



Two chemically distinct light-absorbing pools of urban organic aerosols: A comprehensive multidimensional analysis of trends



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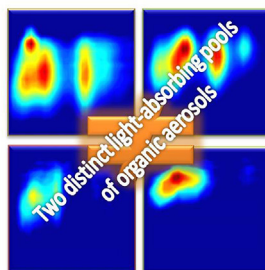
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HIGHLIGHTS

- Chromophoric signature of hydrophobic and size-fractionated organics in aerosols.
- Analytical approach based on a comprehensive multidimensional methodology.
- Two distinct pools of chromophores influence light-absorption of organic aerosols.
- Water-soluble organics chromophores differently affected by sources/aging/seasons.
- Alkaline-soluble organic chromophores have an homogeneous nature across seasons.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 July 2015

Received in revised form

23 November 2015

Accepted 23 November 2015

Available online 11 December 2015

Handling Editor: I. Cousins

Keywords:

Atmospheric aerosols

Alkaline-soluble organic matter

Water-soluble organic matter

Chromophores

Light-absorbing properties

Comprehensive multidimensional analysis

ABSTRACT

The chemical and light-absorption dynamics of organic aerosols (OAs), a master variable in the atmosphere, have yet to be resolved. This study uses a comprehensive multidimensional analysis approach for exploiting simultaneously the compositional changes over a molecular size continuum and associated light-absorption (ultraviolet absorbance and fluorescence) properties of two chemically distinct pools of urban OAs chromophores. Up to 45% of aerosol organic carbon (OC) is soluble in water and consists of a complex mixture of fluorescent and UV-absorbing constituents, with diverse relative abundances, hydrophobic, and molecular weight (Mw) characteristics between warm and cold periods. In contrast, the refractory alkaline-soluble OC pool (up to 18%) is represented along a similar Mw and light-absorption continuum throughout the different seasons. Results suggest that these alkaline-soluble chromophores may actually originate from primary OAs sources in the urban site. This work shows that the comprehensive multidimensional analysis method is a powerful and complementary tool for the characterization of OAs fractions. The great diversity in the chemical composition and optical properties of OAs chromophores, including both water-soluble and alkaline-soluble OC, may be an important contribution to explain the contrasting photo-reactivity and atmospheric behavior of OAs.

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1. Introduction

Atmospheric aerosols have substantially different optical properties, thus altering the absorption and scattering of solar radiation

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(an effect known as direct radiative forcing) (Jacobson, 2001). Aerosols can also act as cloud condensation nuclei (CCN), and thus have an indirect climatic effect through modification of cloud properties (Lohmann and Feichter, 2004; Mahowald et al., 2011; Pöschl, 2005). As reviewed by Kanakidou et al. (2005), the organic aerosol component, in particular the fraction present in submicrometer particle sizes, have an important role in both direct and indirect radiative aerosol forcing. Therefore, understanding the chemical composition and properties of these light-absorbing organic aerosols (OAs) is critical to determine their atmospheric chemistry and climate impacts at both regional and global scales (Jacobson et al., 2000; Laskin et al., 2015).

Drawing a comprehensive picture on fine (diameter < 2.5 μm) OAs composition still is a very challenging task, mostly due to their different mechanisms of formation, sources, atmospheric aging, and complexity of organic structures (Duarte and Duarte, 2011; Noziere et al., 2015). To date, research on the chemical characterization of OAs has been focused mostly on their water-soluble organic matter (WSOM) component. This organic fraction represents a ubiquitous but highly variable fraction (10–80%) of particulate organics in the atmosphere (Zappoli et al., 1999; Decesari et al., 2001; Sullivan et al., 2004; Duarte et al., 2007; Duarte and Duarte, 2011; Matos et al., 2015a; Duarte et al., 2015). Several different off-line and on-line analytical methodologies have been developed and applied to unravel the composition of this OA component (Duarte and Duarte, 2011; Noziere et al., 2015). These efforts have shown that aerosol 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, and phenols, but also amines, amino acids, organic nitrates, and organic sulfates (Duarte et al., 2007, 2008; Pietrogrande et al., 2013; Chalbot et al., 2014 and references therein; Duarte et al., 2015). Despite the increasing efforts to chemically characterize the aerosol WSOM, there is an important pool (14–40%) of this organic fraction that still eludes a satisfactory structural identification by means of the available analytical tools (Duarte and Duarte, 2011, 2013, and references therein). Therefore, the bulk and specific chemical characterization of aerosol WSOM continues to be of utmost importance for exploring its role in the atmosphere.

Knowledge on the chemical identity, sources, and behavior of the non-water-extractable OA fraction is also of considerable interest for understanding the climate-related properties of atmospheric OAs as a whole. Being non-water-extractable, the organic matter contained in this fraction is likely to have a more hydrophobic character than its water-soluble counterpart and, therefore, can be dissolved, for example, in an alkaline medium (in a similar fashion to terrestrial humic substances), although there are some studies reporting the use of organic solvents (e.g., acetonitrile, pyridine, and methanol) for a preliminary assessment of its composition (Nizkorodov et al., 2011; Willoughby et al., 2014). The use of an alkaline following a first ultra-pure water extraction step, is a good alternative to investigate the less polar and presumably 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. More recently, Matos et al. (2015a) 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. It has been suggested that the non-water-extractable OA fraction, where the ASOM is included, may have an *in situ* origin, representing local or regional fresh emissions, thus containing most of the fossil material emitted through human activity (Wozniak et al., 2012; Willoughby et al., 2014; Matos et al., 2015a). Nevertheless, the ASOM fraction still is

a poorly understood fraction which makes its structural characterization a new challenge for the atmospheric research community. Furthermore, little is known about the changes in light-absorbing characteristics of both WSOM and ASOM fractions in relation to their chemical nature (including molecular weight), sources (primary and secondary), and spatiotemporal variability.

In what follows, the objective of this study was to investigate changes in the light-absorbing properties of the chromophoric structures of both WSOM and ASOM fractions, sequentially extracted from fine urban particulate matter (PM_{2.5}) collected in different seasons. The methodology bridges comprehensive two-dimensional separation of both WSOM and ASOM fractions, which simultaneously explore changes in the molecular weight (Mw) and hydrophobicity of these organic fractions, with their intrinsic light-absorbing properties obtained from ultraviolet (UV) absorbance and fluorescence measurements. Reducing the complexity of OAs fractions and adding further analytical dimensions of light-absorbing information has the potential to contribute for a better understanding of the optical properties of OAs, using an urban atmosphere as a case-study. The applied comprehensive separation approach was originally developed to reduce the heterogeneity of standard aquatic fulvic acids (Duarte et al., 2012), and it has been very recently used for constructing a new picture on how size-distinguished aerosol WSOM fractions differ in hydrophobicity during different seasonal events (Matos et al., 2015b). The novelty of the present study is that it takes us one step further in the effort to elicit important and meaningful relationships between size-distinguished fractions of OAs and their UV and fluorescence properties.

2. Material and methods

2.1. Aerosol sampling

A total of 18 high-volume PM_{2.5} samples were collected in pre-fired quartz fiber filters, on a weekly basis (7 days), at the city of Aveiro (40°38'N, 08°39'W), Portugal, between July 2010 and March 2011. Additional information regarding the sampling procedure can be found in section S1, in [Supporting Information \(SI\)](#). The determination of OC and elemental carbon (EC) in each aerosol sample was performed at the Portuguese Agency of Environment, using a Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc.) following a thermo-optical method, described in section S2, in [SI](#).

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

Each collected filter was first extracted with 150 mL of ultra-pure water (18.2 M Ω cm) by mechanical stirring during 5 min plus ultrasonic bath during 15 min. The final obtained slurry was filtered through a hydrophilic polyvinylidene fluoride (PVDF) membrane filter (Durapore[®], Millipore, Ireland) of 0.22 μm pore size. For the ASOM extraction, each retained filter residue obtained from the previous WSOM extraction was soaked in 100 mL of NaOH 0.1 M (Fisher Scientific, UK) under an inert atmosphere (N₂). Then, each residue mixture was placed in an ultrasonic bath for 10 min, acidified with HCl 12 M (Riedel-de Haën, Germany) to pH 3 in order to prevent the oxidation of organic matter, and filtered through a PVDF membrane filter. The dissolved organic carbon (DOC) content of each aqueous and alkaline extract, which was taken as measure of the water-soluble organic carbon (WSOC) and alkaline-soluble organic carbon (ASOC) content of each aerosol sample, respectively, was determined by means of a Shimadzu (Kyoto, Japan) TOC-5000A analyzer. Additional information on DOC analysis can be found in section S2, in [SI](#).

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