Atmospheric Environment 102 (2015) 1–10

Contents lists available at ScienceDirect

Atmospheric Environment

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

# Natural organic matter in urban aerosols: Comparison between water and alkaline soluble components using excitation–emission matrix fluorescence spectroscopy and multiway data analysis

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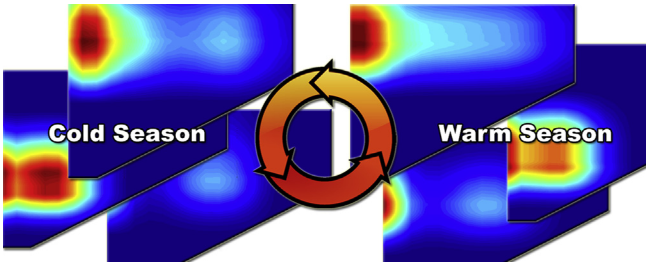
## HIGHLIGHTS

- EEM fluorescence spectroscopy was used to study organic aerosols.
- Water and alkaline soluble components of organic aerosols have been compared.
- The spectral intensity and their seasonal variability have been investigated.
- PARAFAC was used to decompose EEM fluorescence spectra of organic aerosol fractions.
- Possible sources of PARAFAC components from organic aerosols have been suggested.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 15 July 2014
Received in revised form
18 November 2014
Accepted 21 November 2014
Available online 22 November 2014

*Keywords:*
Water-soluble organic matter
Alkaline-soluble organic matter
Atmospheric aerosols
Fluorescence spectroscopy
Emission–excitation matrix
PARAFAC-ALS

## ABSTRACT

Understanding the complexity of Natural Organic Matter (NOM) in atmospheric aerosols has remained an important goal for the atmospheric research community. This work employs a Parallel Factor Model (PARAFAC) with Alternating Least Squares (ALS) algorithm to decompose and further compare sets of excitation-emission matrices fluorescence spectra of Water-soluble and Alkaline-soluble Organic Matter (WSOM and ASOM, respectively), sequentially extracted from urban aerosols collected during different seasons. The PARAFAC-ALS modelling identified three components in both WSOM and ASOM, whose maximum intensities *follow a clear seasonal trend* and which are likely to represent the dominant fluorescent moieties in NOM from urban aerosols. The PARAFAC-ALS modelling also indicated differences *between the colder and warmer seasons* in the fluorescence map of one WSOM component, *which contrast with the results obtained for the ASOM*, where the fluorescence signatures were found to be constant along the seasons, suggesting that the ASOM may have an *in situ* origin.

## 1. Introduction

The fraction of natural organic matter (NOM) in atmospheric aerosols, often referred to as organic aerosols (OA), can be the predominant fraction of fine (diameter <2.5 μm) suspended matter, accounting for 20–90% of the total fine aerosol mass (Kanakidou et al., 2005; Jimenez et al., 2009). After more than a decade of

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http://dx.doi.org/10.1016/j.atmosenv.2014.11.042
1352-2310/

research, it is now well established that OA comprise a multitude of molecular structures, physical properties, and sources (primary and secondary formation) (Duarte and Duarte, 2009). This inherent complexity is nowadays one of the major impairments, not only to an improved understanding of OA chemistry and composition, but also to predict how OA affect the climate system (e.g., Earth's radiative budget and global carbon cycle), atmospheric processes (e.g., cloud formation and lifetime, and secondary aerosol formation), and human health (Pöschl, 2005; Jurado et al., 2008; Heal et al., 2012). Understanding OA significance is, therefore, a focus of major scientific and policy concern.

To date, the overwhelming focus of the atmospheric research community has been on the detailed structural characterization of the water-soluble organic matter (WSOM) from OA. The WSOM represent 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). Several analytical procedures have been developed to study the chemical composition of this water-soluble organic fraction, usually combining total organic carbon analysis, isolation procedures, and off-line characterization by different analytical techniques (e.g., solid- and liquid-state $^{13}$C and $^{1}$H nuclear magnetic resonance (NMR), and high-resolution mass spectrometry (HRMS)) (Sannigrahi et al., 2006; Decesari et al., 2007; Duarte et al., 2007, 2008; Schmitt-Kopplin et al., 2010). As recently reviewed by Duarte and Duarte (2013), most of these studies agree in demonstrating that the aerosol WSOM is, on average, mostly composed of aliphatic structures, but it also has contributions from oxygenated alkyls (e.g. carbohydrate-type structures and alcohols), carboxylic acids, and aromatic structures. These studies have also provided an overview of WSOM composition along different seasons as well as a source attribution (Duarte and Duarte, 2013). Although progress has been made using these protocols for elaborating a model of aerosol WSOM from its functional group composition and a discussion of its possible sources, it is questionable whether the obtained results truly represent the chemical nature of these samples, particularly because a highly variable fraction (14–40%) of the WSOM still eludes structural characterization by means of the currently available high-resolution NMR and MS techniques (Duarte and Duarte, 2011, 2013). Consequently, the majority of the physicochemical properties of these WSOM components, as well as their sources, formation mechanisms, and fate in the atmosphere are still poorly understood.

Besides the water-soluble organic component, the OA also contain water-insoluble organic matter (WIOM), which is often neglected in most field studies and, therefore, left under-characterized. The WIOM may also constitute a highly variable fraction of the total fine aerosol mass and hence may significantly affect the atmospheric behaviour of the air particles. Being insoluble in ultra-pure water, the organic matter contained in this fraction is likely to have a more hydrophobic character 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) (Nizkorodov et al., 2011; Willoughby et al., 2014).

One of the earliest reports in the alkaline-soluble aerosol fraction was carried out by Havers et al. (1998), who performed a direct extraction of the so-called humic-like substances from standard reference air dust and other urban and rural atmospheric particles using 0.1 M sodium hydroxide (NaOH). The authors suggested that this fraction was rich in aliphatic and carbohydrate structures, comparable to humic and fulvic acids from soils and aquatic systems. Since the work of Havers et al. (1998), to the best of our knowledge, only one further work has addressed the alkaline-soluble fraction of OA, but only in quantitative terms: Feczko et al. (2007) obtained the alkaline extractable organic fraction using 0.1 M NaOH on the water treated filter (i.e., following a water extraction). This is a major difference to the procedure of Havers et al. (1998) and, therefore, the results are not comparable. Feczko et al. (2007) reported that the yearly average concentration of alkaline-soluble organic matter (ASOM) fraction can account to up 14% of the aerosol organic carbon. However, nothing is known about its chemical composition and possible sources.

The obvious lack of knowledge on this ASOM leads us to develop new strategies for assessing its chemical features and further comparison to those of the WSOM. For this purpose, this work applies three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy to study the main fluorophores structures of both WSOM and ASOM fractions, sequentially extracted from fine particulate matter ($PM_{2.5}$) collected at an urban location during different seasons. As recently reviewed by Andrade-Eiroa et al. (2013b), this technique has been extensively used for providing important information on the chemical nature, structural groups, conformation, and heterogeneity of chromophoric NOM from different environmental matrices, including also WSOM from aerosols (Duarte et al., 2004; Mladenov et al., 2011). The application of this technique has also increased in the last decade due to the association of multiway chemometric methods, namely parallel factor model (PARAFAC) with an Alternating Least Squares algorithm (ALS) (Murphy et al., 2013).

In this work, we also take advantage of this powerful chemometric tool for decomposing sets of EEM spectra of WSOM and ASOM in order to identify the location and intensity of independent fluorescent components from the PARAFAC-ALS models and, consequently, to characterize the dominant individual fluorescent moieties in both WSOM and ASOM from urban aerosols. From the comparison of the spectral features obtained for each OA fraction, an attempt to identify the most atmospherically-relevant fluorescent structures will be pursued, as well as their variability over seasons.

## 2. Materials and methods

### 2.1. Aerosol sampling

Within two urban aerosol research projects (ORGANOSOL and CN-linkAIR projects), high-volume aerosol samples were collected at the city of Aveiro (40°38′N, 08°39′W), Portugal, on a weekly basis (7 days) in order to collect enough material for subsequent structural characterization. Additional information regarding the sampling procedure can be found in Supporting Information (SI). A total of 60 aerosol samples were collected during an intensive field campaign between November 2009 and January 2014, which were grouped together according to similar ambient conditions, on a total of sixteen groups representative of different seasonal periods. Throughout this intensive sampling period, no attempts were made to control any adsorption/desorption phenomena on the filter. Consequently, some volatilisation/condensation processes may occur on the filter, or particles surface, for semi-volatile organics. Also, oxidation of filter deposited organics by strong oxidants (e.g. ozone) may occur during aerosol collection. Therefore, in a similar fashion to what has been considered in previous works (e.g., Duarte et al. (2007)), the measured concentrations for oxygenated organic species, water-soluble organic carbon (WSOC) in particular, should be considered an upper limit of the true atmospheric levels. Nevertheless, preliminary aerosol sampling campaigns, using the tandem filter method (i.e., sets of two (front and back) quartz fibre filters directly on top of each other), were carried out in order to