the different field campaigns are available in Table S1, in Supporting Information (SI).

In Aveiro, with approximately 60,000 inhabitants, the aerosol sampling occurred at the Campus (Santiago) of the University of Aveiro, on a rooftop approximately 20 m above the ground. The sampling site is located on the west coast of Portugal, 10 km from the Atlantic Ocean, and very close to the city center. An industrial complex, which includes the production of nitric acid, aniline, nitrobenzene and chlorinate compounds, is located 10 km to the North of Aveiro. A total of eight high-volume $\text{PM}_{2.5}$ (particulate matter with aerodynamic diameter $< 2.5 \mu\text{m}$) samples were collected on quartz fibre filters ($20.3 \times 25.4 \text{ cm}$; Whatman QM-A, GE Healthcare Life Sciences), on a weekly basis (7 days in continuum), during July–August 2010 [$n = 3$, Summer (SU)] and December 2010–February 2011 [$n = 5$, Winter (WI)] in order to

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