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^{1}H NMR studies of water- and alkaline-soluble organic matter from fine urban atmospheric aerosols

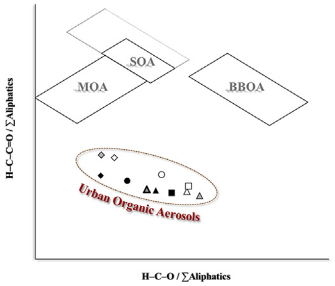
Sónia P. Lopes [a], João T.V. Matos [a], Artur M.S. Silva [b], Armando C. Duarte [a], Regina M.B.O. Duarte [c], *

[a] Department of Chemistry & CESAM, University of Aveiro, 3810-193, Aveiro, Portugal
[b] Department of Chemistry & QOPNA, University of Aveiro, 3810-193, Aveiro, Portugal
[c] Department of Chemistry, CESAM & CICECO, University of Aveiro, 3810-193, Aveiro, Portugal

HIGHLIGHTS

- ^{1}H NMR spectroscopy was used to study urban organic aerosols in $PM_{2.5}$.
- Water and alkaline soluble components of urban organic aerosols have been compared.
- ^{1}H NMR spectral features and their seasonal variability have been investigated.
- Urban OA does not fit marine, secondary and biomass burning source fingerprints.
- Local anthropogenic origin of WSOM and ASOM have been suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

Solution-state ^{1}H NMR spectroscopy was applied to characterize the structural features of water- and alkaline-soluble organic matter (WSOM and ASOM, respectively) sequentially extracted from fine urban atmospheric aerosols collected over different seasons. The objectives of this study were twofold: (i) to compare the functional characteristics of fine aerosol WSOM and the yet unknown ASOM, and (ii) to assess the sources of WSOM and ASOM at an urban location. The ^{1}H NMR analysis confirmed that the WSOM and ASOM fractions hold similar ^{1}H functional groups; however, they differ in terms of their relative distribution throughout the seasons. The winter and autumn samples have a less aliphatic and oxidized character and higher contributions from aromatic groups than those of warmer conditions. The urban aerosol WSOM and ASOM fractions do not fit the established ^{1}H NMR source apportionment fingerprints of marine, secondary, and biomass burning organic aerosols (OAs), exhibiting a smaller relative contribution of carbon-oxygen double bonds, which is indicative of a less oxidized character. These results confirm that the boundaries of the pre-established source categories, especially for secondary and biomass burning OAs, might be different at urban locations, suggesting the need to improve the ^{1}H NMR source apportionment model for including a new fingerprint for urban OAs.

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1. Introduction

Organic aerosols (OAs) represent a large fraction of the mass of fine atmospheric particulate matter and, consequently, may exert a

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* Corresponding author.
E-mail address: regina.duarte@ua.pt (R.M.B.O. Duarte).

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significant impact on climate and human health (Bernstein et al., 2004; Mauderly and Chow, 2008). Depending on its physical and chemical composition, 10–80% of aerosol organic carbon (OC) is water-soluble (Zappoli et al., 1999; Decesari et al., 2001; Sullivan et al., 2004; Duarte et al., 2007, 2015). As recently reviewed by Duarte and Duarte (2013), the water-soluble organic matter (WSOM) in the atmosphere has received much attention from the atmospheric research community, since this fraction 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 WSOM 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 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).

Several different off-line and on-line analytical methodologies have been applied to unravel the structure and composition of aerosol WSOM (Duarte and Duarte, 2011). It has been shown that WSOM 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 (Duarte et al., 2007, 2008; Timonen et al., 2013; Pietrogrande et al., 2013; Chalbot et al., 2014 and references therein). Despite these efforts, there is still a knowledge deficit on aerosol WSOM composition, which further adds to our limited understanding of its fate and impacts on the climate and human health. Therefore, determining the structural composition of aerosol WSOM continues to be of utmost importance for exploring its role in the atmosphere.

Nowadays, the chemical composition, sources, and behavior of the aerosol organic fraction that is not extractable with ultrapure water is emerging as an important research topic when assessing the environmental and health impacts of OAs as a whole. This organic fraction can comprise up to 90% of aerosol OC (Zappoli et al., 1999; Sullivan et al., 2004; Willoughby et al., 2014), and has been indicated to represent local fresh emissions, containing most of the primary fossil material emitted through human activity (Sullivan et al., 2004; Timonen et al., 2013; Willoughby et al., 2014). The available studies rely on the use of high-resolution mass analysis with electrospray ionization and, therefore, they have used organic solvents (e.g. methanol, acetonitrile or pyridine) for extracting the water-insoluble organic species from laboratory generated secondary organic aerosols, SOA (Heaton et al., 2009; Bateman et al., 2010), and ambient rural aerosol samples (Willoughby et al., 2014). In the field aerosol samples, the pyridine extracted a less polar and more aliphatic fraction of the OAs compared to water or acetonitrile, which extracted chemically similar organic matter components (Willoughby et al., 2014). These preliminary studies suggest that the organic solvent-extractable OAs fractions could have molecular characteristics distinct from their water-soluble counterpart. Nevertheless, it must be emphasized that the water- and organic solvent-extracted OC fractions were not sequentially obtained, which means that solvents exhibiting different polarities than water (e.g. methanol and acetonitrile) could still extract similar organic matter components. Anyhow, the questions of the chemical composition and origin of this non-ultrapure water-extractable OAs are far from being resolved.

Based on its own definition, the aerosol organic fraction which is not readily soluble in ultrapure water is expected to have a more hydrophobic character than its water-soluble counterpart. As such, one could presume that this organic fraction can be dissolved in a medium other than an organic solvent. The use of an alkaline medium (e.g. 0.1 M sodium hydroxide, NaOH) following a first ultra-pure water extraction step, could be a good alternative to investigate the less polar and more aliphatic OAs fraction. Adopting this procedure, Feczko et al. (2007) reported that the yearly average concentration of alkaline-soluble organic matter (ASOM) can account to up 14% of the aerosol organic carbon (OC) in six different background European sites. Recently, Matos et al. (2015) reported that the ASOM from fine urban aerosols can account to up 29 and 37% of the particulate OC in cold and warm seasons, respectively. Despite these results, the ASOM fraction still is a poorly understood fraction, which makes its structural characterization a new challenge for the atmospheric research community.

In this work, we employed solution-state ^{1}H NMR spectroscopy to investigate the structural characteristics of the WSOM and ASOM fractions, sequentially extracted from fine atmospheric aerosols collected over different seasons in an urban location at the Western European coast. The fluorescence features of both fractions have been recently studied with the aid of multiway data analysis, where we concluded that the ASOM fraction may have an *in situ* origin. (Matos et al., 2015). In the present study, the acquired ^{1}H NMR data of both aerosol WSOM and ASOM fractions was further interpreted as 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 ASOM, and to understand possible composition variations in both WSOM and ASOM fractions due changes in their sources and seasonal conditions at an urban location.

2. Materials and methods

2.1. Aerosol sampling

A total of 25 fine ($PM_{2.5}$, aerodynamic diameter <2.5 μm) aerosol high-volume samples were collected, on a weekly basis (7 days), at the city of Aveiro (40°38′N, 08°39′W), Portugal, between November 2009 and March 2011. Additional information regarding the sampling procedure can be found in section S1, in Supporting Information (SI). The aerosol samples were grouped together according to similar ambient conditions, on a total of five groups representative of different seasonal periods: Autumn 2009, Summer 2010, Autumn 2010, Winter 2011, and Winter/Spring 2011. The Summer 2010 group was further divided into Summer A 2010 and Summer B 2010, due the high number of forest fires which took place during the second period of this sampling season (8 and 35 fires registered during Summer A and Summer B, respectively). The meteorological data, including air temperature, precipitation, maximum wind velocity, and air masses origin, for each group of aerosol samples are available in Table S1, in SI. The determination of organic carbon (OC) and elemental carbon (EC) in each aerosol sample was performed following a thermo-optical method, described in Section S2, in SI.

2.2. Extraction and isolation of WSOM and ASOM from aerosol samples

An area of 315 cm^2 of each filter was firstly extracted with 150 mL of ultra-pure water (18.2 M Ω cm, filter area to water volume ratio of 2.1 $cm^2\ mL^{-1}$) by mechanical stirring during 5 min plus ultrasonic bath during 15 min. The final slurry obtained was filtered through a hydrophilic polyvinylidene fluoride (PVDF) membrane filter (Durapore®, Millipore, Cork, Ireland) of 0.22 μm pore size. At the end of this filtration step, the slurry residue was washed twice with 20 mL of ultrapure water in order to remove any water-soluble organic carbon (WSOC) still loosely bound to the filter residues. For the ASOM extraction, each slurry residue obtained from the

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