CONTINUOUS REAL-TIME MEASUREMENT OF THE CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICLES IN GREECE USING AEROSOL MASS SPECTROMETRY

A MASTER THESIS
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Abstract

Atmospheric aerosol is an important component of our atmosphere influencing human health, regional and global atmospheric chemistry and climate. The organic component of submicron aerosol contributes around 50% of its mass and is a complex mixture of tens of thousands of compounds. Real-time aerosol mass spectrometry was the major measurement tool used in this work. The Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) can quantitatively measure the chemical composition and size distribution of non-refractory submicron aerosol (NR-PM$_1$). The mass spectra provided by the instrument every few minutes contain information about aerosol sources and processes. This thesis uses the HR-ToF-AMS measurements in two areas of Greece to quantify the contributions of organic aerosol sources to the corresponding organic aerosol levels.

Local and regional air pollution sources were monitored and characterized in two sites during intensive campaigns. The first campaign took place during the fall of 2011 (September 24 to October 23) in Finokalia, Crete, a remote-background coastal site without any major human activity. The aim of the study was to quantify the extent of oxidation of the organic aerosol (OA) during autumn, a season neither too hot nor cold, with reduced solar radiation in comparison to summer. The second one took place during the winter of 2012 (February 26 to March 5), in the third major city of Greece, Patras. The measurements were conducted in the campus of the Technological Educational Institute of Patras (TEI), in order to quantify the severity of the wintertime air pollution problem in the area and its sources. The contributions of traffic and residential wood burning were the foci of that study.

The Finokalia site is isolated and far away from anthropogenic sources of pollution, making it ideal for the study of organic aerosol coming from different directions, usually exposed to high levels of atmospheric oxidants. The fine PM measured during the Finokalia Atmospheric Measurement Experiment (FAME-11) by the AMS and a Multi Angle Absorption Photometer (MAAP) was mostly ammonium sulfate and bisulfate (60%), organic compounds (34%), and BC (5%). The aerosol sampled originated mainly from Turkey during the first days of the study, but also from Athens and Northern Greece during the last days of the campaign. By performing Positive Matrix Factorization (PMF)
analysis on the AMS organic spectra for the whole dataset the organic aerosol (OA) composition could be explained by two components: a low volatility factor (LV-OOA) and a semi-volatile one (SV-OOA). Hydrocarbon-like organic aerosol (HOA) was not present, consistent with the lack of strong local sources.

The second field campaign took place in the suburbs of the city of Patras, 4 km away from the city center during the winter of 2012. During this 10-day campaign, organics were responsible for 70% during the day and 80% during the evening of the total PM$_1$. The OA mean concentration during that period was approximately 20 $\mu$g m$^{-3}$ and reaching hourly maximum values as high as 85 $\mu$g m$^{-3}$. Sulfate ions and black carbon followed with 10% and 7% of the PM$_1$. PMF analysis of the organic mass spectra of PM$_1$ explained the OA observations with four sources: cooking (COA), traffic (HOA), biomass burning (BBOA), and oxygenated aerosol (OOA), related to secondary formation and long range transport. On average, BBOA represented 58% of the total OM, followed by OOA with 18%, COA and HOA, with the last two contributing of the same percentage (12%).
Table of Contents

Abstract .................................................................................................................................................. iii
Table of Contents ..................................................................................................................................... v
Table of Figures ......................................................................................................................................... viii
List of Abbreviations ................................................................................................................................ xii

CHAPTER 1
INTRODUCTION ....................................................................................................................................... 1
  1.1 Atmospheric Particulate Matter (PM) or Aerosols ................................................................. 1
  1.2 Aerosol Properties ...................................................................................................................... 2
    1.2.1 Size distribution ................................................................................................................... 2
    1.1.2 Chemical composition of ambient aerosols ........................................................................... 6
    1.1.3 Secondary Organic Aerosol (SOA) and its Properties ....................................................... 6
  1.3 Thesis objectives and contents ................................................................................................. 8
  1.4 References ................................................................................................................................... 9

CHAPTER 2
INSTRUMENTATION .............................................................................................................................. 12
  2.1 Atmospheric Aerosol Characterization Techniques ............................................................... 12
    2.1.1 Real-Time measurement methods ...................................................................................... 12
    2.2 The Aerosol Mass Spectrometer (AMS) .................................................................................. 13
    2.2.1 Modes of AMS operation ................................................................................................... 18
    2.2.2 Particle Collection Issues .................................................................................................. 19
    2.2.3 Positive Matrix Factorization (PMF) .................................................................................. 20
    2.3 Scanning Mobility Particle Sizer (SMPS) ............................................................................... 22
      2.3.1 Electrostatic Classifier ....................................................................................................... 22
      2.3.2 Condensation Particle Counters (CPC) .............................................................................. 24
    2.4 Multi-angle Absorption Photometer (MAAP) ....................................................................... 25
    2.5 References ............................................................................................................................... 27

CHAPTER 3
ORGANIC AEROSOL IN A REMOTE SITE IN THE EASTERN MEDITERRANEAN .................................... 29
  3.1 Sampling Site and Instrumentation .......................................................................................... 29
  3.2 Measurement Overview ......................................................................................................... 31
    3.2.1 Meteorology .................................................................................................................... 31
    3.2.2 Results ............................................................................................................................. 32
    3.2.3 PMF source apportionment analysis of organic PM ....................................................... 39
CHAPTER 4
WINTERTIME AIR POLLUTION IN PATRAS ......................................................... 50
4.1 Introduction ................................................................................................. 50
4.2 Sampling Site and Instrumentation .............................................................. 50
4.3 Measurement Overview ............................................................................. 51
4.3.1 Meteorology ............................................................................................ 51
4.3.2 Results ..................................................................................................... 52
4.3.3 PMF source apportionment analysis of NR-PM$_1$ ................................... 59
4.4 Conclusions ................................................................................................. 67
4.5 References ................................................................................................... 69

CHAPTER 5
CONCLUSIONS AND FUTURE WORK ............................................................. 72
Table of Figures

**Figure 1.1** The Earth’s global mean energy balance [Kiehl and Trenberth, 1997]. ........................................ 2

**Figure 1.2** Typical number and volume distributions of atmospheric particles in a polluted urban area with the different modes [Seinfeld and Pandis, 2006]. ................................................................. 4

**Figure 1.3** Typical mass and chemical composition distribution of atmospheric particles (Los Angeles, 1987). The accumulation mode mainly consists of sulfate, nitrate, ammonium and organic matter, while the coarse mode is characterized by sodium, chloride, nitrate and a small percent of sulfate. ........................................................................................................ 5

**Figure 1.4** Composition of non-refractory particles smaller than 1 μm in diameter. Organics are in green, sulfates in red, nitrate in blue and ammonium in orange [Zhang, et al., 2007]. .............. 7

**Figure 2.1** Schematic of the principle of operation of time-of-flight aerosol measurements. ...... 13

**Figure 2.2** Schematic of the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer. ................................................................................................................................. 14

**Figure 2.3** FLUENT simulation results illustrating the focusing action of the aerodynamic particle beam forming lens. The results displayed are for 100 nm diameter spheres with a density of 1 gm cm$^{-3}$ [Jayne et al., 2000]. ........................................................................................................ 15

**Figure 2.4** Schematic of the AMS vaporization and ionization regions. ................................. 17

**Figure 2.5** A typical AMS mass spectrum calculated as the difference between the ‘open’ and ‘blocked’ beam positions (here till m/z 120). ......................................................................................... 18

**Figure 2.6** Typical size distribution derived by the AMS. ...................................................... 19

**Figure 2.7** Schematic of PMF analysis of an AMS spectra dataset. The time series of the factors make up the matrix G and the mass spectra of the factors make up the matrix F in Eq. (2) [Ulbrich et al., 2009]. .............................................................. 21

**Figure 2.8** Flow schematic of the Electrostatic Classifier. ........................................................ 23

**Figure 2.9** Flow schematic of a butanol-based CPC (3775). ..................................................... 24

**Figure 2.10** Schematic diagram of the MAAP detector block showing the arrangement of the detectors used relative to the sample collected on the filter. ......................................................... 26

**Figure 3.1** NASA satellite images of Europe and of the island of Crete, indicating the location of the sampling station at Finokalia................................................................. 29

**Figure 3.2** Photograph of the Finokalia station in Crete. ........................................................ 30

**Figure 3.3** Temperature time-series during the the FAME-11 campaign. .............................. 31
Figure 3.4  Average diurnal profiles of the solar radiation during the FAME campaigns. ..........32

Figure 3.5  Number and size distribution time series from FAME-11. The y-axis is the particle diameter and the color indicates the particle number concentration density. ...............................32

Figure 3.6  Time series of PM$_1$ composition (as a percent) and mass concentrations of the major PM$_1$ components measured by the HR-AMS and the MAAP. Source labels point to the origin of the air masses affecting Finokalia at the corresponding periods. .................................33

Figure 3.7  Average composition of PM$_1$ during the 2011 campaign in Finokalia. The small amounts of sea-salt and dust are not included. .................................................................34

Figure 3.8  Average diurnal profiles of the concentrations of the major PM$_1$ components. The error bars correspond to one standard deviation of the measurements. ...............................35

Figure 3.9  The campaign average ambient particle time-of-flight size distributions of the different aerosol species measured by the AMS versus vacuum aerodynamic diameter. .............36

Figure 3.10  Ratios of OM/OC, and atomic O/C and H/C ratios during the FAME-11 campaign. .........................................................................................................................37

Figure 3.11  Average diurnal profiles of OM/OC, O/C and H/C ratios for FAME-11. The error bars correspond to one standard deviation of the measurements. ..........................................................38

Figure 3.12  Comparison (a) of PM$_1$ OM mass from the AMS and filters on the left and (b) of PM$_1$ sulfate mass from the AMS and PM$_{2.5}$ sulfate from filters on the right. .................38

Figure 3.13  The concentration of PMF factors and their average composition at Finokalia site. The contribution of each factor to total OM is also shown (top figure). .................................40

Figure 3.14  Mass spectra of the four OA factors with calculated corresponding atomic ratios. .41

Figure 3.15  Correlation between the hourly averaged OOA factors and particulate sulfate, ammonium, BC and nitrate. The points are time-coloured for the whole campaign. .................................42

Figure 3.16  Average diurnal profiles of the two OOA factors during FAME-11 ..................43

Figure 3.17  Time series of f$_{43}$, f$_{44}$ and f$_{57}$. .................................................................44

Figure 3.18  Average diurnal profiles of f$_{43}$, f$_{44}$ and f$_{57}$. .............................................44

Figure 3.19  Organic aerosol composition in the Ng et al. (2010) triangle plot: f$_{44}$ vs. f$_{43}$, for the OA of the whole FAME-11 campaign. Also, the average OA, LV-OOA and SV-OOA contribution is shown with black dots. .................................................................45

Figure 3.20  Organic aerosol composition in the Ng et al. (2010) triangle plot: f$_{44}$ vs. f$_{43}$. The dots correspond to the average OA of the three FAME campaigns, and to the fragments of OOA factors. .................................................................46
Figure 4.1 Location of sampling sites in the Technological Educational Institute (TEI) and the center of Patras are shown. .................................................................51

Figure 4.2 Left, the location of TEI in Patras. Right, the sampling site in the city centre (top of the white building). .................................................................51

Figure 4.3 Temperature and relative humidity time-series during the campaign. The measurements were taken in Patras center ..................................................52

Figure 4.4 Rose plot of wind speed and wind direction for Patras. ...........................................52

Figure 4.5 The diurnal variation of CE and density of organics .............................................53

Figure 4.6 Total mass concentration NR-PM$_1$ in the TEI site and temperature during the campaign from Patras site ...............................................................54

Figure 4.7 The hourly averaged PM$_1$ composition by the HR-AMS at the TEI site and black carbon measurements of the same period at Patras center. Different scales are used for each species. Also, the contribution of each constituent of the dry PM$_1$ mass is shown. ........................................55

Figure 4.8 Average composition of PM$_1$ during the 2012 campaign in Patras ......................56

Figure 4.9 The campaign-average size distributions of the aerosol species measured by the AMS versus vacuum aerodynamic diameter ..............................................56

Figure 4.10 Average diurnal profiles of the concentrations of the major PM$_1$ components. The error bars correspond to one standard deviation of the measurements. ..........................57

Figure 4.11 Elemental ratio analysis, hourly averaged times series of OM/OC,O/C and H/C ratios. .........................................................................................................58

Figure 4.12 Average diurnal profiles of OM/OC,O/C and H/C ratios........................................59

Figure 4.13 The concentration of PMF factors at the TEI site. Different scales are used for each factor. The contribution of each factor to total OM is shown (top figure). ..............................60

Figure 4.14 Mass spectra of the four OA factors with calculated corresponding atomic ratios. 61

Figure 4.15 Correlation between the hourly averaged BBOA factor and potassium (A.) Also, OOA correlation between particulate sulfate (B.) and ammonium (C.) The points are time-coloured for the whole campaign..............................................................63

Figure 4.16 Average diurnal variation of the four PMF factors. The right y-axis shows the BBOA values, while the left one all the rest ........................................................................64

Figure 4.17 Average diurnal profiles of $f_{43}$, $f_{44}$, $f_{57}$ and $f_{60}$. On the left y-axis is the fraction at m/z 57 and 44 and on the right one the fraction at m/z 60 and 43 ........................................65
**Figure 4.18** Fractions of organic mass fragments 44 ($f_{44}$) and 43 ($f_{43}$) in the Ng triangle (Ng et al., 2010) of this campaign.

**Figure 4.19** Fractions of organic mass fragments 44 ($f_{44}$) and 43 ($f_{43}$) in the Ng triangle (Ng et al., 2010) from Zurich campaign, described in Mohr et al. (2011).
List of Abbreviations

AMS: Aerosol mass spectrometer
BC: Black Carbon
BBOA Biomass-burning organic aerosol
CE: Collection Efficiency
COA: Cooking-related organic aerosol
EI: Electron-impact ionization
HOA: Hydrocarbon-like organic aerosol
HR-ToF-AMS: Aerodyne High-Resolution Time-of-Flight Mass Spectrometer
LST: Local Standard Time
MAAP: Multiangle Absorption Photometer
MS: Mass spectra
m/z: mass-to-charge ratio
NPF: New particle formation
NR-PM$_1$: submicron non-Refractory Particulate Matter
OM: Organic Matter
OOA: Oxygenated organic aerosol
PMF: Positive Matrix Factorization
PM$_1$: Particulate Matter with diameter <1μm
PM$_{2.5}$: Particulate Matter with diameter <2.5μm
PM$_{10}$: Particulate Matter with diameter <10μm
POA: Primary organic aerosol (emitted into the atmosphere directly in the particle phase)
SMPS: Scanning mobility particle sizer
SOA: Secondary organic aerosol (created by chemical reactions leading to a decrease in species volatility and increased partitioning to the particle phase)
WBOA: Wood Burning Organic Aerosol
CHAPTER 1

INTRODUCTION

1.1 Atmospheric Particulate Matter (PM) or Aerosols

Particulate matter (PM or aerosol) is generally defined as a suspension of liquid or solid particles in a gaseous medium. Atmospheric aerosols range in size from a few nanometers in diameter to as much as 100 µm in diameter. Particles larger than 10 µm in diameter tend to settle out of the atmosphere very rapidly, while smaller particles can remain airborne for days.

Aerosols play an important role in Earth’s atmosphere, although they comprise less than 0.000001% of its total volume. They can influence the energy balance of our planet in two ways [Jacob, 1999; Limbeck et al., 2003; Ravishankara, 1997].

I. **Scattering and absorption of sunlight.** Atmospheric aerosols, scatter a significant fraction of sunlight back out into space (Fig.1.1), increasing Earth’s albedo and exerting a cooling influence on the planet (Charlson et al., 1992). At the same time, black carbon (BC) and mineral dust are strong light absorbers (Hansen et al., 2000). Aerosols that absorb sunlight effectively warm the atmosphere. This cooling or warming of the atmosphere as a result of the reflective or absorbent properties of the particles is known as the *direct effect* of particulate matter on climate.

II. **Serving as cloud condensation nuclei.** Cloud condensation nuclei (CCN) or sometimes "cloud seeds" are particles on which water vapor condenses, forming cloud droplets. In the absence of CCN, air reaches saturations of above 400% before cloud droplets form. Clouds with more CCN have more but smaller droplets and are more reflective than those with fewer CCN. By increasing the reflectivity of clouds, atmospheric aerosols are also contributing to cooling (Fig. 1.1) and this is considered as the *indirect effect* of particulate matter on climate.
In addition to their impact on climate, atmospheric aerosols have major negative effects on human health. Both short and long-term exposure of humans to high mass concentrations of particulate matter, with diameter smaller than 2.5 μm (PM$_{2.5}$) increases mortality and morbidity (Dockery et al., 1993). PM$_{2.5}$ can go through the upper respiratory system and enter the lower airways where they are deposited. Aerosols have been also linked to decreased lung function (Gauderman et al., 2000) and bronchitis (Dockery et al., 1996) especially in children and elderly.

### 1.2 Aerosol Properties

#### 1.2.1 Size distribution

Particulate matter existing in air is divided into different categories depending on the size of the particles. For a particle that is spherical, the particle geometric diameter ($D_p$) is used to characterize its size. For a particle that is not spherical, the classical aerodynamic diameter ($D_{ca}$) is defined as the diameter of the spherical particle with a density of 1000 kg m$^{-3}$ that has the same terminal settling velocity as the irregular particle. The classical aerodynamic diameter is given by:
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

\[ D_{ca} = \left( \frac{18u_t \mu}{\rho_p^0 g C_c(D_{ca})} \right)^{1/2} \]  \hspace{1cm} (1.1)

where \( u_t \) is the terminal velocity of the particle, \( \mu \) is the viscosity of air, \( \rho_p^0 \) is the unit density, \( g \) the standard gravity and \( C_c \) the slip correction factor.

For a spherical particle of non-unit density the classical aerodynamic diameter is different from its physical diameter and depends on its density. The aerodynamic diameter of a spherical particle with diameter \( D_p \) and non-unit density depends on the mean free path of the air molecules around it and thus also on pressure. For low pressures, the particle will be in the free molecular regime and the aerodynamic diameter will be proportional to the density of the particle and given by:

\[ D_{va} = D_{ca}/D_p = (\rho_p/\rho_p^0) \]  \hspace{1cm} (1.2)

This diameter is often called the vacuum aerodynamic diameter \( (D_{va}) \) or the free molecular regime aerodynamic diameter of the particle. A number of aerosol instruments that operate at low pressures such as the aerosol mass spectrometer measure the vacuum aerodynamic diameter of particles.

Aerosols smaller than 10 microns in diameter are divided into three categories based on their size: ultrafine, fine, and coarse particles. Ultrafine particles are defined as those having diameters less than 0.1 \( \mu \)m. This fraction has low mass concentration but high number concentration. Fine particles are defined as those smaller than 2.5 \( \mu \)m (they include the ultrafine), while coarse particles are those with diameter from 2.5 to 10 \( \mu \)m. Coarse particles are orders of magnitude fewer in number in comparison to the ultrafine, but have much higher mass concentration.

Fig. 1.2 shows typical number and volume distributions of aerosol in an urban area, which are often approximated as sums of lognormal distributions (Seinfeld and Pandis, 2006). The number distribution usually consists of two modes, the nucleation (diameter less than 10 nm) and the Aitken mode (10 – 100 nm). The nucleation mode is formed only by nucleation of vapors (e.g. sulfuric acid) mainly during the oxidation of precursor gases (e.g. sulfur dioxide). The volume distribution usually has two major modes.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry. 4

(accumulation and coarse). The accumulation (100 nm – 2.5 μm) and coarse (>2.5 μm) modes, have different sources and hence different composition and properties.

![Figure 1.2 Typical number and volume distributions of atmospheric particles in a polluted urban area with the different modes [Seinfeld and Pandis, 2006].](image)

The accumulation mode contains primary particles emitted by combustion, as well as secondary material produced by atmospheric chemistry. It has two sub-modes: the condensation and droplet sub-modes. The coarse mode is formed by mechanical processes and usually consists of dust particles, sea salt, pollen and other mechanically generated particles. A typical mass and chemical composition distribution of atmospheric particles is shown in Fig. 1.3.

Water is an important PM constituent that can account for most of the particulate mass depending on the ambient relative humidity (RH) (Kreidenweis et al., 2001; Spichtinger and Cziczo, 2008). Because PM water content largely depends on the ambient RH and is quite variable, regulatory mass measurements are performed at a fixed low RH.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

Figure 1.3 Typical mass and chemical composition distribution of atmospheric particles (Los Angeles, 1987). The accumulation mode mainly consists of sulfate, nitrate, ammonium and organic matter, while the coarse mode is characterized by sodium, chloride, nitrate and a small percent of sulfate.

Aerosols may be divided into two general categories, based on how they are formed: primary and secondary. Primary aerosols are emitted directly in the particulate phase (solid or liquid) from transportation, industry, power generation, and natural sources such as dust and sea salt. Secondary aerosols are reaction products of precursor gases, mainly SO$_2$, NO$_x$, NH$_3$, and volatile organic compounds (VOCs). The precursor gases become particles by phase changes including absorption and adsorption onto pre-existing particles, chemical reactions with other gases that produce particles and dissolution into water droplets. PM is also categorized as natural or anthropogenic. Aerosols are produced both by living material (e.g. plants, animals or microbes), or non-living (e.g. soil or volcanoes). Major anthropogenic sources include transportation, industry, wood combustion (fireplaces), agricultural activities etc.
1.1.2 Chemical composition of ambient aerosols

Atmospheric particles consist of inorganic ions such as $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{Cl}^-$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{NO}_2^-$, organic compounds (alkanes, alkenes, aldehydes, organic acids, ketones, aromatic, polyaromatic compounds, etc.), oxides of most metals, elemental carbon and water. The carbonaceous component of atmospheric aerosols contains thousands of organic compounds, known as organic carbon (OC), and a graphite-like, dark fraction, which is resistant to oxidation at temperatures below 600 °C known as elemental (EC) or black carbon (BC) (Penner and Novakov, 1996).

Some of the PM components (elemental carbon, dust, metal oxides, sulfate salts) are non-volatile under atmospheric conditions and exist only in the particulate phase. Others are present in significant concentrations in both phases and are called semi-volatile. A typical example is ammonia, a compound found in both gaseous and particulate phase as it reacts with acids (sulfuric, nitric etc.) forming the corresponding salts. Other examples of semi-volatile compounds are water, nitric acid, hydrochloric acid, and a large number of organic compounds.

1.1.3 Secondary Organic Aerosol (SOA) and its Properties

Organic components are emitted to the atmosphere from both biogenic and anthropogenic sources (Hallquist et al., 2009). They consist of volatile, intermediate volatility, semi-volatile and low volatility compounds. Many volatile organic compounds when oxidized produce semi-volatile vapors which are transferred to the particulate phase (Andersson et al., 2001). Primary organic aerosol (POA) refers to the organic compounds which are emitted directly in the particulate phase. Secondary organic aerosol (SOA) is the organic component of particulate matter that was originally emitted in the gas phase, was subsequently oxidized, and then was transferred to the particulate phase.

Despite enormous progress during the last two decades there are still major questions concerning the chemical and physical properties of atmospheric aerosols. Secondary organic compounds are usually the most important components of fine atmospheric particles (Zhang et al., 2007) (Fig. 1.4). Therefore, there is a major need to better understand their sources and processes. This could be succeeded by the use of continuous measurement approaches and quantitative tools that relate mathematically the
measurements of aerosol chemical composition to their sources. In continuous measurements the chemical composition, the number, the volume and the mass distribution and concentration can be measured every few minutes or even faster.

Figure 1.4 Composition of non-refractory particles smaller than 1μm in diameter. Organics are in green, sulfates in red, nitrate in blue and ammonium in orange [Zhang, et al., 2007].

The High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) is state-of-the-art aerosol measurement instrument (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2006, DeCarlo et al., 2006). It measures in real time the chemical composition (sulfate, organics, ammonium, nitrate, chloride and water) of submicron particles and the mass distributions of each species as a function of vacuum aerodynamic diameter. Also, the high-resolution capabilities of this instrument allow the direct separation of most ions from inorganic and organic species at the same nominal mass to charge ratio (m/z), the quantification of several types of organic fragments and the direct identification of organic nitrogen and organosulfur content (DeCarlo et al., 2006). In addition, the organic mass spectra recorded by the AMS can be used as inputs to a number of factor analysis techniques allowing their decomposition into vectors corresponding to the sources of the organic aerosol. This work focuses on ambient aerosol measurements by the HR-ToF-AMS and the additional analysis of the sources of its organic component.
1.3 Thesis objectives and contents

The objective of this thesis is the measurement and characterization of the submicrometer organic aerosol in two sites in Greece. The work focuses on the chemical properties of organic aerosol, its sources and its atmospheric processing.

The Thesis is divided into five chapters. In Chapter 2, the instrumentation and the techniques that were used are discussed. Chapter 3 presents the study of NR-PM$_1$ measured by the HR-ToF-AMS in a remote site, without any human activities nearby, whereas in Chapter 4 the analysis of NR-PM$_1$ in a polluted urban site will be presented. Chapter 5 summarizes the conclusions of this work and suggestions for future work.
1.4 References


Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.


CHAPTER 2

INSTRUMENTATION

2.1 Atmospheric Aerosol Characterization Techniques

There are two basic approaches to measure the aerosol particles. The first one is the most traditional one, in which particles are deposited onto a collection surface (usually a filter or an impaction plate) and are then analyzed in the laboratory with a variety of analytical techniques. The second approach is the in-situ real-time characterization of the particles. The major advantages of the first approach are simplicity, low cost of the sampling devices, and analytical flexibility as the collected material can be analyzed with a variety of techniques. The major disadvantages of the traditional sample collection techniques are the high labor cost of the analysis, the long averaging times, the potential sampling artifacts (e.g. evaporation or adsorption on the filter) and the potential changes of the sampled aerosol in the often long periods between sampling and analysis. In contrast, real-time measurement methods provide almost instantaneous information about the particle concentration, size distribution and/or composition.

In this work we will focus on one of the state-of-the-art real time techniques: aerosol mass spectrometry.

2.1.1 Real-Time measurement methods

In real-time measurement methods the desired property of the aerosol can be derived almost immediately, as the sampling and the analysis is happening within the instrument. Aerosol properties such as mass concentration, number concentration, size distribution, number distribution, opacity, etc., can be measured by different direct-reading instruments. Direct-reading instruments use a sensing region; an aerosol either passes through or is collected in this region. The presence of the particles gives rise to a change in some property of the zone that is detected, followed by the use of a relationship between the detected change and the desired property of the aerosol.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

Optical instruments take advantage the interaction between airborne particles and visible light in a sensing region using the principles of light extinction and light scattering. Their response depends upon the size distribution and refractive index of the particles (Mark et al., 1998). Optical particle counters, photometers, and nephelometers are examples of optical direct-reading instruments.

*Time-of-flight* instruments can provide real-time high-resolution measurement of aerodynamic particle size and size distribution over a wide size range. As shown in Fig. 2.1, air is accelerated in a converging nozzle to a high velocity (>100 m s\(^{-1}\)) at the nozzle exit. Two narrowly focused laser beams are positioned in the jet about 100 μm apart.

**Figure 2.1** Schematic of the principle of operation of time-of-flight aerosol measurements.

Small particles can keep up with the accelerating air in the nozzle and exit with approximately the same velocity as in the air. Larger particles have lower velocities. As a particle passes through the laser beams, a brief pulse of scattered light is detected by a photomultiplier tube. The time interval between the two pulses is used to determine the average velocity of the particle. The larger or heavier the particle is, the lower its velocity in the timing zone will be. With suitable calibration and by knowing the distance (L) between the two laser beams, the particle's aerodynamic diameter can be determined based on the time needed to travel between the two beams.

### 2.2 The Aerosol Mass Spectrometer (AMS)

The Aerosol Mass Spectrometer (AMS) developed by Jayne et al. [2000] and commercialized by Aerodyne Research Incorporated (ARI), can provide continuous quantitative size and composition information for the non-refractory (NR) components of sub-micron atmospheric aerosol in real time. The AMS is capable of directly characterizing ambient aerosols, so no filters or off-line chemical analysis is necessary.
There are several versions of the Aerodyne AMS available, including the Quadrupole AMS (Q-AMS), the Compact Time-of-Flight AMS (C-ToF-AMS), the High-Resolution Time-of-Flight AMS (HR-ToF-AMS) and the Aerosol Chemical Speciation Monitor (ACSM). The Q-AMS is the first version of the instrument and uses a quadrupole mass analyzer. Drewnick et al. (2005) replaced the quadrupole analyzer with a compact time-of-flight mass spectrometer. Even though the C-ToF-AMS has better than unit mass resolution, this resolution is not generally adequate to separate ions of different elemental composition at a nominal mass to charge ratio ($m/z$). The HR-ToF-AMS was introduced by DeCarlo et al. (2006) and can distinguish among ions having the same nominal mass. This new version of the AMS uses a custom-designed Tofwerk AG high-resolution, orthogonal time-of-flight mass spectrometer. Finally, the ACSM is the last AMS introduced (Ng et al., 2011), an instrument ideal for routine monitoring, with many of the capabilities of the classic AMS such as acquisition of unit mass spectra but also with disadvantages including high detection limits, lack of sizing information etc. The HR-ToF-AMS is used in the present work.

![Figure 2.2 Schematic of the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer.](image)

The basic layout of the HR-ToF-AMS is depicted in Fig. 2.2. It consists of four individual, differentially pumped chambers: the aerosol sampling chamber, the particle-
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

Aerosol sampling chamber: Ambient air enters the system through a critical orifice (sampled at a flow rate of approximately 1.4 cm$^3$ s$^{-1}$) and passes through an aerodynamic lens, which focuses particles ranging from approximately 35 nm to 1 μm in size into a narrow beam (Jayne et al., 2000; Zhang et al. 2002; 2004b). This narrow beam (~ 1 mm diameter) created by the lens allows practically 100% particle transmission efficiency to the detector for particles in the size range between 70- 500 nm in diameter and reduced transmission for smaller and larger particles. The lens tube contains six precision orifice lenses with diameter ranging from 5 mm (inner diameter, id) at the entrance to 3 mm (id) at the exit. The first five lenses focus the particles onto the center line, while the final exit aperture is responsible of the supersonic gas expansion and particle acceleration into the vacuum system. The trajectories of 100 nm particles in the lens are shown in Fig. 2.3.

![Figure 2.3](image)

**Figure 2.3** FLUENT simulation results illustrating the focusing action of the aerodynamic particle beam forming lens. The results displayed are for 100 nm diameter spheres with a density of 1 gm cm$^{-3}$ [Jayne et al., 2000].

Particle sizing chamber: After the lens, the aerosol beam enters the particle-sizing differentially pumped chamber, where air is removed by a turbo molecular pump (Varian V-301NAV). A supersonic expansion at the end of the lens accelerates the particles into the sizing region ($10^{-5}$ Torr), where their size is determined by measuring their flight time along a known distance. Smaller particles accelerate to faster velocities while larger ones to slower velocities due to their inertia. A rotating mechanical chopper is located at the front end of the chamber, defining the start time of particle flight. The aerosol beam
passes the chopper wheel, which consists of a rotating disc with two radial slits positioned on a mount that is set in motion by a servo. The chopper can either let the beam pass freely (the ‘open’ position) or completely block it (the ‘blocked’ position, used for background measurements) or let groups of particles pass through at a user-defined rate of 100 - 150 cycles per second (known as the ‘chopped’ position). The position used depends on the mode of operation of the instrument. The end of particle flight is determined by the mass spectrometric detector.

**Particle evaporation and ionization chamber:** The particle evaporation and ionization chamber is connected to the particle sizing chamber through a 3.8 mm orifice. Both chambers are pumped by turbo molecular pumps to a pressure of $2 \times 10^{-5}$ Pa. The particle beam impacts onto a resistively heated surface, the vaporizer, which is located at the downstream end (Drewnick et al., 2005). The vaporizer is built from porous tungsten and its front section has an inverted cone shape (Fig. 2.4). Both the cone shape and the porosity are chosen to decrease the bouncing of the particles. The vaporizer is heated by conduction and its temperature can be tuned in a range from about 250°C up to 1000°C. The typical temperature used is 600°C.

After the impaction of the particles on the vaporizer, the non-refractory (NR) aerosol components are flash vaporized, within 50 – 100 μs. The major NR species include the organics, sulfate, nitrate, ammonium and chloride. Crustal material, sea salt, and black carbon are refractory and are not detected by the AMS.

The resulting vapor molecules are ionized by 70 eV emitted from a tungsten filament located next to the vaporizer. A schematic of the AMS vaporization and ionization regions is shown in Fig. 2.4.
HR-ToF-MS chamber: The resulting positive ions finally enter the HR-ToF-MS chamber, where a custom-designed Tofwerk AG (H-TOF Platform, Thun, Switzerland) high-resolution, orthogonal time-of-flight mass spectrometer is located. The ions are separated according to their mass-to-charge (m/z) ratio. As shown in Fig. 2.2, the HR-ToF-AMS includes ion optics for two modes of operation, referred to as V- and W-modes (DeCarlo et al., 2006). In V-mode ions follow a trajectory from the extraction region into the reflectron and back to the multichannel plate (MCP) detector (effective ion path length, L ≈ 1.3 m). In W-mode, ions exiting the reflectron are directed onto a hard mirror, which focuses them back into the reflectron for a second pass before traveling to the MCP detector (L ≈ 2.9 m). The V-mode is more sensitive, but the W-mode offers higher mass resolution. Signals from the MCP detector are amplified 55 times and are sampled at 1 GHz with an 8-bit analog-to-digital converter (AP240, Acqiris, Geneva, Switzerland).

Each chamber has its own pumping system. The differential pumping of the chambers reduces the sampled gas flow concentrating the particles by a factor of $10^7$ compared to the ambient air. In this way, with the exception of the major components of air (N₂, O₂, Ar, H₂O and CO₂) there is no detectable interference of other vapors in the measured particulate mass spectrum. A turbo pump consists of several turbines in series that rotate at such a speed (several thousand rpm), that in order for a gas molecule to reverse flow without striking a vane, it must be travelling at greater than its anticipated kinetic velocity. In order to achieve a sufficient rotational speed, these pumps must be operated...
at a low pressure (around 2 torr or less), so a diaphragm pump is used to remove the air from their exhaust during operation.

### 2.2.1 Modes of AMS operation

In the standard operating configuration, the AMS alternates between two modes: the *mass spectrum* (MS) and the *time of flight* (ToF) modes. It spends typically 15 seconds in each mode during a cycle, although this is user-defined and can be changed depending on the requirements of the experiment. The data are typically averaged over periods between 2 and 30 minutes. In this study 6 min averages are used, to synchronize the AMS measurements with those of other instruments.

In the MS mode, the mass concentration, the mass spectra and the chemical composition of the aerosol is measured. In this mode, the chopper alternates between the open and blocked positions approximately every 3 seconds while the mass spectrometer continuously scans, typically from *m/z* 0 to 300, at a rate of 1000 per second. In this way, a mass spectrum of the particles and gas beam is obtained by subtracting the average mass spectrum acquired when the chopper is in the blocked position from the average when the chopper is in the open position. The logging and control software records the multiplier signal as a function of *m/z*, generating mass spectra. An example mass spectrum is shown in Fig. 2.5.

![Figure 2.5](image.png)

**Figure 2.5** A typical AMS mass spectrum calculated as the difference between the ‘open’ and ‘blocked’ beam positions (here till *m/z* 120).
In ToF mode, the spinning chopper is in the beam chopped position. The particle beam is blocked most of the time allowing only a small fraction of the particles to pass through and reach the detection chamber. An optical sensor positioned on the chopper mount senses when a slit is in the right position. The time between particle impaction on the heater and detection of the resultant ions is normally of the order of microseconds, which is small compared to the milliseconds required by the particles to travel the length of the ToF region. When the particles reach the detection chamber, their flight time across the sizing chamber is determined, and from this the particle velocity and vacuum aerodynamic diameter are calculated. The mass distribution of the major NR species is depicted in Fig. 2.6.

The HR data analysis in this work was performed using the ToF-AMS analysis software SQUIRREL v1.51C and the HR-ToF-AMS data analysis software Peak Integration by Key Analysis (PIKA v1.10C) (Sueper et al., 2011) adapted in Igor Pro 6.22A (Wavemetrics).

### 2.2.2 Particle Collection Issues

The overall collection efficiency (CE) of the AMS must be quantified, in order to measure the size-resolved chemical composition via the AMS. The fraction of spherical particles that pass through the critical orifice and lens and finally impact the vaporizer, is called transmission efficiency $E_L(d_{va})$, where $d_{va}$ is the vacuum aerodynamic diameter.
Some of the particles, usually non-spherical ones, cannot be detected by the vaporizer as they may be spread of the particle beam in the vacuum chamber. In this case the CE can be decreased. The shape transmission factor, $E_S(d_{va})$, is defined as the fraction of irregularly shaped particles impacting the vaporizer, relative to spheres of the same $d_{va}$ (Huffman et al. 2005). The CE can be also decreased due to the particle bounce on the vaporizer surface before vaporization and detection, $E_B(d_{va})$, particularly for solid particles such as $(\text{NH}_4)_2\text{SO}_4$. The overall collection efficiency, $\text{CE}(d_{va})$ is defined as the product of the above factors:

$$\text{CE}(d_{va}) = E_L(d_{va}) \times E_B(d_{va}) \times E_S(d_{va})$$

Alfarra et al. (2004) determined the CE of six model particles consisting of volatile and non-volatile compounds. The liquid particles (dioctyl-sebacate, oleic acid, and nonylaldehyde) were measured with 100% CE while the other three solid compounds (adipic acid, succinic acid, and pyrene) had a CE=0.2-0.5. The CE of ammonium nitrate particles is close to unity and it is independent of the relative humidity (RH). In contrast, CE of ammonium sulphate is closely related to RH, varying from 1 at high RH to 0.5 or less at moderate RH. So, the phase of the measured by the AMS particle plays a key role. It has become clear that different AMS instruments operating in different environments at different temperatures, under different RH, may have different values of CE. Despite these studies, there are still important issues about the evaluation of CE of ambient aerosol particles.

To deal with the uncertainty of the CE during the field campaigns discussed in this work, we have used the algorithm developed by Kostenidou et al. (2007), which estimates the CE by comparing and matching the volume distributions measured by a SMPS and the mass distributions measured by the AMS. The algorithm calculates also the organic aerosol (OA) density.

### 2.2.3 Positive Matrix Factorization (PMF)

The need of identifying the sources of ambient aerosol resulted in the development and use of the corresponding mathematically analysis techniques. Such a model for factor analysis was proposed by Paatero and Tapper (1994), the positive matrix factorization (PMF), in order to solve the un-mixing matrix problem:
\[ \mathbf{X} = \mathbf{G} \mathbf{F} + \mathbf{E} \quad (2.2) \]

where, \( \mathbf{X} \) is a matrix of measured data, of dimensions \( m \times n \), \( \mathbf{G} \) the first unknown matrix (scores) of dimensions \( m \times p \), \( \mathbf{F} \) the second unknown matrix (loadings) of dimensions \( p \times n \) and \( \mathbf{E} \) is the matrix of residuals (errors). PMF, unlike other factor analysis techniques, produces (by using a least-squares algorithm) a positive solution (the elements of \( \mathbf{G} \) and \( \mathbf{F} \) are constrained to be positive).

PMF was applied for the first time to the organic spectra measured by the AMS, by Lanz, et al. (2007). These authors treated the time-dependent measured organic spectra as the \( \mathbf{X} \) matrix, the resulting constant spectra of the factor (source profiles) as the \( \mathbf{F} \) matrix and the mass contribution of this factor as \( \mathbf{G} \). A schematic of the PMF model is shown in Fig. 2.7.

**Figure 2.7** Schematic of PMF analysis of an AMS spectra dataset. The time series of the factors make up the matrix \( \mathbf{G} \) and the mass spectra of the factors make up the matrix \( \mathbf{F} \) in Eq. (2) [Ulbrich et al., 2009].

In this work, the PMF2 toolkit described by Ulbrich et al. (2009) is used. In this toolkit extra solutions are calculated by the use of different pseudorandom values in the PMF algorithm, called “seeds”.

Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry. 21
One of the challenges present in this analysis is that the number of factors, which correspond to the major aerosol sources affecting the receptor, is typically unknown. In addition, for the correct interpretation of the factors calculated by PMF, a number of tests are performed, such as the comparison of calculated factor spectra to measured reference ones, the correlation of the factor’s resulting time-series with other variables (usually concentrations of other pollutants, but also meteorological variables like wind direction), etc., (Ulbrich et al., 2009). As a result, PMF allows us to deconvolute the organic signal to contributions of various primary and secondary organic sources.

2.3 Scanning Mobility Particle Sizer (SMPS)

The Scanning Mobility Particle Sizer (SMPS) is a system that measures the size distribution of aerosols in the size range from a few nm to hundreds of nm depending on the chosen operation conditions. Particles are classified with an Electrostatic Classifier and their concentration is measured with a Condensation Particle Counter (CPC).

2.3.1 Electrostatic Classifier

The electrostatic classifier consists of a sample pre-conditioner, a bipolar charger and a Differential Mobility Analyzer (DMA). The aerosol first enters the pre-conditioner (usually an impactor or a cyclone), which excludes particles larger than a certain aerodynamic diameter, by inertial impaction. The aerosol flow is accelerated through a nozzle directed at a flat plate, which deflects the flow to form a 90° bend in the streamlines. Particles with sufficient inertia are unable to follow the streamlines and impact on the plate.

In the electrostatic classifier, the Kr-85 bipolar charger (also referred to as neutralizer) exposes the aerosol particles to high concentrations of bipolar ions. The particles and ions undergo frequent collisions until there is a state of equilibrium, in which the particles carry a bipolar charge distribution. The charged aerosol passes from the neutralizer into the main portion of the DMA (Fig. 2.8). The DMA contains two concentric metal cylinders. The polydisperse aerosol and sheath air (particle free air) are introduced at the top of the Classifier and flow down the annular space between the cylinders. The aerosol surrounds the inner core of sheath air, and both flows pass down the annulus with no mixing of the two laminar streams. The inner cylinder, the center rod, is maintained at a
negative voltage, while the outer cylinder is electrically grounded. This creates an electric field between the two cylinders.

The electric field between the two concentric cylinders separates the particles according to their electrical mobility which is inversely related to particle size. Particles with a positive charge move across the sheath flow towards the central rod, at a rate determined by their electrical mobility. Only some particles within a narrow range of electrical mobility have the correct trajectory to exit through the sample slit at the bottom of the center rod of the DMA (Fig. 2.8). These particles are transferred to a particle sensor to determine the particle concentration. Particles with negative charge(s) are repelled towards and deposited on the outer wall, while particles with no charge exit with the bypass air. The size of particles exiting through the slit is determined by the particle charge, central rod voltage, and flows within the DMA. The electrical mobility of these selected particles is a function of flow rates, DMA geometric parameters and the voltage of the center electrode.
2.3.2 Condensation Particle Counters (CPC)

The monodisperse particle stream exiting the DMA is counted by a CPC. In a supersaturated vapor, suspended particles act as nuclei for vapor condensation and may grow to form droplets. This process is referred to as heterogeneous nucleation. The CPC uses this mechanism to measure the number concentration of sub-microneter aerosol particles.

![Flow schematic of a butanol-based CPC (3775).](image)

The saturation ratio of the condensing vapor determines the smallest particle size detected by the CPC. The saturation ratio is defined as the actual vapor partial pressure, $p$, divided by the saturation vapor pressure, $p_s$, at a given temperature $T$. The condensing vapor is either butyl alcohol or water. The relationship between the saturation ratio and the minimal particle size is given by the Kelvin equation:

$$\frac{p}{p_s} = \exp\left(\frac{4\sigma M}{\rho R D_p T}ight) \quad (2.3)$$

where $\sigma$ is the surface tension, $M$ the molecular weight, $\rho$ the density of the liquid, $D_p$ the Kelvin diameter, $R$ the universal gas constant and $T$ the absolute temperature.
The Kelvin diameter is the droplet diameter that will neither grow nor evaporate at the saturation ratio \( p/p_s \). For every droplet size there is a saturation ratio that will exactly maintain the particle size. If the saturation ratio is too small, the particle evaporates; if it is too great, the particle grows.

The butanol-based CPCs promote particle growth using thermal cooling. The water-based CPCs make use of the high diffusivity of water vapor and promote particle growth in the heated condenser. In either case, as the temperature difference between the saturator and the condenser increases, the saturation ratio increases, thereby lowering the minimum particle diameter that can be detected. Once the particles have grown to an optically detectable size (typically, 2 to 3 micrometers), they pass through a light beam and scatter light onto a photodetector.

## 2.4 Multi-angle Absorption Photometer (MAAP)

Aerosol absorption was monitored continuously during our studies by a Multi Angle Absorption Photometer (MAAP, Thermo model 5012; Petzold and Schönlinner 2004). The MAAP measures black carbon mass loadings based on aerosol optical absorption. Like aethalometers, the MAAP makes this measurement on particles collected on a filter substrate. MAAP’s inlet was heated to 70°C prior to analysis in order to remove water and organics.

In the MAAP instrument the optical absorption coefficient of aerosol collected on a filter is determined accounting for multiple scattering effects and absorption enhancement due to reflections from the filter. This calculation is based on the transmitted and reflected phase functions which are defined by directly measured values of transmission, direct and diffuse back scattering. Full details of the algorithms used are given by Petzold et al. (2002; 2004). A schematic of the MAAP optical head is shown in Fig. 2.10. Comparisons between the MAAP technique and the thermal reference method presented by Petzold et al. (2002) for various types of test and ambient aerosol showed that a constant specific absorption can be used to convert the optical absorption coefficient to black carbon mass. The following equation is used by the MAAP instrument to calculate black carbon mass loading:
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

\[ MBC = \frac{(1 - \omega_0) \ln(tr) \text{AREA}}{\sigma_{BC}} \]  

(2.4)

where \( MBC \) is the mass of black carbon deposited on the filter, \( \omega_0 \) is the single scattering albedo (determined from the radiative transfer considerations described above), \( tr \) is the transmittance, \( \text{AREA} \) is the area of the collection spot (equal to 2 cm\(^2\)) and \( \sigma_{BC} \) is the specific absorption of black carbon (6.6 m\(^2\) g\(^{-1}\)). Then the black carbon concentration, \( CBC \) can be calculated by:

\[ CBC = \frac{\Delta MBC}{VOL} \]  

(2.5)

where \( \Delta MBC \) is the difference in \( MBC \) from the previous sample and \( VOL \) is the volume of air sampled.

The MAAP operates at a wavelength of 670 nm, has a 10 s time response, features automatic filter changing based on absolute transmission, and constant sample flow rate (1000 L hr\(^{-1}\)) controlled by a variable speed pump.

**Figure 2.10** Schematic diagram of the MAAP detector block showing the arrangement of the detectors used relative to the sample collected on the filter.
2.5 References


CHAPTER 3

ORGANIC AEROSOL IN A REMOTE SITE IN THE EASTERN MEDITERRANEAN

3.1 Sampling Site and Instrumentation

The Finokalia Aerosol Measurement Experiment (FAME-11) field campaign was conducted in Finokalia, Crete, from September 24 to October 23 in 2011. Finokalia (35° 20'N, 25° 40'E) is a remote coastal site located in northeast Crete (Fig. 3.1). The measurements took place at the Finokalia Station, which is run by the Environmental Chemical Processes Laboratory of the University of Crete (ECPL).

Figure 3.1 NASA satellite images of Europe and of the island of Crete, indicating the location of the sampling station at Finokalia.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

The Finokalia station is located at the top of a hill and at an elevation of 250 m facing the sea. The station is isolated and at least 15 km away from any anthropogenic sources of pollution (Kouvarakis et al., 2000). It is located 60 km northeast of Heraklion, the nearest large urban center (with 150,000 inhabitants), and 400 km southeast of Athens. Additional information about the Finokalia station can be found in Mihalopoulos et al. (1997), Sciare et al. (2003a; b), and Gerasopoulos et al. (2006).

The instrumentation used, included an Aerodyne High-Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS), an Aerodynamic Particle Sizer Spectrometer (APS) and a Scanning Mobility Particle Sizer (SMPS, TSI 3034) for the measurement of the aerosol size distribution, a Multi-Angle Absorption Photometer (MAAP) for the measurement of black carbon and a Tapered Element Oscillating Microbalance (TEOM) for the continuous measurement of the PM$_{2.5}$ and PM$_{10}$ mass concentrations. The SMPS was operating at a set flow rate of 0.5 L min$^{-1}$, limiting the measurable size range to 10-500 nm. The APS measured the size distribution from approximately 400 nm to 10 μm. The HR-ToF-AMS was operating under both the V and W modes to take advantage of the higher sensitivity and higher resolution of each mode respectively (DeCarlo et al., 2006). Filter samples were collected and analyzed off-line, providing a separate measure of the concentration of inorganic and organic aerosol composition for PM$_{1}$ and PM$_{2.5}$. The particles were sampled at ambient relative humidity. Gas-phase monitors for NO$_x$, CO, and CO$_2$ were also used. Meteorological data (temperature, relative humidity, solar radiation, wind speed and direction, etc.) were collected by a dedicated meteorological station.

![Figure 3.2 Photograph of the Finokalia station in Crete.](image-url)
3.2 Measurement Overview

3.2.1 Meteorology

The Finokalia station is a background station, operating constantly since 1993. FAME-11 is the third FAME campaign taking place in Finokalia station. The previous ones were conducted during the summer of 2008 (FAME-08) and the winter of 2009 (FAME-09) (Hildebrandt et al., 2010a; 2011).

During this campaign, the ambient temperature ranged from 12°C to 26°C, while the average temperature was 19°C (Fig. 3.3). There was heavy rain from October 9 to 11, causing major problems to the electrical network of the station. For this reason, the measurements were stopped October 11 to 19 due to repair the power supply at the station.

![Figure 3.3 Temperature time-series during the FAME-11 campaign.](image)

The solar radiation during FAME-11 had the same intensity as the FAME-09 campaign which took place during February/March (Fig. 3.4). Both periods were quite cloudy. On cloud-free days, solar radiation reached a maximum value of 920 W m², while during the summer of 2008 1050 W m² and 1030 W m² during the winter/early spring of 2009.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

3.2.2 Results

Particle size distributions ranging from 10 to 500 nm were monitored via a Scanning Mobility Particle Sizer (SMPS). New particle formation, the spontaneous creation of new nanometer-sized particles in the atmosphere, is often an important source of particle number in remote regions. During the FAME-11 campaign, only one nucleation event was recorded by the SMPS, during October 1. The time series of the number and size distribution, measured via the SMPS is shown in Fig. 3.5.

![Figure 3.4 Average diurnal profiles of the solar radiation during the FAME campaigns.](image)

![Figure 3.5 Number and size distribution time series from FAME-11. The y-axis is the particle diameter and the color indicates the particle number concentration density.](image)

The combination of the number concentration and distribution of particles between 10 and 500 nm in diameter, measured with the SMPS and the AMS data, allowed us to
estimate the time-dependent collection efficiency (CE) for the AMS for every four hours by applying the Kostenidou et al. (2007) algorithm. The CE was found to be on average 0.5, while the average OA density was 1.34 g m\(^{-3}\), determined by the same algorithm. The mass concentrations presented have been corrected for CE (Fig.3.6).

![Graph showing PM\(_1\) composition and mass concentrations](image)

**Figure 3.6** Time series of PM\(_1\) composition (as a percent) and mass concentrations of the major PM\(_1\) components measured by the HR-AMS and the MAAP. Source labels point to the origin of the air masses affecting Finokalia at the corresponding periods.

The hourly averaged PM\(_1\) mass concentrations (in \(\mu g \ m^{-3}\)) of organic aerosol (OA), nitrate, sulphate, ammonium, chloride and black carbon (BC), (from the MAAP) are shown in Fig. 3.6. The dry PM\(_1\) concentration ranged from 0.4 \(\mu g \ m^{-3}\) to 32 \(\mu g \ m^{-3}\) with an average of 10.1 \(\mu g \ m^{-3}\). PM\(_1\) nitrate concentrations measured by the AMS were low during the study (about 0.12 \(\mu g \ m^{-3}\) on average) and similar to FAME-08 (less than 0.1 \(\mu g \ m^{-3}\) on average). Sulfate was the dominant species (46%), followed by organics (34%) and ammonium (14%) (Fig 3.7).

By running the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) analysis, we identified the trajectories of the air masses arriving at the site and the origin of the measured aerosol (Fig. 3.6). During the first part of the campaign, air masses were arriving at the site mainly from Turkey. Air masses coming from Africa appeared on
October 6-7, increasing the PM$_1$ levels, while during the last days of the campaign the air was coming from Athens.

**Figure 3.7** Average composition of PM$_1$ during the 2011 campaign in Finokalia. The small amounts of sea-salt and dust are not included.

The average diurnal profiles for the main PM$_1$ components during the campaign are shown in Fig. 3.8. Sulfate, ammonium and organics had a minimum at around 9:00 but their diurnal profiles were rather flat. This morning minimum could be due to the morning growth of the planetary boundary layer and the mixing of cleaner air from aloft with the dirtier air near the ground. BC shows no significant diurnal variation, indicating the lack of combustion sources, but also the fact that the air aloft had similar BC concentrations than the air near the ground. These differences in composition observed during the morning mixing, suggest that the lower concentrations aloft could be due to cloud processing and removal of the particles that were aloft that did not affect as much the BC containing particles. Overall, the lack of strong diurnal variations is consistent with the absence of local sources near the field site and the fact that most of the PM$_1$ mass is transported to the site from other areas.
The fine PM anion to cation equivalent ratio was found to be smaller than unity and on average 0.77 with a standard deviation of 0.07, indicating that the fine PM was acidic most of the time during the campaign of FAME-11. Similar acidic behavior of the aerosol has been observed for the site in previous measurements (Hildebrandt et al., 2010a; Bougiatioti et al., 2014).

Figure 3.9 presents the campaign average, mass distributions of the ambient aerosol. During FAME-08 the sulfate distribution peaked at 470 nm and organics at 430 nm. The distributions were slightly shifted from each other in the summer of 2008, while in the FAME-11 campaign, all modes were at the same diameter (350 nm), suggesting that the submicrometer particles had similar composition.
The atomic ratios for oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) as well as the ratio for total organic mass to organic carbon mass (OM/OC) can be determined by the HR-ToF-AMS. O/C ratio characterizes the oxidation state of OA. The hourly averaged time series for the three elemental ratios are shown in Fig. 3.10. The average O/C ratio was 0.68±0.09, the H/C ratio was 1.38±0.07 and OM/OC ratio was 2.06±0.1. The OM/OC ratio was lower than in FAME-08 (2.2) but higher than FAME-09 (1.8) (Hildebrandt et al., 2010a; 2011). During October 9 to 11, the OM/OC and O/C ratios reached their minimum value while H/C its maximum. This indicates that relatively fresher aerosol was arriving at the site during that period. During those days heavy rain obliged us to use cars to reach the site and these emissions may have affected the dataset.

The average diurnal profile of each elemental ratio is presented in Fig. 3.11. The H/C ratio does not present any significant variation throughout the day. OM/OC and O/C increase later during the day, as expected from SOA formation associated with the increased photochemistry in the afternoon.
In Fig. 3.12 we compare corrected six hour-averaged AMS sulfate measurements to the PM$_{2.5}$ filter measurements (slope=0.98, $R^2=0.71$). In order to compare the organic mass (OM) measurements from the AMS to the daily averaged organic carbon (OC) measurements from the filters (PM$_1$), the latter were multiplied with the average calculated OM/OC ratio of 2.06. The resulting comparisons for both sulfate and organics are quite encouraging suggesting that the collection efficiency calculated by the Kostenidou et al. (2007) was accurate.
Figure 3.11 Average diurnal profiles of OM/OC, O/C and H/C ratios for FAME-11. The error bars correspond to one standard deviation of the measurements.

Figure 3.12 Comparison (a) of PM$_1$ OM mass from the AMS and filters on the left and (b) of PM$_1$ sulfate mass from the AMS and PM$_{2.5}$ sulfate from filters on the right.
3.2.3 PMF source apportionment analysis of organic PM

The measured organic mass spectra from the HR-AMS were deconvoluted into different components using positive matrix factorization (PMF) analysis (Paatero and Tapper, 1994; Paatero 1999). For this dataset, we have excluded data between October 9 and 11. During those days the heavy rain obliged us to use cars to reach the site. The corresponding emissions have contaminated the organic aerosol measurements which do not represent any more the regional air masses.

Through PMF analysis, it was determined that two factors could represent the data for this campaign dataset. The factors were assigned to Semi-Volatile Oxygenated Organic Aerosol (SV-OOA) and Low-Volatility Oxygenated Organic Aerosol (LV-OOA). These OOA types are mainly characterized by their extent of oxidation (high O/C value). The fact that there was no primary OA (POA) factors identified in the OA over the entire campaign is not uncommon for this location. During FAME-08 the OA measured, was also deconvoluted in two oxygenated OA factors, a more and a less oxidized one (Hildebrandt et al., 2010a). In Fig. 3.13 the hourly time series of the two factors and their contribution to OM are depicted. During the first days of the campaign and when the air masses were coming from Africa (October 6 to 7) LV-OOA is the dominant OA factor with higher concentration. During the middle and last days of the measurements SV-OOA had a bigger contribution to the OM. This may be attributed to the different air masses arriving at the site (from Turkey in the beginning and from Athens in the end) and the different meteorological conditions (it was much colder during the end of the campaign).

The average percentage (by mass) of SV-OOA was 56% and 44% of LV-OOA (Fig. 3.13). In FAME-08 the split of the factors was 41 to 59 split for SV-OOA to LV-OOA, suggesting that during the 2008 summer campaign the OA was more oxidized. Fig. 3.14 shows the mass spectra of the two OOA factors, identified by PMF for the FAME-11 campaign. Oxygenated Organic Aerosol (OOA) is a proxy of secondary OA. Its spectrum is characterized a strong peak at m/z 44 (mostly due to CO$_2^+$) and a lower one at 43 (mostly due to C$_2$H$_3$O$^+$). The intensity of other fragments in its spectrum is low. The more the organic aerosol stays in the atmosphere, the more the fraction of m/z 44 (CO$_2^+$), increases (Ng et al., 2010). OOA represents the chemically aged OA and is mostly due to long range transportation from other areas.
Figure 3.13 The concentration of PMF factors and their average composition at Finokalia site. The contribution of each factor to total OM is also shown (top figure).

Low Volatility Oxygenated Organic Aerosol (LV-OOA, empirical formula $\sim$C$_8$O$_{5.5}$H$_{10}$) is usually strongly correlated with nonvolatile secondary species such as sulfate and has an elevated O/C (0.85 in our case), consistent with regional, heavily aged OA (Jimenez et al., 2009).

Semi Volatile Oxygenated Organic Aerosol (SV-OOA, empirical formula $\sim$C$_8$O$_3$H$_{11}$) is usually correlated with semi-volatile species such as ammonium nitrate and has a lower O/C (0.62 in FAME-11), consistent with less photochemically aged OA.
Hildebrandt et al. (2010a) argued that LV-OOA and SV-OOA, at least in remote areas like Finokalia, do not correspond to different sources or formation processes but rather at the upper and lower limits of the oxidation state of the OOA during the measurement period. PMF uses then these extremes to explain the intermediate states using linear combinations of the corresponding factors. The O:C of the two factors in FAME-11 was 0.62 and 0.85 respectively. During FAME-08, a period with high photochemical activity the corresponding O:C values were 0.6 and 0.9.

LV-OOA during FAME-11 correlated well with sulfate measured by the AMS ($R^2=0.86$) and ammonium ($R^2=0.88$), whereas SV-OOA correlated weakly ($R^2=0.3$) with either of the two species. LV-OOA was correlated also with BC ($R^2=0.62$) something that is rarely observed. SV-OOA showed a good correlation with AMS nitrate ($R^2=0.67$) and chloride ($R^2=0.44$). The corresponding correlation plots are shown in Figure 3.15.

**Figure 3.14** Mass spectra of the four OA factors with calculated corresponding atomic ratios.
The average diurnal profile for both OOA factors is depicted in Fig. 3.16. The LV-OOA concentration reaches a minimum at 10:00 suggesting that the mixing during the morning reduces the average oxidative state of the OA but then starts to increase reaching a maximum at 19:00. The SV-OOA has the opposite temporal profile with a weak maximum at 08:00 and a strong minimum from 16:00 to 19:00. This variation suggests that there is regional photochemical activity converting the SV-OOA to LV-OOA from 10:00 to around 19:00. The LV-OOA diurnal profile is quite similar to that of sulfate but a lot stronger. The maximum average LV-OAA is almost three times as much as the minimum. The LV-OOA and SV-OOA profiles in FAME-11 are qualitatively quite similar to those observed during FAME-08 but a lot stronger. In FAME-08 the maximum LV-OAA was only 50% more than the minimum (Hildebrandt et al., 2010a).
Both OOA factors are highly oxygenated, as evidenced by the large contribution from \( \text{CO}_2^+ \) at \( m/z \) 44 (Aiken et al., 2009). Often, instead of the actual value of mass for each \( m/z \), its fractional contribution is used. So, the fraction of organic mass at \( m/z \) 44, is defined as 
\[
\text{f}_{44} = \frac{[m/z \ 44 \ \text{(in \ \mu g \ m}^{-3})]}{\text{OM (in \ \mu g \ m}^{-3})},
\]
where OM is the total mass concentration of the organic aerosol. Similarly, we define \( \text{f}_{43} \) and \( \text{f}_{57} \). Their hourly time series are depicted in Fig. 3.17. The fraction of organic mass at \( m/z \) 44 (\( \text{f}_{44} \)) was on average \( 0.18 \pm 0.026 \), \( \text{f}_{43} \) was \( 0.056 \pm 0.008 \) and \( \text{f}_{57} \) was \( 0.009 \pm 0.003 \). \( \text{f}_{43} \) is often used as a proxy for moderately oxidized organic aerosol and \( \text{f}_{57} \) is used as a proxy for fresh, hydrocarbon-like organic aerosol (HOA) (Aiken et al., 2009). Their diurnal profiles are shown in Fig. 3.18. The diurnal cycle of \( \text{f}_{44} \) is quite similar to that of sulfate, LV-OOA and \( \text{f}_{44} \) described in Hildebrandt et al. (2010a) for the summer of 2008. It presents two peaks, a smaller one during the early morning hours and a stronger one at around 19:00 in the afternoon, suggesting that organic aerosol becomes more oxidized in the afternoon, when the photochemical activity is higher. The diurnal profile of \( \text{f}_{43} \) is rather flat, without any significant peak throughout the day, and only a small decrease around the evening when \( \text{f}_{44} \) peaks. The diurnal cycle of \( \text{f}_{57} \) is quite stable as well, but a weak peak at around 08:00-11:00 is visible. This may be attributed to the fresh aerosol, emitted from our cars at the bottom of the hill of the site. No evening peak was detected.

**Figure 3.16** Average diurnal profiles of the two OOA factors during FAME-11.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

**Figure 3.17** Time series of $f_{43}$, $f_{44}$ and $f_{57}$.

**Figure 3.18** Average diurnal profiles of $f_{43}$, $f_{44}$ and $f_{57}$. 
In the FAME-11 OA, the LV-OOA component exhibited $f_{43} = 5\%$ and $f_{44} = 21.9\%$; the SV-OOA component exhibited $f_{43} = 6.7\%$ and $f_{44} = 17.4\%$. During FAME-08 one of the OOA components exhibited $f_{43} = 4.5\%$ and $f_{44} = 21.7\%$; the other OOA component exhibited $f_{43} = 6.5\%$ and $f_{44} = 13.1\%$ (Hidebrandt et al., 2011). In the FAME-09 only one OOA factor was derived from PMF analysis and its $f_{43}$ was $4.6\%$ and $f_{44}$ was $16.8\%$. The FAME-11 OOA components are closer to these of FAME-08. The average OOA extent of oxidation of FAME-11 ($f_{43} = 5.9\%$ and $f_{44} = 19.4\%$) was greater than the OOA of FAME-09.

Ng et al. (2010) assembled OA data from AMS measurements in different locations around the world and plotted $f_{44}$ versus $f_{43}$ for the OA. They found that the values of all datasets fell inside the same triangle with the more oxidized OA near the top of the triangle.

![Figure 3.19](image_url)  
**Figure 3.19** Organic aerosol composition in the Ng et al. (2010) triangle plot: $f_{44}$ vs. $f_{43}$, for the OA of the whole FAME-11 campaign. Also, the average OA, LV-OOA and SV-OOA contribution is shown with black dots.
Figure 3.19 depicts the whole campaign’s OA data and also the location of the PMF factors. Figure 3.20 shows the FAME-11 average OA data and also the individual PMF factors for the various campaigns.

![Figure 3.20](image_url)

**Figure 3.20** Organic aerosol composition in the Ng et al. (2010) triangle plot: $f_{44}$ vs. $f_{43}$. The dots correspond to the average OA of the three FAME campaigns, and to the fragments of OOA factors.

### 3.3 Conclusions

The fine PM measured during FAME-11 by the AMS and the MAAP was mostly ammonium sulfate and bisulfate (60%), organic compounds (34%), and BC (5%). During the measurement period PM$_1$ concentrations ranged from 0.42 to 32 μg m$^{-3}$ with an average value of 10±6.8 μg m$^{-3}$. The aerosol sampled originated mainly from Turkey during the first days of the study, but also from Athens and Northern Greece during the last days of the campaign. The OA was oxygenated with an average O/ C ratio of 0.68 and an average OM/OC of 2.06. Only one new particle formation event was recorded for the whole campaign due to the relatively low photochemical activity and the relatively high concentrations. The event occurred during one of the relatively clean sunny periods.
The acidity of the aerosol that signifies the lack of ammonia and other bases like the amines, may have also contributed to this lack of nucleation events.

By performing PMF analysis on the organic spectra for the whole dataset the organic aerosol (OA) composition could be explained by two components: a low volatility factor (LV-OOA) and a semi-volatile one (SV-OOA). Hydrocarbon-like organic aerosol (HOA) was not present, which is consistent with the lack of strong local sources. LV-OOA correlated well with sulfate, ammonium and surprisingly with BC. SV-OOA correlated quite well with nitrate and chloride.

The OA was less oxygenated than during the summertime FAME-08 period due to the lower photochemical activity. There was evidence of significant photochemical processing taking place during daylight hours.
3.4 References


Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry. 49
CHAPTER 4

WINTERTIME AIR POLLUTION IN PATRAS

4.1 Introduction

Patras is the third biggest city of Greece with a population of around 250,000. Previous studies in Patras focused on radioactivity (Papaefthymiou et al., 2005), on monitoring of total suspended particles (Yannopoulos, 2008) and on characterizing the PM$_{2.5}$ composition and the contribution of long range transport (Pikridas et al., 2013). Pikridas et al. (2013) argued that local traffic was not the major contributor to PM$_{2.5}$. Elevated concentrations of organics and potassium during the wintertime, which correlated well with each other, indicated that biomass burning was a major local source. In order to test this hypothesis, an intensive campaign was performed in 2012 to quantify the severity of the problem using real-time measurements and the contribution of residential wood burning.

4.2 Sampling Site and Instrumentation

The sampling location was in the suburbs of the city of Patras (4 km away from the city centre) in the campus of Technological Educational Institute of Patras (TEI) (38°13′N 21°45′E) (Fig. 4.1). The measurements took place during the winter of 2012 (February 26 to March 5).

The instrumentation used in the TEI campus included an Aerodyne High-Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS) and a selection of monitors such as an Aerodynamic Particle Sizer Spectrometer (APS), a Scanning Mobility Particle Sizer (SMPS, TSI 3936L) and a Tapered Element Oscillating Microbalances (TEOM), measuring on-line the aerosol size distribution.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

In addition, a filter sampler and a Multi-angle Absorption Photometer (MAAP) were deployed at the center of Patras (Fig. 4.1) at an elevation of approximately 20 m above sea level, providing information about the spatial distribution of pollution Fig. 4.2.

4.3 Measurement Overview

4.3.1 Meteorology

During the campaign, the ambient temperature ranged from $4^\circ$C to $15.7^\circ$C. The average temperature was $11^\circ$C and, as expected, was anti-correlated with relative humidity (RH) (Fig. 4.3).
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

The wind speed (in m/s) and wind direction (in degrees) distributions in the center of Patras are shown in Fig. 4.4. Zero degrees correspond to north while 90° to the east, 180° to south and 270° to west. Please note that due to the orography of the area these are local wind directions and do not correspond to the overall regional wind patterns.

4.3.2 Results

The combination of the AMS data with ambient number concentration and distribution of particles between 10 and 500 nm in diameter, measured with an SMPS, allowed us to estimate a time-dependent collection efficiency factor (CE) for the AMS for every hour by applying the Kostenidou et al. (2007) algorithm. The density of organics was also...
estimated by the same algorithm and its mean value was 1.45±0.04 g cm$^{-3}$. In Fig. 4.5 the average diurnal variation for both CE and organic density is shown. The mean value of the CE was 0.77±0.05. The estimated CE for this data set is significantly higher than the standard CE of 0.5 used in most studies. One reason for this difference may be that, in other studies, the aerosol is often dried before sampling with the AMS. Drying the particles can change the physical state of the particles from liquid to solid, which may result in increased particle bounce on the vaporizer, decreasing CE (Matthew et al., 2008).

![Graph showing diurnal variation of CE and density of organics.](image)

**Figure 4.5** The diurnal variation of CE and density of organics.

In Fig. 4.6 the hourly total mass concentration of NR-PM$_1$ and the ambient temperature is shown. High PM$_1$ concentrations were observed during the evenings of February 29, March 2, 3 and 4.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

The mass concentrations (in $\mu g\ m^{-3}$) of organic matter (OM), nitrate, sulphate, ammonium, chloride, and black carbon (from the MAAP) are shown in Fig. 4.7. The MAAP was in the center of Patras, about 4 km away from the TEI location. The major component of PM$_1$ was organic matter which increased dramatically reaching levels up to 82 $\mu g\ m^{-3}$ during the evening. The organic aerosol concentration also increased during morning rush hour, but the corresponding concentrations were less than 20 $\mu g\ m^{-3}$. BC closely followed the trend of organic aerosol with maximum BC mass concentration of approximately 8 $\mu g\ m^{-3}$ during nighttime and 4 $\mu g\ m^{-3}$ during rush hour in the mornings. Nitrates followed a similar trend, but sulphate concentrations had smaller fluctuations during the campaign, indicating a different source origin.

In general, organic matter was the most abundant species (73% of PM$_1$) throughout the campaign, followed by sulphate, BC, ammonium and nitrate. The average composition of the main aerosol components is presented in Fig. 4.8.
Figure 4.7 The hourly averaged PM$_1$ composition by the HR-AMS at the TEI site and black carbon measurements of the same period at Patras center. Different scales are used for each species. Also, the contribution of each constituent of the dry PM$_1$ mass is shown.
Figure 4.8 Average composition of PM$_1$ during the 2012 campaign in Patras.

Figure 4.9 shows the average mass distributions for the ambient aerosol for the whole campaign. The modes of the different aerosol species (sulfate, organics, ammonium, chloride and nitrate) are at different diameters, implying that the PM$_1$ particles during the sampling period had different composition at different size ranges.

Figure 4.9 The campaign-average size distributions of the aerosol species measured by the AMS versus vacuum aerodynamic diameter.

The average diurnal profiles for the main NR-PM$_1$ species during the campaign are shown in Fig.4.10. OM and BC show two significant peaks during the day. The first one appeared at around 8:00 am (Local Standard Time, LST), which coincides with the rush
hour traffic and the second one at 19:00 in the evening. During the evening the OM and BC concentrations increased and were responsible for almost 90% of the total NR-PM$_1$ mass, until around midnight. Sulfate shows a rather flat profile during the day, while nitrate presents three peaks, of which two, coincide with those of OM and BC. This suggests that nitrates and OM had at least to some extent, similar sources. The diurnal variation of chloride is not shown here, but it had a major morning peak, which could be due to two olympic-size swimming pools, which are located in a major athletic center, less than 1 km from the sampling site.

![Figure 4.10](image-url) Average diurnal profiles of the concentrations of the major PM$_1$ components. The error bars correspond to one standard deviation of the measurements.

The organic-mass to organic-carbon ratio (OM/OC) and oxygen-to-carbon ratio (O/C) ratio are important characteristics of the organic aerosol. For many years the OM/OC ratio was assumed to be equal to 1.4 (White and Roberts, 1977). A decade ago, Turpin and Lim (2001) recommended values of 1.6 ± 0.2 and 2.1 ± 0.2 for urban and rural areas, respectively. Now it is possible to calculate it by the elemental analysis of the individual organic peaks of the high resolution AMS data. The mean OM/OC ratio was found to be 1.59 with a standard deviation of 0.1 (Fig. 4.11).

The O:C of organic aerosol is a useful metric of the extent of oxidation of the OA and can be calculated from the HR-AMS measurements and increases as the aerosol is exposed to
atmospheric oxidants (Grieshop et al., 2009b; Sage et al., 2008). Also, the elemental analysis gives the hydrogen-to-carbon (H/C) and nitrogen-to-carbon (N/C) ratio. The hourly averaged averaged time series of OM/OC, O/C and H/C ratios are shown in Fig. 4.11.

![Graph showing OM:OC, H:C, and O:C ratios over time.](image)

**Figure 4.11** Elemental ratio analysis, hourly averaged times series of OM/OC, O/C and H/C ratios.

The average O/C ratio was low at $0.33\pm0.07$ and the H/C ratio high at $1.53\pm0.05$. This is consistent with the organic aerosol being heavily dominated by primary emissions (Allan et al., 2010). The estimated N/C ratio (not shown here) was very low at $0.02\pm0.003$. Fig. 4.12 depicts the diurnal variation of OM/OC, O/C, and H/C ratios.
4.3.3 PMF source apportionment analysis of NR-PM$_1$

Positive matrix factorization (Paatero and Tapper, 1994) was applied to the organic aerosol data, measured by the HR-ToF-AMS. The PMF analysis deconvoluted the organic aerosol spectra into four factors. The first one is a Biomass Burning Organic Aerosol (BBOA) factor and was responsible for 58% of the total OM mass during the campaign. It was followed by the Oxygenated Organic Aerosol (OOA) factor representing 18% of the total OM. This factor is generally attributed to aged OA transferred from other areas. The third and fourth factor are Hydrocarbon-like Organic Aerosol (HOA) and Cooking Organic Aerosol (COA) and are both attributed to freshly emitted OM from the combustion of fossil fuels (mainly traffic) or preparation of food, respectively. They both contributed to total OM approximately 12%.

This solution has been evaluated through comparison of the corresponding spectra with literature spectra, the correlation between the factors and time-series of other pollutants, each factor’s diurnal profile and their physical meaning (Zhang et al., 2005c; Ulbrich et al., 2009).

Figure 4.13 presents the hourly averaged time series of the four PMF factors and also their contribution to the total OM. The BBOA concentration increased during the evening.
reaching concentrations up to 65 $\mu$g m$^{-3}$ around midnight and its hourly average value was 10.5 $\mu$g m$^{-3}$.

Figure 4.13 The concentration of PMF factors at the TEI site. Different scales are used for each factor. The contribution of each factor to total OM is shown (top figure).
The BBOA factor had the same trends as the total PM$_1$ with sharp increases after 16:00 pm (Local Standard Time, LST). The OOA factor dominated during the daytime. The OOA varied relatively slowly throughout the campaign and its hourly mean value was 3.2 μg m$^{-3}$ with a maximum value of 10.8 μg m$^{-3}$. The hourly mean value of the HOA factor was 2.1 μg m$^{-3}$ and of COA 2 μg m$^{-3}$. Their maximum hourly values were 15.8 μg m$^{-3}$ for HOA and 20 μg m$^{-3}$ for COA factor. The BBOA, HOA and COA factors correspond to primary sources, whereas the OOA factor to atmospheric processing (secondary OA).

Figure 4.14 shows the mass spectra of the four OA components, identified by PMF for the entire campaign, which are similar to those reported in previous studies (Zhang et al., 2005c; Lanz et al., 2007; Nemitz et al., 2008; Ulbrich et al., 2009). Some m/z’s including 44, 57, and 60 are characteristic of OOA, HOA and BBOA, respectively. These factors are analyzed below.

![Mass spectra of the four OA factors with calculated corresponding atomic ratios.](image)

**Biomass Burning Organic Aerosol (BBOA)**: Typical mass fragments of the BBOA spectrum are m/z 60 and 73, attributed to C$_2$H$_4$O$_2$ and C$_3$H$_5$O$_2$, respectively. The BBOA factor correlates well with K$^+$ ($R^2=0.64$, Fig. 4.14), a biomass burning emission tracer. Its
O:C ratio of 0.29 is higher than for the other primary sources (HOA and COA) and is consistent with the results of Alfarra et al. (2004) and Aiken et al. (2009). BBOA in Patras originates from wood-combustion.

**Oxygenated Organic Aerosol (OOA):** OOA is a surrogate for secondary OA. Its spectrum is characterized by a strong peak at m/z 44 (mostly due to CO$_2^+$) and a lower one at 43 (mostly due to C$_2$H$_3$O$^+$). It does not contain important contributions from marker peaks of other organic aerosol classes. The more the organic aerosol stays in the atmosphere, the more the fraction of m/z 44 (CO$_2^+$), increases (Ng et al., 2010). OOA represents the chemically aged OA and is mostly due to long range transport from other areas. The O:C ratio for OOA for this period was 0.65, consistent with other studies Zhang et al. (2011) and the OM:OC ratio was equal to 2.01. The OOA was correlated reasonably well with particulate ammonium ($R^2=0.61$) and sulfate ($R^2=0.56$, Fig. 4.15). The correlation to nitrate was not as good ($R^2=0.4$).

**Hydrocarbon-Like Organic Aerosol (HOA):** HOA is characterized by ions with the general types C$_n$H$_{2n+1}^+$ and C$_n$H$_{2n-1}^+$. As a result, the HOA spectrum has characteristic peaks at m/z 41, 43, 55, 57, 69, 71, 83 and 85 etc., with little or no signal at 44. The largest peaks are at 43 (C$_3$H$_7^+$) and 57 (C$_4$H$_9^+$) (Fig. 4.14). The mass spectra of HOA are often similar to those of diesel exhaust (Canagaratna et al., 2004; Schneider et al., 2005), and other incomplete combustion sources. The HOA O:C elemental ratio is the lower one (0.1) while the H:C elemental ratio (1.83) is the highest among the PMF factors. The HOA correlation with BC was low ($R^2=0.2$) as the MAAP was monitoring 4 km away.

**Cooking Organic Aerosol (COA):** The COA spectrum has some similarity to that of HOA but is dominated by m/z’s 41 and 55 instead of 43 and 57 (Fig. 4.14). The COA spectra, like the HOA ones are characterized by the ion series: C$_n$H$_{2n+1}^+$ and C$_n$H$_{2n-1}^+$ but also by C$_m$H$_{2m-1}$CO$^+$ (m/z 41, 55, 69, 83...) and C$_m$H$_{2m+1}$CO$^+$ (m/z 29, 43, 57, 71, 85...). The peak of COA concentrations coincide with typical meal times (Fig. 4.16). Its O:C ratio, equal to 0.14 was low but higher than that of HOA. The COA H:C (1.71) was lower than the corresponding one of HOA.
Figure 4.15 Correlation between the hourly averaged BBOA factor and potassium (A.) Also, OOA correlation between particulate sulfate (B.) and ammonium (C.) The points are time-colored for the whole campaign.

The average diurnal profile of the four factors is shown in Fig. 4.16. The BBOA peaks in the evening (maximum of 34 μg m⁻³, at 20:00 LST), which is consistent with residential...
heating. The OOA factor profile is relatively flat, a behavior expected of a pollutant transported to the receptor from other areas. These results are consistent with long term measurements in Patras that supported the importance of transported pollution as a major PM source throughout the year (Pikridas et al., 2013). The HOA factor has two major peaks during the day. Its major peak occurs in the morning (maximum of 7.2 μg m\(^{-3}\), at 20:00 LST) and coincides with the morning traffic. The second peak of HOA appeared in the early evening (4.3 μg m\(^{-3}\), at 19:00 LST) and corresponds to the evening rush hour. COA’s diurnal cycle exhibited a clearly different diurnal profile in comparison to HOA, with one peak in the late evening (6.5 μg m\(^{-3}\), at 22:00 LST) and another one around midday (4 μg m\(^{-3}\), at 13:00 LST) corresponding to mealtimes.

![Figure 4.16 Average diurnal variation of the four PMF factors. The right y-axis shows the BBOA values, while the left one all the rest.](image)

The evolution of individual m/z of the AMS provides additional information. Often, instead of the actual value of mass for each m/z, its fractional contribution is used. For example, if we want to describe the fraction of organic mass at m/z 44 (which mostly corresponds to the CO\(_2^+\) ion), we define \( f_{44} = \frac{[m/z \ 44]}{OM} \) (in μg m\(^{-3}\))/OM (in μg m\(^{-3}\)), where OM is the total mass concentration of the organic aerosol. In addition to the m/z 44 fragment, we will also focus on the fragments at m/z 43, 57 and 60. In Figure 4.17 the average diurnal variation of \( f_{43} \) and \( f_{44} \) is shown. The mean value of \( f_{43} \) was 0.066 with a standard deviation of 0.006 and for \( f_{44} \) was 0.07 ±0.02.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

Figure 4.17 Average diurnal profiles of $f_{43}, f_{44}, f_{57}$ and $f_{60}$. On the left y-axis is the fraction at m/z 57 and 44 and on the right one the fraction at m/z 60 and 43.

The fragments with m/z 43 are primarily C$_2$H$_3$O$^+$ with a smaller contribution from C$_3$H$_7^+$. The fragment with m/z 57 is primarily C$_4$H$_9^+$ with a smaller contribution from C$_3$H$_5$O$^+$. Hence, $f_{43}$ is often used as a proxy for moderately oxidized organic aerosol and $f_{57}$ is used as a proxy for fresh, hydrocarbon-like organic aerosol (HOA) (Zhang et al., 2005a; b; Aiken et al., 2009). The HOA, COA and BBOA PMF factors had low levels of $f_{44}$ which is consistent with the nature of the corresponding sources. On the other hand, the OOA spectrum was dominated by m/z 43 and 44. Increasing $f_{44}$ is linked to photochemical aging (Alfarra et al., 2004; de Gouw et al., 2005). Ng et al. (2010) plotted the $f_{44}$ versus $f_{43}$ from many AMS datasets from around the world. All the measurements fell in a triangular area shown in Fig. 4.18 with the dotted black lines. The measurements from the whole campaign are plotted in Fig. 4.18 together with the location of each PMF factor. The OOA factor found in this study can be characterized as moderately processed, as it is in the right-middle of the triangle, instead of the top corner. Figure 4.19 depicts the Ng triangle and the $f_{43}$ vs. $f_{44}$ results, from a similar study in Zurich (Mohr et al., 2011). These results correspond to another year and place but they are also for wintertime, and like this study, an HOA and a Wood Burning Organic Aerosol (WBOA) factor are present. The consistency of the two studies is encouraging.
Figure 4.18 Fractions of organic mass fragments 44 ($f_{44}$) and 43 ($f_{43}$) in the Ng triangle (Ng et al., 2010) of this campaign.
Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.

4.4 Conclusions

A field campaign took place in the suburbs of the city of Patras, 4 km away from the city center during the winter of 2012. The aim of this campaign was primarily the characterization of the PM$_1$ and secondly, the quantification of the contribution of residential wood burning to local particle pollution. During this 10-day campaign, organics turned out to be responsible for more than 70% during the day and more than 80% during the evening hours of the total PM$_1$. Their mean concentration was roughly 20 µg m$^{-3}$ and they reached an hourly maximum of approximately 85 µg m$^{-3}$. Sulfate ions and black carbon followed with 10% and 7% of the PM$_1$ and they reached an hourly maximum of 6 µg m$^{-3}$ and 8 µg m$^{-3}$, respectively.

PMF analysis applied to the organic mass spectrum of PM$_1$ could explain the observations with four sources: cooking (COA), traffic (HOA), biomass burning (BBOA), and oxygenated aerosol (OOA) related to secondary formation and long range transport. On average, BBOA represented 58% of the total OM, followed by OOA with 18%, COA and HOA, with the last two contributing of the same percentage (12%). Wood burning emissions in Patras are very important during wintertime as BBOA accounts for

Figure 4.19 Fractions of organic mass fragments 44 ($f_{44}$) and 43 ($f_{43}$) in the Ng triangle (Ng et al., 2010) from Zurich campaign, described in Mohr et al. (2011).
42% of the total PM$_{1}$. Many households in Patras, and generally in Greece, have a fireplace or a woodstove, or use exclusively wood instead of central heating for heating purposes. The fact that even near major roads, biomass burning contributes more than traffic during the night hours is characteristic of the relative contributions of the two sources.
4.5 References


Continuous real-time measurement of the chemical composition of atmospheric particles in Greece using aerosol mass spectrometry.


CHAPTER 5

Conclusions and future work

Measurements took place in a remote site during the Finokalia Aerosol Measurement Experiment 2011 (FAME-11) field campaign in Finokalia, Crete. The organic aerosol was oxidized and the mass spectra could be explained by two factors. The first one was a low volatility factor (LV-OOA) and the second a semi-volatile one (SV-OOA). Hydrocarbon-like organic aerosol (HOA), cooking organic aerosol (COA) or fresh biomass burning organic aerosol (BBOA) were not detected. This is consistent with the lack of strong local sources and the relatively fast atmospheric processing of the OA from the corresponding sources to OOA. Aerosol sampled at this remote site had enough time to get sufficiently oxidized (average O/C ratio of 0.68).

A second campaign was conducted in an urban site (Patras), in order to investigate the corresponding organic aerosol sources. OA represent more than 80% of the total PM$_1$ during the night. The maxima levels of PM$_1$ concentrations were close to 100 $\mu$g m$^{-3}$ during polluted nights. Sulfate accounted for only 10% of the PM$_1$. PMF suggested four major sources: biomass burning (58%), cooking (12%), hydrocarbon-like OA mainly from traffic (12%), and aged OA from long-range transport (18%).

With the intention of investigating the local organic sources in an even bigger city, another campaign was also conducted in Athens during the winter of 2013. The analysis of this campaign will be the subject of the future work.