Science of the Total Environment 648 (2019) 430–441

Contents lists available at ScienceDirect

Science of the Total Environment

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

Comparative study of atmospheric water-soluble organic aerosols composition in contrasting suburban environments in the Iberian Peninsula Coast

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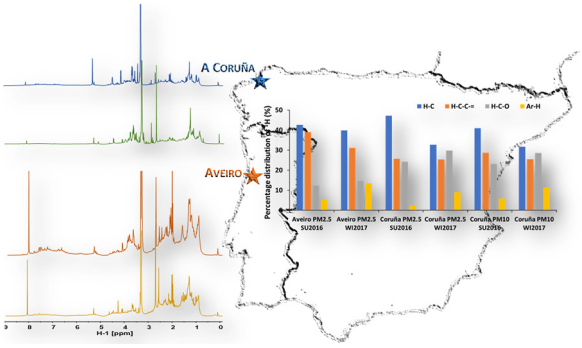
HIGHLIGHTS

- Parallel sampling of aerosol WSOM in Iberian Peninsula Coast: Aveiro vs. A Coruña
- Structural and molecular composition and major sources of WSOM in $PM_{2.5}$ and PM_{10}
- Aveiro impacted by fresh & secondary anthropogenic OAs
- A Coruña impacted by secondary OAs from biogenic, soil dust & anthropogenic sources
- Marine and biomass burning OAs are also important contributors, common to both sites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 April 2018
Received in revised form 26 July 2018
Accepted 13 August 2018
Available online 14 August 2018

Keywords:
Water-soluble organic aerosols
Suburban environments
Chemical and source signatures
NMR spectroscopy
Stable isotopic ($\delta^{13}C$, $\delta^{15}N$) composition
Water-soluble trace metals

ABSTRACT

This study investigates the structural composition and major sources of water-soluble organic matter (WSOM) from $PM_{2.5}$ collected, in parallel, during summer and winter, in two contrasting suburban sites at Iberian Peninsula Coast: Aveiro (Portugal) and Coruña (Spain). PM_{10} samples were also collected at Coruña for comparison. Ambient concentrations of $PM_{2.5}$, total nitrogen (TN), and WSOM were higher in Aveiro than in Coruña, with the highest levels found in winter at both locations. In Coruña, concentrations of PM_{10}, TN, and WSOM were higher than those from $PM_{2.5}$. Regardless of the season, stable isotopic $\delta^{13}C$ and $\delta^{15}N$ in $PM_{2.5}$ suggested important contributions of anthropogenic fresh organic aerosols (OAs) at Aveiro. In Coruña, $\delta^{13}C$ and $\delta^{15}N$ of $PM_{2.5}$ and PM_{10} suggests decreased anthropogenic input during summer. Although excitation-emission fluorescence profiles were similar for all WSOM samples, multi-dimensional nuclear magnetic resonance (NMR) spectroscopy confirmed differences in their structural composition, reflecting differences in aging processes and/or local sources between the two locations. In $PM_{2.5}$ WSOM in Aveiro, the relative distribution of non-exchangeable proton functional groups was in the order: H—C (40–43%) > H—C—C═ (31–39%) > H—C—O (12–15%) > Ar-H (5.0–13%). However, in $PM_{2.5}$ and PM_{10} WSOM in Coruña, the relative contribution of H—C—O groups (24–30% and 23–29%, respectively) equals and/or surpasses that of H—C—C═ (25–26% and 25–29%, respectively), being also higher than those of Aveiro. In both locations, the highest aromatic contents were observed during winter due to biomass burning emissions. The structural composition of $PM_{2.5}$ and PM_{10} WSOM in Coruña

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https://doi.org/10.1016/j.scitotenv.2018.08.171
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is dominated by oxygenated aliphatic compounds, reflecting the contribution of secondary OAs from biogenic, soil dust, and minor influence of anthropogenic emissions. In contrast, the composition of $PM_{2.5}$ WSOM in Aveiro appears to be significantly impacted by fresh and secondary anthropogenic OAs. Marine and biomass burning OAs are important contributors, common to both sites.

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1. Introduction

The study of the water-soluble fraction of organic aerosols (OAs) has been in the spotlight of atmospheric research community due to its effects on aerosol optical depth (Andreae and Gelencsér, 2006; Mladenov et al., 2010; Moise et al., 2015), cloud formation and properties (Martin et al., 2013; Padró et al., 2010; Sun and Ariya, 2006; Wonaschütz et al., 2013), radiation balance (Bond et al., 2013; Laskin et al., 2015; Moise et al., 2015), and atmospheric chemistry (George et al., 2015; Laskin et al., 2015; Mellouki et al., 2015). Atmospheric deposition (wet and dry) is the major pathway for removal of organic carbon (OC) from the atmosphere, thus affecting both atmospheric and land processes, particularly in sensitive ecosystems [e.g., (Witkowska et al., 2016; Witkowska and Lewandowska, 2016; Xie et al., 2016)]. Exposure to OAs has been also linked to a wide range of adverse health effects (e.g., cardiovascular diseases and respiratory problems) (Pöschl, 2005), with many of these toxic effects being attributed to the oxidative or oxidant generating properties of water-soluble organic constituents (Saffari et al., 2014; Verma et al., 2014). Yet, the ability to address the fundamental issues associated with atmospheric chemistry dynamics, climate, and health impact of the water-soluble OAs is limited, mostly because the molecular complexity of aerosol water-soluble organic matter (WSOM) has hindered routine identification of its constituents. Moreover, a myriad of emission sources (natural and anthropogenic) and formation/aging mechanisms (secondary OAs) contribute significantly to the aerosol WSOM burden (Pöschl, 2005), further complicating the molecular characterization of this OAs component.

In Northern Hemisphere midlatitudes, the organic matter may account for 18–70% of tropospheric submicron particulate matter (Zhang et al., 2007), whereas lower percentage values have been reported for Southern Hemisphere locations [e.g., (Duarte et al., 2017b)]. In Europe, the organic matter is also the major single component (15–26%) of both fine and coarse particulate matter ($PM_{2.5}$ and PM_{10}, respectively), with the highest loads being recorded at urban and traffic sites (Putaud et al., 2010). In Southern European regional background and suburban sites, the total carbonaceous fraction [organic matter plus elemental carbon (EC)] is also an important aerosol component, contributing to 28–41% of $PM_{2.5}$ (Duarte et al., 2017a; Pio et al., 2007; Querol et al., 2013, 2009). Notwithstanding these relatively high proportions in ambient PM, the molecular features and source contributions of OAs, including their water-soluble organic component, are still not fully understood. Furthermore, it is also important to note that the water-solubility of OAs from different sources is different [e.g., (Xu et al., 2017)]. Therefore, assessing the water-solubility of ambient OAs and their major structural features would provide not only a better constrain on the types of compounds emitted and/or formed in the atmosphere, but also an in-depth understanding of the contribution from different sources to ambient OAs.

Within Southern Europe, the atmosphere at the Western European Coast supports multiple man-made (e.g., urban, industrial, shipping, and agricultural activities) and climatic (e.g., atmospheric circulation from North Atlantic) stressors with clear socio-economic impacts (Ramos et al., 2016; Russo et al., 2018). As such, the source contributions of OAs at this region are likely to include both primary (sea spray, mineral dust, fossil fuel combustion, wood burning) and secondary (e.g., atmospheric aging and photooxidation) sources (Duarte et al., 2017a, 2015; García-Santiago et al., 2017; Gómez-Carracedo et al., 2015; Lopes et al., 2015; Matos et al., 2017; Moreda-Piñeiro et al., 2015; Viana et al., 2008). However, important questions still remain: (i) how the levels of ambient OAs, in particular of the water-soluble organic fraction, distribute along this region located at the land-sea interface, (ii) how they compare in terms of their structural composition and sources, and (iii) whether would be possible to potentially complement existing OAs source profiles within this region. Hence, this study aims at addressing these three questions, using a multidimensional non-targeted analytical approach (Matos et al., 2017, 2015a), based on one-dimensional (1D) and two-dimensional (2D) solution-state nuclear magnetic resonance (NMR) and excitation-emission matrix (EEM) fluorescence spectroscopies, to investigate the structural composition and major sources of the WSOM from $PM_{2.5}$ samples collected, simultaneously, during summer and winter, in two different suburban sites at the Iberian Peninsula Coast: Aveiro (Portugal) and A Coruña (Spain). PM_{10} samples were also collected concomitantly at A Coruña for comparing and complement the dataset on the main structural features and sources of aerosol WSOM in this suburban location. Stable isotopic ($\delta^{13}C$ and $\delta^{15}N$) and water-soluble trace metals compositions of the bulk $PM_{2.5}$ and PM_{10} samples were also assessed to better understand the contribution of various sources to OAs at the studied locations.

2. Materials and methods

2.1. Aerosol samples collection

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 [Fig. S1, Section S1, in Supporting Information (SI)]. An industrial complex, which includes the production of nitric acid, aniline, nitrobenzene and chlorinate compounds, is located 15 km to the North of Aveiro. A Coruña is a coastal city in the northwest of Spain with a quarter of a million inhabitants. The aerosol measurements were carried out at the urban background site (Oleiros) located near the sea (~0.8 km), and near the neighboring city of A Coruña (located at 8 km) [Fig. S1, Section S1, in SI]. The sampling site is close to a residential area, and in immediate vicinity is agricultural lands, forests and the sea. The main anthropogenic sources are the emissions from traffic and domestic activities, but also industrial emissions can influence air quality in the study area. Because of its proximity to the sea, the local wind pattern is mainly driven by the land-sea breeze. North-westerly synoptic winds are dominant and generally carry relatively clean air from the sea, but other wind directions are also recorded, with a significant contribution to air pollution levels at this site.

In both sampling locations, a total of eight high-volume $PM_{2.5}$ samples (particles with aerodynamic diameter less than 2.5 μm) were simultaneously collected on quartz fibre filters, on a weekly basis (7 days in continuum), during September–October 2016 [$n = 4$, Summer (SU2016)] and January–February 2017 [$n = 4$, Winter (WI2017)] in order to collect enough material for subsequent WSOM characterization. In A Coruña, eight high-volume PM_{10} samples (particles with aerodynamic diameter less than 10 μm) were concomitantly collected in both seasons, following the same sampling procedure. One field blank was collected in each sampling period in order to correct for ambient background $PM_{2.5}$ and PM_{10} mass, total carbon (TC), water-soluble organic carbon (WSOC), total nitrogen (TN), isotopic ($\delta^{13}C$ and $\delta^{15}N$), and water-soluble trace metals levels. This sampling procedure is

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