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

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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 roaster 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
\( \rho \) – Particle density

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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$_1$.

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$_2$O$^+$, 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.
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),

$$\text{Ammonium}_{predicted} = 18 \times \left( \frac{\text{sulfate}}{96} \times 2 + \frac{\text{nitrates}}{62} + \frac{\text{chloride}}{35.45} \right)$$ (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 Klejnnowski, 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$_1$ 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$_4$)$_2$H(SO$_4$)$_2$, (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$, SO$_4^{2-}$, 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.,
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 (Russell 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 9\(^{th}\) – March 13\(^{th}\), 2009) and another during the springtime (April 9\(^{th}\) – May 8\(^{th}\), 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 lens 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).

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 I and they are further discussed in the Papers I–V.
Table 1 – Summary of the instruments used in each site.

<table>
<thead>
<tr>
<th>Instrument / Site</th>
<th>Helsinki spring (Papers I and III)</th>
<th>SPC (Paper II)</th>
<th>Santiago (Paper IV)</th>
<th>Helsinki winter (Paper V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACSM</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>HR-ToF-AMS</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>EC/OC analyzer</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PILS-IC</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM$_1$ samples</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>PM$_{2.5}$ mass analyzer</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>TEOM</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC-$V_{CPH}$</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>DMPS</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC-CF</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>IC-MS</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

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:

\[ x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij} , \]  

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 \( x_{ij} \) 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). \( g_{ip} \) is an element of the \( m \times p \) matrix \( G \) whose columns are the factor TS, \( f_{ij} \) is an element of the \( p \times n \) matrix \( F \) whose rows are the factor profiles (MS), and \( e_{ij} \) 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:

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

where \( \sigma_{ij} \) 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 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 °C) 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.

<table>
<thead>
<tr>
<th>Compound / Site</th>
<th>organics (%)</th>
<th>sulfate (%)</th>
<th>nitrate (%)</th>
<th>ammonium (%)</th>
<th>chloride (%)</th>
<th>BC or EC (%)</th>
<th>Total (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC</td>
<td>32</td>
<td>8</td>
<td>37</td>
<td>16</td>
<td>1</td>
<td>7</td>
<td>10.94</td>
</tr>
<tr>
<td>Santiago de Chile</td>
<td>59</td>
<td>8</td>
<td>14</td>
<td>12</td>
<td>3</td>
<td>3</td>
<td>29.80</td>
</tr>
<tr>
<td>Helsinki spring</td>
<td>45</td>
<td>24</td>
<td>12</td>
<td>10</td>
<td>&lt;1</td>
<td>9</td>
<td>6.6</td>
</tr>
<tr>
<td>Helsinki winter</td>
<td>33</td>
<td>11</td>
<td>33</td>
<td>12</td>
<td>&lt;1</td>
<td>11</td>
<td>6.9</td>
</tr>
</tbody>
</table>

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$_2$H$_2$O$_2^+$, C$_3$H$_6$O$^+$, C$_3$H$_8$N$^+$) 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\textsubscript{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\textsuperscript{-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\textsubscript{2}, 8:00–12:00) largely emitted by the Santiago de Chile vehicle fleet. Thereupon, ammonium nitrate was probably formed by NO\textsubscript{2} conversion to nitric acid (HNO\textsubscript{3}) and further reaction with NH\textsubscript{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.](image)

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$_2$H$_4$O$_2^+$ and C$_3$H$_5$O$_2^+$ (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\textsubscript{x}H\textsubscript{y}O\textsubscript{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](image)

**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⁺, CH₃N⁺, CH₄N⁺, CH₃N, C₂H₃N⁺, C₂H₅N⁺, C₃H₅N⁺, C₂H₆N⁺ 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](image-url) - 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 (C₄H₇O₄) and hydrocarbon (CₓHₓ) also organosulfate fragments such as CHS⁺, CH₃SO₂⁺ and CH₄O₃S⁺ 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 CO₂⁺, CHO⁺ and typical fragments from levoglucosan C₂H₄O₂⁺ and C₃H₅O₂⁺ 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 PM₁ 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 CₓHᵧ, CₓHᵧOᵣ 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 C₂H₄O₂⁺ and C₃H₅O₂⁺ were present in the MS implying that the roasting process also released anhydrosugars. However, an interesting result was that the ratio between the fragments C₂H₄O₂⁺ and C₃H₅O₂⁺ 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 OOA s, 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.
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 enhancement 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\textsubscript{co}=0.85, r\textsubscript{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\textsubscript{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):

\[
Y = 0.88 \times LV - OOA + 0 \times (LV - OOA + MSA) + 1.63 \times LRT - BBOA + 0 \times CROA + 0.96 \times BBOA + 0.14 \times SV - OOA + 0.11 \times HOA ,
\]  

(4)

where Y was the WSOC measured by the TOC-V\textsubscript{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.
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\textsubscript{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 °C. 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, dva) 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).

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$_1$. 
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