CHEMICAL AND SOURCE CHARACTERISATION OF AMBIENT FINE PARTICLES WITH OFF-LINE AND ON-LINE METHODS

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ACADEMIC DISSERTATION in Analytical Chemistry

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Atmospheric aerosols have a significant effect on people and the environment. They cause adverse health effects especially for cardiorespiratory patients. Atmospheric aerosols also affect the Earth’s climate directly by scattering and absorbing solar radiation and indirectly by modifying amounts and properties of clouds. Reliable characterisation and quantification of airborne particles and their sources are essential for developing control strategies for atmospheric pollution and decreasing the uncertainties of estimating particles effects on climate change.

Aerosols can be divided into fine and coarse particles based on their size. This thesis concentrated on fine particles, which are either directly emitted into the atmosphere (primary particles) or formed in the atmosphere through gas-to-particle conversion (secondary particles). The main sources of atmospheric fine particles are natural and anthropogenic combustion, industry and secondary aerosol formation (biogenic and anthropogenic).

The overall objective of this thesis was to investigate the chemical composition of fine particles with different temporal and seasonal time-scales. For this purpose, a variety of different sampling techniques, off-line analytical methods and on-line instruments were used to characterise the main chemical species of fine particles in simultaneous and independent campaigns at several sites mainly in southern Finland but also in South Africa. More specific objectives were to investigate the dominant sources of particulate organic matter in the Helsinki area and chemically characterise the fine particles originating from biomass burning. Determining the effect of air mass origin on the chemical composition and concentration of fine particles was also one of the specific aims.

In this thesis, it was found that the chemical composition of fine particles had strong spatial and temporal variation, although on average the mass concentrations of fine particles were quite similar between different sites. The main components in fine particulate matter in southern Finland was particulate organic matter (POM), followed by sulphate, whereas sulphate had the highest contribution to particulate mass in South Africa. Source apportionment analysis of POM revealed clear primary sources from traffic and from biomass burning. However, the secondary organic aerosol had the largest contribution of POM, even though the campaigns were conducted in specific environments such as residential areas where biomass combustion is commonly used or traffic environments. Occasionally, the contribution of biomass burning organic aerosol increased substantially as ambient air temperature decreased. Additionally, simultaneous measurements pointed out a high contribution of common regional or long-range transported sources over large areas of southern Finland. Similarly, the air mass passing over either clean or polluted areas showed a significant effect on the mass concentrations in Finland and South Africa.
Nimeke

Ilmakehän pienhiukkasten kemiallisen koostumukseen määrittäminen ja lähteiden tarkastelu erillisillä ja jatkuvatoimilla mittauksilla

Tiivistelmä


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Espoo, April 2016

Minna Aurela
### ABBREVIATIONS AND DEFINITIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ACSM</td>
<td>Aerosol chemical speciation monitor</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerosol mass spectrometer</td>
</tr>
<tr>
<td>BBOA</td>
<td>Biomass burning organic aerosol</td>
</tr>
<tr>
<td>BC</td>
<td>Black carbon</td>
</tr>
<tr>
<td>BIC</td>
<td>Bushveld Igneous complex</td>
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<tr>
<td>BLPI</td>
<td>Berner low-pressure impactor</td>
</tr>
<tr>
<td>CC</td>
<td>Carbonate carbon</td>
</tr>
<tr>
<td>CE</td>
<td>Collection efficiency</td>
</tr>
<tr>
<td>CMB</td>
<td>Chemical mass balance</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Particle aerodynamic diameter</td>
</tr>
<tr>
<td>DMPS</td>
<td>Differential mobility particle sizer</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental carbon</td>
</tr>
<tr>
<td>EDXRF</td>
<td>Energy dispersive X-ray fluorescence</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency, USA</td>
</tr>
<tr>
<td>FDMS</td>
<td>Filter Dynamics Measurement System</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>HOA</td>
<td>Hydrocarbon-like organic aerosol</td>
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<tr>
<td>HPAEC</td>
<td>High-performance anion-exchange chromatograph/chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatograph/chromatography</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid chromatograph/chromatography</td>
</tr>
<tr>
<td>LV</td>
<td>Low volatile</td>
</tr>
<tr>
<td>MA, MAs</td>
<td>Monosaccharide anhydride(s)</td>
</tr>
<tr>
<td>MAAP</td>
<td>Multi-angle absorption photometer</td>
</tr>
<tr>
<td>MARGA</td>
<td>Monitor for aerosols and gases in ambient air</td>
</tr>
<tr>
<td>ME-2</td>
<td>Multilinear engine algorithm</td>
</tr>
<tr>
<td>MOUDI</td>
<td>Micro-orifice uniform deposit impactor</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometer/spectrometry</td>
</tr>
<tr>
<td>$m/z$</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitrogen oxides (NO, NO$_2$)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>OC</td>
<td>Organic carbon</td>
</tr>
<tr>
<td>OOA</td>
<td>Oxygenated organic aerosol</td>
</tr>
<tr>
<td>PILS</td>
<td>Particle-into-liquid sampler</td>
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<tr>
<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>PM$_1$</td>
<td>Particles with $D_a &lt; 1 \mu m$; respectively PM$<em>{10}$, PM$</em>{2.5}$, etc.</td>
</tr>
<tr>
<td>PMF</td>
<td>Positive matrix factorisation</td>
</tr>
<tr>
<td>POA</td>
<td>Primary organic aerosol</td>
</tr>
<tr>
<td>POM</td>
<td>Particulate organic matter</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RIE</td>
<td>Relative ionisation efficiency</td>
</tr>
<tr>
<td>SC-OCEC</td>
<td>Semicontinuous OC and EC field analyser</td>
</tr>
<tr>
<td>SMEAR</td>
<td>Station for measuring forest ecosystem – atmosphere relations</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary organic aerosol</td>
</tr>
<tr>
<td>SSR</td>
<td>Smoke-stain reflectometer</td>
</tr>
<tr>
<td>SV</td>
<td>Semivolatile</td>
</tr>
<tr>
<td>TEOM</td>
<td>Tapered element oscillating microbalance</td>
</tr>
<tr>
<td>TC</td>
<td>Total carbon</td>
</tr>
<tr>
<td>TOC-V$_{CPH}$</td>
<td>Total organic carbon analyser with a high-sensitive catalyst</td>
</tr>
<tr>
<td>VI</td>
<td>Virtual impactor</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic carbon compounds</td>
</tr>
<tr>
<td>WINS</td>
<td>Well impactor ninety-six</td>
</tr>
<tr>
<td>WISOC</td>
<td>Water-insoluble organic carbon</td>
</tr>
<tr>
<td>WSOC</td>
<td>Water-soluble organic carbon</td>
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LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an introductory review part, followed by five original research articles. The papers are reproduced with the kind permission of the journals concerned. The references to the articles are indicated in the text by their Roman numerals.


Latest publications of the author on chemical characterisation of ambient particles not included in this thesis


1. INTRODUCTION

During the late 1970s and the 1980s, three environmental issues involving atmospheric air pollution were widely recognised: acid rain, photochemical air pollution (smog) and stratospheric ozone depletion. Nowadays atmospheric particles are at the centre of scientific and political discussions due to the uncertainty surrounding their direct and indirect climate effects (IPCC: Intergovernmental Panel on Climate Change, 2013) and their adverse impacts on human health (Peng et al., 2005), visibility (Watson, 2002) and ecosystems (Matson et al., 2002). In order to estimate the effects of multiphase and multi-component aerosols on climate change, human health and the ecosystem, concentrations and chemical composition of particles should be identified (IPCC 2013, Pope and Dockery 2006 and Brook et al. 2010 and reference herein). Reliable characterisation and quantification of particles and their sources are essential for developing control strategies for atmospheric pollution.

Atmospheric particles can be classified in many ways, e.g. based on their origin (anthropogenic vs natural), size (fine vs coarse) or how they are formed (primary vs secondary). Primary particles are directly emitted into the atmosphere, whereas secondary particles are formed as products of chemical reactions and physical processes occurring in the atmosphere. Atmospheric particles consist of thousands of chemically and physically different components that reflect their sources and atmospheric processes such as ageing (Jimenez et al. 2009). The lifetime of atmospheric particles in the lower troposphere is typically from days to a week depending on their size (Seinfeld and Pandis, 2006). Because of their short lifetime, atmospheric particles are not uniformly distributed over the globe and the chemical composition and concentrations of particles depend greatly on local to regional or long-range transported scale sources. The largest global natural sources of particles are sea salt, mineral dust and secondary production of biogenic organic compounds (Seinfeld and Pandis, 2006, Szidat et al., 2006), whereas the main anthropogenic sources include industrial sources, power generation, transport (Yli-Tuomi et al., 2005, Zhang et al., 2005), small-scale wood combustion (Karvosenoja et al. 2008, Glasius et al, 2006, Szidat et al., 2007, Saarnio et al., 2012) and secondary particle formation from anthropogenic precursor gases. Some of these sources have clear seasonal variation in their emissions; for example, biogenic emissions increase in summertime or emissions from biomass burning may elevate either because
of heating of houses during the wintertime, wildfires during the dry season or prescribed burning in agricultural areas in spring and autumn.

There is no uniform measurement standard or technique available for measuring the chemical composition of particles. To select the most appropriate measurement techniques, it is important to establish which particle chemical characteristics are required and could be done with reasonable efforts and costs. Also, the legislation requires that ambient mass concentrations or emissions of certain components should be determined. The techniques for measuring the chemical composition of particles range from filter or impactor collections and subsequent chemical analyses to highly time-resolved on-line instruments.

In this thesis, I investigate the chemical composition of fine particles and their sources mainly in urban areas in Finland. Additionally, in order to understand the significance of the dispersion of air pollutants, measurements at two rural sites, one located in Finland and the other in South Africa, were included in this thesis. Besides showing the significance of the anthropogenic influence, the rural sites served as places to examine the formation of particles of biogenic origin.

2. OBJECTIVES OF THE STUDY

The general purpose of the thesis was to investigate the chemical composition and sources of fine particles in ambient air. Aerosol measurements were conducted in various environments with different on- and off-line methods. The more specific objectives of the study were:

- to examine how chemical composition and mass concentration of chemical species in fine particles vary temporally (Papers I, II, V) and seasonally (Paper V) in relation to air mass origin (Paper III)
- to investigate the chemical composition of fine particles during biomass burning events (Papers I, III)
- to study how the concentrations of carbonaceous components vary temporally (Papers II and IV), seasonally and during transport between two sites (Paper IV)
- to identify and quantify the sources or processes of particulate organic matter (e.g. hydrocarbon-like, biomass burning or secondary, Paper II)
3. BACKGROUND

3.1. Atmospheric aerosols

Aerosol is generally defined as a suspension of liquid or solid particles in a gaseous medium, outdoor air in the case of this thesis. Although atmospheric particles usually do not have regular shapes, they can be classified based on their aerodynamic diameter \( D_a \). \( D_a \) is defined as a diameter of a spherical particle with a density of 1 g cm\(^{-3}\) that has the same settling velocity as an irregular particle. Atmospheric particles range in size from a few nanometres to as large as 100 \( \mu \)m in diameter. Particles below 0.1 \( \mu \)m are called ultrafine particles, and they usually consist of two particle modes, nucleation and the Aitken mode. Due to their rapid coagulation or Brownian diffusion onto surfaces, the lifetime of these small particles is relatively short (on the order of minutes to days). Larger particles in the size range of 0.1 to 1 \( \mu \)m in diameter can accumulate in the atmosphere because their removal mechanisms are less efficient, and they are called accumulation mode particles. The lifetime of accumulation mode particles in the atmosphere is several days, and during this period they can be transported long distances from their source areas. Particles in the accumulation mode are formed mainly by coagulation of smaller particles, condensation of vapours onto existing particles or cloud processing, and during these mechanisms they growth into their typical size range. As the growth processes are slow in the accumulation mode, they are not reaching the coarse-particle mode sizes in their lifetime. Accumulation mode particles and their precursors can be emitted to the atmosphere from different sources, mainly from incomplete combustion and from biogenic emissions. Together the ultrafine and accumulation modes constitute fine particles. The coarse mode contains particles with a diameter larger than 2.5 \( \mu \)m. Due to the relatively large mass of coarse particles, they have short atmospheric lifetimes because of their rapid gravitational sedimentation and removal caused by inertial forces. Figure 1 shows the typical size ranges for atmospheric particles.
The removal processes of atmospheric species can be grouped into two categories: dry deposition and wet deposition. Dry deposition denotes the direct transfer of gases and particles to the Earth’s surface, whereas in wet deposition, species are in aqueous form when transferred to the surface. Atmospheric particles can serve as condensation nuclei for atmospheric water (cloud or fog droplet formation) or they can be scavenged by droplets. The rate of deposition is slowest for particles of an intermediate size, like accumulation mode size, as mechanisms for deposition are most effective for either very small (ultrafine mode) or very large particles (coarse particles).

In urban areas, aerosols originate mostly from anthropogenic sources. Mass concentrations of fine particles range from 10 $\mu$g m$^{-3}$ to 1 mg m$^{-3}$ in heavily polluted cities in developing countries (Putaud et al., 2010, Hand et al., 2012, He et al., 2001, Ji et al., 2014, Duan et al., 2006). The $\text{PM}_{2.5}$ ($D_0 < 2.5 \mu\text{m}$) mass concentrations in rural background areas containing particles from natural and
transported anthropogenic sources vary from approximately a few \( \mu g \) m\(^{-3}\) to 20 \( \mu g \) m\(^{-3}\) (Putaud et al., 2010, Hand et al., 2012). The concentration and composition of natural background aerosol depends on direct emissions (e.g. wildfires) and gas-to-particle formation from natural sources (biogenic volatile organic carbon compounds). The majority of the fine particulate mass in the atmosphere, both natural and anthropogenic, is formed in the atmosphere from gaseous emissions (Hinds, 1999).

3.2. Health effects of particles

The size of a particle determines how far it can penetrate into the respiratory tract when inhaled. Larger particles are generally filtered in the nose and throat, but particles smaller than about 10 \( \mu m \) (PM\(_{10}\)) can settle in the bronchi and lungs. PM\(_{2.5}\) particles can penetrate deeper into the gas-exchange region of the lungs, and ultrafine particles may pass the blood-air barrier into the bloodstream (Pope and Docherty, 2006). Typically, size-selective sampling of particulate matter (PM) is based on the particle inhalation and deposition processes.

Epidemiological studies indicate that increased concentrations of atmospheric particles cause adverse health effects in urban populations (e.g. Zanobetti and Schwartz, 2009). Still, it is uncertain which aerosol parameters (particle mass, particle number, surface area, particle size, chemical composition or water solubility) are the best indicators of particle harmfulness. Some specific studies have attempted to resolve which components or attributes are most important in determining health effects, but they have not shown unambiguous evidence of the most harmful species/properties (Zanobetti et al., 2014; Boman et al., 2003; Ostro et al., 2011; Dai et al., 2014; Moller, 2011). However, they have given a clear indication that mass alone is not a sufficient metric with which to evaluate the health effects of exposure. Additionally, there seems to be no threshold value for the mass or number concentrations of particles in association with their health effects. Daily mortality has been estimated to increase by 1% per 10 \( \mu g \) m\(^{-3}\) increment of fine particles measured at central urban background sites (WHO, 2005). It has also been estimated that globally the premature mortality rate due to PM\(_{2.5}\) in 2005 was about 2.2 million/year (Lelieveld et al., 2013). The European legislation on air quality set up directives to define the limit value for the maximum mass concentration of PM (PM: both PM\(_{2.5}\) and PM\(_{10}\)) in ambient air. The yearly limit value in the EU member countries for PM\(_{2.5}\) and PM\(_{10}\) is 25 and 50 \( \mu g \) m\(^{-3}\), respectively.
3.3. Climatic effects of particles

It is well known that greenhouse gases warm the atmosphere, but also aerosols have significant influences on the climate. Aerosols have both direct and indirect effects. As a direct effect, aerosols scatter sunlight back into space. As an indirect effect, aerosols in the lower atmosphere modify the size of cloud particles, changing how clouds reflect and absorb sunlight, and thereby affecting the Earth's energy budget. Both these effects cause a cooling influence of particles. At the same time, black carbon (BC) and mineral dust are strong light absorbers (Yang et al., 2009). As opposed to the long-lived greenhouse gases, light-absorbing and scattering particles are referred to as short-lived climate forcers. Particles that absorb sunlight warm the atmosphere. As a global average, the aerosol effect is estimated to result in a net cooling of the atmosphere. This cooling or warming of the atmosphere as a result of the reflective or absorbent properties of particles is the largest source of uncertainty in the estimation of radiative forcing (Figure 2, Stocker et al., 2013).

![Figure 2](image.png)

**Figure 2.** Radiative forcing of components. The horizontal lines indicate the overall uncertainty. Adapted from IPCC (2013).
3.4. Chemical composition of atmospheric fine particles

The chemical composition of fine and coarse particles in the atmosphere differs greatly. Because there is little mass transfer between fine and coarse particles, they exist as two chemically distinct aerosol modes in the atmosphere. Atmospheric fine particles consist of thousands of different components of which the major constituents are inorganic ions (sulphate, nitrate, and ammonium) and carbonaceous compounds (e.g. Solomon et al., 2008 and references therein, Chan and Yao, 2008 and references therein, Zhang et al., 2007, Putaud et al., 2010). The main chemical pathway for the production of fine particles is described briefly in Figure 3. The primary components of coarse particles, which are mainly emitted from mechanical processes, are dust, crustal elements, sea salt and vegetation (Seinfeld and Pandis, 2006).

3.4.1. Inorganic ions

Sulphate, nitrate and ammonium are known as secondary inorganic ions, since they are mainly formed from their precursor gases, sulphur dioxide (SO₂), nitrogen oxides (NOₓ) and ammonia (NH₃), through gas-to-particle conversion. SO₂ is oxidised to sulphate in the gas or aqueous phase with oxidizers such as hydroxyl radical, ozone, H₂O₂ or O₂ with catalyst (Seinfeld and Pandis, 2006). Oxidation in the aqueous phase is much faster than in the gas phase, and the dominant oxidizer in the aqueous phase with low pH is H₂O₂ and with high pH is ozone (Seinfeld and Pandis, 2006). Sulphate is found in the submicron (Dₐ < 1 µm) and supermicron (Dₐ > 1 µm) size ranges, but it is more typical in the submicron size range. The major anthropogenic sources of sulphur are fossil fuel combustion and industrial activities, whereas the natural sources of sulphur are the marine biosphere (marine plankton and sea salt) and volcanos (Finlayson-Pitts and Pitts, 2000).

The source of particulate nitrate is mainly nitric acid, which is formed from NO₃ in the atmosphere. Aerosol nitrate also may be formed directly from reactions of NOₓ on alkaline particles (Herring et al., 1996). However, this process occurs mostly in the coarse fraction. The anthropogenic source of NO₃ is fossil fuel combustion, and in nature, NO₃ is a result of bacterial processes, biological growth and decay, lightning, and forest and grassland fires (Lee et al., 1997). When attached to surfaces, nitric acid is removed rapidly by dry and wet deposition, but it also reacts readily with ammonia to produce ammonium nitrate, or with sea salt or soil to produce compounds such as
sodium nitrate or calcium nitrate in the coarse mode (Pakkanen et al., 1996a). The ammonium nitrate formed is thermally unstable and in dynamic equilibrium with gas-phase ammonia and nitric acid. The formation of ammonium nitrate depends on the availability of ammonia, as the reaction of ammonia with sulphuric acid is predominant (Ansari and Pandis, 1998). However, significant amounts of ammonium nitrate are formed in regions where sulphate levels are low and ammonia and nitrogen oxide emissions are high.

Fertiliser and livestock represent the largest sources of ammonia emissions (EAA, 2014), but emissions from motor vehicles can contribute to ammonia levels, at least in urban areas (Suarez-Bertoa et al., 2014). The main natural source of ammonia, although minor compared to agriculture, is soil (Finlayson-Pitts and Pitts, 2000). The high seasonal variability of agricultural activities and natural sources fluctuate the emissions of ammonia, whereas vehicles-related emissions, although minor in contribution globally, are more stable throughout the year. As mentioned above, ammonia reacts rapidly with sulphuric and nitric acids in the atmosphere and contributes to ambient levels of fine particles. Since sulphate-containing particles deposit much more slowly than either ammonia or nitric acid, the formation of ammonium sulphate particles distributes ammonium over a much larger region than ammonium nitrate does.

### 3.4.2 Carbonaceous matter

Fine particulate carbonaceous matter consists of thousands of different compounds. As the identification of all particulate carbonaceous species is not possible, they are typically divided into three main categories: particulate organic matter (POM), carbonate carbon (CC), and black carbon (BC), which is also called elemental carbon (EC). BC is an optical measurement that is commonly used to denote the extent of light absorption by the sample. BC has no mass unit of its own; rather, the absorption of particles is converted to the mass concentrations of BC, whereas EC usually identifies carbon that does not volatilise below a certain temperature, usually about 500 °C. Although EC and BC are not measures of the same properties of PM, they are often well correlated, although BC or EC concentrations are found to differ by up to a factor of 7 among different methods (Watson and Chow, 2002; Watson et al., 2005).
POM constitutes a major fraction of atmospheric fine PM (Putaud et al., 2010; Zhang et al., 2007), whereas EC is negligible in fine particles in most regions except those under the influence of mineral dust (e.g. Cao et al. 2005). EC represents on average 5–20% of fine particle mass depending greatly on location (Hand et al., 2012, Putaud et al., 2010). EC is exclusively a primary species, and it is formed during incomplete combustion.

POM is composed of organic carbon (OC) and typically elements such as hydrogen, oxygen and nitrogen depending on the molecular composition of organic species in POM. The ratio of POM to OC depends on the origin and age of the POM in the atmosphere. For urban POM, the POM-OC-ratio of 1.6±0.2 and for nonurban POM the ratio of 2.1±0.2 has been recommended (Turpin and Lim, 2001).

POM can be further divided into primary organic aerosol (POA) and secondary organic aerosol (SOA) or into water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC). WISOC compounds are typically from fresh emissions originating from traffic or other local sources. As aerosol ages, it becomes more water-soluble due to oxidation in the atmosphere (Jimenez et al., 2009). Typically, WSOC compounds represent 12–75% of OC (Jaffrezo et al., 2005 and reference herein, Timonen et al., 2008a, Pathak et al., 2011).

POA is composed of a wide range of hydrocarbons, partially oxidised POM, and a wide variety of suspended organic debris and material. Sources of POA include fossil fuel burning, domestic burning, uncontained burning of vegetation (savannah and deforestation fires), agricultural waste and biogenic sources (viruses, bacteria, fungal spores and plant debris). POA is mainly water insoluble whereas SOA is typically more water-soluble (Miyazaki et al., 2006, Timonen et al., 2010). SOA consists typically of compounds bearing multiple oxygenated functional groups (Seinfeld and Pandis, 2006, Clayes et al., 2007, Seinfeld and Pankow, 2003). SOA is formed in the atmosphere via photochemical oxidation of volatile and semivolatile organic compounds emitted from both biogenic and anthropogenic sources and subsequent condensation on pre-existing particle surfaces. In urban areas, anthropogenic volatile organic carbon compounds (VOC) can be the dominant source of SOA, but globally the emissions of biogenic volatile organic compounds comprise 90% of total VOC emissions (Seinfeld and Pankow, 2003, Guenther et al., 1995). SOA’s contribution to POM varies between 49% and 95% (Crippa et al., 2014).
Figure 3. The main atmospheric chemical reactions that contribute to fine particulate matter. HOA, BBOA and OOA mean: hydrocarbon-like organic aerosol, biomass burning organic aerosol and oxygenated organic aerosol, respectively. The components in the red boxes were studied in this thesis. Reaction pathways are compiled from Seinfeld and Pandis (2006).

3.5. Techniques for studying the chemical composition of atmospheric fine particles

The different methods typically used for identifying the chemical composition of fine particles from filters or on-line are presented briefly below and demonstrated in Figures 4 and 5, respectively. Methods that were used in this thesis are indicated.

3.5.1. Off-line instruments

The chemical composition of atmospheric fine particles can be investigated by off-line and on-line methods. Filter-based aerosol sampling with post-sampling chemical analysis is still a very common...
method to investigate the time series of chemical species for an extended period of time. Cascade impactors are still widely used for particle mass size distribution studies. The sampling time with filters and impactors varies with ambient loadings, sampling flow rates and the sensitivities of the analytical methods, but typically it ranges from several hours in urban areas to a day or even longer in clean background conditions. Polytetrafluoroethylene (PTFE) and quartz fibre filters are the most commonly used materials for particle sampling when using filter cassette systems. PTFE filters are suitable for gravimetric mass measurements and various chemical analyses, except for OC. Quartz fibre filters are typically used for OC measurements because of their resistance to high temperatures used in thermoanalytical methods. Polycarbonate film also is used in impactors for determination of the mass size distributions of elements, and aluminium foil is used for the gravimetric mass size distributions. In order to reduce the particle bounce in impactors, impactor substrates are typically greased.

Ion chromatography (IC) is the most applied method for analysing inorganic ions and some organic diacids (e.g. sulphate, nitrate, chloride, ammonium, potassium, sodium, magnesium, calcium and oxalate) from PM samples, and it was used widely in this thesis. The results from different laboratories are usually within ±10% for the major inorganic species, except for calcium, for which the difference can reach 50% (Putaud et al., 2000). In addition to IC, capillary electrophoresis techniques have been used to analyse inorganic ions, mostly from environmental water samples but also from ambient particles (Fukushi et al., 1999). Before the development of a high-capacity cation-exchange column, ammonium was analysed by using a calorimetric method or an ion-selective electrode (Ruoho-Airola et al., 2010; Fukushi et al., 2006). Besides IC, other suitable methods for analysing alkali (e.g. sodium and potassium), or alkaline earth metals (e.g. magnesium and calcium) include atomic absorption spectrometry, inductive coupled mass spectrometry, instrumental neutron activation analysis and particle-induced X-ray emission analysis, which is used also for sulphur analyses (Pakkanen et al., 1993, 1996b, Maenhaut et al., 2011). The four last mentioned methods are suitable also for the trace metal analysis.

Compared to inorganic ions and elements, carbonaceous species (OC, EC, CC) are more difficult to analyse from PM filters or impactor samples as there are no definitive standards for their quantification. The water-soluble fraction of OC is typically analysed by a total organic carbon analyser (Jaffrezo et al., 2005), and thermal-optical methods are widely used to determine total OC
and EC in ambient aerosols (Watson et al., 2005). Both methods were used in this thesis, but mainly the thermal-optical method.

It is widely recognised that OC and EC are operationally defined by the thermal-optical method used, as the temperature program and optical charring correction influence the obtained concentrations of OC and EC. Several intercomparison studies have shown that the uncertainty in the determination of total carbon (TC; sum of OC, EC and CC) is below 25%, but large differences in the concentration of EC measured by different temperature protocols are detected (Cavalli et al., 2010; Watson et al., 2005; Emblico et al., 2012; Schmid et al., 2001). Another method of analysing BC on filter samples, though it is indirect, is the smoke stain reflectometer (SSR), which was used in this thesis during one field experiment. SSR evaluates the amount of BC collected on the filter by converting the reflection of light to an absorption coefficient and finally to mass concentration (Kinney et al., 2000; Hansen et al., 1984).

Individual molecular species in particulate organic fraction are commonly identified and quantified by using gas chromatography–mass spectrometry (GC–MS, Vicente et al., 2012, Schnelle-Kreis et al., 2011; Kowalewski and Gierczak, 2011) and liquid chromatography–mass spectrometry (LC–MS, Samy et al., 2011; Kitanovski et al., 2011; Kampf et al., 2011) including IC. GC-MS is typically used for analysing organic compounds that comprise POA (e.g. hydrocarbons), whereas IC and other types of liquid chromatographies have been used for analysing organic compounds such as levoglucosan or more oxidised ones such as low-molecular-weight dicarboxylic acids (Kerminen et al., 1999, Saarnio et al., 2010a). Typically, organic species identified by chromatographic techniques explain < 20% of the organic mass in PM (Duarte and Duarte 2011). The identification of organic molecular species was not a major focus of this thesis. Only biomass burning tracers, monosaccharide anhydrides (e.g. levoglucosan), were identified. In addition to individual molecular species, the chemical composition of POM can be characterised by using nuclear magnetic resonance spectrometry (Sannigrahi et al., 2006), which determines functional groups or molecular bonds in POM from filters.
3.5.2. On-line instruments

In order to achieve better time resolution and to avoid sampling artefacts typical of filter collection, on-line methods have become more common in the scientific community, especially in the investigating of rapid atmospheric processes and rapidly changing environments. On-line methods for analysing the chemical composition of particles include e.g. Particle Into Liquid Sampler (PILS; Orsini et al. 2003), which can be coupled with different analytical instruments, like IC (Takegawa et al., 2005); high-performance anion exchange chromatography-mass spectrometry (HPAEC-MS, Saarnio et al., 2013); and total organic carbon analyser (Timonen et al., 2010) for analysing components such as typical inorganic ions, major organic ions (like oxalic acid), total water-soluble organic carbon and levoglucosan. A combination of PILS-IC was used in this thesis during a one-year long field experiment. The Monitor for AeRosols and Gases in ambient Air (MARGA; Trebs et al., 2004, ten Brink et al., 2007) measures both water-soluble gases like NH₃, HNO₃, HCl, SO₂ and HONO, and inorganic and organic ions in particles. Water-soluble gases are collected by wet rotating denuders and particles similar to the PILS with the steam-jet aerosol collector (Slanina et al., 2001). Chemical species are analysed by the IC in the MARGA. There is also a monitor for the
particulate metals (EPA 2012) and a semicontinuous OC and EC field analyser (SC-OCEC; Arhami et al. 2006) for carbonaceous species. SC-OCEC was used in a few studies in this thesis. In contrast to the on-line instruments mentioned above, which can determine only one or a few chemical species, the Aerosol Mass Spectrometer (AMS; Jayne et al. 2000, Allan et al., 2003) and the Aerosol Chemical Speciation Monitor (ACSM; Ng et al., 2011a) made it possible to study the overall chemical composition of aerosol with a time resolution ranging from seconds (AMS) to roughly 30 minutes (ACSM). Standard AMS and ACSM measure the mass concentrations of non-refractory submicron aerosols (i.e. sulphate, ammonium nitrate, chloride and POM) that are vaporised under 600 °C. The difference between ACSM and AMS is that AMS is able to measure also the size distributions of chemical species. POM is calculated on the basis of mass spectra of the fragments from different organic compounds. The organic mass spectra can be used further to analyse particles’ sources and oxidation states, as explained later in more detail. Sea salt or mineral dust particles cannot be quantitatively determined because most of them are outside of the instruments’ measured size range (above about 1 µm) and are non-volatile at 600 °C. ACSM was used in this thesis during one study containing four different measurement periods and sites.

Real-time BC measurements are performed by using optical methods, which measure the attenuation of light through a loaded filter. Commonly used instrumentation includes the aethalometer (Magee Scientific, Berkeley, USA, Hansen et al., 1984), the particle soot absorption photometer, (Bond et al., 1999) and the multi-angle absorption photometer (MAAP, Petzold and Schönlinner, 2004). The aethalometer and MAAP were used in a few field experiments in this thesis.
3.5.3. Sampling system and artefacts

Besides accurate analytical methods for resolving the chemical composition of fine particles, one crucial issue is to sample particles in a representative way and understand the sampling artefacts. An ideal aerosol sampling system allows an undisturbed and known sample flow from the environment to the instrumentation with controlled particle size, while preventing condensation or excessive moisture from the sampled aerosol and minimising particle losses. The particle size selection is typically carried out by using cyclones and impactor stages to cut off particles above the wanted aerodynamic size, such as 10 µm, 2.5 µm and 1 µm in PM$_{10}$, PM$_{2.5}$ or PM$_1$, respectively. The aerosol sampling system should also minimise the evaporation of volatile or semivolatile particulate species and prevent the gaseous components’ absorption/adsorption into/onto sampled particles or sampling substrates, e.g. filters.

During the sampling, different processes may alter the original ambient conditions of the aerosol, leading to sampling artefacts. Such processes could include inter-particle interactions, gas-particle interactions and dissociation of semivolatile species. The errors and uncertainties in filter and impactor collections have been extensively studied during the last decades (e.g. Hering and Cass 1999, Pathak and Chan 2005, Viana et al., 2006; Wang and John, 1988). For semivolatile chemical
species, such as ammonium nitrate and some organic species, interference may originate from both the adsorption/absorption of gases onto the filters or into sampled particles and the volatilisation of particles from the filters during sampling, transport or storage. These two artefacts may cancel each other to a certain degree, but filter measurements have shown that positive artefacts usually dominate in OC measurements, whereas for nitrate, negative artefacts are more significant than positive ones (Turpin et al., 1994; Hering and Cass, 1999). The evaporation losses of ammonium nitrate or the adsorptions of gases on certain substrates like PTFE or polycarbonate membrane are lower for impactors than for filter sampling (Wang and John, 1988; Hering et al., 1997).

In order to avoid sampling artefacts, denuders with filter pack systems are used to absorb interfering gases prior to the particle collection and to collect the evaporated PM species with a backup filter. The removal of the gas phase can disturb the gas–particle equilibrium, driving the volatilisation of particulate material from the filter. In the case of OC, the use of denuders has been estimated to increase the evaporation of OC from the filters by 10–16%; however, evaporated OC can be captured using additional quartz fibre or impregnated backup filters (Watson et al., 2009; Subramanian et al., 2004). Nitrate loss from denuded nylon filters has been demonstrated to be negligible but the loss of ammonium is considerable (10–28%), and an additional acid-coated filter or denuder is needed to capture ammonia (Yu et al., 2006). However, the preparation and subsequent chemical analyses of the denuders and back filters are tedious and time consuming. Thus, samplings with single filters and filter pack systems without denuders are common, but in that case the sampling artefacts of (semi)volatile species should be noted.

While on-line methods do not suffer from losses or contamination during storage like off-line methods they may have some similar sampling artefacts as the off-line methods, such as positive artefacts for OC, in case the on-line method is also based on the filter collection like SC-OCEC. In addition, when using short integration times—as the on-line methods typically have—and relatively low flow rates, the mass concentrations may be too low for quantitative detection. In contrast to the positive artefacts in SC-OCEC, the PILS-IC has volatilisation losses for ammonium and also losses in the liquid sampling line (20%, Takegawa et al., 2005; Timonen et al., 2010). In addition, PILS-IC does not have full data coverage over the measurement cycle. Depending on the size of the loop, the flow rate of the transport liquid and the analytical method used, the data coverage is 40–100%. Similarly, data coverage for SC-OCEC is 60–85%, depending on the ratio of the sampling and
analysis time. On-line methods may have also some issues affecting the accuracy of the data. For example, the collection efficiency (CE) of the AMS and ACSM is not 100%; rather, it is estimated on the basis of the chemical composition of the particles and the relative humidity of the sample air (Middlebrook et al., 2012). CE typically varies around 50% and may have a significant effect on the measured mass concentrations. AMS and ACSM also have some uncertainties in estimating the ionisation efficiency for chemical species, especially for organic species. At the moment, only a single relative ionisation value (RIE) is used for all organic species, despite their varying molecular structure, although different values have been presented for simple hydrocarbons and more oxidised organic molecules based on laboratory experiments (Allan et al., 2003). Also, ambient studies have shown that the RIE for POM might depend on the source of the POM (Budisulistiorini et al., 2014).

3.6. Source apportionment methods

Source apportionment methods for PM can be based on either receptor modelling or the combination of emissions inventories and dispersion modelling. The latter approach needs reliable knowledge of the emission sources and volumes, which may be inadequate or unavailable for the environment under evaluation. Receptor modelling is based on statistical analysis of pollutant concentrations measured at a sampling site. It resolves the source types and estimates their contributions to the measured concentrations. Receptor modelling can further be divided to different approaches like 1) enrichment factor analysis, in which the ratio of measured chemical components is compared to the reference material (e.g. particle composition versus crustal abundance, Lin et al., 2015); 2) the tracer-based method, which can distinguish for example, fossil from non-fossil carbon in PM using the ratio of $^{14}$C and $^{12}$C (e.g. Szidat et al., 2007); 3) chemical mass balance (CMB), in which source profiles are known and compared with the measured species at the site (e.g. Yin et al., 2010); 4) principal component analysis (e.g. Lin et al., 2015); 5) positive matrix factorisation (PMF, Paatero, 1997); and 6) the multilinear engine algorithm (ME-2), which is the combination of PMF and CMB (Lanz et al., 2008). The latter is used in this thesis and is explained more closely below.

ME-2 with a custom software tool has especially been developed to identify the sources of POM measured with an ACSM (Canonaco et al., 2013). The most common factors for POM, obtained with ME-2 or PMF from the ACSM or AMS data, are a) hydrocarbon-like organic aerosol (HOA), which is considered to represent POA from fossil fuel combustion i.e. traffic; b) cooking-related
organic aerosol, which has spectral features similar to those of POA from fossil fuel combustion and a distinctive diurnal pattern; c) biomass burning organic aerosol (BBOA) correlated with biomass burning emission tracers and elevated peaks at a mass-to-charge ratio (m/z) of 60 and 73 in the mass spectra; d) low volatile oxidised organic aerosol (LV-OOA), which is interpreted as a surrogate for regional and long-range transported, aged POM; and e) semivolatile oxidised organic aerosol (SV-OOA), which is interpreted as a surrogate for less photochemically aged POM (Zhang et al., 2011).

4. EXPERIMENTAL

4.1. Measurements sites

In this thesis, the chemical composition of fine particles was examined in various environments with different temporal resolutions. Year-round off-line PM$_1$ measurements were conducted at the rural SMEAR II site (SMEAR: Station for Measuring Ecosystem-Atmosphere Relationships) in Hyytiälä, Finland, and at the urban background site (SMEAR III) in Helsinki, Finland (Paper IV). In addition to off-line methods, on-line methods were also used at SMEAR III (Paper V). Half-year measurements with different off-line methods and sampling time durations were also carried out at an urban background site in Kotka, Finland, with simultaneous measurement at SMEAR III in Helsinki (Paper I). Furthermore, this thesis contains short-term on-line measurements conducted in different areas in Helsinki (Paper II) and off-line measurements conducted a rural area (savannah) in South Africa (Paper III). The details of the sites and periods are given in Table 1 and briefly described below.

Urban sites:

SMEAR III is located on a small hill 5 km northeast from the centre of Helsinki and 150 m east from a densely trafficked road (60 000 vehicles/day) (Järvi et al., 2009).

Kotka is located on the northern coast of the Gulf of Finland, 130 km east of Helsinki. A six-month field campaign was carried out in a central urban background location at a schoolyard surrounded
mainly by three-storey apartment buildings at a distance of 15–30 m from the station. The nearest slow-traffic road was situated 15 m away from the station.

**The Residential I site** was situated approximately 20 km northeast from downtown Helsinki. The site was surrounded by detached houses. No major roads went through the area, and the nearest motorway was approximately 1.2 km east of the site.

**The Residential II site** was situated in a low-lying area of detached housing approximately 20 km west from downtown Helsinki. No main roads ran through the area. The closest highway was situated approximately 3 km south of the site.

**The Curbside site** was situated in downtown Helsinki beside a moderately trafficked road (23000 vehicles/working day). The constant rows of buildings on both sides of the road affected the dispersion of the aerosols, although one big crossing was close to the site.

**The Highway site** was situated near a heavily trafficked highway (5 m from the edge of the first lane), which is the inner ring road around Helsinki, approximately 10 km from downtown Helsinki. The traffic density was approximately 69 000 vehicles/working day.

*Rural sites:*

**SMEAR II** is located in a rural area of Southern Finland, Hyytiälä, within a boreal forest. Tampere (population 213 000) is the closest larger town, 50–60 km south-west of the station. The station has an extensive set of continuing atmospheric measurements (Kulmala et al., 2001).

**Botsalano** game reserve in North West Province, South Africa, was equipped with a mobile station for atmospheric measurement (Laakso et al., 2008). This setting can be considered a dry savannah regional background site, with no major local anthropogenic sources.
Table 1. Sites and periods of the ambient measurements used in this thesis.

<table>
<thead>
<tr>
<th>Country</th>
<th>City/locality, site</th>
<th>Site type</th>
<th>Measurement period</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finland</td>
<td>Helsinki, SMEAR III</td>
<td>Urban background</td>
<td>14 Nov. 2004–12 May 2005</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14 Feb. 2007–18 Feb. 2008</td>
<td>IV</td>
</tr>
<tr>
<td>Finland</td>
<td>Kotka</td>
<td>Urban background</td>
<td>14 Nov. 2004–12 May 2005</td>
<td>I</td>
</tr>
<tr>
<td>Finland</td>
<td>Helsinki</td>
<td>Residential</td>
<td>17 Feb.–16 March 2011</td>
<td>II</td>
</tr>
<tr>
<td>Finland</td>
<td>Espoo</td>
<td>Residential</td>
<td>12 Jan.–28 Feb. 2012</td>
<td>II</td>
</tr>
<tr>
<td>Finland</td>
<td>Helsinki</td>
<td>Curbside</td>
<td>1 Dec. 2010–7 Jan. 2011</td>
<td>II</td>
</tr>
<tr>
<td>Finland</td>
<td>Helsinki</td>
<td>Highway</td>
<td>18 Oct.–5 Nov. 2012</td>
<td>II</td>
</tr>
<tr>
<td>Finland</td>
<td>Hyytiälä, SMEAR II</td>
<td>Rural background</td>
<td>14 Feb. 2007–18 Feb. 2008</td>
<td>IV</td>
</tr>
<tr>
<td>South Africa</td>
<td>Botsalano</td>
<td>Rural background</td>
<td>9–15 Oct. 2007</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 Jan.–5 Feb. 2008</td>
<td>III</td>
</tr>
</tbody>
</table>

4.2. Off-line measurements

Several off-line sampling methods were used in this thesis. The main sampling methods are compiled in Table 2 and briefly presented below.

Table 2. Sampling methods used in this thesis. UBG: urban background

<table>
<thead>
<tr>
<th>Sampling method</th>
<th>Sampling duration</th>
<th>Substrate</th>
<th>Site</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA WINS</td>
<td>24 h</td>
<td>PTFE</td>
<td>Kotka, UBG</td>
<td>I</td>
</tr>
<tr>
<td>VI-1</td>
<td>4 day</td>
<td>PTFE</td>
<td>Kotka, UBG</td>
<td>I</td>
</tr>
<tr>
<td>VI-2</td>
<td>4 day</td>
<td>PTFE+nylon</td>
<td>Kotka, UBG</td>
<td>I</td>
</tr>
<tr>
<td>VI-3</td>
<td>4 day</td>
<td>2×quarzt fibre</td>
<td>Kotka, UBG</td>
<td>I</td>
</tr>
<tr>
<td>Filter cassette</td>
<td>24 h/72 h</td>
<td>2×quartz fibre</td>
<td>SMEAR III, UBG</td>
<td>I, IV, V</td>
</tr>
<tr>
<td>Filter cassette</td>
<td>24 h/72 h</td>
<td>2×quartz fibre</td>
<td>SMEAR II, rural</td>
<td>IV</td>
</tr>
<tr>
<td>BLPI</td>
<td>4 day</td>
<td>Aluminium foil</td>
<td>Kotka, UBG</td>
<td>I</td>
</tr>
<tr>
<td>MOUDI</td>
<td>72 h</td>
<td>Aluminium foil</td>
<td>SMEAR III, UBG</td>
<td>V</td>
</tr>
<tr>
<td>Dekati PM10</td>
<td>24 h</td>
<td>Quartz fibre</td>
<td>South Africa, rural</td>
<td>III</td>
</tr>
</tbody>
</table>
4.2.1. Sampling techniques

An EPA (Environmental Protecting Agency, USA) well impactor ninety-six (WINS, Peters et al., 2001) sampler was used to collect 24-h PM$_{2.5}$ particles at a flow rate of 16.7 l min$^{-1}$ on a daily basis. Particles with $D_a > 2.5$ µm were impacted into the oiled surface and particles with $D_a < 2.5$ µm were collected in prewashed PTFE filters (ø 47 mm, pore size 3 µm, Millipore Ireland B.V., Carrigtwohill, Ireland). The EPA-WINS sampler was used in a six-month campaign conducted at an urban background site in Kotka, Finland (Paper I).

A virtual impactor (VI, Loo and Cork, 1988) classifies particles in two size ranges: fine (PM$_{2.5}$) and coarse (PM$_{2.5-10}$, 2.5 µm $< D_a < 10$ µm). After a PM$_{10}$ inlet, discriminate particles larger than 10 µm, sample air (16.67 l min$^{-1}$) is divided into two flows: the major flow (15.03 l min$^{-1}$), which only carries fine particles, and the minor flow (1.67 l min$^{-1}$), which carries all of the coarse particles and 10% of the fine particles. Both flows are filtered resulting in two particle size fractions in separate filters. Three VIs were used in the six-month campaign at the urban background site in Kotka, Finland (Paper I). The pre-washed PTFE filters (same type as in EPA-WINS) were used in two of the VI units, whereas the third VI was loaded with two quartz fibre filters (ø 47 mm, Whatman QMA, Maidstone, UK). This tandem quartz filter method was used to estimate and correct the positive artefacts caused by the adsorption of gaseous organic compounds on the filters. One VI had a nylon (ø 47 mm, Nylasorb 1.0µm, Ann Arbor, MI, USA) backup filter behind the PTFE-filter to capture HNO$_3$, which is formed when NH$_4$NO$_3$ is evaporated from the loaded filter and decomposed into HNO$_3$ and NH$_3$. VI was used to collect four-day (from Monday to Friday) samples.

Filter cassette systems (Pall Life Sciences) were used to collect submicron particles using two preheated quartz fibre filters (Ø 47 mm Tissuquartz, PALL or Whatmann QMA) placed in series. The four upper stages of a Berner low pressure impactor (BLPI; Berner and Lürzer, 1980, described later) were used to cut off supermicron particles. The sampling duration was mainly 24 h on working days and 72 h from Friday to Monday. The filter cassette system was used at SMEAR II (Paper IV) and at SMEAR III (Papers I, IV and V).

The BLPI (Berner and Lürzer, 1980) is a cascade impactor that divides particles into ten size fractions. The aerodynamic 50% cut-off diameters (corresponding to 50% collection efficiency) are...
7.5, 3.5, 1.8, 0.94, 0.53, 0.32, 0.16, 0.093, 0.067 and 0.035 µm (Hillamo and Kauppinen, 1991). Four-day (from Monday to Friday) samples were collected at a flow rate of 25 l min\(^{-1}\). The substrate material was aluminium foil greased with Apiezon L vacuum grease. The BLPI was used in the six-month campaign conducted at the urban background site in Kotka, Finland (Paper I).

The micro-orifice uniform deposit impactor (MOUDI) is also a cascade impactor that divides particles into nine size fractions, with the cut-off diameters of the impactor stages being 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 µm (Marple et al., 1991). It has much higher absolute stage pressures than low pressure impactors, which is expected to reduce, though not necessarily eliminate, losses of semivolatile material. The duration of each MOUDI collection was typically 72 h, the flow rate was 30 l min\(^{-1}\) and the material of the substrates was aluminium foil. The MOUDI was used at SMEAR III in 2006–2007 and its results are briefly presented in Paper V.

The Dekati PM10 impactor is a three-stage cascade impactor that separates particles into four different size fractions, with the impactor cut points at 10, 2.5 and 1 µm. The particles in the Dekati impactor were collected using Ø 25 mm quartz fibre filters (Tissuquartz, PALL) in three impactor stages \((D_a > 1 \mu m)\), whereas particles smaller than 1 µm diameter were collected on the same filter material but with a larger diameter filter \((Ø 47 \text{ mm quartz fibre filter})\). The sampling flow rate was 30 l min\(^{-1}\), and the sampling duration was typically approximately 24 h. The Dekati PM10 impactor was used at the rural savannah site in South Africa for two short campaigns in 2007 and 2008 (Paper III).

### 4.2.2. Chemical analyses

The sample treatment and analytical techniques for fine PM are presented in this section. Table 3 compiles the instruments used and the descriptions of the methods can also be found in Papers I–V. Except for trace elements, all of the chemical analyses were conducted at the Finnish Meteorological Institute.
Table 3. Off-line chemical and physical analyses used in this thesis.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Determined component</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCEC analyser</td>
<td>OC, EC</td>
<td>I, III–V</td>
</tr>
<tr>
<td>IC</td>
<td>SO₄²⁻, NO₃⁻, Cl⁻, oxalate, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺</td>
<td>I, III, V</td>
</tr>
<tr>
<td>HPAEC-MS</td>
<td>Monosaccharide anhydrides (e.g. levoglucosan)</td>
<td>II, III</td>
</tr>
<tr>
<td>LC-MS</td>
<td>Monosaccharide anhydrides (e.g. levoglucosan)</td>
<td>I</td>
</tr>
<tr>
<td>TOC-VCPH</td>
<td>WSOC</td>
<td>V</td>
</tr>
<tr>
<td>EDXRF</td>
<td>Al, Br, Ca, Cl, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Si, Sr, Ti, V, Zn</td>
<td>I</td>
</tr>
<tr>
<td>SSR</td>
<td>BC</td>
<td>I</td>
</tr>
<tr>
<td>microbalance</td>
<td>Gravimetric mass</td>
<td>I, V</td>
</tr>
</tbody>
</table>

4.2.2.1. Carbonaceous fraction

The concentrations of particulate OC and EC were analysed using a thermal-optical OCEC aerosol analyser (Sunset Laboratory Inc., Tigard, OR, US, Birch and Cary, 1996). The thermal analytical technique splits carbon into fractions according to their volatility. In the first stage, OC is desorbed from the quartz fibre filter through progressive heating under a pure He stream. However, a fraction of OC chars and forms pyrolysed OC during that stage. In the second phase, the sample is heated in temperature steps under a mixture of 90% He–10% O₂ (HeOx phase), during which pyrolysed organic and EC are desorbed. In order to correct for the pyrolysis effect, the analyser measures the transmittance of a 658 nm laser beam through the filter media. The split point, which separates OC and pyrolysed OC from EC, is determined as a point when the laser signal returns to its initial value. After being vaporised in several temperature steps, OC, EC and pyrolysed OC are catalytically converted first to CO₂ and then to CH₄, which is quantified with a flame ionisation detector. At the end of each analysis, a fixed volume of calibration gas (5% CH₄ in helium) is injected into the instrument to correct possible variations in the analyser’s performance.

The operating parameters of the OCEC aerosol analyser vary depending on the thermal protocol used during the analysis. In this thesis, modified NIOSH (Papers I and V), EUSAAR_1 (Papers III and IV) and EUSAAR_2 (Paper III) protocols were used (Table 4, Cavalli et al., 2010). The EUSAAR-2 protocol differs from the EUSAAR-1 protocol by having more temperature steps during the HeOx phase, which improves the determination of the split between OC and EC. The
helium phase is equal in both EUSAAR protocols. The modified NIOSH protocol clearly has higher temperatures in the helium phase than the EUSAAR protocols.

Table 4. Temperature protocols used to analyse samples in this thesis.

<table>
<thead>
<tr>
<th>step</th>
<th>mod NIOS T, duration (°C, s)</th>
<th>EUSAAR-1 T, duration (°C, s)</th>
<th>EUSAAR-2 T, duration (°C, s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He1</td>
<td>310, 90</td>
<td>200, 180</td>
<td>200, 180</td>
</tr>
<tr>
<td>He2</td>
<td>475, 90</td>
<td>300, 180</td>
<td>300, 180</td>
</tr>
<tr>
<td>He3</td>
<td>615, 90</td>
<td>450, 180</td>
<td>450, 180</td>
</tr>
<tr>
<td>He4</td>
<td>800, 90</td>
<td>650, 180</td>
<td>650, 180</td>
</tr>
<tr>
<td>HeOx1</td>
<td>550, 45</td>
<td>550, 240</td>
<td>500, 120</td>
</tr>
<tr>
<td>HeOx2</td>
<td>625, 45</td>
<td>850, 120</td>
<td>550, 120</td>
</tr>
<tr>
<td>HeOx3</td>
<td>700, 45</td>
<td>700, 70</td>
<td></td>
</tr>
<tr>
<td>HeOx4</td>
<td>775, 45</td>
<td></td>
<td>850, 80</td>
</tr>
<tr>
<td>HeOx5</td>
<td>850, 45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HeOx6</td>
<td>890, 120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HeOx: mixture of 10% oxygen in helium

BC was analysed from the EPA-WINS samples using a smoke stain reflectometer (Model M34D, Diffusion Systems, London, UK) in Paper I. The average reflectance of two measurements was converted into the adsorption coefficient, following the guidance in ISO9835 (1993). Finally, the absorption coefficient was converted into BC using a correlation analysis between filter blackness measurements and corresponding aethalometer readings.

4.2.2.2. Ions

Selected inorganic ions (sulphate, nitrate, chloride, sodium, ammonium, potassium, magnesium and calcium) and oxalate were analysed using a Dionex IC (DX-500 or ICS-3000, Dionex, Sunnyvale, USA) with a conductivity detector. An AS11 or AS17 column was used to separate anions, and the eluent was either NaOH or KOH. For cations, the column was either CS12 or CS12A, with an eluent of methane sulphonic acid. Chemically (Paper I) or electrolytically (Papers III–V) regenerated suppressors were used to decrease the background signal and increase the signal of the analyte. The substrates (PTFE, Nylasorb, quartz fibre, aluminium foils) were extracted with
deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA) before the analyses. Before the water extraction, the PTFE filters used at the urban background site in Kotka (Paper I) were first wetted with a small amount of methanol to reduce the hydrophobic effect of the material. The sample solutions were filtered before analysis to remove insoluble material. The total volume of the extract was typically 5 or 10 ml.

4.2.2.3. Monosaccharide anhydrides

Monosaccharide anhydrides (MAs), such as levoglucosan, mannosan and galactosan, were analysed using a Dionex ICS-3000 system coupled to a quadrupole mass spectrometer (Dionex MSQ™). The analytes were separated using a Dionex CarboPac™ PA10 column, an electrolytically regenerated suppressor and a KOH eluent. A mass spectrometer with electrospray ionisation was used to detect MAs. The samples for the MA analyses were extracted with Milli-Q water similarly to the method used for ions. A detailed description of the HPAEC-MS method is presented by Saarnio et al. (2010a). The MAs were analysed using the HPAEC-MS method in Papers II and III, whereas in Paper I, the MAs were analysed using LC coupled with an ion trap mass spectrometer (Agilent Technologies SL, Santa Clara, CA, USA, Dye and Yttri, 2005). Two Atlantis (150 mm, Waters, Milford, MA, USA) columns were used in series to separate different isomers of MAs. The eluent was deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA). In the LC-MS analysis, the samples were extracted with a 2-mL mixture of tetrahydrofuran and water (1:1) in an ultrasonic bath for 30 min. The sample solutions were filtered before the analyses.

4.2.2.4. Water-soluble organic carbon

In Paper V, WSOC was analysed using the total organic carbon analyser with a high sensitivity catalyst (TOC-VCPH, Shimadzu). The substrates (quartz fibres or aluminium foils) were extracted with deionised water (15 ml, Milli-Q Gradient A10, Millipore, Billerica, MA, USA) and the sample solutions were filtered before analysis. The extractions were acidified and bubbled with helium to remove inorganic carbon (carbonates, hydrogen carbonates and dissolved carbon dioxide) before they were injected into an oven. In the oven, the carbon was catalytically oxidised to CO₂ at 680°C, and the CO₂ produced was detected by a sensitive NDIR-detector. A detailed description of the analytical method is presented in the paper by Timonen et al. (2008b).
4.2.2.5. Trace elements

The concentrations of trace elements (Al, Br, Ca, Cl, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Si, Sr, Ti, V and Zn) were analysed using an energy dispersive X-ray fluorescence (EDXRF, Tracor Spectrace 5000). The PTFE substrates were excited by radiating them with a low-power Rh-anode X-ray tube, and the characteristic X-ray radiation was detected with a Si(Li) detector. The measured intensities were converted into elemental concentrations. EDXRF is particularly well suited for fast, non-destructive, sensitive and multi-elemental analysis of ambient aerosols. The results of the trace metal analysis were utilised briefly in Paper I.

4.2.3. Gravimetric method

The PTFE filters (Paper I) and aluminium foils (Paper V) were weighed with a Mettler M3 microbalance (Mettler Instrumente AG, Zurich, Switzerland) that had a resolution of 1 µg. The samples were allowed to stabilise on the weighing bench for 30–60 min before being weighed. As the measured masses, especially for the impactor substrates, are typically quite small, the relative humidity, temperature and pressure of the ambient air and the static charge of the sample can have a significant role. The temperature and relative humidity were recorded, but not adjusted, and the electrostatic charges of the filters were eliminated with Po-210 radioactive sources. Each filter was weighed twice and the criterion for valid weighing was that the mass readings were within 2 µg of each other. The weighing was repeated if the criterion was not fulfilled.

4.3. On-line measurements

A description of the on-line measurements used in this thesis to investigate the chemical composition and physical properties of fine particles is presented in this section and in Papers I–V. The information about the instruments used is compiled in Table 5.
Table 5. On-line instruments of measuring particles in this thesis.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Determined component</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-OCEC</td>
<td>OC, EC, BC</td>
<td>I, IV, V</td>
</tr>
<tr>
<td>PILS-IC</td>
<td>Cl(^-), NO(_3)^-, SO(_4)^{2-}, Na(^+), NH(_4)^+, K(^+), oxalate, MSA</td>
<td>V</td>
</tr>
<tr>
<td>ACSM</td>
<td>POM, Cl(^-), NO(_3)^-, SO(_4)^{2-}, NH(_4)^+</td>
<td>II</td>
</tr>
<tr>
<td>MAAP</td>
<td>BC</td>
<td>II</td>
</tr>
<tr>
<td>Aethalometer</td>
<td>BC</td>
<td>I, V</td>
</tr>
<tr>
<td>TEOM</td>
<td>Gravimetric mass (PM(_{2.5}))</td>
<td>II</td>
</tr>
<tr>
<td>TEOM+FDMS</td>
<td>Gravimetric mass (volatile and non-volatile)</td>
<td>I, V</td>
</tr>
<tr>
<td>FH 62 I-R</td>
<td>Gravimetric mass by β-attenuation</td>
<td>I, II</td>
</tr>
<tr>
<td>SHARP</td>
<td>Gravimetric mass by light scattering and β-attenuation</td>
<td>II</td>
</tr>
<tr>
<td>DMPS</td>
<td>Size distribution of particle (PM(_{1}))</td>
<td>III, IV</td>
</tr>
</tbody>
</table>

4.3.1 Organic and elemental carbon

A SC-OCEC (Sunset Laboratory Inc., Oregon, US) was used to measure the concentrations of OC and EC on-line. The operation of a SC-OCEC is quite similar to that of the thermal-optical OCEC aerosol analyser used for the filters, described earlier in Section 4.2.2.1. In short, SC-OCEC collects a particle sample on a quartz filter located in the quartz oven. After the sampling period, the deposited particles are heated in a helium and HeOx-phase atmosphere in the oven. The vaporised carbon compounds formed in the oven are purged to a MnO\(_2\) catalyst, where they are further oxidised to carbon dioxide and quantified with a non-dispersive infrared (NDIR) detector. At the end of each analysis, an external standard was automatically injected through the system to correct possible variations in the instrument’s performance.

The sample flow of the SC-OCEC was 9 l min\(^{-1}\), and a cyclone was used to cut off particles with \(D_a > 1\) μm prior to the sampling. A parallel plate carbon denuder (Sunset Laboratory Inc., OR, US) was used in-line before the instrument to remove organic gases. The time resolution was either two or three hours, and consisted of 100–160 minutes of sample collection and 20 minutes of sample analysis. An instrumental blank, which consisted of two minutes of sampling and subsequent analysis, was taken every night. In addition to the thermally determined OC and EC, the instrument also measured refractory carbon optically (denoted as BC) with the laser (660 nm). The time resolution for the BC was one minute.
4.3.2. Ions

The main inorganic ions were analysed on-line using the PILS-IC (Paper V). The operation principles of the PILS are described in detail in Orsini et al. (2003). Briefly, particles and water steam are simultaneously fed into the PILS, where particles grow by water supersaturation as they move across a conical shape cavity surrounded by passive cooling elements. At the other end of the cavity, the grown particles impact a quartz-glass surface. The surface is rinsed with a flow of water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA) containing a known concentration of lithium fluoride (LiF) as an internal standard. Liquid from the PILS was directly fed into the 1 000 μl loops of two ICs, one for anions and the other one for cations (Dionex ICS-2000, Dionex, Sunnyvale, CA, USA). With the PILS-IC system, the concentrations of Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}^{2−}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, oxalate and methane sulphonate (MSA) could be determined with a 15-min time resolution.

A VI modified from the design of Loo and Cork (1988), with a cut-off size of 1.3 μm was used to cut off the coarse particles upstream of the PILS measurements. Gaseous compounds (ammonia and acidic gases) were removed before the PILS measurements with three annular denuders (one coated with 3% phosphoric acid and two with 1% potassium hydroxide). The denuders were changed every second week to ensure that all gaseous compounds were effectively removed.

4.3.3. Non-refractory chemical species

An ACSM (Aerodyne Research Inc., Ng et al., 2011a) was used to determine the mass concentrations of non-refractory sub-micron aerosol species (POM, nitrate, sulphate, ammonium and chloride). The instrument consists of a particle sampling inlet, three vacuum chambers and a residual gas analyser mass spectrometer. In the particle sampling inlet, particles are focussed into a narrow particle beam using an aerodynamic lens system. After being transmitted through the chambers, the beam is directed into a hot tungsten oven (~600 °C) where the particles are flash-vaporised, ionised with a 70-eV electron impact ioniser and detected with a quadrupole mass spectrometer. Particle-laden and particle-free air is sampled interchangeably to determine the contribution of the gas-phase components to the total signal. In this thesis, ACSM data were averaged over ~30-min intervals for
each measurement point. A collection efficiency value of 0.5 was used in this study to account for the particle losses in the instrument. The data acquisition software provided by the manufacturer was used to process the data to obtain the total organic and inorganic (i.e., $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{NH}_4^+$, and $\text{Cl}^-$) particle mass concentrations. Ng et al. (2011a) discuss the calculation of the concentrations from the ACSM data in further detail. The comparison of ACSM to different instruments has been widely studied in the paper of Budisulistiorini et al. (2014).

4.3.4. Black carbon

BC concentration was measured using a MAAP (Thermo Electron Corporation, Model 5012) in Paper II, an aethalometer (AE-16 or AE42-2-HP-P3, Berkeley, CA, USA) in Papers I and V, and a SC-OCEC (see 4.3.1) in Paper IV. The MAAP determines the absorption coefficient ($\sigma_{AP}$) of the particles deposited onto a filter by a simultaneous measurement of transmitted and backscattered light. The backscattered light is measured to correct the scattering effects of the aerosols on the filter. The instrument uses a wavelength of 637 nm, as determined by Müller et al. (2011). The $\sigma_{AP}$ is converted to BC mass concentrations by using the mass absorption cross section of 6.6 m$^2$ g$^{-1}$ (Petzold and Schönlinner, 2004). The aethalometer uses a wavelength of 880 nm to measure the attenuation of light through the filter, which for atmospheric fine particles is mainly due to BC. The light attenuation changes due to the absorption of particles onto the filter. BC mass concentrations are calculated from the attenuation coefficient using the default mass absorption cross section of 16.6 m$^2$ g$^{-1}$ (Hansen et al., 1984). The inlet cut point for the MAAP was 1 µm (PM$_1$) and for the aethalometer 2.5 µm (PM$_{2.5}$).

4.3.5. Mass concentrations

PM$_{2.5}$ mass concentrations were measured with monitors based on $\beta$-attenuation (FH 62 I-R, Thermo Fisher, USA), a combination of light-scattering and $\beta$-attenuation (SHARP 5030, Thermo Fisher, USA) or a tapered element oscillating microbalance technique (TEOM 1400ab or 1400A, Thermo Fisher, USA).

The attenuation of $\beta$-rays (Kr-85 source) by a filter in the FH 62 I-R monitor is directly related to the amount of mass on the filter. The inlet is heated to 35 °C to avoid water condensation on the
filter. This process not only leads to the loss of water, but certain semivolatile compounds such as ammonium nitrate can also evaporate. This monitor was used in Papers I and II.

A SHARP monitor combines light-scattering photometry and β-attenuation (C-14 source) in one instrument. Similar to the FH 62 I-R monitor, the sample tube was heated (35 °C) to avoid condensation. This monitor was used in Paper II.

The TEOM technique is used to measure the mass concentration of PM in the air. The change in the oscillation frequency over time is used to directly measure the accumulation of mass on the filter located on the top of the tapered oscillating glass rod. In line with other mass monitors, the sample tube of TEOM was heated (30 °C). A TEOM 1400ab was used in Paper II, and a TEOM 1400a equipped with a Filter Dynamics Measurement System (FDMS) was used in Papers I and V. The FDMS TEOM first measures the non-volatile mass of particles that have passed through a drier. After this, the semivolatile portion of the sample is independently measured from the total incoming sample by using a filter to remove particles. The combination of TEOM and FDMS can therefore measure both the volatile and non-volatile particles. To ensure equivalent results, the PM$_{2.5}$ monitoring data from different instruments were corrected using empirical calibration equations according to European standards (Waldén et al., 2010).

The mass concentration of PM$_1$ was measured indirectly in Papers III and IV using a Differential Mobility Particle Sizer (DMPS; a Hauke-type Differential Mobility Analysers and TSI model 3025 and 3010 Condensation Particle Counters), which measured the distribution of particle numbers by size. The particle number concentration of each DMPS size channel was converted to a volume concentration assuming spherical particles, multiplied by the estimated particle density and summed to obtain the total mass concentration of particles below 840 nm. The particle density value was calculated from the analysed chemical composition for each sample using an approach suggested by Saarnio et al. (2010b) and varied from 1.38 to 1.75 g cm$^{-3}$ (Paper III), or using the particle density value of 1.48 g cm$^{-3}$ obtained from Saarnio et al. (2010b, Paper IV).
4.4. Data analysis methods

The data obtained from the off- and on-line measurements were treated using two methods: source analysis of POM (Paper II) and chemical mass closure of fine particles (Paper I). The sources and characteristics of POM were investigated using ME-2 and the custom software tool SoFi (version 4.6, Canonaco et al., 2013). By using the source apportionment method, POM can be divided into factors representing different particle sources, such as engine emissions from traffic, biomass burning and cooking, or into factors that represent components with similar chemical characteristics, such as LV- and SV-OOA. In ME-2, the user can constrain the factor profiles and/or time series to a chosen extent. Constraining is typically used if the environmentally reasonable number of factors are not satisfactory separated from each other. When using constraints, users input prior information about known factor profile(s) (and/or time series) to the program. The resolved factor is allowed to vary from the reference one (input) based on the $a$-value. For example, if $a = 0.1$ when constraining a mass spectral profile, all of the $m/z$s in the fit profile can vary by as much as $-10\%$ to $+10\%$ of the input mass spectrum profile. According to the source apportionment guidelines of ME-2, a reference HOA mass spectrum should be constrained first, if the constraint is needed (Crippa et al., 2014). Both unconstrained and constrained ($a = 0.1$) factor profiles were used in Paper II.

The number of factors in the dataset is unknown, and the final number of factors is defined by the user in ME-2. The number of factors is selected based on the unexplained variation, changes in the Q-value (the total sum of the squares of the scaled residuals), the comparison of mass spectra with the AMS mass spectra database (Ng et al., 2011b) and/or information (e.g. temporal or diurnal variation) on auxiliary species such as BC, inorganic ions, NO$_x$ and meteorological information. Two- and three-factor solutions were used in Paper II.

The gravimetrically-measured particulate mass was reconstructed from the sum of analysed or estimated chemical components. This method, called a chemical mass closure, was used to determinate of the relative contribution of different components and sources to the fine particulate mass. In Paper I, the chemical components of fine particles were divided into five classes: secondary inorganic ions (ammonium, non-sea-salt sulphate and nitrate), sea salt, soil, elemental carbon and POM. The concentrations of sea salt and nss-SO$_4$ were estimated from the concentration of sodium based on standard sea water composition (Brewer, 1975). The measured OC
concentration was multiplied by 1.6 to estimate the concentration of POM (Turpin and Lim, 2001), and the soil-related components (Si, Al, Fe, Ca and K) were calculated as their oxides (Brook et al., 1997).

5. RESULTS

5.1. Chemical composition of atmospheric fine particles

The average chemical compositions of the fine particles from the urban and rural environments are presented as pie charts in Figure 6. On average, the sums of the chemically analysed species were quite similar at all the sites, varying between 8 and 14 µg m\(^{-3}\). Typically, the analysed mass covered 50–95% of the total mass determined using the gravimetric method, mass concentrations monitors or estimation of the number size distribution data. The analysed mass had the lowest contribution to the total mass at the Residential I site, but since BC was not measured there, it was not accounted for in the analysed mass. Usually, the main reason for the difference between the analysed and total mass was a difference in size fractions—the analysed mass may have had cut-off of 1 µm, whereas the monitored mass concentrations mainly had a cut-off at 2.5 µm. No clear seasonal variation was found in the concentrations of fine particle mass, but differences in the concentrations and contributions of individual species were detected. The highest concentrations of ions, OC and EC were measured during winter, but the highest contribution of OC was detected in summer.

The organic fraction had the largest contribution to the total mass at all of the sites except the rural site in South Africa. The campaign-average concentration for POM varied from 3.5 to 6.4 µg m\(^{-3}\), constituting 39–55% of the analysed components. In South Africa, sulphate had the highest contribution to the total mass, followed by POM. On average, sulphate concentrations displayed large variation between the sites, ranging from 0.6 to 3.9 µg m\(^{-3}\), corresponding to contributions from 7% to 44% of the total mass. Typically, the sum of the secondary inorganic ions and POM had similar contributions to the mass.

Nitrate concentrations were extremely low in South Africa. Particulate nitrate was most likely missing because of the gas-to-particle partitioning of ammonium nitrate, as the South Africa
campaigns were performed in summer and spring, when the air temperature favoured ammonium nitrate to be mostly in its gas phase.

BC constituted approximately 10% of the particle mass at the urban background sites, whereas the contribution was much higher (25%) at the Highway site, where engine emissions from traffic were large. At the rural savannah site, the contribution (3%) and concentration of BC (0.29 kg m⁻³) were very small.

Figure 6. Chemical composition of fine particles in different environments. The results were compiled from Papers I, II, III and V. The cut-off of fine particles was 2.5 μm in Kotka and 1 μm at the other sites. BC was not measured at the Residential I site. UBG: urban background.

Although the average chemical composition of fine particles seemed to be very similar at all the sites, at least in Finland, the temporal pattern of the different components shows that they had clear variations in their concentrations and mass contributions. For example, the POM concentrations and contributions displayed day-to-day variation ranging from 0.5 to 29.6 kg m⁻³ and from 16 to 88%, respectively (Papers I and V). Even larger mass concentrations were observed when analyses with higher time resolution were performed with on-line measurements (Papers II and V). With the on-
line instruments, the time resolution of the chemical characterisation of the fine particles improved significantly, allowing detailed investigations of the emissions’ sources and the particles’ transformation processes. The highest mass concentrations were obtained during wildfire episodes in May and August 2006. Examples of the chemical composition of fine particles with different time resolutions are presented in Figure 7.

**Figure 7.** Examples of the chemical composition of fine particles using on-line (upper panel) and off-line (lower panel) methods. The results were compiled from Papers I, II, III and V.
5.2. Carbonaceous fraction

Particulate carbonaceous matter can be separated into OC and EC (or BC). In the urban background sites, 30% of the TC was in the form of EC, on average (Papers I, II, IV, V), whereas the EC fractions in the rural sites were clearly lower (11% and 14% in Papers III and IV, respectively) and was higher at the Highway site (40%; Paper II). If the majority of OC and EC is emitted from primary sources, then their emission rates will be similar and the sources of carbonaceous particles can be roughly estimated based on the ratio of OC to EC. However, if there is more than one main primary source, such as traffic and biomass burning together, then the ratio of OC to EC will not be constant and the sources cannot be distinguished from each other. In the urban background sites, the main source of EC was obviously traffic. This can be seen from the diurnal variation of EC (Figure 8), which showed the highest concentrations at times of high traffic volume (Papers II, IV and V). However, the comparison of the diurnal profiles of EC and NO\textsubscript{x} in different seasons showed evidence of additional sources beyond traffic during winter (Paper IV). In Finland, wood is typically used for supplementary heating in detached housing areas during cold seasons, and most likely the combustion of wood was an additional local source of EC during winter. OC did not have any diurnal trend in urban areas, but individual subcategories of POM did (Paper II). The source apportionment results for POM will be discussed later. The diurnal trends of EC and OC are presented in Figure 8.

Although the interpretation of the ratio of OC to EC is not straightforward, the average ratio of OC to EC at the rural areas i.e. savannah site (Paper III) and SMEAR II (Paper IV), was significantly higher (7.5 and 9.6, respectively) than in the urban areas of Helsinki or Kotka (2.3–3.2, Papers I, II, IV and V). This was likely due to the large contribution of SOA to POM and the low concentrations of EC at the rural sites. High OC-to-EC ratios of up to 16 have also been observed in other rural/remote areas (Gelenchér et al., 2007; Querol et al., 2013).

As already mentioned, EC forms during incomplete combustion processes and is always primary; thus, EC concentrations decrease with dilution, whereas SOA formation can increase OC concentrations and hence OC-to-EC ratios. High OC-to-EC ratios were also observed during the biomass-burning events (7–10, Papers I, III, V), in emission measurements of wood burning and in ambient wildfire smoke (6–10, Calvo et al., 2015; Saarnio et al., 2010b; Formenti et al., 2003),
whereas clearly lower OC-to-EC ratios (1–3) were detected for primary combustion-generated aerosols (Polidori et al., 2006; Querol et al., 2013). At the urban sites, the lowest average OC-to-EC ratio was obtained at the Highway site (Paper II), indicating large emissions of primary particles from traffic. The ratio of OC to EC, especially at the Highway site was lower during the daytime than in the early morning hours (Figure 8), when there was no traffic and the concentration of EC was mostly related to regional background EC. At the Highway site, OC was calculated from POM measured by ACSM by dividing the concentration of POM by 1.6 (Turpin and Lim, 2001). The average OC-to-EC ratios measured during different campaigns are collected in Figure 9.

![Figure 8](image)

**Figure 8.** Diurnal variation of EC, OC and OC-to-EC ratio. OC was calculated by dividing the POM measured at the Residential, Highway and Curbside sites by 1.6. The results were compiled from Papers II, IV and V.

In Paper IV, simultaneous measurements of OC and EC at the urban background site (SMEAR III) and the rural site (SMEAR II) showed significantly higher concentrations of OC and EC at the urban site. However, the concentrations of OC had a high correlation between the sites (Pearson correlation coefficient R=0.9). Also, a high correlation in daily PM$_{2.5}$ mass concentrations was obtained between Kotka and Helsinki in Finland, suggesting that the air masses were well mixed.
over a large area of southern Finland (Paper I). There were no clear seasonal variations in the OC concentrations at the SMEAR sites, although for both sites, the concentrations were somewhat higher in winter than in summer. EC had the lowest concentrations in summer. At SMEAR III in Helsinki, the ratio between OC and EC had no clear seasonal variation, whereas at rural SMEAR II, the ratio of OC to EC increased significantly during summer. This indicates a prominent formation of secondary biogenic organic aerosol at the rural site (SMEAR II) in summer.

![Figure 9](image)

**Figure 9.** The average ratios of OC to EC in fine particles during the campaigns. Results are compiled from Papers I, III, IV and V. BB means biomass burning events (wildfires, see Figure 7).
5.3. Case studies

5.3.1 Biomass burning

In Papers I and III, biomass burning events (a forest fire and a field-burning experiment involving savannah grass and branches, respectively) were studied more thoroughly. During the study conducted at the urban background site in Kotka (Paper I), a wildfire episode originating from the western part of Russia was observed that lasted a total of 12 days. The highest 1-h average mass concentration of PM$_{2.5}$ was almost 90 µg m$^{-3}$ during the episode, which can be compared to the campaign mean of 11 µg m$^{-3}$. The contribution of POM to PM$_{2.5}$ mass increased to 45–77% from its non-episodic average value of 37%, and the concentrations of typical biomass burning markers i.e. levoglucosan, potassium and oxalate, increased 3–5-fold, with respect to the campaign mean. Similar results, with high concentrations of POM, MAs (e.g. levoglucosan), potassium and oxalate, were observed at the rural site in South Africa (Paper III), where a biomass-burning experiment was performed. Potassium was mainly in the form of KCl, which has typically been detected in fresh smoke from burning savannah grass (Gao et al., 2003). The ratios of different MAs were also investigated in the field-burning experiment in South Africa (Paper III). Depending on the biomass material burned, different ratios of levoglucosan to mannosan or galactosan were produced. In the biomass-burning experiment, the burned material—savannah grass and branches—produced similar ratios of levoglucosan to mannosan (16–17) and levoglucosan to galactosan (14–17), as had been observed in laboratory experiments with savannah grass and acacia wood (levoglucosan/mannosan: 22, levoglucosan/galactosan: 15, Inuma et al., 2007).

5.3.2 The impact of air mass origin

The air mass backward trajectories were obtained using the NOAA HYSPLIT backward trajectory model (Rolph, 2016). The routes of arriving masses were studied especially in Papers III and IV. Either 72-h or 96-h backward air mass trajectories were calculated to arrive at every third hour (Paper IV) or every hour (Paper III) of sampling, with an arrival height of 100 m above the ground.
Figure 10. Air mass history of the ambient case studies: a) regional background, b) Waterberg overpass and c) Western BIC (Bushveld Igneous Complex) overpass. The abbreviations for the provinces are LP: Limpopo, GR: Gauteng, MP: Mpumalanga, FS: Free State, NC: Northern Cape, and NW: North West. The figure is slightly modified from Paper III.

The influence of the air mass origin on the observed chemical composition of PM$_1$ was studied in the rural site in South Africa (Paper III). Backward trajectory calculations defined well characterised source regions. Three different cases were chosen for detailed investigation: 1) air masses with a regional background, 2) air masses influenced by the coal-fired power station in Waterberg and 3) air masses influenced by the silicon- and platinum-group metal smelters in
western Bushveld Igneous Complex (BIC, Figure 10). The observed PM$_1$ mass concentrations were significantly lower for the background air masses (2.9 µg m$^{-3}$) when compared to the events, which contained air masses influenced by anthropogenic sources (7.6–13.4 µg m$^{-3}$). The observed sulphate concentrations were 14 or 37 times larger when the air mass had passed over the Waterberg and BIC areas, respectively, when compared to the clean background air. The coal-fired power station in Waterberg does not remove SO$_x$ or NO$_x$ from flue gas. Therefore, the case data from the coal-fired power station will be very valuable as a reference point when the new coal-fired power station with de-SO$_x$ and de-NO$_x$ technology starts to operate in the area.

The influence of air mass origin on the carbonaceous fraction was studied in Paper IV, in which the concentrations and contributions of OC and EC were measured simultaneously at the rural site (SMEAR II) and the urban background site (SMEAR III). SMEAR II is located 220 km north-west from SMEAR III. A total of four cases were selected for further investigation (Figure 11). Three cases had clearly elevated OC concentrations at the rural site; during those cases, the air mass routes passed over the urban background site on the way to the rural site. In terms of annual averages, the OC concentration was 60% higher at the urban background site than at the rural site. However, during these events, the OC concentrations approached each other, with the difference being only 15–20% between the sites. The main sources for OC seemed to be common for both of the sites. The larger OC concentrations measured at the urban background site were caused by engine emissions from local traffic.

The fourth case contained air masses from Arctic areas that reached the rural site before reaching the urban background site. Typically, Arctic flows contain very clean air, which was detected as low concentrations of OC and EC at both sites during the fourth case. During the Arctic flow, the concentration differences for OC were much lower between the sites than average, but the contribution of local sources was still seen at the urban background site.
Figure 11. Air mass history at SMEAR II (rural) and SMEAR III (urban background). Case studies with high OC and EC concentrations (a–c), and low OC and EC concentrations (d). The OC and EC concentrations are in units of µg m\(^{-3}\). The figure was slightly modified from Paper IV.

5.4. Source apportionment of particulate organic matter

The source apportionment of POM was studied in the Helsinki metropolitan area (Paper II). Aerosol composition was measured using ACSM at four different sites: two of them were suburban
residential areas, and the other two were traffic sites, one at a downtown kerbside (Curbside site) and the other at a suburban highway edge (Highway site). Using the ME-2 algorithm with the custom software tool SoFi, a three-factor solution was found to describe the sources of POM most reliably at the Highway and residential sites (Residential I and II). The identified factors were HOA, OOA and BBOA, based on the reference mass spectra presented in the literature and by using auxiliary species such as BC, NO\textsubscript{x} and/or inorganic ions. The HOA factor was dominated by ions related to aliphatic hydrocarbons e.g. \textit{m/z} 41, \textit{m/z} 43, \textit{m/z} 55, \textit{m/z} 57, \textit{m/z} 67, \textit{m/z} 69, \textit{m/z} 71, \textit{m/z} 81, \textit{m/z} 83 and \textit{m/z} 85 (Zhang et al., 2005). HOA is typically emitted by combustion engines, such as from motor vehicles, and is believed to mainly come from lubricating oils (Canagaratna et al., 2004). HOA was correlated well with other combustion-related components, e.g. NO\textsubscript{x} and BC (Pearson correlation coefficients \textit{R}=0.74–0.92), indicating that it was mostly related to vehicle emissions. Multiple studies have shown OOA to be a good surrogate for SOA, correlating well with secondary species (Zhang et al., 2005). The Pearson correlation coefficient between OOA and ammonium was 0.71–0.77. OOA at all of the sites had very high contributions of \textit{m/z} 44, which is mainly CO\textsubscript{2}\textsuperscript{+} fragments, typically from the thermal decarboxylation of organic acid groups, and \textit{m/z} 18, a fragment of H\textsubscript{2}O\textsuperscript{+}, implying the thermal breakdown of carboxylic acid on the vaporizer. The high contribution of these fragments indicated highly oxidised POM. The characteristic \textit{m/z}s for BBOA are typically 29, 60 and 73, which are associated with the fragmentation of levoglucosan and other anhydrous sugars making them good tracers for biomass-burning emissions (Alfarra et al., 2007). In addition to these specific fragments, BBOA had high contributions of \textit{m/z} 44 and \textit{m/z} 18. The BBOA may have been a mixture of BBOA and OOA, long-range transported BBOA, partly processed BBOA or an instrument-related feature (Timonen et al., 2013, Crippa et al., 2013, Fröhlich et al., 2015).

At the Residential I and II sites, the reference spectrum for constraining the HOA factor was used to improve the separation between HOA and BBOA. The reference mass spectrum of HOA was taken from an earlier study conducted at the urban background site in Helsinki (SMEAR III, personal communication with Samara Carbone). BBOA could not be extracted from the data in the Curbside campaign. The signal at \textit{m/z} 60—which is related to biomass combustion—was noisy, and its contribution to total POM (\textit{f}60:0.4\%) was very close to the background level (0.3\%, Cubison et al., 2011). The mass spectra of the individual factors were very similar at all four sites (Figure 12) and correlated well (Pearson correlation coefficient \textit{R}= 0.92–0.98).
Figure 12. Mass spectra of ME-2 factors HOA, BBOA and OOA at two residential and two traffic sites in the Helsinki metropolitan area in Finland. The reference mass spectrum of HOA was taken from an earlier study and was used at the Residential I and II sites. The figure was adapted from Paper II.

OOA had the highest contribution to POM at all of the sites (50–67%). OOA did not have any diurnal trend, indicating that it was mostly regionally distributed or long-range transported. The contribution of HOA was larger at the traffic sites than at the residential sites, as can be expected. The concentration of BBOA was clearly highest at the Residential I site due to local wood-burning emissions and concurrently observed poor vertical mixing (winter inversion). BBOA had a clear
dependency on temperature. The contribution of BBOA to POM increased substantially during low ambient temperatures, especially at the Residential I and Highway sites (Figure 13). Although the temperature was not very low during the Highway campaign, which was conducted in autumn, the contribution of BBOA to POM was significant (60–78%) as the temperature decreased below 0 °C. The mass concentrations and contributions of ME-2 factors studied in Paper II are presented in Figure 13.

![Mass concentrations and contributions of ME-2 factors in Helsinki metropolitan area, Finland. The black lines represent the ambient temperature in the lower panel. The figure was adapted from Paper II.](image)

**Figure 13.** Mass concentrations (average) and contributions (averages and time series) of ME-2 factors in Helsinki metropolitan area, Finland. The black lines represent the ambient temperature in the lower panel. The figure was adapted from Paper II.

### 6. REVIEW OF THE PAPERS AND AUTHOR’S CONTRIBUTION

**Paper I** describes the chemical characterisation of the urban PM analysed with different on-line and off-line methods. This study was conducted from November 2005 to May 2006 in Kotka, Finland. The campaign was a part of multidisciplinary HIPPU study, in which, a personal exposure study
among ischemic heart disease patients, a toxicological cell study and an epidemiological panel were utilised, in addition to the detailed chemical composition of the particles. I handled the samples and performed the chemical analysis of the particles (ions, OC and EC), except for the analyses of the MAs and trace metals. I was responsible for analysing the PM composition data and writing the article.

**Paper II** presents the chemical composition of the submicron particles and the sources of POM in the Helsinki metropolitan area using a relatively new monitoring technique, ACSM, based on aerosol mass spectrometry. The study was conducted during the years 2010–2012 at four different sites. I operated the on-line instruments and conducted the data and source apportionment analyses. Also, I wrote the paper.

**Paper III** focusses on enhancing the knowledge of the chemical composition of particles at a regional background location in South Africa. The site is occasionally exposed to emissions from coal-fired power stations and/or to large mining and pyrometallic smelting activities. Two short sampling campaigns were conducted in October 2007 and Jan–Feb 2008. I did not attend the campaigns in South Africa, but I prepared the particle samplers for the measurements. I performed a majority of the chemical (ions, OC and EC) and data analyses. Additionally, I wrote the paper, with the help of the local co-authors from South Africa.

**Paper IV** presents the OC and EC concentrations in PM$_1$ measured for a year at a rural forested site in southern Finland, in Hyytiälä (SMEAR II), and at the urban background site in Helsinki (SMEAR III). The seasonal variation of the carbonaceous particles had not been studied previously at SMEAR II. I prepared the samplers and performed the chemical analysis (OC and EC). In addition, I was responsible for analysing the data and writing the article.

**Paper V** describes the results of the yearlong on-line and off-line measurements conducted at the urban background site in Helsinki, Finland (SMEAR III). The seasonal variation of the chemistry of PM$_1$ particles was studied, and the off-line and on-line methods were compared. In this paper, I contributed to the measurements and maintenance of the on-line instruments (PILS-IC, SC-OCEC), and performed much of the chemical analyses (partly ions, OC and EC).
7. SUMMARY AND CONCLUSIONS

The primary focus of this thesis was to investigate the chemical composition of atmospheric fine particles. The more specific focus was to characterise the sources or origins of the fine particles, especially the organic fraction. For this purpose, I conducted several measurement campaigns with various off-line and on-line instruments. On a campaign-average basis, the mass concentrations of fine particles were quite similar to each other in the studied areas but had a lot of temporal variation. A similar temporal trend for PM$_{2.5}$ in two cities in southern Finland indicated high contributions of regional or long-range transported sources to the PM$_{2.5}$. In Finnish urban and rural sites, the fine particles consisted mostly of organic matter, whereas at the rural site in South Africa, sulphate had the highest contribution to fine PM, followed by organic matter. The high contribution of sulphate was related to the impact of industrial emissions in South Africa.

The sources of particulate organic matter (POM) in the Helsinki metropolitan area were studied using factor analysis (ME-2), which revealed primary organic aerosol (POA) i.e. traffic and biomass burning, and secondary organic aerosol (SOA) as clear factors. POA had distinct diurnal variations, whereas the diurnal trend of SOA was flat, indicating long-range transport or regionally distributed POM. SOA had the largest contribution to POM (50–67%), even though the campaigns were conducted at specific environments, like in residential or traffic areas. However, the contribution of biomass burning to POM occasionally increased substantially. Such events occurred during cold ambient temperatures, during which the BBOA contribution to POM was around 50% or even higher versus 25–30% on average. The HOA contribution to the POM was 15–33%.

The studies of carbonaceous matter in Finland showed that common sources for OC in the rural and urban background areas existed, but both areas also had local sources, like traffic in the urban area and biogenic organic aerosol in the rural environment. Evidence of the clear contribution of biomass burning to organic matter during winter was also presented.

Although the interpretation of the ratio of OC to EC is not straightforward, it may give an indication of their sources. At the rural sites, the OC-to-EC ratio was two to three times the value in the urban areas. Similarly, higher ratios were observed during the biomass-burning events, whereas low ratios were observed near the traffic emissions. Also, there were differences in OC-to-EC ratio between
the seasons. The OC-to-EC ratio was significantly higher during summer than during the other seasons, indicating that biogenic sources had considerable influence on OC during summer.

Different cases were studied to understand the significance of the origin of the particles on the chemical composition. The chemical composition or mass concentration of PM may differ significantly, depending on the air mass origin. During biomass-burning events in Finland, the mass concentrations of fine particles increased almost 10-fold and typical biomass burning markers were identified. In South Africa, the concentrations of sulphate increased by a factor of 14 or 37 times, when compared with the clean background air during air mass flows over the coal-fired power plant or during industrial mining activities.

To conclude, this thesis contains the results of long-term off-line and on-line measurements of the fine particle chemistry in urban and rural areas. The thesis also includes data obtained from short-term campaigns providing information on different sources and meteorology affecting the particle chemistry at the measured area. Today several methods exist to determine the physical properties or chemical compositions of aerosols. However, more information is still needed on the properties of particles to understand the sources of primary anthropogenic and biogenic emissions and how they are processed in the atmosphere and affect air quality or climate. To fulfil this need, the chemistry of precursor gases and particles should be measured simultaneously.
REFERENCES


Characterization of urban particulate matter for a health-related study in southern Finland

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Particulate matter was physically and chemically characterized in November 2005–May 2006 concurrently with an epidemiological study among cardiac patients in Kotka, Finland. The daily PM\textsubscript{2.5} concentrations (campaign mean 10.6 µg m\textsuperscript{-3}) typically displayed a similar pattern to that in Helsinki, suggesting that the air masses were well-mixed over a large area of southern Finland. There were occasionally increased short-term PM\textsubscript{2.5} and particle number concentrations, most likely due to emissions from local industrial sources. A strong relationship was detected between high particle number concentrations (> 30 000 cm\textsuperscript{-3}) and north-easterly winds. PM\textsubscript{2.5}, black carbon (BC) or nitrogen oxides (NO\textsubscript{x}) did not show corresponding connection. The mean contribution of local traffic to BC and NO\textsubscript{x} were estimated at 30% and 55%, respectively, during the campaign. The main chemical component of PM\textsubscript{2.5} was particulate organic matter (37% ± 14%) followed by non-sea-salt sulphate (26% ± 11%), whereas main component of PM\textsubscript{2.5-10} was soil-derived crustal material (49% ± 11%).

Introduction

Epidemiological studies indicate that increased concentrations of atmospheric particles cause adverse health effects in urban populations. Still, it is uncertain which aerosol parameters, such as particle mass, particle number, surface area, particle size, chemical composition or water solubility, are the best indicators of harmfulness. There seems to be no threshold value for the mass or number concentration of particles in association with health effects. Daily mortality has been estimated to increase by 1% per each 10 µg m\textsuperscript{-3} increment of fine particles (PM\textsubscript{2.5}; mass of particles smaller than 2.5 µm in aerodynamic diameter) measured at a central urban background site.
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The mortality estimate doubles and is about six-fold for the same increment as five-day mean and the mean of several years, respectively (Pope and Dockery 2006).

Urban fine particulate aerosol is a mixture that consists of primary particulate matter emitted directly from local sources and of secondary material formed in the atmosphere from gas-phase precursors. The origins of urban PM$_{2.5}$ include local combustion and non-combustion emissions from traffic (Yli-Tuomi et al. 2005), small-scale wood combustion (Karvosenoja et al. 2008), industrial sources and even vegetation in warm seasons (Szidat et al. 2004), as well as mixtures of similar emissions transformed during regional or long-range transport (LRT) of air masses. In Helsinki, Finland, 64%–76% of the atmospheric PM$_{2.5}$ has been estimated to be from LRT (Karpinnen et al. 2004). One frequent source of LRT in the spring and summer in southern Finland are wildfire emissions typically originating from the Baltic countries, Belarus, Ukraine and western Russia (Niemi et al. 2004, 2005, 2009, Sillanpää et al. 2005, Saarikoski et al. 2007).

Spatial and temporal variations in particle number and mass concentrations, including chemical composition, were investigated at many different urban and rural sites (Putaud et al. 2004, Aalto et al. 2005, Sillanpää et al. 2006, Puustinen et al. 2007). However, the combination of health related studies with detailed aerosol measurements, allowing chemical mass closure, are uncommon (Happo et al. 2008, Jalava et al. 2008). Using receptor modelling in Helsinki, Lanki et al. (2006) showed that local traffic and oil combustion are more harmful sources of PM$_{2.5}$ to ischemic heart disease (IHD) patients than LRT or the soil source. Penttinen et al. (2006) reported similar results on the source-related effects of PM$_{2.5}$ on the respiratory health of asthmatic subjects in Helsinki.

In the multidisciplinary HIPPU study in Kotka, Finland, different online and offline physical and chemical measurement methods were used in connection to a six-month epidemiological panel and personal exposure study among ischemic heart disease patients and parallel high-volume particulate sampling for a toxicological cell study. This kind of highly integrated, prospective study has not been done before in Finland and they are rare also elsewhere. However, a multidisciplinary retrospective analysis on urban air pollution and health had previously been made (Ghio 2004). It was well-motivated to investigate urban air particles and health also elsewhere in Finland than in Helsinki, because it is unclear, to what extent the PM$_{2.5}$ and particle number concentrations associated health outcomes in Helsinki, e.g. increased respiratory and stroke mortality (Kettunen et al. 2007, Halonen et al. 2009) as well as increased hospital emergency room visits for respiratory and cardiac causes (Halonen et al. 2008, 2009), could be generalized for other cities in southern Finland. In Helsinki, the local and regional emissions contributing to PM$_{2.5}$ have been estimated to originate mainly from traffic, residential wood combustion and oil combustion (Vallius et al. 2003, Saarikoksi et al. 2008), because industrial emissions are very small, and the energy production and district heating are effectively maintained by large coal- and gas-fuelled plants with efficient emission control.

The principal objective of the present study was to chemically and physically characterize urban air particulate matter in Kotka, which is a city in southern Finland, where the local industries, the commercial harbours, and the transport sector were hypothesized to affect particle properties. A second objective was to compare in simultaneous measurements the contributions of local sources vs. regional transport and LRT to the particulate mixture in Kotka and Helsinki. The results from this work will be utilized in the analysis of the contributions of different sources to personal PM$_{2.5}$ exposure, to changes in inflammatory markers in patients’ blood circulation, and to the toxicological properties of the urban air particulate samples. The results from the epidemiological and toxicological studies are not presented in this paper.

Material and methods

Sampling site and measurement period

The six-month field campaign was carried out between 14 November 2005 and 12 May 2006.
in the city centre of Kotka, Finland (60°28’N, 26°56’E, 25 m a.s.l.) that is located on a small island, called Kotkansaari, on the northern coast of the Gulf of Finland, 130 km east of Helsinki. A transportable station for air quality monitoring and particulate sampling was placed in a central urban background location of Kotkansaari, on a schoolyard surrounded mainly by three-storey apartment buildings at a distance of 15–30 m. The nearest slow traffic road was situated 15 m away from the station. The distance of the major road with inbound traffic into the city was 1000 m west of the station. The sample intakes were about 5–6 m above the level of the nearest street.

The monitoring site was carefully selected to best represent the local environments (e.g. topography, micrometeorology) and local particle sources (e.g. car traffic, residential wood burning, energy plant for district heating, industries, harbours) in the vicinity of the homes of the cardiac patients participating in the six-month epidemiological panel study. All these subjects were living on Kotkansaari within a distance of less than two kilometres from the air-quality monitoring station.

The total particulate emissions from a variety of industrial activities, including energy production, and from traffic in Kotka in 2006 were estimated at 560 and 22 t a⁻¹, respectively (Kotka Environment Centre 2007). The main industrial activities in Kotka were a foundry and factories in connection to the production of paper, pulp, glass and glass fibre. The main point source in the area, a pulp mill, accounting for approximately 70% of the industrial primary particle mass emissions in the city (Kotka Environment Centre 2007), was 3 km north to north-east of the air-quality monitoring station. Other major local sources included the harbour activities. The main port (Mussalo), which is the largest container port in Finland, was in the sector south to south-west of the station at a distance of 4 km. The nearest harbour (City Terminal) was situated about 1 km north-east of the monitoring station. The total amount of goods traffic in all ports of the Kotka area was approximately 9 Mt in 2006. The population in Kotka was about 55 000 (2006).

In order to assess the contribution of the local industry to ambient particles in Kotka, the campaign data were compared with the data collected in parallel in Helsinki. The monitoring site in Helsinki, SMEAR III station (60°12’N, 24°58’E, 26 m a.s.l.), was located at a distance of about 5 km north-east of Helsinki downtown. A major road with high levels of traffic (60 000 cars day⁻¹) was at a distance of less than 200 m from the station to the east. The estimated total annual particle emissions in Helsinki were in 2006 about 1000 t (Helsinki Metropolitan Area Council 2007). The main sources of the emissions were traffic (28%), energy production (33%), and domestic wood combustion for heating of houses and sauna stoves (29%).

**High-time-resolution measurements**

In Kotka, the PM₂.₅ mass and particle number concentrations were measured with high-time-resolution by using a β-attenuation particulate matter mass monitor (Eberline FH62-IR, Eberline Instruments Santa Fe, NM, USA) and a condensation particle counter (CPC; TSI Model 3022, Shoreview, MN, USA), respectively. The CPC used in this study could detect particles larger than 20 nm in diameter and the averaging time was one minute. The averaging time for PM₂.₅ measurement was 1 h.

Black carbon (BC) was measured with five-minute time resolution using an aethalometer (AE 42-2-HP-P3, Berkeley, CA, USA) with a flow rate of 16.7 l min⁻¹ (Hansen et al. 1982). The aethalometer was equipped with a cyclone removing particles larger than 2.5 µm (aerodynamic diameter) from the sample air. Black carbon equivalent concentrations were calculated from the light absorption using a coefficient of 16.6 m² g⁻¹.

The NOₓ (NO and NO₂) was measured with a chemiluminescence method (AC-30M Environment S.A, Poissy, France). Data for the meteorological parameters in Kotka such as wind direction and speed, temperature, humidity, and pressure, were recorded in an automatic weather station, which was situated at a distance of 1.5 km south to south-east of the monitoring station. The route of arriving air masses was estimated using the NOAA HYSPLIT backward trajectory model (Draxler and Rolph 2003).
In Helsinki, the PM$_{2.5}$ mass, particle number, NO$_x$ (NO and NO$_2$), and BC were measured with a tapered element oscillating microbalance (TEOM©, Thermo Fisher Scientific Inc. Waltham, MA, USA), a CPC (TSI Model 3022, Shoreview, MN, USA), a chemiluminescence analyzer (TEI 42S analyzer, Thermo Fisher Scientific Inc. Waltham, MA, USA) and an aethalometer (AE-16, Magee Scientific Company, Berkeley, CA, USA), respectively. The particle number size distribution was measured with twin Differential Mobility Particle Sizer (DMPS 3025 and 3010).

At both sites, the measurement period for NO, NO$_2$ and particle number concentration covers most of the time between 14 November 2005 and 12 May 2006. The measurement of PM$_{2.5}$ in Kotka and in Helsinki, and of BC in Helsinki started later, i.e. 15 December 2005, 27 January 2006, and 19 March 2006, respectively. The BC measurements in Kotka had a break between 20 January and 19 March 2006 due to technical failure.

Particle sampling

An EPA-WINS sampler (Peters et al. 2001) operated at a flow rate of 16.7 l min$^{-1}$ was used to collect 24-h PM$_{2.5}$ samples on a daily basis. The particles were sampled on prewashed (methanol and deionised) polytetrafluoroethylene (PTFE) filters (diameter 47 mm, pore size 3 µm, type FS, Millipore Ireland B.V., Carrigtwohill, Ireland). The total number of daily samples was 175.

Four-day (from Monday to Friday) Berner low-pressure impactor (BLPI; Berner and Lürzer 1980, Hillamo and Kauppinen 1991) samples were collected in parallel with three virtual impactors (VI; Loo and Cork 1988). The BLPI divides particles into 10 size fractions at a flow rate of 25 l min$^{-1}$. The aerodynamic 50% cut-off diameters of the BLPI stages are 7.5, 3.5, 1.8, 0.94, 0.53, 0.32, 0.16, 0.093, 0.067, and 0.035 µm. Aluminium foil greased with Apiezon L vacuum grease was used as a collection substrate in the BLPI. The VI collected particles at a flow rate of 16.7 l min$^{-1}$ in two size ranges: fine (PM$_{2.5}$, particle diameter < 2.5 µm) and coarse (PM$_{2.5-10}$, 2.5 µm < particle diameter < 10 µm) particles. The uppermost cut-off of coarse particles in the VI and BLPI was made with a PM$_{10}$ inlet manufactured according to the design of Liu and Pui (1981). For comparison of the data with the PM$_{2.5}$ or PM$_{2.5-10}$ samples from the VI, the BLPI stages 1–7 (0.035–1.8 µm) and 8–10 (1.8–10 µm) were summed up and classified as fine and coarse particles, respectively. The prewashed PTFE filters (same type as in EPA-WINS) were used in two of the VI units whereas the third VI was loaded with two pre-cleaned (heated at 550 °C for 4–5 hours) quartz fibre filters (Ø 47 mm, Whatman QMA, Maidstone, UK). One of the VIIs had a nylon (Ø 47 mm Nylasorb, 1.0 µm, PALL, Ann Arbor, MI, USA) backup filter below the PTFE filter to collect HNO$_3$, which is formed when semivolatile NH$_4$NO$_3$ collected on the aerosol filter evaporates and decomposes. A total of 78 (3 × 26) VI samples and 25 BLPI samples were collected.

Sub-micrometer particulate matter samples (particle diameter < 1 µm) were collected at the SMEAR-III station in Helsinki using two quartz fibre filters (Ø 47 mm, Whatman Q-MA, Maidstone, UK) in series in a filter cassette system (Pall Life Sciences, Ann Arbor, MI, USA). The four upper stages of the Berner low-pressure impactor (BLPI; Berner and Lürzer 1980) were used to cut off the super-micrometer particles. The flow rate was 80 l min$^{-1}$. The PM$_1$ filter samples were collected during 2 February–12 May 2006. The sampling duration was mainly 24 h on working days and 72 h over the weekends. For particle size distribution determination, 14 Micro-orifice uniform deposit impactor (MOUDI: Marple et al. 1991, Timonen et al. 2008a) measurements were made during February–May 2006. The sampling time was mostly three days and the flow rate was 30 l min$^{-1}$.

Gravimetric and chemical analyses

The PTFE filters and aluminium foils were weighed on a Mettler M3 microbalance (Mettler Instrumente AG, Zurich, Switzerland) before and after sampling. The filters were allowed to stabilize inside a laminar flow bench for about 30 minutes before weighing. During the measurement period the temperature and relative humid-
ity in the weighing room varied in the range of 23.2 ± 0.6 °C and 18.2% ± 8.1%, respectively. Electrical discharger (Mettler Toledo, HAUG, Leinfelden-Achterdingen, Germany) and Po-210 (1U400 static master, NRD, Grand Island, NY, USA) radioactive source were used to eliminate electrostatic charges of the filters. The samples were stored in a freezer at −20 °C, until they were chemically analysed.

Organic (OC) and elemental carbon (EC) were analysed from quartz-fibre filters of the VI using a thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc. Tigard, OR, USA). The instrument uses a two-phase thermal method to separate organic and elemental carbon. During heating in the first phase, some of the organic carbon is pyrolysed and not evaporated from the filter. In the second phase, pyrolysed and elemental carbon are oxidized to volatile form. An optical correction was made to separate pyrolysed and elemental carbon (Viidanoja et al. 2002). In order to correct for a positive artefact caused by adsorption of gas phase organic material on quartz filters, two filters, one upon the other, were used in sample collection. The particulate organic carbon was calculated by subtracting the backup value (~ gas phase organics) from the value of the front filter. The uncertainty of the TOA method was estimated to be 5% for OC and 15% for EC in concentrations above the quantification limit.

In addition to high-time-resolution aethalometer measurements, BC was analysed from the 24-h EPA-WINS samples by using a smoke stain reflectometer (SSR, Model M34D, Diffusion Systems, London, UK). The average reflectance of two measurements was converted into an absorption coefficient a by following the guidance in ISO9835 (1993). Finally, the absorption coefficient was converted into black carbon (BC) using the linear calibration equation obtained from a correlation analysis between filter blackness measurements and corresponding aethalometer readings (Hansen et al. 1984). Because of a contamination risk during the blackness measurements, only a half of each PTFE filter was used in the SSR measurement. The other half of the filter was used in ion chromatographic analyses.

A quarter or a half of the PTFE filters of EPA-WINS (24-h sample) and of the VI (4-day sample) and of the aluminium foils of the BLPI (4-day sample) were analysed for selected ions by an ion chromatography (DX500, Dionex Corporation, Sunnyvale, CA, USA). The anions (Cl−, NO3−, SO42−, and oxalate) were analysed using an AS11 column and 1–20 mM sodium hydroxide eluent with a flow rate of 1.5 ml min−1. Cations (Na+, NH4+, K+, Mg2+, and Ca2+) were analysed using a CS12 column and 20 mM methanesulfonic acid eluent with a flow rate of 1.2 ml min−1. The BLPI samples were extracted with 10 ml of deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA). A piece of a PTFE filter was first wetted with methanol (0.5 ml) to reduce the hydrophobic effect of the filter and then extracted with 9.5 ml of deionised water. Based on the test solutions, the uncertainty of the ion chromatographic analysis was estimated to be 5%–10% depending on the ion to be analysed.

Monosaccharide anhydrides (MAs = sum of levoglucosan, mannosan and galactosan) were analysed using a liquid chromatograph coupled to an ion trap mass spectrometer (LC-MS, Agilent Technologies SL, Santa Clara, CA, USA) (Dye and Yttri 2005). To separate different isomers of the MAs, two columns (Atlantis, 150 mm, Waters, Milford, MA, USA) one after the other were used at 7 °C. The eluent was deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA) with a flow rate of 0.1 ml min−1. An electrospray ionization technique was used and the monitored ion was m/z = 161. Before analysis, a piece (1 cm2) of the exposed quartz filter was extracted with a 2 ml of the mixture of tetrahydrofuran and deionised water (1:1) in ultrasonic bath for 30 min, and then the sample solutions were filtered (IC-Acrodisk 13 mm, 0.45 µm, PALL, Ann Arbor, MI, USA). The uncertainty of the LC-MS method has been estimated at 20% (Saarikoski et al. 2007).

The concentrations of trace elements (Al, As, Br, Ca, Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Si, Sr, Ti, V and Zn) in the 4-day VI samples were determined by using an energy-dispersive X-ray fluorescence method (ED-XRF, Tracor Spectrace 5000: Spolnik et al. 2004). The accuracy and precision of this analytical method was estimated to be on the average of 14% and 4%, respectively (Sillanpää et al. 2005).

The concentrations of OC, EC, MA and ions were determined from the quartz filters of the
SMEAR-III station, using the analytical methods described above. The blank concentrations of sodium and calcium in the filter material of the PM$_1$ samples were too high to allow determination of these ions typically existing mainly in the coarse particulate fraction.

**Chemical mass closure**

The chemical components of the particulate samples were divided into seven classes: ammonium ($\text{NH}_4^+$), nitrate ($\text{NO}_3^-$), non-sea-salt sulphate (nss-$\text{SO}_4^{2-}$), sea salt (SS), soil (SOIL), elemental carbon (EC) and particulate organic matter (POM) (Table 1). Nss-$\text{SO}_4^{2-}$ and sea salt concentrations were calculated with the help of standard seawater composition (Brewer 1975) and assuming that all the sodium originates from the sea. The latter assumption is not entirely true for fine particles, because sodium is also emitted from some combustion sources. Thus, the value of SS in fine particles may be slightly overestimated. The measured OC concentrations were multiplied by a factor of 1.6 to obtain an estimate for total particulate organic matter (POM) mass concentration (Turpin and Lim 2001). Typical soil-related elements, Si, Al, Fe, Ca and K, appear predominantly as oxides in the atmosphere (Brook *et al.* 1997). The SOIL concentrations were calculated from the results of the ED-XRF-analyses (4-day VI samples).

The time resolution of fine particle mass (PM$_{2.5}$), ions and reflectance (BC) obtained from filter samples was 24 h. The 24-h OC concentration was estimated on the basis of the measured 4-day OC concentrations and 24-h oxalate concentrations. As the Pearson correlation coefficient between OC and oxalate was very high ($0.98, n = 26$) and oxalate is one of the major compounds in secondary organic aerosol and in biomass combustion smoke, the 24-h OC concentration could be estimated relatively accurately for the chemical mass closure assessment. Daily fine particle SOIL concentrations were simply set equal to the 4-day SOIL results calculated from the trace metal analysis. The daily BC values were calculated from the high-time-resolution aethalometer readings and from the reflectance values of the 24-h EPA-WINS filters. The chemical mass closure of coarse particles was based on the 4-day VI and BLPI sample data.

The chemical mass closure of PM$_1$ in Helsinki included ammonium, nitrate, sulphate, EC and POM. The soil and the sea-salt contributions to PM$_1$ could not be calculated because of the high blank values of sodium and calcium in quartz filters as compared with the relatively small concentration of these ions in this particulate size range.

**Quality control**

The PM$_{2.5}$ concentration was measured by an automatic monitor (data calculated as 1-h average values) and using filter methods (24-h average with EPA-WINS and 4-day average with VI), and an approximate PM$_{2.5}$ concentration was obtained by summing up stages 1 to 7 of the BLPI (uppermost cut-off diameter < 1.8 µm; 4-day average value). The online method was based on $\beta$-attenuation and the others were based on gravimetric determinations. The correlation coefficients (0.95–0.98) and slopes (0.875–1.04) for different instruments showed that the PM$_{2.5}$ mass concentrations measured with the different

<table>
<thead>
<tr>
<th>Component</th>
<th>Fine particles (24-h)</th>
<th>Coarse particles (4-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4^+$</td>
<td>$[\text{NH}_4^+]$</td>
<td>$[\text{NH}_4^+]$</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>$[\text{NO}_3^-]$</td>
<td>$[\text{NO}_3^-]$</td>
</tr>
<tr>
<td>nss-$\text{SO}_4^{2-}$</td>
<td>$[\text{SO}_4^{2-}] - 0.246[\text{Na}^+]$</td>
<td>$[\text{SO}_4^{2-}] - 0.246[\text{Na}^+]$</td>
</tr>
<tr>
<td>SS</td>
<td>3.248[Na$^+$]</td>
<td>3.248[Na$^+$]</td>
</tr>
<tr>
<td>SOIL</td>
<td>$[\text{Fe}_2\text{O}_3] + [\text{Al}_2\text{O}_3] + [\text{SiO}_2] + [\text{CaO}] + [\text{K}_2\text{O}]$</td>
<td>$[\text{Fe}_2\text{O}_3] + [\text{Al}_2\text{O}_3] + [\text{SiO}_2] + [\text{CaO}] + [\text{K}_2\text{O}]$</td>
</tr>
<tr>
<td>EC</td>
<td>BC (aethalometer or reflectance)</td>
<td>EC</td>
</tr>
<tr>
<td>POM (1.6OC) (µg m$^{-3}$)</td>
<td>$1.6 \times (33.78[\text{oxalate}] + 0.46)$</td>
<td>1.6[OC]</td>
</tr>
</tbody>
</table>
techniques were highly comparable with each other. During the wildfire episode between 1 and 5 May 2006, the 4-day filter samples were overloaded, which reduced the flow rate and might have slightly changed the particle cut off diameter for some part of the sampling period.

Corresponding comparisons for the ions determined from the 24-h EPA-WINS and the 4-day VI and BLPI fine particle samples by ion chromatography were made and, with most of the ions, there was a relatively good agreement between the three datasets. For Na⁺, NH₄⁺, K⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻ and oxalate, the Pearson correlation coefficients and the slopes were 0.75–0.98 and 0.66–1.14, respectively. The deviations from each other were due to the sum of uncertainties in sampling, storage and analytical procedure. Fine particle calcium ion concentration seemed to be unreliable to measure. This was most likely due to a variable calcium concentration in blank filters and generally low calcium concentration in fine particulate samples, especially in PM₁₀.

Although there was a good correlation in fine particle nitrate between the three instruments, the backup filter concentration in VI showed that almost half of the nitrate (average 46%) had evaporated from the 4-day PFTE filters during particulate sampling. The 24-h EPA-WINS nitrate concentrations were on average 12% smaller than the total nitrate concentration (front + backup) in the 4-day VI-PM₂.₅ samples. As the evaporated fine particle nitrate was measured only from the 4-day VI-PM₂.₅ samples and the evaporation varied substantially (range of backup NO₃⁻/total NO₃⁻: 0.15–0.87), these results could not be utilized for the correction of nitrate in each 24-h sample.

The coarse particle sampling with one of the VI units was not operating correctly after maintenance service in the middle of the campaign, and these results had to be discarded. During that period the coarse particle ion concentrations were calculated from the BLPI (stages 8–10). According to comparison between the BLPI-PM₁₀–₈–₁₀ and the VI-PM₂.₅–₁₀ data, the ionic concentrations correlated (n = 13) reasonably well with each other. For coarse particle mass, Na⁺, K⁺, Mg²⁺, Cl⁻, NO₃⁻, and SO₄²⁻, the Pearson correlation coefficients and the slopes between the different instruments were 0.85–0.98 and 0.81–1.38, respectively. The correlation was relatively low for ammonium (r = 0.64), but its concentration in most coarse particle stages was below quantification level. Other coarse particle constituents (OC, EC and elements) were analysed from the two other VIs.

Due to a technical problem in the aethalometer, the BC data were not available between 20 January and 19 March. During that period the BC concentration was calculated from the smoke stain reflectometer analyses of the 24-h EPA-WINS PM₂.₅ samples. The Pearson correlation coefficient between the 24-h BC concentrations (aethalometer) and the absorption coefficients (reflectometer) of the 24-h VI-PM₂.₅ samples was 0.94.

**Results and discussion**

**High-time-resolution measurements**

The average concentrations of PM₂.₅, BC, particle numbers and gaseous NO and NO₂ at the urban background stations in Kotka and Helsinki are summarised in Table 2.

**PM₂.₅ concentration and source apportionment**

The average PM₂.₅ concentration calculated from the 1-h values in Kotka was 10.6 µg m⁻³ for the period 15 December 2005–12 May 2006. For comparison, the average PM₂.₅ value measured with TEOM© in Helsinki (27 January–12 May 2006) was 13.9 µg m⁻³ (Table 2). The annual average PM₂.₅ concentrations in European cities have a 10-fold range (4–40 µg m⁻³) as reviewed by Putaud et al. (2004), who also have shown that Nordic countries have the lowest mass concentrations.

The daily PM₂.₅ concentrations were roughly on the same level and displayed a similar pattern in Kotka and Helsinki (Fig. 1a), which suggests that regional transport and LRT of well-mixed air masses had major contributions to particulate air pollution in southern Finland. The local sources of fine particles did not seem to have
Table 2. The campaign mean values of 1-h average PM$_{2.5}$, BC, NO and NO$_2$ (µg m$^{-3}$) and particle number (CPC, cm$^{-3}$) concentrations in Kotka and in Helsinki during 14 November 2005–12 May 2006 (PM$_{2.5}$ from 15 December 2005). The PM$_{2.5}$ and BC measurements started in Helsinki on 27 January and 19 March 2006, respectively. The values of parallel sampling periods are shown in parentheses. The lower particle size cut off for CPC in Kotka was 20 nm and in Helsinki 10 nm.

<table>
<thead>
<tr>
<th></th>
<th>Kotka</th>
<th></th>
<th></th>
<th>Helsinki</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>Mean</td>
<td>SD</td>
<td>$n$</td>
<td>Mean</td>
<td>SD</td>
<td></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>3531 (2487)</td>
<td>10.6 (11.8)</td>
<td>9.2</td>
<td>PM$_{2.5}$</td>
<td>2518</td>
<td>13.9 (13.9)</td>
<td>11.1</td>
</tr>
<tr>
<td>BC</td>
<td>2530 (1342)</td>
<td>0.75 (0.80)</td>
<td>0.64</td>
<td>BC</td>
<td>1342</td>
<td>1.40 (1.40)</td>
<td>2.05</td>
</tr>
<tr>
<td>NO</td>
<td>4802 (3699)</td>
<td>6.2 (6.5)</td>
<td>13.5</td>
<td>NO</td>
<td>3887</td>
<td>9.0 (10.1)</td>
<td>19.3</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>4713 (3612)</td>
<td>20.2 (21.7)</td>
<td>18.4</td>
<td>NO$_2$</td>
<td>3886</td>
<td>26.3 (29.6)</td>
<td>18.0</td>
</tr>
<tr>
<td>CPC</td>
<td>3973 (3785)</td>
<td>7062 (6951)</td>
<td>7015</td>
<td>CPC</td>
<td>4097</td>
<td>12819 (12263)</td>
<td>10872</td>
</tr>
</tbody>
</table>

Fig. 1. (a) 24-h average PM$_{2.5}$ concentrations in Kotka and in Helsinki during December 2005–May 2006. (b) An example of rapidly increased PM$_{2.5}$ events during one month in Kotka.
any remarkably different influences on the daily PM$_{2.5}$ concentrations in the two cities, but some short-lasting impacts differing from each other were found in the 1-h concentration (Fig. 1b). This good general agreement between the Kotka and Helsinki data is likely due to the fact, that both of the monitoring sites are located on the coast of the Gulf of Finland, and had obviously very similar diurnal mixing conditions.

In Kotka, the diurnal cycle of PM$_{2.5}$ was rather flat (not shown), which suggests LRT dominance over the local sources of fine particle emissions. Long lasting (> 24 h), elevated PM$_{2.5}$ concentrations (≥ 20 µg m$^{-3}$) were detected mostly when air masses, as estimated by backward trajectories (NOAA HYSPLIT MODEL), were coming from the Baltic countries, Belarus, Ukraine, Russia and other countries in eastern Europe. Biomass combustion aerosol, originating from small-scale wood heaters of households, may be regionally significant in Finland especially during cold seasons (Saarikoski et al. 2008). The contribution of biomass burning to PM$_{2.5}$ in Kotka was derived from other studies. According to Puxbaum et al. (2007), the ratio of biomass combustion OC to levoglucosan varies a lot depending on the type of wood used and on the burning conditions. In this study, two ratios, 9.2 and 9.8, were used, as they are derived from a recent field measurement in Helsinki (Saarikoski et al. 2008) and from a recent laboratory study on the flue gas of a small masonry heater (Frey et al. 2009), respectively. The ratio from the laboratory study was calculated from a combination of results, where total combustion consists of 75% normal and 25% smouldering combustion. The used ratios of biomass combustion OC to levoglucosan were assumed to be the most suitable ones for Finnish urban environments, but as a large range of values (1.9–23.5) has been presented in the literature (Puxbaum et al. 2007), the uncertainty in the current estimation may be large.

Our rough estimate showed that, in Kotka, approximately one quarter of the urban air POM originated from biomass burning, which equals 8%–9% (range 2%–18%) of the PM$_{1.5}$ mass. The estimation was done from 4-day VI-PM$_{2.5}$ samples collected during weekdays. The contribution of biomass burning to urban PM$_{2.5}$ may be even higher during weekends, when people spend more time at home and use more often their masonry heaters and sauna stoves. The wildfire episode originating from western Russia in the spring 2006 was excluded from this calculation.

As discussed earlier, the local emissions may have had only occasionally some temporary effects on the PM$_{2.5}$ concentration in Kotka. The maximal local contribution was estimated from cases ($n = 7$), where the PM$_{2.5}$ concentration increased rapidly in Kotka but was not elevated in Helsinki. The highest PM$_{2.5}$ concentration during such event was compared with the concentration preceding the event. Only cases, where this preceding PM$_{2.5}$ concentration was below the campaign mean, were processed. The local contribution to the PM$_{2.5}$ concentration during the events was estimated to be 65%–80%. No common factors such as wind direction or wind speed, or elevated NOx, BC or particle number concentration were found to appear in parallel to these events.

**Particle number concentrations**

The particle number concentrations above 20 nm in size varied between 300 and 49 000 cm$^{-3}$ in Kotka and the mean concentration was approximately 7000 cm$^{-3}$ (Table 2). In urban background sites all over Europe, daily mean particle number concentrations ranging between $10^4$ and $6 \times 10^4$ cm$^{-3}$ have been recorded (Paatero et al. 2005). The particle numbers have a strongly inverse relationship with the distance to the nearest road with busy traffic (Pakkanen et al. 2006, Puustinen et al. 2007).

The difference between the number concentrations in Kotka and in Helsinki (Table 2) was at least partly due to the different cut-off size (Kotka 20 nm, Helsinki 10 nm), as the particle number size distribution data in Helsinki showed that on average 45% of the particles were below 20 nm in size and 33% of them were between 7 and 20 nm. According to Laakso et al. (2003), approximately 50% of the particles (size range 10–400 nm) in an urban background area of Helsinki in 1999–2001 were detected in the
nucleation mode (10–25 nm). As car engines are an important source of the nucleation mode and also Aitken mode (30–90 nm) particles (Laakso et al. 2003), some of the traffic-related particles may not have been detected in Kotka. On the other hand, the centre of Kotka had generally much less traffic in vicinity to the monitoring site than the site in Helsinki.

The contribution of traffic to particle number concentration was studied in relation to diurnal variation. It turned out that the diurnal variation in Kotka was almost insignificant. The ratio of the highest diurnal mean value to the lowest diurnal mean value was only 1.3 during weekdays, while it was nearly 4 in Helsinki. The mean ratio in Helsinki lowered to approximately to 3, if particles below 20 nm were excluded, but still the diurnal variation clearly existed. Simultaneous measurement in the urban background station in Helsinki (SMEAR III) displayed a clear diurnal variation that followed the rush hours in traffic with the highest number concentrations between 07:00 and 09:00 (Fig. 2). A significant correlation of the diurnal variation in particle number with the traffic intensity was also detected in other urban sites (Morawska et al. 2002, Tuch et al. 2003, Ketzel et al. 2004, Stanier et al. 2004). One possible reason, why there was no obvious diurnal variation in particle number concentration in Kotka, is that the nucleation mode particles were not measured. On the other hand, other local sources may have played an important role in ultrafine particle emissions.

Other than traffic-related sources for particle number were studied from the cases, where air-pollution events were detected in Kotka but not in Helsinki. The limit concentration for a source event was chosen to be 18 500 cm$^{-3}$, which was twice the standard deviation plus the median concentration (Ziemba et al. 2006). Another criterion was that the event should last at least two or more hours. A set of 6–10 events, which fulfilled the criteria, were detected in December 2005 (Fig. 3). These events probably indicated a local emission source other than usual traffic and/or weather conditions with limited atmospheric mixing. It was expected that a local source would also increase black carbon and/or NO$_x$ concentration, but there was no significant correlation of particle number concentration with BC or NO$_x$. Correspondingly, there were also no significant correlations with meteorological parameters such as temperature, relative humidity, wind speed or wind direction.

The association of 1-h average particle number concentration with the wind direction (N, NE, E, SE, S, SW, W and NW) was also investigated to estimate the influence of point sources such as factories or power plants (Table 3). The clearest correlation was detected between particle number concentrations over 30 000 cm$^{-3}$ and north-easterly winds. 70% of these elevated concentrations were measured when the wind was blowing from the north-east. The PM$_{2.5}$, NO$_x$ or BC concentrations did not correlate with the highly elevated particle number concentrations.

![Figure 2](image-url) Diurnal pattern of 1-h average black carbon (BC) (µg m$^{-3}$) and particle number (cm$^{-3}$) concentrations during weekdays in Kotka and in Helsinki during 14 November 2005–12 May 2006. The lower cut-off size of particles in Kotka was 20 nm and in Helsinki 10 nm.
Also particle number concentrations above the daily mean (10 000 cm\(^{-3}\)) were detected more frequently during northerly, north-easterly and easterly winds. Only few cases with particle number concentration over 20 000 cm\(^{-3}\) were detected for wind direction from the south to the north-west.

The main local point source of industrial particle emissions, a sulphate pulp mill, was located 3 km north to north-east of the station. A more precise wind direction analysis showed that the pulp mill was not exactly in the location, wherefrom the highest particle number concentrations seemed to transport (wind direction 52.5°–67.5°). There were two other sulphate pulp mills, one located 1.5 km and the other 13 km from the site in a sector of 45°–90°. It should be noticed that the wind direction and the particle measurements were not conducted at the same site, which means that small differences in wind direction may have occurred between the two sites.

**Black carbon and NO\(_x\) concentrations**

The main source of atmospheric BC in cities is fossil fuel combustion, especially combustion in diesel engines. BC consists of elemental carbon (EC) and highly polymerized organic matter. In many European cities, BC is strongly related to traffic and it is among the most important contributors to both PM\(_{2.5}\) and PM\(_{10}\) (Pakkanen

### Table 3

<table>
<thead>
<tr>
<th>Wind direction</th>
<th>&lt; 10000</th>
<th>10000–20000</th>
<th>20000–30000</th>
<th>&gt; 30000</th>
<th>Total n</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>187</td>
<td>75</td>
<td>21</td>
<td>1</td>
<td>284</td>
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<tr>
<td>NE</td>
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<td>366</td>
</tr>
<tr>
<td>S</td>
<td>315</td>
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</tr>
<tr>
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<td>8</td>
<td>2</td>
<td>0</td>
<td>522</td>
</tr>
<tr>
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<td>582</td>
<td>26</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>470</td>
<td>65</td>
<td>1</td>
<td>0</td>
<td>536</td>
</tr>
</tbody>
</table>
In Kotka, the EC concentrations (4-day filter samples) and the BC concentrations (aethalometer and 24-h filter samples) correlated highly with each other (Pearson correlation coefficients 0.97 and 0.89, respectively). The campaign mean EC-to-BC ratio was 0.95. BC was moderately correlated with PM$_{2.5}$ ($r = 0.73$), while the correlation coefficients were smaller (range 0.37–0.66) with the other air quality parameters (NO, NO$_2$ and number concentration) measured on-line. A clear correlation was occasionally detected between the BC and the particle number concentrations, and between the BC and NO$_x$ concentrations, indicating a common local source such as traffic.

The difference between the higher daytime average concentrations and the lower nighttime average concentrations in Kotka was not large (Fig. 2), which implies the influence of several BC sources. The 24-h-averaged time trends in BC in Helsinki and Kotka were occasionally similar to each other, indicating similar mixing conditions of local air pollution or some common fine particle sources in regional transport or LRT of air pollution (Fig. 4). Pakkanen et al. (2000) estimated that the long-range transported BC is on average about 0.4 µg m$^{-3}$, which is assumed to represent the average regional background over southern Finland. A rough estimate can be done by assuming that the lowest diurnal value in Kotka represents the background value with a minimal influence of local traffic and other local sources. In this study, the lowest value was 0.56 µg m$^{-3}$ at 02:00 (all days included), which is consistent with the value reported by Pakkanen et al. (2000) before subtracting the estimated values of night time traffic and local sources (other than traffic). By subtracting the background concentration, which includes some night time traffic, from the campaign mean value, the contribution of local traffic to BC in Kotka can be estimated at about 30%.

The local traffic influence on BC concentrations was supported by the observations on NO and NO$_2$, both showing clear diurnal variation. The highest NO$_2$ concentrations were detected during rush hours, and the morning values were generally higher than the afternoon values. NO was peaking one hour later and high concentrations were lasting longer. Subtraction of the minimum diurnal values from the campaign mean concentration, as done with BC, showed that contributions of local traffic to NO and NO$_2$ were approximately 60% and 50%, respectively.

**Chemical mass closure**

The chemical mass closures for 24-h PM$_{2.5}$ (campaign mean 9.7 ± 6.6 µg m$^{-3}$) and 4-day PM$_{2.5-10}$...
Urban particulate matter and health

In Figs. 5 and 6, respectively. The identified aerosol components accounted on average for 95% ± 14% of the PM$_{2.5}$ mass and 89% ± 21% of the PM$_{2.5-10}$ mass.

**Carbonaceous compounds**

The 24-h POM was over half of the time, i.e. in 63% of the samples, the largest component of fine particles in Kotka and correlated highly with PM$_{2.5}$ concentration ($r = 0.86$). The average contribution of POM to PM$_{2.5}$ mass was 37% ± 14%. The POM concentration varied between 0.9 and 29.6 µg m$^{-3}$ (average 3.6 ± 4.1 µg m$^{-3}$). The POM concentrations were typically below 9 µg m$^{-3}$, except during the wildfire episode in spring 2006 (Fig. 5). Similar values (POM 1.0–25.1 µg m$^{-3}$, 72-h PM$_{1}$ samples) were measured in Helsinki in spring 2006 (Timonen et al. 2008b). POM was also for 76% of the time the largest component of PM$_{1}$ in December 2005–May 2006 in Helsinki. Diacids, mainly oxalic acid, and levoglucosan each comprised approximately 2% of POM (range 0.2%–3.5%) in Kotka.

The campaign mean BC contribution to PM$_{2.5}$ mass was 8% ± 3% in 24-h sampling (Fig. 5). The contribution of BC to PM$_{2.5}$ with 1-h time resolution in Kotka varied from 1% to 64% (average 9%). The BC and PM$_{2.5}$ ratios with 1-h time resolution were calculated only for PM$_{2.5}$ values over 2 µg m$^{-3}$. Values below that were considered as inaccurate. The highest ratios (over 20%) were measured mostly at PM$_{2.5}$ concentrations lower than the campaign mean, referring to local BC emissions and to limited mixing conditions. During LRT events both the PM$_{2.5}$ and the BC concentrations were increased.

The campaign mean of daily EC-to-POM ratios for PM$_{2.5}$ (0.27 ± 0.16) in Kotka was close to a typical value measured in urban background stations (Viana et al. 2006). The average contributions and concentrations of POM and EC

![Fig. 5. Chemical mass closure of fine (PM$_{2.5}$) particle concentrations and the relative contribution (%) of different mass components in Kotka during 14 November 2005–12 May 2006. The sampling time was 24 h for PM$_{2.5}$.](image)
to coarse particle mass were 16% ± 6% and 0.70 ± 0.60 µg m⁻³ and 2% ± 1% and 0.09 ± 0.01 µg m⁻³, respectively.

Secondary inorganic compounds

The nss-SO₄²⁻ (26% ± 11%) was a dominant secondary inorganic ion in PM₂.₅ followed by ammonium (8% ± 3%) and nitrate (4% ± 3%) (Fig. 5). The mean 24-h average concentrations with standard deviations for nss-SO₄²⁻, ammonium and nitrate were 2.4 ± 1.7, 0.80 ± 0.63 and 0.40 ± 0.47 µg m⁻³, respectively. In approximately 40% of the measurements, the contribution of nss-SO₄²⁻ to PM₂.₅ mass was larger than that of POM. In Helsinki, the corresponding value was 30% in PM₁.

Equivalent concentrations of NH₄⁺ and nss-SO₄²⁻ in Kotka showed equal amounts indicating that they were in the form of (NH₄)₂SO₄. The amount of NH₄NO₃ seemed to be very low, as no excess NH₄⁺ was left after (NH₄)₂SO₄ formation. However, some of the NH₄NO₃ may have evaporated during sample collection. The amount of evaporated nitrate was not measured for the 24-h samples. The ion charge equivalent ratio of analysed anions to cations was around unity (1.10 ± 0.22) indicating that the fine particles were close to neutral or slightly acidic.

The total contribution of secondary ions to 4-day PM₂.₅–₁₀ mass was 9% ± 6%, nitrate being the largest (6% ± 1%) component, followed by nss-SO₄²⁻ (3% ± 1%) (Fig. 6). The 4-day mean concentrations with standard deviations of nitrate and nss-SO₄²⁻ were 0.23 ± 0.20 and 0.11 ± 0.03 µg m⁻³, respectively. The NH₄ concentrations were almost negligible. The equivalent calculation suggested that nitrate was mostly in the form of NaNO₃.

Sea salt and soil material

Sea salt (SS) (0.45 ± 0.36 µg m⁻³) had mostly a moderate contribution to 24-h PM₂.₅ (7% ± 9%),

---

**Fig. 6.** Chemical mass closure of coarse (PM₂.₅–₁₀) particle concentrations and the relative contributions (%) of different mass components in Kotka during 14 November 2005–12 May 2006. The sampling time was 4 days for PM₂.₅–₁₀.
but occasionally there were days when the contribution was 20%–49% of the PM$_{2.5}$ mass (Fig. 5). During these events, the PM$_{2.5}$ concentrations (1.8–7.8 µg m$^{-3}$) were below the average and the SS concentrations were twice (0.96 ± 0.42 µg m$^{-3}$) as high as the mean SS. According to backward trajectories, the air masses were coming mostly from the clean arctic areas such as the Norwegian or Arctic Seas. Some overestimation may be involved in these high contributions, because of the assumption that all the sodium is coming from the sea. A minor fraction of fine particulate sodium may also be emitted by combustion processes. However, the 4-day size distribution measurements showed that only a very small fraction of sodium was in the ultrafine size-range (Table 4), where combustion-related sodium particles are typically found. Also the number concentrations of particles or NO$_x$ concentrations were not elevated during these days, as it would be expected if sodium originated from local pulp mills. The elevated sodium concentration may be partly explained by resuspended road salt that is spread over the main routes to prevent frost and ice forming on the road surface. On average, 70% of the sodium was in particles over 0.94 µm in size (stages 7–10).

The mean SS contribution to 4-day PM$_{2.5-10}$ was 12%, but the range was wide (1%–44%) (Fig. 6). The SS concentrations in PM$_{2.5-10}$ varied between 0.08 and 1.21 µg m$^{-3}$ (0.39 ± 0.30 µg m$^{-3}$). Soil-derived material accounted for 3% ± 2% and 49% ± 19% of the PM$_{2.5}$ and PM$_{2.5-10}$ mass, respectively (Figs. 5 and 6). The mean concentrations with standard deviation for soil material in fine and coarse particles were 0.34 ± 0.27 and 2.95 ± 3.61 µg m$^{-3}$, respectively.

Trace metals

Trace metals, excluding the soil-related compounds, accounted together for less than 1% of the 4-day PM$_{2.5}$ and PM$_{2.5-10}$ mass. The average concentrations of Zn (14 ± 13 ng m$^{-3}$), V (5.3 ± 2.7 ng m$^{-3}$), Mn (2.7 ± 1.5 ng m$^{-3}$) and Pb (5.5 ± 3.3 ng m$^{-3}$) in PM$_{2.5}$ in Kotka were comparable to those reported by Pakkanen et al. (2001) for Helsinki. The concentrations of some other interesting species such as As, Cu and Ni were mainly below the quantification limit. Because of the long sampling time, no detailed source analysis was done.

Size distribution of PM mass and ions

The size distribution of particulate mass and ion content was categorized into three size classes: 0.035–0.16 µm, 0.16–1.8 µm and 1.8–10 µm, which roughly represented the ultrafine, accumulation and coarse particles. The corresponding impactor stages were 1–3, 4–7 and 8–10. On the average, most of the mass was in the size range of 0.16–1.8 µm (59% ± 14%). The ultrafine and coarse particles had on average 10% ± 4% and 31% ± 16% of the mass, respectively. The main ions in ultrafine and accu-

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Table 4. Size-segregated average (± SD) masses and ion concentrations (ng m$^{-3}$) and their relative contributions (%) in different size fractions of PM$_{10}$ in Kotka ($n = 25$). $D_p$ refers to particle diameter.

<table>
<thead>
<tr>
<th>Component</th>
<th>Ultrafine $D_p &lt; 0.16 \mu m$</th>
<th>Accumulation $0.16 &lt; D_p &lt; 1.8 \mu m$</th>
<th>Coarse $D_p &gt; 1.8 \mu m$</th>
<th>Ultrafine $D_p &lt; 0.16 \mu m$ contribution (%) to mass conc.</th>
<th>Accumulation $0.16 &lt; D_p &lt; 1.8 \mu m$ contribution (%) to mass conc.</th>
<th>Coarse $D_p &gt; 1.8 \mu m$ contribution (%) to mass conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM $^{a}$</td>
<td>1600 ± 1100</td>
<td>9600 ± 6700</td>
<td>5000 ± 3800</td>
<td>10 ± 4</td>
<td>59 ± 14</td>
<td>31 ± 16</td>
</tr>
<tr>
<td>SO$_{4}^{2-}$</td>
<td>201 ± 136</td>
<td>2435 ± 1847</td>
<td>120 ± 56</td>
<td>13 ± 6</td>
<td>27 ± 11</td>
<td>4 ± 3</td>
</tr>
<tr>
<td>NO$_{3}^{-}$</td>
<td>69 ± 72</td>
<td>478 ± 666</td>
<td>240 ± 206</td>
<td>4 ± 2</td>
<td>5 ± 3</td>
<td>6 ± 5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>5 ± 2</td>
<td>37 ± 40</td>
<td>118 ± 113</td>
<td>0.4 ± 0.2</td>
<td>0.6 ± 1.1</td>
<td>3 ± 4</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>84 ± 63</td>
<td>783 ± 554</td>
<td>10 ± 10</td>
<td>5 ± 2</td>
<td>8 ± 3</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>5 ± 4</td>
<td>124 ± 64</td>
<td>123 ± 92</td>
<td>0.4 ± 0.3</td>
<td>2 ± 2</td>
<td>4 ± 3</td>
</tr>
<tr>
<td>K$^+$</td>
<td>11 ± 9</td>
<td>81 ± 57</td>
<td>14 ± 9</td>
<td>0.7 ± 0.2</td>
<td>0.9 ± 0.3</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1 ± 1</td>
<td>10 ± 5</td>
<td>16 ± 11</td>
<td>0.1 ± 0.1</td>
<td>0.1 ± 0.1</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1 ± 1</td>
<td>26 ± 14</td>
<td>97 ± 68</td>
<td>0.1 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>2 ± 1</td>
</tr>
</tbody>
</table>
mulation particles were sulphate, followed by ammonium and nitrate (Table 4). Corresponding average values were measured with Micro-orifice uniform deposit impactor (MOUDI, Marple et al. 1991) in Helsinki during February–May, 2006 (n = 14). Sulphate, ammonium and nitrate covered 20% ± 11%, 9% ± 4% and 6% ± 5% from the mass in accumulation mode and 12% ± 7%, 7% ± 2% and 4% ± 3% in the ultrafine mode, respectively. The contribution of sulphate to particle mass in accumulation mode was higher in Kotka (27% ± 11%) than in Helsinki (20% ± 11%). However, the average mass concentrations of sulphate in Kotka (2.4 µg m⁻³) and in Helsinki (2.1 µg m⁻³) were about same in this particle size range. The difference in the ratio of sulphate to mass in accumulation particles was mainly due to the lower POM concentration in Kotka as compared with that in Helsinki.

Nitrate was most frequently the main watersoluble coarse particle component followed by sulphate and chloride. These three ions accounted together for 13% of the coarse particle mass. According to VI-samples (PM_{2.5-10}), half of the coarse mass was soil-related material. There were no major differences in the chemical components of coarse mode particles between Kotka and Helsinki.

**Wildfire episode**

The biomass smoke episode observed in April and May 2006 was exceptionally long compared to episodes in other recent years (Niemi et al. 2009), lasting for about 12 days (25 April–7 May). The wildfire episode increased substantially the mean spring (March–May) PM_{2.5} concentration that was 11.8 µg m⁻³ with and 8.8 µg m⁻³ without the episode. The two highest 1-h PM_{2.5} concentrations (4 May at 06:00 and 6 May at 07:00) were almost 90 µg m⁻³ and the highest 24-h value (3–4 May) was almost 60 µg m⁻³. The contribution of POM to PM_{2.5} mass varied between 45% and 77% (average 56%) during the smoke episode, while the campaign mean contribution was slightly below 40%, when all the samples were included. This indicates that the POM concentrations increased substantially during the biomass smoke episode.

The concentrations of typical biomass combustion markers, levoglucosan and potassium, during the smoke episode were approximately three-fold, and that of oxalate over five-fold as compared with their campaign mean values. Potassium and oxalate have also other sources than biomass combustion, but when appearing together with increased levoglucosan concentration they are likely to originate from this source (Sillanpää et al. 2005). The BC concentration was 2-fold the campaign mean value during the episode, and the concentration time trend followed very closely that of PM_{2.5} (Fig. 7). Also NO₂ had a somewhat similar trend to that of BC, but there was no significant correlation between NO and BC. The same wildfire smoke episode affected also Helsinki, where real-time chemical composition measurements and dispersion modelling were conducted by Saarikoski et al. (2007).

**Summary and conclusions**

This work is part of the HIPPU project, which contained central site ambient aerosol measurements in an industrial city of Kotka in southern Finland, together with simultaneous monitoring of personal air-pollution exposure and resultant systemic inflammation and cardiac effects in ischemic heart disease patients. The paper presents results from a 6-month field campaign with on-line (PM_{2.5}, BC, particle number, NO₂ and NO) aerosol measurements and off-line chemical characterization (mass, water-soluble ions, elemental carbon, organic carbon, trace metals, levoglucosan and reflectance). Comparison with simultaneous aerosol measurement data in Helsinki was made to assess the importance of regional emissions and long-range transport (LRT) of particulate pollution in relation to different local sources such as traffic, small-scale biomass combustion, industries, power and heat production, and harbours.

The campaign mean PM_{2.5} concentration in Kotka was 10.6 µg m⁻³ and the main chemical component was particulate organic matter (POM: 1.6 × organic carbon; 37% ± 14%), followed by non-sea-salt sulphate (26% ± 11%). The main component of PM_{2.5-10} mass (mean concentration 4.2 µg m⁻³) was soil-related mineral compounds.
Half of the PM$_{10}$ mass was in the accumulation mode. During a spring episode of transnational wildfire smoke the concentrations of PM$_{2.5}$, POM, BC and typical biomass combustion tracers such as levoglucosan, potassium and oxalate were highly increased. At the same time, there was the maximal appearance of spring road-dust in PM$_{2.5-10}$.

Typical traffic-related measures such as particle number and black carbon (BC) concentrations showed that local traffic was occasionally but not continuously their major source. The contribution of local traffic to BC was estimated to be 30%, while those to NO and NO$_2$ were higher, 60% and 50%, respectively. In addition to traffic, the other typical particulate source in high latitude urban areas is small-scale biomass combustion. A quarter of POM was estimated to originate from biomass use, which equals to 8%–9% of the PM$_{2.5}$ mass.

High particle number concentrations (over 30 000 cm$^{-3}$) without PM$_{2.5}$, NO$_x$ or BC involvement were clearly correlated with north-easterly winds, but no single source or explanation to that phenomenon could be identified. Several local point sources, including several large sulphate pulp mills, were located in that specific direction.

When compared with that in Helsinki, the mean PM$_{2.5}$ concentration during simultaneous measurements was 15% lower in Kotka, while the corresponding differences in mean BC, NO and NO$_2$ concentrations were −43%, −36% and −27%, respectively. The 24-h average PM$_{2.5}$ concentrations showed similar patterns of variation in both cities, but the hourly PM$_{2.5}$ concentrations varied much less in Kotka. The variations in BC concentrations differed from each other in the two cities. In addition, the particle number concentrations did not show a clear diurnal variation in Kotka like they did in Helsinki.

Thus, LRT and regional emissions were the dominant sources of PM$_{2.5}$ in Kotka, although industrial activities (paper and pulp mills), power plants and busy harbours were located in the city, some of them even in vicinity to the sampling site. As LRT was the major source of PM$_{2.5}$ in Kotka, it will be possible to analyze the health effects related to this source in the patients of the concurrent health study more clearly than in Helsinki, where local traffic has always been a much more prominent source than presently in Kotka. Moreover, the effects on health of different LRT aerosol compositions can also be investigated, as there was a 12-day-long episode of transnational wildfire smoke during the present field campaign. The central suburban site of air quality monitoring and particulate sampling was highly representative of the local environments (e.g. topography, micrometeorology) and local particle sources (car traffic, residential wood burning, energy plant for district heating, industries, harbours) in vicinity to the homes of the cardiac patients, as all of them were living within two kilometres from the monitoring site.
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Chemical and Source Characterization of Submicron Particles at Residential and Traffic Sites in the Helsinki Metropolitan Area, Finland

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ABSTRACT

Chemical characterization of non-refractory submicron particles (NR-PM₁) and source apportionment of organic aerosols (OA) were carried out at four different sites in the Helsinki metropolitan area, Finland, using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM). Two of the sites represented suburban residential areas, whereas the other two were traffic sites, one in a curbside in downtown and the other one in a suburban highway edge. The residential and the curbside measurements were conducted during the winter, but the highway campaign was carried out in the autumn. NR-PM₁ were composed mainly of organics (40–68% in the different sites), followed by sulphate (11–34%), nitrate (12–16%), ammonium (7.8–8.5%) and chloride (0.24–1.3%). The mean concentrations of NR-PM₁ were quite similar during the winter campaigns (10.1–12.5 µg/m³), but NR-PM₁ was clearly lower during the autumn campaign at the highway site (6.0 µg/m³) due to the meteorology (favourable mixing conditions), small concentrations of long-range transported particles and non-intensive heating period locally and regionally. Using a multilinear engine algorithm (ME-2) and the custom software tool Source Finder (SoFI), the organic fraction was divided into two or three types of OA representing hydrocarbon-like organic aerosol (HOA), oxygenated organic aerosol (OOA), and in three sites, biomass burning organic aerosol (BBOA). At the downtown traffic site (Curbside), BBOA could not be found, probably because most of the local wood burning occurs in the suburban areas of the Helsinki region. OOA had the largest contribution to OA at all the sites (50–67%). The contribution of HOA was higher at the traffic sites (25–32%) than at the residential sites (15–18%). At the suburban residential and highway sites, the contribution of BBOA was high (25–30%). Especially during cold periods, very high BBOA contributions (~50%) were observed at the residential sites.

Keywords: Chemical composition; Source apportionment; Fine particles; ACSM.

INTRODUCTION

Atmospheric aerosols play a key role in climate change. Particles scatter and absorb light, and they serve condensation surfaces for water vapour, affecting cloud formation, precipitation rates and indirect climatic effects due to clouds (IPCC, 2013). Some of the particles are semi-volatile, and they can modify the trace gas composition and impact gas-phase reaction pathways through heterogeneous reaction in the atmosphere. Aerosols also have adverse effects on human health, as fine aerosols can penetrate deep into the lungs. Even a short-term exposure to outdoor fine particulate matter is associated with increased risk of death and emergency admission to the hospital (e.g., Atkinson et al., 2014). A 10 µg/m³ increment in particulate matter < 2.5 µm (PM₂.₅) has been associated with an increase in the risk of death, but the mass concentration alone is not sufficient to evaluate the health effects of particles, as certain chemical components and sources are more harmful than others (Zanobetti et al., 2014). Specific sources like traffic, coal, oil and biomass combustion, soil or road dust have shown positive correlation with mortality or to adverse health effects (Ostro et al., 2011; Dai et al., 2014; Uski et al., 2014; Zanobetti et al., 2014).

Chemical composition of fine particles in urban areas has been studied extensively all over the world. The main contributors to PM are organic materials followed by sulphate, nitrate, ammonium and black carbon (e.g., Putaud et al., 2004; Zhang et al., 2007; Chan and Yao, 2008 and references therein), but the sources for the chemical components may differ depending on local and regional

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emissions and how the air masses are drifting. One major source of fine particles in many urban environments is the transportation sector (e.g., Zhang et al., 2005). Biomass burning in fireplaces and stoves is often another significant particulate matter source, especially during winter in residential areas (Glasius et al., 2006; Szidat et al., 2007), whereas the prescribed burning may have a significant role in agricultural areas also effecting urban areas (Jimenez et al., 2006). Other sources of particulate matter are industry, cooking, power generation, biogenic hydrocarbon emissions and the secondary material formed through chemical reactions (Zhang et al., 2007; Mohr, et al., 2012).

In the Helsinki metropolitan area, vehicular traffic is the most significant local particle source affecting urban air quality (Pirjola et al., 2012; Soares et al., 2014). Also, the effects of wood combustion on local air quality can be considerable, especially during periods of low vertical mixing due to stagnant weather conditions, as the release height of the emissions is typically low and the combustion in domestic heating appliances is incomplete (Saarikoski et al., 2008; Saarnio et al., 2012). Wood combustion is widely used as a supplementary source of heating at detached-housing areas in winter in the Helsinki area. Additionally, a large portion of fine particles originates from long-range transport (LRT) in the Helsinki metropolitan area. The concentrations of LRT particles are highest when aerosols are transported from the polluted areas of Eastern Europe, whereas the lowest LRT levels are observed when air masses originate from the Atlantic Ocean (Niemii et al., 2004, 2005; Saarikoski et al., 2007; Saarnio et al., 2010a).

The objective of this study was to characterize the chemical composition and sources of submicron particulate matter (PM$_x$) in the Helsinki metropolitan area, Finland, by deploying a relatively new monitoring technique based on aerosol mass spectrometry (Aerodyne Aerosol Chemical Speciation Monitor, ACSM). This study was conducted during the years 2010–2012 at four different sites, including two suburban detached-housing areas (Residential I and Residential II), a curbside site in downtown (Curbside) and a suburban highway edge (Highway). Organic aerosol (OA) data was analysed in detail by applying a multilinear engine algorithm (ME-2, Canonaco et al., 2013) for organic mass spectra in order to explain the main sources of OA in the Helsinki area. So far, the combination of ACSM or AMS (aerosol mass spectrometer) and ME-2 with Source Finder (SoFi) has been used only in few studies (e.g., Canonaco et al., 2013; Crippa et al., 2014).

**METHODS**

**Description of the Sites**

The measurements were conducted at four different sites around the Helsinki metropolitan area (Fig. 1). The population of the Helsinki metropolitan area is about 1 million. The Residential I site was situated approximately 20 km northeast from downtown Helsinki. The site was surrounded by detached houses. It is quite typical to use wood burning as a supplementary heating source in Finnish detached housing areas, and most of the houses have their own fireplaces.

![Fig. 1. Map of the sampling sites and major roads in the Helsinki metropolitan area. The Curbside was situated in the downtown area of Helsinki.](image)

There were no main roads through the area, but the nearest motorway was approximately 1.2 km east of the site. Measurements at the Residential I site were conducted from 17 February to 16 March 2011.

The Residential II site was situated in a low-lying area of detached housing approximately 20 km west from Helsinki downtown. There were no main roads through the area. The closest highway was situated approximately 3 km south of the site. Measurements at the Residential II site were performed from 12 January to 28 February 2012.

The Curbside site was situated in downtown Helsinki beside a quite heavily trafficked road (23000 vehicles/working day). A lot of the vehicles in downtown are related to transportation and work-related drives throughout the day. There were constant rows of buildings on both sides of the road affecting the dispersion of aerosols, although there was one big crossing close to the site. Measurements at Curbside were carried out from 1 December 2010 to 7 January 2011.

The Highway site was situated near a heavily trafficked highway (5 m from the edge of the first lane), which is the inner ring road around Helsinki, approximately 10 km from Helsinki downtown. The traffic density was approximately 69 000 vehicles/working day. Measurements at the Highway site were conducted from 18 October to 5 November 2012.

**Instrumentation**

**Aerosol Chemical Speciation Monitor**

The aerosol chemical speciation monitor (Aerodyne Research Inc., Ng et al., 2011a) is able to routinely characterise non-refractory sub-micron aerosol species (NR-PM$_x$: sum of organics, nitrate, sulphate, ammonium and chloride). The instrument consists of a particle sampling inlet, three vacuum chambers and a residual gas analyser mass spectrometer. In the particle sampling inlet, particles are focussed into a narrow particle beam by using an aerodynamic lens system. After being transmitted through chambers, the beam is directed into a hot tungsten oven (~600°C) where particles are flash- vapourised, ionised with a 70 eV electron impact ioniser and detected with a...
quadrupole mass spectrometer. ACSM can measure with a time resolution from 15 minutes upward, and in this study, a time resolution of approximately 30 min was used. The comparison of ACSM to different instruments has been widely studied in the paper of Budisulisitorini et al. (2014). In order to account for the particle losses in the vaporizer, a collection efficiency (CE) of 0.5 has been widely used in aerosol mass spectrometry techniques (Canagaratna et al., 2007). A CE = 0.5 was also used in this study, but it was calculated also based on the Middlebrook et al. (2011). There were some occasions, when high aerosol acidity was achieved. However, most of the time the calculated CE was 0.5. Additionally, there were some uncertainties in the calculation of the acidity of the aerosols. At the time of the measurements campaigns the ACSM was not calibrated for sulfate, only for ammonium and nitrate, and therefore the relative ionization efficiency (RIE) for sulfate was not measured. In this study, the RIE value of 1.2 was used for sulfate that seems to be at the high end, as RIE values of 1–1.2 for sulfate were measured since spring 2013. Uncertainties of the calculations of sulfate concentrations have been presented by Budisulisitorini et al. (2014). There are also other factors like high ammonium nitrate molar fraction or high relative humidity that affects the CE, but in this study they were not present.

**Multi-Angle Absorption Photometer**

The black carbon (BC) concentration was measured using a multi-angle absorption photometer (MAAP, Thermo Electron Corporation, Model 5012). The MAAP determines the absorption coefficient (σAP) of the particles deposited on a filter by a simultaneous measurement of transmitted and backscattered light. The σAP is converted to BC mass concentrations by the instrument firmware using the mass absorption cross section of 6.6 m2/g (Petzold and Schönlinner, 2004). The inlet cut point for the MAAP was 1 μm (PM1). BC concentrations were measured at every site, but due to the poor data coverage caused by technical problems, the data from the Residential I site are not presented here.

**Other Air Quality and Meteorological Data**

PM2.5 concentrations were measured with monitors based on β-attenuation (FH 62 I-R, Residential I and Curbside sites), combination of light-scattering and β-attenuation (SHARP 5030, Residential II site) or with a tapered element oscillating microbalance technique (TEOM 1400 AB, Highway site). The PM2.5 monitoring data of different instruments was corrected using calibration equations to ensure equivalent results according to European standards (Waldén et al., 2010). NO and NO2 concentrations were measured with a chemiluminescence analyser (Horiba APNA360/370). 24-h filter samples (PM10) were collected at the Residential I site every third day (n = 4) and levoglucosan (1,6-anhydro-β-D-glucopyranose), selected ions and benzo(a)pyrene (BaP) were analysed by using a high performance anion-exchange chromatograph coupled with mass spectrometer, an ion chromatograph and a gas chromatograph coupled with mass spectrometer, respectively (Saarnio et al., 2010b; Vestenius et al., 2011; Teimilä et al., 2014). Local meteorological data was recorded at an urban background site (SMEAR III) 5 km northeast from downtown Helsinki.

**ACSM Data Analysis**

The organic aerosol fraction was investigated by using ME-2 and the custom software tool SoFi version 4.6 (Canonaco et al., 2013). ME-2 allows exploring the solution space much more widely than positive matrix factorization (PMF). Especially the solutions in ME-2 can be rotated in directions that make sense and not arbitrarily as done with fpeak in PMF. By using the source apportionment method, organic aerosols can be divided into factors representing different particle sources like traffic, biomass burning and cooking, or into factors that represent components with similar chemical characters, such as low-volatility (LV) and semi-volatile (SV) oxygenated organic aerosol (OOA).

The number of factors in the dataset is unknown, and the final number of factors in the ME-2 is defined by the user. The number of factors was selected based on the unexplained variation, changes in the Q-value (the total sum of the squares of the scaled residuals), the comparison of mass spectra with the AMS mass spectra database (Ng et al., 2011b) and/or by using auxiliary species such as BC, inorganic ions, NOx, and meteorological information.

In ME-2, the user can constrain factor profiles and/or time series to a chosen extent. According to the guidelines of source apportionment by ME-2, a reference hydrocarbon like organic aerosol (HOA) mass spectrum should be constrained first if the constraint is needed (Crippa et al., 2014). Because primary organic aerosol components (HOA and biomass burning organic aerosol BBOA) were not separated clearly with unconstrained ME-2 analyses in the residential sites, the constrained factor profile of HOA was used.

In the paper of Crippa et al. (2014), reference spectra for constraining were taken from the measurements done in Paris, where HOA and organic aerosol from cooking (COA) were nicely separated (Crippa et al., 2013). As the COA factor has not been identified in Helsinki in earlier studies (Timonen et al., 2013; Carbone et al., 2014), the reference HOA mass spectrum was deployed from the measurement done by Carbone et al. (2014) at an urban background site in Helsinki instead of the reference HOA spectrum from Crippa et al. (2013). In the study of Carbone et al. (2014), high resolution data was presented, but unit mass resolution mass spectrum of HOA was calculated for the purpose of this study. HOA mass spectrum was used as an input data with an a-value of 0.1. The a-value determines the extent to which the output is allowed to vary from the input, i.e. an a-value of 0.1 means that the contributions of the mass spectral ions concentrations are allowed to vary only up to 10%. Different a-values were tested (0.05–0.3) to find the most reasonable one (not shown).

In the Residential I campaign, some periods with very low concentrations (approximately 30% of the data points) were excluded from the factor analyses, as the explained variation over the period with low concentrations was below the reasonable value (< 75%, Canonaco et al., 2013).
RESULTS AND DISCUSSION

Mass Concentrations and Chemical Composition of Fine Particles

The mean concentrations of NR-PM$_1$, calculated by summing up all chemical species measured by the ACSM (organics, nitrate, sulphate, ammonium, chloride), were quite similar during the wintertime campaigns (Residential I, Residential II and Curbside), whereas the mean NR-PM$_1$ concentration was clearly lower during the autumn campaign conducted at the Highway site (Table 1; Fig. 2). The low NR-PM$_1$ concentrations during the Highway campaign were mainly caused by the very low level of LRT background aerosol (the small concentrations of typical secondary LRT components such as sulphate, ammonium and nitrate are also visible in Fig. 2). In general, fine particle concentrations during these four campaigns were quite low compared to concentrations measured in large cities like Beijing (Sun et al., 2012, NR-PM$_1$: 50 µg/m$^3$) or Santiago de Chile (Carbone et al., 2013, NR-PM$_1$: 30 µg/m$^3$) but comparable to the measurements done e.g. at the urban background sites in Helsinki (Carbone et al., 2014, NR-PM$_1$: 7 µg/m$^3$), Atlanta (Budisulistiorini et al., 2014, NR-PM$_1$: 14–17 µg/m$^3$) or Grenoble (Lanz et al., 2010, NR-PM$_1$: 15 µg/m$^3$).

On the basis of the campaign averages, organic material made up from 50 to 67% of total mass measured with the ACSM, followed either by sulphate (winter campaigns) or nitrate (autumn campaign), ammonium and chloride (Fig. 2). Organics had the largest contribution during the autumn campaign, and the contribution of sulphate was the smallest. In the Helsinki metropolitan area, sulphate is typically long-range transported and at the beginning of the autumn campaign, air masses came to the Helsinki metropolitan area from Scandinavian countries and the Arctic Ocean (HYSPLIT model: Draxler and Rolph, Rolph, not shown), where anthropogenic SO$_2$ emissions are low.

NR-PM$_1$ measured by the ACSM comprised roughly from 50 to 80% of the PM$_{2.5}$, which is consistent with the other observations (e.g., Sun et al., 2012). Different chemical species may have slightly different distribution in PM$_1$ and PM$_{2.5}$ depending on the locations and seasons. For example PM$_1$/PM$_{2.5}$ ratio for organic matter (or organic carbon), sulphate, nitrate and ammonium typically ranges from 0.5 to 0.8 (Liu et al., 2012; Perrone et al., 2014 and reference herein). However, in the measurements done by Budisulistiorini et al. (2014), the mass concentrations of NR-PM$_1$ (ACSM) were 50–110% higher than PM$_{2.5}$, and it was speculated that in addition to known evaporative losses of the semi-volatile components in filter-based methods, ACSM has deficits in calibrating procedures. The smallest contribution of NR-PM$_1$ to PM$_{2.5}$ was obtained at the Residential I site. The reason for the small contribution could be large BC concentrations at that site due to local wood-burning emissions. Unfortunately, that cannot be confirmed, as the BC data was available only for a short period of the campaign (not shown in Fig. 2). At the other residential site, the ratio of BBOA to BC was on average 0.8, indicating that BC concentrations at Residential I site may be as high as or even higher than BBOA concentrations. A similar value (0.8) has been presented also in the paper Crippa et al. (2013). The source apportionment analysis will be discussed later. The contribution of BC to PM$_{2.5}$ was 10, 16 and 17% at the Residential II, Curbside and Highway sites, respectively. By summing NR-PM$_1$ and BC-PM$_1$, the contribution of measured chemical species increased up to 86–99% (excluding Residential I site). Other components that were not measured by ACSM and can have a minor contribution to the PM$_{2.5}$ mass were potassium and calcium, which can be associated with smoke aerosols (Li et al., 2003), sodium and chloride, that are present in sea salt, as well as aluminosilicates (e.g., Si, Al and Fe oxides) that are typical components of street dust particles. However, the difference between the measured chemical species and PM$_{2.5}$ was likely to be mostly due to the difference in the size ranges (PM$_1$ vs. PM$_{2.5}$), the uncertainty in the collection efficiency and the RIE values for chemical species.

The Pearson correlation coefficient, r, between NR-PM$_1$ and PM$_{2.5}$ was high during the winter campaigns (0.87–0.90) and moderate in the autumn campaign conducted at the Highway site (0.80). At the Highway site, BC had quite a high contribution to the PM$_{2.5}$ (17%); therefore, the correlation between chemical species and PM$_{2.5}$ improved when BC was included in chemical components (r: 0.90). Similar or even higher correlations have been found between ACSM and filter-based method of PM$_{2.5}$ and PM$_1$ in Atlanta (Budisulistiorini et al., 2014).

Source Apportionment of Organic Aerosols

The ME-2 algorithm and SoFi-tool were used to explore the sources and origins of organic aerosol. A three-factor

Table 1. The concentrations (mean ± stdev) in µg/m$^3$ during the campaigns.

<table>
<thead>
<tr>
<th>Species</th>
<th>Residential I</th>
<th>Residential II</th>
<th>Curbside</th>
<th>Highway</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>19.3 ± 18.1</td>
<td>14.6 ± 9.9</td>
<td>14.5 ± 9.7</td>
<td>9.19 ± 6.83</td>
</tr>
<tr>
<td>NR-PM$_1$</td>
<td>10.1 ± 9.5</td>
<td>11.2 ± 8.1</td>
<td>12.5 ± 7.6</td>
<td>5.96 ± 3.97</td>
</tr>
<tr>
<td>BC</td>
<td>-</td>
<td>1.55 ± 1.80</td>
<td>1.84 ± 1.65</td>
<td>1.97 ± 2.16</td>
</tr>
<tr>
<td>organics</td>
<td>5.25 ± 5.88</td>
<td>5.33 ± 4.22</td>
<td>6.37 ± 3.92</td>
<td>4.01 ± 2.98</td>
</tr>
<tr>
<td>sulfate</td>
<td>1.87 ± 1.67</td>
<td>2.37 ± 1.61</td>
<td>2.94 ± 2.14</td>
<td>0.57 ± 0.37</td>
</tr>
<tr>
<td>nitrate</td>
<td>1.54 ± 1.57</td>
<td>1.90 ± 1.93</td>
<td>2.01 ± 1.53</td>
<td>0.84 ± 0.82</td>
</tr>
<tr>
<td>ammonium</td>
<td>0.77 ± 0.64</td>
<td>1.10 ± 0.81</td>
<td>0.99 ± 0.67</td>
<td>0.49 ± 0.42</td>
</tr>
<tr>
<td>chloride</td>
<td>0.08 ± 0.15</td>
<td>0.05 ± 0.06</td>
<td>0.18 ± 0.65</td>
<td>0.05 ± 0.07</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>37.3 ± 41.1</td>
<td>33.5 ± 48.3</td>
<td>98.7 ± 95.2</td>
<td>81.2 ± 85.4</td>
</tr>
</tbody>
</table>

*sum of organics, sulfate, nitrate, ammonium and chloride measured with the ACSM.*
solution was found to represent most reliably the sources of organic aerosol at both the residential sites and at the Highway site. The four-factor solution resulted in split factors, without identifying a unique factor profile. The time series were similar between the two split factors. Factors were identified as OOA, BBOA and HOA based on the reference mass spectra presented in literature (e.g., Ng et al., 2011b). In the Curbside campaign, only HOA and OOA were found, as BBOA could not be extracted from the data. The signal at m/z 60, which is related to biomass combustion, was very noisy without any reasonable time series or diurnal cycle; therefore, constraint of BBOA was not attempted. The average fraction of m/z 60 to organics (f60) was very close to the estimated background level of f60 (0.3%, Cubison et al., 2011) even in higher organic loadings. The reason BBOA was not seen in the Curbside campaign remained unclear. Most of the local wood burning occurs in the suburban areas of the Helsinki region further away from downtown, but it was still expected to extract the BBOA factor in the Curbside campaign.

OOA is generally dominated by secondary organic aerosols (SOA) formed in the atmosphere from gas-to-particle conversion. OOA factor could not be further separated to distinct factors in any of the campaigns due to fact that the measurements were done in winter and autumn when ambient temperature and light intensity are low. Typically, more than one OOA component has been found for the datasets collected in summer because of more intense photochemistry, higher ambient temperatures, and larger temperature changes in summer than in winter promote separation (Lanz et al., 2010). The OOA factor at all the sites had very high contributions of m/z 44, which is mainly the CO$_2$ fragment typically from thermal decarboxylation of organic acid groups (Alfarra et al., 2004), and m/z 18, a
fragment of $\text{H}_2\text{O}^+$ implying the thermal breakdown of the carboxylic acid on the vaporizer, indicating highly oxidised organic aerosol that is considered a low-volatility oxidised organic aerosol (Fig. 3).

The mass spectra of individual factors were very similar between the sites, and they correlated well (Pearson correlation $r = 0.92$–0.98). Also, the mass spectra of OOA and HOA were very similar to the reference mass spectra of LV-OOA and HOA presented by Ng et al. (2011b), respectively (Table 2). The BBOA mass spectra had a much higher contribution of $m/z$ 18 and $m/z$ 44 than the mean BBOA mass spectrum in Ng et al. (2011b).

One method to assess the oxidation state of organic aerosol is to plot the fraction of $m/z$ 43 to organics ($f_{43}$) versus the fraction of $m/z$ 44 to organics ($f_{44}$, respectively; Ng et al., 2010; Fig. 4). It can be seen from the figure that, in general, OA has larger $f_{44}$, and therefore is more oxidised, at the Residential I site than at the Highway and Curbside sites. At the Residential II site, on the other hand, OA varied least, especially for $f_{43}$. By looking at the individual ME-2 SoFi factors, it can be seen that OOA had the largest $f_{44}$ (0.21–0.30) and corresponding O:C ratios (0.87–1.2, Ng et al., 2010), with the highest values observed for the residential sites. All OOAs are located in the highly oxidised LV-OOA region in the triangle plot where, e.g., fulvic and humic acids are also found. All these $f_{44}$ and O:C ratios for OOA were higher than in multiple field studies (Ng et al., 2010) or even at a very similar site in Helsinki (Timonen et al., 2013; Carbone et al., 2014). The higher ratios may be due to different instruments, as the previous measurements in Helsinki were performed using the high-resolution AMS with time-of-flight detector (ToF). The quadrupole detector used in the ACSM is much less sensitive than the ToF detector in the AMS. However, $f_{44}$ at the Curbside site (0.21) was quite similar to that measured in New York with the ACSM (0.19; Ng et al., 2011a). BBOA had slightly larger $f_{43}$ values than OOA but much smaller $f_{44}$ values. The observed O:C ratios for BBOA (0.4–0.5) were also slightly higher than presented in the literature (e.g., 0.21–0.32; Saarikoski et al., 2012; Timonen et al., 2013; Carbone et al., 2014). It is possible that the BBOA is LRT BBOA (Timonen et al., 2013), a mixture of BBOA and OOA or can be partly processed BBOA (Crippa et al., 2013), as the BBOA factors in all three sites had quite large $f_{44}$ and $f_{18}$, although elevated $f_{44}$ has also been observed for primary wood combustion sources (Alfarra et al., 2007). HOA presented the lowest O:C ratios at all the sites.

**Residential Areas**

OOA constituted more than half of organic aerosols at both the residential sites (Residential I 55 ± 22% and
Table 2. Comparison of factors and auxiliary data calculated as Pearson correlation coefficient r. Means of the factors (*) presented by Ng et al. (2011b). The term “sec ions” is the sum of main inorganic ions (sulfate, nitrate and ammonium) as a unit of an equivalent concentration. Coefficients with values over 0.70 have been bolded.

<table>
<thead>
<tr>
<th></th>
<th>Residential I</th>
<th>Residential II</th>
<th>Curbside</th>
<th>Highway</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.76</td>
<td>0.78</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.75</td>
<td>0.78</td>
<td>0.78</td>
<td>0.74</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.82</td>
<td>0.84</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>0.77</td>
<td>0.71</td>
<td>0.71</td>
<td>0.53</td>
</tr>
<tr>
<td>BC sulphate</td>
<td>0.71</td>
<td>0.76</td>
<td>0.92</td>
<td>0.82</td>
</tr>
<tr>
<td>nitrate</td>
<td>0.29</td>
<td>0.76</td>
<td>0.36</td>
<td>0.30</td>
</tr>
<tr>
<td>ammonium</td>
<td>0.31</td>
<td>0.72</td>
<td>0.72</td>
<td>0.59</td>
</tr>
<tr>
<td>chloride</td>
<td>0.71</td>
<td>0.74</td>
<td>0.74</td>
<td>0.38</td>
</tr>
<tr>
<td>sec ions</td>
<td>0.53</td>
<td>0.74</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td>LV-OOA*</td>
<td>0.23</td>
<td>0.46</td>
<td>0.24</td>
<td>0.22</td>
</tr>
<tr>
<td>HOA*</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>BBOA*</td>
<td>0.70</td>
<td>0.72</td>
<td>0.76</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Fig. 4. f43 versus f44 triangle plots for different sites and for the identified ME-2 factors (▲, ● and ■). The dotted lines define the triangular space where ambient OA usually falls. The triangle plot is described detail in Ng et al. (2010).

Residential II 55 ± 19%, Fig. 5). Also, the diurnal patterns of OOA were very similar at both the sites, without any significant trend over the day (Fig. 6). The OOA component has been shown to be a good surrogate of SOA in multiple studies, correlating well with secondary species (e.g., Zhang et al., 2005). In this study, OOA correlated with ammonium at both the residential sites (Fig. 7 and Table 2) and with sulphate at the Residential II site (Table 2). The precursor gas, ammonia, is emitted from agricultural and some natural sources. In Finland, those sources are quite limited in winter; therefore, ammonium can be considered mainly as long-range transported. The good correlation between OOA and ammonium indicates that also OOA originates mostly from LRT. Although the correlation between sulphate and OOA were poor at the Residential I site, it is very likely that part of the sulphate is long-range transported together with ammonia. During the cold period, there was an excess of sulphate up to 70% compared to ammonium, and the inorganic aerosol was acidic (main anion sulphate), referring to some local or regional sulphur dioxide (precursor sulphate) sources. Aerosol at the Residential II site was quite neutral despite the ambient temperature.

The contributions and concentrations of constrained HOA factor were rather similar at both the residential sites: 15 ± 7% of OA and 1.2 ± 1.3 µg/m³ at the Residential I site and 18 ± 9% and 0.92 ± 0.89 µg/m³ at the Residential II site (Fig. 5). The contribution of HOA was very similar to the campaign carried out in January/March 2009 in Helsinki (Carbone et al., 2014), whereas it was higher than during the campaigns done in non-urban environments (Crippa et al., 2014). The ambient temperature did not seem to have any influence on the concentration or contribution of HOA at the Residential II site, whereas at the Residential I site the highest HOA concentrations were detected together with low ambient temperatures (Figs. 5 and 7).

The HOA factor correlated well with nitrate at the Residential II site and NOₓ (NO + NO₂) at both the sites, which is quite typical, as HOA and NOₓ usually have a common source, traffic (Fig. 7 and Table 2). However, NOₓ also correlated slightly with BBOA at the Residential I site (Table 2), and similar diurnal trends were detected for HOA, BBOA and NOₓ at the Residential I site, with pronounced peaks in the morning and evening (Fig. 6). Similar time series of HOA and BBOA and pronounced morning and evening peaks for BBOA have also been detected during winter inversions in Zürich (Lanz et al., 2008). For HOA and BBOA, the evening peak was clearly higher than the morning peak, whereas NOₓ had a larger peak in the morning. NOₓ also has sources other than traffic, like heating plans and energy production, which, however, were not located in the vicinity. The diurnal profile of HOA at the Residential II site was rather flat, ranging from an early morning value of 0.7 µg/m³ to an evening value of 1.2 µg/m³ at 8 p.m. (Fig. 6). The broad “morning and evening peaks” (7 a.m.–1 p.m. and 3–9 p.m.) were probably a consequence of the combination of rush hours and stable meteorological conditions.
conditions with low air temperatures, which hamper the dispersion of pollutants.

The mean contributions of BBOA to OA were quite similar at both the residential sites (Residential I 30 ± 18% and Residential II 27 ± 17%), but the mean concentration at the Residential I (2.8 ± 4.25 µg/m$^3$) site was almost double that of the Residential II site (1.6 ± 2.2 µg/m$^3$). Some data was excluded from the Residential I site, as the factor analyses could not be performed reliably if all the data were included. Those excluded periods had low mass concentrations and therefore would have decreased the mean BBOA concentration if included in the analysis. Clearly lower contributions of BBOA were achieved in wintertime in Paris, Helsinki (urban background) and Manchester (12–18%; Allan et al., 2010; Crippa et al., 2013; Carbone et al., 2014) than in this study for residential areas.

**Fig. 5.** Concentrations (averages) and contributions (averages and time series) of ME-2 factors (OOA, HOA and BBOA) at Curbside, Residential I, Residential II and Highway sites in the Helsinki metropolitan area, Finland. Black line is to ambient temperature.

**Fig. 6.** Diurnal profiles of ME-2 factors and some auxiliary components in four different sites.
Temperature had a clear effect on the concentration and the contribution of BBOA at the Residential I site, whereas that kind of behaviour was not seen at the Residential II site. At the beginning of the Residential I campaign, cold and stagnant weather conditions occurred and temperature decreased below –20°C during the nights and stayed below –10°C during the daytime (Fig. 5). The temperature profile for the Residential II site was very different. During the Residential II campaign, the weather was quite mild and rainy (sleeting and snowing), although in the middle of the campaign there were a few days with very low temperatures. The highest BBOA concentrations were measured during those cold days at the Residential II site (Figs. 5 and 7). Chloride correlated with BBOA at the Residential I site (Fig. 7 and Table 2). It has been noticed earlier that there is potassium chloride (KCl) in young smoke, whereas aged smoke contains more potassium nitrate (KNO₃) and potassium sulphate (K₂SO₄) (Liu et al., 2000; Li et al., 2003). This conversion has been presented to be quite fast (Li et al., 2003). The sources for biomass burning smoke were very close to the Residential I site, as there were several residential houses in the vicinity of the site and smoke from chimneys was regularly seen during the campaign. The clear indication of biomass burning smoke was also seen in the concentrations of levoglucosan, potassium and BaP (Fig. 8). The typical biomass burning tracer, levoglucosan, had higher concentrations during the cold period than right after it when temperature increased. Also, the concentrations of potassium and BaP were elevated at the same time. The correlation between BaP and levoglucosan has been shown to be very strong in small-house areas in Finland (Kousa et al., EAC, 2012).

Sulphate correlated with BBOA at the Residential I site (Table 2). The ratio of BBOA to sulphate increased as the concentration of BBOA increased (not shown), which indicated that BBOA increased relatively more than sulphate, and the main origin of sulphate was probably other than BBOA. The origin of sulphate may be from other heating systems like district heat produced by coal or heavy oil in power plants. The heavy oil is used as an additional heating source during cold weather periods, at least in the Helsinki metropolitan area. Furthermore, sulphate and BBOA are also present in LRT aerosols which are mixed with pollutants from local sources.

Traffic Sites
Similar to the residential sites, OOA had the highest contribution to OA at the traffic sites, (Curbside 67 ± 14% and Highway 50 ± 19%; Fig. 5). The diurnal pattern of OOA was relatively independent of the time of the day (Fig. 6).
The time series of the OOA correlated with ammonium and sulphate at both the traffic sites and with nitrate at the Curbside site (Fig. 7 and Table 2). The ion balance was quite neutral at the Highway site, whereas it was mainly acidic at the Curbside site. There were no local emissions that would have explained the differences observed in acidity at the different sites, but meteorology and variation in emissions of precursor gases likely affected the concentrations of secondary inorganic ions and thus to the ion balance.

The contribution of HOA to OA was 33 ± 14% at the Curbside site and 25 ± 17% at the Highway site, with no correlation between ambient temperature and the concentrations or contributions of HOA. The diurnal trends of HOA, BC and NOₓ and their time series were similar, indicating common emission sources (Figs. 6 and 7). NOₓ is strongly associated with vehicle exhaust, and the diurnal pattern at the Highway site was quite typical for other traffic sites (Sun et al., 2011). During the rush hours, the HOA concentrations were elevated, and the morning peak was more pronounced than the evening peak. The morning and afternoon rush hour peaks were not seen at the Curbside site, maybe because the traffic flow near the Curbside site is quite constant throughout the day and/or the dispersion of aerosols was poor.

The mean contribution of BBOA to OA was 25 ± 15% at the Highway site and slightly smaller than at the Residential sites. Highest BBOA concentrations and contributions were measured with low ambient temperature, but such a clear trend as at the Residential I site was not seen (Fig. 5). In general, the weather was quite mild (temperature between −7 and 13°C) during the campaign. Two clear BBOA episodes were detected at the Highway site during the night of October 25–26 and on the evening of October 27 when temperature decreased below 0°C (Figs. 5 and 7). During those periods, the contribution of BBOA to OA was between 60 and 78%. BBOA seemed to be quite fresh during those days, as the concentrations of chloride were elevated together with BBOA. From the Curbside data, BBOA could not be extracted, probably because domestic wood burning is limited in downtown Helsinki and other sources dominate the composition of OA.

SUMMARY AND CONCLUSIONS

The chemistry of non-refractory submicron particles (NR-PM₁₀) was investigated in four measurement campaigns at different environments in the Helsinki metropolitan area, Finland. Two of the campaigns were conducted in the suburban residential areas (Residential I and II sites), one in downtown (Curbside site) and one beside the suburban highway (Highway site). Campaigns were conducted either in winter (Residential I & II and Curbside) or in autumn (Highway). The detailed aerosol chemistry was characterised with approximately 30 min time resolution by using the Aerodyne Aerosol Chemical Speciation Monitor. The sources of organics were further examined by the multilinear engine algorithm (ME-2) and the custom software tool Source Finder (SoFi). Auxiliary aerosol chemical components (inorganics, black carbon) and NOₓ concentrations were used to interpret the sources and origins of different factors produced by ME-2.

The mean concentrations of NR-PM₁₀, i.e., the sum of components deployed from the ACSM, were quite similar for the campaigns carried out in wintertime (10.1–12.5 µg/m³), whereas the concentration was 40–50% lower during the autumn campaign (6.0 µg/m³) conducted at the Highway site due to the low background concentration levels. The low background levels were likely caused by meteorology, origin of air masses and non-intensive heating period locally and regionally. On the basis of the whole study, organics had the highest contribution to NR-PM₁₀ (54 ± 14%), followed by sulphate (21 ± 11%), nitrate (15 ± 8%), ammonium (9 ± 5%) and chloride (1.0 ± 2.2%). The contribution of black carbon to PM₂.₅ was 13% on average, having the highest concentrations and contributions at the traffic sites. The sum of NR-PM₁₀ and BC accounted for almost all of PM₂.₅.

Organic fractions at four sites were divided into two or three distinct types of organic aerosol, representing HOA that was likely to be related to fresh vehicle exhaust, BBOA that mostly originated from local residential wood burning and OOA. The mass spectra of individual factors were very similar between the sites, although different approaches to the ME-2 tool were used: HOA was either constrained (residential sites) or not constrained (traffic sites). It seems that constraining was needed in the environments that were less affected by traffic. BBOA was not constrained, as it was separated without constraining at the Residential and the Highway sites, whereas at the Curbside site the biomass tracer (m/z 60) was not resolved from the background signal.
OOA had the largest contribution to organic aerosol at all the sites (50–67%) correlating with all or some of the secondary inorganic components, which indicates that OOA was mostly regionally distributed and long-range transported. The contributions of HOA were higher at the traffic sites (25–32%) than at the residential sites (15–18%). The time series and diurnal trends of HOA followed those of NO$_x$ and BC. The concentration of BBOA was clearly highest at the Residential 1 site (2.8 µg/m$^3$) due to local wood burning emissions and cold weather. The detection of chloride together with BBOA supported the hypothesis that a significant fraction of BBOA was likely to be fresh and from local sources. BBOA had clear dependency on temperature. The contribution of BBOA was almost half of OA when temperature was low (below −15°C) at the Residential 1 site and as large as 60–78% during the cold autumn nights (below 0°C) at the Highway site. At the downtown traffic site (Curbside), BBOA could not be found, probably because most of the local wood burning occurs in the suburban small-house areas of the Helsinki region.

This study displayed an extensive chemical characterization of submicron aerosol particles at residential and traffic-related environments. It presented that online monitoring of PM$_1$ chemical composition with ACSM provides new quantitative information on the sources of aerosol. That data is valuable for local authorities dealing with the air quality issues in urban areas. However, this study also showed that in a rather clean urban environment, like in the Helsinki metropolitan area, long-range transported or regionally distributed pollutants often dominate the concentration and the composition of PM, even though the measurements are carried out next to well-known particle sources (traffic, residential wood burning), resulting in relatively similar chemical composition and source apportionment for PM regardless of the location of the measurement site. In those cases, the measurement period needs to be long enough (probably at least several months) to obtain a sufficient amount of data with varying source contributions in order to achieve reliable source apportionment analysis. That can be accomplished by novel, low-maintenance monitoring instruments like the ACSM.

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The composition of ambient and fresh biomass burning aerosols at a savannah site, South Africa

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Abstract

Atmospheric aerosols play a key role in climate change and also have adverse health impacts. Since South Africa is a rapidly developing country with increasing urbanization and industrial growth, information on the quality of ambient air is important. In this study the chemical composition of ambient particles and the particles in fresh biomass burning plumes were studied at a savannah environment in Botsalano, South Africa. The results indicated that Botsalano was regularly impacted by air masses that had passed over several large point sources. Air masses that had passed over the coal-fired Matimba power station in the Waterberg or over the platinum group metal smelters located in the western Bushveld Igneous Complex had increased sulphate concentrations in the submicron ranges which were 14 to 37 times higher when compared to air masses that had passed over rural areas only. Due to the limited nature of this type of data in literature for the interior regions of southern Africa, this report serves as a valuable reference for other studies. The biomass burning study showed that potassium in fresh smoke of savannah grass is most likely mainly in the form of KCl. Clear differences were also found in the ratio of potassium and levoglucosan in the smouldering and flaming phases. The results highlight the need for more comprehensive chamber experiments of the different fuel types used in southern Africa, in order to confirm the ratio of important biomass burning tracer species that can be used in source apportionment studies in the future.
Introduction

Concerning air quality, Africa is one of the least studied continents in the world. Extensive aerosol measurements have been carried out in southern Africa within the framework of the SAFARI 92, SAFARI 2000 and EUCAARI campaigns.\textsuperscript{1,2} The first two campaigns concentrated mainly on biomass burning emissions and regional transport through the atmosphere, whereas the EUCAARI campaign focused on understanding the interactions of climate and air pollution around the world. However, many air pollution measurements conducted in South Africa have been focused on nucleation events, trace gases and/or optical properties of aerosols and lesser extend on the chemistry of the particles.\textsuperscript{3-8} A few studies on the chemical characterization or source apportionment of ambient aerosols have been conducted in Tanzania during wet and dry seasons and in Kenya in different environments.\textsuperscript{9-13} However, very few studies in addition to the SAFRARI 2000 campaign, which covered multiple studies in southern Africa have been published that concentrated on the chemical characterization of aerosols in South Africa.\textsuperscript{1,14} The most recent long-term measurements of aerosol chemical composition were conducted relatively close (approximately 100 km) to the Johannesburg-Pretoria megacity conurbation, where different source regions were determined and the chemical characteristics of organics were investigated.\textsuperscript{15-16}

The main objective of this paper is to enhance the level of knowledge with regard to the chemical composition of particles at a regional background location in the North West Province of South Africa, for which only sparse information on the air quality is available. This chosen location is also downwind of the Waterberg area on the dominant anti-cyclonic circulation route of air mass movement in this part of South Africa. The construction of a large new coal-fired power station (Medupi Power Station), in addition to the currently operational coal-fired power station in the Waterberg area (Matimba Power Station) necessitates the need for such measurements to serve as reference in the future. In addition, background aerosol chemical compositional information is also important since South Africa is a developing country with increasing urbanization and industrial growth.
The sampling site was chosen to represent a relatively clean background area, with very little local pollution, giving us an opportunity to investigate how the chemical composition of aerosols changed depending on the origin of the air masses. As far as the authors could assess there are not any other aerosol chemical composition studies published for this important area. Earlier studies focused on the physical properties of aerosols at the site. In this study we concentrated mainly on submicron particles since the particles originating from anthropogenic and natural wild fire combustion sources are typically below 1 µm in aerodynamic size. In addition to considering the aerosol chemical composition of regional air masses, a biomass burning experiment was also conducted onsite to investigate the chemical composition of aerosols originating from a fresh biomass burning plume.

**Experimental**

**Site description and measurement periods**

A mobile station for atmospheric measurement was deployed in the Botsalano game reserve in the North-West Province, South Africa (25.541S, 25.754E, 1424 m AMSL). This setting can be considered as a dry savannah regional background site, with no major local anthropogenic sources. In Figure 1 the main large sources around the measurements site have been presented. Briefly, the sector from north to south, in an easterly direction, contains several large sources. Possibly, one of the largest regional pollution source areas is the mining and pyrometallurgical smelting activities in the western limb of the Bushveld Igneous Complex (BIC). The ambient measurements that are reported in this paper were carried out in two short campaigns during 9-15 October 2007 (local spring) and 30 January – 5 February 2008 (local summer). The meteorological conditions of Botsalano during the campaigns are presented in Figure 2. The beginning of the spring campaign was slightly colder than the summer campaign; otherwise the seasons had very similar temporal variation in temperatures. The relative humidity and temperature was on average 19 and 22% higher during the summer campaign than in the spring campaign, respectively. The summer and spring campaign
represented typical seasons compared to the study Laakso et al., (2008) at the same site in 2006-2007.\textsuperscript{17}

In addition to the ambient samples, a small-scale biomass burning measurement experiment was also performed. During the biomass burning experiment organic materials, consisting mainly of dry grass and branches collected upwind of the site, were burned. The distance between the sampling equipment and the fire was approximately 50 m. Two samples were collected. The first sample was taken of the main plume that was sampled for 44 min, while the second sample that was taken over a period of 124 min during the period when the fire intensity and fuel amount was lower.

**Measurements**

The samples were collected with a three-stage cascade impactor with aerodynamic cut-off diameters of 10, 2.5 and 1 µm followed by a backup filter (Dekati®PM10). The PM10 inlet was used for cutting off particles greater than 10 µm. The collection substrates were pre-heated quartz fibre filters (Tissuquartz, PALL). The sampling flow rate was 30 L min\textsuperscript{-1}, while the sampling duration was approximately 24 h, except during the biomass burning experiment, when shorter sampling periods were utilised.

**Chemical analysis**

Organic carbon (OC) and elemental carbon (EC) were analysed from a 1 cm\textsuperscript{2} punch out of the quartz fibre filters using a thermal optical carbon analyser (TOA; Sunset Laboratory Inc. Tigard, OR, USA). The instrument uses a two-phase thermal method to separate OC and EC (EUSAAR\textsubscript{1} and EUSAAR\textsubscript{2}).\textsuperscript{23} Optical correction was performed in order to separate pyrolysed organic carbon from elemental carbon.

The sampled submicron particles (PM\textsubscript{1}) had uniform deposition on the filters, but the larger size fractions (particles > 1 µm) were not uniformly spread. However, a previous study indicated that unevenly spread samples yielded acceptable results, when applying optical correction for impactor samples.\textsuperscript{24} Therefore these samples were also analysed.
The amount of gaseous organic carbon collected on the filters were not measured, and hence not subtracted for the concentrations of OC. The overall uncertainty of the TOA method was estimated to be 10% for OC and 20% for EC in concentrations above the quantification limit.

The field blank concentrations of OC for the backup filters (PM$_1$), calculated for a one-day sampling period, were just above the detection limit during spring (0.07 µg m$^{-3}$) and summer (0.10 µg m$^{-3}$) campaigns, respectively. For the impactor stages the combined corresponding blank concentrations were 0.08 µg m$^{-3}$ and 0.09 µg m$^{-3}$ during the spring and summer campaigns, respectively. The blank concentration of EC was below the detection limit for the impactor stages (0.02 µg m$^{-3}$) and for the backup filters (0.07 µg m$^{-3}$). The measured OC concentrations were multiplied by a factor of 1.6 to obtain an estimate for total particulate organic matter (POM) mass concentration.$^{25}$

The remaining portion of the quartz filters were analysed with ion chromatography (IC) in order to determine selected ions: chloride (Cl$^-$), nitrate (NO$_3^-$), sulphate (SO$_4^{2-}$), oxalate, sodium (Na$^+$), ammonium (NH$_4^+$), potassium (K$^+$), magnesium (Mg$^{2+}$) and calcium (Ca$^{2+}$). The uncertainty of the IC analysis was estimated according to the analysis of standards being 5-10% depending on the ion analysed. The field blank concentrations of each of the ions in the backup- and impactor stages filters were 0.018 µg m$^{-3}$ and 0.008 µg m$^{-3}$, respectively during both the campaigns and the determination limit were below 0.002 µg m$^{-3}$ for all of them.

Concentrations of monosaccharide anhydrides (levoglucosan, galactosan and mannosan) collected on backup (PM$_1$) filters were measured using an IC coupled to a quadrupole mass spectrometer.$^{26}$ The blank concentrations of monosaccharide anhydrides were below the determination limit (1-5 µg L$^{-1}$), which corresponded to 0.001-0.005 µg m$^{-3}$ for a 24 h sample.
**Auxiliary data**

Earlier publications\textsuperscript{17,19} presented detailed descriptions of the measurements at Botsalano including meteorological parameters (temperature, pressure, relatively humidity, precipitation, wind speed and wind direction), trace gas concentrations (SO\textsubscript{2}, NO/NO\textsubscript{x}, CO and O\textsubscript{3}) and submicron aerosol particle size distribution with a Differential Mobility Particle Sizer (DMPS) consisting of a Vianna-type Differential Mobility Analyser and TSI model 3010 Condensation Particle Counter.

Total mass concentration of PM\textsubscript{1} was not measured directly, but was estimated from the DMPS size distribution in the size range from 10 to 840 nm. Particle number concentration of each DMPS size channel was converted to volume concentration assuming spherical particles, multiplied by the estimated particle density and summed to obtain the total mass concentration of particles below 840 nm. The particle density value was calculated from the analysed chemical composition for each sample by using an approach suggested by Saarnio et al.\textsuperscript{27} and it varied from 1.38 to 1.75 g cm\textsuperscript{-3}.

**Air mass history**

Air mass backward trajectories were calculated using the NOAA HYSPLIT backward trajectory model.\textsuperscript{28} The 96 h backward air mass trajectories were calculated to arrive on every hour of sampling, with an arrival height of 100 m above the ground.

**Results and discussion**

**Overall ambient air results**

The overview of the meteorological pattern in Botsalano has been shown that the north-easterly wind direction had the highest frequency.\textsuperscript{19} This can be expected, since the meteorological pattern over the interior of South Africa is dominated by an anticyclonic circulation pattern.\textsuperscript{29} Secondly, although Botsalano is a background site without significant local air pollution point sources, it is regularly impacted by air masses that have passed over several large point sources. Especially the Matimba coal fired power station at Lephalale in the Waterberg, the silicon and platinum group metal (PGMs)
smelters near Polokwane, the PGM smelters in the Northam/Thabazimbi area, and the city of Gaborone are situated on the dominant anticyclonic circulation path for air masses arriving at Botsalano. The mining and metallurgical activities in the western region as lying on the axis between the towns of Brits and Rustenberg (Bushveld Igneous Complex, BIC) are also likely to impact the site regularly.

The PM\textsubscript{1} mass concentrations calculated from the DMPS results varied between 1.4 and 21.5 µg m\textsuperscript{-3} (mean 11.3 ± 5.3 µg m\textsuperscript{-3}), whereas the total concentrations of all analysed components varied between 2.9 and 14.5 µg m\textsuperscript{-3} (mean 9.0 ± 3.2 µg m\textsuperscript{-3}). The lowest concentrations had the highest differences between the mass concentrations estimated from DMPS and the sum of analysed components (Figure 3). However, the mean ratio between them was 0.84, and they correlated well (Pearson r = 0.93). This implies that the chemical components analysed essentially comprised the total mass of the PM\textsubscript{1} fraction. The lower mass concentration derived from DMPS likely due to lower cut off of the particle size compared to the PM sampler (840 nm vs 1 µm).

Figure 4 presents the PM\textsubscript{1} fractional concentrations of the analysed components for the combined, as well as the individual spring and summer campaigns. Considering the combined campaigns (both spring and summer), sulphate had the highest individual component concentration, i.e. 44% or 3.9 ± 2.3 µg m\textsuperscript{-3} (Table 1). POM was the second highest component, i.e. 39% or 3.5 ± 0.6 µg m\textsuperscript{-3}, while two main cations, ammonium and potassium contributed 11 and 2% (Table 1). The rest of the components combined contributed approximately 4%. The equivalent ratio of sulphate to main cations for PM\textsubscript{1} indicated that sulphuric acid was not neutralised totally. The average contribution of sulphate in Botsalano was higher than what was measured during measurement campaigns of approximately one year in different environments in Europe, China and at Welgegund near Potchefstroom in South Africa\textsuperscript{15,30,31} However, at Welgegund in South Africa a similar contribution has been noticed during the wet season or in shorter campaigns at rural or remote sites in USA, Ireland or Japan\textsuperscript{15,32} According to aerosol mass spectrometer (AMS) studies the overall average contribution of submicron sulphate
and organic matter around the world are 32% (range 10-67%) and 45% (range 18-70%), respectively.\textsuperscript{32}

A relative comparison of the spring and summer campaigns indicate that POM was the dominant component during spring, while sulphate dominated in summer. Sulphate concentrations were clearly higher during the summer campaign than during the spring campaign, whereas the POM concentrations did not vary significantly between two seasons (Table 1). It is well known that oxidation of SO\textsubscript{2} to sulphate occurs faster at higher relatively humidity as observed during summer than in the drier period. Also the concentration of SO\textsubscript{2} and the ratio of SO\textsubscript{2} and sulphate support this interpretation, being clearly lower during the summer campaign than during the spring campaign, which indicates faster removal of SO\textsubscript{2} (Table 1). The meteorological data for Botsalano, confirming the afore-mentioned relative humidity levels, have previously been presented.\textsuperscript{17} It has also been suggested that ozone (O\textsubscript{3}) concentrations could have a positive correlation to sulphur conversion rate.\textsuperscript{33} However, in our study the O\textsubscript{3} concentrations did not have significant difference between the summer (range 17-63 ppb) and spring campaign (range 11-58 ppb), although the average solar radiation in summer was on average 28 % higher than in spring.

The EC level during the spring campaign was substantially higher compared to the summer campaign (Table 1), which confirms the influence of combustion during spring. Although the concentrations of levoglucosan, a biomass burning marker\textsuperscript{34}, were always relatively low, it was substantially higher during the spring campaign than in the summer campaign, with mean values of 0.010 and 0.006 µg m\textsuperscript{-3}, respectively. Additionally, CO, which can be used as a gaseous tracer of combustion\textsuperscript{35}, had similar trends with means of 145 ppb and 92 ppb during the spring and summer campaigns, respectively.

As previously mentioned, it was found that the total concentration of the components analysed was a good approximation for the total PM\textsubscript{1} mass, as calculated from DMPS data. Additionally, PM\textsubscript{1} particle depositions on the filters were uniform, while the larger size fractions were not. Since mass closure could not be performed for the PM\textsubscript{1-2.5} and
PM$_{2.5-10}$ size fractions, these fractions are not individually discussed in detail, but only in comparison with the PM$_1$ fraction. Figure 5 shows the analysed components for the different size fractions for the combined spring and summer ambient air sampling campaigns. From this data it is obvious that SO$_4^{2-}$, POM, NH$_4^+$, EC and K$^+$ were predominantly found in the PM$_1$ size fraction, while NO$_3^-$ occurred mostly in the coarser fractions. This size fraction analysis clearly indicates that the fine faction (PM$_1$) is dominated by the water soluble chemical compounds. Soil components, which were not analysed in this study, are likely to comprise the majority of the coarser fractions.

**Ambient air case studies**

In the previous paragraphs it was established that the analysed chemical compounds were mainly found in the fine fraction (in PM$_1$). In addition, the mass balance could only be calculated for the PM$_1$ fraction. Therefore the subsequent case studies focus mainly on the PM$_1$ results.

**Case study 1: Air masses that had passed over the regional background**

According to backward air mass trajectory analysis, there was one sampling day (9-10 October 2007) when the air masses arrived at Botsalano from the south-west. In this direction there are no large air pollution point sources, apart from the town of Mafikeng (population approximately 260 000), as is indicated in Figure 6a.

**Case study 2: Air masses that had passed over the Waterberg**

On three days during the sampling campaigns (11-12, 12-13 & 14-15 October 2007) air masses were likely to have been influenced by the coal-fired power station at Lephalalale in the Waterberg, i.e. Matimba Power Station, without having an influence from any other large point sources (Figure 6b). The significance of this case study data is due to the current commissioning of a second coal fire power station, i.e. Medupi Power Station, in the Waterberg area. The Matimba Power Station does not have equipment for removing sulphur and nitrogen gases from the emissions (de-SO$_x$ and de-NO$_x$), while the newly constructed Medupi Power Station will include such technology although it is not yet clear if it will be implemented during initial commissioning. This case study data could in
future serve as a valuable reference for other studies in this area to compare the concentrations of particles with and without the NO\textsubscript{x} and SO\textsubscript{x} removal.

**Case study 3: Air masses that had passed over the western BIC**

On two days during the sampling campaign (30 January-1 February 2008) the air masses arriving at Botsalano passed directly over the two closest PGM smelters in the western BIC lying to the east of Rustenberg (Figure 6c). These air masses were also likely to have travelled over the PGM and silicon smelters near Polokwane, but not over any other large air pollution point sources. The large air pollution point sources in the western BIC are mainly a mixture of ferrochrome and PGM smelters, as well as base metal refineries.\textsuperscript{20} The sampled air masses therefore do not represent all the types of point sources occurring in the western BIC, but they represent the PGM smelters occurring in this region.

**Comparison of case studies**

In Table 1 the comparative results for the three case studies identified are listed. From these results it is clear that the background air masses sampled were substantially cleaner compared to the anthropogenically influenced air masses, notwithstanding the possible influence of pollution from Mafikeng on the background air masses sampled. The total concentrations of the components measured in the PM\textsubscript{1} fraction, which was also found to be a good approximation of the total PM\textsubscript{1} mass as indicated earlier, were 2.9, 7.6 and 13.4 µg m\textsuperscript{-3} for the regional background, Waterberg overpass and the western BIC overpass, respectively. The anthropogenic influence of the large points sources on the chemical composition of the PM\textsubscript{1} fraction become apparent especially when the sulphate compositions are considered. The regional background had sulphate concentration of only 0.2 µg m\textsuperscript{-3} while the Waterberg overpass during spring campaign and Western BIC overpass during summer campaign, air masses had the levels of 2.8 and 7.5 µg m\textsuperscript{-3}, respectively. During the Western BIC event the sulphate to SO\textsubscript{2} ratio was higher indicating faster oxidation of SO\textsubscript{2} than on average during the summer campaign or longer transport time. The temperature and relative humidity during the event were similar as the
averages, but the wind speed was lower. During the Waterberg event the sulphate to SO$_2$ ratio was similar than the spring average.

**Samples from biomass burning experiments**

During the ambient air sampling campaigns no clear biomass burning plume could be identified, hence no ambient biomass burning plume case study is presented. The spring sampling season in mid-October was well past the peak activity of regional biomass burning, so the biomass burning influences in the air masses were not expected. The highest levoglucosan concentration was 0.030 µg m$^{-3}$, which was one order of magnitude lower than background concentration (0.3 µg m$^{-3}$) measured during the SAFARI 2000 campaign that was conducted in a period when large scale regional biomass combustion occurred.$^{35}$ Biomass burning is a very important air pollution source in southern Africa, having both air quality and climate change implications. To augment the ambient data already presented in this paper, data of a biomass burning experiment conducted is subsequently presented.

A fractional distributional graph of the time weighted average of the various components analysed in the two biomass burning plume samples gives an overall indication of the relative importance of the components in fresh biomass burning plumes, which are presented in Figure 7. From this data it is clear that POM is much higher than the other components in the PM$_1$ fraction. It is realised that some of the detected OC might have been gaseous OC, since the amount of gaseous OC was not measured. The amount of gaseous OC in ambient measurement has been presented to be 6-19%.$^{9,27,37}$ In our study approximately a quarter of the analysed OC was vaporized during the first temperature step of the TOA analysis (T=75-200 °C), implying that these compounds were the most volatile. Some of these components might therefore have been gaseous OC absorbed/adsorbed into the filter substrate or onto the particles collected on it. Notwithstanding this possibility, the dominance of POM in the PM$_1$ fraction remains evident. This is important, since it indicates that organic components released by biomass combustion during the dry season in southern Africa could play an important role during new particle formation and subsequent growth. This is in contrast to the wet season in
southern Africa, when biogenic activities are mainly responsible for the release of organic components. The situation in southern Africa is therefore completely different compared to European and North American conditions, where biogenic activity are the main source of atmospheric organic compounds at least in rural areas. The chemical and physical characteristics in the atmosphere are therefore likely to differ substantially. The dominant contribution of POM to PM$_{1}$ aerosol from biomass burning smokes clearly support the findings of a recent paper focussing specifically on the effect of biomass burning plumes on the formation and growth of ambient atmospheric aerosols in southern Africa from long term data$^{38}$.

Apart from high POM contribution in PM$_{1}$ (81%) other differences between biomass burning plume samples and other samples were the concentrations or the contributions of monosaccharide anhydrides, oxalate and potassium, which can be attributed as biomass burning tracers.$^{36}$ Their concentrations increased significantly during the biomass burning event compared to the ambient samples. The concentration of submicron oxalate during biomass burning event increased almost four fold compared to the average of the ambient samples. However, the relative contribution of oxalate to POM (0.1%) was smaller than the contribution thereof to the combined ambient samples (2.7%). The contribution of K$^{+}$ in PM$_{1}$ during biomass burning (4-5%) doubled compared to the ambient samples (2%).

The ratios of monosaccharide anhydrides give information of the biomass burning material. The ratios of levoglucosan to mannosan and levoglucosan to galactosan in the first plume were 17.1 and 14.0, respectively, and in the second plume 16.4 and 17.4, respectively, which were quite similar to measured values in laboratory experiments, during which savannah grass with acacia wood was burned (levoglucosan to mannosan ratio of 21.7 and levoglucosan to galactosan ratio of 15.2).$^{39}$ It has been reported that fresh smoke of savannah grass contains potassium chloride (KCl) particles, while aged smoke contain potassium sulphate (K$_{2}$SO$_{4}$) and potassium nitrate (KNO$_{3}$).$^{36,40}$ Cl$^{-}$ was the most abundant anion (3%) in the first plume followed by sulphate (2%) and nitrate (1%). These results indicate that the most of the K$^{+}$ was most likely present as KCl. The calculation of equivalent ratios showed that there was an excess of K$^{+}$ compared to Cl$^{-}$,
SO$_4^{2-}$ and NO$_3^-$. However, if SO$_4^{2-}$ was assumed to react first with NH$_4^+$, there was no excess sulphate left for K$^+$. The additional K$^+$ might therefore be present as carbonaceous material (like K$_2$CO$_3$) that has been detected in another biomass burning study in southern Africa.$^{41}$

Since components analysed in the coarse fractions (PM$_{1.2.5}$ and PM$_{2.5-10}$) are unlikely to approach mass closure, these results are therefore only presented in a comparative manner to the PM$_1$ results (Figure 8). From these results the dominance of the PM$_1$ fraction in the overall PM$_{10}$ chemical composition in fresh biomass burning plumes is evident. Over 90% of the POM, EC, K$^+$, Cl$^-$, SO$_4^{2-}$ and NH$_4^+$ammonium were in a PM$_1$ fraction. NO$_3^-$, Na$^+$ and oxalate were mainly in the PM$_1$ fraction (62-83%), whereas at least 50% of Ca$^{2+}$ was in the PM$_1$ fraction.

**Conclusions**

Size segregated aerosol samples were collected using a three-stage impactor with backup filter at a relatively clean savannah environment at Botsalano Game Reserve, South Africa. The backup filter collected particles below 1 µm. Other size ranges were > 10 µm, 2.5-10 µm and 1-2.5 µm. Two campaigns were performed, i.e. one in spring (9-15 October 2007) and another in summer (30 January – 5 February 2008), and during which 11 sets of impactor samples with typically 24-h sampling time were collected. In addition to these ambient measurements, a simple biomass burning experiment was also performed to determine the chemical composition of fresh biomass burning fire plumes. Organic and elemental carbon, selected ions and monosaccharide anhydrides (e.g. levoglucosan) were analysed. These components essentially comprised the total mass of the PM$_1$ fraction.

Results of the ambient air masses indicated that sulphate, organic carbon, ammonium, elemental carbon and potassium were mostly associated with fine particles (PM$_1$). Other components (sodium, chloride, nitrate and oxalate) were divided into fine and coarse fractions, but their concentrations were very small. POM was the dominant component
during spring, while sulphate dominated in summer. Some indications of different oxidation rate of SO$_2$ between the seasons were found explaining the higher sulphate concentrations in summer campaign. Substantially higher elemental carbon concentrations in spring demonstrated the occurrence of more combusting processes compared to the summer campaign.

Although Botsalano is a background site, it is regularly impacted by air masses that have passed over several large point sources. The anthropogenic influence of the large points sources on the chemical composition of the PM$_1$ fraction become apparent, at least when the sulphate compositions are considered. The air mass passing over the coal-fired power station in Waterberg or the PMG smelter increased the sulphate concentrations 14 or 37 times compared to the background air. Characterization of especially the air masses that had passed over the Waterberg area is very important since an additional large coal-fired power station is being commissioned at present (2015). The data presented here can in future be compared with similar studies done after the commissioning of the aforementioned new coal-fired power station, as well as after the de-SO$_x$ and de-NO$_x$ technology of the new power station have become operational, to assess the impact of such large industrial developments in this area.

The biomass burning study confirmed that potassium in fresh biomass plumes is most likely mainly in the form of KCl, not K$_2$SO$_4$ and KNO$_3$. Clear differences were also found in the ratio of potassium and levoglucosan in the smouldering and flaming phases. The data highlight the need for more comprehensive chamber type experiments of the major fuel types, as to confirm the ratio of important biomass burning tracer species. Such information can in future be used to better quantify the contribution of biomass burning in source apportionment studies.
References


**Captions**

Figure 1: Geographical map of southern Africa indicating the location of the Botsalano measurement site (25.541S, 25.754E), as well as the location of large air pollution point sources. The abbreviations for the provinces are LP: Limpopo, GP: Gauteng, MP: Mpumalanga, FS: Free State, NC: Northern Cape, NW: North West

Figure 2: Meteorological parameters (temperature, relative humidity, wind speed, wind direction, and precipitation) during the campaigns.

Figure 3: Mass concentrations of particles estimated from DMPS and the sum of the analysed components colour coded by the total particle number concentration (# cm\(^{-3}\)).

Figure 4: Combined PM\(_1\) fractional component composition for both ambient sampling campaigns, as well as the fractional component composition of the individual ambient spring and summer sampling campaigns.

Figure 5: Comparison of PM\(_1\), PM\(_{1-2.5}\) and PM\(_{2.5-10}\) compositional analysis for the combined ambient campaigns.

Figure 6: Air mass history of the identified ambient case studies investigated: a) regional background, b) Waterberg overpass, c) Western BIC overpass. The abbreviations for the provinces are LP: Limpopo, GP: Gauteng, MP: Mpumalanga, FS: Free State, NC: Northern Cape, NW: North West.

Figure 7: Time weighted combined PM\(_1\) fractional component composition the biomass burning plumes sampled.

Figure 8: Comparison of PM\(_1\), PM\(_{1-2.5}\) and PM\(_{2.5-10}\) compositional analysis for the combined time weighted average biomass burning plumes sampled.

Table 1: Concentrations of particles (µg m\(^{-3}\)) and gases (ppb) for the spring, summer, mean and identified ambient case studies investigated. Case Study 1: Regional background, Case Study 2: Waterberg overpass, Case Study 3: Western BIC overpass. Biomass burning experiments were excluded.
Table 1

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<td>N/A</td>
</tr>
<tr>
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<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>Mg$^{2+}$</td>
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<tr>
<td>Cl$^-$</td>
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<td>BDL</td>
<td>0.005</td>
<td>0.003</td>
<td>BDL</td>
<td></td>
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<tr>
<td>Total$^5$:</td>
<td>7.62</td>
<td>10.66</td>
<td>8.97</td>
<td>2.93</td>
<td>7.56</td>
<td>13.36</td>
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<td>SO$_2$ (g)</td>
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<td>0.93</td>
<td>0.05</td>
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<tr>
<td>NO$_x$ (g)</td>
<td>2.70</td>
<td>1.94</td>
<td>2.37</td>
<td>2.11</td>
<td>2.66</td>
<td>1.62</td>
</tr>
<tr>
<td>CO (g)</td>
<td>144</td>
<td>94</td>
<td>123</td>
<td>93</td>
<td>146</td>
<td>92</td>
</tr>
<tr>
<td>O$_3$ (g)</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>29</td>
<td>35</td>
<td>30</td>
</tr>
</tbody>
</table>

*Oxalate is also included in POM analysis
N/A: not analysed
BDL: below determination limit
$^5$Total particles excluding oxalate
$^5$g: gaseous compounds
Fig1.
Fig 2.
Fig 3.
Fig 4.
Fig 5.
Fig 6.

a) Regional background

b) Waterberg overpass

c) Western BIC overpass
Fig 7.
Fig 8.
Carbonaceous aerosol at a forested and an urban background sites
in Southern Finland

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b University of Helsinki, Department of Physics, PO. Box 64, 00014 University of Helsinki, Finland

1. Introduction

Organic carbon (OC) and elemental carbon (EC) constitute a major fraction of atmospheric particulate matter, but only a minor
fraction of organic matter (OM) has been identified and quantified
to individual compounds (Pataud et al., 2004; Oliveira et al.,
2007; Dutton et al., 2009). OC is of both primary and secondary origin,
while EC is exclusively a primary species. Although OC and EC
concentrations have been investigated for many different urban,
rural and remote sites (Malm et al., 2004; Viana et al., 2006, 2007;
Harrison and Yin, 2008; Schwarz et al., 2008; Sciare et al., 2008;
Yttri et al., 2007, 2009), the measurements, where gaseous
organic artefact is taken into account, are sparse in northern Europe
(Viidanoja et al., 2002; Saarikoski et al., 2005; Yttri et al., 2009).

In this study OC and EC concentrations in PM1 (particulate
matter < 1 μm in aerodynamic diameter) were measured for a year
at a rural forested site in southern Finland in Hyytiälä (SMEAR II:
Station for Measuring Forest Ecosystem-Atmosphere Relations) and
at an urban background site in Helsinki (SMEAR III). The distance
between the sites is 220 km. In Helsinki, as also detected at other
sites around the Europe (Szidat et al., 2006; Gelencsér et al., 2007),
secondary organic aerosol has been typically the dominant OC
source during summer whereas biomass combustion has been one
of the main sources during winter (Saarikoski et al., 2008). In
Hyytiälä local anthropogenic sources are rare. In summer biogenic
volatile organic carbon (BVOC) emissions have been assessed to
have a large influence to particulate OC concentrations (Tunved
et al., 2006, 2008).

There have not been previous long-term OC measurements in
Hyytiälä even though the aerosol chemical composition in Hyytiälä
has been studied in short campaigns several times e.g. by using an
aerosol mass spectrometer (AMS; Raaikainen et al., 2009) or by
filters/impactors (Saarikoski et al., 2005; Cavalli et al., 2006). Most
of the campaigns in Hyytiälä have been conducted in springtime
(e.g. Allan et al., 2006) when new particle formation typically

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(P. Aalto), Petri.Keronen@helsinki.fi (P. Keronen), Karri.Saarnio@fmi.fi (K. Saarnio),
Kimmo.Teilola@fmi.fi (K. Teinilä), Markku.Kulmala@helsinki.fi (M. Kulmala), Risto.
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occurs more frequently, but the results from the long-term OC measurements have not been reported previously.

The objective of this paper was to compare OC and EC concentrations between the urban background site and the forested site with different sources for carbonaceous particulate matter. Additionally, as this is the first study investigating OC and EC concentrations in Hyytiälä over all the seasons, the seasonal variation will elucidate the sources of carbonaceous particulate matter in Hyytiälä. The third objective was to estimate how OC and EC concentrations changed during the transport between the sites, when they were both affected by the same air masses.

2. Experimental

2.1. Measurement sites and sampling

The aerosol measurements were done in Hyytiälä (61°51′ N, 24°17′ E, 179 m ASL) and in Helsinki (60°12′ N, 24°57′ E, 30 m ASL) at SMEAR II and SMEAR III stations, respectively. The measurements were conducted from 14 February 2007 to 18 February 2008.

Hyytiälä site is located in a rather homogenous stand of Scots pine on a flat terrain at Hyytiälä Forestry Field Station of the University of Helsinki 220 km northwest from Helsinki (Kulmala et al., 2001). The site represents a background area of Southern Finland. Occasionally measurements are affected by the station site. The urban background site is located on a small hill 5 km northeast from the centre of Helsinki and 150 m east from a densely trafficked road (60 000 vehicles/day) (Jarvi et al., 2009). The area between the road and the station is forested. The population of the Helsinki Metropolitan Area is about 1 million. The main local anthropogenic particle emission sources affecting the surface fine particle concentrations are traffic and during winter season domestic wood combustion.

Ambient particulate matter samples were collected using two pre-cleaned (heated at 800 °C for 4–5 h) quartz fibre filters (Ø 47 mm Tissuquartz, Pall) placed in series in a filter cassette system (Pall Life Sciences) at both sites. The four upper stages of the Berner low pressure impactor (BLPI; Berner and Lürzer, 1980) were used to cut off supermicrometer particles (Saarikoski et al., 2008). The sampling duration was mainly 24 h on working days and 72 h over weekends. The measurement height was 5 m from the ground surface. The flow rate of the BLPI was 80 l min⁻¹ in Hyytiälä. In Helsinki the flow after the BLPI was divided into two lines, one for the quartz filter samples and the other for the polytetrafluoroethylene filter samples (not discussed in this paper) both lines having a flow of 40 l min⁻¹.

2.2. Organic and elemental carbon analysis

OC and EC were analyzed from the quartz fibre filters using a thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc.). The instrument uses a two-phase thermal method (EUSAAR-1 short; Cavalli et al., 2010) to separate OC and EC (Vidanoja et al., 2002). The optical correction was performed in order to separate pyrolysed organic carbon from elemental carbon. In the sampling a tandem filter method was used to estimate and to correct absorption of gaseous compounds on the filters. The particulate OC concentration was calculated by subtracting the concentration of the back-up filter from that of the front filter. The amount of gaseous OC (back-up filter) of total OC (front filter) was similar in Hyytiälä (3–39%, average 17%) and Helsinki (3–35%, average 16%). The ratio of back-up to front filter was typically lower for a higher sample load since the OC load on the back-up filter was rather constant and independent of OC load on the front filter. Additionally, the ratio of back-up to front filter OC increased slightly from winter to summer mostly because the average OC concentrations on backup filters were higher during summer than winter. The uncertainty of the analyzer was estimated to be 10% for OC and 20% for EC.

In Helsinki the OC and EC concentrations were also measured using a semicontinuous OC/EC analyzer (Sunset Laboratory Inc., Saarikoski et al., 2008) from 14 February 2007 to 1 November 2007 and from 11 December 2007 to 18 February 2008. The time-resolution for the semicontinuous analyzer was either two or three hours. Instrumental blank, which consisted of two minutes sampling and subsequent analysis was taken every night at 02:00 or 03:00 depending on the time-resolution. In addition to the thermally determined OC and EC, the instrument measured also black carbon (BC) optically with the laser (660 nm). The time-resolution for BC was one minute, but BC results were averaged over the OC sampling time. Strong correlations were observed for the filter and the semicontinuous measurements (Fig. 1). The Pearson correlation coefficient (r) was 0.95 for OC and 0.93 for EC with the mean ± SD filter-to-semicontinuous ratio of 0.96 ± 0.22 and 0.97 ± 0.20 for OC and EC, respectively.

2.3. Auxiliary data

Total mass concentration of PM1 was not measured directly but it was calculated from the results of Differential Mobility Particle Sizer (DMPS; a Hauke-type Differential Mobility Analyzers and TSI model 3025 and 3010 Condensation Particle Counters), which measured particle number size distribution. Particles, with diameter below 1 μm were summed up and converted to mass concentration using the particle density value of 1.48 g cm⁻³ at both sites (Saarnio et al., 2010). PM1 results were averaged to one hour.

Selected ions (sulphate, nitrate, chloride, oxalate, sodium, ammonium and potassium) were analysed for Hyytiälä samples during one month between March 26 and April 30, 2007 by an ionchromatography (Dionex ICS-3000). A piece of quartz filter (1 cm²) was extracted with 5 mL of Milli-Q water. AS17/CS12A analytical columns (4 mm i.d. × 250 mm length), 500/300 μl loops.
ASRS/CRS ultra II suppressors and KOH/MSA eluent were used for anions/cations.

Local meteorological data were recorded at both sites. The routes of arriving air masses during four events were obtained using the NOAA HYSPLIT backward trajectory model (Draxler and Rolph, 2003). 72-h backward air mass trajectories were calculated every third hour eight times per day. The arrival level was 100 m above the ground. NO and NOx concentrations were measured in Helsinki with a chemiluminescence analyser (TEI 42S, Thermo Fisher Scientific, Waltham, MA, USA). NO2 concentration was calculated as a difference between NOx and NO. This method converted other reactive nitrogen oxide species (e.g. PAN) into NO and thus the NOx signal should be considered as an upper estimate for NO + NO2 concentration. Detection limits for NO and NOx were 0.1 ppb.

3. Results and discussion

3.1. Annual concentrations and the seasonal variation of OC and EC

In 95% of the samples OC concentrations were higher in Helsinki than in Hyytiälä (Fig. 1). The range of OC concentrations was quite similar in Helsinki and in Hyytiälä, 0.4–6.1 and 0.1–5.6 μg m⁻³ respectively, but the annual average was much higher in Helsinki (1.8 μg m⁻³) than in Hyytiälä (1.1 μg m⁻³). There were no clear seasonal variations in the OC concentrations, although for both the sites the concentrations were somewhat higher in winter than in other seasons (Table 1). The high OC concentrations in winter could result from the large contribution of biomass burning (Saarikoski et al., 2008; Szidat et al., 2006), the poor mixing of emissions as well as a higher contribution of semivolatile OC in particulate phase (discussed later) during the cold season compared to the warm season. Besides biomass burning in winter there is a significant contribution of traffic to the OC concentrations in Helsinki throughout the year (Saarikoski et al., 2008). However, the effect of local traffic was not shown in the diurnal profile of OC in Helsinki (Fig. 2a), even though 15–27% of OC has been attributed to traffic on annual basis (Saarikoski et al., 2008).

Although there was no clear seasonal variation for particulate OC, the variation was seen in the back-up filter concentrations of OC (gaseous and semivolatile OC). The average OC concentration on back-up filters was almost threefold higher during summer (0.27 μg m⁻³) than during winter (0.10 μg m⁻³) in Hyytiälä. The corresponding summer (0.37 μg m⁻³) and winter (0.20 μg m⁻³) values were higher in Helsinki, but the difference was the same. The higher OC concentrations on back-up filters in summer suggested that higher temperatures favoured semi-volatile OC being in the vapor phase instead of particle phase. Although there was clear seasonal differences in the back-up filter OC concentrations the variation between the seasons was not large enough to induce a seasonal variation for the measured ambient OC concentrations.

Correlation between Hyytiälä and Helsinki sites was high for OC ($r = 0.9$, Fig. 3a). High correlations might be due to the same main sources affecting in Hyytiälä and Helsinki and/or similar meteorology at the sites or the original sources could be different but the air masses were well-mixed over the southern Finland. Also long range transport (LRT) has a significant contribution to OC concentrations in Finland. In the study of Saarikoski et al. (2008) they estimated that on annual basis 24% of OC was from the LRT in Helsinki. The OC correlation did not differ significantly between the

<table>
<thead>
<tr>
<th>Season</th>
<th>Site</th>
<th>OC (μg m⁻³)</th>
<th>EC (μg m⁻³)</th>
<th>Site/instrument</th>
<th>OC (μg m⁻³)</th>
<th>EC (μg m⁻³)</th>
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</thead>
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<tr>
<td>All</td>
<td>Hyytiälä</td>
<td>1.1 ± 0.9</td>
<td>0.18 ± 0.19</td>
<td>Helsinki</td>
<td>1.8 ± 1.1</td>
<td>0.77 ± 0.56</td>
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<td>(0.68 ± 0.63)</td>
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<td>0.64 ± 0.33</td>
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</tr>
<tr>
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<td>0.89 ± 0.75</td>
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<td>(1.5 ± 1.3)</td>
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</tr>
<tr>
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<td>0.77 ± 0.45</td>
</tr>
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<td>Semicont.</td>
<td>(2.0 ± 1.6)</td>
<td>(0.63 ± 0.57)</td>
</tr>
</tbody>
</table>

Fig. 2. Average diurnal variation of OC (a) and EC (b) during different seasons in Helsinki (14 February–1 November 2007 and 11 December 2007–18 February 2008). Only weekdays are included.

Table 1
Annual (14 February 2007–18 February 2008) and seasonal mean (spring: March–May, summer: June–August, autumn: September–November, winter: December–February) concentrations of OC and EC in PM$_\text{10}$ at the forested (Hyytiälä) and at the urban background (Helsinki) sites. The results of the semicontinuous OC/EC measurements in Helsinki (14 February–1 November 2007 and 11 December 2007–18 February 2008) are in parentheses.
seasons (Fig. 3a), however, the slope for the summer period was smaller than for the other seasons. It can be assumed that there is a considerable influence of biogenic OC on both Helsinki and Hyytiälä sites in summer but as there are no other major local sources in Hyytiälä, biogenic OC could have a larger effect on OC concentrations in Hyytiälä than in Helsinki in summertime.

As the OC concentrations were most of the time higher in Helsinki, there was an excess of $0.5–0.8\, \mu g\, m^{-3}$ of OC in Helsinki (Fig. 3a; intercept values) throughout the year. The intercept value differing from zero indicated that OC had local sources in Helsinki (mostly traffic) but also the transport of OC probably favoured the Helsinki site more than the Hyytiälä site. The intercept value was lowest in summer showing the potential large contribution of biogenic OC in Hyytiälä and Helsinki.

EC concentrations were always significantly higher in Helsinki ($0.1–4.2\, \mu g\, m^{-3}$, average $0.77\, \mu g\, m^{-3}$) than in Hyytiälä ($0.02–1.5\, \mu g\, m^{-3}$, average $0.18\, \mu g\, m^{-3}$; Fig. 1). Both sites had the lowest EC concentrations in summer (Table 1) that might derive from slightly lower traffic volume and less biomass burning in summer than in the other seasons, and by better dilution of particles because of higher mixing height. The highest season-mean EC concentrations were observed in winter and in autumn in Hyytiälä and Helsinki, respectively (Table 1).

EC concentrations had weaker correlation between the sites than those of OC (Fig. 3b). Weak correlation was expected as in Helsinki there was a significant local EC source (traffic) that was almost totally lacking in Hyytiälä. The contribution of traffic to EC concentrations in Helsinki can be seen in the average diurnal profile of EC (Fig. 2b). EC has a strong maximum during morning rush hour at 6–9 am and a minimum during the night. However, in winter the diurnal profile was different; the EC concentrations started to increase after the night minimum and stayed high with only a gradual decrease during the day. This might be caused by poor vertical mixing during winter and/or combination of traffic and other EC sources (e.g. biomass burning), which had different diurnal profiles than traffic. In order to verify this hypothesis the diurnal trend of NO$_x$ was calculated. NO$_x$ has been used as an indicator for traffic emission whereas the NO$_x$ emission from wood combustion has been stated to be low compared to traffic emissions (Glasius et al., 2006). NO$_x$ showed similar diurnal profile as EC except in winter (not shown). In winter the profile of NO$_x$ was similar to those in other seasons suggesting that there was another EC source that affected the diurnal trend of EC in winter.

**Fig. 3.** Scatter plots of the forested site (Hyytiälä) vs. urban background site (Helsinki) for OC (a) and EC (b) during different seasons. $r$ – Pearson correlation coefficient.
The contribution of LRT to EC in Helsinki was estimated from the Hyytiälä EC data assuming that in Hyytiälä EC was mainly from LRT and at least the same amount of LRT EC was observed in Helsinki. The contribution of LRT to EC concentrations was 16\%–31\% of the total EC in Helsinki depending on the season.

OC had a high correlation with the calculated PM$_1$ data at both sites (Hyytiälä: $r = 0.94$ and Helsinki: 0.94) regardless of the seasons, whereas EC and PM$_1$ were less correlated ($r = 0.79$ in Hyytiälä and $r = 0.69$ in Helsinki). The contribution of OC to PM$_1$ mass was significant, being higher in Hyytiälä (annual average 23\%) than in Helsinki (18\%), whereas the contribution of EC to PM$_1$ was higher at more traffic related Helsinki-site (9\%) than at forested Hyytiälä-site (4\%). It was quite surprising that the OC to PM$_1$ ratio had only a weak seasonal trend in Hyytiälä (Fig. 4). The ratio was slightly higher in summer than in winter; however, May was an exception. In May the OC to PM$_1$ ratio was clearly lower (18\%) than in other months of the year. In May the air masses came to Hyytiälä mostly from the west to north sector from the clean marine areas. Therefore there could have been a lot of sea salt in particles even though it doesn’t usually contribute to PM$_1$ but rather to coarse particle size. Excluding May, quite even OC to PM$_1$ ratio could result from the fact that there are different main sources in different seasons; the biogenic emissions affect in summer and the biomass burning emissions affect in winter. The LRT has no seasonal favour in Finland, although the chemical composition and hence the OC to PM$_1$ ratio may vary depending on the origin. For EC to PM$_1$ ratio there was no seasonal trend in Helsinki but in Hyytiälä there was a distinct trend with much lower ratios in summer than in the other seasons (Fig. 4) resulting from the much lower EC concentrations in Hyytiälä in summertime (Fig. 1, Table 1).

Although extensive chemical composition was not studied throughout the campaign, the one month study in spring 2007 (March 26–April 30) in Hyytiälä showed that the contribution of inorganic ions was slightly lower (37\%) than the contribution of particulate organic matter (51\%, POM = OC × 1.6, Turpin and Lim, 2001). This indicated that aerosols in Hyytiälä contained also other than carbonaceous components. The sum of analyzed components was on the average 85\% of the calculated PM$_1$ mass during the one month study in 2007.

3.2. Comparison of OC and EC to other studies

Only a few studies have been addressed to over one year measurements of OC and EC in Scandinavia (Ricard et al., 2002; Viidanoja et al., 2002; Yttri et al., 2007; Saarikoski et al., 2008) and three of them were accounted for the positive sampling artefact. Two of the measurements were conducted in Helsinki, one at SMEAR III (Saarikoski et al., 2008) and the other at a more traffic-influenced site (Viidanoja et al., 2002) both giving higher OC (3.0 and 2.5 mg m$^{-3}$, respectively) and EC (0.89 and 1.2 mg m$^{-3}$, respectively) concentrations than in this study. The differences could be caused by normal year-to-year variations (e.g. biomass burning episodes in 2006), by different locations of the experimental sites (urban vs. urban background) and different cut-off sizes (PM$_1$ vs. PM$_{2.5}$, PM$_{2.5}$ in Viidanoja et al., 2002).

Before this study OC and EC have been measured in Hyytiälä only for short periods. During one month measurement campaign in May 2004, OC concentrations (PM$_1$) were quite similar (0.4–5.1 mg m$^{-3}$) as during this campaign, whereas EC range

Fig. 5. Scatter plots of OC vs. EC during different seasons at the forested site (Hyytiälä) and urban background site (Helsinki).

Fig. 6. OC to EC ratio and the daily mean temperature in Hyytiälä (a) and Helsinki (b) between 14 February 2007 and 18 February 2008. Sampling time was mainly 24 h (weekdays) or 72 h (weekends).
(0.08–0.5 \mu g m^{-3}) was narrower in May 2004 (Saarikoski et al., 2005). Extensive over a year lasting measurements have been conducted at high latitudes areas in Europe, however these measurements have different cut-off size (PM10) and correction for the positive artefact has not been performed (Yttri et al., 2007).

3.3. Correlation between OC and EC and OC/EC ratio

The origin of the carbonaceous particles can be roughly estimated on the basis of the ratio between OC and EC concentrations (Turpin and Huntzicker, 1995). If the major fractions of OC and EC are emitted by a dominant primary source (e.g., vehicle emissions), the correlation between OC and EC concentrations should be high because the relative rates of OC and EC emission would be proportional to each other. However, if there were more than one main primary source (e.g. biomass burning and traffic), the OC to EC ratio is not constant and the sources of OC are almost impossible to estimate (Szidat et al., 2006).

OC concentrations had rather weak correlation with EC concentrations at the urban background Helsinki-site ($r = 0.59$) but clearly higher correlation was detected at the forested Hyytiälä –site ($r = 0.83$; Fig. 5). The correlations were quite similar during non-summer seasons ($r = 0.92–0.94$) and much higher than during summer ($r = 0.74$) in Hyytiälä. The high correlation in Hyytiälä was likely due to the high influence of LRT and biomass burning to both OC and EC concentrations whereas the lower correlation in summer indicated that also other sources existed with different OC to EC ratios (e.g. biogenic OC with no EC emissions). The weak correlation in Helsinki suggested that OC and EC had several sources with different OC to EC ratios that varied in time.

![Fig. 7. Examples of the air mass trajectories calculated by a HYSPLIT backward trajectory model for the samples with high OC and EC concentrations (a–c) and with low OC and EC concentrations (d).](image-url)
On annual basis the OC to EC ratio was almost three times higher in Hyytiälä (7.4) than in Helsinki (2.5). In Hyytiälä the seasonal average ratio varied from 4.8 to 13 being over twofold higher in summer than in the other seasons. The OC to EC ratio began to increase in April, was highest in June and decreased back to lower level in September (Fig. 6a). The same pattern as for the OC to EC ratio has also been seen in the six month study of the VOC emission rates of Scotch pines in Hyytiälä (Tarvainen et al., 2005). VOC emissions rates were very high in spring, somewhat lower in early summer and high again in late summer with gradual decrease in autumn. These observations together with the summer maximum in the growth rate of nucleation mode particles (Kulmala et al., 2004) and the indication that newly formed particles have contained lots of organic material (O'Dowd et al., 2002) suggest that biogenic OC had a high contribution to particulate OC in late-spring and summer in Hyytiälä.

In contrast to Hyytiälä, the OC to EC ratio in Helsinki did not have clear seasonal trend (Fig. 6b). The season-average ratios were similar in winter, spring, and summer (2.6–2.8) whereas in autumn it was slightly lower (2.0). The reason for the lack of seasonal variation in Helsinki could be due to the fact that the contribution of biogenic OC to total OC was lower in Helsinki than in Hyytiälä whereas that of traffic was significant in Helsinki throughout the year.

3.4. Case studies

According to the backward trajectories the highest OC concentrations in Hyytiälä originated mainly from the area of Eastern Europe. These high concentrations occurred together with the high EC concentrations, which was not unexpected as OC and EC had a high correlation at least during nonsummer months in Hyytiälä. In addition to Hyytiälä high OC and EC concentrations events were also detected in Helsinki and the origin was obviously mainly the same as in Hyytiälä. The transport of air masses was studied for three samples which had high OC concentrations in Hyytiälä (above three times the annual mean OC). Examples of high OC concentration events are presented in Fig. 7a–c. Samples were collected in January 8–9, 2008 (Fig. 7a), January 15–16, 2008 (Fig. 7b) and September 25–26, 2007 (Fig. 7c) and they were chosen so that the air masses passed the Metropolitan area of Helsinki on the way to Hyytiälä. For all the samples air masses originated from the narrow sector in the Eastern Europe. The OC concentrations ranged from 3.3 to 3.9 and EC concentrations from 0.30 to 0.74 μg m⁻³ in Hyytiälä whereas the OC and EC concentrations were higher in Helsinki with the difference between the sites in the range of 0.51–0.75 μg m⁻³ and 0.60–1.04 μg m⁻³ for OC and EC, respectively. The ratio of this excess OC and EC in Helsinki was 0.73–1.1, which was close to the value obtained by Saarikoski et al. (2008) for traffic particles (0.71).

The difference in the concentrations between the sites was also studied for air masses flows from the Arctic areas. During the Arctic flows the air masses came usually from the higher latitude to the lower ones reaching Hyytiälä before Helsinki. As the air masses were not passing over significant sources during the transport to the sites, OC and EC concentrations were very low. An example of the clean air mass sample (December 12–13, 2007) is presented in Fig. 7d. The OC and EC concentrations were 0.55 and 0.17 μg m⁻³ in Hyytiälä, respectively, whereas the corresponding OC and EC concentrations were only 0.11 and 0.26 μg m⁻³ higher in Helsinki, respectively, than in Hyytiälä. The differences in concentrations between Helsinki and Hyytiälä were clearly lower in this one event than obtained from the comparison of all OC and EC data (intercepts in Fig. 3).

4. Summary and conclusions

Organic and elemental carbon concentrations were measured from the submicrometer particles for one year (14 February 2007–18 February 2008) at an urban background station in Helsinki (SMEAR III) and at a rural forested station in Hyytiälä (SMEAR II), Finland. The sites are 220 km apart from each other. As the uncertainties in the OC and EC measurements are well known, two main ways to minimize the uncertainties in the sampling and analysis were taken into account. Tandem filter measurement system was used to estimate the positive artefact of OC and the separation of charred OC to EC was done by the optical correction. The EC and with a few exceptions the OC concentrations were always higher in Helsinki than in Hyytiälä. The annual mean OC concentration in Helsinki was 1.8 μg m⁻³ and in Hyytiälä 1.1 μg m⁻³ being over 60% higher in Helsinki than in Hyytiälä. The mean EC concentration was very low in Hyytiälä (annual mean 0.18 μg m⁻³) being 23% of the annual mean EC concentration in Helsinki (0.77 μg m⁻³). The contribution of OC to PM₁ was significant and much higher in Hyytiälä (23%) than in Helsinki (18%) whereas the contribution of EC to PM₁ was over twofold higher in Helsinki (9%) than in Hyytiälä (4%).

High correlation for OC between the sites pointed out that the main OC sources, the transport from the same source areas and/or the meteorology were common for both sites. OC correlation did not have significant seasonal variations; however, in summer OC concentrations were more equal at the sites reflecting biogenic contribution to OC at both sites. Also the OC to PM₁ ratio did not have clear seasonal variation, which could result from the different main sources affecting in different seasons at both sites. Compared to OC EC had weaker correlation between the sites as the local traffic in Helsinki had clear contribution to EC concentrations. In winter there were also other main EC sources and these sources were impossible to separate with this data set.

The annual mean OC to EC ratio was threefold higher in Hyytiälä than in Helsinki. The OC and EC concentrations did not have significant seasonal variation, but in Hyytiälä the OC to EC ratio increased from winter to summer. The ratio was over twofold higher in summer compared to the other seasons’ mean value suggesting that biogenic emissions had considerable influence to OC in summer in Hyytiälä. In Helsinki the ratio did not have a seasonal trend.

Acknowledgements

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References


Seasonal and diurnal changes in inorganic ions, carbonaceous matter and mass in ambient aerosol particles in an urban, background area

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Concentration and composition of the fine particulate matter (PM) was measured using various online methods for 13 months in an urban, background area in Helsinki, Finland. Seasonal differences were found for ions and carbonaceous compounds. Biomass burning was found to increase inorganic ion and elemental carbon (EC) concentrations in winter, whereas organic carbon (OC) contribution was highest during summer due to secondary aerosol formation. Diurnal cycles, with maxima between 06:00 and 09:00, were recorded for EC and nitrate due to traffic emissions. In addition, the concentrations measured with the online and offline PM sampling devices were compared using regression analysis. In general, a good agreement ($r^2 = 0.60–0.95$) was found. During the year-long measurements, on average 65% of PM$_{2.5}$ was identified by submicron chemical analyses (ions, OC, EC). As compared with filter measurements, the high resolution measurements provided important data on short pollution plumes and diurnal changes.

Introduction

Atmospheric aerosols are produced by several anthropogenic and natural sources. The major constituents of atmospheric aerosol particles are inorganic ions (sulfate, nitrate, and ammonium) and carbonaceous compounds (e.g. Solomon et al. 2008 and references therein, Bond et al. 2013). Aerosol composition is depending on the source, but it is also affected by the physico-chemical processes like aging in the atmosphere and aerosol removal processes (Jimenez et al. 2009). In order to estimate the effects of multi-phase and multi-component aerosol particles on the climate change, human health and ecosystem, concentrations and chemical compositions of aerosol particles should be known (Pope and Dockery 2006, IPCC 2007, Brook et al. 2010).

Processes in the atmosphere are rapid and traditional PM-filter collections with long collection times do not provide an adequate picture of the constantly-evolving situation. The new online analyzing methods, such as particle-into-liquid sampler (PILS; Orsini et al. 2003), the...
aerosol mass spectrometer (AMS; Jayne et al. 2000, Allan 2003) or the semi-continuous OC/EC aerosol carbon analyzer (RT-OCEC; Arhami et al. 2006) have provided a possibility to study aerosol chemistry and size distribution with high time resolutions. High-time-resolution instruments have also facilitated studies of variety of fast-changing properties like gas/particle partitioning, water solubility and oxygenation state, as well as diurnal changes and sources of ambient aerosol particles (Kondo et al. 2007, Henning et al. 2008, Dunlea et al. 2009). The errors and uncertainties in filter collections were extensively studied during the last decades (e.g. Hering and Cass 1999, Pathak and Chan 2005, Viana et al. 2006a). Different kinds of sampling artifacts have to be taken into account in online measurements, and due to the short integration times, concentrations to be determined in these online samples are very low and often close to determination limits of the analyzing methods (Parshintsev et al. 2009, Timonen et al. 2010).

In this study, the chemical composition of ambient fine particulate matter (PM$_{1}$) was measured at an urban background station for a year in order to determine PM sources and describe seasonal and diurnal changes of inorganic ions, carbonaceous matter and PM mass (PM$_{2.5}$) in ambient aerosol particles. In addition, results of the online methods for PM mass and individual compounds were compared with concentrations measured from the traditional filter samples in order to increase the understanding of collection artifacts in both measurements methods.

**Material and methods**

**Measurement site**

The SMEAR III station (60°12´N, 24°58´E, 26 m a.s.l.) is situated in an urban, background area approximately 5 km from the Helsinki city center. The SMEAR III station is surrounded by the Kumpula University Campus, small forest area and a road. The aerosol, trace gas and flux measurements have been conducted at the SMEAR III station since it was established in 2004 (Järvi et al. 2009). The main local sources of fine particles at SMEAR III are traffic, wood combustion (residential heating in winter) and secondary aerosol formation (Saarikoski et al. 2008, Timonen et al. 2008, Järvi et al. 2009, Saarnio et al. 2010, Saarnio et al. 2012). In addition, long-range-transported pollution or biomass-burning emissions from wildfires occasionally elevate PM concentrations (Karppinen et al. 2004, Niemi et al. 2009). Local meteorological data were obtained from the Finnish Meteorological Institute weather station (Vaisala, Milos 500) situated next to the SMEAR III station.

**Online measurements**

The Particle-Into-Liquid Sampler (PILS; Table 1) was developed for rapid automated online aerosol collection (Webet et al. 2001, Orsini et al. 2003). PILS combined with two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA) was used to collect aerosol samples directly to the liquid phase and to analyze concentrations of major ions online. A Virtual Impactor (VI; Loo and Cork 1988) with a cut-off size of 1.3 µm was used to remove coarse particles before PILS measurements. Gaseous compounds (ammonia and acidic gases) were removed before PILS measurements with three annular denuders (one coated with 3% phosphoric acid and two with 1% potassium hydroxide). The denuders were changed every second week to ensure that all gaseous compounds were effectively removed. The operation principle of PILS is described in detail in Orsini et al. (2003). Briefly, aerosol and water steam is simultaneously fed into PILS, where particles grow as they move across a conical shape cavity. At the other end of the cavity the grown particles impact a quartz-glass surface. The surface is rinsed with water (Milli-Q, Millipore Gradient A10) containing a known concentration of lithium fluoride (LiF) as an internal standard. Liquid from PILS was directly fed into the loops of two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA). The 1000 µl loops were used to collect a representative samples for subsequent IC analyzes. With the PILS-IC system the concentrations of Cl$^{-}$, NO$_{3}^{-}$, SO$_{4}^{2-}$, Na$^{+}$, NH$_{4}^{+}$, K$^{+}$, oxalate and methane sulphonate (MSA) could be determined with a 15-min time resolution. The quantification limit for the ions was 2.5 ng ml$^{-1}$,
which equals the air concentration of 0.05 µg m⁻³. The uncertainty of the ion concentrations measured with the PILS-IC system was estimated to be 15% for all analyzed ions.

A semi-continuous OC/EC carbon aerosol analyzer (RT-OCEC, Sunset Laboratory Inc., Oregon, US, Table 1) was used to measure the concentrations of elemental and organic carbon with 3-h time resolution. The sample flow was 9.2 l min⁻¹ in order to collect a representative sample for the subsequent thermal analysis. A cyclone was used to cut off particles with aerodynamic diameter > 1 µm and a parallel plate carbon denuder (Sunset Laboratory Inc., OR, US) was used in-line before the instrument to remove organic gases. The method is described in detail by Turpin et al. (1990) and Birch and Cary (1996). Briefly, during one measurement cycle the instrument collects a sample for 164 minutes. After the sampling period, the deposited particles are heated in a quartz oven where the elemental and organic carbon concentrations are individually quantified. The vaporized carbon compounds formed in the oven are purged to MnO₂ catalyst where they are further oxidized to carbon dioxide and quantified with a non-dispersive infrared (NDIR) detector. In addition the RT-OCEC measures optical EC with one minute time resolution using the laser light transmission values measured before and after the analysis cycle. A predetermined calibration factor, based on numerous ambient measurements, is used to convert laser attenuation to EC mass on the filter. Due to the small average concentrations in Helsinki, the measurements of total carbon (TC; Thermal EC + OC) and optical EC were considered more reliable and therefore the “Optical OC” concentrations (Optical OC = TC – optical EC) were used in the comparison. The uncertainty of the measured OC and EC concentrations was estimated to be 20%.

A tapered Element Oscillating Microbalance (TEOM® 1400a; Rupprecht and Patashnick (1991); see Table 1) equipped with a Filter Dynamics Measurement System (FDMS) was used to continuously measure the PM₁₅₅ mass concentration. In FDMS TEOM, the flow is first directed through the Sample Equilibration System (SES) dryer to TEOM and nonvolatile mass is measured. In the next stage, the flow goes through a filter, where PM is removed, and mass volatilized from the collection filter is measured. The mass evaporated from the filter is added to nonvolatile mass to achieve a real PM₁₅₅ concentration. A Virtual Impactor (VI, Loo and Cork 1988) was used before the TEOM to cut off large particles (aerodynamic diameter > 2.5 µm). The uncertainty of the PM concentrations measured with TEOM was estimated to be 10%. All TEOM data shown in this article are FDMS TEOM PM₁₅₅ data, i.e., they are corrected for evaporative losses.

### Table 1. Used instruments, measurement periods, cutoff sizes, and mean ± SD and maximum concentrations of each chemical species (OC, EC, BC, major ions, total PM mass) measured with the online instruments during the intensive measurement campaign. Detailed description of the measurement devices and methods are given in the reference articles.

<table>
<thead>
<tr>
<th>Component/instrument</th>
<th>Cutoff size (µm)</th>
<th>Measurement period</th>
<th>Mean ± SD (µg m⁻³)</th>
<th>Maximum (µg m⁻³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC, EC/RT-OCEC</td>
<td>1</td>
<td>17 Jun. 2006–28 Feb. 2007</td>
<td>OC: 2.0 ± 2.5</td>
<td>41</td>
<td>Turpin et al. (1990), Bae et al. (2007), Saarikoski et al. (2008)</td>
</tr>
<tr>
<td>Major ions/PILS-IC</td>
<td>1</td>
<td>9 Feb. 2006–28 Feb. 2007</td>
<td>NH₄⁺: 0.85 ± 0.81</td>
<td>NH₄⁺: 10</td>
<td>Weber et al. (2001), Orsini et al. (2003), Sorooshian et al. (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄²⁻: 0.77 ± 1.0</td>
<td>SO₄²⁻: 27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>K⁺: 0.10 ± 0.07</td>
<td>K⁺: 2.7</td>
<td>Hansen et al. (1984), Weingartner et al. (2003)</td>
</tr>
<tr>
<td>BC/aethalometer</td>
<td>2.5</td>
<td>3 Jul.–27 Dec. 2006</td>
<td>1.0 ± 0.8</td>
<td>5.7</td>
<td></td>
</tr>
</tbody>
</table>

*Due to technical problems, there was a break in PILS-IC data from 28 November 2006 to 26 January 2007.*
A single-wavelength aethalometer (model AE-42, Magee Scientific; see Table 1) using the wavelength of 880 nm was used to measure the black-carbon concentrations. Time resolution of the measurements was 5 minutes and the flow rate 5 l min⁻¹. A cyclone was used to remove particles larger than 2.5 µm in aerodynamic diameter. Black-carbon equivalent mass concentrations were calculated from the absorption measurements of the aethalometer data using a mass absorption efficiency of 16.6 m² g⁻¹. The uncertainty of the BC concentrations measured with aethalometer was estimated to be 10%.

#### PM₁ filter measurements

PM₁ filter samples were collected using a filter cassette system. A Berner low pressure impactor (BLPI stages 8–11; Berner and Lürzer, 1980) was used in-line to remove supermicron particles. The flow rate was adjusted to 80 l min⁻¹. Two pre-fired (12 h, 500 °C) quartz-fiber filters (Whatman Q-MA 47 mm) were placed in series to a filter cassette. A sample was collected to the front filter and the backup filter was used to evaluate the sampling artifacts. The collection times were 24 and 72 hours during weekdays and weekends, respectively. During episodes of elevated particle concentrations, a shorter collection time (12 hours) was used in order to avoid overloading of the filters. Altogether 297 samples were collected during the year-long campaign. In the PM₁ filter collections, denuders were not used in-line.

A 1-cm² piece was cut from each sample for each analyzing method (Table 2). The organic and elemental carbon (OC and EC) concentrations were determined with the thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon, US) using the thermal-optical transmittance method (TOT). The method is described in detail by Saarikoski et al. (2007). Water-soluble organic carbon (WSOC) was analyzed using Shimadzu’s total-organic carbon analyzer TOC-V CPN (Timonen et al. 2008). Main inorganic ions (Cl⁻, NO₃⁻, SO₄²⁻, oxalate, NH₄⁺, K⁺) were analyzed using Dionex DX-500 or ICS-3000 ion chromatography systems (Dionex, Sunnyvale, USA; Teinilä et al. 2004, Aurela et al. 2011). Concentrations measured for the back-up filters were subtracted from those of the front filters for OC and WSOC by assuming that they were only adsorbed gas-phase components of the sample air (positive artifacts) and the adsorption was equal in the front and back-up filters. For WSOC and OC, the backup-to-front-filter ratios were (mean ± SD) 5.6% ± 6.4% and 10% ± 6.6%, respectively. The backup-to-front-filter ratios for ions were 1.3% ± 1.8% (ammonium), 3.9% ± 3.7% (potassium), 4.4% ± 7.1% (sulfate), 4.3% ± 4.8% (chloride), 4.4% ± 4.8% (nitrate), and 4.5% ± 4.8% (sulfate).

<table>
<thead>
<tr>
<th>Component/instrument</th>
<th>Mean ± SD (µg m⁻³)</th>
<th>Maximum (µg m⁻³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC, EC (Sunset OCEC aerosol carbon analyzer)</td>
<td>OC: 2.5 ± 2.7</td>
<td>OC: 16</td>
<td>Turpin et al. (1990), Birch and Cary (1996), Viidanoja et al. (2002)</td>
</tr>
<tr>
<td>WSOC (Shimadzu TOC-V CPN)</td>
<td>WSOC: 1.5 ± 1.7</td>
<td>10.65</td>
<td>Viana et al. (2006b), Timonen et al. (2008)</td>
</tr>
<tr>
<td>Major Ions (Dionex ICS-2000)</td>
<td>NH₄⁺: 0.712 ± 0.632</td>
<td>NH₄⁺: 3.96</td>
<td>Teinilä et al. (2004), Saarikoski et al. (2008), Timonen et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>NO₃⁻: 0.50 ± 0.58</td>
<td>NO₃⁻: 3.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO₄²⁻: 1.88 ± 1.41</td>
<td>SO₄²⁻: 6.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K⁺: 0.087 ± 0.16</td>
<td>K⁺: 2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ox: 0.09 ± 0.09</td>
<td>Ox: 0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSA: 0.03 ± 0.05</td>
<td>MSA: 0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl⁻: 0.01 ± 0.05</td>
<td>Cl⁻: 0.5</td>
<td></td>
</tr>
<tr>
<td>Total mass/calculated = 1.6OC + EC + ions</td>
<td>8.17 ± 6.76</td>
<td>38.53</td>
<td></td>
</tr>
</tbody>
</table>
± 5.0% (oxalate) and 42% ± 33% (nitrate). For ions the backup-to-front-filter ratios were used only to evaluate the magnitude of measurement artifacts in filter collections. For filter measurements, the mass was calculated as a sum of all ions, EC and particulate organic matter (POM), which was calculated from the OC concentration (POM = 1.6 × OC; Turpin and Lim 2001, Saarnio et al. 2010).

Size-segregated samples were collected with a Micro-Orifice Uniform Deposit Impactor (MOUDI, Marple et al. 1991, Timonen et al. 2008). Altogether 45 collections were made, approximately one in each week during the campaign. The aerodynamic cut-off diameters of the impactor stages were 0.056, 0.100, 0.18, 0.32, 0.56, 1.00, 1.8, 3.2 and 5.6 µm. The collection time was typically 72 hours. Gravimetric mass, WSOC and ions were analyzed from the MOUDI samples (Timonen et al. 2008).

The ion, carbonaceous compound and PM concentrations of semi-continuous/continuous measurements (RT-OCEC, PILS-IC, TEOM and aethalometer) were compared using regression analysis with those obtained from the PM1 filter measurements.

Results and discussion

Comparison between online instruments and filter sampling

Inorganic ions

For main ions, sulfate, nitrate and ammonium the concentrations were well above the quantification limits and the PILS-IC ion concentrations agreed well with those from the filter samplings ($r^2 = 0.80–0.87$; Table 3). Sulfate, ammonium and nitrate concentrations were 16%, 14% and 37% lower, respectively, than those measured with PILS. We noted that substantial concentrations of nitrate (front/backup filter ratio 42%) was found from the backup filter in the filter collections.

Ion concentrations measured with PILS-IC were compared with the filter sampling results only in a few other studies. Typically sulfate and ammonium concentrations measured from the filter correlate well with the PILS-IC concentrations, but for nitrate the agreement is poor (Orsini et al. 2003, Kuokka et al. 2007). Ma et al. (2004) compared the ion concentrations measured with a micro-orifice impactor and PILS-IC, and found that the correlation was relatively high, but also the concentrations measured with PILS-IC were lower by 10% ± 5%, 11% ± 8%, and 18% ± 5% for sulfate, ammonium, and nitrate, respectively. Laboratory tests have shown that the collection efficiency of PILS is good (Orsini et al. 2003). However, it has been shown that the collection efficiency depends on volatility of the compounds, since the semi volatile species evaporate in PILS as a result of latent heat of condensation and convective heating of the sampled air (Sorooshian et al. 2006). Sorooshian et al. (2006) found that the average collection efficiency for all species from a variety of aerosols exceeded 96% except for ammonium (88%) when compared with simultaneous measurements carried out with a differential

<table>
<thead>
<tr>
<th>Component</th>
<th>Slope</th>
<th>Intercept</th>
<th>$r^2$</th>
<th>Sample number</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$ (PM$_1$ vs. PILS-IC)</td>
<td>0.84</td>
<td>0.45</td>
<td>0.87</td>
<td>214</td>
</tr>
<tr>
<td>NO$_3^-$ (PM$_1$ vs. PILS-IC)</td>
<td>0.63</td>
<td>0.02</td>
<td>0.80</td>
<td>187</td>
</tr>
<tr>
<td>NH$_4^+$ (PM$_1$ vs. PILS-IC)</td>
<td>0.86</td>
<td>0.05</td>
<td>0.82</td>
<td>212</td>
</tr>
<tr>
<td>OC (PM$_1$ vs. RT-OCEC)</td>
<td>0.77</td>
<td>0.23</td>
<td>0.95</td>
<td>165</td>
</tr>
<tr>
<td>EC (PM$_1$ vs. RT-OCEC)</td>
<td>0.57</td>
<td>0.27</td>
<td>0.60</td>
<td>167</td>
</tr>
<tr>
<td>EC vs. BC (RT-OCEC vs. aethalometer)*</td>
<td>1.31</td>
<td>0.06</td>
<td>0.92</td>
<td>1127</td>
</tr>
</tbody>
</table>

* the cutoffs for EC and BC are PM$_1$ and PM$_{2.5}$, respectively. The regression parameters were calculated using 3-h averages.
mobility analyzer (DMA). When compared with other online measurements (e.g., DMA, AMS), PILS-IC has been shown to measure nitrate acceptably (Sorooshian et al. 2006, Bae et al. 2007, Timonen et al. 2010).

It seems likely that evaporation of nitrate compounds from filter samples was the main cause of lower nitrate concentrations measured from filter samples. In addition to volatilization, other differences in the two methods, PILS-IC and PM$_1$ filters, are likely causing part of the variation seen in the nitrate concentrations in this study. In filter methods, particles remain in the filter material long time after collection. Evaporation of semi-volatile compounds from the filter and adsorption of gases onto the filter material during the collection can have a large effect on the ion concentrations measured from the filter (Hering and Cass, 1999, Viana et al. 2006a). In PILS-IC, the sample is mixed with supersaturated water vapor and subsequently impacted onto a quartz plate within seconds (Orsini et al. 2003). In addition, it must be noted that at low concentrations (0.05–0.1 µg m$^{-3}$) near the compounds’ quantification limits, the ion concentrations measured with IC are also highly uncertain.

Fine PM concentrations

The TEOM PM$_{2.5}$ mass concentrations were compared with the PM$_1$ mass calculated for 24-hour filter measurements that were carried out in parallel at the SMEAR III. The mean ± SD mass concentration for PM$_1$ was 7.8 ± 6.5 µg m$^{-3}$. The ratio between PM$_1$ (filters) and PM$_{2.5}$ (TEOM) was 0.62 ± 0.51. The difference can be due to the different cutoff sizes (PM$_1$ and PM$_{2.5}$) and possibly also due the evaporation of semi-volatile compounds from the PM$_1$ filter during collection. PM$_{2.5}$ measurements with the TEOM equipped with both the SES and the FDMS systems have been shown to compare very well to other real-time automatic analyzers counting semi-volatile matter (Grover et al. 2006, Wilson et al. 2006). For this study, the mass between PM$_1$ and PM$_{2.5}$ can be evaluated also from the MOUDI results. The mass ratios between PM$_1$/PM$_{1.8}$ and PM$_1$/PM$_{3.2}$ in MOUDI were (mean ± SD) 0.83 ± 0.10 and 0.68 ± 0.15, indicating that on average 17% of PM$_{1.8}$ mass was between PM$_1$ and PM$_{1.8}$ and 32% of PM$_{3.2}$ mass between PM$_1$ and PM$_{3.2}$. Assuming that the mass is equally distributed between PM$_{1.8}$ and PM$_{3.2}$, the mass between PM$_1$ and PM$_{2.5}$ would be 25% of the PM$_{2.5}$ mass that is close to the difference found between PM$_1$ and PM$_{2.5}$ (30%). Some uncertainty in this approach is due to the fact that the collection efficiency curves in the impactor are not step functions, but this is difficult to quantify.

Carbonaceous matter

For OC the semi-continuous and the filter sampling methods gave quite similar concentrations. The OC concentrations measured with the RT-OCEC were on average 10% greater than those of the filters for OC (Table 3) but the correlation between the RT-OCEC OC and the filter sampling OC was very good ($r^2 = 0.95$). However, larger differences between the RT-OCEC BC and BC analyzed from the PM$_1$ filters were found (slope = 0.57, $r^2 = 0.60$). This is likely affected by higher uncertainty associated with small BC concentrations, both in filters and online sampling. Similar behavior for OC was observed also by Sciare et al. (2010). In both methods (RT-OCEC and PM$_1$ filters collections), particles were collected on filters, but in RT-OCEC gas-phase components were removed before the filter with a parallel plate carbon denuder. In the filter sampling, absorption of gas-phase compounds on filters was taken into account by subtracting the OC concentration of the backup filter from the result of the front filter. In addition to the gaseous compounds, part of the semi-volatile organic components that evaporated from the front filter was subsequently absorbed on the backup filter and considered the gas-phase components and subtracted from the particulate-phase OC. That can underestimate the amount of particulate-phase OC determined from the filter samples. In the RT-OCEC, semi-volatile organic components were included in OC since the two filters were used back to back and analyzed simultaneously. One major difference between online and filter measurements was the storage time. The filter samples were stored in a freezer from days to weeks prior to their analy-
sis, whereas the online samples were analyzed directly after the collection. Also, the efficiency of the denuder in front of the RT-OCEC can partly explain the larger concentrations of OC measured with the RT-OCEC than using the filter sampling. A mean value of the measured denuder break-through and the blank values (0.80 µg m⁻³) were subtracted from the RT-OC. However, denuder efficiency may change with time or it can depend on the concentrations of gaseous components. The more detailed analyzes of the sources of OC during this campaign has been published by Saarikoski et al. (2008).

Optically measured EC was also compared with black carbon (BC) measured with the aethalometer. On average the concentration of EC (RT-OCEC) was only 78% of that of BC (aethalometer). This difference is partly due to the different cut-off diameters of the RT-OCEC (1 µm) and aethalometer (2.5 µm), resulting in a slightly different size fraction and possibly in a different chemical composition of particles measured. Also the used wavelengths were different: 660 nm for the RT-OCEC and 880 nm for the aethalometer. The mass absorption efficiency used to calculation the BC mass was 16.6 m² g⁻¹ for the aethalometer, whereas the calibration of RT-EC had been performed by the manufacturer. Despite all the differences in measurements, a very good correlation ($r^2 = 0.92$) was found between the RT-OCEC BC concentration and BC measured with the aethalometer, whereas the calibration of RT-EC had been performed by the manufacturer. The BC results from the semi-continuous ECOC carbon analyzer have previously been shown to agree well with the BC results of other online instruments (e.g. Kanaya et al. 2008, Solomon et al. 2008 and references therein).

**Seasonal and diurnal variations in PM concentrations and composition**

During this campaign, the PM$_{2.5}$ mass concentration was 13.8 ± 11.4 µg m⁻³ (mean ± SD; see Table 1) and the ratio between PM$_1$ (PM$_1$ filter samples) and PM$_{2.5}$ (TEOM PM$_{2.5}$) was 0.62 ± 0.51. During this measurement period, the ratio between non-volatile mass and PM$_{2.5}$ was 0.82 ± 0.52, suggesting that on average 18% of mass was volatile at the temperature of TEOM SES (30 °C). In Finland, for most of the time the temperature is below 30 °C, thus this represents the maximum value for semi-volatile matter. No clear seasonal variation was found in the PM$_1$ or PM$_{2.5}$ mass. The measured PM$_{2.5}$ mass concentrations were slightly higher than those measured typically in Finland at urban, background sites (mean PM$_{2.5}$ values in 2001 in urban and urban, background sites were 9.6 and 8.2 µg m⁻³; see Laakso et al. 2003). The main reason for the slightly higher concentration can be partly explained by the monitoring methods used (FDMS-TEOM in this paper and other monitor types in Laakso et al. 2003). Furthermore, also the biomass burning episodes elevated average PM concentrations.

In general, the PM chemical composition followed expected trends in OC, sulfate, nitrate, ammonium, EC being the major components of fine particulate matter (Niemi et al. 2004, Sillanpää et al. 2005a, 2005b) during the 13 month measurement period (Fig. 1). Sulfate was the most abundant ion, with an average concentration of 1.74 µg m⁻³ (Table 1). The average concentrations of NO$_3^-$, NH$_4^+$ and K$^+$ were 0.77, 0.85 and 0.10 µg m⁻³, respectively (Table 1). The concentrations of potassium and oxalate in the PILS-IC measurements were very low for most of the year, being above the quantification limit only 20% and 30% of the time, respectively. Elevated potassium concentrations (up to 0.5 µg m⁻³; not shown) were measured only during the two biomass burning episodes (Saarikoski et al. 2007, Saarnio et al. 2010). For sodium and chloride, the concentration in the PILS-IC measurements were for most of the time (> 80%) below the quantification limit as can be expected for a fine PM fraction. The concentrations of OC and optical EC were 2.0 ± 2.5 and 0.74 ± 0.64 µg m⁻³ (mean ± SD), respectively (Table 1). OC correlated with PM$_{2.5}$ ($r^2 = 0.70$). Highest 3-h average OC concentrations (up to 41 µg m⁻³) were measured during two biomass burning episodes.

**Diurnal variation**

Since the time resolution for EC and OC was three hours, also the ion and PM$_{2.5}$ mass concentrations were averaged to the corresponding time
Fig. 1. Comparisons between online and PM₁ filter measurements of OC, ammonium, nitrate, sulfate and EC from 9 February 2006 to 28 February 2007. Sampling time for the PM₁ filters was approximately 24 hours during week- days and 72 hours on weekends, and the ion results of the online instruments were averaged to corresponding time periods.

Fig. 2. Measured concentrations of major ions, EC, POM and PM₂.₅ for 3-h averages. The amount of volatile PM is evaluated based on FDMS TEOM results and the mass between PM₁ and PM₂.₅ is evaluated from simultaneous MOUDI collections.

periods. The values measured during biomass burning episodes (April–May and August 2006) were excluded from the data, when seasonal and diurnal variations were studied. No diurnal variation was found for POM, ammonium and sulfate (Fig. 2). The diurnal variation in PM₂.₅ measured with TEOM was weak (Fig. 2). Most evident diurnal variation was recorded for EC which had the highest concentration at 06:00–09:00 and the lowest one at 03:00–06:00 (Fig. 2). Of the ions, only nitrate had the diurnal variation with a peak concentration between 06:00 and 09:00. Diurnal cycles of nitrate depend on available atmospheric ammonia of the specific location (Seinfeld and Pandis 1998). Similar nitrate behavior to the one found during our experiment was also recorded in previous studies (e.g. Hennigan et al. 2008, Poulain et al. 2011). It seems that the morning peak of nitrate was not related to changes in meteorological variables (Fig. 3), but was more likely caused by the increased traffic emissions during rush hour. The concentration of nitrate was the lowest in the afternoon and in the evening. The lower concentrations in the afternoon were probably caused by the increased mixing layer height. In the study of Järvi et al. (2008)
in Helsinki, it was found that also black carbon, which is non-volatile, quite systematically had lower concentrations during afternoon. Concurrently with increased mixing layer height, the ambient temperature was increasing, that may have decreased nitrate concentrations by transferring particle-phase nitrate into the gas-phase.

The difference between weekdays and weekends was also studied. Of all the chemical components only EC varied clearly on the weekday-to-weekend bases. On weekdays, EC concentrations started to raise at 06:00 simultaneously with the increasing traffic volumes. EC concentrations remained at high level until the evening rush hour was over at around 18:00. Minimum EC concentrations were recorded at night between 00:00 and 03:00. During weekends, the diurnal variation of EC was minimal. The diurnal cycle of EC, with maximum at weekdays during the rush hours, indicates that traffic was likely the major source of EC. However, EC had a slightly different diurnal variation in different seasons. In summer and autumn, the concentrations of EC decreased sharply after the morning peak at 06:00–09:00, whereas in winter the concentrations stayed at higher level until the night (Fig. 4), probably because of the more stable boundary layer height during the day. For OC, the diurnal variation was only found in summer (Fig. 4). Similar to nitrate in autumn (Fig. 5), the concentrations of OC in summer were lowest in the afternoon and early evening due to the efficient mixing of pollutants and transfer of particle-phase OC to gas-phase.

**Seasonal variation**

To study the seasonal differences, one month was chosen to represent each season: February for winter, April for spring, June for summer and September for autumn. Seasonal differences during the measurement campaign were large. The highest ion, EC and OC concentrations were measured during the winter and the highest nitrate concentration during both winter and spring (Figs. 4 and 5). This is in line with the result of Ruoho-Airola (2012) who found a clear seasonal cycle in ambient sulphur and nitrogen concentrations in clean, background areas with a maximum in February. Potassium has been used as a tracer for biomass burning (Khalil and Rasmussen 2003). The concentrations of potassium were highest in winter (excluding the forest fire episodes) and lowest in summer, indicating that the local biomass burning for domestic heating likely increased aerosol concentrations during the winter. Biomass burning has been shown to affect PM concentration during the cold season in Finland (Saarnio et al. 2012). In addition to biomass burning, the high secondary ion concentrations recorded during the winter could represent long-range transported aerosol particles.

The lowest concentrations of all compounds, except of OC, were measured during the summer. Therefore, the average contribution of OC was largest during the summer. Also, a clear seasonal cycle was found for the OC/EC ratio. During the summer, the OC/EC ratio was on average 4.5, whereas during the autumn and winter it was...
smaller than 3. This is in line with the results of Aurela et al. (2011) who found a clear increase in the OC/EC ratio during summer due to biogenic emission at a background site. The EC concentrations were $82\% \pm 41\%$ (mean ± SD) higher during the winter than during the summer. The high EC concentrations during the winter were likely caused by traffic emissions from the nearby road or biomass burning from domestic heating, amplified by weak atmospheric mixing during the winter. There were clear differences in both nitrate concentrations and its diurnal cycles during the different seasons (Fig. 5). There was a morning peak in the nitrate concentration during the winter and spring. The afternoon decrease in the nitrate concentration was clearly seen in the autumn, whereas in the summer no diurnal cycle was observed. For ammonium, no seasonal or diurnal variation was detected, even though during the summer slightly lower concentrations were recorded in the evening (Fig. 5).

Seasonal differences in ion balance

The equivalent ratio of cations to anions was calculated for the PM$_1$ filter samples and PILS-IC ion concentrations (Fig. 6). For PM$_1$, this ratio was quite stable: $0.9 \pm 0.2$ (mean ± SD). For PILS-IC, the ratio was $1.05 \pm 0.3$ being higher in the summer (from July to September) than in the winter. The maximum cation-to-anion ratio (monthly average 1.4) was found for the biomass burning episode in August (see Saarnio et al. 2010). The amount of excess ammonium was calculated from the ammonium concentration by subtracting first the amount of ammonium sulfate (for simplicity all ammonium is assumed to be ammonium sulfate without contribution of ammonium bisulfate; if part of sulfate was in the form of ammonium bisulfate the amount of excess ammonium would be larger), then ammonium nitrate and finally ammonium chloride. It was found that most of the time ammo-
nium was in the forms of ammonium sulfate and ammonium nitrate. However, in the summer from June to September, substantial amount of excess ammonium was recorded. The amount of excess ammonium was found to increase as temperatures increased (Fig. 7). At the same time, as the relative amount of ammonium increased, the contribution of nitrate to the total mass decreased (Fig. 7). The temperature dependency of nitrate was likely caused by nitrate partition into the gas phase with increasing temperature. Occasional high cation-to-anion ratios have also been found

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**Fig. 5.** Average ammonium (a) and nitrate (b) concentrations for each hour of day during the measurement campaign (9 February 2006–28 February 2007).

**Fig. 6.** Monthly average cation-to-anion ratios based on the PILS-IC and PM, filter measurements from February 2006 to February 2007.
in other studies. Weber et al. (2001) found that the cation-to-anion ratio seem to be dependent on the particle source. They measured cation-to-anion ratios below 1 for local pollution episodes and ratios of up to 4 for clean air masses with low (10 µg m⁻³) ambient aerosol concentrations.

**Real-time mass closure**

A real-time mass closure (i.e. the ratio between chemically analyzed compounds and gravimetric mass) was constructed by comparing the chemical components measured by online methods (PILS-IC and RT-OCEC) with PM₂.₅ measured by TEOM. Only the major ions (sulfate, nitrate and ammonium) were used to construct the mass closure. The RT-OCEC was measured with a time resolution of 3-h and therefore also the data from PILS-IC and TEOM were averaged over the same periods. Excluding the measurements when one or more of the instruments was not running properly, the total number of data points was 1225. Similar to the filter collections, a multiplier of 1.6 was used to convert the measured organic carbon to particulate organic matter.

During February 2007, 90% of the PM₂.₅ mass was identified by chemical analyses (Fig. 8). During the year-long measurement period, on average 65% of PM₂.₅ was identified by the chemical analyses of PM₁. No seasonal differences in the degree of the achieved mass closure results were found. However, the difference between the analyzed and measured mass was largest when the PM₂.₅ concentration was low. Especially for the PM₂.₅ concentrations below 5 µg m⁻³, the degree of the achieved mass closure varied significantly (0.1–1.95). At that concentration level, all the instruments were running close to their detection limits giving high total uncertainty for the mass closure. When the concentrations were > 15 µg m⁻³, the mass closure result was not larger than 1.2, but it could still be as low as 0.22. For the largest concentrations (> 50 µg m⁻³) the mass closure was in range 0.85–1.0, however, the number of data points was very limited (n = 4). The used multiplier to convert carbon to particulate organic matter has an effect on the results of mass closure. The OM/OC ratio depends on the source and age of aerosols and can range typically from 1.2 to 2.5 (Turpin and Lim, 2001, Jimenez et al. 2009, Saarnio et al. 2010). An estimated value 1.6 was used based on the previous studies and recommendation of Turpin and Lim (2001). The reconstruction of mass measured by TEOM has previously been studied e.g. by Schwab et al. (2006) in US. They found that the difference between mass reconstructed from filter samples and measured by TEOM was on average less than 10%. But similarly to our case, they recorded a large variation in how the mass closure was reached.

**Summary and conclusions**

Long time-series of the PM chemical composition determined with high-time-resolution meas-
measurement devices in sub-arctic conditions are rare. In this study, measurements of major chemical components in fine particles were conducted at an urban, background station in Finland from February 2006 to February 2007 in order to investigate diurnal and seasonal changes in the PM concentration and composition. In addition, concentrations obtained from online measurement devices were compared with those from the traditional filter collections in order to increase the understanding of collection artifacts in both measurement approaches.

In addition to regional and long-range transported aerosols, the sources of PM during the measurement were biomass burning, SOA formation and traffic. The contribution of ions and EC were largest in the winter due to emissions from biomass burning that is used for domestic heating during the cold season. The contribution of OC was largest during the summer, likely due to more pronounced SOA formation. The PM ion balance was 1.05 ± 0.3 (mean ± SD), being higher during the summer (from July to September) than winter. During the summer from June to September, substantial amount of excess ammonium was recorded. The amount of excess ammonium was found to increase as temperatures increased, whereas the contribution of nitrate to the total mass decreased, likely due to changes in nitrate partitioning between the gas and aerosol phases.

The aerosol chemical composition measured from the PM$_1$ filter samples compared well with the concentrations measured with the online instruments. Volatility of the measured compounds and differences in the measurement techniques were the main reasons for the differences between the online and offline methods. Also, a different cutoff sizes used in the measurements (PM$_1$ and PM$_{2.5}$) affected the measured concentrations. The ratio between PM$_1$ (filter) and PM$_{2.5}$ (TEOM) was 0.62 ± 0.51. The difference in the cutoff sizes (PM$_1$ and PM$_{2.5}$) explained on average 25% of the unexplained mass, whereas the volatilized mass fraction (≤ 18%) explained the remaining unexplained mass. A real-time mass closure was constructed by using the PM$_{2.5}$ mass concentrations from TEOM, ion concentrations from PILES-IC and carbonaceous matter concentrations measured with the RT-OCEC. The analyzed submicron compounds (ions, POM, EC) represented on average 65% of the PM$_{2.5}$ mass.

Nitrate concentrations were found to peak in early morning, during the rush hours. There was a morning peak in the nitrate concentration during the winter and spring. The afternoon decrease in the nitrate concentration could be clearly seen during the autumn, whereas no diurnal cycle was found during the summer. Also EC had a clear diurnal cycle, with a maximum during the morning rush hour.

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