CHARACTERIZATION AND SOURCES OF ATMOSPHERIC PARTICLES IN DIFFERENT POPULATION DENSITY ENVIRONMENTS

A Dissertation by

MICHAEL PIKRIDAS

For the award of the degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF PATRAS

OCTOBER 2012
Acknowledgements

I would like to acknowledge professor Spyros Pandis, for his guidance through the course of my Ph.D. studies. His advices and ideas were the cornerstone of this work.

I would also like to acknowledge prof. Riipinen Ilona, for her advices and help over particle formation were essential in my understanding of the phenomena.

The LAQS group members Kalli Florou, Maria Tsiflikiotou, Anna Siampani, Magda Psichoudaki, Christos Kaltsonoudis, Vaggelis Louvaris and Carnegie Mellon members Gabriella Farnham Engelhart and Lea Hindebrandt for their support during intensive sampling campaigns was essential. Special thanks to Dr. Evangelia Kostenidou with which I shared problems and opinions during my Ph. D. studies.

This thesis is not based only on personal measurements but also on results shared by other groups around the world, which I acknowledge for their effort to provide quality data.
Abstract

The objective of this study is to improve our understanding of the number and mass sources of ambient aerosol. A number of field campaigns were conducted that include the recently developed aerosol mass spectrometer (AMS) and air ion spectrometer (AIS). The AMS provides temporal high resolution measurements of the chemical composition of ambient particles and the AIS information on charged particles of diameter smaller than 40 nm. Particles in the atmosphere are either emitted directly or formed in situ by precursor gases. Sulfuric acid, whose main source in cloud free air is the photo-oxidation of SO$_2$, has been identified as a key component of ambient nucleation. It is well established that other species, the identity and role of which is not clear, may be also involved. Nucleation is favored in environments of intense sunlight, low particulate and high SO$_2$ concentrations.

Finokalia is a remote coastal site in the eastern Mediterranean. During a month-long campaign that took place during May 2008, the site was found to lack strong local sources but was heavily influenced by long range transport. Back trajectory analysis identified five source regions (Athens, Greece, Africa, other continental and marine), each of which influenced the composition and properties of particles with diameters lower than 1 μm (PM$_1$) differently. Marine air masses had the lowest PM$_1$ concentrations and continental air masses from the Balkans, Turkey and Eastern Europe the highest. Highly soluble (approximately 80%) organics in water and increased organic carbon to elemental carbon ratio correlated positively with ozone indicated that PM$_1$ organics were highly oxidized. No detectable traces of hydrocarbon-like organic aerosol were found. These results suggest strongly that PM$_1$ organics were transported to Finokalia and were oxidized in the 6-36 hours of transport from the source areas to Crete in the strongly oxidizing environment of Eastern Mediterranean.

At Finokalia, during summer, despite the high solar intensity, low particle and relatively high SO$_2$ concentrations, nucleation was not frequent. Nucleation events were favored by air masses that crossed land before reaching the site. More frequent nucleation events were observed during winter when solar intensity was lower compared to summer. The variability in nucleation frequency observed at Finokalia can be explained by ammonia involvement in the nucleation process. Ternary nucleation theory predicts that a third constituent, other than sulfuric acid and water, is involved and typically ammonia is considered as that. Pre-existing aerosol, if acidic, will absorb
ammonia within a matter of minutes and therefore nucleation will not occur. Our results indicate that nucleation at Finokalia occur only when particles were neutral, consistent with the ternary nucleation hypothesis. Even though this does not prove that ammonia participates in the stable cluster, it suggests that it may be involved in the process. Other components, such as amines, that co-vary with ammonia may also be involved.

Gas-phase ammonia was exhausted if the air mass spent significant time over the sea, but air masses that passed over land just before arriving at the site can pick up ammonia and therefore nucleation is favored during these conditions. The main difference between summer and winter is that during summer SO$_2$ is oxidized fast enough so that particles are acidic most of the time. In the winter because photochemistry is significantly slower, there is less sulfate around, so there is enough ammonia left in the gas phase to participate in nucleation. In this case the lack of SO$_2$ may prevent nucleation.

Ambient particle size distributions were measured in Paris, France. Monitoring was conducted in the city center along with two satellite suburban stations, located 16 and 18 km away each on opposite directions, two mobile laboratories, and one aircraft during July 2009 (summer) and 15 January till 15 February 2010 (winter). Airborne measurements showed increased number concentrations downwind of Paris coupled with increases in black carbon. These were attributed to PM emissions of the Paris area and are referred henceforth as the “Paris plume”. During summer the plume was found to reach at least 200 km but due to air traffic restrictions it could not be followed further. The number concentration of the upwind suburban was a factor of 3 lower than in the city centre. During winter, number concentration of the plume was found to decrease exponentially with distance. At distances greater than 60 km from the city center the number concentration was similar to that observed during summer at the same distance from the city.

New particle formation (NPF), the process that involves both the formation of new particles (nucleation) and growth to detectable sizes was investigated in Paris. NPF was found to be prevented mainly by the surface area of pre-existing aerosol, on which low volatility vapors condense, called the condensational sink. During summer, NPF was observed half of the campaign days at two sites. The observed frequency was lower at the third ground site mainly due to interferences by nearby traffic which did not allow clear event identification. NPF was also observed at a 600 m altitude, either simultaneously with NPF identified on the ground or along one side the Paris plume at
the same elevation. During winter NPF was not observed due to higher condensational sink and lower solar intensity, consistent with summer observations that indicated NPF to be limited by pre-existing aerosol.

Typically the population density of an area is considered to reflect its particulate matter concentrations. Particulate mass concentrations in Paris were found, during summer, to be similar with those of Finokalia, even though the first is a megacity with over 10,000,000 inhabitants and the latter is a remote area with no notable human activity. Our results in Paris and Finokalia indicate that aerosol levels may increase dramatically due to transported particulate matter. At Finokalia, a receptor site, the surrounding source regions, located more than 100 km away, dictated the aerosol mass concentration.

Observations in both Paris and Finokalia were derived out of month-long intensive campaigns which were costly. Therefore, a cost-effective methodology that assesses both local and transported particulate sources was needed. Such a methodology was developed and implemented for the case study area of Patras, Greece. The method development and evaluation was stepwise and the information gathered in each step allowed the better planning of the next step.

In Patras, local vehicular traffic contributed on average 10-14% of the mass of particles smaller than 10 μm in diameter. Other local sources were found to contribute approximately 20% of particles smaller than 2.5 μm in diameter (PM_{2.5}). During winter the contribution of local sources increased approximately to 35%. The contribution of long range transport to the PM_{2.5} was 80% during spring and summer and decreased to 70% during autumn. During winter the contribution of transported PM decreased further to half of the PM_{2.5}. Overall long range transport was the most significant source of PM at the area. During winter, when the contribution of local sources peaked, PM_{2.5} was found to increase sharply during nighttime due to diesel and wood combustion for heating purposes. The organic aerosol concentration alone was found to exceed 80 μg m\(^{-3}\) and black carbon concentrations exceeded that of sulfate. These surprisingly high concentrations, for a medium-size city, are partially due to inversion layer height decrease during night when domestic heating peaks.
# Table of Contents

**Chapter 1**

**Introduction**

1.1 Atmospheric Aerosol and their Properties .......................................................... 1  
1.2 Nucleation in the Atmosphere ........................................................................ 3  
1.3 Particulate Source Apportionment Methods ................................................... 6  
1.4 Objectives and Scopes of this Thesis .............................................................. 8  
1.5 References ..................................................................................................... 9  

**Chapter 2**

**Background Measurements in a costal site in the Eastern Mediterranean**

2.1 Abstract ......................................................................................................... 13  
2.2 Introduction ................................................................................................... 14  
2.3 Site Description ............................................................................................. 15  
2.4 Campaign Objectives .................................................................................... 16  
2.5 Overview of Measurements .......................................................................... 16  
   2.5.1 Meteorology ....................................................................................... 16  
   2.5.2 PM Inorganic Composition ............................................................... 19  
   2.5.3 Aerosol Mass Spectrometry ................................................................. 20  
   2.5.4 PM Carbonaceous Material ................................................................ 21  
   2.5.5 Organic Aerosol Volatility .................................................................. 21  
   2.5.6 PM Size Distribution ......................................................................... 22  
   2.5.7 Water and Hydrosopicity ................................................................... 22  
   2.5.8 PM Optical Properties ......................................................................... 22  
   2.5.9 Gaseous Species .................................................................................. 23  
   2.6 Overview of Measurements ............................................................................ 23  
   2.6.1 Statistical Analysis .............................................................................. 23  
   2.6.2 Source Region Analysis ...................................................................... 23  
   2.6.3 Meteorology ....................................................................................... 25  
   2.6.4 PM Inorganic Composition ............................................................... 28  
   2.6.5 Organic PM ........................................................................................ 31  
   2.6.6 PM Size Distribution ......................................................................... 33  
   2.6.7 Gaseous Species .................................................................................. 36  
2.7 Conclusions .................................................................................................... 36  
2.8 References ...................................................................................................... 38  

**Chapter 3**

**New particle formation at a remote site in the Eastern Mediterranean**

3.1 Abstract ......................................................................................................... 41  
3.2 Introduction ................................................................................................... 41  
3.3 Experimental ................................................................................................. 44  
   3.3.1 Sampling Site ...................................................................................... 44  
   3.3.2 Measurement Period .......................................................................... 44  
   3.3.3 Instrumentation ................................................................................... 44  
   3.3.4 Sulfuric Acid Approximation ............................................................... 45  
   3.3.5 Retroplume Analysis .......................................................................... 46  
   3.3.6 Particle Formation Event Categorization ............................................ 48
3.3.7. Nucleation Event Characteristics .......................................................... 48
3.4 Results and Discussion ............................................................................. 53
  3.4.1. Nucleation Event Seasonal Cycle ....................................................... 53
  3.4.2. Condensational Sink ..................................................................... 55
  3.4.3. Growth and Ion Formation Rates ............................................... 56
  3.4.4. Retropulse Analysis of New Particle Formation .............................. 57
  3.4.5. Cations to Anions Ratio During Nucleation Events ...................... 57
  3.4.6. SO₂ and Sulfuric Acid Proxy During the Two Intensive Campaigns .... 61
3.5 Comparison with Other Studies ............................................................... 63
3.6 Conclusions .............................................................................................. 64
3.7 References ................................................................................................. 66

Chapter 4
Number Concentrations and Sources in a Modern Megacity
  4.1 Abstract .................................................................................................... 70
  4.2 Introduction ............................................................................................. 70
  4.3 Sampling Sites ......................................................................................... 72
  4.4 Instrumentation ....................................................................................... 75
  4.5 Methods .................................................................................................. 75
    4.5.1. Particle Formation Event Categorization ........................................ 75
    4.5.2. Duration of Nucleation Events ....................................................... 79
    4.5.3. Condensational Sink ..................................................................... 79
    4.5.4. Intercomparison of Aerosol Sizing Instruments .............................. 80
    4.5.5. Meteorology ................................................................................... 80
  4.6 Number Concentration at the Ground Sites ............................................. 82
    4.6.1. Fixed Measurements ..................................................................... 82
    4.6.2. Mobile Measurements .................................................................. 84
  4.7 New Particle Formation on the Ground ................................................... 87
  4.8 Airborne Measurements ......................................................................... 89
  4.9 Summary and Conclusions .................................................................... 95
  4.10 References ............................................................................................ 97

Chapter 5
Characterization of the Origin of Fine Particulate Matter in a Medium Size Urban Area in the Mediterranean
  5.1 Abstract .................................................................................................. 100
  5.2 Introduction ............................................................................................ 100
  5.3 The Test Case: Patras, Greece ................................................................. 102
  5.4 Is there a problem? Step 1: Daily Average PM₁₀ levels ......................... 103
  5.5 Potential Sources – Hourly PM Variation ............................................. 104
  5.6 Filter-based Composition Measurements – Constraints on the PM Sources . 105
  5.7 The Role of Transported Pollution ....................................................... 109
  5.8 Pinning Down Local Sources ................................................................. 112
  5.9 Comparison with Other Sites ................................................................. 119
  5.10 Conclusions and Discussion ................................................................ 120
  5.11 References ............................................................................................ 122
Chapter 6
Summary and Future Work
6.1 Summary ..................................................................................................... 125
6.2 Future work ................................................................................................. 128

Appendix A
Instrumentation
A.1 Scanning Mobility Particle Sizer (SMPS) .................................................... 129
A.2 Air Ion Spectrometer (AIS) ........................................................................ 130
A.3 Aerosol Mass Spectrometer (AMS) ............................................................. 131
A.4 Proton Transfer Reaction Mass Spectrometry (PTR-MS)............................ 132
A.5 Nephelometry ............................................................................................. 132
A.6 Tapered Element Oscillating Microbalance (TEOM) ................................. 133
A.7 Quality Assurance – Quality Control ......................................................... 134
A.8 References .................................................................................................. 135

Appendix B
Σύνοψη διδακτορικής διατριβής ................................................................. 136
Curriculum Vitae ............................................................................................... 148
List of Figures

Figure 1.1 Typical number and volume distributions of atmospheric particles with the different modes

Figure 1.2 Typical mass distribution and chemical composition of atmospheric particles (Los Angeles, 1987). The accumulation mode mainly consists of sulfate, nitrate, ammonium and organics and the coarse mode is characterized by sodium, chloride, nitrate and some sulfate

Figure 1.3 H$_2$SO$_4$-H$_2$O binary nucleation rate (cm$^{-3}$ s$^{-1}$) as a function of $N_{H_2SO_4}$, calculated from classical binary nucleation theory (Kulmala and Laaksonen 1990): (a) relative humidity= 20%; (b) RH=50%; (c) RH=80%; (d) RH=100%

Figure 1.4 The chemical composition of charged nucleating clusters at 292K (35p.p.t.v. NH$_3$)(c) and 292K (230p.p.t.v. NH$_3$)(d). The cluster spectra are averaged over the steady-state nucleation period. To simplify the figures, only the overall envelopes are shown for organic species. The concentrations are approximately corrected for detection efficiency. (Kirby et al., 2011)

Figure 1.5 Example of footprint potential emission sensitivity (PES) from 20-day retroplume calculations with the particle dispersion model FLEXPART in backward mode. A continental air mass that crosses Paris is mapped

Figure 2.1 NASA satellite images of Europe and of the island of Crete, indicating the location of the sampling station at Finokalia

Figure 2.2 Source region analysis: flowchart of the description path

Figure 2.3 Source region analysis based on FLEXPART footprint plots. Air masses were categorized based on their source region using PES of their footprint residence time plots (Stohl et al., 2005). A trajectory was attributed to a category if the source region had a PES value above 0.9 ns kg$^{-1}$ in the corresponding footprint plot

Figure 2.4 Daily averages of ambient temperature (a), relative humidity (b), light intensity (c) and wind speed (d) during May 4 to June 8. Red lines indicate the median, boxes represent the upper and lower quartile and the whiskers extend to the most extreme data points. From May 19 to May 21 (source region Africa) average daily temperature increased and relative humidity decreased

Figure 2.5 Average diurnal variation in ambient temperature (a), relative humidity (b), light intensity (c) and wind speed (d)

Figure 2.6 Time series of PM$_1$ aerosol composition measured by the Q-AMS. Different scales are used for each graph
Figure 2.7  Daily average of PM$_{1.3}$ and PM$_{1.3-10}$ during the study, based on filter measurements. OM was calculated as OC×2.2 according to Hildebrandt et al. (2010). Crustal concentration is calculated using iron as a surrogate according to Sciare et al. (2005). Other is the sum of PO$_4^{3-}$ and K$^+$………………………………………………..30

Figure 2.8  Mass fraction of PM$_{1.3}$ over PM$_{10}$ mass as a function of time………………31

Figure 2.9  Percentage of water soluble OC based on PM$_1$ filter measurements. On average 80% of OC was water soluble……………………………………………………………..32

Figure 2.10  OC versus EC as determined by PM$_1$ filters. The slope of the OC versus EC line was 5.4 (blue points) for the study period with the exception of May 19-May 21 (source region Africa), when it was equal to 2.8 (black points)…………………………33

Figure 2.11  OC/EC as a function of time. Ozone and OC/EC are moderately correlated and have a time lag of one day…………………………………………………………33

Figure 2.12  Campaign average of number, surface area and volume distribution. Error bars represent one standard deviation from the average……………………………………34

Figure 2.13  Time series of number, surface area and volume concentrations for N$_{10}$-500……………………………………………………………………………………35

Figure 2.14  Daily averages of acidic gaseous species (SO$_2$, HNO$_3$)…………………………36

Figure 3.1  Source regions used in the retroplume analysis (Greece, Turkey, West Crete, East Crete and Marine). The sampling station (Finokalia) and Athens (population approximately 5 million people) are also denoted on the map……………………………………47

Figure 3.2  SMPS and AIS measurements during a nucleation event day (19 March 2009) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2)………49

Figure 3.3  SMPS and AIS measurements during an undefined day (13 May 2008) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2)……………………….49

Figure 3.4  SMPS and AIS measurements during a non-event day (5 May 2008) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2)……………………….50

Figure 3.5  PM$_1$ cations to anions ratio (in equivalents) distribution for FAME-08 and -09 from 08:00-16:00 (a,c) and the cations to anions distribution during new particle formation events and undefined events for FAME-08 and -09 (b,d) based on Q-AMS measurements……………………………………………………………………..51
Figure 3.6  Monthly frequency of nucleation events and undefined events. A minimum of events and undefined is observed during August and September and a maximum in February and March.

Figure 3.7  Average diurnal profile of the condensation sink (CS) during event (red), undefined (green) and non-event (blue) days. The CS of event and undefined days is on average about half of the CS of non-event days. The CS values are based on dry DMPS data and have been corrected for hygroscopic growth.

Figure 3.8  Hourly averaged PM$_1$ cations to anions ratio during FAME-08 and -09. Red area corresponds to the estimated uncertainty (two standard deviations). Dashed line represents neutrality. Dust events have been excluded from the analysis and are not shown in these two graphs.

Figure 3.9  Cations to anions ratio for FAME-08 and -09 from 08:00 to 16:00 (UTC+2). Blue edged dots correspond to “non-events” for FAME-08 (a) and FAME-09 (c), red to “events” and green to “undefined” for FAME-08 (b) and FAME-09 (d). Dashed lines correspond to one standard deviation from unity in the case of FAME-09 and two standard deviations in the case of FAME-08. Solid line corresponds to neutral aerosol.

Figure 3.10  Cations to anions ratio during the nucleation event of 1 June 2008 at Finokalia. The beginning and end of the event is noted on the graph. Red area corresponds to the estimated uncertainty (two standard deviations). Dashed line represents neutrality. Time of day corresponds to local standard time (UTC+2).

Figure 3.11  Filter based SO$_2$ measurements and condensation sink calculations during the two intensive campaigns. Red and green areas correspond to events and undefined respectively.

Figure 3.12  Sulfuric acid concentration estimated based on SO$_2$ measurements, photolysis frequency of NO$_2$ (J$_{NO2}$) and the condensation sink (CS). Red and green areas correspond to nucleation and undefined events, respectively.

Figure 4.1  Population density and administrative map of Paris. Outlined in red is Ile de France and in green Ile de Paris. The three ground stations (SIRTA, LHVP and GOLF) are depicted with black dots. The map is also separated into sectors depicted by dashed blue lines, formed by concentric circles centered at kilometer zero of Paris (48.8534°N 2.3488°E). The radius of the circles is 0.15, 0.25, 0.4, 0.6, 0.8 and 1 degrees of latitude (one degree being equal to 111.1 km approximately), which corresponds to 16.7, 27.8, 44.4, 66.7, 88.9 and 111.1 km.

Figure 4.2  Trajectories of the ATR-42 aircraft during the summer campaign. Solid colored lines correspond to a different flights.

Figure 4.3  Size distribution measurements during a nucleation event (12 July 2009) in all ground sites. (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1).
Figure 4.4  Size distribution measurements during an undefined event (10 July 2009). (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1)…………………………………………………………...78

Figure 4.5  Size distribution measurements during a non-event (29 July 2009). (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1)………………………………………………...…………78

Figure 4.6  Nucleation analysis results during summer and winter for all ground sites. Events, non-events, undefined and lack of data are depicted in blue, grey, light blue and white, respectively……………………………………………...…………….79

Figure 4.7  Number concentration comparison of ambient particles between 20 – 500 nm between the FMPS of MoLa and of the three ground sites for summer (top) and winter (bottom). Comparison with LHVP was conducted only by MOSQUITA during the summer. The scale factor between MoLa and MOSQUITA during the summer was equal to 1.1 ($R^2=0.9$) which yields a scale factor of 1.02 between MoLa and the SIRTA sizing instruments. The intercomparison time between MoLa and MOSQUITA during summer and between MoLa and SIRTA during both campaigns was 8 hours. The intercomparison period of MOSQUITA and MoLa with the LHVP sizing instrument was 24 and 10 hours during summer and winter, respectively…………………………81

Figure 4.8  Wind direction rose plots during the summer and winter campaigns at each of the ground sites. Each rose corresponds to angle bin of $\pi/18$ (ie 0- $\pi/18$, $\pi/18$ - $2\pi/18$, etc) and concentric circles at each site correspond to 5% frequency to provide an estimate of the direction’s intensity. Wind speed, in $c$, corresponding to each size bin is color coded inside each rose. Wind speeds below 1 m s$^{-1}$ have been omitted from the graph……………………………………………………………………………………………………82

Figure 4.9  Number concentration diurnal profiles of summer (left) and winter (right) campaigns, concerning for size ranges between 20-30 nm, 30-100 nm and 100-500 nm. Different scales are used………………………………………………………………………………………………………..84

Figure 4.10  Grand average distributions for summer (red) and winter (blue) campaigns of all ground sites. No scaling factor has been applied…………………………84

Figure 4.11  Number concentrations of the two satellite sites during summer and winter with respect to air mass direction at each site. The angles which indicate that the air mass traveled through the city center prior reaching the site are depicted with red. The horizontal dashed black line corresponds to the campaign average for each site. Periods with wind speed below unity were omitted from the analysis…………………85

Figure 4.12  Number concentration with respect to distance from the city center measured by the mobile platforms. During summer (red) little variability was observed contrary to winter (blue) when the aerosol population decreased exponentially with distance…………………………………………………………………………………………………………………………86
Figure 4.13  Condensational sink of the three ground sites during July 2009. Red and green bars indicate the event and undefined periods, respectively……………………….89

Figure 4.14  Number distribution time series when a nucleation event was identified at SIRTA and/or LHVP but not at GOLF………………………………….90

Figure 4.15  Number concentration decay of the Paris plume with distance (red dots), monitored at an altitude of approximately 600 m above ground during summer. Polynomial fit (black line) was added to guide the eye……………………………………………………92

Figure 4.16  Flight trajectories during 9 and 21 July 2009. Black carbon and number concentrations are color coded. Black carbon concentrations are used as tracers of the Paris plume (a, c). Increased number concentration was observed outside of the plume. During July 9 (b) the area where the number concentration increase was located upwind (the direction of the plume indicates wind direction) and NPF was identified at all ground sites. During July 21 (d) the particle number increase was observed along the plume. NPF was not observed at any of the ground sites…………………………………93

Figure 4.17  Downwelling solar irradiance (top), condensational sink (middle) and isoprene concentration (bottom) comparison of the Paris plume with areas on either side when high particle concentrations were observed in one side outside of the plume. Differences among these areas were not observed with respect condensational sink, isoprene and solar irradiance…………………………………………………………….94

Figure 5.1  Map of south­east Europe indicating the location of Patras, the urban area under investigation. The rural sampling station at Vouprasio is also shown……102

Figure 5.2  Monthly average PM$_{10}$ concentrations from January 2004 till December 2004 measured at the city center. Error bars correspond to one standard deviation of the monthly average. The dashed line is the annual European PM$_{10}$ standard of 40 μg m$^{-3}$. The number on top of each bar corresponds to the exceedances each month of the European daily PM$_{10}$ standard of 50 μg m$^{-3}$. No measurements were available for May………………………………………………………………………………….103

Figure 5.3  Diurnal cycles of PM$_{10}$ mass concentrations of weekdays (black line) and weekends (red line) during warmer (April - September) and colder (October - March) months……………………………………………………………………105

Figure 5.4  Monthly boxplots of temperature (top) during December 2009 to May 2012. Data used are of 10 min resolution. Red lines indicate the median, boxes represent the upper and lower quartile and the whiskers extend to the most extreme data points. Total monthly precipitation (bottom) for the corresponding period……………………….107

Figure 5.5  PM$_{2.5}$ average monthly composition from December 2008 till May 2012. Dashed line corresponds to the annual average of 22.3±11.8 μg m$^{-3}$………………108

Figure 5.6  Average PM$_{2.5}$ monthly compositions at the urban center (not-textured) and a rural background site (textured). Measurements at both sites correspond to the same sampling dates spanning from June 2011 to May 2012………………………….109
Figure 5.7  Seasonal comparison among three Mediterranean sites for sulfate (a) and OC (b). Urban center measurements are shown in blue and range from December 2008 till May 2012, rural measurements shown in green ranging from June 2011 till May 2012 and remote background measurements with brown conducted from July 2004 till July 2006 (Koulouri et al., 2008)………………………………………………..110

Figure 5.8  Seasonal contribution of regional transport (not textured) and local sources (textured) to the PM$_{2.5}$ components………………………………………………………….111

Figure 5.9  PM$_{1}$ composition of (a) organics; (b) sulfate; (d) ammonium and (e) nitrate from 26 February to 5 March by a HR-AMS at the urban background site and black carbon measurements (c) of the same period at the urban center. Different scales are used for each species. The contribution of each constituent of the dry PM$_{1}$ mass is shown in (f)……………………………………………………………………115

Figure 5.10  PM$_{1}$ diurnal profiles of (a) organics, (b) sulfate, (d) ammonium, (e) nitrate and (f) potassium by a HR-AMS and of SO$_{2}$ measurements (c) from 26 February to 5 March at the urban background site. Vertical lines correspond to rush hour traffic and of the nighttime increase observed………………………………………………..116

Figure 5.11  Three-hour average PM$_{2.5}$ mass (FDMS-TEOM) versus light scattering coefficient (nephelometer) at the urban background and urban center, respectively. The two instruments located 3.5 km away exhibit good correlation (R$^2$=0.61) indicating that both sites were susceptible to the same sources. The light scattering coefficient of particles is expected to correlate with particle mass concentration provided by TEOM, but the correlation of the two instruments is complicated by the drying methods used. The two instruments were deployed at the same place for 5 days and exhibited good correlation (R$^2$=0.77, not shown) and an average scattering efficiency of 2.8 m$^2$ g$^{-1}$ (dashed red line)……………………………………………………………………117

Figure 5.12  Diurnal profile of PM$_{2.5}$ mass at the urban background site from 26 February to 5 March. The profile exhibits two peaks, one at 08:00 and one at 20:30. Black carbon monitored at the urban center exhibits the same peaks indicating that combustion sources were involved in both cases………………………………………………117

Figure 5.13  Night and day average number, surface and volume distributions from 21 February 2012 to 9 March 2012. The aerosol number, surface and volume concentrations increased by a 3-4 fold at night compared to day without a significant mode shift…………………………………………………………………………118
List of Tables

Table 1.1  PM air quality standards for U.S.A and E.U. ..........................3
Table 2.1  Summary of FAME-08 measurements........................................17
Table 2.2  Source region analysis for meteorological, physical and chemical properties.................................................................26
Table 3.1  Growth rates and condensational sink in Finokalia during April 2008 – April 2009............................................................55
Table 3.2  Summary of retroplume analysis..................................................57
Table 4.1  Summary of MEGAPOLI measurements during both campaigns.................................................................76
Table 4.2  Summary of the aerosol distributions of the three ground sites during the MEGAPOLI summer and winter campaign and characteristics of NPF during summer.................................................................83
Chapter 1

Introduction

1.1 Atmospheric Aerosol and Their Properties

Aerosols, also known as particulate matter (PM), are solid and liquid particles suspended in a gaseous medium. Ambient aerosols are an important and ubiquitous component of Earth’s atmosphere because they are linked with climate change due to their ability to scatter and absorb light and to act as cloud condensation nuclei (CCN) thus significantly affecting the earth’s albedo (Twomey, 1977; Albrecht, 1989; Lohmann and Feichter, 2005). Atmpspheric particles smaller than 100 nm have low mass but high number concentrations. Particles above 100 nm are orders of magnitude fewer in number but involve almost all the mass. Fig. 1.1 shows a typical number and volume distribution of ambient aerosol, which is often the sum of lognormal distributions (Seinfeld and Pandis, 1998). The number distribution includes two modes, nucleation (<10 nm) and Aitken (10 – 100 nm). The nucleation mode exists only if new particles are formed in situ by the oxidation of precursor gases, a process that will be discussed in Section 1.2. The volume distribution also involves two major modes; the accumulation (100 nm – 2.5 μm) and coarse (>2.5 μm) modes which have different sources and hence different composition and properties. Accumulation mode particles derive from the coagulation of particles in the nucleation mode, the condensation of vapors onto existing particles and from the cloud processing of particles.

The coarse mode is formed by mechanical processes and usually consists of human-made and natural dust particles, sea salt and other mechanically generated particles. This difference in sources is also depicted in the composition of the two modes. The accumulation mode mainly consists of sulfate, nitrate, ammonium, and organics and the coarse mode is dominated by oxides of crustal elements, sodium, chloride, nitrate, and some sulfate (Fig. 1.2). Another important PM constituent is water which can account for most of the particulate mass depending on the ambient RH (Kreidenweis et al., 2001; Spichtinger and Cziczo, 2008). Because PM water content largely depends on RH, mass measurements are performed at a fixed low RH.
Figure 1.1: Typical number and volume distributions of atmospheric particles with the different modes. (Seifeld and Pandis, 2006)

Figure 1.2: Typical mass distribution and chemical composition of atmospheric particles (Los Angeles, 1987). The accumulation mode mainly consists of sulfate, nitrate, ammonium and organics and the coarse mode is characterized by sodium, chloride, nitrate and some sulfate.

A link between human health and PM mass has been established for several decades. One of the most notable pollution events is the Great Smog of 1952 that took place in London from 5 to 9 December 1952, causing 4000 premature deaths (Stegeman et al., 2002). Several studies since have indicated that elevated particulate matter (PM) concentrations are related with increased mortality (Pope et al., 1991; 2009). Fine particles with diameter smaller than 2.5 µm (PM$_{2.5}$) are mainly responsible for this
association (Pope et al., 2009; Schwartz et al., 1996; Wang et al., 2008). A strong correlation of airborne particulate matter (PM) levels and mortality (Dockery et al., 1993; Pope et al., 2009) has been observed resulting on legislation of PM levels in ambient air. These levels differ from country to country and are often exceeded in urban areas where anthropogenic emissions are high. Table 1.1 summarizes legislation concerning PM in the European Union and U.S.A.

Table 1.1. PM air quality standards for U.S.A and E.U.

<table>
<thead>
<tr>
<th>Type</th>
<th>Limit</th>
<th>Applies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily PM$_{10}$</td>
<td>50 $\mu$g m$^{-3}$ less than 35 times per annum</td>
<td>1-Jan-2005</td>
</tr>
<tr>
<td>Daily PM$_{10}$</td>
<td>50 $\mu$g m$^{-3}$ less than 7 times per annum</td>
<td>1-Jan-2015</td>
</tr>
<tr>
<td>Annual PM$_{10}$</td>
<td>40 $\mu$g m$^{-3}$</td>
<td>1-Jan-2005</td>
</tr>
<tr>
<td>Annual Target PM$_{2.5}$</td>
<td>25 $\mu$g m$^{-3}$</td>
<td>1-Jan-2010</td>
</tr>
<tr>
<td>Annual PM$_{10}$</td>
<td>50 $\mu$g m$^{-3}$ three year average</td>
<td>Revoked</td>
</tr>
<tr>
<td>Daily PM$_{10}$</td>
<td>150 $\mu$g m$^{-3}$ less than 4 times in 3 years</td>
<td></td>
</tr>
<tr>
<td>Daily PM$_{2.5}$</td>
<td>35 $\mu$g m$^{-3}$ 98% in 3 years</td>
<td>1-Jan-2006</td>
</tr>
<tr>
<td>Annual PM$_{2.5}$</td>
<td>15 $\mu$g m$^{-3}$ three-year average</td>
<td></td>
</tr>
</tbody>
</table>

1.2 Nucleation in the Atmosphere

The formation of new particles by homomolecular nucleation does not occur unless the vapor phase is supersaturated. The situation changes when two or more vapor species are present, none of which is supersaturated: nucleation may take place as long as the participating vapor species are supersaturated with respect to a liquid solution droplet. The formation rate of new clusters in a binary nucleation system follows Eq. 1.1.

\[ J = C \exp\left(-\frac{\Delta G^*}{kT}\right) \]

Eq 1.1
where $\Delta G^*$ is the free energy required to form a critical nucleus, $C$ is a kinetic factor, $k$ the Boltzmann constant and $T$ temperature. $\Delta G^*$ can be calculated at the saddle point in the three-dimensional space formed by $\Delta G$ and the two monomers concentration of the cluster. In the atmosphere it has been established that sulfuric acid and water participate in new particle formation (NPF) but the calculated nucleation rates under ambient conditions ($C_{\text{H}_2\text{SO}_4}=10^5$ - $10^6$ molecules cm$^{-3}$) are of the order of $10^{-4}$ - $10^{-2}$ cm$^{-3}$ s$^{-1}$ (Fig. 1.3) which is more than two orders of magnitude lower than those observed in the field (Kulmala and Laaksonen, 1990).

![Figure 1.3. H$_2$SO$_4$-H$_2$O binary nucleation rate (cm$^{-3}$ s$^{-1}$) as a function of NH$_2$SO$_4$, calculated from classical binary nucleation theory (Kulmala and Laaksonen 1990): (a) RH= 20%; (b) RH=50%; (c) RH=80%; (d) RH=100%.](image)

Several mechanisms have been proposed to close the gap between the calculated and observed nucleation rates. Kulmala et al. (2006) proposed that clusters are readily available but are activated under favorable conditions. This theory predicts that the critical cluster involves a single molecule of sulfuric acid based on nucleation rate measurements that indicate a power law dependence of $n$ between $J_3$ (formation rate of 3 nm clusters) and the sulfuric acid concentration, where $n$ has been shown not to exceed 2 (Weber et al., 1996; Kulmala et al., 2004b). According to the nucleation theorem the slope of nucleation rate vs. concentration of the nucleating vapour (ie $n$) determines the number of molecules in the critical cluster (Kashchiev, 1982). Because the $J_1$ (the stable cluster formation rate) dependence cannot exceed that of $J_3$ it was assumed by Kulmala et al. (2006) that only one molecule of sulfuric acid is enough to
form a stable cluster. Nucleation rates can be expressed as a function of the concentration of the available clusters:

\[ J_{\text{act}} = kN_{\text{clusters}} \]  \hspace{1cm} \text{Eq. 1.2}

where \( k \) is a kinetic constant that has been shown to vary significantly, even from day to day at the same location. It has been suggested that this variation may be due to the organics concentration (Metzger et al., 2010). Even though measurements in urban (Sihto et al., 2006) and rural (Riipinen et al., 2007) areas are consistent with cluster activation theory, model simulations for sulfur rich areas fail to reproduce the observed NPF events (Jung et al., 2008).

The effect of ions on NPF is known for more than a century (Wilson, 1895). Ion induced nucleation theory predicts that a cluster may be stabilized by the presence of an ion regardless of its polarity. This decreases the energy \( \Delta G^* \) required to form the critical cluster. The ion production rate \( Q \) is a key parameter since it will determine the concentration of ions available for participation in the process. At ground level only a 1% - 30% of the observed nucleation rates can be attributed to ion-induced nucleation (Manninen et al., 2010). Vana et al. (2006) reported than only weak NPF (when less than average number of particles is produced) could be explained by ion-induced nucleation theory, while model simulations in an urban area failed to reproduce NPF using ion-induced nucleation theory (Jung et al., 2008).

There has been evidence that the critical cluster on many cases does not consist of two but three components, the so called ternary nucleation theory. The theory predicts that the cluster involves a basic species whose presence considerably decreases the equilibrium vapor pressure of sulfuric acid above the solution surface (Coffman and Hegg, 1995). Ammonia has been often considered to be the third constituent. The enhancement of sulfuric acid nucleation is supported by laboratory studies (Berndt et al., 2010; Ehn et al., 2010; Erupe et al., 2011; Kirby et al., 2011). NPF at coastal areas has often been explained by iodine oxides (O’Dowd et al., 2002a, 2002b) that are produced from the oxidation of biogenic emissions of iodine vapors. Marine algae are responsible for these emissions during low tide periods. Kirby et al. (2011), as part of the CLOUD experiment at CERN, managed to monitor the composition of the stable cluster which comprised of ammonium bisulfate under ambient conditions and is consistent with theoretical calculations of the stable cluster (Napari et al., 2002).
Figure 1.4. The chemical composition of charged nucleating clusters at 292K (35p.p.t.v. NH$_3$)(c) and 292K (230p.p.t.v. NH$_3$)(d). The cluster spectra are averaged over the steady-state nucleation period. To simplify the figures, only the overall envelopes are shown for organic species. The concentrations are approximately corrected for detection efficiency. (Kirby et al., 2011).

1.3 Particulate Source Apportionment Methods

Ambient particles can be either directly emitted in the atmosphere or formed by oxidation of precursor gases. In order to distinguish between the two the first are referred to as “primary particles” and the latter as “secondary”. Ambient particulate mass is also distinguished based on its origin as anthropogenic and biogenic and can be further categorized based on its source (i.e. diesel exhaust particles, food cooking, biomass burning, etc). The contribution of each source can be evaluated through the use of chemical compounds that are relatively resistant to chemical transformations, typically referred to as “tracers”. Elemental composition has been widely used in such a manner (Miller et al., 1972; Hopke et al., 1976; Gordon, 1980; Cass and McRae, 1983) but is mainly limited to coarse particles and particles from few specific sources. Several source-specific organic compounds have been also used as tracers (Hildeman et al., 1991; Schauer et al., 1996). If the composition of the source is not well characterized with respect to the tracers or if the tracers react in the atmosphere, only qualitative information can be extracted.
Another way to account for particulate sources is the use of Chemical Transport Models (CTMs). CTMs use emission data and meteorological information and simulate atmospheric reactions, dispersion, and removal to predict pollutant concentrations. The model predictions are evaluated by comparisons against measured concentrations. CTMs provide, for each site, high resolution temporal information on chemical composition and contribution of local sources but are subjected to errors because of the model input and the potentially incomplete understanding of the simulated processes (Gaydos et al., 2007).

The lifetime of a particle depends mainly on its size and may range from minutes, for particles greater than 10 μm in diameter, to days for submicrometer particles (Seinfeld and Pandis, 2006). Depending on their lifetime, and thus their size, ambient aerosol can be transported hundreds to thousands of kilometers away from its source (Stohl et al., 2002). During transport atmospheric particles are subjected to chemical and physical transformations (Donahue et al., 2006). Both tracers and CTMs have been used to account for long range transport of pollutants, with the latter used more widely.

CTMs were initially used to account for transport of gas-phase pollutants such as O₃ (Berntsen et al., 1999; Jacob et al., 1999; 2003; Auvray and Bey, 2005) but are also used to account for dust transport (Tegen et al., 1994; Perry et al., 1997; Karyampudi et al., 1999; Kallos et al., 2006) and fine PM (Pandis et al., 1992; 1993; Gaydos 2005; Wangstrom et al., 2011). A semi-quantitative “source oriented” approach is to establish forward or backward trajectories from source or receptor locations of interest, respectively. This is possible via trajectory models, such as FLEXTRA (Seibert and Frank, 2004), FLEXPART (Stohl et al., 2005), HYSPLIT (Draxler and Hess, 1998), STILT (Lin et al., 2003) and ATMOS (Arndt and Carmichael, 1995) and others, which describe the paths taken by air parcels. The paths are compared against a measured quantity in order to establish a potential source-receptor link.

FLEXPART releases a large number of “particles” over the sampling time at the desired location, and calculates their trajectories using stochastically modeled turbulent fluctuations superimposed on the grid scale winds. In backward mode, the cloud of particles is called a retroplume. The output consists of four dimensional gridded data and is thus much more complex than a simple trajectory. Hence special visualization and analysis techniques are necessary for interpreting FLEXPART’s output. A quantity used is the ‘potential emission sensitivity’ distribution (PES). The value of PES (in units of s kg⁻¹) in a particular grid cell is proportional to the particle residence time in that
cell. For a backward simulation, it is a measure for the simulated mixing ratio at the receptor that a source of unit strength (1 kg s$^{-1}$) in the respective grid cell would produce. Thus FLEXPART not only provides air mass trajectories but gives additional information on aerosol diffusion and dispersion. An example of the output of FLEXPART is shown in Fig. 1.5.

Semi-empirical methods can be used to assess for local or transported PM. As an example, the diurnal profile difference between weekdays and weekdays provides information on vehicular traffic. Tsimpidi et al. (2011) in their analysis of pollution in Mexico city suggested that the minimum diurnal values are a zeroth order estimate of the background concentrations for the area of interest. This enables distinction between local and transported sources contribution at the area of interest. Even though simplistic, these methods are easy to implement and provide rough estimates of the PM sources of the area under investigation.

**Figure 1.5.** Example of footprint potential emission sensitivity (PES) for Paris from 20-day retroplume calculations with the particle dispersion model FLEXPART in backward mode. Continental air masses that arrives in Paris are mapped.

### 1.4 Objectives and Scope of this Work

The scope of this thesis is to improve our understanding of the sources of ambient aerosol number and mass concentrations. In Chapter 2 the remote area of Finokalia is investigated. Finokalia is an ideal background site for southeast Europe. Because no strong local source was identified at the area and the aerosol concentrations depend on air mass origin. In Chapter 3 nucleation, the major particle number source will be examined for Finokalia. The seasonal nucleation pattern and frequency in the area will be investigated combining chemical composition measurements, thermodynamic theory
and statistics. In Chapter 4 the effect of Paris, France on its surroundings is examined. New particle formation (NPF) is assessed and the frequency of events is explained. Finally in Chapter 5, particulate mass sources affecting Patras, Greece are quantified.

Each location examined represents a different environment. Finokalia is remote, Paris is a megacity and Patras lies in between. The source receptor relationships are examined for all cases and the similarities and differences are characterized.

1.5 References


Chapter 2

Background Measurements in a Coastal Site in the Eastern Mediterranean*

2.1 Abstract

A month (May 4 to June 8, 2008) of ambient aerosol, air ion and gas phase sampling (Finokalia Aerosol Measurement Experiment 2008, FAME-08) was conducted at Finokalia, on the island of Crete, Greece. The purpose of the study was to characterize the physical and chemical properties of aged aerosol and to investigate new particle formation. Measurements included aerosol and air ion size distributions, size-resolved chemical composition, organic aerosol thermal volatility, water uptake and particle optical properties (light scattering and absorption). Statistical analysis of the aerosol mass concentration variations revealed the absence of diurnal patterns suggesting the lack of strong local sources. Sulfates accounted for approximately half of the particulate matter less than 1 micrometer in diameter (PM$_1$) and organics for 28%. The PM$_1$ organic aerosol fraction was highly oxidized with 80% water soluble. The supermicrometer particles were dominated by crustal components (50%), sea salt (24%) and nitrates (16%). The organic carbon to elemental carbon (OC/EC) ratio correlated with ozone measurements but with a one-day lag. The average OC/EC ratio for the study period was equal to 5.4. For three days air masses from North Africa resulted in a 6-fold increase of particulate matter less than 10 micrometers in diameter (PM$_{10}$) and a decrease of the OC/EC ratio by a factor of 2. Back trajectory analysis, based on FLEXPART footprint plots, identified five source regions (Athens, Greece, Africa, other continental and marine), each of which influenced the PM$_1$ aerosol composition and properties. Marine air masses had the lowest PM$_1$ concentrations and air masses from the Balkans, Turkey and Eastern Europe the highest.

2.2 Introduction

Elevated particulate matter (PM) concentrations have been related with increased mortality (Pope et al., 1991; 2009). Fine particles with diameter smaller than 2.5 μm (PM$_{2.5}$) are mainly responsible for this association (Pope et al., 2009; Schwartz et al., 1996; Wang et al., 2008). PM is also linked with climate change because of the particles’ ability to scatter and absorb light and to act as cloud condensation nuclei (CCN) thus significantly affecting the earth’s albedo (Twomey, 1977; Albrecht, 1989; Lohmann and Feichter, 2005).

Even though the importance of PM has been recognized for several decades, there are still significant gaps in our understanding of its sources and atmospheric transformations. It is well established that gaseous sulfuric acid plays a central role in atmospheric nucleation (Kulmala and Kerminen, 2008), but it alone cannot account for the observed nucleation rates in sulfur poor environments (Kulmala et al., 2004; Stanier et al., 2004a). The hygroscopicity of inorganic salts has been investigated extensively but our knowledge of the water uptake of particles consisting of organic-inorganic mixtures is still incomplete (Cruz and Pandis, 2000; Dick et al, 2000; Meyer et al, 2009). Semi-volatile organic compounds (primary or secondary) partition between the gas and particulate phases. Understanding the partitioning of these organic compounds has been recognized as one of the major challenges in our efforts to quantify the rates of formation of secondary organic particulate matter (Robinson et al., 2007). There is little information about the volatility of these organic compounds especially as the aerosol ages in the atmosphere (Kanakidou et al., 2005, Hallquist et al., 2009). As a part of the EUCAARI (Kulmala et al., 2009) project the Finokalia Aerosol Measurement Experiment 2008 (FAME-08) was designed to address the above issues by collecting measurements of ultrafine, fine and coarse particles, by monitoring water uptake, size resolved PM composition and size resolved volatility of aged organic aerosol that was transported to Crete from Europe, Asia and Africa.

The Eastern Mediterranean basin is a good area for the investigation of the properties of aged PM (Mihalopoulos et al., 1997; Sciare et al., 2003a; Gerasopoulos et al., 2006). The three major sources of PM in the area are particles and its gaseous precursors from industrialized areas in the Balkans and Eastern Europe (Sciare et al. 2003a; 2003b), Saharan dust transported from the south (Moulin et al., 1998; Kalivitis et al., 2007), and sea spray (Koulouri et al., 2008; Kouvarakis et a., 2002; Sciare et al.,...
Long range transport from Europe contributes significantly to non-sea-salt sulfate (Sciare et al., 2003a) with biogenic emissions of marine origin being the second most important contributor (Mihalopoulos et al., 1997; Kouvarakis et al., 2002). The majority of aerosol studies in the eastern Mediterranean are focused on megacities such as Athens (Bartzis et al., 2004) and not on remote areas. Few attempts have been made to characterize the PM size distribution away from the urban centers (Lazaridis et al., 2008; Eleftheriadis et al., 2006; Kalivitis et al., 2008) and even fewer to link composition with size (Kavouras and Stephanou, 2002; Schneider et al., 2004; Koulouri et al., 2008). Particle formation has been investigated but without any instrumentation to monitor particles below 10 nm (Kalivitis et al., 2008). There is almost no information about the water uptake of PM in the area.

FAME-08 combined filter-based methods with continuous measurements of number distribution and chemical composition including water in order to assess the physical, chemical and optical properties of “aged” PM. In this overview we briefly describe the full set of measurements of FAME-08 with experimental procedures described in Section 2.5. In Section 2.6 there is an overview of the experimental results including analysis of the diurnal patterns of the various pollutants and analysis of source regions affecting the site during the measurement period. A synthesis of the results is presented in Section 2.7.

2.3 Site Description

Finokalia (35° 24’ N, 25° 60’ E) is a remote coastal station located in the southeast of the Mediterranean Sea on the island of Crete, Greece (Fig. 2.1). The nearest large urban center is Heraklion with 150,000 inhabitants located 50 km west of Finokalia. The Finokalia station is located at the top of a hill at an elevation of 230 m facing the sea. There is no notable human activity at a range of approximately 15 km (Kouvarakis et al., 2000).

Figure 2.1. NASA satellite images of Europe and of the island of Crete, indicating the location of the sampling station at Finokalia.
2.4 Campaign objectives

FAME-08 was designed in order to improve our understanding of the physical, chemical and optical properties of aged European aerosol as it is transported from central to southeastern Europe. Its objectives were:

1. Characterization of the PM size, surface area, volume distribution and its physicochemical properties.
2. Characterization of PM chemical composition as a function of size.
3. Improved understanding of the mechanisms of in-situ formation of particles in this area.
4. Quantification of the role of organic matter in the water uptake by PM as a function of aerosol age.
5. Linking the volatility of PM with age, sources, and source areas.

2.5 Overview of measurements

FAME-08 was conducted from May 4 to June 8, 2008 and provided continuous measurements of physical and chemical characteristics of PM, air ions, gaseous species and meteorological parameters. The frequency, resolution and the exact operation period of each method are summarized in Table 2.1.

2.5.1 Meteorology

Temperature and relative humidity (MP101A Humidity-Temperature, ROTRONIC), wind speed and direction (05103 Wind Monitor, NovaLynx Corporation), and UV intensity (Pyranometer CM3, Kipp & Zonen) were monitored with a 5 minute resolution throughout the campaign. A source region analysis was conducted and the categories used were named by the region from which the air originated: Marine, Africa, Greece, other continental and Athens. Athens was separated from Greece in order to investigate whether the effect of this megacity could be detected at the field site, about 400 km away. We categorized the air masses based on their source region using the footprint potential emission sensitivity (PES) from 20-day retroplume calculations with the particle dispersion model FLEXPART in backward mode (Stohl et al., 2005), with three hour resolution. Additional information about PES calculations can be found in Seibert and Frank (2004). A retroplume, a replacement for simple back trajectory calculations in the
<table>
<thead>
<tr>
<th>Variable</th>
<th>Instrument</th>
<th>Group</th>
<th>Resolution</th>
<th>Period of Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerosol Size Distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (10-500 nm)</td>
<td>TSI 3080 SMPS a</td>
<td>CAPS b</td>
<td>10 min</td>
<td>May 4 - May 28</td>
</tr>
<tr>
<td>Aerosol Number Distribution (10-500 nm)</td>
<td>TSI 3034 SMPS a</td>
<td>U. of Aegean</td>
<td>3 min</td>
<td>May 8 - June 8</td>
</tr>
<tr>
<td>Positive/Negative Ion Size Distribution (0.8-40 nm)</td>
<td>Aerosol Ion Spectrometer</td>
<td>U. of Helsinki</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td><strong>Aerosol Chemical Composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Water</td>
<td>DAASS c</td>
<td>CAPS b</td>
<td>10 min</td>
<td>May 4 - May 28</td>
</tr>
<tr>
<td>PM1 (non refractory) Size Resolved Composition</td>
<td>Q-AMS d</td>
<td>PSI c /CAPS b</td>
<td>3 min</td>
<td>May 8 - June 7</td>
</tr>
<tr>
<td>Water Soluble Ions</td>
<td>Steam Sampler</td>
<td>U. of Patras</td>
<td>17 min</td>
<td>May 6 - June 8</td>
</tr>
<tr>
<td>PM_{1.3} and PM_{10} Inorganic Ions</td>
<td>Virtual Impactor with Ion Chromatography/ICP-MS b</td>
<td>ECPL f</td>
<td>Daily</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>PM_{1} OC/EC</td>
<td>ECPL Sampler with Sunset Laboratories Carbon Analyzer</td>
<td>ECPL f</td>
<td>Daily</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>PM_{1} WSOC</td>
<td>ECPL Sampler with Shimadzu TOC-Vesh i</td>
<td>ECPL f</td>
<td>Daily</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td><strong>Aerosol Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light Scattering (wet/dry)</td>
<td>Radiance Research Integrating Nephelometer (Model M903)</td>
<td>ECPL f</td>
<td>5 min</td>
<td>May 4 - June 7</td>
</tr>
<tr>
<td>Light Scattering (3 wavelengths)</td>
<td>Integrating Nephelometer (TSI MODEL 3563 )</td>
<td>U. of Aegean</td>
<td>5 min</td>
<td>May 4 - June 7</td>
</tr>
<tr>
<td>Organic Aerosol Volatility</td>
<td>Thermodenuder</td>
<td>CAPS b</td>
<td>20 min</td>
<td>May 8 - June 8</td>
</tr>
<tr>
<td>Absorption</td>
<td>Magee Scientific Aethalometer (Model AE-20)</td>
<td>ECPL f</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>Absorption</td>
<td>PSAP (Particle Soot Absorption Photometer)</td>
<td>ECPL f</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
</tbody>
</table>
Table 2.1 (continued)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Instrument</th>
<th>Group</th>
<th>Resolution</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gaseous Species</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>Thermo electron Model 49C</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 7</td>
</tr>
<tr>
<td>O₃</td>
<td>Dasibi Model 1008 RS</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 7</td>
</tr>
<tr>
<td>CO</td>
<td>Thermo electron Model 48C</td>
<td>ECPL</td>
<td>30 min</td>
<td>May 15 - June 7</td>
</tr>
<tr>
<td>SO₂, HNO₃, HCl</td>
<td>Impregnated Glass Fiber Filters with IC analysis</td>
<td>ECPL</td>
<td>6 hrs</td>
<td>May 4 - June 6</td>
</tr>
<tr>
<td>NH₃</td>
<td>Impregnated Paper Filters with IC analysis</td>
<td>ECPL</td>
<td>6 hrs</td>
<td>May 4 - June 6</td>
</tr>
<tr>
<td><strong>Meteorology</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>MP101A Humidity-Temperature</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>Light intensity</td>
<td>Pyranometer CM3</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>Temperature</td>
<td>MP101A Humidity-Temperature</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>05103 Wind Monitor</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
<tr>
<td>Wind Direction</td>
<td>05103 Wind Monitor</td>
<td>ECPL</td>
<td>5 min</td>
<td>May 4 - June 8</td>
</tr>
</tbody>
</table>

*a SMPS: Scanning Mobility Particle Sizer; b CAPS: Center for Atmospheric Particle Studies at Carnegie Mellon University; c DAASS: Dry-Ambient Aerosol Size Spectrometer; d Q-AMS: Quadrupole Aerosol Mass Spectrometer; e PSI: Paul Scherrer Institut; f ECPL: Environmental Chemical Processes Laboratory (University of Crete); g IC: Ion chro-matography; i TOC: Total Organic Carbon; h ICP-MS: Inductively Coupled Plasma Mass Spectrometry.
interpretation of atmospheric trace substance measurements (Stohl et al., 2002), was attributed to a region if that region had a PES value above 0.9 ns kg$^{-1}$. For periods in which more than one source region had PES values above the threshold, we attributed that air mass to that region which had the larger area with PES value above the threshold. In order to characterize a retroplume as marine, all PES values above 0.9 ns kg$^{-1}$ had to be located either over sea or over the island of Crete. The marine aerosol that passed over Crete before reaching the field site was not significantly different in composition from the aerosol that was strictly marine and therefore the two were lumped together. A retroplume was characterized as other continental if it was associated with west Turkey or the central and northern Balkans. A flowchart of the decision path is presented in Fig 2.2.

![Flowchart of decision path](image)

**Figure. 2.2** Source region analysis: flowchart of the decision path.

### 2.5.2 PM Inorganic Composition

A custom made virtual impactor (Loo and Cork, 1988) was used to collect particles with diameters less than 1.3 μm (PM$_{1.3}$) and particles with diameters between 1.3 and 10 μm (PM$_{1.3-10}$) daily on Teflon filters (Millipore, Fluoropore membrane filters of 3.0 μm pore size). All collected filters were divided in half and extracted in ultrasonic bath with 20 ml of nanopure water for 45 min for the determination of water soluble ions (Koulouri et al., 2008). For the analysis of anions a Dionex AS4A-SC column was
used, with isocratic elution at 2.0 ml min⁻¹ of Na₂CO₃/NaHCO₃ as eluent. For the analysis of organic anions, an AS11 analytical column was used, with NaOH (0.1–3.5 mM) as eluent in a gradient mode. For the analysis of cations a CS12-SC column was used, under isocratic conditions with 20 mM MSA eluent and flow rate of 1.0 ml min⁻¹. All ion species were detected by conductivity detectors. PM₁ inorganic components were also monitored by a Quadrupole- Aerosol Mass Spectrometer with details provided below.

The PM₁,3-10 filters were also analyzed for trace metals. An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) was applied to measure concentrations of Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb (Koulouri et al., 2008). The digestion procedure was performed in Teflon vessels (DAP – 60K, 60 ml/40 bar) in a microwave digestion system (Berghof MWS - 2). An internal standard (In, CPI International, S4400-1000241) was added to the digested samples before the ICP-MS analysis (Koulouri et al., 2008).

PM₂.₅ semi-continuous measurements of water soluble inorganic ions were conducted by a steam sampler-ion chromatograph at a flow rate of 16.7 Lpm. The system consisted of three parts: (1) a set of annular diffusion denuders (URG-2000) to remove water soluble gaseous species (e.g. NH₃, SO₂, HNO₃), (2) a steam-jet aerosol collector (Khlystov et al., 1995) and (3) two ion chromatographs (IC’s) (Metrohm 761 Compact IC) for quantitative mass analysis of anions and cations respectively. A LiF solution of known concentration was mixed with the sample at a flow of 0.1 ml min⁻¹ prior to analysis, as an internal standard. The cations and anions IC were equipped with 1000-μl and 200-μl sample loops respectively.

2.5.3 Aerosol Mass Spectrometry

A Quadrupole Aerosol Mass Spectrometer (Q-AMS) from Aerodyne, Inc. was used to measure non-refractory (NR) PM₁ chemical composition semi-continuously (Jayne et al., 2000; Jimenez et al., 2003). The instrument determined the size distributions of sulfate, nitrate, chloride, ammonium, water and organics. The calibration of the instrument is described by Hildebrandt et al. (2010). Applying the Kostenidou et al. (2007) algorithm, a total collection efficiency factor (CE) was estimated for the AMS for every two hours. The average CE for the ambient PM during
the campaign was equal to 0.85. A more detailed description of the CE analysis can be found in Lee et al. (2010).

2.5.4 PM Carbonaceous Material

PM$_1$ was collected on quartz fiber filters (Whatman QMA, 1851-047), on a daily basis using a custom-built sampler described by Saarikoski et al. (2008). PM$_1$ organic and elemental carbon (OC and EC) was measured using a modification of the NIOSH thermal–optical transmission method, using a carbon analyzer (Sunset Laboratory Inc., Oregon). The method has two distinct phases to differentiate between OC and EC. During the first phase (OC phase) the sample is kept in a helium atmosphere and heated in four steps, reaching 650°C, while the second phase (oxygen or EC phase) has two consecutive temperature steps, reaching 850°C. Ambient and thermally denuded organic aerosol was also monitored by the Q-AMS (Hildebrandt et al., 2010).

Water soluble organic carbon (WSOC) was measured daily using a Shimadzu $V_{\text{C,SH}}$ Total Organic Carbon (TOC) analyzer and PM$_1$ filters (Whatman QMA, 1851-047). A punch of 1 cm$^2$ was extracted with 15 ml of nanopure water for 45 min, filtered (Ion Chrom Acrodisc 13, 0.45 μm) for the retention of the non-soluble species and analyzed with the TOC (Sciare et al., 2008). All soluble carbon containing compounds in the solution were oxidized to form carbon dioxide, which was then measured by a non-dispersive infrared (NDIR) gas analyzer. Next, the inorganic carbon was measured, by acidifying the sample and converting all the carbonates, hydrogen carbonates and dissolved carbon dioxide to carbon dioxide, which was volatilized by bubbling air through the sample. The produced carbon dioxide was also measured by the NDIR. The water-soluble organic carbon is the difference between the total and inorganic carbon.

2.5.5 Organic Aerosol Volatility

The volatility of the organic aerosol was measured using a thermodenuder system built based on the design of An et al. (2007). The aerosol flow was directed alternately, via a system of solenoid valves, either through the thermodenuder (set at a predefined temperature) or through a bypass line. In order to avoid recondensation of organic vapors, activated charcoal (4-14 mesh, Sigma Aldrich) was used in the cooling stage. At the end of the thermodenuder, the aerosol path was split in two lines and particles were sent to a Scanning Mobility Particle Sizer (SMPS) and the Q-AMS for real-time measurement of the aerosol size distribution and chemical composition, respectively.
The volatility was then determined by comparing the residual aerosol after the thermodenuder to the aerosol that was passed through the bypass (Lee, 2010).

2.5.6 PM size Distribution

The PM number size distributions were monitored by:

1. An Air Ion Spectrometer (AIS) which monitored the number size distribution of charged particles in the range of 0.8 to 40 nm (Mirme et al., 2007);
2. Two standard SMPS systems (TSI 3936L, TSI 3034) that monitored fine PM in the size range of 10 nm to 500 nm. The TSI 3034 SMPS monitored the size distribution of ambient and thermally denuded particles in sequence in a temperature controlled environment, while the TSI 3936L was part of the Dry-Ambient Aerosol Size Spectrometer (DAASS) which alternately monitored the distribution of ambient and dried (RH<30%) aerosols at ambient temperature (Stanier et al., 2004b).

2.5.7 Water and Hydroscopicity

The ability of ambient fine particles to absorb water and grow was measured using the Dry-Ambient Aerosol Size Spectrometer (DAASS), (Stanier et al., 2004b). The aerosol path was alternated, via a system of solenoid valves, between the low relative humidity (RH) and ambient conditions. Low RH (<30%) was achieved by sampling ambient air through a system of Nafion dryers prior to measurement by an SMPS (TSI 3936L). The water content of aerosols from 10 nm to 500 nm was computed as the difference in particle volume distributions at ambient RH and at low RH (Khlystov et al., 2005). The DAASS was kept at ambient temperature under a weatherproof sunshade. A fan was employed to ensure constant circulation of ambient air around the instruments.

2.5.8 PM Optical Properties

Aerosol absorption was monitored continuously by two instruments: a Magee Scientific Aethalometer (Model AE-20) and a Particle Soot Absorption Photometer (Radiance Research) operated at 3 wavelengths. Two nephelometers (Radiance Research Integrating Nephelometer, Model M903) were also used connected in series by a diffusion drier. These two nephelometers were kept under a weatherproof sunshade in order to ensure that operation was under ambient temperature and RH. Temperature and RH were measured at the inlet of each instrument. The first nephelometer measured
the scattering coefficient at ambient conditions and the second at low RH. A third nephelometer (TSI Model 3563) measured the scattering coefficient at three wavelengths in a controlled environment.

2.5.9 Gaseous Species

Continuous measurements of O$_3$ by two instruments (Thermo Electron Model 49C, Dasibi Model 1008 RS) and CO (Thermo Electron Model 48C) using high-sensitivity gas analyzers were conducted. Glass fiber filters (GFF Whatman, 1822047) were soaked in a citric acid-glycerol solution for the measurement of gas-phase NH$_3$, and paper filters (Whatman, 1441047) were soaked in sodium carbonate/ glycerol solution, for the measurement of gaseous acids (HCl, H$_2$SO$_4$, HNO$_3$). These filters were downstream of bulk PM collecting filters (Millipore Fluoropore membrane filters, 0.45 μm) and were replaced every six hours.

2.6 Overview of Measurements

2.6.1 Statistical Analysis

For the source region analysis two statistical tests were employed. First, one-way analysis of variance (ANOVA) was employed to reveal if any of the source region contributions had statistically significant differences, at the 99% confidence level ($\alpha=0.01$), compared to the rest. If the ANOVA test showed that such a difference existed then the Tukey-Kramer test was employed for every possible combination of source regions at a confidence level of 99%. Unlike ANOVA, which can only be used to look for at least one different pair among a group without being able to indicate which pair is different, the Tukey-Kramer test can indicate which differences between pairs of groups are significant at a given confidence level, for an uneven dataset and without confidence loss (Wheater and Cook, 2000). The ANOVA test was also employed to find if statistically significant diurnal variation existed at the 95% confidence level (Hildebrandt et al., 2010).

2.6.2 Source Region Analysis

Marine aerosol that passed over Crete before reaching the field site had a similar composition as the aerosol that did not pass over Crete. This fact suggests that the local, Cretan sources, influencing the field site are not significant and that the marine aerosols are affected by the naval activity of the Mediterranean.
The origins of the air masses reaching the sampling site during the experiment are given in Fig. 2.2. The PM concentrations and meteorological conditions grouped by source region are shown in Table 2.2.

Meteorological variables, such as local temperature and relative humidity, changed significantly only when African air masses arrived at the site. Average temperature was on average 4°C higher and relative humidity was on average 16% lower for these periods with African influence. For the rest of the periods the local meteorology was not correlated with the air mass origin.

PM$_1$ sulfate concentrations measured by the AMS were statistically different among all source regions at the 99% level. Air masses passing over Athens resulted in the highest PM$_1$ sulfate (7.5±2.2 μg m$^{-3}$), followed by Greece (6.8±3.0), other continental (5.9±2.8 μg m$^{-3}$), African (5.0±1.7 μg m$^{-3}$) and marine air masses (3.0±1.3 μg m$^{-3}$) (Hildebrandt et al., 2010). The significance of sulfate long-range transport to the area of Finokalia is quite evident from these results, as well as the influence of Athens to the site. PM$_1$ ammonium in marine air masses was statistically lower (1.0±0.4 μg m$^{-3}$) than that from the other source regions (>1.7 μg m$^{-3}$). PM$_1$ nitrate concentrations measured by the AMS were low during the study (less than 0.1 μg m$^{-3}$ on average) and were statistically similar for air masses coming from Athens, Greece, other continental...
and marine source regions. There was a statistically significant increase of PM$_1$ nitrate for African air masses which may be attributed to the increased nitrate content of dust, although it is mostly of supermicron size. Acidity of PM$_1$, defined here as the ratio of AMS ammonium to sulfate (in molar equivalents), was statistically equal for African, marine and other continental source regions but was significantly higher for Greece and Athens ($\alpha=0.01$). A small fraction of the AMS sulfate could be in the form of organosulfates (Farmer et al., 2010), but all approaches (AMS, filter-based, steam-sampler) used in the study consistently showed that the fine PM was acidic during most of FAME-08.

AMS organic aerosol in air masses from Athens and other continental (not Greece) origin (3.2±1.0 μg m$^{-3}$) was statistically higher than that from Greece (2.6±0.7 μg m$^{-3}$). Organic aerosol contributions were statistically smaller when they originated from Africa (2.1±0.8 μg m$^{-3}$) and marine areas (1.9±0.8 μg m$^{-3}$).

Number concentrations of air masses from Athens, Greece and of other continental origin were statistically the same but higher by 25% than those of marine and African origin. Air ions below 2 nm followed by AIS were statistically similar for all source regions ($\approx520±150$ cm$^{-3}$), with the exception of Africa (662±225 cm$^{-3}$) which was statistically higher. Aerosol absorption (522 nm) was higher for aerosols originating from Africa (8.5±3.4 Mm$^{-1}$) than for all other source regions. This is probably due both to the increased EC concentrations measured during that period and to the high dust levels which can also absorb radiation. Lower absorption was found for air masses originating from Athens and other continental source regions (5.7±1.6 Mm$^{-1}$).

2.6.3 Meteorology

The daily and diurnal variations of meteorological variables are shown in Fig. 2.4 and 2.5, respectively. All diurnal profiles are given with respect to local standard time (UTC+2). The lowest ambient temperature at the site was 12°C and the highest 30.5°C while the average temperature was 20°C. The average daily ambient temperature increased during the study as we moved from late spring to early summer (Fig. 2.4a).The maximum temperature occurred in the afternoon (2-5 pm) and the minimum in the late night (3-6 am).

Relative humidity varied greatly (Fig. 2.4b) having an average value for the study equal to 63%, with a minimum of 18% and a maximum of 99.8%. The diurnal profile of
Table 2.2. Source region analysis for meteorological, physical and chemical properties.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Instrument</th>
<th>Marine</th>
<th>North Africa</th>
<th>Athens</th>
<th>Greece</th>
<th>Continental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average±</td>
<td>Number of</td>
<td>Average±</td>
<td>Number of</td>
<td>Average±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>std</td>
<td>values</td>
<td>std</td>
<td>values</td>
<td>std</td>
</tr>
<tr>
<td>PM₁ Sulfate (μg/m³)</td>
<td>Q - AMS</td>
<td>3.0±1.3</td>
<td>590</td>
<td>5.0±1.7</td>
<td>134</td>
<td>7.5±2.2</td>
</tr>
<tr>
<td>PM₁ Ammonium (μg/m³)</td>
<td>Q - AMS</td>
<td>1.0±0.4</td>
<td>590</td>
<td>1.7±0.6</td>
<td>134</td>
<td>2.1±0.6</td>
</tr>
<tr>
<td>PM₁ Nitrate (μg/m³)</td>
<td>Q - AMS</td>
<td>0.08±0.06</td>
<td>590</td>
<td>0.10±0.08</td>
<td>134</td>
<td>0.08±0.04</td>
</tr>
<tr>
<td>Acidity¹</td>
<td>Q - AMS</td>
<td>0.89±0.19</td>
<td>590</td>
<td>0.90±0.12</td>
<td>134</td>
<td>0.75±0.08</td>
</tr>
<tr>
<td>PM₁ Organics (μg/m³)</td>
<td>Q - AMS</td>
<td>2.1±0.8</td>
<td>590</td>
<td>1.9±0.8</td>
<td>134</td>
<td>3.2±0.9</td>
</tr>
<tr>
<td>Number Concentration (cm⁻³)</td>
<td>SMPS</td>
<td>2403±952</td>
<td>1825</td>
<td>2435±1075</td>
<td>167</td>
<td>3034±1043</td>
</tr>
<tr>
<td>Air Ions (&lt;2 nm) (cm⁻³)</td>
<td>AIS</td>
<td>561±170</td>
<td>4452</td>
<td>662±225</td>
<td>684</td>
<td>511±1853</td>
</tr>
<tr>
<td>Aerosol Absorption (Mm⁻¹)</td>
<td>PSAP</td>
<td>4.6±1.7</td>
<td>4001</td>
<td>8.5±3.4</td>
<td>579</td>
<td>5.9±1.5</td>
</tr>
<tr>
<td>T (°C)</td>
<td>Rotronic</td>
<td>19.0±3.2</td>
<td>4594</td>
<td>24.8±3.1</td>
<td>684</td>
<td>19.6±3.4</td>
</tr>
<tr>
<td>RH (%)</td>
<td>Rotronic</td>
<td>64.6±19.8</td>
<td>4575</td>
<td>46.5±22.4</td>
<td>682</td>
<td>61.6±20.1</td>
</tr>
</tbody>
</table>

¹ PM₁ acidity defined here as the ratio of ammonium to sulfate in molar equivalents as measured by the Q-AMS.
Figure 2.4. Daily averages of ambient temperature (a), relative humidity (b), light intensity (c) and wind speed (d) during May 4 to June 8. Red lines indicate the median, boxes represent the upper and lower quartile and the whiskers extend to the most extreme data points. From May 19 to May 21 (source region Africa) average daily temperature increased and relative humidity decreased.

Figure 2.5. Average diurnal variation in ambient temperature (a), relative humidity (b), light intensity (c) and wind speed (d).
relative humidity had no statistically significant variation at the 95% confidence level (Fig. 2.5b).

During FAME-08 solar radiation was intense reaching a maximum value of 1049 W m\(^{-2}\), while daily maxima always exceeded 850 W m\(^{-2}\). The average solar intensity diurnal profile maximum was 950 W m\(^{-2}\) at 12:00 (Fig. 2.5d). Wind speed was on average 4.6 m s\(^{-1}\) and no statistically significant diurnal pattern (at the 95% level) was observed (Fig. 2.5c) during FAME-08, indicating no influence from land/sea breeze effects.

### 2.6.4 PM Inorganic Composition

PM\(_1\) sulfate and ammonium measured by the Q-AMS correlated well with those from PM\(_{1.3}\) filters (\(R^2 = 0.95\) and 0.86 respectively), thus the bias of the Q-AMS measurements due to the potential existence of organosulfates and organonitrates is limited (Farmer et al., 2010). Nitrate did not correlate well because it was associated mainly with NaNO\(_3\) and with sizes above the AMS size cut-off. Nitrate concentrations in the PM\(_1\) fraction were low, typically below 0.1 μg m\(^{-3}\) while in PM\(_{10}\) it was on average 3.9 μg m\(^{-3}\).

Fig. 2.6 shows the PM\(_1\) sulfate, ammonium, nitrate and organics mass concentrations during the study. One-way ANOVA concluded that none of these species exhibited statistically significant diurnal variations (at the 95% level) indicating the lack of strong local aerosol sources (Hildebrandt et al., 2010).

Sulfate was the dominant constituent of PM\(_1\) accounting for approximately half of the measured PM\(_1\) mass (average concentration 4.7 μg m\(^{-3}\)) ranging from a minimum of 0.7 μg m\(^{-3}\) to a maximum of 15.5 μg m\(^{-3}\). Sulfate concentrations below 1.6 μg m\(^{-3}\) were always associated with air masses of marine origin while concentrations above 10 μg m\(^{-3}\) were associated with Athens, Greece and other continental sources. Ammonium, which was strongly correlated with sulfate (\(R^2=0.9\) based both on filters and Q-AMS data), accounted for 16% of the average PM\(_{1.3}\) mass (average concentration 1.3 μg m\(^{-3}\)). EC accounted for 2% of the average PM\(_{1.3}\) mass and the rest of the inorganic species (e.g. nitrate, phosphate, sodium, potassium, calcium, magnesium and chloride) for 7%. Similar behavior concerning fine inorganic composition is exhibited in other European natural background sites where sulfate is typically the dominant constituent followed by ammonium. This is unlike urban and rural sites where organics dominate (Putaud et al., 2004). Campaign average sulfate concentrations are above the annual average reported for European natural background and elevated sites by a factor of 2-3 (Putaud et al.,
Figure 2.6 Time series of PM$_1$ aerosol composition measured by the Q-AMS. Different scales are used for each graph.

2004; Lanz et al., 2009). These high sulfate levels are likely due to the high photochemical activity in the Eastern Mediterranean during the late spring, summer and...
early fall, and to the relatively high SO$_2$ emissions in the Balkans, Turkey and Eastern Europe.

PM$_{1.3}$ and PM$_{1.3-10}$ inorganic composition based on filter measurements are presented in Fig. 2.7. The coarse (PM$_{1.3-10}$) fraction was dominated by crustal components (50%) and nitrate (16%). Sulfate, Na$^+$ and Cl$^-$ contributed approximately 10% each to the average coarse mass.

**Figure 2.7.** Daily average of PM$_{1.3}$ and PM$_{1.3-10}$ during the study, based on filter measurements. OM was calculated as OC*2.2 according to Hildebrandt et al. (2010). Crustal concentration is calculated using iron as a surrogate according to Sciare et al. (2005). Other is the sum of PO$_4^{3-}$ and K$^+$. PM$_{1.3}$ accounted on average for 47% of the PM$_{10}$ mass (Fig. 2.8), reaching 75% on May 17 and 27. The minimum contribution (21%) was observed when air masses originating from Africa caused a three-day Saharan dust event which started on May 19 and ended on May 21. During the event the PM$_{10}$ calcium concentration increased significantly along with the concentrations of other trace metals.

During this study PM$_{10}$ Na$^+$ and Mg$^{2+}$ correlated well with each other (R$^2$=0.76), indicating a common origin. Previous studies (Mihalopoulos et al., 1997; Kouvarakis et
al., 2002) have also reported similar correlations and have attributed both constituents mainly to sea salt. PM$_{10}$ Cl$^-$ and Na$^+$ correlated well ($R^2=0.87$) with an average Cl$^-$/Na$^+$ mass ratio equal to 0.87. This ratio is lower by a factor of 2.1 than the typical seawater composition, indicating a deficit in Cl$^-$. This is probably due to the reactions of acids with sea salt that release hydrogen chloride (Seinfeld and Pandis, 2006), which is often observed in polluted coastal areas such as Finokalia (Mihalopoulos et al., 1997).

During this campaign ICP-MS-determined Al, Ca and Fe for PM$_{1.3-10}$ correlated well with each other ($R^2>0.83$) indicating a common crustal origin (Sciare et al., 2005). Because ICP-MS did not provide measurements of Si and because our findings were similar to those of Sciare et al. (2005), we used their approach to determine the dust contribution, which is based on iron instead of the sum of oxides algorithm of Malm et al. (1994). The rest of the elements determined by ICP-MS were typically below 0.01 μg m$^{-3}$ with the exception of Zn, which had an average concentration of 0.1 μg m$^{-3}$. ICP-MS analysis was not conducted for the PM$_1$ fraction as recent studies in the same area have indicated that the elemental concentrations of crustal origin in this size fraction are close to zero (Koulouri et al., 2008).

The particles during FAME-08 always contained water according to both the Q-AMS and the DAASS, even when RH was low. Similar hygroscopic behavior during summer months has been reported before for sulfate rich PM (Klystov et al., 2005).

### 2.6.5 Organic PM

In order to convert OC to organic matter (OM), OC was multiplied by 2.2 based on the AMS analysis of Hildebrandt et al. (2010). This value is consistent with the suggestions of Turpin and Lim (2001) for aged aerosol. Q-AMS organics and filter PM$_1$ OM correlated well ($R^2=0.79$). OM represented 28% (average concentration 2.3 μg m$^{-3}$)
3) of the PM$_1$ mass on average. Finokalia is similar to other European rural and background sites, where OM represents 20-30% of the PM$_{2.5}$ concentration (Putaud et al., 2004) and different than elevated remote sites where OM represents about half of the PM$_1$ mass (Lanz et al., 2009). The ANOVA test revealed a lack of diurnal pattern of the total organic aerosol measured by the Q-AMS, yet the fraction of the total organic aerosol mass due to fragments at $m/z$ 43 and 44 exhibited diurnal patterns of similar phase (Hildebrandt et al., 2010). The mass fragment at $m/z$ 44 mostly corresponds to the CO$_2^+$ ion and can be used as a measure of the extent of oxidation. A detailed analysis of the organic aerosol measured by the AMS during FAME-08 is presented in Hildebrandt et al. (2010).

The water soluble fraction of the PM$_1$ organic content was on average 79.5±7.8% (Fig. 2.9). This large percentage of water soluble carbon supports our hypothesis that organic PM at Finokalia was highly aged. Furthermore, Q-AMS data analysis concluded that $m/z$ 44 contributed on average 18% to the total organic mass (Hildebrandt et al., 2010) which points to a highly oxidized organic aerosol, typical for highly aged air masses (Jimenez et al., 2009).

The PM$_1$ filter based OC/EC slope was equal to 5.4 (Fig. 2.10) for the study period, with the exception of May 19 to May 21 where the slope was equal to 2.8 due to the high EC concentrations in the African air mass. An OC/EC slope equal to 5.4 suggests that a significant fraction of the organic PM is secondary, while a value of 2.8 indicates that the secondary formation is limited (Cabada et al., 2004; Lim and Turpin, 2002). All of the organic aerosol was oxygenated (OOA) during FAME-08; hydrocarbon-like organic aerosol (HOA) was not present in detectable amounts (Hildebrandt et al., 2010). Considering that sources influencing Finokalia are expected

![Figure 2.9. Percentage of water soluble OC based on PM$_1$ filter measurements. On average 80% of OC was water soluble.](image)
to contain HOA, these results suggest that HOA was converted to OOA in the 6-36 hours of transport from the source areas to Crete. The OC/EC ratio correlates moderately ($R^2=0.2$) with daily average ozone, but a time lag between the ozone peak and the OC/EC ratio was observed (Fig. 2.11). Using a time lag of one day the correlation increased ($R^2=0.44$) suggesting that the oxidation of organics does not take place near the site but away from it. Similar findings have been reported for urban areas (Cabada et al., 2004).

**Figure 2.10.** OC versus EC as determined by PM$_1$ filters. The slope of the OC versus EC line was 5.4 (blue points) for the study period with the exception of May 19-May 21 (source region Africa), when it was equal to 2.8 (black points).

**Figure 2.11.** OC/EC as a function of time. Ozone and OC/EC are moderately correlated and have a time lag of one day.

### 2.6.6 PM Size Distribution

Average number, surface area and volume size distributions are presented in Fig. 2.12. The SMPS-measured average number distribution was centered at 90 nm, the surface area distribution at 245 nm and the volume distribution at approximately 300 nm. Diurnal profiles of number, surface area and volume distributions did not exhibit any trends, which is consistent with the lack of local sources of particles. The average total number concentration was 2690±1072 cm$^{-3}$ (Fig. 2.13). Particles below 50 nm did
not contribute significantly to the number concentrations ($N_{10-50}=337\pm296$ cm$^{-3}$) contrary to larger fractions ($N_{50-100}=1044\pm581$ cm$^{-3}$, $N_{100-500}=1309\pm590$ cm$^{-3}$). Finokalia exhibits very similar behavior to the European natural background sites where average number concentrations vary between 3000 and 5000 cm$^{-3}$ and are centered above the 10-30 nm reported for urban, near-urban and rural sites (Van Dingenen et al., 2004).

**Figure 2.12.** Campaign average of number, surface area and volume distribution. Error bars represent one standard deviation from the average.

Source region analysis concerning number concentration indicates higher contributions from Athens, Greece and other continental source regions than for air masses of marine and African origin. $N_{10-50}$ was also influenced by nucleation and growth of particles. During FAME-08 six nucleation events took place, according to AIS measurements, accompanied by growth of the particles to the Aitken mode. Typical air ion number concentration between 2 nm to 20 nm was near zero on non event days and reached up to 100-300 cm$^{-3}$ during a nucleation event. An analysis of approximately a year of ion measurements at Finokalia including the FAME-08 period can be found in Manninen et al. (2010).

### 2.6.7 Gaseous Species

Daily average concentrations of SO$_2$ and HNO$_3$ never exceeded 220 and 400 ppt respectively (Fig. 2.14). SO$_2$ and HNO$_3$ levels were below the detection limit (20 ppt) for 109 and 13 of the 180 analyzed samples, accounting for 61% and 7% of the duration of the campaign, respectively. The average concentrations of the values above the detection limit were $81\pm70$ ppt for SO$_2$ and $178\pm100$ ppt for HNO$_3$. The low SO$_2$/sulfate ratio (average = 0.06) suggests that the conversion of SO$_2$ to sulfate is almost complete by the time that the air masses arrive at Crete. Hildebrandt et al. (2010) estimated a
maximum OH value of $1.5 \times 10^7$ molecules cm$^{-3}$, which corresponds to a SO$_2$ consumption rate of 6.3% per hour in this environment. Several SO$_2$ plumes were observed with concentrations reaching levels above 1 ppb. Most of these plumes were associated with transport from coal-fired power plants in northwest Turkey (Canakkale area) and the Peloponnese (Megalopoli area).
2.7 Conclusions

A month of ambient particulate and gas phase sampling was conducted at a remote area in the Eastern Mediterranean in order to characterize the properties and temporal variability of PM. The lack of statistically significant diurnal variation in the bulk concentration of all constituents monitored by the Q-AMS and in the number concentrations suggests the absence of strong local sources. The coarse (PM$_{1.3-10}$) fraction was dominated by crustal matter (50%) and sea salt (24%). The dominant PM$_1$ constituents were sulfate and organics, accounting for 55% and 28% of the dry mass, respectively. The FAME-08 period was characterized by relatively high sulfate levels compared to those reported in other European background sites, and the sub-micrometer particles were acidic during most of the time.

On average 80% of the PM$_1$ organic aerosol was water soluble and its OC/EC ratio was equal to 5.4, indicating that the organic aerosol content was mainly secondary and highly oxidized. This conclusion is supported by the Q-AMS analysis of the PM$_1$ organics presented by Hildebrandt et al. (2010). These authors reported that hydrocarbon-like organic aerosol was not detected because all of it had reacted during the one day of transport from the mainland. The OA was highly oxidized and had a surprisingly invariant AMS spectrum regardless of the source region. Hildebrandt et al.
(2010) concluded that atmospheric oxidation of OA appears to converge to a highly oxidized organic aerosol, regardless of the original organic aerosol source. The OC/EC ratio was found to correlate ($R^2=0.44$) moderately with the average ozone concentration of the previous day.

Analysis of retroplumes obtained from a particle dispersion model in backward mode combined with statistical tests was conducted and five source regions were identified (Athens, Greece, other continental, Africa, marine). The hot and dry air masses originating from Africa resulted in an increase in temperature by 4°C and a decrease in relative humidity by 16% on average. Air masses from Africa were also associated with increased dust concentrations, increased aerosol absorption, increased concentrations of small air ions (<2 nm), lower ozone and a decrease of the OC/EC ratio by half. Source regions Athens, Greece and other continental were associated with higher sulfate, organic and number concentrations. Air masses of marine origin had the lowest concentrations for all PM$_1$ species.
2.8 References


Chapter 3

New particle formation at a remote site in the Eastern Mediterranean *

3.1 Abstract

A year (6-April-2008 to 14-April-2009) of particulate monitoring was conducted at a remote coastal station on the island of Crete, Greece in the Eastern Mediterranean. 58 regional new particle formation events were observed with an Air Ion Spectrometer (AIS), half of which occurred during the coldest months of the year (December-March). Particle formation was favored by air masses arriving from the west that crossed Crete or southern Greece prior to reaching the site and also by lower-than-average condensational sinks (CS). Aerosol composition data, which were acquired during month-long campaigns in the summer and winter, suggest that nucleation events occurred only when particles were neutral. This is consistent with the hypothesis that a lack of NH₃, during periods when particles are acidic, may limit nucleation in sulfate-rich environments. Nucleation was not limited by the availability of SO₂ alone, as nucleation events often did not take place during periods with high SO₂ or H₂SO₄ concentrations. The above results support the hypothesis that an additional reactant (other than H₂SO₄) plays an important role in the formation and/or growth of new particles. Our results are consistent with NH₃ being this missing reactant.

3.2 Introduction

Formation of new particles in the atmosphere is frequently observed at many different sites around the world (Kulmala et al., 2004) and is of interest due to the particles’ effect on radiative forcing, cloud formation and lifetime (Charlson and Heitzenberg, 1995). Even though sulfuric acid has been identified as a key component in aerosol formation and growth (Kulmala and Laaksonen, 1990), it is clear that other chemical compounds often participate in the formation and growth of new particles (Kulmala et al., 2004). Ammonia, amines, iodine and organics have been suggested as potential candidates in different environments (Ball et al., 1999; Kulmala et al., 2002; Jimenez et al., 2003; Jung et al., 2008; Benson et al., 2009; 2011; Berndt et al., 2010;

Erupe et al., 2011), but due to instrumentation limitations the composition of the fresh nuclei remains unknown. The recently developed Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer (API-TOF, Tofwerk AG) can measure the chemical composition of the naturally charged fraction of ions (Junninen et al., 2010) and may contribute to our understanding of the particle formation process (Ehn et al., 2010).

The sulfuric acid – water binary nucleation rates (Kulmala and Laaksonen, 1990; Laaksonen, 1999; Vehkamaki et al., 2002) often appear to be too low to explain observed nucleation rates in the planetary boundary layer (Weber et al., 1999). Ternary nucleation theory (Korhonen et al., 1999; Kulmala et al., 2002; Napari et al. 2002; Merikanto et al., 2007) includes ammonia whose presence considerably decreases the equilibrium vapor pressure of sulfuric acid above the solution surface (Coffman and Hegg, 1995). Ternary nucleation theories have also been used as a basis for the development of second-generation semi-empirical parameterizations (Jung et al., 2008) that try to correct the original rates that appear to be too high compared with ambient observations (Kulmala et al., 2002). According to Jung et al. (2006) nucleation does not occur in sulfur rich (regarding sulfur rich areas where the sulfate concentration exceeds that of organics and hence the sulfate to organics ratio exceeds unity) areas if there is not enough ammonia to neutralize all particulate sulfate. If sufficient NH$_3$ is present then nucleation ends when ammonia is consumed following the condensation of sulfuric acid into the newly formed and pre-existing particles. This however does not reflect the composition of the stable cluster which in the same study is predicted to include two molecules of ammonia and two of sulfuric acid and hence is acidic.

Ion-induced nucleation results in early cluster stabilization via condensation onto pre-existing ions and typically occurs at higher altitudes (Lovejoy et al., 2004). Observations from a variety of European sites suggest that ion-induced mechanisms are not enough to explain the observed 2 nm particle formation rates (Manninen et al., 2010). Kulmala et al. (2000; 2006) proposed that thermodynamically stable clusters are always present but grow only at favorable conditions. Kinetic nucleation theory assumes the formation of dimers as potential particle formation nuclei (Lushnikov and Kulmala, 1998). Particle concentrations during nucleation events vary within the boundaries predicted by the cluster activation and kinetic nucleation theory at a remote site in a boreal forest (Sihto et al., 2006) and in a polluted environment (Riipinen et al., 2007). Recent smog chamber experiments indicate that semi-volatile organic compounds may also be affecting the nucleation process (Metzger et al., 2010). Recent
studies on the formation and composition of the smallest observable particles depict however, an important role of basic gases (such as NH₃ and amines) as cluster stabilizing agents (Berndt et al., 2010; Ehn et al., 2010; Erupe et al., 2011).

Besides the presence or absence of certain compounds, nucleation is also affected by meteorological parameters. It is a photo-induced phenomenon and mainly occurs during daytime under direct sunlight while the presence of clouds acts as an inhibitor (Stanier et al., 2004; Boy and Kulmala, 2002). Even though theoretical models predict that increasing relative humidity (RH) results in higher nucleation rates (Kulmala et al., 2002) ambient measurements show that, indirectly, increasing RH can be a nucleation inhibitor. The surface area of existing particles increases as the ambient RH increases and high RH values are also often connected with cloudy conditions (Vehkamaki et al., 2004; Lyobovtseva et al., 2005).

In a previous work particle formation was investigated at Finokalia (the site of our measurements) for a two month period but without monitoring particles below 18 nm (Kalivitis et al., 2008). The three nucleation events which occurred during that period took place in air masses arriving from the west and resulted in an 80-100% increase of the particle number concentration. Coastal particle formation has been investigated extensively along the Irish coastline where it is driven by low tides. The observed nucleation in Mace Head is consistent with ternary nucleation rates with IO₂ as the third constituent (O’Dowd et al., 2002b; O’Dowd and de Leeuw, 2007). At Bodega Bay, California, nucleation has been also associated with ocean upwelling and occurs only close to the shore. Because the phenomenon is limited in space, observed newly formed particles in the coastal site did not grow to the Aitken mode (Wen et al., 2006).

In this paper we test the hypothesis that a third reactant other than sulfuric acid and water is involved in new particle formation. We focus especially on the role of NH₃ which has been suggested as a potential candidate for the third reactant. We study events that occurred between April 2008 and April 2009 at a remote coastal station located in the southeast of the Mediterranean Sea on the island of Crete, Greece, and we try to characterize them in terms of aerosol composition and seasonality. We will test the hypothesis that nucleation events at Finokalia are not limited by the sulfuric acid availability or the condensation sink but mainly by the ammonia levels. We will utilize aerosol thermodynamic theory and the available aerosol composition measurements to identify periods of practically zero (<1 ppt) gas-phase ammonia concentrations.
Synthesizing these findings we will try to explain the unexpected seasonal pattern and frequency of nucleation events at the area.

3.3 Experimental

3.3.1 Sampling Site

Measurements were conducted at the Finokalia station (35°24’ N 25°60’ E) which belongs to the network of European Supersites for Atmospheric Aerosol Research (EUSAAR). The station is located at a remote coastal site in the southeast of the Mediterranean Sea on the island of Crete, Greece at a top of a hill in the steep slope of a mountain reaching all the way to the sea. The nearest large urban center is Heraklion with 150,000 inhabitants, located 50 km west of Finokalia. No notable human activity is present at a range of approximately 15 km from the site (Kouvarakis et al., 2000). There are very few trees and little vegetation in the surrounding area. Most of the aerosol at the site is transported from the surrounding regions (Greece, Turkey, Northern Africa, Eastern and Central Europe) (Pikridas et al., 2010). Tidal amplitudes in the Mediterranean Sea (and hence at Finokalia) are of the order of a few centimeters (El-Gizery, 2010).

3.3.2 Measurement Period

Particle formation events were followed for one year (April-08 to April-09) during which two intensive campaigns took place, the Finokalia Aerosol Measurement Experiment -2008 and -2009 (FAME-08 and FAME-09), both part of the EUCAARI intensive campaigns (Kulmala et al., 2009). FAME-08 took place in the early summer (4 May to 8 June) (Pikridas et al., 2010), while FAME-09 took place during the late winter (25 February to 26 March 2009) (Hildebrandt et al., 2010b).

The main objective of the EUCAARI field campaigns was the understanding of the interactions of climate and air pollution, and involved a number of ground monitoring sites including Finokalia. Measurements were performed at different locations in Europe from April 2008 to May 2009. FAME-08 and -09 were month-long campaigns at Finokalia that provided more extensive measurements during the summer and winter, respectively.

3.3.3 Instrumentation

For the one year period under investigation an Air Ion Spectrometer (AIS) (Mirme et al., 2007) was used to monitor air ions ranging from 0.8 to 40 nm in diameter. The AIS measures simultaneously the positive and negative ion distributions from 3.2 to
0.0013 cm² V⁻¹ s⁻¹ (approximately 0.8-40 nm diameter). The spectrometer tends to overestimate low concentrations of cluster ions. This is caused by a natural production of small ions (< 1 nm, 10 to 100 cm⁻³) inside the spectrometer. Particle number size distributions of dried ambient aerosol (RH<40%) were monitored using a custom-made Differential Mobility Particle Sizer (DMPS) (Birmili et al., 1999) at a size range of 9-900 nm. The AIS measures only the naturally charged particles and therefore its measured concentrations are much lower than that of the Scanning Mobility Particle Sizer (SMPS) or DMPS for the same size range. AIS and SMPS/DMPS measurements were corrected for diffusion losses within the instruments and care was taken to minimize the diffusion losses in the sampling lines. Also meteorological parameters (RH, temperature, solar irradiance, wind speed) were monitored throughout the campaign.

During the two intensive campaigns, the size distribution of aerosol at ambient relative humidity was also monitored by a SMPS (TSI model 3034 – FAME-08; TSI model 3080 – FAME-09) and the size-resolved chemical composition of ambient non-refractory particulate matter of diameter less than 1 μm (PM₁) was measured, without drying of the air samples, using a Quadropole – Aerosol Mass Spectrometer (Q-AMS) from Aerodyne Research, Inc. (Jayne et al., 2000; Canagaratna et al., 2007). The calibration of the Q-AMS and the analysis of the spectra during both campaigns are discussed in detail by Hildebrandt et al. (2010a; b).

Ambient composition of particulate matter of diameter less than 1.3 μm (PM₁,₃) was monitored using filters (Millipore, Fluoropore membrane filters of 3.0 μm pore size) with daily resolution during FAME-08 and FAME-09 and found to correlate well (R²=0.95 for sulfate and 0.86 for ammonium) with Q-AMS measurements (Pikridas et al., 2010). Gaseous acidic species (SO₂, HNO₃) were monitored using alkaline impregnated filters positioned after the particulate filters with 6-hour and 12-hour resolution during FAME-08 and FAME-09, respectively. During both campaigns the inorganic semi-volatile (e.g. nitates) concentrations were low (<0.1 μg m⁻³). The particle composition based on the filter analysis has been presented by Pikridas et al. (2010).

3.3.4 Sulfuric Acid Approximation

For each campaign a sulfuric acid proxy was calculated based on the SO₂ measurements, the photolysis frequency of NO₂ (J_NO₂) and the calculated CS. Hildebrandt et al (2010a) used the photolysis frequency of NO₂ to estimate the concentration of the OH radical at Finokalia, based on the correlations of Berresheim et
Following the same procedure we estimated the OH radical concentration and combined it with the SO$_2$ measurements and the calculated condensational sink (see Section 3.3.7) to estimate the sulfuric acid concentration according to:

$$[H_2SO_4] = k_{OH} \frac{[SO_2][OH]}{CS}$$  \hspace{1cm} (3.1)

where $k_{OH}$ is the reaction constant of SO$_2$ with the OH radical and is equal to $8.5 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 298 K (DeMore et al., 1997); (OH) and (SO$_2$) are the concentrations of OH and SO$_2$, respectively and $CS$ is the condensational sink. Eq. 3.1 is based on the assumptions that the oxidation of SO$_2$ with the hydroxyl radical is the only sulfuric acid source, the major sink is the condensation of sulfuric acid onto the existing aerosol surface and the system is at pseudo-steady-state. At Finokalia these assumptions are valid (Bardouki et al., 2003). These authors using an equation similar to Eq. 3.1 based on similar SO$_2$ filter measurements found very good correlation ($R^2=0.85$) of the predicted H$_2$SO$_4$ concentrations with values measured by a CIMS. This is due to the fact that the Finokalia site is remote and therefore pollutant concentrations change relatively slowly (compared to sites close to sources). Therefore, the available SO$_2$ filter based measurements for Finokalia should provide a fair estimate of sulfuric acid concentrations.

The uncertainty of this approximation is a combination of the measurement uncertainty of the SO$_2$, the condensation sink calculation, and of J$_{NO_2}$. In this work we used the same methods as Bardouki et al. (2003), hence we expect the same overall uncertainty. Since the work of Bardouki et al. (2003) is based on summer measurements the approximation uncertainty is expected to be higher when applied to winter periods. An increase in the uncertainty of the approximation is also expected if the filter resolution is lower than the six hour one proposed by Bardouki et al. (2003).

### 3.3.5 Retroplume Analysis

Following the source region approach of Pikridas et al. (2010) we categorized the air masses sampled at the station based on their source region using the footprint potential emission sensitivity (PES) from 20-day retroplume calculations with the particle dispersion model FLEXPART in backward mode (Stohl et al., 2005), with three hour resolution. Additional information about PES calculations can be found in Seibert and Frank (2004). A retroplume was attributed to a region if that region had a PES value above 0.9 ns kg$^{-1}$. For periods in which more than one source region had PES values above the threshold, we attributed the air mass to the region though which the
retroplume passed last before reaching the site. The categories used were named by the region from which the air originated: Marine, Greece, other continental, West Crete and East Crete (Fig. 3.1). In order to characterize a retroplume as marine, all PES values above 0.9 ns kg\(^{-1}\) had to be located over the sea.

![Fig. 3.1. Source regions used in the retroplume analysis (Greece, Turkey, West Crete, East Crete and Marine). The sampling station (Finokalia) and Athens (population approximately 5 million people) are also denoted on the map.](image)

For each source region \(i\) the normalized frequency \(F_i\) of nucleation was calculated as:

\[
F_i = N_{i, \text{total}} \frac{N_i}{N_{i, \text{total}}} \tag{3.2}
\]

where \(N_i\) is the number of nucleation event retroplumes associated with the source region \(i\), \(N_{i, \text{total}}\) is the sum of all retroplumes associated with this source region and \(N_{\text{total}}\) is the number of retroplumes investigated regardless of source region, equal to 1046 in this study. The normalized frequency \(F_i\) corresponds to the number of nucleation events per year if the wind was always coming from the source region \(i\).
3.3.6 Particle Formation Event Categorization

The observation period was divided into particle formation event days, non-event days and undefined days. The data classification follows closely the work of Manninen et al. (2010), which combined the classification schemes introduced by Dal Maso et al. (2005) and Hirsikko et al. (2007). In this work, however, we chose to concentrate on the regional nucleation events that show clear condensational growth (event classes I and II in Manninen et al., 2010). In general, a day is classified as a regional particle formation event day if a nucleation mode is present for several hours and grows continuously during the course of the day. In this work the appearance of a nucleation mode corresponds to an increase of the charged particle concentration in the 2-10 nm range above 15 cm$^{-3}$ for more than an hour. The concentration of charged particles in this range is typically much less than 10 cm$^{-3}$. If no traces of a nucleation mode are seen, a day is classified as a non-event day. Days that did not clearly belong to either of the aforementioned categories were classified as undefined, including those during which a particle burst was picked up by the AIS without subsequent condensational growth and those during which the nucleation mode is not clear. Days during which particle formation was measured by the AIS, but not the SMPS are included in the undefined days. Some of the days regarded as “undefined” by Manninen et al. (2010) are in this work considered as “non-event” days.

AIS positive and negative-ion along with SMPS measurements during typical event, undefined and non-event days are presented in Fig. 3.2, 3.3 and 3.4, respectively. Particle formation was identified by an increase of concentration in the 2 to 10 nm range, which was less than 10 cm$^{-3}$ on non-event days, and the subsequent growth of the freshly-formed nucleation mode. Because the concentration of air ions is typically low from 2 to 10 nm, it provides a very sensitive way to follow nucleation events. This distribution of naturally charged air ions (Fig. 3.2) is not unique at Finokalia but has been observed elsewhere (Manninen et al., 2010).

3.3.7 Nucleation Event Characteristics

Event Duration: In order to calculate the duration of an event, the total number concentration of air ions with diameter between 2 and 10 nm versus time was followed and fitted to a normal distribution (Hirsikko et al., 2005). The beginning and end of an event was determined by the initial increase and maximum of the total number concentration fit, respectively. Decrease of the number concentration implies that the
Figure 3.2. SMPS and AIS measurements during a nucleation event day (19 March 2009) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).

Figure 3.3. SMPS and AIS measurements during an undefined day (13 May 2008) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).
Figure 3.4. SMPS and AIS measurements during a non-event day (5 May 2008) at Finokalia. SMPS (top) distribution ranging from 10 nm to 500 nm. Positive (bottom) and negative (middle) ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).

rate of particle production is lower than the combined rates of coagulation and particle growth above 10 nm or that the air mass is getting diluted; it does not necessarily imply that the rate of production is zero. Thus, our calculated end of particle formation is a lower-bound estimate. This procedure minimizes bias of new particle formation (NPF) duration due to various discrepancies such as measurement uncertainty or dispersion/dilution changes in the air mass.

* Aerosol Acidity: PM$_1$ water soluble ions at Finokalia correspond approximately to half of the mass for this size range, on an annual basis, followed by organics that account for 33% (Koulouri et al., 2008). Water soluble ions are dominated by sulfate and ammonium while the concentration of other PM$_1$ ions (nitrate, chloride) is typically below 0.2 μg m$^{-3}$. Thus, Finokalia is a sulfate rich site, especially during the summer when PM sulfate concentrations reach their highest values and dominate the PM$_1$ composition. Unlike PM sulfate concentrations, gas phase sulfur (namely SO$_2$) concentration is typically below 1 ppb (Bardouki et al., 2003). PM$_1$ acidity at Finokalia is practically equal to the ratio of ammonium to sulfate and nitrate in molar equivalents due to lack of other ions for this size range (Pikridas et al., 2010), assuming that all nitrate is inorganic. However, the ratio is not very different when we assume that all nitrate was organic (i.e. inorganic nitrate = 0) since nitrate concentrations were low.
Refractory material accounts on an annual average basis for 2% of the PM$_1$ (Koulouri et al., 2008). Therefore we can exclude refractory material from our PM$_1$ acidity analysis without significant error. Using this definition of particle acidity, neutral particles have ratios equal to unity while acidic particles have ratios smaller than unity.

The classification of a period as “neutral” or acidic is complicated by the measurement errors of the corresponding ion concentrations. To characterize this error we have taken advantage of the fact that the acidity ratio cannot exceed unity. Assuming that measurements are not biased and that the random error for neutral periods is normally distributed around unity, we estimated the standard deviation of the distribution based on values of the ratio exceeding unity (Fig. 3.5). The above simplification is valid only if ammonia is the dominant basic species present to neutralize acidic particles. It is not true if other basic species, such as Ca$^{2+}$, compete with ammonia. This is the case during dust events when the coarse mode increases dramatically and contributes significantly even to the PM$_1$ mass (Pikridas et al., 2010). During each intensive campaign one dust event occurred during which no nucleation events were observed, and have been excluded from our analysis.

![Figure 3.5. PM$_1$ cations to anions ratio (in equivalents) distribution for FAME-08 and -09 from 08:00-16:00 (a,c) and the cations to anions distribution during new particle formation events and undefined events for FAME-08 and -09 (b,d) based on Q-AMS measurements.](image-url)
**Growth rate:** The diameter growth rates (GR) of the newly-formed particles are related to the condensational flux of vapors onto the nucleation mode aerosol. Particle growth rates were determined from the AIS ion data for 1.5-3, 3-7, and 7-20 nm particles with the method introduced by Hirsikko et al. (2005). First, a normal distribution function was fitted to the time series of the particle concentration in each of the AIS size channels. Then, the times \( t_{\text{max}} \) corresponding to the maximum concentration in the size channels (characterized by their geometric mean size \( D_p \)) were determined from the fits, and GR values were obtained by a linear least-squares fit to the resulting \( (t_{\text{max}}, D_p) \) data. When the method of maximum concentrations is used, the effect of charging rate to growth rate is small (Yli-Juuti et al., 2011) provided that the charged fraction stays the same during the growth, which is possible by analyzing only one size bin at the time. Both polarities were analyzed separately but because of the higher negative ion concentrations our analysis will be based on them.

In addition to the size-dependent GRs obtained from the AIS data, we determined daily GR values for > 10 nm particles from the SMPS data. This analysis was done using the method introduced by Dal Maso et al. (2005), where the growth rate is determined by following the evolution of the geometric mean size of the nucleation mode.

**Condensation and coagulation sink:** The capability of the existing aerosol population to remove vapors and freshly formed particles can be described by the condensational (CS) and coagulation sinks \( \text{CoagS}(D_p) \) respectively (Kulmala et al., 2001; Dal Maso et al., 2005). CS is defined as the condensational loss rate constant of vapors, whereas \( \text{CoagS}(D_p) \) is a similar loss rate constant for particles with size \( D_p \) due to coagulation with larger particles. The values of condensation and coagulation sinks are closely coupled (both being roughly proportional to the aerosol surface area), so only the CS values were calculated to describe the background aerosol population. The CS values were calculated based on the DMPS/SMPS data and the properties of the condensable vapors are assumed to be similar to sulfuric acid, without accounting for hydration, leading to a maximum estimate.

The coarse fraction (above \( \text{PM}_{10} \)) is alkaline and acts as a sink for sulfuric acid vapors, due to the reactions with sea salt and dust (Pikridas et al., 2010). Ammonium concentrations in the coarse fraction were typically low and accounted for less than 2% of the coarse mass during FAME-08 (Pikridas et al., 2010) and less than 1% on an annual basis (Koulouri et al., 2008). \( \text{PM}_{\text{coarse}} \) filter-based measurements were made
during the FAME studies. The FAME-08 results are discussed in Pikridas et al. (2010). The sea-salt concentrations in the area have also been discussed by Mihalopoulou et al. (1997) and Koulouri et al. (2008). Briefly, the sea-salt PM\textsubscript{10} concentrations were a few micrograms per cubic meter and did not exceed 5 \( \mu \text{g m}^{-3} \). The average PM\textsubscript{1} concentration was 10 \( \mu \text{g m}^{-3} \). Therefore the coarse mode (with the exception of the dust event periods) had modest contribution (usually less than 20%) to the condensation sink.

The DMPS data corresponded to dried aerosol and were corrected for the hygroscopic growth of the particles in order to calculate the CS. Water uptake was calculated using the Extended - Aerosol Inorganic Model II (E-AIM) (Carslaw et al., 1995; Clegg et al., 1998; Massucci et al., 1999). The inorganic PM\textsubscript{1.3} monthly average concentrations for sulfate, ammonium, and nitrate based on filter measurements (Koulouri et al., 2008), were used as inputs for E-AIM in conjunction with RH and temperature measurements at ambient and dry conditions. The aerosol composition at Finokalia is quite stable (with the exception of dust events) and so use of the monthly average is a good first order approximation for the CS calculation. Hygroscopic growth was then estimated assuming volume additivity (Engelhart et al., 2010).

3.4 Results and Discussion

3.4.1 Nucleation Event Seasonal Cycle

During one year at Finokalia 58 particle formation events and 48 undefined events were observed, the monthly frequency of which is presented in Fig. 3.6. Nucleation events are favored during the colder months (December-March) when half of the events occurred. The normalized event frequency during those months was above 8 month\(^{-1}\) with the exception of January, when seven undefined events occurred. The lowest event frequency was during August, corresponding to only one nucleation day. During the rest of the study, event frequency ranged between 3 and 6 month\(^{-1}\). Similar low nucleation frequency during August and September has been observed in other sulfur rich regions (Stanier et al., 2004). The undefined frequency minimum occurred in September and the maximum in February, following a similar pattern as that of events.
Figure 3.6. Monthly frequency of nucleation events and undefined events. A minimum of events and undefined is observed during August and September and a maximum in February and March.

Fig 3.7. Average diurnal profile of the condensation sink (CS) during event (red), undefined (green) and non-event (blue) days. The CS of event and undefined days is on average about half of the CS of non-event days. The CS values are based on dry DMPS data and have been corrected for hygroscopic growth.
3.4.2 Condensational Sink

Yearly average “ambient” CS was equal to \((14\pm 15.9) \times 10^{-3} \text{ s}^{-1}\), being 80% higher than the corresponding dry CS, which was equal to \((7.8\pm 5.3) \times 10^{-3} \text{ s}^{-1}\). Both the “ambient” and dry annual averages are higher than the ambient CS reported for the coastal site of Mace Head \((5.5 \times 10^{-3} \text{ s}^{-1})\) and Hyytiälä in the boreal forest \((4.8 \times 10^{-3} \text{ s}^{-1})\) (Dal Maso et al., 2002). The CS was lower on event and undefined days than non-event days (Fig. 3.7). On average, the lowest CS values on event days occur around 08:00 (Local standard time, UTC+2), coinciding with the time nucleation events typically start, and increase linearly at a rate of \(0.3 \times 10^{-3} \text{ s}^{-1} \text{h}^{-1}\) due to growth of both the preexisting aerosol and of the newly formed particles (Fig. 3.7).

Contrary to this overall trend, in May 2008 (FAME-08) and March 2009 (FAME-09) the CS of event days was statistically similar to the non-event ones, as shown in Table 3.1, suggesting that the CS was not the factor limiting nucleation during these periods.

<table>
<thead>
<tr>
<th>Table 3.1. Growth rates and condensational sink in Finokalia during April 2008 – April 2009.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Month</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Jan-09</td>
</tr>
<tr>
<td>Feb-09</td>
</tr>
<tr>
<td>Mar (FAME-08)</td>
</tr>
<tr>
<td>Apr(08,09)</td>
</tr>
<tr>
<td>May (FAME-09)</td>
</tr>
<tr>
<td>Jun-08</td>
</tr>
<tr>
<td>Jul-08</td>
</tr>
<tr>
<td>Aug-08</td>
</tr>
<tr>
<td>Sep-08</td>
</tr>
<tr>
<td>Oct-08</td>
</tr>
<tr>
<td>Nov-08</td>
</tr>
<tr>
<td>Dec-08</td>
</tr>
<tr>
<td>Annual</td>
</tr>
</tbody>
</table>

*The CS of non-events is the average CS from 08:00-16:00 (Local standard time, UTC+2); b No DMPS data are available; c DMPS measurements are available only for one day.

During January 2009 a small number of events are observed, as shown in Fig. 3.6, due to the high condensational sink values of that month. Yet the seasonal variation of the CS cannot fully explain the observed NPF frequency. During August 2008 NPF frequency was at its minimum, but the highest monthly average CS was observed during October and November of the same year. CS during May 2008 and February 2009 is similar yet NPF frequency is four times higher during the latter.
3.4.3 Growth and Ion Formation Rates

The highest daily-growth rates were observed during the hottest months of the year (May 2008 to July 2008) (Table 1) reaching as high as 14 nm h\(^{-1}\) on 25 May 2008 and on 16 June 2008. The annual average growth rate of the study period was equal to 5.4±3.5 nm h\(^{-1}\). The smallest growth rates were observed during December 2008 (≤2 nm h\(^{-1}\)). Daily-growth rates at a boreal forest follow a similar seasonal pattern (Dal Maso et al., 2005), yet the annual average is about half than that of Finokalia (3 nm h\(^{-1}\)). Size-dependent growth rates were also calculated for three size ranges; 1.5-3 nm, 3-7 nm and 7-20 nm and the average growth rate for each size range was 3.6±1.1 nm h\(^{-1}\), 6.9±3.9 nm h\(^{-1}\) and 7.5±5.8 nm h\(^{-1}\), respectively. The size-dependent growth rates of the two larger size ranges typically exhibited higher values than the corresponding smaller size growth rates. The Kelvin effect is clearly one of the potential explanations for this behavior. Differences in the chemical composition of the particles can lead also to differences in the interactions between the condensing vapors and the particles and therefore affect the resulting condensation rates. This behavior, for example, can also occur during organic vapor condensation. As more and more vapors condense onto the particles, the Raoult effect lowers the equilibrium vapor pressures of condensable vapors, and enhances their condensational flux to the particles. Finally, it is also possible that the apparent size dependence is in fact a dependence on time. In this case the increase in the growth rates could result from a temporal increase in the concentrations of the condensable vapors. Our lack of understanding of the identity of the condensing vapors (other than sulfuric acid and ammonia) limits our ability to test the above explanations.

The calculated size-dependent growth rates during one FAME-08 event and one FAME-09 event were a factor of six or more higher than the rate that can be explained by condensation of sulfuric acid. Even if this analysis is based on only two events it suggests that species other than sulfuric acid may be dominating the growth of these fresh nanoparticles in Finokalia. Riipinen et al. (2011) reached similar conclusions for forested areas in Finland and Canada.

The average ion formation rates at 2 nm in Finokalia were around 0.08 ions cm\(^{-3}\) s\(^{-1}\) for both the positive and the negative ions with a range of 0.02 to 0.1 ions cm\(^{-3}\) s\(^{-1}\). A more detailed discussion of the growth rates and the ion formation rates for 12 European sites during the EUCAARI project can be found in Manninen et al. (2010).
**3.4.4 Retroplume Analysis of New Particle Formation**

Nucleation is a photo-induced phenomenon, thus only the retroplumes corresponding to arrival times between 08:00 and 17:00 (Local standard time, UTC+2) were investigated. Since we used retroplumes with 3-hour resolution, three retroplumes were investigated each day. The summary of the retroplume analysis is presented in Table 3.2. West and north-west winds favor NPF. The retroplumes which passed over Greece had the highest normalized frequency of an event (123 year⁻¹), followed by those associated with west Crete (101 year⁻¹). The majority of source region “Greece” events were associated with the Peloponnese (southeast Greece). The normalized frequency of undefined events was independent of the origin of the air mass (Table 3.2).

<table>
<thead>
<tr>
<th>Airmass Origin</th>
<th>West Crete</th>
<th>Greece</th>
<th>Turkey</th>
<th>East Crete</th>
<th>Marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retroplumes</td>
<td>216</td>
<td>161</td>
<td>298</td>
<td>185</td>
<td>186</td>
</tr>
<tr>
<td>Events</td>
<td>21</td>
<td>19</td>
<td>6</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Normalized Event</td>
<td>102</td>
<td>123</td>
<td>21</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Undefined</td>
<td>11</td>
<td>6</td>
<td>13</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Normalized Undefined</td>
<td>53</td>
<td>39</td>
<td>39</td>
<td>51</td>
<td>45</td>
</tr>
</tbody>
</table>

Pikridas et al. (2010) reported that PM₁ aerosol mass concentration and composition during FAME-08 were statistically similar for air masses that passed over Crete and for air masses that did not. Yet, a large difference in the normalized frequency of nucleation events exists: the frequency is much higher for air masses which passed over Crete than for those which did not. This is consistent with the hypothesis of a missing reactant which has sources over land. When the air mass does not pass over Crete, it is conceivable that this reactant is exhausted by the time that the air masses reach Finokalia and nucleation does not take place.

The effect of sea breeze affecting nucleation was also examined. Because of the surrounding terrain the winds at Finokalia are consistently NW to N. Therefore no correlation among the local wind direction and events or undefined periods was noted.

**3.4.5 Cations to Anions Ratio During Nucleation Events**

We would like to test the hypothesis that new particles form only when enough ammonia is present to neutralize fine particulate acids and an excess is available. Accurate measurements of gas-phase ammonia at sub-100 ppt levels are extremely difficult. We will rely instead on the accumulation mode particle acidity as an indirect
measure of the availability or lack of ammonia in the gas phase. The submicrometer inorganic particles equilibrate with the gas phase in a matter of minutes (Seinfeld and Pandis, 2006; Takahama et al., 2004). Therefore if they are acidic, all the gas-phase ammonia has been transferred to the particulate phase (its equilibrium concentration is practically zero) and there is no gas-phase ammonia available for participation in the ternary nucleation process (Jung et al., 2006). If however, the accumulation mode particles are neutral then according to aerosol thermodynamics there can be gas-phase ammonia present. E-AIM calculations using Q-AMS measurements from different periods of the study as input showed that during the “acidic periods” the ammonia mixing ratio was below or near the 1 ppt level, while when particles were neutral the ammonia mixing ratio increased sharply near or above the ppb level. Therefore the acidity of the accumulation mode can be used as a sensitive indicator of the existence or lack thereof of ammonia in the gas phase. In this case ternary nucleation should not occur if the PM$_1$ is acidic. This can be tested using the AMS PM$_1$ composition measurements.

The above argument applies to the accumulation mode particles. The coarse particles equilibrate with the gas phase much slower (timescales of hours) and therefore are not usually in equilibrium with the gas phase (Wexler and Seinfeld, 1992; Meng and Seinfeld, 1996). This is the case often over the ocean where acidic accumulation mode particles coexist with alkaline coarse mode particles (Capaldo et al., 2000). During nucleation events the fresh particles (assuming ternary nucleation) are acidic, while the accumulation mode particles are neutral according to the simulations of Jung et al. (2006). However, as the fresh particles grow to larger sizes they get neutralized by the available ammonia.

The hourly averaged PM$_1$ cations to anions ratio (C/A) in equivalents of the two intensive campaigns (FAME-08 and FAME-09), based on Q-AMS measurements, is presented in Fig 3.8. The campaign-average PM$_1$ C/A ratio was equal to 0.85 and 0.91 for FAME-08 and FAME-09 respectively. On several occasions (usually low concentration periods), during both campaigns, the ratio exceeded unity which was attributed to measurement uncertainty. The uncertainty for the C/A ratio was estimated to be 0.08 and 0.25 for FAME-08 and FAME-09 respectively (Fig. 3.5). The uncertainty of the FAME-09 C/A was greater than that of FAME-08 by a factor of 3 due to small PM$_1$ concentrations measured, which were often close to the limit of detection in the case of ammonium (<0.1 μg m$^{-3}$) (Drewnick et al., 2009).
During one third of the FAME-08 study, PM$_1$ C/A was below 0.84 and typically associated with air masses from Greece. On three periods the C/A ratio dropped below 0.5 (May 12 21:00 – May 13 10:00, May 24 13:20 – May 24 22:10, May 25 10:55 – May 25 23:00). On all three occasions the ratio dropped due to an increase in sulfate content which was not accompanied by an increase in ammonium. Likely the sources of sulfur include the power plants of Canakkale in Turkey and of Megalopoli in Greece as well as the city of Athens.

During FAME-08, the C/A ratios during all events and “undefined” days were above 0.84 and therefore, considering the measurement uncertainty, the particles were neutral (Fig. 3.9).

As an example, the C/A ratio of the June 1 2008 nucleation event is shown in Fig. 3.10. From midnight to 7 am, the C/A ratio was a little below 0.84, thus particles were acidic. The C/A ratio increased above 0.84 from 08:30 till 10:00, reaching 0.95, and new particles were formed. The event’s end coincided with a sharp C/A ratio decrease after 10:00.
Due to the large uncertainty of the C/A ratio during FAME-09 no definite conclusion could be made regarding particle acidity (Fig. 3.8). The average PM$_1$ C/A of all events and undefined FAME-09 periods was above 0.9 and individual measurements within the nucleation periods were within one standard deviation from unity (Fig. 3.9). Both these findings suggest that particles were neutral at least during the nucleation periods.

Our analysis therefore supports the hypothesis that nucleation events in this sulfur rich region occur during periods when the aerosol is neutral and NH$_3$ exists in the gas phase. On the other hand events do not occur, when the aerosol becomes acidic and the gas phase NH$_3$ is zero. While this does not prove that NH$_3$ is involved in particle formation it is consistent with this hypothesis. Other chemical compounds that covary with NH$_3$, such as amines, may also be involved. Amines are also gas-phase bases and therefore would have zero concentrations during periods when the fine PM is acidic.

There are no noteworthy local sources of NH$_3$ as no major agricultural activity occurs in the area. The main source of NH$_3$ and ammonium is long range transport as indicated by the very good correlation of NH$_4^+$ with non-sea-salt sulfate ($R^2=0.89$,
Koulouri et al., 2008). The annual average concentration of NH$_3$ in the area has been reported to be 315±136 ppt (Kouvarakis et al., 2001).

![Figure 3.10.](image)

**Figure 3.10.** Cations to anions ratio during the nucleation event of 1 June 2008 at Finokalia. The beginning and end of the event is noted on the graph. Red area corresponds to the estimated uncertainty (two standard deviations). Dashed line represents neutrality. Time of day corresponds to LST (UTC+2).

### 3.4.6 SO$_2$ and Sulfuric Acid Proxy During the Two Intensive Campaigns

Filter based SO$_2$ measurements were conducted during both intensive campaigns and are presented in Fig. 3.11. During both campaigns, the sources of SO$_2$ were the same, but the photochemistry and weather differed and thus the oxidation rates were quite different.

FAME-08 SO$_2$ measurements were presented by Pikridas et al. (2010). In brief, out of the 180 analyzed samples of FAME-08, 71 were above the detection limit (20 ppt), with an average campaign concentration equal to 81±70 ppt, using 20 ppt as the value for the samples which were below the detection limit. Nucleation events during that time (marked with red in Fig. 3.11) occurred when SO$_2$ levels were low and typically below or near the detection limit. On several occasions during FAME-08 (such as 20 May, 24 May, 4 June and June 8) when sunlight activity was intense, SO$_2$ levels ranged from 200 to 300 ppt and the condensational sink was low ($4-5\times10^{-3}$ s$^{-1}$), yet no event occurred. This supports our hypothesis that nucleation at Finokalia, during FAME-08, was not limited by photochemistry, sulfuric acid production or the condensational sink.
Figure 3.11. Filter based SO$_2$ measurements and condensation sink calculations during the two intensive campaigns. Red and green areas correspond to events and undefined respectively.

Figure 3.12. Sulfuric acid concentration estimated based on SO$_2$ measurements, photolysis frequency of NO$_2$ ($j_{NO2}$) and the condensation sink (CS). Red and green areas correspond to nucleation and undefined events, respectively.
During FAME-09 average SO$_2$ concentrations were 211±194 ppt and nucleation occurred with SO$_2$ concentrations ranging from 200 ppt to 450 ppt. SO$_2$ concentrations during FAME-09 nucleation events were more than a 10-fold higher than those of FAME-08 suggesting that low SO$_2$ concentrations could be limiting nucleation during FAME-09. The sulfuric acid concentration was estimated based on filter-based SO$_2$ measurements, photolysis frequency of NO$_2$ ($J_{NO2}$) and CS using Eq. 3.1 and is presented on Fig. 3.12. The estimated concentrations are in fair agreement with the sulfuric acid concentrations measured during the MINOS campaign (July-August 2001) at Finokalia (Bardouki et al., 2003).

Nucleation events during FAME-08 (marked with red in Fig. 3.12) occurred when the estimated H$_2$SO$_4$ concentrations were 5×10$^5$ -2×10$^6$ molecules cm$^{-3}$, typically lower than those during undefined days (7×10$^5$ - 6×10$^6$ molecules cm$^{-3}$) and lower than the average concentration of non-event days (3×10$^6$ molecules cm$^{-3}$). This supports our hypothesis that nucleation at Finokalia, during FAME-08, was not limited by photochemistry, sulfuric acid production or the condensational sink.

Contrary to FAME-08, during FAME-09 nucleation events occurred under higher (≈10$^7$ molecules cm$^{-3}$) than average (1.2±3.0×10$^6$ molecules cm$^{-3}$) estimated sulfuric acid concentrations, indicating that sulfuric acid production was one of the factors limiting nucleation during the winter.

3.5 Comparison with Other Studies

Nucleation in coastal areas like Mace Head has often been explained by iodine oxides (O’Dowd et al., 2002a, b) that are produced from the oxidation of biogenic emissions of iodine vapors. Marine algae are responsible for these emissions during low tide periods. These events are characterized by very high nucleation rates but small growth of the resulting particles to larger sizes (O’Dowd and Hoffmann, 2005). Links between tidal amplitudes and coastal nucleation have been observed at various sites (O’Dowd et al., 2002b; Russell et al., 2007; Whitehead et al., 2009). However, other studies in coastal areas where tidal amplitude is significant have reported that the nucleation events were not related to tide height (Modini et al., 2009; Coe et al., 2000).

The land morphology in the area around Finokalia is quite different from Mace Head with the steep slopes of the mountains extending all the way to the water. At the same time the tidal amplitude is very small. As a result, the nucleation events are very different in the two locations (e.g., the particle formation rates are orders of magnitude smaller in Finokalia, the growth of the particles is quite different, etc). At Mace Head
nucleation is due to a point or line source and often the growth of the nucleated particles cannot be followed (Vana et al., 2008), while at Finokalia most events follow the typical “banana shape” growth pattern. In addition to these our trajectory analysis indicates that nucleation in Finokalia is favored when the air mass spends most of its time over land. If nucleation was driven by algae emissions the Marine source region should have been favored. This leads to the important conclusion that even in coastal environments the formation and growth of ultrafine particles can be quite different.

Several coastal studies have taken into account the air mass history in order to explain NPF (Coe et al., 2000; Lee et al., 2008; Modini et al., 2009). A coastal site at west Korea has reported nucleation to be favored by westerly winds that cross the shorelines of China and Korea (Lee et al., 2008). At the Norfolk coast of the United Kingdom nucleation occurred when the air masses crossed over a certain area. It was found that the air mass was enriched with SO₂ followed by oxidation that caused nucleation (Coe et al., 2000). In the case of Finokalia, air mass history showed that west and northwest winds favored nucleation. We have assumed that the air mass is enriched with a missing reactant which we did not identify. Our analysis suggests that it could be ammonia or a species that co varies with it.

At Agnes Water, Australia the air mass history was shown not to affect nucleation, but nucleation was favored by sea breeze (Mondini et al., 2009). At Finokalia, due to the surrounding terrain the local wind direction is predominantly N-NW. As a result the wind direction patterns of events, undefined and non-events were identical.

Recently it has been reported that isoprene may act as a nucleation inhibitor in clean forest environments, if the ratio of emitted isoprene to monoterpene carbon is greater or equal to 10 (Kanawade et al., 2011). However, there are few trees in the area around Finokalia (it is by no means a forest) and the surrounding flora consists of a few low-level bushes and plants that survive in this dry climate.

3.6 Conclusions

A year of ambient particulate monitoring was conducted at a remote area in the Eastern Mediterranean in order to characterize new particle formation. Particle formation periods were categorized into event, non-event, and undefined days based on their characteristics. Undefined and event days are most frequent during February and March (winter) and least frequent during August and September (summer). Nucleation events are mainly associated with air masses arriving from the west and passing over
Crete, favored typically by lower than average CS. During the summer intensive campaign (FAME-08), all event and undefined particle formations occurred when particles were neutral under low SO$_2$ concentrations (<40 ppt) compared to the average (93 ppt).

During the winter intensive campaign (FAME-09) due to the large uncertainty of the C/A ratio, almost the whole study is consistent with neutral particles. Nucleation events occurred under higher SO$_2$ concentrations (360 ppt) compared to the average (220 ppt) indicating that the SO$_2$ concentrations were limiting to some extent particle formation during that period.

Our explanation of the unexpected seasonal variation of nucleation frequency (more events during the winter than during the summer) is that the availability of ammonia (or something that may covary with it like the amines) is limiting the frequency of the events. The main difference between summer and winter is that during the summer the SO$_2$ is oxidized fast enough so that particles are acidic most of the time. The available gas-phase ammonia is transferred to the particulate phase trying to neutralize the acid. There is more sulfate than ammonia available, so the system runs out of gas-phase ammonia. During summertime periods favorable for nucleation (high sulfuric acid, low particle surface area) the lack of ammonia (or amines) results in no nucleation events. In the winter when the photochemistry is significantly slower, there is significantly less sulfate around, so there is enough ammonia to neutralize it and some is left in the gas phase to participate in nucleation. When the right conditions appear, nucleation events take place. Air masses that pass over land just before arriving at the site can pick up ammonia and therefore nucleation is favored during these conditions.
3.7 References


Chapter 4
Ultratine Particle Sources and In-situ Formation in a European Megacity

4.1 Abstract

Ambient particulate matter size distributions were measured in Paris, France during summer (July 2009) and winter (15 February – 15 March 2010) at three fixed ground sites and using two mobile laboratories and one airplane. The campaigns were part of the MEGAPOLI project. New particle formation (NPF) was observed only during the summer. NPF occurred at the Paris center and a suburban site on half of the campaign days due to low condensational sink \((10.7\pm5.9\times10^{-3}\text{s}^{-1})\), which was driving the frequency of events at the two sites. NPF was also observed at 600 m altitude simultaneously with regional events identified on the ground. Increased particle number concentrations were measured outside of the Paris plume, and were attributed to NPF. The Paris plume was identified at least 200 km away from the Paris center during summer. The effect of Paris was different on the two suburban sites. During summer the site which was mainly downwind was not affected much by Paris emissions due to both local sources but also higher background number concentrations. The number concentration at the second site, which was mainly upwind during summer, increased by a factor of three when it was downwind of Paris. During winter, number concentration at the Paris center was on average \(1.3\pm0.7\times10^4\ \text{cm}^{-3}\), and decreased on the ground exponentially with distance. Further than 60 km, the number concentration was similar to that observed during summer. The number concentration at both suburban sites increased during winter when they were downwind of Paris by at least 50%.

4.2 Introduction

Urban areas in developed regions have been growing annually 0.7% in population since 2005 and account for more than 70% of the total population of the planet in 2010 (UN, 2011). In this work, following the definition of the Organization for Economic Co-operation and Development, urban areas correspond to a population density greater than 150 inhabitants per km\(^2\). Several of these urban areas have increased in size to mega-centers, attracting more than 5 million inhabitants. This has led to an increasing demand for transportation, energy and industrial activity that result in concentrated
emission of gases and particulate matter (PM) impacting local air quality (Molina and Molina, 2004; Molina et al., 2004; Lawrence et al., 2007; Gurjar et al., 2008). Atmospheric particles and trace gases in polluted environments have been linked with increasing mortality (Pope and Dockery, 2006) thus affecting life quality. Fine particles with diameter smaller than 2.5 µm (PM$_{2.5}$) are mainly responsible for this association (Pope et al., 2009; Wang et al., 2008).

Aerosol particles can change climate patterns and the hydrological cycle on regional and global scales (Chung et al., 2005; Lohmann and Feichter, 2005; IPCC, 2007). Primary particles, which usually dominate particle number concentrations, have a larger effect on climate, compared for example with nucleated particles, because they have a much higher probability of becoming cloud condensation nuclei (Pierce and Adams, 2007). However, the uncertainties in the primary emission rates and sizes are still large. On a global scale new particle formation (NPF) dominates the total aerosol number concentration as it occurs almost worldwide (Kulmala et al., 2004). The mechanism behind this major particle formation process is still not understood. This uncertainty has a direct impact on our understanding of the role of nucleated particles in climate change (Pierce and Adams, 2009). NPF is often a regional phenomenon covering areas of several hundred km$^2$ (Vana et al., 2004; Stanier et al., 2004; Komppula et al., 2006) but it can be space-restricted when at least one source of the nucleating vapors is space limited, as it has been observed in coastal sites (Wen et al., 2006).

During the past decade a number of studies reported ambient PM number concentrations in urban areas, spanning from a few months (Hering et al., 2007; Wang et al., 2010; Dunn et al., 2004; Baltensperger et al., 2002; McMurry et al., 2005), to one or more years (Woo et al., 2001; Alam et al., 2003; Shi, 2003; Stanier et al., 2004b; Wu et al., 2007; Rodriguez et al., 2005; Watson et al., 2006; Wåhlin, 2009). The majority of studies are based on observations from one or at most two static stations, assuming that these stations are representative of the area under investigation. Most of these studies have found higher concentrations during the winter due to increased energy demand along with a diurnal pattern that peaks due to morning rush hour traffic during weekdays but not on weekends.

NPF has been often observed in urban areas (Woo et al., 2001; Laasko et al., 2003; Tuch et al., 2003; Stanier et al., 2004a; Watson et al., 2006; Wu et al., 2008).
Growth and nucleation rates are seldomly reported in these studies (McMurry, 2000; Qian et al., 2007).

During the “Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation” (MEGAPOLI) project measurements were conducted in and around the largest megacity in Europe, Paris. Gas and particulate phase measurements from three fixed ground sites, two mobile laboratories and one airplane, were collected for both summer 2009 and winter 2010. The residence time of the air mass over land was found to influence PM mass levels; with the higher residence times leading to higher PM levels (Freutel et al., 2012). As a result air masses from the Atlantic, which were dominating during the summer campaign, led to relatively clean conditions (Freutel et al., 2012). Cooking was identified as a significant local source of Paris during summer with vehicular traffic being second (Beekman et al., 2012). During winter residential heating was found to be a major source of Paris.

In this work we focus on the particulate number concentrations in Paris and its surroundings during both (summer and winter) campaigns. The effect of the Paris megacity on its surroundings will be assessed together with the spatial extent of its influence. The frequency and spatial characteristics of new particle formation events are investigated.

4.3 Sampling Sites

Two month long campaigns during summer (1 July to 31 July 2009) and winter (15 January to 15 February 2010) were conducted. They included monitoring of the aerosol size distribution along with composition, coupled with gas phase and meteorological monitoring.

The city of Paris, called Ile de Paris (IDP), is an urbanized area covering about 3000 km² and the largest metropolitan city in Europe including more than 10 million inhabitants. The city is surrounded by rural areas and no urbanized center can be found at a radius of 80 km. The administrative boundaries of IDP and the greater Paris area called Ile de France (IDF) are shown in Fig. 4.1 with the population density map of the area.
Figure 4.1 Population density and administrative map of Paris. Outlined in red is Ile de France and in green Ile de Paris. The three ground stations (SIRTA, LHVP and GOLF) are depicted with black dots. The map is also separated into sectors depicted by dashed blue lines, formed by concentric circles centered at kilometer zero of Paris (48.8534°N 2.3488°E). The radius of the circles is 0.15, 0.25, 0.4, 0.6, 0.8 and 1 degrees of latitude (one degree being equal to 111.1 km approximately), which corresponds to 16.7, 27.8, 44.4, 66.7, 88.9 and 111.1 km.

Detailed aerosol measurements were conducted at an urban, and two sub-urban sites (shown on Fig. 4.1). The Site Instrumental de Recherche par Télédétection Atmosphérique (SIRTA, 48° 43’ 5” N 2° 12’ 26” E) is located in Palaiseau, 20 km south of IDP in a semi-urban environment inside the campus of Ecole Polytechnique. The site is surrounded by highways at 3-6 km distance in all wind directions. The Laboratoire d’Hygiène de la Ville de Paris (LHVP, 48° 49’ 11” N 2° 21’ 35” E) is located inside IDP. Measurements in LHVP were performed on a terraced roof 14 m above ground level. This site is a station of the AIRPARIF air quality monitoring network and is representative of the Paris urban background air pollution (Sciare et al., 2010; Favez et al., 2007). Finally the sub-urban station at Golf de la Poudrerie (GOLF, 48° 56’ 2” N 2° 32’ 49” E) was located 20 km northwest of IDP near a golf course and a forested park.

Two mobile laboratories were operated by the Max Planck Institute for Chemistry (Drewnick et al., 2012) and the Paul Scherrer Institute (Bukowiecki et al., 2002; Weimer et al. 2009) named MoLa and MOSQUITA respectively. These were moving
around IDF focusing on the air quality interactions between Paris and its surroundings. MoLa was stationed at GOLF during both campaigns and monitored either moving or stationed, while MOSQUITA was stationed at SIRTA and monitored only when in motion.

The airborne measurements were performed by an ATR-42 aircraft, operated by the French Service des Avions Français Instrumentés pour la Recherche en Environnement. Each flight included a circle around IDF followed by crossing the expected Paris plume multiple times, always at a constant altitude of 600 and 800 m above sea level for the summer and winter campaign, respectively. Flights were performed on 11 out of the 31 days of the summer MEGAPOLI campaign. Fig. 4.2 shows the flight patterns and sampling days of the ATR-42 during the summer campaign. Flights days were selected based on the ambient particulate levels observed on the ground. Higher PM concentrations were favored thus the observed properties are expected to be biased. During winter two flights per sampling day were conducted for three days. The first flight included a trip around IDF and the second, following a flight similar with the summer, monitoring the Paris plume.

Figure 4.2. Trajectories of the ATR-42 aircraft during the summer campaign. Solid colored lines correspond to a different flights.
4.4 Instrumentation

The available particle sizing instrumentation is summarized in Table 4.1. At SIRTA, particle size distributions ranging from 10 to 500 nm were monitored via a Scanning Mobility Particle Sizer (SMPS). The sampling inlet was located approximately at 4 m above ground and the aerosol was dried using a Nafion dryer. At the same site an Air Ion Spectrometer (AIS; Mirme et al., 2007) monitored the size distribution of positive and negative air ions of diameters ranging from 0.8 to 40 nm. To minimize particle losses the sampling line was smaller than 30 cm. A Differential Mobility Analyzer (DMPS) monitored, close to AIS, number size distributions ranging from 6 to 800 nm. At LHVP, the sampling inlet was located 6 m above ground and the aerosol sample was dried entering a DMPS which monitored the size distribution from 3 to 630 nm. At GOLF, the aerosol size distribution was monitored with an Electrical Aerosol Spectrometer (EAS) and sampling was conducted 8 m above ground.

MoLa, when stationed at GOLF, monitored aerosol size distribution via a Fast Mobility Particle Sizer (FMPS). The aerosol inlet was located at the same height with the stationary measurements. MOSQUITA monitored the number size distribution from 6 to 520 nm via a FMPS during summer and via an Ultra High Sensitivity Aerosol Spectrometer (UHSAS) during winter. The UHSAS monitored the size distribution ranging from 60 nm to 1 μm. The size distribution of ambient aerosol was monitored at an altitude via an FMPS during summer. The FMPS monitors particles ranging from 5 nm to 500 nm, yet the lower cutoff size was 20 nm due diffusion losses inside the sampling line. Aerosol number concentration was monitored directly during summer and winter flights using a condensation particle counter (CPC; TSI Model 3010) and a ultrafine CPC (Model 3025), respectively.

4.5 Methods

4.5.1 Particle Formation Event Categorization

Particle formation events have been categorized based on the concentration of 1.6 – 7.5 nm air ions (Hiirsiko et al., 2007; Vana et al., 2008) and on the concentration of total ambient particles below 25 nm (Stanier et al., 2004a; Dal Maso et al., 2005). At SIRTA both air ions and ambient particles were measured and therefore we used for
<table>
<thead>
<tr>
<th>Variable</th>
<th>Instrument</th>
<th>Group</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ATR-42</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (20 - 500 nm)</td>
<td>TSI 3091 FMPS(^a)</td>
<td>LaMP(^b)</td>
<td>1 sec</td>
</tr>
<tr>
<td>Absorption</td>
<td>PSAP(^e)</td>
<td>LaMP(^b)</td>
<td>1 sec</td>
</tr>
<tr>
<td>Trace Gas Concentration</td>
<td>HS PTR-QMS 500(^d)</td>
<td>CNRS(^e)</td>
<td>1 sec</td>
</tr>
<tr>
<td>Aerosol Number Concentration</td>
<td>TSI 3025 CPC(^f)</td>
<td>CNRM(^g)</td>
<td>1 sec</td>
</tr>
<tr>
<td>Absorption</td>
<td>PSAP(^e)</td>
<td>CNRM(^g)</td>
<td>1 sec</td>
</tr>
<tr>
<td><strong>MoLa</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (5–500 nm)</td>
<td>TSI 3091 FMPS(^a)</td>
<td>MPIC(^h)</td>
<td>1 min</td>
</tr>
<tr>
<td>Absorption</td>
<td>Thermo 5012 MAAP(^i)</td>
<td>MPIC(^h)</td>
<td>1 min</td>
</tr>
<tr>
<td>PAH concentration</td>
<td>Echo Chem PAS 2000(^j)</td>
<td>MPIC(^h)</td>
<td>1 min</td>
</tr>
<tr>
<td><strong>MOSQUITO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (5–500 nm)</td>
<td>TSI 3091 FMPS(^a)</td>
<td>PSI(^h)</td>
<td>1 sec</td>
</tr>
<tr>
<td>Absorption</td>
<td>PSI(^h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SIRTA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (10–500 nm)</td>
<td>SMPS(^k)</td>
<td>CMU(^l)</td>
<td>10 min</td>
</tr>
<tr>
<td>Aerosol Number Distribution (6–800 nm)</td>
<td>DMPS(^m)</td>
<td>UoH(^n)</td>
<td>9 min</td>
</tr>
<tr>
<td>Positive/Negative Ion Size Distribution (0.8–40 nm)</td>
<td>NAIS(^o)</td>
<td>UoH(^n)</td>
<td>3 min</td>
</tr>
<tr>
<td><strong>LHVP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (3–630 nm)</td>
<td>DMPS(^m)</td>
<td>IfT(^p)</td>
<td>10 min</td>
</tr>
<tr>
<td>Trace gas concentration</td>
<td>HS PTR-QMS 500(^d)</td>
<td>U. de Provence</td>
<td>2 min</td>
</tr>
<tr>
<td><strong>GOLF</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Number Distribution (5 nm–1 μm)</td>
<td>EAS(^q)</td>
<td>MPIC(^h)</td>
<td>1 min</td>
</tr>
</tbody>
</table>

\(^a\) FMPS: Fast Mobility Particle Sizer; \(^b\) LaMP: Laboratoire Meteorologie Physique; \(^c\) PSAP: Particle Soot Absorption Photometer; \(^d\) HS PTR-QMS: High Sensitivity Proton Transfer Reaction-Quadrupole Mass Spectrometer; \(^e\) CNRS: Centre national de la recherche scientifique; \(^f\) CPC: Condensation Particle Counter; \(^g\) CNRM: Centre National de Recherches Météorologiques; \(^h\) MPIC: Max Plank Institute for Chemistry; \(^i\) MAAP: Multi Angle Absorption Photometer; \(^j\) SMPS: Scanning Mobility Particle Sizer; \(^k\) CMU: Carnegie Mellon University; \(^m\) DMPS: Differential Mobility Particle Sizer; \(^n\) UoH: University of Helsinki; \(^o\) NAIS: Neutral Air Ion Spectrometer; \(^p\) IfT: Leibniz Institute for Tropospheric Research; \(^q\) EAS: Electrical Aerosol Spectrometer.
SIRTA two classification schemes, one based solely on ambient particles following the classification scheme of Dal Maso et al. (2005) and one that includes air ions, following the classification scheme of Hirsikko et al. (2007). In both cases, the observation period was divided into particle formation event days, non-event days and undefined days. In general, a day is classified as event day if a nucleation mode is present for several hours and grows continuously during the course of the day. If no traces of a nucleation mode are seen, a day is classified as a non-event day. Days that did not clearly belong to either of the aforementioned categories were classified as undefined. Examples of event, undefined and non-event days are shown on Fig. 4.3, 4.4 and 4.5, respectively.

Figure 4.3. Size distribution measurements during a nucleation event (12 July 2009) in all ground sites. (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1).

During July 12\textsuperscript{th}, a nucleation mode, appeared at 2 p.m. (LST) simultaneously at all ground sites (Fig. 4.3). Nucleation was observed approximately one hour earlier after the solar intensity increased by a factor of 4, along with air ion concentration increase in the size range between 1.6 – 7.5 nm. During July 10\textsuperscript{th}, an increase in number concentration above 10 nm was measured at LHVP and SIRTA at 2 p.m. (LST) simultaneously (Fig. 4.4). It was unclear whether the mode appeared at GOLF due to interferences by local sources. Particle growth was not continuous at all sites and the mode disappeared abruptly after approximately three hours, even though the direction of the wind did not change at this time. Air ion bursts, at SIRTA, in the size range between
1.6 – 7.5 nm did not follow a distinct pattern but were random. As a result it was unclear whether NPF occurred at the sites or somewhere else and the day was classified as undefined everywhere. During July 29, the condensation sink was rather high 9.0±1.7×10⁻³ s⁻¹, 20.3±9.7×10⁻³ s⁻¹ and 14.4±4.1×10⁻³ s⁻¹ at SIRTA, LHVP and GOLF respectively, when NPF was expected to occur (8 a.m. – 4 p.m. LST). These sink values were above the summer average for all sites (see Section 4.5.3).

Figure 4.4. Size distribution measurements during an undefined event (10 July 2009). (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1).

Figure 4.5. Size distribution measurements during a non-event (29 July 2009). (a) AIS measurements in SIRTA, (b) SMPS measurements at SIRTA, (c) DMPS measurements at LHVP, (d) EAS measurements at GOLF. Time of day corresponds to local standard time (UTC+1).
As a result no nucleation mode was observed at all sites (Fig. 4.5). A summary of the particle formation categorization can be found in Fig. 4.6.

Figure 4.6. Nucleation analysis results during summer and winter for all ground sites. Events, non-events, undefined and lack of data are depicted in blue, grey, light blue and white, respectively.

4.5.2 Duration of Nucleation Events

The duration of nucleation events in SIRTA was calculated based on AIS following the procedure described by Hirsikko et al. (2005) and Pikridas et al. (2012). In brief a normal distribution was fitted to the concentration of air ions with diameters between 2-5 nm. The beginning of the event was determined by the initial increase of the air ion concentration and the end by the peak of the normal distribution. Decrease of the number concentration implies that the rate of particle production is lower than the combined rates of coagulation and particle growth above 10 nm or that the air mass is getting diluted; it does not necessarily imply that the rate of production is zero. Thus, our calculated event-end is a lower bound estimate.

4.5.3 Condensational Sink

The condensation sink (CS) is defined as the condensational loss rate constant of vapors. The CS values were calculated based on the aerosol number size data and the properties of the condensable vapors are assumed to be similar to those of sulfuric acid, without accounting for hydration, leading to an upper limit estimate. If the aerosol sample was dried prior to sampling, the diameter growth was estimated using the Extended Aerosol Inorganic Model II (E-AIM, http://www.aim.env.uea.ac.uk/
aim/aim.php; Carslaw et al., 1995; Clegg et al., 1998; Massucci et al., 1999). The hourly averaged inorganic concentrations for sulfate, ammonium, nitrate measured by the AMS and ambient RH, were used as inputs to the model, neglecting organic particulate related water. The volume growth factor was determined following the method of Engelhart et al. (2011) which assumes that all submicrometer particles grow similarly by neglecting Kelvin effects. The diameter growth factor was calculated as the cubic root of the volume growth factor and was applied to the whole particle range.

4.5.4 Intercomparison of Aerosol Sizing Instruments

Because each aerosol sizing instrument monitored different size ranges (Table 4.1), only the 10-500 nm range where all particle size monitoring instruments overlapped could in principle be used for intercomparisons. The EAS, located at GOLF, had one bin between 10-20 nm which was omitted, limiting the intercomparison size range between 20 – 500 nm. In order to characterize differences between instruments during both campaigns, MoLa visited each site for several hours (8-10 h) during each campaign. The sizing instruments of the two mobile laboratories were also compared for 8 hours and the difference in number concentration between the two was 10% on average ($R^2=0.9$). From each comparison a scaling factor was determined and used to scale the number concentration of each instrument to that measured by the MoLa’s FMPS, which is used as a reference in this study. The summary of the comparison results is shown in Fig. 4.7. During the summer campaign a direct comparison between the DMPS based on LHVP and the FMPS at MoLa was not conducted, instead an intercomparison with MOSQUITA, which lasted 24 hours, was used to determine the scale factor. The largest differences between the sizing instruments were observed during winter at LHVP and GOLF which was close to 20%. The rest of the comparisons showed differences equal or lower than 10%.

4.5.5 Meteorology

During summer, the lowest ambient temperature was 12°C, observed at SIRTA and GOLF, and the highest 33°C, observed at LHVP. Average temperatures during summer were 18.7, 21.1 and 19.7 °C at SIRTA, LHVP and GOLF, respectively. On average ambient temperature was higher inside the city center by at least 1°C compared to the suburban sites. RH ranged between 35% and 90% in all sites. Diurnal variations of RH and temperature were similar at all sites during the summer. There were several cloudy periods and cloud coverage in the various sites was different. On cloud free days
solar radiation reached 900 W m\(^{-2}\) during summer, while on several occasions daily maxima were less than 600 W m\(^{-2}\).

**Figure 4.7.** Number concentration comparison of ambient particles between 20 – 500 nm between the FMPS of MoLa and of the three ground sites for summer (top) and winter (bottom). Number concentration by MoLa was averaged according to each sizing instrument’s resolution (see Table 4.1). Comparison with LHVP was conducted only by MOSQUITA during the summer. The scale factor between MoLa and MOSQUITA during the summer was equal to 1.1 (R\(^2\)=0.9) which yields a scale factor of 1.02 between MoLa and the SIRTA sizing instruments. The intercomparison time between MoLa and MOSQUITA during summer and between MoLa and SIRTA during both campaigns was 8 hours. The intercomparison period of MOSQUITA and MoLa with the LHVP sizing instrument was 24 and 10 hours during summer and winter, respectively.

During the winter campaign, average ambient temperature was 2.6±3.6, 3.3±3.4 and 1.2±3.5°C at GOLF, LHVP and SIRTA respectively. RH varied from 40% to 90% and exceeded 95% on several occasions at all sites. Hourly average global solar irradiance did not exceed 400 W m\(^{-2}\) during the winter campaign and did not exceed 100 W m\(^{-2}\) on 14 of the 32 campaign days.

Fig. 4.8 shows the wind direction distribution at all sites, for each campaign. Wind direction during summer was predominantly SW at LHVP and GOLF and W at SIRTA (Fig. 4.8) indicating that air masses often crossed the city center before reaching GOLF and that SIRTA was mostly upwind of the city. During winter wind direction was a lot more variable with the wind coming from both NE and W (Fig 4.8). During
the winter campaign SIRTA was often influenced by air masses that crossed the urban area before reaching the site, while during the summer it was usually upwind of the Paris center.

![Wind direction rose plots](image)

**Figure 4.8.** Wind direction rose plots during the summer and winter campaigns at each of the ground sites. Each rose corresponds to angle bin of \(\pi/18\) (i.e. 0- \(\pi/18\), \(\pi/18\) - 2\(\pi/18\), etc) and concentric circles at each site correspond to 5% frequency. Wind speed, in m s\(^{-1}\), is color coded inside each rose. Wind speeds below 1 m s\(^{-1}\) have been omitted from the graph.

### 4.6 Number Concentration at the Ground Sites

#### 4.6.1 Fixed Measurements

Average number concentrations between 20 – 500 nm, for all ground sites during both campaigns, are summarized in Table 4.2. On average the N\(_{20}\) concentrations (concentration above 20 nm) during winter were 50-60% higher than during summer in all sites. The highest concentrations were observed at the urban center (LHVP) followed by the mostly downwind urban background station (GOLF). The average ratio of LHVP to GOLF were 1.17 during both campaigns, while the ratio of the urban station to the rural site (SIRTA) was 1.87 and 1.80 during summer and winter, respectively.

The number concentration in all sites followed the same diurnal pattern during both campaigns (Fig. 4.9). The pattern involved an increase in concentration during morning traffic hours which peaked at approximately between 7 and 10 a.m. (LST) during summer and winter respectively, along with a second peak during nighttime, between 8 and 9 p.m. (LST) during both campaigns. Such patterns are typical of urban areas. The magnitude of the peaks varied depending on site and period. The increase corresponding to rush hour traffic compared to the minimum concentrations observed
from 3-4 a.m. (LST) was 65%, 80% and 25% at GOLF, LHVP and SIRTA respectively, during summer and 155%, 135% and 120% during winter. The nighttime increase ranged from 20%-50% for both campaigns at all sites.

**Table 4.2.** Summary of the aerosol number concentration of the three ground sites and characteristics of NPF.

<table>
<thead>
<tr>
<th>Site</th>
<th>Average Number Concentration (&gt;20 nm) 1000/cm³</th>
<th>Increase in Number Concentration due to NPF (%)</th>
<th>Growth Rate (nm/h)</th>
<th>Site</th>
<th>Average Number Concentration (&gt;20 nm) 1000/cm³</th>
<th>Increase in Number Concentration due to NPF (%)</th>
<th>Growth Rate (nm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOLF</td>
<td>7.6±3.7</td>
<td>11.5±3.7</td>
<td>207±137</td>
<td>6.1±1.8</td>
<td>LHVP</td>
<td>8.9±4.3</td>
<td>13.5±6.7</td>
</tr>
</tbody>
</table>

*a An individual scale factor has been applied to each sizing instrument to convert it to that of MoLa, which was used as a reference in this study.

During summer particles ranging from 30 to 100 nm dominated the N₂₀ concentration (Fig. 4.9) accounting for 50%-60% at all ground sites. On the other hand during winter particles from 20 to 30 nm accounted for 47% and those from 30-100 nm for 37% at all sites. Particles above 100 nm accounted for less than 20% of N₂₀ during both campaigns at all sites. These differences are due to the shift of the Aitken mode of the distributions to lower sizes during the winter. Grand average distributions for each campaign and site are shown in Fig. 4.10.

To investigate the impact of emissions in the center of Paris on number concentrations on the two satellite sites (GOLF, LHVP) the measurements have been separated with respect to wind direction, excluding periods when the wind speed was below 1 m s⁻¹ (Fig. 4.11). Taking into account that the area is relatively flat, it was assumed that the urban center influences each of the satellite sites at certain wind directions (215±30º and 65±30º for GOLF and SIRTA, respectively), noted with red on Fig. 4.11. During summer, the highest number concentrations at SIRTA were observed when the air masses crossed the city center (9.0±1.4×10³ cm⁻³) and the lowest when the wind originated from the opposite direction (3.4±0.3×10³ cm⁻³) resulting in an increase of the number concentration by a factor of 3. This suggests that the background N₂₀ SW of Paris was quite low (3,400 cm⁻³ on average) and that when SIRTA was downwind of Paris its N₂₀ was similar to that in LHVP. Contrary to SIRTA at GOLF the N₂₀ number concentration was not affected by the wind direction during the summer. Black carbon measurements were consistent with this result. The high N₂₀ when the GOLF site was
upwind of Paris could be due to both local sources but also higher background concentrations in the area NE of Paris during the summer.

During winter at GOLF, air masses from the city center increased the aerosol number level by 50% compared to the average. During the same period at SIRTA air masses crossing the center increased the aerosol concentration by a factor of 2 compared to the average.

### 4.6.2 Mobile Measurements

The majority of mobile measurements were conducted downwind of the Paris center in order to characterize its effect on the megacity surroundings. As a result the reported concentrations for each area do not correspond to the average but are positively biased.

![Figure 4.9](image)

**Figure 4.9.** Number concentration diurnal profiles of summer (left) and winter (right) campaigns, concerning for size ranges between 20-30 nm, 30-100 nm and 100-500 nm. Different scales are used.
Figure 4.10. Grand average distributions for summer (red) and winter (blue) campaigns of all ground sites. No scaling factor has been applied. Different diameter scales are used.

During nighttime, when the vans were stationed at their individual base, concentrations in urban environments are expected to be lower than average (Fig. 4.9). Measurements when the vans were stationed at their individual base were negatively biased and omitted from this spatial variability analysis, thus ensuring that mobile measurements were taken at the same periods. While on the road, the exhaust of other vehicles often influenced measurements that were omitted.

Figure 4.11. Number concentrations of the two satellite sites during summer and winter with respect to air mass direction at each site. The angles which indicate that the air mass traveled through the city center prior reaching the site are depicted with red. The horizontal dashed black line corresponds to the campaign average for each site. Periods with wind speed below 1 m s⁻¹ were omitted from the analysis.
In order to omit a measurement, a steep increase of the particle number concentration corresponding to a distribution with number mode diameter approximately equal to 50 nm, coupled with steep increase of black carbon concentration should be observed. Mobile measurements were separated based on location, into concentric circles of 0.15, 0.25, 0.4, 0.6, 0.8 and 1 degrees of latitude (one degree being equal to 111.1 km approximately), which corresponds to 16.7, 27.8, 44.4, 66.7, 88.9 and 111.1 km radius, centered at kilometer zero of Paris (the official Paris center which corresponds to an island near Notre Dame de Paris) shown in Fig. 4.1. The radius of the two inner circles includes the urban center and IDP. During summer little variability was observed in the MoLa measurements in the N-E of Paris with increasing distance (Fig. 4.12). During winter the number concentrations of the the corresponding to the city center, was higher by 150% compared to the summer and the concentration decreased exponentially with distance (Fig. 4.12). Number concentrations extending further than approximately 60 km from the city center were similar during summer and winter. The city area influence extended up to approximately 60 km during the winter.

The mobile laboratory’s results do not imply that Paris did not affect its surrounding during summer; it implies that the effect of the city was similar to the average effect of local or transported pollution sources and therefore no significant variation was observed.

**Figure 4.12.** Number concentration with respect to distance from the city center measured by the mobile laboratory (MoLa) N to E of Paris. During summer (red) little variability was observed contrary to winter (blue) when the aerosol population decreased exponentially with distance.
4.7 New Particle Formation on the Ground

During the summer campaign air ion bursts between 2-5 nm were picked up by the NAIS at SIRTA on a daily basis with the exception of July 29th, based on both polarities. Concentrations of positively charged particles between 2 to 10 nm were higher by one order of magnitude compared to negative ones. In this work we report NPF categorization based on the negative polarity which provided a more sensitive way of identifying nucleation events.

During the summer campaign 16, 14 and 7 NPF event days were identified in SIRTA, LHVP and GOLF, respectively. If two events, identified at SIRTA by AIS, when particles above 10 nm were not monitored are included, the number of “events” at SIRTA rises to 18. Typically when an “event” occurred at SIRTA it also took place at the city center (Fig. 4.6). The difference in the number of events between the two sites is mainly due to instrument failure at LHVP which did not allow monitoring of the size distribution and therefore the frequency between these sites was similar (55% and 56% at SIRTA and LHVP, respectively). Nucleation events, if identified at two or more of the ground sites, would always occur practically simultaneously. The ambient number concentration \(N_{20}\) increased on average by a factor of 2 at the two suburban sites during these events. At the urban center (LHVP) the average increase for the same size fraction was 46±15%.

The highest daily growth rate (17.6 nm h\(^{-1}\)) was observed at SIRTA on July 4th during a regional event observed at all ground sites while the lowest growth rate (1.6 nm h\(^{-1}\)) was observed on July 15th at LHVP, where typically lower daily growth rates compared to the two satellite sites were observed. The average growth rate was 5.5±4.1 nm h\(^{-1}\), 4.6±1.9 nm h\(^{-1}\) and 6.1± 1.8 nm h\(^{-1}\) at SIRTA, LHVP and GOLF, respectively during the summer campaign (Table 2). Growth rates for events that occurred on all sites on the same day were 8.3±5.6 nm h\(^{-1}\), 4.5±2.0 nm h\(^{-1}\) and 5.9± 2.4 nm h\(^{-1}\) at SIRTA, LHVP and GOLF, respectively.

During July 28th nocturnal particle formation was observed at SIRTA, which was identified by increase of the ion number concentration in the 1.25–1.66 nm size range. An apparent growth of cluster ions to larger diameters than the upper limit of the preexisting ion pool was evident but air ions did not grow above 2 nm. Nocturnal nucleation has been observed in remote areas (Junninen et al., 2008; Kalivitis et al., 2012; Hirsikko et al., 2012) and has been linked to the presence of monoterpenes (Ortega et al., 2012).
The condensation sink during the summer campaign for all sites is shown on Fig. 4.13, where event and undefined days are also marked with blue and light blue respectively. The condensational sink during winter was on average $21.5\pm14.4\times10^{-3}\,\text{s}^{-1}$, $17.0\pm8.6\times10^{-3}\,\text{s}^{-1}$ and $12.3\pm6.8\times10^{-3}\,\text{s}^{-1}$ at GOLF, LHVP and SIRTA respectively. The high condensation sink in conjunction with the low solar intensity (see Section 4.5.5) prevented nucleation during winter and no event was identified. During summer the sink was half than in the winter at GOLF and SIRTA ($11.7\pm11.6\times10^{-3}\,\text{s}^{-1}$ and $5.7\pm3.5\times10^{-3}\,\text{s}^{-1}$ respectively) and 30% lower at LHVP ($12.8\pm7.5\times10^{-3}\,\text{s}^{-1}$). During summer at SIRTA and LHVP events occurred under lower than average condensational sink by 45% and 25% respectively. Undefined events at both sites occurred under average sink and non-event days were associated with 25-30% higher sink compared to the average. All these indicate that the condensation sink influenced the frequency of events at both sites.

Solar intensity influence on NPF, even though important at all sites, was more notable at SIRTA and LHVP, where the solar intensity during events was on average 30% and 20% higher compared to non-event days, respectively. At GOLF, during non-event days solar intensity was higher by 8% compared to events.

At GOLF, 7 events could be identified corresponding to a monthly frequency of 23%. The event frequency difference between GOLF and the other two ground stations was partially due to a higher frequency (23%) of undefined days (Fig. 4.6). This inability was largely due to interferences by nearby traffic. When no event was identified at all sites the condensation sink at GOLF, was double ($14.7\pm4.5\times10^{-3}\,\text{s}^{-1}$) compared to event days ($7.3\pm0.8\times10^{-3}\,\text{s}^{-1}$), indicating that, similarly to the other sites, the sink was inhibiting NPF. On several occasions (July 2, 6, 8, 19, 23, 28), NPF was identified at LHVP and SIRTA but not at GOLF (Fig. 4.14).

During these days condensation sink values at GOLF were similar to event days and lower by 30% compared to the campaign average, indicating that at least the sink was not suppressing NPF. On two occasions (July 6 and 8) the sizing instrument provided a continuous mode below 30 nm, either due to electrometer noise or local interferences, which prevented identification of NPF. Both days were listed as non-event days but NPF may have occurred. During July 2 and 19, a nucleation mode was observed at LHVP and SIRTA for more than an hour but nucleated particles did not grow above 20 nm (Class II events based on Dal Maso et al., 2005). During the same time, at GOLF the nucleation mode was not observed yet it is uncertain whether
nucleation occurred and particles did not grow to detectable size or NPF did not occur, thus both days were

![Figure 4.13. Condensational sink of the three ground sites during July 2009. Red and green bars indicate the event and undefined periods, respectively.](image)

listed as non-events. During July 23 NPF was identified at SIRTA but not at LHVP due to instrument failure. Air masses crossed SIRTA before reaching GOLF and a fresh Aitken mode appeared at the latter after 3 h. Wind direction was constant during that time and the lag was consistent with the time needed for an air mass to travel between the two sites at the observed wind speeds. Similar to July 23, on July 28 NPF was identified at SIRTA and LHVP. At GOLF a new mode appeared after approximately 3 h. Thus the event frequency difference among GOLF and the other two sites is mainly due to local interferences and uncertainty in identifying nucleation events.

### 4.8 Airborne Measurements

Airborne measurements during the summer and winter showed increased number concentrations downwind of Paris coupled with increases in black carbon. These were attributed to PM emissions of the Paris area and are referred henceforth as the “Paris plume”. Increased concentrations of toluene and benzene, both of which are of anthropogenic origin were also encountered in these plumes. The number concentrations for the summer airborne measurements correspond to particles larger than 20 nm (N_{20}). Particles smaller than 20 nm were not detected due to diffusion losses. The plume average number concentration during the summer campaign was 10,000 cm^{-3} which was 45% higher than the observed background concentrations (6,900 cm^{-3}).
Figure 4.14. Number distribution time series when a nucleation event was identified at SIRTA and/or LHVP but not at GOLF.
cm$^{-3}$) outside of the plume. These high background N$_{20}$ concentrations in this N to E quadrant where the all of the summer flights but one took place are consistent with the ground (fixed and mobile) observations. The plume and N-E background number concentrations were 11% and 44% higher than those of the Paris center and SIRTA for the summer campaign, respectively.

Airborne measurements clearly provide a more sensitive way to characterize the plume since areas outside the plume were omitted. Due to air traffic restrictions the plume was not followed closer than a 50 km distance from the Paris center. Airborne measurements were conducted on days when pollution was above average, thus the sample is positively biased. Ground mobile laboratories were not restricted in such a manner and sampled closer the city center. On the ground, monitoring was conducted on during the whole campaign providing a more representative sample but separating the plume from the background was not possible. During summer little variation of the number concentration was observed with distance below 100 km in this N to E area from the city center. During the same period the number concentration at an altitude was found to decay with distance (Fig. 4.15).

According to the airborne measurements inside the plume the concentration was reduced by approximately 15% in the area from 30 to 90 km from the Paris center. According to the ground measurements (Fig. 4.12) the reduction was 16% suggesting that the measurements are in general consistent. During all summer flights, with the exception of July 25, “hot spots” outside of the Paris plume where particle number concentrations similar or higher to those of the Paris plume were identified without increase in black carbon or anthropogenic VOC’s (benzene, toluene). The “hot spots” where the particle number increase occurred have been separated into three groups based on their location as “upwind”, “alongside” and “local”. During winter no hot spots were identified, consistent with ground measurements where no NPF was identified.

The “upwind” class occurred upwind of Paris four times, always near IDP (Fig. 4.16b) and simultaneously with regional nucleation events observed at least in two of the ground sites. The N$_{20}$ concentration increases were thus attributed to NPF. On average N$_{20}$ concentrations were 50% higher, compared to the plume. Because this class occurred opposite of the Paris plume and the flights followed the plume, the extent of this area could not be assessed. The time the upwind class was identified was consistent
with the time particles grew above 20 nm in diameter, the lowest detected size, on the ground on all occasions.

The “alongside” class occurred along one side of the Paris plume at an average 40 km distance from the plume edge and was attributed to NPF. The average number concentration increase of this class compared to that of the plume, for the same days, was 4% and 130% compared to the background. The area connecting the plume and this class always exhibited at least 20% lower concentrations than the two. Because the number concentration in the area between the plume and the alongside class was always lower than the number concentration of the class, we rule out that these observations were the result of diffusion (Fig. 4.16b). The alongside class was identified on four flights (July 1, 15, 21, 28), two of which were non-event days for all ground sites and two when NPF was identified at SIRTA and LHVP, but not at GOLF. The high N_{20} areas covered approximately 3,000 km² along the plume.

In order to investigate why particle number concentration increased only on one side of the plume during these flights, each flight path, was separated into the three areas; the area with high N_{20} outside of the plume, the plume area and the area in the other side of the plume, where no increase in particle number was observed. The observed differences between the two sides of the plume with respect to the condensation sink, solar intensity and isoprene, which has been reported as a potential inhibitor of NPF in forested areas (Kiendler-Scharr et al., 2009; Kanawade et al., 2011),
were 12%, 5% and 6% respectively (Fig. 4.17) which are not significant. As a result these three variables cannot explain why NPF occurred only on one side of the plume. Other components such as benzene, toluene, monoterpenes, methacrolein, methyl vinyl ketone, O₃, CO and meteorological parameters such as temperature and RH were investigated in order to identify differences between the two sides of the plume. Differences in all the investigated parameters were approximately 10% or lower. These events clearly require more investigation with instrumentation that can sample much smaller particles than the N₂₀.

**Figure 4.16.** Flight trajectories during 9 and 21 July 2009. Black carbon and number concentrations are color coded. Black carbon concentrations are used as tracers of the Paris plume (a, c). Increased number concentration was observed outside of the plume. During July 9 (b) the area where the number concentration increase was located upwind (the direction of the plume indicates wind direction) and NPF was identified at all ground sites. During July 21 (d) the particle number increase was observed along the plume. NPF was not observed at any of the ground sites.

The “local” class was the most frequent (6 out of the 11 flights), occurred always at the north coast of France above the city of Fecamp. Because the local class was always associated with this specific area the particle number increase was attributed to a local source.
Figure 4.17. Downwelling solar irradiance (top), condensational sink (middle) and isoprene concentration (bottom) comparison of the Paris plume with areas on either side when high particle concentrations were observed in one side outside of the plume. Differences among these areas were not observed with respect condensational sink, isoprene and solar irradiance.
During winter only the total number particle concentration was monitored aloft and no information on the number size distribution was available. During the three winter flights, plume number concentration was 45% higher than the background.

4.9 Summary and Conclusions

Ambient aerosol number concentrations were monitored at the city center of the Paris megacity along with two satellite suburban stations, located 16 and 18 km away each on opposite directions, two mobile laboratories and one aircraft during July 2009 (summer) and 15 January till 15 February 2010 (winter).

During summer, the N$_{20}$ (the number concentration higher than 20 nm) at the city center was 1.2 and 1.9 times higher than in the downwind and upwind suburban sites, respectively. Particles ranging from 30-100 nm dominated the aerosol number accounting for 50-60% of N$_{20}$ at all sites. The Paris plume was identified at an altitude of 600 m, using black carbon as a tracer, as far as 200 km away from the city center. The number concentration was found to decrease linearly (R$^2$=0.94) with distance. Average plume N$_{20}$ was 10,000 cm$^{-3}$ and the average concentrations outside of the plume was 6,900 cm$^{-3}$, which corresponds to a 45% increase.

During summer at SIRTA, N$_{20}$ increased to 9,000 cm$^{-3}$ when the site was downwind of Paris and decreased to 3,400 cm$^{-3}$ when the site was upwind. At GOLF, located at approximately the same distance from the city center as SIRTA but on different direction, no difference was observed with respect to air masses crossing or not Paris before reaching the site, suggesting a high local background in the NE quadrant.

NPF was observed at all sites during summer. At SIRTA and LHVP an event was identified on half of the campaign days and at GOLF once every four campaign days. The lower frequency of events at GOLF was mainly due to interferences of nearby traffic and instrument limitations which did not allow clear event identification. NPF occurred during periods of lower condensational sink by 45%, 25% and 50% at SIRTA, LHVP and GOLF respectively compared to each site’s average. The condensation sink was a controlling factor for the frequency of events. Solar intensity was higher by 30% and 20% on event days compared to non-event days at SIRTA and LHVP, respectively. At GOLF, solar intensity was higher by 8% during non-event days compared to event days. On average NPF increased N$_{20}$ by a factor of 2 at the two suburban sites and less than 50% at the city center. Average summer campaign daily growth rates at the three sites were 5.5, 4.6 and 6.1 at nm h$^{-1}$ at SIRTA, LHVP and GOLF respectively. These average growth rates were not statistically different.
During summer increased particle number concentrations were identified outside of the Paris plume at 600 m altitude. On four occasions the particle increase was located upwind of the ground stations simultaneously with regional NPF observed on the ground at least in two of the sites. As a result the increase was attributed to NPF. Increased particle number concentrations were also identified along one side of the plume on four occasions. A number of parameters were investigated including condensational sink, solar irradiance, anthropogenic and biogenic VOC’s among others, as possible explanations for this assymetry. All differences were approximately 10% or lower, so none of these could explain the observations.

During winter N$_{20}$ at LHVP was 1.2 and 1.8 times higher than in the downwind and upwind suburban sites, respectively similar to summer. During winter the absolute concentrations were increased almost by 50-60% at all sites compared to summer. Particles from 20 to 30 nm accounted for 47% on average and those from 30 to 100 nm for 37%. N$_{20}$ was found to decrease exponentially with distance from the Paris center. At distances from the city center greater than 60 km N$_{20}$ was 6,000 cm$^{-3}$ which was similar to the N$_{20}$ observed during summer at the same distance from the city. At SIRTA, when the site was upwind N$_{20}$ increased by a factor of 2 compared to when it was upwind. At GOLF the relative increase was 50%.

During winter the higher condensational sink and lower solar intensity compared to summer prevented NPF to occur.
4.10 References


Beekman et al., Will regional emissions control fine particulate matter levels in future megacities? Submitted to PNAS.


Zhijun Wu, Min Hu, Peng Lin, Shang Liu, Birgit Wehner, Alfred Wiedensohler, Particle number size distribution in the urban atmosphere of Beijing, China, Atmos. Environ. 42, 7967–7980, 2008.
Chapter 5
Characterization of the Origin of Fine Particulate Matter in a Medium Size Urban Area in the Mediterranean

5.1 Abstract
A multi-stage methodology for investigating particulate pollution is developed and implemented for the case study area of Patras, Greece. Initially a low cost particulate matter mass monitor was used to assess aerosol mass concentrations and it was found that the city, despite its small size (population around 200,000) and lack of heavy industry, violates both the daily and annual European Union PM standards. Increased PM$_{10}$ concentrations were observed during the winter but local vehicular traffic was estimated to account for only 12±4% of the PM$_{10}$ concentration on an annual basis. In the second stage PM$_{2.5}$ chemical composition was measured at the urban center and biomass burning was identified as a major PM source during the colder months. In the third stage PM$_{2.5}$ concentration and chemical composition was also followed at a mostly upwind rural site around 40 km from the city. The transported pollution was found to account for 50% of the PM$_{2.5}$ during winter and for more than 70% during the rest of the year. Almost all of the sulfates and 40-90%, depending on the season, of the organic aerosol are transported to the city from other areas. In the last stage, an intensive campaign took place during winter in order to quantify PM sources during the most polluted period. Nighttime sharp increases of the aerosol levels were observed with organic aerosol levels exceeding 80 μg m$^{-3}$. Fossil fuel and local biomass combustion emissions for domestic heating were responsible for these levels.

5.2 Introduction
Over the past decades a number of studies have indicated a strong correlation of airborne particulate matter (PM) and mortality (Dockery et al., 1993; Pope et al., 2009) resulting in legislation of PM levels in ambient air. The concentrated emissions in urban areas are the result of the increased demand for energy (e.g., heating), transportation and industrial activity. Air quality and pollution have been traditionally treated as local problems, yet there has been increasing evidence of the contribution of regional sources.
In a number of areas local air quality can be impacted by pollution generated elsewhere to the extent that critical levels may be exceeded (Lelieveld et al., 2002).

A number of commercially available continuous monitors can measure the concentrations of gas phase compounds or PM mass concentrations. They are widely used for regulatory air quality monitoring of pollutants such as O$_3$, NO$_x$ and SO$_2$, along with monitoring of mass concentration of particles smaller than 10 (PM$_{10}$) or 2.5 μm (PM$_{2.5}$). However these monitors provide limited information about the sources of pollution and therefore the causes of air quality standards exceedance. Continuous PM chemical composition monitoring is still a challenge due to the increased cost of the corresponding instrumentation.

In parallel to continuous monitoring filter-based methods provide information both on PM mass and chemical composition. The resolution and frequency can vary from hours to days depending on the ambient concentration of the pollutant under investigation and the required information. The cost of the corresponding instrumentation is reasonable but the cost of sample collection and chemical analysis can be significant if a lot of samples are analyzed. Typically for assessing ambient PM, 24-hour sampling once every 6 days is used.

In this work a multi-stage methodology for investigating the sources of fine PM will be presented and implemented on the case study area of Patras, Greece. Patras is an urban area with around 200,000 inhabitants, with local traffic assumed to be the major contributor to local air quality problems. Previous studies in Patras either focused on radioactivity (Papaeftihymiou et al., 2005) or on monitoring total suspended particles (Yannopoulos, 2008) without accounting for composition. The concentration of PM$_{2.5}$ water soluble ions has been reported by Danalatos and Glavas (1999) and Glavas et al. (2008). The majority of the previous measurements have been conducted in a site situated 10 km away (mostly downwind) from the urban center and did not provide information about the sources affecting the urban area itself. There is little or no information about the levels and sources of organic PM in the area.

As a first step, PM$_{10}$ levels were assessed by the Greek Environmental Agency in order to examine compliance with European air quality legislation. We use this information to quantify the magnitude of the problem and to test the hypothesis that local vehicular traffic is a major source. During the second phase PM composition was monitored in order to gain additional information about the sources of pollution. As a third step simultaneous measurements at the city center and 40 km away were
conducted in order to quantify the contribution of long range transport. Finally, as a last step, an intensive campaign designed to quantify the magnitude of local sources took place during the most polluted period. Following this approach the cost and complexity increases from step to step, starting from operating low cost automatic monitors, typical of regulatory monitoring, and finishing with small scale intensive campaigns using state-of-the-art instrumentation. The information gathered in each step is evaluated allowing the better planning of the next step. The proposed methodology can be used in other areas facing PM problems.

5.3 The Test Case: Patras, Greece

The city of Patras has around 200,000 inhabitants and is located at the foothills of a 2 km mountain, overlooking the Gulf of Patras (Fig. 5.1). The most notable activity is the harbor located near (< 1 km) the city center and a small industrial zone located 16 km southwest of the city center. The industrial zone includes a number of light industries (pharmaceuticals, food and beverages, etc). The only heavy industry is a cement factory located 16 km NE (mostly downwind) of the city center. The closest metropolitan area is Athens located 220 km east of Patras.

Figure 5.1. Map of south-east Europe indicating the location of Patras, the urban area under investigation. The rural sampling station at Vouprasio is also shown.
Minimum average monthly temperatures are observed during January and February reaching 11.5°C and 11.3°C, respectively. The highest average monthly temperature (26.9°C) is observed during summer. During the colder months of the year (October to March) precipitation increases compared to summer when precipitation is scarce. Information concerning the monthly variations of meteorological variables can be found in the supplementary information.

5.4 Is there a problem? Step 1: Daily Average PM$_{10}$ levels

PM$_{10}$ mass concentration was monitored using a beta attenuation monitor (FAG, FH 62 IN, Eberlin Germany) at Patras center (38° 14’ 46” N, 21°. 44’ 08” E) at ground level from January 1 to December 31, 2004. The daily PM$_{10}$ standard of 50 µg m$^{-3}$ was exceeded 75 times within 2004 at this urban kerbside station, which is twice the number allowed on an annual basis (35 exceedances) according to European standards. This daily limit was exceeded 58 times during the colder months (October to March), but was not exceeded during August and April. The other 17 exceedances took place during June, July and September.

Annual average PM$_{10}$ concentration was 42.3±14.7 µg m$^{-3}$ which exceeded the annual European PM$_{10}$ standard of 40 µg m$^{-3}$. Mean monthly concentrations of all the cold months were equal or above the annual average and the annual PM$_{10}$ standard of 40 µg m$^{-3}$ (Fig. 5.2), with the exception of January 2004 (35.3 µg m$^{-3}$). During the warmer months of the year PM$_{10}$ levels were below the annual average standard, with the exception of September.

![Figure 5.2. Monthly average PM$_{10}$ concentrations from January 2004 till December 2004 measured at the city center. Error bars correspond to one standard deviation of the daily average. The dashed line is the annual European PM$_{10}$ standard of 40 µg m$^{-3}$. The number on top of each bar corresponds to the exceedances each month of the European daily PM$_{10}$ standard of 50 µg m$^{-3}$. No measurements were available for May.](image-url)
This first level analysis of daily PM levels indicates that the urban area under investigation has a PM pollution problem mainly during the colder months of the year. Potential local sources are vehicular traffic and industrial activity. Due to the different behavior of the colder months of the year (October to March) compared with the warmer ones (April to September), we will investigate these two periods separately.

5.5 Potential Sources – Hourly PM Variation

The average PM$_{10}$ diurnal profiles of weekends and weekdays during warmer and colder months are presented in Fig. 5.3. During weekdays of the warmer months a maximum ($51.2\pm20.1$ μg m$^{-3}$) was observed from 8-9 a.m. Local Standard Time (LST) during morning traffic rush hour. This was 20 μg m$^{-3}$ more than the daily minimum concentrations ($31.0\pm11.0$ μg m$^{-3}$) observed from 5-6 a.m. LST. Two weaker maxima were present during 12 - 2 p.m. and 9-10 p.m. LST. Both of these could be explained by increases in the local traffic during the end of the workday and in the evening. The daily average PM$_{10}$ during weekends was 6% lower compared to weekdays. The morning traffic peak was less pronounced ($44.8\pm3.5$ μg m$^{-3}$) and a fourth peak was present from 2-3 a.m (time when the night entertainment often ends). The early afternoon peaks and early night peaks were almost the same as in the weekdays. The average hourly concentration, even during weekends, always exceeded 30 μg m$^{-3}$ suggesting a potentially high background of PM$_{10}$ concentration.

During the weekdays of the colder months, the PM$_{10}$ profile exhibited two maxima, the first during rush hour (9 a.m. LST) equal to $57.6\pm31.4$ μg m$^{-3}$ and the second at 9 p.m. (LST) equal to $59.3\pm32.0$ μg/m$^3$. A concentration minimum was observed from 4 to 6 a.m LST, similar to the warmer months. During weekends, the morning peak was weak and the actual maximum was in the early afternoon (1-2 p.m. LST). A nighttime peak was also observed at 9 p.m. (LST) following the nighttime trend of weekdays, but the concentration was on average lower by 6 μg m$^{-3}$. During the colder months the diurnal concentrations were higher by $30\pm8\%$ after the rush hour peak was observed (ie after 9 a.m., LST) compared to the warmer months of the year.

Assuming that the difference between the weekdays and weekends diurnal profile between 7 a.m. and 2 p.m. (LST) is due to local traffic and by subtracting the concentrations of the two, the overall effect of vehicular traffic can be assessed. This analysis suggests that local vehicular traffic increases PM levels by $12\pm4\%$ on average during the year. During the colder months vehicular traffic contribution was 14% on
average and during the warmer months it is 10%. Taking into account that measurements were carried out at a ground kerbside location in the city center these results probably reflect the upper limit for the city.

The observed average diurnal profiles always exceed 25 µg m⁻³. Tsimpidi et al. (2011) in their analysis of pollution in Mexico city suggested that these minimum values are a zeroth order estimate of the background concentrations for the area of interest. If this is the case, approximately 80% of the PM during the warmer months and 60% during the colder months were due to transport of pollution to the city. The accuracy of this simplistic estimate will be investigated in a Section 5.7.

**5.6 Filter-based Composition Measurements – Constraints on the PM Sources**

PM₂.₅ mass and composition measurements were conducted from December 2008 till May 2012 at an elevation of approximately 20 m above ground at the city center. A filter sampler (MetOne SASS) was used to collect PM₂.₅ samples for chemical analysis. Five samples were collected simultaneously at a flowrate of 6.7 L min⁻¹. The sampling lasted typically 24 h except during intensive sampling periods when the resolution was increased to 12 h. Teflon filters (Whatman 7582 004 0.2 µm pore size) were weighed.
(Kern ABT 120-5DM) before and after sampling in a temperature and humidity controlled glovebox where they remained for 24 h before weighing. Temperature was kept at 25±1°C and relative humidity (RH) ranged from 30% to 35%. Two filters were weighed for each sampling period and the balance was calibrated prior to sampling using internal or external standard weights. One teflon filter from each sampling period was extracted in a ultrasonic bath with 20 ml of nanopure water for 30 min for the determination of water soluble ions (Koulouri et al., 2008). For the analysis of anions a Metrosep A Supp5 column was used, with isocratic elution with 0.7 ml min⁻¹ of Na₂CO₃/NaHCO₃ as eluent. For the analysis of cations a Metrosep C4 column was used, under isocratic conditions with HNO₃/dipicolinic acid eluent and flow rate of 0.9 ml min⁻¹.

PM₂.₅ organic (OC) and elemental carbon (EC) were measured using a modification of the NIOSH thermal-optical transmission method and a carbon analyzer (Sunset Laboratory Inc., Oregon) on quartz filters (Pall 2500 QAO-UP). The method employs lower temperature setpoints in the first steps of analysis in order to reduce charring of organics (Yu et al., 2002). Further details about the method can be found in Pikridas et al. (2010). OC was multiplied by 1.6, for all seasons, to estimate the organic matter concentration (Turpin and Lim, 2001).

Particulate water was not measured directly but was estimated by the Extended Aerosol Inorganic Model III (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php; Carslaw et al., 1995; Clegg et al., 1998; Massucci et al., 1999) at the RH during weighing using the water soluble ions’ concentrations as input (Rees et al., 2004; Tsyro et al., 2005). Water soluble PM₂.₅ calcium was used as a tracer for dust in the same size fraction and its concentration was multiplied by 11 to estimate the mass concentration of dust (Sciare et al., 2005).

The average PM₂.₅ mass concentration of the 141 samples collected was 21.2±9.7 μg m⁻³, while that based on the sum of the PM₂.₅ components was 22.2±11.1 μg m⁻³. On an annual average basis, PM₂.₅ represented 55±16% of the PM₁₀. The PM₂.₅ fraction increased during the winter to 66±19% due to removal of coarse particles by the more frequent precipitation (Fig. 5.4) and by addition of emissions of fine PM.

The annual average PM₂.₅ concentration of 22.3±11.8 μg m⁻³ (at RH <35%) exceeds the USEPA air quality annual standard (three year average smaller than 15 μg m⁻³). The current European Union annual PM₂.₅ target of 25 μg m⁻³ was not exceeded based on the sum of components under RH equal to 50% (24.5±19.9 μg m⁻³).
highest PM$_{2.5}$ concentrations during 2009-2012 were observed from November to February and the lowest in June, consistent with the 2004 PM$_{10}$ measurements. PM$_{2.5}$ concentration during the warmer and colder months was 19.5±2.8 μg m$^{-3}$ and 25.3±6.2 μg m$^{-3}$, respectively. This 30% increase during winter was mainly due to increased organic content.

![Figure 5.4](image)

*Figure 5.4.* Monthly boxplots of temperature (top) during December 2009 to May 2012. Data used are of 10 min resolution. Red lines indicate the median, boxes represent the upper and lower quartile and the whiskers extend to the most extreme data points. Total monthly precipitation (bottom) for the corresponding period.

During the four years of measurements at the urban center the daily PM$_{2.5}$ standard of 35 μg m$^{-3}$ was exceeded 25 times, 24 of which were during the colder months of the year and only one exceedance during the warmer months. On average the composition when the daily PM$_{2.5}$ standard was exceeded, was characterized by higher organic and potassium concentrations, indicating that biomass burning could have been involved.

The annual average PM$_{2.5}$ organic mass concentration was equal to 10.7 μg m$^{-3}$. Organic mass concentration in the summer (7.2±1.6 μg m$^{-3}$) was half than in the winter (14.2±5.2 μg m$^{-3}$). Organics comprised of 47% of the annual average PM$_{2.5}$. The contribution of organics increased to 57% during the colder months. The annual average EC concentration was equal to 1.9 μg m$^{-3}$ and the monthly variation of EC followed that of organics. The ratio of OC to EC was on average equal to 2.7, which is half of the ratio reported for more remote locations in the eastern Mediterranean basin using the same method (Pikridas et al., 2010). The average monthly PM$_{2.5}$ composition based on the filter measurements is shown in Fig. 5.5.
The concentration of organics during winter of the first two years (2009-2010) of this study was on average 11.1±2.9 \( \mu g \) m\(^{-3}\) but doubled (22.2±5.5 \( \mu g \) m\(^{-3}\)) the corresponding periods of the latter two years (2011-2012). Similarly, potassium and EC concentrations also doubled resulting in an overall increase of the PM\(_{2.5}\), during the colder months by 70%. No significant difference was observed in the concentrations of the remaining PM\(_{2.5}\) components during winter and in the concentration of all components during summer.

Sulfate was the second most abundant PM\(_{2.5}\) constituent comprising 16% (3.8±1.0 \( \mu g \) m\(^{-3}\)) of the annual average mass. Highest concentrations were observed during the warmer months of the year (4.6±0.5 \( \mu g \) m\(^{-3}\) on average). Potassium, a tracer for biomass burning (Zhang et al., 2010), shows good correlation (R\(^2\)=0.79) with PM\(_{2.5}\) mass during the winter but no correlation (R\(^2\)=0.08) is observed during the summer.

Summarizing, composition analysis showed that the high winter concentrations were due to increased organic PM content. The positive correlation of potassium with PM\(_{2.5}\) indicates that a biomass combustion source was also involved. This result is further supported by the increase of EC and potassium the last two years of this study along with the increase in organic content.
5.7 The Role of Transported Pollution

The term “long range transport” includes transport of pollutants over hundreds or thousands of kilometers (Stohl et al., 2002; Wild, 2004; Auvray and Bey, 2005; Sciare et al., 2008). In order to assess the role of transport, measurements were performed in Vouprasio (38° 04' 17" N, 21° 23' 56" E), a rural background site located 36 km SW of the city simultaneously with the urban center from June 2011 till May 2012. A total of 63 samples were analyzed from each site. At the rural site, a filter sampler (MetOne Super-SASS) was used to collect four PM$_{2.5}$ filters with a resolution of 24 hours at a flowrate of 6.7 L min$^{-1}$. All teflon and quartz filters collected at the rural site were treated as discussed in Section 5.6.

The average sulfate concentration at the rural site was 4.3±2.8 μg m$^{-3}$. The monthly difference in sulfate at the rural site and the Patras center never exceeded 1.5 μg m$^{-3}$ (Fig. 5.6) regardless of season indicating a common source. The average nitrate concentration at the rural site (0.26±0.19 μg m$^{-3}$) was lower than that in the city center (0.39±0.27 μg m$^{-3}$) for the same time period. During the warmer months the difference between the two sites was less than 0.1 μg m$^{-3}$. During the colder months, when increased concentrations were observed at both sites (0.6±0.2 μg m$^{-3}$ and 0.4±0.2 μg m$^{-3}$ at the urban and rural sites, respectively), the concentration of nitrate at the city center exceeded on average 0.2 μg m$^{-3}$ that of the rural site.

![Figure 5.6. Average PM$_{2.5}$ monthly compositions at the urban center (not-textured) and a rural background site (textured). Measurements at both sites correspond to the same sampling dates spanning from June 2011 to May 2012.](image-url)
Figure 5.7. Seasonal comparison among three Mediterranean sites for sulfate (a) and OC (b). Urban center measurements are shown in blue and range from December 2008 till May 2012, rural measurements shown in green ranging from June 2011 till May 2012 and remote background measurements with brown conducted from July 2004 till July 2006 (Koulouri et al., 2008).

The average organic aerosol concentration, at the rural site, was 8.4±5.1 μg m⁻³. At the city center organics concentration was consistently higher throughout the year. During the colder months the average concentration at the rural site was 10.0±2.7 μg m⁻³ on average, which was approximately half of the observed organics concentration for the same sampling days at the city center. During the warmer months the average concentration at the rural site was 6.0±1.6 μg m⁻³ on average, 33% lower than the concentrations observed at the city center.

Monthly average potassium concentrations maxima and minima were observed in January (0.68±0.53 μg m⁻³) and June (0.03±0.03 μg m⁻³) at the rural site, respectively. Potassium concentrations during the cold months of the year at the urban center were higher by 44% on average, compared to the rural site, indicating the presence of local contribution in addition to regional transport.

The pollution transported to Patras originates from sources at different distances. A rough estimate on the contribution of sources that are hundreds of kilometers away can be obtained by comparing the average levels of Patras with those of Finokalia (35°
20° N, 25° 40' E), a remote station located on the island of Crete, Greece (Mihalopoulos et al., 1997; Kouvarakis et al., 2000). Finokalia, located approximately 500 km SSE of Patras, lacks strong local particulate sources (Sciare et al., 2008; Pikridas et al., 2010) and can be considered as a European background station.

Seasonal differences among the urban, rural and background (Finokalia) sites are shown on Fig. 5.7. Differences among sulfate concentrations at the three sites were less than 1.5 μg m⁻³ regardless of season. These differences indicate that similar sulfate sources were affecting the three sites. This is consistent with model simulations that indicate that SO₂ is transported to the Mediterranean basin where sulfate is produced due to the intense photochemical activity (Fountoukis et al., 2011).

At Finokalia, organic aerosol has been found to be highly oxygenated and is considered aged (Hildebrandt et al., 2010). On average the OC concentrations at Finokalia do not vary significantly with season (Koulouri et al., 2008) and the variations observed are linked with air mass origin (Sciare et al., 2008; Pikridas et al., 2010). Contrary to Finokalia, OC in Patras exhibits seasonality with much higher concentrations during the colder months (Section 5.6). The rural background site is influenced by a variety sources over continental Greece including agricultural activities, biogenic secondary organics aerosol, etc. OC concentrations at the rural site are consistently higher than in Finokalia but lower than in the city. On average the ratio of PM₂.₅ at Finokalia and Patras was approximately 0.44-0.50 throughout the year, except during winter when it decreased to 0.23.

![Image of Figure 5.8](image-url)  
**Figure 5.8.** Seasonal contribution of regional transport (not textured) and local sources (textured) to the PM₂.₅ components.
The differences between Patras and Vouprasio, concerning OC, provide a rough estimate of its transport to the city and a means to calculate the overall contribution of transported and locally produced OC. Following the same approach, we also account for transported and local EC. Sulfate concentrations between the two sites are similar throughout the year and it can be assumed that practically sulfate is the result of transport. The amount of ammonium that corresponds to that of sulfate was also considered to be the result of transport. Nitrate and the corresponding ammonium concentrations are treated the same way as OC. Dust and other minor PM$_{2.5}$ components, such as Na$^+$, were lumped as “other local sources”. The contribution of local traffic was also assessed based on the PM$_{10}$ kerbside measurements, discussed on Section 5.5. The results of this rough analysis are shown in Fig. 5.8

Transported PM accounted for 80% during summer and spring corresponding to an average concentration of PM$_{2.5}$ of 12.0 $\mu$g m$^{-3}$ and 14.1 $\mu$g m$^{-3}$, respectively. This contribution was reduced to 67% and 48% during autumn and winter (12.7 $\mu$g m$^{-3}$ on average for both periods), respectively. On average transported pollution contributed approximately 12-13 $\mu$g m$^{-3}$ of dry PM$_{2.5}$ mass on an annual basis, which is close to EPA’s annual PM$_{2.5}$ standard of 15 $\mu$g m$^{-3}$. The standard is exceeded if water is also accounted. Local traffic accounted for 15% of PM$_{10}$ during winter and autumn and for 10% of PM$_{10}$ during summer and spring. The remaining 10%, 10%, 15% and 35% during spring, summer autumn and winter, respectively is due to local sources other than traffic.

Based solely on diurnal profiles of PM$_{10}$ measurements, presented in Section 5.4, the contribution of transported PM was estimated to be around 80% and 60% during the warmer and colder months of the year. In this section, based on PM$_{2.5}$ composition measurements inside and upwind of the city, the overall contribution of transport during warmer (April to September) and colder (October to March) months was estimated to be 76% and 60%, respectively. The two methods are consistent suggesting that the approach based on the seasonal diurnal profiles gives reasonable results.

5.8 Pinning Down Local Sources

The observed PM$_{2.5}$ was attributed to transported PM, local traffic and “other local sources” in the previous sections. The contribution of other local sources appears to be smaller during spring and summer, however during winter they contribute around 40% of the PM$_{2.5}$. Biomass burning has been identified as a major candidate because of the
high organic aerosol and its correlation with K. In order to identify other potential sources an intensive campaign was held. From 20 February to 5 March 2012 measurements were performed at the urban center and at an urban background station (38°13′14″N, 21°44′28″E) located 3.5 km SW of the center at an elevation of 10 m above ground.

**Urban Center.** The urban center station was equipped with a filter sampler (described in Section 5.6) operating at 12 h resolution, a nephelometer (Aurora – 1000F, Ecotech) and gas monitors measuring CO₂ (Teledyne Model 360E). Aerosol absorption was monitored continuously by a Multi Angle Absorption Photometer (MAAP, Thermo model 5012; Petzold and Schönlinner 2004). MAAP’s inlet was heated to 70°C prior to analysis in order to remove water and organics.

**Urban Background.** The urban background station was equipped with a High Resolution Aerosol Mass Spectrometer (HR-AMS) from Aerodyne, Inc. (Jayne et al., 2000; Jimenez et al., 2003), monitoring the chemical composition of non-refractory (NR) particulate matter with diameter less than one μm (PM₁) without drying the sample from 26 February to 5 March. The HR-AMS is described in detail in DeCarlo et al. (2006). The instrument determined the size distributions of sulfate, nitrate, chloride, potassium, ammonium and organics. Ambient PM₁ potassium concentrations were calculated using a custom software tool, supplied by the manufacturer, whose purpose is to speciate and quantify HR-AMS data (De Carlo et al., 2006). Applying the Kostenidou et al. (2007) algorithm, a total collection efficiency factor (CE) was estimated for the AMS for every two hours. Average CE during daytime 8 a.m. to 6 p.m. was approximately 0.65, while after 6 p.m. till midnight the CE was approximately unity. Between midnight and 8 a.m. CE varied between 0.65 and 1 depending on the day.

The dried PM₂.₅ mass was monitored continuously by a Tandem Element Oscillating Microballance (TEOM; Thermo model 1405-DF; Patashnick and Rupprecht, 1991). The daily average mass concentration was also measured by a Federal Reference Method (FRM) sampler (Partisol-2000, Rupprecht & Patashnick Co., Inc.) which sampled on one PTFE filter at a flowrate of 16.7 L min⁻¹. The filter was weighed and analyzed for inorganic ions according to the procedures described in Section 5.6.

Ambient number concentration and distribution of particles between 10 and 500 nm in diameter were measured with a Scanning Mobility Particle Sizer (SMPS, TSI
SO₂ (Teledyne Model 100EU) was also monitored throughout the sampling period.

The hourly averaged composition of PM₁, as given by the HR-AMS and MAAP is shown in Fig. 5.9. Organics concentration was 15.6±17.8 μg m⁻³ and dominated the PM₁ contributing on average 63% of the PM₁ mass during the campaign. The organics contribution increased after 6 p.m. (LT) exceeding 80 μg m⁻³ on several occasions which corresponded to an increase of 80%. The sulfate concentration was on average 1.8±0.9 μg m⁻³ and never exceeded 6 μg m⁻³. The average nitrate concentration was equal to 1.2±1.2 μg m⁻³. Nitrate exhibited equal or higher concentration than sulfate during early morning (7-9 a.m. LT) or at night after 6 p.m. (LT).

After 6 p.m. LT the PM₁ organics increased by an order of magnitude followed by increase in nitrate while the sulfate concentration remained stable or decreased. The average PM₁ potassium concentration, provided by the AMS, was 1.0±0.8 μg m⁻³ and the highest concentrations were observed during nighttime following closely the temporal variations of organics (R²=0.69) including the sharp nighttime increase (Fig. 5.10).

The PM₂.₅ mass concentration was on average 35.8±28.0 μg m⁻³ at the urban background site correlating well (R²=0.61, 3 hour average) with the scattering coefficient (70.6±68.2 Mm⁻¹ on average) measurements (a proxy of the fine aerosol mass) monitored at the urban center for the same size fraction. Since the two instruments were 3.5 km away, this correlation indicates that both sites were susceptible to similar fine PM sources (Fig. 5.11).

The diurnal profile of PM₂.₅ mass showed a peak during rush hour traffic followed by a sharp increase after 6 p.m. LT. Black carbon concentration, located 3.5 km away at the urban center, also followed the variations of the PM₂.₅ mass at the urban background site (Fig. 5.12) indicating that the source behind the sharp increase at night involved combustion. Average BC concentration was 1.9±1.7 μg m⁻³. The highest BC concentrations were observed at night (typically above 5 μg m⁻³ and reaching as high as 10 μg m⁻³) often exceeding those of sulfate. SO₂ peaked during rush hour traffic and during the night following the sharp increase of BC, PM₂.₅ and organics mass. SO₂ is emitted during combustion of fossil fuels and biomass. Biomass combustion results in the emission of 0.1 to 0.4 g SO₂ per kg of dry fuel depending on the type of biomass (Andreae and Merlet, 2001; UK Emission Factors Database, 2010; Akagi et al., 2011). In special cases, such as tropical and extratropical forests, emission factors reaching 1 g
Figure 5.9. PM$_1$ composition of (a) organics; (b) sulfate; (d) ammonium and (e) nitrate from 26 February to 5 March by a HR-AMS at the urban background site and black carbon measurements (c) of the same period at the urban center. Different scales are used for each species. The contribution of each constituent of the dry PM$_1$ mass is shown in (f).
Figure 5.10. PM$_1$ diurnal profiles of (a) organics, (b) sulfate, (d) ammonium, (e) nitrate, and (f) potassium by a HR-AMS and of SO$_2$ measurements (c) from 26 February to 5 March at the urban background site. Vertical lines correspond to rush hour traffic and of the nighttime increase observed.
Figure 5.11. Three-hour average PM$_{2.5}$ mass (FDMS-TEOM) versus light scatter coefficient (nephelometer) at the urban background and urban center, respectively. The two instruments located 3.5 km away exhibit good correlation ($R^2=0.61$) indicating that both sites were susceptible to the same sources. The light scattering coefficient of particles is expected to correlate with particle mass concentration provided by TEOM, but the correlation of the two instruments is complicated by the drying methods used. The two instruments were deployed at the same place for 5 days and exhibited good correlation ($R^2=0.77$, not shown) and an average scattering efficiency of 2.8 m$^2$ g$^{-1}$ (dashed red line).

Figure 5.12. Diurnal profile of PM$_{2.5}$ mass at the urban background site from 26 February to 5 March. The profile exhibits two peaks, one at 08:00 and one at 20:30. Black carbon monitored at the urban center exhibits the same peaks indicating that combustion sources were involved in both cases.
SO₂ per kg of dry fuel have been reported (Andreae and Merlet, 2001). During fossil fuel combustion, almost all sulfur in the fuel is oxidized into SO₂ (Vaaraslahti et al., 2004) thus the SO₂ emission factor depends largely on the fuel sulfur content (De Fre et al., 1994). As a result fossil fuel combustion EF’s vary by 3 orders of magnitude (0.015 to 54 g/kg fuel consumed; UK Emission Factors Database, 2010) for sulfur concentrations from 2 to 2000 ppm or more. In Greece legislated sulfur levels in liquid fossil fuels are below 15 ppm but in practice the sulfur content could be an order of magnitude higher because marine fuel is used to an unknown extent. Because SO₂ peaks during rush hour traffic and potassium does not, we assume that it derives mainly from fossil fuel combustion. During nighttime, potassium peaks along with SO₂ indicating that biomass was also involved along with diesel combustion, which is the primary heating agent in the area. Since the sulfur content of fuel in the area may vary by an order of magnitude or more, the biomass and fossil fuel contribution of the nighttime increases cannot be directly distinguished.

Average number concentration of particles ranging from 10 to 500 nm during the campaign was 24±28×10³ cm⁻³. The number concentration was lower during daytime (before 6 p.m. LT) and was on average 15±15×10³ cm⁻³ but increased by a 3-fold during the night to 51±38×10³ cm⁻³. Even though the number concentration increased during the night the number mode diameter did not change substantially (Fig. 5.13). Average surface and volume concentrations of PM₀.₅ during the campaign were 780±1155 μm² cm⁻³ and 21±37 μm³ cm⁻³ respectively, and concentration of both increased during the night by a factor of 4.

Figure 5.13. Night and day average number, surface and volume distributions from 21 February 2012 to 9 March 2012. The aerosol number, surface and volume concentrations increased by a 3-4 fold at night compared to day without a significant mode shift.

PM₂.₅ mass, PM₁ organics, BC, SO₂ and K were found to increase sharply during nighttime indicating that combustion sources are active at night. Biomass and diesel combustion were identified as a possible sources. Diesel is primarily used for heating in
the area. The high emissions with the low nighttime mixing layer heights contributed to the observed nighttime increase.

5.9 Comparison with Other Sites

The annual average PM$_{2.5}$ concentration at the urban center site (22.3±11.8 μg m$^{-3}$) was similar to those measured at urban sites around Europe that range from 14 to 32 μg m$^{-3}$ (Van Dingenen et al., 2004). Many urban and near urban European sites exhibit increased PM$_{2.5}$ mass concentrations in the winter compared to the summer by 25-50%, probably due to higher energy demand, sharing a common trend with Patras. Annual PM$_{2.5}$ sulfate concentration (3.5±2.3 μg m$^{-3}$) was similar to other urban sites (Putaud et al., 2004), but higher than European natural and rural sites. Annual average organics concentration (10.5±8.5 μg m$^{-3}$) is higher than in the European urban, near city and rural sites reported by Putaud et al. (2004).

Transported PM$_{2.5}$ in Paris, a megacity with a population of 10.5 millions, was found to account approximately for 70% of the total PM$_{2.5}$ on an annual basis, similar to Patras (Beekman et al., 2012). During winter, in Paris, PM$_1$ mass increased more than a factor of 2 compared to summer and biomass burning was identified during winter as a major source accounting for 40-45% of the organic aerosol content. Despite the similarities of the two urban areas, PM$_1$ concentration in Paris during summer was lower than 8 μg m$^{-3}$ on average and during winter ranged between 15.2 μg m$^{-3}$ and 18.5 μg m$^{-3}$. The corresponding concentrations for PM$_{2.5}$ in Patras was 22 μg m$^{-3}$ and 30 μg m$^{-3}$ for summer and winter, respectively. The main reason that a medium size city exhibits higher concentrations than a megacity is their location. Paris, located near the Atlantic ocean, is influenced by marine air masses, which are relatively clean compared to continental ones (Freutel et al., 2012). Patras, due to its location, is more frequently influenced by continental air masses that result in higher background concentrations than Paris. During winter, at both cities, domestic heating increased PM levels. Paris is located in a flat terrain, contrary to Patras that is located between two large mountains. Under favorable conditions in Patras (e.g., low wind speed, low boundary depth) emitted particles are “trapped” and accumulate as long as the sources persist.
5.10 Conclusions and Discussion

A multi-stage methodology was employed to investigate particulate sources in an urban area. Following this approach the cost and complexity increases from step to step. During the first step, ambient PM levels were assessed and it was concluded whether the area under investigation has a problem. The contribution of local vehicular traffic and transported pollution was roughly estimated but other sources were not identified. At the second step, the seasonal behavior and composition of PM$_{2.5}$ was determined. Biomass burning was identified as a winter source, but it could not be concluded whether it was local or transported. At the third step local and transported PM contribution was determined and biomass burning was identified as a local source. Our estimated contribution of transported PM was similar with the rough estimate using only a continuous mass monitor in the first step. Finally, during the most polluted period a small campaign was held and the temporal behavior of fine PM was investigated. Frequent high fine PM concentrations were observed during nighttime due to domestic heating emissions. Domestic heating and especially biomass burning was identified as the source that drives PM levels to exceed legislated standards at least during winter.

Patras, a medium size urban area of 200,000 inhabitants, despite its size, violates both the EU and EPA air quality standards concerning PM$_{10}$ and PM$_{2.5}$ respectively. Higher levels of PM$_{2.5}$ and PM$_{10}$ were identified during the colder months (October to March) when the majority of violations were identified. Local vehicular traffic contributed on average 12±4% of the PM$_{10}$. Taking into account that the measurements were located at a kerbside, these are upper bound estimates indicating that traffic is a relatively small source in the area. During the colder months the vehicular traffic contribution increased to 14% on average and during the warmer months it was reduced to 10%.

Local sources other than traffic, were found to contribute approximately 20% and the rest was attributed to long range transport. The contribution of local sources increased to 37% during winter. Organic aerosol which comprised almost half (47%) of the PM$_{2.5}$ mass correlated well ($R^2=0.79$) with potassium during winter indicating that biomass burning contributed significantly to local PM levels. Potassium concentrations doubled when the PM$_{2.5}$ mass exceeded the U.S. EPA daily standard. Potassium concentrations 40 km away from the city at a rural background site were lower by 44% on average than in the city center during the colder months. This suggests that biomass
emissions were located inside the urban area and were not due to agricultural biomass waste combustion that takes place at rural areas around the city the same period.

Even though long range transported PM, is not enough to exceed legislated standards (only one exceedance in 4 years of the daily U.S. EPA daily standard during summer), it provides high background concentrations that are the basis for exceedances. When the high background concentrations are coupled with strong local sources, eg during winter in Patras, legislated standards are readily violated.

Domestic heating was identified as the dominant winter source and was found to increase PM levels sharply during nighttime. Two fuels are commonly used in the area, diesel and wood. Due to uncertainties in the sulfur content of the fossil fuel actually burned the contribution of either source could not be accurately quantified. On several occasions during nighttime, the organic aerosol alone was found to exceed 80 µg m⁻³ and black carbon concentrations exceeded those of sulfate. These surprisingly high concentrations, for a medium-size city, are the combination of the inversion layer that decreases during night when domestic heating peaks. Because the city is located between two high mountains the emitted PM is “trapped” and accumulates as long as the source persists and the wind does not disperse the air mass.

Acknowledgements: The authors would like to acknowledge D., Sakipis, D., Tsokolis, G., Katsi, E., Viliou, M., Papaioannou, P., Mpakoulas, and M., Tsiflikiotou for their assistance in collecting samples. Dr. C. Lagouvardos and Dr. V. Kotroni of the Institute of Environmental Research & Sustainable Development of the National Observatory of Athens for providing the meteorological data used in this study.
References


Beekman et al., Will regional emissions control fine particulate matter levels in future megacities? Submitted to PNAS.


Tsyro, S. G.: To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM\textsubscript{10} and PM\textsubscript{2.5}? Atmos. Chem. Phys., 5, 515–532, doi:10.5194/acp-5-515-2005, 2005.


Chapter 6
Summary and Future Work

6.1 Summary

The goal of this thesis was the improvement of our understanding of the ambient particulate number and mass sources. Finokalia, a remote area in the southeast Mediterranean was investigated and the lack of strong local sources was shown. High sulfate levels compared to those reported in other European background sites were reported. On average 80% of the PM$_1$ organic aerosol was water soluble and its OC/EC ratio was equal to 5.4, indicating that the organic aerosol content was mainly secondary and highly oxidized. Moderate correlation ($R^2=0.44$) of the OC/EC ratio with the average ozone concentration of the previous day, suggested that the oxidation of organics takes place away from the site. Analysis of air mass trajectories reaching the site combined with statistical tests identified five source regions (Athens, Greece, other continental, Africa, marine). Source regions Athens, Greece and other continental were associated with higher sulfate, organic and number concentrations. Air masses of marine origin had the lowest concentrations for all PM$_1$ species.

New particle formation was followed at Finokalia for one year. Particle formation periods were categorized into event, non-event, and undefined days based on their characteristics. Undefined and event days are most frequent during February and March (winter) and least frequent during August and September (summer). Nucleation events were mainly associated with air masses arriving from the west and passing over Crete, favored typically by lower than average condensational sink.

During the summer intensive campaign which took place during May 2008, all event and undefined particle formations occurred when particles were neutral under low SO$_2$ concentrations (<40 ppt) compared to the average (93 ppt). During the winter intensive campaign, which took place during the February 2009, due to the large uncertainty of the C/A ratio, almost the whole study was consistent with neutral particles. Nucleation events occurred under higher SO$_2$ concentrations (360 ppt) compared to the average (220 ppt) indicating that the SO$_2$ concentrations were limiting to some extent particle formation during that period. The seasonal pattern of NPF and the overall event frequency could not be explained by meteorology or SO$_2$ concentration alone.
Our explanation of the unexpected seasonal variation of nucleation frequency (more events during the winter than during the summer) is that the availability of ammonia (or something that may covary with it like the amines) is limiting the frequency of the events. During winter, due to lower photochemical activity, which resulted in lower sulfuric acid production rate, particles were consistently neutral and NPF was more frequent. During summer the ammonia levels were not sufficient to neutralize the sulfuric acid produced and particles were mainly acidic. NPF would occur only under periods when particles were neutral. Air masses that pass over land just before arriving at the site can pick up ammonia and therefore nucleation is favored during these conditions. These results suggest that ammonia is involved in NPF, but does not imply participation in the stable cluster.

Ambient aerosol number concentrations were monitored at the city center of the Paris megacity along with two satellite suburban stations, located 16 and 18 km away each on opposite directions, two mobile laboratories and one aircraft during July 2009 (summer) and 15 January till 15 February 2010 (winter). During the summer campaign, PM$_1$ mass concentrations were comparable with those of Finokalia during May 2008. During summer at one of the suburban sites (SIRTA), the number concentration increased by a factor of 3 when the site was downwind compared to when it was upwind. Contrary to SIRTA, at the other suburban site (GOLF), the number concentration was not affected by wind direction during summer.

NPF was observed at all sites during summer. At SIRTA and the Paris center (LHVP) an event was identified on half of the campaign days and at GOLF once every four campaign days. The lower frequency of events at GOLF was mainly due to interferences of nearby traffic and instrument limitations which did not allow clear event identification. Condensation sink was mainly controlling the frequency of events at all sites. The Paris plume was identified at an altitude of 600 m, using black carbon as a tracer, as far as 200 km away from the city center. Increased particle number concentrations were identified outside of the Paris plume during summer. On four occasions the particle increase was located upwind of the ground stations simultaneously with regional NPF observed on the ground at least in two of the sites. As a result the increase was attributed to NPF. Increased particle number concentrations were also identified along one side of the plume on four occasions but only two were associated with NPF on the ground.
During winter number concentration was higher by approximately 50-60% compared to summer at all sites. At distances from the city center greater than 60 km the number concentration was similar with that observed during summer at the same distance from the city. At SIRTA, when the site was upwind $N_2$ increased by a factor of 2 compared to when it was upwind. At GOLF the relative increase was 50%. During winter the higher condensational sink and lower solar intensity compared to summer prevented NPF to occur.

Two areas (Paris, Finokalia) have been characterized via summer and winter month-long campaigns, but little or no information was acquired for the rest of the year. A multi-stage method for assessing particulate sources was developed and implemented at Patras, Greece. Initially a low cost particulate matter mass monitor was used to assess aerosol mass concentrations and it was found that the city, despite its small size (population around 200,000) and lack of heavy industry, violates both the daily and annual European Union PM standards. Increased PM$_{10}$ concentrations were observed during the winter but local vehicular traffic was estimated to account for only 12±4% of the PM$_{10}$ concentration on an annual basis. In the second stage PM$_{2.5}$ chemical composition was measured at the urban center and biomass burning was identified as a major PM source during the colder months. The PM$_{2.5}$ concentration during winter was higher by 50% the latter two years (2011-2012) of the study compared to the same periods of the first two years (2009-2010).

In the third stage PM$_{2.5}$ concentration and chemical composition was also followed at a mostly upwind rural site around 40 km from the city. The transported pollution was found to account for 50% of the PM$_{2.5}$ during winter and for more than 70% during the rest of the year. Almost all of the sulfates and 40-90%, depending on the season, of the organic aerosol are transported to the city from other areas. Even though long range transported PM, is not enough to exceed legislated standards, it provides high background concentrations that are the basis for exceedances. When the high background concentrations are coupled with strong local sources, eg during winter in Patras, legislated standards are readily violated. In the last stage, an intensive campaign took place during winter in order to quantify PM sources during the most polluted period. Nighttime sharp increases of the aerosol levels were observed with organic aerosol levels exceeding 80 μg m$^{-3}$. Fossil fuel and local biomass combustion emissions for domestic heating were responsible for these levels.
6.2 Future work

The major PM sources in Patras have been quantified, yet the effect of domestic cooking has not been assessed, even though they are present. Domestic cooking quantification may result from statistical analysis of AMS data or by tracking cholesterol, the tracer for cooking. During the colder months, sharp PM increase during nighttime was observed with diesel and biomass combustion being mainly responsible. The relative contribution of each to the increase was not determined. In order to distinguish the two a tracer, specific to only one of the sources should be monitored. Levoglucosan results from biomass combustion and is a suitable tracer for this purpose. Positive matrix factorization of AMS data may also be used to quantify the two sources.

In this work a semi-empirical method was used to quantify local traffic. Hopanes, resulting from the lubricant of combustion engines, have been used as tracers of vehicular traffic. The tracer method provides more robust results and distinguishes vehicular traffic from diesel combustion for domestic heating, since in the latter the combustion engine does not use lubricant.

The importance of ammonia in NPF was shown. Ammonia concentrations in the pptv level can trigger NPF and therefore a high resolution method that monitors ammonia in the pptv level is needed. A method that provides high resolution particulate ammonium concentrations has been developed and tested against the steam jet aerosol collector. The same method can be used to monitor gas phase ammonia. In order to examine NPF the detection limit of the method should be decreased.

The relation between NPF and urban plumes is not well understood. City plumes can potentially inhibit, due to the high condensational sink, or trigger, due to the high SO$_2$ concentrations, NPF. During July 2009 in Paris, NPF was identified outside of the plume always upwind of Paris. Evidence was given that NPF took place along one side of the plume, without explaining why NPF did not occur on either side. Further investigation of urban plumes should be conducted in order to establish a positive or negative relation with NPF.
A.1 Scanning Mobility Particle Sizer (SMPS)

The Scanning Mobility Particle Sizer (SMPS) measures the mobility of a charged particle in an electric field. Particles enter the SMPS via an impactor whose primary function is to remove larger particles that carry more than a single charge. The pressure drop across the impactor, which is proportional to the square of the flow rate, is used by a volume flowmeter to measure the sample flow. Particles entering the system are neutralized (using a radioactive source which primarily is Kr-85 or less often Po-210) such that they have a Fuchs equilibrium charge distribution and then enter a column where the polydisperse aerosol is classified according to electrical mobility. The geometry of the column allows classification of the polydispersed aerosol into different sizes. Two geometries have been widely used in this work, the long and nano columns of TSI Inc which can classify aerosols from 10 nm – 1 μm and 3 nm – 150 nm, respectively. Regardless of geometry, every column contains two concentric metal cylinders. The inner rod, is maintained at a controlled negative voltage, while the outer cylinder is electrically grounded creating an electric field between the two cylinders. As the inner rod voltage changes the diameter of particles that go through a slit at the bottom of the column changes, providing at the exit particles with very narrow diameter range. The size of particles exiting through the slit is being determined by the charge, central rod voltage, and flow within the DMA:

\[ D_p = \left(1 + Kn \alpha + \beta e^{\frac{q_{sh}}{Kn}}\right) \frac{2neVL}{3 \mu q_{sh} \ln \frac{r_2}{r_1}} \]  \hspace{1cm} \text{A.1.1} \]

where \(n\) is the number of elementary charges on the particle, \(e\) is the elementary charge \((1.6 \times 10^{-19} \text{ Coulomb})\), \(\alpha = 1.142\), \(\beta = 0.558\), \(\gamma = 0.999\), \(Kn\) the Knudsen number which is given by \(2\lambda/D_p\), \(\lambda\) the gas mean free path, \(\mu\) is the gas viscosity, \(D_p\) is the particle diameter cm, \(q_{sh}\) is sheath air flow rate (equal to excess air flow rate), \(r_2\) is the outer radius of annular space \((1.961 \text{ cm for the Long DMA and 1.905 cm for Nano DMA})\), \(r_1\) is the inner radius of the annular space \((0.937 \text{ cm for the Long DMA and 0.937 cm for} \)
the Nano DMA, V is the average voltage on the inner center rod in volts, L the length between exit slit and polydisperse aerosol inlet (44.37 cm for Long DMA and 5 cm for the Nano DMA).

In the case of the SMPS the voltage changes gradually. In a Differential Mobility Particle Sizer (DMPS) the voltage steps through predetermined values. The monodisperse distribution that exits the DMA moves to a Condensation Particle Counter (CPC) which measures the particle concentration at that size.

A CPC counts aerosol particles after growing them via condensation. An aerosol stream (monodisperse or polydisperse) is guided to a heated tube saturated with the vapors of the working fluid (n-butanol or ultra pure water). The aerosol stream moves to a condenser (tube of low temperature) where the particles grow by condensation of the cooled vapors. The saturation ratio of the condensing vapor, which is guided by the temperature difference between the saturator and the condenser, determines the smallest particle size detected by the CPC as described by the Kelvin equation (Eq. A.1.2).

\[
\frac{p}{p_s} = \exp\left(\frac{4\sigma M}{\rho RTD_p}\right)
\]  

A.1.2

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 saturation ratio is defined as the actual vapor partial pressure, \(p\), divided by the saturation vapor pressure, \(p_s\), at a given temperature. 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 where they are counted.

A. 2 Air Ion Spectrometer (AIS)

Air ions ranging from 0.8 - 40 nm are classified according to their mobility diameter similar to a DMA (Mirme et al., 2007). The AIS contains two annulus analyzers consisting each of an ion repulsive inner electrode and ion collecting outer electrode. The collecting electrodes of each annulus consist of 21 electrically isolated sections each connected to an electrometer. The zero drift and noise level of each electrometer are recorded. Particle free air is injected at each annulus which is recycled from each column in order to maintain similar gaseous characteristics.

The ions moving in the radial electric field of the mobility analyzers precipitate on the different sections of the inner electrode according to their mobility. The electric
currents carried over these sections by ion fluxes are measured by electrometers and form the output signals vector of the AIS. The design is based on the theory of the aspiration method (Tammet, 1970).

### A. 3 Aerosol Mass Spectrometer (AMS)

The AMS (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2006) is used to monitor the composition of non refractory PM$_1$ (NR-PM$_1$) in real time. Practically only a small fraction of particles smaller than 20 nm and larger than 800 nm (aerodynamic diameter) is analyzed. The aerosol stream enters the instrument via a critical orifice and is focused into a particle beam by a series of aerodynamic lenses. Particles smaller than 20 nm are lost by diffusion while a large fraction of particles greater than 800 nm is lost inside the lenses. The particle beam that has been created goes through a chopper the operation of which determines the 3 instrument modes.

At the Time-of-Flight Mode (ToF mode) the chopper is in the beam chopped position and only a fraction of the particle beam is allowed to reach the detector. As particles travel they are forced to spread out according to their size as a result of the supersonic expansion caused by the final aperture of the lens. While in this mode the mass distribution as a function of the vacuum aerodynamic diameter is monitored.

At the Mass Spectrum mode (MS mode) the chopper is open allowing all aerosol to go through thus increasing the mass that reaches the detector providing with mass concentrations and mass spectra.

The third mode is a simple alteration between the ToF and MS modes, providing both mass spectra and sizing. After the particle beam leaves the chopper it is volatilized by impacting on a heated surface (typically set at 600 °C). Refractory material such as black carbon, calcium salts and metal oxides among others cannot volatilize and therefore the AMS measures only non refractory particle composition. After the particles have been volatilized into gases they are ionized by electron impaction. The resulting ions are analyzed by a standard quadropole mass spectrometer detecting the positive ion fragments generated by the electron impact ionization.

Calculating the aerosol concentration is complicated by particle bounce at the vaporizer. Therefore the Collection Efficiency (CE) of the AMS has to be determined at every scan. CE depends on morphology and composition. Spherical liquid particles tend to have higher CE than solid particles. Kostenidou et al. (2007) has provided an
algorithm that can compute CE along with particle density by means of bilinear interpolation, provided that the data are coupled with SMPS measurements of the corresponding size fraction. In this work the AMS will monitor ambient particles instead of dried and the CE will be calculated using the Kostenidou et al. (2007) algorithm instead of assuming a CE equal to 0.5 for dry ambient particles (Zhang et al., 2005).

A. 4 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

A PTR-MS provides on-line measurements of trace organic gas-phase components with concentrations as low as a few pptv (Hansel et al., 1995). The detection is based on reactions of H_3O^+ ions, which perform non-dissociative proton transfer to most of the common volatile organic compounds (VOCs). All compounds that have a proton affinity smaller than water (165.2 kcal mol\(^{-1}\)) do not react and hence all components present in clean air are not fragmented or ionized. Because clean air does not react with H_3O^+ it can be used as the carrier gas instead of using an inert carrier (e.g. He) which would result in diluting the sample with corresponding loss in sensitivity.

High density of H_3O^+ ions is generated via a hollow-cathode ion source, from which ions are extracted into a short “source drift region” filled with water vapor. The ions reach the reaction region filled with the air and the trace constituents to be analyzed. Only a small amount of the trace gases reacts with the ions guided to a mass spectrometer for identification.

A. 5 Nephelometry

Two nephelometers (NGN-nephelometer, Ecothech Aurora 1000F) were employed in this work to monitor PM after the sample was heated at 50°C to remove most of the water content. Nephelometers measure the light scattered by particulates (dust/aerosol) in the air by shining light through sample air and measuring the deflected light (scattering) using the Beer-Lambert law:

\[ I = I_0 e^{-\sigma_{ext} x} \quad \text{A.5.1} \]

where \( I_0 \) is the initial light intensity, \( I \) is the intensity after distance \( x \), \( \sigma_{ext} \) is the attenuation, or extinction coefficient. The larger \( \sigma_{ext} \), the more rapidly the light is
attenuated. The light source sits inside a matt-black tube containing baffles to minimize reflected light and it is assumed that the attenuated light is primarily due to scattering by particles, resulting in $\sigma_{\text{ext}}$ being equal to $\sigma_{\text{scat}}$.

Ambient particles are composed of constituents that absorb light (black carbon, iron oxides) and produce measurement bias which is relatively small in the case of ambient aerosols. Mie theory is used to involve PM$_{2.5}$ mass and the extinction coefficient $\sigma_{\text{scat}}$. Yet the intensity of scattered radiation by a polydisperse aerosol distribution is not simply linearly related to dry aerosol mass concentration, but rather a function of the size distribution parameters, aerosol density and index of refraction. The nephelometers used in this study were calibrated using gases (CO$_2$, SUVA 134a refrigerant) are accurate and precise enough to make measurements of the PM$_{2.5}$ aerosol scattering coefficient.

A. 6 Tapered Element Oscillating Microbalance (TEOM)

TEOM is designed to provide real time particulate concentrations measurement. In this work a 1405-DF TEOM model was used. Ambient air is drawn through a virtual impactor that separates particles into PM$_{2.5}$ and PM$_{2.5-10}$ (PM coarse). In order for the virtual impactor to work properly an initial 16.7 Lpm flowrate should be established upstream of which 12 Lpm are bypass flow, 3 Lpm go through the PM$_{2.5}$ path and the rest 1.67 through the coarse channel. The aerosol stream regardless of size fraction is guided to a nafion dryer where it is dried. The sample is guided to a valve system that alternates periodically (6 min). During base sampling the aerosol stream is also heated to 50 °C to remove any extra water and is oriented towards a hollow tapered glass element without any other treatment. The mass measurement is derived from changes in the resonate frequency of the filter and glass element, as particulates are deposited. During reference sampling the aerosol stream is cooled to 4 °C to avoid any evaporation and is again guided to the tapered elements. The difference between base and reference sampling is the actual measurement. TEOM provides rolling average measurements of 10 points resulting in one hour measurement lag.

Care must be taken that the instrument is held under a controlled environment with temperature below 25 °C and that the temperature does not fluctuate significantly. Measurements at ambient RH that exceed 90% should be omitted because of insufficient drying. Care must be taken that the instrument noise during measurement at each tapered element does not exceed 0.1%.
A. 7 Quality Assurance – Quality Control

PM$_{2.5}$ filters were collected on PTFE (Whatman 0.2 and 1.0 μm pore size) and quartz (Pallflex, Tissuquartz 2500QAO-UP) substrates for measuring the water soluble ionic composition and bulk organics, respectively. In order to assess artifacts laboratory, travel and field blank filters were collected at least once every two months and a quartz filter was placed downstream of a PTFE filter during sampling to assess for absorbed organic vapors. In order to minimize evaporation bias all filters were collected within a few hours after sampling and were immediately stored in clean petri dishes. All quartz filters were thermally treated at 500 °C for 24 h and were folded in pre-cleaned aluminum foil. All filters were stored at room temperature in petri dishes prior to sampling and were refrigerated at -12 °C after sampling.

Water soluble ion concentration of the blanks were close or below the detection limit of the method (≈10 ppb in solution or 0.02 μg m$^{-3}$) for ions related to dust and sea salt particles (Ca$^{2+}$, Na$^{+}$, Cl$^{-}$) and never exceeded 0.1 μg m$^{-3}$. The rest of the ions exhibited concentrations below the detection limit. Blank levels of OC were 0.04±0.04 μgC m$^{-3}$, 0.07±0.07 μgC m$^{-3}$ and 0.4±0.7 μgC m$^{-3}$ for laboratory, travel and field blanks, respectively and were mainly due to absorption of organic gases in the field and during the cooling stage of the thermal treatment. EC could not be quantified in laboratory and travel blanks while field blanks concentrations were equal to 0.03±0.06 μgC m$^{-3}$ and are probably due to pyrolysis of the carbon content during analysis.
A. 8  References
Σύνοψη Διδακτορικής Διατριβής

Η παρούσα διδακτορική διατριβή έχει ως στόχο να βελτιώσει την γνώση μας για τις πηγές αριθμού και μάζας αιωρούμενων ατμοσφαιρικών σωματιδίων. Για το σκοπό αυτό χρησιμοποιήθηκε ο φασματογράφος μάζας αιωρούμενων σωματιδίων (Aerosol Mass Spectrometer, AMS) και ο αναλυτής ατμοσφαιρικών ιόντων (Air Ion Spectrometer, AIS). Το πρώτο παρέχει πληροφορίες για την χημική σύσταση των αιωρούμενων σωματιδίων με διάμετρο μικρότερος του ενός μικρού (PM1) ενώ το δεύτερο την κατανομή αριθμού σωματιδίων με διάμετρο 0.8-40 nm.

Μετρήσεις Υποβάθρου σε Παραθαλασσιο Σταθμό στην Ανατολική Μεσόγειο

Η Φινοκαλία είναι μια απομακρυσμένη τοποθεσία στα βόρεια παράλια της Κρήτης. Κατά την διάρκεια ενός μήνα εντατικών μετρήσεων τον Μάιο του 2008, δεν εντοπίστηκαν ισχυρές τοπικές πηγές αντίθετα η προέλευση των αερίων μαζών καθόριζε την σχετική χημική σύσταση των αιωρούμενων σωματιδίων. Πέντε περιοχές προέλευσης των αιωρούμενων σωματιδίων ταυτοποιήθηκαν και ονομάστηκαν με βάση το όνομα της τοποθεσίας ως “Αθήνα”, “Ελλάδα”, “Ηπειρωτική Ευρώπη”, “Αφρική” και “Θαλάσσα”. Η σειρά αναφοράς ακολουθεί την μέση αύξηση μάζας των PM1 στην Φινοκαλία συμφωνα με την ανάλυση. Οι συγκεντρώσεις των θαλάσσιων PM1 ήταν κατά μέσο όρο οι χαμηλότερες ενώ αντίστοιχα οι αέριες μάζες που προέρχονταν από την Αθήνα εμφανίζονταν υψηλές συγκεντρώσεις.

Οι οργανικές ενώσεις των PM1 στην περιοχή διαλύονταν στο νερό σε ποσοστό 80%, ενώ ο λόγος οργανικού προς στοιχειακό άνθρακα βρέθηκε υψηλός (5.4 κατά μέσο όρο) και συσχετίστηκε θετικά με τις συγκεντρώσεις ήζοντος (R²=0.44) στην περιοχή (Εικόνα 1). Όλες οι παραπάνω παρατηρήσεις και αποτελούν ισχυρές ενδείξεις από αποθέματα στην περιοχή (Εικόνα 1). Οι οργανικές ενώσεις των PM1 στην περιοχή διαλύονταν στο νερό σε ποσοστό 80%, ενώ ο λόγος οργανικού προς στοιχειακό άνθρακα βρέθηκε υψηλός (5.4 κατά μέσο όρο) και συσχετίστηκε θετικά με τις συγκεντρώσεις ήζοντος (R²=0.44) στην περιοχή (Εικόνα 1). Όλες οι παραπάνω παρατηρήσεις και αποτελούν ισχυρές ενδείξεις από αποθέματα στην περιοχή (Εικόνα 1).
Σχηματισμός Φρέσκων Σωματιδίων σε Απομακρυσμένη Περιοχή της Ανατολικής Μεσογείου

Περιοχή της Ανατολικής Μεσογείου

Στην Φινοκαλιά, παρόλη την υψηλή ένταση φωτός, τις χαμηλές συγκεντρώσεις σωματιδίων και τις υψηλές συγκεντρώσεις SO2 η συχνότητα ατμοσφαιρικής πυρηνογένεσης ήταν χαμηλή. Οι αέριες μάζες που φτάνουν στην Φινοκαλιά και έχουν περάσει κανένα χρόνο πάνω από στερία εμφανίζουν υψηλότερη συχνότητα πυρηνογένεσης σε σχέση με τον μέσο όρο. Σε αυτή την περίπτωση διαδραματίζουν και οι περιοχές προέλευσης “Ελλάδα” και “Αθήνα”, όπου εμφανίζονται και οι υψηλότερες συγκεντρώσεις σωματιδίων, παρόλη την υψηλή ένταση φωτός που έχουν εμφανιστεί στη σειρά των σωματιδίων. Αυτά η συχνότητα πυρηνογένεσης σε σχέση με την περιοχή παρατηρείται ευέλικτη και ενδεικτική μεταφερόμενης ρύπανσης.
Εικόνα 2. Μηνιαία συχνότητα πυρηνογενέσεων και περιόδοι όπου δεν είναι απόλυτα βέβαιο ότι πυρηνογένεση έλαβε χώρα. Ελάχιστη συχνότητα πυρηνογενέσεων παρατηρήθηκε τον Αύγουστο και τον Σεπτέμβριο και μέγιστη συχνότητα τον Φεβρουάριο και Μάρτιο.

Το καλοκαίρι τα σωματίδια με διάμετρο μικρότερο από 1 μμ είναι οξινά εξαιτίας της υψηλής παραγωγής θειικού οξέως που συμπυκνώνεται στα προϋπάρχοντα σωματίδια. Η διαθέσιμη αμμωνία καταναλώνεται μέσα σε μερικά λεπτά και τα επίπεδα της θα παραμείνουν μηδενικά εφόσον δεν εξουδετερωθούν πλήρως τα οξινά σωματίδια. Πυρηνογένεση λαμβάνει χώρα μόνο όταν, κάτω από κατάλληλες συνθήκες, τα σωματίδια έχουν εξουδετερωθεί πλήρως (Εικόνα 3). Αντίθετα τον χειμώνα τα σωματίδια εμφανίζονται ουδέτερα. Η χαμηλότερη ένταση φωτός συνεπάγεται και χαμηλότερη παραγωγή θειικού οξέως και η διαθέσιμη αμμωνία είναι ικανή να εξουδετερώσει τα σωματίδια. Οι αέριες μάζες που διασχίζουν στεριά ευνοούν την πυρηνογένεση γιατί εμπλουτίζονται με αέρια αμμωνία. Η παραπάνω εξήγηση δεν αποδεικνύει ότι η αμμωνία συμμετέχει στον σχηματισμό του σταθερού πυρήνα. Συστατικά που ακολουθούν τις διακυμάνσεις της αμμωνίας, όπως οι αμίνες, μπορούν να αναλάβουν αυτό τον ρόλο.
Εικόνα 3. Λόγος κατιόντων προς ανιόντων για το καλοκαίρι (FAME-08) και τον χειμώνα (FAME-09) από τις 08:00 το 16:00 (UTC+2). Τα μπλε σημεία αντιστοιχούν σε περιόδους που δεν συνέβαινε πυρηνογένεση για το καλοκαίρι (a) και για τον χειμώνα (c). Τα κόκκινα σημεία αντιστοιχούν σε περιόδους πυρηνογένεσης και τα πράσινα σε περιόδους όπου πυρηνογένεση δεν ήταν βέβαιο αν συνέβη ή όχι. Για το καλοκαίρι (b) και τον χειμώνα (d). Στικτές γραμμές αντιστοιχούν σε δύο τυπικές αποκλίσεις από την μονάδα για το καλοκαίρι και μία τυπική απόκλιση από την μονάδα για το χειμώνα. Η συνεχής γραμμή αντιστοιχεί σε ουδέτερα σωματίδια.

Συγκεντρώσεις Αριθμού και Πηγές σε μια σύγχρονη Μεγαλούπολη

Μετρήσεις κατανομής αιωρούμενων σωματιδίων έλαβαν χώρα στο Παρίσι τον Ιούλιο του 2009 και μεταξύ 15 Ιανουαρίου 2010 και 15 Φεβρουαρίου 2010. Οι μετρήσεις συμπεριλάμβαναν τρεις επίγειους σταθμούς σταθμούς μετρήσεων (ένας στο κέντρο της πόλης και δύο σε ημιαστικές περιοχές σε ίση απόσταση και αντίθετη κατεύθυνση σε σχέση με το κεντρικό σταθμό), δύο κινητά εργαστήρια και ένα αεροπλάνο.

Η συγκέντρωση αριθμού N_{20} (σωματίδια με διάμετρο μεγαλύτερο των 20 nm) το καλοκαίρι ήταν 2.1 και 1.9 φορές υψηλότερη στο κέντρο του Παρισιού σε σχέση με τους δύο ημιαστικούς σταθμούς. Στο ίδιο περίοδο, η αντίθετη κατεύθυνση στην συγκέντρωση αριθμού αιωρούμενων σωματιδίων κατά 200% όταν οι αέριες μάζες διέσχιζαν το Παρίσι πριν φτάσουν σε αυτόν σε σχέση με την αντίθετη κατεύθυνση. Για τον χειμώνα, δεν διαπιστώθηκε συσχέτιση μεταξύ N_{20} και διαδρομής των αερίων μαζών.
Αυτό οφείλεται κυρίως στην μεγάλη συγκέντρωση υποβάθρου βόρεια και ανατολικά του Παρισιού.

Ονομάζουμε θύσανο του Παρισιού τις εκπομπές που προέρχονται από το Παρίσι και χαρακτηρίζονται από υψηλές συγκέντρωσεις αριθμού και ανθρωποποιημένων οργανικών αερίων. Κατά τις εναέριες μετρήσεις την καλοκαιρινή περίοδο ο θύσανος χαρτογραφήθηκε χρησιμοποιώντας τον στοιχειακό άνθρακα ως ανιχνευτή και ταυτοποιήθηκε σε απόσταση 200 km από το Παρίσι. Η συγκέντρωση αριθμού στον θύσανο ήταν, κατά μέσο όρο, αυξημένη 45% σε σχέση με την τις συγκεντρώσεις υποβάθρου. Στον θύσανο η συγκέντρωση αριθμού ελαττωνόταν γραμμικά με την απόσταση από το Παρίσι.

Πυρηνογένεση παρατηρήθηκε τις μισές ημέρες της καλοκαιρινής περιόδου, τόσο στο κέντρο του Παρισιού όσο και στον ένα ημιαστικό σταθμό. Στον δεύτερο σταθμό, που επηρεαζόταν από μεγαλύτερο βαθμό από το το Παρίσι, δεν ταυτοποιήθηκαν τόσο συχνά πυρηνογενέσεις, λόγω παρεμβολών από την παρακείμενη κυκλοφοριακή κίνηση. Κατά μέσο όρο η συγκέντρωση αριθμού N₂₀ διπλασιάστηκε στους ημιαστικούς σταθμούς και αυξήθηκε 25% στο κέντρο του Παρισιού εξ’ αιτίας της πυρηνογένεσης. Σε όλους τους σταθμούς η συχνότητα πυρηνογένεσης ήταν σημαντικά εξαρτώμενη από τη διαθέσιμη επιφανή συμπύκνωση. Όταν αυτή ήταν υψηλή η συχνότητα του φαινομένου σήμανε γραμμικά με την απόσταση από το Παρίσι. Η ένταση του ηλιακού φωτός, παρατηρήθηκε γραμμικά με την αυξήση της συγκέντρωσης αριθμού αλλά χωρίς ανάλογη αύξηση στα επίπεδα του στοιχειακού άνθρακα. Το καλοκαίρι στις 10 από τις 11 πτήσεις ταυτοποιήθηκαν μια ή περισσότερες περιοχές εκτός θύσανου με αυξημένη συγκέντρωση αριθμού αλλά χωρίς ανάλογη αύξηση στα επίπεδα του στοιχειακού άνθρακα. Με βάση τα χαρακτηριστικά κάθε περιοχής, ταυτοποιήθηκαν τρεις κατηγορίες περιοχών. Η πρώτη κατηγορία περιλαμβάνει περιοχές όπου η αύξηση αριθμού συμπίπτει με πυρηνογένεση στο έδαφος σε τουλάχιστον δυο από τους τρεις επίγειους σταθμούς. Οι περιοχές ήταν πάντα αντίθετα στην κατεύθυνση του ανέμου σε σχέση με το Παρίσι και κοντά στους επίγειους σταθμούς. Ο χρόνος που γινόταν αντιληπτή η αύξηση συνέπεσε με τον χρόνο που η διάμετρος των σωματιδίων στο έδαφος αυξανόταν πάνω από τα 20 nm (η κατώτερη ανιχνευόμενη διάμετρος κατά τις πτήσεις). Συνεπώς οι αυξήσεις αυτές αποδόθηκαν σε πυρηνογένεση. Η συχνότερη κατηγορία αφορούσε αύξηση σε συγκεντρώσεις αριθμού πάνω από μια συγκεκριμένη περιοχή βορειοδυτικά του Παρισιού και αποδόθηκε σε τοπική πηγή.
Σε τέσσερις περιπτώσεις παρατηρήθηκε αύξηση στις συγκεντρώσεις αριθμού κατά μήκος του θύσανου (Εικόνα 4) και σε μέση απόσταση 40 km από αυτόν από την μία πλευρά, καλύπτοντας έκταση περίπου ίση με 3000 km². Η συγκέντρωση αριθμού μεταξύ του θυσάνου και της περιοχής αυξημένης συγκέντρωσης ήταν στατιστικά ίση. Η περιοχή που συνέδεε τις δύο προαναφερόμενες εμφάνιζε πάντα χαμηλότερες συγκεντρώσεις αριθμού (130% κατά μέσο όρο) σε σχέση με τον θύσανο υποδεικνύοντας πως το φαινόμενο δεν οφείλεται σε διάχυση.

Εικόνα 4. Τροχιά πτήσεων στις 9 και 21 Ιουλίου 2009. Συγκεντρώσεις στοιχειακού άνθρακα και αριθμού σωματιδίων αντιπροσωπεύονται με χρωματισμούς. Ο στοιχειακός άνθρακας χρησιμοποιείται ως ανιχνευτής του θυσάνου του Παρισιού (a, c). Υψηλές συγκεντρώσεις αριθμού παρατηρούνται εκτός του θυσάνου. Κατά τις 9 Ιουλίου (b) η περιοχή όπου η αύξηση της συγκέντρωσης αριθμού παρατηρείται βρίσκεται αντίθετα της φοράς του ανέμου (η κατεύθυνση του θυσάνου αντιπροσωπεύει και την κατεύθυνση του ανέμου) ενώ πυρηνογένεση λαμβάνει χώρα σε όλους τους επίγειους σταθμούς. Στις 21 Ιουλίου (d) η αύξηση της συγκέντρωσης αριθμού παρατηρήθηκε κατά μήκος του θυσάνου. Πυρηνογένεση δεν έλαβε χώρα σε κανένα επίγειο σταθμό.

Από τις τέσσερις πτήσεις, όπου η συγκέντρωση αριθμού ήταν αυξημένη κατά μήκος του θυσάνου, οι δύο συσχετίζονταν με πυρηνογένεση στο έδαφος σε τουλάχιστον δύο από τους επίγειους σταθμούς ενώ στις υπόλοιπες δύο δεν παρατηρήθηκε πυρηνογένεση στο έδαφος. Για να ερευνηθεί γιατί αυξημένες συγκεντρώσεις αριθμού παρατηρούνταν μόνο από την μία μεριά του θυσάνου, η περιοχή της αυξημένης συγκέντρωσης αριθμού συγκρίθηκε με την αντιδιαμετρική της σε σχέση με τον θύσανο για ανθρωπογενές και βιογενή οργανικά αέρια, διαθέσιμη

141
επιφάνειας συμπύκνωσης, NOₓ, O₃, CO μαζί με μετεωρολογικές μεταβλητές όπως υγρασία, θερμοκρασία και ένταση φωτός. Καμία διαφορά δεν ξεπέρασε το 10% και συνεπώς αυτές οι μεταβλητές δεν εξήγησαν το φαινόμενο.

Την χειμερινή περίοδο οι συγκεντρώσεις αριθμού στο κέντρο του Παρισιού ήταν κατά μέσο όρο 13,000 cm⁻³, αυξημένες κατά 60% σε σχέση με το καλοκαίρι (8,900 cm⁻³). Οι συγκεντρώσεις στο κέντρο ήταν 1.2 και 1.8 φορές υψηλότερες σε σχέση με τους δύο ημιαστικούς σταθμούς. Οι συγκεντώσεις αριθμού στους δύο ημιαστικούς σταθμούς αυξάνονταν κατά 50% και 200% σε σχέση με τις ελάχιστες για κάθε σταθμό ξεχωριστά, όταν οι αέριες μάζες σχετίζονταν με το κέντρο του Παρισιού. Οι συγκεντρώσεις αριθμού ακολουθούσαν εκθετική μείωση συναρτήσεις από το Παρίσι. Σε απόσταση 60 km οι συγκεντρώσεις αριθμού είναι παρόμοιες με αυτές της καλοκαιρινής περιόδου (6,000 cm⁻³) (Εικόνα 5).

Εικόνα 5. Συγκέντρωση αριθμού συναρτήσει της απόστασης από το Παρίσι, σύμφωνα με το κινητό εργαστήριο. Το καλοκαίρι (κόκκινο) δεν παρατηρήθηκε σημαντική μεταβολή σε αντίθεση με τον χειμώνα (μπλε) όπου η συγκέντρωση αριθμού μειώνεται εκθετικά μειωμένη συναρτήσεις απόστασης.

Χαρακτηρισμός των Πηγών Λεπτόκοκκων Ατμοσφαιρικών Σωματιδίων σε μια Μετρίου Μεγέθους Αστική Περιοχή της Μεσογείου

Η πληθυσμική πυκνότητα θεωρείται αντιπροσωπευτική, σε ένα βαθμό, των σωματιδικών συγκεντρώσεων μιας περιοχής. Τους καλοκαιρινούς μήνες το Παρίσι έχει την ίδια περίοδο συγκέντρωση PM₁ με την Φινοκαλλία παρόλο που η τελευταία είναι
μια απομακρυσμένη περιοχή χωρίς σημαντική ανθρώπινη δραστηριότητα, ενώ το Παρίσι μια μεγαλούπολη 10,000,000 κατοίκων. Για τον χαρακτηρισμό τόσο της Φινοκαλίας όσο και του Παρισιού πραγματοποιήθηκαν μηνιαίες εντατικές μετρήσεις τον χειμώνα και το καλοκαίρι. Τέτοιου τύπου μετρήσεις είναι πολυέξουδες και δεν δίνουν πληροφορίες για τις περιόδους ενδιάμεσα των εντατικών μετρήσεων. Στη Φινοκαλία αναδείχθηκε η σημασία των μεταφερόμενων σωματιδίων και η συμβολή τους στα επίπεδα ΑΣ. Το Παρίσι αντίθετα, είναι τόσο δέκτης μεταφερόμενων σωματιδίων, όσο και πηγή. Μια μέθοδος ελέγχου των σωματιδιακών πηγών, τοπικών και μεταφερόμενων, που θα μπορεί να εφαρμοστεί σε ποικίλου τύπου περιοχές είναι χρήσιμη. Με κατάλληλο σχεδιασμό το κόστος εφαρμογής μπορεί να είναι υποπολλαπλάσιο αυτού των εντατικών μετρήσεων. Μια τέτοια μέθοδος αναπτύχθηκε και εφαρμόστηκε στην περιοχή της Πάτρας. Η μέθοδος είναι κλιμακωτή και τα συμπεράσματα από κάθε βήμα χρησιμοποιούνται για να σχεδιαστεί το επόμενο.

Αρχικά η μάζα των αιωρούμενων σωματιδίων με διάμετρο μικρότερο των 10 μm (ΑΣ10) μετρήθηκε με συσκευή συνεχούς λειτουργίας. Σκοπός ήταν να αποκομίσουμε πληροφορίες σχετικά με τις συγκεντρώσεις μάζας των σωματιδίων στην περιοχή υπό έλεγχο. Λαμβάνοντας υπόψη πως οι διακυμάνσεις στα ημερήσια προφίλ οφείλονται σε τοπικές πηγές, ποσοτικοποιήθηκε η συνεισφορά της τοπικής κίνησης. Με βάση την ελάχιστη συγκέντρωση ημερησίων προφίλ ποσοτικοποιήθηκε και η συνεισφορά των μεταφερόμενων σωματιδίων στις συγκεντρώσεις μάζας της Πάτρας. Παρόλο που αυτή η μέθοδος υπόκειται σε σημαντικά σφάλματα, έδωσε μια πρώτη εικόνα του προβλήματος. Το επόμενο βήμα ήταν ο χαρακτηρισμός της σύστασης των αιωρούμενων σωματιδίων στην περιοχή. Σκοπός ήταν η διάκριση των σημαντικότερων ενώσεων και οι πηγές τους (π.χ. ιόντα καλίου είναι ενδεικτικά καύση βιομάζας). Για να διακρίνουμε μεταξύ μεταφερόμενης και τοπικής συνεισφοράς των αιωρούμενων σωματιδίων ταυτόχρονο μετρήσεις στην περιοχή υπό έλεγχο και μακριά από αυτή, σε περιοχή υποβάθρου, ελαβαν χώρα παράλληλα. Είναι σημαντικό οι τοπικές πηγές στην περιοχή υποβάθρου να είναι περιορισμένες. Το τελευταίο στάδιο της μεθόδου συμπεριλαμβάνει μια περίοδο εντατικών μετρήσεων όταν οι σωματιδιακές συγκέντρώσεις είναι οι υψηλότερες του έτους.

Η Πάτρα, μια μεσαίων μεγέθους πόλη, παραβιάζει τα θεσμοθετημένα ΡΜ10 ημερήσια όρια της Ε.Ε. Μετρήσεις έλαβαν χώρα στο κέντρο της πόλης, αρχικά στο επίπεδο του εδάφους. Οι περισσότερες παραβιάσεις (58 από τις 75) εντοπίστηκαν την ψυχρότερες τοιχώματος και συμπεριλαμβάνει μια περίοδο εντατικών μετρήσεων όταν οι σωματιδιακές συγκέντρώσεις είναι οι υψηλότερες του έτους.
υψηλότερα επίπεδα PM10. Συγκρίνοντας το ημερήσιο προφίλ των καθημερινών και των αργών ποσοτικοποιήθηκε η συνεισφορά της τοπικής κίνησης που ήταν ίση με 12±4% (ετήσιος μέσος όρος). Θεωρώντας ως συγκεντρώσεις υποβάθρου τις μικρότερες συγκεντρώσεις των οριαίων προφίλ εκτιμήθηκε πως η συνεισφορά των τοπικών πηγών είναι 20% τους θερμούς μήνες (Απρίλιος - Σεπτέμβριος) και αυξάνει τους ψυχρούς μήνες σε 37%.

Εικόνα 6. Μέση μηνιαία σύσταση ΑΣ2.5 από τον Δεκέμβριο 2008 μέχρι Μάιο 2012. Η στική γραμμή αντιπροσωπεύει τον ετήσιο μέσο όρο που είναι ίσος με 22.3±11.8 μg m-3.

Η μέση ετήσια συγκέντρωση PM2.5 στην Πάτρα για την περίοδο μεταξύ Δεκεμβρίου 2008 και Μαίου 2012 ήταν 22.3±11.8 μg m-3 κατά μέσο όρο. Η μισή περίπου μάζα (47%) αντιστοιχεί σε οργανικές ενώσεις. Η συγκέντρωση των οργανικών διπλασιάστηκε το 2011 και 2012 σε σχέση με το 2009-2010 και ως αποτέλεσμα αυξήθηκαν και οι συγκεντρώσεις των PM2.5 κατά 70%. Η δεύτερη πιο σημαντική ένωση ήταν τα θειικά ιόντα που αντιστοιχούσαν στο 16% της μάζας των PM2.5. Οι συγκεντρώσεις καλίου συσχετίζονται (R2=0.79) με τις αντίστοιχες των οργανικών PM2.5 μόνο τον χειμώνα, όταν παρατηρούνται οι υψηλότερες συγκεντρώσεις PM2.5. Επιπλέον, οι συγκεντρώσεις καλίου ήταν διπλάσιες όταν οι συγκεντρώσεις PM2.5 υπερέβαλαν τα 35 μg m-3 (το ημερήσιο όριο PM2.5 στις Η.Π.Α.). Αυτοί οι συσχετισμοί υποδεικνύουν την καύση βιομάζας ως βασική πηγή σωματιδίων. Δεν είναι όμως εφικτό να ταυτοποιήσουμε αν η καύση βιομάζας είναι τοπική πηγή ή αν μεταφέρονται σωματίδια από απομακρυσμένες πηγές. Οι μέσες μηνιαίες συγκεντρώσεις των PM2.5 δίνονται στην Εικόνα 6.
Εικόνα 7. Εποχιακή συνεισφορά μεταφερόμενων σωματιδίων και τοπικών πηγών στη συνολική σύσταση PM$_{2.5}$ της Πάτρας.

Για να επιτευχθεί διάκριση μεταξύ τοπικών πηγών και μεταφερόμενων σωματιδίων, μετρήσεις έλαβαν χώρα παράλληλα με την δειγματοληψία στην Πάτρα, 40 km νοτιοδυτικά της Πάτρας, στο οικισμό Ν. Βουπρασίου για ένα χρόνο. Οι συγκεντρώσεις θειικών μεταξύ των δύο τοποθεσιών δεν διέφεραν σημαντικά όλο το έτος, υποδεικνύοντας πως τα θειικά ιόντα είναι αποτέλεσμα μεταφοράς και σε μικρότερο βαθμό in situ οξείδωσης. Οι συγκεντρώσεις οργανικών στην Πάτρα είναι συστηματικά υψηλότερες από ότι στο σταθμό υποβάθρου, όλο το έτος. Τον χειμώνα είναι 50% υψηλότερες ενώ το καλοκαίρι 33%. Οι συγκεντρώσεις καλίου είναι παρόμοιες του θερμού μήνες στις δύο τοποθεσίες ενώ είναι αυξημένες κατά 44% τους ψυχρούς μήνες του έτους στην Πάτρα. Όλα τα παραπάνω υποδεικνύουν την παρουσία ισχυρών σωματιδιακών πηγών στην Πάτρα. Συνολικά τα μεταφερόμενα συνιστούν το 80% των συνολικών στην Πάτρα. Με βάση την σύγκριση των δύο σταθμών καταλήξαμε στην Εικόνα 7 όπου διαχωριστήκε η σύσταση τοπικών και μεταφερόμενων σωματιδίων. Τα μεταφερόμενα σωματίδια είναι η σημαντικότερη πηγή στην περιοχή της Πάτρας. Αν και οι συγκεντρώσεις των μεταφερόμενων σωματιδίων δεν είναι από μόνες τους ικανές να
προκαλέσουν υπέρβαση των θεσμοθετημένων ορίων (μία υπέρβαση των PM2.5 ορίων ταυτοποιήθηκε τους θερινούς μήνες και τα τέσσερα έτη μετρήσεων) εισήγονται για τις υψηλές συγκεντρώσεις υποβάθρου στην περιοχή. Σε συνδυασμό με μία ισχυρή τοπική πηγή οι συγκεντρώσεις πιο εύκολα υπερβαίνουν τα θεσμοθετημένα όρια.

Μικρής διάρκειας εντατικές μετρήσεις έλαβαν χώρα από τις 20 Φεβρουαρίου μέχρι τις 5 Μαρτίου 2012, με σκοπό τον χαρακτηρισμό των τοπικών πηγών στην Πάτρα την περίοδο των υψηλότερων συγκεντρώσεων. Ραγδαία αύξηση των συγκεντρώσεων μάζας PM1, και PM2.5 παρατηρήθηκε σε σχεδόν καθημερινή βάση μετά τις 6 μ.μ. (τοπική ώρα). Οι αυξήσεις λάμβαναν χώρα ταυτόχρονα σε 2 σημεία μέσα στον αστικό υπό μορφή περιοχή 3.5 km. Συνεχείς μετρήσεις μάζας PM2.5 έλαβαν χώρα και στους δύο σταθμούς δειγματοληψίας. Τα δύο όργανα εμφάνισαν ικανοποιητική συσχέτιση (R2=0.61, 3-ωροι μέσοι όροι) υποδεικνύοντας ότι οι πηγές και οι δύο σημεία δειγματοληψίας ήταν κοινές. Η συγκέντρωση μόνο των PM2.5 οργανικών ζεσπισίες συγγράρει τα 80 μg m⁻³ ενώ τα συνολικά PM2.5 τα 100 μg m⁻³. Παράλληλα με τη ραγδαία νυχτερινή αύξηση, η συγκέντρωση του καυσιακού άνθρακα και των νιτρικών ιών ήταν υψηλότερη αυτής των θειικών ιών. Παράλληλα αυξάνονταν και τα ιόντα καλίου. Στην Εικόνα 8 δίνονται τα ημερήσια προφίλ καθ' όλη την περίοδο δειγματοληψίας του SO2, καλίου, οργανικών, θειικών, αμμωνίου και νιτρικών, από το AMS. Η αύξηση της συγκέντρωσης του στοιχειακού άνθρακα υποδυκνύει πως εμπλέκεται μία πηγή καύσης. Η συγκέντρωση του θειικού ιών παρατηρήθηκε κατά την περίοδο καύσης βιομάζας για οικιακή θέρμανση. Το συνηθέστερο καύσιμο για αυτό τον σκοπό είναι το πετρέλαιο. Για να ξεχωρίσουμε την συνεισφορά της κάθε πηγής καύσης χρησιμοποιήσαμε το SO2 ως άνιχνευτή ορυκτών καυσίμων. Ο διαχωρισμός θα ήταν εφικτός αν η μέση περιεκτικότητα στην καυσίμοι ήταν γνωστή. Αυτό είναι απαραίτητο αφού το SO2 δεν παράγεται αποκλειστικά από ορυκτά καύσιμα αλλά και από καύση βιομάζας σε μικρότερο όμοιο τοπίο.
Εικόνα 7. Ημερήσιο προφίλ PM$_1$ (α) οργανικών, (β) θειικών, (γ) αμμωνίου, (δ) νιτρικών ιόντων και (ε) ξιφίου από το AMS μαζί με το προφίλ του SO$_2$ (ζ) για την περίοδο από 26 Φεβρουαρίου μέχρι 5 Μαρτίου στον ημιαστικό σταθμό των ΤΕΙ Πάτρας. Κάθε γραμμή αντιστοιχεί στην περίοδο υψηλής κίνησης και στην ραγδαία νυχτερινή αύξηση.
Curriculum Vitae

Date of Birth

22 September 1981

Current Position

Institute of Chemical Engineering (ICE-HT) Foundation for Research & Technology-Hellas (FORTH) Stadiou St., Platani, P.O. Box 1414, 26504, Patras, Greece

Contact

Off: (+30) 2610 965313
Cell: (+30) 6932 166012
email: mpikridas@gmail.com
mpikridas@chemeng.upatras.gr

EDUCATION

<table>
<thead>
<tr>
<th>Date</th>
<th>Qualification</th>
<th>Institution</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>09/2006 - 11/2009</td>
<td>M.Sc. in Chemical Engineering</td>
<td>University of Patras, Greece</td>
<td></td>
</tr>
<tr>
<td>09/1999 - 07/2004</td>
<td>B. Sc. (Diploma) in Chemistry</td>
<td>School of Natural Sciences,</td>
<td>Aristotle University of Thessaloniki, Greece</td>
</tr>
</tbody>
</table>

WORK EXPERIENCE

<table>
<thead>
<tr>
<th>Date</th>
<th>Position</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/2006-2/2008</td>
<td>Teaching Assistant</td>
<td>Ordinary Differential Equations (2 semesters) Laboratory of Analytical Chemistry</td>
</tr>
<tr>
<td>10/2005-4/2006</td>
<td>Supervisor Analyst in the Army Oil Analysis Program (AOAP)</td>
<td></td>
</tr>
<tr>
<td>04/2004</td>
<td>Pre-Olympic games (Doping Control Escort)</td>
<td></td>
</tr>
<tr>
<td>08/2004</td>
<td>Olympic Games (Doping Control Escort)</td>
<td></td>
</tr>
</tbody>
</table>

COMPUTER SKILLS

- MATLAB (Advanced), LabView (Basic), Linux (Basic), MS-Office (Excellent)
- MS-Windows 3.1, 9x, Me, XP (Pro), Vista (Home), 7 (Pro)

SCIENTIFIC INSTRUMENTATION

- SMPS (Various models), AIS (Airel Ltd), PSM (Airmodus), APS (TSI 3321), OPS (TSI 3330), Sunset Analyzer (Lab Model), IC (Metrohm 761), MAAP (Thermo 5012), TEOM (Thermo 1405DF), Nephelometer (Ecotech 1000F, NGN-3a), SASS (MetOne), GC-MS (Varian CP-3800)

LANGUAGES

- Greek (native speaker), English (fluent, teaching licence), French (basic), German (basic)

PROFESSIONAL AFFILIATIONS

- Hellenic Association for Aerosol Research
- Hellenic Association of Chemistry
**Publications**


**Conference Presentations**

- Hiking, reading