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CHEMICAL CHARACTERIZATION OF URBAN BACKGROUND AEROSOL USING ONLINE AND FILTER METHODS

Hilkka Timonen

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Abstract

In order to evaluate the influence of ambient aerosol particles on cloud formation, climate and human health, detailed information about the concentration and composition of ambient aerosol particles is needed. The duration of aerosol formation, growth and removal processes in the atmosphere range from minutes to hours, which highlights the need for high-time-resolution data in order to understand the underlying processes.

This thesis focuses on characterization of ambient levels, size distributions and sources of water-soluble organic carbon (WSOC) in ambient aerosols. The results show that in the location of this study typically 50-60 % of organic carbon in fine particles is water-soluble. The amount of WSOC was observed to increase as aerosols age, likely due to further oxidation of organic compounds. In the boreal region the main sources of WSOC were biomass burning during the winter and secondary aerosol formation during the summer. WSOC was mainly attributed to a fine particle mode between 0.1 – 1 µm, although different size distributions were measured for different sources. The WSOC concentrations and size distributions had a clear seasonal variation.

Another main focus of this thesis was to test and further develop the high-time-resolution methods for chemical characterization of ambient aerosol particles. The concentrations of the main chemical components (ions, OC, EC) of ambient aerosol particles were measured online during a year-long intensive measurement campaign conducted on the SMEAR III station in Southern Finland. The results were compared to the results of traditional filter collections in order to study sampling artifacts and limitations related to each method. To achieve better a time resolution for the WSOC and ion measurements, a particle-into-liquid sampler (PILS) was coupled with a total organic carbon analyzer (TOC) and two ion chromatographs (IC). The PILS-TOC-IC provided important data about diurnal variations and short-time plumes, which cannot be resolved from the filter samples.

In summary, the measurements made for this thesis provide new information on the concentrations, size distributions and sources of WSOC in ambient aerosol particles in the boreal region. The analytical and collection methods needed for the online characterization of aerosol chemical composition were further developed in order to provide more reliable high-time-resolution measurements.

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Ilmakehän pienhiukkasten kemiallisen koostumuksen määrittäminen käyttäen suodatin- ja jatkuvatoimisia mittauksia

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Tiivistelmä

Ilmakehän aerosolit sisältävät pienhiukkasia, joiden koko, pitoisuus sekä kemiallinen koostumus täytyy tuntea, jotta niiden vaikutuksia pilvien muodostumiseen, ilmastoon ja terveyteen voidaan arvioida. Uusien aerosolihiukkasten synty-, kasvu- ja poistumisprosessit ovat nopeita, kestoltaan usein vain muutamista minuuteista tunteihin, minkä takia kemiallisen koostumuksen määrittämiseen tarvitaan jatkuvatoimisia, hyvän aikaresoluution tarjoavia laitteita.

Tämä työ keskittyy aerosolihiukkasten vesiliukoisen orgaanisen hiilen pitoisuuden, kokojakaumien sekä lähteiden tarkasteluun Pohjois-Euroopan boreaalisella vyöhykkeellä. Vesiliukoisen orgaanisen hiilen päälähteet olivat biomassan palamisessa syntyneet hiukkaset talvella ja sekundääristen aerosolihiukkasten muodostuminen kesällä. Helsingissä SMEAR III -mittausasemalla tehdyissä mittauksissa pienhiukkasissa (Dp < 1µm) vesiliukoisen orgaanisen hiilen osuus oli keskimäärin 50–60 % orgaanisesta hiilestä. Vesiliukoisten yhdisteiden määrän havaittiin kasvavan aerosolin iän kasvaessa johtuen todennäköisesti orgaanisten yhdisteiden hapettumisesta ja siten muuntumisesta vesiliukoisemmiksi. Vesiliukoisen hiilen kokojakaumissa valtaosa vesiliukoisesta hiilestä oli akkumulaatiomoodissa, 0.1-1 µm:n kokoisissa hiukkasissa. Mitatut vesiliukoisen orgaanisen hiilen kokojakaumat olivat erilaisia eri lähteistä peräisin oleville hiukkasille. Vesiliukoisen orgaanisen hiilen määrässä ja kokojakaumissa havaittiin myös selkeää vuodenaikaisvaihtelua.

Toisena päätavoitteena tässä työssä oli testata ja edelleen kehittää jatkuvatoimisia reaaliaikaisia mittausmenetelmiä aerosolien kemiallisen koostumuksen määrittämiseksi. Aerosolien pääkomponenttien (epäorgaaniset ionit, orgaaninen ja epäorgaaninen hiili) pitoisuuksia mitattiin reaaliaikaisesti vuoden ajan SMEAR III -asemalla Etelä-Suomessa. Uutta on se, että koostumuksen muutokset tunnetaan tarkasti ajan funktiona, jolloin päästölähteiden selvittäminen on oleellisesti helpompaa kuin aiemmin. Yhdistämällä PILS-keräin ionikromatografiin ja orgaanisen hiilen kokonaispitoisuutta mittaavaan laitteistoon mahdollistettiin ionien ja vesiliukoisen orgaanisen hiilen hiukkaspitoisuuksien samanaikainen määritys hyvällä aikaresoluutiolla, sekä saatiin uutta tietoa vesiliukoisen hiilen ja ionien vuorokausivaihtelusta ja lyhytkestoisista pitoisuuden muutoksista.

Tässä tutkimuksessa tuotettiin uutta tietoa vesiliukoisen orgaanisen hiilen pitoisuuksista, kokojakaumista ja lähteistä Pohjois-Euroopassa. Näytteenkeräys- ja analyysimenetelmiä kehitettiin edelleen jatkuvatoimiseksi, jolloin lähes reaaliaikaiset aerosolien kemiallisen koostumuksen mittaukset tulivat mahdolliseksi.

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ABBREVIATIONS

AMS	Aerosol mass spectrometer
APS	Aerodynamic particle sizer
BC	Black carbon
BLPI	Berner low pressure impactor
CE	Collection efficiency
CPC	Condensation particle counter
D_a	Particle aerodynamic diameter
DMPS	Differential mobility analyzer
EC	Elemental carbon
FA	Fulvic acid
FDMS	Filter dynamics measurement system
HA	Humic acid
HR-ToF-AMS	High-resolution time-of-flight mass spectrometer
HULIS	Humic-like substances
IC	Ion chromatograph
IPCC	Intergovernmental Panel on Climate Change
LC-MS	Liquid chromatograph mass spectrometer
LRT	Long-range transport
MA	Monosaccharide anhydrides
MOUDI	Micro-orifice uniform deposit impactor
m/z	Mass to charge -ratio
NDIR	Non-dispersive infrared
NPOC	Non-purgeable organic carbon
OC	Organic carbon
OM	Organic matter (OC*1.6)
PILS	Particle-into-liquid sampler
PM	Particulate matter
PMF	Positive matrix factorization
POA	Primary organic aerosol
RT-ECOC	Semi-continuous ECOC carbon aerosol analyzer
SMEAR	Station for measuring forest ecosystem – atmosphere relations

SOA	Secondary organic aerosol
TEOM	Tapered element oscillating micro-balance
TOA	Thermal-optical carbon analyzer
TOC	Total organic carbon
TOT	Thermal-optical transmittance
VI	Virtual impactor
WISOC	Water-insoluble organic carbon
WSOC	Water-soluble organic carbon
WSPOM	Water-soluble particulate organic matter

Contents

List of publications

This thesis consists of an introductory review, followed by five research articles. Papers **II**, **III**, **IV**, and **V** are reprinted under the Creative Commons Attribution 3.0License and paper **I** is reproduced with the permission from the journal. In the introductory part, these papers are cited according to their roman numerals. In addition to the articles, some unpublished data has been used in the results section.

I Timonen, H. J., Saarikoski, S. K., Aurela, M. A., Saarnio, K. M., and Hillamo, R. E. J.: Water-soluble organic carbon in urban aerosol: concentrations, size distributions and contribution to particulate matter, Boreal Env. Res., 13, 335–346, 2008.

II Timonen, H., Saarikoski, S., Tolonen-Kivimäki, O., Aurela, M., Saarnio, K., Petäjä, T., Aalto, P. P., Kulmala, M., Pakkanen, T., and Hillamo, R.: Size distributions, sources and source areas of water-soluble organic carbon in urban background air, Atmos. Chem. Phys., 8, 5635–5647, 2008.

III Timonen, H., Aurela, M., Carbone, S., Saarnio, K., Saarikoski, S., Mäkelä, T., Kulmala, M., Kerminen, V.-M., Worsnop, D. R., and Hillamo, R.: High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS, Atmos. Meas. Tech., 3, 1063–1074, 2010.

IV Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., and Hillamo, R.: Sources of organic carbon in fine particulate matter in northern European urban air, Atmos. Chem. Phys., 8, 6281-6295, 2008.

V Timonen, H., Aurela, M., Saarnio, K., Frey, A., Saarikoski, S., Teinilä, K., Kulmala, M., and Hillamo, R.: Monitoring of inorganic ions, carbonaceous matter and mass with online and offline methods, Submitted.

1. INTRODUCTION

The term aerosol means solid or liquid particles suspended in a gas. The size of aerosol particles ranges from nanometer-size molecular clusters to particles with diameters larger than 100 µm. Aerosol particles originate from anthropogenic (e.g. traffic, industry etc.) and natural (e.g. volcanoes, sea, leaf, dust) sources, and they are further divided to primary and secondary particles according to their formation mechanisms. Primary aerosol particles are emitted directly to atmosphere in particulate form from the source (e.g. combustion, volcanic eruptions and wind-driven suspension of soil, mineral dust, sea salt and biological materials), whereas secondary particles are formed in the atmosphere via gas-to-particle conversion processes (e.g. nucleation, condensation and heterogeneous and multiphase chemical reactions) (Seinfeld and Pandis, 1998). Ambient aerosol particles have an effect on our everyday life. According to the Intergovernmental Panel on Climate Change (IPCC), aerosol particles have a poorly constrained effect on climate (IPCC, 2007). The aerosol particles cool the climate by scattering sunlight back to space, whereas some particles can absorb radiation and thus warm the atmosphere. Indirectly particles affect climate due to their ability to act as cloud condensation nuclei influencing the lifetime and albedo of clouds (IPCC, 2007). Fine particulate matter (PM) has been also associated with several adverse health effects, which depend on particle concentrations and compositions (e.g. Pope and Dockery, 2006, Tainio et al., 2010). Large concentrations of aerosol particles during pollution plumes, e.g. smokes drifting from forest fires, clearly reduce visibility (Hand and Malm, 2007).

In order to understand the effects of multi-phase and multi-component aerosol particles on human health, radiative budget and climate, a more thorough knowledge on chemistry of atmospheric aerosol particles is needed. Traditionally, the chemical composition of aerosol particles has been measured from filters. Typically the collection time in the filter collections has ranged from 12 to 48 hours to gain enough mass for the subsequent analyzes. In addition to the poor time resolution, a problem with the filter collections has been sampling artifacts (absorption of gases on the filter, evaporation of collected PM from the filter and alteration of compounds collected on the filter) during the collection, storage and analyses. Over the last years, online measurement devices have developed to a great extent. By using multiple instruments, chemical characterization of ambient aerosol particles can be achieved with a high time resolution. The aerosol mass spectrometer (AMS) has been a large improvement for the existing methods. With the AMS, the chemical composition (main ions and organics) and size distributions of aerosol particles can be measured with a few-minute time resolution (Allan et al., 2003, DeCarlo et al., 2006). Also the specific mass to charge (*m/z*) ratios can be used as tracers for the known sources. So far a chemical characterization on a molecular level cannot be solved from the AMS data due to the fact that atmosphere is composed of a huge amount of different types of molecules that have overlapping signals. The particle-into-liquid sampler (PILS) has been developed to collect aerosol particles directly into liquid. The achieved liquid sample can be directly fed to a desired analyzer. Typically the PILS has been combined with ion chromatographs or a total organic carbon analyzer (Sullivan et al., 2006, Peltier et al., 2007, 2008) and occasionally the liquid chromatography mass spectrometry (HPLC-MS) (Parshintsev et al., 2010) or spectrometers (Rastogi et al., 2009, Hecobian et al., 2010) are also used. The semi-continuous ECOC carbon aerosol analyzer can be used to thermally measure concentrations of organic and inorganic carbon (Arhami et al., 2006). Typically sampling time resolution from 1 to 4 hours is used depending on measured concentrations. Also a variety of monitoring instruments like tapered element oscillating micro-balance (TEOM), aethalometer or multiangle absorption photometer (MAAP), measuring aerosol properties with time resolution from minutes to hours, have been developed. Despite of new methods, the full chemical characterization of ambient aerosols on molecular level is still inadequately known. Using multiple methods, typically 5-20 % of organic mass can be identified on molecular level, whereas the rest remains unknown (Pio et al., 2001, Decesari et al., 2006, Aggarwal and Kawamura, 2009).

This thesis presents results from aerosol chemical composition measurements made at the urban background station (SMEAR III) situated in Helsinki, Southern Finland. A special attention is paid on the characterization of water-soluble fraction of aerosol particles. The used online methods were further developed to enable a chemical characterization of ambient aerosol particles with high time resolution.

2. OBJECTIVES OF THIS STUDY

The overall objective of this study was to test and further develop high-time-resolution methods for determination of chemical composition of atmospheric aerosol particles and to study the sources and physico-chemical properties of WSOC in urban background environment. Before this study, only a very limited number of WSOC measurements had been performed in northern Europe.

The specific objectives of this thesis were:

- to develop a method for the determination of water-soluble organic carbon concentrations of ambient aerosol samples collected on filter
- to explore the variations of WSOC concentrations and size distributions, and to evaluate the sources and atmospheric processes affecting WSOC concentrations
- to develop and test a method for online measurement of WSOC and ions
- to assess the validity of semicontinuous/continuous measurements by comparing the results of the online methods with those obtained by the PM_1 filter measurements
- to find out the water-solubility of different organic fractions found by applying the positive matrix factorization (PMF) on high-resolution aerosol mass spectrometer (AMS) data

3. LITERATURE REVIEW ON RECENT WSOC MEASUREMENTS

3.1. Aerosol chemical composition and WSOC

Ambient aerosol particles comprise of a mixture of substances originating from a variety of diverse activities, including fuel combustion (from vehicles, power generation, and industrial facilities), biomass burning (forest fires, agricultural burning, heating) and industrial processes. In addition to this, a large number of biogenic sources, e.g. sea spray, volcanic emissions, windblown soil, influence aerosol concentrations. Primary particles are directly introduced into the atmosphere, whereas the secondary aerosol particles are formed in atmosphere from gaseous compounds (Seinfeld and Pandis, 1998). The major constituents of atmospheric aerosol particles are inorganic ions, carbonaceous compounds, trace metals and particle-bound water. The composition is mostly depending on the source, but it is also affected by the physico-chemical processes like aging in the atmosphere and aerosol removal processes.

The inorganic ions in the atmosphere are well characterized. The concentration of major ions (sulfate, nitrate, chloride, oxalate, sodium, ammonium, potassium, magnesium and calcium) can be measured from filter samples with an ion chromatograph or online with e.g. PILS-IC system, or by an aerosol mass spectrometer with a time resolution of 2-15 minutes. The major ions sulfate, nitrate and ammonium are mostly formed by gas-to-particle conversion from their precursor gases SO_2, NO_x and NH_3. Trace metals represent typically less than 2% of the aerosol mass, depending on source of aerosol (Seinfeld and Pandis, 1998). The major sources of trace metals in the atmosphere are anthropogenic, such as industrial and different kind of combustion processes.

Carbonaceous compounds exist in three different forms in ambient aerosol particles: organic carbon (OC), elemental carbon (EC) and carbonate minerals. Elemental carbon represents typically 5-25% of fine particle mass (Viidanoja et al., 2002, Park et al., 2005). Elemental carbon is also called black carbon (BC) or soot, depending on the used analyzing method. Typically the term EC is used for thermally analyzed carbon, the term BC for optically measured carbon and soot refers to measurements with a morphological detection like the electron microscopy. Elemental carbon is produced in various combustion processes (e.g. biomass burning and fuel burning) due to incomplete burning and is therefore always primary material. Carbonate minerals (e.g. $CaCO_3$) have crustal origin and are typically found mainly in coarse particles (Li et al., 2000). The organic fraction of ambient aerosol particles offers a challenge. Typically it represents 10-70 % of fine particulate mass (Saxena and Hildemann, 1996). The organic fraction consists of a large number (1000 to 10000) of structurally different compounds, originating from various sources and with wide range of chemical and physical characteristics. The number of carbon atoms in carbon chains varies from two to several tens, and the chain structure varies from aliphatic to branched and aromatic structures (Saxena and Hildeman, 1996, Decesari et al., 2000). Also the chemical properties like solubility, hygroscopicity, polarity and volatility vary (Seinfeld and Pandis, 1998). These large differences make chemical analysis of organic matter tedious. Using multiple methods, typically 10-20 % of organic mass can be identified, whereas the rest remains unknown (Pio et al., 2001, Decesari et al., 2006, Aggarwal and Kawamura, 2009). Despite the obvious significance of organic carbon in aerosol particles, the sources, atmospheric processing and removal are still poorly known.

The organic fraction can be further divided into the water-soluble and water-insoluble fractions. The water-insoluble compounds are typically fresh emissions, originating from traffic or other local sources. As aerosol ages, it has been observed to become more water-soluble due to further oxidation (Jimenez et al., 2009). The water-soluble organic fraction represents typically 25-75 % of the total organic mass (Jaffrezo et al., 2005 and references therein, Pathak et al., 2011). The measured WSOC concentrations range from very small concentrations (0.5-2 $\mu g\ m^{-3}$) measured in clean background areas (e.g. Cavalli et al., 2006) up to very high concentrations (10-75 $\mu g\ m^{-3}$) measured typically for biomass burning influenced aerosol particles (e.g. Decesari et al., 2006, Ram and Sarin, 2011). Water-soluble compounds affect the hygroscopicity of particles and thus on their ability to absorb water from the gas phase. When particles grow, they are more likely to scatter light and more likely to form cloud droplets, thus influencing the radiative forcing of climate through the direct and indirect effects. Water-solubility may also influence the toxicity of PM.

3.2. Sources of WSOC

Biomass burning (forest fires as well as biomass burning for domestic heating) is known to produce large amounts of fine particulate OC and a substantial fraction of this OC is water-soluble (Decesari et al., 2006, Saarnio et al., 2010). Levoglucosan is often used as a tracer for WSOC emitted from biomass combustion.

In the absence of biomass burning emissions, secondary aerosol formation has been shown to be the major source of WSOC (Miyazaki et al., 2006, Kondo et al., 2007). In boreal areas, biogenic volatile organic compounds emitted by the boreal forest, have been shown to have a large influence to WSOC and OC concentrations in a summer time when the biogenic activity is high (Tunved et al., 2006), whereas in urban areas due to increased biomass burning anthropogenic contribution to SOA formation can be important (Szidat et al., 2006, 2009, Offenberg et al., 2007). It has been observed that continuous formation of secondary organic aerosol from biogenic VOCs takes place during transport over forested areas (Tunved et al., 2006). Also following nucleation, oxidation products of monoterpenes and possibly also sesquiterpenes have been shown to condense on particles of all sizes in measurable quantities (Laaksonen et al., 2008). Chamber experiments have shown that monoterpene oxidation products enrich into the smallest particles (Anttila et al., 2006). Some of the major oxidation products of biogenic VOCs have been observed to be water-soluble compounds (Cavalli et al., 2006).

3.3. Seasonal and diurnal changes in WSOC

Clear seasonal trends have been observed in most WSOC measurements. For urban locations, the maximum WSOC concentrations in fine particles have been observed to occur in winter and the minimum in summer (Ho et al., 2006, Viana et al., 2006). For marine and mountain sites, the highest WSOC concentrations have been measured in summer (Pio et al., 2007, Yoon et al., 2007).

Diurnal changes of WSOC are different for different locations, likely due to different prevailing sources during the measurements. Samy et al. (2010) observed higher concentration of WSOC at night than during daytime. They concluded that the increased daytime convective mixing of local primary emissions decrease the concentrations and therefore larger concentrations of WSOC are measured at night time. Ram and Sarin, (2011) observed a night-time increase in the concentrations of carbonaceous species, but found higher WSOC/OC ratios during the day due to enhanced secondary organic aerosol (SOA) formation. WSOC has been observed to have a correlation with temperature and relative humidity (Hennigan et al., 2008), both having diurnal cycles.

3.4. Chemical characterization of WSOC

The chemical characterization of WSOC has been problematic. It is known that the water-soluble compounds are typically oxygenated, polar, multifunctional compounds (Decesari et al., 2000). Because of the large number of organic species in the atmosphere, some of which reside in gas and particle phases, a measurement of WSOC that is comprehensive, phase-specific, and speciated on a molecular level is difficult. There are some major components (diacids, monosaccharide anhydrides, etc.) that are relatively easy to measure, whereas the rest remain typically unknown.

There are several different approaches to characterize the water-soluble fraction of OC. Decesari et al. (2001) have developed a method where the WSOC compounds are divided into three different classes: neutral/basic compounds (e.g. pinonaldehyde, levoglucosan), mono- and dicarboxylic acids (e.g. nonandioic acid and 3-hydroxy butanoic acid) and polyacids (e.g. fulvic acid). The method is based on a chromatographic separation and subsequent functional group analysis by proton NMR. By this approach they have been able to categorize up to 80 % of WSOC to these classes (Decesari et al., 2006). Another approach is to classify WSOC into hydrophilic (more soluble in water) and hydrophobic (less soluble in water) fractions (Duarte and Duarte, 2005; Sullivan and Weber, 2006). While the definitions of these fractions are operational, they are closely related to the carbon chain length and the number of functional groups per molecule. Hydrophilic organic compounds are highly oxygenated, with low molecular weights, typically with a number of carboxyl, carbonyl, or other groups per molecule. These compounds tend to be highly soluble in water. Hydrophobic organic compounds tend to be longer in carbon chain length, and less hygroscopic.

Based on recent studies, humic-like substances, called HULIS due to their observed similarities to terrestrial humic acids, are known to contribute up to 60% of WSOC mass (Salma et al., 2007 and references therein). HULIS is believed to affect aerosol properties, such as surface activity, hygroscopic growth, ability to nucleate cloud droplets, and light absorption (Graber and Rudich, 2006, Asa-awuku et al., 2008, Ziese et al., 2008). HULIS is known to consist of high-molecular weight, polydisperse macromolecules containing aromatic and aliphatic structures, as well as carbonyl, phenyl hydroxyl and methyl groups (Graber and Rudich, 2006, Salma and Lang, 2008). It has been observed that atmospheric HULIS has a much lower molecular weight than terrestrial humic (HA) and fulvic acids (FA) (Kiss et al., 2003, Samburova et al., 2005), but functional groups are remarkably similar to HA and FA, especially in terms of carboxylic acids and carbohydrate-like substances (Stone et al., 2009). The elemental composition of HULIS has been measured to be C:H:O:N= 22:32:10:1 (molar ratios) by Salma et al. (2007). However, the exact chemical composition is unknown. Comparison of results is difficult because of differences in collection, extraction and analyzing methods of HULIS. Large concentrations of HULIS are known to be produced in biomass burning (Asa-awuku et al., 2008, Salma et al., 2010). Also secondary aerosol formation from gas phase VOCs followed by oligomerization is believed to be a source of HULIS (Graber and Rudich, 2006).

A large number of different organic acids have been found to contribute to the WSOC mass. The most abundant forms are monocarboxylic acids (e.g. acetic, formic, methanesulfonic, lactic, glyoxylic and glyceric acids) and diacids (e.g. oxalic, succinic and malonic acid). Monocarboxylic acids have multiple sources, including both biomass burning and biogenic emissions (Chebbi and Carlier, 1996). Monocarboxylic acids are mostly in gas phase because of their high vapor pressure, whereas diacids are mainly in particulate phase due to their low vapor pressure. Oxalic acid is the most abundant of diacids, representing typically 1-3 % of the fine mode WSOC (Huang et al., 2006). It has multiple sources ranging from traffic to biomass burning. Trace amounts (a few ng m^{-3}) of tricarboxylic acids (citric and tricarballylic acids) are typically found in water-soluble fraction (Decesari et al., 2006).

Monosaccharide anhydrides (levoglucosan, galactosan and mannosan) are water-soluble compounds known to be formed in biomass burning. Levoglucosan, formed in thermal breakdown of cellulose, is commonly used as a tracer for biomass burning. When polluted air masses have been influenced by biomass burning, such as small-scale combustion or wild land fires, very high levoglucosan mass concentrations have been measured (Yttri et al., 2005, Jordan et al., 2006, Saarikoski et al., 2007, Saarnio et al., 2010). In addition to anhydrides, small concentrations of sugars (e.g. glucose and xyloce) and sugar alcohols (glycerol, sorbitol) have been measured in ambient aerosol particles affected by biomass burning (e.g. Graham et al., 2002).

Oxidation of biogenic VOCs, such as α-pinene, β-pinene, isoprene and sesquiterpenes emitted by boreal forest, are known to produce a large variety of water-soluble compounds like acids and aldehydes (Kourtchev et al., 2005, Cavalli et al., 2006).

In addition to the compound classes mentioned above, a large variety of individual compounds and compound classes have been identified. However, the amounts are typically very small (few ng m^{-3}) (Saxena and Hildeman, 1996).

3.5. Size distributions of WSOC

The size of the aerosol particles varies from a nanometer up to 100 µm. Due to the large size range of aerosol particles, their size distributions are typically expressed on a logarithmic scale. Due to formation, transformation and removal processes affecting ambient aerosol particles, particles typically concentrate on certain size ranges called modes. The smallest of the size modes is the nucleation mode, with size from nanometer molecular clusters to 20 nm particles. Nucleation mode particles are formed by the clustering of low-volative vapours and the subsequent growth of these cluster by vapour condensation (Kulmala et al., 2000). The Aitken mode ($0.02\ \mu m < D_p < 0.1\ \mu m$) is typically the smallest mode detected by impactor measurements. The Aitken mode includes small primary particles originating from combustion processes as well as particles grown from the nucleation mode. Particles with an aerodynamic diameter below 0.1 µm are called ultrafine particles. The accumulation mode ($0.1\ \mu m < D_p < 1\ \mu m$) is a dominating mode for the submicron particulate mass in ambient measurements. The sources of accumulation mode particles are typically combustion processes and growth of Aitken mode particles. Due to weak removal processes of accumulation mode particles, particulate mass accumulates to this mode. The sum of ultrafine and accumulation mode particles constitute fine particles. The coarse particles are usually natural particles, such as salt from sea spray, debris from vegetation and windblown dust or mechanically-generated anthropogenic particles. Due to their large size of particles the removal processes for coarse particles (settling and impaction) are effective and their residence time in atmosphere is short.

Size distributions of WSOC have been studied in different environments, for example by roadside, in background areas, coastal sites and marine environments (e.g. Yu et al., 2004; Decesari et al., 2005; Tursic et al., 2006; Bao et al., 2009). Matta et al. (2003) measured the size distributions of WSOC for one year in Po Valley, Italy. A decrease in the contribution of all carbonaceous species to the particulate mass as the particle size increases has been observed in measurements made in urban environments (e.g. Bologna; Matta et al., 2003 and Shenzhen; Huang et al., 2006). A smaller WSPOM/mass –ratio in the supermicron particles can be affected by the fact that the mass in large particles is mainly crustal material that is not water-soluble. Recently, WSOC size distributions of biomass burning emissions have been studied. The studies clearly indicate that biomass burning emissions elevated the WSOC concentrations, especially in fine particles (Agarwal et al., 2010, Wang et al., 2011). The measurements of WSOC size distribution have been done by using different types of impactors with different filters and by using different extraction methods and different analyzing techniques (direct analyses by total organic carbon analyzers or indirect analyses with thermal-optical EC/OC analyzer). A comparison of the results is difficult due to different collection and analytical methods.

Conducted studies indicate that the sources, concentrations, seasonal and diurnal changes of WSOC as well as the size distributions are location-specific, and thus measurements in different environments are needed. Experimental data on WSOC in ambient air is still limited, and the behavior of WSOC is not well characterized because emission, production, and transport processes of aerosol particles have dynamic timescales ranging from minutes to hours, yet the time resolution of measurements is typically from 1 to 3 days. This situation emphasizes the need for time-resolved aerosol measurements, which can provide data that lead to a much better understanding of the properties and sources of WSOC.

4. MATERIALS AND METHODS

4.1. Measurement site

All of the measurements included in this thesis were conducted at the SMEAR III station (60°12’N, 24°58’E, 26 m above sea level; Järvi et al., 2009), belonging to the SMEAR (Station for Measuring Ecosystem-Atmosphere Relationship) measurement network. The SMEAR I is a remote background station in Värriö, the SMEAR II is a rural background station in Hyytiälä, the SMEAR III station is an urban background station situated in Helsinki and the SMEAR IV is a measurement station situated at elevated location (306 m asl) in a semi-urban area in Kuopio. The SMEAR III station (an air conditioned container and a 31 m high measurement tower) is situated next to the buildings of the Finnish Meteorological Institute and the University of Helsinki, five kilometers northeast from the central Helsinki. On the eastern side of the station lies a busy road (approximately 50000 cars daily) and a small forested area is located on the western side. Since 2004, when the measurement station was established, continuous measurements of gas and particle properties have been conducted at the SMEAR III station.

Physical and chemical properties of ambient aerosol particles and gas phase components are continuously measured at the SMEAR III station. The total mass of aerosol particles is measured with a tapered element oscillating micro-balance (TEOM, model 1400a + FDMS) and the concentrations of EC and OC are measured with a semicontinuous EC/OC carbon aerosol analyzer. In addition, physical properties of ambient aerosol particles are measured with a condensation particle counter (CPC), differential mobility analyzer (DMPS), and aerodynamic particle sizer (APS). Ozone (O_3) is measured using the TEI 49 analyzer, nitrogen oxides (NO_x) using the TEI 42S analyzer with molybdenum thermal converter and nitrogen monoxide (NO) using the TEI 42S analyzer. Nitrogen dioxide (NO_2) concentration is calculated by subtracting the NO concentration from that of NO_x. Carbon monoxide (CO) is measured using the Horiba APMA 360 analyzer and sulfur dioxide (SO_2) is measured using the Horiba APSA360.

The main local sources of fine particles at the SMEAR III station are traffic, biomass combustion for residential heating in winter and secondary aerosol formation (Papers II, IV; Järvi et al., 2009; Saarnio et al., 2010). Long-range transported emissions, pollution and biomass burning emissions from wild fires affect particle concentrations occasionally (Niemi et al., 2004).

4.2. Meteorological data

Local meteorological data were obtained from the Vaisala, Milos 500, weather station situated next to the SMEAR III station. The ambient temperature was measured using the Pt100 (Pentronic Ab) sensor, relative humidity was measured with the HMP45D (Vaisala Oyj) sensor, and global radiation with the CM11 (Kipp & Zonen) sensor.

To establish the potential source areas of the measured aerosol particles, 120-h air mass back trajectories were calculated for the sampling periods using the FLEXTRA model (Stohl and Wotawa, 1995).

4.3. Measurement campaigns

All the data presented in this thesis was collected during two intensive campaigns. During the 2006-2007 intensive measurement campaign (February 9, 2006 to February 28, 2007), the concentrations of main chemical components (OC, EC, WSOC, ions), size distributions of WSOC, ions and gravimetric mass were measured for a year in order to study the sources and transformation processes as well as diurnal and seasonal changes of ambient aerosol particles (Papers I-IV). The deployed instruments, measured components and collection times for the filter and online measurements are given in Tables 1 and 2.

Table 1. Online measurements during the intensive measurement campaign from February 2006 to February 2007.

Component/ property	Instrument	Cutoff size (µm)	Time resolution	Measurement period
Total mass	TEOM	2.5	30 min	9.2.2006-28.2.2007
OC, EC	RT-ECOC	1	3 h	17.6.2006-28.2.2007
Major Ions	PILS	1	15 min	9.2.2006-28.2.2007
BC	Aethalometer	1	2 min	3.7.-27.12.2006

Table 2. Filter measurements during the intensive measurement campaign from February 2006 to February 2007.

Component/ property	Sampling device	Analytical instrument	Time resolution
Major ions	Filter cassette	Dionex ICS-2000	24 h
WSOC	Filter cassette	Shimadzu TOC-V_{CPH}	24 h
OC, EC	Filter cassette	Sunset ECOC aerosol carbon analyzer	24 h
MA	Filter cassette	LC-MS, Agilent 1100 Series	24 h
Gravimetric mass	MOUDI	Mettler M3 microbalance	72 h
Major ions	MOUDI	Dionex ICS-2000	72 h
WSOC	MOUDI	Shimadzu TOC-V_{CPH}	72 h

The state-of-art online measurement devices, High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), PILS combined with total organic carbon analyzer and two ion chromatographs (PILS-TOC-IC), Semicontinuos EC/OC carbon aerosol analyzer (RT-ECOC) and a tapered element oscillating micro-balance (TEOM) were used to measure aerosol chemical composition during the spring 2009 campaign (April 9 to May 28, 2009). The measurement times and analyzed compounds and properties are collected to Table 3.

Table 3. The instruments, their time resolution and analyzed components during spring 2009 intensive campaign

Component/property	Instrument	Cutoff size (µm)	Time resolution	Measurement period
Ions, OC, mass	HR-ToF-AMS	1	2 min	9.4.-8.5.2009
Ions, WSOC	PILS-TOC-IC	1	WSOC: 6 min Ions: 15 min	25.4-28.5.2009
OC, EC	RT-ECOC	2.5	3 h	continuous measurements
PM	TEOM	2.5	1 h	continuous measurements

4.4. Filter measurements

4.4.1. PM_1

The PM_1 samples were collected using two pre-fired quartz (Whatman Q-MA 47 mm) filters in sequence in a filter cassette (Gelman Sciences). The PM_1 filter collections were made from February 9, 2006 to February 28, 2007 (N=297). The front filter was used to collect the aerosol sample and the back filter to estimate the absorption of gaseous compounds to the quartz filter during the collection. The semivolatile compounds evaporated from the front filter can also add mass to the backup filter. Using this experimental setup, these two artifacts cannot be separated. Based on previous studies, the absorption of gaseous compounds was estimated to have larger effects on our results, and thus the results of backup filter were subtracted from the results of the front filter. On overall the concentrations in of backup filters were very small (Table 4), except for nitrate. It seems likely that semivolatile nitrate evaporates from filters during collection and absorbs to the backup filter. The collection time was approximately 24 hours during weekdays and 72 h during weekends. In order to remove the particles with an aerodynamic diameter (D_a) > 1 µm, four stages (8–11) of the Berner low pressure impactor (BLPI; Berner and Lürzer, 1980) were installed in line prior to the filter cassette. The flow rate was 80 l min^{-1} to collect representative sample for the subsequent chemical analyses. A 1-cm^2 piece of filter was used for each chemical analysis (For description of methods see section 4.5).

Table 4. Average concentrations of major components in front and backup filters

Ion	Concentration in front filter (µg m^{-3})	Concentration in backup filter (µg m^{-3})	Backup/ front filter ratio (%)
Sulfate	1.80	0.08	4.4 ± 7.1
Nitrate	0.36	0.15	42 ± 33
Ammonium	0.71	0.01	1.3 ± 1.8
Potassium	0.075	0.002	3.9 ± 3.7
EC	0.91	-	-
OC	2.50	0.25	10 ± 6.6
WSOC	1.50	0.08	5.6 ± 6.4
MA	0.09	-	-

4.4.2. MOUDI

The micro-orifice uniform deposit impactor (MOUDI, Marple et al., 1991) was used to collect size-segregated samples at the SMEARIII station from February 2006 to February 2007. The MOUDI collections (45 altogether) were made approximately once a week. To collect a representative sample for the subsequent chemical analyses, the collection time was approximately 72 hours. Shorter collection times (12-48 hours) were adopted when ambient concentrations were higher. Pre-weighed aluminum foils were used as a collection substrate. Before collection the foils were washed with deionized water (Millipore A10, gradient) and dried in an oven (120 °C), in order to reduce the blank values. The collected samples were weighed with the Mettler M3 Microbalance (Mettler Instruments AG, Zurich, Switzerland) right after collection and refrigerated until analyzed. In addition to the gravimetric mass, major ions and water-soluble organic carbon were analyzed from the MOUDI samples.

4.5. Chemical analysis of filter samples

4.5.1. TOC-V_{CPH} total organic carbon analyzer

The WSOC analyzes were done by using a TOC-V_{CPH} organic carbon analyzer (Shimadzu) with a high sensitive catalyst (platinum on quartz wool) (Papers I-IV). The non-purgeable organic carbon (NPOC) method was used in order to remove carbonate carbon and carbon dioxide from the samples before analysis. In the NPOC-method volatile components may evaporate from the sample during the bubbling. However, the effect for aerosol samples is expected to be very minor, because the volatile fraction escapes from the sample already during the collection.

In the NPOC-method, WSOC is firstly extracted from the filter with deionized water. The sample-solution is drawn through a plastic tube to a syringe. The acid addition (1 % 2 M HCl) and helium bubbling (1.5 minutes) are done in the syringe. The acid is used to convert all inorganic carbon to carbon dioxide (CO_2), which evaporates from the sample solution prior to analysis. After the bubbling the sample is injected into an oven, where it is catalytically oxidized to carbon dioxide at 680 °C. CO_2 is detected with a non-dispersive infrared (NDIR) detector. Each sample is measured three times and the average of the measured values is calculated. A quite large injection volume (500 µl) is used because of the expected relatively small concentrations of WSOC, especially in the size-segregated impactor samples. The syringe and sample lines are washed twice with the sample solution between the samples. Approximately 10 ml of the sample is needed. The measurement time is approximately 15 minutes. Prior to the analyses, the TOC-V_{CPH} analyzer was calibrated with a series of potassium hydrogen phthalate standards (200-10000 µg l^{-1}, N=10).

The detection limit for the TOC-V_{CPH} is 4 µg l^{-1} and the standard deviation of the repeated measurements is less than 1.5 % (values given by the manufacturer). The measurement error resulting from the TC content in the water (used to make the solutions) and in the blank filters is typically much greater than the error resulting from the system blank value. The estimated error in the measurements is 15 % for atmospheric concentrations smaller than 2 µg m^{-3} and 10 % for the concentrations larger than 2 µg m^{-3}.

4.5.2. Ion chromatography

The ions (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, oxalate, succinate and malonate) were analyzed using Dionex DX500 (Papers I, II, IV), ICS-2000 (Papers III-V) or ICS-3000 (Papers I, II, IV) ion chromatographs. In an ion chromatograph the sample liquid is injected into a carrier fluid, eluent. The eluent and sample liquid go through a column containing a stationary fixed material (adsorbent). The separation is based on different partitioning of ions between the stationary adsorbent and the moving eluent/analyte mixture. The detection is based on conductivity of the mobile phase. The sample was extracted from filters by gently rotating the sample in deionized water for 15 minutes. The ion chromatographs had AG11/CG12A guard columns, AS11/CS12A analytical columns, ASRS/CSRS ultra II suppressors and NaOH and MSA eluents for anions and cations, respectively. Large loops (typically 500 µl for anions and 300 µl for cations) were used due to the small concentrations of ions in samples. In the ICS-2000 and ICS-3000 systems an AS17 anion column was used instead of AS11 and the anion eluent was potassium hydroxide (KOH). In addition the ICS-2000 and ICS-3000 systems had automatic eluent generators. A runtime of 15 minutes was used in order to separate the ions satisfactorily. Based on daily test samples, the uncertainty of the IC analyses of the filters is on order of 5-10 % for all the analyzed ions.

4.5.3. LC-MS

The LC-MS (Agilent 1100 Series, Trap SL, Agilent Technologies, USA) was used to determine the concentrations of monosaccharide anhydrides (MA, levoglucosan, galactosan and mannosan) from PM$_1$ samples during the 2006-2007 intensive campaign (Papers I, II, IV). Liquid chromatography–mass spectrometry (LC-MS) is an analytical technique where liquid chromatography is used to separate the analyzed components, and mass spectrometry is used to properly identify them. Prior to the analyses, the MAs were extracted from the filters with 2 ml of a mixture of tetrahydrofuran and water (1:1). The used injection volume was 2 µl and the eluent was deionized water with a flow rate of 0.1 ml min^{-1}. Two LC-columns were used in series (Atlantis dC18 3 µm, 2.1 mm of inner diameter and 150 mm in length, Waters). A negative electrospray technique was used for ionization. The mass-to-charge ratio (*m/z*) of the monitored ion was 161.

4.5.4. TOA

A thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon) was used to determine concentrations of both organic and elemental carbon (OC and EC) from PM_1 samples. The method is described in detail by Birch and Cary (1996). The analysis is based on a thermal-optical transmittance method (TOT). The instrument uses a two-phase thermal method to separate OC and EC. Firstly, the sample is purged with helium and the temperature is raised from room temperature to 900 °C in four consecutive steps, which is considered to burn all OC. In the next stage the sample is kept in an oxygen-helium mixture (1:49) and heated from 600 °C to 800 °C in order to determine EC. The vaporized compounds are catalytically oxidized to CO_2 and then reduced to CH_4, and the amount of carbon evolved is quantified with a flame ionization detector. An optical correction is applied for the separation of pyrolyzed OC from EC. The used temperature program was similar to the well-known NIOSH (The National Institute for Occupational Health and Safety) program, except for the last temperature step in the helium phase. The temperature of this last step was decreased from 870 °C to 800 °C in order to reduce a premature evolution of EC in the helium mode (Subramanian et al., 2006).

4.6. Online methods

4.6.1. PILS

The particle-into-liquid sampler has been developed for a rapid automated on-line measurement of ambient aerosol bulk composition (Weber et al., 2001, Orsini et al., 2003).

The PILS is typically coupled with either an ion chromatograph or a total organic carbon analyzer (e.g. Kondo et al., 2007, Gilardoni et al., 2007). The measurement campaigns were typically short in duration, from weeks to months and most of the PILS measurements were conducted in the United States. Due to the high time resolution, the PILS is suitable for mobile measurements e.g. in airplanes (Sorooshian et al., 2007), or trains (TROICA-9 experiment at the Trans-Siberian railway; Kuokka et al., 2007) or in ships (De Gouw et al., 2008).

The design and the operating principle of the PILS have been described in detail by Orsini et al. (2003). Shortly, aerosol particles are mixed with water vapor at their arrival to the conical shape cavity. As the particles go through the space, moisture is condensed on particles and they grow. After the cavity droplets are focused by a tapered wall to go through a nozzle. The nozzle directs the sample flow containing the droplets to impact onto a quartz surface. The spreading jet of air forces the impacted droplets to the perimeter of the quartz plate. The impaction plate is washed off with a steady stream of the transport liquid containing internal standard (lithium fluoride, LiF). During the collection, liquid that has been condensed onto aerosol particles and a small amount of water condensing out of the saturated air to the quartz impaction surface dilutes the transport liquid. Based on the LiF concentration prior and after the PILS this dilution is taken into account and the aerosol concentration can be accurately calculated. Laboratory tests have shown that the collection efficiency of the PILS is greater than 95% for particles between 0.03 and 6.0 µm (Orsini et al., 2003).

4.6.1.1. PILS-IC

A particle-into-liquid sampler combined with two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA) was used to collect ambient aerosol samples and to analyze the concentrations of major ions online from February 9, 2006 to February 28, 2007 (Paper V). Coarse particles were removed before the PILS by using a virtual impactor (VI; Loo and Cork, 1988) with a cut-off size of 1.3 µm. Gaseous compounds (ammonia and acidic gases) were removed prior to the PILS with three annular denuders, one coated with phosphoric acid (H_3PO_4 3 %) and two coated with potassium hydroxide (KOH 1 %). The denuders were changed every second week to ensure that all gaseous compounds were effectively removed. The liquid from the PILS was directly fed to the loops of two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA). The 1000 µl loops were used to collect representative sample for subsequent IC analyses. With the PILS-IC system, the concentrations of sulfate, nitrate, chloride, sodium, ammonium, potassium, oxalate and methane sulphonate (MSA) could be determined with a 15 minute time resolution. The quantification limit for the ions was 2.5 ng ml^{-1}, which equals to air concentration of 0.05 µg m^{-3}. The uncertainty of the PILS-IC results was estimated to be 15 % for all of the analyzed ions.

4.6.1.2. PILS-TOC-IC

In the PILS-TOC-IC system (paper III) a liquid sample from one PILS (Metrohm Peak Inc) was shared by the Shimadzu TOC-V$_{CPH}$ analyzer and two Dionex ICS-2000 ion chromatographs to enable simultaneous high-time-resolution measurements of WSOC and water-soluble ions (Fig. 1). The concentrations of WSOC and ions were measured with the PILS-TOC-IC during the spring 2009 campaign for a month (April 25 - May 28, 2009).

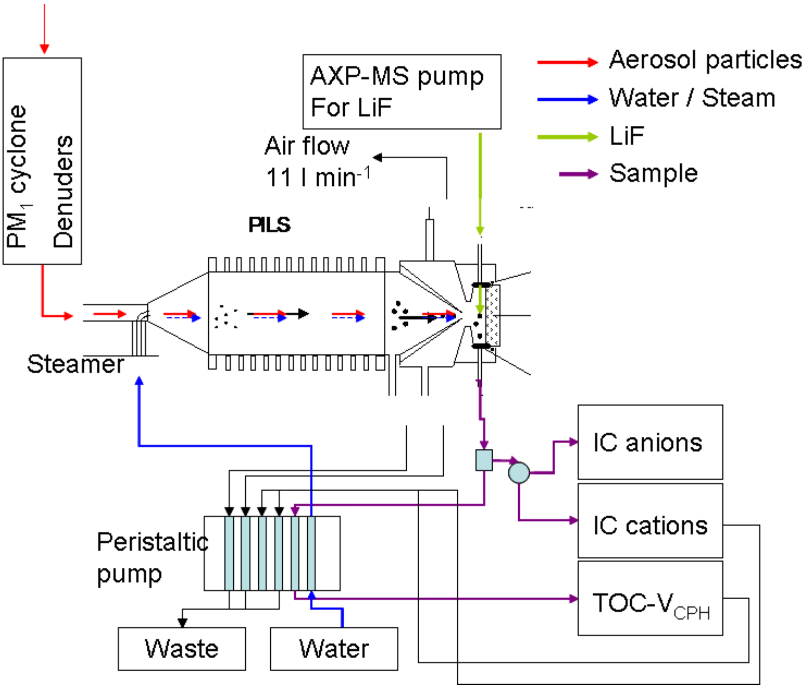

Figure 1. Measurement setup for PILS-TOC-IC (Particle-into-liquid sampler combined with TOC-V$_{CPH}$ and two ion chromatographs)

A cyclone (sharp cut cyclone SCC 1.829, BGI Inc. USA) was used to cut off supermicron particles (D_a > 1 µm) prior the PILS. After the cyclone, the sample flow (11 l min^{-1}) was directed through a parallel plate carbon filter denuder (Sunset Laboratory Inc., Portland, OR) and an annular denuder (URG-2000, 30x242 mm, Chapel Hill, NC) coated with H_3PO_4 to remove gaseous organic components and ammonia from the sample. After the denuders, the line was divided into a sample line and blank line. The sample-line fed the airflow directly to the PILS. In the blank-line the airflow was directed first through a PTFE filter (type FS, diameter 47 mm, pore size 3 µm, Millipore, Ireland) and subsequently fed to the PILS. When blank values were measured, a valve was used to force the airflow through a PTFE filter. The blank value was measured for approximately one hour every day during the weekdays. Dilution of the sample liquid in the PILS impaction plate was calculated from the IC measurements using the LiF concentration prior and after the PILS and the same multiplier was used for the WSOC results. After impaction to the quartz surface, the sample-liquid was delivered into a debubbler to remove air and to divide the liquid-flow into two separate lines. One of the lines was directed to the TOC-V_{CPH} analyzer and the other was split between two ion chromatographs.

4.6.2. Semicontinuos EC/OC carbon aerosol analyzer

A semicontinuous EC/OC carbon aerosol analyzer (Sunset Laboratory Inc, Oregon) was used to measure the concentrations of elemental carbon (EC) and organic carbon (OC) with a three hour time resolution (Papers II-V). The sample is collected to a filter mounted in the instrument for 160 minutes. After the collection, the sample is purged with helium while the temperature is increased step-wise to 850º C. The vaporized organic carbon is converted to CO_2 in the oxidizing oven (MnO_2). The CO_2 is subsequently detected with a non-dispersive infrared (NDIR) detector system. At the second stage the sample is purged with a helium-oxygen mixture while the temperature is increased again to 850 ºC to oxidize the elemental carbon from the filter. The CO_2 is detected with the NDIR detector.

4.6.3. Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; DeCarlo et al., 2006) was used to determine the concentrations of major species (POM, sulfate, nitrate, chloride, and ammonium) in the fine particulate matter during the spring 2009 campaign (Paper III). The HR-ToF-AMS measurements were done from April 9 to May 8, 2009 at the SMEAR III station. In the HR-ToF-AMS, aerosol particles are sampled through an aerodynamic lens. The aerodynamic lens forms a narrow particle beam that is transmitted into the detection chamber, in which the non-refractory species are flash-vaporized upon impact onto a hot surface (600ºC) under high vacuum. After electron impact ionization (70 eV) the composition is subsequently analyzed with time-of-flight mass spectrometer.

The HR-ToF-AMS has two ion optics modes. The V-mode is a single-reflection configuration with higher sensitivity and lower resolving power (up to ~2000 at *m*/*z* 200), and the W-mode is a two-reflectron configuration with higher resolving power (up to ~4000 at *m*/*z* 200) but lower sensitivity. The time resolution of the AMS was set to 5 minutes and the instrument was alternating between the V-mode (2.5 min) and the W-mode (2.5 min). In this study, five-minute average results of the unit mass resolution data from V-mode were used. The detection limits for submicrometer aerosol particles are < 0.04 µg m^{-3} for all species in the V-mode and < 0.4 µg m^{-3} in the W-mode. A collection efficiency (CE) value is required for the estimation of aerosol mass concentration measured by the AMS. Based on recent studies collection efficiency of aerosol mass spectrometer is affected by particle incomplete vaporization, lens transmission effects (impaction, diffusion, and focusing) and particle phase and morphology (Matthew et al., 2008, Cross et al., 2009). Based on comparison with other instruments (PILS, RT-ECOC, TEOM) and previous studies (Canagaratna et al., 2007 and references therein) a collection efficiency of 0.5 was used for the data.

4.6.4. TEOM

During the 2006-2007 campaign (Papers I, II, IV, V) a tapered Element Oscillating Microbalance equipped with a Filter Dynamics Measurement System (FDMS) (TEOM© 1400a, Patashnick and Rupprecht, 1991) was used to continuously measure $PM_{2.5}$ mass concentration. In the Tapered Element Oscillating Microbalance (TEOM) the sample is collected to a filter that is placed on top of the oscillating tapered cone. The oscillation frequency of the cone depends on the weight of the sample on the filter and therefore the increase in mass can be calculated from the changes in the oscillation frequency. In the FDMS TEOM the flow is directed through the Sample Equilibration System (SES) dryer to the TEOM for the first six minutes and the nonvolatile mass is measured. For the next six minutes the flow goes through a filter, where all the particles are removed, and the mass volatilized from the collection filter is measured. The mass evaporated from the filter is added to nonvolatile mass to achieve a real $PM_{2.5}$ concentration. A virtual impactor (VI, Loo & Cork, 1988) was used prior to the TEOM to cut off large particles ($D_p > 2.5$ µm).

During the spring 2009 campaign (Paper III) the TEOM model 1400ab (Rupprecht & Patashnick Co. Inc, USA) was used. The results of the TEOM are not corrected for evaporation of semivolatile aerosol compounds. A $PM_{1.3}$ virtual impactor (VI; Modified from Loo and Cork, 1988) was used to cut off the supermicron particles. In comparison with the other instruments, 30 minute average data were used. $PM_{2.5}$ measurements with the TEOM equipped with both the SES and the FDMS systems have shown to compare very well with other real-time automatic analyzers accounting semivolatile matter (Grover et al., 2006, Wilson et al., 2006). Based on the results of Grover et al. (2006), Wilson et al. (2006) and comparison with other instruments measuring parallel, the uncertainty of the PM mass concentrations measured with the TEOM was estimated to be 10 % for TEOM+FDMS system and 20% for TEOM.

4.6.5. Aethalometer

A single-wavelength aethalometer (model AE-42, Magee Scientific; Hansen et al., 1984) using the wavelength of 880 nm was used to measure black carbon concentrations. The time-resolution of the measurements was five minutes and the flow rate was 5.0 $l\ min^{-1}$. 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 using a mass absorption efficiency of 16.6 $m^2\ g^{-1}$. Based on the comparison with other instruments, the uncertainty of the results was estimated to be 20 %.

4.7. Data analysis

A positive matrix factorization method (PMF) was used to explore the sources or similar chemical characteristics of organics obtained from the HR-ToF-AMS. Also the sources of OC and WSOC during 2006-2007 campaign were evaluated using PMF. The PMF is a least-squares-based factor analysis model, where the goal is to resolve the mixture of sources that contributes to PM samples. The PMF has been used extensively for a source apportionment of ambient particulate matter (e.g. Aiken et al., 2009; Gu et al., 2011). The PMF method is described in detail by Paatero (1997 and 1999).

The EPA PMF 1.1 program was used to run the PMF on the 2006-2007 OC data (Paper IV). The samples collected during intensive forest fire episodes were excluded from the data set, after which the data consisted of 230 samples and 11 variables (OC, WSOC, EC, levoglucosan, sulfate, oxalate, ammonium, potassium, ozone, nitrogen monoxide and nitrogen dioxide). The best fit was found for four factors, explaining 88–100% of the variation. The uncertainties used for the PMF analysis were in range of 5–15%, the lowest percentage estimated for sulfate and the largest for WSOC and levoglucosan.

The IGOR 6.11 (Wavemetrics, Lake Oswego, OR), Squirrel 1.47 and PIKA 1.10 (Sueper, 2009) were used to analyze the spring 2009 campaign HR-ToF-AMS data. The PMF analysis (Lanz et al., 2007, Ulbrich et al., 2009) was conducted for both unit mass resolution and high-resolution spectra of the V-mode of organics. The results of the V-mode high-resolution spectra were better, and hence only those are used in this thesis.

5. RESULTS AND DISCUSSION

5.1. New method for quantifying WSOC

Previously, two different methods have commonly been used for the determination of WSOC from samples collected on filters. The WSOC can be extracted from filter with water and the WSOC content of water-solution can be analyzed (e.g. Miyazaki et al., 2006, Salma et al., 2007, Peltier et al., 2008). Indirectly, WSOC can be measured with a thermal method by measuring first the total organic carbon concentration on the filter and then extracting WSOC fraction from a filter and analyzing the concentration of WISOC remaining on filter (WSOC=TC-WISOC) (e.g. Szidat et al., 2006, Yttri et al., 2009).

In order to test the suitability of the new NPOC-method to WSOC analyses the results of TOC-V_{CPH} (direct extraction) were compared with those of TOA (WSOC indirectly measured; WSOC=TC-WISOC) (N=11). The agreement between the methods, TOA and TOC-V_{CPH}, was good and independent of the concentration level of carbon on the filter (Fig.2).

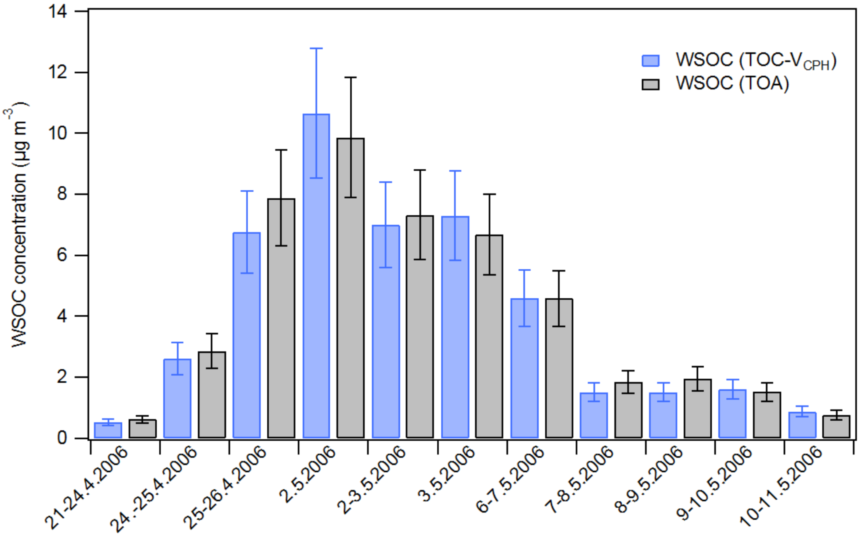

Figure 2. WSOC concentrations measured from the same sample with two different instruments, TOA and TOC-V_{CPH}

For TOA, the sum of WSOC and WISOC was close to the corresponding OC (average ± standard deviation was 97 ± 7.6 % of OC). It seems that both methods give reliable results, but compared with the thermal-optical method, the advantage of the TOC-V_{CPH} analyzer is that the WSOC analysis can be done directly from the water solution. It is easier and more accurate to extract the sample by water and to measure WSOC from a primary water-solution. The direct WSOC analysis also minimizes the contamination risk.

The WSOC results of two different collection methods, the MOUDI (72 h sampling duration) and the PM_1 filter samples (24-72 h sampling duration), were in a good agreement (r=0.99; Fig. 3). The MOUDI PM_1 WSOC result was 101 ± 19 % (average ± standard deviation) of the corresponding PM_1 result. The results of PM_1 filters and MOUDI were comparable also for the inorganic ions. The measured sulfate concentration for the MOUDI samples was 89 ± 17 % of the corresponding PM_1 samples.

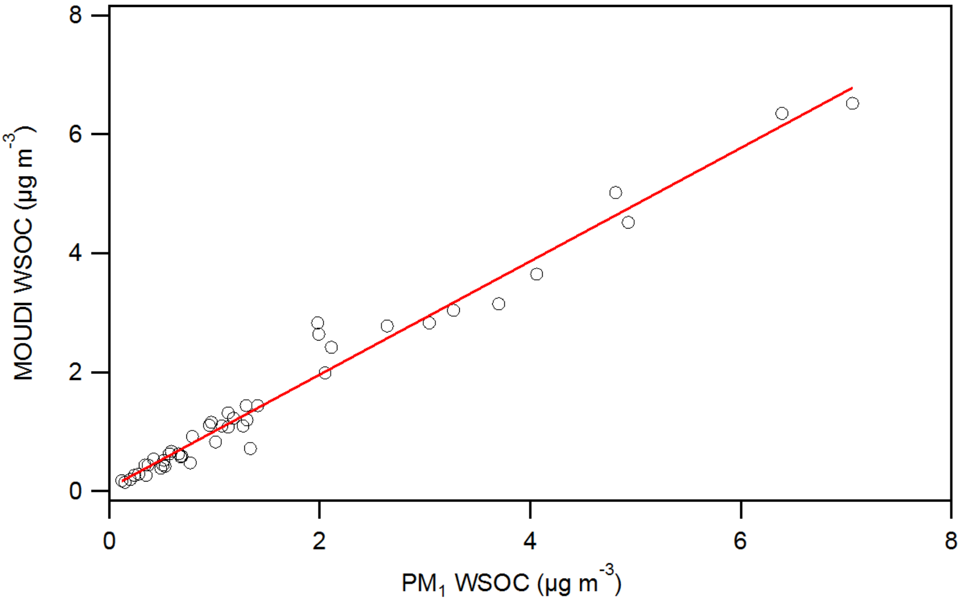

Figure 3. Correlation between WSOC concentrations measured from collected MOUDI and PM_1 samples.

5.2. Water-soluble organic carbon

Although WSOC is one of the major components of ambient aerosol particles, only a small number of papers have been published about WSOC measurements. To our knowledge, long-term measurements of WSOC have not been previously conducted in northern Europe. One of the aims of this study was to explore the properties of WSOC fraction in the northern Europe boreal region and to determine the factors affecting the WSOC concentrations. The PM_1 concentration and size distributions of WSOC were measured for a period of one year (Paper II). In order to estimate the amount of particulate organic matter (WSPOM), WSOC concentrations were multiplied by estimated average molecular weight per carbon weight in aerosol particles. For simplicity, the constant ratio of 1.6 was used in this work, based on calculations published by Turpin and Lim, (2001) and Saarnio et al. (2010), but the ratio may vary and is likely to be higher e.g. depending on the aerosol aging.

Figure 4 represents time series of WSOC, OC and WSOC/OC –ratio. The WSOC concentration was 1.47 ± 1.72 µg m^{-3} (average ± standard deviation), but it showed a large variation. The largest values, up to 11 µg m^{-3}, were measured during the forest fire episodes in spring and autumn. During the measurement campaign, on average 56 % of OC was water-soluble.

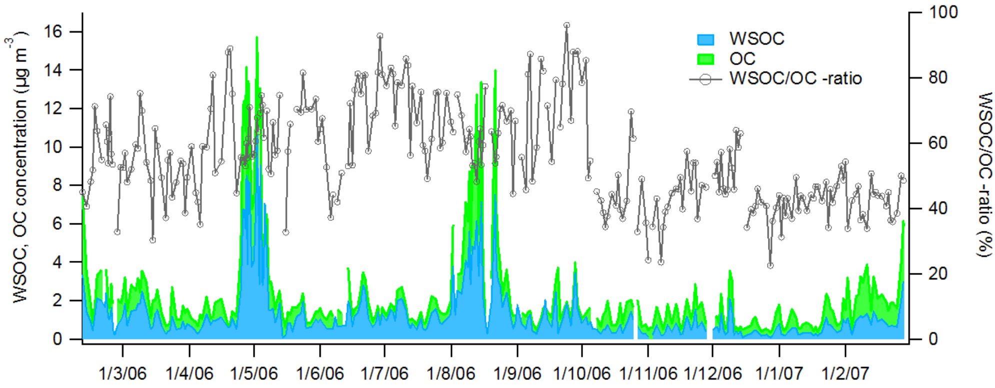

Figure 4. Concentrations of WSOC and OC and the WSOC/OC -ratio from March 2006 to February 2007 at SMEAR III in Helsinki. OC and WSOC were analyzed from the daily PM_1 filter samples.

The WSOC/OC –ratio had a clear seasonal variation, the lowest mean WSOC/OC –ratios being observed in winter (0.46) and the highest (0.70) in summer (the WSOC/OC -ratios measured during the biomass burning episode were excluded from the calculations of the seasonal WSOC/OC –ratios).

Before this work, no long-term measurements of WSOC size distributions in the northern European boreal region have been published, although this region has been recognized as one of the most effective emitters of biogenic VOCs (Hakola et al., 2003, Tunved et al., 2006). In this study, measured WSOC size distributions were clearly bimodal with a dominating accumulation mode between 0.1-1 µm and a small coarse mode (Paper II). Figure 5 represents the concentrations of WSPOM, inorganic ions and unidentified mass in the fine (PM_1) and coarse (PM_1-PM_{10}) fractions (upper and lower panels, respectively).

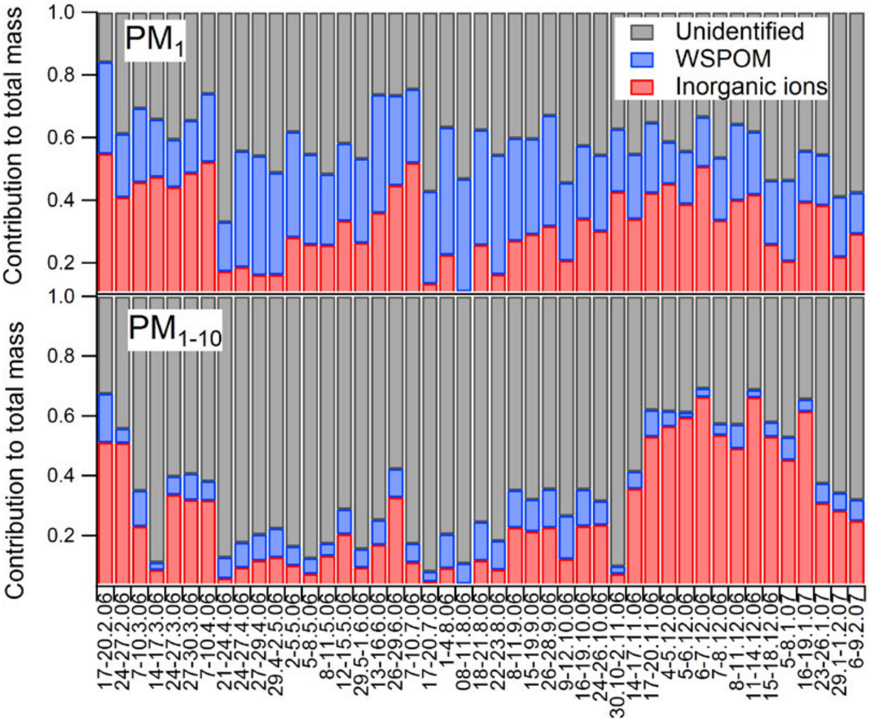

Figure 5. The contributions of WSPOM, inorganic ions and mass in fine (PM_1, upper panel) and coarse fractions ($PM_{1-10,}$ lower panel) for each MOUDI collection

The unidentified fraction contains water-insoluble compounds (e.g. elemental carbon, water-insoluble organic carbon and trace metals) that were not measured from MOUDI samples. In the size distributions, most of the WSOC is attributed to submicron particles. Water-soluble particulate organic matter (WSPOM, WSOC multiplied by 1.6) comprised 25 ± 7.7 % and 7.5 ± 3.4 % of aerosol PM_1 mass and the PM_{1-10} mass, respectively. Inorganic ions contributed 33 ± 12 % and 28 ± 19 % of the analyzed PM_1 and PM_{1-10} aerosol mass, respectively.

5.3. Sources of water-soluble organic carbon in European boreal region

In order to achieve a better understanding of the variability in the size-distributions of WSOC, the samples were divided into five categories according to air-mass back trajectories and the results from the chemical analyses. The categories represented the most likely sources of particulate matter (PM) and WSOC in Finland: long-range transported (LRT) aerosol particles, biomass burning aerosol particles originating from wild land fire episodes and local small-scale wood combustion, and particles originating from marine areas and from the clean arctic areas (Paper II). Clear differences in the WSOC concentrations and size distributions originating from these different sources were observed (Fig 6), demonstrating that concentrations and size distributions of WSOC are dependent on the source and age of aerosol particles.

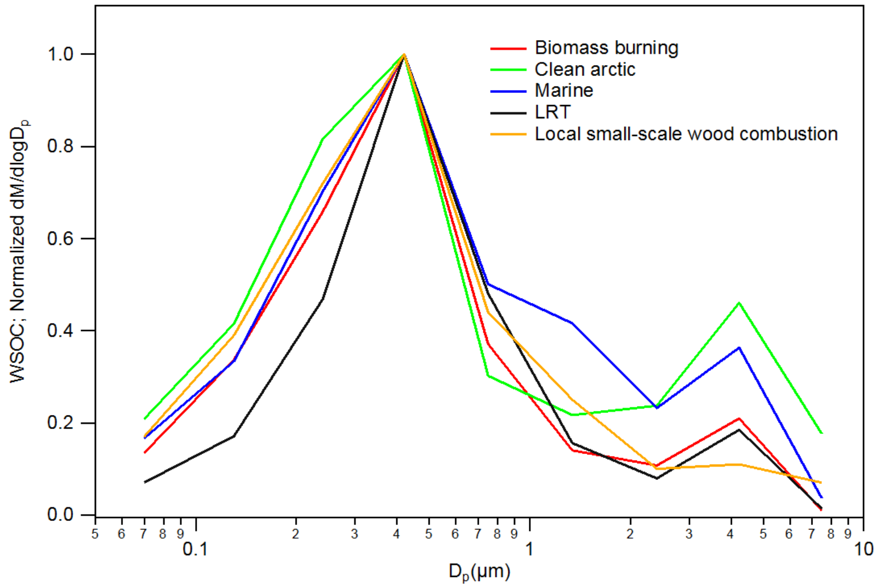

Figure 6. The size distributions of WSOC measured for aerosol particles emitted from different source areas

Biomass burning emissions are a major source of ambient aerosol particles especially during winter time in Finland (Paper IV). Long-range transported biomass burning emissions from forest fires in southern Russia or Europe are typically observed during spring and summer time. In 2006 two major biomass burning episodes (April 25-May 10, 2006 and August, 1-28, 2006) were observed (Saarikoski et al. 2007, Saarnio et al. 2010). High WSOC concentrations were measured during the biomass burning episodes. Also the relative amount of water-soluble organic compounds was elevated compared with PM and the sum of inorganic ions, indicating that large amounts of water-soluble organic compounds were produced during the burning process itself or during the subsequent atmospheric transportation (Fig. 7). From the size distributions, the enrichment of WSOC in ultrafine particles was observed both in the aerosol particles originating from the wild land fire areas and local small-scale combustion for residential heating (Fig. 6). Clear differences between local biomass burning (domestic heating) emissions and long-range transported emissions were seen. Larger WSOC/OC –ratios (on average 0.64) were observed for aerosol particles originating from the wild land fires than for particles originating from the local small-scale combustion (on average 0.49). The smallest WSOC/OC –ratios (on average 0.30) were measured in laboratory for fresh biomass burning emissions from a small masonry heater (Frey et al., 2008). This indicates that atmospheric oxidation processes increase the water-solubility of the organic compounds as aerosol particles ages during the long-range transport.

The highest WSOC concentrations together with high WSOC/mass and WSOC/OC -ratios were measured in summer, especially in the ultrafine particles (Paper II, IV). The observations support the idea that a higher biogenic activity will increase the condensation growth of aerosol particles and therefore increase the mass of particles (Kulmala et al., 2004). It seems that a substantial amount of mass that condenses on particles is water-soluble, or is transformed to a water-soluble form by oxidation after condensation.

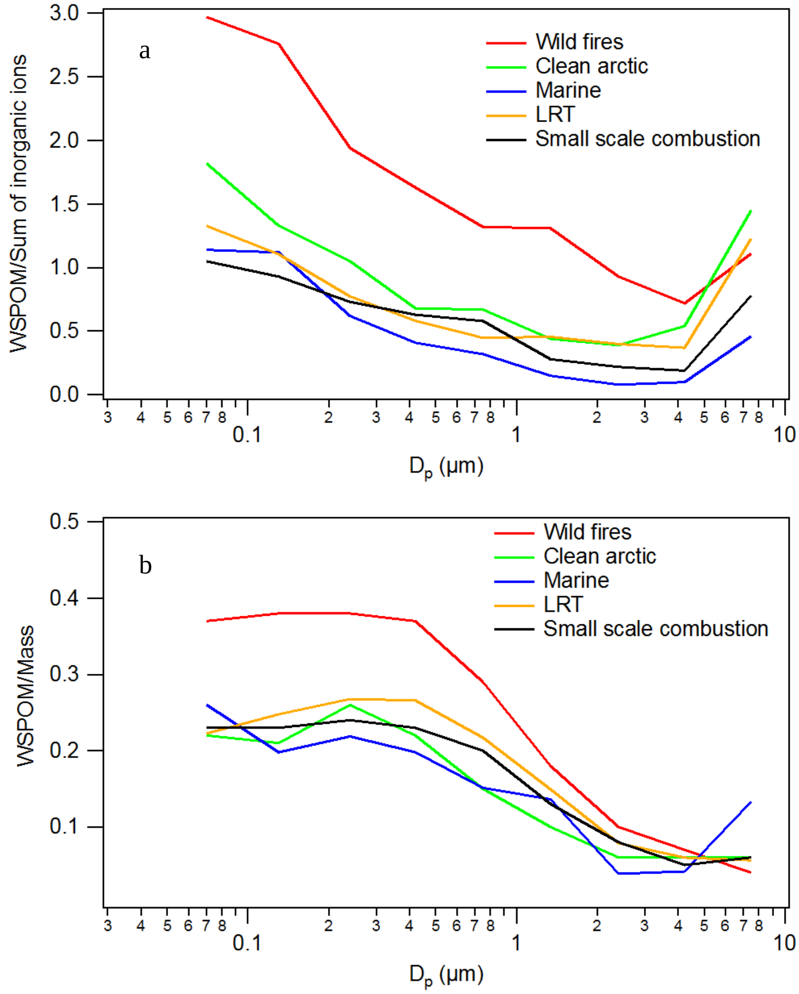

Figure 7. The WSPOM/sum of inorganic ions (a) and WSPOM/mass –ratios (b) for different source areas observed during the MOUDI collections.

During the LRT episodes the size distributions of WSOC were typically dominated by accumulation mode particles originating from various primary and secondary sources along the way to the measurement site (Fig. 6). The size distributions of WSOC and sulfate were similar, indicating that WSOC was clearly internally mixed with sulfate in the LRT particles. Typically both condensation and cloud processing accumulate material to the accumulation mode as a function of time, which also explains enrichment of the WSOC into the accumulation mode.

5.4. Water-solubility of the organic aerosol emitted from different sources

A big problem with the filter collections is their poor time resolution. Due to the low time resolution filter methods do not provide enough information in order to satisfactorily explain the constantly evolving situation in atmosphere. In order to achieve a better time resolution for WSOC and ion measurements, a particle-into-liquid sampler was coupled with a total organic carbon analyzer (TOC) and two ion chromatographs (IC) to enable high-time-resolution measurements of water-soluble ions and water-soluble organic carbon by a single sampling and analytical set-up (Paper V). During the spring 2009 measurement campaign, the characteristics, sources and water-solubility of submicron organic aerosol (OA) were studied using the online measurement devices, PILS-TOC-IC, RT-ECOC, TEOM and HR-ToF-AMS.

The new high-time-resolution measurement system, PILS-TOC-IC, was able to provide essential chemical and physical information about fast changes in the composition, concentrations and likely sources of the water-soluble fraction of atmospheric aerosol. The high time resolution (6 min for WSOC and 15 min for ions) of the measurements provided data that could follow the rapid changes in WSOC and ion concentrations. Also, by coupling one PILS simultaneously to two instruments, the amount of work is reduced and the reliability of the measurements is increased. The high-time-resolution data of WSPOM enables observation of diurnal variations and comparison of the data with gas-phase compounds typically measured continuously as well as with the meteorological data. Moreover, the online sample analyses minimized the contamination risk (common in handling and storage of samples in offline methods) and the sampling artifacts (like evaporation and absorption of organic gases).

The results of PILS-TOC-IC were compared with the results of the HR-ToF-AMS (Fig. 8). For sulfate, nitrate and ammonium, the correlation between the PILS-TOC-IC and AMS was excellent (0.93, 096 and 0.96, respectively). Also the POM (AMS) and WSPOM (PILS-TOC-IC) results correlated reasonably (r=0.66).

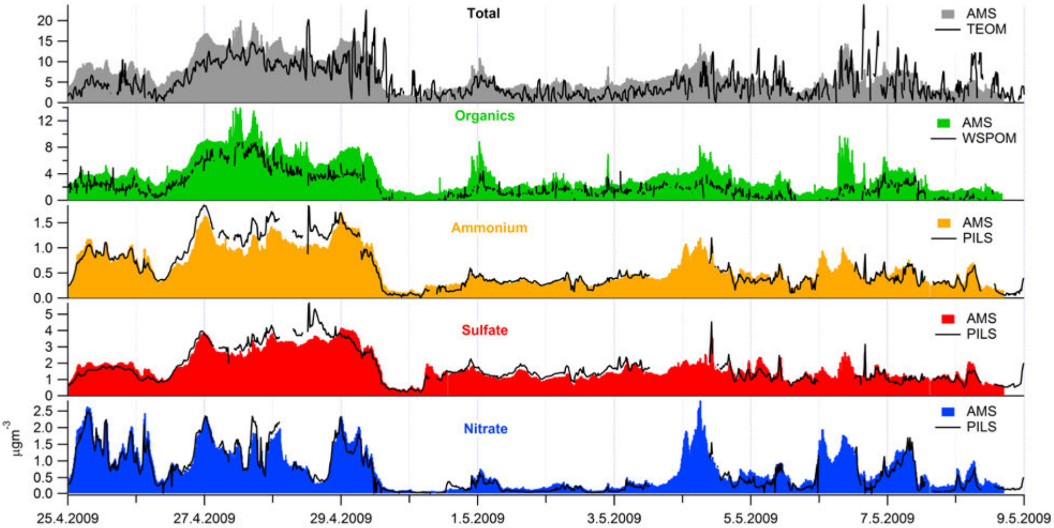

Figure 8. Concentrations of major ions and WSPOM (using conversion factor 1.6 to convert WSOC to WSPOM) measured by PILS-TOC-IC and AMS from April 25 to May 8, 2009. PILS-TOC-IC (ions, WSPOM) and TEOM (total mass) results are marked with the black line. AMS results are marked with colors (blue=nitrate, red=sulfate, yellow=ammonium, green= total organics, grey = total mass i.e. sum of ions and organics).

Similar sources or atmospheric processes affecting the concentration of organic aerosol were investigated by applying Positive Matrix Factorization (PMF) on the high-resolution spectra of the HR-ToF-AMS organics. Altogether 9 factors were needed to describe the variation in the dataset (Fig. 9). The factors were compared to measured reference mass spectra and were correlated with tracer species of the aerosol and gas phase measurements from collocated instruments. The identified factors included hydrocarbon-like OA (HOA), less oxygenated semivolatile OOA II, local and long-range transported biomass burning OA (local and LRT BBOA). Four factors represented oxygenated fraction of OA. OOA 1a and OOA 1b represented typical highly oxidized fraction, with low volatility and a mass spectrum similar to fulvic acid. In addition to these, one OOA I included MSA (called OOA I + MSA), indicating that aerosol might originate from the Baltic Sea. It was also noticed that the wind direction was from the sea (S and SW) when contribution of the OOA I + MSA factor was higher. In addition PMF found one OOA I with a clear nitrogen signal (N-content OOA I). One factor was observed to represent the emissions from a nearby coffee roastery, since its mass spectra (MS) resembled that of caffeine (NIST Chemistry WebBook, http://webbook.nist.gov/chemistry). Additionally, the wind direction during high contribution of that factor was always from the coffee roastery located only 2 km from the SMEAR III.

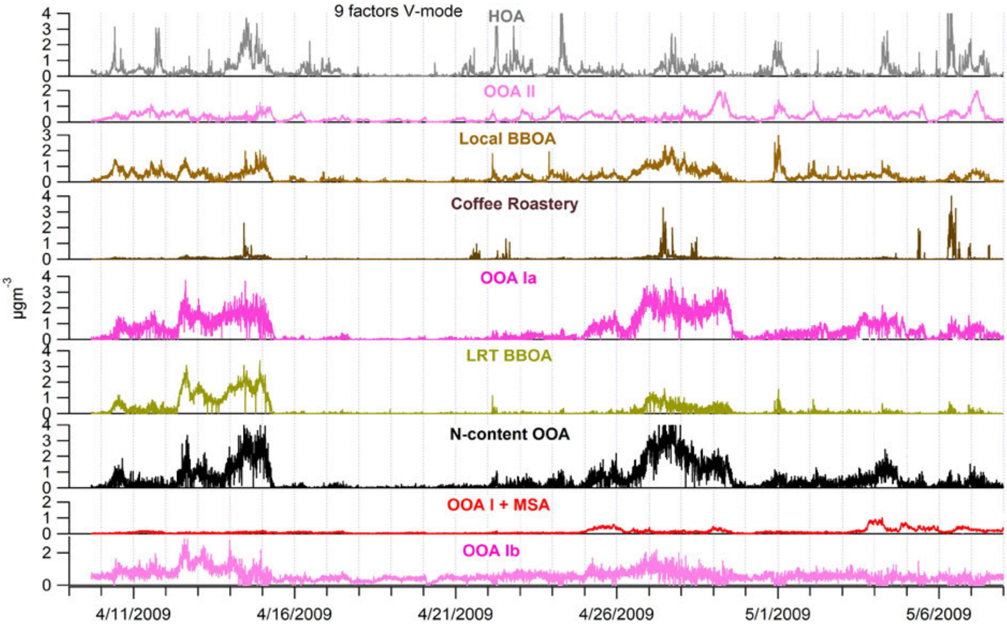

Figure 9. The time series of factors during the spring 2009 campaign

The OM to OC –ratios were calculated for each factor. High OM:OC ratios (1.9-2.1) were observed for highly oxidized water-soluble fractions, whereas this ratio was clearly lower (1.2-1.4) for local fresh sources, like traffic (Table 5). For the local BBOA and LRT BBOA, the OM:OC –ratios were 1.5 and 1.9, thus indicating that the OM:OC –ratio increases as the aerosol ages.

Table 5. OM:OC –ratios for each factor during spring 2009 campaign

Factor	OM:OC -ratio
OOA Ib	1.9
OOA I + MSA	2.0
N-content OOA I	2.1
LRT BBOA	2.0
OOA Ia	2.1
Coffee Roastery	1.4
Local BBOA	1.6
OOA II	1.4
HOA	1.2

Simultaneous measurements of WSOC and AMS organics provided a possibility to evaluate the solubility of organic fractions recognized by PMF. In this study, the factors representing highly oxidized aerosol particles or originating from biomass burning (OOA Ia, N-Content OOA I, LRT BBOA and local BBOA) were clearly correlated with WSPOM (r= 0.77-0.86), whereas HOA, coffee roastery, OOA Ib, OOA II, and OOA I + MSA had clearly lower correlation with WSPOM (r=0.1-0.4). The concentration of WSPOM cannot be directly derived from the AMS results. However, using the PMF factors, the time series of WSPOM could be reconstructed from the AMS data (Fig. 10). Multiple Linear Regression (IGOR 6.11) was used to estimate the coefficients a, b, c, d, e, f, g, h and i in the following equation:

$$Y=a*X_1 + b*X_2 + c*X_3 + d*X_4 + e*X_5 + f*X_6 + g*X_7 + h*X_8 + i*X_9.$$

The following multipliers were obtained for the factors:
WSPOM= 0.66 * OOA Ib + (-0.42) * OOA I + MSA + 0.88 * N-Content OOA I + 0.98 * LRT BBOA + 0.66 * OOA Ia + 0 * coffee roastery + 0.86 * BBOA + 0.33 * OOA II + 0.16 * HOA.

The correlation between the reconstructed WSPOM and the measured WSPOM was good (r=0.93), indicating that the amount of water-soluble organic carbon can be extracted from the AMS data. However, further studies are needed to test the applicability of the multipliers in different environments with different sources.

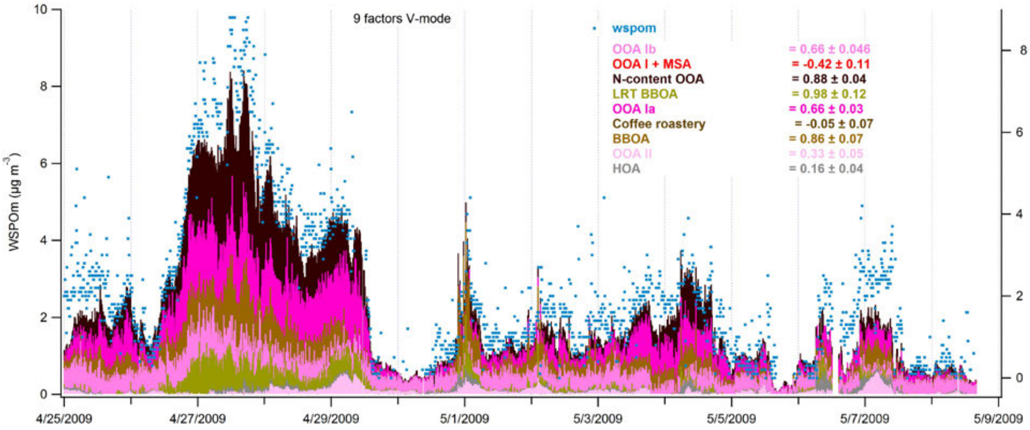

Figure 10. The measured time-series of WSPOM (PILS-TOC-IC) and the WSPOM time-series reconstructed from the PMF factors derived from the AMS POM data.

5.5. High-time-resolution measurements of ions and carbonaceous compounds

Year-long intensive measurements of chemical composition (PILS-IC, RT-ECOC and TEOM) of submicrometer particles were conducted at the SMEAR III urban background station in Finland 2006-2007. The aim of the study was to measure diurnal and seasonal changes in the composition of ambient aerosol particles and to compare the results of the online measurement devices with to those of traditional PM_1 filter collections in order to validate the new online methods and to study the sampling artifacts.

The errors and uncertainties in filter collections have been studied extensively during the last decades (e.g. Hering and Cass, 1999, Pathak and Chan 2005, Viana et al., 2006), but online methods offer new challenges. The online sample collection methods are relatively novel and different kind of sampling artifacts have to be taken into account. Due to the short integration times, concentrations to be determined in these online samples are very low and often close to the detection limits of the analyzing methods.

The results of the PILS agreed well with the filter measurements for non-volatile species (e.g. sulfate), but larger discrepancies were observed for semivolatile nitrate and ammonium.

Sulfate measured from the filters was 18 % higher than that from the PILS-IC, whereas nitrate and ammonium were 41 and 9.1 % lower when compared to the PILS results. Due to short collection times (15 min) in the PILS, many species like oxalate, sodium and chloride concentrations were most of the time too low and could not be quantified accurately.

The results of RT-ECOC correlated well (r =0.98) with the OC and EC measured from the PM_1 filters. For OC the results of the RT-ECOC were on average 10 % larger than those of the filters. EC results measured from PM_1 filter samples, BC measured by RT-ECOC and BC measured with aethalometer correlated well.

Long time series provided information about the diurnal and seasonal changes. A clear diurnal cycle was observed only for nitrate and EC, with maxima between 06:00 and 09:00 AM local time (Fig 11. diurnal cycle for nitrate). For nitrate the peak in concentration in the morning was most pronounced when the nitrate concentrations were large in winter and spring. The decrease in the afternoon could clearly be seen in fall, but in summer the nitrate concentrations had no diurnal changes. The diurnal cycle of EC, with a clear maximum at weekdays during the rush hour (06:00 and 09:00 AM local time), indicates that traffic was likely to be the major source of EC. A similar diurnal cycle for BC has been measured in SMEARIII in previous study by Järvi et al. (2008).

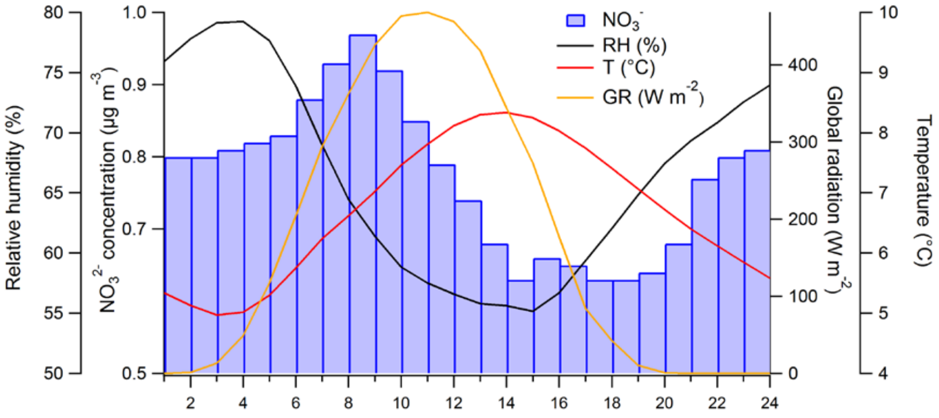

Figure 11. The diurnal cycle of nitrate, RH (%), T (°C) and global radiation (W m^{-2})

The seasonal differences in aerosol composition during the measurement campaign were substantial. The largest ion, EC and OC concentrations were measured during winter. The lowest concentrations for all compounds, except for OC, were measured in summer. Therefore, the average contribution of OC was largest in summer. The high potassium concentrations in winter indicate that the local biomass burning for domestic heating was likely to elevate aerosol particle concentrations in winter. The EC concentrations were 82 ± 41 % higher in winter than in summer, on average. This is an indication of extra source in winter (wood combustion) coinciding poorer mixing than during summer.

6. REVIEW OF PAPERS AND AUTHOR’S CONTRIBUTION

Paper I describes the method developed to measure the concentration of WSOC in ambient aerosol samples and the first results. The WSOC results of the new method were observed to correlate well with the results measured with the thermal method. I developed the method and analyzed the samples. I also wrote the article.

Paper II contains the chemical characterization (gravimetric mass, ions, WSOC) of year-long measurement period of size-segregated samples collected with a MOUDI impactor conducted at the SMEAR III station. Different size distributions were measured for aerosol particles originating from different sources or source areas. Also large seasonal differences in the size distributions and in the contribution of WSOC were observed. I was in charge of the MOUDI-collections, I did the WSOC analyzes as well as wrote the article.

Paper III describes the new online method, PILS-TOC-IC, developed to measure WSOC and ion concentrations of ambient aerosol particles online. The results of PILS-TOC-IC were compared to those of other parallel online measurements, HR-ToF-AMS, RT-ECOC and TEOM. The online measurements provided information about the sources and formation mechanisms of ambient aerosol particles. I was responsible for developing the method as well as sample collection in co-operation with my colleagues. I wrote the article about these measurements.

Paper IV describes the results of year-long measurements of OC, WSOC and EC in 2006-2007. The sources of OC and WSOC were studied using PMF. The main sources of OC and WSOC were SOA, biomass burning, LRT and traffic. The contribution of SOA was significantly larger for WSOC than for OC. In this paper I mainly contributed to the sampling and chemical analyses.

Paper V describes the results of the year long PILS-IC, RT-EC/OC, aethalometer and TEOM measurements conducted at the SMEAR III station. The results of the online methods were compared to those of daily filter samples. Measured long time series provided information about seasonal and diurnal changes as well as about differences between the used measurement techniques. I contributed to the sampling and chemical analyses along with my colleagues and I wrote the paper.

7. SUMMARY AND CONCLUSIONS

The main focus of this thesis was to characterize WSOC in an urban background environment in a boreal region and to further develop the existing methods to enable online measurements of water-soluble fraction (ions and WSOC) of atmospheric aerosol particles. The measurements of this thesis were made during two intensive campaigns.

Firstly, a method for the WSOC measurements was developed and tested. The TOC-V_{CPH} analyzer provided a fast and reliable method for WSOC determination from ambient aerosol samples collected on filter. The results of this new method were comparable with those of the thermal (TOA) method. The measurement campaigns provided information on WSOC concentrations, size distributions, characteristics and sources. WSOC was one of the main components in atmospheric aerosol particles, representing typically 50-60 % of OC and 25 % of the fine PM. The largest WSOC/OC -ratios were measured for the long-range transported pollution, indicating that the aging of particles increases the amount of WSOC due to further oxidation. WSOC had a bimodal size distribution with a clear accumulation mode below 1 µm of particle aerodynamic diameter and minor coarse mode at sizes >1 µm. The PM_1 concentrations of WSOC were dependent on the source of aerosol particles. Low concentrations (< 1 µg m^{-3}) were typically measured for particles originating from arctic or marine areas, whereas larger concentrations (1-5 µg m^{-3}) were measured for long-range transported aerosol particles and aerosol particles originating from biomass burning. WSOC was observed to have a seasonal cycle with a maximum in summer, likely due to SOA formation from biogenic VOC emissions. In winter biomass burning was the main source of WSOC.

Due to the obvious need for data with a better time resolution, a method was further developed to enable online measurement of WSOC and ions with a good time resolution. Parallel to the WSOC measurements a suite of state-of-art devices (HR-ToF-AMS, PILS-IC, RT-ECOC, filter and impactor sampling) were used to get a chemical characterization of ambient aerosol particles during the measurement periods. Due to the good time resolution of all measurements, the results can be compared and they will complement each other. High-time-resolution data also makes it possible to study variations in concentrations and sources.

The AMS data analyzed with the PMF provided an important tool for the characterization of organic fraction of ambient aerosol particles. The concentration of WSOC was observed to correlate well with highly oxidized and aged fractions such as long-range transported biomass burning particles. In addition, high OM:OC ratios (1.9-2.1) were observed for the highly oxidized water-soluble fractions. The organics originating from local sources like traffic (HOA) did not correlate with WSOC and the observed OM:OC ratios were clearly lower (1.2-1.4).

The differences between filter collections and online methods were studied by comparing the results of simultaneous measurements. For non-volatile compounds, the results of online methods correlated well with the results analyzed from filters. Larger discrepancies were observed for semivolatile compounds, like nitrate. The online methods were observed to provide reliable and important data, especially on diurnal changes as well as on short pollution plumes.

To conclude, this thesis contains results of the first long-term measurements of WSOC in boreal region, northern Europe. The PILS sampling method provided a fast and reliable way for the online observation of ions and WSOC. Online measurement presented important data about temporal variations that cannot be resolved from filter data.

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