FINNISH METEOROLOGICAL INSTITUTE
CONTRIBUTIONS
No. 105

CHEMICAL CHARACTERIZATION AND SOURCE APPORTIONMENT OF SUBMICRON AEROSOL PARTICLES WITH AEROSOL MASS SPECTROMETERS

Samara Carbone

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation in Physics

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in Physicum auditorium E204, Gustaf Hällströminkatu 2, on April 5th, 2014, at 13 o’clock.

Finnish Meteorological Institute
Helsinki, 2014

Author's address: Finnish Meteorological Institute
P.O. Box: 503, FI-00101 Helsinki, Finland
samara.carbone@fmi.fi

Supervisors: Research Professor Risto Hillamo, Ph.D
Finnish Meteorological Institute

Professor Markku Kulmala, Ph.D
Department of Physics, University of Helsinki

Professor Douglas R. Worsnop, Ph.D
Department of Physics, University of Helsinki
Finnish Meteorological Institute
Aerodyne Research Inc.

Reviewers: Associate Professor Qi Zhang, Ph.D
Department of Environmental Toxicology, University of California, Davis

Associate Professor Annele Virtanen, Ph.D
Department of Applied Physics, University of Eastern Finland

Opponent: Associate Professor Joakim H. Pagels, Ph.D
Department of Design Sciences, Lund University

Custos: Professor Veli-Matti Kerminen
Department of Physics, University of Helsinki

ISBN 978-951-697-817-1 (paperback)
ISSN 0782-6117
Unigrafia Oy
Helsinki 2014

978-951-697-818-8 (pdf)
http://ethesis.helsinki.fi
Helsingin yliopiston verkkojulkaisut
Helsinki 2014

Acknowledgements

The research work presented here was accomplished at the Finnish Meteorological Institute, Air Quality/Atmospheric Composition Research Departments, from September 2008 to April 2014. The research studies were funded by Helsinki Energy, Ministry of Traffic and Communication, TEKES, and Graduate School in Physics, Chemistry, Biology, and Meteorology of Atmospheric Composition and Climate Change (University of Helsinki). They are gratefully acknowledged.

I want to thank the Heads of the Department, Professors Yrjö Viisanen, Jakko Kukkonen and Heikki Lihavainen for the opportunity to be part of the Air Quality/Atmospheric Composition Research Departments. I am most grateful to Prof. Risto Hillamo who brought me all the way from Brazil and believed in my capabilities and entrusted me enormous responsibility. Thanks also for the guidance. I want to thank Prof. Douglas Worsnop for his wise scientific advices and a few non-scientific too. He made me see that there is always more in the datasets I analyze, especially in terms of number of ions and PMF factors. I am also grateful to Prof. Markku Kulmala for his support over the course of my post-graduate studies.

I want to thank the reviewers of this thesis, Professors Qi Zhang and Annele Virtanen for their interesting suggestions and contribution to this thesis. I appreciate that Prof. Joakim Pagels has kindly promised to be my official opponent in the public examination of this thesis. I am also grateful to Prof. Veli-Matti Kerminen for being the Custos and for taking such good care of the final details of this thesis.

Kiitos paljon, my work colleagues, Karri, Anna, Minna, Sanna and Hilkka for reading my papers, helping with the ‘hundreds’ of field experiments we participated in, discussions and company during this journey. Thanks to my *hupi* collegaues, Mika, Joana, Anna and Curtis for the brave ideas in organizing the entertainment in the events of our department, pikkujoulu, movie evenings, Laskiaispäivää!

I thank Donna, Manjula and Sally for their patience during my introduction to mass spectrometry and software tools. They gave me hope when I thought all was lost concerning data analysis. Thanks a lot, girls!

Thanks to Tania, Misha, Flavia, Jana, Emilie, Danielle, Zuzana, Katti, Essi, Johanne, Ilona, Vishnu, Kata, Francisco, Pekka, Val and Mari who promoted a balanced state of mind during these years. Your contribution to this research study is larger than you think. Thanks for sharing your dreams, crazy ideas and time with me. You filled an important gap in my life!

E finalmente eu quero agradecer a minha família pelo apoio e amor incondicional sempre!

Helsinki, March 2014

Samara Carbone

Abbreviations and definitions

ACSM – Aerosol Chemical Speciation Monitor

BBOA – Biomass burning organic aerosol

BC – Black carbon

CCOA – Coal combustion organic aerosol

COA – Cooking organic aerosol

CROA – Coffee roastery organic aerosol

EC – Elemental carbon

EI – Electron impact

HKI – Helsinki

HOA – Hydrocarbon-like organic aerosol

HR-MS – High resolution-mass spectrum

HR-ToF-AMS – High resolution Time-of-Flight Aerosol Mass Spectrometer

LRT – Long-range transport

LRT-BBOA – Long-range transported biomass burning organic aerosol

LV-OOA – Low-volatility oxygenated organic aerosol

LV-OOA+MSA – Low-volatility oxygenated organic aerosol plus methanesulfonic acid

m/z – Mass-to-charge ratio

NOA – Nitrogen-containing organic aerosol

NR-PM_1 – Non-refractory particulate matter below 1 µm in diameter

OA – Organic aerosol

OC – Organic carbon

OOA – Oxygenated organic aerosol

PM – Particulate matter

PM_1 – Particulate matter below 1 µm in diameter

PM_{10} – Particulate matter below 10 µm in diameter

$PM_{2.5}$ – Particulate matter below 2.5 µm in diameter

R-PM_1 – Refractory PM_1

SP-AMS – Soot Particle Aerosol Mass Spectrometer

SPC – San Pietro Capofiume

SV-OOA – Semi-volatile oxygenated organic aerosol

UMR-MS – Unit-mass resolution mass spectrum

USACH – University of Santiago de Chile

WISOM – Water-insoluble organic matter

WSOM – Water-soluble organic matter

ρ – Particle density

Content

List of publications

I. Timonen, H., Aurela, M., **Carbone, S**., Saarnio, K., Saarikoski, S., Mäkelä, T., Kulmala, M., Kerminen, V.-M., Worsnop, D. R.: High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS, Atmospheric Measurement Techniques, 3, 1063-1074, 2010.

II. Saarikoski, S., **Carbone, S**., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L., Trimborn, A., Facchini, M. C., Fuzzi, F., Hillamo, R. and Worsnop, D.: Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy. Atmospheric Chemistry and Physics, 12, 8401-8421, 2012.

III. Timonen, H., **Carbone**, **S**., Aurela, M., Saarnio, S., Saarikoski, S., Kulmala, M., Worsnop, D. R. and Hillamo, R.: Analysis of the behavior of submicrometer water-soluble organic carbon in urban background air, Journal of Aerosol Science, 56, 61-77, 2013.

IV. **Carbone, S**., Saarikoski, S., Frey, A., Reyes, F., Reyes, P., Castillo, M., Gramsch, E., Oyola, P., Jayne, J., Worsnop, D. R. and Hillamo, R.: Chemical Characterization of Submicron Aerosol Particles in Santiago de Chile, Aerosol and Air Quality Research, 13, 462-473, 2013

V. **Carbone, S.**, Aurela, M., Saarnio, K., Saarikoski, S., Timonen, H., Frey, A., Sueper, D., Ulbrich, I. M., Jimenez, J. –L., Kulmala, M., Worsnop, D. R., Hillamo, R.: Wintertime aerosol chemistry in sub-arctic urban air. Aerosol Science and Technology, 48(3), 313-323, 2014.

Other related publications not included in this thesis

Gilardoni, S., Massoli, P., Giulianelli, L., Rinaldi, M., Paglione, M., Pollini, F., Lanconelli, C., Poluzzi, P., **Carbone, S**., Hillamo, R., Russell, L. M., Facchini, M. C, Fuzzi, S., Fog scavenging of organic and inorganic aerosol in the Po Valley, Atmos. Chem. Phys. Discuss., 14, 4787-4826, 2014.

Paglione, M., Saarikoski, S., **Carbone, S**., Hillamo, R., Facchini, M. C., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., Moretti, S., Tagliavini, E., Swietlicki, E., Stenström, K. E., Prévôt, A: S: H., Massoli, P., Canaragatna, M., Worsnop, R., Decesari, S.: Primary and secondary biomass burning aerosols determined by proton nuclear magnetic resonance (H-NMR) spectroscopy during the 2008 EUCAARI campaign in the Po Valley (Italy), Atmos. Chem. Phys. Discuss., 13, 33343–33401, 2013.

Frey, A. K., Saarnio, K., Lamberg, H., Mylläri, F., Karjalainen, P., Teinilä, K., **Carbone, S**., Tissari, J., Niemelä, V., Härinen, A., Rautiainen, J., Kytoämäki, J., Artaxo, P., Virkkula, A., Pirjola, L., Rönkkö, T., Keskinen, J., Jokiniemi, J., Hillamo, R.: Optical and Chemical Characterization of Aerosols Emitted from Coal, Heavy and Light Fuel Oil, and Small-Scale Wood Combustion, Environ. Sci. Technol., 48, 827–836, 2014.

Happonen, M., Mylläri, F., Karjalainen, P., Frey, A., Saarikoski, S., **Carbone, S**., Hillamo, R., Pirjola, L.: Size distribution, chemical composition and hygroscopicity of fine particles emitted from an oil-fired heating plant, Environ. Sci. Technol., 47(24), 14468–14475, 2013.

Timonen, H., Aurela, M., **Carbone, S.**, Saarnio, S., Frey, A., Saarikoski, S., Teinilä, K., Kulmala, M., Hillamo, R.: Seasonal and diurnal changes in inorganic ions, carbonaceous matter and mass in ambient aerosol particles at urban background area, In press, Bor. Environ. Res., 2014.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., **Carbone, S**., Capes, G., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Di Marco, C. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt, L., Hillamo, R., Jimenez, J. -L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A. –M., Kulmala, M., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, L., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy. Atmos. Chem. Phys. Discuss., 13, 23325–23371, 2013.

Saarnio, K., Teinilä, K., Saarikoski, S., **Carbone, S.**, Gilardoni, S., Timonen, H., Aurela, M., Hillamo, R.: Online determination of levoglucosan in ambient aerosols with particle-into-liquid sampler – high-performance anion-exchange chromatography – mass spectrometry (PILS–HPAEC–MS), Atmos. Meas. Tech., 6, 2839 –2849. 2013.

Andrade, M. F., Fornaro, A., Dias de, E. F., Mazzoli, C. R., Martins, L. D., Boian, C., Oliveira, M. G. L., Peres, J., **Carbone, S**., Alvalá, P., Leme, N. P.: Ozone sounding in the Metropolitan Area of São Paulo, Brazil: Wet and dry season campaigns of 2006, Atmos. Environ., 61, 627–640, 2012.

Backman, J., Rizzo, L. V., Hakala, J., Nieminen, T., Manninen, H. E., Morais, F., Aalto, P. P., Siivola, P. P., **Carbone, S**., Hillamo, R., Artaxo, P., Virkkula, A., Petääjä, T. and Kulmala, M.: On the diurnal cycle of urban aerosols, black carbon and the occurrence of new particle formation events in springtime São Paulo, Brazil. Atmos. Chem. Phys., 12, 11733–11751, 2012.

Kerminen, V. M., Niemi, J. V., Timonen, H., Aurela, M., Frey, A., **Carbone, S**., Saarikoski, S., Teinilä, K., Hakkarainen, J., Tamminen, J., Vira, J., Prank, M., Sofiev, M. and Hillamo, R.: Characterization of a volcanic ash episode in southern Finland caused by the Grimsvötn eruption in Iceland in May 2011, Atmos. Chem. Phys., 11, 12227–12239, 2011.

Knote, C., Brunner, D., Vogel, H., Allan, J., Asmi, A., Äijälä, A., **Carbone**, **S**., van der Gon, H. D, Jimenez, J. L., Kiendler-Scharr, A., Mohr, C., Poulain, L., Prévôt, S. H. A., Swietlicki, E. and Vogel, B. Towards an online-coupled chemistry-climate model: evaluation of COSMO-ART, Geosci. Model Dev., 4, 1077–1102, 2011.

1. Introduction

Particulate matter consists of a complex mixture of liquid and solid small particles suspended in the air. They have been consistently demonstrated to provoke adverse effects to human health and to affect the global climate directly or indirectly (Pope and Dockery, 2006; IPCC, 2013)

With respect to the importance of particulate matter (PM) on human health, a countless number of studies suggest a relation between short-term and long-term effects of human exposure to elevated levels of PM and an increase in hospital admissions, cardiopulmonary diseases, and mortality (Riediker et al., 2004; Pope and Dockery, 2006; Dominici et al., 2006). In terms of specific chemical compounds, metals were highlighted as important for the development of pulmonary and cardiovascular diseases. Metals may also be involved in PM-induced allergic sensitization, while soluble organic compounds appear to be implicated in PM-induced allergy and cancer (Schwarze et al., 2006).

Concerning the PM role in global climate, aerosol particles scatter and absorb solar radiation, which can have cooling or heating effects on the atmosphere and an impact on visibility (Nazarenko and Menon, 2005; Ramanathan et al., 2007; Romanou et al., 2007). Aerosol particles are also involved in the formation of clouds and precipitation as cloud condensation and ice nuclei. Changes in properties of ambient aerosol particles, number concentration and size distribution, alter cloud albedo (Norris and Wild, 2007) and can suppress or enhance precipitation (Nober et al., 2003; Tao et al., 2007; Phillips et al., 2002).

PM is composed of sulfate, nitrate, ammonium, minerals, metals, black carbon, and organic compounds often referred as organic matter (Rogge et al., 1993). The variability in PM levels and composition makes its study difficult. For example, organic matter is composed of an enormous number of compounds containing a variety of different functional groups.

PM composition have been intensively investigated, mainly with offline instruments, which provide only limited time-resolution information (typically 12–24 hours) and increase the possibility of artifacts in sampling and storage (Hering and Cass, 1999; Pakkanen and Hillamo, 2002; Pathak and Chan, 2005; Viana et al., 2006). For this reason, the use of online instruments is increasing. The Aerodyne aerosol mass spectrometer (AMS) is, to date, one of the few field-deployable instruments that provides simultaneously high-time resolution (from seconds to minutes) and quantitative size-resolved chemical information from refractory (soot-particle aerosol mass spectrometer, SP-AMS) and non-refractory (high-resolution time-of-flight aerosol mass spectrometer, HR-ToF-AMS) PM_1. In addition, the instrument provides chemical mass-size-distribution information.

Moreover, PM is related to different origins and formation processes. Often PM matter is classified as primary or secondary: depending if it is directly emitted into the atmosphere or formed by gas-to-particle conversion of volatile organic compounds (VOC) after their oxidation. Concerning the origin, the atmospheric PM may have natural or anthropogenic sources. Globally, natural sources of PM are dominating (Guenther et al., 2006). Anthropogenic sources have been intensively investigated in the last decades due to its interference in the global climate and human health.

The identification of sources and determination of their contribution to PM has become more important due to the strict legislation standard levels imposed by environmental agencies. For example, the 24-hour mean standard for $PM_{2.5}$ is currently 25 µg m^{-3} (EU, 2008) and it will be reduced to 20 µg m^{-3} in the year 2020 (EU, 2008). In this context, the use of receptor models might be useful in achieving the limits of the new legislation. In addition to identification of sources, the receptor models can be used to study individual air-pollution episodes and emission inventories, contributing to creation of effective air-quality-control strategies.

This thesis covers field and laboratory studies. In the field studies, the chemical composition of the PM_1 at three different sites during four field studies were characterized using instruments based on the AMS technique. The receptor model PMF was used to characterize in more detail the organic aerosol (OA) fraction of the non-refractory particulate PM (NR-PM_1). However, because in some studies only the NR-PM_1 fraction was measured by the AMS, elemental carbon or black carbon data from the thermal-optical carbon analyzer (Sunset Laboratory Inc.) were used to achieve the PM_1 mass closure. In addition, laboratory experiments were conducted to test the new SP-AMS and its feasibility to measure metals.

Objectives

The overall objective of this study was to investigate in more detail chemical characteristics of ambient particulate matter and its sources. Studies made in laboratory and during field campaigns were used to study composition of fresh emissions, changes during aging, and finally composition of submicron PM observed in ambient air. The more specific objectives of the study were:

- ✓ to obtain new insights on the chemical composition of submicron aerosol particles at different locations using high-time resolution mass spectrometers;
- ✓ to characterize in more detail the OA fraction and its sources in high time-resolution using PMF;
- ✓ to estimate the oxidation and processing of OA in the atmosphere where anthropogenic and natural emissions co-exist;
- ✓ to use measurements of different aerosol properties – e.g. water-solubility, refractory, volatility character, acidity, and size distribution – to obtain more information about the PM_1 composition and sources;
- ✓ to develop a method for the detection of trace metals in aerosol particles with the SP-AMS.

2. Background information

2.1 Mass spectrometry principles

Mass spectrometry is an analytical technique that determines the mass-to-charge (m/z) ratios of gas-phase ions by making them pass through known electric or magnetic fields and analyzing their resultant motion. In other words, it is used to separate the components of a sample by their mass. The technique has wide application and it has been used in the discovery of drugs, food control, forensic science, natural products, atomic physics, and air pollution (Hoffmann, 2007).

A mass spectrometer usually contains the following elements: a sample inlet to introduce the compound that is analyzed, an ionization source to produce ions from the sample, one or several mass analyzers to separate the various ions based on their m/z values, a detector to count the ions emerging from the last analyzer, and finally a data-processing system that produces the mass spectrum in a suitable form.

Another important fact concerning mass spectrometry is the generation of fragments. That is, after producing molecular ions, those can fragment due to excessive energy transfer during the ionization process, which is the case of the electron impact (EI) ionization. What it means is that the resulting mass spectrum instead of being only composed of molecular signals, will also contain signals of fragments of molecules. Nevertheless, in the case of EI ionization the signal of different fragments can be used to identify a specific molecule (Hoffmann, 2007).

In the air-pollution field, the use of mass spectrometers to identify PM composition has been a long tradition. Cautreels and Cauwenberghe (1967) used a mass spectrometer coupled to an ion chromatograph to identify over 100 organic compounds in PM. Mukai et al. (1990) used a mass spectrometer to measure platinum in airborne PM. Examples of more recent mass spectrometers used to measure PM are the ATOFMS (aerosol time-of-flight aerosol mass spectrometer, Prather et al., 1994), the AMS (aerosol mass spectrometer, Jayne et al., 2000), and the APi-ToF (atmospheric pressure interface time-of-flight mass spectrometer, Junninen et al., 2010). The latter measures atmospheric cluster ions. Figure 1 illustrates an average ambient mass spectrum of PM, where the typical fragments from air (N_2^+, H_2O^+, O_2^+, OH^+, N^+, O^+, and Ar^+) are dominant. A closer analysis reveals the fragments of the compounds nitrate, sulfate, ammonium, chloride, and organics present in the aerosol phase.

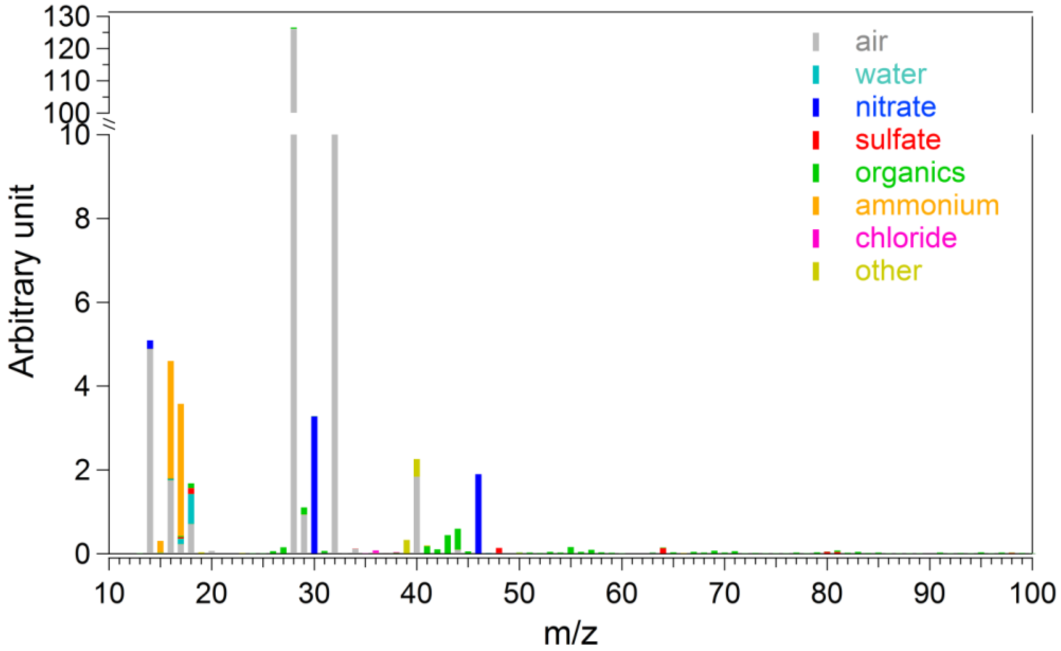


Figure 1 – Ambient PM mass spectrum in arbitrary units.

2.2 Particulate matter (PM)

PM has been classified into four main groups according to size distribution, where diameter is ‘d’: the nucleation mode (d < 0.01 µm), the Aitken mode (0.01 µm < d < 0.1 µm), the accumulation mode (0.1 µm < d < 2.5 µm) and the coarse mode (d > 2.5 µm) (Seinfeld and Pandis, 2006). These three first modes also denote the so-called fine mode (Seinfeld and Pandis, 2006). The nucleation and Aitken modes are more important in terms of number of particles, while the accumulation and coarse modes are the most important in terms of mass. For an individual particle, the mass increases from the nucleation to the coarse mode. The particles in the nucleation and Aitken modes grow into larger sizes, typically into the accumulation size range, by vapor condensation or coagulation with other particles. The particles in the accumulation mode account for most of the visibility effects (Covert et al., 1980) and present a relatively long lifetime due to efficient removal mechanisms for the nucleation mode particles (condensational growth and losses to larger particles due to coagulation) and the coarse mode particles. The particles in the coarse mode present elevated sedimentation velocity and for this reason are quickly removed from the atmosphere by dry deposition. Those particles are present in re-suspended dust (soil or roads), sea-spray, plants, volcanoes, agriculture, and industrial processes (Romo-Kröger et al., 1994; Allen et al., 2001; Seinfeld and Pandis, 2006).

Large attention has been given to the particles in the submicron range – that is particles smaller than 1 µm (PM_1) – due to the poor understanding of their chemical composition, morphology, size-distribution, and state of mixing. The PM_1 levels and composition in the atmosphere depend strongly on meteorological conditions, type of emission, and proximity to the source.

2.3 Chemical composition of PM_1

PM_1 comprises carbonaceous material (organic and black carbon), sulfates, nitrates, ammonium, chloride, metals, metal oxides, sea salt, and water. In field studies, the four first comprehend most of the particulate mass, typically larger than 80% (Krivacsy et al., 2001; Henning et al., 2003; Theodosi et al., 2011). The largest fraction of PM_1 is usually divided into carbonaceous material and inorganic fraction.

2.3.1 Inorganic fraction

The inorganic PM_1 fraction is well characterized in the literature. The major inorganic ions in atmospheric PM_1 are sulfate, nitrate, ammonium, and chloride. The corresponding compounds after neutralization in the atmosphere are often found in form of the ammonium sulfate, ammonium nitrate, and ammonium chloride (Seinfeld and Pandis, 2006). In the absence of the substantial amounts of metallic salts, particle neutralization can be investigated through a comparison between the ammonium concentration measured and the ammonium concentration predicted: using the measured sulfate, nitrate, and chloride concentrations, and respective molar weight as shown in Equation 1 (Zhang et al., 2007a),

$$Ammonium_{predicted} = 18 \times \left(\frac{sulfate}{96} \times 2 + \frac{nitrate}{62} + \frac{chloride}{35.45}\right) \qquad (1)$$

The neutralized aerosol condition is present if the ratio (ammonium measured to ammonium predicted) is about the unity, indicating that there is enough ammonium to neutralize the anions, i.e., sulfate, nitrate, and chloride.

Additional inorganic compounds such as potassium, calcium, and sodium have been also identified in PM_1 – however, usually in much lower concentrations (Rogula-Kozłowska and Klejnowski, 2013) and consequently in most cases they do not play an important role in aerosol neutralization. The importance of potassium and sodium can become more relevant during episodes of biomass burning or marine origin (Saarnio et al., 2012; Ovadnevaite et al., 2012).

2.3.2 Carbonaceous material

Carbonaceous material is mainly derived from incomplete biomass and fossil fuels combustion and consists of organic carbon (OC) and black or elemental carbon (Bond et al., 2004). The appropriate definition of the latter depends on the instrumental method utilized for its measurement. For example, elemental carbon (EC) is the term used when the technique involves thermal methods, however if the detection is optical then the black carbon (BC) is an appropriate term. Despite the small concentrations often reported in the literature (few percents of PM_1), this compound is directly connected to global radiative forcing due to its absorbing properties (Ramanathan and Carmichael, 2008).

The OC can be converted into organic matter (OM) or organic aerosol (OA) through a multiplying factor, which varies in most cases from 1.6±0.2 and 2.1±0.2 for urban and aged non-urban aerosol, respectively (Turpin and Lim, 2001). The organic fraction makes up most of the carbonaceous material and in several studies it is the dominant compound in PM_1 (Zhang et al., 2007b). In a compilation of 37 datasets worldwide, Zhang et al. (2007b) observed that the average organic fraction PM ranges from 20 to 70%. Another peculiarity concerning the organic mass fraction is the large variability of chemical species it contains. That is, the organic fraction is not composed of a single organic compound, but the sum of molecules mainly composed of the atoms of carbon, hydrogen, oxygen, and nitrogen grouped in different organic functional groups (acids, di-acids, alcohols, ketones, and so on).

The organic fraction can be further classified according to its solubility in water as water-soluble organic matter (WSOM) and water-insoluble organic matter (WISOM) (Saxena and Hildemann, 1996). The water-solubility is an important property in the characterization of OA since it is related to particle hygroscopicity, a property that represents the particle’s ability to take up water. A large fraction of the OA (25–75%) is water-soluble (Jaffrezo et al., 2005; Pathak et al., 2011; Papers I and III) and it enhances with particle age in the atmosphere due to oxidation processes (Jimenez et al., 2009). The water-soluble OA has been characterized as oxygenated, polar and composed of multifunctional compounds such as monocarboxylic acids, diacids, aldehydes and monosaccharide anhydrides (Decesari et al., 2000; Kourchev et al., 2005; Cavalli et al., 2006; Henningan et al., 2008).

The WISOM corresponds to compounds that present low solubility in water (below 1 g of solute in 100 g of water; Saxena and Hildemann, 1995). In the atmosphere the WISOM is composed of large molecules (>C9), such as n-alkanes, polycyclic aromatic hydrocarbons (PAHs), cholesterol, and other steroids (Saxena and Hildemann, 1996; and references therein).

2.3.3 Metals

Although metals are normally present in small concentrations in ambient measurements, typically ng m^{-3} (Allen et al., 2001; Pakkanen et al., 2001; Gao et al., 2002; Querol et al., 2007), their adverse impacts on human health are important (Schwarze et al., 2006; EEA air quality report, 2013). Ambient measurements in three different sites in United Kingdom presented the following metals distributed throughout the fine and accumulation modes, Zn, Cu, Sn, Se, Pb, Co, Mn, Ni, Cd, and Hg (Allen et al., 2001), where most of them are among the United States Environmental Protection Agency (EPA) list of hazardous air pollutants. In other three sites in New York City, the metal concentrations measured in $PM_{2.5}$ ranged from 0.85–36 ng m^{-3} for Cu, 0.26–18 ng m^{-3} for Ni, 0.080–2.6 ng m^{-3} for Sb, and 1.4–87 ng m^{-3} for Zn (Gao et al., 2002). In an urban site in Helsinki, the concentration of 29 different metals in the PM_1 and the highest concentrations were obtained by Fe, Al, Ca, Na, K, V, Cr, and Zn, which ranged from 6 to 56 ng m^{-3} (Pakkanen et al., 2001).

2.4 Sources of PM_1

PM_1 has been related to primary and secondary aerosols, where the primary corresponds to the sources that are directly emitted into the atmosphere as particles, while the secondary corresponds to the particles that are formed through oxidation of volatile organic compounds. In addition, both can be further divided into natural and anthropogenic sources. When emitted into the atmosphere, the PM_1 can be local (1–10 km), regional (>100 km) or be long-range transported from remote areas (>1000 km) (Seinfeld and Pandis, 2006). The latter is often responsible for elevated PM_1 levels at locations where the local emissions are low (Niemi et al., 2009).

2.4.1 Primary aerosol

The main natural sources of aerosols in the atmosphere are biogenic, oceanic, and biomass burning. Primary biogenic aerosol emission consists of pollen, bacteria, fungal and fern spores, viruses, and fragments of animals and plants (Simoneit and Mazurek, 1982; Deprés et al., 2007). Those particles range from few tens of nanometers to millimeters and are responsible for an emission of about 1000 Tg yr^{-1} (Jaenicke, 2005). Penner (1995) estimated that plant fragments and microorganisms contribute with 56 Tg yr^{-1} to the global emission rate of fine particulate matter. For comparison other sources of submicron aerosol particles, such as sea-salt and sea-spray represent 24 and 8.2 Tg yr^{-1}, respectively (Vignati et al., 2010), while open biomass burning emissions (carbonaceous material) were estimated to be 25.86 Tg yr^{-1} (Lamarque et al., 2010).

Among the anthropogenic primary sources are fuel combustion for transportation and energy production, biomass burning, cooking, and industrial processes (Seinfeld and Pandis, 2006; Querol et al., 2007; He et al., 2004). In China, besides the technological improvements, the industrial sector represented 46% of the $PM_{2.5}$ emissions in the year 2005 (5.97 Tg). The emissions were followed by the residential sector with 33.8% (4.39 Tg) (Lei et al., 2011). In terms of carbonaceous aerosol, the residential sector contributed to 47-69% of BC and 81-92% of OC emitted in China in the same year (Lei et al., 2011). In Spain, Minguillón et al. (2011) using the radiocarbon ^{14}C technique

(Currie, 2000) estimated that, on average, 72–89% and 28–44% of EC and OC, respectively, had a fossil fuel origin in the two sites investigated.

Both biogenic and anthropogenic primary sources have been shown to be very substantial in the production of secondary organic aerosol (SOA, Griffin et al., 1999; Carlton et al., 2009).

2.4.2 Secondary aerosol

Secondary aerosol species typically dominate in the composition of PM as a result of physical (nucleation, condensation, and evaporation) and chemical processes (photochemistry and oxidation) in the atmosphere (Finlayson-Pitts and Pitts Jr., 2000). In Europe, secondary aerosol particles represent a majority of $PM_{2.5}$ mass (Putaud et al., 2010; Kim et al., 2011). Secondary aerosol is composed of organic (secondary organic aerosols, SOA) and inorganic compounds (mainly ammonium sulfate and ammonium nitrate) from natural and anthropogenic sources.

In the aerosol phase, sulfate can be present in solid and aqueous forms ($(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$, NH_4HSO_4, SO_4^-, HSO_4^-), typically neutralized by ammonia (NH_3), depending on the availability of the latter and water (Seinfeld and Pandis, 2006). The origin of the sulfur can be natural or anthropogenic. Anthropogenic sulfur is emitted by fuel combustion processes in the form of sulfur dioxide (SO_2), which can further react with OH and HO_2 radicals and in the presence of water vapor to be rapidly converted into sulfuric acid (Stockwell and Calvert, 1983; Seinfeld and Pandis, 2006). Sulfuric acid (aqueous phase) can react with NH_3 and form the salt ammonium sulfate. Sulfate can be also formed by atmospheric oxidation of biogenic organic sulfur compounds, in particular dimethyl sulfide (DMS) in the oceanic air (Spicer et al., 1996; Bruyn et al., 1998).

Nitrate, often present in the PM_1, is commonly found in the forms of ammonium nitrate or sodium nitrate, which will be dependent on nitric acid reacting with NH_3 or the salt sodium chloride (NaCl). The latter takes place in areas close to sea water where the presence of NaCl is abundant. The reaction with NH_3 may happen in environments where the concentration of this gas is high (and sulfate is low): for example close to animal waste, agricultural areas (due to the use of fertilizers), and industries. Nitric acid in urban environments is a product of nitrogen oxide gas (NO): largely emitted by vehicle exhaust, which is easily oxidized in the atmosphere and converted into nitric acid (Seinfeld and Pandis, 2006). In remote areas, nitrates can also result from natural sources such as biological activity (Robinson and Robbins, 1970).

The SOA sources and formation pathways have been intensively investigated due to the enormous number of precursors and chemical reactions involved. The precursors are typically volatile, semi volatile organic compounds (VOCs), and primary aerosol particles. They are emitted by natural (plants and ocean) and anthropogenic (fuel combustion, industries, biomass burning) activities and are oxidized in the atmosphere e.g. by ozone, OH and nitrate radicals, yielding SOA (Finlayson-Pitts and Pitts Jr., 2000; Seinfeld and Pandis, 2006). SOA represent a large mass fraction of secondary aerosols in the atmosphere. For example, near Riverside the SOA was observed to represent, on average 74% of PM_1, with maximum of 90% in the midday period (Docherty et al., 2008). Also in two sites close to Beijing (urban and rural) OC concentrations were mostly secondary (74–80%), (Guo et al., 2012). Among anthropogenic sources, several studies show that biomass burning and fossil fuel combustion produce potential precursors for SOA formation (Rusell et al., 2011; Yee et al., 2013). In the case of fuel combustion, gasoline emissions were shown to be more relevant than diesel (Bahreini et al., 2012). In addition to the anthropogenic, biogenic sources can represent a significant fraction of the secondary OC. Fu et al. (2010) observed that, on average 58–63% (day and nighttime) of the secondary OC measured in the central eastern China had biogenic origin mainly from isoprene, α/β-pinenes and β-caryophyllene precursors.

3. Materials and Methods

3.1 Sites characterization

3.1.1 San Pietro Capofiume, Italy

The San Pietro Capofiume (SPC) measurement station is a rural station located at the Po Valley in Italy, 40 km northeast from Bologna (44º39’ N, 11º37’ E, 10 m a.s.l., Decesari et al., 2001, Figure 2), surrounded by agricultural areas. The region of the Po Valley is recognized as the most industrialized and populated region of Italy. Unfortunately, it is also recognized as one of the most polluted regions of Europe (Sofiev et al., 2011; Paper II; EEA air quality report, 2013), where the poor ventilation caused mainly by the mountain chains (Alps in the north and west and the Apennines in the south) is responsible for accumulating pollutants over the valley (Squizzato et al., 2013).

The measurements were carried out during the springtime (March 31st – April 20th, 2008). During this time, large variations in meteorological conditions (relative humidity (RH), air temperature, and wind direction) were observed from daytime to nighttime. For example, the air temperature varied between 3 and 21 ºC (on average 12.2 ºC) and the relative humidity between 28 and 98% (on average 70%) during the whole period of the campaign. In addition, a drastic increase in the mixing-layer height was observed during most of the days around 11:00 (local summer time).

3.1.2 Santiago de Chile, Chile

The main site in Santiago was the USACH (University of Santiago de Chile) station, which was located inside the University of Santiago de Chile campus (33º 27’ S, 70º 41’ W, 567 m a.s.l., Figure 2). The metropolitan area of Santiago de Chile has 36% of the population of the whole country (~5 million inhabitants) and it is located in a valley surrounded by the Andes mountains on the east and north sides and by hills on the west side. Similar to the Po Valley, the complex topography is responsible for hampering air pollution dispersion and exceeding the PM levels recommended by the WHO (2006). The measurements were carried out during the transition from winter to springtime (August 17th – November 23rd, 2011). During that period, the air was relatively dry (65%) while the air temperatures presented strong diurnal cycle from –2 to 31 ºC and weak winds (2 m s^{-1}).

3.1.3 Helsinki, Finland

The SMEAR III station is located 5 km at north of Helsinki downtown (60º 12' N, 24º 57' E, 30 m a.s.l., Järvi et al., 2009) and is considered as an urban background station (observations vary dramatically with wind direction). Its operation consists of continuous measurements of gases, aerosol particles, and meteorological variables. The Metropolitan area of Helsinki (Figure 2) is the most populated region of Finland with about 1 million inhabitants. Helsinki is situated in the coastal area of Baltic Sea and large boreal forest areas are by far the dominant land-cover, i.e. north of Helsinki.

Two field campaigns, one during the wintertime (January 9th – March 13th, 2009) and another during the springtime (April 9th – May 8th, 2009) were carried out at this station. The wintertime was characteristic, for very low air temperatures (from –16 to +5 ºC), elevated RH values, and short number of hours of sunshine (caused by both cloudiness and northern latitude). During the springtime, the air temperatures were higher (from –5 to +20 ºC), RH was lower, and the number of hours of sunshine was substantially larger (3–4 times, Pirinen et al., 2012).

Figure 2 – Map showing the locations of the three sites used in the field experiments: Santiago de Chile in Chile, San Pietro Capofiume in Italy, and Helsinki in Finland.

3.2 Measurements

3.2.1 Aerosol Mass Spectrometers

3.2.1.1 ACSM

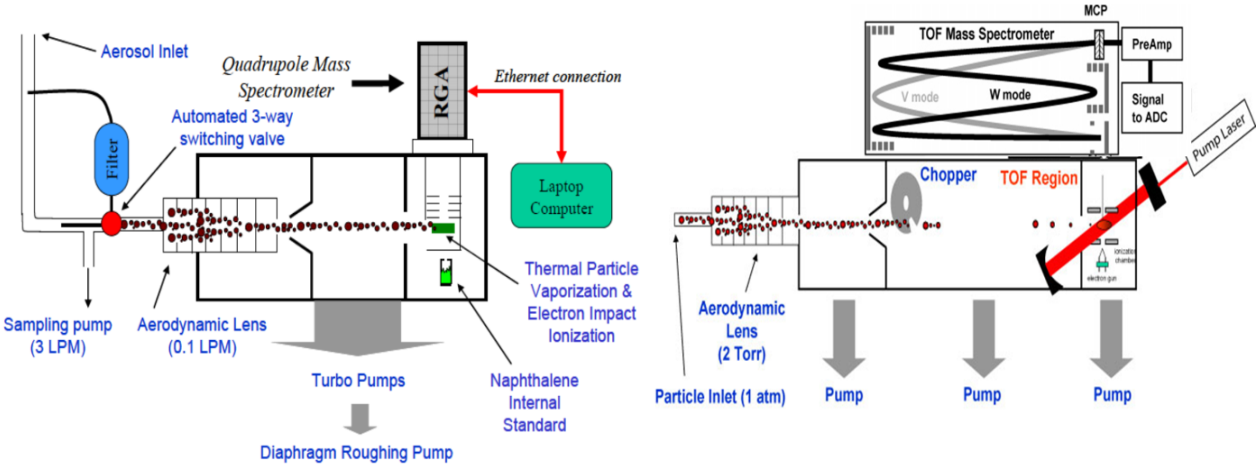
The aerosol chemical speciation monitor (ACSM, Aerodyne Research Inc.) is able to routinely characterize non-refractory submicron aerosol species such as organics, nitrate, sulfate, ammonium, and chloride with the time resolution from 15 minutes upwards (Ng et al., 2011). The instrument consists of a particle-sampling inlet, three vacuum pumps (Pfeiffer: two HP300 and one HP80) and one backup diaphragm pump (Vacuubrand, MD1), three vacuum chambers, and a residual gas analyzer mass spectrometer. Particles are first focused by using an aerodynamic lenses system into a narrow particle beam, which is transmitted through three vacuum chambers. In the third chamber, the particle beam is directed into a hot tungsten oven (600°C) where particles are flash-vaporized, ionized with a 70 eV electron impact ionizer, and detected with a quadrupole mass spectrometer (Figure 3a).

3.2.1.2 HR-ToF-AMS

The Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (Aerodyne Research Inc., Billerica, MA, USA; DeCarlo et al. (2006), hereinafter referred to as “AMS”) measures the same non-refractory particles as the ACSM. In fact, it contains the same aerodynamic lenses, vaporizer and ionizer setup. However, the presence of a chopper after the inlet allows particle size distribution information to be obtained (PToF mode). Moreover, additionally to the backup pump the AMS also contains 5 turbo molecular pumps (Varian: two V-300 and three V-70) to guarantee an extremely low pressure inside the instrument. Another difference concerns the detector in the AMS is that a microchannel plate detector (MCP) is used. The MCP consists of a plate with many parallel channels (4–25 µm in diameter) where each channel acts as an independent electron multiplier. This type of detector is responsible for faster response time and an increase in the dynamic range. In addition, with the time-of-flight mass spectrometer detector much higher mass resolution is achieved, which enables the separation of different ion with similar mass-to-charge ratio, whereas with the ACSM only unit mass resolution data can be obtained. In addition to the PToF mode other two modes are available, V and W, where the first is more sensitive to lower concentrations and the second mode allows higher mass resolution and a better separation of the ions, Figure 3b.

3.2.1.3 SP-AMS

The Soot-Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc., USA; Onasch et al., 2012) consists of a combination of two well-characterized instruments: the Aerodyne AMS and the single particle soot photometer (SP2; Droplet Measurement Technologies, CO, USA). In the SP-AMS an intracavity Nd:YAG laser vaporizer (1064 nm), based on the design used in the SP2 instrument, was incorporated into the HR-ToF-AMS. The addition of laser enables vaporization of refractory particles, specifically laser-light absorbing refractory black carbon (rBC) particles that are not detected in the standard AMS or ACSM. The new laser vaporizer does not interfere with the standard tungsten vaporizer used in the HR-ToF-AMS instrument. Therefore, the SP-AMS instrument can be operated with the laser vaporizer alone, with both the laser and tungsten vaporizers, or just with the tungsten vaporizer. When operated with both vaporizers, the laser is modulated on and off, in order to measure refractory black carbon and the associated less refractory particulate material in addition to the standard AMS non-refractory particulate measurements (Figure 3b).



(a) (b)

Figure 3 – Diagram of the aerosol chemical speciation monitor (ACSM) (a) and soot-particle aerosol mass spectrometer (SP-AMS) (b).

3.2.2 Complementary aerosol instrumentation

Other instruments were used to complement the information obtained by the aerosol mass spectrometers, such as the TEOM (tapered element oscillating microbalance, model 1400ab), PILS-TOC-IC (Particle-into-liquid sampler coupled with two ion chromatographs, Saarikoski et al., 2008; Paper I), DMPS (differential mobility particle sizer, the configuration used was described in more detail in Järvi et al., 2009), Semicontinuous EC/OC carbon aerosol analyzer (Sunset Laboratory Inc., Portland, OR), PM_1 filter collections (gravimetric analysis, ion chromatography connected to a conductivity detector (IC-CD and mass spectrometry (IC-MS)), and $PM_{2.5}$ mass analyzer. Those instruments are summarized in Table 1 and they are further discussed in the Papers I–V.

Table 1 – Summary of the instruments used in each site.

Instrument / Site	Helsinki spring (Papers I and III)	SPC (Paper II)	Santiago (Paper IV)	Helsinki winter (Paper V)
ACSM			X	
HR-ToF-AMS	X	X		X
EC/OC analyzer	X	X	X	X
PILS-IC	X			X
PM_1 samples	X	X		X
$PM_{2.5}$ mass analyzer			X	
TEOM	X			X
TOC-V_{CPH}	X	X		X
DMPS	X			X
IC-CD		X		X
IC-MS		X		X

3.3 Data processing

The aerosol mass spectrometers datasets were processed with Igor Pro 6 (Wavemetrics, Lake Oswego, OR) software. Sueper (2008) has developed two data-management utilities that provide an easier interface to the users; Squirrel (SeQUential Igor data RetRiEvaL) and Pika (Peak Integration by Key Analysis). Different versions of Squirrel and Pika were used in this study and are available at http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html.

3.4 Positive Matrix Factorization

The positive matrix factorization (PMF) was introduced by Paatero and Tapper (1994) and since then it has been applied to different environmental areas to investigate different phenomena of data variability (Juntto and Paatero, 1994; Anttila et al., 1995; Hopke et al., 1999). One application of PMF is in the identification of sources of ambient PM (Hopke et al., 1999; Viana et al., 2008). In the literature, most of the studies investigate the sources of the inorganic ions (nitrate, ammonium, sulfate, and chloride), trace elements and sea-salt collected by off-line measurements (mainly PM_{10} and $PM_{2.5}$ filter samples) with PMF. For this reason, the lack of information concerning OA sources motivated Lanz et al. (2007) to apply PMF to the submicron OA fraction measured by the AMS. The results identified 6 different factors of OA (OOA types I and II, HOA, charbroiling, wood burning, and a minor source) where the OOA type I and HOA were in-line with the results obtained by the deconvolution of the AMS OA proposed by Zhang et al. (2005). The use of large datasets, such as the datasets obtained by the AMS instruments, required the development of a custom software tool to examine the PMF solutions. Hence, the PET (PMF evaluation tool) was created (Ulbrich et al., 2009) and since then, the chemical composition of OA has been widely investigated at different locations (Aiken et al., 2008; Papers II-V; Ng et al., 2010; Mohr et al., 2010; Zhang et al., 2011; Sun et al., 2012).

PMF is a bilinear unmixing receptor model that follows certain rules to be physically meaningful (Henry, 1991). The predicted source compositions and contributions must be non-negative, that is, a source cannot have a negative percentage of an element or emit a negative mass. Also, the sum of the predicted elemental mass contributions for each source must be less than or equal to the total measured mass for each element (mass conservation principle). In the PMF model, the input data matrix is assumed to be comprised of the linear combination of factors with constant profiles that have varying contributions across the dataset, which is represented by Equation 2:

$$x_{i\,j} = \sum_p g_{i\,p} \times f_{p\,j} + e_{i\,j}\ , \tag{2}$$

where i and j subscripts refer to the row and column indices in the matrix, p refers to the number of factors in the solution, and $x_{i\,j}$ is an element of matrix X. The matrix X corresponds to an ensemble of mass spectra (MS) in mass concentration (μg m^{-3}) measured in time series (TS) with the AMS and have $m \times n$ dimension (*m*=rows, *n*=columns). $g_{i\,p}$ is an element of the $m\ x\ p$ matrix G whose columns are the factor TS, $f_{i\,j}$ is an element of the $p \times n$ matrix F whose rows are the factor profiles (MS), and $e_{i\,j}$ is an element of the $m \times n$ matrix E. The matrix E represents the residuals not fit by the model for each experimental data point (E=X – GF). The PMF algorithm requires no priori information about G and F, it iteratively fits F and G to the data using the least-square approach, which minimizes the sum of the least squares of the Q function, Equation 3:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{\sigma_{ij}}\right)^2 , \tag{3}$$

where $\sigma_{i\,j}$ is an element of the $m \times n$ measured errors of the elements in the matrix X, i.e. the estimated errors from each AMS measurement. One important remark is that, the rows in F (MS) were normalized to sum 1, which is different from the original PMF applications (EPA PMF), where the sum of the different rows in F will sum 1.

3.4.1 Determination of the number of factors

Each factor in PMF represents of a fixed source type (or in the case of the AMS data, different oxidation states of organic aerosol) with varying contribution and the determination of the number of factors in a solution must be determined by the user. For this reason the value of a fit parameter of Q normalized as a function of the number of factors was shown to be useful in estimating the minimum number of factors in a solution (Ulbrich et al., 2009). However, most studies have shown that the best way to estimate the number of factors is combining this parameter with additional external data. Examples of external data are meteorological variables, backward wind trajectories, concentration of gases, and concentration of aerosol particles not included in the input data matrix. This approach was used in all PMF applications in the papers of the current thesis.

3.5 Laboratory experiments

Laboratory experiments were used to evaluate the feasibility of the SP-AMS in measuring metals. In addition to the SP-AMS, also a constant output atomizer (TSI model 3076), a silicon drier (Topas 25 cm), a differential mobility analyzer (DMA, TSI model 3080) and the condensation particle counter (CPC, TSI model 3772) constituted the instrument setup. Polydisperse submicron aerosol particles containing known concentrations of Regal black (a substance that produces similar MS to the soot emitted by traffic, Onasch et al., 2012) and 13 different concentration standards of metals (2% in nitric acid each, Sigma-Aldrich) were generated by the atomizer, dried in a silicon drier, size-selected by the DMA (300 nm in mobility diameter), counted by the CPC and corresponding signal (in Hz) measured by the SP-AMS.

4. Results and discussions

4.1 PM_1 composition

The aerosol particles that evaporate inside the AMS (vaporizer temperature approximately 600 ºC) were defined as non-refractory (NR) particles and the mass concentration measured as NR-PM_1 (Allan et al., 2004; Takegawa et al., 2006). Several studies in the literature, based on the comparison with additional instrumentation such as DMPS, TEOM, and gravimetric analysis, confirmed that the NR-PM_1 particles measured by the AMS comprised the major fraction of the PM_1 (DeCarlo et al., 2008; Sun et al., 2012; Zhang et al., 2011). In fact, most of the PM_1 is accounted when BC is included into the mass fraction (Huffman et al., 2009; Papers I–V).

4.1.1 Inorganic fraction

The average mass fraction of the inorganic ions (nitrate, sulfate, ammonium, and chloride) for each field experiment is presented in Table 2. The largest concentrations were obtained in the urban site of Santiago de Chile, while the lowest were obtained at the Helsinki site during the springtime. The anions (nitrate, sulfate, and chloride) and the cation (ammonium) were used to estimate the acidity in the PM_1 (Zhang et al., 2007a). For instance, during the Helsinki wintertime, the measurements suggested that the PM_1 was acidic most of the time (67% of the measurements, Paper V), while in the other three studies the aerosol was mostly neutralized.

Table 2 – Total mass concentration and average concentration for organics, sulfate, nitrate, ammonium, chloride, and EC or BC for the four field experiments.

Compound / Site	organics (%)	sulfate (%)	nitrate (%)	ammonium (%)	chloride (%)	BC or EC (%)	Total ($\mu g\ m^{-3}$)
SPC	32	8	37	16	1	7	10.94
Santiago de Chile	59	8	14	12	3	3	29.80
Helsinki spring	45	24	12	10	<1	9	6.6
Helsinki winter	33	11	33	12	<1	11	6.9

Additional compounds such as sodium, potassium, and calcium were measured with the PILS-IC in Helsinki (both campaigns) and IC-CD (in PM_1 filter samples) at the SPC site. In the two Helsinki campaigns the sum of those ions represented less than 1% of PM_1, while in the SPC it represented about 1%. The low contribution of those compounds indicated small uncertainty in assuming only ammonium as the main cation in the calculation of the neutralization balance.

4.1.2 Carbonaceous fraction

The sum of organics and BC represented on average 39%, 62%, 54%, and 44% of PM_1 at the sites, SPC, Santiago de Chile, HKI spring and wintertime, respectively, Table 2. Those results are in agreement with Zhang et al. (2007b) who reported a variation of the organic fraction (in NR-PM_1) between 18–70% in 25 different sites investigated in the northern hemisphere.

The wide variety of different fragments that the organic fraction contains is illustrated in Figure 4 with an average organic mass spectrum for a short period during the Helsinki wintertime campaign. In addition, when the same mass spectrum was investigated with higher resolution (HR-MS, Figure 4b) it was possible to observe that different ions were present in the same unit of mass. The ions were grouped in families based on their chemical constitution (C, H, N, and O), indicated by different colors. For example, the investigation in further detail of one individual unit of mass (m/z 58) revealed the presence of three different organic ions ($C_2H_2O_2^+$, $C_3H_6O^+$, $C_3H_8N^+$) that were not identified in the UMR-MS (Figure 4a).

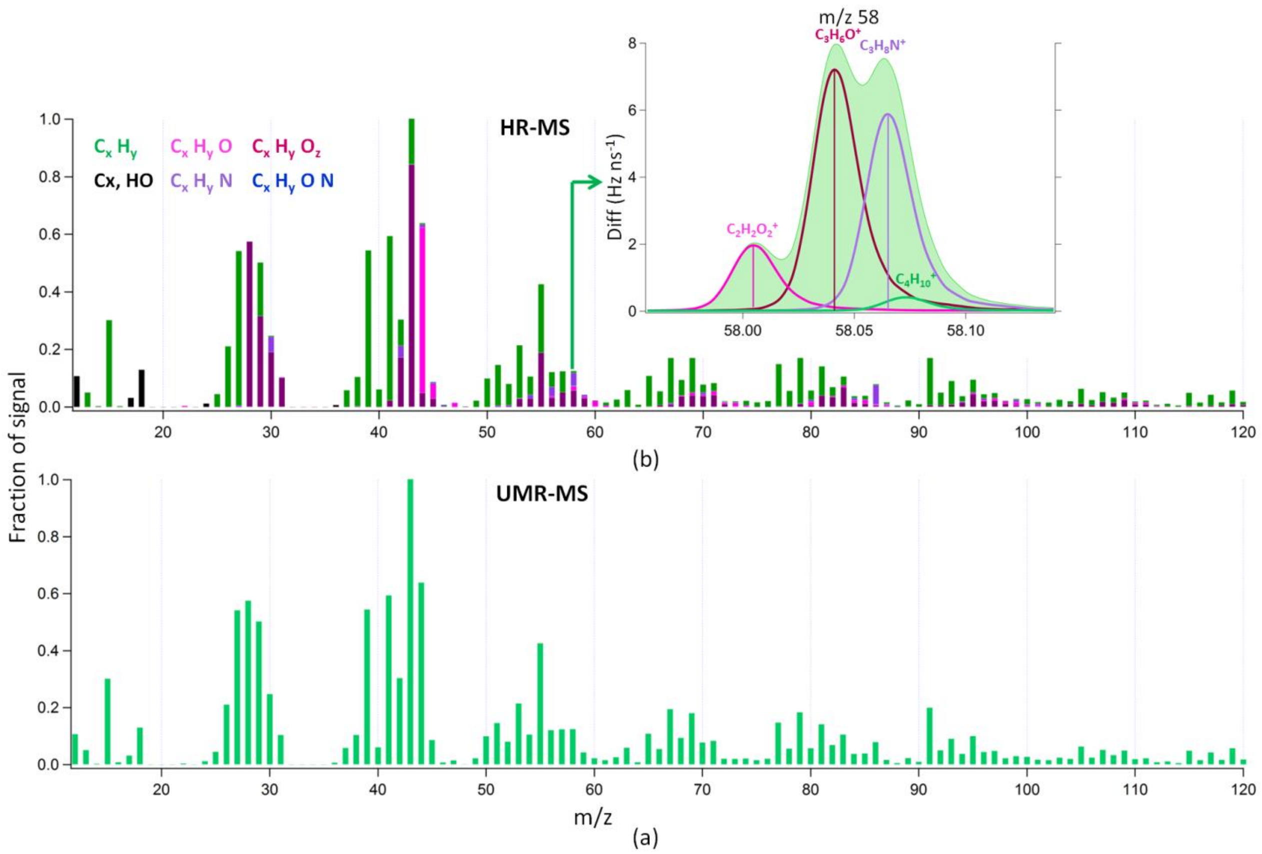


Figure 4 – Ambient mass spectrum of organics in unit mass resolution (UMR) (a) and in high-resolution (HR) (b). The m/z 58 was zoomed in to show the different fragments it contains. The shaded green area in (b) represented the total OA signal for this m/z.

4.2 PM_1 sources and components

4.2.1 Diurnal profile

High time-resolution of aerosol mass spectrometry measurements enable the determination of diurnal profiles of different chemical compounds in the PM. The determination of the diurnal profiles is helpful in the identification of chemical processes and sources involved. This information was used in Papers I–V. One example of its application was the diurnal profiles measured during the Helsinki wintertime campaign (Figure 5). The organics presented a rather stable behavior throughout the day, with the exception of two small broad peaks, one in the morning that followed the morning rush hour (in agreement with BC) and another in the evening, which was probably related to the use of biomass burning for domestic heating (Saarnio et al., 2012). Similar behavior was observed during the springtime (Paper III). At the SPC and Santiago de Chile sites, the diurnal development of the mixing layer (sometimes also called planetary boundary layer, PBL) seemed to cause a diurnal cycle with larger amplitude with mass concentrations much higher during the night and morning times (Paper II and IV). Moreover, in Santiago de Chile a clear enhance in organics concentration in the morning (8:00–9:00h) is likely related to traffic emissions.

Stable diurnal concentrations of sulfate were observed in the SPC and Helsinki field experiments. In Helsinki, this is due to the low local anthropogenic emissions of SO_2. Since the major coal-fired power plants in Finland employ desulfurization process, the measured sulfate is most likely regional or LRT. This fact was confirmed in Paper V with auxiliary data from atmospheric transport models and backward wind trajectories. In Santiago de Chile an increase of less than 1 µg m^{-3} in the afternoon could be related to local industrial activities (Paper IV).

In Santiago de Chile the ammonium nitrate diurnal concentrations presented a clear increase between 9:00–15:00h. This increase occurred after elevated concentrations of nitrogen oxide (NO, 7:00–10:00h) and nitrogen dioxide (NO_2, 8:00–12:00) largely emitted by the Santiago de Chile vehicle fleet. Thereupon, ammonium nitrate was probably formed by NO_2 conversion to nitric acid (HNO_3) and further reaction with NH_3 from industrial and agricultural emissions. In the Helsinki and SPC sites, an elevated concentration of ammonium nitrate in the early mornings could be related to aloft entrainment of ozone and/or nitric acid gases (Weimer et al., 2006) and PBL break-up, respectively.

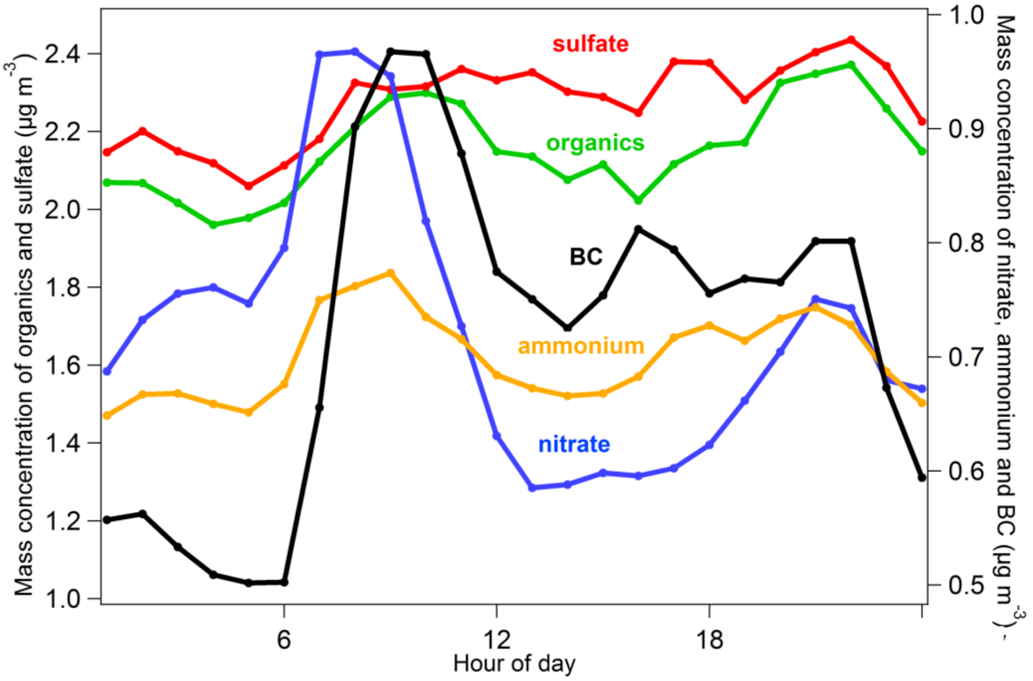


Figure 5 – Average diurnal profiles of the compounds sulfate, nitrate, ammonium, organics, and BC in Helsinki during the wintertime.

In addition, a clear diurnal cycle for traffic emissions in Helsinki was observed. From the elemental analysis the value of the ratio between the atoms hydrogen and carbon (H:C) had a maximum between 06:00 and 09:00 in the morning and a minimum in the afternoon. In terms of black carbon concentrations, the same morning peak was observed for the BC concentrations. In order to evaluate the effect of traffic to the H:C ratio, the diurnal cycle of the H:C ratio was calculated separately for weekdays, Saturdays, and Sundays. The peak in value of H:C during the morning rush hour was seen only during weekdays (Paper III).

4.2.2 Components of OA

A more detailed analysis of the vast composition of the organic fraction is possible using PMF. When PMF is applied to the AMS organic fraction data, each factor obtained does not necessarily represent a different source; instead it represents a different *component* of OA. This is because the variables employed in the input data matrix (m/z values) represent not only atmospheric molecules, but also their fragments. Therefore, each component will contain a group of molecules and fragments with certain common characteristics.

Eleven different components were identified among the four field experiments, where seven of them consisted of the oxygenated organic aerosol components (OOA); OOA type *a* (OOA-a), OOA type *b* (OOA-b), OOA type *c* (OOA-c), low volatile OOA (LV-OOA), semi-volatile OOA (SV-OOA), LV-OOA containing methanesulfonic acid (LV-OOA+MSA). In addition to the OOAs also the nitrogen-containing OA (NOA), long-range transported biomass burning OA (LRT-BBOA), BBOA, hydrocarbon-like OA (HOA), and coffee roastery OA (CROA) were identified.

4.2.2.1 Typical OA components

Experimental data have demonstrated that some components are intimately related to specific sources. For instance, the HOA component has been related to traffic emissions due to the similarity with the mass spectrum obtained from this type of emission (Canagaratna et al., 2004). An agreement between the diurnal profiles of HOA and BC, which is a product from incomplete combustion and tracer for traffic were verified in most studies in this thesis (Papers II–V).

Conversely, the BBOA component has been related to burning of several types of raw materials, forest, agricultural crops, and different types of wood (Mohr et al., 2009; Lee et al., 2010; Cubison et al., 2011). Moreover, the BBOA concentrations were shown to follow potassium and levoglucosan time series (Aiken et al., 2008; Papers II and V). The latter consists of an anhydrosugar present in plants and therefore emitted during the incomplete burning process. Its signal in the AMS is typically measured in the form of the fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$ (m/zs 60 and 73 in UMR, Scheneider et al., 2006; Alfarra et al., 2007). Large variability concerning the main fragments of BBOA in the MS can be found in the literature (Lanz et al., 2007; Aiken et al., 2008). The main reasons are the variety of raw materials used for burning, the burning conditions and atmospheric evolution. Later on, a different component was identified the cooking organic aerosol (COA) whose MS is composed of fragments typically present in both MS, HOA, and BBOA (Mohr et al., 2009; Mohr et al., 2012). The BBOA was observed in all the four experiments. During the Helsinki wintertime this component presented excellent agreement with levoglucosan concentrations suggesting local and regional wood combustion as the main source of BBOA. A moderate agreement between BBOA and levoglucosan was also observed during the SPC campaign.

Another component frequently identified in field studies is the OOA, which is composed of the most oxygenated fragments in the MS, typically the $C_xH_yO_z$ (where x, y and z ≥ 1). The OOA can be further divided into low-volatility OOA (LV-OOA) and semi-volatile OOA (SV-OOA). In some studies they present an agreement when compared to the secondary inorganic aerosol compounds sulfate (less volatile) and nitrate (more volatile), (Ulbrich et al., 2009) or to the sum of them (Sun et al., 2010; Paper IV). The SV-OOA and LV-OOA were identified in all the sites with the exception of the SPC site, which presented the three OOA components, OOA-a, OOA-b and OOA-c, however not the SV-OOA. The ability to separate different components of OOA was related to the high-oxidized state of the aerosol particles (Ng et al., 2010), typical from the Po Valley region where the pollutants accumulate over time.

In Santiago de Chile, different volatile character of the OOAs was confirmed when those components were evaluated as a function of ambient temperature. The SV-OOA concentrations decreased with the temperature increase, while opposite behavior was observed by the LV-OOA, Figure 6, indicating higher volatile character of the SV-OOA. More detailed characterization of those two components will be provided in the next section.

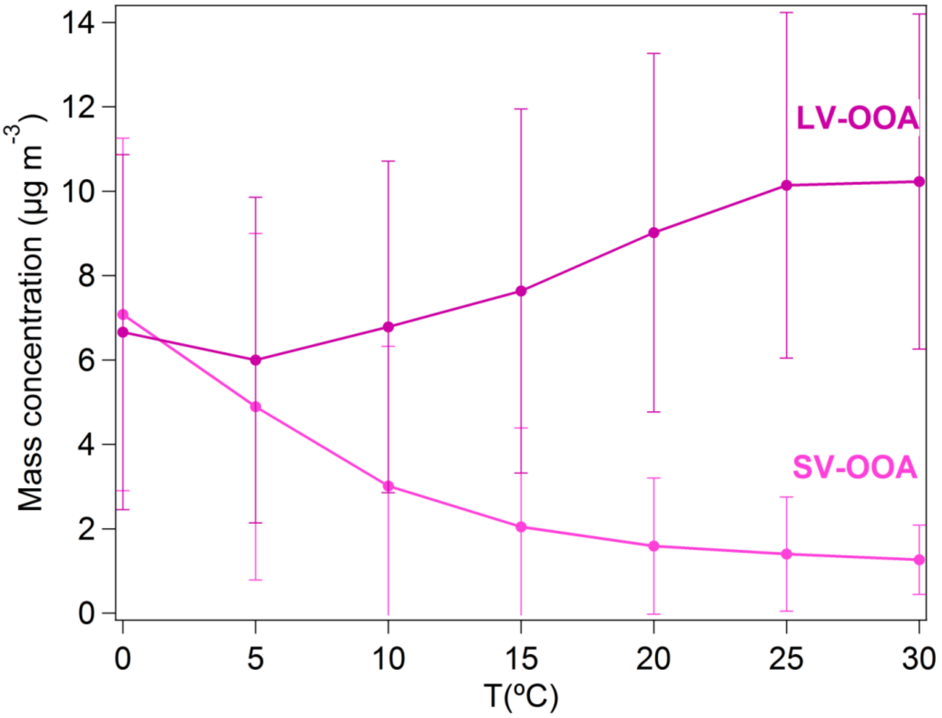


Figure 6 – Average mass concentration of the OA components LV-OOA and SV-OOA as a function of the air temperature during the Santiago de Chile field campaign.

4.2.2.2 Less typical components

Some OA components have been less frequently identified in field studies, such as coal combustion OA (CCOA, Sun et al., 2013), cooking OA (COA, Mohr et al., 2012), nitrogen-containing OA (NOA, Sun et al., 2011; Papers II and V), methanesulfonic acid-containing LV-OOA (LV-OOA+MSA, Paper III), LRT biomass burning OA (LRT-BBOA) and coffee roastery OA (CROA, Papers III and V).

The NOA has been related to very distinct sources. In the Helsinki site this component was observed to comprise up to 29% of the OA fraction during the wintertime and was related episodes of high air relative humidity and low visibility, Figure 7 (Paper V). The low air temperatures typical from the wintertime could have facilitated low-molecular weight and highly water-soluble nitrogen-containing fragments, such as alkyl amines to stay in the particulate phase (Sellegri et al., 2005). In the SPC site, the NOA was also obtained and associated with MSA concentrations, which suggested marine contribution to this component. In Papers II and V the major nitrogen-containing fragments were CHN^+, CH_3N^+, CH_4N^+, CH_5N, $C_2H_3N^+$, $C_2H_4N^+$, $C_3H_8N^+$, $C_2H_6N^+$ most likely from amine functional group and fragmentation of organonitrates in smaller extent. In the case of amines (tertiary) those were demonstrated through laboratory experiments to be able to form significant yields of SOA (Murphy et al., 2007). In the urban environments of Mexico City and New York City this component was related to industrial and marine origin, respectively (Aiken et al., 2008; Sun et al., 2011).

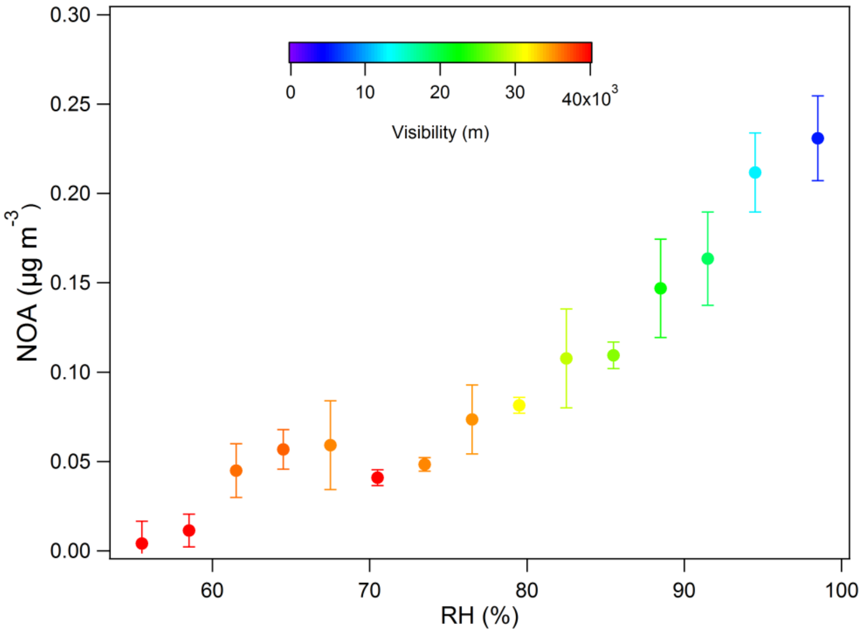


Figure 7 – NOA component concentrations as a function of the air relative humidity and colored by visibility.

In Paper III a quite oxygenated component containing fragments from MSA was identified and called LV-OOA+MSA. In addition to oxygenated ($C_xH_yO_z$) and hydrocarbon (C_xH_y) also organosulfate fragments such as CHS^+, $CH_3SO_2^+$ and $CH_4O_3S^+$ were present in the mass spectrum this component. A marine component with similar O:C and OM:OC ratios was observed in Paris (Crippa et al., 2013), where it contributed on average to 15% of OA. MSA was measured with the AMS over the sub-arctic north east Pacific Ocean as internally mixed particles centered at 475 nm (Phinney et al., 2006). In the same study the presence of MSA in the submicron size range was also confirmed by MOUDI measurements.

Another high-oxygenated component observed during the springtime in Helsinki was the LRT-BBOA (Paper III). The presence of oxygenated fragments CO_2^+, CHO^+ and typical fragments from levoglucosan $C_2H_4O_2^+$ and $C_3H_5O_2^+$ in the MS, suggested that this component could represent a more oxidized fraction of the BBOA. In fact, the largest contribution from this component occurred at the same time when large smoke from forest fires in the southern and eastern Europe was observed with MODIS sensor (onboard the NASA EOS Terra satellite) and the air back-trajectories showed that those air masses reached southern Finland (Paper I). During the same period PM_1 was close to 20 µg m^{-3} (Paper I) and the LRT-BBOA presented good agreement with the WSOC (r=0.8) suggesting that this component could comprise a significant fraction of WSOC.

The CROA was identified in Papers III and V and represented local emissions from two coffee roasteries located at 2 and 10 km from the site of observations in Helsinki. This component was composed of C_xH_y, $C_xH_yO_z$ and nitrogen-containing fragments. In fact, in both studies CROA was the richest in the N:C, 0.04 and 0.08 for winter and springtime, respectively. Furthermore, the fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$ were present in the MS implying that the roasting process also released anhydrosugars. However, an interesting result was that the ratio between the fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$ was lower for CROA (=1.1) than to BBOA (=2.1), which could be due to the low temperatures used during the roasting process or presence of different anhydrosugars.

With respect to the different characteristics of each OA component HOA, BBOA, and CROA likely represent the POA, while the OOAs, LRT-BBOA, NOA, and LV-OOA+MSA represent the SOA. This assumption is probably not exact; however, it provides a good estimation concerning the origin of those components. When classified this way the OA measured in the four field campaigns was mostly secondary (Figure 8), suggesting fast aerosol processing in the atmosphere even in sites when the solar radiation was extremely low. This fact suggested the presence of strong oxidants in the atmosphere of Helsinki during the wintertime and/or the importance of the presence of water, which facilitates chemical reactions in the aqueous phase.

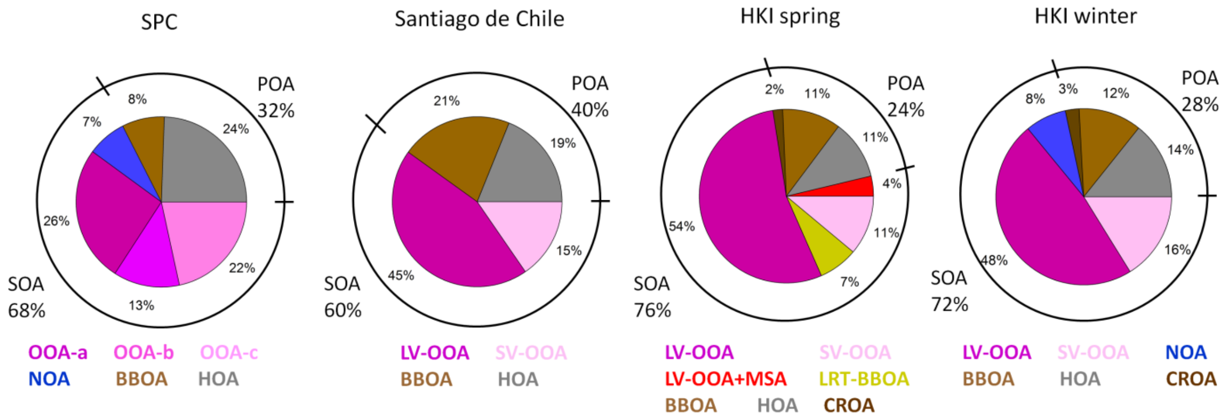


Figure 8 – OA components contributions for each field experiment further classified as POA and SOA.

4.2.3 Aerosol evolution in the atmosphere

When gases and POA are emitted into the atmosphere they will evolve by physicochemical processes, such as oxidation, volatilization, condensation of further products, and mixing of air masses and thus become more oxidized, less volatile, and more hygroscopic, thus leading to OOA formation, where the two OOAs, LV-OOA, and SV-OOA represent different components of SOA (Jimenez et al., 2009). The oxidation process has been highlighted in the investigation of the OA evolution and different diagnostics permit its evaluation, f_{44} vs f_{43} (Ng et al., 2010), Van Krevelen diagram (Heald et al., 2010) and oxidation state OS_C (Kroll et al., 2011).

The presence of fragments with different amount of oxygen (CO_2^+ and $C_2H_3O^+$) in the LV-OOA and SV-OOA components made Ng et al. (2010) use f_{44} (a ratio between m/z 44 and organics) and f_{43} (similar with m/z 43) in order to investigate the aging of the OA components in 25 different locations. The evaluation of different datasets resulted in the determination of a triangle space, an area in the graph where the SV-OOA component evolved into LV-OOA. The LV-OOA was located on the top region of the triangle together with the highly-oxygenated products humic-like substances (Hulis) and fulvic acid. In this thesis, similar behavior was observed for the four field experiments (Figure 9) where all the OOAs were clustered on the most oxidized region of the triangle.

Another interesting point is that the BBOAs and HOAs found in Papers II–V (Figure 9) clustered around similar regions of the triangle, both with similar amount of f_{44}, however HOA presented higher amount of f_{43}. Moreover, CROA also clustered around the BBOA area confirming the similarities between the roasting and biomass burning processes. In Paper III the BBOA revealed the presence of two distinct origins, one local likely from domestic heating and another LRT BBOA from forest fires in eastern Europe. This component did not cluster around the BBOA area probably due to its high oxidized character and distinct source.

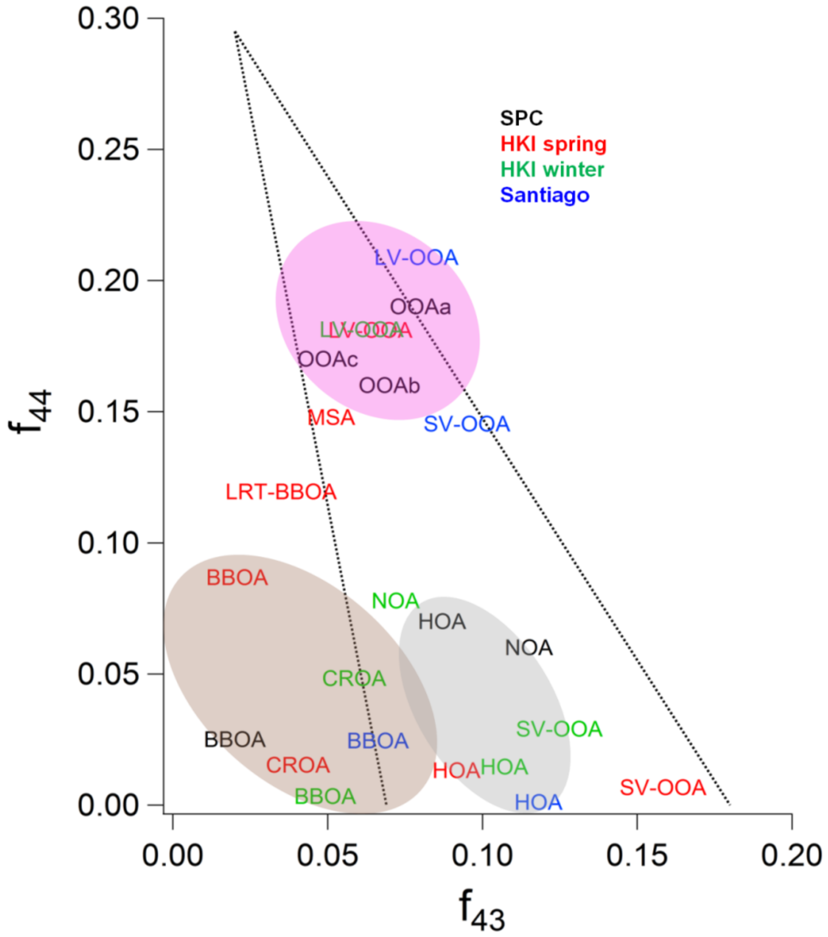


Figure 9 – Average f_{44} and f_{43} of each OA component in the four field experiments.

The effects of the photo-oxidation were also observed in Santiago de Chile and in Helsinki sites. A clear increase of the LV-OOA compared to the SV-OOA in the OA mass fraction was verified throughout the campaigns with the increase in the number of hours of sunshine (Papers IV and V). Such a change was probably a consequence of increased photochemical reactions and consequent enhance in the formation of atmospheric oxidants such as OH and peroxide radicals, ozone and nitrate radical important in the formation of SOA (Finlayson-Pitts and Pitts Jr., 2000; Seinfeld and Pandis, 2006).

4.2.4 Water-soluble organic carbon reconstruction

Water-solubility is an important property of OA that is not possible to obtain directly from the AMS data. Only a few studies have been published in which parallel high time-resolution WSOC and AMS measurements were conducted. Kondo et al. (2007) measured submicron aerosol properties with an AMS and PILS-TOC and they found that the signal at m/z 44 and the derived OOA mass concentrations were highly correlated.

Xiao et al. (2011) suggested to estimate the WSOC from the AMS OA components LV-OOA and SV-OOA. They found a good correlation (R=0.79) between measured and predicted WSOC concentrations. During the Helsinki springtime campaign, seven different OA components were identified and among them there were components representing local and long-range transported biomass burning, which has been considered as one of the main sources of WSOC (Miyazaki et al., 2006; Kondo et al., 2007). In fact, WSPOM correlated with CO and oxalate (r_{co}=0.85, $r_{oxalate}$=0.82) during episodes of LRT biomass burning smoke, indicating that the latter could be a substantial source of WSPOM (Paper I). In Paper III all OA components were used to reconstruct the WSOC-fraction. In the AMS results the OA components represented organic matter, therefore they were converted to organic carbon concentration using the observed OM:OC ratios (Table 1, Paper V) in order to be comparable with the TOC-V_{CPH} analyzer, which measured water-soluble fraction of organic carbon.

It is likely that all compounds extracted by PMF have water-soluble and water-insoluble fraction. Thereupon, the multiple linear regression (Igor 6.11) was used to estimate the coefficients for the OA components needed to reconstruct the WSOC fraction (Equation 4):

$$\begin{aligned} Y = {} & 0.88 \times LV - OOA + 0 \times (LV - OOA + MSA) + 1.63 \times LRT - BBOA + 0 \times CROA + \\ & 0.96 \times BBOA + 0.14 \times SV - OOA + 0.11 \times HOA \ , \end{aligned} \tag{4}$$

where Y was the WSOC measured by the TOC-V_{CPH} analyzer. The LV-OOA+MSA and CROA coefficients presented small negative values and for this reason were forced to be zero. The time series of the reconstructed WSOC presented good agreement with the measured WSOC (r=0.93), Figure 10. The results suggested elevated contribution of LV-OOA and BBOA's to the WSOC.

The low coefficient obtained for the LV-OOA+MSA indicated that this component is mostly water-insoluble. Although MSA itself is typically found in the WSOC fraction (Decesari et al., 2001) several studies reported that the submicron aerosol particles over the marine air were dominated by the WIOM fraction (O'Dowd et al., 2004; Cavalli et al., 2004; Facchini et al., 2008). It has been suggested that the OM transfer from the water surface to the atmosphere is facilitated by the bubble-bursting processes (Gershey, 1983; Facchini et al., 2008). Thus, it is most likely the reason for the water-insolubility character of this component.

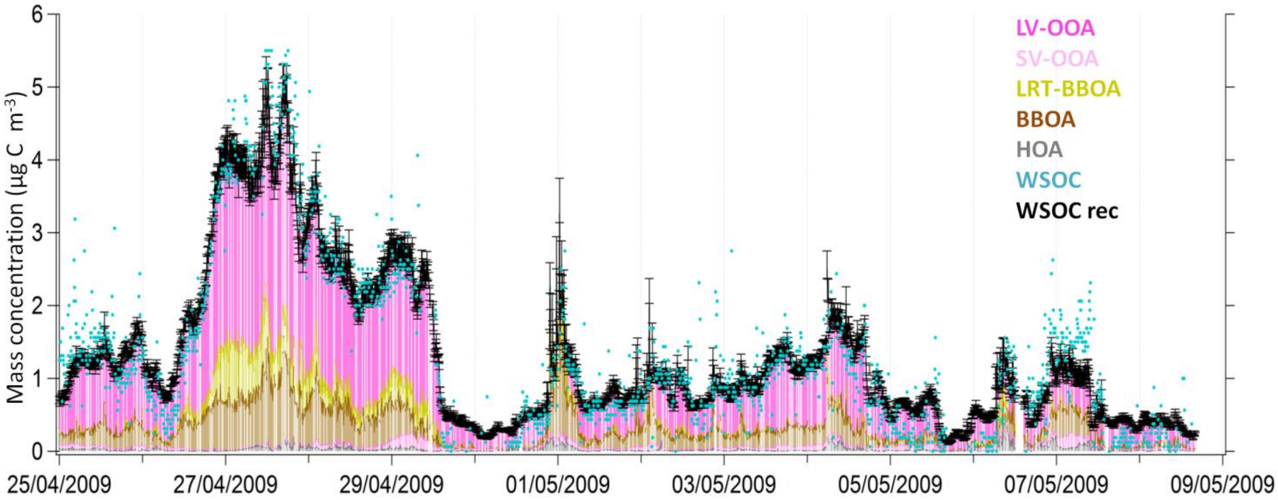


Figure 10 – Measured concentrations of WSOC (PILS-TOC-IC) and WSOC concentrations reconstructed from the PMF factors derived from the AMS organic fraction.

4.2.5 Refractory PM_1, characterization of rBC and trace metals with the SP-AMS

The refractory fraction of PM_1 is composed mainly of BC, metals, oxides, and sea-salt. In ambient studies their contribution to PM_1 is usually below 15% (Huang et al., 2010; Crippa et al., 2013, Papers II–V). In emission studies of fuel combustion by vehicles or of power and heat production, the R-PM_1 can represent up to 90% depending on the fuel and burning conditions employed (Happonen et al., 2013). Also elements, such as Na, V, Fe, Cr, and Ni has been found in the PM_1 fraction of heavy fuel oil emission (Sippula et al., 2009). Moreover, in emission studies when the changes in the chemical composition can be rapid due to characteristics of the burning process, an instrument that allows chemical characterization with high time-resolution, such as the SP-AMS, is extremely beneficial.

One example of mass size distribution (UMR) obtained with the SP-AMS during a field campaign in the SPC is depicted in Figure 11. The mass size distribution of the compound rBC were represented by the m/z 36, similar to proposed by Massoli et al. (2012). The m/z 36 was scaled according to the total rBC signal.

Although the detection of rBC by the SP-AMS was described by Onasch et al. (2012), the detection of metals remained uncharacterized. For this reason, the current thesis summarizes the main characteristics in the detection of the trace metals Na, Al, Ca, V, Cr, Fe, Mn, Ni, Cu, Zn, Rb, Sr, and Ba. Laboratory experiments conducted with metal solutions and generation of monodisperse (mobility diameter, d_m=300 nm) aerosol particles proved the feasibility of the detection of metals though the isotopic patterns, Figure 12 (Carbone et al., in preparation). For example, the isotopes ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, ^{138}Ba, which corresponded to 99.79% of the total mass of Ba were identified by the SP-AMS with similar isotopic compositions as reported by NIST database

(Watson et al., 2004). The ratios between the measured isotopic compositions and the NIST database are displayed in Figure 12.

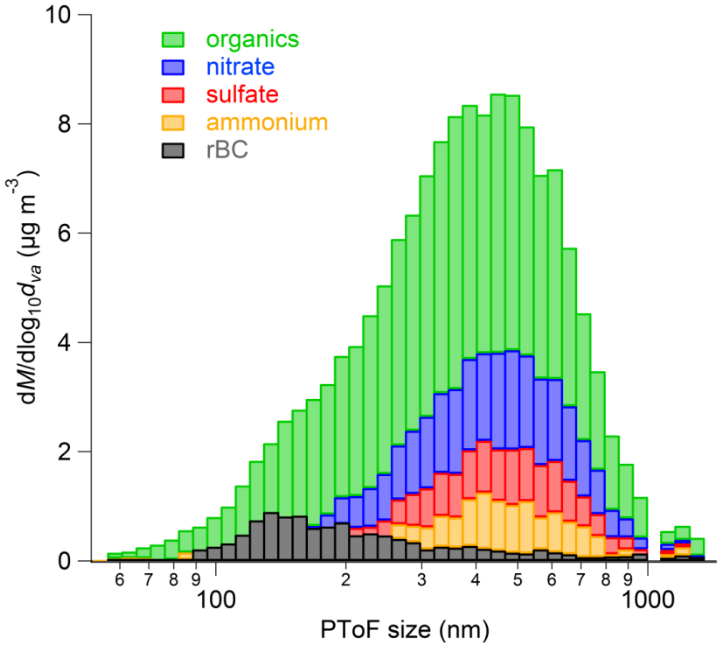


Figure 11 – Ambient average mass size distribution of the compounds organics, nitrate, ammonium, sulfate, and rBC measured by the SP-AMS during a field study in the SPC site during the summer time in the year 2012. The different compounds are stacked on each other.

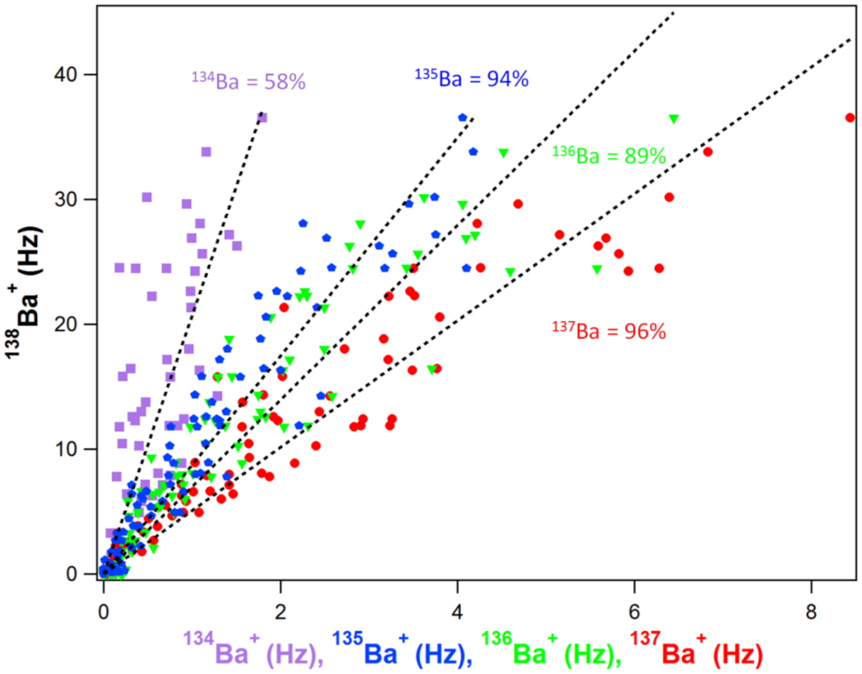


Figure 12 – Average signal of the barium isotopes measured by the SP-AMS in the laboratory. The percentages represent the ratio of the isotopic compositions measured and the theory.

An interesting feature during the quantification process was that some metals (Rb, Na, Ba, Sr, Al, Ca, V, Cr) presented the ionization efficiency relative to C_3 much higher than predicted by the theory, from 2 to 100 times higher. The explanation is that those metals were being surface ionized on the hot surface of the rBC particles, typically around 4000 ºC. Thereupon, the overestimation was due to two parallel ionization processes occurring concomitantly, surface ionization, and electron impact ionization. The first was much more efficient for low ionization energy ions. This fact was verified when the experiment was repeated under similar conditions, however with tungsten vaporizer and ionizer off. Further details and results on the quantification process, relative ionization efficiency values, of each metal measured by the SP-AMS are discussed in Carbone et al. (in preparation).

Another important characteristic of the metals was that in mass spectrometry they present negative mass defect. That is, they are located on the right side of the nominal mass and in most cases separated from the hydrocarbon and oxygenated fragments, which facilitates their identification in the MS. One mass spectrum measured by the SP-AMS during a study to investigate heavy fuel oil power plant emissions illustrates the mass defect of the different fragments of organics, nitrate, sulfate, ammonium, rBC and the metals, Figure 13.

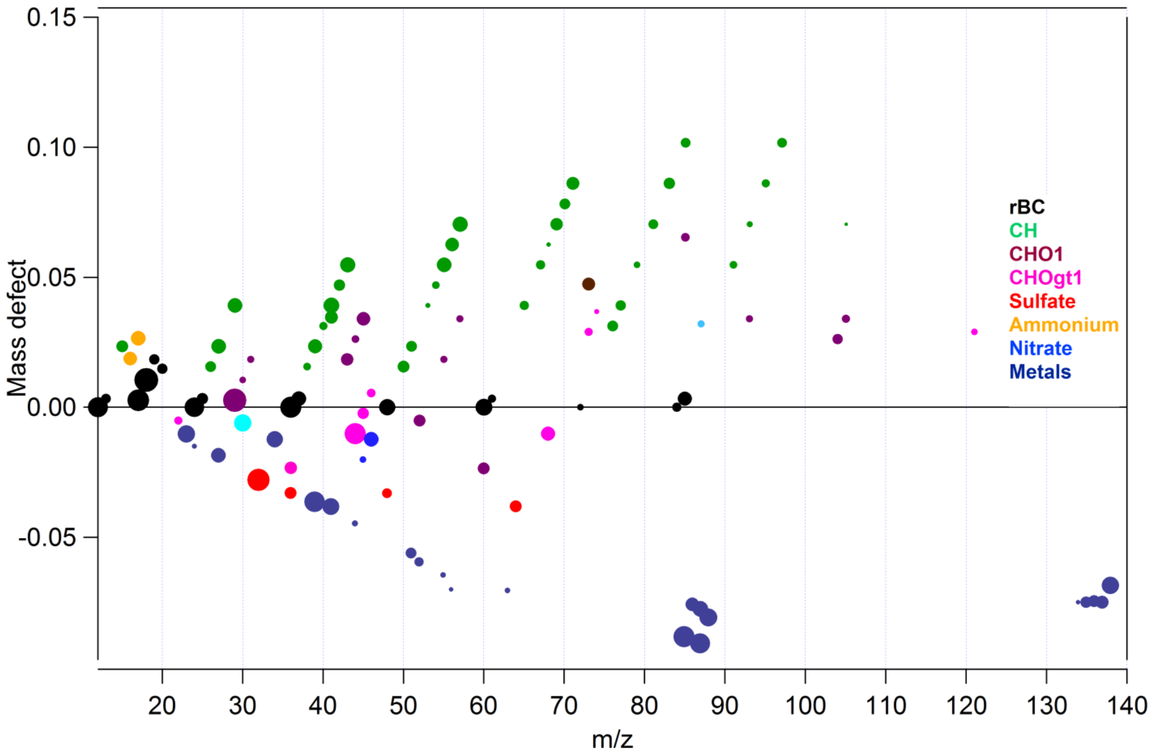


Figure 13 – Average mass defect measured for a heavy-fuel oil power plant emission.

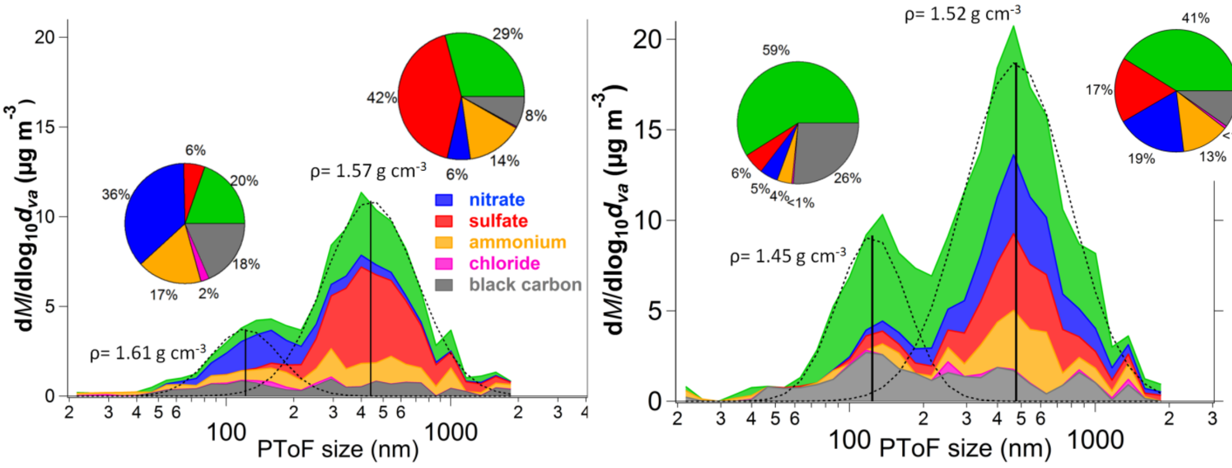
4.3 Chemically-solved aerosol size distribution

Instruments such as DMPS provide high time-resolution (typically of the order of minutes) size distribution information of PM. However, it does not provide information concerning the chemical composition of PM. In the case of other offline instruments such as, filter sampling information regarding the composition is possible, however with much lower time resolution (12–24 hours). Hence, the AMS fills an important gap in aerosol science providing both chemical composition information and high time-resolution, typically a few minutes in ambient datasets depending on the mass load. One drawback in the AMS concerning mass size distribution data is the limitation imposed by the aerodynamic lenses in the inlet in which a 100% transmission only occurs from 70–500 nm (in vacuum aerodynamic diameter, d_{va}) decreasing rapidly before and after that (Jayne et al., 2000). For this reason, in cases when the accumulation mode is centered at the edges of the lenses transmission, part of the mass will not be measured.

High time-resolution size distribution measurements enabled characterization of chemical composition of externally mixed aerosol where different size modes originated from different sources. One interesting application in determining the size-resolved chemical composition of the different aerosol modes is that those might be related to different sources. To illustrate this fact, Figure 14 shows the average mass size distributions for two short episodes during the Helsinki wintertime. On both mass size distributions two modes are evinced, a lower and an accumulation mode centered at ~130 and 470 nm, respectively. The compositions of the two lower modes are more contrasting than in the accumulation modes of each episode. The lower mode of the first episode was dominated by nitrate (36%), whereas the organics dominated the mass fraction of this mode in the second episode (59%). When the lower mode of the first episode was investigated more closely the presence of this mode during morning rush hours indicated that it was likely from traffic emissions (Paper V).

During the second episode, the average mass spectrum of each mode was obtained and revealed that the lower mode was dominated by the fragments also found in the CROA MS (m/zs 67, 82, 109, and 194) suggesting that this mode was mostly related to emissions from the coffee roasteries.

Another important consequence of the different chemical composition in the lower modes was the difference in the aerosol densities. The density in each mode was calculated assuming the average concentration for each compound and the following values of 1.78, 1.72, 1.72, 1.52, and 1.77 g cm^{-3} for sulfate, nitrate, ammonium, chloride, and BC, respectively (Lide, 1991; Park et al., 2004). The average density of organics during the whole experiment was estimated based on the oxygen to carbon (O:C) and hydrogen to carbon (H:C) ratios from elemental analyses of AMS data (Kuwata et al., 2012) and the value 1.19±0.1 g cm^{-3} was used. The high amount of nitrate in the first episode resulted in higher aerosol density (σ=1.61 g cm^{-3} for the first episode and 1.45 g cm^{-3} for the second), which suggested that the AMS could be overestimating the mass in this mode due to the acidity and therefore a correction for the collection efficiency factor (CEF) might be needed for this mode. A CEF based on the parameterization proposed by Middlebrook et al. (2012) was applied in this study (Paper V). However, that did not contain a correction for the different modes. The elevated fraction of nitrate and likely acidic character could have implications on the particles hygroscopicity and SOA formation (Gao et al., 2004; Khlystov et al., 2005).



(a) (b)

Figure 14 – Average mass size distributions of the main aerosol components, organics, nitrate, sulfate, ammonium, chloride, and BC (the fragment $C_4H_9^+$ was used as surrogate to BC, Zhang et al., 2004) measured by the AMS for two episodes in Helsinki during the wintertime (Paper V).

5. Review of papers and author's contribution

Paper I describes a new online method, PILS-TOC-IC, developed to measure WSOC and ion concentrations of ambient aerosol particles online. The results of the PILS-TOC-IC were compared to other parallel online measurements, AMS, semi-continuous EC/OC and TEOM. The online measurements provided insights about the sources and formation mechanisms of ambient aerosol particles. I operated the AMS during the field campaign, analyzed the AMS data and participated in the preparation of the paper.

Paper II presents a comprehensive chemical characterization of PM_1 over the Po Valley (SPC) with AMS and filter sampling. The latter was analyzed to investigate EC, OC, WSOC, inorganic ions, organic acids and levoglucosan with the techniques, IC-CD, IC-MS, and HPAEC-MS. Insights concerning the aerosol processing and application of PMF to the OA are described. I have analyzed the AMS data, including the PMF analysis, and participated to the preparation of the paper.

Paper III investigates the water-solubility character of the OA in Helsinki springtime using the AMS. It contains the water-solubility reconstruction from the AMS OA components. Moreover, the local and LRT origin of the OA were discussed. I operated the AMS during the field campaign, processed and analyzed the data, including the PMF application. I also participated to preparation of the paper.

Paper IV contains a description of the PM_1 chemical composition in a long-term field campaign in Santiago de Chile with the ACSM. It also describes the OA evolution throughout the campaign and verified the semi-volatile character of the SV-OOA. I participated in the instrumentation setup, data processing and analysis (including the PMF application), and wrote the paper.

Paper V provides information concerning the chemical composition of PM_1 in a sub-arctic urban environment during the wintertime. It provided a detailed description of the OA components and further investigation on the size-resolved chemical composition of three distinct episodes. I operated the AMS during the field campaign, processed and analyzed the AMS data (including the PMF application), and wrote the paper.

6. Conclusions

Field studies and laboratory experiments were performed with three different high time-resolution aerosol mass spectrometers aiming to better characterize the PM_1 composition and sources. The field studies were performed at three different sites: rural, urban, and background urban with the HR-ToF-AMS and ACSM, instruments that measured only the NR-PM_1. For this reason the new SP-AMS was further characterized in order to evaluate its feasibility to detect trace metals.

PMF was applied to the mass spectrometers datasets and 11 different components of the OA were identified, 6 types of OOAs, one containing substantial organosulfate fragments from MSA, LRT-BBOA, NOA, local BBOA, CROA, and HOA. The last three most likely represent the POA, while the others represent the SOA. The OM was dominated by aerosol particles of secondary origin (65%). The elevated contribution of SOA during the Helsinki wintertime, the time of the year when the solar radiation is extremely low, suggested the presence of strong atmospheric oxidants, and the importance of water in the OA oxidation process.

Moreover, when the OA components were investigated as a function of their levels of oxidation in the atmosphere (f_{44} vs f_{43}) all the OOAs were clustered on the uppermost region of the triangle diagnostic representing the highly oxidized fraction of the OA. In addition, the BBOAs and HOAs clustered around similar regions of the triangle, both with similar values of f_{44}, however different for f_{43}. The CROA also clustered around the BBOA region suggesting similarities between the roasting and burning processes. The BBOA revealed the presence of two distinct origins, one local likely from domestic heating and another LRT BBOA from forest fires in eastern Europe. The LRT BBOA component did not cluster around the BBOA area probably due to its high oxidized character and distinct source.

Different properties of the PM_1 were investigated and revealed more information about its composition and sources. A comparison of the AMS data with those from additional instrumentation indicated that most of the PM_1 was NR. The water-solubility of the OM indicated that the LV-OOA and the LRT-BBOA were the most water-soluble components. The SV-OOA presented clear semi-volatile character when investigated as a function of the local air temperature, decreasing in concentration with the air temperature enhance. Concerning the aerosol neutralization, in most sites the results indicated enough ammonium to neutralize the major inorganic anions, except for Helsinki during wintertime when the aerosol particles were acidic most of the time. The size-resolved chemical composition was investigated in detail to different episodes and revealed internally and externally mixed aerosol particles in two different modes, an accumulation (~470 nm) and a lower mode (~130nm). The different modes were composed of different compounds and suggested a rather acidic lower mode mainly dominated by nitrate most likely from local traffic emissions.

In addition to the field studies, laboratory experiments were accomplished in order to characterize the feasibility of detection of trace metals by the SP-AMS. The determination of isotopic patterns and the relative ionization efficiencies for 13 different metals successfully confirmed this possibility. Furthermore, the negative mass defect, typical from metals, was observed useful in their identification in the MS. The measurement of trace metals by the SP-AMS represents a step forward in the study of sources and might be extremely useful in the next source apportionment studies.

However, a few points remain not fully understood. The origin and composition of the nitrogen compounds in the NOA found in Helsinki and the true functional groups that compose each OA component remain unknown. In addition, other refractory materials, such as oxides and metal oxides remain uncharacterized and could be relevant in certain applications, for instance in emission studies. Source apportionment using the metals measured by the SP-AMS could be powerful in the identification of natural and anthropogenic sources of PM_1.

References

Alfarra, M. R., Prévôt, A. S. H., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., Schreiber, D., Mohr, M., and Baltensperger, U.: Identification of the mass spectral signature of organic aerosols from wood burning emissions, Environ. Sci. Technol., 41, 5770–5777, 2007.

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty, K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A., Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan, V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P., Molina, L. T., Sosa, G., Jimenez, J. L.: Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine particle composition and organic source apportionment, Atmos. Chem. Phys., 9, 6633–6653, 2009.

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aeros. Sci., 35, 909–922, 2004.

Allen, A. G., Nemitz, E., Shia, J. P., Harrison, R. M., Greenwood, J. C.: Size distributions of trace metals in atmospheric aerosols in the United Kingdom, Atmos. Environ., 35, 4581–4591, 2001.

Anttila, P., Paatero, P., Tapper, U., Järvinen, O.: Source identification of bulk wet deposition in Finland by positive matrix factorization, Atmos. Environ., 29, 1705–1718, 1995.

Bahreini, R., Middlebrook, A. M., Gouw, J. A., Warneke, C., Trainer, M., Brock, C. A., Stark, H., Brown, S. S., Dube, W. P., Gilman, J. B., Hall, K., Holloway, J. S., Kuster, W. C., Perring, A. P., Prevot, A. S. H., Schwarz, J. P., Spackman, J. R., Szidat, S., Wagner, N. L., Weber, R. J., Zotter, P., Parris, D. D.: Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass, Geophys. Res. Lett., 39, L06805, 2012.

Bruyn, W. J. D., Bates, T. S., Cainey, J. M., Saltzman, E. S.: Shipboard measurements of dimethyl sulfide and SO2 southwest of Tasmania during the first aerosol characterization experiment (ACE 1), J. Geophys. Res., 103(D13), 16703–16711, 1998.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, D14203, 2004.

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., Worsnop, D. R.: Chase Studies of Particulate Emissions from in use New York City Vehicles, Aeros.. Sci. Technol., 38, 555–573, 2004.

Carlton, A. G., Wiedinmyer, C., Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987–5005, 2009.

Carbone, S., Onasch, T., Timonen, H., Saarikoski, Saarnio, K., S., Sueper, D., Worsnop, D., Hillamo, R.: Trace metals characterization with the SP-AMS: detection and quantification, in preparation.

Cavalli, F., Facchini, M. C., Decesari, S., Emblico, L., Mircea, L., Jensen, M. N. R., Fuzzi, S.: Size-segregated aerosol chemical composition at a boreal site in southern Finland, during the QUEST project, Atmos. Chem. Phys., 6, 993–1002, 2006.

Cavalli, F., Facchini, M. C., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J.-P., Dell'Acqua, A.: Advances in identification of organic matter in marine aerosol. J. Geophys. Res., 109, 2004.

Cautreels, W., Van Cauwenberghe, K.: Determination of organic compounds in airborne particulate matter by gas chromatography-mass spectrometry, Atmos. Environ., 10(6), 447–457, 1967.

Covert, D. S., Waggoner, A. P., Weiss, R. E., Ahlquist, N. C., Charlson, R. J.: Atmospheric aerosols, humidity, and visibility, Adv. Environ. Sci. Technol., 9, 1980.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A. and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, Atmos. Chem. Phys., 11,12049–12064, 2011.

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., José, N., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, Atmos. Chem. Phys., 13, 961–981, 2013.

Currie, L. A.: Evolution and multidisciplinary frontiers of 14C, aerosol science, Radiocarbon, 42, 115–126, 2000.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., Jimenez, J. L.: Field-deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal. Chem. 78, 8281–8289, 2006.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, C., Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 9, 4987–5005, 2008.

Decesari, S., Facchini, M. C., Fuzzi, S., Tagliavini, E.: Characterizations of water-soluble organic compounds in atmospheric aerosols: a new approach, J. Geophys. Res. 105, 1481–1489, 2000.

Decesari, S., Facchini, M. C., Matta, E., Lettini, F., Mircea, M., Fuzzi, S., Tagliavini, E., and Putaud, J.-P.: Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy, Atmos. Environ., 35, 3691–3699, 2001.

Després, V. R., Nowoisky, J. F., Klose, M., Conrad, R., Andreae, M. O., Pöschl, U.: Characterization of primary biogenic aerosol particles in urban, rural, and high-alpine air by DNA sequence and restriction fragment analysis of ribosomal RNA genes, Biogeoscienc., 4, 1127–1141, 2007.

Docherty, K. S., Stone, E. A., Ulbrich, I. M., DeCarlo, P. F., Snyder, D. C., Schauer, J. J., Peltier, R. E., Weber, R. J., Murphy, S. M., Seinfeld, J. H., Eatough, D. J., Grover, B. D., and Jimenez, J. L.: Apportionment of primary and secondary organic aerosols in Southern California during the 2005 study of organic aerosols in riverside (SOAR), Environ. Sci. Technol., 42, 7655–7662, 2008.

Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., Samet, J. M.: Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases, J. Americ. Medic. Assoc., 295(10), 1127–1134, 2006.

Environmental European Agency report: Air Quality in Europe - report 2013, Denmark, available at http://www.eea.europa.eu/publications/air-quality-in-europe-2013, 2013.

European Committee, Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, available at: http://eur-lex.europa, 2008.

Finlayson-Pitts, B. J. and Pitts Jr., J. N.: Chemistry of the upper and lower atmosphere, Academic Press, San Diego, 2000.

Facchini, M. C., Rinaldi, M., Decesari,S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., O’Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, 2008.

Fu, P., Kawamura, K., Kanaya, Y., Wang, Z.: Biogenic contributions of biogenic volatile organic comounds to the formation of secondary organic aerosols over Mt. Tai, Central East China, Atmos. Environ. 44, 4817–4826, 2010.

Gao, Y., Nelson, E. D., Field, M. P., Ding, Q., Li, H., Sherrell, R. M., Gigliotti, C. L., Ry, D. A. V., Glenn, T. R., Eisenreich, S. J., Characterization of atmospheric trace elements on $PM_{2.5}$ particulate matter over the New York-New Jersey harbor estuary, Atmos. Environ. 36, 1077–1086, 2002.

Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., Seinfeld, J., H.: Partcile phase acidity and oligomer formation in secondary organic aerosol, Environ. Sci. Technol., 38, 6582–6589, 2004.

Gershey, R. M.: Characterization of seawater organic matter carried by bubble-generated aerosols, Limnol. Oceanogr., 28, 309–319, 1983.

Griffin, R. J., Cocker, D. R., Flagan, R. C., Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104, 3555–3567, 1999.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys., 6, 3181–3210, 2006.

Guo, S., Hu, M., Guo, Q., Zhang, X., Zheng, M., Zheng, J., Chang, C. C., Schauer, J. J., Zhang, R.: Primary Sources and Secondary Formation of Organic Aerosols in Beijing, China, Environ. Sci. Technol., 46, 9846–9853, 2012.

Happonen, M., Mylläri, F., Karjalainen, P., Frey, A., Saarikoski, S., Carbone, S., Hillamo, R., Pirjola, L., Häyrinen, A., Kytömäki, J., Niemi, J. V., Keskinen, J., Rönkkö, T.: 2013, Size Distribution, Chemical Composition, and Hygroscopicity of Fine Particles Emitted from an Oil-Fired Heating Plant, Environ. Sci. Technol., 24, 14468–14475, 2013.

He, L.-Y., Hu, M., Huang, X.-F., Yu, B.-D., Zhang, Y.-H., Liu, D.-Q.: Measurement of emissions of fine particulate organic matter from Chinese cooking, Atmos. Environ., 38, 6557–6564, 2004.

Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., Farmer, D. K., Artaxo, P., Weinheimer, A. J.: A simplified description of organic aerosol composition and implications for atmospheric aging. Geophys. Res. Lett., 37, L08803, 2010.

Henning, S., Weingartner, E., Schwikowski, M., Gaggeler, H. W., Gehrig, R., Hinz, K. P., Trimborn, A., Spengler, B., Baltensperger, U.: Seasonal variation of water-soluble ions of the aerosol at the high-alpine site Jungfraujoch (3580 m asl), J. Geophys. Res., 108 (D1), 4030, 2003.

Hennigan, C. J., Bergin, M. H., Dibb, J. E., Weber, R. J.: Enhanced secondary organic aerosol formation due to water uptake by fine particles, Geophys. Res. Lett., 35, L18801, 2008.

Hering, S., Cass, G.: The magnitude of the bias in the measurement of $PM_{2.5}$ arising from volatilization of particulate nitrate from Teflon filters, J. Air Waste Manag. Assoc., 49, 725–733, 1999.

Henry, R. C. in: Hopke, P. K. (Ed.), Multivariate Receptor Models in Receptor Modeling for Air Quality Management, Elsevier, New York, 117–148, 1991.

Hopke, P. K., Xie, Y, Paatero, P.: Mixed multiday analysis of airborne particle composition data, J. Chemom., 1999, 13, 343–352.

Hoffmann, E., Stroobant, V.: Mass Spectrometery – Principles and Applications. 3rd ed. John Wiley & Sons, Ltd., Chichester, England, 2007.

Huang, X.-F., He, L.-Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L.-W., Liu, X.-G., Zhang, Y.-H., Jayne, J. T., Ng, N. L., Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 10, 8933–8945, 2010.

Huffman, J. A., Docherty, K. S., Aiken, A. C., Cubison, M. J., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Jayne, J. T., Worsnop, D. R., Ziemann, P. J., Jimenez, J. L.: Chemically-resolved aerosol volatility measurements from two megacity field studies. Atmos. Chem. Phys., 9, 7161–7182, 2009.

IPCC, 2013: Summary for Policymakers. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA

Khlystov, A., Stanier, C. O., Takahama, S., Pandis, S. N.: Water content of ambient aerosol during the Pittsburgh Air Quality Study, J. Geophys. Res., 110, D07S10, doi:10.1029/2004JD004651, 2005.

Kim, Y., Sartelet, K., Seigneur, C.: Formation of secondary aerosols over Europe: comparison of two gas-phase chemical mechanisms, Atmos. Chem. Phys., 11, 583–598, 2011.

Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo. J. Geophys. Res., 112, D011203, 2007.

Krivacsy, Z., Gelencsér, A., Kiss, G., Mészáros, E., Molnár, A., Hoffer, A., Mészáros, T., Sárvári, Z., Temesi, D., Varga, B., Baltensperger, U., Nyeki, S., Weingartner, E.: Study on the chemical character of water soluble organic compounds in the fine atmospheric aerosol at the Jungfraujoch, J. Atmos. Chem., 39, 235–259, 2001.

Kourtchev, I., Ruuskanen, T., Maenahut, W., Kulmala, M., Claeys, M.: Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland, Atmos. Chem. Phys., 4, 2761–2770, 2005.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nat. Chem., 3, 133–139, 2011.

Kuwata, M., Zorn, S. R., Martin, S.T.: Using elemental ratios to predict the density of organic material composed of carbon, hydrogen, and oxygen, Environ. Sci. Technol., 46, 787–794, 2012.

Jaenicke, R.: Abundance of cellular material and proteins in the atmosphere, Sci., 308, 73–73, 2005.

Jaffrezo, J. L., Aymoz, G., Delaval, C., Cozic, J.: Seasonal variations of the water-soluble organic carbon mass fraction of aerosol in two valleys of French Alps, Atmos. Chem. Phys., 5, 2809–2821, 2005.

Järvi, J., Hannuniemi, H., Hussein, T., Junninen, H., Aalto, P. P., Hillamo, R., Mäkelä, T., Keronen, P., Siivola, E., Vesala, T., Kulmala, M.: The urban measurement station SMEAR III: Continuous monitoring of air pollution and surface-atmosphere interactions in Helsinki, Finland. Bor. Environ. Res. 14(suppl. A), 86–109, 2009.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., Worsnop, D. R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. Aeros. Sci. Technol., 33, 49–70, 2000.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Sci., 326, 1525–1529, 2009.

Juntto, S., Paatero, P.: Analysis of daily precipitation data by positive matrix factorization, Environmetr., 5, 127–144, 1994.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Aardenne, J. V., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, K., Vuuren, D. P.: Historical (1850-2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, 2010.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503–1522, 2007.

Lei, Y., Zhang, Q., He, K. B., Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990-2005, Atmos. Chem. Phys., 11, 931–954, 2011.

Lide, D.R.:. CRC Handbook of Chemistry and Physics, CRC Press Inc, USA, 1991.

Lee, T., Sullivan, A. P., Mack, L., Jimenez, J. L, Kreidenweis, S. M., Onasch, T. B., Worsnop, D. R., Malm, W, Wold, C. E., Hao, W. M., Collett, J. L.: Variation of Chemical Smoke Marker Emissions During Flaming vs. Smoldering Phases of Laboratory Open Burning of Wildland Fuels, Aeros. Sci. Technol., 44(9), i–v, 2010.

Junninen, H., Ehn, M., Patäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., Worsnop, D. R.: Atmos. Meas. Tech., 3, 1039–1053, 2010.

Massoli, P., Fortner, E. C., Canagaratna, M. R., Williams, L. R., Zhang, Q., Sun, Y., Schwab, J. J., Trimborn, A., Onasch, T. B., Demerjian, K. L., Kolb, C. E., Worsnop, D. R., Jayne, J. T.: Pollution Gradients and Chemical Characterization of Particulate Matter from Vehicular Traffic near Major Roadways: Results from the 2009 Queens College Air Quality Study in NYC, Aeros. Sci. Technol., 46, 1201–1218, 2012.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., Canagaratna, M. R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, Aeros. Sci. Technol., 46, 258–271, 2012.

Minguillón, M. C., Perron, N., Querol, X., Szidat, S., Fahrni, S., Alastuey, A., Jimenez, J. L., Mohr, C., Ortega, A., Day, D. A., Lanz, V. A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Penuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J., Baltensperger, U., Prevot, A. S. H.: Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain, Atmos. Chem. Phys., 11, 12067–12084, 2011.

Miyazaki, Y., Kondo, Y., Takegawa, N., Komazaki, Y., Kawamura, K., Mochida, M., Okuzawa, K., Weber, R. J.: Time-resolved measurements of water-soluble organic carbon in Tokyo, J. Geophys. Res.,111, D23206, 2006.

Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbrich, I. M., Hannigan, M., and Jimenez, J. L.: Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor vehicles with high-resolution aerosol mass spectrometry and comparison with ambient and chamber observations, Environ. Sci. Technol., 43, 2443–2449, 2009.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prévôt, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, Atmos. Chem. Phys., 12, 1649–1665, 2012.

Mukai, H., Ambe, Y., Morita, M.: Flow injection inductively coupled plasma mass spectrometry for the determination of platinum in airborne particulate matter, J. Anal. At. Spectrom., 5, 75–80, 1990.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C. and Seinfeld, J. H.: Secondary aerosol formation from atmospheric reactions of aliphatic amines. Atmos. Chem. Phys., 7, 2313–2337, 2007.

Nazarenko, L. and Menon, S.: Varying trends in surface energy fluxes and associated climate between 1960 and 2002 based on transient climate simulations, Geophys. Res. Lett., 32(22), 2005.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., Worsnop, D. R.: Organic aerosol components observed in northern hemispheric datasets from aerosol mass spectrometry, Atmos. Chem. Phys., 10, 4625–4641, 2010.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aeros. Sci. Tech., 45, 770–784, 2011.

Niemi, J. V., Saarikoski, S., Aurela, M., Tervahattu, H., Hillamo, R., Westphal, D. L., Aarnio, P., Koskentalo, T., Makkonen, U., Vehkamäki, H., Kulmala, M.: Long-range transport episodes of fine particles in southern Finland during 1999–2007, Atmos. Environ., 43, 1255–1264, 2009.

Nober, F. J., Graf, H.-F., Rosenfeld, D.: Sensitivity of the global circulation to the suppression of precipitation by anthropogenic aerosols, Glob. Planet. Chan., 37, 57–80, 2003.

Norris, J. R., Wild, M.: Trends in aerosol radiative effects over Europe inferred from observed cloud cover, solar "dimming" and solar "brightening", J. Geophys. Res., 112(D8), 2007.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., Putaud, J.-P.: Biogenically driven organic contribution to marine aerosol, Nat., 431, 676–680, 2004.

Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., Worsnop, D. R.: Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application, Aeros. Sci. Technol., 46, 804–817, 2012.

Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G., Worsnop, D. R., O'Dowd, C.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, J. Geophys. Res., 117, D16201, 2012.

Pakkanen, T. A., Kerminen, V.-M., Korhonen, C. H., Hillamo, R., Aarnio, P. Koskentalo, T., Maenhaut, W.:. Use of atmospheric elemental size distributions in estimating aerosol sources in the Helsinki area, Atmos. Environ., 3, 55537–5551, 2001.

Pakkanen, T., Hillamo, R.: Comparison of sampling artifacts and ion balances for a Berner low-pressure impactor and a virtual impactor, Bor. Environ. Res., 7, 129–140, 2002.

Paatero, P., Tapper, U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetr., 5, 111–126, 1994.

Park, K., Kittelson, D. B., Zachariah, M. R., McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates. J. Nanopart. Res., 6, 267–272, 2004.

Pathak, R. K., Chang, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of $PM_{2.5}$ in filter-based samplers, Atmos. Environ., 39, 1598–1607, 2005.

Pathak, R. K., Wang, T., Ho, K. F., Lee, S. C.: Characteristics of summertime $PM_{2.5}$ organic and elemental carbon in four major Chinese cities: Implications on high acidity for water-soluble organic carbon (WSOC), Atmos. Environ., 45, 318–325, 2011.

Penner, J. E.: Carbonaceous aerosols influencing atmospheric radiation: Black and organic carbon, in: Aerosol Forcing of Climate, edited by: Charlson, R. J. and Heintzenberg, J., Wiley and Sons, Chichester, 91–108, 1995.

Phillips, V. T. J., Alan, T. W. C., Blyth, M., Latham, J.: The influence of aerosol concentrations on the glaciation and precipitation of a cumulus cloud, Quarter. J. Roy. Meteorol. Soc., 128(581), 951–971, 2002.

Phinney, L., Leaitch, W. R., Lohmann, U., Boudries, H., Worsnop, D. R., Jayne, J. T., Toom-Sauntry, D., Wadleigh, M., Sharma, S., Shantz, N.: Characterization of the aerosol over the sub-arctic northeast Pacific Ocean. Deep-Sea Research Part II, 53, 2410–2433, 2006.

Pirinen, P., Simola, H., Aalto, J., Kaukoranta, J. P., Karlsson, P., Ruuhela, R.: Tilastoja Suomen ilmastosta 1981-2010. Finnish Meteorological Institute, Finland, p. 83, 2012.

Prather, K. A., Nordmeyer, T., Salt, K.: Real-time characterization of individual aerosol particles using time-of-flight mass spectrometry, Anal. Chem., 66, 1403–1407, 1994.

Pope, C. A., Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manag. Assoc., 56(6), 709–742, 2006.

Putaud, J. P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F.: A European aerosol phenomenology – 3: Physical and chemical characteriatics of particulate matter from 60 rural, urban, and kerbside sites across Europe, Atmos. Environ., 44, 1308–1320, 2010.

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, P., de la Rosa, J., Sánchez de la Campa, A., Artinano, B., Salvador, P., Garcia Dos Santos, S., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillon, M. C., Monfort, E., Gil, J. I., Inza, A., Ortega, L. A., Santamaria, J. M., Zabalza, J.: Source origin of trace elements in PM from regional background, urban and industrial sites of Spain, Atmos. Environ., 41, 7219–7231, 2007.

Ramanathan, V., Li, F., Ramana, M. V., Praveen, P. S., Kim, D., Corrigan, C. E., Nguyen, H., Stone, E. A., Schauer, J. J., Carmichael, G. R., Adhikary, B., Yoon, S. C.: Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing, J. Geophys. Res. Atmos., 112(D22), 27, 2007.

Ramanathan, V., Carmichael, G.: Global and regional climate changes due to black carbon, Nat. Geosci., 1, 221–227, 2008.

Riediker, M., Cascio, W. E., Griggs, T. R., Herbst, M. C., Bromberg, P. A., Neas, L., Williams, R. W., Devlin, R. B.: Particulate Matter Exposure in Cars Is Associated with Cardiovascular Effects in Healthy Young Men, Am. J. Respir. Crit. Care Med., 169, 934–940, 2004.

Robinson, E., Robbins, E. C.: Gaseous Nitrogen Compound Pollutants from Urban and Natural Sources, J. Air Pollut. Contr. Assoc., 20(5), 303–306, 1970.

Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., Simoneit, B. R. T.: Quantification of urban organic aerosols on a molecular level: Identification, abundance and seasonal variation, Atmos. Environ., 27, 1309–1330, 1993.

Romanou, A., Liepert, B., Schmidt, G. A., Rossow, W. B., Ruedy, R. A., Zhang, Y.: 20th century changes in surface solar irradiance in simulations and observations, Geophys. Res. Lett., 34(5), 2007.

Rogula-Kozlowska, W., Klejnowski, K.: Submicrometer aerosol in rural and urban backgrounds in southern Poland: primary and secondary components of PM_1, Bull. Environ. Contam. Toxicol., 90, 103–109, 2013.

Romo-Kröger, C. M., Morales, J. R., Dinator, M. I., Llona, F.: Heavy metals in the atmosphere coming from a copper smelter in Chile, Atmos. Environ., 28(4), 705–711, 1994.

Russell, L. M., Bahadura, R., Ziemann, P. J.: Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles, PNAS, 3516–3521, 108, 9, 2011.

Saarnio, K., Niemi, J. V., Saarikoski, S., Aurela M., Timonen, H., Teinilä, K., Myllynen, M., Frey, A., Lamberg, H., Jokiniemi, J., Hillmao, R.: Using monosaccharide anhydrides to estimate the impact of wood combustion on fine particles in the Helsinki Metropolitan Area, Bor. Env. Res., 17, 163–183, 2012.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., Hillamo, R.: Sources of organic carbon in PM_1 in Helsinki urban air, Atmos. Chem. Phys., 8, 6281–6295, 2008.

Saxena, P., Hildemann, L. M.: Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, J. Atmos. Chem., 24, 57–109, 1996.

Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M. O., and Kirchner, U.: Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles, Int. J. Mass. Spectrom., 258, 37–49, 2006.

Schwarze, P. E., Øvrevik, J., Lång, M., Refsnes, M., Nafstad, P., Hetland, R. B., Dybing, R.: Particulate matter properties and health effects: consistency of epidemiological and toxicological studies, Hum. Experim. Toxicol., 25, 559–579, 2006.

Sellegri, K., Hanke, M., Umann, B., Arnold, F., Kulmala, M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, Atmos. Chem. Phys., 5, 373–384, 2005.

Simoneit, B. R. T., Mazurek, M. A.: Organic matter of the troposphere-II. Natural background of biogenic lipid matter in aerosols over the rural western United States, Atmos. Environ., 16, 2139–2159, 1982.

Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J.: Comparison of particle emissions from small heavy fuel oil and woodfire boilers. Atmos. Environ., 43, 4855–4864, 2009.

Spicer, C. W., Kenny, D. V., Chapman, E., Busness, K. M., Berkowitz, C. M.: Observations of dimethyl sulfide over western North Atlantic Ocean using an airborne tandem mass spectrometer, J. Geophys. Res., 101(D22), 19137–29147, 1996.

Sofiev, M., Prank, M., and Baklanov, A. (Eds.): Influence of Regional Scale Emissions on Megacity Air Quality, MEGAPOLI Scientific Report 11–12, available at: http://megapoli.dmi.dk/publ/MEGAPOLI sr11-12.pdf, 2011.

Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., Pavoni, B.: Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy), Atmos. Chem. Phys., 13, 1927–1939, 2013.

Stockwell, W. R., Calvert, J. G.: The mechanism of the HO-SO_2 reaction, Atmos. Environ., 17, 2231–2235, 1983.

Seinfeld, J. H., Pandis, S. N.: Atmospheric chemistry and physics. From air pollution to climate change. 2nd ed. John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2006.

Sueper, D.: ToF-AMS High Resolution Analysis Software – Pika, availabel at: http://cires.colorado.edu/jimenez-group/wiki/index.php/ToF-AMS Analysis Software, 2008.

Sun, J., Zhang, Q., Canagaratna, M. R., Zhang, Y., Ng, N. L., Sun, Y., Jayne, J., Zhang, X., Zhang, X., Worsnop, D. R.: Higly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, Atmos. Environ., 44(1), 131–140, 2010.

Sun, Y.-L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W.-N., Bae, M.-S., Hung, H.-M., Hogrefe, O., Frank, B., Rattigan, O. V., Lin, Y.-C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass spectrometer, Atmos. Chem. Phys., 11, 1581–1602, 2011.

Sun, Y.-L., Wang, Z., Dong, H., Yang, T., Li, J., Pan, X., Chen, P., Jayne, T.P.: Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor, Atmos. Environ., 51, 250–259, 2012.

Sun, Y.-L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., Li, J., Jia, J. J.: Aerosol composition, sources and processes during wintertime in Beijing, China, Atmos. Chem. Phys., 13, 4577–4592, 2013.

Takegawa, N., Miyakawa, T., Kondo, Y., Jimenez, J. L., Zhang, Q., Worsnop, D. R., Fukuda, M.: Seasonal and diurnal variations of submicron organic aerosols in Tokyo observed using the Aerodyne aerosol mass spectrometer (AMS). J. Geophys. Res., 111, D11206, http://dx.doi.org/ 10.1029/2005JD006515, 2006.

Tao, W. K., Li, X., Khain, A., Matsui, T., Lang, S., Simpson, J.: Role of atmospheric aerosol concentration on deep convective precipitation: Cloud-resolving model simulations, J. Geophys. Res. Atmos., 112(D24), 2007.

Theodosi, C., Grivas, G., Zarmpas, P., Chaloulakou, A., Mihalopoulos, N.: Mass and chemical composition of size-segregated aerosols (PM1, PM2.5, PM10) over Athens, Greece: local versus regional sources, Atmos. Chem. Phys., 11, 11895–11911, 2011.

Turpin, B.J., Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. Aeros. Sci. Technol., 35, 602–610, 2001.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., Jimenez, J. L.: Interpretation of organics components from Positive Matrix Factorization of aerosol mass spectrometric data. Atmos. Chem. Phys., 9, 2891–2918, 2009.

Viana, M., Chi, X., Maenhaut, W., Cafmeyer, J., Querol, X., Alastuey, A., Mikuska, P., Vecera, Z.: Influence of sampling artefacts on measured PM, OC, and EC levels in carbonaceous aerosols in an urban area, Aeros. Sci. Tech., 40, 107–117, 2006.

Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A. S. H., Hueglin, C., Bloemen, H., Wåhlin, P., Vecchi, R., Miranda, A. I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R.: Source apportionment of particulate matter in Europe: A review of methods and results, J. Aeros. Sci., 39, 827–849, 2008.

Vignati, E., Facchini, M. C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., O'Dowd, C. D.: Global scale emission and distribution of sea-spray aerosol: sea-salt and organic enrichment, Atmos. Environ., 44(5), 670–677, 2010.

Xiao, R., Takegawa, N., Zheng, M., Kondo, Y., Miyazaki, Y., Miyakawa, T., Hu, M., Shao, M., Zeng, L., Gong, Y., Lu, K., Deng, Z., Zhao, Y., Zhang, Y. H.: Characterization and source apportionment of submicron aerosol with aerosol mass spectrometer during the PRIDE-PRD 2006 campaign, Atmos. Chem. Phys., 11, 6911–6929, 2011.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., Jimenez, J. L.: Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry, Environ. Sci. Technol., 38, 4797–4809, 2004.

Zhang, Q., Alfarra, M. R., Worsnop, R. D., Allan, J., Coe, H., Canagaratna, M., Jimenez, J. L.: Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, Environ. Sci. Technol., 39, 4938–4952, 2005.

Zhang, Q., Jimenez, J. L., Worsnop, D. R., Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, Environ. Sci. Technol., 41, 3213–3219, 2007a.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, 2007b.

Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., Shen, X. J., Yang, S.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, Tellus, 63B, 382–394, 2011.

Zhang, Q., Jimenez, J. L., Canagaratna, M., Ng, N. L., Ulbrich, I., Worsnop, D. and Sun, Y. L.: Understanding Organic Aerosols via Factor Analysis of Aerosol Mass Spectrometry: a Review, Analytic. Bioanalytic. Chem., 401, 3045–3067, 2011.

Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmos. Chem. Phys., 13, 8019–8043, 2013.

Watson, P. R., Van Hove, M. A., Hermann, K.: NIST Surface Structure Database - Ver. 5.0 National Institute of Standards and Technology, Gaithersburg, MD, 2004.

Weimer, S., Drewnick, F., Hogrefe, O., Schwab, J. J., Rhoads, K., Orsini, D., Canagaratna, M., Worsnop, D. R., Demerjian, K. L.: Size-selective nonrefractory ambient aerosol measurements during the Particulate Matter Technology Assessment and Characterization Study–New York 2004 Winter Intensive in New York City, J. Geophys. Res, 111, D18305, 2006.

WHO, 2006. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide: Global Update 2005 (Summary of risk assessment), WHO/SDE/PHE/OEH/06.02. URL: http://www.euro.who.int/Document/E87950.pdf

Finnish Meteorological Institute Contributions

1. Joffre, Sylvain M., 1988. Parameterization and assessment of processes affecting the long-range transport of airborne pollutants over the sea. 49 p.
2. Solantie, Reijo, 1990. The climate of Finland in relation to its hydrology, ecology and culture. 130 p.
3. Joffre, Sylvain M. and Lindfors, Virpi, 1990. Observations of airborne pollutants over the Baltic Sea and assessment of their transport, chemistry and deposition. 41 p.
4. Lindfors, Virpi, Joffre, Sylvain M. and Damski, Juhani, 1991. Determination of the wet and dry deposition of sulphur and nitrogen compounds over the Baltic Sea using actual meteorological data. 111 p.
5. Pulkkinen, Tuija, 1992. Magnetic field modelling during dynamic magne- tospheric processes. 150 p.
6. Lönnberg, Peter, 1992. Optimization of statistical interpolation. 157 p.
7. Viljanen, Ari, 1992. Geomagnetic induction in a one- or two-dimensional earth due to horizontal ionospheric currents. 136 p.
8. Taalas, Petteri, 1992. On the behaviour of tropospheric and stratospheric ozone in Northern Europe and in Antarctica 1987-90. 88 p.
9. Hongisto, Marke, 1992. A simulation model for the transport, transformation and deposition of oxidized nitrogen compounds in Finland — 1985 and 1988 simulation results. 114 p.
10. Taalas, Petteri, 1993. Factors affecting the behaviour of tropospheric and stratospheric ozone in the European Arctic and Antarctica. 138 p.
11. Mälkki, Anssi, 1993. Studies on linear and non-linear ion waves in the auroral acceleration region. 109 p.
12. Heino, Raino, 1994. Climate in Finland during the period of meteorological observations. 209 p.
13. Janhunen, Pekka, 1994. Numerical simulations of E-region irregularities and ionosphere-magnetosphere coupling. 122 p.
14. Hillamo, Risto E., 1994. Development of inertial impactor size spectroscopy for atmospheric aerosols. 148 p.
15. Pakkanen, Tuomo A., 1995. Size distribution measurements and chemical analysis of aerosol components. 157 p.
16. Kerminen, Veli-Matti, 1995. On the sulfuric acid-water particles via homogeneous nucleation in the lower troposphere. 101 p.
17. Kallio, Esa, 1996. Mars-solar wind interaction: Ion observations and their interpretation. 111

p.

18. Summanen, Tuula, 1996. Interplanetary Lyman alpha measurements as a tool to study solar wind properties. 114 p.

19. Rummukainen, Markku, 1996. Modeling stratospheric chemistry in a global three-dimensional chemical transport model, SCTM-1. Model development. 206 p.

20. Kauristie, Kirsti, 1997. Arc and oval scale studies of auroral precipitation and electrojets during magnetospheric substorms. 134 p.

21. Hongisto, Marke, 1998. Hilatar, A regional scale grid model for the transport of sulphur and nitrogen compounds. 152 p.

22. Lange, Antti A.I., 1999. Statistical calibration of observing systems. 134 p.

23. Pulkkinen, Pentti, 1998. Solar differential rotation and its generators: computational and statistical studies. 108 p.

24. Toivanen, Petri, 1998. Large-scale electromagnetic fields and particle drifts in time-dependent Earth's magnetosphere. 145 p.

25. Venäläinen, Ari, 1998. Aspects of the surface energy balance in the boreal zone. 111 p.

26. Virkkula, Aki, 1999. Field and laboratory studies on the physical and chemical properties of natural and anthropogenic tropospheric aerosol. 178 p.

27. Siili, Tero, 1999. Two-dimensional modelling of thermal terrain-induced mesoscale circulations in Mars' atmosphere. 160 p.

28. Paatero, Jussi, 2000. Deposition of Chernobyl-derived transuranium nuclides and short-lived radon-222 progeny in Finland. 128 p.

29. Jalkanen, Liisa, 2000. Atmospheric inorganic trace contaminants in Finland, especially in the Gulf of Finland area. 106 p.

30. Mäkinen, J. Teemu, T. 2001. SWAN Lyman alpha imager cometary hydrogen coma observations. 134 p.

31. Rinne, Janne, 2001. Application and development of surface layer flux techniques for measurements of volatile organic compound emissions from vegetation. 136 p.

32. Syrjäsuo, Mikko T., 2001. Auroral monitoring system: from all-sky camera system to automated image analysis. 155 p.

33. Karppinen, Ari, 2001. Meteorological pre-processing and atmospheric dispersion modelling of urban air quality and applications in the Helsinki metropolitan area. 94 p.

34. Hakola, Hannele, 2001. Biogenic volatile organic compound (VOC) emissions from boreal deciduous trees and their atmospheric chemistry. 125 p.

35. Merenti-Välimäki, Hanna-Leena, 2002. Study of automated present weather codes.153 p.

36. Tanskanen, Eija I., 2002. Terrestrial substorms as a part of global energy flow. 138 p.

37. Nousiainen, Timo, 2002. Light scattering by nonspherical atmospheric particles. 180 p.
38. Härkönen, Jari, 2002. Regulatory dispersion modelling of traffic-originated pollution. 103 p.
39. Oikarinen, Liisa, 2002. Modeling and data inversion of atmospheric limb scattering measurements. 111 p.
40. Hongisto, Marke, 2003. Modelling of the transport of nitrogen and sulphur contaminants to the Baltic Sea Region. 188 p.
41. Palmroth, Minna, 2003. Solar wind – magnetosphere interaction as determined by observations and a global MHD simulation. 147 p.
42. Pulkkinen, Antti, 2003. Geomagnetic induction during highly disturbed space weather conditions: Studies of ground effects 164 p.
43. Tuomenvirta, Heikki, 2004. Reliable estimation of climatic variations in Finland. 158 p.
44. Ruoho-Airola, Tuija, 2004. Temporal and regional patterns of atmospheric components affecting acidification in Finland. 115 p.
45. Partamies, Noora, 2004. Meso-scale auroral physics from groundbased observations. 122 p.
46. Teinilä, Kimmo, 2004. Size resolved chemistry of particulate ionic compounds at high latitudes. 138 p.
47. Tamminen, Johanna, 2004. Adaptive Markov chain Monte Carlo algorithms with geophysical applications. 156 p.
48. Huttunen, Emilia, 2005. Interplanetary shocks, magnetic clouds, and magnetospheric storms. 142 p.
49. Sofieva, Viktoria, 2005. Inverse problems in stellar occultation. 110 p.
50. Harri, Ari-Matti, 2005. In situ observations of the atmospheres of terrestrial planetary bodies. 246 p.
51. Aurela, Mika, 2005. Carbon dioxide exchange in subarctic ecosystems measured by a micrometeorological technique. 132 p.
52. Damski, Juhani, 2005. A Chemistry-transport model simulation of the stratospheric ozone for 1980 to 2019. 147 p.
53. Tisler, Priit, 2006. Aspects of weather simulation by numerical process. 110 p.
54. Arola, Antti, 2006. On the factors affecting short- and long-term UV variability. 82 p.
55. Verronen, Pekka T., 2006. Ionosphere-atmosphere interaction during solar proton events. 146 p.
56. Hellén, Heidi, 2006. Sources and concentrations of volatile organic compounds in urban air. 134 p.
57. Pohjola, Mia, 2006. Evaluation and modelling of the spatial and temporal variability of particulate matter in urban areas. 143 p.

58. Sillanpää, Markus, 2006. Chemical and source characterisation of size-segregated urban air particulate matter. 184 p.

59. Niemelä, Sami, 2006. On the behaviour of some physical parameterization methods in high resolution numerical weather prediction models. 136 p.

60. Karpechko, Alexey, 2007. Dynamical processes in the stratosphere and upper troposphere and their influence on the distribution of trace gases in the polar atmosphere. 116 p.

61. Eresmaa, Reima, 2007. Exploiting ground-based measurements of Global Positioning System for numerical weather prediction. 95 p.

62. Seppälä, Annika, 2007. Observations of production and transport of NOx formed by energetic particle precipitation in the polar night atmosphere. 100 p.

63. Rontu, Laura, 2007. Studies on orographic effects in a numerical weather prediction model. 151 p.

64. Vajda, Andrea, 2007. Spatial variations of climate and the impact of disturbances on local climate and forest recovery in northern Finland. 139 p.

65. Laitinen, Tiera, 2007. Rekonnektio Maan magnetosfäärissä – Reconnection in Earth's magnetosphere. 226 s.

66. Vanhamäki, Heikki, 2007. Theoretical modeling of ionospheric electrodynamics including induction effects. 170 p.

67. Lindfors. Anders, 2007. Reconstruction of past UV radiation. 123 p.

68. Sillanpää, Ilkka, 2008. Hybrid modelling of Titan's interaction with the magnetosphere of Saturn. 200 p.

69. Laine, Marko, 2008. Adaptive MCMC methods with applications in environmental and geophysical models. 146 p.

70. Tanskanen, Aapo, 2008. Modeling of surface UV radiation using satellite data. 109 p.

71. Leskinen, Ari, 2008. Experimental studies on aerosol physical properties and transformation in environmental chambers. 116 p.

72. Tarvainen, Virpi, 2008. Development of biogenetic VOC emission inventories for the boreal forest. 137 p.

73. Lohila, Annalea, 2008. Carbon dioxide exchange on cultivated and afforested boreal peatlands. 110 p.

74. Saarikoski, Sanna, 2008. Chemical mass closure and source-specific composition of atmospheric particles. 182 p.

75. Pirazzini, Roberta, 2008. Factors controlling the surface energy budget over snow and ice. 141 p.

76. Salonen, Kirsti, 2008. Towards the use of radar winds in numerical weather prediction. 87 p.

77. Luojus, Kari, 2009. Remote sensing of snow-cover for the boreal forest zone using microwave radar. 178 p.

78. Juusola, Liisa, 2009. Observations of the solar wind-magnetosphere-ionosphere coupling. 167 p.

79. Waldén, Jari, 2009. Meteorology of gaseous air pollutants. 177 p.

80. Mäkelä, Jakke, 2009. Electromagnetic signatures of lightning near the HF frequency band. 152 p.

81. Thum, Tea, 2009. Modelling boreal forest CO_2 exchange and seasonality. 140 p.

82. Lallo, Marko, 2010. Hydrogen soil deposition and atmospheric variations in the boreal zone. 91 p.

83. Sandroos, Arto, 2010. Shock acceleration in the solar corona. 116 p.

84. Lappalainen, Hanna, 2010. Role of temperature in the biological activity of a boreal forest. 107 p.

85. Mielonen, Tero, 2010. Evaluation and application of passive and active optical remote sensing methods for the measurement of atmospheric aerosol properties. 125 p.

86. Lakkala, Kaisa, 2010. High quality polar UV measurements : scientific analyses and transfer of the irradiance scale. 156 p.

87. Järvinen, Riku, 2011. On ion escape from Venus. 150 p.

88. Saltikoff, Elena, 2011. On the use of weather radar for mesoscale applications in northern conditions. 120 p.

89. Timonen, Hilkka, 2011. Chemical characterization of urban background aerosol using online and filter methods. 176 p.

90. Hyvärinen, Otto, 2011. Categorical meteorological products : evaluation and analysis.138 p.

91. Mäkelä, Antti, 2011. Thunderstorm climatology and lightning location applications in northern Europe. 158 p.

92. Hietala, Heli, 2012. Multi-spacecraft studies on space plasma shocks. 132 p.

93. Leinonen, Jussi, 2013. Thunderstorm climatology and lightning location applications in northern Europe.

94. Gregow, Hilppa, 2013. Impact of strong winds, heavy snow loads and soil frost conditions on the risks to forests in Northern Europe. 178 p.

95. Henriksson, Svante, 2013. Modeling key processes causing climate change and variability. 98 p.

96. Valkonen, Teresa, 2013. Surface influence on the marine and coastal Antarctic atmosphere. 114 p

97. Saarnio, Karri, 2013. Chemical characterisation of fine particles from biomass burning. 180 p.

98. Honkonen, Ilja, 2013. Development, validation and application of numerical space environment models. 148 p.

99. Siljamo, Pilvi, 2013. Numerical modelling of birch pollen emissions and dispersion on regional and continental scales. 156 p.

100. Anekallu, Chandrasekhar, 2013. Energy conversion across the Earth's magnetopause observations. 166 p.

101. Riihelä, Aku, 2013. The surface albedo of the arctic from space optical imagers: retrieval and validation. 164 p.

102. Lindgvist, Hannakaisa, 2013. Atmospheric ice and dust: from morphological modeling to light scattering. 154 p.

103. Tuomi, Laura, 2014. (valmisteilla / in preparation)

104. Portin, Harri, 2014. Observations of aerosols, clouds and their interactions at Puijo measurement station. 133 p.

105. Carbone, Samara, 2014. Chemical characterization and source apportionment of submicron aerosol particles with aerosol mass spectrometers. 135 p.