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Persistence of urban organic aerosols composition: Decoding their structural complexity and seasonal variability[☆]

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ABSTRACT

Organic Aerosols (OAs) are typically defined as highly complex matrices whose composition changes in time and space. Focusing on time vector, this work uses two-dimensional nuclear magnetic resonance (2D NMR) techniques to examine the structural features of water-soluble (WSOM) and alkaline-soluble organic matter (ASOM) sequentially extracted from fine atmospheric aerosols collected in an urban setting during cold and warm seasons. This study reveals molecular signatures not previously decoded in NMR-related studies of OAs as meaningful source markers. Although the ASOM is less hydrophilic and structurally diverse than its WSOM counterpart, both fractions feature a core with heteroatom-rich branched aliphatics from both primary (natural and anthropogenic) and secondary origin, aromatic secondary organics originated from anthropogenic aromatic precursors, as well as primary saccharides and amino sugar derivatives from biogenic emissions. These common structures represent those 2D NMR spectral signatures that are present in both seasons and can thus be seen as an "annual background" profile of the structural composition of OAs at the urban location. Lignin-derived structures, nitroaromatics, disaccharides, and anhydrosaccharides signatures were also identified in the WSOM samples only from periods identified as smoke impacted, which reflects the influence of biomass-burning sources. The NMR dataset on the H–C molecules backbone was also used to propose a semi-quantitative structural model of urban WSOM, which will aid efforts for more realistic studies relating the chemical properties of OAs with their atmospheric behavior.

1. Introduction

Decoding the structural features of the organic fraction in fine atmospheric aerosols ($PM_{2.5}$, aerodynamic diameter < 2.5 μm) has remained an important goal for the atmospheric research community. The Organic Aerosol (OA) fraction can account for more than 40% of the total fine aerosol mass in urban and continental areas (Jimenez et al., 2009; Kanakidou et al., 2005), and has profound effects on radiative climate forcing (Kanakidou et al., 2005; Yu et al., 2006), atmospheric chemistry (George et al., 2015; Laskin et al., 2015), and human health (Davidson et al., 2005; Mellouki et al., 2015). The chemical composition and physical properties of OA and their dynamic change in the atmosphere have been the subject of extensive research over the past two decades (Duarte and Duarte, 2011; Nozière et al., 2015). Coping with OA complexity is still, however, a major impairment in advancing our understanding about its molecular composition, as well as its physical properties, sources, transformation, and climatic impact (Duarte and Duarte, 2011; Nozière et al., 2015). Investigating the chemical properties of OA components is also relevant at urban areas, where their ambient concentrations and hazards properties are linked to adverse health effects (Heal et al., 2012).

The most extensively studied OA fraction is the water-soluble component. The water-soluble organic matter (WSOM) represent a highly variable amount (10–80%) of the total particulate organics in the atmosphere (Zappoli et al., 1999; Decesari et al., 2001; Sullivan et al., 2004; Duarte et al., 2007; Lopes et al., 2015) and, therefore, can have an important role in several atmospheric processes: e.g., influencing how particles act as cloud condensation nuclei (Dinar et al., 2006; Padró et al., 2010); contributing to the

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absorption of solar radiation at varying degrees, and thus atmospheric heating (Dinar et al., 2008; Mladenov et al., 2010); and acting as a source of organic carbon (OC) to surface waters, thus influencing the global carbon cycle (Jurado et al., 2008). The most relevant methodologies applied to unravel the chemical and structural composition of WSOM have been widely reviewed (Chalbot and Kavouras, 2014; Duarte and Duarte, 2011, 2015; Graber and Rudich, 2006; Nozière et al., 2015), and usually include a combination of total OC analysis, isolation and/or separation procedures, and functional group analysis by different advanced analytical techniques (e.g., infrared spectroscopy, nuclear magnetic resonance [NMR] spectroscopy, and high-resolution mass spectrometry). It has been shown that WSOM might consist of a highly diverse suite of oxygenated compounds, including dicarboxylic acids, keto-carboxylic acids, aliphatic aldehydes and alcohols, saccharides, anhydrosaccharides, aromatic acids, phenols, but also amines, amino acids, organic nitrates, and organic sulfates (Duarte et al., 2008, 2007; Timonen et al., 2008; Duarte and Duarte, 2015; Lopes et al., 2015). The studies published thus far on the aerosol WSOM have also highlighted the seasonal variation of the chemical features of this aerosol organic fraction. In this regard, using ^{1}H NMR spectroscopy for characterizing WSOM samples, Decesari et al. (2001) reported that acidic compounds (mono- and di-carboxylic acids and polyacidic compounds) were far more abundant than the neutral ones in all seasons, with polycarboxylic acids being the most abundant class of WSOM in spring, fall, and winter, while the mono/di-acids are dominant in summer. Recently, Chalbot et al. (2016) concluded on the different contribution of specific types of carbon functional groups to WSOM for different seasons in an urban location. The aromatic structures were most abundant in fall and winter, hinting the potential contribution of combustion sources, whereas the H—C—O carbon was the dominant WSOM contributor in spring and summer, reflecting the contribution of pollen and other biogenic particles in spring, and secondary OA formation and/or atmospheric aging of primary OA in summer. Duarte et al. (2015) also reported a seasonal variation of urban carbonaceous aerosols, including the WSOM, with the highest concentrations being found during colder seasons. Using solid-state ^{13}C NMR analysis, these authors concluded that winter and autumn samples are distinct from those of warmer conditions, in that they have a less aliphatic and oxidized character and higher contributions from aromatic functional groups. The urban WSOM samples from colder periods were found to be clearly impacted by biomass combustion sources, but including also more aged compounds of probable secondary origin. Despite the improved understanding on the seasonal variation of the chemical features of aerosol WSOM, there is still a deficit knowledge on the structural and molecular signatures of the different OA sources, as well as on their seasonal pattern.

In addition to the WSOM, OA can also contain an organic fraction with a more hydrophobic character and, consequently, not readily soluble in ultra-pure water. It has been suggested that this organic fraction might 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). In order to further investigate its content and structural composition, different groups of authors have used an alkaline solution (i.e. 0.1 M NaOH) on the water treated filters (i.e., following a first ultra-pure water extraction step) to extract the less polar, but still somewhat acidic, OA fraction (Feczko et al., 2007; Matos et al., 2015a; Lopes et al., 2015). Feczko et al. (2007) reported that the yearly average concentration of alkaline-soluble organic matter (ASOM) can account up to 14% of the aerosol OC at six different background European sites. Matos et al. (2015a) showed that the fluorescent features of urban aerosol ASOM are more constant throughout the year than those of the WSOM, suggesting that ASOM may be enriched in fluorescent compounds with an *in situ* origin. Using solution-state ^{1}H NMR spectroscopy, Lopes et al. (2015) suggested that WSOM and ASOM fractions from fine urban aerosols hold similar proton functional groups, but they differ in terms of their relative distribution throughout the year. Yet, the structural characteristics of both WSOM and ASOM components and the actual differences and/or commonalities between these two OA fractions remain poorly defined. Understanding the organic composition at the structural level and how the different functional groups are distributed within the OA is of utmost importance, mostly because such chemical features determines the atmospheric behavior of OA (Laskin et al., 2015; Nozière et al., 2015).

To advance the understanding of the molecular nature of WSOM and ASOM fractions, this study uses a combination of 2D NMR techniques, namely gradient-selected $^{1}H-^{1}H$ homonuclear Correlation Spectroscopy (*g*COSY), gradient-selected $^{1}H-^{13}C$ Heteronuclear Single Quantum Coherence (*g*HSQC), and gradient-selected $^{1}H-^{13}C$ Heteronuclear Multiple Bond Correlation (*g*HMBC), to identify the main substructures present in these two fractions, which have been sequentially extracted from fine urban aerosols collected over two different seasons. Such multifaceted approach was used for providing additional understanding of the structural dynamics of both aerosol WSOM and ASOM fractions, as well as deciphering their major sources over seasons. The spectral data and derived structural features were also used to build a semi-quantitative model of the most atmospherically-relevant structures in urban aerosol WSOM.

2. Materials and methods

2.1. Aerosol sampling, extraction, and isolation of WSOM and ASOM samples

Within the framework of two urban aerosol research projects (ORGANOSOL and CN-linkAIR projects), a total of 12 high-volume $PM_{2.5}$ samples were collected on a rooftop approximately 20 m above the ground at the campus of University of Aveiro (40°38′N, 8°39′W), which is located at about 7 km from the coast on the outskirts of the city of Aveiro (Portugal), with approximately 78.400 inhabitants and an urban area of approximately 197 km^2. The sampling site is located 1 km away from the A25 motorway, and adjacent to a residential area and a salt pans area of the Lagoon of Ria de Aveiro. An industrial complex, which includes the production of nitric acid, aniline and nitrobenzene, is about 10 km north of Aveiro. The sampling site is impacted by both marine air masses travelling from the Atlantic Ocean and anthropogenic emissions from vehicular transport, residential, and industrial sources (Duarte et al., 2017). The $PM_{2.5}$ samples were collected between June 2010 and August 2010 (summer season, 7 samples) and between December 2010 and February of 2011 (winter season, 5 samples), on a weekly basis (i.e., each $PM_{2.5}$ sample was collected during 7 days in continuum), on pre-fired (at 500 °C) quartz-fiber filters (20.3 × 25.4 cm; Whatman QM-A, Maidstone, UK) with an airflow rate of 1.13 $m^3\ min^{-1}$. Throughout the sampling periods no attempts were made to control any adsorption/desorption phenomena on the filters. Consequently, some volatilization/condensation processes may occur on the filter and particles surface for semi-volatile organics. Also, oxidation by strong oxidants (e.g. ozone) of filter deposited organics may occur during aerosol collection. Therefore, in a similar fashion to what has been considered in previous works (e.g. Duarte et al. (2007) and Lopes et al. (2015)), the concentrations and chemical features for oxygenated organic