



## A one-year record of carbonaceous components and major ions in aerosols from an urban kerbside location in Oporto, Portugal



Danilo Custódio<sup>a</sup>, Mário Cerqueira<sup>a,\*</sup>, Célia Alves<sup>a</sup>, Teresa Nunes<sup>a</sup>, Casimiro Pio<sup>a</sup>, Valdemar Esteves<sup>b</sup>, Daniele Frosini<sup>c</sup>, Franco Lucarelli<sup>d</sup>, Xavier Querol<sup>e</sup>

<sup>a</sup> Department of Environment & Centre for Environmental and Marine Studies (CESAM), University of Aveiro, 3810-193 Aveiro, Portugal

<sup>b</sup> Department of Chemistry & Centre for Environmental and Marine Studies (CESAM), University of Aveiro, 3810-193 Aveiro, Portugal

<sup>c</sup> Department of Chemistry, University of Florence, 50019 Sesto Fiorentino, Florence, Italy

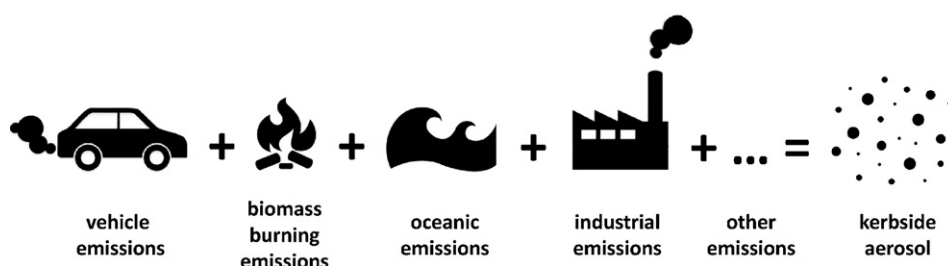
<sup>d</sup> Department of Physics and Astronomy, University of Florence, 50019 Sesto Fiorentino, Florence, Italy

<sup>e</sup> Institute of Environmental Assessment and Water Research, Spanish Research Council, 08034 Barcelona, Spain

### HIGHLIGHTS

- Fine aerosol composition was investigated at a kerbside site during one year.
- PM<sub>2.5</sub> composition was strongly influenced by vehicle exhaust and biomass burning.
- Organic acids were associated with both natural and anthropogenic sources.
- (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was dominant in summer due to an increase in secondary aerosol formation.
- NaCl was dominant in winter due to an increase of sea salt transport from the ocean.

### GRAPHICAL ABSTRACT



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### ABSTRACT

PM<sub>2.5</sub> aerosol samples were collected from January 2013 to January 2014 on the kerbside of a major arterial route in the city of Oporto, Portugal, and later analyzed for carbonaceous fractions and water soluble ions. The average concentrations of organic carbon (OC), elemental carbon (EC) and water soluble organic carbon (WSOC) in the aerosol were 6.2 μg/m<sup>3</sup>, 5.0 μg/m<sup>3</sup> and 3.8 μg/m<sup>3</sup>, respectively, and fit within the range of values that have been observed close to major roads in Europe, Asia and North America. On average, carbonaceous matter accounted for 56% of the gravimetrically measured PM<sub>2.5</sub> mass. The three carbon fractions exhibited a similar seasonal variation, with high concentrations in late autumn and in winter, and low concentrations in spring. SO<sub>4</sub><sup>2-</sup> was the dominant water soluble ion, followed by NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, oxalate, Ca<sup>2+</sup>, Mg<sup>2+</sup>, formate, methanesulfonate and acetate. Some of these ions exhibited a clear seasonal trend during the study period. The average OC/EC ratio for the entire set of samples was 1.28 ± 0.61, which was consistent with a significant influence of vehicle exhaust emissions on aerosol composition. On the other hand, the average WSOC/OC ratio was 0.67 ± 0.23, reflecting the influence of other emitting sources. WSOC was highly correlated with nssK<sup>+</sup>, a tracer of biomass combustion, and was not correlated with nssSO<sub>4</sub><sup>2-</sup>, a species associated with secondary processes, suggesting that the main source of WSOC was biomass burning. Most of the SO<sub>4</sub><sup>2-</sup> was anthropogenic in origin and was closely associated with NH<sub>4</sub><sup>+</sup>, pointing to the formation of secondary aerosols. Na<sup>+</sup>, Cl<sup>-</sup> and methanesulfonate were clearly associated with marine sources while NO<sub>3</sub><sup>-</sup> was related with combustion of both fossil and non-fossil fuels. Mixed sources explained the occurrence of the other water soluble ions.

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\* Corresponding author.

E-mail address: [cerqueira@ua.pt](mailto:cerqueira@ua.pt) (M. Cerqueira).

## 1. Introduction

Exposure to atmospheric aerosols in urban areas has been linked to adverse health effects related primarily to the respiratory and cardiovascular systems (Dominici et al., 2006; Martinelli et al., 2013). The urban aerosol is made up of primary particles — emitted directly into the atmosphere from anthropogenic and natural sources — and secondary particles — formed in the atmosphere from gas to particle conversion, condensation of gases on preexisting particles, and heterogeneous reactions (Calvo et al., 2013; Pöschl, 2005). In the urban atmosphere primary anthropogenic sources include traffic, domestic fuel combustion, industrial activities and construction works, while primary natural sources comprise sea salt, soil dust and biological debris (Calvo et al., 2013; Pöschl, 2005). Owing to the variety of sources, urban aerosol consists of a complex mixture of chemical constituents such as carbonaceous matter, soluble inorganic salts and acids, insoluble mineral dust, trace metals and water (Calvo et al., 2013). However, the chemical properties of urban aerosols differ significantly between background and roadside atmospheres. A number of studies conducted during the last years indeed indicate that the chemical composition of aerosol samples collected at the roadside level is strongly influenced by fresh tailpipe emissions, re-suspended road dust, and brake and tyre wear (Amato et al., 2011; Aurela et al., 2015; Furuşjö et al., 2007; Bukowiecki et al., 2010; Mirante et al., 2014; Pant and Harrison, 2013; Weinbruch et al., 2014). The proximity to road traffic emissions has been linked to increased morbidity and mortality in some epidemiological studies (Hoek et al., 2001; Hoffman et al., 2009). In addition, traffic also represents an important source of gaseous precursors of secondary aerosols, which may account for a significant fraction of the total particulate mass, as suggested by many source apportionment studies carried out in urban areas (Cusack et al., 2013; Guo et al., 2014; Liu et al., 2014; Voutsas et al., 2014). The rate at which aerosol formation takes place is strongly dependent on atmospheric and meteorological conditions, which implies dissimilarities among geographical regions (Jimenez et al., 2009). This is particularly important in urban areas of Southern European countries that are characterized by a complex meteorology (e.g. intense solar radiation, low rainfall) which favors gas-to-particle conversion processes (Reche et al., 2011). Despite advances on this topic, we do not yet have a full understanding about the composition and origin of particles collected in the proximity of busy roads. Specifically, to our knowledge, there is no information available regarding the seasonal variation of source contributions to aerosol mass collected at these sites. This shortage of information is hindering the development of effective measures to reduce human exposure to aerosol particles in heavily trafficked roads.

The work presented in this paper is intended to provide comprehensive information about the seasonal variation of fine aerosol chemical composition (with a focus on carbonaceous matter and water soluble ions) at the roadside level in a typical medium sized southern European city (Oporto, Portugal) and complements the recent study of Amato et al. (2016) who described source apportionment results for aerosol samples collected in Southern European cities during the AIRUSE LIFE+ project. Finally, the present work will be of crucial interest to further understand the origin of aerosol particles and therefore for the adoption of measures and new strategies to ensure better air quality in urban areas.

## 2. Sampling and analytical methods

### 2.1. Study site and aerosol sampling

Oporto is located in northern Portugal, near the mouth of the Douro River (Fig. 1). The city has a population of about 240,000 (INE, 2011), and the urban area, which extends beyond its administrative limits, has a population of about 1.3 million in a land area of 389 km<sup>2</sup>, making it the country's second largest city after the capital. Oporto is the center

of an important industrial, commercial and touristic region, as well as a major communication and transportation hub in the northwestern Iberian Peninsula.

Aerosol sampling was conducted from the 5th of January 2013 to the 24th of January 2014 on the rooftop of an air quality monitoring station (41°09'46"N; 8°35'27"W) located on the kerbside of a major arterial route (Fernão de Magalhães Avenue) connecting the Inner Circular Highway to the city centre. The avenue runs in a northeast-southwest direction and the station is located on the northwest kerbside. Two aerosol samplers fitted with PM<sub>2.5</sub> size selective inlets were used in parallel: a low-volume sampler, operated at a flow rate of 2.3 m<sup>3</sup>/h and equipped with a Pall PTFE filter; and a high volume sampler, operated at a flow rate of 1.13 m<sup>3</sup>/min and equipped with a pre-fired (550 °C, 5 h) Whatman QM/A quartz fiber filter. The PTFE filters were used for the determination of aerosol mass concentration and for the chemical analysis of water soluble ions whilst the quartz fiber filters were used for the analysis of organic carbon, elemental carbon and water soluble organic carbon. The sampling period was 24 h and the frequency was set to one sample every three days.

### 2.2. Analytical methods

The mass concentration of particulate matter was determined by gravimetry. Before sampling, the filters were conditioned for at least 24 h in a room with constant humidity (50 °C) and temperature (20 °C) and then weighed with an electronic microbalance with a sensitivity of 0.01 mg, in accordance with the European Standard EN14907:2005 (CEN, 2005). After collection, the filters were re-conditioned, re-weighed and stored at −20 °C until the chemical analysis. The EC and OC particulate fractions accumulated in the filters were measured by the thermal optical method previously described by Pio et al. (2011). The uncertainty based on triplicate analysis of sample filters was <5%. The detection limits were 30 ng/m<sup>3</sup> for OC and 3 ng/m<sup>3</sup> for EC.

For the analysis of water soluble organic carbon, two 9 mm punches taken from a sample filter were subjected to extraction with 20 mL of UV-oxidized high-purity water under ultrasonication for 20 min at room temperature. The liquid extract was filtered, with a 0.45 µm PTFE syringe filter, to remove insoluble particles and filter debris. The filtrate was then acidified with a 2 M HCl solution (2%,  $V_{\text{acid}}/V_{\text{sample}}$ ), purged with ultra-pure nitrogen, to remove dissolved volatile inorganic carbon and volatile organic species, and analyzed for WSOC using a total organic carbon analyzer (Shimadzu TOC-5050A). Water insoluble organic carbon (WIOC) was calculated as the difference between OC and WSOC. The triplicate analysis of standards indicated an uncertainty of 4%. The method detection limit was 50 ng/m<sup>3</sup>.

For the analysis of water-soluble ions, a quarter of Teflon filter was subjected to extraction with 13 mL of Milli-Q ultrapure water under ultra-sonication for 15 min at room temperature. The liquid extracts were then filtered with a 0.45 µm pore PTFE syringe filter to remove insoluble particles, and analyzed using three Dionex ion chromatography systems equipped with electrochemical suppression. The cations ammonium (NH<sub>4</sub><sup>+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) were determined using an IonPac CG12A guard column and a CS12A analytical column with 10 mM H<sub>2</sub>SO<sub>4</sub> as the eluent. The anions chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) were measured with an IonPac AG4A guard column and an AS4A analytical column with a Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> (1.8 and 1.7 mM, respectively) buffer solution as the eluent. The anions fluoride (F<sup>-</sup>), formate (HCOO<sup>-</sup>), acetate (CH<sub>3</sub>COO<sup>-</sup>), methanesulfonate (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and glycolate (HOCH<sub>2</sub>COO<sup>-</sup>) were determined with an IonPac AG11 and an IonPac AS11 column by gradient elution with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution from 0.075 mM to 2.5 mM as eluent. The analytical uncertainty based on triplicate measurements of standards was <5%. The detection limits were in the range of 0.1 to 1 ng/m<sup>3</sup>.

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