CHEMICAL CHARACTERISATION OF FINE PARTICLES FROM BIOMASS BURNING

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Title
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Abstract

Biomass burning has lately started to attract attention because there is a need to decrease the carbon dioxide (CO_2) emissions from the combustion of fossil fuels. Biomass is considered as CO_2 neutral fuel. However, the burning of biomass is one of the major sources of fine particles both at the local and global scale. In addition to the use of biomass as a fuel for heat energy production, biomass burning emissions can be caused, e.g. by slash-and-burn agriculture and wild open-land fires. Indeed, the emissions from biomass burning are crucially important for the assessment of the potential impacts on global climate and local air quality and hence on human health. The chemical composition of fine particles has a notable influence on these impacts.

The overall object of this thesis was to gain knowledge on the chemistry of fine particles that originate from biomass burning as well as on the contribution of biomass burning emissions to the ambient fine particle concentrations. For this purpose novel analytical methods were developed and tested in this thesis. Moreover, the thesis is based on ambient aerosol measurements that were carried out in six European countries at 12 measurement sites during 2002–2011. Additionally, wood combustion experiments were conducted in a laboratory. The measurements included a wide range of techniques: filter and impactor samplings, offline chemical analyses (chromatographic and mass spectrometric techniques, thermal-optical method), and online measurements of particles' physical properties and chemical composition (incl. particle number and mass concentrations and size distributions, concentrations of carbonaceous components, water-soluble ions, and tracer compounds).

This thesis presents main results of different studies aimed towards chemical characterisation of fine particle emissions from biomass burning. It was found that wood combustion had a significant influence on atmospheric fine particle concentrations in the Helsinki Metropolitan Area in the cold season. Especially in the residential areas local wood combustion emissions were occasionally substantial. A notable contribution of particles originating from wood combustion was detected both at suburban and urban areas caused by emissions that were distributed regionally or they were long-range transported. In addition to the wood combustion emissions, transported smokes from open-land fires in Russia and the Baltic countries affected the air quality in Helsinki in the warm season. Source-specific tracer compounds were used in the thesis for identifying the biomass burning source of fine particles. The most used tracer compounds were anhydrosugars (levoglucosan, mannosan, and galactosan) that originate specifically in the pyrolysis of cellulose and hemicelluloses, the main components of plant biomass.

In summary, the sampling and analytical methods needed for the online chemical characterisation of fine particles from biomass burning were developed in order to provide precise and prompt high-time-resolution information on biomass burning emissions. The results and the implications of this thesis provide new information on the concentrations and sources of fine particles in the boreal region.

ILMATIETEEN LAITOS

Nimeke
Biomassan palamisesta peräisin olevien pienhiukkasten kemiallinen määrittäminen

Tiivistelmä

Yleinen kiinnostus biomassan palamista kohtaan on kasvanut viime aikoina. Kiinnostuksen kasvun taustalla on tarve vähentää fossiilisten polttoaineiden aiheuttamia hiilidioksidipäästöjä (CO_2), sillä biomassaa pidetään CO_2-päästöjen suhteen neutraalina polttoaineena. Biomassan palaminen on kuitenkin yksi merkittävimmistä pienhiukkaslähteistä niin paikallisella tasolla kuin maa-ilmanlaajuisestikin. Sen lisäksi että biomassaa poltetaan lämpöenergian tuottamiseksi, syntyy biomassan palamisen päästöjä myös mm. kulotuksista ja metsäpaloista. On olennaista tietää, millaisia vaikutuksia biomassan palamisella on ilmastoon sekä paikalliselle ilmanlaadulle ja sitä kautta ihmisten terveydelle. Pienhiukkasten kemiallisella koostumuksella on huomattava merkitys näihin vaikutuksiin.

Tämän väitöskirjan yleisenä tavoitteena oli selvittää laaja-alaisesti biomassan palamisesta peräisin olevien pienhiukkasten kemiallista koostumusta sekä biomassan palamisen vaikutusta ilmakehän pienhiukkaspitoisuuksiin. Tätä tarkoitusta varten kehitettiin uusia analyyttisiä menetelmiä, joita testattiin ulkoilman pienhiukkasilla. Väitöskirjan aineisto perustuu hiukkasmittauksiin, joita tehtiin kuudessa Euroopan maassa 12:lla eri mittauspaikalla vuosien 2002–2011 aikana. Lisäksi tutkimukseen kuului laboratoriossa tehtyjä puunpolttokokeita. Mittausvälineistö koostui laajasta valikoimasta erilaisia tekniikoita: suodatin- ja impaktorinäytteenkeräyksiä, laboratoriossa tehtäviä analyysejä (kromatografisia ja massaspektrometrisiä tekniikoita, termis-optinen menetelmä) sekä mittauksia, joilla kyettiin mittaamaan lähes ajantasaisesti hiukkasten fysikaalisia ominaisuuksia ja kemiallista koostumusta (mm. hiukkasten lukumäärä- ja massapitoisuutta ja -kokojakaumia, sekä hiilipitoisten ainesosien, vesiliukoisten ionien ja merkkiaineiden pitoisuuksia).

Väitöskirjassa esitellään tärkeimmät tutkimustulokset, jotka tähtäävät biomassan palamisesta peräisin olevien pienhiukkasten kemialliseen karakterisointiin. Havaittiin, että puunpoltolla on merkittävä osuus ilmakehän pienhiukkaspitoisuuksiin pääkaupunkiseudulla kylmänä vuodenaikana. Erityisesti pientalovaltaisilla alueilla paikallisten puunpolton päästöjen osuus oli ajoittain huomattavan suuri. Puunpoltosta peräisin olevien joko alueellisesti levinneiden tai kaukokulkeutuneiden pienhiukkasten osuus oli huomattava sekä pientalo- että kaupunkikeskusalueilla. Puunpolton hiukkaspäästöjen lisäksi Venäjältä ja Baltiasta kulkeutuneet metsäpalo- ja kulotussavut heikensivät ajoittain ilman laatua Helsingissä, erityisesti lämpimän kauden aikana. Lähdespesifisiä merkkiaineita käytettiin tässä väitöskirjassa biomassan palamisen tunnistamiseen ilmakehän pienhiukkasista. Kasvibiomassan pääkomponenttien eli selluloosan ja hemiselluloosien palamisessa muodostuvat anhydrosokerit (levoglukosaani, mannosaani ja galaktosaani) olivat eniten käytetyt merkkiaineet tässä väitöskirjassa.

Väitöskirjassa kehitettiin näytteenkeräys- ja analyyttisiä menetelmiä, jotta biomassan palamisesta peräisin olevien pienhiukkasten kemiallista koostumusta pystyttäisiin havainnoimaan täsmällisesti entistä paremmalla aikaresoluutiolla. Tässä tutkimuksessa tuotettiin uutta tietoa pohjoisten alueiden pienhiukkasten pitoisuuksista ja lähteistä.

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ABBREVIATIONS AND DEFINITIONS

AMS	Aerosol mass spectrometer
APS	Aerodynamic particle sizer
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BkF	Benzo[k]fluoranthene
BC	Black carbon
BLPI	Berner low-pressure impactor
CE	Collection efficiency
CPC	Condensation particle counter
D_a	Aerodynamic diameter
DMA	Differential mobility analyser
DMPS	Differential mobility particle sizer
D_p	Particle diameter
EC	Elemental carbon
ESI	Electrospray ionisation
GC	Gas chromatograph/chromatography
HPAEC	High-performance anion-exchange chromatograph/chromatography
HPLC	High-performance liquid chromatograph/chromatography
HR-ToF-AMS	High-resolution time-of-flight aerosol mass spectrometer
HVCI	High-volume cascade impactor
IC	Ion chromatograph/chromatography
i.d.	Inner diameter
IdP	Indeno[1,2,3-cd]pyrene
ISTD	Internal standard
LOD	Limit of detection
LOQ	Limit of quantification
LRT	Long-range transport
MA, MAs	Anhydrosugar/-s (levoglucosan, mannosan, and galactosan)

me-β-ara	Methyl-β-D-arabinopyranoside
MOUDI	Micro-orifice uniform deposit impactor
MS	Mass spectrometer/spectrometry
m/z	Mass-to-charge ratio
NO_x	Nitrogen oxides (NO, NO_2)
OC	Organic carbon
PAH, PAHs	Polycyclic aromatic hydrocarbon/-s
PILS	Particle-into-liquid sampler
PM	Particulate matter
PM_1	Particles with D_a <1 µm; respectively PM_{10}, $PM_{2.5}$, $PM_{0.2}$, etc.
POM	Particulate organic matter
PTFE	Polytetrafluoroethylene (Teflon)
PUF	Polyurethane foam
RSD	Relative standard deviation
SC-OC/EC	Semicontinuous OC/EC field analyser
SD	Standard deviation
SIM	Selected ion monitoring
SMEAR	Station for measuring forest ecosystem – atmosphere relations
SOA	Secondary organic aerosol
SO_x	Sulphur oxides (SO, SO_2, etc.)
TEOM	Tapered element oscillating microbalance
TC	Total carbon
TOA	Thermal-optical carbon analyser
TOC-V_{CPH}	Total organic carbon analyser with a high-sensitive catalyst
VI	Virtual impactor
VOC	Volatile organic compounds
WISOC	Water-insoluble organic carbon
WSOC	Water-soluble organic carbon

Contents

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.

I   Saarnio K., Teinilä K., Aurela M., Timonen H. and Hillamo R. (2010) High-performance anion-exchange chromatography–mass spectrometry method for determination of levoglucosan, mannosan, and galactosan in atmospheric fine particulate matter. *Anal. Bioanal. Chem.* **398**, 2253–2264, doi:10.1007/s00216-010-4151-4.

II   Saarnio K., Teinilä K., Saarikoski S., Carbone S., Gilardoni S., Timonen H., Aurela M. and Hillamo R. (2013) Online determination of levoglucosan in ambient aerosols with Particle-into-Liquid Sampler – High-Performance Anion-Exchange Chromatography – Mass Spectrometry (PILS–HPAEC–MS). *Atmos. Meas. Tech. Discuss.* **6**, 5495–5527, doi:10.5194/amtd-6-5495-2013.

III   Saarnio K., Aurela M., Timonen H., Saarikoski S., Teinilä K., Mäkelä T., Sofiev M., Koskinen J., Aalto P.P., Kulmala M., Kukkonen J. and Hillamo R. (2010) Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe. *Sci. Total Environ.* **408**, 2527–2542, doi:10.1016/j.scitotenv.2010.03.010.

IV   Saarnio K., Niemi J.V., Saarikoski S., Aurela M., Timonen H., Teinilä K., Myllynen M., Frey A., Lamberg H., Jokiniemi J. and Hillamo R. (2012) Using monosaccharide anhydrides to estimate the impact of wood combustion on fine particles in the Helsinki Metropolitan Area. *Boreal Environ. Res.* **17**, 163–183.

V   Saarnio K., Sillanpää M., Hillamo R., Sandell E., Pennanen A.S. and Salonen R.O. (2008) Polycyclic aromatic hydrocarbons in size-segregated particulate matter from six urban sites in Europe. *Atmos. Environ.* **42**, 9087–9097, doi:10.1016/j.atmosenv.2008.09.022.

Other biomass-burning-related publications of the author <u>not</u> included in this thesis:

Saarikoski S., Sillanpää M., Timonen H., <u>Saarnio K.</u>, Teinilä K., Sofiev M., Karppinen A., Kukkonen J. and Hillamo R. (2007) Chemical composition of aerosols during a major biomass burning episode in northern Europe in spring 2006: Experimental and modelling assessments. *Atmos. Environ.* **41**, 3577–3589.

Saarikoski S., Sillanpää M., <u>Saarnio K.</u>, Hillamo R., Pennanen A.S. and Salonen R.O. (2008) Impact of biomass combustion on urban fine particulate matter in central and northern Europe. *Water Air Soil Poll.* **191**, 265–277.

Tissari J., Lyyränen J., Hytönen K., Sippula O., Tapper U., Frey A., <u>Saarnio K.</u>, Pennanen A.S., Hillamo R., Salonen R.O., Hirvonen M.-R. and Jokiniemi J. (2008) Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. *Atmos. Environ.* **42**, 7862–7873.

Frey A., Tissari J., <u>Saarnio K.</u>, Timonen H., Tolonen-Kivimäki O., Aurela M., Saarikoski S., Makkonen U., Hytönen K., Jokiniemi J., Salonen R.O. and Hillamo R. (2009) Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater. *Boreal Env. Res.* **14**, 255–271.

Vasconcellos P.C., Souza D.Z., Sanchez-Ccoyllo O., Bustillos J.O.V., Lee H., Santos F.C., Nascimento K.H., Araújo M.P., <u>Saarnio K.</u>, Teinilä K. and Hillamo R. (2010). Determination of anthropogenic and biogenic compounds on atmospheric aerosol collected in urban, biomass burning and forest areas in São Paulo, Brazil. *Sci. Total Environ.* **408***, 5836–5844.

Lamberg H., Nuutinen K., Tissari J., Ruusunen J., Yli-Pirilä P., Sippula O., Tapanainen M., Jalava P.I., Makkonen U., Teinilä K., <u>Saarnio K.</u>, Hillamo R., Hirvonen M.-R. and Jokiniemi J. (2011) Physicochemical characterization of fine particles from small-scale wood combustion. *Atmos. Environ.* **45**, 7635–7643.

Reche C., Viana M., Amato F., Alastuey A., Moreno T., Hillamo R., Teinilä K., <u>Saarnio K.</u>, Seco R., Peñuelas J., Mohr C., Prévôt A.S.H. and Querol X. (2012). Biomass burning contributions to urban aerosols in a coastal Mediterranean City. *Sci. Total Environ.* **427–428**, 175–190.

Other publications of the author <u>not</u> included in this thesis:

Shimmo M., <u>Saarnio K.</u>, Aalto P., Hartonen K., Hyötyläinen T., Kulmala M. and Riekkola M.-L. (2004) Particle size distribution and gas-particle partition of polycyclic aromatic hydrocarbons in Helsinki urban area. *J. Atmos. Chem.* **47**, 223–241.

Kuokka S., Teinilä K., <u>Saarnio K.</u>, Aurela M., Sillanpää M., Hillamo R., Kerminen V.-M., Pyy K., Vartiainen E., Kulmala M., Skorokhod A.I., Elansky N.F. and Belikov I.B. (2007) Using a

moving measurement platform for determining the chemical composition of atmospheric aerosols between Moscow and Vladivostok. *Atmos. Chem. Phys.* **7**, 4793–4805.

Riipinen I., Sihto S.-L., Kulmala M., Arnold F., Dal Maso M., Birmili W., Saarnio K., Teinilä K., Kerminen V.-M., Laaksonen A. and Lehtinen K.E.J. (2007) Connections between atmospheric sulphuric acid and new particle formation during QUEST III – IV campaigns in Heidelberg and Hyytiälä. *Atmos. Chem. Phys.* **7**, 1899–1914.

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

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

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

Aurela M., Sillanpää M., Pennanen A., Mäkelä T., Laakia J., Tolonen-Kivimäki O., Saarnio K., Yli-Tuomi T., Aalto P., Salonen I., Pakkanen T., Salonen R. and Hillamo R. (2010) Characterization of urban particulate matter for a health-related study in southern Finland. *Boreal Env. Res.* **15**, 513–532.

Timonen H., Aurela M., Carbone S., Saarnio K., Saarikoski S., Mäkelä T., Kulmala M., Kerminen V.-M., Worsnop D.R. and Hillamo R. (2010) 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.

Aurela M., Saarikoski S., Timonen H., Aalto P., Keronen P., Saarnio K., Teinilä K., Kulmala M., and Hillamo R. (2011) Carbonaceous aerosol at a forested and an urban background sites in Southern Finland. *Atmos. Environ.* **45**, 1394–1401.

Timonen H., Aurela M., Saarnio K., Frey A., Saarikoski S., Teinilä K., Kulmala M. and Hillamo R. (2011) Monitoring of inorganic ions, carbonaceous matter and mass in ambient aerosol particles with online and offline methods. *Atmos. Meas. Tech. Discuss.* **4**, 6577–6614.

Timonen H., Carbone S., Aurela M., Saarnio K., Saarikoski S., Ng N.L., Canagaratna M.R., Kulmala M., Worsnop D.R. and Hillamo R. (2013) Characteristics, sources and water-solubility of ambient submicron organic aerosol in springtime in Helsinki, Finland. *J. Aerosol Sci.* **56**, 61–77.

1. INTRODUCTION

Aerosol is a mixture of different sized suspended liquid or solid particles and the gas surrounding the particles. The size of an aerosol particle varies from few nanometres to several tens of micrometres. Aerosol particles affect climate and visibility, as well as air quality that is associated with the health effects of aerosols. The increasing level of particles may cause significant increase of human morbidity and mortality (e.g. Dockery et al., 1993; Pope et al., 2002). The health effects of particles depend on various factors, e.g. on their size, that defines the location at which they deposit within the respiratory system, and on their chemical composition.

Atmospheric particles can be formed in natural processes or caused by humans. One of the main particle sources at the global scale is biomass burning. The quantity, size, and composition of the emitted particles depend strongly on the combustion conditions as well as the quality of the burning material. On the boreal latitudes, like in Finland, wood combustion in residential houses is a major local biomass burning source. Other biomass burning sources in Finland are long-range transported smoke plumes from residential heating in Central and Eastern Europe and agricultural and wildfires in Russia and Eastern Europe.

The use of biomass to produce energy and heat is encouraged to increase in Finland. An increase in biomass use as an energy source holds the potential to reduce the emissions of fossil fuel combustion, since biomass combustion is currently not considered to affect the carbon dioxide (CO_2) balance in the atmosphere. However, one of the major problems with the biomass combustion is its tendency to emit an abundance of fine particles. For example in Finland, it has been estimated that 25% of all fine particle emissions originate from domestic wood combustion (Karvosenoja et al., 2008). If the amount of small-scale wood combustion increases and the heating of the houses with firewood becomes an everyday routine, the ambient fine particle concentrations will probably increase, especially in built-up residential areas. However, modern combustion appliances produce particulate emissions to a lesser extent and with different chemical composition than conventional combustion appliances.

Because of their impacts on climate and human health, the size distribution and chemical composition of fine particle emissions from biomass burning are essential to know. Additionally, there is a need for defining the contribution of biomass burning to the air particulate levels. Numerous emission and atmospheric studies have shown that source-specific compounds are useful to track the sources of particulate emissions.

Anhydrosugars, such as levoglucosan, mannosan, and galactosan, are compounds formed exclusively in the thermal degradation of plant biomass (e.g. Shafizadeh, 1984) and therefore they are commonly used as source-specific tracers for biomass burning. In addition to anhydrosugars, the particulate emissions from biomass burning consist of a wide range of other organic compounds, e.g. polycyclic aromatic hydrocarbons (PAHs), as well as elemental carbon (EC), and ash-forming compounds.

This thesis summarises the methodologies and results from several fine particle studies related to biomass burning in Finland. The term biomass is used in this thesis only for chemically unconverted plant biomass, not e.g. for biofuels. The thesis includes method development to improve the analytics of biomass burning particles with offline and online techniques. The main sampling and analytical methods are presented. The focus was in determining the biomass burning tracer compounds quantitatively and in solving the chemical composition of biomass burning aerosol. The results include data from the ambient measurements affected by the emissions from residential wood combustion and long-range transported smoke plumes from open-land fires, and laboratory measurements of the emissions from biomass combustion experiments. The thesis is complemented with a study of PAHs in size-segregated PM measured at six urban environments in Europe.

2. OBJECTIVES OF THE STUDY

The use of biomass energy is encouraged in Finland because of the pressure to use biofuels instead of fossil fuel. Biomass is a carbon neutral source of renewable energy; however, burning of biomass produces fine particles. The overall objective of this study was to gain knowledge on the chemistry of fine particles in low-tropospheric aerosols, especially of those that originate in biomass burning.

The specific objectives of this thesis were:

- to develop and validate a fast analytical method for the determination of anhydrosugars (called also as monosaccharide anhydrides (MAs); levoglucosan, mannosan, and galactosan) in fine particle samples (**Paper I**);

- to extend the method for the analysis of MAs from an offline technique to a reliable online application, in order to be able to detect the short-term changes in the aerosol composition caused by biomass burning (**Paper II**);

- to compare online and offline techniques in the research of short-term smoke plumes, and to study the differences of fresh and aged particles from open-land fires (**Paper III**);

- to estimate the contribution of wood combustion to ambient fine particles in different temporal and spatial scales in the Helsinki Metropolitan Area using the data of anhydrosugar concentrations (**Paper IV**);

- to study the polycyclic aromatic hydrocarbons in size-segregated particulate matter in urban background air of six European cities, and to assess the representativeness of benzo[a]pyrene (BaP) as a universal marker of total and genotoxic polycyclic aromatic hydrocarbons (PAHs) (**Paper V**).

3. THEORETICAL BACKGROUND

3.1. Atmospheric aerosols

Aerosol is a suspension of solid or liquid particles, or both, in the surrounding gas. In atmospheric aerosols, the surrounding gas is air. The term *particulate matter* (PM) refers to the solid and liquid phase of the aerosols.

3.1.1. Particle properties and sources

Aerosol particles are usually presented as a *size distribution* of four modes (Fig. 1): the nucleation ($D_p < 0.01$ µm), Aitken (0.01 µm $< D_p < 0.1$ µm), accumulation (0.1 µm $< D_p < 2$ µm), and coarse ($D_p > 2$ µm) particle modes (Seinfeld and Pandis, 2006). Particles in the nucleation and Aitken modes are called as *ultrafine particles* ($PM_{0.1}$). When the size range is extended to include the accumulation mode particles in addition to the ultrafine particles, they are called as *fine particles* or PM_1 or $PM_{2.5}$ depending on the upper limit of the size range (1 and 2.5 µm, respectively). When the size range is further extended to include larger particles up to the particle diameter of 10 µm, the size range is called as *thoracic particles* (PM_{10}) since this particle range includes the particles that are able to enter the human thoracic airways (lower regions of the respiratory tract) (Finlayson-Pitts and Pitts, 2000). The particles in the larger-particle mode of thoracic particles are simply called as *coarse particles* (PM_{1-10} or $PM_{2.5-10}$).

Ultrafine particles have the majority of particles by number, but because of their small size, they typically account only a few percent of the total particulate mass. Once emitted into or formed in the atmosphere, particles can grow by vapour condensation or by coagulation with other particles (Seinfeld and Pandis, 2006). The lifetime of nucleation mode particles is relatively short due to their rapid coagulation. Small particles may also diffuse on the surfaces or act as nucleation sites for the droplets.
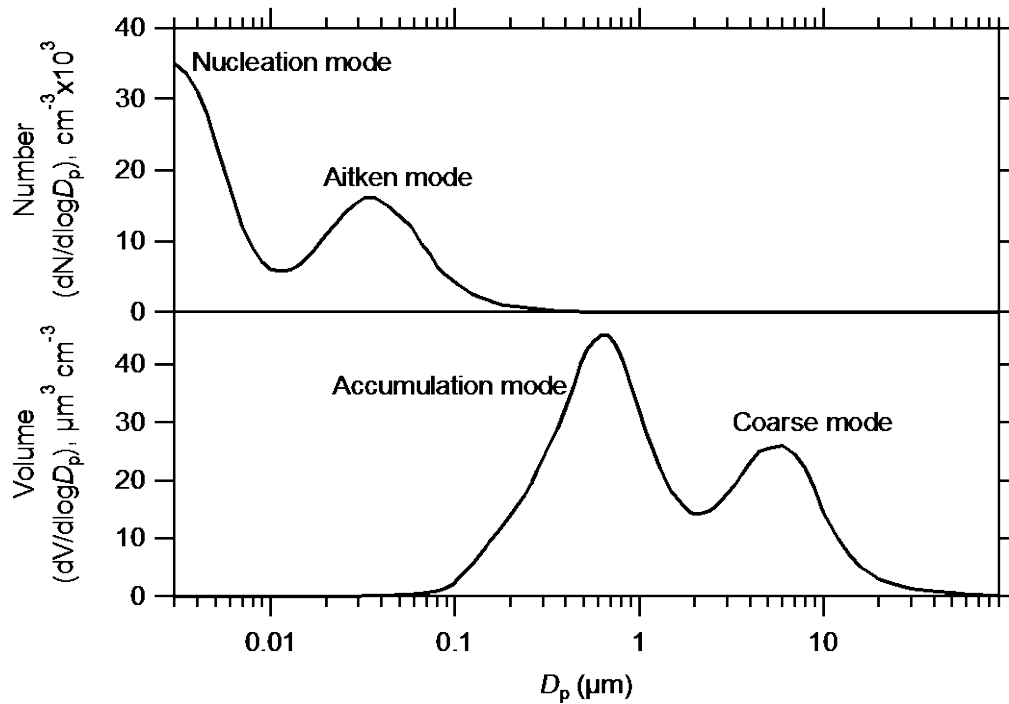
Figure 1. An example of typical number (upper) and volume size distributions (lower) of atmospheric particulate matter with the different modes (adapted from Seinfeld and Pandis (2006)).

The accumulation mode makes up usually a significant fraction of atmospheric particle mass and it often has the largest surface area (Finlayson-Pitts and Pitts, 2000). The lifetime of accumulation mode particles is typically many days and they can be transported long distances in the atmosphere (Hinds, 1999). The removal of accumulation mode particles is by washout or rainout. The coarse mode particles are typically small in particle number but high in particulate mass. Due to their large size, coarse particles are generally removed from the lower atmosphere in few hours or in a day by sedimentation or impaction.

Particle shapes vary from spherical liquid particles to cubic seasalt or cylindrical fibre particles (Hinds, 1999). The shape can also be more complex such as agglomerated chains or clusters. Combustion particles often have an agglomerated structure (Flagan and Seinfeld, 1988).

Atmospheric aerosol particles can be divided into two classes according to their formation mechanisms: *primary particles* have been emitted into the atmosphere directly from the sources, whereas *secondary particles* are produced in the atmosphere (Seinfeld and Pandis, 2006). Prima-

ry fine particles originate from different combustion processes, such as biomass burning, vehicles, and industrial activities. Different mechanical processes (e.g. soil-related dust, seasalt, and biogenic production) produce primary coarse particles. A significant fraction of the particulate mass in the atmosphere is formed through a gas-to-particle conversion. Secondary PM can be classified into sulphur-containing compounds, nitrogen-containing compounds, and organic compounds. *Secondary organic aerosol* (SOA) is formed by the mass transfer to the particulate phase of low-vapour-pressure products of the oxidation of organic gases and by heterogeneous pathways (Jacobson et al., 2000; Kalberer et al., 2004).

Particles can also be divided according to the source; *natural sources* (e.g. sea-sprays, volcanoes, biogenic production, lightning-caused open-land fires, etc.), and *anthropogenic sources* (e.g. traffic, industry, land use, wood combustion, slash-and-burn agriculture, etc.) (Hinds, 1999). In general, primary fine particles originate mainly from anthropogenic sources or wildfires.

Once particles are emitted into or formed in the atmosphere, they start to mix with the particles from the other sources. Aerosol is diluted and there occur transformations, e.g. oxidation and degradation. Particles can also be transported even thousands of kilometres (Hinds, 1999). However, the transport distance is dependent on the particle size and the meteorological conditions. *Long-range transport* (LRT) is classified as one of the typical sources of particles in ambient measurements (e.g. Saarikoski et al., 2008b).

3.1.2. Chemical composition of atmospheric particles

Chemical composition of particles is strongly dependent on the sources they are emitted from. In general, atmospheric aerosol particles contain carbonaceous material, sulphates, nitrates, ammonium, crustal species, seasalt, metal oxides, hydrogen ions, and water (Seinfeld and Pandis, 2006). From these species organic carbon (OC), elemental carbon (EC), sulphate, ammonium, and certain transition metals are found predominantly in the fine particles (Table 1). Nitrate can be found in both the fine and coarse aerosol fraction. Crustal material, including silicon, calcium, magnesium, aluminium, and iron, and biogenic particles (pollen, spores, plant fragments) are usually in the coarse aerosol fraction.

Table 1. The typical main sources and chemical components in three particulate size ranges in Europe (Sillanpää et al., 2006; Salonen and Pennanen, 2007).

	Ultrafine particles	Accumulation particles	Coarse particles
Main sources	Combustion Engine exhaust Nucleation Gas-to-particle conversion Vegetation emissions	Combustion Biomass burning Industry Energy production Agglomeration and hygroscopic growth of ultrafine particles Photochemical transformation Secondary aerosols Resuspension	Mechanically generated particles Sea salt Resuspension Windblown dust Biogenic material
Main components	EC OC SO_4^{2-} (Trace metals)	SO_4^{2-} NH_4^+ NO_3^- EC OC H_2O (Trace metals)	Si Al Ca Fe Na Cl NO_3^- OC

Carbonaceous fraction often makes up a significant part of PM. Carbonaceous compounds are classified based on their carbon-content to subfractions of EC and OC, and OC is divided furthermore into water-soluble OC (WSOC) and water-insoluble OC (WISOC) based on the water-solubility of the compounds (Saxena and Hildemann, 1996).

EC has a chemical structure similar to graphite and it is only formed in combustion processes (Kuhlbusch, 1995). EC is analysed by a thermal method whereas similar component is called as black carbon (BC) if the determination is made optically. EC can also be called as soot.

Dissimilar to EC, particulate OC is not a single component but the sum of carbon atoms in organic compounds. OC is emitted directly from sources (primary organic aerosol) or formed in the atmosphere from gaseous precursors (SOA) (Kanakidou et al., 2005). In order to convert OC to particulate organic matter (POM), that refers to the mass of all organic compounds in particles, Turpin and Lim (2001) have recommended using a multiplying factor of 1.6 ± 0.2 for urban aerosols, a factor of 2.1 ± 0.2 for aged non-urban aerosols and 2.2–2.6 for aerosols heavily im-

pacted by wood smoke based on the molecular weight per carbon weight ratio (MWt/CWt). The main factor contributing to the variation of POM-to-OC ratios is the oxygen content in organic compounds (Pang et al., 2006). Many oxygen-containing organic compounds are typically water-soluble and they have MWt/CWt in the range of 1.5–3.8 (Saxena and Hildemann, 1996; Turpin and Lim, 2001; Pang et al., 2006). On the contrary, most of the water-insoluble organic compounds, e.g. PAHs, long-chained *n*-alkanes and *n*-alkanoic acids, have low MWt/CWt, i.e., 1.0–1.5.

The chemical composition of atmospheric particles may vary remarkably depending on the environment; for example, the chemical composition of particles in remote environments differs from that in urban environments. In a study by Putaud et al. (2010), chemical composition of fine and coarse aerosol fractions were compared from 60 rural, urban, and kerbside sites across Europe. It was found that there were regional differences in PM characteristics between Northwestern, Central and Southern Europe in addition to the classification of site types: the contribution of mineral dust to all PM size fractions is larger in Southern Europe, that of sea salt to PM_{10} is larger in Northwestern Europe, and ratio of total carbon to PM_{10} is generally larger in Central Europe. However, the main constituents of both PM_{10} and $PM_{2.5}$ are generally POM, sulphate and nitrate all over Europe but there is a decreasing gradient in sulphate and nitrate contribution to PM_{10} when moving from rural to urban to kerbside sites. In contrast, the ratio of total carbon to PM_{10} increases from rural to kerbside sites.

The vicinity of particle sources naturally influences the chemical composition of ambient air PM; e.g. marine aerosols contain remarkably sea salt (O'Dowd and de Leeuw, 2007) whereas close to a combustion source, flue gas emissions dominate in the chemical composition of atmospheric aerosol. The chemical composition of particles originating from biomass burning is described in more detail in Sect. 3.2.4.

3.1.3. Environmental and health impacts of aerosols

Fine particles affect the climate directly by absorbing and scattering sunlight. Elemental carbon-containing fine particles are known to absorb sunlight, thus contributing to global warming. In contrast, sulphate particles scatter sunlight, and therefore have a cooling effect (IPPC, 2007). Besides influencing on the optical properties of the atmosphere, the soot particles deposited onto the snow and ice surfaces affect the earth's albedo, thus accelerating the melting of snow and ice. In addition, fine particle emissions affect the climate indirectly through their influence on cloud formation. These effects are strongly dependent on the chemical properties of aerosols (IPCC, 2007).

In addition to the climatic effects, the aerosols have also effects on the air quality and visibility. The decreased air quality causes serious risks to human health from exposure to PM (WHO, 2006). The atmospheric pollution has adverse effects on breathing and respiratory systems: lung tissue damages, cancer, and even premature deaths. The elderly, children, and people with chronic lung disease, influenza, or asthma, are especially sensitive to the effects of PM. Epidemiological studies have most often given stronger exposure-response relationships for mortality and morbidity outcomes in association with ultrafine and fine particles than PM_{10} (e.g. Chuang et al., 2005). Ultrafine particles have been suggested to pose a great risk to human health due to their high number concentration in urban environments and potential to penetrate from the lung alveoli into the blood circulation (Delfino et al., 2005). However, there is increasing debate that particulate number or mass concentration may not be the most appropriate exposure parameter for the assessment of health risks of atmospheric pollution (Forsberg et al., 2005). For instance, many aromatic compounds, commonly identified in particles from incomplete combustion, are suspected genotoxic agents and carcinogens, and some of them may also cause acute health effects (WHO, 1998; EC 2001).

3.2. Biomass burning

Biomass burning, as a term, encompasses all burning of biogenic material from plants, such as trees, grasses, crop residues, and chemically unconverted biomass fuel (wood logs, pellets). Globally, biomass burning is an important primary source of soot and organic PM that absorbs and scatters incident solar radiation, affects the earth's albedo as well as decreases visibility (Simoneit et al., 1999). CO_2 is the most significant single factor that intensifies the greenhouse effect (IPCC, 2007). The CO_2 that is formed in biomass burning is reused in the growth of new biomass material, and therefore the net effect of biomass burning on the atmospheric CO_2 balance is zero. However, methane (CH_4) that is formed in incomplete burning of biomass is a significant greenhouse gas.

The two major sources of biomass burning emissions in Finland are residential biomass burning (small-scale wood combustion) (e.g. Karvosenoja et al., 2008; Ahtoniemi et al., 2010; **Paper IV**) and the smoke plumes from open-land fires in the Eastern European countries which are occasionally transported to Finland (Niemi et al., 2009; **Paper III**). Pollution from biomass burning was one of the first occupational and residential hazards: early humans must have been exposed to large amounts of carcinogenic compounds from the smoke of open fires in caves, huts and tents (Andreae, 1991). As late as in the youth of our parents, some people have still lived certain periods in chimneyless huts in Finland. In less developed countries, residential and occupational exposure to biomass burning smoke is still a major problem.

According to the 'Europe 2020' strategy, the use of renewable energy has to increase to 38.5% in Finland by 2020 (Ministry of Finance, 2012). This requires an increase in all kinds of biomass energy. An increase in biomass use as an energy source holds the potential to reduce the global greenhouse gas emissions since biomass burning is currently not considered to affect the CO_2 balance in the atmosphere, as opposed to the use of fossil fuels. However, both biomass and fossil fuel combustion can release varying amounts of gaseous and particulate emissions into the atmosphere.

3.2.1. Chemical composition of plant biomass

Biomass is primarily composed of carbon (C), hydrogen (H), and oxygen (O) because the main chemical compounds in plant biomass are cellulose ($(C_6H_{10}O_5)_n$), hemicelluloses ($C_xH_yO_z$), and lignin ($C_xH_yO_z$) (Pettersen, 1984; Van Loo and Koppejan, 2008). Other components such as nitrogen (N), sulphur (S), and chlorine (Cl) are less than 1% of dry matter. In addition to the main carbohydrate components and lignin, some extractives (e.g. fats, waxes, resins, terpenes, and starches) and ash forming components exist in plant biomass (Pettersen, 1984). The extractive content gives plants their colours and odours (Pettersen, 1984).

Cellulose is a glucan polymer consisting of linear chains of several hundred to over ten thousand units of 1,4-β-bonded anhydrous glucose (Pettersen, 1984). It is a crystalline, strong polymer that is resistant to hydrolysis. Cellulose is an important structural component of the primary cell wall of plants. The structural diagram of a portion of a glucan chain is presented in Fig. 2.
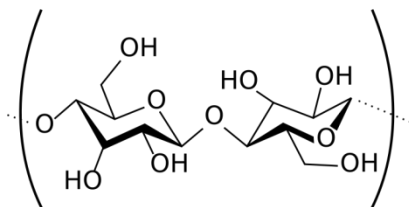
Figure 2. Partial molecular structure of cellulose.

Hemicelluloses is a group of polysaccharides such as xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan that are synthesised in plants almost entirely from glucose, mannose, galactose, xylose, and arabinose, as well as from 4-O-methylglucuronic acid, and galacturonic acid residues (Pettersen, 1984). Hemicelluloses have a random, amorphous structure with little strength. Generally, hemicelluloses are of much lower molecular weight (60–200 sugar units) than cellulose and appear to contribute as a structural component in the plant.

Lignin is a phenolic substance consisting of an irregular array of variously bonded hydroxyl- and methoxy-substituted phenylpropane units (Pettersen, 1984). Lignin fills the spaces in the plant cell wall between cellulose and hemicelluloses.

Plant classes differ according to their chemical composition; e.g. woody tissue is structurally composed mainly of cellulose (40–45% of the dry weight), hemicelluloses (20–35%), and lignin (15–30%) (Pettersen, 1984). However, different plant species in the same class may contain the main components in different ratios. Additionally, the composition of hemicelluloses varies widely among different plant species; it is different in coniferous trees (also called as softwood; e.g. pine and spruce) from those in broad-leaved trees (hardwood; e.g. birch), and moreover, from those in grasses and herbs (Simoneit et al., 1999; Schädel et al., 2010).

3.2.2. Biomass burning process

Burning, or combustion, is a complex process involving chemical and physical reactions, and transfer of mass and heat. Generally in burning, fuel reacts with oxygen releasing heat energy.

Ignition is the first step of a biomass burning process. During ignition the biomass fuel starts to oxidise in raising temperature. Moisture will evaporate at low temperatures (< 100 °C) (Van Loo and Koppejan, 2008). After ignition a *flaming* phase starts. It involves hydrolysis, oxidation, and dehydrating processes. The moist biomass is getting warmer and it reaches the point, in which most of the water contained in the biomass is evaporated. Along with the drying, the temperature of the biomass continues increasing and the pyrolysis begins at about 200 °C (Van Loo and Koppejan, 2008). Pyrolysis can be defined as thermal devolatilisation in the absence of an externally supplied oxidising agent (Van Loo and Koppejan, 2008). In pyrolysis, the large molecules of biomass (cellulose, hemicelluloses, and lignin) are degraded, and plenty of combustible gases, liquid tarry substances, and some inert gases are formed (Shafizadeh, 1984). At about 400 °C, most of the volatiles are gone and the devolatilisation rate decreases rapidly until the temperature reaches 500 °C (Van Loo and Koppejan, 2008). Most of the pyrolysis products are burnt with flame due to oxygen in air. Flaming is commonly known as the real burning phase.

The production of volatiles leaves a solid residue that is a material of various stages of charring and carbonisation. *Smouldering* is a phase in which there is enough heat to decompose the reactive char into some products. Smouldering combustion is a surface process in which oxygen diffuses to the surface and reacts exothermally with carbon at > 450 °C (Reid et al., 2005). If temperature is increased to about 650–700 °C and above, CO can convert to CO_2 if oxygen exists sufficiently. When the burning process ends, the rest of the biomass that was not burnt into gaseous or particulate emissions is left as the residual ash. The descriptions of different stages of burning are summarised in Table 2.

Table 2. Characteristics of the stages of biomass burning (Reid et al., 2005; Chan et al., 2011).

Stage of burning		Process	Process characteristics
Flaming stage	Solid phase	Drying/distilling process	Water and volatile contents are removed or diffused into the inner layers of bulk material
		Pyrolysis process	Starts at about 150–200 °C Below 200 °C the process is endothermic Above 200 °C the process is exothermic Dehydrocellulose decomposition takes place
		Glowing burning	Starts at about 450 °C if oxygen is present Resulting in char being oxidised
	Gas phase	The flame	The emitted volatiles are converted to combustion products of low-molecular weight
Smouldering stage		Smouldering process	A low-temperature process Takes place at concentrations of oxygen as low as 5% Can proceed over days under conditions of high moisture

Properties of the fuel have an important influence on the quality of the burning. The burning of a biomass item depends on its chemical, structural, and physical properties. Also the moisture content of the biomass fuel determines the burning process. If the moisture content of fuel is high, fuel does not spontaneously react and some amount of energy is needed to evaporate the water (Van Loo and Koppejan, 2008). This reduces the heating value of the fuel and decreases the efficiency of the burning (Jenkins et al., 1998). On the other hand, low moisture content causes the fuel to burn faster leading to incomplete burning, which increases smoke particle formation.

Although the characteristics of biomass fuels vary largely, there are some common properties which make them generally different from fossil solid fuels. Biomass fuels have typically higher volatile material content and lower char content than coal (Van Loo and Koppejan, 2008). Also the heating values of the biomass fuels are generally significantly lower than in fossil fuels and therefore the biomass burning temperatures are usually below those of fossil fuel. Third, biomass ashes contain high amounts of volatile material such as alkali metals, especially potassium, of which a large fraction volatilises during burning process forming fine particles (Valmari, 2000). With low temperatures (< 500 °C) only organically bound alkali metals are released, while the major fraction of alkali release occurs at temperatures > 600 °C and usually mainly in the char burning phase (Valmari, 2000).

3.2.3. Emissions from biomass burning

Emissions from biomass burning include a wide range of gases and particles. It has been estimated that biomass burning contributes to 40% of the CO_2, 32% of the carbon monoxide (CO), 21% of the nitrogen oxides (NO_x), 12% of the ammonia (NH_3), 38% of the ozone (O_3), 39% of the particulate OC, and >86% of the EC emissions released by all sources globally (Andreae, 1991). In a recent study by Bond et al. (2013), the contribution of biomass burning to the atmospheric BC was estimated to be about 37% at the global scale.

Theoretically, when carbon in biomass burns completely only CO_2 is formed. If the burning is incomplete, also CO and diverse hydrocarbons (C_xH_y) are formed (Simoneit, 2002). CO indicates that the burning has been unfinished, there has been deficiency of oxygen or the gases have reacted with embers (Andreae and Merlet, 2001). The presence of hydrocarbons in flue gases is nearly always a sign of incomplete burning (Demirbas, 2004).

NO_x are produced during combustion (Demirbas, 2004). The nitrogen of NO_x can originate from the fuel at lower temperatures and from air at high temperatures. The temperature in biomass burning is rarely high enough to cause NO_x formation from combustion air. The formed NO_x and volatile organic compounds (VOC) can take part in the SOA formation in the atmosphere (e.g. Camredon et al., 2007). Sulphur in biomass oxidises to sulphur oxides (SO_x) in combustion (Van

Loo and Koppejan, 2008). SO_x and NO_x are also involved in the formation of fine ash particles. Sulphur and chlorine in biomass can form sulphuric (H_2SO_4) and hydrochloric acid (HCl) (Van Loo and Koppejan, 2008).

Organic compounds emitted from biomass burning can occur both in gaseous and particulate phases. They are typically divided into VOC and POM. One of the most important VOC from biomass burning is methane (Johansson et al., 2004), which is a very strong greenhouse gas with the warming effect 21-fold that of CO_2 (Seinfeld and Pandis, 2006). Aerosol from incomplete biomass burning may contain liquid or tarry parts that are products from the gas-to-particle conversion of organic compounds during the cooling of the emission gases (Tissari, 2008). Organic vapours may also condense on the existing particles rather than forming new particles via nucleation.

Soot particles are formed mainly in the flame from organic pyrolysis gases (Tissari, 2008). In the biomass combustion, the mixing of combustion gases and air is often insufficient. Therefore the flame zone contains fuel-rich areas where soot is formed. In wood combustion, the decomposition products of lignin have been suggested to play an important role in the soot formation (Fitzpatrick et al., 2008). The soot formation mechanisms are complex and there are different proposed mechanisms. The soot formation is proposed to be at lower temperatures from aromatic hydrocarbons directly by growing into graphic-like structure or soot formation takes place at higher temperatures where both aliphatic and aromatic hydrocarbons first fragment followed by the polymerisation of the fragments into larger molecules forming soot (Amann and Siegla, 1981). Most of the soot particles are burnt in the oxygen-rich zone in the flame but a minor part of the soot particles is released as agglomerates composed of very stable EC spherules of about 30–50 nm (Ishiguro et al., 1997).

In sufficient burning conditions, fine particle emissions are formed mainly by the vaporisation of ash-forming elements from the biomass fuel (Sippula et al., 2007). The formation of fine ash particles begins by a homogenous nucleation when the temperature decreases after the flame and the vapour pressure of ash species decreases (Jokiniemi et al., 1994). Most mineral compounds are bound to the organic structure of the biomass and are easily released during the pyrolysis.

Potassium, sulphur, chlorine, and sodium are very volatile ash-forming species in biomass (Knudsen et al., 2004). Also calcium and zinc may volatilise in the flame.

The variation in the properties of the burning material, terrain, weather, and the form of burning leads to different size and chemical distributions of particles emitted from biomass burning (e.g. McDonald et al., 2000; Chen et al., 2007; Fuzzi et al., 2007; **Paper III**). The majority of the particles from biomass burning have been reported to be smaller than 2.5 µm in diameter (e.g. Artaxo et al., 2002; Frey et al., 2009; **Paper III**). The particle size in the direct emissions from biomass burning is typically from 30 to 200 nm (Hays et al., 2002; Hedberg et al., 2002; Demirbas, 2004; Reid et al., 2005). In a laboratory study by Frey et al. (2009), wood combustion with a masonry heater was tested with sufficient (normal combustion) and insufficient combustion conditions (smouldering combustion). The maximum in the particle mass size distribution was detected at 100 nm with normal and at 300–700 nm with smouldering combustion. Coarse particles (1–10 µm) in biomass burning emissions are formed from low volatile ash compounds and partially unburnt char. Very large coarse particles (>10 µm) are formed from residual ash particles that are carried upwards by the gas flow (Wiinikka, 2005).

3.2.4. Chemical composition of particles from biomass burning

As discussed in the previous section, the chemical composition of particles from biomass burning depends largely, e.g. on the conditions of fuel and the quality of burning. In general, the contribution of carbonaceous fraction is relatively high, especially, if the burning has been incomplete. If the burning has been efficient, the emitted particles contain typically lots of ash-forming components. For example, the following components have been found in the particles from biomass burning: sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+), zinc (Zn), EC, and POM (e.g. Saarikoski et al., 2007; Frey et al., 2009; Maenhaut et al., 2011; **Papers I-IV**).

A wide range of organic compounds has been identified to form POM in the fine particle emissions from biomass burning, e.g. *n*-alkanes and *n*-alkenes, *n*-alkanols and *n*-alkanals, alkanoic, alkenoic, and alkanedioic acids, methyl-alkanoates and -alkenoates, guaiacols, syringols, and

other substituted benzenes and phenols, dimers and lignans, PAHs, alkyl-PAHs, and oxy-PAHs, sugar derivatives, coumarins and flavonoids, furans, recin acids, diterpenoids, phytosteroids, triterpenoids, and other compounds (Fine et al., 2002; 2004). Two specific groups of organic compounds are discussed below in more detail.

Polar organic compounds

Biomass burning is a complex process in which cellulose, hemicelluloses, and lignin decompose producing different emission products in different phases of process. At temperatures < 300 °C, cellulose overcomes depolymerisation, dehydration, fragmentation, and finally oxidation to lead to char formation (Shafizadeh, 1984). At temperatures > 300 °C, cellulose overcomes bond-splitting by transglycosylation, fission, and disproportionation reactions into anhydrosugars and volatile products, such as levoglucosan and other anhydrosugars (Shafizadeh, 1984; Simoneit, 1999). The decomposition of hemicelluloses occurs at 180–340 °C (Lv et al., 2010). At this stage, lignin is degraded into monomers, such as coumaryl, vanillyl, and syringyl moieties (Simoneit, 1993). Some of the decomposition products of cellulose, hemicelluloses, and lignin are used as tracer compounds for biomass burning (presented in more detail in Sect. 3.2.5).

Several organic acids (mono-, di- and polycarboxylic acids) have been found from biomass burning originated particles (Mayol-Bracero et al., 2002). For example oxalic, malonic, and succinic acid (analysed as ions) have been measured in transported wild fire smokes (Sillanpää et al., 2005a; Saarikoski et al., 2007; **Paper III**). Malic acid was noticed to have a similar behaviour to levoglucosan in deforestation fire smokes suggesting that they were both formed in the same aerosol formation process when the low-volatile organic vapours were condensed; levoglucosan directly in the smokes emitted by deforestation fires and malic acid when the vapours from the fires and the biogenic emissions were photo-oxidised (Claeys et al., 2010). Also the term of HULIS (humic-like substances) has been connected to biomass burning aerosols (e.g. Mayol-Bracero et al., 2002; Hoffer et al., 2006). HULIS is possibly composed of water-soluble poly-acidic compounds (Decesari et al., 2000).

Toxic organic compounds

Combustion of biomass is a potential source of several organic air toxins, e.g. formaldehyde, benzene, PAHs, furans, and dioxins (Andreae and Merlet, 2001; Lavric et al., 2004; Lemieux et al., 2004; Piazzalunga et al., 2013). PAHs are formed in the oxygen-deficit area of a flame where polymerization rather than oxidation occurs (Flagan and Seinfeld, 1988). PAHs are of great interest because of their adverse health effects. Exposure to PAHs increases the risk of cancer, and in animal experiments, PAHs have given raise to immunologic and reproductive effects (Boström et al., 2002). Dioxins and furans are persistent environmental pollutants that are very toxic and potent carcinogens (WHO, 2010). They are released into the atmosphere by biomass burning and other combustion sources. For example, polychlorodibenzo-p-dioxins and -furans have been found in the emissions from biomass combustion (Lavric et al., 2004; Piazzalunga et al., 2013).

In urban air, more than 100 PAHs have been identified (Hytönen et al., 2009). Their properties, like saturation vapour pressures, vary greatly. At room temperature in equilibrium, bicyclic species are present in the gas phase, compounds formed of seven or more benzene rings in the particle phase, and intermediate PAHs in both phases (Seinfeld and Pandis, 2006). Partitioning depends also, e.g. on ambient air temperature, concentrations in the gas phase, and the chemical composition of the particles (Shimmo et al., 2004; Tsapakis and Stephanou, 2005).

In a Finnish wood combustion experiment by Hytönen et al. (2009), 11 particle-phase PAHs contributed 0.7% to the PM emission from normal and 2.1% from smouldering combustion. In many countries, residential wood combustion has been found to cause a great proportion of emissions of PAHs. In Finland, residential combustion, of which wood combustion has a very large share, was estimated to cause 64% (11 tons/year) of the total emission of four PAHs (BaP, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), and indeno[1,2,3-cd]pyrene (IdP)) in 2003 (Koskinen et al., 2005). In Sweden it was estimated that residential wood combustion produces about 60% of the PAHs emissions (Boström et al. 2002). Based on radiocarbon analysis of atmospheric PAHs, biomass combustion contributed about 50% to the total PAHs in the atmosphere at a Swedish background site but only about 10% at two southern European background sites in Greece and Croatia (Mandalakis et al. 2005). Increased levels of PAH concentrations have also been reported in forest fire smokes (e.g. Anttila et al., 2008).

3.2.5. Tracers of biomass burning

Some elemental and organic compounds are specific for certain sources and therefore they have been used for the identification and quantification of different aerosol sources. A good tracer is specific for its source and it is persistent and stable enough in atmospheric conditions. In addition, the optimum tracer could be used quantitatively; however, in biomass burning, the conditions of the fuel and the quality and the phase of burning affect the chemical composition of the emitted aerosol. The components that are used for tracing the biomass burning sources are listed below:

Decomposition products of cellulose and hemicelluloses

In the pyrolysis of cellulose and hemicelluloses, anhydrous sugar compounds, such as levoglucosan, mannosan, and galactosan, are produced (Fig. 3).
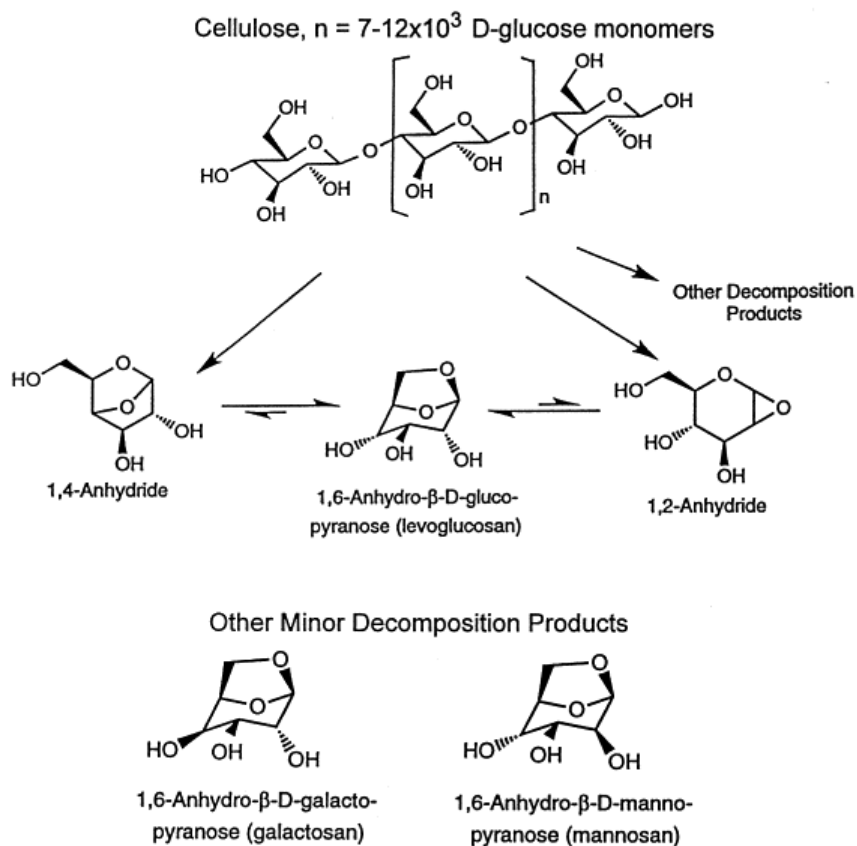
Figure 3. Schematic representation of the major decomposition products during the pyrolysis of cellulose and hemicelluloses (adapted from Shafidazeh (1984) and Elias et al. (2001)).

Levoglucosan (1,6-anhydro-*β*-D-glucopyranose) is formed in the decomposition of cellulose and hemicelluloses whereas mannosan (1,6-anhydro-*β*-D-mannopyranose) and galactosan (1,6-anhydro-*β*-D-galactopyranose) from hemicelluloses only (Shafizadeh, 1984; Simoneit, 2002). Levoglucosan is typically the most abundant of these three isomers. Also other anhydrosugars can be formed in the pyrolysis of cellulose and hemicelluloses, such as 1,6-anhydro-*β*-D-glucofuranose (Claeys et al., 2010). According to chemical classification these compounds are lactols. In atmospheric sciences these compounds are commonly called as anhydrosugars or monosaccharide anhydrides (MAs) and therefore also in this thesis.

Due to their low vapour pressures, MAs are mainly in particulate phase in the atmosphere (Oja and Suuberg, 1999). MAs are generally considered as relatively stable compounds in atmospheric conditions (Simoneit et al., 1999; Fraser and Lashmanan, 2000; Khalil and Rasmussen, 2003; Jordan et al., 2006). However, it was noticed during a research cruise from English Channel to the Antarctic coast (Saarnio et al., 2006) that only low concentration of levoglucosan was detected in the samples collected near the western coast of Africa and the Equator whereas the concentrations of other biomass burning tracers were high and the smoke odour was detected. It was assumed that strong solar irradiation and high ambient temperature affects the stability of levoglucosan. Later studies (Hennigan et al., 2010; Hoffmann et al., 2010) demonstrated that the reason for levoglucosan degradation is the high concentration of gas-phase hydroxyl (OH) radical. OH radicals are typically generated in the troposphere by the influence of sunlight (Seinfeld and Pandis, 2006).

The amount of levoglucosan in particles has been used to calculate the contribution of biomass burning to atmospheric aerosols (e.g. Zdrahál et al., 2002; Yttri et al., 2005; Puxbaum et al., 2007; Wang et al., 2007; Saarikoski et al., 2008a). The characteristic concentration ratios of levoglucosan or MAs to PM or OC have been obtained in laboratory studies (e.g. Rogge et al., 1998; Schauer et al., 2001; Fine et al., 2002; 2004; Iinuma et al., 2007; Frey et al, 2009). However, it has been suggested that due to its dependency on combustion conditions levoglucosan cannot be used as a quantitative tracer for the amount of combusted wood, at least if solely levoglucosan has been used as a tracer (Hedberg et al., 2006). Levoglucosan or MAs were used as biomass burning tracers in **Papers I**, **II**, **III**, and **IV**. Additionally, the ratio of levoglucosan to other

MAs was utilised in separating local wood combustion emissions from transported smokes from open-land fires (**Paper IV**).

Decomposition products of lignin

Substituted phenols, including alkylphenols and methoxyphenols, are a class of biomass burning tracers that originate from the pyrolysis of lignin (Simoneit et al., 1993; Iinuma et al., 2010). For example, syringyl compounds have been found from hardwood smoke and guaiacyl compounds in softwood smoke (Kjällstrand and Petersson, 2001). Unlike MAs, these compounds can be found both in gaseous and particulate phase due to their wide range of volatilities.

PAHs

Several PAHs have been identified in wood combustion emissions and in ambient air in wood-heated residential areas (Ramdahl, 1983; Hays et al., 2003). These are alkylated phenanthrene compounds with the main compound 1-methyl-7-isopropylphenanthrene (trivial name retene) formed by the thermal degradation of resin compounds in the coniferous wood. Also the ratios of some particulate PAHs have been suggested to be characteristic of biomass burning (e.g. Li and Kamens, 1993; Rogge et al., 1993; Simcik et al., 1999; Tang et al., 2005). Assessment of the emission sources using certain PAHs ratios was tested in **Paper V** where the use of PAHs as source-specific tracers was discussed.

Dicarboxylic acids

Elevated concentrations of oxalate have been measured in biomass burning particles (e.g. Sillan-pää et al., 2005a; Saarikoski et al., 2007; Kundu et al., 2010; Zhang et al., 2010). However, in summertime, dicarboxylic acids are also formed by the secondary organic aerosol formation (e.g. Huang et al., 2006). Sillanpää et al. (2005a) noticed that oxalate corresponded well with other biomass burning signatures and also with the other dicarboxylic acids (succinate, malonate). Dicarboxylic acid concentrations were elevated both in fine and coarse fraction suggesting that the acids were probably condensed on the existing particles. Oxalate was utilised in **Paper III** to trace biomass burning emissions.

Potassium (K)

Increased concentration of K has been reported for the biomass burning emissions (e.g. Hedberg et al., 2002; Khalil and Rasmussen, 2003; Saarikoski et al., 2007; Frey et al, 2009; Kaivosoja et al., 2013). The amount of K is dependent on the combustion conditions; K is emitted into particulate phase mainly in the flaming phase with high temperature whereas in incomplete burning it remains in residual ash (Werther et al., 2000). In **Paper III**, K was used to indicate the biomass burning origin of the particles. Similar to dicarboxylic acids, K may also originate from the other sources.

Zinc (Zn)

Zn has been observed to have a significant contribution in wood burning emissions (Hedberg et al., 2002). In a wood combustion experiment by Frey et al. (2009), Zn contributed 94% to the sum of the analysed trace elements on average. However, Zn is also emitted by coal-fired power plants and other industrial activities (Braga et al., 2005).

Chloride (Cl⁻)

Cl^- has been identified as one of the main ions in biomass combustion particles (e.g. McDonald et al., 2000; Frey et al., 2009). Potassium chloride (KCl) occurs in fresh smoke whereas increased amounts of potassium sulphate (K_2SO_4) and potassium nitrate (KNO_3) are present in aged smoke. Cl^- was measured from the smoke plumes in **Paper III**.

Methyl halides, such as methyl chloride (CH_3Cl), are formed predominantly in the smouldering stage of biomass burning from chlorine in biomass, probably because of the reaction between methanol and HCl catalysed at glowing char surfaces (Reinhardt and Ward, 1995) or by radical reactions in flames. It has been shown that CH_3Cl in gas-phase correlates well with the biomass burning emissions (Andreae and Merlet, 2001; Khalil and Rasmussen, 2003).

Elemental carbon (EC)

Particulate EC (or BC or soot) is formed in the flame from organic gases (Tissari, 2008), so it can be used as a tracer of combustion. However, it is not a specific tracer for combustion of biomass because it is formed in combustion of fossil fuels as well. The EC-to-OC ratio can also be used as an indicator of the burning temperature because the formation of EC increases at high

temperatures (Khalil and Rasmussen, 2003). Similarly to K, particulate EC is formed in efficient flaming burning, whereas in insufficient burning or smouldering a wide range of organic compounds are emitted into atmosphere instead of EC (Khalil and Rasmussen, 2003; Frey et al., 2009). The use of EC and the EC-to-OC ratio as biomass burning tracers was studied in **Paper III**.

Radiocarbon (^{14}C)

The sources of atmospheric aerosols have been evaluated also by measuring radiocarbon ^{14}C (e.g. Szidat et al., 2006; Gilardoni et al., 2011). The isotope ^{14}C is formed in the atmosphere and it is quickly oxidized to $^{14}CO_2$ which is taken up by plants through photosynthesis. Thus, ^{14}C is incorporated into all land-living plants (Sheffield et al., 1994; Szidat et al., 2004). When a plant dies, the exchange of carbon with the surrounding environment ends and the $^{14}C/^{12}C$ ratio begins to decrease following the radioactive decay (half-life of 5730 ± 40 years) of the ^{14}C isotope. This decay is slow compared to the life time of plants, but it is fast compared to fossil material time scale. As a consequence, the $^{14}C/^{12}C$ ratio in fossil fuels is zero and the isotopic ratio in atmospheric aerosol depends on the relative contribution of fossil and non-fossil carbon and on the age of modern carbon sources.

Tar balls

Smouldering conditions of biomass burning may produce tar balls (Pósfai et al., 2004). Tar ball is a distinct carbonaceous particle type of soot that can be identified in individual particle analysis by electron microscopy. Tar balls have been detected in LRT smokes from open-land fires (Niemi et al., 2005).

Biomass burning tracer fragments with AMS

In Aerodyne aerosol mass spectrometer (AMS) measurements, mass-to-charge ratios (*m/z*) of 60 (mostly $C_2H_4O_2^+$) and 73 (mostly $C_3H_5O_2^+$) have been shown to be associated with biomass burning (e.g. Schneider et al., 2006; Alfarra et al., 2007; Lee et al., 2010). These may originate from levoglucosan and other MAs but also from the sugar compounds emitted from several sources. The fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$ were compared with levoglucosan concentrations in **Paper II**.

3.2.6. Small-scale wood combustion in Finland

Most of the detached houses in Finland have a fireplace that is used for heating and pleasure. In the cities, the use of district heating is common but in the areas with no district heating system or related, residential wood combustion can be the main heating system. The residential wood fuel consumption has increased 29% in ten years from year 2000 in Finland (METLA, 2010). The use of biomass energy, also in households, is encouraged in Finland because of the pressure to use biofuels instead of fossil. For instance, it is possible to get some financial support to replace an oil or electricity heating system with a heating system based on renewable energy (e.g. biomass combustion, ground or air source heat pumps). Investments are also allocated in the development of the modern technology combustion appliances but no regulations yet exist for PM emissions from residential biomass combustion appliances in Finland.

The emission measurement experiments have showed that the appliance type, fuel, and operational practices affect clearly the fine PM emissions (Tissari et al., 2008; Frey et al., 2009; Lamberg et al., 2011). In good combustion conditions (e.g. with a modern pellet burner), the fine PM emission factors are low and the major part of the fine PM consists of inorganic compounds. With traditional small-scale combustion appliances (e.g. masonry heaters and sauna stoves), the quality and quantity of emissions are strongly dependent on operational practices.

It has been estimated that residential wood combustion accounted for 25% of the primary $PM_{2.5}$ emissions in Finland in 2000 (Karvosenoja et al., 2008). In wintertime the contribution can be much higher. In Sweden it was assessed that wood combustion produces 20–90% of the fine particle emissions in winter (Boman et al., 2003). In Denmark in a residential area without a district heating system, wood combustion resulted in local particle levels comparable to those measured in streets with heavy traffic (Glasius et al., 2006). Also the concentrations of PAHs can be several times higher at the residential area than in the background because of residential wood combustion (Hellén et al., 2008). Small-scale wood combustion can affect air quality not only locally but also regionally or even further away. Due to the lack of local sources in urban background of Helsinki, the reason for the increased levels of wood combustion emissions was found to be regional distribution or LRT or both (**Papers II**, **IV**).

3.2.7. Smoke plumes transported to Finland from open-land fires

Open-land fires exist all around Europe every year (Saarikoski and Hillamo, 2013). Lightning can cause wildfires but most of the fires are ignited by humans, either intentionally as a part of local agriculture or accidentally. Burning of fields as a cultivation technique before the new growing season is forbidden in the European Union but it is commonly used in the eastern European countries and Russia in springtime. The smokes from open-land fires are occasionally transported from these areas to Northern Europe, including Finland.

The number and timing of fires vary with years, which is mainly caused by the differences in the meteorological conditions. Typically the smokes from open-land fires are transported to Finland during the warm season (Niemi et al., 2009). In spring, from March to May, the fires are mostly agricultural whereas in the late summer, from July to September, the smokes are primarily caused by wildfires. The durations of the smoke episodes detected in Finland have varied from few hours to several days and weeks. During the 21st century, the LRT smoke episodes have been reported at several sites over Finland from years 2002 (Niemi et al., 2004; 2005; Sillanpää et al, 2005; Jalava et al., 2006; Hänninen et al., 2009), 2004 (Niemi et al., 2006; Saarikoski et al., 2008a), 2006 (Saarikoski et al., 2007; Timonen et al., 2008b; Anttila et al., 2008; Aurela et al., 2010; **Papers III**, **IV**), 2007 (Niemi et al., 2009; Maenhaut et al., 2011), 2008 (Hyvärinen et al., 2011), 2009 (Timonen et al., 2010; Yttri et al., 2011), and 2010 (Mielonen et al., 2012; Portin et al., 2012). Saarikoski and Hillamo (2013) have compiled an extensive review on the transported wildfire smokes detected in the Northern Europe.

4. EXPERIMENTAL

4.1. Research sites

The measurements presented in this thesis were carried out both in ambient air and in laboratory conditions. Ambient measurements were conducted to investigate the influence of biomass burning on ambient particles whereas in laboratory measurements the chemistry of wood burning particles was examined in controlled atmosphere.

4.1.1. Ambient air measurements

The measurements included in this thesis were conducted at 12 sites in six countries (Fig. 4).
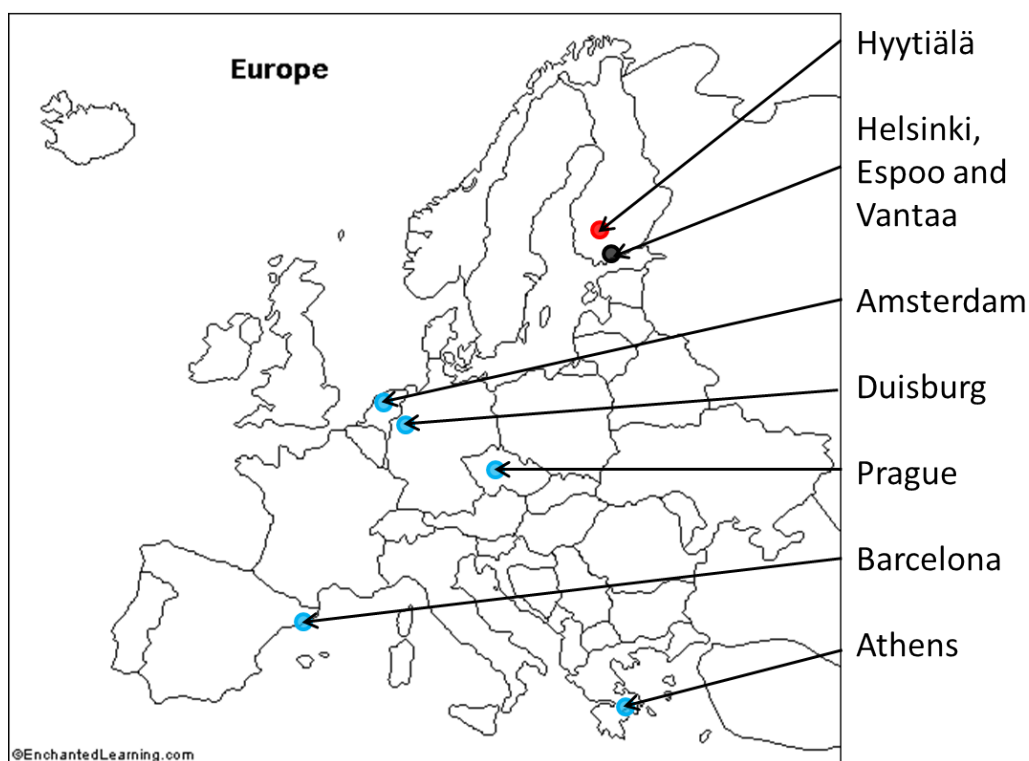
Figure 4. Locations of the ambient measurements included in this thesis. Red dot stands for sampling of MAs and blue sampling of PAHs. Black dot equals a wide range of measurements and samplings, including samplings of MAs and PAHs.

The details of the measurement sites and periods are given in Table 3. Most of the studies included measurements at the SMEAR III station in Helsinki (**Papers I**, **II**, **III**, **IV**). SMEAR III is an urban background station located next to the building of Finnish Meteorological Institute (4 km north of the centre of Helsinki). In **Papers I** and **II**, analytical methods were developed and tested at SMEAR III. In **Paper I**, the results from SMEAR II, the rural background station situated in Hyytiälä, are also presented. In **Paper III**, LRT smokes from wildfires were measured at SMEAR III. In **Paper IV**, the measurements were made, in addition to SMEAR III, at two other urban background sites in Helsinki and three residential sites over the Helsinki Metropolitan Area in order to estimate the contribution of wood combustion on ambient fine particles. In **Paper V**, the measurements were made at urban background sites in six European cities to measure PAHs in size-segregated PM.

Table 3. Sites and periods of the ambient measurements used in this thesis.

Country	City/locality, site	Site type	Measurement periods	Paper
Finland	Helsinki, Kumpula (SMEAR III)	Urban background	15–23 Dec. 2005	**IV**
			10 Feb. 2006–28 Feb. 2007	**III, IV**
			8–19 Dec. 2008	**I, IV**
			14 Jan.–13 Mar. 2009	**I, IV**
			16 Feb.–25 Mar. 2011	**II**
	Helsinki, Kallio	Urban background	21 Mar.–12 May 2003	**V**
			1 Oct.–24 Dec. 2008	**IV**
			2 Feb.–30 Mar. 2009	**IV**
	Helsinki, West Harbour	Urban background	22 Nov.–24 Dec. 2008	**IV**
	Helsinki, Vartiokylä	Residential	2 Feb.–30 Mar. 2009	**IV**
	Espoo, Lintuvaara	Residential	1 Jan.–30 Dec. 2005	**IV**
	Vantaa, Itä-Hakkila	Residential	1 Oct.–24 Dec. 2008	**IV**
	Juupajoki, Hyytiälä (SMEAR II)	Rural background (Boreal forest)	28 Mar.–27 Apr. 2007	**I**
Czech Republic	Prague	Urban background	29 Nov. 2002–16 Jan. 2003	**V**
Germany	Duisburg	Urban background	4 Oct.–21 Nov. 2002	**V**
Greece	Athens	Urban background	2 Jun.–21 Jul. 2003	**V**
Netherlands	Amsterdam	Urban background	24 Jan.–13 Mar. 2003	**V**
Spain	Barcelona	Urban background	28 Mar.–19 May 2003	**V**

4.1.2. Wood combustion experiments

The study of **Paper IV** included wood combustion experiments conducted in the emission research laboratory of the University of Eastern Finland in Kuopio. Two different materials were burnt: wood logs (birch) and coniferous pellets (mainly pine). The experiments were made with three different small-scale combustion appliances: a pellet boiler (pellets), a conventional heat-storing masonry heater (logs), and a sauna stove (logs). The pellet boiler represented a modern technology that is not yet widely used in Finland whereas sauna stove and masonry heater represented the typical wood combustion methods (Tissari et al., 2008; Lamberg et al., 2011). The detailed description of the combustion procedure was given in Lamberg et al. (2011). The emitted combustion air from the continuously operating pellet boiler was diluted with the dilution ratio of ~100 and four 4-h samples were collected. Six combustion tests were performed for the sauna stove (sampling duration 55 min) and five for the masonry heater (65 min). These samplings contained the emissions from an ignition batch and two addition batches. The dilution ratio was ~900 for the masonry heater emissions and ~2000 for the sauna stove.

4.2. Sampling techniques

4.2.1. Size-segregated sampling

The size-segregated sampling is based on the inertia of particles in curvilinear motion (Hinds, 1999). The sample air flow is passed through a nozzle and the output jet is directed against a flat plate. The flow streamlines make a curve and the particles whose inertia exceeds a certain value cannot follow the streamlines impacting on the flat plate while the particles with a smaller aerodynamic diameter stay in the air flow. This property is utilised in inertial impactors.

Several devices that utilise inertia for size-segregation were used during the course of this study:

Micro-Orifice Uniform Deposit Impactor (MOUDI) is a cascade impactor that enables the collection of several size-classes (Marple at al., 1991). At each stage, jets of particle laden air exiting from nozzles impinge on an impaction plate. Smaller particles with less inertia to impact proceed on to the next stage where the nozzles are smaller, the air velocity through the nozzles is

higher and finer particles are collected. This continues on through the cascade impactor until the smallest particles are collected at the after-filter. A 9-stage MOUDI with a PM_{10} inlet was used to collect size-segregated samples of biomass burning smokes at the SMEAR III station in **Paper III**. The aerodynamic cut-off sizes of the MOUDI stages were 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, and 10 µm, the sample flow rate was 30 L min^{-1}, and the sampling duration was typically 72 h (Timonen et al., 2008a; 2008b). The sampling substrates (47 mm) were made of aluminium foil that was washed with deionized water and baked at 120 °C before sampling.

High-Volume Cascade Impactor (HVCI) is a suitable sampling device when a large amount of size-segregated PM needs to be collected, particularly for toxicological tests (Sillanpää et al., 2003). HVCI has been used for collecting ambient samples of urban (Pennanen et al., 2007) and wild fire emissions (Jalava et al., 2006) and for sampling of emissions of wood combustion experiments (Jalava et al., 2010). HVCI was used in **Paper V** to separate the particles in the urban background air of six European cities into four size-ranges: ultrafine ($PM_{0.2}$), accumulation ($PM_{0.2-1}$), intermediate ($PM_{1-2.5}$) and coarse particles ($PM_{2.5-10}$). The sampling flow rate was 850 L min^{-1}. Particles in the three largest size ranges were collected on polyurethane foam substrates (PUF; Antistatic foam 87035K13, McMasterCarr, NJ, USA), and those in the smallest size range on glass fibre filter (Munktell MGA, Munktell Filter AB, Sweden).

Berner Low-Pressure Impactor (BLPI; Berner and Lürzer, 1980) is a cascade impactor that was used in **Papers I**, **II**, and **IV**. BLPI was modified by removing the lower stages and using the upper stages as a pre-impactor for filter sampling (described in Sect. 4.2.2).

In *Virtual Impactor* (VI), the sample air flow is divided into two flows after the accelerating nozzle: major (90%) and minor flow (10%). The smaller particles follow the curving stream of the major flow whereas the larger particles stay in the minor flow that is directed vertically from the nozzle. Instead of impacting the particles on a plate, the separated flows can be collected on filters. VI has been used for filter sampling, e.g. of wildfire emissions (Sillanpää et al., 2005a). In **Paper III**, a VI was used as a pre-impactor before the online coupling of a particle-into-liquid sampler and ion chromatographs. The cut-off diameter of major flow particles was 1 µm with the total air flow rate of 16.7 L min^{-1}.

Cyclones can be used for removing the coarse fraction of particles from the sample air flow. The sample air is drawn into the cyclone through an inlet that is tangential to the cylindrical part of the cyclone (Hinds, 1999). The inlet geometry causes the air to rotate around in the cyclone before exiting at the top centre of the cyclone. The larger particles are deposited on the walls during the rotation due to their centrifugal motion. In **Paper II** a cyclone (sharp cut cyclone SCC1.829, BGI Inc.) was used to cut off the super-micrometer particles before PM_1 mass measurement at TEOM. In **Paper III** the sampling line of the OC/EC field analyser was equipped with a cyclone that had a cut-off at 1 µm with a flow rate of 9.2 L min^{-1}.

In **Paper II** the fine particles for the online measurement were sampled from ambient air through a *size-selective inlet* (Digitel LVS/PM) that removed the particles with an aerodynamic diameter larger than 1 µm.

4.2.2. Filter sampling

Particulate samples were collected on *filters* from the ambient air at SMEAR III (**Papers I**, **II**, **III**, **IV**) and at SMEAR II (**Paper I**), as well as from the wood combustion emissions in the emission research laboratory of the University of Eastern Finland (**Paper IV**).

In the ambient air samplings, the four upper stages of BLPI were used prior to the filter sampling to remove particles larger than 1 µm. The PM_1 samples were collected i) with a filter cassette system (Gelman Sciences) having two pre-fired (800 ºC, 4 hours) quartz filters (47 mm, Pall, Tissuquartz) one upon the other (front + backup) with the flow rate of 80 L min^{-1} (**Papers I**, **III**, **IV**), or ii) by dividing the sample flow in two after the BLPI and using two filter cassette systems in parallel; one with a PTFE membrane filter (47 mm, 3.0 µm FS, Fluoropore™, Millipore, Ireland) and the other with two pre-fired quartz filters (47 mm, Tissuquartz™, Pall Life Sciences, MI, USA) one upon the other with the flow rate of 40 L min^{-1} for each filter cassette (**Papers I**, **II**, **IV**). The typical sampling duration was 10–24 hours on working days and 24–72 hours over the weekends.

Different from the ambient air samplings, the five upper stages of BLPI were used with the flow rate of 25 L min^{-1} to remove the supermicron particles in the wood combustion experiments

(**Paper IV**). The PM_1 samples were collected on PTFE filters. The sampling duration was four hours for pellet burner, 55 minutes for sauna stove, and 65 minutes for masonry heater samples.

In **Paper IV**, PM_{10} samples were collected at the sites in the Helsinki Metropolitan Area, other than SMEAR III, for 24 hours using automatic samplers: Micro PNS samplers with PTFE filters or a Wedding sampler with PTFE coated glass fibre filters.

4.3.   Gravimetric analysis

To determine the mass of the sampled PM_1, the PTFE filters were weighed before and after the sampling with a Mettler Toledo UMT2-balance (readability of 1 µg; Mettler Toledo GmbH, Switzerland). The filter samples were weighed in **Papers I**, **II**, and **IV**.

4.4.   Chemical analyses

Sample treatment and analytical techniques used for the studied particle-phase components are presented in this section. The descriptions can also be found in **Papers I-V**. Analytical techniques for filter and impactor samples are listed in Table 4.

Table 4. Offline chemical analyses used in this thesis.

Instrument	Determined component	Manufacturer	Paper
TOA	EC, OC	Sunset Laboratory Inc.	**III**
TOC-V$_{CPH}$	WSOC	Shimadzu Corp.	**III**
HPLC–MS	Levoglucosan, MAs	Agilent Technologies	**III, IV**
HPAEC–MS	Levoglucosan, MAs	Dionex Corp.	**I, II, IV**
GC–MS	PAHs	Agilent Technologies	**V**
IC	Cl^-, NO_3^-, SO_4^{2-}, oxalate, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Dionex Corp.	**III**

4.3.1. Organic and elemental carbon (OC/EC)

The concentrations of OC and EC in samples collected on quartz filters were determined with a *thermal-optical carbon analyser* (TOA; Carbon analyser, Sunset Laboratory Inc.; Birch and Cary, 1996) in **Paper III**. The analysis was based on thermal-optical transmittance method. The instrument used a two-phase thermal method to separate OC from EC. First, a 1–1.5 cm^2 piece of filter sample was purged with helium (He), and the oven temperature was raised from room temperature to 800 °C using four steps in He atmosphere (310 °C (90s) – 475 °C (90s) – 615 °C (90s) – 800 °C (90s)). During this phase all organic compounds and carbonate carbon were expected to evaporate from the filter. After the first phase the oven was cooled shortly. In the second phase, the oven temperature was increased again in a mixture of O_2 and He (1:49) (550 °C (45s) – 625 °C (45s) – 700 °C (45s) – 775 °C (45s) – 850 °C (45s) – 890 °C). During this phase the possibly remaining organic compounds and EC evaporated from the sample. The evaporated compounds were catalytically oxidised to CO_2 and then reduced to CH_4, and the amount of carbon evolved was quantified with a flame ionisation detector. Part of OC was pyrolised on the filter into compounds resembling EC during the first phase of the thermal analysis. This was corrected optically by measuring the laser light transmittance through the sample during the analysis as the transmittance was decreased by charring of OC. The split between the charred OC and EC was determined in the second phase as the transmittance reached its initial value. The detection limit (LOD) for both EC and OC was about 1 $\mu g \, cm^{-2}$.

4.3.2. Water-soluble organic carbon (WSOC)

WSOC concentration was determined using a *total carbon analyser with a high-sensitive catalyst* (TOC-V$_{CPH}$, Shimadzu) (**Paper III**). An Al-foil sample or a piece of a quartz filter sample was extracted with deionised water. The non-purgeable OC method was used to remove carbonate and CO_2 from the sample before the determination: The sample solution (500 µL) was drawn to the syringe of the analyser in which acid addition (1% 2M HCl) and He bubbling were done. The acid converted all inorganic carbon to CO_2. After the bubbling, the sample was injected into the oven where the sample was catalytically oxidised to CO_2 at 680 °C and CO_2 was detected with a non-dispersive infrared detector. The WISOC fraction was calculated by subtracting the analysed WSOC from the analysed OC (by TOA). The LOD for the TOC-V$_{CPH}$ was 4 $\mu g \, L^{-1}$ and SD of

the repeated measurements was less than 1.5%. The measurement error resulting from the total carbon content in the water used in the sample solutions and in the blank filters was typically much bigger than the error resulting from the system blank value. The estimated error was 15% or 10% for the atmospheric concentrations under or above 2 μg m^{-3}, respectively.

4.3.3. Anhydrosugars (MAs)

Two techniques were used for the determination of levoglucosan, mannosan, and galactosan: *high-performance liquid chromatography–mass spectrometry* (HPLC–MS) and *high-performance anion-exchange chromatography–mass spectrometry* (HPAEC–MS). Both HPLC–MS and HPAEC–MS methods used selected ion monitoring (SIM) at *m/z* 161 for determination of MAs.

HPLC–MS method was based on the method presented by Dye and Yttri (2005) and it was described in detail in Saarikoski et al. (2007) and it was used in **Papers III** and **IV**. A filter sample piece was extracted with a 2-mL mixture of tetrahydrofuran–water (1:1, v/v) with 30-min ultrasonic agitation, and filtered. The used column system consisted of two Atlantis™ dC$_{18}$-columns (2.1 mm *i.d.* × 150 mm length, 3 μm; Waters) in line and deionised water was used as an eluent. Electrospray ionisation (ESI) and ion trap MS were used (Agilent Technologies SL).

HPAEC–MS method was developed, validated, and presented in detail in **Paper I**. More about this method is presented in Sect. 5.1.1. It was used in **Papers I**, **II**, and **IV**. In this method, a piece of filter sample was extracted with 5 mL of deionized water with internal standard (ISTD) and with 15-min rotation, and filtered. The used column system consisted of CarboPac™ PA10 guard and analytical columns (2 mm *i.d.* × 50/250 mm length, respectively; Dionex) and the eluent was produced by a KOH eluent generator. Ionisation technique was ESI and the MS was equipped with a quadrupole mass analyser. The LOD was 2 ng mL^{-1} for levoglucosan and 1 ng mL^{-1} for mannosan and galactosan.

4.3.4. Polycyclic aromatic hydrocarbons (PAHs)

A *gas chromatograph coupled to a mass spectrometer* (GC–MS) was used for the analysis of PAHs in **Paper V**. The particulate samples for the PAH analysis were collected with HVCI on PUF strips and glass fibre filters. The samples were extracted twice with methanol using ultrasonic agitation. All 14 samples per campaign were pooled to form a single ultrafine ($PM_{0.2}$), fine ($PM_{0.2-2.5}$; i.e., $PM_{0.2-1}$ and $PM_{1-2.5}$ combined) and coarse ($PM_{2.5-10}$) particulate sample to represent each 7-week campaign. The methanol extracts were concentrated with a rotary evaporator. The concentrated methanol extract containing $PM_{0.2}$ particles was filtered. All the concentrated methanol extracts were divided into glass tubes and finally evaporated to dryness under nitrogen flow. The sample extraction procedure was validated in earlier studies, using NIST standard reference materials (Jalava et al., 2005; 2006). The concentrations of indicator PAHs in the reference materials were within ±40% of the certified values provided by NIST.

The dry particulate samples were dissolved in dichloromethane and analysed using GC–MS and SIM technique (HP 5970B/HP 5890 GC, Agilent Technologies, Germany). The analytical method was described in detail by Sandell et al. (1999). The column used was a DB-17 (0.25 mm *i.d.* $\times$ 30 m length, phase thickness of 0.15 µm; Agilent J&W GC Column, Agilent Technologies, USA). The quantification was conducted using the ISTD method, and the response factors were calculated against standard solutions at three levels containing 28 parent or substituted PAHs and one oxygen- and three sulphur-containing polyaromatic heterocyclic compounds. The quantification limit (LOQ) for individual PAHs was around 0.0002 ng m^{-3}.

4.3.5. Ions

Inorganic ions and oxalate were determined by two *ion chromatographs* (IC; Dionex DX-500/ICS-3000) (**Paper III**). The analysed ions were Cl^-, NO_3^-, SO_4^{2-}, oxalate, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. The samples were collected on quartz filters. A 1-cm^2 piece of a filter was extracted with 5 mL of deionized water, shaken for 10 minutes, and filtered prior to analysis. The anions were separated using a column system, consisted of guard and analytical columns (AG11/AS11, 4 mm *i.d.* $\times$ 50/250 mm length; Dionex), NaOH or KOH eluent (in DX500 or ICS-3000 instrument, respectively) with a concentration gradient, and either chemical suppression with H_2SO_4 (DX500) or electrochemical suppression (ASRS ULTRA II, 4 mm; ICS-3000). The

cations were analysed using guard and analytical columns (CG12/CS12A; 4 mm *i.d.* $\times$ 50/250 mm length; Dionex), an isocratic MSA eluent, and electrochemical suppression (CSRS ULTRA II, 4 mm). Conductivity cells were used for the detection of the ions. The eluents for the DX500 instruments were prepared manually whereas the ICS-3000 system had automatic eluent generators. Large sample loop sizes (500 µL for anions and 300 µL for cations) were used due to the small concentrations of ions in the samples. The LOQ was 1–5 ng mL^{-1} depending on the ion.

4.5. Online measurements

A description of the online measurements used in this thesis for the investigation of the physical properties and chemical composition of particles is presented in this section. The descriptions can also be found in **Papers II**, **III**, and **IV**. The information of the used instruments is collected in Table 5.

Table 5. Online instruments used in this thesis.

Instrument	Measured component	Manufacturer	Paper
TEOM$^{©}$ 1400a, 1400ab	PM_1, $PM_{2.5}$, $PM_{2.5-10}$	Patashnick & Rupprecht; Thermo Fischer Scientific Inc.	**II, III, IV**
Grimm Model 180 Ambient Dust Monitor	$PM_{2.5}$	Grimm Aerosol Technik GmbH & Co	**IV**
Particulate Monitoring Instrument FH 62 I-R	$PM_{2.5}$, PM_{10}	ESM Andersen Instruments GmbH	**IV**
CPC	Particle number	TSI Inc.	**III**
DMPS	Particle number size distribution (D_p 3–1000 nm)	TSI Inc.	**III**
APS	Particle number size distribution (D_a 0.5–20 µm)	TSI Inc.	**III**
SC-OC/EC	EC, OC	Sunset Laboratory Inc.	**III**
PILS–IC	Cl^-, NO_3^-, SO_4^{2-}, oxalate, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Metrohm Peak Inc. (PILS), Dionex Corp. (IC)	**III**
PILS–HPAEC–MS	Levoglucosan	Metrohm Peak Inc. (PILS), Dionex Corp. (HPAEC–MS)	**II**
HR-ToF-AMS	NO_3^-, SO_4^{2-}, NH_4^+, $C_2H_2O_2^+$, $C_3H_5O_2^+$, organics	Aerodyne Research Inc.	**II**

4.5.1. Measurements of physical properties of particles

Particulate mass monitors

TEOM instruments (TEOM 1400ab, Thermo Fischer Scientific Inc., Germany; TEOM 1400a, Rupprech & Patashnik, USA) were used in **Papers II-IV** to measure the concentrations of the PM_1, $PM_{2.5}$, and $PM_{2.5–10}$ in the air. TEOM uses the tapered element oscillating microbalance technique for the direct mass measurement on a filter with real-time data output.

A *Grimm Model 180 Ambient Dust Monitor* (Grimm Aerosol Technik GmbH & Co., Germany) was used to determining the $PM_{2.5}$ concentration in real time in ambient air in **Paper IV**. The instrument uses an optical technique, based on light scattering, for the determination of particulate mass.

FH 62 I-R Particulate Monitors (ESM Andersen Instruments GmbH, Germany) were used for measuring the $PM_{2.5}$ and PM_{10} concentrations in ambient air in **Paper IV**. The instrument collects particulate mass directly on a filter and uses radiometric technology (beta gauge) for simultaneous mass determination.

Devices for particle number and size distribution measurement

Total number concentration of aerosol particles was measured by using a *condensation particle counter* (CPC; TSI Model 3022) in **Paper III**. CPC measures the number concentration by saturating the aerosol by water or alcohol vapour and cooling it to enlarge the particles so they can be easily detected by optical methods.

The particle number size distribution was measured in **Paper III**. The dried aerosol was measured in the size range of 3–1000 nm (mobility diameter) with a twin *differential mobility particle sizer* (DMPS; TSI Models 3025 (size range of 3–10 nm) and 3010 (10–1000 nm)). Both instruments used a Hauke-type differential mobility analyser (DMA) that classifies particles according to their electrical mobility, and a CPC for particle detection. The larger size range of particles with the aerodynamic diameter (D_a) of 0.5–20 µm was measured using an *aerodynamic particle sizer* (APS; TSI Model 3321). In APS, particles are focused into the centre of a jet of sheath air

and they are accelerated in a nozzle. After the nozzle two laser beams detect the flight-time of the particles. The velocity of the particles is dependent on their aerodynamic size.

4.5.2. Semicontinuous OC/EC analyser

A *semicontinuous OC/EC field analyser* (SC-OC/EC; Model 3, Sunset Laboratory Inc., Oregon, USA) was used to measure online the OC and EC concentrations in PM_1 with a 3-hour time resolution (**Paper III**). SC-OC/EC resembled the carbon analyser designed for laboratory use (TOA; Sect. 4.3.1.) but SC-OC/EC included also the aerosol sampling system. The instrument was equipped with a cyclone that had cut-off at 1 µm with a flow rate of 9.2 L min^{-1} and a parallel plate carbon filter denuder that removed organic gas-phase components from the sample air. The particle samples were collected on the filter situated in the oven of the instrument for 164 minutes after which the sample was analysed with the thermal-optical method. Measurements started every day at 12 a.m., 3:17 a.m., 6 a.m., 9 a.m., 12 p.m., 3 p.m., 6 p.m., and 9 p.m. local time. A daily 2-minute blank sample was collected (at 3 a.m.) and analysed. OC was determined in He-phase with two temperature steps: 300 ℃ (80 s) and 650 ℃ (90 s). EC was determined subsequently in O_2/He-phase (1:49) with three steps: 550 ℃ (30 s), 650 ℃ (45 s), and 850 ℃ (90 s). In addition to thermally determined OC and EC, instrument also measured optical EC (EC_{opt}) with the laser (660 nm). The time resolution for EC_{opt} was three minutes, but instrument also calculated the average result for the selected sampling time. By subtracting optical EC_{opt} from thermally determined total carbon (TC; thermal OC + thermal EC), "optical" OC can be obtained (Saarikoski et al., 2008b). In **Paper III**, the difference between the EC concentration analysed from the PM_1 filters and comparably averaged online measured EC_{opt} concentration was 3.7% whereas the corresponding difference between the EC concentration from the filters and averaged online EC measured thermally was 12%. Additionally, the EC concentrations were probably too low to be determined thermally and therefore the instrumental blank values obtained for thermal EC varied. Only the results of EC_{opt} and "optical" OC were used in **Paper III**.

4.5.3. PILS

Particle-into-Liquid Sampler (PILS) is a device for the online collection of the samples of water-soluble compounds in aerosols (Weber et al., 2001). The design and operation of PILS has been described by Orsini et al. (2003). Briefly, particles in sample flow are mixed with hot water vapour at their arrival into the conical shape cavity of the PILS body. When the particles go through the space, moisture is condensed on particles and they grow in size. After the cavity, the droplets are focused to go through a nozzle that directs the sample flow onto an impaction plate of quartz. The spreading jet of air forces the impacted droplets to the perimeter of the quartz plate. The impaction plate is flushed with a steady stream of transport solution containing ISTD. During the collection, the liquid that was condensed onto the particles and a small amount of water condensing out of the saturated air to the impaction plate dilutes the transport solution. Based on the ISTD concentration before and after PILS, the dilution is taken into account and the aerosol concentration can be accurately calculated. The most useful feature of PILS is that it produces a liquid aerosol sample flow that can be introduced to several analytical devices, e.g. ion chromatographs, analysers for WSOC, or liquid wavelength capillary cell and absorbance spectrophotometry (e.g. Orsini et al., 2003; Sullivan et al., 2004; Rastogi et al., 2009; Timonen et al., 2010). One of the aims of this study was to connect PILS with HPAEC–MS, in order to determine levoglucosan concentrations online with a high time resolution.

PILS–HPAEC–MS

The HPAEC–MS method (described in Sect. 4.3.3. and in **Paper I**), originally designed for the offline analyses, was further developed for the online analysis of levoglucosan with particle-into-liquid sampler (PILS–HPAEC–MS) in **Paper II.** The details about the PILS–HPAEC–MS method development are given later in Sect. 5.1.2. Fine particles were sampled from ambient air through a size-selective inlet (Digitel LVS/PM) that removed the particles larger than 1 µm. The air flow (16.7 L min^{-1}) was directed to PILS where the particles impacted onto the impaction plate. Impaction plate was flushed with a steady stream of a standard solution (130 µL min^{-1}) containing ISTD (methyl-β-D-arabinopyranoside) and the standard addition of levoglucosan after which the solution was split at a debubbler unit. The flow rate of the effluent that was directed to

the sample loop (50 µL) of the HPAEC instrument was 70 µL min^{-1}. Then the sample was automatically injected into the column for the analysis. During the time required for the sample elution and detection (less than eight minutes), the sample loop was flushed and filled with the following sample. The HPAEC–MS instrument was the same as used in a laboratory. The analysis program that was 15 minutes in the laboratory was shortened to eight minutes for the PILS–HPAEC–MS system (described in Sect. 5.1.2).

PILS–IC

PILS followed by the IC analysis was used for the continuous determination of the ion composition of aerosol particles (**Paper III**). The online system consisted of three annular denuders in series (URG-2000, 30 mm × 242 mm, Chapel Hill, NC), a VI (cut-off at 1 µm), a PILS, two ion chromatographs for anion and cation determination (Dionex ICS-2000), and an 8-channel peristaltic pump. Two of the denuders were coated with KOH (1%) solution and one with H$_3$PO$_4$ (3%) solution to remove acidic and basic gases, respectively, from the sample air flow. The VI major flow (15 L min^{-1}), with the particles smaller than 1 µm, was directed into PILS. The impacted particles were transported from the collection plate of PILS with an internal standard solution (LiF) and delivered after a debubbler unit into two sample loops (1000 µl), one for anion and the other for cation determination. The analysed ions were Cl$^-$, NO$_3^-$, SO$_4^{2-}$, oxalate, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, and Ca^{2+}. The time resolution of the PILS–IC method was 15 minutes. The analytical equipment in ICS-2000 and the analysis programs were similar to those used in ICS-3000 (presented in Sect. 4.3.5).

4.5.4. Aerosol mass spectrometer

A *High Resolution Time-of-Flight Aerosol Mass Spectrometer* (HR-ToF-AMS; Aerodyne Research Inc.; DeCarlo et al., 2006) was used in **Paper II** for the comparison of biomass burning tracers from the online measurements. A detailed description of the method is given by Timonen et al. (2010; 2013) and Saarikoski et al. (2012). The time resolution of the HR-ToF-AMS measurements was six minutes. The collection efficiency (CE) of 0.5 was used in order to calculate

the ambient concentrations of the chemical species (SO_4^{2-}, NO_3^-, NH_4^+, $C_2H_2O_2^+$, $C_3H_5O_2^+$, organics) from the HR-ToF-AMS data. CE depends on several factors, e.g. particle chemical composition and relative humidity (Middlebrook et al., 2012) but according to Timonen et al. (2010) a CE=0.5 is valid for the HR-ToF-AMS data collected in Helsinki in springtime.

4.6. Supporting data and methods

The local meteorological data, including air temperature, wind speed, and wind direction, was measured at the weather station next to SMEAR III station in Kumpula, Helsinki (**Papers II, IV**). Visibility was measured using a Vaisala FD12P weather sensor at the Kaisaniemi weather station located 4 km south of SMEAR III station in the downtown of Helsinki (**Paper III**). In the study of six European cities (**Paper V**), the data of air quality and meteorological parameters (O_3, air temperature, and global radiation) were acquired by the local air quality administration.

The backward air mass trajectories were achieved using HYSPLIT (NOAA Air Resources Laboratory; Draxler and Rolph, 2013) (**Paper II**) and FLEXTRA (Stohl and Wotawa, 1995) (**Paper IV**) trajectory models.

The Fire Assimilation System (Sofiev et al., 2009) and the SILAM modelling system (Sofiev et al., 2006, 2008) were used in **Paper III** for evaluation of the emission fluxes from wildfires.

5.   RESULTS

The results of this thesis are divided into four parts. The first part summarises the results from the development of offline and online methods for MAs. In the second part online and offline techniques are compared in the ambient measurements. Part three describes the characteristics of fine particles from small-scale combustion and in smoke plumes transported from open-land fires. The results are complemented with the fourth part summarising the findings on PAHs in size-segregated PM in urban background air from six European cities.

5.1.   Developed analytical methods

One of the specific aims of this study was to develop a fast and simple analytical method for the analysis of MAs. The method needed to be suitable for the further development from an offline technique to an online method. In literature, several techniques have been used for the determination of MAs, such as GC or HPLC coupled to MS (e.g. Schkolnik and Rudich, 2005, and references therein; Dye and Yttri, 2005) or HPAEC with pulsed amperometric detection (e.g. Engling et al., 2006; Caseiro et al., 2007; Iinuma et al., 2007; Puxbaum et al., 2007). Earlier in our laboratory, HPLC–MS was used for the analysis of MAs from filters (used in **Papers III** and **IV**); however, the instrument was not suitable to be taken on the field measurements. Therefore, an ICS-3000 instrument was upgraded with an ESI/MS detector in order to create a new, completely water-based method for the analysis of MAs (used in **Papers I** and **II**).

5.1.1. HPAEC–MS

A new analytical method for the fast and easy determination of MAs was developed by combining the separation of analytes by a high-performance anion-exchange chromatograph with a detection of quadrupole mass spectrometer using electrospray ionisation (HPAEC–MS) (**Paper I**).

Sample preparation method was only a rotation for 15 min. The extraction efficiency was tested by extracting the samples twice and analysing both the extracts separately. In the latter extract,

less than 0.6% of MAs was found. Therefore, only a single extraction was chosen. The sample preparation procedure was tested further with the simultaneously collected ambient PM_1 samples both on quartz and PTFE filters, and compared to the extraction with 30 min of ultrasonic agitation. It was found that the difference between the extractions by rotation and by ultrasonic agitation was insignificant for both the quartz and PTFE filters. However, the measured concentrations from the PTFE filters were on average 4% higher for levoglucosan and 9% for mannosan than from the quartz filters (Fig. 5a). The measured galactosan concentrations were on average 8% lower from the PTFE than the quartz filters. Because the results were fairly similar to the two filter materials, the use of water as an extraction agent seemed to be suitable for PTFE too, despite its hydrophobicity.

MAs were detected by monitoring m/z 161 and the ISTD (^{13}C-labelled levoglucosan) by m/z 167. The operating parameters of MS were chosen so that minimum fragmentation and best sensitivity were achieved. However, the high probe temperature caused a slight dehydration of galactose, glucose, and mannose forming galactosan, levoglucosan, and mannosan. Thus it was important to elute monosaccharides during the desired analysis time; otherwise carry-over peaks might exist in the following analysis overlapping with the peaks of MAs and causing incorrect results.
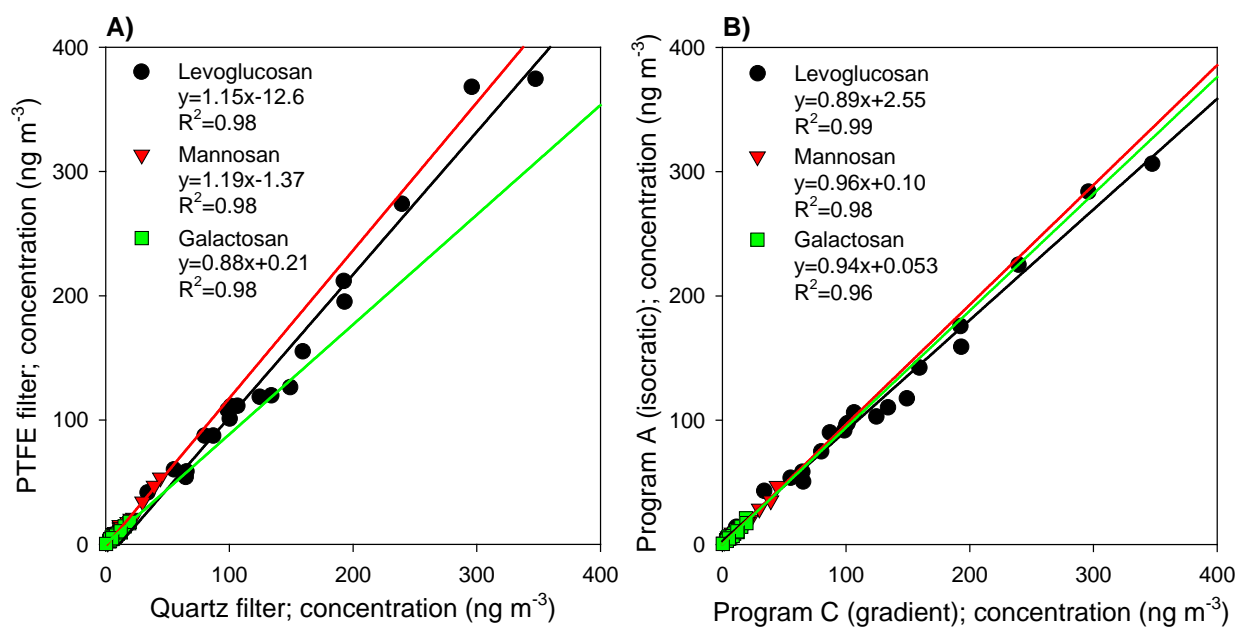
Figure 5. Comparison of simultaneously collected ambient PM_1 samples on the quartz and PTFE filters (**a**), and the comparison of the tested analysis programs A and C (**b**).

An isocratic program and programs with a concentration gradient were tested for the separation of MAs and other sugar compounds. Using Program A (isocratic eluent 2 mM, flow rate of 0.250 mL min^{-1}), the MAs isomers were separated and, additionally, mono- and disaccharides and some of the polyols were separated. The run-time for eluting all the selected compounds was nearly 25 min. However, the goal was to develop a fast method for a routine analysis of MAs and not to analyse other sugar compounds but to get them out of the column as quickly as possible. In order to accelerate the elution of the compounds after MAs, gradient elution programs were tested (Programs B and C). In Program C, the best peak shapes were achieved by using a flow rate of 0.200 mL min^{-1} and the starting eluent concentration of 0.5 mM. After the eluent gradient, an isocratic step with a high eluent concentration was added for cleaning out the compounds that have high retention to the stationary phase. Therefore the analysis run was shortened to 15 min (0.5 mM (1 min) – 2.375 mM min^{-1} (to 10 mM) – 65 mM (6 min) – 0.5 mM (4 min); flow rate 0.200 mL min^{-1}) by advancing the cleaning step, whereupon mono- and disaccharides were incompletely separated. The Programs A and C were compared by using 20 ambient PM$_1$ samples collected on quartz filters (Fig. 5b). The differences between the two programs were minor. The chromatographic and validation parameters for the HPAEC–MS method with the separation program C are given in Table 6 (the determination of the parameters presented in **Paper I**).

Table 6. Summary of chromatographic and validation parameters of the HPAEC–MS method.

	Levoglucosan	Mannosan	Galactosan
Peak resolution (in the linear range)	1.57 – 1.04	3.31 – 2.35	n.a.
Asymmetry (in the linear range)	1.13 – 1.39	1.19 – 1.32	1.14 – 1.37
Linear range (ng mL^{-1})	5 – 370	1 – 20	1 – 10
Coefficient of determination in the linear range (%)	99.95	99.63	99.64
Detection limit, LOD (ng mL^{-1})	2	1	1
Quantification limit, LOQ (ng mL^{-1})	5	3	3
Determination range (ng mL^{-1}), with quadratic fitting	5 – 2000	3 – 400	3 – 400
Precision (% RSD), standard solution	3.9	4.5	5.9
Precision (% RSD), PM$_1$ sample	4.3	8.5	8.3
Accuracy (%, recovery), quartz filter samples	94 ± 4	103 ± 4	101 ± 6

For some reason, levoglucosan had a lower response at MS than mannosan and galactosan. The higher LOD and LOQ values for levoglucosan than for two other MAs might be due to that reason, and additionally, due to ion suppression that is caused by the co-elution of other compounds (ISTD, and possible sugar-alcohols in samples) with levoglucosan, which decreases the sensitivity. The overall method uncertainties were about 12–15% for each MAs.

5.1.2. PILS–HPAEC–MS

The sampling by PILS was combined with HPAEC–MS (developed in **Paper I**) to enable an online analysis of levoglucosan in ambient aerosol with an enhanced time resolution (**Paper II**). The operational description of the sampling procedure was described above in Sect. 4.5.3. The sampling line did not include denuders because levoglucosan is primarily in particle phase in the ambient temperature (Oja and Suuberg, 1999). The sample loop was filled in less than one minute and the sample was automatically injected into the column for the analysis. During the time required for the elution and detection of MAs, the sample loop was flushed and filled with the following sample.

In order to get data with a highest possible time resolution, the HPAEC–MS analysis time was chosen to be less than in the offline method (15 min). MAs elute in less than eight minutes with an isocratic eluent (2 mM KOH; 0.250 mL min^{-1}) but there is a possibility that the later eluting monosaccharides may overlap with MAs in the following analysis runs. It was earlier seen that monosaccharides slightly dehydrate during ionisation and form MAs (**Paper I**). However, glucose was not found in wintertime PM$_1$ filter samples and therefore the shorter run-time was considered suitable for the PILS–HPAEC–MS method. A minor drawback with this method is that the achieved data are only semicontinuous and the chromatograms represent less than one minute sampling of every eight minutes period.

Methyl-β-D-arabinopyranoside (me-β-ara) was used as ISTD in the PILS–HPAEC–MS method, because its retention time differs from levoglucosan, and therefore it does not cause ion suppression in levoglucosan determination like levoglucosan-$^{13}C_6$. The consumption of ISTD is notable

in the PILS–HPAEC–MS method, and as an inexpensive chemical, me-*β*-ara is also an economical option. The ISTD concentration of 100 ng mL^{-1} was most suitable for the method.

In the PILS–HPAEC–MS method, the LOD and LOQ values were estimated to be 5–10 ng mL^{-1} (21–42 ng m^{-3} in ambient air) and 20–30 ng mL^{-1} (84–126 ng m^{-3}), respectively. The linear range of the HPAEC–MS method was from 5 to about 200 ng mL^{-1} when me-*β*-ara was used as ISTD. Moreover, the determination of the higher levoglucosan concentrations up to about 500 ng mL^{-1} succeeded using the quadratic calibration curve. The determination range of the PILS–HPAEC–MS method was from LOQ to 500 ng mL^{-1} (from 84–126 ng m^{-3} to about 2.1 µg m^{-3}).

The limitation of the PILS–HPAEC–MS method was the determination of levoglucosan of low concentrations. The average wintertime concentration of levoglucosan in the ambient urban background air of Helsinki is on the same concentration level as the estimated LOQ value of the PILS–HPAEC–MS method. Therefore a standard addition method was tested to improve the analytical range of the levoglucosan determination. With the standard addition of 50 ng mL^{-1} also the small concentrations of levoglucosan could be determined (Fig. 6; period E). The PILS–HPAEC–MS method was not capable of measuring mannosan and galactosan, due to their significantly lower concentrations in ambient air. In **Papers I** and **IV**, levoglucosan contributed on average 86% to the sum of MAs in Helsinki.
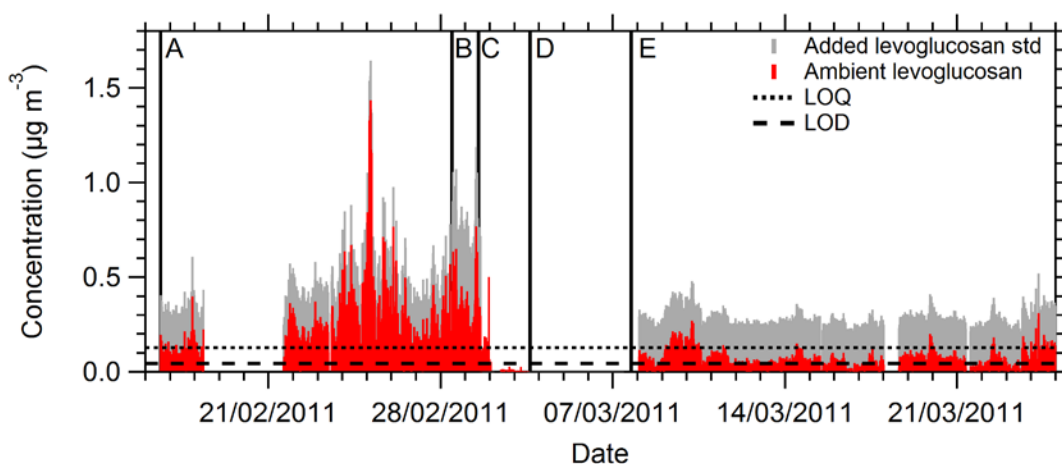
Figure 6. Ambient levoglucosan concentrations during the method development campaign and the changes in the analytical conditions. The concentrations of ISTD and standard addition, respectively (ng mL^{-1}): (A) 50, 50; (B) 50, 100; (C) 50, 0; (D) 100, 0; (E) 100, 50.

5.2.   Comparison between online and offline techniques

Biomass burning related particles were measured simultaneously with online and offline tech-niques in two of the papers of this thesis. In **Paper II**, ambient fine particle concentrations were measured at SMEAR III in winter 2011. Levoglucosan was determined online with PILS–HPAEC–MS and offline with the filter samples. The correlation between the online and offline techniques was good but PILS–HPAEC–MS somewhat underestimated the concentrations of levoglucosan giving on average 20% lower results than those obtained from the filters with HPAEC–MS (Fig. 7).
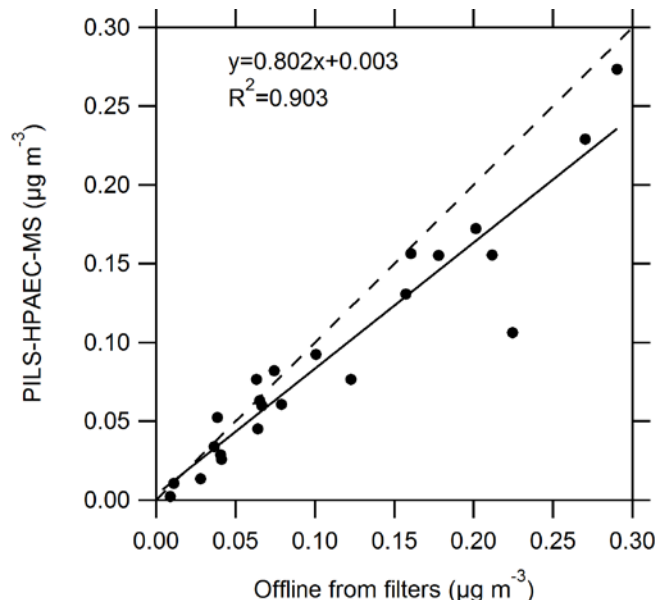
Figure 7. Comparison of levoglucosan concentrations measured online with PILS–HPAEC–MS (averaged to filter samplings) and offline with the filters analysed with HPAEC–MS (n=23).

In **Paper III**, LRT smoke plumes were studied at SMEAR III using the online techniques (SC-OC/EC, PILS–IC) and the filter samples with the offline analysis (TOA, IC) for EC, OC, and ions. The time resolution was 3 h for SC-OC/EC and 15 min for PILS–IC whereas the filters were collected for 10–72 hours. In order to compare the online and offline techniques in the re-search of short-term plumes, the results of online measurements were averaged to the corre-sponding the filter samplings (Table 7).

Table 7. Average concentrations ($\pm$ SD) of chemical species ($\mu g\ m^{-3}$) from the analyses of PM_1 filter samples (**a**) and online determinations averaged to the PM_1 filter sampling times (**b**) during the plumes (PLU), the non-plume times (NON), the whole episodic period of plumes (EPI=PLU+NON), and on the reference period (REF).

	PLU	NON	EPI	REF
a) offline analysis of filter samples				
EC	1.3 ($\pm$ 0.35)	0.85 ($\pm$ 0.31)	1.0 ($\pm$ 0.40)	0.65 ($\pm$ 0.24)
OC	8.7 ($\pm$ 3.2)	3.5 ($\pm$ 1.4)	6.1 ($\pm$ 3.6)	1.6 ($\pm$ 0.71)
Oxalate	0.24 ($\pm$ 0.083)	0.14 ($\pm$ 0.026)	0.19 ($\pm$ 0.076)	0.093 ($\pm$ 0.060)
Sulphate	2.0 ($\pm$ 0.90)	1.7 ($\pm$ 0.41)	1.9 ($\pm$ 0.71)	1.4 ($\pm$ 1.2)
Nitrate	0.68 ($\pm$ 0.38)	0.45 ($\pm$ 0.41)	0.56 ($\pm$ 0.40)	0.31 ($\pm$ 0.26)
Ammonium	0.86 ($\pm$ 0.43)	0.67 ($\pm$ 0.23)	0.77 ($\pm$ 0.35)	0.54 ($\pm$ 0.54)
Potassium	0.075 ($\pm$ 0.037)	0.041 ($\pm$ 0.011)	0.058 ($\pm$ 0.032)	0.036 ($\pm$ 0.046)
b) online measurements averaged to the filter samples				
EC	1.3 ($\pm$ 0.34)	0.85 ($\pm$ 0.33)	1.1 ($\pm$ 0.40)	0.73 ($\pm$ 0.26)
OC	12.3 ($\pm$ 4.0)	6.0 ($\pm$ 4.1)	9.5 ($\pm$ 5.1)	2.6 ($\pm$ 1.1)
Oxalate	0.17 ($\pm$ 0.076)	0.060 ($\pm$ 0.032)	0.10 ($\pm$ 0.082)	0.040 ($\pm$ 0.024)
Sulphate	2.8 ($\pm$ 1.1)	2.1 ($\pm$ 0.55)	2.3 ($\pm$ 1.0)	1.5 ($\pm$ 1.8)
Nitrate	0.74 ($\pm$ 0.40)	0.57 ($\pm$ 0.55)	0.59 ($\pm$ 0.48)	0.34 ($\pm$ 0.42)
Ammonium	1.8 ($\pm$ 0.65)	1.3 ($\pm$ 0.35)	1.4 ($\pm$ 0.65)	0.80 ($\pm$ 0.84)
Potassium	0.096 ($\pm$ 0.054)	0.046 ($\pm$ 0.020)	0.062 ($\pm$ 0.049)	0.040 ($\pm$ 0.052)

SC-OC/EC measured systematically higher concentrations for OC than TOA. When the SC-OC/EC results for OC were averaged over the filter sampling times, the average OC concentrations were about 1.5-fold to the TOA results. The difference was partly methodological: i) SC-OC/EC was equipped with a gas-removing denuder but possibly part of the gaseous compounds have passed the denuders during the high-concentration plumes and thus have caused positive artefacts for online determination; ii) particle-bound components were analysed more promptly in the online analysis whereas during the filter sampling evaporation and/or adsorption of semi-

volatile organic material may have occurred due to the long sampling time; iii) to remove the positive sampling artefact in the filter sampling, the concentration of OC on back-up filter was subtracted from the front filter concentration that may have caused an underestimation of particulate OC. The back-up correction was on average ($\pm$ SD) $6.0 \pm 1.4\%$ during the plumes and $15 \pm 4.1\%$ during the reference period. The concentrations of EC were quite similar from the online and offline techniques.

Oxalate concentrations from the online and offline techniques corresponded well during the plumes. When the oxalate concentration was low, the results with PILS–IC were about half of those from the filters. Oxalic acid formation may happen during the filter sampling: particle-bound glyoxylic acid may be oxidised and concurrently longer-chain dicarboxylic acids may decay forming oxalic acid (Sorooshian et al., 2006). Besides formation on the filter during the sampling, the lower concentration of oxalate in the online analysis could be explained by the fact that at times the concentrations of oxalate were close to LOQ in the PILS–IC method, which increased the determination uncertainty of oxalate. Oxalate might also have degraded in the hot vapour during the PILS sampling.

The online and offline techniques corresponded relatively well for sulphate and nitrate, showing slightly higher concentrations with the online technique. Notably higher concentrations of ammonium were measured with PILS–IC than from filters that could be partly due to highly hydrophilic ammonia passing the denuders. The potassium ion concentration was higher with PILS–IC than with filters but only during the plumes.

The online methods measured the alteration between the short-term plumes and non-plume times more specifically than it was able using filter samples that were roughly divided into plume- and non-plume-samples.

In general, online measurements presented valuable data on temporal variations that could not be obtained with the filter sampling. However, conventional filter and impactor techniques enable sampling of larger air volumes and hence larger amounts of PM than online techniques. Large amounts of PM may be needed for analysis of trace components. It can be concluded than online and offline techniques complemented one another.

5.3. Characteristics of biomass burning emissions

5.3.1. Anhydrosugars

Levoglucosan, either alone or as a part of the sum of three MAs, was the most widely used tracer for biomass burning emissions in this thesis. For example, during the LRT smokes from open-land fires in August 2006, levoglucosan concentration was 18-fold compared to the reference period on average (**Paper III**). The concentrations of other tracer components also increased but not as significantly: the increase was 4.2-fold for oxalate, 3.0-fold for K^+, and 2.1-fold for Cl^- and for EC. The increase of $PM_{2.5}$ mass (3.5-fold) and OC (8.0-fold) were higher than those of some of the tracer compounds.

In **Paper IV**, the concentrations of MAs were measured at three urban background sites and at three suburban residential small-house areas in the Helsinki Metropolitan Area in selected periods during 2005–2009. Excluding the episodes of the LRT smokes, levoglucosan and MAs also had a seasonal dependence; the highest concentrations were measured during the cold season when there is need for additional heating, and the meteorological conditions cause more often stagnant situations (temperature inversion) that prevent the mixing of the emissions (**Papers I**, **II**, **IV**). Similarly to seasonal differences, the day-to-day differences are related to ambient temperature that is reflected both in the quantity of wood combustion emissions and in atmospheric mixing of emissions. A clear spatial variation was observed in the area; the measured concentrations were typically higher at suburban sites than at urban sites. The higher concentrations at suburban sites were estimated to originate mainly from local wood combustion. The local emissions could have be seen at the suburban sites but they were diluted and/or mixed before the same air-masses reached the urban sites or the local emissions from suburbs did not drift to the urban sites, and therefore the concentrations of MAs were notably lower there.

Even though the data set was limited, a slight day-of-the-week variation was observed during the cold season. The medians of MAs were higher on Wednesdays and Saturdays at the suburban sites (Fig. 8a) and on Saturdays at the urban sites (Fig. 8b) that could be explained at least partly by the fact that those two are the days when sauna stoves are traditionally heated in Finland but presumably most of the concentrations of MAs are caused by masonry heaters.
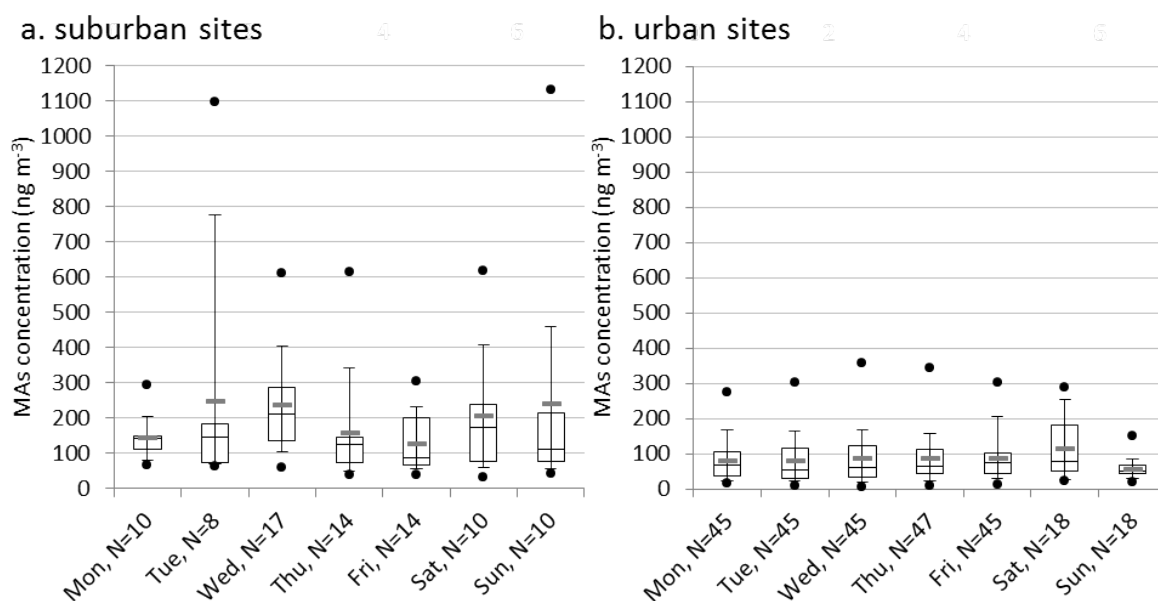
Figure 8. Day-specific variation in MAs concentration at suburban (**a**) and urban sites (**b**). The median (black line inside the boxes), 25 and 75 percentile values (box lower and upper limits), 10 and 90 percentile values (error bars), the highest and the lowest values (black dots), and the mean value (grey horizontal bar) are presented for each day of the week during the cold season.

MAs were also studied from the wood burning emissions in the laboratory where three combustion appliances and two wood fuels were tested (**Paper IV**). The emission factor of MAs was 7.9 and 3.3 mg kg^{-1} fuel when birch wood logs were burnt in a sauna stove and in a masonry heater, respectively. The emission factor of MAs was much lower (0.025 mg kg^{-1} fuel) when the fuel was coniferous pellets (mainly of pine) and the used burner was a modern pellet boiler.

It was observed that the measured proportions of MAs in the combustion emissions (Table 8b) corresponded well with the proportions of monosaccharides (Table 8a) that were calculated from the composition of cellulose and hemicelluloses in birch and pine trees (Pettersen, 1984). It was assumed that glucose, mannose, and galactose in biomass produce levoglucosan, mannosan, and galactosan in the same ratio in pyrolysis, and therefore the ratios of MAs can be used for the estimation of the type of the burnt biomass. The measured proportions of MAs in ambient air corresponded mainly well with those calculated for the estimated firewood usage in Finland (Table 8). During the episodes of the LRT smokes in 2006 (**Paper III**), the proportions of MAs differed from the typical ambient proportions (Table 8) (**Paper IV**). The ratio of levoglucosan to galactosan was much lower during the plumes than during other times. That was probably because of

burning of foliar material in open-land fires whereas wood logs are burnt in residential combustion.

Table 8. Average calculatory proportions of monosaccharides in tree species (**a**), measured average proportions of MAs in combustion experiments (**b**) and in ambient air particles (**c**), and estimated proportions of MAs based on monosaccharides in the firewood used in Finland (**d**).

a) Calculatory proportions in tree species (%)					Glucose	Mannose	Galactose
Pine tree					77	18	5
Birch tree					95	4	1
b) Material	**Burner type**	**Conditions**		**Sample type**	**Levogl. (%)**	**Mannosan (%)**	**Galactosan (%)**
Pine pellet	Pellet boiler	Efficient combustion		PM$_1$	82.7	13.5	3.7
Birch log	Masonry heater	Conventional batch combustion		PM$_1$	92.0	5.7	2.4
Birch log	Sauna stove	Inefficient batch combustion		PM$_1$	95.0	3.0	2.0
c) Site	**Description**	**Sampling period**		**Sample type**	**Levogl. (%)**	**Mannosan (%)**	**Galactosan (%)**
SMEAR III	Urban backg.	Cold season 2006–7		PM$_1$	79.0	12.2	8.8
SMEAR III	Urban backg.	Warm season 2006		PM$_1$	75.8	12.1	12.1
SMEAR III	Wildfires	Spring 2006		PM$_1$	70.9	11.5	17.6
SMEAR III	Wildfires	August 2006		PM$_1$	66.8	12.4	20.9
SMEAR III	Urban backg.	Cold season 2008–9		PM$_1$	85.8	9.7	4.5
Lintuvaara	Residential	Cold season 2005		PM$_{10}$	79.1	11.9	9.0
Lintuvaara	Residential	Warm season 2005		PM$_{10}$	75.2	16.0	8.8
Itä-Hakkila	Residential	Oct.–Dec. 2008		PM$_{10}$	82.0	12.0	6.0
Vartiokylä	Residential	Feb. –Mar. 2009		PM$_{10}$	83.9	10.6	5.5
Kallio	Urban backg.	Oct.–Dec. 2008		PM$_{10}$	82.4	11.4	6.1
Kallio	Urban backg.	Feb. –Mar. 2009		PM$_{10}$	82.4	12.1	5.5
West harbour	Urban backg.	Nov.–Dec. 2008		PM$_{10}$	82.5	11.2	6.3
SMEAR II	Rural forest	Spring 2007		PM$_1$	82.5	10.9	6.6
d) Estimated produced proportions (%)					**Levogl.**	**Mannosan**	**Galactosan**
From firewood usage in Finland (METLA, 2010)					86	11	3

5.3.2. Contribution of wood combustion to ambient particles

Typically source-specific estimations are made using factor analysis techniques, such as positive matrix factorisation that uses a wide range of chemical values (e.g. Saarikoski et al., 2008b). The estimates of the contribution of biomass burning to atmospheric aerosols have also been calculated based solely on the amount of levoglucosan in particles (e.g. Zdráhal et al., 2002; Yttri et al., 2005; Puxbaum et al., 2007; Wang et al., 2007; Saarikoski et al, 2008a).

In **Paper IV**, the contribution of wood combustion to ambient particles was estimated in the Helsinki Metropolitan Area. A ratio for $PM_{2.5}$-to-MAs (24.4 ± 9.2) was derived by using the results from the previous studies (Viidanoja et al., 2002; Frey et al., 2009; **Paper III**) in order to estimate the contribution of wood combustion to ambient $PM_{2.5}$. The concentrations of MAs and PM were measured at three urban background sites and at three suburban residential small-house areas in selected periods during 2005–2009. These data were utilised to study the impact of wood combustion on ambient PM concentration levels.

The average contribution of wood combustion emissions to fine particles ranged from 18% to 29% at the urban sites and from 31% to 66% at the suburban sites in cold season (October–March). At the urban sites, the wood combustion particles were estimated to be caused by regional distribution whereas at the suburban sites both local wood combustion and regionally distributed emissions from wood combustion contributed to the PM concentration. The local wood combustion emissions were estimated to cause occasionally even 10–15 µg m^{-3} of additional daily mean concentration of $PM_{2.5}$ while the average of the additional daily concentration of $PM_{2.5}$ was about 1–3 µg m^{-3} during the cold season depending on the site.

5.3.3. Transported emissions from wildfires

In 2006 two major episodes of transported smokes from open-land fires were detected in Helsinki. The first episode was a 12-day period in April–May with nearly constantly upraised level of particles transported from agricultural fires with the transport time of 1–4 days and it was characterised in detail by Saarikoski et al. (2007). The second episode period that lasted nearly whole August, was a series of short-duration, high-concentration plumes from forest and bog fires close to Finland. The second episode is discussed more closely in this thesis (**Paper III**).

During the episode in August 2006, the highest measured $PM_{2.5}$ mass concentration was 180 µg m^{-3} (30-min average). The size distributions measured by DMPS and APS as well as the ion and WSOC determinations from the MOUDI and filter samples showed that the major growth in PM concentration during the plumes was caused by the particles smaller than 1 µm and by the contribution of POM. The WSOC-to-OC ratio was lower during the smoke plumes than at other times (Fig. 9). That implied that the particulate matter did not have oxidised greatly during the transportation, which agreed well with the fact that the smoke plumes originated relatively close to the observation site and the chemical mass closure (Fig. 9) could be attained by using a relatively low POM-to-OC conversion factor of 1.6 during the smoke plumes. Individual plumes differed from each other. During some of the plumes, the mass size distribution of PM changed and the chemical composition of PM changed along with size distribution, which was mainly due to mixing of wild-fire smokes with other emissions.
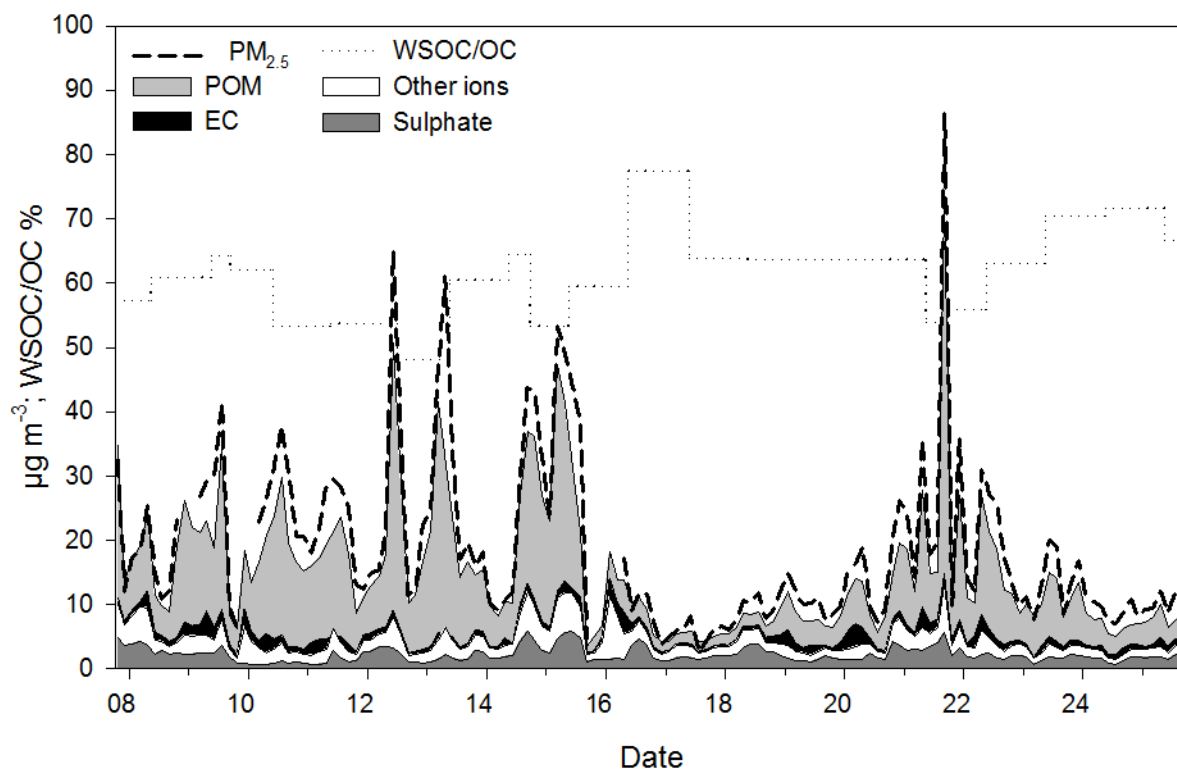
Figure 9. Chemical mass closure for fine particles during the episode of fresh smoke plumes detected at SMEAR III in August 2006. All online values were averaged to 3-hour time resolution. The WSOC/OC ratio is based on the PM_1 filter samples analysed offline.

The episodes in April-May and in August were compared with each other in **Paper III**. The concentrations of K^+ and EC did not increase during the August plumes as much as during the spring episode. In the spring episode, the K^+-to-OC ratio was 3.3-fold and EC-to-OC ratio 1.6-fold compared to the plumes of the August episode period implying that the two episode periods did not have differences in burning material only, but also the form of burning was different. Burning material in spring was mostly dry and easily burning hay and crop residue from the previous season. In August, due to burning of fresh vegetation, the quality of burning was more like smouldering emitting a lot of OC instead of EC. Another difference between the two episodes was found in the contribution of water-soluble organic carbon. In spring the WSOC-to-OC ratio was larger during the plumes than in the reference period whereas in August the WSOC-to-OC decreased during the plumes. That can be explained by the age of the plumes as in August the fires were close to Finland, and the transport time was short, but in May-April the smoke particles were much more aged.

5.4. Study of PAHs in urban background particles

PAHs were investigated in size-segregated particulate samples collected in a series of 7-week sampling campaigns in Europe 2002–2003 (Duisburg – autumn, Prague – winter, Amsterdam – winter, Helsinki – spring, Barcelona – spring, Athens – summer) (**Paper V**). The PAH contents were determined from the $PM_{0.2}$, $PM_{0.2-2.5}$, and $PM_{2.5-10}$ samples of the six campaigns.

PAHs in urban background air particles

The PAH concentrations were high (PM_{10}-PAH 9.9–55 ng m^{-3}) in the autumn and winter campaigns compared to the spring and summer samples (PM_{10}-PAH 2.9–5.2 ng m^{-3}). In Prague, the contribution of PAHs to PM was highest in $PM_{0.2}$, whereas in the five other cities the PAH contribution was highest in $PM_{0.2-2.5}$ (Fig. 10). PAHs with four rings had a large contribution (41–47% of total PAH concentration in PM_{10}) to the total PAHs in each of the campaigns. In the cold season campaigns, the contributions of the 5- and 6-ring PAHs, many of which are suspected carcinogens or genotoxic agents, became prominent in the fine (28–45%) and ultrafine (41–65%) size ranges.
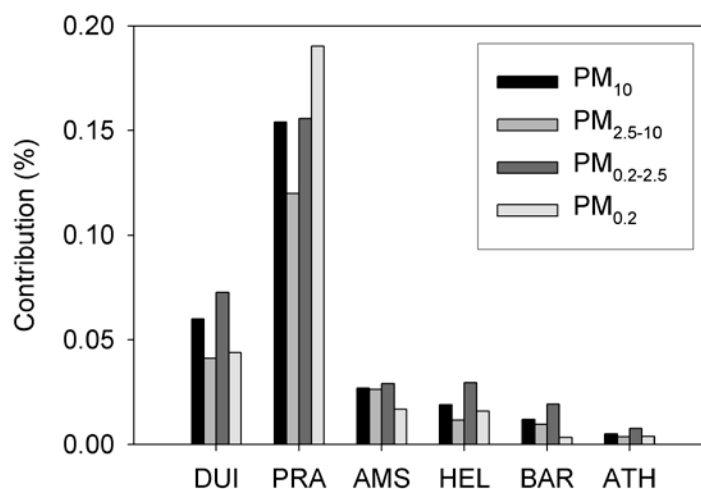
Figure 10. Relative contribution of total PAHs to all thoracic particles (PM_{10}), and to the coarse ($PM_{2.5-10}$), fine ($PM_{0.2-2.5}$), and ultrafine ($PM_{0.2}$) size range. DUI = Duisburg, PRA = Prague, AMS = Amsterdam, HEL = Helsinki, BAR = Barcelona, ATH = Athens.

Assessment of PAH emission sources

Major sources of PAHs, especially in large urban areas, are gasoline and diesel vehicles, coal and oil combustion as well as biomass combustion (Rogge et al., 1993; Finlayson-Pitts and Pitts, 2000; EC, 2001). Since the HVCI samples were pooled to represent each 7-week campaign in **Paper V**, the determination of any single short-term PAH emission source was not possible. Nevertheless, the hints of the sources were searched by using the ratios of some particulate PAHs. Based on the PAH ratios biomass burning was a possible source in the Helsinki spring and Prague winter campaigns. Previous studies from the same campaigns has suggested that biomass burning had a higher contribution to $PM_{2.5}$ in Prague, Amsterdam, and Duisburg (cold-season campaigns) than in Helsinki, Barcelona, and Athens (warm-season campaigns) (Sillanpää et al., 2005b; 2006; Saarikoski et al., 2008a). It was noticed that individual PAHs or their ratios cannot be regarded as highly specific indicators for emission sources due to several reasons: i) PAHs originate from a large variety of combustion sources with only slightly different emission profiles from each other, ii) PAHs' vapour pressure and reactivity have large variabilities, iii) atmospheric particulate PAHs concentration depends on the ambient temperature and solar radiation intensity as well as the total ambient particulate mass concentration, iv) a long sampling duration may change the particulate PAH composition – particularly semivolatile compounds –

collected on the sample substrate, and v) sample treatment techniques can cause inaccuracy in the determination results.

Use of BaP as a marker compound

Benzo[a]pyrene (BaP) has been suspected to be one of the most potent carcinogenic and geno-toxic PAHs (WHO, 1998) and it has been regarded as a marker of total PAHs and genotoxic PAHs (EC, 2001). The representativeness of BaP was tested in **Paper V**. The contribution of BaP concentration to the total PAH concentration in PM_{10} and its three sub-size ranges is pre-sented in Fig. 11. Besides not having a constant BaP-to-total PAH concentration ratio in any par-ticulate size range, BaP had no significant correlation with any individual PAH or a group of different size PAHs. This observation did not support the use of BaP as a marker for total PAHs. The concentration ratio of BaP to the sum of six genotoxic PAHs (benz[a]anthracene, BbF, BkF, BaP, dibenz[a,h]anthracene, and IdP) was also investigated to assess how well BaP represented the genotoxic PAHs in $PM_{2.5}$ and in PM_{10}. The ratios of were not constant; they were highest in the cold-season and lowest in the warm-season campaigns. Also the contributions of other geno-toxic PAHs were tested similarly; the ratio of BkF to the sum of six genotoxic PAHs was most stable in all measured size ranges and therefore BkF seemed to be a better representative for genotoxic PAHs than BaP.
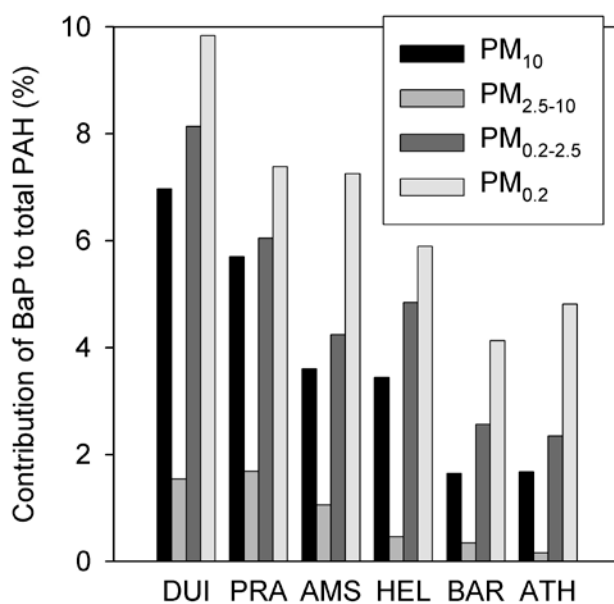
Figure 11. Relative contribution of BaP to the total PAHs in all thoracic particles (PM_{10}), and in the coarse ($PM_{2.5–10}$), fine ($PM_{0.2–2.5}$), and ultrafine ($PM_{0.2}$) size ranges.

6.   REVIEW OF PAPERS AND AUTHOR'S CONTRIBUTION

Paper I describes an analytical method (HPAEC–MS) that was developed for the determination of MAs in atmospheric aerosols from the filter samples. The method was validated and it was used for measuring the concentrations of MAs from the samples collected at two background sites in Southern Finland. I participated in the development of the method, sample collection and analysis of the samples with the co-authors. I made the validation of the method, analysed the data, and wrote the article.

Paper II presents an online application of the HPAEC–MS method with the PILS for nearly real-time determination of levoglucosan in atmospheric aerosol. The results achieved with this method were compared to those measured concurrently with other techniques to confirm the accuracy of the new online method. I participated in the development of the method with the co-authors. I made most of the practical work in the field testing of PILS–HPAEC–MS, and analysed the data in this study. AMS measurements and data analysis were done by the co-authors. I wrote the article.

In **Paper III** two types of open-land smokes were studied: aged smokes mainly from agricultural fires in spring and relatively fresh smoke plumes from late-summer forest and bog fires. The chemical composition and physical properties of fine particles in fresh smoke plumes from wildfires were studied in detail. A wide range of online measurements was used to characterise the particles chemically and physically in individual plume events. The chemical online results were compared to the respective filter samples. Additionally, satellite observations and a dispersion model were utilised for the evaluation of the emission fluxes from wildfires. I participated in the samplings and chemical analyses with the co-authors. I analysed the data from the chemical and physical measurements, and wrote the article except for the parts concerning modelling of fire emissions and atmospheric dispersion.

Paper IV describes the spatial and temporal variation of wood combustion particles in the Helsinki Metropolitan Area. The concentrations of MAs and PM were used to demonstrate the dif-

ferences between the urban and suburban areas as well as local and regional transport of biomass burning aerosols. In addition, the proportions of the MAs isomers in the ambient samples were compared to those measured in wood combustion experiments conducted in the laboratory. I participated in the sampling of ambient and combustion experiment samples and in conducting chemical analyses with the co-authors. I was responsible for analysing the data and writing the article.

Paper V presents the results of a study in which PAHs were determined in size-segregated particulate samples from six European cities at different seasons. The study was a part of a project in which an in-depth chemical and toxicological characterisation of size-segregated particulate matter was conducted. Large differences were detected in PAH concentrations and distributions between the cities, seasons, and particle size-classes. I did not participate in the samplings or chemical analyses. I made the data analysis and had the principal responsibility in writing the article.

7.   SUMMARY AND IMPLICATIONS

The primary focus of this thesis was to investigate the chemistry of fine particles that originate from biomass burning. For this purpose new analytical methods were developed and several measurement campaigns were conducted. Specific tracer compounds were used to identify the biomass burning origin of the particles.

Anhydrosugars (MAs; levoglucosan, mannosan, and galactosan) are specific tracer compounds for biomass burning emissions. A new method for the analysis of these compounds was developed using HPAEC–MS. The method was validated and tested with the filter samples of ambient fine particles and from wood combustion emissions. The advantages of the HPAEC–MS method are that there are reasonably small needs for sample preparation, water is used as the extracting agent, the analysis method is fast and simple, and it has a wide determination range. The use of

MS as a detector enables the method to be also used for the analysis of some polyols and on demand other sugar compounds, too.

The HPAEC–MS method was extended from an offline technique to an online method by combining it with a Particle-into-Liquid Sampler. The novel PILS–HPAEC–MS method enabled the measurement of airborne levoglucosan concentration with eight minutes' time resolution. A fairly good agreement in levoglucosan concentrations using the filter and PILS samplings showed that the PILS–HPAEC–MS method is able to measure the short-term changes in the levoglucosan concentrations whereas that information is lost in the integrating filter samples. The developed methods make a good addition to the research fields of biomass burning and of atmospheric aerosols. Especially, the novel online method makes a notable input on the measurements of aerosols because not many studies exist with high-time-resolution data of levoglucosan.

The major source of biomass burning emissions in Finland is residential wood combustion, especially in the cold season, but the LRT smoke plumes can affect the ambient concentrations occasionally. The impact of wood combustion on fine particles in the Helsinki Metropolitan Area was studied by deriving a multiplying factor for MAs; the average contribution of wood combustion emissions to fine particles ranged from 18% to 29% at the urban sites and from 31% to 66% at the suburban sites in cold season. Based on the spatial variation between the suburbs and urban areas, the quantity of emissions from local wood combustion at suburbs could be estimated. The contribution of regional distribution and/or LRT of emissions from wood combustion was substantial to the total emissions from wood combustion both at the urban and suburban sites. The measured proportions of MAs isomers separated residential wood combustion emissions from those that were from open-land fires.

The highest PAH concentrations as well as the highest contributions of PAHs to PM were found in the cold-season campaigns and especially in the fine and ultrafine particle size ranges. The ratios of PAHs were tested for the source assessment but the uncertainty was relatively large for them. The use of BaP as a marker PAH for the total PAHs and for genotoxic PAHs was also inspected and it was found that BaP is not always the most representative PAH for those purposes.

To conclude, this thesis contains results of several biomass burning related studies of fine atmospheric aerosols. Novel analytical methods were developed for aerosol research and new information on the chemical composition of biomass burning particles was achieved. Online measurements complemented the traditional filter measurements by presenting valuable data on temporal variations that cannot be obtained with the filter sampling.

8. FUTURE OF THE RESEARCH FIELD

Biomass burning is an important topic to be studied because nowadays humans are a major contributor to biomass burning. It is essential to know how biomass burning will affect the Earth's environment and climate on a wide spatial and temporal scale. It is already known that biomass burning is one of the major sources of fine atmospheric particles globally.

Today several methods exist for the determination of physical properties and chemical composition of aerosol particles. There is a trend to develop and increase the amount of online measurements, also in the study of biomass burning tracers. Aerosol mass spectrometric techniques provide quantitative information on size and chemical mass loading in real-time for aerosol particles. This kind of data is useful in source apportionment analysis that is typically not that sensitive to the emission rates of tracer components.

In Finland, the use of renewable energy, such as wood combustion is currently increasing. If the amount of small-scale wood combustion increases and the heating of the houses with firewood becomes an everyday routine, the ambient PM concentrations will probably increase. This emphasises the need to regulate strict PM emission limitations for new residential wood combustion appliances. For instance, if the use of modern pellet boilers and modern technology heat-storing fireplaces increases in new housings and the use of traditional combustion appliances decreases, the PM emission can fall significantly. However, pellet boilers are expensive and pellet storages require a lot of space. Therefore the fireplaces and sauna stoves will probably remain as the main methods for supplementary heating and pleasure in Finland in the near future. Later in future, the

changes in combustion appliances, technique and material may alter the amount and composition of wood burning emissions; for example MAs are produced to a lesser extent in efficient combustion, which poses new challenges for source apportionment studies and for the long-term trend monitoring of wood burning aerosols in ambient air. However, MAs remain as valid tracers for incomplete burning from conventional combustion appliances and from open-land fires as well.

The research field needs more investigations on different burning situations with several fuels and combustion appliances, including modern low-emission applications, to determine the differences in the chemical composition of the emissions. Both online and offline techniques should be utilised in the investigations in order to get a comprehensive view on the chemical composition of the fine particle emissions from biomass burning in the future.

REFERENCES

Ahtoniemi P., Tainio M., Tuomisto J.T., Karvosenoja N., Kupiainen K., Porvari P., Karppinen A., Kangas L. and Kukkonen J. (2010) Health Risks from Nearby Sources of Fine Particulate Matter: Domestic Wood Combustion and Road Traffic (PILTTI). National Institute for Health and Welfare (THL), Report 3/2010. 60 p.

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

Amann C.A. and Siegla D.C. (1981) Diesel particulates – What they are and why. *Aerosol Sci. Technol.* **1**, 73–101.

Andreae M.O. (1991) Biomass burning: its history, use, and distribution and its impact on environmental quality and global climate. In: Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, Levine J.S. (ed.), MIT Press, Cambridge, MA, USA, pp. 1–21.

Andreae M.O. and Merlet P. (2001) Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cy.* **15**, 955–966.

Anttila P., Makkonen U., Hellén H., Kyllönen K., Leppänen S., Saari H. and Hakola H. (2008) Impact of the open biomass fires in spring and summer of 2006 on the chemical composition of background air in south-eastern Finland. *Atmos. Environ.* **42**, 6472–6486.

Artaxo P., Martins J.V., Yamasoe M.A., Procópio A.S., Pauliquevis T.M., Andreae M.O., Guyon P., Gatti L.V. and Leal A.M.C. (2002) Physical and chemical properties of aerosols in the wet and dry seasons in Rondônia, Amazonia. *J. Geophys. Res.* **107**(D20), 8081.

Aurela M., Sillanpää M., Pennanen A., Mäkelä T., Laakia J., Tolonen-Kivimäki O., Saarnio K., Yli-Tuomi T., Aalto P., Salonen I., Pakkanen T., Salonen R. and Hillamo R. (2010) Characterization of urban particulate matter for a health-related study in southern Finland. *Boreal Env. Res.* **15**, 513–532.

Berner A. and Lürzer C. (1980) Mass size distributions of traffic aerosols at Vienna. *J. Phys. Chem.* **84**, 2079–2083.

Birch M.E. and Cary R.A. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* **25**, 221–241.

Boman B.C., Forsberg A.B. and Järvholm B.G. (2003) Adverse health effects from ambient air pollution in relation to residential wood combustion in modern society. *Scand. J. Work Env. Hea.* **29**, 251–260.

Bond T.C., Doherty S.J., Fahey D.W., Forster P.M., Bernsten T., DeAngelo B.J., Flanner M.G., Ghan S., Kärcher B., Koch D., Kinne S., Kondo Y., Quinn P.K., Sarofim M.C., Schultz M.G., Schultz M., Venkataraman C., Zhang H., Zhang S., Bellouin N., Guttikunda S.K., Hopke P.K., Jacobson M.Z., Kaiser J.W., Klimont Z., Lohmann U., Schwarz J.P., Shindell D., Storelvmo T., Warren S.G. and Zender C.S. (2013) Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res.-Atmos.* **118**, 5380–5552.

Boström C.-E., Gerde P., Hanberg A., Jernström B., Johansson C., Kyrklund T., Rannug A., Törnqvist M., Victorin K. and Westerholm R. (2002) Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Persp.* **110**, 451–488.

Braga C.F., Teixeira E.C., Meira L., Wiegand F., Yoneama M.L. and Dias J.F. (2005) Elemental composition of PM_{10} and $PM_{2.5}$ in urban environment in South Brazil. *Atmos. Environ.* **39**, 1801–1815.

Camredon M., Aumont B., Lee-Taylor J. and Madronich S. (2007) The $SOA/VOC/NO_x$ system: an explicit model of secondary organic aerosol formation. *Atmos. Chem. Phys.* **7**, 5599–5610.

Caseiro A., Marr I.L., Claeys M., Kasper-Giebl A., Puxbaum H. and Pio C.A. (2007) Determination of saccharides in atmospheric aerosol using anion-exchange high-performance liquid chromatography and pulsed-amperometric detection. *J. Chrom. A* **1171**, 37–45.

Chan C.-Y., Engling G., Sang X. and Zhang T. (2011) Biofuel combustion emissions – Chemical and physical smoke properties. *Environmental Impact of Biofuels*, Dos Santos Bernardes M.A. (ed.),

ISBN: 978-953-307-479-5, InTech, doi:10.5772/23430. Available from: http://www.intechopen.com/books/environmental-impact-of-biofuels/biofuel-combustion-emissions-chemical-and-physical-smoke-properties

Chen L.W.A., Moosmüller H., Arnott W.P., Chow J.C., Watson J.G., Susott R.A., Babbitt R.E., Wold C.E., Lincoln E.N. and Hao W.M. (2007) Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environ. Sci. Technol*. **41**, 4317–4325.

Chuang K.J., Chan C.C., Chen N.T., Su T.C., Lin L.Y. (2005) Effects of particle size fractions on reducing heart rate variability in cardiac and hypertensive patients. *Environ. Health Pers.* **113**, 1693–1697.

Claeys M., Kourtchev I., Pashynska V., Vas G., Vermeylen R., Wang W., Cafmeyer J., Chi X., Artaxo P., Andreae M.O. and Maenhaut W. (2010) Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions. *Atmos. Chem. Phys.* **10**, 9319–9331.

DeCarlo P.F., Kimmel J.R., Trimborn A., Northway M., Jayne J.T., Aiken A.C., Gonin M., Fuhrer K., Horvath T., Docherty K.S., Worsnop D.R. and Jimenez J.L. (2006) Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* **78**, 8281–8289.

Decesari S., Facchini M.C., Fuzzi S. and Tagliavini E. (2000) Characterization of water soluble organic compounds in atmospheric aerosol: a new approach. *J. Geophys. Res.* **105**, 1481–1489.

Delfino R.J., Sioutas C. and Malik S. (2005) Potential role of ultrafine particles in associations between airborne particle mass and cardiovascular health. *Environ. Health Pers.* **113**, 934–946.

Demirbas A. (2004) Combustion characteristic of different biomass fuels. *Prog. Energ. Comb.* **30**, 219–230.

Dockery D.W., Pope C.A. III, Xu X., Spengler J.D., Ware J.H., Fay M.E., Ferris B.G. Jr. and Speizer F.E. (1993) An association between air pollution and mortality in six U.S. cities. *N. Engl. J. Med.* **329**, 1753–1759.

Draxler R.R. and Rolph G.D. (2013) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/ HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.

Dye C. and Yttri K.E. (2005) Determination of monosaccharide anhydrides in atmospheric aerosols by use of high-performance liquid chromatography combined with high-resolution mass spectrometry. *Anal. Chem.* **77**, 1853–1858.

EC (2001) Working Group on Polycyclic Aromatic Hydrocarbons. Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position paper. EC/DG Environment.

Elias V.O., Simoneit B.R.T., Cordeiro R.C. and Turcq B. (2001) Evaluating levoglucosan as an indicator of biomass burning in Carajás, Amazônia: a comparison to the charcoal record. *Geochim. Cosmochim. Acta* **65**, 267–272.

Engling G., Carrico C.M., Kreidenweis S.M., Collett J.L. Jr., Day D.E., Malm W.C., Lincoln E., Hao W.M., Iinuma Y. and Herrmann H. (2006) Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection. *Atmos. Environ.* **40**, S299–S311.

Fine P.M., Cass G.R. and Simoneit B.R.T. (2002) Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the Southern United States. *Environ. Sci. Technol.* **36**, 1442–1451.

Fine P.M., Cass G.R. and Simoneit B.R.T. (2004) Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States tree species. *Environ. Engin. Sci.* **21**, 705–721.

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

Fitzpatrick E.M., Jones J.M., Pourkashanian M., Ross A.B., Williams A., Bartle K.D. (2008) Mechanistic aspects of soot formation from the combustion of pine wood. *Energy Fuels* **22**, 3771–3778.

Flagan R.C. and Seinfeld J.H. (1988) Fundamentals of air pollution engineering. Prentice Hall, NJ, USA.

Forsberg B., Hansson H.-C., Johansson C., Areskoug H., Persson K. and Järvholm B. (2005) Comparative health impact assessment of local and regional particulate air pollutants in Scandinavia. *Ambio* **34**, 11–19.

Fraser M.P. and Lakshmanan K. (2000) Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. *Environ. Sci. Technol.* **34**, 4560–4564.

Frey A.K., Tissari J., Saarnio K.M., Timonen H.J., Tolonen-Kivimäki O., Aurela M.A., Saarikoski S.K., Makkonen U., Hytönen K., Jokiniemi J., Salonen R.O. and Hillamo R.E.J. (2009) Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater. *Boreal Env. Res.* **14**, 255–271.

Fuzzi S., Decesari S., Facchini M.C., Cavalli F., Emblico L., Mircea M., Andreae M.O., Trebs I., Hoffer A., Guyon P., Artaxo P., Rizzo L.V., Lara L.L., Pauliquevis T., Maenhaut W., Raes N., Chi X., Mayol-Bracero O.L., Soto-García L.L., Claeys M., Kourtchev I., Rissler J., Swietlicki E., Tagliavini E., Schkolnik G., Falkovich A.H., Rudich Y., Fisch G. and Gatti L.V. (2007) Overview of the inorganic and organic composition of size-segregated aerosol in Rondônia, Brazil, from the biomass-burning period to the onset of the wet season. *J. Geophys. Res.* **112**, D01201.

Gilardoni S., Vignati E., Cavalli F., Putaud J.P., Larsen B.R., Karl M., Stenström K., Genberg J., Henne S. and Dentener F. (2011) Better constraints on sources of carbonaceous aerosols using a combined 14C – macro tracer analysis in a European rural background site. *Atmos. Chem. Phys.* **11**, 5685–5700.

Glasius M., Ketzel M., Wåhlin P., Jensen B., Mønster J., Berkowicz R. and Palmgren F. (2006) Impact of wood combustion on particle levels in a residential area in Denmark. *Atmos. Environ.* **40**, 7115–7124.

Hänninen O.O., Salonen R.O., Koistinen K., Lanki T., Barregard L. and Jantunen M. (2009) Population exposure to fine particles and estimated excess mortality in Finland from an East European wildfire episode. *J. Expo. Sci. Environ. Epidemiol.* **19**, 414–422.

Hays M.D., Geron C.D., Linna K.J., Smith N.D. and Schauer J.J. (2002) Speciation of gas-phase and particle emissions from burning of foliar fuels. *Environ. Sci. Technol.* **36**, 2281–2294.

Hays M.D., Smith N.D., Kinsey J., Dong Y. and Kariher P. (2003) Polycyclic aromatic hydrocarbon size distribution in aerosols from appliances of residential wood combustion as determines by direct thermal desorption-GC/MS. *J. Aerosol Sci.* **34**, 1061–1084.

Hedberg E., Kristensson A., Ohlsson M.C., Johansson P.-Å., Swietlicki E., Vesely V., Widequist U. and Westerholm R. (2002) Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmos. Environ.* **36**, 4823–4837.

Hedberg E., Johansson C., Johansson L., Swietlicki E. and Brorström-Lundén E. (2006) Is levoglucosan a suitable quantitative tracer for wood burning? Comparison with receptor modelling on trace elements in Lycksele, Sweden. *J. Air Waste Manage. Assoc*. **56**, 1669–1678.

Hellén H., Hakola H., Haaparanta S., Pietarila H. and Kauhaniemi M. (2008) Influence of residential wood combustion on local air quality. *Sci. Total Environ.* **393**, 283–290.

Hennigan C.J., Sullivan A.P., Collett J.L. Jr. and Robinson A.L. (2010) Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. *Geophys. Res. Lett.* **37**, L09806.

Hinds W.C. (1999) Aerosol technology: properties, behavior, and measurement of airborne particles. 2nd ed., John Wiley & Sons, Inc., New York, USA.

Hoffer A., Gelencsér A., Guyon P., Kiss G., Schmid O., Frank G.P., Artaxo P. and Andreae M.O. (2006) Optical properties of humic-like substances (HULIS) in biomass-burning aerosols. *Atmos. Chem. Phys.* **6**, 3563–3570.

Hoffmann D., Tilgner A., Iinuma Y. and Herrmann H. (2010) Atmospheric stability of levoglucosan: a detailed laboratory and modelling study. *Environ. Sci. Technol.* **44**, 694–699.

Huang X.F., Yu J.Z., He L.Y. and Yuan Z. (2006) Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms. *J. Geophys. Res.* **111**, D22212.

Hytönen K., Yli-Pirilä P., Tissari J., Gröhn A., Riipinen I., Lehtinen K.E.J. and Jokiniemi J. (2009) Gas-particle distribution of PAHs in wood combustion emission determined with annular denuders, filter, and polyurethane foam adsorbent. *Aerosol Sci. Technol.* **43**, 442–454.

Hyvärinen A.-P., Kolmonen P., Kerminen V.-M., Virkkula A., Leskinen A., Komppula M., Hatakka J., Burkhart J., Stohl A., Aalto P.P., Kulmala M., Lehtinen K.E.J., Viisanen Y. and Lihavainen H. (2011) Aerosol black carbon at five background measurement sites over Finland, a gateway to the Arctic. *Atmos. Environ.* **45**, 4042–4050.

Iinuma Y., Brüggemann E., Gnauk T., Müller K., Andreae M.O., Helas G., Parmar R. and Herrmann H. (2007) Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *J. Geophys. Res.* **112**, D08209.

Iinuma Y., Böge O., Gräfe R. and Herrmann H. (2010) Methyl-nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. *Environ. Sci. Technol.* **44**, 8453–8459.

IPCC (2007) Summary for Policymakers. In: Climate change 2007: The Physical Science Basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate Change (Solomon S., Qin D, Manning M., Chen Z., Marquis M., Averyt K.B., Tignor M. and Miller H.L. (eds.)). Cambridge University Press, Cambridge, UK and New York, NY, USA.

Ishiguro T., Takatori Y. and Akihama K. (1997) Microstructure of diesel soot particles probed by electron microscopy: first observation of inner core and outer shell. *Combust. Flame* **108**, 231–234.

Jacobson M.C., Hansson H.-C., Noone K.J. and Charlson R.J. (2000) Organic atmospheric aerosols: review and state of the science. *Rev. Geophys.* **38**, 637–651.

Jalava P.I., Salonen R.O., Hälinen A.I., Sillanpää M., Sandell E. and Hirvonen M.-R. (2005) Effects of sample preparation on chemistry, cytotoxicity, and inflammatory responses induced by air particulate matter. *Inhal. Toxicol.* **17**, 107–177.

Jalava P.I., Salonen R.O., Hälinen A.I., Penttinen P., Pennanen A.S., Sillanpää M., Sandell E., Hillamo R. and Hirvonen M.-R. (2006) In vitro inflammatory and cytotoxic effects of size-segregated samples collected during long-range transport of wildfire smoke to Helsinki. *Toxicol. Appl. Pharm.* **215**, 341–353.

Jalava P.I., Salonen R.O., Nuutinen K., Pennanen A.S., Happo M.S., Tissari J., Frey A., Hillamo R., Jokiniemi J. and Hirvonen M.-R. (2010) Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. *Atmos. Environ.* **44**, 1691–1698.

Jenkins B.M., Baxter L.L., Miles T.R. Jr. and Miles T.R. (1998) Combustion properties of biomass. *Fuel Process. Technol.* **54**, 17–46.

Johansson L.S., Leckner B., Gustavsson L., Cooper D., Tullin C. and Potter A. (2004) Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. *Atmos. Environ.* **38**, 4183–4195.

Jokiniemi J., Lazaridis M., Lehtinen M. and Kauppinen E. (1994) Numeral simulation of vapour-aerosol dynamics in combustion. *J. Aerosol Sci.* **25**, 429–446.

Jordan T.B., Seen A.J. and Jacobsen G.E. (2006) Levoglucosan as an atmospheric tracer for wood smoke. *Atmos. Environ.* **40**, 5316–5321.

Kaivosoja T., Jalava P.I., Lamberg H., Virén A., Tapanainen M., Torvela T., Tapper U., Sippula O., Tissari J., Hillamo R., Hirvonen M.-R. and Jokiniemi J. (2013) Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale. *Atmos. Environ.* **77**, 193–201.

Kalberer M., Paulsen D., Sax M., Steinbacher M., Dommen J., Prevot A.S.H., Fisseha R., Weingartner E., Frankevich V., Zenobi R. and Baltensberger U. (2004) Identification of polymers as major components of atmospheric organic aerosols. *Science* **303**, 1659.

Kanakidou M., Seinfeld J.H., Pandis S.N., Barnes I., Dentener F.J., Facchini M.C., Van Dingenen R., Ervens B., Nenes A., Nielsen C.J., Swietlicki E., Putaud J.P., Balkanski Y., Fuzzi S., Horth J.,

Moortgat G.K., Winterhalter R., Myhre C.E.L., Tsigaridis K., Vignati E., Stephanou E.G. and Wilson J. (2005) Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **5**, 1053–1123.

Karvosenoja N., Tainio M., Kupiainen K., Tuomisto J.T., Kukkonen J. and Johansson M. (2008) Evaluation of the emissions and uncertainties of PM2.5 originated from vehicular traffic and domestic wood combustion in Finland. *Boreal Env. Res.* **13**, 465–474.

Khalil M.A.K. and Rasmussen R.S. (2003) Tracers of wood smoke. *Atmos. Environ.* **37**, 1211–1222.

Kjällstrand J. and Petersson G. (2001) Phenolic antioxidants in wood smoke. *Sci. Total Environ.* **277**, 69–75.

Knudsen J.N., Jensen P.A. and Dam-Johansen K. (2004) Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy Fuels* **18**, 1385–1399.

Koskinen P., Silvo K., Mehtonen J., Ruoppa M., Hyytiä H., Silander S. and Sokka L. (2005) Preliminary assessment of releases of certain hazardous substances in Finland. The Finnish Environment 801, Finnish Environment Institute. In Finnish, English abstract. Edita Prima Ltd., Helsinki.

Kuhlbusch T.A.J. (1995) Method for determining black carbon in residues of vegetation fires. *Environ. Sci. Technol.* **29**, 2695–2702.

Kundu S., Kawamura K., Andreae T.W., Hoffer A. and Andreae M.O. (2010) Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.* **10**, 2209–2225.

Lamberg H., Nuutinen K., Tissari J., Ruusunen J., Yli-Pirilä P., Sippula O., Tapanainen M., Jalava P., Makkonen U., Teinilä K., Saarnio K., Hillamo R., Hirvonen M.-R. and Jokiniemi J. (2011) Physico-chemical characterization of fine particles from small-scale wood combustion. *Atmos. Environ.* **45**, 7635–7643.

Lavric E.D., Konnov A.A. and Ruyck J. (2004) Dioxin levels in wood combustion – a review. *Biomass Bioenerg.* **26**, 115–145.

Lee T., Sullivan A.P., Mack L., Jimenez J.L., Kreidenweis S.M., Onasch T.B., Worsnop D.R., Malm W., Wold C.E., Hao W.M. and Collett J.L. Jr. (2010) Chemical smoke marker emissions during flaming and smoldering phases of laboratory open burning of wildland fuels. *Aerosol Sci. Technol.* **44**, i–v.

Lemieux P.M., Lutes C.C. and Santoianni D.A. (2004) Emissions of organic air toxins from open burning: a comprehensive review. *Prog. Energ. Comb.* **30**, 1–32.

Li C.K. and Kamens R.M. (1993) The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmos. Environ.* **27A**, 523–532.

Lv G.-j., Wu S.-b. and Lou R. (2010) Kinetic study of the thermal decomposition of hemicellulose isolated from corn stalk. *BioResources* **5**, 1281–1291.

Maenhaut W., Nava S., Lucarelli F., Wang W., Chi X. and Kulmala M. (2011) Chemical composition, impact from biomass burning, and mass closure for $PM_{2.5}$ and PM_{10} aerosols at Hyytiälä, Finland, in summer 2007. *X Ray Spectr.* **40**, 168–171.

Mandalakis M., Gustafsson Ö., Alsberg T., Egebäck A.-L., Reddy C.M., Xu L., Klanova J., Holoubek I. and Stephanou E.G. (2005). Contribution of biomass burning to atmospheric polycyclic aromatic hydrocarbons at three European background sites. *Environ. Sci. Technol.* **39**, 2976–2982.

Marple V.A., Rubow K.L. and Behm S.M. (1991) A Microorifice Uniform Deposit Impactor (MOUDI): Description, calibration and use. *Aerosol Sci. Technol.* **14**, 434–446.

Mayol-Bracero O.L., Guyon P., Graham B., Roberts G., Andreae M.O., Decesari S., Facchini M.C., Fuzzi S. and Artaxo P. (2002) Water-soluble organic compounds in biomass burning aerosols over Amazonia. 2. Apportionment of the chemical composition and importance of the polyacidic fraction. *J. Geophys. Res.* **107**, D20.

McDonald J., Zielinska B., Fujita E., Sagabiel J., Chow J. and Watson J. (2000) Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol.* **34**, 2080–2091.

METLA, Finnish Forest Research Institute. Finnish Statistical Yearbook of Forestry (2010) [in Finnish with English summary]. Official Statistics of Finland, 164 p.

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

Mielonen T., Portin H., Komppula M., Leskinen A., Tamminen J., Ialongo I., Hakkarainen J., Lehtinen K.E.J. and Arola A. (2012) Biomass burning aerosols observed in Eastern Finland during the Russian wildfires in summer 2010 – Part 2: remote sensing. *Atmos. Environ.* **47**, 279–287.

Ministry of Finance (2012) Europe 2020 –Strategy. Finland's National Programme, Spring 2012. *Ministry of Finance Publications* 16c/2012, Juvenes Print, Tampereen Yliopistopaino Oy, 46 p.

Niemi J.V., Tervahattu H., Vehkamäki H., Kulmala M., Koskentalo T, Sillanpää M. and Rantamäki M. (2004) Characterization and source identification of a fine particle episode in Finland. *Atmos. Environ.* **38**, 5003–5012.

Niemi J.V., Tervahattu H., Vehkamäki H., Martikainen J., Laakso L., Kulmala M., Aarnio P., Koskentalo T, Sillanpää M. and Makkonen U. (2005) Characterization of aerosol particle episodes in Finland caused by wildfires in Eastern Europe. *Atmos. Chem. Phys.* **5**, 2299–2310.

Niemi J.V., Saarikoski S., Tervahattu H., Mäkelä T., Hillamo R., Vehkamäki H., Sogacheva L. and Kulmala M. (2006) Changes in background aerosol composition in Finland during polluted and clean periods studied by TEM/EDX individual particle analysis. *Atmos. Chem. Phys.* **6**, 5049–5066.

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

O'Dowd C.D. and de Leeuw G. (2007) Marine aerosol production: a review of the current knowledge. *Phil. Trans. R. Soc. A* **365**, 1753–1774.

Oja V. and Suuberg E.M. (1999) Vapor pressures and enthalpies of sublimation of D-glucose, D-xylose, cellobiose, and levoglucosan. *J. Chem. Eng. Data* **44**, 26–29.

Orsini D.A., Ma Y., Sullivan A., Sierau B., Baumann K. and Weber R.J. (2003) Refinements to the particle-into-liquid-sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. *Atmos. Environ.* **37**, 1243–1259.

Pang Y., Turpin B.J. and Gundel L.A. (2006) On the importance of organic oxygen for understanding organic aerosol particles. *Aerosol Sci. Technol.* **40**, 128–133.

Pennanen A.S., Sillanpää M., Hillamo R., Quass U., John A.S., Branis M., Hůnová I., Meliefste K., Janssen N.A.H., Koskentalo T., Castaño-Vinyals G., Bouso L., Chalbot M.-C., Kavouras I.G. and Salonen R.O. (2007) Performance of a high-volume cascade impactor in six European urban environments: Mass measurement and chemical characterization of size-segregated particulate samples. *Sci. Total Environ.* **374**, 297–310.

Pettersen R.C. (1984) The chemical composition of wood. In: The Chemistry of Solid Wood, ed. Rowell R.M. *Adv. Chem. Ser.* **207**, American Chemical Society, Washington, DC, pp. 57–126.

Piazzalunga A., Anzano M., Collina E., Lasagni M., Lollobrigida F., Pannocchia A., Fermo P. and Pitea D. (2013) Contribution of wood combustion to PAH and PCDD/F concentrations in two urban sites in Northern Italy. *J. Aerosol Sci.* **56**, 30–40.

Pope C.A. III, Burnett R.T., Thun M.J., Calle E.E., Krewski D., Ito K. and Thurston G.D. (2002) Lung cancer, cardiopulmonary mortality and longterm exposure to fine particulate air pollution. *J. Am. Med. Assoc.* **287**, 1132–1141.

Portin H., Mielonen T., Leskinen A., Arola A., Pärjälä E., Romakkaniemi S., Laaksonen A., Lehtinen K.E.J. and Komppula M. (2012) Biomass burning aerosols observed in Eastern Finland during the Russian wildfires in summer 2010 – Part 1: in-situ aerosol characterization. *Atmos. Environ.* **47**, 269–278.

Pósfai M., Gelencsér A., Simonics R., Arató, Li J., Hobbs P.V. and Buseck P.R. (2004) Atmospheric tar balls: Particles from biomass and biofuel burning. *J. Geophys. Res.* **109**, D06213.

Putaud J.-P., Van Dingenen R., Alastuey A., Bauer H., Birmili W., Cyrys J., Flentje H., Fuzzi S., Gehrig R., Hansson H.C., Harrison R.M., Herrmann H., Hitzenberger R., Hüglin C., Jones A.M., Karper-

Giebl A., Kiss G., Kousa A., Kuhlbusch T.A.J., Löschau G., Maenhaut W., Molnar A., Morena T., Pekkanen J., Perrino C., Pitz M., Puxbaum H., Querol X., Rodriguez S., Salma I., Schwarz J., Smolik J., Schneider J., Spindler G., ten Brink H., Tursic J., Viana M., Wiedensohler A. and Raes F. (2010) A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ.* **44**, 1308–1320.

Puxbaum H., Caseiro A., Sánchez-Ochoa A., Kasper-Giebl A., Claeys M., Gelencsér A., Legrand M., Preunkert S. and Pio C. (2007) Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *J. Geophys. Res.* **112**, D23S05.

Ramdahl T. (1983) Retene – a molecular marker of wood combustion in ambient air. *Nature* **306**, 580–582.

Rastogi N., Oakes M.M., Schauer J.J., Shafer M.M., Majestic B.J. and Weber R.J. (2009) New technique for online measurement of water-soluble Fe(II) in atmospheric aerosols. *Environ. Sci. Technol.* **43**, 2425–2430.

Reid J.S., Koppmann R., Eck T.F. and Eleuterio D.P. (2005) A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* **5**, 799–825.

Reinhardt T.E. and War D.E. (1995) Factors affecting methyl chloride emissions from forest biomass combustion. *Environ. Sci. Technol.* **29**, 825–832.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. and Simoneit B.R.T. (1993) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* **27**, 636–651.

Rogge W.F., Hildemann L.M., Mazurek M.A. and Cass G.R. (1998) Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* **32**, 13–22.

Saarikoski S. and Hillamo R. (2013) Wildfires as a source of aerosol particles transported to the northern European regions. Urban Air Quality in Europe, Viana M. (ed.), *Hdb. Env. Chem.* **26**, 101–122, doi: 10.1007/698_2012_169.

Saarikoski S., Sillanpää M., Sofiev M., Timonen H., Saarnio K., Teinilä K., Karppinen A., Kukkonen J. and Hillamo R. (2007) Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessments. *Atmos. Environ.* **41**, 3577–3589.

Saarikoski S.K., Sillanpää M.K., Saarnio K.M., Hillamo R.E., Pennanen A.S. and Salonen R.O. (2008a) Impact of biomass combustion on urban fine particulate matter in central and northern Europe. *Water Air Soil Poll.* **191**, 265–277.

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

Saarikoski S., Carbone S., Decesari S., Giulianelli L., Angelini F., Canagaratna M., Ng N.L., Trimborn A., Facchini M.C., Fuzzi S., Hillamo R. and Worsnop D. (2012) Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy. *Atmos. Chem. Phys.* **12**, 8401–8421.

Saarnio K., Saarikoski S., Sillanpää M., Kuokka S., Virkkula A. and Hillamo R. (2006) Levoglucosan associated with biomass burning in atmospheric aerosols. Proceedings of the NOSA 2006 Conference, Vehkamäki H., Bergman T., Julin J., Salonen M. and Kulmala M. (eds.). *Report Series in Aerosol Science* **83**, 330–334.

Salonen R.O. and Pennanen A.S. (2007) The impact of fine particles on health. Views and conclusions from the FINE Particles – Technology, Environment and Health Technology Programme, P. Herring (ed.). Original Finnish version by T. Paukku (ed.). Tekes, Finland.

Sandell E., Kiviranta A., Tuominen J. and Aarnio P. (1999) Concentration levels of polycyclic aromatic hydrocarbons (PAHs) in ambient air in Finland. *Fresenius Environ. Bullet.* **8**, 567–575.

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

Schädel C., Blöchl A., Richter A. and Hoch G. (2010) Quantification and monosaccharide composition of hemicelluloses from different plant functional types. *Plant Physiol. Bioch.* **48**, 1–8.

Schauer J.J., Rogge W.F., Hildemann L.M., Cass G.R. and Simoneit B.R.T. (1996) Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **30**, 3837–3855.

Schkolnik G. and Rudich Y. (2005) Detection and quantification of levoglucosan in atmospheric aerosols: A review. *Anal. Bioanal. Chem.* **385**, 26–33.

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

Seinfeld J.H. and Pandis S.N. (2006) Atmospheric Chemistry and Physics. From Air Pollution to Climate Change. 2nd ed. John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

Shafizadeh F. (1984). The chemistry of pyrolysis and combustion. In: The Chemistry of Solid Wood, ed. Rowell R.M. *Adv. Chem. Ser.* **207**, American Chemical Society, Washington, DC, pp. 489–529.

Sheffield A.E., Gordon G.E., Currie L.A. and Riederer G.E. (1994) Organic, elemental, and isotopic tracers of air pollution sources in Albuquerque, NM. *Atmos. Environ.* **28**, 1371–1384.

Shimmo M., Saarnio K., Aalto P., Hartonen K., Hyötyläinen T., Kulmala M. and Riekkola M.-L. (2004) Particle size distribution and gas-particle partition of polycyclic aromatic hydrocarbons in Helsinki urban area. *J. Atmos. Chem.* **47**, 223–241.

Sillanpää M., Hillamo R., Mäkelä T., Pennanen A.S. and Salonen R.O. (2003) Field and laboratory tests of a high volume cascade impactor. *J. Aerosol Science* **34**, 485–500.

Sillanpää M., Saarikoski S., Hillamo R., Pennanen A., Makkonen U., Spolnik Z., Van Grieken R., Koskentalo T. and Salonen R.O. (2005a) Chemical composition, mass size distribution and source analysis of long-range transported wildfire smokes in Helsinki. *Sci. Total Environ.* **350**, 119–135.

Sillanpää M., Frey A., Hillamo R., Pennanen A.S. and Salonen R.O. (2005b) Organic, elemental and inorganic carbon in particulate matter in six urban environments in Europe. *Atmos. Chem. Phys.* **5**, 2869–2879.

Sillanpää M., Hillamo R., Saarikoski S., Frey A., Pennanen A., Makkonen U., Spolnik Z., Van Grieken R., Braniš M., Brunekreef B., Chalbot M.-C., Kuhlbusch T., Sunyer J., Kerminen V.-M., Kulmala M. and Salonen R.O. (2006) Chemical composition and mass closure of particulate matter at six urban sites in Europe. *Atmos. Environ.* **40**(S2), 212–223.

Simcik M.F., Eisenreich S.J. and Lioy P.J. (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* **33**, 5071–5079.

Simoneit B.R.T., Rogge W.F., Mazurek M.A., Standley L.J., Hildemann L.M. and Cass G.R. (1993) Lignin pyrolysis products, lignin, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environ. Sci. Technol.* **27**, 2533–2541.

Simoneit B.R.T., Schauer J.J., Nolte C.G., Oros D.R., Elias V.O., Fraser W.F., Rogge W.F. and Cass G.R. (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* **33**, 173–182.

Simoneit B.R.T. (2002) Biomass burning – a review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* **17**, 129–162.

Sippula O., Hytönen K., Tissari J., Raunemaa T. and Jokiniemi J. (2007) Effect of wood fuel on the emissions from a top-feed pellet stove. *Energy Fuels* **21**, 1151–1160.

Sofiev M., Siljamo P., Valkama I., Ilvonen M. and Kukkonen J. (2006) A dispersion modelling system SILAM and its evaluation against ETEX data. *Atmos. Environ.* **40**, 674–685.

Sofiev M., Galperin M. and Genikhovich E. (2008) Construction and evaluation of Eulerian dynamic core for the air quality and emergency modeling system SILAM. In: Borrego C., Miranda A.I., eds. *NATO Science for Peace and Security Series C: Environmental Security. Air Pollution Modeling and its Application XIX.* Springer, pp. 699–701.

Sofiev M., Vankevich R., Lötjönen M., Prank M., Petukhov V., Ermakova T., Koskinen J. and Kukkonen J. (2009) An operational system for the assimilation of satellite information on wild-land fires for the needs of air quality modelling and forecasting. *Atmos. Chem. Phys.* **9**, 6833–6847.

Sorooshian A., Varutbangkul V., Brechtel F.J., Ervens B., Feingold G., Bahreini R., Murphy S.M., Holloway J.S., Atlas E.L., Buzorius G., Jonsson H., Flagan R.C. and Seinfeld J.H. (2006) Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004. *J. Geophys. Res.-Atmos.* **111** (D23), D23S45.

Stohl A. and Wotawa G. (1995) A method for computing single trajectories representing boundary layer transport. *Atmos. Environ.* **29**, 3235–3239.

Sullivan A.P., Weber R.J., Clements A.L., Turner J.R., Bae M.S. and Schauer J.J. (2004) A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site. *Geophys. Res. Lett.* **31**, L13105.

Szidat S., Jenk T.M., Gäggeler H.W., Synal H.-A., Fisseha R., Baltensberger U., Kalberer M., Samburova V., Wacker L., Saurer M., Schikowski M. and Hajdas I. (2004) Source apportionment of aerosols by ^{14}C measurements in different carbonaceous particle fractions. *Radiocarbon* **46**, 475–484.

Szidat S., Jenk T.M., Synal H.-A., Kalberer M., Wacker L., Hajdas I., Kasper-Giebl A. and Baltensberger U. (2006) Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C. *J. Geophys. Res.* **111**, D07206.

Tang N., Hattori T., Taga R., Igarashi K., Yang X., Tamura K., Kakimoto H., Mishukov V.F., Toriba A., Kizu R. and Hayakawa K. (2005) Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. *Atmos. Environ.* **39**, 5817–2826.

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

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

Timonen H., Aurela M., Carbone S., Saarnio K., Saarikoski S., Mäkelä T., Kulmala M., Kerminen V.-M., Worsnop D.R. and Hillamo R. (2010) 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.

Tissari J. (2008) Fine particle emissions from residential wood combustion. Kuopio Univeristy Publications C. Natural and Environmental Sciences 273, Kopijyvä, Kuopio, Finland, 63 p.

Tissari J., Lyyränen J., Hytönen K., Sippula O., Tapper U., Frey A., Saarnio K., Pennanen A.S., Hillamo R., Salonen R.O., Hirvonen M.-R. and Jokiniemi J. (2008) Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. *Atmos. Environ.* **42**, 7862–7873.

Tsapakis M. and Stephanou E.G. (2005) Occurence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environ. Pollut.* **133**, 147–156.

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

Valmari T. (2000) Potassium behaviour during combustion of wood in circulating fluidised bed power plants. VTT Publication 414, Otamedia Oy, Espoo, Finland.

Van Loo S. and Koppejan J. (2008) The handbook of biomass combustion and co-firing. Earthscan, London, UK; Sterling, VA, USA.

Viidanoja J., Sillanpää M., Laakia J., Kerminen V.-M., Hillamo R., Aarnio P. and Koskentalo T. (2002) Organic and black carbon in $PM_{2.5}$ and PM_{10}: 1 year of data from an urban site in Helsinki, Finland. *Atmos. Environ.* **36**, 3183–3193.

Wang Q., Shao M., Liu Y., William K., Paul G., Li X., Liu Y. and Lu S. (2007) Impact of biomass burning on urban quality estimated by organic tracers: Guangzhou and Beijing as cases. *Atmos. Environ.* **41**, 8380–8390.

Weber R.J., Orsini D., Daun Y., Lee Y.-N., Klotz P.J. and Brechtel F. (2001) A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol Sci. Technol.* **35**, 718–727.

Werther J., Saenger M., Hartge E.U., Ogada T. and Siagi Z. (2000) Combustion of agricultural residues. *Prog. Energy Comb. Sci.* **26**, 1–27.

WHO (World Health Organization) (1998) Selected non-heterocyclic polycyclic hydrocarbons. Geneva: WHO International Programme on Chemical Safety (IPCS): 1998. Environmental Health Criteria 202.

WHO (2006) Air Quality Guidelines. Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. WHO Regional Office for Europe, Copenhagen.

WHO (2010) Dioxins and their effect on human health. Fact sheet N°225, May 2010.

Wiinikka, H. (2005) High temperature aerosol formation and emission minimisation during combustion of wood pellets. PhD thesis, Department of Applied Physics and Mechanical Engineering, Luleå University of Technology.

Yttri K.E., Dye C., Slørdal L.H. and Braathen O.-A. (2005) Quantification of monosaccharide anhydrides by liquid chromatography combined with mass spectrometry: application to aerosol samples from an urban and a suburban site influences by small-scale wood burning. *J. Air Waste Manage. Assoc.* **55**, 1169–1177.

Yttri K.E., Simpson D., Nøjgaard J.K., Kristensen K., Genberg J., Stenström K., Swietlicki E., Hillamo R., Aurela M., Bauer H., Offenberg J.H., Jaoui M., Dye C., Eckhardt S., Burkhart J.F., Stohl A. and Glasius M. (2011) Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites. *Atmos. Chem. Phys.* **11**, 13339–13357.

Zdrahál Z., Oliveira J., Vermeylen R., Claeys M. and Maenhaut W. (2002) Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations. *Environ. Sci. Technol.* **36**, 747–753.

Zhang X., Hecobian A., Zheng M., Frank N.H. and Weber R.J. (2010) Biomass burning impact on $PM_{2.5}$ over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis. *Atmos. Chem. Phys.* **10**, 6839–6853.

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