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Jorge**

**Carbono particulado na atmosfera: distribuição,
envelhecimento e deposição húmida**

**Particulate carbon in the atmosphere: distribution
aging and wet deposition**



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Particulate carbon in the atmosphere: distribution aging and wet deposition

Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica do Doutor Mário Miguel Azevedo Cerqueira, Professor Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro, e a co-orientação da Doutora Teresa Filomena Vieira Nunes, Professora Associada do Departamento de Ambiente e Ordenamento da Universidade de Aveiro.

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“Nothing is more fatal to the knowledge raise than to presume that our views are ultimate. In this world, as more we know more remains to explore and there is always a new thesis to conquer”

palavras-chave

aerossol, carbono orgânico, carbono elementar, carbono orgânico, carbono orgânico solúvel, carbono orgânico insolúvel, atmosfera de fundo, atmosfera urbana, processos atmosféricos, deposição húmida

resumo

Nas últimas décadas foram desenvolvidos vários estudos sobre a circulação atmosférica da matéria carbonácea. Contudo, apesar dos esforços da comunidade científica, não se conseguiu ainda compreender detalhadamente a composição e a formação do aerossol carbonáceo no ar ambiente, o que reflete a grande variedade de fontes emissoras e a complexidade dos processos de transformação que ocorrem na atmosfera. Acresce ainda que se sabe muito pouco sobre um caso particular do aerossol de carbono: as partículas carbonáceas em suspensão no ar interior. Outra componente do ciclo do carbono que tem merecido pouca atenção da comunidade científica é a remoção das partículas carbonáceas da atmosfera.

Este trabalho tem como objetivo principal contribuir para um melhor conhecimento sobre as fontes, processos de transformação e remoção da matéria carbonácea presente na atmosfera. As concentrações de matéria particulada, carbono orgânico (CO) e carbono elementar (CE) foram medidas simultaneamente no ar interior e exterior de residências localizadas em áreas urbanas e sub-urbanas da região nordeste de Portugal Continental. Os valores médios da razão entre as concentrações no ar interior e exterior (I/E) para o CO foram superiores a 1 para as residências com ocupantes, mostrando que as fontes interiores, como a confeção de alimentos, a queima de biomassa e o movimento de pessoas, influenciaram fortemente os teores de CO. Pelo contrário, obtiveram-se valores médios próximos de 1 para a razão I/E do CE, excluindo uma residência de fumadores, sugerindo que as concentrações deste componente eram controladas por fontes externas, muito provavelmente o tráfego automóvel e a queima de biomassa. A composição do aerossol foi também avaliada durante um ano num local confinante com uma estrada de tráfego intenso na cidade do Porto. Verificou-se que as principais fontes emissoras de partículas eram o tráfego automóvel, as poeiras do solo e a queima de biomassa. Muitos dos constituintes do aerossol mostraram variações temporais bem marcadas, as quais foram relacionadas com a variabilidade sazonal das fontes emissoras, dos processos atmosféricos e das condições climáticas. Procedeu-se ainda à recolha de amostras de precipitação e posterior caracterização química num local de fundo do arquipélago dos Açores e num local urbano da cidade do Porto. A principal fonte do CE nos Açores é o transporte a longas distâncias a partir das áreas continentais que envolvem o Atlântico Norte. Os teores de carbono orgânico insolúvel tiveram origem tanto em emissões locais como no transporte a longas distâncias. As concentrações de matéria carbonácea no Porto mostraram-se substancialmente superiores às que tinham sido medidas em áreas remotas de Portugal, indicando uma contaminação significativa por atividades antropogénicas.

Keywords

aerosol, elemental carbon, organic carbon, dissolved organic carbon, water insoluble organic carbon, background atmosphere, urban atmosphere, atmospheric processes, wet deposition

Abstract

During the last decades a significant number of studies was performed about the cycling of carbonaceous matter in the atmosphere. Despite the efforts of the scientific community, a full understanding about the composition and formation of carbonaceous aerosol in ambient air was not yet achieved, reflecting the great variety of emitting sources and the complexity of transformation processes in the atmosphere. In addition, very little is known about a specific type of carbonaceous aerosol: the indoor carbonaceous aerosol. Removal of particulate carbonaceous matter from the atmosphere is another component of the carbon cycle that has received poor attention from researchers.

The main aim of this work was to contribute to a better understanding of the sources, transformation processes and removal of atmospheric carbonaceous matter. Particulate matter, organic carbon (OC) and elemental carbon (EC) concentrations were measured simultaneously in the indoor and outdoor air of residences located in urban and sub-urban areas of northwestern Mainland Portugal. Average indoor to outdoor ratios (I/O) for OC were higher than 1 in occupied residences, showing that indoor sources, such as cooking, smoking, biomass burning and movement of people, strongly influenced indoor OC concentrations. In contrast, I/O ratios for EC were close to 1, except for a smokers' residence, suggesting that indoor concentrations were mainly controlled by outdoor sources, most likely from vehicular emissions and biomass burning. Aerosol composition was also evaluated during one year in a kerbside site located in a busy road of Oporto. Road traffic, local dust and biomass burning were found to be the most important sources of aerosol particles. Most of the aerosol constituents exhibited well-defined temporal variations, which were related with the seasonal variability of source strengths, atmospheric processes and climatic conditions. In addition, precipitation samples were collected and characterized for chemical constituents at a background site in the Azores Islands and an urban site in the city of Oporto. Transport from continental areas bordering the North Atlantic Ocean were the main source of EC in the Azores. Both local emissions and long-range transport explained the levels of water soluble organic carbon found in the same samples. Concentrations of carbonaceous matter in Oporto were considerably higher than those measured before in other background areas in Portugal, indicating a significant atmospheric contamination by anthropogenic activities.

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CHAPTER 1

General Introduction

1. 1. Properties and sources of carbonaceous aerosol

Carbonaceous matter comprise a large and highly variable fraction of the atmospheric aerosol and consists of organic carbon (OC), elemental carbon (EC) or black carbon (BC) and inorganic carbonate carbon (CC). EC and BC are often used interchangeably to denote roughly the same refractory and light-absorbing fraction of carbonaceous matter; when this fraction is quantified with a thermal method it is normally named EC and when it is measured with an optical method is named BC.

EC presents a chemical structure similar to graphite and is a primary species produced by the incomplete combustion of biomass and fossil fuels. EC is a strong light-absorbing material, and therefore can have significant direct and indirect climatic effects, including absorption of incoming and outgoing solar radiation, hence contributing to warming of the atmosphere, decreasing the albedo of snow and ice due to deposition of EC particles, therefore increasing absorption and accelerating melting, and changing the properties and distribution of clouds, with effects on cloud reflectivity and precipitation patterns (Hansen and Nazarenko, 2004; Jacobson, 2001).

OC is a complex mixture of hundreds of organic compounds, which is not completely resolved, including, aliphatic and aromatic hydrocarbons, aldehydes, ketones, alcohols and carboxylic acids (Calvo et al., 2013). OC has both a primary and a secondary origin. Primary OC particles of natural origin include plant spores and pollen, vegetation debris, microorganisms, soil organic matter and marine aerosols (Calvo et al., 2013; Després et al., 2012). Biomass and fossil fuel burning are the two most important sources of anthropogenic primary OC aerosols. The share of OC and EC emitted during combustion processes depends on various conditions, including temperature, fuel composition and moisture, and relative humidity (Bond et al., 2004). In general, EC prevails in emissions from high temperature fires, such as diesel engines, and OC is more abundant in emissions from smoldering flames, such as wildfires.

Secondary OC particles are produced from gas to particle conversion of volatile organic compounds, either by the condensation of low vapor pressure compounds or from physical or chemical adsorption of gaseous species on aerosol particles. The formation of secondary organic aerosol depends on several chemical and meteorological factors, such as the concentrations of gaseous precursors, the presence of atmospheric oxidants, the characteristics of pre-existing aerosols, air temperature and relative humidity. Secondary organic aerosol can be formed from both natural and anthropogenic gaseous volatile organic

compounds. The most relevant sources of gaseous precursors are vegetation, animals, wildfires, combustion of fossil fuels, vehicle exhaust, oil extraction and refining, natural gas extraction and refining and chemical industries.

In contrast to EC, the OC fraction of aerosol particles is not light absorbing. But OC particles are very efficient at scattering light, and therefore reduce the amount solar radiation that is absorbed by the Earth's surface (Lin et al., 2014).

Water soluble organic carbon (WSOC) represents a significant fraction (20 to 80%) of OC particulate matter (Jaffrezou et al., 2005; Park and Cho, 2011). WSOC has been mostly associated with the production of secondary organic aerosol (Sullivan et al., 2004; Yang et al., 2005). However, primary contributions to WSOC ambient concentrations, particularly biomass burning emissions, have also been documented (Viana et al., 2008; Wonaschütz et al., 2011). Given the water affinity of this organic carbon fraction, WSOC is expected to influence the formation of cloud condensation nuclei and hence on cloudiness and surface temperature.

CC is another form of primary carbonaceous matter that is emitted to the atmosphere, mainly as a result of soil dust suspension and construction/demolition works. It is usually not considered in atmospheric chemistry studies, particularly those focusing on fine particles, due to a low contribution to the aerosol mass load and also due the absence of a robust method to determine CC concentrations in atmospheric particles (Karanasiou et al., 2011).

1.2. Aging and distribution of carbonaceous aerosols in the atmosphere

After emission into the atmosphere, carbonaceous particles experience a set of physical and chemical transformations, including changes in their size, structure and chemical composition (aerosol aging). Common processes involved in the modification of primary organic carbon aerosols are adsorption of volatile organic compounds (Kroll et al., 2005), reaction of atmospheric oxidants at the particle's surface (de Gouw and Lovejoy, 1998), and photochemical degradation (Mang et al., 2008). Freshly emitted EC aerosols also experience aging by condensation of gaseous species (Moteki et al., 2007), coagulation with preexisting aerosols (Johnson et al., 2005) and reaction with gaseous oxidants (Zuberi et al., 2005). In general, primary carbonaceous aerosols have low water affinity. However, aging processes can convert the hydrophobic carbonaceous particles in hydrophilic ones (Liu et al., 2011; Tritscher et al., 2011). This transformation has important implications in the way aerosols interact with water and on the subsequent removal from the atmosphere by the action of

hydrometeors. Therefore, aging processes are expected to significantly affect the distribution and burden of carbonaceous particles in the atmosphere.

EC aerosol particles and a significant fraction of OC aerosol particles are sufficiently small to be removed from the atmosphere immediately after production. Indeed, the lifetime of fine carbonaceous aerosols is generally of the order of a few days, which explains the uneven distribution of both carbon fractions at the Earth's surface. Global model simulations, along with field data, show that carbonaceous aerosols originating from fossil fuel combustion and biomass combustion are common throughout the year over Europe, North America and Asia. Carbonaceous aerosols emitted from biomass burning also spread over vast areas of central and southern Africa, South America and Southeast Asia, particularly during the dry season. In contrast with the accumulation over continental areas, OC and EC particles are scarcer over marine regions or the Earth's poles (Cooke et al., 2002; Takemura et al., 2000).

1.3. Removal of carbonaceous aerosols from the atmosphere.

Carbonaceous aerosols are removed from the atmosphere by wet deposition (the incorporation of particles in clouds and precipitation and the subsequent transport to the surface) and dry deposition (the transport of particles from the atmosphere to the surface without interaction with clouds and precipitation). The relative importance of these deposition processes depends of various factors, including the physical and chemical properties of particles, the amount of precipitation in the region and the type of terrain and surface cover. In areas with abundant precipitation removal of carbonaceous aerosol from the atmosphere is clearly dominated by wet deposition (Cerqueira et al., 2010). Wet scavenging of carbonaceous aerosols include in-cloud processes, when aerosol particles act as cloud condensation nuclei or ice nuclei, and below-cloud processes, when aerosol particles are intercepted by falling rain droplets or snowflakes. Scavenging of carbon species from the atmosphere by wet deposition is strongly dependent on the affinity of chemicals with water. Although EC can acquire hydrophilic properties by chemical aging (Liu et al., 2011; Tritscher et al., 2011), fresh EC is known to be hydrophobic, thus its scavenging ratio tends to be lower than those commonly found for more soluble atmospheric constituents, such as OC, that comprises a significant fraction of water-soluble compounds and consequently facilitates the transfer of organic particles into hydrometeors. Not surprisingly, estimates of scavenging ratios show that EC is removed from the atmosphere less efficiently than OC (Cerqueira et al., 2010).

1.4. Motivation and objectives

The present thesis aims to increase the current knowledge about the cycling of carbonaceous matter in the atmosphere. During the last two decades a significant number of studies was performed covering this subject, with a particular focus on aerosol composition in outdoor air and the origin of atmospheric particulate matter. Despite the efforts of the scientific community, a full understanding about the composition and formation of carbonaceous aerosol particles in ambient air was not yet achieved, reflecting the great variety of emitting sources and the complexity of transformation processes in the atmosphere. In addition, few attention has been paid to carbonaceous aerosol in indoor air. Humans spend most of their time in confined spaces, hence it is critically important to explore the origin and chemical composition of indoor inhalable particles. Removal of particulate carbonaceous matter from the atmosphere is another step of the carbon cycle that has received very little attention from researchers. Wet deposition is known to play an important role at cleaning the atmosphere but current information on carbonaceous matter in precipitations is still poorly documented. This scarcity of data about wet deposition fluxes of particulate carbon is an important limitation to validate regional and global models that simulate transport and concentration of this aerosol constituent.

Specific objectives of this thesis include:

- to investigate the relationships between indoor and outdoor concentrations of PM₁₀, OC and EC concentrations and describe relevant sources of particulate matter in the indoor air of residences in Portugal;
- 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);
- to characterize aerosol sources and estimate their relative contribution to the mass of suspended particles in the atmosphere of Oporto;
- to characterize the seasonal variation of WIOC and EC concentrations and investigate the sources of these carbon fractions in rain samples collected in a remote marine area (Azores Islands);
- to characterize major chemical constituents (organic and inorganic) in rain samples, investigate their sources and explore the interactions between rain and suspended particles in a typical urban site (Oporto);

- to estimate wet deposition fluxes of major carbon fractions in two sites with contrasting levels of atmospheric contamination.

1.5. Outline of the thesis

The thesis is organized in seven chapters. Chapter 1 presents a brief introduction about the sources, composition, distribution and removal of carbonaceous aerosols, along with the motivation, objectives and outline of the thesis. The following five chapters have the format of scientific articles, four of which were already published or submitted to international journals with peer review.

Chapter 2 presents the first description of particulate matter (PM_{10}) and associated carbonaceous fractions in the indoor air of residential homes in Portugal. The characteristics and the relationships between indoor and outdoor concentrations of particulate matter, organic carbon and elemental carbon were investigated

Chapter 3 describes the seasonal variation of major aerosol constituents (carbon fractions and water soluble organic and inorganic ions) in Oporto, Portugal. The study was based on more than one hundred $PM_{2.5}$ samples collected at a kerbside site and explores the time variation of factors contributing to aerosol formation in an urban area.

Chapter 4 is also focused on the Oporto aerosol composition. An in depth characterization of the chemical properties of $PM_{2.5}$ and PM_{10} aerosol samples collected simultaneously in Oporto was performed and a receptor model was applied to investigate the contribution of different sources to the aerosol load in a large urban area. Both studies about the Oporto aerosol were performed within the framework of AIRUSE LIFE Project, the main objective of which was to test and develop specific measures to improve air quality in southern Europe.

Chapter 5 presents the first long term study about wet deposition of particulate carbon to a remote marine area (Azores Islands). Water insoluble carbon was measured in rain samples and the results were used to investigate sources of carbon and to estimate wet deposition fluxes into the Central North Atlantic Ocean.

Chapter 6 is also focused on the chemistry of precipitation. Rain samples were continuously collected during one year at a kerbside site in Oporto and analyzed for major chemical constituents. In this study sources of chemical species in rain were described, the incorporation of aerosol particles by rain was explored and wet deposition fluxes quantified.

Finally, Chapter 7 provides a compilation of the main conclusions of this thesis.

1.6. Contribution of the candidate to jointly authored articles presented in this thesis

As stated above, five out of seven chapters of the present thesis have the format of scientific articles. The contribution of the candidate to each one of the articles is given below:

Chapter 2: contribution to study design; sample collection in two out of four investigated homes; contribution to PM₁₀, EC and OC measurement in samples from two homes; and participation in data analysis and article writing.

Chapter 3: significant contribution to study design and sampling site preparation; collection of aerosol samples during one year (together with another team member); analysis of carbon fractions and water soluble ions in the whole set of aerosol samples; significant contribution to data analysis and interpretation; and participation in article writing.

Chapter 4: significant contribution to study design and sampling site preparation; collection of aerosol samples during one year (together with another team member); analysis of carbon fractions, water soluble ions and elements in the whole set of aerosol samples (he stayed a few weeks at the University of Florence to perform ion chromatography and PIXE analysis); statistical and source apportionment analysis of data.

Chapter 5: in charge of continuous rain sampling during the study period at the Azores; analysis of carbon fractions at the University of Aveiro; data analysis and interpretation; and contribution to article writing.

Chapter 6: significant contribution to study design and sampling site preparation; collection of rain samples during one year (together with another team member); analysis of carbon fractions and water soluble ions in the whole set of rain samples; data analysis and interpretation; and article writing.

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CHAPTER 2

Indoor and outdoor suspended particulate matter and associated carbonaceous species at residential homes in northwestern Portugal

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Abstract

Particulate matter with an aerodynamic diameter equal to or less than 10 μm (PM_{10}), organic carbon (OC) and elemental carbon (EC) concentrations were measured simultaneously in the indoor and outdoor air of 4 residences located in urban and sub-urban areas from northwestern Portugal. The residences were studied with occupants. One of them was also studied without any indoor activity, taking advantage of the fact that occupants moved into a new home. 48-h aerosol samples were collected on quartz fibre filters with low-volume samplers equipped with size selective inlets. The filters were weighed and thereafter analysed for OC and EC using a thermal-optical transmittance method. The average indoor and outdoor PM_{10} concentrations in the occupied residences were $71.9 \pm 38.3 \mu\text{g}/\text{m}^3$ and $54.0 \pm 13.3 \mu\text{g}/\text{m}^3$, respectively. Despite the higher abundance of PM_{10} indoors, outdoor sources were found to be significant contributors to indoor concentrations. An estimation based on data from the residence studied under different occupancy conditions indicated that outdoor sources can supply 68% of the indoor PM_{10} mass concentration. Average indoor to outdoor (I/O) ratios for OC ranged from 1.7 to 5.6 in occupied residences, showing that indoor sources, like cooking, smoking and cleaning, strongly influenced indoor OC concentrations. In contrast, I/O ratios for EC were close to 1, except for a smokers' residence, suggesting that indoor concentrations were mainly controlled by outdoor sources, most likely from vehicular emissions and residential biomass burning.

2.1. Introduction

Exposure to particulate matter in ambient air has been linked to diverse health effects, particularly within the respiratory and cardiovascular systems (Brunekreef and Holgate, 2002; Pope III et al., 2002). Since people in industrialized countries spend 80 to 90% of their time indoors and most of that time is spent at home, personal exposure to particulate matter mainly occurs in the indoor residential environment. Particles in the indoor air of residences

originate from a variety of sources. Common indoor sources include cooking, smoking, cleaning, biomass burning in fireplaces and stoves, handling of fibre containing materials and movement of people (Abt et al., 2000a; Cerqueira et al., 2010; Nasir and Colbeck, 2013; Polidori et al., 2007; Ward and Noonan, 2008). Another important source of indoor particulate matter is air transport from the outdoor by infiltration and ventilation processes (Abt et al., 2000b; Riley et al., 2002).

During the last years many studies were conducted in Europe to assess human exposure to residential aerosol particles and to describe its sources, physical properties and chemical composition (e.g. Fischer et al., 2000; Jones et al., 2000; Monn et al., 1997; Stranger et al., 2007). However, these studies were focused on residences from central and northern Europe, which means that little or no information is available for residences located in the southern part of this continent. This lack of information is of particular concern in the light of the current knowledge about the aerosol spatial distribution over Europe. Exceedances of the EU daily limit value for PM_{10} are common in southern European countries (Mitsakou et al., 2008; Moreno et al., 2005; Pederzoli et al., 2010; Querol et al., 2008), due to local dust resuspension and mineral dust intrusions from African desert regions, thus suggesting a significant contribution of outdoor sources to residential indoor PM_{10} levels.

This paper reports the first quantitative description of particulate matter (PM_{10}) concentrations and associated carbonaceous fractions (OC and EC) in the indoor air of residences in Portugal. The aims of this study were to: (1) assess exposure to particulate matter in urban and sub-urban residences in Portugal; (2) investigate the relationships between indoor and outdoor concentrations of PM_{10} , OC and EC concentrations; (3) describe relevant sources of particulate matter in the indoor air of investigated residences.

2.2. Experimental

2.2.1 Sampling sites

The study was conducted in four homes located in the cities of Aveiro (population 45 000) and São João da Madeira (population 21 000), both located in northwestern Portugal. The homes were selected to reflect different indoor sources (cooking, smoking, presence of pets, fireplace utilization, etc.) and outdoor environments (urban density, traffic intensity, etc). Three homes were located in blocks of flats and one was a terraced house. They were all studied with occupants. One of them was also studied without any indoor activity, taking advantage of the fact that occupants moved into a new home. Doors and windows provided

natural ventilation in all the cases. They were normally closed and were opened only for short time periods (a few hours per days) according to occupants' requirements. The exception was home 2, with a door linking the kitchen to a roof terrace that was frequently opened. A summary with the main characteristics of sampling sites used in this study is presented in Table 2.1.

Kitchen was selected for sampling indoors because these rooms are known to have diverse sources of air particles and because occupants spend much of their time inside it. In many Portuguese homes the kitchen is a communal area which is not only used for cooking but also for eating, relaxing and socializing. Outdoor sampling was conducted at the same height above ground as indoor sampling using a balcony (a terrace was used in home 2) at the front of the building.

2.2.2 Sampling method

Indoor and outdoor PM₁₀ measurements were performed simultaneously with two MiniVol™ TAS samplers from AirMetrics (Eugene, Oregon, USA). The MiniVol is a low-volume portable sampler equipped with an air pump, a rotameter, a flow rate controller and a programmable timer. In operation, air is drawn through a size selective inlet and then through a filter pack fitted to the top of the sampler in order to selectively collect aerosol particles in the PM₁₀ size range. The size-selective inlets were located at about 160 cm above the floor in order to get samples within the breathing air zone of the occupants. Aerosol samples were taken at a flow rate of 5 L min⁻¹ for 48 hours. The filters used for the concentration of particles were made of quartz fibre (Whatman QMA, 47 mm diameter). These were previously combusted at 550 °C for 4 h to remove organic contaminants. A total of 7 pairs of filter samples were gathered per residence.

Table 2. 1 - Summary details of sampling sites used in this study

Site	Study period	Location	Site condition	home type	floor	occupants	smokers	pets	cooker type	fireplace use	ventilation
Home 1A	Feb. - Mar. 2011	Aveiro / city centre	near road with medium traffic flow	apartment	4	5	No	no	gas	no	natural
Home 1B	Jan. - Feb. 2012	Aveiro / city centre	near road with medium traffic flow	apartment	4	0	No	no	not used	no	natural
Home 2	Apr. 2011	Aveiro / suburb	near road with medium traffic flow	apartment	6	3 - 5	No	dog	gas	no	natural
Home 3	May 2011	Aveiro / city centre	near road with high traffic flow	apartment	4	4	3	cat	gas	no	natural
Home 4	Mar. 2011	São João da Madeira / suburb	far from busy roads	terraced house	-	3 - 4	No	dog & cat	gas	wood burning	natural

2.2.3 Analysis

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%) then weighed on an electronic microbalance with a sensitivity of 0.01 μg . After collection, the filters were re-conditioned, re-weighed and stored at -20 °C until they could be chemically analysed.

The EC and OC particulate fractions accumulated in filters were measured by the thermal optical method previously described by Castro et al. (1999). The system comprises a quartz tube with two heating zones, a laser and a non dispersive infrared (NDIR) CO₂ analyzer. A punch of the filter sample is placed vertically inside the quartz tube within the first heating zone, which is then heated to 600 °C in a nitrogen atmosphere to vaporize the organic fraction of particles. EC is determined by sequential heating at 850 °C in a nitrogen/air atmosphere. The second heating zone is filled with cupric oxide and maintained at 850 °C during the entire analysis process to guarantee the total oxidation of the volatilized carbon to CO₂, which is quantified continuously by the NDIR analyzer. Correction for the pyrolysis contribution to EC from OC is achieved by monitoring the transmission of light through the filter with the laser beam. The OC/EC split is set when the transmittance reaches the same value as the one at the beginning of the analysis. Pyrolytic carbon (PC) is calculated from the mass of CO₂ emitted during the second heating phase, under the gas flow containing O₂, until the recovery of filter light transmittance.

2.3. Results and Discussion

2.3.1 Mass concentrations

A summary of PM₁₀ measurements is shown in Table 2.2. Exposure to particulate matter in occupied residences was higher indoors than outdoors (an average of about 30%). The highest indoor concentrations (average of 116±57 $\mu\text{g}/\text{m}^3$) were found in home 3. The presence of 3 smokers and poor ventilation conditions seems to explain these results. Significant differences in PM₁₀ concentrations between non-smokers and smokers residences were also described previously. Breysse et al. (2005) reported an average increase of 88% in PM₁₀ concentrations after investigating indoor air at 91 residences in Baltimore, USA, and Chao and Wong (2002) an increase of 19% in urban residences of Hong Kong, China. Studies

performed in European countries have also consistently reported increased PM₁₀ concentrations (average of 5% to 93%) in residences with smokers (Phillips et al., 1997, 1998, 1999; Stranger et al., 2007).

Table 2. 2 - Average, standard deviation, indoor to outdoor ratios and Pearson correlation coefficients for PM₁₀ mass concentrations measured in the five homes. Bold values indicate statistically significant correlation coefficients ($p < 0.05$).

	PM ₁₀ (µg/m ³)		I/O	R
	Indoor	Outdoor		
Home 1A	52.6 ± 7.0	46.9 ± 8.7	1.1 ± 0.1	0.90
Home 1B	35.7 ± 12.0	45.5 ± 13.5	0.8 ± 0.1	0.98
Home 2	59.9 ± 6.5	63.6 ± 14.6	1.0 ± 0.2	0.31
Home 3	116.4 ± 57.2	49.9 ± 13.1	2.5 ± 1.6	-0.06
Home 4	58.6 ± 10.3	55.8 ± 12.2	1.1 ± 0.1	0.95
Overall average*	71.9 ± 38.3	54.0 ± 13.3	1.4 ± 1.0	-

* for occupied homes only

The lowest concentrations, on the other hand, were found in home 1B (average of 36 µg/m³), a result of the absence of indoor activities. Data from this residence show an average PM₁₀ decrease of 32% from the occupied to the unoccupied condition. This is comparable to the 50% decrease reported by Nasir and Colbeck (2013) in an unoccupied living room from an UK suburban location. Average concentrations from home 1 measured during periods without indoor activity (condition B) can be used as indicative of the contribution of outdoor sources to indoor PM₁₀ concentrations measured in periods of indoor activity (condition A). This is an acceptable approximation because outdoor concentrations in home 1 were quite similar during both conditions A and B. Therefore, 68% of the mass resulted from outdoor sources and only 32% was generated indoors. Indoor sources in this residence include, among other housework activities, movement of people, cooking and cleaning.

I/O ratios have been previously employed to describe the differences between the indoor and outdoor environments (Jones et al., 2000; Monn et al., 1997; Stranger et al., 2007). Average I/O ratios in this study ranged from 0.8 to 2.5. The lowest value was found in home 1B in line with the absence of indoor sources, and the highest in home 3, indicating that smokers were the main source of particles indoors. Homes 1A, 2 and 4 had ratios close to 1, suggesting a significant influence of outdoor sources on indoor PM₁₀ concentration. Since windows (or door, in home 2) were opened at least a few hours per day, it is not difficult for particles

originating outdoors to get into these residences. Correlation analysis between indoor and outdoor measurements was used to further support this finding. The correlation coefficient was very high in home 1 (for both conditions A and B) and in home 4, confirming that outdoor particulate matter is a significant contributor to residential indoor concentrations. In addition, the magnitude of r values provides evidence that outdoor air was basically the only one source of particles inside the unoccupied residence. Poor correlations were found in homes 2 and 3, due to a higher influence of indoor sources.

Comparative data for indoor and outdoor PM_{10} concentrations in industrialized countries are presented in Table 2.3. Indoor concentrations in Portugal were higher than those measured before in countries from central and northern Europe (Jones et al., 2000; Monn et al., 1997). The same tendency was observed for outdoor concentrations, suggesting that outdoor sources might be important contributors to indoor air pollution levels. As mentioned before in this paper, exceedances to PM_{10} concentration limits fixed in the European Directive 2008/50/CE are quite frequent in southern European countries due to a high mineral dust load in ambient air (Mitsakou et al., 2008; Moreno et al., 2005; Pederzoli et al., 2010; Querol et al., 2008). This dust excess seems to be the source of a significant background level of particulate matter in the indoor air of residences located in Portugal.

Indoor concentrations from this study were lower than those reported previously for East Asian countries. This difference is related to cultural practices and living styles. Chinese style of cooking with high emissions of oily fumes and incense burning are common home activities in that part of the world and are known to strongly influence indoor PM_{10} levels (Lung et al., 2007). In addition, uncontrolled industrial and traffic emissions are responsible for high levels of outdoor particles in Asian cities, which then can get into residences (Chao and Wong, 2002).

2.3.2 OC and EC concentrations

A summary of OC and EC measurements is shown in Table 2.4. The highest average indoor OC concentrations were found in home 3 ($27 \pm 18 \mu\text{g}/\text{m}^3$), the smokers' residence, and the lowest in home 2 ($10 \pm 1 \mu\text{g}/\text{m}^3$), a residence with a very high ventilation rate. OC concentrations for occupied residences were about 2.5 times higher indoors than outdoors. This can be attributed to a variety of sources, which are known to release considerable amounts of organic particles into residential indoor air, including smoking (Na and Cocker III, 2005), cooking (Polidori et al., 2007, Abt et al., 2000a), biomass burning (Ward and Noonan, 2008) and handling of textiles (Cerqueira et al., 2010). Similar indoor and outdoor concentrations

(average I/O ratio of 1.0) were found in the unoccupied residence, suggesting that all the indoor OC resulted from outdoor infiltration of particles. The very high correlation factor for this residence ($r=0.96$) confirms the absence of OC indoor sources.

Table 2. 3 - Indoor and outdoor PM₁₀ mass concentrations reported before in industrialized countries.

Location	Number of homes and area type	PM ₁₀ (µg/m ³)			Reference
		Indoor	outdoor	I/O	
Birmingham, United Kingdom	4; urban area (flats near roadside)	29.2	19.5	1.6	Jones et al. (2000)
	2; urban area (flats in multi-storey block)	40	19.3	2.1	
	1; rural area	35.3	16.0	2.5	
Zürich, Switzerland	residential area with low indoor activity ^a	10.8	15.2	0.71	Monn et al. (1997)
	residential area with normal indoor activity ^a	32.8	23.4	1.40	
	residential area with indoor smokers ^a	26.9	14.6	1.84	
Amsterdam, The Netherlands	18; urban area (high-traffic street)	37	43	0.86 ^b	Fischer et al. (2000)
	18; urban area (low-traffic street)	22	36	0.61 ^b	
Antwerp, Belgium	15; urban and suburban areas	39	41	0.95	Stranger et al. (2007)
Athens, Greece	3; urban area: - warm period	35	52	0.7 ^b	Diapouli et al. (2011)
	- cold period	32	54	0.6 ^b	
Hong Kong, China	34; urban area (mixed indoor and outdoor activities)	63.3	69.5	0.91 ^b	Chao and Wong (2002)
Taipei, Taiwan	45; urban (residential, commercial, mixed) and industrial areas	79.8	95.5 ^c	0.84	Lung et al. (2007)

^a number of homes not specified by authors

^b ratio calculated from average indoor and outdoor values

^c average of 41 outdoor measurements

EC was clearly less abundant than OC in indoor and outdoor air. The highest average EC concentration was found again in the smokers' residence. High values were also measured in the unoccupied residence but this was clearly related with the infiltration of EC from outdoor sources, as demonstrated by the average I/O ratio, which was equal to 1.0, and the high correlation factor between the two sets of data ($r=0.78$). I/O ratios closer to 1, together with high correlation factors ($r>0.70$) were found in homes 2 and 4, showing that EC was generated outdoors, most likely from vehicular emissions and biomass burning. A dominant outdoor origin for EC was reported before in studies about the characteristics of carbonaceous indoor aerosols (Cao et al., 2005; 2012; Ho et al., 2004; Na and Cocker III, 2005).

Table 2. 4 - Average, standard deviation, indoor to outdoor ratios and Pearson correlation coefficients for OC and EC concentrations measured in the five homes.

	OC ($\mu\text{g}/\text{m}^3$)		EC ($\mu\text{g}/\text{m}^3$)		I/O		r	
	Indoor	Outdoor	Indoor	Outdoor	OC	EC	OC	EC
Home 1A	12.2 \pm 1.5	6.2 \pm 1.0	2.3 \pm 0.5	2.3 \pm 0.7	2.0 \pm 0.3	1.1 \pm 0.3	0.4	-0.21
Home 1B	15.9 \pm 3.1	16.2 \pm 5.2	3.7 \pm 1.2	3.7 \pm 1.3	1.0 \pm 0.1	1.0 \pm 0.2	0.96	0.78
Home 2	10.4 \pm 1.3	6.5 \pm 2.0	1.8 \pm 1.0	1.8 \pm 1.0	1.7 \pm 0.5	1.1 \pm 0.3	0.24	0.7
Home 3	27.3 \pm 18.2	5.0 \pm 2.5	3.9 \pm 1.5	1.9 \pm 1.4	5.6 \pm 2.0	2.9 \pm 1.6	0.79	0.93
Home 4	10.9 \pm 2.7	6.1 \pm 3.5	2.2 \pm 1.2	2.7 \pm 1.3	2.3 \pm 1.2	0.8 \pm 0.2	0.94	0.93
Overall average*	15.2 \pm 11.3	5.9 \pm 2.4	2.5 \pm 1.3	2.2 \pm 1.1	2.9 \pm 1.9	1.5 \pm 1.2	-	-

* for occupied homes only.

The contribution of OC and EC to PM_{10} concentrations, together with the OC/EC ratios are presented in Table 2.5. The percentages of OC in PM_{10} for occupied residences ranged from 18 to 25% in indoor air and from 10 to 13% in outdoor air. This is indicative of a significant contribution of OC sources to indoor PM_{10} mass concentration. However, the highest percentage of OC in PM_{10} was observed in the unoccupied residence indoor air. At least in part, this might be explained by the chemical composition of outdoor air, which was the main source of indoor particles and was richer in OC during the sampling period without occupants

than in the period with occupants. In addition, the percentage of OC increases from outdoor to indoor air, suggesting that particles going indoors were mainly generated from OC sources. This is likely to occur since OC is known to be prevalent in the fine fraction of outdoor aerosol (Duarte et al., 2008) and fine particles infiltrate more efficiently indoors than coarse particles (Abt et al., 2000b).

Average EC concentrations accounted for only 4 to 11 % of the PM₁₀ mass concentration indoors and 3 to 8 % outdoors, in line with a lower abundance of EC than OC in ambient air.

Table 2. 5 - Average and standard deviation of percentage of OC and EC in PM₁₀ together with OC/EC ratios in the five homes.

	OC/PM ₁₀ (%)		EC/PM ₁₀ (%)		OC/EC	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Home 1A	23.5 ± 3.7	13.3 ± 1.4	4.3 ± 0.8	5.0 ± 2.2	5.6 ± 1.4	2.9 ± 0.8
Home 1B	46.4 ± 7.2	35.4 ± 3.1	10.6 ± 1.5	8.4 ± 2.4	4.5 ± 0.9	4.5 ± 1.2
Home 2	17.5 ± 2.2	10.6 ± 3.7	3.0 ± 1.5	2.9 ± 1.6	7.9 ± 5.7	5.5 ± 6.3
Home 3	25.1 ± 12.1	9.8 ± 3.8	3.8 ± 1.2	3.7 ± 2.2	6.7 ± 2.6	3.8 ± 3.4
Home 4	18.5 ± 2.9	10.6 ± 5.3	3.6 ± 1.6	4.9 ± 2.0	6.0 ± 2.8	2.2 ± 0.8
Overall average*	21.1 ± 7.0	11.1 ± 3.8	3.7 ± 1.3	4.1 ± 2.1	6.5 ± 3.4	3.6 ± 3.7

* for occupied homes only.

The ratio of OC/EC has been widely used to study the origin and transformation processes of carbonaceous aerosol in a variety of outdoor atmospheres. Minimum OC/EC ratios in the range of 1.1 to 1.4 for PM₁₀ aerosol samples are common in urban background air and ratios exceeding these values are indicative of the presence of secondary organic carbon (Pio et al., 2011). Outdoor OC/EC ratios found in this study were higher than 1.4 and compare well with the average ratios reported before for the background atmospheres of Portuguese cities (Lisbon, Oporto and Coimbra), that were in the range of 2.4 to 5.1 (Pio et al., 2011), thus pointing to the occurrence of secondary organic aerosols. Higher average OC/EC ratios were found in the indoor air of occupied residences, which might be attributed to the strength of OC sources such as smoking, cooking and movement of people. Finally, it is worth to mention the convergence of results between indoor and outdoor OC/EC ratios in the unoccupied residence. This is not surprising, following the above reported findings that I/O ratios for OC

and EC were equal to 1.0, but it also emphasizes the common origin of carbon particles collected indoors and outdoors.

2.4. Conclusions

Although the number of investigated cases was not large, this paper reports the first comprehensive research about PM₁₀ and associated carbon fractions in the indoor air of residences in Portugal. The main conclusions from the present study are summarised as follows:

- exposure to PM₁₀ in occupied residences was higher indoors than outdoors and maximum exposure was found within a smokers' residence;
- a significant influence of outdoor sources on indoor PM₁₀ concentration was found in occupied residences without smokers, reflecting the efficiency of natural ventilation conditions.
- PM₁₀ mass concentrations in the indoor air of residences in Portugal were higher than those reported before in central and northern Europe, which might be the result of a higher input of mineral dust from outdoor sources;
- the average contribution of OC to PM₁₀ in the indoor air of occupied residences ranged was 21%. A higher contribution (46%) was found in the unoccupied residence, showing that fine particles, with a high content in OC, infiltrate more easily indoors than coarse particles, with a high mineral content;
- OC concentrations were higher indoors than outdoors in the occupied residences, showing the influence of indoor sources like smoking, cooking and cleaning;
- EC concentrations accounted for an average of only 3.7% of the PM₁₀ mass concentration in the indoor air of occupied residences;
- main sources of EC in non-smokers residences were located outdoors.

This study has also shown that more research is needed to better understand human exposure to indoor particulate matter in southern European countries. Future studies should focus on the origin of particles and the contribution of mineral dust to indoor particulate matter levels.

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CHAPTER 3

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

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Abstract

PM_{2.5} 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/m³, 5.0 µg/m³ and 3.8 µg/m³, 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_{2.5} mass. The three carbon fractions exhibited a similar seasonal variation, with high concentrations in late autumn and in winter, and low concentrations in spring. SO₄²⁻ was the dominant water soluble ion, followed by NO₃⁻, NH₄⁺, Cl⁻, Na⁺, K⁺, oxalate, Ca²⁺, Mg²⁺, 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⁺, a tracer of biomass combustion, and was not correlated with nssSO₄²⁻, a species associated with secondary processes, suggesting that the main source of WSOC was biomass burning. Most of the SO₄²⁻ was anthropogenic in origin and was closely associated with NH₄⁺, pointing to the formation of secondary aerosols. Na⁺, Cl⁻ and methanesulfonate were clearly associated with marine sources while NO₃⁻ was related with combustion of both fossil and non-fossil fuels. Mixed sources explained the occurrence of the other water soluble ions.

3.1. 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). 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. 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. 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; Furusjö 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 from 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. (2015) 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.

3.2. Sampling and analytical methods

3.2.1 Study site and aerosol sampling

Oporto is located in northern Portugal, near the mouth of the Douro River (Figure 3.1). The city has a population of about 240000 (2011 census), and the urban area, which extends beyond its administrative limits, has a population of about 1.3 million in a land area of 389 km², 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.

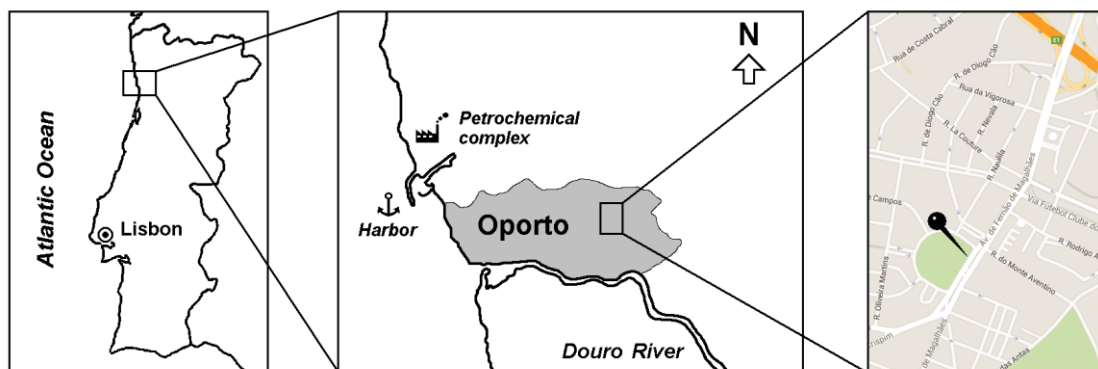


Figure 3.1 Map showing the location of sampling site in Oporto, Portugal.

Aerosol sampling was conducted from the 5th of January 2013 to the 24th of January 2014 in 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_{2.5} size selective inlets were used in parallel: a low-volume sampler, operated at a flow rate of 2.3 m³/h and equipped with a Pall PTFE filter; and a high volume sampler, operated at a flow rate of 1.13

m³/min and equipped with a pre-fired (550 °C, 5h) Whatman QM/A quartz fiber filter. The PTFE filter was used for the determination of aerosol mass concentration and for the chemical analysis of water soluble ions whilst the quartz fiber filter was 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.

3.2.2 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).

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 2M 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.

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 (NH₄⁺), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺) and magnesium (Mg²⁺) were determined using an IonPac CG12A guard column and a CS12A analytical column with 10 mM H₂SO₄ as the eluent. The anions chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻) and oxalate (C₂O₄²⁻) were measured with an IonPac AG4A guard column and an AS4A analytical column with a Na₂CO₃/NaHCO₃ (1.8 and 1.7 mM, respectively) buffer solution as the eluent. The anions fluoride (F⁻), formate (HCOO⁻), acetate (CH₃COO⁻), methanesulfonate (CH₃SO₃⁻) and glycolate (HOCH₂COO⁻) were determined with an IonPac AG11 and an IonPac AS11 column by gradient elution with Na₂B₄O₇ solution from 0.075

mM to 2.5 mM as eluent.

The non-sea-salt ion concentrations were calculated by the following equation, assuming that the chemical composition of sea-salt particles is the same as that of seawater and that soluble Na^+ in aerosol particles comes solely from seawater,

$$\text{nssX} = X - (X/\text{Na})_{\text{sw}} \times \text{Na}^+$$

where nssX is the mass concentration of non-sea salt ion X in the aerosol particles, $(X/\text{Na})_{\text{sw}}$ is the mass ratio of component X to Na in seawater (Millero, 2013) and Na^+ is the mass concentration of sodium in the aerosol particles.

3.2.3 Meteorology

The climate of Oporto is strongly influenced by the seasonal movement of the Azores anticyclone. During autumn and winter, the anticyclone is usually located south of the Azores Islands and low pressure systems track across the North Atlantic causing cold and wet weather in Oporto. During late spring and summer, the northward movement of the anticyclone prevents the transport of cold air and the formation of precipitation. The temperature range in Oporto is characteristic of a maritime climate but summer rainfall is so scarce that the city can also be included in the Mediterranean climate region from this point of view.

Table 3.1 presents a summary of meteorological data recorded at the monitoring site with a wireless weather station (Vantage Pro2 Plus, Davis Instruments). Weather conditions were typical of Oporto city based on climatological averages (IPMA, 2015). The daily average temperature ranged from 10.2 °C in winter to 21.9 °C in summer. In contrast, the daily average relative humidity varied from 66% in summer to 84% in winter. Precipitation was mostly accumulated in winter and the total precipitation amount during the sampling period was 1319 mm, comparing well with the annual average rainfall of 1237 mm recorded in Oporto during the period 1981-2010 (IPMA, 2015). Strong winds from the Atlantic (north-west sector) were common during winter and early spring and alternating sea/land breezes formed in summer. These wind conditions show that most of the time the airflow influencing the sampling site, which was located on the northwest side of the road, was not arriving directly from the traffic sources. Therefore, the sampling site should be regarded as a kerbside with a significant urban background influence.

Table 3. 1 - Average, standard deviation and range (min-max) of meteorological parameters recorded at the Oporto kerbside site during the study period.

	Temperature (°C)	Relative humidity (%)	Precipitation (mm/day)	Wind speed (m/s)	Prevailing wind direction
Winter	10.2±2.0 (6.1-14.3)	84±10 (53-98)	7.4±10.2 (0.0-46.0)	5.3±2.9 (1.0-16.4)	NW, NE
Spring	14.1±2.6 (8.7-21.8)	76±13 (41-97)	3.9±8.8 (0.0-45.4)	5.3±2.1 (1.1-11.5)	NE, NW
Summer	21.9±3.8 (16.2-31.8)	66±18 (32-90)	0.2±1.3 (0.0-12.7)	3.7±1.1 (1.1-6.6)	NE, NW
Autumn	15.2±4.7 (6.1-26.2)	80±14 (46-97)	4.6±9.5 (0.0-45.5)	3.4±1.7 (0.2-8.7)	SW, SE

2.4 Data analysis

The aerosol composition was examined by means of summary statistics and correlation analysis. The application of the Shapiro-Wilk test indicated that chemical parameters did not follow a normal distribution. This led to the use of the nonparametric Spearman's rank correlation coefficient to assess the relationships between aerosol constituents.

3.3. Results and discussion

A total of 125 low volume and the same number of high volume PM_{2.5} samples were collected and analyzed during this study. Table 3.2 presents a statistical summary of PM_{2.5}, carbon fractions and water soluble ions concentrations, while Figures 3.2 and 3.3 show the seasonal variation of these parameters. The variation of PM_{2.5} and major aerosol chemical constituents as a function of wind direction and speed is illustrated in Figure 3.4. Table 3.3 presents a Spearman's correlation coefficient matrix between aerosol constituents.

3.3.1 PM_{2.5} mass concentration

The PM_{2.5} mass concentration varied from 6.2 to 87.7 µg/m³ with an average of 26.7±16.1 µg/m³ (Table 3.2). These concentrations fall within the range of values reported before for other kerbside sites in Oporto (Oliveira et al., 2010; Slezakova et al., 2007) and in other European cities (Putaud et al., 2010). PM_{2.5} mass concentrations obtained in this study were 30 to 40% higher than those recorded a few years ago in the Oporto background atmosphere (Oliveira et al., 2010), which suggests a significant contribution of traffic sources to the aerosol load. The monthly variation of aerosol mass concentrations shows maxima in winter and summer (Fig. 3.2). Winter values might be attributed to unfavorable meteorological conditions

for the dispersion of air pollutants (stagnant atmosphere), while the summer values were probably related to wildfire emissions in the surrounding area of Oporto. According to the national authority in the field of forest protection (ICNF - *Instituto da Conservação da Natureza e das Florestas*), Northern Portugal was highly affected by wildfires during the summer of 2013 (Figure S1 of supplementary data). 27 large fires (burnt area >100 ha) were recorded in the Oporto district between the 11st of August and the 21st of September, burning 8752 ha of woodlands and shrublands (ICNF, 2014).

The polar plot distribution (Fig. 3.4) shows that the major sources of PM_{2.5} were located inland, in an area that extends to the southwest of the sampling site. This distribution appears to be associated with traffic emissions from the nearby road but may also be related with other sources, including biomass burning and local dust. The role of these sources as contributors to aerosol production in Oporto was emphasized in the source apportionment study of Amato et al. (2015). Indeed, they found that traffic, biomass burning and local dust were the most important sources of fine particles, accounting for 39%, 18% and 15%, respectively, of the PM_{2.5} aerosol mass.

Fig. 3.5 shows the monthly variation of PM_{2.5} mass concentration along with the contribution of noncarbonated total carbonaceous mass (EC+OM) and inorganic mass (WSII) to total aerosol mass concentration. EC concentrations were obtained directly from the analytical instrument data determination. The contribution of total organic matter (OM) was estimated by multiplying the measured OC concentrations by a factor of 1.4. This factor is higher than the OM/OC ratio of 1.2 reported for fresh vehicle emissions (Aiken et al., 2008), which were expected to be the major source of aerosols at the study site. However, as further described in this work, there was evidence of a high fraction of oxygenated organic species in the aerosol samples collected in Oporto and consequently this might explain the OM/OC ratio within the range of values described for urban areas strongly impacted by vehicle emissions (Bae et al., 2006; Brown et al., 2013). Finally, the contribution of total water soluble inorganic ions (WSII) was calculated by summing the measured inorganic ions concentrations. On average, carbonaceous matter (EC+OM) accounted for 52% of the gravimetrically measured PM_{2.5} mass (minimum of 41% in spring and maximum of 62% in winter) in good agreement with what has been observed in other European kerbside sites (Putaud et al., 2010). The total concentration of WSII plus the concentration of carbonaceous matter accounted for 74% of the PM_{2.5} concentration. The remaining chemically unaccounted mass fraction can be attributed to minerals and trace elements as well as particle-bound water.

Table 3. 2 - Annual and seasonal concentrations of PM_{2.5}, carbon fractions and water soluble ions (in units of µg/m³) in aerosols from Oporto.

	Winter		Spring		summer		autumn			
	avg±stdev	Range	avg±stdev	Range	avg±stdev	Range	avg±stdev	Range	avg±stdev	range
PM _{2.5}	26.7±16.1	6.2-87.7	26.7±16.5	8.2-75.6	18.8±8.2	6.9-35.9	33.2±17.5	8.7-87.7	27.3±16.7	6.2-75.6
OC	6.2±4.8	0.8-26.5	7.7±6.0	1.6-26.5	3.4±1.8	0.9-8.7	7.1±4.8	1.5-22.9	5.9±4.1	0.8-19.2
EC	5.0±3.1	0.6-16.5	5.6±3.1	0.6-15.2	3.0±1.5	0.9-6.0	4.7±3.1	1.1-12.9	6.6±3.1	1.2-16.5
WSOC	3.8±2.7	0.8-13.8	4.4±2.9	0.8-11.5	2.1±1.1	0.8-5.7	4.4±2.9	0.9-13.8	4.0±2.5	0.8-10.9
WIOC	2.4±2.5	BDL-15.7	3.5±3.3	BDL-15.7	1.3±1.0	BDL-3.0	2.7±2.1	0.6-9.5	2.0±1.9	BDL-8.3
Cations										
Na ⁺	0.54±0.43	0.08-2.61	0.72±0.61	0.08-2.61	0.59±0.34	0.09-1.61	0.43±0.27	0.08-1.19	0.38±0.23	0.10-1.09
K ⁺	0.21±0.17	0.02-1.12	0.25±0.16	0.06-0.65	0.10±0.06	0.02-0.23	0.23±0.21	0.03-1.12	0.26±0.16	0.07-0.69
Ca ²⁺	0.14±0.14	BDL-0.79	0.08±0.08	BDL-0.41	0.11±0.08	0.01-0.30	0.24±0.20	0.02-0.79	0.13±0.10	0.03-0.42
Mg ²⁺	0.06±0.04	BDL-0.25	0.06±0.05	BDL-0.25	0.07±0.04	0.01-0.15	0.08±0.06	0.00-0.25	0.04±0.02	0.01-0.11
NH ₄ ⁺	0.62±0.70	BDL-3.74	0.56±0.65	BDL-3.57	0.53±0.59	BDL-2.51	0.89±0.97	0.10-3.74	0.48±0.39	0.10-1.43
Anions										
F ⁻	0.005±0.010	BDL-0.078	0.010±0.016	BDL-0.078	0.007±0.004	BDL-0.020	0.002±0.003	BDL-0.012	0.001±0.001	BDL-0.005
Cl ⁻	0.61±0.70	BDL-4.38	1.11±0.95	0.01-4.38	0.51±0.53	BDL-2.17	0.23±0.24	BDL-1.13	0.47±0.36	0.08-1.65
NO ₃ ⁻	1.14±1.12	0.09-7.48	1.55±1.40	0.11-7.48	0.84±0.84	0.09-4.38	0.86±0.74	0.16-3.61	1.24±1.13	0.17-4.97
SO ₄ ²⁻	1.95±1.80	0.14-12.10	1.09±0.60	0.41-2.80	1.85±1.26	0.14-6.26	3.33±2.70	0.90-12.10	1.69±1.14	0.78-6.07
oxalate	0.17±0.14	0.01-0.68	0.15±0.12	0.02-0.58	0.10±0.07	0.01-0.30	0.25±0.14	0.04-0.60	0.21±0.17	0.03-0.68
formate	0.040±0.037	BDL-0.211	0.040±0.038	BDL-0.154	0.015±0.010	BDL-0.040	0.056±0.045	BDL-0.211	0.050±0.026	0.014-0.100
acetate	0.012±0.012	BDL-0.088	0.012±0.016	BDL-0.088	0.005±0.006	BDL-0.026	0.008±0.010	BDL-0.031	0.019±0.010	0.004-0.039
MS ⁻	0.031±0.034	BDL-0.267	0.012±0.019	BDL-0.099	0.038±0.030	BDL-0.113	0.057±0.045	0.019-0.267	0.021±0.016	0.002-0.076
glycolate	0.008±0.013	BDL-0.060	0.004±0.010	BDL-0.053	BDL±BDL	BDL-BDL	0.014±0.017	BDL-0.060	0.015±0.012	BDL-0.045
nssSO ₄ ²⁻	1.82±1.82	BDL-12.08	0.91±0.63	0.15-2.78	1.71±1.27	BDL-6.07	3.22±2.71	0.75-12.08	1.59±1.14	0.65-5.91
nssK ⁺	0.19±0.17	BDL-1.11	0.22±0.17	0.04-0.62	0.08±0.06	BDL-0.20	0.21±0.21	0.01-1.11	0.24±0.17	0.06-0.69
nssCa ²⁺	0.12±0.14	BDL-0.78	0.05±0.08	BDL-0.40	0.09±0.08	BDL-0.27	0.22±0.20	0.07-0.78	0.12±0.10	0.01-0.40

BDL - below detection limit

Table 3. 3 - Spearman's correlation coefficients (r) of major aerosol constituents in aerosols from Oporto during winter (grey cells) and summer (white cells). Bold values indicate statistically significant correlation coefficients ($p < 0.05$).

	PM _{2.5}	OC	EC	WSOC	WIOC	Na ⁺	Mg ²⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	oxalate	formate	acetate	MS ⁻	nssSO ₄ ²⁻	nssK ⁺	nssCa ²⁺
PM _{2.5}		0.89	0.76	0.87	0.58	-0.14	0.65	0.03	0.08	0.33	0.18	0.73	0.74	0.80	-0.28	0.18	0.86	0.82
OC	0.88		0.78	0.91	0.78	-0.12	0.60	0.07	0.05	0.40	0.12	0.76	0.83	0.77	-0.21	0.12	0.83	0.82
EC	0.77	0.82		0.78	0.58	0.04	0.82	-0.42	0.30	0.33	-0.28	0.39	0.62	0.60	-0.49	-0.27	0.73	0.85
WSOC	0.86	0.93	0.80		0.57	-0.04	0.71	0.04	0.19	0.43	0.16	0.81	0.85	0.80	-0.21	0.16	0.91	0.86
WIOC	0.74	0.90	0.71	0.70		-0.12	0.35	0.26	-0.10	0.37	0.25	0.57	0.47	0.42	0.02	0.26	0.48	0.54
Na ⁺	-0.19	-0.34	-0.40	-0.38	-0.22		0.33	-0.30	0.82	0.44	-0.27	-0.21	0.03	-0.17	0.15	-0.27	0.08	-0.15
Mg ²⁺	-0.05	-0.29	-0.33	-0.27	-0.24	0.72		-0.32	0.54	0.44	-0.13	0.38	0.60	0.61	-0.36	-0.13	0.76	0.78
NH ₄ ⁺	0.74	0.70	0.62	0.68	0.55	-0.43	-0.24		-0.56	0.22	0.92	0.52	0.11	0.15	0.65	0.92	-0.02	-0.10
Cl ⁻	-0.01	-0.18	-0.28	-0.24	-0.02	0.91	0.69	-0.28		0.28	-0.50	-0.16	0.08	-0.02	-0.17	-0.50	0.31	0.08
NO ₃ ⁻	0.85	0.80	0.73	0.74	0.70	-0.24	-0.08	0.91	-0.09		0.30	0.49	0.46	0.44	0.23	0.30	0.53	0.32
SO ₄ ²⁻	0.50	0.34	0.29	0.33	0.18	-0.26	0.02	0.79	-0.19	0.62		0.62	0.19	0.31	0.52	1.00	0.12	0.04
oxalate	0.70	0.66	0.64	0.68	0.46	-0.47	-0.21	0.92	-0.37	0.83	0.76		0.74	0.81	0.16	0.62	0.72	0.62
formate	0.49	0.46	0.37	0.50	0.30	-0.20	0.06	0.57	-0.07	0.53	0.43	0.72		0.79	-0.18	0.19	0.76	0.71
acetate	0.06	0.18	0.20	0.30	-0.08	-0.29	0.01	0.23	-0.29	0.19	0.05	0.37	0.53		-0.23	0.31	0.78	0.75
MS ⁻	0.33	0.28	0.32	0.33	0.08	-0.17	-0.08	0.61	-0.16	0.48	0.68	0.65	0.37	0.18		0.52	-0.26	-0.37
nssSO ₄ ²⁻	0.47	0.40	0.40	0.43	0.17	-0.52	-0.21	0.81	-0.49	0.60	0.93	0.82	0.46	0.18	0.68		0.12	0.04
nssK ⁺	0.72	0.72	0.68	0.75	0.50	-0.45	-0.18	0.86	-0.32	0.84	0.61	0.91	0.69	0.44	0.47	0.69		0.83
nssCa ²⁺	0.66	0.58	0.52	0.63	0.38	-0.48	-0.15	0.64	-0.36	0.63	0.49	0.71	0.53	0.36	0.25	0.52	0.72	

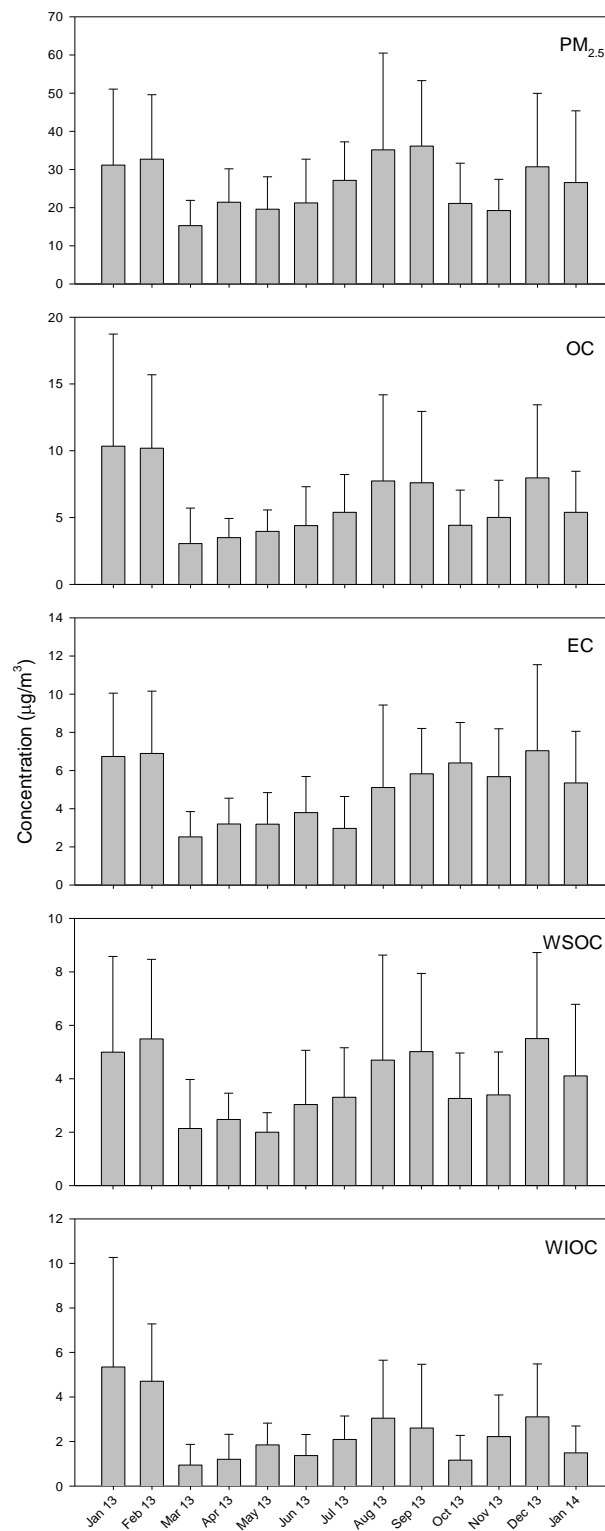


Figure 3 2 - Monthly average variations of mass (PM_{2.5}), organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC) and water insoluble organic carbon concentrations in aerosols from Oporto.

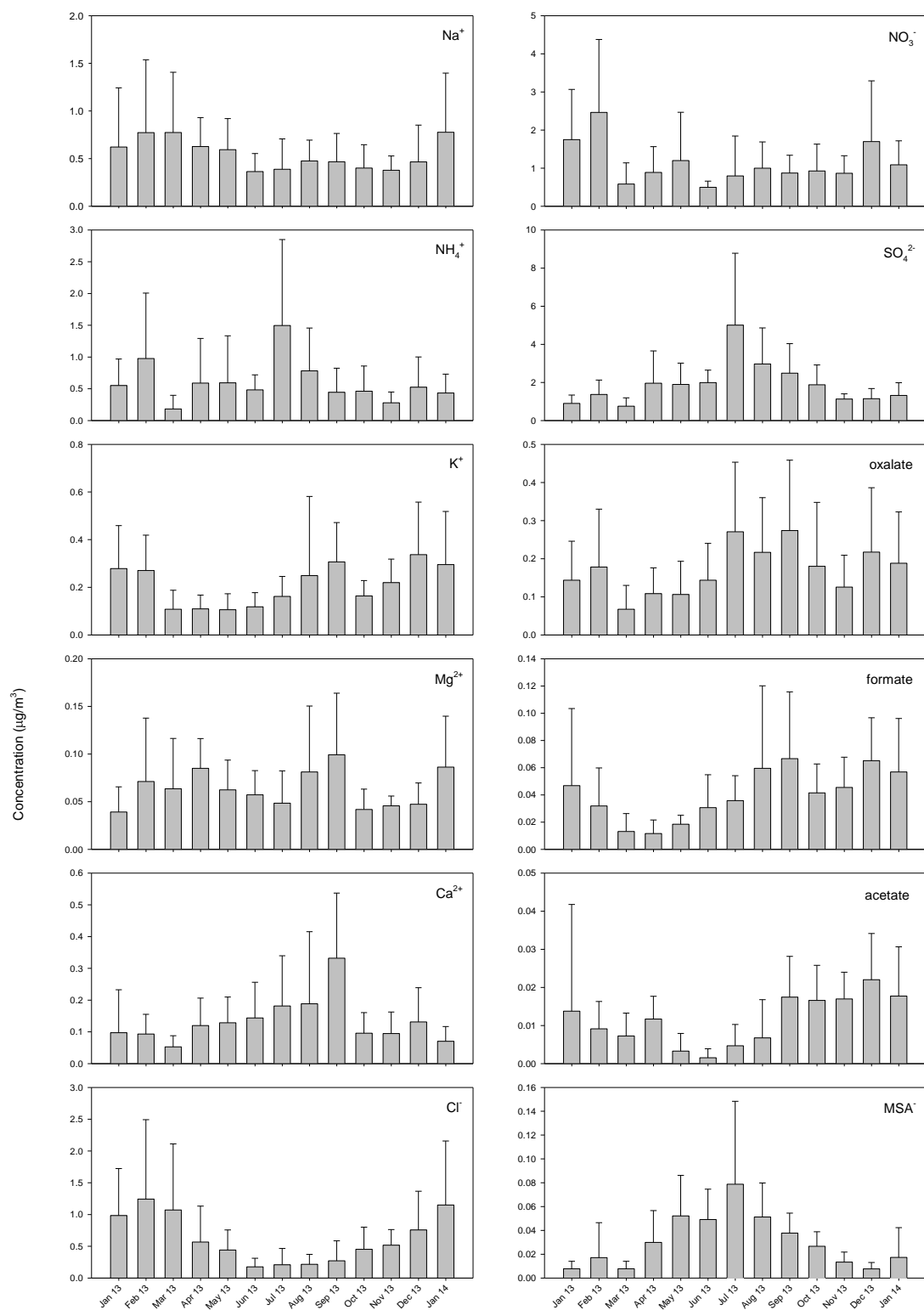


Figure 3.3 - Monthly average variations of major water soluble ions concentrations in aerosols from Oporto.

3.3.2 Organic carbon and elemental carbon

The average concentrations of OC and EC observed in Oporto were $6.2 \pm 4.8 \mu\text{g}/\text{m}^3$ and $5.0 \pm 3.1 \mu\text{g}/\text{m}^3$ respectively (Table 3.2), and are in the lower end of the range of values that has been observed close to major roads in Europe, Asia and North America (Kim et al., 2003; Lee et al., 2006; Pio et al., 2011; Ruellan and Cachier, 2001; Yu, 2002). Both carbon fractions exhibited high concentrations in late autumn and in winter (Fig. 3.2) – probably reflecting an input of emissions from residential biomass burning for heating purposes, combined with unfavorable dispersion conditions – and low concentrations in spring. OC concentrations were also high during summer and were probably related with an increase in secondary organic aerosol formation and with emissions from wildfires in the Oporto region. OC and EC concentrations were well correlated throughout the year ($r=0.82$ in winter and $r=0.78$ in summer). This is not surprising given their similar seasonal patterns and polar plots, which reveal common sources (most likely vehicle exhaust and biomass burning emissions), and the same removal processes for the two species.

The OC/EC ratio has been used as a first indication of carbonaceous aerosol sources, mainly to distinguish between primary sources and atmospheric transformation processes. Ratios ranging from 2 to 5 are commonly observed in urban background atmospheres and are assumed to indicate a significant contribution of secondary aerosol sources (Pio et al., 2011; Querol et al., 2013). Ratios lower than 1 are consistently observed in roadway tunnels and are assumed to describe the composition of fresh traffic emissions (Pio et al., 2011). The average OC/EC ratio for the entire sampling period in Oporto was 1.28 ± 0.61 . The comparison with previous observations (Pio et al., 2011) shows that this value is consistent with a significant influence of recent traffic emissions on aerosol composition. Fig. 3.6 presents the monthly variation of OC/EC ratios. The highest values were found during summer, suggesting an increase in the secondary formation of OC from the photochemical oxidation of volatile organic compounds or the input of smoke plumes from wildfires, which are known to exhibit high OC/EC ratios (Pio et al., 2008; Vicente et al., 2012). On the other hand, the lowest values were recorded in autumn followed by spring, which is indicative of a lower production of OC from secondary processes and from residential biomass combustion.

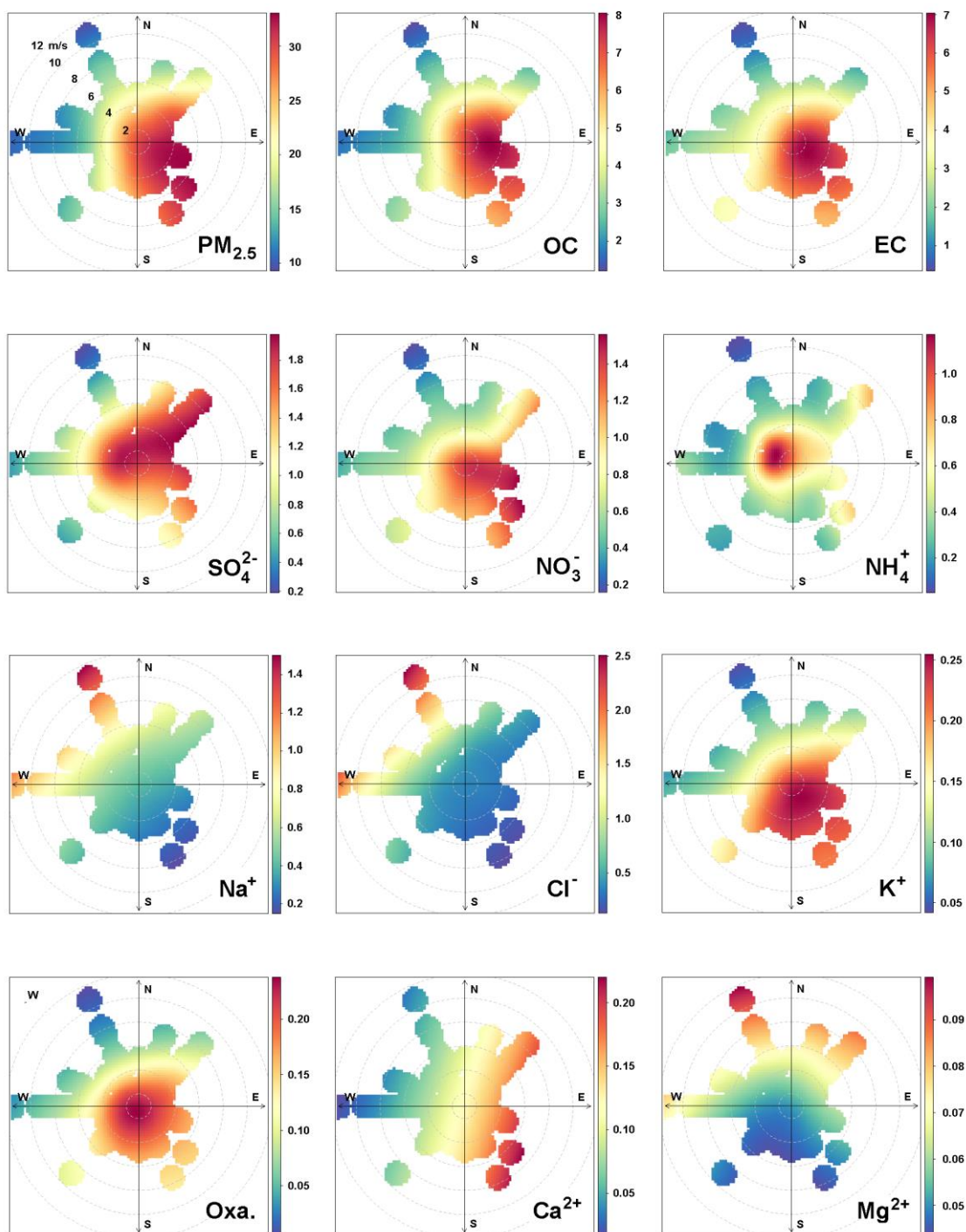


Figure 3. 4 - Polar plots of $\text{PM}_{2.5}$ and major chemical constituents as a function of wind direction and speed in Oporto. Concentrations are in units of $\mu\text{g}/\text{m}^3$.

The EC-tracer method (Pio et al., 2011) has been used to estimate the contribution of secondary organic aerosol to organic carbon concentrations. However, one of the conditions necessary to get correct estimates of secondary OC is that the contribution of primary sources of OC and EC other than fossil fuel combustion is negligible. This is clearly not the

case with the Oporto aerosol samples which were found to be strongly contaminated with biomass burning emissions.

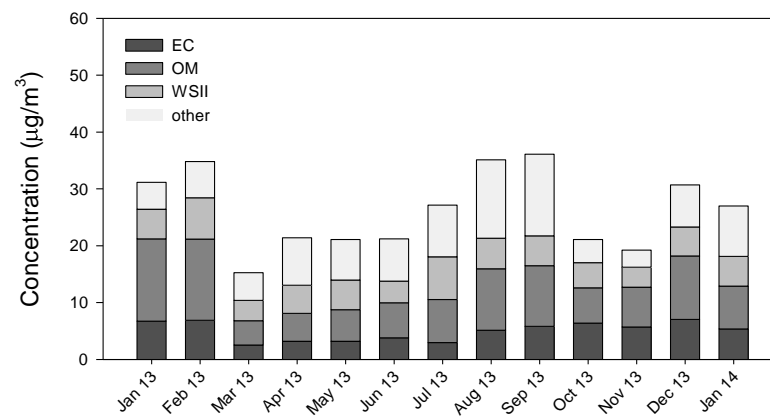


Figure 3.5 - Contribution of carbonaceous mass (EC+OM) and inorganic mass (WSII) to PM_{2.5} mass concentration.

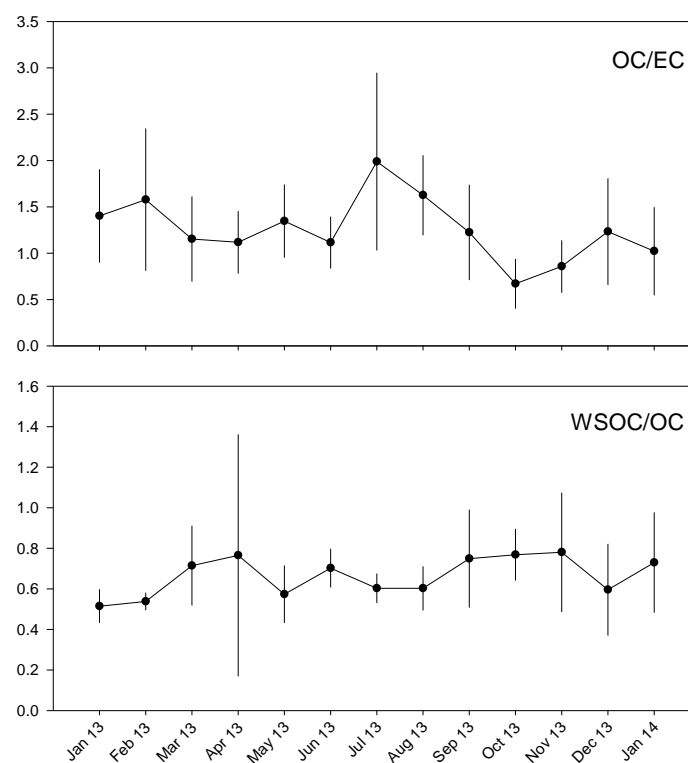


Figure 3. 6 - Monthly average variation of OC/EC and WSOC/OC concentration ratios in Oporto.

3.3.3 Water soluble and water insoluble organic carbon

During the study period WSOC concentrations varied from 0.8 to 13.8 $\mu\text{g}/\text{m}^3$ with a global average of $3.8 \pm 2.7 \mu\text{g}/\text{m}^3$. These values compare well with those described in the literature for roadside and urban atmospheres (Park and Cho, 2011 and references therein). The seasonal variation was similar to that described above for OC, with high concentrations in late autumn and in winter and low concentrations in spring (Fig. 3.2).

The WSOC/OC ratio has been used to investigate the origin of carbonaceous matter in aerosols and particularly to evaluate the extent of formation of secondary organic carbon (e.g. Park and Cho, 2011). In general, the WSOC fraction increases from less than 0.20 in roadside or urban sites, in the vicinity of fossil fuel sources, to more than 0.75 in rural and remote sites (Jaffrezo et al., 2005; Pio et al., 2007; Park and Cho, 2011). In this study, the global WSOC/OC ratio was 0.67 ± 0.23 , thus contrasting with the above general trend. This might result from differences among previously investigated roadside sites, located in Paris and Hong Kong (Ruellan and Cachier, 2001; Yu, 2002) and that of Oporto, particularly in what concerns traffic volumes and corresponding emissions of primary pollutants. This explanation is sustained by the magnitude of average OC concentrations, which was 2.0 to 5.5 times higher than those observed in the present study. In other words, rather than being totally dominated by fresh primary emissions from vehicles, OC aerosol in the Oporto roadside reflects the influence of various emitting sources. WSOC was highly correlated with nssK^+ ($r=0.75$ in winter and $r=0.91$ in summer), a tracer of biomass combustion, and was not correlated with nssSO_4^{2-} (Table 3.3), a species associated with secondary processes, indicating that the main sources of WSOC were domestic wood combustion and wildfires. This is in line with the above mentioned observations of Amato et al. (2015), who found that biomass burning was a major source of fine particles in Oporto. The role of biomass burning as a contributor to the WSOC content of aerosol particles was also previously emphasized in the studies of Viana et al. (2008) and Wonaschütz et al. (2011).

A seasonal variation for the WSOC/OC ratio with high values in summer and low values in winter, and therefore strongly related with the seasonal change of photochemical activity, has been described in urban background sites (Park and Cho, 2011; Du et al, 2014). No clear seasonal trend was observed for the WSOC contribution to OC during the present study (Fig. 3.6), probably because the seasonal pattern of secondary WSOC was masked by the higher inputs of primary WSOC.

WIOC was well correlated with both WSOC and EC and, to a lesser extent, with nssK^+ , indicating that the three carbon fractions share a common combustion source and confirming

that most of the particulate carbon originates from biomass burning activities. The WIOC/EC ratio was in the range of 0.24, in autumn, and 0.64, in winter and summer. These results reflect the lower relative contribution of WIOC to OC, when compared to WSOC, and contrast with other observations in urban areas where the influence of vehicular emissions on aerosol composition is stronger (Favez et al., 2008; Miyazaki et al., 2006; Yu, 2002).

3.3.4 Water soluble ionic components

SO_4^{2-} was the dominant water soluble anion (global average of $1.95 \mu\text{g}/\text{m}^3$), followed by NO_3^- ($1.14 \mu\text{g}/\text{m}^3$), Cl^- ($0.61 \mu\text{g}/\text{m}^3$), oxalate ($0.17 \mu\text{g}/\text{m}^3$), formate ($0.040 \mu\text{g}/\text{m}^3$), methanesulfonate ($0.031 \mu\text{g}/\text{m}^3$) and acetate ($0.012 \mu\text{g}/\text{m}^3$). The dominant water soluble cation was NH_4^+ ($0.62 \mu\text{g}/\text{m}^3$), followed by Na^+ ($0.54 \mu\text{g}/\text{m}^3$), K^+ ($0.21 \mu\text{g}/\text{m}^3$), Ca^{2+} ($0.14 \mu\text{g}/\text{m}^3$) and Mg^{2+} ($0.064 \mu\text{g}/\text{m}^3$) (Table 3.2).

Na^+ and Cl^- are tracers of sea salt and both exhibited a seasonal variation with the highest concentrations in winter and the lowest in summer (Fig. 3.3). This is in agreement with the winter prevalence of marine air flow which transports sea salt aerosols to the sampling site. In addition, wind speed over the North Atlantic is known to be consistently higher during winter, thus causing an increase in the sea salt content of coastal aerosol (Yoon et al., 2007). The polar plot distributions also provide evidence for the marine source of Na^+ and Cl^- , since both graphs clearly show transport from the Atlantic Ocean, with maxima under strong west and northwesterly winds. It is also worth noting that the Cl^- seasonal trend is better defined than that of Na^+ . This is due to the well known summer Cl^- depletion in sea salt aerosol. The typical summer weather conditions favor the formation of HNO_3 from the oxidation of NO_2 by OH radical, and from the vaporization of NH_4NO_3 aerosol particles, which then reacts with NaCl and results in the volatilization of Cl^- , as HCl (Bardouki et al., 2003; Pio et al., 1996).

The biogenic fraction of sulfate measured in Oporto was estimated with the linear relationship between air temperature and the methanesulfonate (MS^-) to non-sea-salt sulfate ratio described by Bates et al. (1992) for the remote South Pacific Ocean atmosphere ($\text{MS}^-/\text{nssSO}_4^{2-}$ (in %) = $-1.5T$ (in °C) + 42.2). Recently, this relationship was also suggested to be applicable to the atmosphere over the Atlantic Ocean (Lin et al., 2012). Using the average winter and summer surface air temperatures in Oporto (10 and 19 °C respectively) $\text{MS}^-/\text{nssSO}_4^{2-}$ ratios of 0.27 and 0.14, respectively, are expected for the biogenic sulfate fraction. Combining these ratios with MS^- concentrations, contributions of 3 and 15% of biogenic sulfate to total sulfate are obtained for the winter and summer seasons, respectively. Given that ssSO_4^{2-} accounts for 22% of total sulfate in winter and 5 % in summer, we demonstrate

that 75 to 80% of total sulfate measured in Oporto during this study is anthropogenic in origin.

The time variation of SO_4^{2-} showed a maximum in summer and a minimum in winter (Fig. 3.3). In this case, the seasonal variation of biogenic sulfur emissions from the ocean cannot be the unique explanation for this time variation since biogenic sulfate is also a minor contributor to total sulfate and the difference between summer and winter average concentrations is higher than $2 \mu\text{g}/\text{m}^3$. Although not statistically significant, the difference suggests that the summer increase is likely related with the secondary formation of sulfate, which tends to be higher in the summer months, when solar radiation and photochemical activity are more intense (Seinfeld and Pandis, 1998). SO_4^{2-} was mostly associated with winds from the northeast and southeast sectors (Fig. 3.4), probably due to emissions from the large number of medium sized industries that spread in the region that surrounds Oporto – including metallurgical, metal processing and chemical – or long range transported emissions from continental areas in Europe. The source apportionment analysis of Amato et al. (2015) has also identified the Oporto oil refinery, located about 10 km NW of the sampling site, as a possible source of sulfur in aerosols but that conclusion cannot be confirmed by the polar plot distribution of SO_4^{2-} .

The seasonal variation of NH_4^+ also shows a peak in summer, but this time trend is expected to reflect the impact of NH_3 emissions from biological sources in urban areas, which include humans, sewage systems and garbage containers (Reche et al., 2012). The NH_4^+ polar plot shows a maximum associated with low wind speed, thus suggesting an urban source of NH_3 and the subsequent local or regional formation of secondary aerosols.

In contrast to NH_4^+ , the highest NO_3^- concentrations were observed during winter (Fig. 3.3). This observation might be at least partially explained by an increase in NO_x emissions from biomass burning for heating purposes combined with the typical winter conditions of a temperate climate region. The polar plot distribution of NO_3^- (Fig. 3.4) shows that concentrations increase under the influence of southeasterly winds and closely resembles that of other pollutants strongly affected by vehicular exhaust ($\text{PM}_{2.5}$, OC and EC). Therefore, oxidation of NO_x emitted during the combustion of fossil fuels by motor vehicles might be a significant source of NO_3^- throughout the year.

Sea salt from the ocean surface was a small but significant contributor to the atmospheric concentrations of total K^+ (18%). This contribution was in the range of 9% in summer to 30% in spring. Both K^+ and nssK^+ concentrations were higher in late autumn/winter, in line with an increase in biomass combustion for heating purposes, and in summer, due to wildfires.

Ca^{2+} concentrations peaked in summer (Fig. 3.6) suggesting that dry weather conditions favored the resuspension of soil and road dust. Sea salt Ca^{2+} comprised on average 32% of total Ca^{2+} concentrations. Seasonally, this contribution was higher in winter (51%) than in summer (15%), in accordance with the above mentioned time variation of marine airflow over the sampling site. The polar plot distribution (Fig. 3.4) shows that Ca^{2+} originated mostly west of the sampling site and the highest concentrations were recorded under the maximum wind speeds. This distribution shows that Ca^{2+} in fine aerosols can be emitted by nearby sources, like road dust resuspension, or more distant sources, which may include construction and demolition works or agricultural soils.

No clear seasonal trend was observed for Mg^{2+} , but the highest monthly average values were recorded in summer (Fig. 3.3), most likely as a consequence of an increase in soil dust inputs to the atmosphere. This is sustained by the fact that the aerosol $\text{Mg}^{2+}/\text{Na}^{+}$ mass ratio ranges from a minimum of 0.12 ± 0.09 in winter, which is in agreement with that of sea salt (0.12), to a maximum of 0.21 ± 0.19 in summer. The polar plot distribution (Fig. 3.4) confirms that Mg^{2+} has both continental and marine sources.

Methanesulfonate in marine and coastal atmospheres is mainly the result of gas-phase oxidation of dimethylsulfide (DMS) which is a breakdown product of cellular solutes produced by some species of marine phytoplankton (Andreae et al., 2003). MS^{-} in Oporto exhibited a well-marked seasonal cycle with the highest concentrations in summer and the lowest in winter (Fig. 3.3). This time trend was reported before in North Atlantic coastal sites (Pio et al., 1996; Yoon et al., 2007) and reflect the seasonal cycles of primary productivity in the oceanic waters.

Oxalate was the most abundant water soluble carboxylate identified in fine aerosol particles, followed by formate, acetate and glycolate. On average, the oxalate mass concentration accounted for 74% of the total carboxylates mass concentration. Together, the average contribution of the four carboxylate species to WSOC (on a carbon mass basis) was only 1.8%. Both results compare fairly well with previous studies about the distribution of carboxylates in fine aerosols from urban areas (Wang et al., 2007; Yang et al., 2005).

Oxalate has been reported to originate from primary emissions of biomass burning (Yamasoe et al., 2000) and from the atmospheric conversion of precursor gases, of both natural and anthropogenic origin, into secondary aerosols (Legrand et al., 2007). Additionally, there is strong evidence that vehicle exhaust is not a primary source of oxalic acid (Huang and You, 2007). In this study oxalate was found to be well correlated with nssK^{+} , particularly in winter ($r=0.91$), suggesting that biomass burning was a source of oxalate at the sampling site.

Moderate to high correlations were detected between oxalate and the inorganic species nssSO_4^{2-} , NO_3^- and NH_4^+ . This is in agreement with other studies about the aerosol composition over the UK and East Asian countries (Laongsri and Harrison, 2013; Yu et al., 2005) and indicates that secondary processes are also important sources of oxalate. On the other hand, oxalate was modestly correlated with EC ($r=0.64$ in winter and $r=0.39$ in summer). Poor correlations between these two aerosol constituents were also reported in the above mentioned studies of Laongsri and Harrison (2013) and Yu et al. (2005) and were indicative of a lower contribution of road vehicle emissions to atmospheric oxalate levels. The polar plot distribution of oxalate differs from those of $\text{PM}_{2.5}$, OC, EC and NO_3^- , which were intensely related with vehicle exhaust emissions. In this case, the association between high concentrations and low wind speed points to the occurrence of local sources, including biomass burning for heating purposes or secondary aerosol processes.

Formate and acetate concentrations in aerosols have been scarcely reported in the literature. This is due to the fact that formic and acetic acids have a high vapor pressure at common ambient air temperatures and consequently both species strongly accumulate in the gas-phase (Bardouki et al., 2003; Souza et al., 1999; Talbot et al., 1988). In the present study, the time variation of formate concentration exhibited low values in spring and high values in summer and late autumn/winter, which points to a significant contribution of biomass burning sources of formic acid. This is supported by the good correlation between formate and the biomass burning tracer nssK^+ ($r=0.76$ in summer and $r=0.69$ in winter).

The seasonal variation of acetate was not completely coincident with that of formate (Fig. 3.3). However, acetate was found to be well correlated with formate in summer ($r=0.79$), suggesting that these two aerosol components may share common sources. Biomass burning is supposed to contribute to the atmospheric levels of acetate, but the correlation analysis between acetate and nssK^+ concentrations suggests that this contribution is only important during the warm season ($r=0.78$ in summer and $r=0.44$ in winter).

The relative abundance of formic and acetic acids in the atmosphere is known to be dependent on the emitting source. Although not consistently observed, it has been documented that emissions from fossil fuel combustion, biomass burning and vegetation have a higher proportion of acetic acid while atmospheric processes are associated to a higher proportion of formic acid (e.g. Talbot et al., 1988; Servant et al., 1991; Souza et al., 1999). Therefore, the formate to acetate ratio (F/A) in aerosols has been used to investigate the contribution of primary sources (F/A values lower than 1) and secondary sources (F/A values higher than 1) to the atmospheric levels of carboxylate species (Wang et al., 2007; Tsai

et al., 2013). F/A values of 3 during winter and 9 during summer were found during this study, indicating a prevalence of atmospheric reactions over direct emissions. However, these results contrast with the aforementioned high correlation between both monocarboxylate species and nssK^+ , and therefore call into question the adequacy of the formate to acetate ratio to distinguish primary and secondary sources of atmospheric carboxylic acids.

3.3.5 Mass balance for water soluble inorganic species

A compound mass balance was computed using the method described by Mirante et al. (2014) in order to identify the dominant water soluble inorganic species in the Oporto aerosol. To perform this balance the following rules were applied:

- 1) Na^+ was considered to originate only from sea salt and was firstly balanced with sulphate to form sodium and magnesium sea salt sulfates, with ratios dependent from sea salt composition;
- 2) excess (free) sodium r^2 and magnesium are associated with chloride in proportions equivalent to sea water, until any of the ions (generally chloride) is totally spent;
- 3) NH_4^+ is preferentially associated with free (non sea salt) SO_4^{2-} , as $(\text{NH}_4)_2\text{SO}_4$ (Seinfeld and Pandis, 1998); in the case of an excess of NH_4^+ with respect to SO_4^{2-} , the free NH_4^+ is balanced firstly with NO_3^- and secondly with Cl^- , to form ammonium nitrate and chloride;
- 4) any free NO_3^- , after balancing with NH_4^+ , is associated sequentially with sea salt cations (free Na^+ and Mg^{2+} , after step (2)), in proportions equivalent to sea water, and with soil cations (Ca^{2+} , K^+ , and Mg^{2+});
- 5) any free SO_4^{2-} is also sequentially associated with free sea salt and soil cations (Na^+ , Mg^{2+} , Ca^{2+} , and K^+); if any SO_4^{2-} remains free after this step it is considered as non-reacted sulphuric acid;
- 6) any free Cl^- , after steps (2) and (3), is sequentially associated with Ca^{2+} and K^+ , being supposed to result from soil or from reaction of gaseous HCl with soil particles;
- 7) after previous balances any free Ca^{2+} , Mg^{2+} and K^+ are considered as non-reacted soil particles.

Results from this balance are shown in Table 3.4. NaCl was the dominant water soluble inorganic species in winter and was clearly more abundant in this season than in summer. The observed difference is related with the above mentioned intensification of sea salt transport from the ocean during the cold season and with the summer interaction between NaCl and HNO_3 to form HCl. The relevance of this interaction is evident from the abundance of NaNO_3 ,

which is the second largest contributor to the mass of water soluble inorganic species in summer.

The contribution of $(\text{NH}_4)_2\text{SO}_4$ to the mass of inorganic compounds was 51% in summer and decreased to 21% in winter. These results are in line with those of the correlation analysis given in Table 3.4. Indeed, the association between NH_4^+ and nssSO_4^{2-} was found to be higher in summer ($r=0.92$) than in winter ($r=0.81$), indicating an increase in the formation of secondary aerosols during the sunny season, promoted by a higher input of anthropogenic precursors from continental areas and an increase in photochemical activity. During winter the abundance of aerosol precursors is lower and sulfuric and nitric acids compete for ammonia to form ammonium salts.

Table 3. 4 - Average concentrations of water soluble inorganic compounds (in units of $\mu\text{g}/\text{m}^3$) during winter and summer in Oporto.

Compound	Winter	Summer
$(\text{Na}_2)_{\text{ss}}\text{SO}_4$	0.21	0.12
$(\text{Mg})_{\text{ss}}\text{SO}_4$	0.10	0.033
$(\text{Na})_{\text{ss}}\text{Cl}$	1.4	0.31
$(\text{Mg})_{\text{ss}}\text{Cl}_2$	0.14	0.053
$(\text{NH}_4)_2\text{SO}_4$	1.1	3.24
NH_4NO_3	1.0	0.039
NH_4Cl	0.022	0.000
NaNO_3	0.32	0.72
$\text{Mg}(\text{NO}_3)_2$	0.046	0.15
$\text{Ca}(\text{NO}_3)_2$	0.26	0.15
KNO_3	0.35	0.028
CaSO_4	0.010	0.58
K_2SO_4	0.044	0.25
Na_2SO_4	0.000	0.11
MgSO_4	0.000	0.029
H_2SO_4	0.011	0.22
CaCl_2	0.019	0.000
KCl	0.10	0.001

The mass balance also revealed that NH_4NO_3 was a major aerosol constituent in winter, accounting for 19% of the mass of inorganic compounds and, in contrast, that summer

aerosol was practically devoid of NH_4NO_3 . HNO_3 produced from the atmospheric oxidation of NO_x is known to be stabilized by reaction with NH_3 . Ammonium nitrate (NH_4NO_3) formed from this reaction accumulates in the fine aerosol mode and is also known to be thermally stable under the low ambient temperature and high relative humidity conditions that are common in the winter months. The seasonal change of weather conditions promotes the summer volatilization of NH_4NO_3 into gaseous ammonia and nitric acid. The occurrence of these processes is sustained by the results of the correlation analysis. Indeed, NO_3^- and NH_4^+ concentrations were highly correlated in winter ($r=0.91$) and not correlated in summer ($r=0.22$).

Also evident in Table 3.4 is the higher abundance of CaSO_4 , K_2SO_4 , Na_2SO_4 and H_2SO_4 in summer than in winter. The observed difference shows that ammonia and sea salt concentrations are insufficient to completely neutralize H_2SO_4 produced in summer. Suspended soil particles containing Ca^{2+} and K^+ carbonates are more abundant under the typical dry summer conditions in Oporto and play an important role as H_2SO_4 neutralizers. However, the atmospheric concentration of alkaline species is apparently scarce to ensure the full consumption of H_2SO_4 .

3.4. Conclusions

$\text{PM}_{2.5}$ aerosol samples were collected at a kerbside site of Oporto, Portugal, during a period of approximately one year, and then analyzed for carbonaceous components and major water soluble ions. The general conclusion of this work is that although the sampling site was located near a major arterial road, the aerosol composition reflects the influence of a variety of sources besides vehicle emissions, including biomass burning, atmospheric processes, oceanic emissions, dust resuspension and industrial activities. The role of biomass burning as a source of kerbside aerosol was not evident in previous studies performed in Oporto (Oliveira et al., 2010; Slezakova et al., 2007). However, the present work demonstrates that this source should be taken into account for the future definition of emission abatement measures.

More specific conclusions include the following:

- $\text{PM}_{2.5}$ and carbon fractions concentrations were in good agreement with values reported in the literature for the kerbside of heavily trafficked roads;
- $\text{PM}_{2.5}$, OC and WSOC exhibited pronounced seasonal variations with peak levels in winter and summer most likely related with biomass burning for heating purposes and wildfires, respectively;

- on average, the carbonaceous matter accounted for 52% of the $PM_{2.5}$ mass concentration and the concentration of carbonaceous matter plus the total concentration of inorganic matter accounted for 74% of the $PM_{2.5}$ mass concentration;
- the average OC/EC and WSOC/OC ratios and the results of the correlation analysis indicated that $PM_{2.5}$ composition was strongly influenced by vehicle exhaust and biomass burning activities, respectively;
- the origin and the seasonal variation Na^+ and Cl^- , with peak concentrations in winter, was clearly associated with the occurrence of airflow transport from the North Atlantic;
- SO_4^{2-} was mainly derived from anthropogenic sources and peak values were found in summer suggesting an increase in the formation of secondary aerosol; the non-sea-salt fraction of SO_4^{2-} was also found to be associated with NH_4^+ , particularly in summer, further sustaining the possibility of secondary aerosol production;
- the formation and lift-up of dust particles under dry weather conditions was likely to be an important source of Ca^{2+} and Mg^{2+} ; a marine source was also identified for Mg^{2+} ;
- methanesulfonate presented a well-defined seasonal variation, consistent with the seasonal cycle of primary productivity in the North Atlantic waters;
- oxalate was the most abundant water soluble carboxylate identified in fine aerosol particles; the origin of oxalate was probably associated with biomass burning as well as secondary process in the atmosphere;
- biomass burning was identified as an important source of formate and, to a lesser extent, of acetate;
- among the aerosol water soluble inorganic constituents, $(NH_4)_2SO_4$ was dominant in summer and NaCl was prevalent in winter.

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CHAPTER 4

Source apportionment of particulate matter in Oporto

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Abstract

This chapter reports the results of the source apportionment of PM₁₀ and PM_{2.5} conducted at an urban traffic site (Oporto, Portugal). After collecting 125 PM₁₀ and PM_{2.5} 24h samples from January 2013 to February 2014 simultaneously, these were analysed for the contents of OC, EC, anions, cations, major and trace elements and levoglucosan. The USEPA PMF5 receptor model was applied to these dataset. Road traffic (as sum of vehicle exhaust, vehicle non-exhaust and traffic-related secondary nitrate) is unequivocally the most important source of PM₁₀ and PM_{2.5}. The total annual mean contribution from road traffic to PM₁₀ is high (22%), corresponding to an absolute value of 12.7 µg/m³. For PM_{2.5} the contribution of traffic emissions increases to 31% (10.3 µg/m³ as annual mean). Local dust (19%) and biomass burning (14%) are the second and third most important sources of PM₁₀. In PM_{2.5} the contribution of biomass burning increases to 18% and that of local dust decreases to 15%. Other significant anthropogenic sources are: secondary sulphate (10% in PM₁₀ and 13% in PM_{2.5}); industries, mainly metallurgy contributing 4% of PM₁₀ (5% in PM_{2.5}); and secondary nitrate, emitted from multiple sources such as industries. Natural contributions consist of sea salt (16% of PM₁₀ and 5% in PM_{2.5}). During high pollution days, road traffic is the largest source of PM₁₀ and PM_{2.5}: 36% to PM₁₀ and 35% to PM_{2.5}. Biomass burning is the second most important source during high pollution episodes (25% of PM₁₀ and 33% of PM_{2.5}). During those days, local dust is also quite important (27-22%).

4.1 Introduction

Atmospheric Particulate Matter (PM) concentrations can vary widely due to different climatic conditions and local features such as anthropogenic source types, emission rates, long range

transport and dispersion patterns. (Pey et al., 2013; Hoyle et al., 2011; Manders et al., 2010; Hodzic et al., 2007).

Urban PM₁₀ concentrations show significant variability across Europe as reported by routine monitoring networks (EEA, 2013). For PM_{2.5} the spatial variability across Southern Europe is less known because in most air quality zones it is not as widely measured as PM₁₀. As a consequence, there is limited information on the geographical variability of the coarse fraction (PM_{10-2.5}), which is often linked to local sources and whose evidence of health concern is increasing (Brunekreef and Forsberg, 2005).

However, bulk PM concentrations only, without the necessary chemical characterization of collected samples and source apportionment analysis, does not allow for an in depth investigation of sources limiting the scope for air quality management purposes. In face of this challenge, this study, created the first comprehensive dataset of Oporto city for PM₁₀ and PM_{2.5} levels and composition aiming to characterize the PM sources and contributions in one of the largest urban area of the Iberia Peninsula. This work was developed within the framework of AIRUSE LIFE Project, the main objective of which is to test and develop specific measures to improve air quality in southern Europe, targeted to meet air quality standards and to approach as closely as possible the WHO guidelines.

4.2 Methods

4.2.1 PM sampling and measurements

Aerosol samples were collected in a typical urban traffic site, located in Praça Francisco Sá Carneiro (41°09'46.10'' N; 8°35'26.95'' W), in a station of the National Air Quality Network, QualAr. It is located in the eastern side of Porto city, next to the Fernão de Magalhães Avenue and at 600 meters from the Inner Circular Motorway (Figure 4.1).

Two low volume samplers (TECORA) operating at 2.3 m³/h collected PM₁₀ and PM_{2.5} onto 47 mm diameter Teflon filters. A parallel PM_{2.5} and PM_{2.5-10} sampling was carried out by a high-volume sampler operating at 66.8 m³/h with an Andersen PM₁₀ sampling head and Sierra impaction plates, enabling the sequential collection of PM_{2.5-10} and PM_{2.5} samples onto quartz micro-fiber filters (Whatman was used from the beginning until 7 July 2013. After this date, filters from Pall were used).

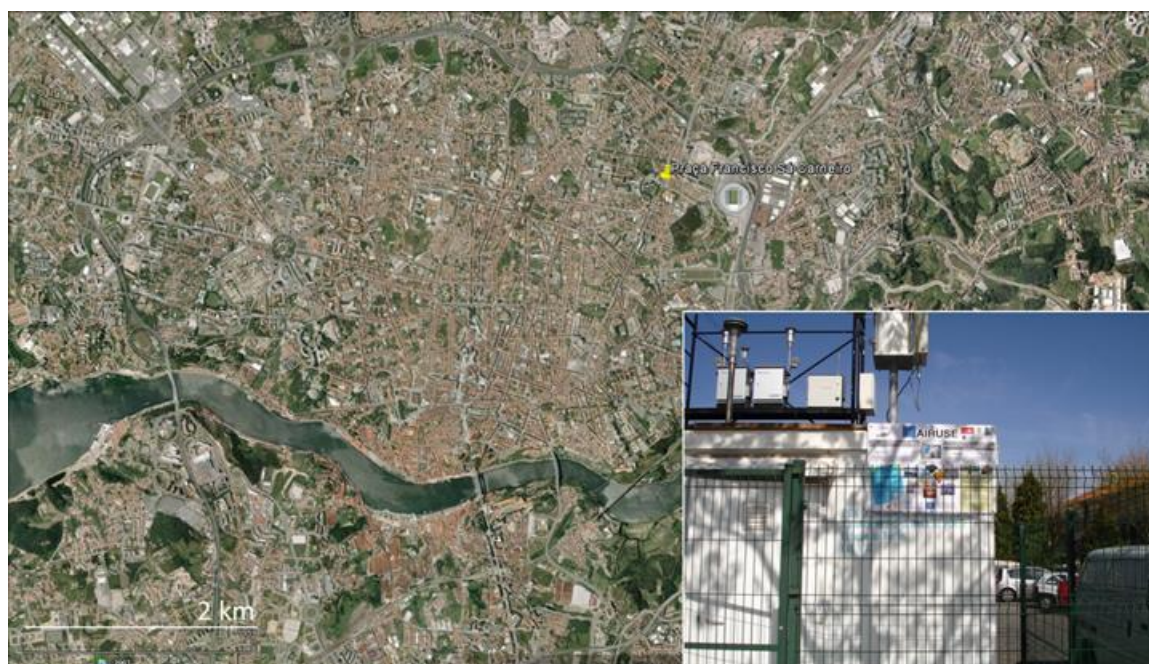


Figure 4.1 - Location of the Oporto monitoring site

Hourly samplings of $PM_{2.5}$ and $PM_{2.5-10}$ were carried out by means of the STREAKER sampler during 4 weeks from the end of January to the beginning of March 2013 and during 3 weeks in June-July 2013. The Streaker sampler (Figure 4.2), allows the collection of coarse and fine aerosol (i.e. $PM_{2.5-10}$ and $PM_{2.5}$, respectively) with 1-hour time resolution (D'Alessandro et al., 2003). With this sampler, the aerosol coarse and fine fractions are collected, respectively, on a Kapton foil and a Nuclepore filter, which are paired on a cartridge that rotates at constant speed for a week so that a circular continuous deposit of particular matter ("streak") is produced on both stages.

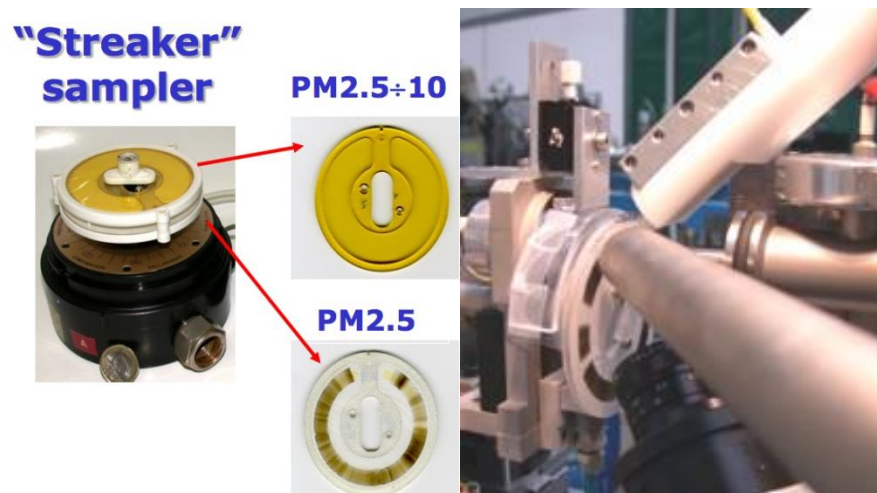


Figure 4.2 - The streaker sampler with collection foils (left) and their PIXE analysis (right).

4.2.3 Sample treatment and analysis

Before sampling, quartz microfiber filters were previously combusted at 550 °C for 5 h to remove organic contaminants and conditioned for 48 h at 20 °C and 40% of relative humidity. Weights of blank filters were measured three times every 24 h by means of a microbalance (1 µg sensitivity). After sampling, filters were brought back to the laboratory to be weighed two more times every 24 hours of conditioning at the same temperature and relative humidity as the first weighing and kept in aluminum foils.

Once the weights of samples were determined, filters were destined for several analytical determinations. These procedures are briefly listed below, according to the different species analyzed:

- Major elements and trace elements were determined:
 - In Teflon filters by different techniques: PIXE (Particle Induced X-Ray Emission), without any pretreatment (Lucarelli et al., 2014); after acid digestion (5 ml HF, 2.5 ml HNO₃, 2.5 ml HClO₄) of 1/2 of each filter, consecutively by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) (Querol et al., 2001) to assure comparability between the two techniques; by ICP-AES after digestion with HNO₃-H₂O₂ in a microwave oven according to the EU method EN14902:2005 (Traversi et al., 2014);
 - In quartz filters by ICP-MS and ICP-AES after acid digestion (5 ml HF, 2.5 ml HNO₃, 2.5 ml HClO₄) of 1/4 of each filter (Querol et al., 2001);
- Water soluble ions by IC (Ion Chromatography), after extraction in 20 ml of MilliQ water (with ultrasonic bath for 30 min) of ¼ of filter;
- On quartz filters organic carbon (OC) and elemental carbon (EC) by thermal/optical analysis in a thermo-optical transmission system described in detail elsewhere (Pio et al., 2011, 1998).
- On the PM_{2.5} quartz filters levoglucosan, by means of Ion Chromatography after extraction in 10 ml of MilliQ water (with ultrasonic bath for 30 min) on 1.5 cm² punch from quartz filter.

As concerns the samples with hourly resolution, collected with the streaker sampler, they were analyzed by PIXE at the LABEC laboratory of Florence (Italy) (Figure 4.2), using a beam spot (2 mm²) corresponding to one hour of aerosol sampling on the streaker. These measurements allow for the determination of the elemental concentrations (atomic number $Z > 10$) with hourly time resolution.

Some elements were detected by different techniques; this guaranteed a quality assurance check of the obtained data.

4.2.4. Source apportionment

Source apportionment studies of atmospheric particulate matter are often performed by means of receptor models that are based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{jk} \quad i=1,2,\dots,m \quad j=1,2,\dots,n \quad (4.1)$$

where x_{ij} is the concentration of the species j in the i^{th} sample, g_{ik} is the contribution of the source k in the i^{th} sample and f_{jk} is the concentration of the species j in source k . Equation (4.1) can be also expressed in matrix form as $\mathbf{X}=\mathbf{GF}^T$. If f_{jk} are known for all the sources then the Chemical Mass Balance (CMB) can be applied (Watson et al., 1984), as for this model the experimental profiles of all major sources are needed. When both g_{ik} and f_{jk} are unknown, factor analysis (FA) techniques such as *Principal Components Analysis* (PCA) (Thurston and Spengler, 1967; Henry and Hidy, 1979) and *Positive Matrix Factorization* (PMF) (Paatero and Tapper, 1994) are used for solving equation (4.1). PMF can be solved with the Multilinear Engine (ME-2) developed by Paatero (1999) and implemented in the version v5 of the US EPA PMF (<http://www.epa.gov/heasd/research/pmf.html>).

In this study, the US EPA PMF v5 was applied. Since the method is a weighted least-squares method, individual estimates of the uncertainty in each data value are needed. The uncertainty estimates were based on the approaches by Polissar et al., (2008) and Amato et al., (2009). Species which retain a significant signal were separated from the ones dominated by noise, following the signal-to-noise (S/N) criterion defined by Paatero and Hopke (2003). Species with $S/N < 0.2$ are generally defined as bad variables and removed from the analysis and species with $0.2 < S/N < 2$ are generally defined as weak variables and down weighted by a factor of 3. Nevertheless, since S/N is very sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit was used as complementary criterion.

Once the source contributions were obtained, these were plotted in polar coordinates as a function of wind direction and speed by means of the PolarPlot function available in the OpenAir software (Carslaw, 2012; Carslaw and Ropkins, 2012).

4.3 Results

4.3.1 Source apportionment

Therefore this subchapter is only focused on the source apportionment results. The best PMF solution was found pooling PM₁₀ and PM_{2.5} samples in a single input matrix for PMF, comprising 226 samples, 27 strong species (EC, OC, levoglucosan, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, NO₃⁻, Li, As, Rb, Sb and Ba), 6 weak species (V, NH₄⁺, Cd, Sn, La and Pb) and setting PM as total variable with 400% uncertainty (US EPA, 2014). The distribution of residuals, G-space plots, Fpeak values and Q values were explored for solutions with number of factors varying between 6 and 9. The most reliable solution was found with 8 factors/sources, adding an extra 7% uncertainty and a minimum (base run) Q robust value of 7040.4, found over 30 runs (seed number 30), which exceeded the theoretical Q value (5800) by 21%. Species concentrations were reconstructed within 79-104%.

Constraints were added to the base run solution. Such constraints were of both physical and chemical nature and aimed at reducing the rotational ambiguity of the PMF problem, driving the solution towards a priori information based on mass conservation principle or partial knowledge of emission sources (Amato et al., 2009; Paatero and Hopke, 2008). More specifically, in the case of Oporto, the following constraint was introduced: Pulling the difference of source contributions between PM₁₀ and PM_{2.5} to zero, only for those days and sources where PM_{2.5} contribution was higher than PM₁₀ contribution in the base run solution. The % of dQ was set at 5% for each constraint and the converged results used totally 2.9% dQ.

The 8 sources identified in Oporto (Figure 4.3) were: Biomass burning (BB), Secondary nitrate (SNI), Heavy oil and secondary sulphate (HOS), Mineral (MIN), Sea salt (SEA), Industrial (IND), Vehicle non-exhaust (NEX), and Vehicle exhaust (VEX).

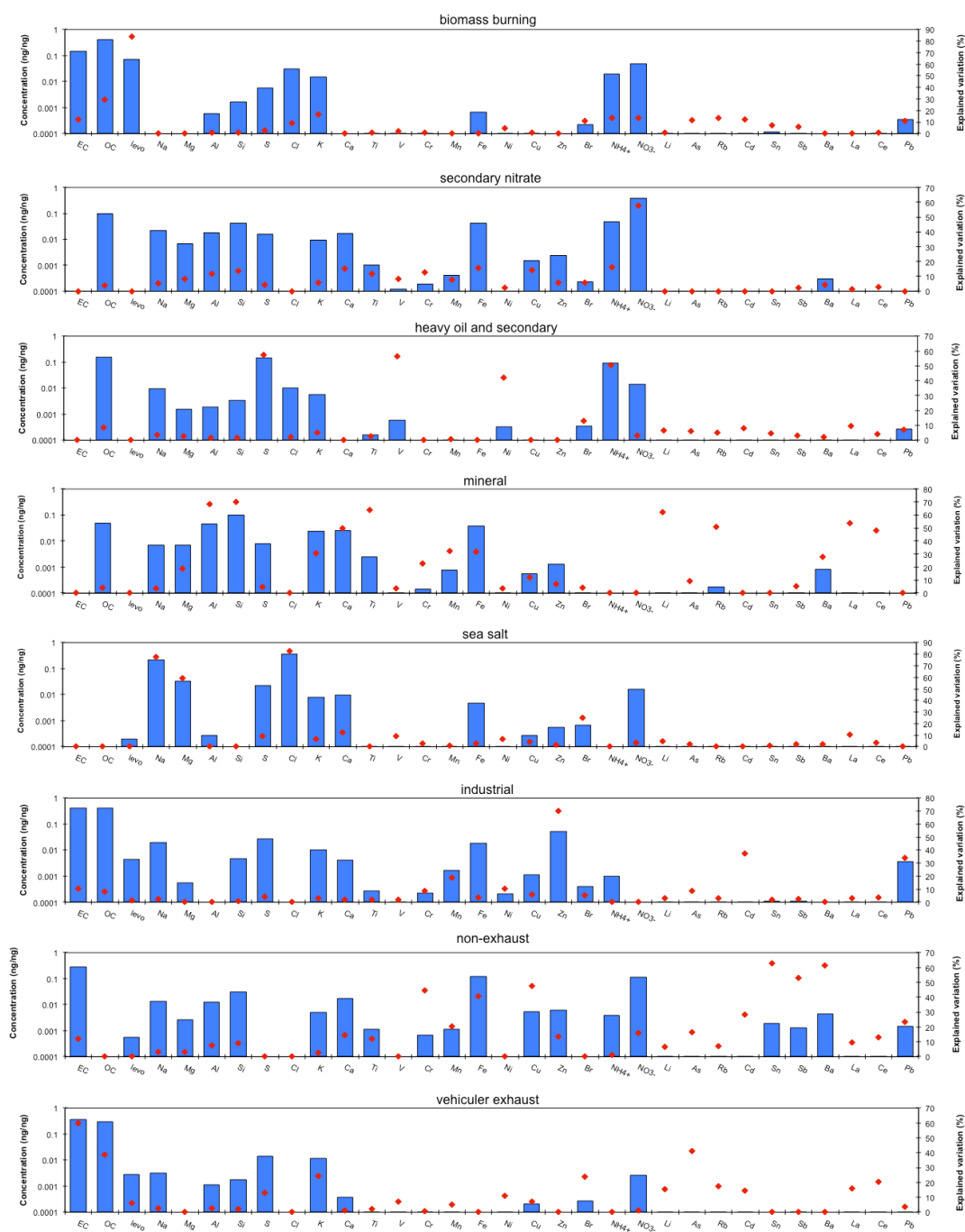


Figure 4. 3 - PMF factors profiles obtained in Oporto (concentration in blue and explained variation in red).

Biomass burning (BB) comprises levoglucosan, the traditional tracer of this source (84% of explained variation), as well as OC (29% of OC explained variation) and EC (11%) (Figure 4.3). A high OC/EC ratio (2.9) is also characteristic of biomass burning emissions (Gonçalves et al., 2010). The presence of K (17% of explained variation), another BB tracer, helps corroborating the assignment to this source. Lower proportions of ammonium, nitrate and chloride were also associated with this source. Although, on average, the contribution of BB explains 17% of

the PM_{2.5} mass throughout the sampling campaign (Figure 4.4), the impact is especially high in the winter months, due to the generalized use of wood for residential heating (Figure 4.5). It should be noted that results from a survey questionnaire carried out in the early fall of 2010 to assess residential wood combustion (RWC) practices in the 18 districts of mainland Portugal revealed that emissions of PM_{2.5} from RWC in the country represented 30% of the primary PM_{2.5} emissions reported in official inventories. In the Oporto district, which, in addition to the municipality with the same name, encompasses another 17 municipalities, it was estimated that about 250 kton of wood are annually burnt by householders for heating purposes, which contributes to the emission of 1.3 kton/year of PM_{2.5} (Gonçalves et al., 2012). The contribution of BB to PM is also higher in September (Figure 4.5). Several wildfires were registered in the Oporto district in this particularly hot and dry month. According to the Institute for Nature Conservation and Forests (ICNF, 2014), this district recorded the highest number of occurrences and one of the largest burnt areas.

The Secondary nitrate (SNI) factor explained about 16% of NH₄⁺ and most of the variance of NO₃⁻ (58%) (Figure 4.3). NO_x emissions from road traffic and industrial plants represent the primary source (Oliveira et al., 2010), although, in winter, biomass burning could also contribute to the detection of NH₄⁺ and NO₃⁻ in the particulate phase (Calvo et al., 2015). On an annual basis, the SNI contributions to PM₁₀ and PM_{2.5} were, on average, 3.2 and 1.4 µg/m³, respectively (ratio PM_{2.5}/PM₁₀ of 0.44), including a proportion of semi volatile organic aerosols, which easily condense on the high surface area of ammonium nitrate particles (Figures 4.4 and 4.5). Although in winter ammonium nitrate formation is favored by low temperature and higher humidity and in summer it is volatilized more quickly due to higher temperature, a marked seasonality is not observed (Figure 4.5). This is likely related to the fact that in summertime wildfires represent an additional source of nitrate precursors.

The factor Heavy oil and secondary (HOS) was traced by V and Ni (Figure 4.4), but also had a high contribution from SO₄²⁻ and NH₄⁺. When the sampling site, in particular, and the city center, in general, is under the influence of NW winds, one of the major sources of these constituents could be the refinery, which began operating in 1970. It is a crude oil industrial processing plant that has an annual installed capacity of 4.5 million tons and produces a wide range of products including fuels, lubricants, aromatics (BTX) for the petrochemical industry, industrial solvents and petroleum waxes. Emissions from ships in the harbor, located at short distance from the refinery, may represent another source. Source contributions for this factor were generally higher in summer than in winter (Figure 4.5) due to the higher photochemical activity during warmer months. Annual average contributions to PM₁₀ and PM_{2.5} were 3.5

(10%) and 3.3 (13%) $\mu\text{g}/\text{m}^3$, respectively. These constituents are concentrated in fine particles (ratio $\text{PM}_{2.5}/\text{PM}_{10}$ of 0.97) (Figures 4.4 and 4.5).

The Mineral (MIN) factor was identified by the typical crustal species, such as Al, Si, Ca, Li, Ti, Rb, Ce, La (all with explained variation above 50%), Cr, Mn, Fe, Ba and K (above 20%) (Figure 4.3). The MIN source represents a mixture of diverse contributions, mainly from fugitive and diffuse emissions (e.g. soil resuspension and constructions works). The overall composition of the Mineral factor reveals a significant enrichment in Ca, Fe and K when compared to the average crust composition (Rahn, 1976; Mason, 1966), indicating an anthropogenic component. Ca-rich particles may originate from concrete or limestone. Additionally potassium, beside from biomass burning, may result, together with Fe, from particle traffic emissions (Lawrence et al., 2013), as it may be deposited on the roads and resuspended afterwards. The overall MIN contribution was 6.3 $\mu\text{g}/\text{m}^3$ (18%) to PM_{10} and 3.8 $\mu\text{g}/\text{m}^3$ (15%) to $\text{PM}_{2.5}$ levels. The mean $\text{PM}_{2.5}/\text{PM}_{10}$ ratio of 0.63 indicates a considerable fraction on fine particles.

The Sea salt (SEA) factor, traced by Na^+ , Cl^- and Mg^{2+} (Figure 4.4), is associated with sea spray aerosol. It contributes, on average, 5.5 (16%) and 1.1 (4%) $\mu\text{g}/\text{m}^3$, respectively, to PM_{10} and $\text{PM}_{2.5}$. The $\text{PM}_{2.5}/\text{PM}_{10}$ ratio (0.21) reveals the dominance of these sea spray components in coarse particles. Sea salt particles are more abundant in winter, when Atlantic winds pick up (Figures 4.4 and 4.5).

The Industrial (IND) factor, traced by Zn (70% of explained variation), also encompasses substantial percentages of Cd, Pb and Mn (Figures 4.3 and 4.6). Mean contributions to PM_{10} and $\text{PM}_{2.5}$ concentrations were, for both size fractions, 1.2 - 1.3 $\mu\text{g}/\text{m}^3$, corresponding to 4% and 5% respectively (Figure 4.4). No discernible seasonality is observed (Figure 4.5). Previous works carried out in Oporto, in which principal component analysis has been applied to the aerosol chemical composition databases, also pointed out industrial sources, probably related to refuse incineration or metallurgy, as a separate factor that had a strong contribution from Zn, Pb and Mn (Oliveira et al., 2010; Pio et al., 1998).

The Vehicle non-exhaust (NEX) factor is traced by the aforementioned brake wear metals/metalloids (Cu, Ba, Cr, Fe, Sn and Sb), which individually explained 45-63% of the variation (Figure 4.3). NEX emissions accounted for 2.9 $\mu\text{g}/\text{m}^3$ (8%) of PM_{10} and only 1.3 $\mu\text{g}/\text{m}^3$ (5%) of $\text{PM}_{2.5}$ levels (Figure 4.4). A $\text{PM}_{2.5}/\text{PM}_{10}$ ratio of 0.45 denotes the predominance of brake and tire wear components in coarse particles. Differently to the MIN source, NEX contributions were rather constant over the year with slightly higher values in winter (Figure

4.5). A similar observation was reported by Amato et al. (2009) for an urban site in Barcelona, suggesting low seasonal variation of NEX emissions (Figures 4.4 and 4.5).

Vehicle exhaust (VEX) comprises organic particles (38% of OC explained variation) from tailpipes, as well as EC (60%) (Figure 4.3). The ratio OC/EC of 0.64 reveals a predominance of primary organic aerosol (Alves et al., 2015) from fuel incomplete combustion in vehicle engines. The presence of K (24% of variation), S (13%) and Br (24%) is also noted. Potassium is found in all unleaded fuels (Spencer et al., 2006). It is also used as an antifreeze inhibitor and as an additive in some oil types. Sulphur is a naturally occurring component of crude oil and is found in both gasoline and diesel. However, recent pollution reduction strategies have forced to lessen the sulphur content of fuels to near-to-zero levels. Sulphur is also used in engine oil anti-wear additives (Fitch, 2004). Before leaded fuels were phased out, bromine was used to prepare 1,2-di-bromoethane, which was an anti-knock agent. However, this use has declined as lead has gradually been removed from fuel. Bromine compounds are now being tested in batteries for electric cars, designed to produce zero emissions. Average source contributions from Vehicle exhaust were around $8.0 \mu\text{g}/\text{m}^3$ for both size fractions, corresponding to 23% of PM_{10} and 32% of $\text{PM}_{2.5}$ levels. The average $\text{PM}_{2.5}/\text{PM}_{10}$ ratio of 0.99 reveals an overwhelming contribution of exhaust particulate constituents to the lowest size fraction, which is related to the very fine mode of motor exhaust particles (Figures 4.4 and 4.5). Furthermore, besides representing the most significant source to particulate matter levels, the contribution of Vehicular Exhaust emissions did not show significant variations between seasons, emphasizing a constancy in traffic patterns, which overlaps the seasonal weather and atmospheric dynamics. Traffic has been also pointed out as the main contributor to atmospheric particulate levels in previous sampling campaigns (Oliveira et al., 2010).

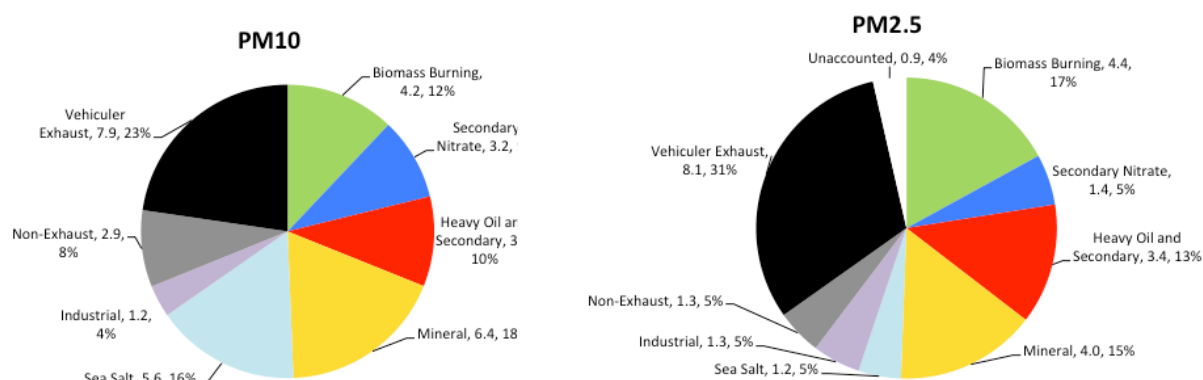


Figure 4. 4 - Pie chart of the identified source contributions ($\mu\text{g}/\text{m}^3$ and %) to PM_{10} and $\text{PM}_{2.5}$ in Oporto

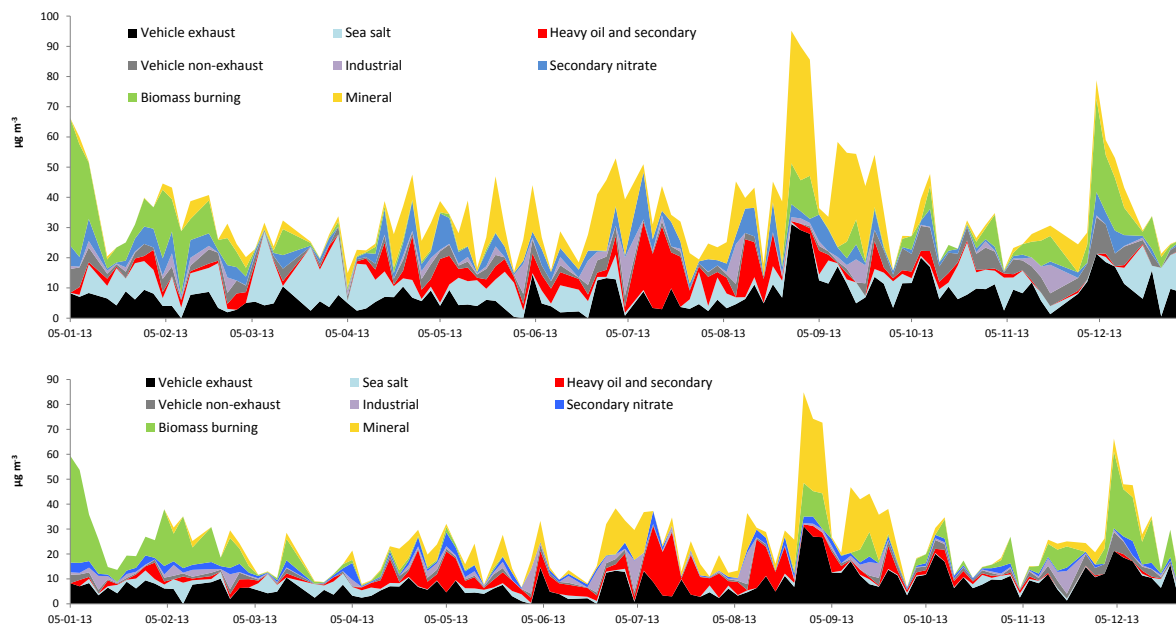


Figure 4. 5 - Time variability of source contributions to PM₁₀ (top) and PM_{2.5} (bottom) in Oporto.

The total contribution from traffic can be estimated as the sum $(VEX)+(NEX)+0.6*(SNI)$, which results in 12.8 and 10.3 $\mu\text{g}/\text{m}^3$ in PM₁₀ (37%) and PM_{2.5} (41%), respectively. This indicates a clear preponderance of urban traffic emissions in Porto, at least in the vicinity of the sampling site. Oliveira et al. (2010) estimated that direct vehicle emissions and road dust resuspension contributed with 44–66% to the fine aerosol and with 12 to 55% to the coarse particle mass at two contrasting sites in the center of the city of Porto (roadside and urban background), showing typically highest loads at roadside. The assumption that 60% of SNI originates from road traffic is based on NO_x emission estimates from the inventory of The North Regional Coordination and Development Commission for different sectors, sources, and activities (DAO-UA/CCDR-N, 2009).

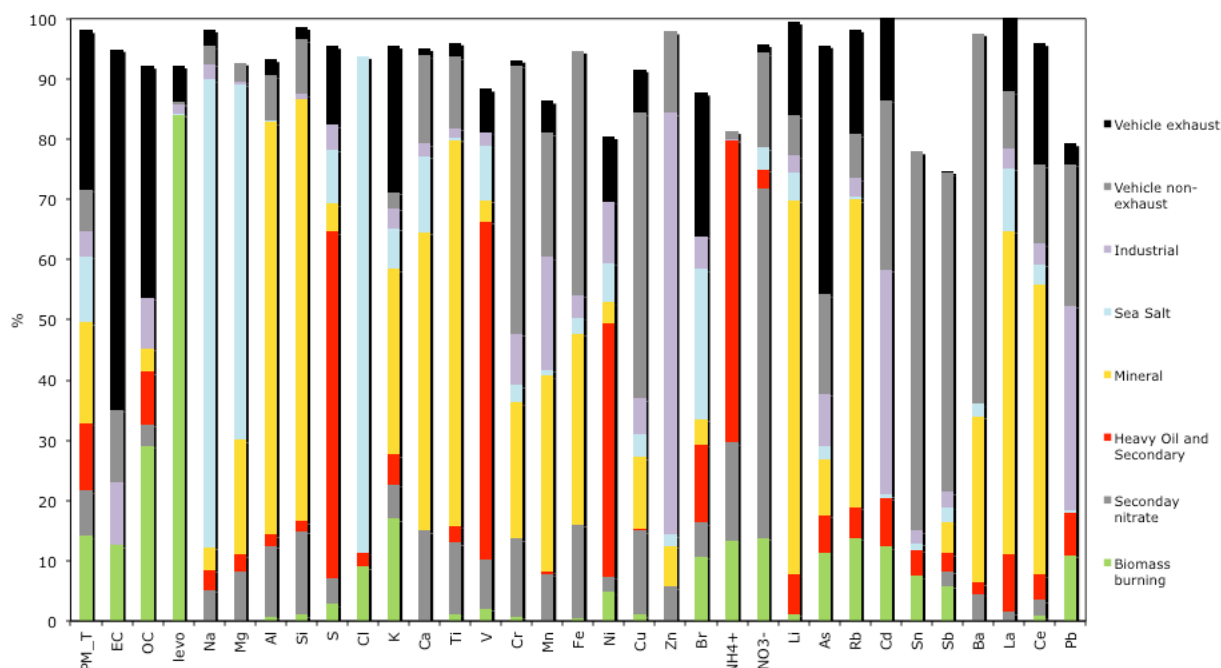


Figure 4. 6 - Source fingerprints in Oporto. Average of PM₁₀ and PM_{2.5} samples.

Finally, average source contributions to PM₁₀ and PM_{2.5} during the days in which PM₁₀ concentration is above 50 µg/m³ are reported in Table 4.1. Traffic (as sum of VEX, NEX and 60% of secondary nitrates), Biomass burning (as sum of BB and 16% of secondary nitrates) and Mineral dust are the sources which give the most relevant contribution.

Table 4. 1 - Source contribution (%) to PM₁₀ and PM_{2.5} in Oporto during the days in which PM₁₀ concentration is above 50 µg/m³.

	PM ₁₀	PM _{2.5}
	%	%
Sea salt	3	<1
Saharan dust	<1	<1
Local dust	27	22
Heavy oil & secondary	5	2
Veh. non-exhaust	6	3
Veh. Exhaust	25	30
Veh. Nitrate	5	2
Industrial	2	1
Non-traffic nitrate	2	1
Biomass burning	25	33
Unaccounted	-	5

The error associated with source contribution estimates were calculated based on the standard error of the coefficients of a multiple regression between the daily PM concentration (independent variable) and the eight source contributions for that day (dependent variables). As a result we obtained the symmetric error for each source contribution (Table 4.2).

Table 4. 2 - Annual average source contributions and standard error ($\mu\text{g}/\text{m}^3$) in Oporto.

	PM₁₀	PM_{2.5}
	Annual mean contribution \pm standard dispersion	
Vehicle exhaust (VEX)	7.9 \pm 0.7	8.1 \pm 0.7
Vehicle non-exhaust (NEX)	2.9 \pm 0.5	1.3 \pm 0.2
Secondary nitrate (SNI)	3.2 \pm 0.4	1.4 \pm 0.2
Heavy oil & secondary sulphate (HOS)	3.4 \pm 0.2	3.3 \pm 0.2
Industrial (IND)	1.2 \pm 0.2	1.3 \pm 0.2
Biomass burning (BB)	4.2 \pm 0.2	4.4 \pm 0.2
Mineral (MIN)	6.3 \pm 0.3	3.8 \pm 0.2
Sea salt (SEA)	5.5 \pm 0.4	1.1 \pm 0.4

Figure 4.7 shows the variation of source contributions as a function of wind speed and direction with quickly gaining a graphical impression of potential source influences. The vector daily averages of wind data are used in order to match the 24-h resolution of source contributions. Eight plots are shown, each one including PM₁₀ and PM_{2.5} source contributions in order to improve the statistical significance.

The Secondary nitrate (SNI), Heavy oil and secondary (HOS), Vehicle exhaust (VEX) and non-exhaust (NEX) plots show maxima with low wind speed, suggesting nearby sources with higher impact under stagnant atmospheric conditions. In addition to nearby sources, the Biomass Burning (BB) plot also reveals higher contribution when the winds blow from the southeast to southwest sectors, likely transporting plumes from large residential areas on the outskirts or from neighbor municipalities (e.g. Vila Nova de Gaia) with energy use patterns more similar to those of rural counties. The intense daily traffic from suburban dormitories, such as Gaia, to the Oporto city center, is the likely cause of the high concentrations from SNI, NEX and VEX associated with southerly and southeast winds. The Sea salt (SEA) source shows a clear transport from the Atlantic Ocean, under westerly winds. Low to moderate contributions from Industrial and Mineral (MIN) sources are associated with transport from the northeast to the southeast sectors (Figure 4.7). An unknown number of small metallurgical industries, smelters, woodworking industries (including furniture

manufacturing) and other familiar industries are spread by inland neighboring municipalities in this northeast to southeast sector (e.g. Gondomar, Valongo, Paredes).

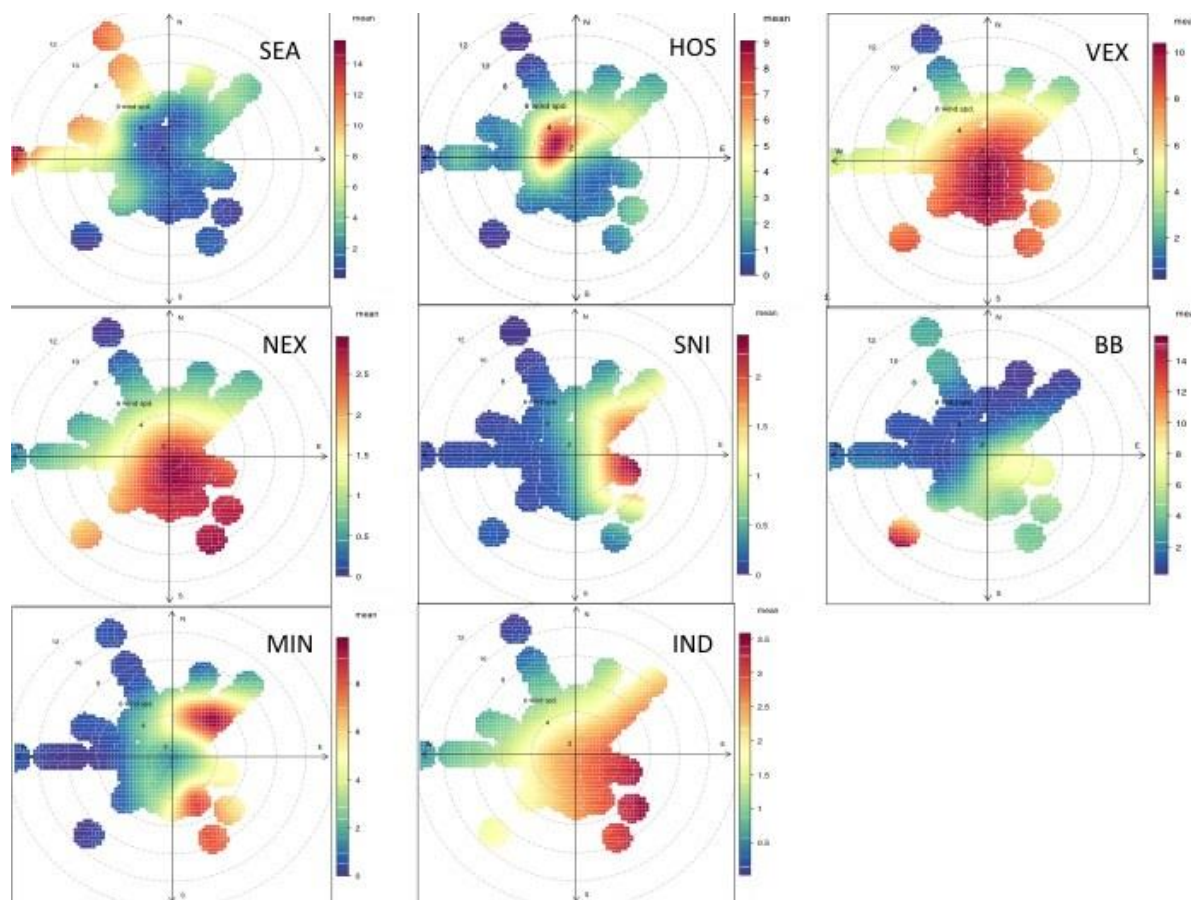


Figure 4. 7 - Plots of daily source contributions as a function of wind speed and direction particulate matter in Oporto: (BB) Biomass burning, (SNI) Secondary nitrate, (HOS) Heavy oil & secondary, (MIN) Mineral, (SEA) Sea salt, (IND) Industrial, (NEX) Vehicle non-exhaust and (VEX) Vehicle exhaust.

4.3.2 Source apportionment during high pollution days

In order to evaluate the origin of particles during high pollution days, similar sources were combined in fewer categories and pie charts were created for the annual mean and for days exceeding the limit of $50 \mu\text{g}/\text{m}^3$ (Figure 4.8). On an annual basis, road traffic is, as expected, the most important source of PM_{10} (38%) and $\text{PM}_{2.5}$ (39%). Another 19% and 13% of PM_{10} mass are related to mineral and sea salt particles, respectively, mostly contributing to the coarse aerosol fraction. Biomass burning, that is mainly associated with residential wood combustion, accounts for 14% of the PM_{10} levels, representing 18% of $\text{PM}_{2.5}$. Heavy oil and secondary sulphate constituents, which encompass emissions from shipping and a petro-refinery complex, contribute to 10% and 13% in PM_{10} and $\text{PM}_{2.5}$, respectively (Figure 4.8).

When the mean source contributions that have been estimated with the annual dataset are compared with the assignments for days exceeding the limit of $50 \mu\text{g}/\text{m}^3$, some features

stand out (Figure 4.8). The contribution from biomass burning to PM_{2.5} and PM₁₀ doubles on exceedance days, whilst the input from traffic and sea salt decrease in relation to the overall average. It is worth noting that approximately half of the exceedances were recorded in late August and early September, when intense wildfires struck the region. The other half was registered in winter months, indicating the input from residential wood combustion to the atmospheric particulate loads. The contribution from mineral dust also increases during exceedance days. The highest contributions from this source to the particulate matter levels were observed during the intense wildfire period, suggesting soil dust entrainment into the smoke aerosols. Post-fire soil erosion may also have contributed to enhanced PM₁₀ and PM_{2.5} concentrations.

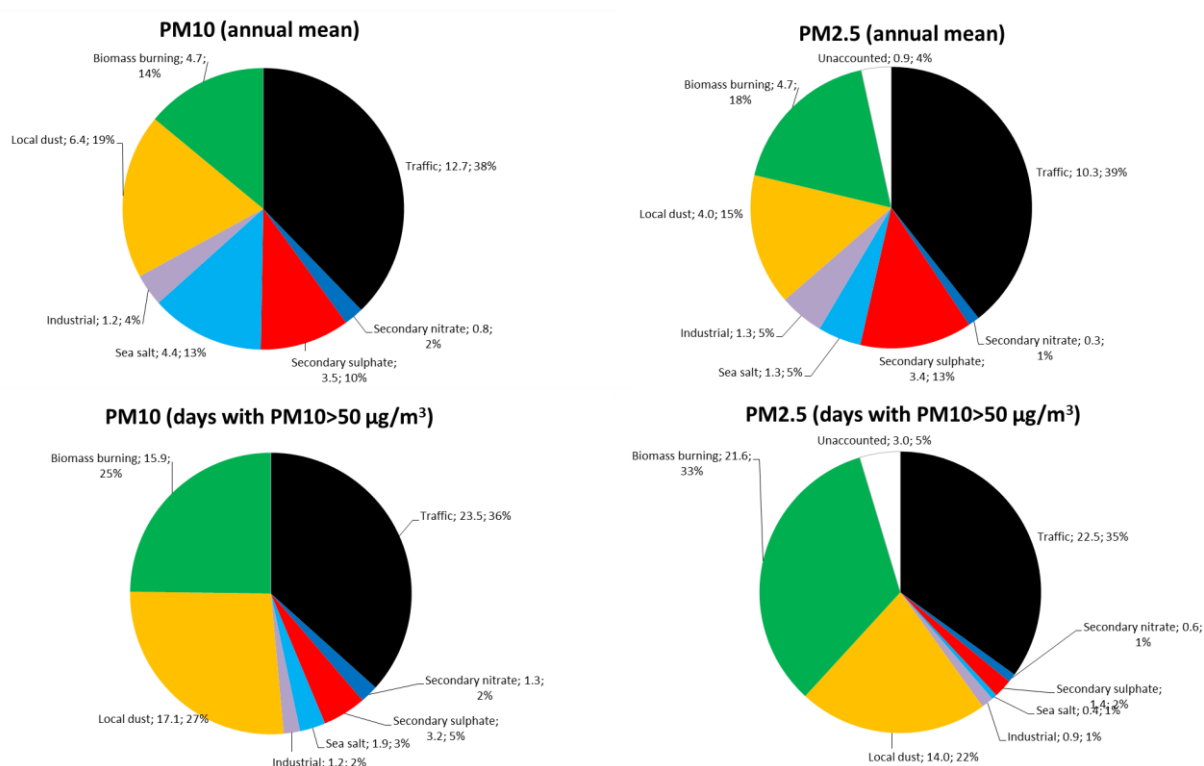


Figure 4. 8 - Simplified pie chart of source contributions (µg/m³ and %) to PM₁₀ and PM_{2.5} in Oporto. Annual mean (top). Days with PM₁₀ > 50 µg/m³ (bottom)

4.3.3 Validation of PMF results from daily data with hourly data

Using hourly data from the streaker-PIXE, six and five factors were identified in the fine and in the coarse fraction, respectively: traffic, aged sea salt, mineral dust and industry in both fractions; secondary sulphate (including a contribution from heavy oil) and biomass burning in the fine fraction; fresh sea salt in the coarse fraction.

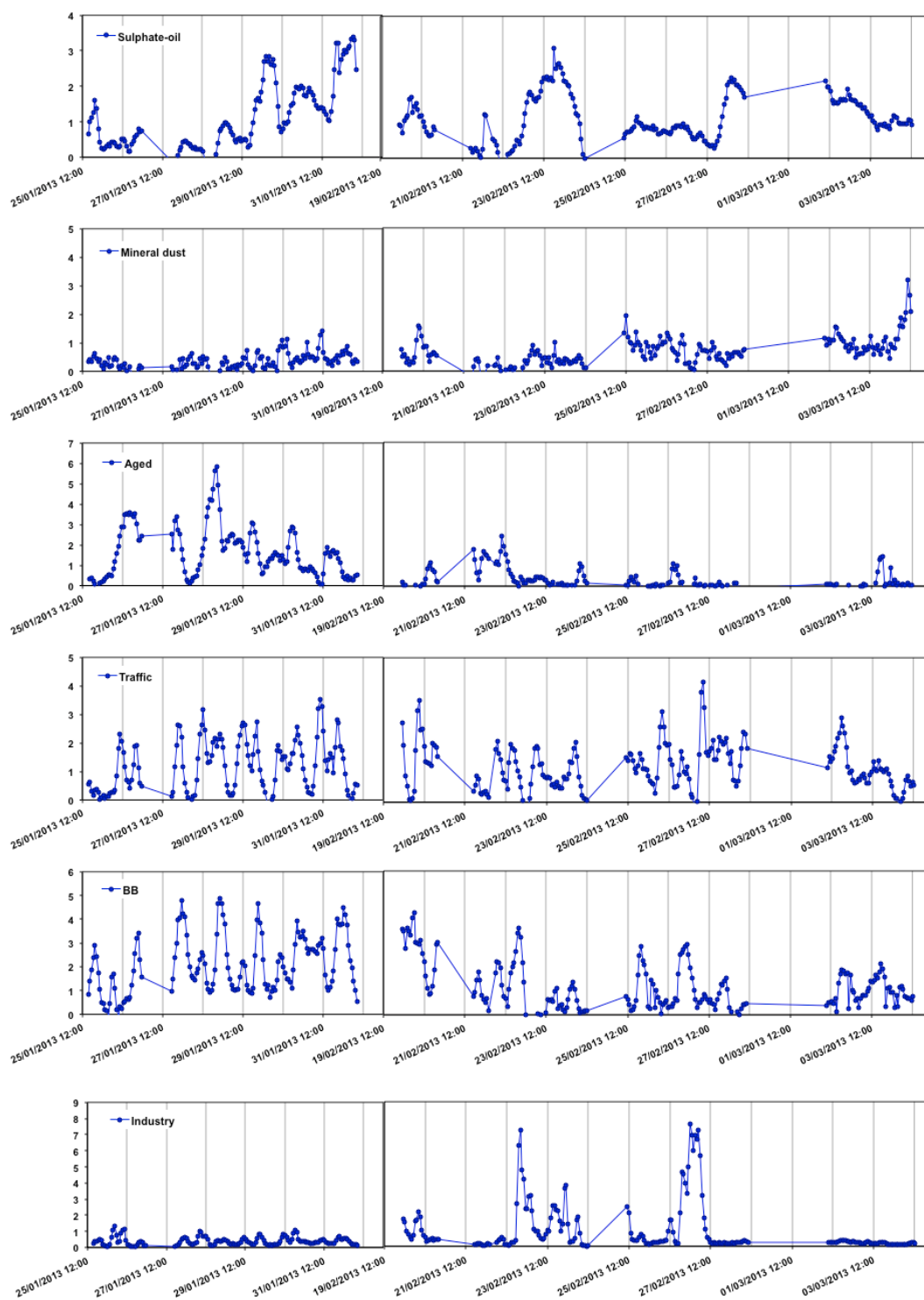


Figure 4. 9 - Time variability of source contributions in Oporto for the winter streaker campaign (arbitrary units, a.u.).

The traffic source is mainly traced by Fe, Cu and, to a lesser extent Mn, in both the fine and coarse fractions; nevertheless, the coarse fraction profile of this source is heavily characterized also by Cr, Ni, Rb, Zr and Ba. The interpretation of these profiles as a traffic source is also reinforced by the daily time trends, showing peaks in both the fractions during

the traffic rush hours (Figures 4.9 and 4.10); further, the source polar plots suggest a local emission for this source, that is near to the sampling site, which is actually characterized as a traffic site (Figure 4.11). The traffic source identified by the use of the streaker corresponds to the Vehicle non-exhaust source (NEX) resolved on the daily data; the difference between the fine and coarse source profiles shows that the road dust that is re-suspended by traffic and the contribution from direct brake and tire wear is higher in the coarse fraction. The Vehicle exhaust source (VEX) cannot be identified, as its main tracers, EC and OC, cannot be detected by PIXE.

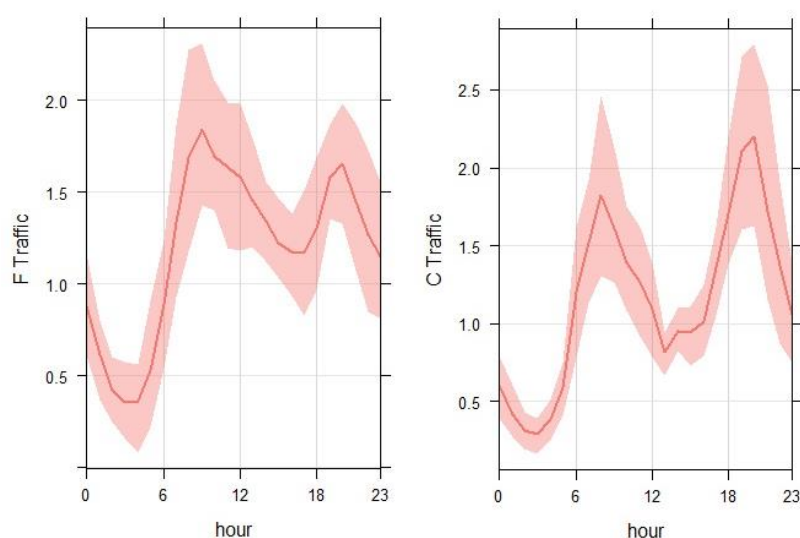


Figure 4. 10 - Daily time trends of the traffic source (a.u.), in the fine (F) and coarse (C) fractions in Oporto.

As for the daily samples, the PMF on the streaker hourly data identified, in both fractions, the contribution of the Industry (IND) emissions: Zn and, to a lesser extent, Pb mainly characterize this source. The time trend for this source shows sharp peaks always occurring around 11pm, probably linked to a specific phase of an industrial process (Figure 4.12). The polar plots for this source point to a location of the emission of this source close to the sampling site. Within the city and nearby there are several industries, most of them of small scale and not properly inventoried, whose welding, metalworking, foundry and metallurgical activities may contribute to the emission of non-ferrous metals.

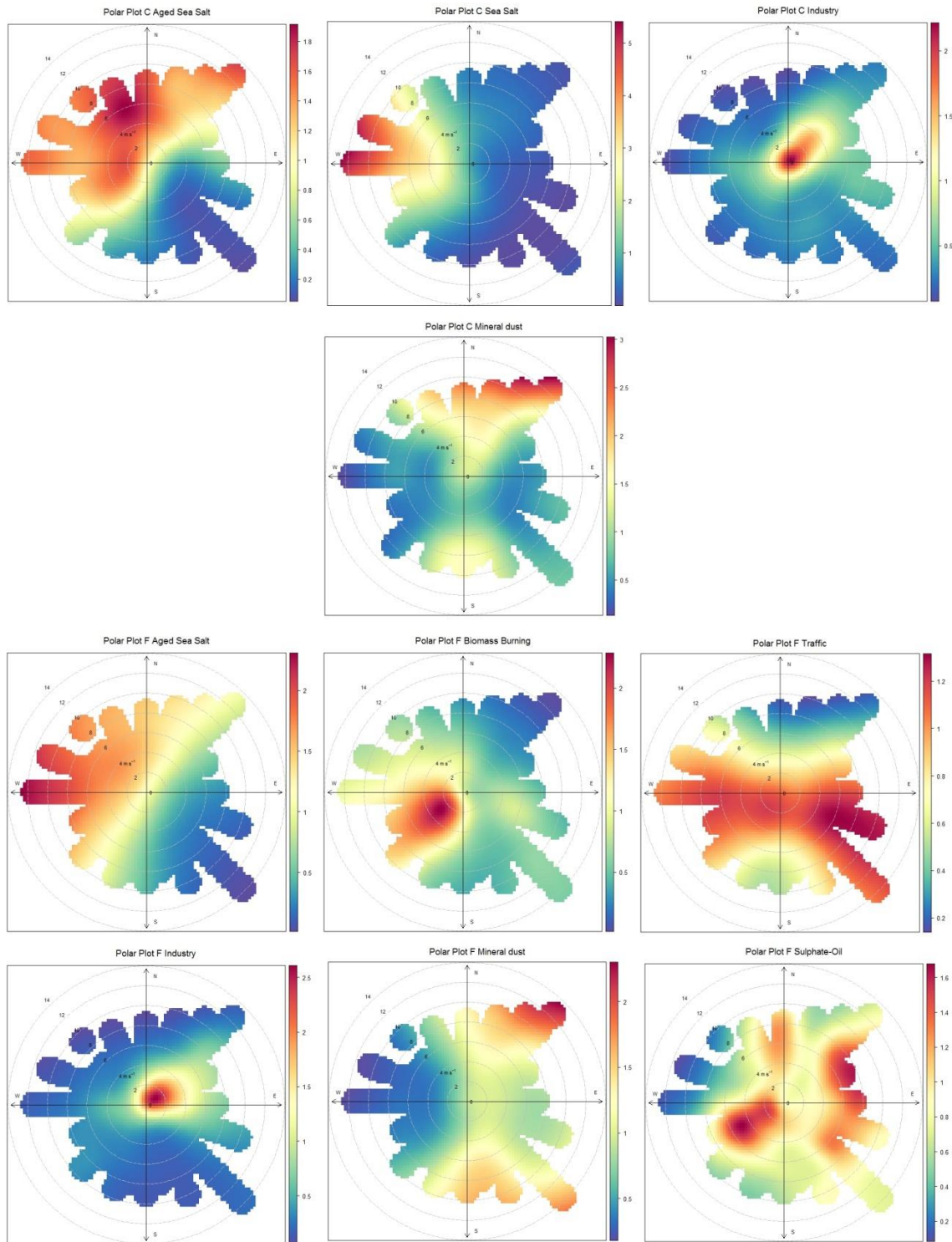


Figure 4. 11 - Polar plots of hourly source contributions (a.u.) in Oporto, for the fine (F) and coarse (C) fractions.

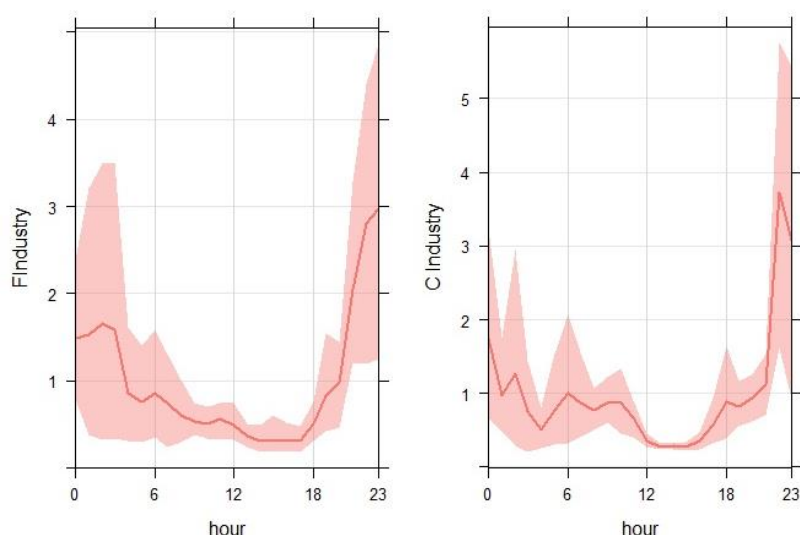


Figure 4. 12 - Daily time trends of the Industry source (a.u.), in the fine (F) and coarse (C) fractions in Oporto.

The Biomass burning (BB) source is mainly characterized by K, and, to a lesser extent, by Cl, Pb and Ni. The time trend of this source (Figure 4.9) supports the interpretation of this factor as BB for domestic heating: the average daily time trend (Figure 4.13) clearly shows a sharp increase of the contribution of this source in the late afternoon, when most of the fireplaces are lit, and a slow decrease after some hours, as fires extinguish during the night. The polar plot shows a local origin for this source, with a prevailing influence from the south-western sector, where most of the Oporto city is located. In addition, winds from this direction transport the plumes from the biggest suburban dormitory of the metropolitan area (Vila Nova de Gaia). This municipality, with more than 300,000 inhabitants, spreads over an area of about 168 km², encompassing many parishes with deeply rooted rural habits.

As for the daily samples, the PMF on the streaker hourly data identified, in the fine fraction, a Heavy oil and secondary sulphate (HOS), characterized by S and, to a lesser extent, by Ni and V. This factor has a daily trend with maxima during the night and minima during the day, mainly driven by the meteorological conditions, indicating a regional rather than a local source; this is also confirmed by the polar plot (Figure 4.11). These characteristics (time trend and polar plot) are typical of aerosol with secondary origin. The polar plot does not show any clear prevailing emission direction; nevertheless during the streaker sampling weeks somehow relevant sources appear to be located NE and SW with respect to the sampling site. The northeast direction appears to be also linked to the Industrial source (see above); in the SW direction there is the Douro River, with some ship traffic along and anchorages on its mouth: however, the cargo vessel dock is located at the international harbor of Leixões, NW

from the sampling site. Another major source to the Northwest is the refinery, a crude oil industrial processing plant. The observed direction, and the daily time trend, could be the result of the recirculation of air masses over the coast, due to the diurnal variation of the land/sea breezes combined with a channeling effect by the river.

Concerning the secondary aerosol, it is worth noting that the secondary nitrates source, identified with the daily samples, cannot be found in the streaker hourly data as its main tracer, nitrate, cannot be detected by PIXE, which is almost the only analytical technique applicable on the streaker samples.

The Mineral dust profile is characterized by crustal markers as Si, Al, Ca, Ti, K, Mn and Na; the enrichment factors (EF), calculated with respect to Al using the average continental crust composition reported by (Mason, 1966; Rahn 1976), are close to 1, thus reinforcing the interpretation of this source as mineral dust. This source does not show any clear daily/time trend; nevertheless, the slight tendency to higher contributions during the day rather during the night (Figure 4.13) points to the possible emission of dust also during anthropogenic activities such as construction, demolition works and releases from buildings and other surfaces through weathering and other erosive processes. No Saharan dust intrusions were present during the weeks when the streaker sampler was used. The polar plots show a minimum contribution for this source from West, consistent with the geography of Oporto, as in that direction the city faces the Atlantic Ocean.

In the streaker hourly data, the PMF identified two sea salt sources: the Aged sea salt (SEA) is present in both the fine and coarse fractions, whereas the Fresh sea salt (FSS) is identified only in the coarse fraction. Both these sources are characterized by typical sea salt elements like Na, Mg, S, Ca and Br, but differ for their Cl content, as the aged sea salt is depleted in Cl with respect to data reported in literature for seawater (Bowen, 1979). The polar plot for the FSS shows high contributions in correspondence with air masses coming straight from the Atlantic Ocean (west), while the SEA source appear linked to air masses originating from the Ocean but transiting over the north-western and northern sectors, that is reaching sampling site after passing over the land, sometimes over long distances (e.g. from North Portugal).

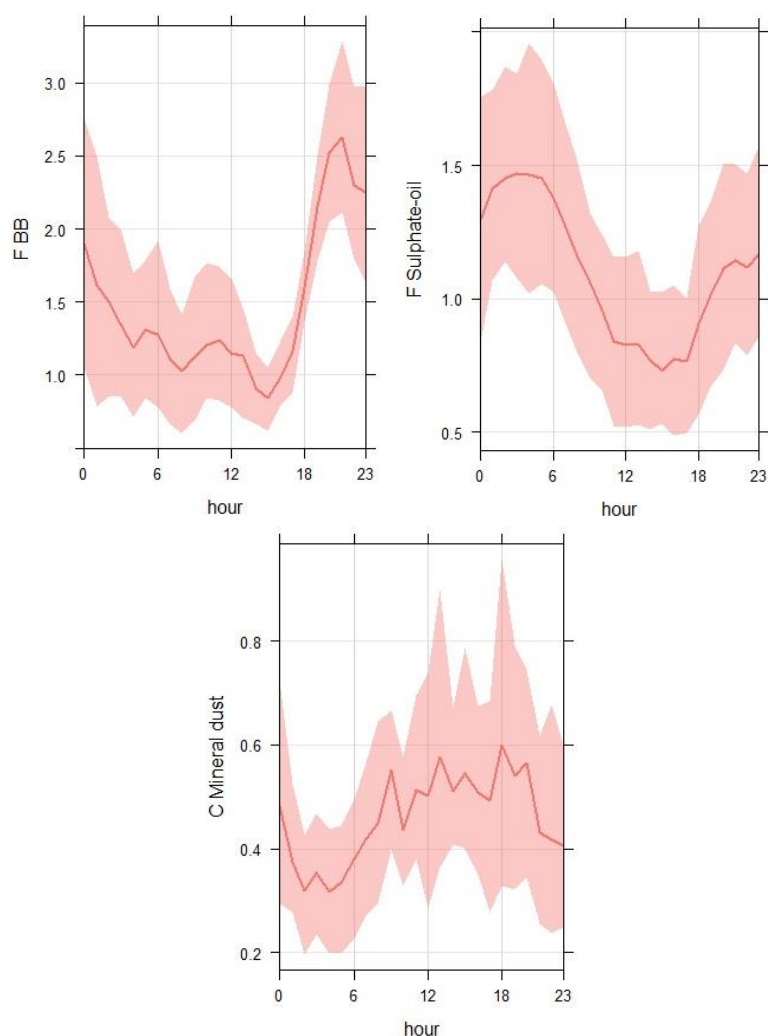


Figure 4. 13 - Daily time trends of the Biomass burning (BB), Heavy oil & secondary sulphate and Mineral dust sources (a.u.) at Oporto.

4.4 Conclusions

The USEPA PMF5 receptor model was applied to a set of aerosol data recorded during one year at a traffic site in Oporto. Road traffic is the most important contributor to PM_{10} and $PM_{2.5}$. Local dust (19%) and biomass burning (14%) are the second and third most important sources of PM_{10} . In $PM_{2.5}$ the contribution of biomass burning increases to 18% and that of local dust decreases to 15%. Other significant anthropogenic sources are: secondary sulphate industries, mainly metallurgy, and secondary nitrate, emitted from multiple sources such as industries. During high pollution days, road traffic and biomass burning are the largest sources of PM_{10} and $PM_{2.5}$. Biomass burning is the second most important source during high pollution episodes (days exceeding the limit of $50 \mu\text{g}/\text{m}^3$). As for the daily samples, the application of PMF to the streaker hourly data permitted the identification, in both aerosol fractions, of biomass burning practices in Oporto, with a sharp increase in the contribution of

this source in the late afternoon. Daily time trends also show a clear contribution of traffic sources with two daily peaks associated with rush hours. Other anthropogenic contributors to aerosol mass were addressed to local or regional sources.

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CHAPTER 5

Wet deposition of particulate carbon to the Central North Atlantic Ocean

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Abstract

Elemental carbon (EC) and water-insoluble organic carbon (WIOC) concentrations were measured in wet-only precipitation samples collected on Terceira Island (Azores, Portugal) between December 2009 and October 2010, to investigate temporal variations, source regions and wet deposition fluxes. The global volume-weighted average (vwa) concentrations were $134 \pm 19 \mu\text{gC L}^{-1}$ for WIOC and $15.0 \pm 1.6 \mu\text{gC L}^{-1}$ for EC, which fall within the range of values that have been found in the European background atmosphere. The WIOC concentration exhibited a temporal variation over the study period with a minimum in winter (vwa $88 \pm 16 \mu\text{gC L}^{-1}$) and a maximum in summer (vwa $477 \pm 86 \mu\text{gC L}^{-1}$). This trend was due to the higher dilution effect of winter rains and possibly to an increase of biogenic particulate carbon incorporation during the growing season. A different temporal variation was observed for the EC concentration with a minimum in summer (vwa $4.2 \pm 3.3 \mu\text{gC L}^{-1}$) and a maximum in spring (vwa $17.5 \pm 2.2 \mu\text{gC L}^{-1}$). The observed trend was mainly related to changes in atmospheric circulation patterns over the Azores. A backward trajectory analysis was applied to identify possible source regions of particulate carbon. The highest WIOC and EC concentrations were associated with air masses that persisted for more than four days over the Central North Atlantic Ocean and with air masses arriving from Europe, respectively. Lower concentrations were observed in samples collected under the influence of back-trajectories from North America. Despite the lower abundance of particulate carbon, the wet deposition fluxes were higher for this group of samples, which reflects the higher amount of precipitation that is normally associated with air masses arriving in the Azores from the west and northwest sectors.

5.1. Introduction

Atmospheric aerosols contain a significant amount of carbonaceous matter, which is commonly classified into two major fractions: elemental carbon (EC) and organic carbon (OC). EC is a primary species that is derived from the incomplete combustion of fossil fuels and

biomass. OC originates from primary and secondary sources. Primary OC is produced from combustion processes, similarly to EC emissions, or mechanical processes that release organic materials, such as pollen, spores, plant debris, microorganisms, soil and sea spray, into the atmosphere. Secondary OC, in turn, is produced from gas-to-particle conversion of the oxidation products of volatile organic compounds (Seinfeld and Pankow, 2003).

Wet deposition is known to play a dominant role in removing particulate carbon from the atmosphere (Ducret and Cachier, 1992; Cerqueira et al., 2010). However, current information on the spatial and temporal variabilities of particulate carbon in precipitation is still scarce, which is an important limitation to: assessing anthropogenic impacts on land and ocean carbon biogeochemistry (Jurado et al., 2008); and validating global models that simulate the transport and concentration of carbonaceous aerosols, thus affecting predictions of the anthropogenic forcing of aerosols on climate (Cooke et al., 2002; Croft et al., 2005).

Previous measurements have shown that wet deposition of particulate carbon is more significant in the vicinity of emission sources (Ducret and Cachier, 1992; Cerqueira et al., 2010), which are known to be concentrated in inland areas. However, recent model estimates by Jurado et al. (2008) also suggest that the global oceans are important receptors of EC and OC incorporated into precipitation (more than 50 Tg C y⁻¹), therefore, new research on particulate carbon wet deposition fluxes should be extended to oceanic areas.

This study reports the first long-term measurements of water-insoluble organic carbon (WIOC) and elemental carbon wet deposition fluxes at a remote marine site. The aims of this study were to: (1) characterize the seasonal variation of WIOC and EC concentrations in rain collected on Terceira Island (Azores, Portugal); (2) explore the processes that determine the seasonal pattern of WIOC and EC concentrations in rain; (3) conduct source apportionment analysis of WIOC and EC in rain; and (4) quantify the wet deposition fluxes of particulate carbon to the Central North Atlantic Ocean.

5.2. Material and Methods

5.2.1 Site description

The Azores archipelago is a set of nine volcanic islands located in the Mid-Atlantic Ridge, approximately 1500 km from mainland Portugal and 1900 km from North America (Fig. 5.1). The climate of the islands is strongly influenced by the seasonal movement of the Azores anticyclone. In late spring and summer, the high-pressure cell is located southwest of the islands, which causes a general subsidence flow that inhibits upward vertical motions and

therefore the occurrence of precipitation. During autumn and winter, the anticyclone moves south of the Azores and low pressure systems track across the region and cause wet and stormy weather.

Sampling was performed at the José Agostinho Observatory (JAO), which is located north of the town of Angra do Heroísmo and at the south coast of Terceira Island ($38^{\circ}39'32''$ N; $27^{\circ}13'23''$ W; 74 m above sea level). The observatory is part of the World Meteorological Organization (WMO) synoptic network (WMO ID 08511) and the Global Atmosphere Watch program (GAW ID: ANG) of the WMO. The monthly average temperature at JAO for the time period of 1981 - 2010 ranged from 13.8°C (February) to 22.2°C (August). During the same period, the average monthly precipitation amount ranged from 29 mm (July) to 155 mm (December), and the average annual precipitation was 1099 mm. Approximately 65% of the annual precipitation is concentrated during the months of October to March, which are considered the rainy months (IPMA, 2014).

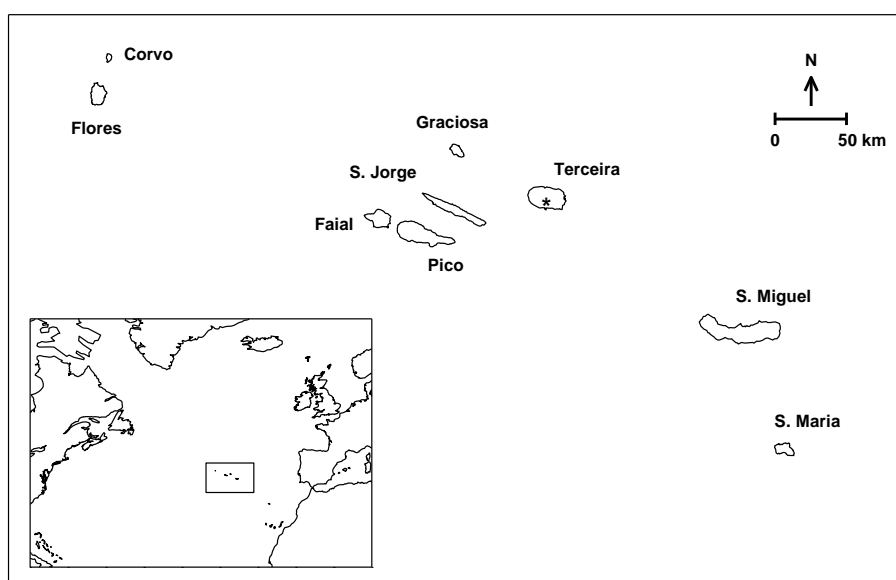


Figure 5. 1 - Map of the Azores archipelago, North Atlantic, with the sampling site marked (*)

5.2.2 Sampling and analysis

Daily rain water samples were collected between 20 December 2009 and 28 October 2010 with an Eigenbrodt model UNS130/E automatic wet-only collector. The sampler consists of a glass funnel with an open area of 500 cm^2 , which is connected to a 5 L glass storage bottle, a movable lid and a precipitation sensor to control the start and stop of each collection period.

Prior to use, all the collector components that may come in contact with the samples were cleaned with water, followed by rinses with distilled and deionized water.

For the analysis of EC, WIOC and WITC (water insoluble total carbon), a liquid aliquot was filtered through a quartz fiber filter (Whatman QMA), which was previously ignited at 550 °C for 5 hours. The sample filtration was achieved by using a stainless steel filter unit equipped with a mask to concentrate the particles onto a circular spot that was 10 mm in diameter. The filter was then dried at an ambient temperature inside a desiccator for approximately 24 hours and stored frozen until the analysis was conducted at the University of Aveiro. Possible sources of error associated with the sampling and filtration processes and precautions to minimize the errors are addressed by Cerqueira et al. (2010). The EC and OC particulate fractions accumulated in the filters were measured by the thermal-optical method described in detail by Castro et al. (1999) and Pio et al. (2011). This method was previously used to quantify carbonaceous matter extracted from rain and snow samples (Cerqueira et al., 2010).

5.2.3 Air mass trajectories

Four-day back-trajectories arriving at the JAO location at altitudes of 500 m, 1000 m and 1500 m above sea level (a.s.l.) were calculated for every rain event using the HYSPLIT model (Draxler and Rolph, 2012). Model runs were performed with meteorological data from the Global Data Assimilation System (GDAS) archives. The mid-point of the rain sampling period was selected as the arrival time at JAO.

To investigate the source regions of particulate carbon in rain, each set of daily trajectories was subjectively classified according to the prevailing air mass origin and transport pathway into the following 5 groups:

- North America: air masses originating over Southern Canada, the United States of America or Mexico
- Arctic: air masses originating over Northern Canada, Arctic Ocean, Greenland or the area north of the British Islands
- Europe: air masses originating over continental Europe
- Azores: air masses originating over the North Atlantic in the area located to the north and west of the Azores that travel strictly over the ocean and arriving at the JAO location after a clockwise turn
- North Atlantic: the remaining air masses originating over the North Atlantic that travel strictly over the ocean before arriving at JAO location.

5.3. Results and Discussion

5.3.1 Precipitation data

In total, 103 daily precipitation samples were collected throughout the study period, most of which (69) were collected during the winter and spring (Fig. 5.2). The average volume of the precipitation events ranged from 3 mm day⁻¹ in summer to 12 mm day⁻¹ in winter and spring. The total accumulated precipitation was 972 mm, which is somewhat lower than the average annual precipitation at JAO (1099 mm). The seasonal distribution of the accumulated precipitation was as follows: 508 mm in winter, 310 mm in spring, 53 mm in summer and 100 mm in autumn. Fig. 5.3 presents a four-day back-trajectory analysis of air masses that arrived at 1000 m a.s.l. during all precipitation events sampled at JAO in different seasons. The seasonal variation of precipitation events and precipitation amount were linked to the dynamics of the Azores anticyclone. From winter to early spring, the anticyclone was usually located southwest of the islands. Under these conditions, precipitation in the Azores was the result of the convergence of cold and dry air from the North American continent and the Polar region with warm and moist air from the tropics. During summer, the anticyclone moved northwards, which blocked the transport of cold air and consequently the formation of convective precipitation. Occasional showers, which are common during this time of the year, were triggered by the orographic uplift of moist air over the islands.

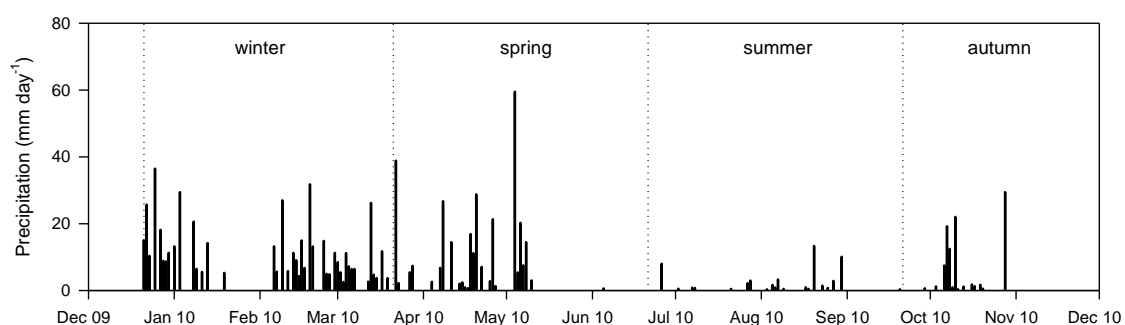


Figure 5. 2 - Time series of the daily precipitation at JAO during the study period.

5.3.2 Carbon concentrations in precipitation

WIOC, EC and WITC concentrations in precipitation collected at JAO are listed in Table 1. The global volume-weighted average concentrations found during this study were $134 \pm 19 \mu\text{gC L}^{-1}$ for WIOC and $15.0 \pm 1.6 \mu\text{gC L}^{-1}$ for EC. These values were 1.2 and 4.8 times higher,

respectively, than those measured in 2003 and 2004 in the Azores during the CARBOSOL project (Cerqueira et al., 2010). The observed differences, which are only significant for the EC, are not surprising given that particulate carbon concentrations previously reported were based on a limited number of samples (a set of 7) which may have biased the results. Even so, the data from the present study fit within the range of values that have been found in the European background atmosphere (average values are from 2.8 to 31 $\mu\text{gC L}^{-1}$ for EC and from 98 to 358 $\mu\text{gC L}^{-1}$ for WIOC; Ducret and Cachier, 1992; Cerqueira et al., 2010).

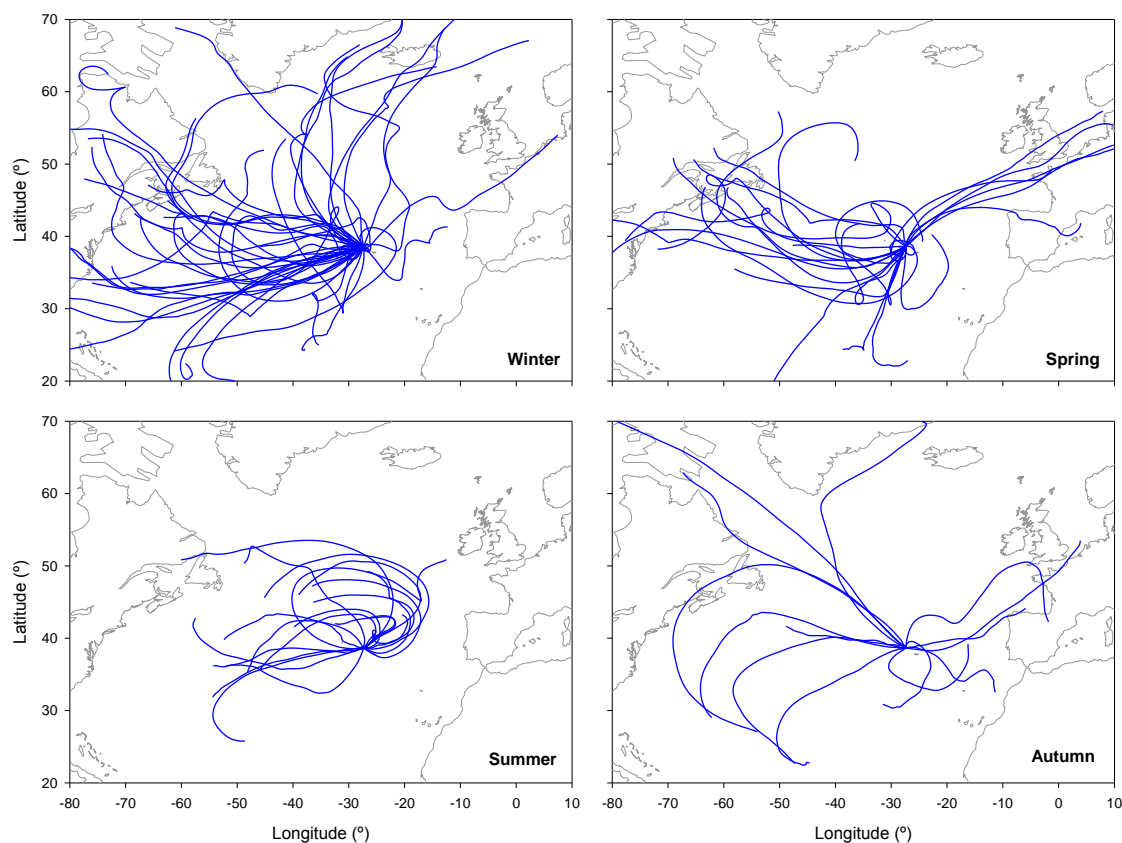


Figure 5.3 - Four-day back-trajectories arriving at 1000 m a.s.l. during the precipitation events sampled at JAO.

Comparison data from other marine areas than the Azores are not yet available. However, dissolved organic carbon (DOC) was previously measured in rain samples from various island sites (Kieber et al., 2002, and references therein). The average WIOC concentration in the Azores corresponds to approximately 20-50% of the average DOC concentration at those sites. This result is comparable to the range of WIOC/DOC values reported in the modelling work of Jurado et al. (2008) for island and coastal locations (12-68%) and indicates that WIOC

wet deposition fluxes should not be ignored when studying the cycle of organic carbon through the marine atmosphere.

Table 5. 1 - Seasonal volume-weighted average (vwa), volume-weighted standard deviation (vw σ), simple average and range (within brackets) of WIOC, EC and WITC concentrations in precipitation at JAO.

Season	N	WIOC	EC		WITC	
		($\mu\text{gC L}^{-1}$)	($\mu\text{gC L}^{-1}$)		($\mu\text{gC L}^{-1}$)	
		vwa \pm vw σ	average	vwa \pm vw σ	Average	vwa \pm vw σ average
Winter	43	88 \pm 16 (23-503)	108	15.2 \pm 1.8 (3.1-57)	19	103 \pm 17 (31-543)
Spring	26	89 \pm 13 (26-636)	215	17.5 \pm 2.2 (5.4-236)	48	107 \pm 14 (31-871)
Summer	20	477 \pm 86 (120-10426)	1309	4.2 \pm 3.3 (0.0-46)	5.1	482 \pm 87 (120-10473)
Autumn*	14	324 \pm 151 (66-1475)	618	11.9 \pm 6.8 (0.0-85)	12	336 \pm 156 (81-1481)
Overall	103	134 \pm 19 (23-10426)	438	15.0 \pm 1.6 (0.0-236)	23	149 \pm 20 (31-10473)

* the monitoring period was shorter than the season length

The average contribution of EC to the WITC in rain was 13%. This share is approximately 2 to 4 times lower than that of continental background aerosols (Pio et al., 2007) and suggests that wet deposition processes are more efficient at removing WIOC than removing EC from the atmosphere. Evidence of significant differences in the wet scavenging efficiency of these two species was described by Cerqueira et al. (2010). However, the relative contribution of both carbon fractions to WITC is the result of a complex balance between emission, transformation and removal processes. EC in the Central North Atlantic atmosphere is essentially the result of the long-range transport of air masses originating in continental areas, because EC emissions from the ocean or from human activities at the surface of the ocean are thought to be negligible. Although EC particles freshly emitted by combustion processes are mostly hydrophobic, atmospheric ageing processes, such as mixing with secondary species or chemical reactions, may convert these particles to hydrophilic aerosols (Tritscher et al., 2011; Zhang et al., 2008; Zuberi et al., 2005). Thus, EC emitted in continental areas and transported to the Central North Atlantic Ocean is expected to be significantly removed from the atmosphere by wet deposition processes (along with dry deposition processes) before being transported to the Azores. However, a large fraction of OC aerosols

from continental areas is water soluble (Pio et al., 2007), which also facilitates removal from the atmosphere by wet deposition during transport over the Atlantic Ocean. Given that most of the EC and WIOC particles emitted in continental areas were most likely lost during the air mass transit to the Azores and that the share of EC was lower than that of WIOC in rain sampled at JAO, the ocean appears to act as a source of organic carbon to the local atmosphere. This possibility is further discussed in the next section.

5.3.3 Temporal variation of concentrations

The results from this study exhibit a temporal variation in the concentrations of particulate carbon fractions (Table 5.1 and Fig. 5.4). The volume-weighted average WIOC concentrations varied between a minimum of $88 \pm 16 \mu\text{gC L}^{-1}$ in winter and a maximum of $477 \pm 86 \mu\text{gC L}^{-1}$ in summer. Interestingly, the sampling events with high precipitation volumes (typical of the winter and spring seasons) exhibited lower WIOC concentrations than those with lower precipitation volumes (typical of the summer season). This effect is evident from the regression analysis between the logarithm of the WIOC concentration and the logarithm of precipitation amount (Fig. 5.5(a)). The model obtained from the analysis, which had a standard error of $0.33 \mu\text{gC L}^{-1}$ and a correlation coefficient (r) of -0.80, was

$$\log_{10}(WIOC) = (2.77 \pm 0.05) - (0.77 \pm 0.06) \times \log_{10}(\text{precipitation}).$$

The model shows that dilution is an important factor that controls the WIOC content of precipitation. Additionally, these results indicate that organic particles are efficiently scavenged from the atmosphere at the onset of rain events and are then diluted by subsequent rainfall. Similar observations were previously reported for other water-soluble organic and inorganic species (e.g., André et al., 2007; Falkowska et al., 2008; Yan and Kim, 2012).

Another possible factor that may play an important role in determining seasonal WIOC differences is the input of biogenic organic carbon from the oceans. The organic carbon contribution to submicrometer aerosol over the North Atlantic Ocean is known to vary seasonally and is higher during the spring to autumn period when the biological activity in the oceanic surface waters is more intense (O'Dowd et al., 2004). Most of the organic carbon in the submicrometer marine aerosol is water-insoluble and has a significant contribution from phytoplankton exudates (Facchini et al., 2008). Breaking waves were suggested to exert an overwhelming influence on the organic carbon content of sea spray aerosol (Quinn et al., 2014). However, this influence was not evident in the Azores samples, otherwise, the WIOC concentrations in rain should also exhibit high values during the winter season, when wind

conditions are more favorable for sea spray formation. Biogenic emissions from Terceira Island soils and plants were reported to peak during the growing season (Alves et al., 2007) and are also possible contributors to the WIOC content of precipitation.

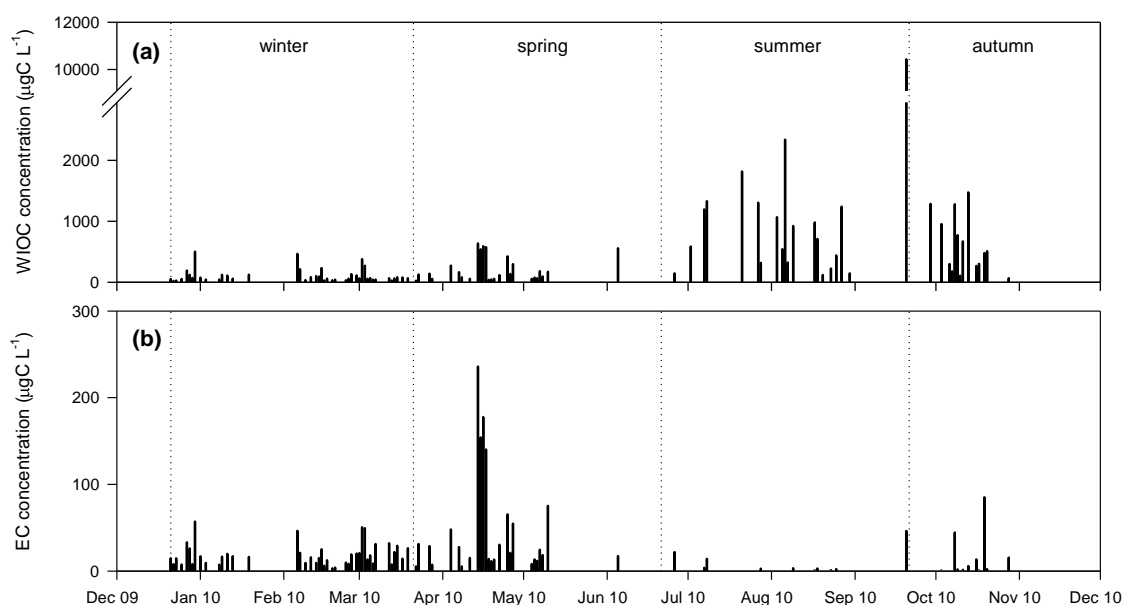


Figure 5. 4 - Time series of WIOC concentrations (a) and EC concentrations (b) in precipitation at JAO during the study period.

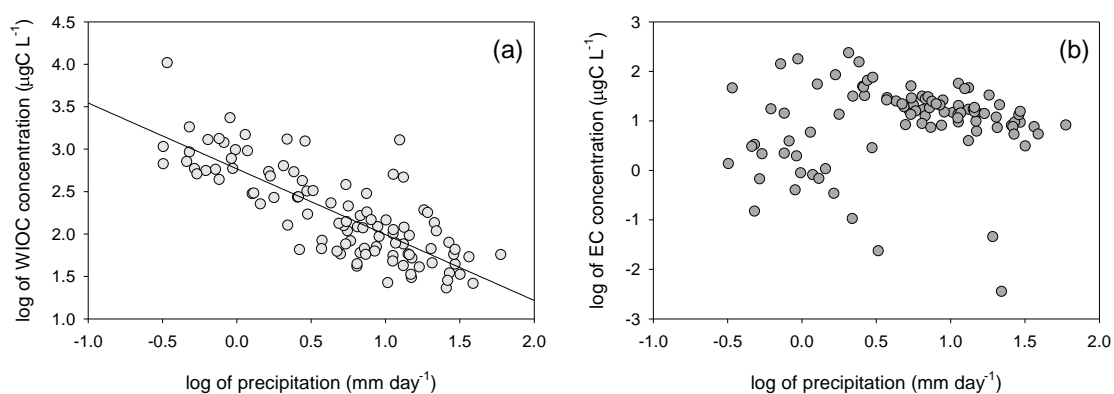


Figure 5. 5 - Log–log plots of the relationship between the WIOC concentration and the daily precipitation amount (a) and between the EC concentration and the daily precipitation amount (b)

A different trend was observed for EC, which had a minimum volume-weighted average concentration of $4.2 \pm 3.3 \mu\text{gC L}^{-1}$ in summer and a maximum of $17.5 \pm 2.2 \mu\text{gC L}^{-1}$ in spring (Table 5.1 and Fig. 5.4(b)). The reported differences do not reflect any seasonal pattern of sources, given that EC emissions above the North Atlantic waters (from islands or ship traffic)

should have only a minor significance compared to emissions from continental areas surrounding it. On the other hand, EC concentrations are not significantly affected by the time variation of the daily precipitation amount. This is evident from the plot shown in Fig. 5.5(b), in which the logarithm of the EC concentration does not display any correlation with the logarithm of daily precipitation amount. These results suggest that EC particles are not as efficiently scavenged from the atmosphere as WIOC particles, even though EC particles can acquire hydrophilic properties by chemical ageing (Tritscher et al., 2011; Zhang et al., 2008; Zuberi et al., 2005). As explained in more detail in the following section, the seasonal patterns in air mass transport are the main factor that controls the EC concentrations in precipitation in the Azores area.

5.3.4 Effects of air mass origin on concentrations

Fig. 5.6(a) presents the volume-weighted average WIOC concentrations for samples associated with the different classes of back-trajectories. The highest WIOC concentrations ($596 \pm 118 \mu\text{gC L}^{-1}$) were obtained in rain samples collected exclusively under the influence of air mass transport around the Azores, which mostly occurred during summer. These values are linked to the above mentioned decrease of precipitation volumes and increase of marine biogenic carbon incorporation during the growing season. Relatively lower values were found in samples associated with back-trajectories from North America ($94 \pm 20 \mu\text{gC L}^{-1}$) and were comparable to values observed in rain samples that were collected during background maritime air masses originating over the ocean, which mostly occurred during the non-growing season (North Atlantic class; $91 \pm 12 \mu\text{gC L}^{-1}$). These results suggest that most of the WIOC emitted to the North American atmosphere and exported to the North Atlantic with the prevailing winds was already lost when the air masses arrived at the Azores longitude. However, the remaining WIOC is an important contributor to global wet deposition fluxes as discussed in the following section.

Fig. 5.6(b) shows a different variation pattern for the volume-weighted average EC concentrations. The concentration values associated with the Azores group of back-trajectories were very low ($1.5 \pm 0.6 \mu\text{gC L}^{-1}$) and among the lowest measured in rain samples (Ducret and Cachier, 1992; Cerqueira et al., 2010). These results confirm that the Azores area is not a source of EC to the atmosphere and that air masses persisting over the Central North Atlantic Ocean become nearly devoid of EC. Such a small summer value should be regarded as a background concentration for the Azores atmosphere. In contrast, air masses arriving in the Azores from the European continent display the highest EC concentrations ($41 \pm 13 \mu\text{gC L}^{-1}$).

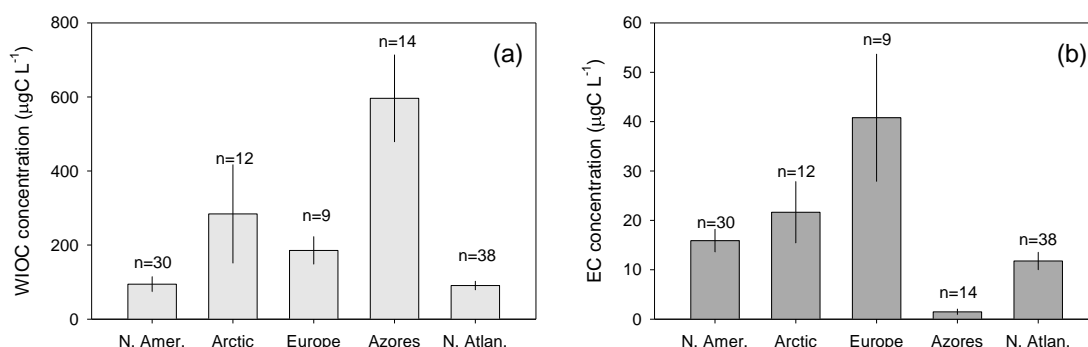


Figure 5. 6 - Volume-weighted average ($\mu\text{gC L}^{-1}$) concentrations and volume-weighted average standard deviations for WIOC (a) and EC (b) as a function of air mass back-trajectory class. The n values above the bars indicate the number of sampled events associated with each class.

The transport of EC was particularly intense with air masses originating in populated and industrialized regions of northern and Central Europe. A careful analysis of these back-trajectories indicates that air masses take less than 2 days to travel from coastal Europe to the Azores. Rain events associated with trajectories arriving from North America, which is known to be an important source region of EC to the global atmosphere, displayed a volume-weighted average EC concentration that was approximately 3 times lower than that of the European class of rain samples. The location of Terceira Island, which is farther from the east coast of North America (≈ 2300 km) than from the west coast of Europe (≈ 1500 km), may explain the observed difference. A longer distance means that more time is required for the air masses to reach the Azores (usually more than 3 days), and the probability of EC particles being removed from the atmosphere is greater. However, the volume-weighted average EC concentration in the North American group of samples ($16 \pm 2 \mu\text{gC L}^{-1}$) was significantly higher than that of the Azores samples, thus, the transport time of 3 to 4 days was insufficient to ensure the complete removal of EC from the atmosphere. The results from this section clearly demonstrate that air mass origin is a dominant factor of the temporal variation of EC concentrations on Terceira Island.

5.3.5 Wet deposition fluxes

Wet deposition fluxes were calculated on a daily basis by multiplying individual event concentrations by the event precipitation amount. The time variation of WIOC and EC wet deposition fluxes is shown in Fig. 5.7, and the seasonal average values (calculated as the

simple average of the daily fluxes) are shown in Table 5.2. WIOC wet deposition was higher in winter and early spring, decreased in summer and increased again during autumn. Note that the autumn value is biased by an outlier; if the outlier is removed, the average decreases to $458 \pm 835 \mu\text{gC m}^{-2} \text{ day}^{-1}$, which is comparable to the winter value. The observed trend contrasts with the temporal variation of WIOC concentrations (i.e. the maximum occurs in summer) and demonstrates that the magnitude of wet deposition fluxes in the Azores is mostly controlled by the amount of precipitation. The results of the back-trajectory analysis presented in Fig. 5.3 indicate that winter air masses arriving at JAO generally originated from the west and northwest sectors. For that reason, during the study period, North America was the main source region of WIOC deposited by rain to the Azores. The time variation of the EC daily fluxes corresponds well with that of WIOC: higher atmospheric inputs to the surface occur during the rainy months. However, the spring to summer decrease was more pronounced because EC particles were nearly absent from the rain during summer (the EC concentration levels were close to the limit of detection of the analytical method used in this study). According to the above-mentioned temporal distribution of backward trajectories, North America was also the largest EC exporter region to the Azores. Although the highest EC concentrations were found in samples collected under the influence of air mass transport from Europe, this continent was only a small contributor to the global EC wet deposition flux, due to the lower amount and frequency of precipitation events.

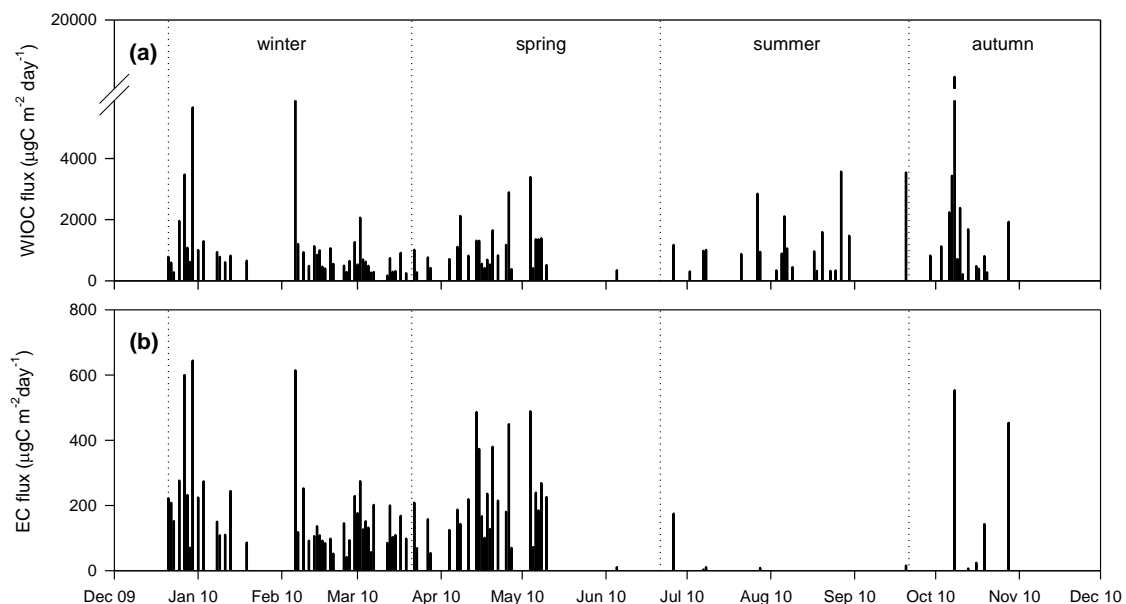


Figure 5. 7 - Time series of WIOC daily wet deposition fluxes (a) and EC daily wet deposition fluxes (b) at JAO during the study period.

Table 5. 2 - Seasonal average and standard deviation of WIOC, EC and WITC wet deposition fluxes at JAO.

Season	WIOC ($\mu\text{gC m}^{-2} \text{ day}^{-1}$)	EC ($\mu\text{gC m}^{-2} \text{ day}^{-1}$)	WITC ($\mu\text{gC m}^{-2} \text{ day}^{-1}$)
Winter	496 \pm 989	85 \pm 130	576 \pm 1097
Spring	301 \pm 626	59 \pm 116	360 \pm 733
Summer	276 \pm 697	2 \pm 18	278 \pm 701
Autumn*	877 \pm 2643	32 \pm 116	909 \pm 2734
Overall	419 \pm 1188	47 \pm 108	465 \pm 1259

* the monitoring period was shorter than the season length

As far as the authors know, to date, there are no measurements of WIOC and EC wet deposition fluxes into oceanic waters to compare with the results of the present study. The modelling study of Jurado et al. (2008) is the only study that provides estimates for these fluxes based on satellite measurements of climatological data and aerosol concentrations and literature scavenging ratios. Average values of $0.53 \text{ mgC m}^{-2} \text{ day}^{-1}$ for organic carbon (soluble and insoluble) and $0.10 \text{ mgC m}^{-2} \text{ day}^{-1}$ for black carbon were estimated for a latitude band extending from 30° N to 60° N . The magnitude of these values is comparable to that of the measurements performed in the Azores, despite the uncertainty associated with model predictions of wet deposition fluxes. Predictions are uncertain due to the scarce information on the distribution of particulate carbon concentrations over the oceans and the use of the same value for the scavenging ratios of organic and black carbon aerosols.

5.4. Conclusions

This study reports the first long-term measurements of WIOC and EC concentrations in precipitation collected at a remote marine site and contributes to a better understanding of particulate carbon removal from the atmosphere. WIOC and EC concentrations in precipitation in the Azores were within the range of values previously reported for the European background atmosphere. A temporal variation was observed for both particulate carbon fractions: the WIOC concentrations were lower in winter than in summer, which was related to the dilution effect of winter rains and possibly to a higher input of biogenic organic carbon during the growing season; the EC concentrations were higher in winter and spring than in summer, which reflects the seasonality of the long-range transport of air pollutants to the Azores. The summer maximum WIOC concentrations were observed under the influence of air masses with a long residence time over the Central North Atlantic Ocean, which further supports the possibility of organic carbon incorporation from marine and island sources. The

same samples exhibited the lowest EC concentrations, which reflects the absence of major combustion sources over the North Atlantic waters. The maximum EC concentrations were associated with air masses arriving from populated and industrialized areas in Europe and taking less than 2 days to travel to the Azores. The wet deposition fluxes were higher during the rainy months compared with the dry months, and North America was found to be the main source region of particulate carbon deposited by rain into the Azores region.

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CHAPTER 6

Rain water chemistry at an urban kerbside site in Oporto

Abstract

Rain water samples were collected continuously during one year at a traffic site in Oporto, Portugal, and analysed for water soluble organic and inorganic ions, dissolved organic carbon (DOC), water soluble inorganic carbon (WIOC) and elemental carbon (EC). Cl^- and Na^+ were the prevailing ions in rain, accounting, on average, for 46.6% and 25.7% of the total mass of measured water soluble ions. DOC was the dominant carbon fraction, while EC and WIOC accounted for only about 5 and 30%, respectively, of the total mass of carbon in rain. The EC levels observed in Oporto were 3 to 8 times higher than those reported before for background coastal and marine sites in Portugal, pointing to a significant contamination of the Oporto atmosphere by anthropogenic sources of carbonaceous matter. Principal Component Analysis (PCA) was applied to precipitation data to differentiate sources affecting the chemical composition of rainwater in Oporto. Three main sources were identified: sea-salt; secondary atmospheric processes; and vehicle exhaust. Rain chemistry data were combined with aerosol chemistry data, also measured at the same site, in order to calculate scavenging ratios for atmospheric constituents. The highest scavenging ratio values were found for Na^+ , Cl^- and Mg^{2+} and the lowest for oxalate, WIOC and EC, which was mainly a consequence of differences in the affinity of chemical species for water.

6.1. Introduction

Wet deposition is an important scavenging process for the removal of air pollutants from the atmosphere and the subsequent accumulation in Earth's surface. Various factors influence the chemical composition of precipitation, including local and regional emissions of air pollutants, long range transport of air pollutants, geographical location, meteorological conditions, and atmospheric processes.

During the last decades a huge number of studies was performed to investigate the chemical composition of rain and to evaluate wet deposition fluxes of atmospheric pollutants. However, most of these studies were focused on water soluble inorganic chemical constituents, which usually require easily accessible analytical methods. By contrast, scarce studies were dedicated to investigate water soluble organic chemicals and even scarcer is the research about water insoluble chemical constituents.

Na^+ , Cl^- and Mg^{2+} are abundant species in rain water, particularly in coastal areas, due to sea spray emissions (Moreda-Piñeiro et al., 2014; Vásquez et al., 2003; Pio et al., 1991). NO_3^- and the non-sea salt part of SO_4^{2-} in rain have been associated with the atmospheric conversion of precursor gases, such as NO_x and SO_2 emitted from anthropogenic sources (Seinfeld and Pandis, 2007). Ca^{2+} has been related to soil emissions while K^+ has been associated to both soil and biomass burning emissions (Huang et al., 2010; Arsene et al., 2007). NH_4^+ inputs to rain are mainly a consequence of emissions from livestock production and fertilizer application (Mouli et al., 2005). Water soluble and insoluble organic species in rain originate from a variety of sources, including fossil and non-fossil fuel combustion, biogenic processes and industrial processes (Avery et al., 2006; 2001; Bauer et al., 2003). Finally, elemental carbon in precipitation has been linked to natural and anthropogenic fuel combustion (Custódio et al., 2014).

In these study, one year precipitation sampling was performed in Oporto, Portugal, with the purpose of: (1) obtaining a comprehensive characterization of rain water chemical composition, including the measurement of DOC, WIOC, EC, soluble organic and inorganic ions; (2) identifying sources of chemical constituents in precipitation; (3) studying the interaction between aerosol particles and rainwater; and (4) estimating wet deposition fluxes of selected chemical constituents.

6.2. Material and methods

6.2.1. Site description

Oporto is located in northern Portugal, near the mouth of the Douro river. The city has a population of about 240000 (2011 census), and the urban area, which extends beyond its administrative limits, has a population of about 1.3 million in a land area of 389 km², 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.

Rain sampling was conducted from 5 January 2013 to 24 January 2014 in the rooftop of an air quality monitoring station (41° 09' 46"N; 8° 35' 27" W; Figure 1) located on the kerbside of a major arterial route (Fernão de Magalhães Avenue) connecting the Inner Circular Highway to the city centre, Figure S. 2 (Supplementary Data).

6.2.2. Sampling and analysis

An Eigenbrodt model UNS130/E automatic wet-only collector was used for daily collection of rain samples. The sampler consists of a glass funnel with an open area of 500 cm², which is connected to a 3 L glass storage bottle, a movable lid and a precipitation sensor to control the start and stop of each collection period. Prior to use, all the collector components that may come in contact with the samples were cleaned with water, followed by rinses with distilled and deionized water.

For the analysis of EC and WIOC the precipitate was filtered through a quartz fiber filter (Whatman QMA), which was previously ignited at 550 °C for 5 h. The sample filtration was achieved by using a stainless steel filter unit equipped with a mask to concentrate the particles onto a circular spot that was 10 mm in diameter. The filter was then dried at an ambient temperature inside a desiccator for approximately 24 h and stored frozen until the analysis. Possible sources of error associated with the sampling and filtration processes and precautions to minimize the errors are addressed by Cerqueira et al. (2010). The EC and WIOC particulate fractions accumulated in the filters were measured by the thermal–optical method described in detail by Pio et al. (2011) and Castro et al. (1999). This method was previously used to quantify carbonaceous matter extracted from rain and snow samples (Cerqueira et al., 2010).

For the analysis of DOC, an aliquot of the filtered water sample was acidified with a 2M 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 injected in a total organic carbon analyzer (Shimadzu TOC-5050A)

Water-soluble ions were analyzed using three Dionex ion chromatography systems equipped with electrochemical suppression after sample filtration with a 0.45 µm pore PTFE syringe filter, to remove insoluble particles. The cations ammonium (NH₄⁺), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺) and magnesium (Mg²⁺) were determined using an IonPac CG12A guard column and a CS12A analytical column with 10 mM H₂SO₄ as the eluent. The anions chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻) and oxalate (C₂O₄²⁻) were measured with an IonPac AG4A guard column and an AS4A analytical column with a Na₂CO₃/NaHCO₃ (1.8 and 1.7 mM, respectively) buffer solution as the eluent. The anions fluoride (F⁻), formate (HCOO⁻), acetate (CH₃COO⁻), methanesulfonate (CH₃SO₃⁻) and propionate (CH₃CH₂COO⁻) were determined with an IonPac AG11 and an IonPac AS11 column by gradient elution with Na₂B₄O₇ solution from 0.075 mM to 2.5 mM as eluent.

The non-sea-salt ion concentrations were calculated by the following equation,

assuming that the chemical composition of sea-salt incorporated in rain is the same as that of seawater and that soluble Na^+ in rain comes solely from seawater,

$$\text{nssX} = X - (X/\text{Na})_{\text{sw}} \times \text{Na}^+$$

where nssX is the mass concentration of non-sea salt ion X in rain, $(X/\text{Na})_{\text{sw}}$ is the mass ratio of component X to Na in seawater and Na^+ is the mass concentration of sodium in rain.

6.2.3. Quality control

The ion balance method was applied to check the quality of data from chemical analyses. The average ratio between the sum of cations and the sum of anions of individual samples was found to be 0.99 ± 0.12 . In addition a significant correlation ($r=0.998$; $p<0.0001$) was observed between the sum of cations and the sum of anions (Figure 6.1). Both results are indicative of the completeness of chemical analyses.

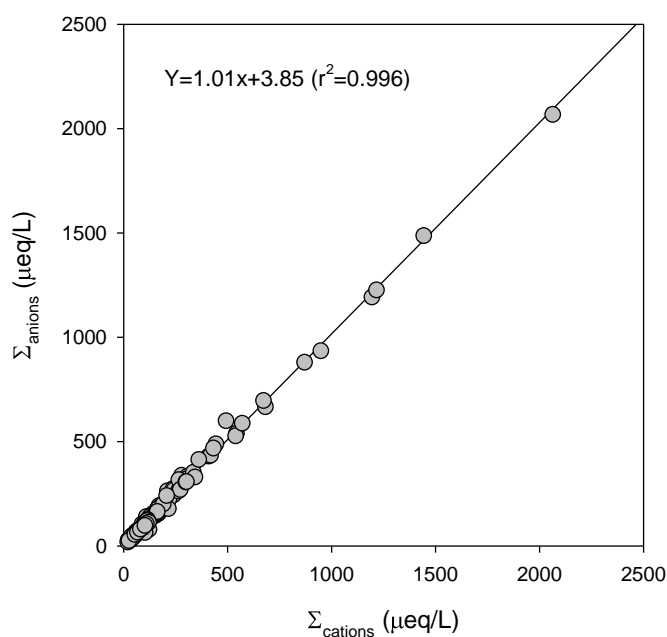


Figure 6.1 – Linear regression between the sum of cations and the sum of anions.

6.3. Results and discussion

6.3.1. Chemical composition

A summary of meteorological data recorded at the monitoring site was given in chapter 3. Precipitation was mostly accumulated in winter and the total precipitation amount during the sampling period was 1319 mm. 124 precipitation samples were collected in Oporto: 58 in winter, 33 in spring, 5 in summer and 28 in autumn.

Table 6.1 presents a statistical summary of annual and seasonal concentrations of DOC, WIOC, EC and water soluble ions in precipitation samples. Figure 6.2 shows the relative distribution of water soluble ionic species in rain.

Volume-weighted average concentrations of carbon fractions found in this study were 507 $\mu\text{gC.L}^{-1}$ for DOC, 224 $\mu\text{gC.L}^{-1}$ for WIOC and 38 $\mu\text{gC.L}^{-1}$ for EC. DOC was clearly the dominant carbon fraction. EC and WIOC accounted for only about 5 and 30%, respectively, of the total mass of carbon. The dominance of DOC over the other forms of carbon is typical of precipitation samples (Cerqueira et al., 2010).

The EC levels observed in Oporto were 3 to 8 times higher than those reported before for background coastal and marine sites in Portugal (Custódio et al., 2014; Cerqueira et al., 2010), pointing to a significant contamination of the Oporto atmosphere by anthropogenic sources of carbonaceous matter. For WIOC and DOC the ratio of concentrations between Oporto and these background sites was not so high, probably reflecting the diversity of organic carbon sources, particularly a significant incorporation of biogenic carbon in background rain.

WIOC and EC were found to be moderately correlated ($r=0.84$), suggesting common sources for these two carbon fractions. An average WIOC/EC ratio of 12 was obtained in the Oporto rain samples, which is much higher than the average ratio observed in aerosol samples (less than 1; see chapter 3). These results clearly point to a low scavenging efficiency of EC by rain.

Cl^- and Na^+ were the dominant ions in rain samples from Oporto. Together, these two species accounted for more than 72 % of the average ionic mass in rain. The abundance of these species is indicative of a strong contribution of sea-salt to the mass composition of rain and has been observed in other coastal sampling sites (e.g. Moreda-Piñeiro et al., 2014; Vázquez et al., 2003). SO_4^{2-} was the third most abundant ion in rain, accounting for 12 % of the total ionic mass. About half of this sulfate mass originated from sea-salt. The other half is expected to be the result of anthropogenic sources and, to a minor extent, from biogenic sources, like the oxidation of oceanic dimethyl sulfide.

Table 6.1 Annual and seasonal concentrations of carbon fractions and water soluble ions in rain from Oporto (µg/L).

	Overall			Winter			Spring			summer			autumn		
	avg±stdev	range	vwa	avg±stdev	range	Vwa	avg±stdev	Range	vwa	avg±stdev	range	vwa	avg±stdev	Range	vwa
WIOC	368±738	11-5852	224	372±784	36-5852	230	376±842	39-4472	176	183±114	11-289	171	384±558	13-2560	280
EC	54±94	BDL-799	38	59±109	2.4-799	37	37±50	BDL-278	21	20±16	BDL-46	25	71±106	BDL-508	65
DOC	790±761	152-4367	507	630±555	152-3029	412	785±730	164-3138	511	1205±741	446-2484	1213	1034±1015	180-4367	606
cations															
Na ⁺	3662±5208	158-36303	3526	5236±65451	58-36303	5391	1397±1135	202-4785	1618	1409±544	584-1968	1105	3032±3617	158-16775	1654
K ⁺	221±352	19-2806	202	303±472	31-2806	298	105±82	28-418	109	154±67	89-266	161	180±158	19-579	104
Ca ²⁺	250±285	27-1638	209	285±317	34-1638	294	147±139	27-573	108	175±68	62-234	91	295±317	58-1596	158
Mg ²⁺	410±550	22-3855	386	568±690	22-3855	609	174±129	23-497	176	172±62	65-215	98	357±397	41-1902	183
NH ₄ ⁺	374±573	2.8-5055	245	376±726	2.8-5055	260	384±410	25-1623	224	168±38	129-230	141	391±348	68-1365	256
anions															
F ⁻	3.2±6.4	BDL-42	2.6	4.3±8.5	BDL-42	4.0	1.6±1.6	BDL-6.3	1.0	2.6±2.2	0.3-6.2	0.9	2.5±3.5	BDL-14	1.5
Cl ⁻	6603±9343	247-64206	6301	9460±11672	247-64206	10092	2385±2040	354-8600	2741	2439±965	1087-3761	1590	5579±6626	264-28828	2773
NO ₃ ⁻	763±1155	99-9958	503	758±1406	99-9958	585	739±887	186-3814	410	452±71	334-520	316	847±852	114-2866	463
SO ₄ ²⁻	1721±1926	232-11398	1474	2134±2434	306-11398	2094	1168±1144	347-6301	941	817±276	405-1132	523	1561±1120	232-5085	869
oxalate	13±18	BDL-127	8.0	11±19	BDL-127	7.4	14±13	2.9-61	8.8	18±15	BDL-42	16	15±21	2.2-69	6.9
formate	84±108	BDL-825	64	86±91	BDL-570	70	76±41	8.6-190	71	130±147	19-380	42	83±164	7.6-825	46
acetate	100±182	13-1396	75	127±205	13-1396	100	54±33	16-130	46	72±49	30-155	32	93±217	16-1172	59
MS ⁻	5.9±6.3	BDL-36	4.8	5.0±6.4	BDL-36	4.5	8.3±5.5	1.9-28	6.7	9.6±11.9	1.5-30	2.6	4.8±4.8	BDL-20	3.5
propion.	6.8±10.3	BDL-78	5.1	8.4±11.9	BDL-78	6.4	5.9±6.0	2.6-34	4.5	BDL	BDL	BDL	4.9±10.5	BDL-57	3.4
nssSO ₄ ²⁻	808±1178	BDL-7908	607	831±1437	BDL-7908	720	819±1091	165-5941	542	465±141	258-640	309	802±591	192-2370	479

Acetate and formate were the dominant water soluble organic ions, followed by oxalate, propionate and MS^- . Acetate and formate accounted for 44.7 % and 40.7 % of the total mass of organic ions analyzed, respectively. Together, the average contribution of the five organic species to dissolved organic carbon (on a carbon mass basis) was less than 2 %. The prevalence of acetate and formate over the other organic ions has been observed in other studies about the chemistry of precipitation (Song and Gao, 2009; Avery et al., 2006) and contrasts with the relative distribution of organic ions in the aerosol phase, which is usually characterized by a higher prevalence of oxalate (see chapter 5). The volume weighted average concentrations of acetate, formate and oxalate found in this study compare well with values reported before for background atmospheres (Vet et al., 2014 and references therein) and were a factor of 2 to 5 times lower than values reported for polluted urban atmospheres (Vet et al., 2014 and references therein), suggesting that clean Atlantic air masses strongly influence the chemistry of rain in Oporto.

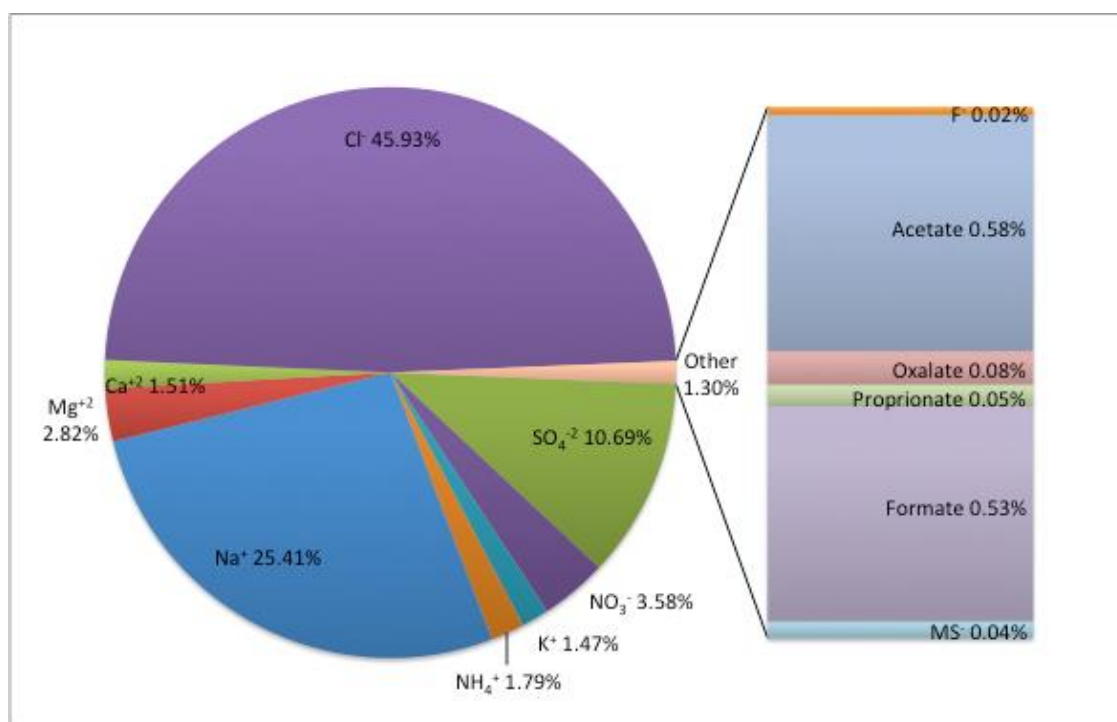


Figure 6.2 Relative distribution of water soluble ions mass concentration in rainwater.

6.3.2. Enrichment factor analysis

In order to further investigate the sources of Cl^- , SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+} in rain, enrichment factors (EF) relative to Na^+ were calculated using the following equation:

$$EF = \frac{(X/Na^+)_{rain}}{(X/Na^+)_{seawater}}$$

where X is the ions of interest. The results are presented in Table 6.2.

Table 6.2 Mass ratios of selected ions vs. Na^+ in rain compared with seawater ratios (Millero, 2013).

	Cl^-/Na^+	SO_4^{2-}/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+
Rain	1.74	0.82	0.10	0.12	0.13
Seawater	1.80	0.25	0.04	0.04	0.12
EF	0.97	3.28	2.50	3.00	1.08

The EF values show that sea-salt was the only source of Cl^- and Mg^{2+} . On the other hand, rain water was enriched in Ca^{2+} , SO_4^{2-} and K^+ relative to Na^+ as compared to seawater. The Ca^{2+} enrichment might be related with crustal sources and that of SO_4^{2-} and K^+ with anthropogenic activities (fossil and non-fossil fuel combustion processes, respectively). A seasonal variation was observed for the EF of Ca^{2+} , with the highest values in summer, suggesting a higher input of dust from soil suspension during the dry season.

6.3.3. Principal component analysis

Principal Component Analysis (PCA) was applied to total precipitation data to differentiate sources affecting the chemical composition of rainwater in Oporto. The selected principal components were those that showed eigenvalues above 0.8. From the PCA analysis six principal components were extracted (Table 6.3).

The first principal component (PC1), which explains 46% of the total variance, is characterized by high contributions of sodium, chloride and magnesium ions, indicating an important sea-salt influence on rain composition. The second principal component (PC2) accounted for 23% of the total variance and has high loadings of species usually associated to secondary atmospheric processes, such as ammonium, nitrate, nss-sulfate, methylsulfonate and oxalate. The third principal component (PC3) explained 14% of the total variance and is characterized by a high contribution of insoluble carbon fractions and, to a minor extent, dissolved organic carbon.

Table 6.3 Factor loadings and total variance obtained by principal component analysis. Values lower than 1 are not shown.

	PC1	PC2	PC3	PC4	PC5	PC6
WIOC		15.00	83.36	1.64		
EC			98.91	1.09		
DOC		50.97	24.15	2.70	4.76	17.42
Na ⁺	96.28	1.50			2.21	
Ca ²⁺	49.50	36.96		5.47		3.13
Mg ²⁺	95.57	3.22			1.21	
NH ₄ ⁺	7.78	84.48	1.72			6.02
nssK ⁺	4.52	1.23			94.26	
F ⁻	11.70	15.77		3.64	12.79	47.76
Cl ⁻	96.96	1.36			1.68	
NO ₃ ⁻	6.59	85.23				3.28
Oxalate		73.43		8.81		
Formate		16.91		78.64		2.69
Acetate	8.15	50.45		9.44		31.96
MS ⁻	2.47	79.39		18.13		
propion.	9.23	45.59	3.79	17.39		24.01
nssSO ₄ ²⁻	5.44	74.54			20.02	
Variance (%)	46	23	14	5	4	4

The high loading of EC suggests a dominant contribution from combustion processes, most likely with a strong contribution from vehicle exhaust. The fourth principal component (PC4) accounted for 5% of the total variance and is distinguished by a high load of formate. The origin of this chemical species has been linked to a variety of sources, including direct anthropogenic emissions, biogenic emissions and secondary atmospheric processes (Avery et al., 2006; 2001). In this case the origin of formate is unclear. Principal component 5 (PC5), explaining 4% of the variance, was identified as biomass burning combustion, based upon the high load of nssK⁺. Principal component 6 (PC6) is characterized by a high loading of fluoride and acetate, pointing to a significant contribution from an industrial source.

6.3.4. Air mass effects

The concentration of soluble and insoluble species in precipitation is a complex function of the diversity of pollutant sources and atmospheric processes. One of the most important processes affecting rain composition is known to be the origin of air masses at a sampling site (e.g. Custódio et al., 2014; Yan and Kim, 2012; Avery Jr. et al. 2006). The variation of major

rain chemical constituents as a function of local wind direction and speed are shown in Figures 6.3 and 6.4. These polar plot distributions were used to identify the source region of chemicals measured in rain samples collected in Oporto. Na^+ , Cl^- and Mg^+ present a similar spatial distribution with the highest concentrations associated to winds from the northwest sector, which is clearly an indication that these ions are related with sea-salt emissions from the Atlantic Ocean.

DOC, EC, WIOC, NH_4^+ , NO_3^- , nssSO_4^{2-} and oxalate concentrations in rain increased under low wind speed conditions, which suggests a local origin for these chemical species. This local source of insoluble carbon is not surprising since that Principal Component Analysis pointed to a common traffic source and sampling was performed at a short distance from a busy road. DOC, NH_4^+ , NO_3^- , nssSO_4^{2-} and oxalate also exhibited a common distribution with maxima associated with low wind speed, but these species were probably related with secondary aerosol formation, as described in chapter 6.3.3.

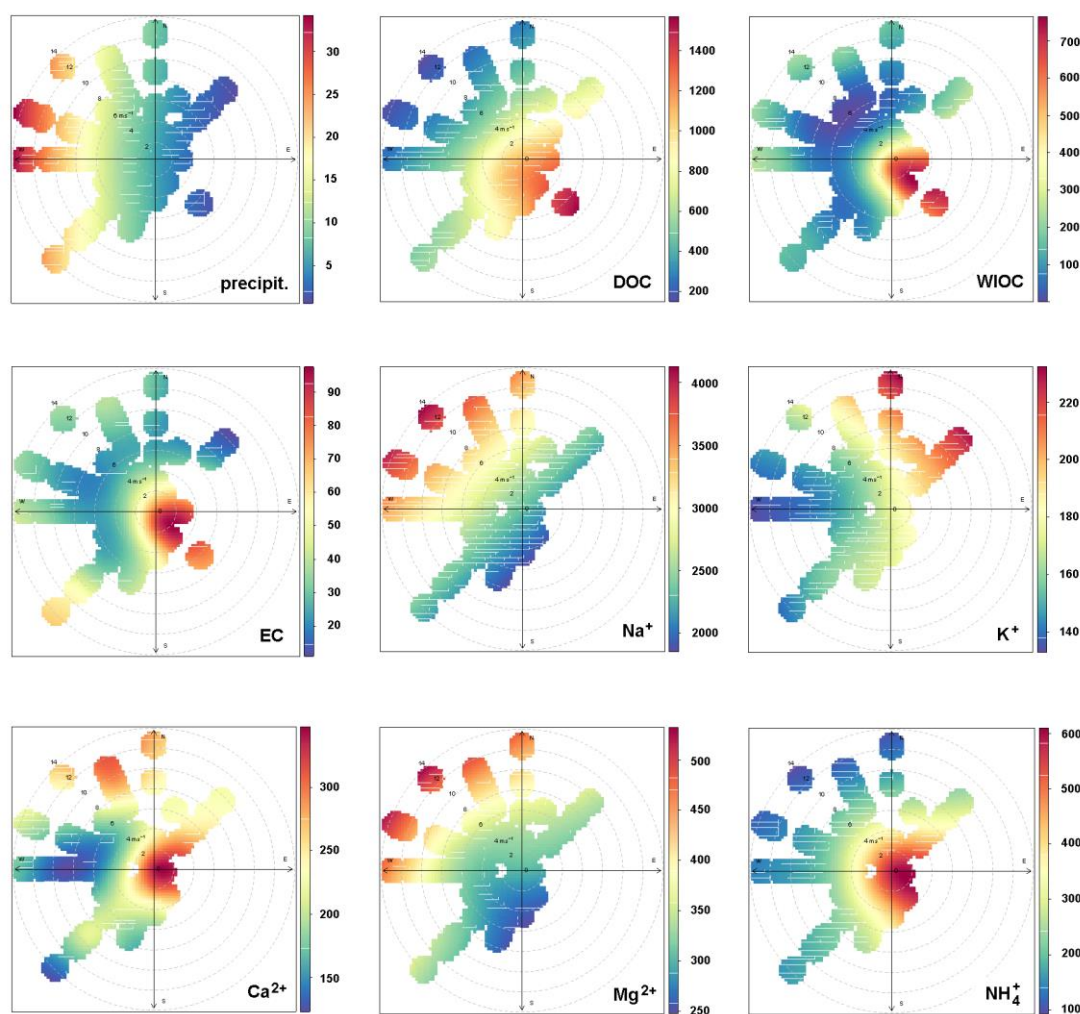


Figure 6. 3 - Polar plots of precipitation, carbon fractions and cations as a function of wind direction and speed in Oporto. Precipitation is in units of mm and concentrations are in units of ng/L.

The sources of formate, acetate, propionate and Fluoride were located inland. The polar plot distribution suggests a common origin, but this contradicts the results of the Principal Component Analysis, that separated the formate source from the sources of the other chemical constituents.

The origin of Ca^{2+} and K^{+} was also located inland but their polar plot distribution suggest independent sources.

MS^{-} seems to have at least two sources: a marine, as indicated by westerly winds; and a continental, which was more relevant during stagnant conditions.

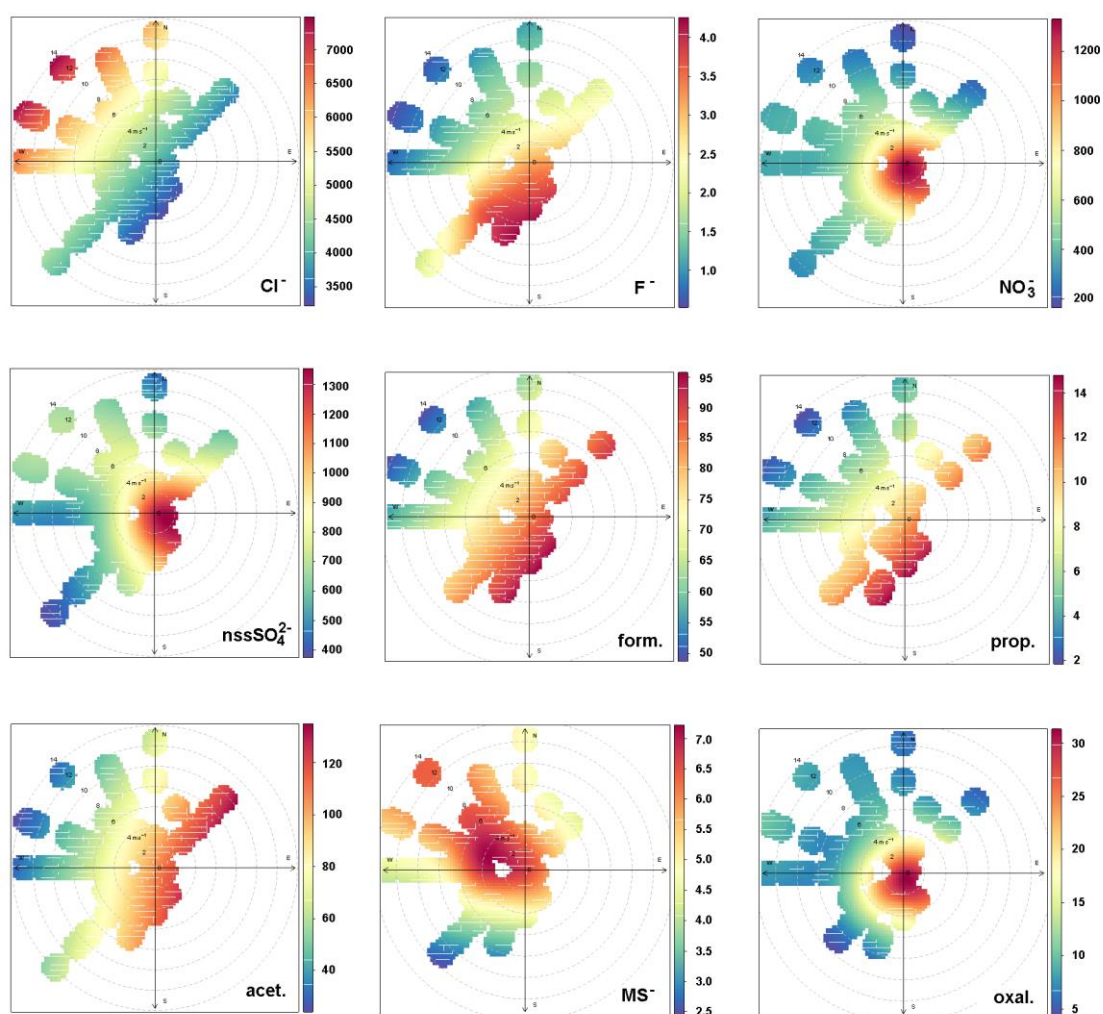


Figure 6.4 - Polar plots of anions as a function of wind direction and speed in Oporto. Concentrations are in units of ng/L.

6.3.5. Scavenging ratios

The concept of scavenging ratio has been used to quantify the tendency of a species to be removed from the atmosphere by precipitation. The volume based scavenging ratio (ω_v) can be calculated by the equation (Kasper-Giebl et al., 1999)

$$\omega_v = C_p \times \rho_w / C_a$$

where C_p is the concentration of the species in precipitation ($\mu\text{g kg}^{-1}$), C_a is the concentration of the species in air ($\mu\text{g m}^{-3}$) and ρ_w is the density of water (1000 kg m^{-3}). The calculation of ω_v is based on the assumption that the concentration of a species in precipitation is directly related to the concentration of the same species in air.

In this study scavenging ratios were calculated using individual pairs of concentration in precipitation and in air. Concentrations in air were estimated from $\text{PM}_{2.5}$ aerosol samples collected at the same site and over the same time period. A detailed description of aerosol sampling and analytical methods was given in chapter 3. The average scavenging ratios for major chemical species in Oporto are shown in Table 6.4.

Table 6.4 Average scavenging ratios for rain chemical constituents in Oporto.

	$\omega \times 10^{-6}$
EC	0.018 ± 0.023
WIOC	0.396 ± 0.705
WSOC	0.367 ± 0.372
Na^+	6.89 ± 9.96
K^+	1.86 ± 2.27
Ca^{2+}	6.09 ± 6.50
Mg^{2+}	8.11 ± 8.82
NH_4^+	1.63 ± 1.53
F^-	2.73 ± 6.16
Cl^-	8.62 ± 11.55
NO_3^-	1.48 ± 1.73
SO_4^{2-}	1.91 ± 1.88
Oxalate	0.251 ± 0.221
Formate	3.33 ± 4.01
Acetate	9.89 ± 10.30
MS^-	0.582 ± 0.790

ω_v values ranged between 1.8×10^4 , for EC, and 9.9×10^7 for acetate. The observed range of values, spanning several orders of magnitude, was expected since many factors can influence the magnitude and variability of ω_v , such as particle-size distributions and solubilities,

precipitation rates and amounts, droplet accretion processes, air mass trajectories and gas-phase scavenging (Galloway et al., 1993 and references therein). Because of many influencing factors, ω_v can range over several orders of magnitude even for a single species at a single location.

High scavenging ratios in Oporto were found for the ionic species Na^+ , Cl^- and Mg^{2+} . This can be explained by the dominant sea-salt origin of these species in aerosol particles from Oporto (chapter 3) and by the high solubility of sea-salt in water. These results might also be reflecting the size distribution of sea-salt, which is known to peak in the coarse mode, and the fact that scavenging ratios were calculated with $\text{PM}_{2.5}$ data. High scavenging ratios were also found for formate and acetate. These values are related with the high vapor pressure of formic and acetic acids, which explains their low prevalence in the form of aerosol particles, and the high solubility of both acids in water. In contrast with the above results, oxalate, WIOC and particularly EC exhibited the lowest scavenging ratios of the group of chemical species investigated in Oporto. This is not surprising, given that oxalic acid is less soluble in water than monocarboxylic acids and that WIOC and EC have low affinity for water.

The ω_{EC} found in this study (urban traffic site) is about ten times lower than the value reported by Cerqueira et al. (2010) for a coastal background site, in Aveiro, also in Portugal, under a strong influence of Atlantic air masses. According to Galloway et al. (1993) a significant spatial and temporal variance in scavenging ratios can be observed due to several factors, including the physical and chemical state of aerosol. Regarding the Oporto site, it is worth to emphasize that carbonaceous aerosol mass has a significant contribution from local sources, like vehicle and biomass burning emissions (chapter 4), which means that more fresh and hydrophobic particles are expected to be found in the urban atmosphere, and therefore lower scavenging ratios should be found in Oporto than in Aveiro. In the case of ω_{WIOC} , the Oporto value was about five times higher than reported before for Aveiro, showing that other factors are explaining a stronger incorporation of WIOC in rain in the urban site.

6.3.6 - Wet deposition fluxes of carbon species

The atmospheric deposition of carbonaceous matter has become a core issue in studies about the cycling of carbon through the atmosphere (e.g. Jurado et al., 2008). However, current information on the deposition fluxes of carbon to Earth's surface is still scarce. Estimates of carbon deposition by wet deposition were performed in Oporto taking into account individual values of precipitation amount and DOC, WIOC and EC concentrations in rain (Table 6.5).

The annual flux deposition of total carbon in Oporto was $1045.2 \text{ mg C m}^{-2} \text{ yr}^{-1}$, corresponding to $691.4 \text{ mg C m}^{-2} \text{ yr}^{-1}$ as DOC, $302.3 \text{ mg C m}^{-2} \text{ yr}^{-1}$ as WIOC and $51.5 \text{ mg C m}^{-2} \text{ yr}^{-1}$ as EC. The seasonal variation of wet deposition fluxes shows that most of the carbon (about 42 %) is transported to the surface during winter, in contrast with the summer fluxes, which accounted for only 7% of the total carbon wet deposition.

There are not many published results to compare with data from this study. EC and WIOC wet deposition fluxes in the urban site of Oporto were higher than most of the average values reported by Cerqueira et al. (2010) for European remote sites (EC fluxes in the range of 5 to $38 \text{ mg C m}^{-2} \text{ yr}^{-1}$) and WIOC fluxes in the range of 61 to $378 \text{ mg C m}^{-2} \text{ yr}^{-1}$). In what concerns DOC, the Oporto fluxes were 2.8 times lower than the average values described by Yan and Kim (2012) for Seoul, Korea ($1.9 \text{ g C m}^{-2} \text{ yr}^{-1}$).

Table 6. 5. Wet deposition fluxes of carbon species in Oporto (mg C m^{-2}).

	total carbon	DOC	WIOC	EC
Winter	438.5	280.0	136.1	22.4
Spring	251.4	182.9	61.3	7.2
Summer	74.8	64.5	9.0	1.3
Autumn	251.4	159.9	74.3	17.3
Annual	1045.2	691.4	302.3	51.5

6.4. Conclusions

This study reports the chemical composition of rain at a kerbside location in Oporto, Portugal. 124 rain samples were collected, most of them during the winter season. Information from the chemical analysis of these samples lead to the following conclusions:

- Na^+ and Cl^- were the prevailing ions, accounting for more than 70% of the total mass of measured water soluble ions;
- most of the carbon investigated in precipitation was in the dissolved form;
- formate and acetate ions were the dominant organic species identified in rain, but carboxylic acids species accounted just for 32% of the total mass of dissolved organic carbon;

- EC was a minor constituent of precipitation, however average concentrations of these carbon fraction indicate a significant contamination of the Oporto atmosphere by combustion processes;
- three main sources controlled the chemical composition of rain: sea-salt; secondary atmospheric processes; and vehicle exhaust;
- scavenging ratios ranged over three orders of magnitude; the highest value was found for Cl⁻ and the lowest for EC, reflecting significant differences in the hydrophobic properties of atmospheric chemical constituents.

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CHAPTER 7

CONCLUSIONS

Atmospheric carbonaceous aerosols, from both natural and anthropogenic sources, have significant effects on air quality, visibility, atmospheric chemistry and Earth's radiation budget. However, the cycling of these carbonaceous aerosols through the atmosphere and the corresponding environmental effects are very difficult to analyze and describe due to the variety of emitting sources, transformation processes, transport mechanisms and removal routes. This study focused on suspended carbon particles and was intended to contribute to the ongoing efforts of the scientific community to better elucidate the complex role of these particles during their transport through the atmospheric reservoir. The main conclusions from this study are summarized below.

Regarding the indoor aerosol composition:

- Exposure to PM_{10} in occupied residences was higher indoors than outdoors and maximum exposure was found within a smokers' residence; the PM_{10} mass concentrations in the indoor air of residences in Portugal were higher than those reported before in central and northern Europe, which might be the result of a higher input of mineral dust from outdoor sources;
- The average contribution of OC to PM_{10} in the indoor air of occupied residences ranged was 21%. A higher contribution (46%) was found in the unoccupied residence, showing that fine particles, with a high content in OC, infiltrate more easily indoors than coarse particles, with a high mineral content;
- OC concentrations were higher indoors than outdoors in the occupied residences, showing the influence of indoor sources like smoking, cooking and cleaning;
- EC concentrations accounted for an average of only 3.7% of the PM_{10} mass concentration in the indoor air of occupied residences; the main sources of EC in non-smokers residences were located outdoors.

About the aerosol composition in Oporto:

- Road traffic was the most important contributor to PM_{10} and $PM_{2.5}$ sampled in the Oporto kerbside; local dust (19%) and biomass burning (14%) were the second and third most important sources of PM_{10} ; in $PM_{2.5}$ the contribution of biomass burning increased to 18% and that of local dust decreased to 15%; other significant anthropogenic sources were: secondary sulphate industries, mainly metallurgy, and secondary nitrate, emitted from multiple sources such as industries;

- PM_{2.5}, OC and WSOC exhibited pronounced seasonal variations with peak levels in winter and summer, most likely related with biomass burning for heating purposes and wildfires, respectively;
- oxalate was the most abundant water soluble carboxylate identified in fine aerosol particles; the origin of oxalate was probably associated with biomass burning as well as secondary process in the atmosphere; biomass burning was identified as an important source of formate and, to a lesser extent, of acetate;
- among the aerosol water soluble inorganic constituents, (NH₄)₂SO₄ was dominant in summer, reflecting an increase in secondary aerosol formation, and NaCl was prevalent in winter, associated with the occurrence of airflow transport from the North Atlantic;

In what concerns the chemical composition of rain:

- A temporal variation was observed for both EC and WIOC concentrations in rain samples from the Azores. The EC time trend reflected the seasonal variation of long-range air mass transport and the WIOC time trend was related with local or regional inputs of biogenic carbon and the seasonal variation of weather patterns over the North Atlantic.
- The wet deposition fluxes of particulate carbon were higher during the rainy months compared with the dry months, and North America was found to be the main source region of particulate carbon deposited by rain into the Azores region;
- Carbonaceous matter in rain from Oporto was dominated by dissolved organic carbon; EC was a minor chemical constituent of rain but average concentrations of these carbon fraction indicate a significant contamination of the Oporto atmosphere by combustion processes;
- Scavenging ratios ranged over three orders of magnitude; the highest value was found for Cl⁻ and Na⁺ and the lowest for EC, reflecting significant differences in the hydrophobic properties of atmospheric chemical constituents.

SUPPLEMENTARY DATA

Supplementary Data S1

Wildfire emissions in the surrounding area of Oporto during the summer of 2013, Chapter 3.

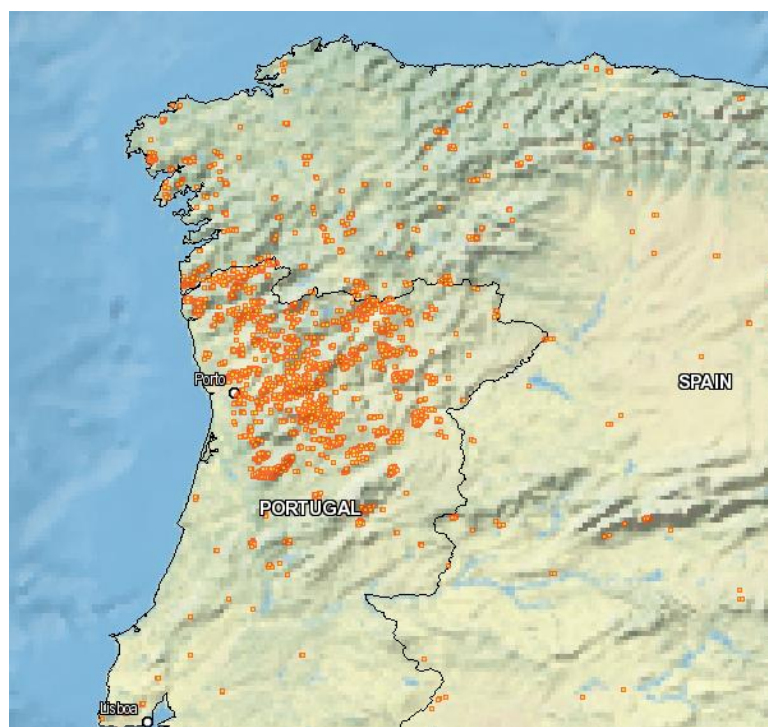


Figure S. 1 - MODIS fire counts (<https://firms.modaps.eosdis.nasa.gov/firemap/>) in northwestern Iberia between 11/08/2013 and 21/09/2013.

Supplementary Data S2

Chapter 6.



Figure S. 2 – Sampling equipment on the rooftop of the air quality monitoring station (41° 09' 46''N; 8° 35' 27'' W) located at the kerbside of Fernão de Magalhães Avenue.