Using monosaccharide anhydrides to estimate the impact of wood combustion on fine particles in the Helsinki Metropolitan Area

Karri Saarnio[1], Jarkko V. Niemi[2)3)], Sanna Saarikoski[1], Minna Aurela[1], Hilkka Timonen[1], Kimmo Teinilä[1], Maria Myllynen[2], Anna Frey[1], Heikki Lamberg[4], Jorma Jokiniemi[4)5)] and Risto Hillamo[1]

[1] *Finnish Meteorological Institute, Air Quality Research, P.O. Box 503, FI-00101 Helsinki, Finland*
[2] *Helsinki Region Environmental Services Authority (HSY), P.O. Box 100, FI-00066 HSY, Finland*
[3] *Department of Environmental Sciences, P.O. Box 65, FI-00014 University of Helsinki, Finland*
[4] *University of Eastern Finland, Fine Particle and Aerosol Technology Laboratory, P.O. Box 1627, FI-70211 Kuopio, Finland*
[5] *VTT Technical Research Centre of Finland, Fine Particles, P.O. Box 1000, FI-02044 VTT, Finland*

The spatiotemporal variation of ambient particles under the influence of biomass burning emissions was studied in the Helsinki Metropolitan Area (HMA) in selected periods during 2005–2009. Monosaccharide anhydrides (MAs; levoglucosan, mannosan and galactosan), commonly known biomass burning tracers, were used to estimate the wood combustion contribution to local particulate matter (PM) concentration levels at three urban background sites close to the city centre, and at three suburban sites influenced by local small-scale wood combustion. In the cold season (October–March), the mean MAs concentrations were 115–225 ng m^{-3} and 83–98 ng m^{-3} at the suburban and urban sites, respectively. In the warm season, the mean MAs concentrations were low (19–78 ng m^{-3}), excluding open land fire smoke episodes (222–378 ng m^{-3}). Regionally distributed wood combustion particles raised the levels over the whole HMA while particles from local wood combustion sources raised the level at suburban sites only. The estimated average contribution of wood combustion to fine particles (PM$_{2.5}$) ranged from 18% to 29% at the urban sites and from 31% to 66% at the suburban sites in the cold season. The PM measurements from ambient air and combustion experiments showed that the proportions of the three MAs can be utilised to separate the wildfire particles from residential wood combustion particles.

Introduction

Residential wood combustion or, more generally, biomass burning is a remarkable source of fine particulate matter (PM$_{2.5}$, particles with aerodynamic diameter smaller than 2.5 μm) emissions throughout Europe (e.g. May *et al.* 2009, Niemi *et al.* 2009, Szidat *et al.* 2009, Krecl *et al.* 2010).

Editor in charge of this article: Veli-Matti Kerminen

It is estimated that residential wood combustion can produce locally 20%–90% of the wintertime fine particle emissions (Boman *et al.* 2003) and that it is responsible for 33% of the total primary carbonaceous emissions in Europe (Krecl *et al.* 2010). In several studies, heating with wood was associated with harmful health effects (Boman *et al.* 2003, Schreuder *et al.* 2006, Naeher *et al.* 2007, Bølling *et al.* 2009, Jalava *et al.* 2010).

Wood combustion has recently been studied in several European locations, e.g. in Austria (Caseiro *et al.* 2009), Germany (Puxbaum *et al.* 2007, Bari *et al.* 2010), Denmark (Glasius *et al.* 2006, 2008), Norway (Yttri *et al.* 2005, 2009), and Sweden (Hedberg *et al.* 2006, Krecl *et al.* 2007, 2010). For example, 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). The highest contribution of wood burning to ambient PM concentration is typically found during the cold season due to residential heating with wood, amplified by poor mixing in the wintertime boundary layer (e.g. Puxbaum *et al.* 2007, Saarikoski *et al.* 2008a). Especially during periods of low vertical mixing due to stagnant weather conditions, the effects of wood combustion on local air quality can be considerable. The most serious local impacts of wood smoke are usually observed in the densely populated small house areas of suburbs or villages (Glasius *et al.* 2006). However, wood burning emissions may also be transported long distances and cause significant increases in PM concentrations on a regional level (e.g. Niemi *et al.* 2009, Mochida *et al.* 2010).

Residential wood combustion accounted for 25% of the primary $PM_{2.5}$ emissions in Finland in 2000 (Karvosenoja *et al.* 2008). The residential wood fuel consumption increased in Finland over the last years: the increase being almost 29% from 2000 (45 PJ) to 2009 (58 PJ) (METLA 2010). The use of biomass energy, also in households, is encouraged by the Finnish government, because of the pressure to use biofuels instead of fossil fuel. For instance, it is possible to get some financial support to replace an oil or electric heating system with a heating system based on renewable energy (e.g. biomass, heat

pumps). Investments are also allocated in the development of modern-technology combustion appliances, but no regulations yet exist for PM emissions from residential biomass-combustion appliances in Finland.

In the Helsinki Metropolitan Area (HMA), heating of buildings is mainly based on extensive district heating system, which has only a minor impact on air quality thanks to effective emission control methods and high emission height. On the other hand, in suburban small-house areas of the HMA, large amounts of PM are emitted from wood burning, e.g. in heat-storing fireplaces and sauna stoves (HSY 2010a). Saarikoski *et al.* (2008a) estimated that in Helsinki 41% of organic carbon (OC) in PM_1 originates from wood combustion during winter, whereas only 3.4% during summer. However, the study did not give any information on the potential spatial variation in biomass burning aerosols at different urban and suburban sites of the HMA.

Monosaccharide anhydride isomers (MAs; i.e., levoglucosan, mannosan, and galactosan) are shown to be specific tracer compounds for biomass combustion, such as residential wood combustion and open land fires (e.g. Simoneit 2002, Yttri *et al.* 2005, Saarikoski *et al.* 2008a, Niemi *et al.* 2009, Saarnio *et al.* 2010a) because they are produced exclusively during the thermal breakdown of cellulose and diverse hemicelluloses (Simoneit 2002). In a laboratory study by Fraser and Lakshmanan (2000), levoglucosan did not degrade over a period of 10 days when exposed to acid-catalysed hydrolysis. However, there has recently been a debate about atmospheric stability of levoglucosan (Hennigan *et al.* 2010, Hoffmann *et al.* 2010). For example, Hennigan *et al.* (2010) showed that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when biomass burning particles are exposed to the typical summertime concentration of hydroxyl radicals (1×10^6 molecules cm^{-3}). Additionally, Hedberg *et al.* (2006) suggested that levoglucosan is not suitable as a quantitative tracer due to its dependency on combustion conditions. Despite these limitations, MAs concentrations showed to be valuable in tracking the biomass combustion emissions (Saarikoski *et al.* 2008a).

High-time-resolution information about wood combustion has been recently gained by

using online methods, such as measuring certain mass-to-charge ratios (m/z) of organic mass fragments with the aerosol mass spectrometer (AMS) (e.g. Schneider *et al*. 2006, Lee *et al*. 2010). Unfortunately, the AMS methods cannot separate the mass fragments of MAs from those that originate from other sugar compounds. Furthermore, the AMS methods cannot separate different MAs isomers, i.e. levoglucosan, mannosan, and galactosan. The isomer ratios of MAs in ambient air may provide valuable information for the source identification of biomass burning aerosols.

The objective of this study was (1) to study the variation in MAs concentrations at urban and suburban sites in the HMA at different temporal scales, (2) to analyse the spatial variation of MAs concentrations for local and regional emission sources, (3) to quantify the impact of biomass combustion on PM concentrations, and (4) to compare the ambient proportions of MAs isomers with those from wood combustion experiments to identify the type of biomass that was burnt. This is the first study that demonstrates the differences between urban and suburban areas as well as local and regional transport of biomass burning aerosols in the HMA.

Experimental methods

Site description

The HMA is located in the boreal region on the coast of the Baltic Sea. The city centre of Helsinki (60°10´N, 24°58´E) is surrounded from the west, north, and east by residential areas, while in the south the closest inhabited areas are over 70 km away on the Estonian coast of the Baltic Sea. The population of the HMA is about one million. Long-range transport (LRT) is the main source of fine particles in ambient air in the HMA, whereas traffic, residential wood combustion, energy plants and industrial processes are the most important local emission sources (Saarikoski *et al*. 2008a). The main heating sources of the buildings in the area are district heating (78%), electric heating (10%), and oil (8%) (HSY 2010b). The rest includes wood combustion and other individual heating systems. Dis-

trict heat is mainly produced with fossil fuels. The number of detached houses is about 65 000 and approximately 90% of them have some kind of a fireplace. Small-scale wood combustion appliances are used for supplementary heating and for pleasure purposes as well. The use of heat-storing fireplaces is most common during the cold season but sauna stoves are heated throughout the year.

The current study was based on measurements that were conducted in the HMA in selected periods during the years 2005–2009 (Table 1). The research sites included three urban background sites in Helsinki: the SMEAR III station in Kumpula (in this study called as URB-1), Kallio station (URB-2), and West Harbour of Helsinki (URB-3); and three suburban sites in the areas of detached housing without district heating: Lintuvaara (SUB-1), Itä-Hakkila (SUB-2), and Vartiokylä (SUB-3). The locations of the sites are presented in Fig. 1, which also illustrates the density of detached houses in the area.

Mass measurements and filter samplings

Information on the measurements and filter samplings at the sites are given in Table 1. The sampling height at all the sites was 4 m above ground level. The online mass concentrations of $PM_{2.5}$ were measured with the following instruments: a Grimm Model 180 Ambient Dust Monitor (Grimm Aerosol Technik GmbH & Co., Germany) at SUB-2 and at SUB-3, a Tapered Element Oscillating Microbalance (TEOM 1400ab; Thermo Fischer Scientific Inc., Germany) at URB-2, and a Particulate Monitoring Instrument FH 62 I-R (ESM Andersen Instruments GmbH, Germany) at URB-3. These different PM measurement instruments have passed a test against a reference method, and their results are reliably comparable after using calibration functions (Waldén *et al*. 2010). At URB-1 in 2006–2007, the online mass concentration of $PM_{2.5}$ was measured using a TEOM 1400a (Rupprech & Patashnik, USA) equipped with a Filter Dynamics Measurement System (FDMS) to measure the fraction of semi-volatile PM (Saarikoski *et al*. 2007). At URB-1 in 2008–2009, the mass
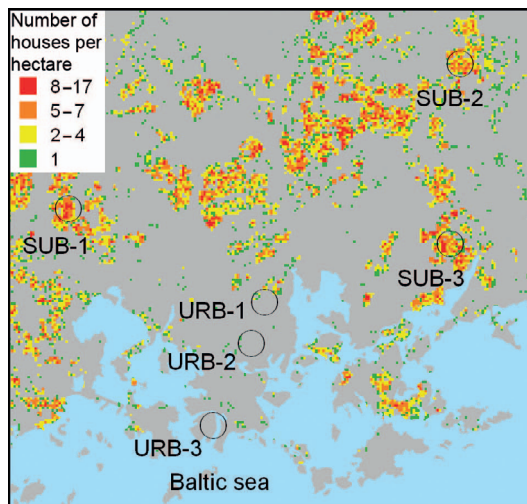
Fig. 1. Site locations (marked with circles with diameter of 1 km) and the density of detached houses in the HMA.

concentration of PM_1 was determined from poly-tetrafluoroethylene (PTFE) filters by weighing them before and after sampling using a Mettler Toledo UMT2 micro-balance (Mettler Toledo GmbH, Switzerland). At SUB-1, the online mass concentrations of PM_{10} were measured with a FH 62 I-R (ESM Andersen Instruments GmbH, Germany).

Filter samples were collected for the determination of MAs. The PM_1 sampling duration at URB-1 was typically 10–24 hours on working days and 10–72 hours over weekends with the manual sample exchange typically at 08:00 and/or 18:00. The sampling procedures used were presented by Saarikoski *et al*. (2008a) (samplings during 2006–2007) and by Saarnio *et al*. (2010b) (2008–2009). At the other sites, the filter sampling was conducted for PM_{10} with sampling duration of 24 hours starting at midnight. Micro PNS samplers with PTFE filters were used at

Table 1. Information on the sites, samplings and measurements.

Site name	Distance from city centre	Site description	Local fine PM emission sources	Sampling periods	Filter sampling[a]	Measured PM size-class
SUB-1 (Lintuvaara)	10 km NW	Suburban area of detached housing	Small-scale wood combustion[b]	1 Jan.– 30 Dec. 2005	PM_{10}; 24 h; occasionally	PM_{10}
SUB-2 (Itä-Hakkila)	16 km NE	Suburban area of detached housing	Small-scale wood combustion[b]	1 Oct.– 24 Dec. 2008	PM_{10}; 24 h; every 4 days	$PM_{2.5}$
SUB-3 (Vartiokylä)	10 km ENE	Suburban area of detached housing	Small-scale wood combustion[b,c]	2 Feb.– 30 Mar. 2009	PM_{10}; 24 h; every 2 or 4 days	$PM_{2.5}$
URB-1 (Kumpula)	4 km NNE	Urban background (university campus)	Traffic[d]	(a) 10 Feb. 2006– 28 Feb. 2007; (b) 8–19 Dec. 2008, 14 Jan.– 13 Mar. 2009	PM_1; typically 10–24 h (few samplings over weekend); continuously	(a) $PM_{2.5}$; (b) PM_1
URB-2 (Kallio)	2 km NNE	Urban background (dwelling zone in central area)	Traffic[b,c]	1 Oct.– 24 Dec. 2008, 2 Feb.– 30 Mar. 2009	PM_{10}; 24 h; every 2 or 4 days	$PM_{2.5}$
URB-3 (West Harbour)	1.5 km SW	Urban background (harbour area)	Ships, traffic[b]	22 Nov.– 24 Dec. 2008	PM_{10}; 24 h; every 4 days	$PM_{2.5}$

[a] Filter samples for analysis of MAs (PM size-class; duration; and frequency of the samplings).
[b] YTV (2009).
[c] HSY (2010a).
[d] Saarikoski *et al*. (2008).

URB-2, URB-3, SUB-2 and SUB-3. At SUB-1, samples were collected using a Wedding sampler with PTFE coated glass fibre filters. MAs are principally found in the fine fraction of particles (Yttri *et al*. 2005, Engling *et al*. 2006, Frey *et al*. 2009). In the burn tests by Engling *et al*. (2006), approximately 98.8% of levoglucosan was in $PM_{2.5}$ with the majority in sub-micron particles. Yttri *et al*. (2005) found that 80% of MAs was associated with particles smaller than 1 μm in ambient air in a small Norwegian town. Since in the present study MAs were determined from different filter materials and from samples having different PM size-classes, it was estimated that the comparison of the results had an uncertainty of 20%.

The local meteorological data, including air temperature, wind speed, and wind direction (WD), were recorded at URB-1. The FLEXTRA trajectory model (Stohl and Wotawa 1995) was used to investigate the main directions and the routes of the air masses. Four-day backward-trajectories were calculated at noon each day at the arrival pressure level of 950 hPa representing about 500 m height. The sources of aerosol particles were considered in a regional scale, so the accuracy of the trajectory calculations with the chosen parameters was sufficient to reveal the differences in source directions.

Analysis of MAs

Two analysis protocols were used for analysis of MAs: The samples from the years 2005–2007 were analyzed with liquid chromatography–mass spectrometry (LC-MS) and those from years 2008–2009 with high-performance anion-exchange chromatography–mass spectrometry (HPAEC-MS). The LC-MS method was adapted from Dye and Yttri (2005) and it was presented earlier by Saarikoski *et al*. (2007). The samples were extracted with 2-ml of a tetrahydrofuran–water mixture (1:1, v/v) with 30-min ultrasonic agitation, and filtered. The used column system consisted of two Atlantis™ C_{18}-columns in line (Waters) and deionized water was used as an eluent. Electrospray ionization (EI) and ion trap MS were used (Agilent Technologies SL). The HPAEC-MS method was validated and pre-

sented in detail by Saarnio *et al*. (2010b). In this method, the samples were extracted with 5 ml of deionized water with internal standard and with 15-min shaking, and filtered. The used column system consisted of CarboPac™ PA10 guard and analytical columns (Dionex) and the eluent was produced by a KOH eluent generator. The ionization technique was EI and the MS was equipped with a quadrupole mass analyzer. Both LC-MS and HPAEC-MS methods used *m/z* 161 for determination of MAs.

Multiplying factor for estimating wood combustion impact

The impact of wood combustion on ambient PM concentrations in the HMA could be roughly estimated using MAs concentrations with a multiplying factor (MF). MF was derived from previous ambient-environment studies and estimated uncertainties (Δ) by assuming that 83% ± 3% (mean ± Δ) of MAs is levoglucosan (levo) in the HMA (average range in this study) and by using the ratio of biomass-burning originated OC (BB-OC) to levoglucosan [9.2 ± 0.9 (mean ± Δ); positive matrix factorization (PMF) results in urban Helsinki in winter by Saarikoski *et al*. (2008a)], and estimating the contribution of OC to $PM_{2.5}$. The OC concentration was converted to particulate organic matter (POM) by multiplying it by 1.6 ± 0.2 (mean ± Δ) (Turpin and Lim 2001, Saarnio *et al*. 2010a). The contribution of POM to $PM_{2.5}$ is the most crucial factor that largely depends on the material combusted and the combustion technique. In combustion experiments with a masonry heater, the POM-to-$PM_{2.5}$ contribution ranged between 33% (good combustion) and 67% (smouldering combustion) (Frey *et al*. 2009). In the present study, no ambient OC concentration was measured, and therefore the POM-to-$PM_{2.5}$ contribution had to be estimated. Viidanoja *et al*. (2002) found that in the ambient air in Helsinki the POM-to-$PM_{2.5}$ contribution is approximately 50%. That value was used with the uncertainty of 17 percentage units, which is the difference between POM-to-$PM_{2.5}$ contribution presented by Viidanoja *et al*. (2002) and that in good and smouldering combustions given by Frey *et al*. (2009). By combing

the abovementioned factors, a semi-quantitative MF was derived for MAs:

$$MF = \frac{\dfrac{levo}{MAs} \times \dfrac{BB\text{-}OC}{levo} \times \dfrac{POM}{OC}}{POM / PM_{2.5}} \quad (1)$$

$$= \frac{0.83 \times 9.2 \times 1.6}{0.5} = 24.4$$

The uncertainty of MF (ΔMF) was calculated using the following equation:

$$\Delta MF = MF \times \left[\left(\frac{\Delta \dfrac{levo}{MAs}}{\dfrac{levo}{MAs}} \right)^2 + \left(\frac{\Delta \dfrac{BB\text{-}OC}{levo}}{\dfrac{BB\text{-}OC}{levo}} \right)^2 + \left(\frac{\Delta \dfrac{POM}{OC}}{\dfrac{POM}{OC}} \right)^2 + \left(\frac{\Delta \dfrac{PM_{2.5}}{POM}}{\dfrac{PM_{2.5}}{POM}} \right)^2 \right]^{0.5} \quad (2)$$

$$= 24.4 \times \left[\left(\frac{0.03}{0.83} \right)^2 + \left(\frac{0.9}{9.2} \right)^2 + \left(\frac{0.2}{1.6} \right)^2 + \left(\frac{0.17}{0.5} \right)^2 \right]^{0.5}$$

$$= 24.4 \times 0.38 = 9.2$$

This MF and its uncertainty were used for MAs concentration to estimate indicatively the $PM_{2.5}$ concentration originated from wood combustion (BB-$PM_{2.5}$):

$$BB\text{-}PM_{2.5} = MAs \times (MF \pm \Delta MF)$$
$$= MAs \times (24.4 \pm 9.2) \quad (3)$$

It must be emphasized that this kind of use of a multiplying factor is very crude and it includes a wide range of uncertainty but, nonetheless, it enables the estimation of the order of local wood combustion impact on the PM concentration.

Wood combustion experiments in laboratory

The study included wood combustion experiments conducted in an emission research laboratory. The detailed description of the combustion procedure is given in Lamberg *et al.* (2011). Two

different materials were burnt: wood logs made of birch and coniferous pellets made mainly of pine. The experiments were conducted with three different small-scale combustion appliances: a pellet boiler (pellets), a conventional heat-storing masonry heater (wood logs) and sauna stove (wood logs). The sauna stove and masonry heater represented the typical wood combustion methods used in Finland (Tissari *et al.* 2008, Lamberg *et al.* 2011). The pellet boiler represented a modern technology that is not yet widely used in Finland. The dilution ratio of the combustion air emitted from the pellet boiler was about 100. 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. The diluted PM_1 emissions were sampled on PTFE filters using the five uppermost stages of a Berner low-pressure impactor first to remove the particles larger than 1 μm. The sample flow rate was 25 l min^{-1}. The filters were weighed before and after sampling using a Mettler Toledo UMT2 micro-balance, and MAs were analysed with HPAEC-MS (as described earlier).

Results and discussion

Temporal variation

Seasonal variation

MAs were determined from the filter samples collected in the HMA in selected periods during 2005–2009 (Table 2), including two one-year campaigns at SUB-1 in 2005 and at URB-1 in 2006–2007 (Fig. 2). The measurements were classified either as warm season (April–September) or cold season (October–March) periods to demonstrate the typical MAs concentration levels at the suburban and urban sites in the HMA (Table 2). In the cold season, the mean MAs concentrations were 115–225 ng m^3 and 83–98 ng m^3 at the suburban and the urban sites, respectively. In the warm season, the measurements were only conducted at one suburban
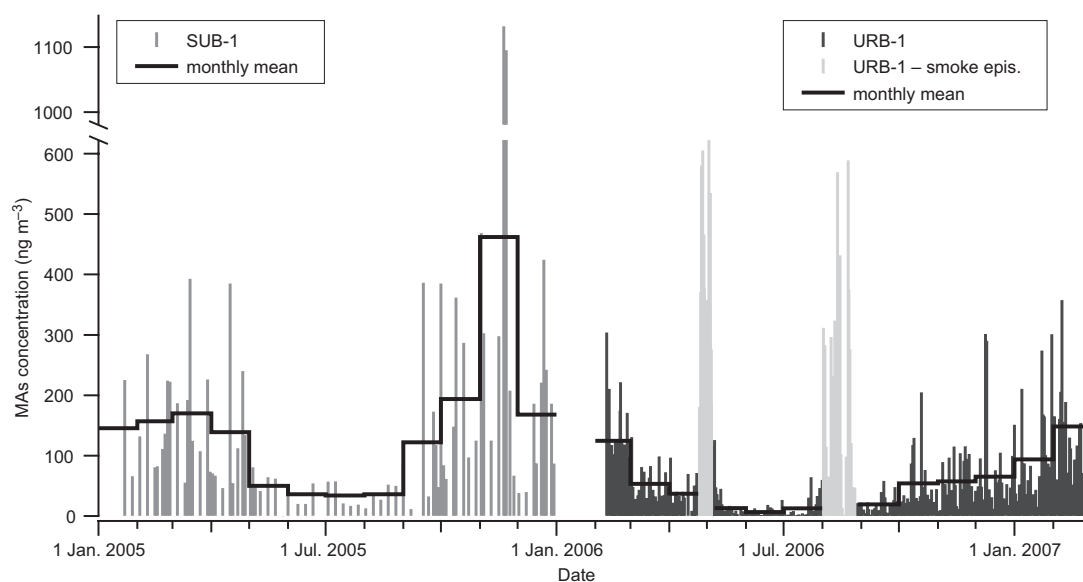
Fig. 2. Concentrations of MAs in the HMA during 2005–2007. In order to distinguish the long-range-transported open land fire smoke episodes from the seasonal variation, they are presented separately (light-grey bars). The concentrations of MAs were determined from PM_{10} filter samples at SUB-1 (grey bars) and from PM_1 at URB-1 (dark-grey bars). Additionally, the monthly mean concentrations are presented with horizontal black lines.

(SUB-1) and one urban site (URB-1), and as expected, the mean MAs concentrations were quite low in the warm season (19–78 ng m³), excluding the wildfire smoke episode periods (222–378 ng m⁻³). Since SUB-1 and URB-1 were the only sites where MAs concentrations were measured throughout the year, we focused on these sites to describe in more detail the sea-

sonal variation of MAs and PM concentrations.

The concentration of MAs showed a clear seasonal variation at both sites with the highest concentrations during winter and the lowest in summer (Fig. 2). The seasonal variation in the PM concentration was not seen as clearly as in the concentration of MAs, especially, at URB-1 (Fig. 3). This was mainly due to different emis-

Table 2. Average concentrations of MAs and PM in the HMA during 2005–2009. n = number of filter samples.

Site	Sampling season or period	Sample type	n	MAs (ng m⁻³)	Measured PM size-class	PM^a (ng m⁻³)
SUB-1	Warm season (Apr.–Sep. 2005)	PM_{10}	35	78	PM_{10}	22.6
SUB-1	Cold season (Jan.–Mar., Oct.–Dec. 2005)	PM_{10}	43	225	PM_{10}	27.3
SUB-2	Cold season (Oct.–Dec. 2008)	PM_{10}	22	215	$PM_{2.5}$	8.2
SUB-3	Cold season (Feb.–Mar. 2009)	PM_{10}	21	115	$PM_{2.5}$	9.6
URB-1	Warm season (Apr.–Sep. 2006)[b]	PM_1	105	19	$PM_{2.5}$	9.5
URB-1	Wildfire smokes (Apr.–May 2006)	PM_1	20	378	$PM_{2.5}$	35.5
URB-1	Wildfire smokes (Aug. 2006)	PM_1	12	222	$PM_{2.5}$	21.6
URB-1	Cold season (Feb.–Mar. 2006, Oct. 2006–Feb. 2007)	PM_1	153	84	$PM_{2.5}$	10.3
URB-1	Cold season (Dec. 2008–Mar. 2009)	PM_1	131	90	PM_1	9.3
URB-2	Cold season (Oct.–Dec. 2008)	PM_{10}	22	85	$PM_{2.5}$	8.6
URB-2	Cold season (Feb.–Mar. 2009)	PM_{10}	21	83	$PM_{2.5}$	11.1
URB-3	Cold season (Nov.–Dec. 2008)	PM_{10}	9	98	$PM_{2.5}$	9.5

[a] PM concentration from only those days when the filter samples were collected.

[b] Season without major episodes of long-range transported wildfire smokes.
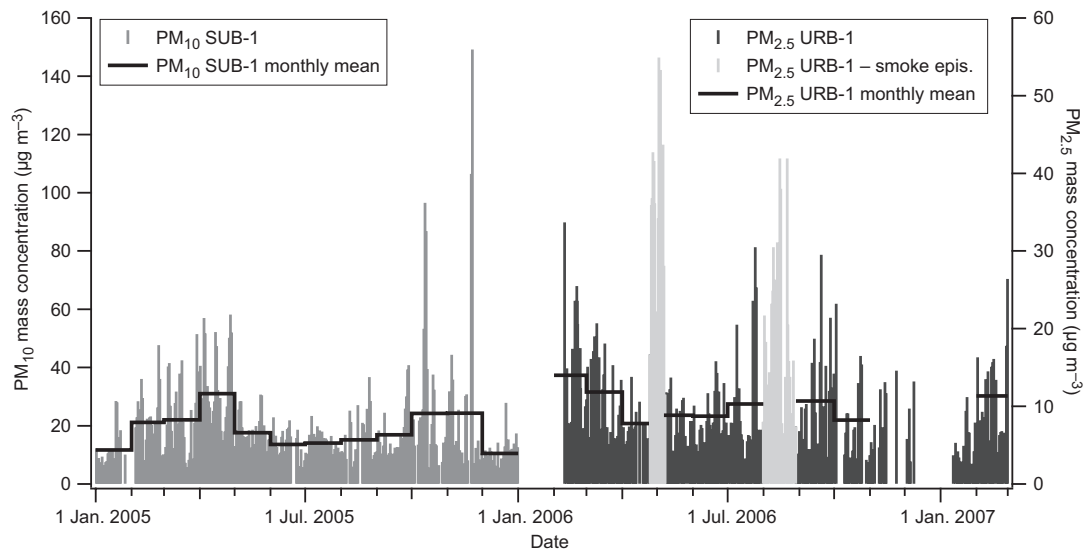
Fig. 3. Daily mean PM concentrations in the HMA during 2005–2007. The long-range-transported open land fire smoke episodes are presented separately (light-grey bars). The mass concentration of PM_{10} was measured at SUB-1 (grey bars, left axis) and $PM_{2.5}$ at URB-1 (dark-grey bars, right-hand side axis). The monthly mean concentrations are presented with horizontal black lines. Due to instrumental problems, data for the end of 2006 was discontinuous.

sion sources during different seasons. At this latitude, secondary organic aerosol formation from biogenic precursors and small-scale wood combustion are the major sources of PM during the warm and cold seasons, respectively (Saarikoski *et al*. 2008a). Other important emission sources in the HMA are traffic and LRT throughout the year (Saarikoski *et al*. 2008a) as well as coarse road dust in spring (Anttila and Salmi 2006). At SUB-1, where wood combustion is a local emission source, a notable influence of wood combustion on the PM concentration was seen (Figs. 2 and 3). Occasionally, the MAs concentration behaved similarly to the PM concentration at both urban and suburban sites, implying that wood combustion was a major source of PM in the area at the time. Besides wood combustion, long-range-transported open land fire smokes occasionally raised the levels of MAs and PM, e.g. during spring and summer 2006 (Saarikoski *et al*. 2007, Saarnio *et al*. 2010a) (Figs. 2 and 3).

The contribution of MAs to PM_{10} at SUB-1 in 2005 and MAs to $PM_{2.5}$ at URB-1 in 2006–2007 had a similar seasonal variation as did the concentration of MAs. During those periods, the correlation coefficient (Pearson's *r*) between MAs and PM_{10} at SUB-1 was 0.66,

and between MAs and $PM_{2.5}$ at URB-1 its was 0.71. At SUB-1, the monthly mean contribution of MAs to PM_{10} was at its highest in December 2005 (monthly mean contribution 1.7%) and at its lowest in August 2005 (0.2%). At URB-1, the monthly mean MAs-to-$PM_{2.5}$ contribution was highest in January 2007 (1.9%) and lowest in June 2006 (0.1%). The mean MAs-to-$PM_{2.5}$ contributions were somewhat lower than those reported previously for Helsinki by Saarikoski *et al*. (2008b): 0.98% in spring 2003, 3.0% in autumn 2003, 2.0% in winter 2004, 2.3% in spring 2004, and 0.95% in summer 2004.

Local meteorological conditions can affect remarkably the emissions and concentrations of PM and MAs that may be seen as greater seasonal means. Therefore, year-to-year comparisons are not straightforward. For example, the concentration of MAs was exceptionally high on 21–22 November 2005, when a strong temperature inversion occurred in the area. The accumulation of local wood combustion emissions in the ambient air was evident at SUB-1 with daily mean concentrations of 1.1 μg m^{-3} for MAs (Fig. 2) and 150 μg m^{-3} for PM_{10} (Fig. 3). This was the highest 24-h ambient MAs concentration ever measured in the HMA and in Finland. These

samples, collected during the meteorological inversion, raised the monthly mean concentration of MAs to 0.46 μg m^{-3} while the median of the samples was 0.30 μg m^{-3}. High daily MAs concentrations (up to 0.63 μg m^{-3}) were also observed in 2006 at URB-1 due to long-range-transported smokes from wildfires. Typically, high daily concentrations of PMs at the urban sites in the HMA are caused by long-range-transported particles or road dust (mainly coarse particles), not by local wood combustion (Anttila and Salmi 2006, Niemi *et al*. 2009).

Day-of-week variation

Similarly to seasonal differences between the cold and warm seasons, the day-to-day differences are related to ambient temperature that is reflected both in quantity of wood combustion emissions and in atmospheric mixing of emissions. The data from the three suburban (Fig. 4a) and three urban sites (Fig. 4b) were combined to show the differences in MAs concentrations between the days of the week during the cold season (October–March).

At the suburban sites, the range of the concentrations of MAs was three to four times larger than at the urban sites. That was mainly due to the local wood combustion at the suburban sites. The dataset for the suburban sites was limited and therefore there were large differences between the weekdays. However, stagnant conditions can cause high concentrations of MAs if wood combustion exists (Fig. 4). Those high concentrations increased remarkably the mean of the measured values as compared with their median. Therefore here, it is more convenient to compare the day-specific medians. The higher medians of MAs on Wednesdays and Saturdays than on other days of the week at the suburban sites (Fig. 4a) can be explained (at least partly) by the fact that in Finland those two are the days when sauna stoves are traditionally heated. At the urban sites, the MAs concentrations were somewhat elevated on Saturdays even though the variation in concentrations was large (Fig. 4b).

Saarnio *et al*. (2010b) found a clear difference between the weekends and weekdays at URB-1 in winter 2008–2009 when the MAs concentration during the weekends ($n = 31$) was on average 58% higher than during the weekdays ($n = 83$). However, at the same site during the cold season in 2006–2007 ($n = 30$ and $n = 115$, respectively), the respective difference was only 4%.

Night/day variation

Typically MAs are analyzed from filter samples with sampling times of several hours or days. To our best knowledge and excluding our previous study (Saarnio *et al*. 2010b), no studies presenting information on the night/day variation in the ambient MAs concentrations from small-scale wood combustion exist. The present study was based mainly on 24-h samples, except for URB-1 where sampling durations varied. The filter samplings were conducted continuously, with the sample exchange in the morning and in the evening (typically at 08:00 and 18:00, respectively), at the URB-1 site during the winter 2008–2009 and during one week in February 2006. The concentrations of MAs in the nighttime samples ($n = 64$) were on average only 12% higher than those in the daytime samples ($n = 65$) during the winter 2008–2009 (Saarnio *et al*. 2010b), and 8% in February 2006 ($n = 5$ and $n = 5$, respectively).

The difference in MAs concentrations between day and night is more distinct at the suburban sites than at the urban sites probably because the emission sources of MAs at the suburban sites are closer to the measuring point. In this study, the samplings of the MAs concentrations at the suburban sites were conducted with a 24-h time-resolution and not on a daily basis and, therefore, the above hypothesis could not be confirmed. However, based on the changes in the concentration of PM$_{2.5}$, it could be observed that in the suburban areas wood combustion raised the particulate concentrations, especially in the evenings (data not shown here) when people spend more time at home. Additionally, lower ambient temperature at night increases the need for heating, and at the same time the atmospheric mixing is less efficient, causing higher ambient concentrations. For example at SUB-2, the concentration of PM$_{2.5}$ rose typically in the evening
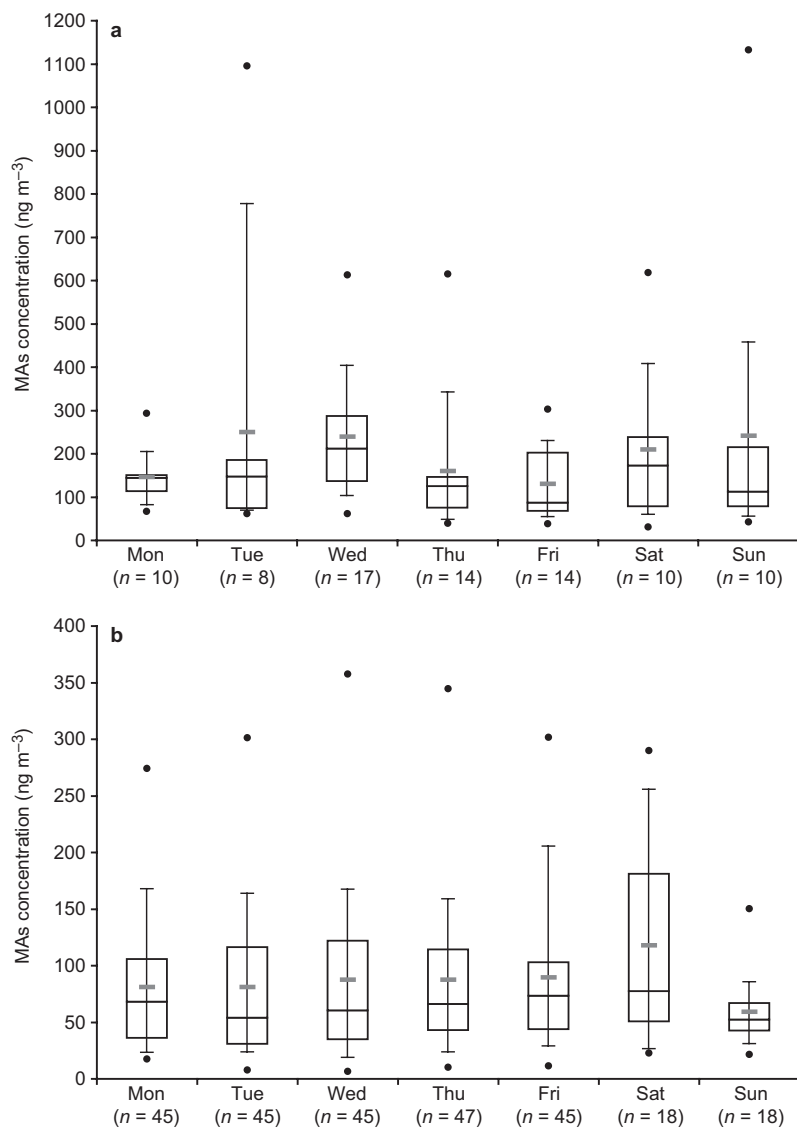
Fig. 4. Day-specific variation in MA concentrations at (**a**) suburban and (**b**) urban sites. The median (black line inside the boxes), 25 and 75 percentile values (box lower and upper limits), 10 and 90 percentile values (error bars), the maximum and the minimum values (black dots), and the mean value (grey horizontal bar) are presented for each day of the week during the cold season (October–March).

(18:00–23:00). At the same time, the respective concentration at the urban sites of the HMA was clearly lower.

Spatial variation

During the cold season (October–March) in 2008–2009, the samplings were conducted concurrently in the suburban areas (SUB-2 and SUB-3), where residential wood combustion is a major local-emission source, and at the urban background sites (URB-1, URB-2, and URB-3),

where no local wood combustion exists or it is only a minor source at the local scale. Even though URB-3 is directly exposed to marine winds, the MAs concentrations were only slightly lower (mean ± SD = 12% ± 19%) than those measured at URB-2 which is situated 2 km inland from the city centre (Fig. 5). The concentrations of MAs were on the same level also at the third urban background site, URB-1, 4 km inland from the city centre. The similarity of the MAs concentrations in the parallel samplings at different urban sites implied that there were not major local wood combustion sources in the
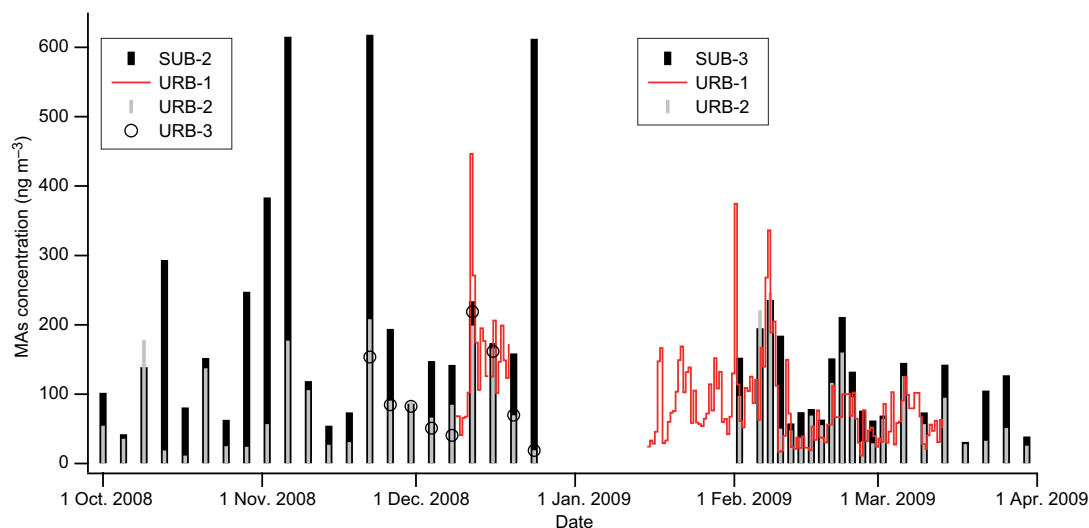
Fig. 5. Concentrations of MAs at SUB-2 and SUB-3 (thick black bars), URB-1 (red line), URB-2 (thin grey bars), and URB-3 (circles) during the cold season in 2008–2009. The sampling duration was 24 hours at all sites except at URB-1 where it was mostly 10 or 14 hours.

urban areas. Instead, fine particles containing MAs in the urban areas of Helsinki were mainly regionally distributed or long-range transported.

In October–December 2008 the concentration of MAs was on average 4.7 times higher at SUB-2 than at URB-2, whereas in February–March 2009 it was only 1.6 times higher at SUB-3 than at URB-2. Obviously, there are differences in various suburbs but also the remarkable difference between SUB-2 and SUB-3 can be caused by the locations of the sampling sites; the SUB-2 sampling site was totally surrounded by detached houses while the SUB-3 site was only partly surrounded by houses due to a small green area beside the site. Furthermore, there might be large differences in the amounts of wood combustion emissions from surrounding houses but they were not studied in this work.

Combining the concurrent concentrations of MAs at the urban and suburban sites with observed meteorology and the calculated four-day backward-trajectories, the samples were divided into two categories even though the dataset was limited ($n = 43$): (1) fine particles mainly from regional sources (with a horizontal scale from about ten to several hundred kilometres) or from LRT (from several hundreds to over thousand kilometres), and (2) fine particles assessed to be mainly caused by local wood-

combustion sources close to suburban sites (distance up to few kilometres).

Regionally distributed wood combustion particles

The particulate matter was expected to be regionally distributed, either from the emission sources in the surrounding region or long-range transported from farther afield, when the concentrations of MAs were fairly similar both at the urban and suburban sites (Fig. 5). Meteorological data and backward-trajectories showed that during such periods the air masses were mainly from east or south, i.e. WD was from the eastern or southern sector and the route of the air masses was mainly over Russia and/or eastern and/or central Europe, which means that the biomass burning emissions may be transported to the HMA. These cases included both samples of low and relatively high concentration of MAs. During these sampling periods, the mean concentration of MAs and the average MAs-to-$PM_{2.5}$ contribution were only slightly higher at the suburban sites than at URB-2 at the same time (Table 3). The somewhat higher contributions at the suburban sites could be explained by different PM sources, e.g. the influence of local

wood combustion at suburban sites and traffic at urban sites.

Fine particles from local wood combustion

When the air masses came from north and/or west (i.e. WD was from northern or western sector and the backward-trajectories showed the route of air masses coming mainly over the Scandinavia and/or the Arctic Sea, which means that the air was relatively clean), the concentrations of MAs were often clearly higher at the suburban than at the urban sites. During these events, both ambient temperature and wind speed were lower than during the events with southern and eastern air masses. Therefore, those high concentrations of MAs at the suburban sites were estimated to originate mainly from local wood combustion. The local emissions could be registered 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 the suburbs did not drift to the urban sites, and therefore the concentrations of MAs were notably lower there.

There were remarkable differences in the contributions of MAs to $PM_{2.5}$ between the suburban sites, especially SUB-2, and the urban background sites when fine particles were caused mainly by local wood combustion (Table 4). The mean concentration of MAs and the average MAs-to-$PM_{2.5}$ contribution were clearly higher at the suburban sites than at URB-2 at the same time. The sites SUB-2 and SUB-3 are both located in the middle of residential areas but remarkably higher concentrations of MAs

were detected at SUB-2 (Fig. 5). The difference between SUB-2 and SUB-3 could result from the locations of the sampling sites in the suburbs as explained earlier.

These results were in line with the contributions measured previously in the Nordic countries. The average MAs-to-$PM_{2.5}$ contribution was 2% at an urban background site in the HMA in winter 2004 (Saarikoski *et al.* 2008b). In Denmark, the average contribution of MAs to $PM_{2.5}$ was 3.6% in a residential area and 1.7% at a background site (Glasius *et al.* 2008) while in Norway, the average contribution of MAs to PM_{10} was 3.1% in a residential area and 0.6% in urban background of Oslo in winter (Yttri *et al.* 2005).

Impact of wood combustion on PM concentration

The data on MAs and PM concentrations during the cold season (October–March) were used to estimate semi-quantitatively the contribution of wood combustion to ambient PM concentrations. During the warm season, open land fire smokes occasionally drift to the HMA (Niemi *et al.* 2009) that would complicate the estimation. Additionally, it has been proposed that MAs are more stable in the atmosphere in winter when solar radiation is low and there are less hydroxyl radicals that might react with levoglucosan in the air (Hennigan *et al.* 2010, Hoffmann *et al.* 2010).

The impact of wood combustion on ambient PM concentrations in the HMA was roughly estimated using the measured MAs concentrations and the multiplying factor derived in this study

Table 3. Average MAs concentrations and MAs-to-PM contributions in the cold season samples when biomass burning particles were mainly regionally distributed or long-range transported.

Site	Period	n	MAs conc. (μg m^{-3})	MAs-to-PM (%)
SUB-2	Oct.–Dec. 2008	14	0.12	1.6
URB-2	Oct.–Dec. 2008	14	0.09	0.9
URB-3	Nov.–Dec. 2008	6	0.10	0.9
SUB-3	Feb.–Mar. 2009	13	0.12	1.1
URB-2	Feb.–Mar. 2009	13	0.10	0.7

Table 4. Average MAs concentrations and MAs-to-PM contributions in the cold-season samples when biomass burning particles at the suburban sites originated mainly from local sources.

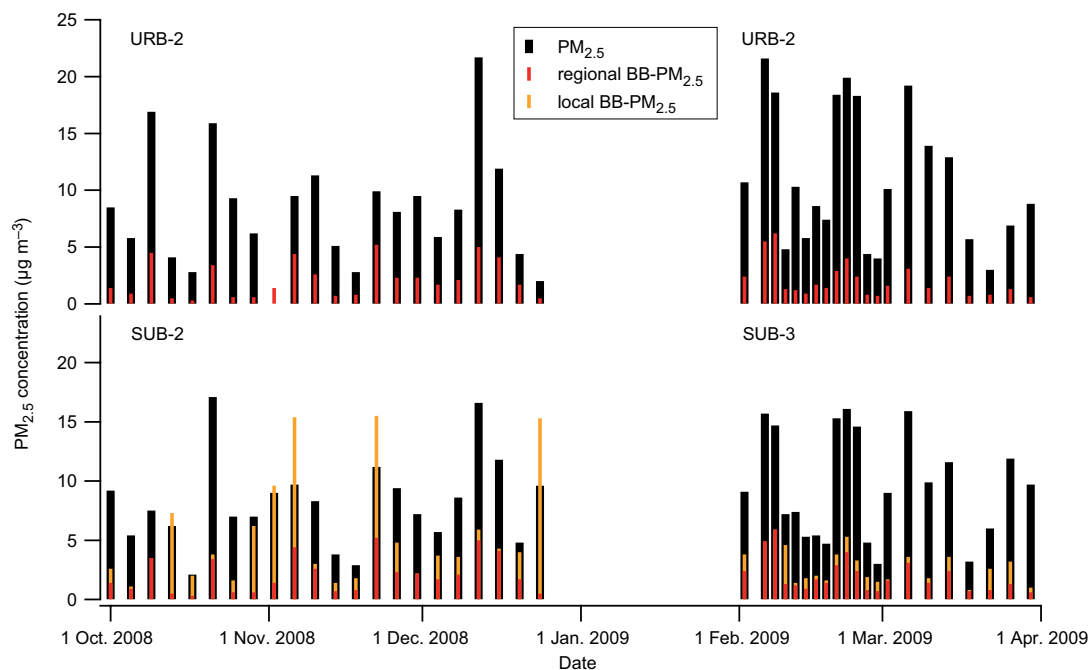| Site	Period	n	MAs conc. (μg m^{-3})	MAs-to-PM (%)
SUB-2	Oct.–Dec. 2008	8	0.38	4.6
URB-2	Oct.–Dec. 2008	8	0.08	1.0
URB-3	Nov.–Dec. 2008	3	0.09	1.3
SUB-3	Feb.–Mar. 2009	8	0.11	1.6
URB-2	Feb.–Mar. 2009	8	0.06	0.8

Fig. 6. PM$_{2.5}$ concentrations (black bars) with the estimation of the PM$_{2.5}$ concentrations caused by wood combustion (BB-PM$_{2.5}$) in regional scale (red bars) and from local sources (orange bars) at URB-2 (upper part), and at SUB-2 and SUB-3 (lower part) during the cold season in 2008–2009.

(MF ± ΔMF = 24.4 ± 9.2). In October–December 2008, the average of the estimated contribution of wood combustion to PM$_{2.5}$ (BB-PM$_{2.5}$) was clearly higher at SUB-2 than at URB-2 (Fig. 6) or at URB-3. The high contribution at SUB-2 was obviously due to major emissions from local wood combustion. However, when the local wood-combustion emissions dominated, the BB-PM$_{2.5}$ was occasionally overestimated. It could be stated that the multiplying factor of 24.4 was too high for fresh emissions from wood combustion. In ambient aerosol that is heavily impacted with fresh wood-combustion emissions (like SUB-2 occasionally), the POM-to-PM$_{2.5}$ contribution is presumably higher than 50%, and therefore the multiplying factor would be smaller. In February–March 2009, the difference in BB-PM$_{2.5}$ between SUB-3 and URB-2 was not as large as between SUB-2 and URB-2 in October–December 2008. Both the measured PM$_{2.5}$ and the estimated BB-PM$_{2.5}$ showed a fairly similar pattern at SUB-3 and URB-2 (Fig. 6), yet the PM$_{2.5}$ concentration was somewhat higher at URB-2 while the estimated BB-PM$_{2.5}$ was typically higher at SUB-3. The similarity indicated

that the fine particles were mainly regionally distributed at those two sites. The minor differences were presumably caused by traffic at URB-2 and by wood combustion at SUB-3.

The average PM concentrations caused by wood combustion were 2.0–2.4 μg m^{-3} (contribution to total PM concentration 18%–29%) and 2.8–5.6 μg m^{-3} (27%–66%) at the urban and suburban sites, respectively (Table 5). The urban areas of the HMA were assumed to be influenced by wood combustion emissions only on a regional scale, not by local wood combustion. Therefore, the estimated regional BB-PM$_{2.5}$ concentration at URB-2 (i.e. regional background concentration) could be subtracted from the values obtained simultaneously at the suburban sites (SUB-2 or SUB-3), in order to estimate the PM$_{2.5}$ concentration and the contribution of local wood-combustion emissions at the suburban sites (i.e. "hotspot" concentration) (Fig. 6 and Table 5). At the suburban sites, average contributions of local and regional wood combustion to the total PM$_{2.5}$ concentrations were 11%–41% (local BB-PM 0.8–3.2 μg m^{-3}) and 20%–25% (regional BB-PM 2.0–2.2 μg m^{-3}), respectively

(Table 5). Due to local wood combustion in the cold season, the concentration of $PM_{2.5}$ at SUB-2 was higher than at the urban sites in the HMA influenced by traffic.

During the measurements of the present study, only two 24-h samples were estimated to exceed the WHO guideline limit for the daily mean concentration of $PM_{2.5}$ (25 μg m^{-3}; WHO 2006) purely because of wood combustion (excluding the open land fire smokes). The exceedance took place at SUB-1 in November 2005 when the temperature inversion occurred. However, wood combustion was more often a secondary reason for exceedance together with LRT and/or local traffic emissions. At SUB-2, the local wood combustion emissions caused occasionally even 10–15 μg m^{-3} of additional daily mean concentration of $PM_{2.5}$. The most dramatic difference between the urban and suburban samples, and at the same time the highest $PM_{2.5}$ concentration from local wood combustion was detected at SUB-2 at Christmas Eve (the last sample from SUB-2 in Fig. 6) when fireplaces and sauna stoves are used frequently in small-house areas.

A wide range of emission factors are given in the literature for levoglucosan and MAs (e.g. Engling *et al.* 2006, Iinuma *et al.* 2007, Schmidl *et al.* 2008b). Schmidl *et al.* (2008b) found relatively high emission factors of levoglucosan for several wood species in Austria. Caseiro *et al.* (2009) used those factors in estimation of the wood combustion contribution to ambient PM concentrations in three Austrian cities. In that study, a multiplying factor of 10.7 for the lev-

oglucosan concentration was used to calculate the concentration of wood-smoke PM. However, the ratio of levoglucosan to PM emissions from wood combustion is dependent on the type of wood (e.g. Engling *et al.* 2006, Caseiro *et al.* 2009) and also on the combustion technique (e.g. Frey *et al.* 2009). In the combustion experiment carried out by Frey *et al.* (2009), the contribution of levoglucosan to emitted PM was clearly lower than in the tests by Schmidl *et al.* (2008b); being 3.0% ± 1.2% in normal combustion, and 2%–3% in smouldering combustion when birch logs were burnt in a conventional masonry heater (Frey *et al.* 2009), and therefore the $PM_{2.5}$-to-levoglucosan factor was about 33 and $PM_{2.5}$-to-MAs about 25. The multiplying factor from the combustion experiment by Frey *et al.* (2009) was comparable to that derived in the present study (24.4 ± 9.2), assuming that MAs-to-PM ratios measured in the laboratory conditions do not change during dilution. In other European studies, for example Puxbaum *et al.* (2007) used a multiplying factor of 7.35 for levoglucosan to estimate the contribution of wood combustion to OC and thereby attained the contribution of 18.0%–68.4% in winter at the CARBOSOL sites. Bari *et al.* (2010) estimated that levoglucosan contributes 3.7% to PM_{10} and thus the relative contribution of wood heating to wintertime ambient PM_{10} pollution was estimated to be 59% ± 41% in a residential area near Stuttgart in southern Germany.

Typically source-specific estimations are made using factor analysis techniques, such as

Table 5. Estimated mean (± uncertainty Δ) concentrations of PM from wood combustion (BB-PM) and mean contributions (± with uncertainty) of wood combustion to PM concentration during the cold season. The multiplying factor (24.4) **for converting** MAs to BB-PM was derived from Eq. 1 for $PM_{2.5}$ size class, which decreases the accuracy of the results for other size classes (PM_{10} and PM_1).

Site	Period	Size-class	BB-PM (μg m^{-3})	BB-PM (%)	Regional BB-PM (%)	Local BB-PM (%)
SUB-1	Jan.–Mar., Oct.–Dec. 2005	PM_{10}	5.6 (± 2.1)	27 (±10)		
SUB-2	Oct.–Dec. 2008	$PM_{2.5}$	5.2 (± 2.0)	66 (± 25)	25 (± 10)	41 (± 16)
SUB-3	Feb.–Mar. 2009	$PM_{2.5}$	2.8 (± 1.1)	31 (± 12)	20 (± 8)	11 (± 4)
URB-1	Oct. 2006–Feb. 2007	$PM_{2.5}$	2.0 (± 0.8)	29 (± 11)	29 (± 11)	
URB-1	Dec. 2008–Mar. 2009	PM_1	2.3 (± 0.9)	24 (± 9)	24 (± 9)	
URB-2	Oct.–Dec. 2008	$PM_{2.5}$	2.1 (± 0.8)	24 (± 9)	24 (± 9)	
URB-2	Feb.–Mar. 2009	$PM_{2.5}$	2.1 (± 0.8)	18 (± 7)	18 (± 7)	
URB-3	Nov.–Dec. 2008	$PM_{2.5}$	2.4 (± 0.9)	26 (± 10)	26 (± 10)	

PMF that uses a wide range of chemical values (e.g. Saarikoski *et al.* 2008a). In the PMF analysis presented by Saarikoski *et al.* (2008a), the source apportionment was made for OC in fine particles in Helsinki showing a 41% contribution of wood combustion to OC (and hence for POM, as well) in winter. With the estimation that approximately 50% of fine particles consisted of POM, the contribution of wood combustion to fine particles in that study was 20.5%. That value was relatively close to the contributions estimated for the urban sites in the present study (18%–29%; Table 5). Therefore, it could be concluded that the semi-quantitative estimations were at a fairly correct level.

Proportions of the MAs isomers

Different plant species contain monosaccharides in different proportions (e.g. Pettersen 1984, McKendry 2002; *see* also Table 6), and they may produce MAs isomers in the same proportions when the plant species are burnt. In order to study the production of the MAs isomers from different wood species that are typically burned in Finnish households, we conducted wood combustion experiments in a laboratory. In those experiments, particulate emissions of two wood materials were measured. The proportions of the MAs isomers from birch-log combustion experiments (average emission factor of MAs 7.9 mg kg^{-1} fuel and 3.3 mg kg^{-1} fuel from a sauna stove and from a masonry heater, respectively; Table 6) were close to the proportions of respective monosaccharides in birch wood (glucose 95%, mannose 4%, galactose 1%; Pettersen 1984). Emissions of MAs from combustion of coniferous pellets (mainly of pine) in a modern pellet boiler were extremely low (average emission factor of MAs 0.025 mg kg^{-1} fuel), which gave a large uncertainty to the interpretation of the results. However, the proportions of MAs from coniferous pellets differed from that of birch logs (Table 6) and was roughly comparable to the proportions of the three monosaccharides in pine (77% of glucose, 18% of mannose and 5% of galactose; Pettersen 1984). Based on the comparison of the proportions of the original monosaccharides in plant species and the produced MAs, it was concluded that the pro-

portions of MAs can be utilised to estimate what kind of biomass material was burnt.

In real life, a single species is rarely burnt and therefore the MAs in ambient PM are typically from mixtures of several plant species. In the present study, the proportions of the MAs in ambient air was studied from all the samples collected during 2005–2009 (Table 7). There seemed to be a difference in the proportions when the analysis method was changed. The proportions of mannosan and, especially, galactosan in the samples from January 2005 to February 2007 analysed with LC-MS were higher than in samples analysed with a validated HPAEC-MS method (Saarnio *et al.* 2010b). The latter proportions were relatively close to the proportions that was crudely estimated based on the firewood usage in Finland [86%/11%/3% for levoglucosan/mannosan/galactosan; Saarnio *et al.* (2010b)]. That estimation did not include the use of waste wood (mostly coniferous species from construction sites) as firewood. However, based on the similarity of this crude estimation and the measured proportions of MAs in ambient air, it can be assumed that the monosaccharides in a plant species produce MAs in the same proportions when the plant is burnt. The proportions of MAs in the HMA air somewhat differed from those reported for the urban background and residential area in Norway (Yttri *et al.* 2005) (Table 7). There, the contribution of galactosan to MAs was minimal, obviously suggesting that the composition of burnt wood species in Norway was different to that in the HMA and the surrounding regions.

During the cold season 2008–2009, the proportions of the MAs isomers were fairly similar at all sites in the HMA (Table 7). Therefore, it could be assumed that the composition of the combusted firewood was reasonably uniform in southern Finland. However, by comparing the seasonal variation in the proportions of MAs at URB-1 and SUB-1, the greater change in proportions was noticed at the urban site. Even though in Finland firewood is used throughout the year (e.g. sauna stoves also in summertime), the transported smokes from open land fires in eastern Europe occasionally dominate during the warmer half of the year (Niemi *et al.* 2009). The influence of transported PM from trans-

Table 6. Average proportions of MAs in combustion experiments.

Material	Burner type	Conditions	Sample type	Levoglucosan (%)	Mannosan (%)	Galactosan (%)	References
Coniferous pellet (mainly of pine)	Pellet boiler	Efficient combustion	PM_1	82.7	13.5	3.7	This study
Birch log	Conventional masonry heater	Conventional batch combustion	PM_1	92.0	5.7	2.4	This study
Birch log	Sauna stove	Inefficient batch combustion	PM_1	95.0	3.0	2.0	This study
Softwood	Fireplace		$PM_{2.5}$	79.1	17.4	3.5	Fine *et al.* (2004)
Pine	Open chamber		$PM_{0.05-10}$	68.2	13.6	18.2	Iinuma *et al.* (2007)
Ponderosa pine	Chamber	Flaming	$PM_{2.5}$	70.2	27.5	2.3	Engling *et al.* (2006)
Ponderosa pine	Chamber	Smouldering	$PM_{2.5}$	73.7	23.9	2.4	Engling *et al.* (2006)
Ponderosa pine needles	Stack		$PM_{2.5}$	73.2	19.7	7.2	Engling *et al.* (2006)
Pine with needles	Open chamber		$PM_{0.05-10}$	75.2	13.3	11.5	Iinuma *et al.* (2007)
Spruce with needles	Open chamber		$PM_{0.05-10}$	78.0	5.5	16.5	Iinuma *et al.* (2007)
Spruce	Tiled stove		PM_{10}	73.5	20.6	5.8	Schmidl *et al.* (2008b)
Oak	Tiled stove		PM_{10}	90.8	6.3	2.9	Schmidl *et al.* (2008b)
Oak	Chamber	Flaming	$PM_{2.5}$	93.4	3.4	3.3	Engling *et al.* (2006)
Oak	Chamber	Smouldering	$PM_{2.5}$	81.9	2.5	15.6	Engling *et al.* (2006)
Leaves	Open air		PM_{10}	50.6	9.3	40.1	Schmidl *et al.* (2008a)
German peat	Open chamber		$PM_{0.05-10}$	77.7	11.3	11.0	Iinuma *et al.* (2007)

Table 7. Average proportions of MAs in ambient air samples.

Site	Description	Sampling period	Sample type	Levoglucosan (%)	Mannosan (%)	Galactosan (%)	References
SUB-1	Residential	Cold season (Jan.–Mar., Oct–Dec. 2005)	PM_{10}	79.1	11.9	9.0	This study
SUB-1	Residential	Warm season (Apr.–Sep. 2005)	PM_{10}	75.2	16.0	8.8	This study
SUB-2	Residential	Oct.–Dec. 2008	PM_{10}	82.0	12.0	6.0	This study
SUB-3	Residential	Feb.–Mar. 2009	PM_{10}	83.9	10.6	5.5	This study
URB-1	Urban background	Cold season (Feb.–Mar. 2006, Oct. 2006–Feb. 2007)	PM_1	79.0	12.2	8.8	Saarikoski et al. (2008a); this study[b]
URB-1	Urban background	Warm season (Apr.–Oct. 2006)[a]	PM_1	75.8	12.1	12.1	Saarikoski et al. (2008a); this study[b]
URB-1	Wildfire smokes	Apr.–May 2006	PM_1	70.9	11.5	17.6	Saarikoski et al. (2007); this study[b]
URB-1	Wildfire smokes	Aug. 2006	PM_1	66.8	12.4	20.9	Saarnio et al. (2010a); this study[b]
URB-1	Urban background	Cold season (Dec. 2008–Mar. 2009)	PM_1	85.8	9.7	4.6	Saarnio et al. (2010b)
URB-2	Urban background	Oct.–Dec. 2008	PM_{10}	82.4	11.4	6.1	This study
URB-2	Urban background	Feb.–Mar. 2009	PM_{10}	82.4	12.1	5.5	This study
URB-3	Urban background	Nov.–Dec. 2008	PM_{10}	82.5	11.2	6.3	This study
Oslo, Norway	Urban background	Nov.–Dec. 2001	PM_{10}	79.0	19.5	1.4	Yttri et al. (2005)
Elverum, Norway	Residential	Jan.–Mar. 2002	PM_{10}	77.5	22.1	0.4	Yttri et al. (2005)
Upper Midwest, USA	Residential burning	Winter 2004–2005	$PM_{2.5}$	86.2–91.0	6.2–9.7	2.2–4.6	Sullivan et al. (2011a, 2011b)
Upper Midwest, USA	Wildfire and prescribed burning	Summer 2004	$PM_{2.5}$	83.4–92.2	4.8–11.4	2.9–6.8	Sullivan et al. (2011a, 2011b)
ME, USA	Forest fire smokes	Jun.–Jul. 2002	TSP	83.4	13.8	2.8	Medeiros et al. (2006)
MT, USA	Wildfire smokes	Summer	$PM_{2.5}$	78.3	15.0	6.7	Ward et al. (2006)
Siberia, Russia	Forest fires	Oct. 2004	$PM_{2.5}$	69.9	11.1	19.3	Kuokka et al. (2007)

[a] Season without the major episodes of long-range transported wildfire smokes.
[b] Proportions of MAs not published earlier.

ported smokes could be seen more distinctively at URB-1 that at SUB-1 where the transported smokes were mixed with the local wood combustion emissions.

The proportions of MAs altered having the highest levoglucosan/galactosan ratio in the cold season and lowest in the summer. The lowest levoglucosan/galactosan ratio was measured during the long-range transported open land fire smokes in April–May and August 2006 (Table 7). This can be assumed to be caused partly by burning of foliar material in the fires: dry and agricultural biomass like straw and grass from the previous season in the episode in April–May 2006, and bog peat and fresh forest containing plant material of leaves and branches as well as woody material and undergrowth in August 2006. Schmidl *et al*. (2008a) showed that high concentrations of galactosan exist when foliar material burns (Table 6). Comparable proportions of MAs to that recorded during the transported open land fire smokes in Helsinki in 2006 was measured, e.g. from forest fires in Siberia (Kuokka *et al*. 2007) whereas in forest fires in USA (Medeiros *et al*. 2006, Ward *et al*. 2006) the proportions of MAs was closer to that from the firewood usage in Finland (Table 7). Sullivan *et al*. (2011a, 2011b) did not find any major differences in MAs proportions between the summer (wildfires and prescribed burning) and winter (residential burning) in the Upper Midwest (USA). However, based on the difference in the proportions of MAs in the air samples of the present study, the open land fire smokes from Russia and other eastern European countries were separated from the local wood combustion emissions in Finland.

Summary and conclusions

The concentrations of MAs and PM 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. The concentration of MAs showed a clear seasonal variation with the maximum in winter and the minimum in summer, excluding open land fire smoke episodes. The highest average concentrations of MAs appeared

especially at suburban sites on Wednesdays and Saturdays when sauna stoves are traditionally heated in Finland. The concentration of MAs also showed clear spatial variation in the area; the measured concentrations were typically higher at the suburban sites than at the urban sites.

The concentration of MAs was used to estimate semi-quantitatively the contribution of wood combustion to fine particles. A multiplying factor of 24.4 ± 9.2 (mean ± uncertainty Δ) was derived for MAs from the previous studies and the results showed a fairly good agreement at the urban sites with the previously published contributions of wood combustion emissions to fine particle concentrations. However, the factor of 24.4 seemed to be too high for fresh emissions at a suburban site. The average cold season (October–March) 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. At the urban sites, the wood combustion particles were estimated to be caused by regional distribution only, whereas at suburban sites both local wood combustion and regionally distributed emissions from wood combustion contributed to the PM concentration. The contribution of regionally-distributed fine particles from wood combustion was notable over the whole area. The contribution of local wood combustion differed between the suburban sites that might have been due to different wood-combustion practices in different places as well as the location of the sampling site in the suburbs. The local wood-combustion emissions were estimated to occasionally cause an addition of even 10–15 μg m^{-3} to the daily mean concentration of PM$_{2.5}$ while, depending on the site, the average the addition to the daily concentration of PM$_{2.5}$ during the cold season was about 1–3 μg m^{-3}.

The study included wood combustion experiments in a laboratory that supported the interpretation of the ambient air measurements. The combustion experiments showed that by comparing the proportions of the three MAs isomers, the transported open land fire smokes can be separated in the HMA from the local wood combustion, which facilitates the source-specific estimations. The experiments with a modern pellet boiler indicated that MAs had very low emission factors

and, therefore, MAs are not as usable as source-specific tracers for emissions from efficient biomass combustion like they are for emissions from traditional wood combustion appliances.

In Finland, the use of renewable energy, such as wood combustion is encouraged to increase. 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 introduce 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 housing areas, and the use of traditional combustion appliances decreases, the PM emission could fall significantly. However, pellet boilers are expensive and pellet storage requires a lot of space. In the near future, fireplaces and sauna stoves will probably remain as the main methods for supplementary heating and pleasure in the HMA. Therefore, there is a clear need to give more information to residents on low-emission combustion technique (e.g. burning methods and habits, use of dry and clean wood). Also financial support is needed in densely populated areas, in order to replace combustion appliances that produce high emissions. In future, changes in combustion appliances, technique and material may alter also the amount and the composition of emissions from wood burning; for example MAs are produced to a lesser extent in efficient combustion, which poses new challenges to source-apportionment studies and to the long-term trend monitoring of wood-burning aerosols in ambient air.

References

Anttila P. & Salmi T. 2006. Characterizing spatial and temporal patterns of urban PM_{10} using six years of Finnish monitoring data. *Boreal Env. Res.* 11: 467–479.

Bari M.A., Baumbach G., Kuch B. & Scheffknecht G. 2010. Temporal variation and impact of wood smoke pollution on a residential area in southern Germany. *Atmos. Environ.* 44: 3823–3832.

Bølling A.K., Pagels J., Yttri K.E., Barregard L., Sallsten G., Schwarze P.E. & Boman C. 2009. Health effects of residential wood smoke particles: the importance of combustion conditions and physicochemical particle properties. *Particle Fibre Toxicol.* 6: 29.

Boman B.C., Forsberg A.B. & Järvholm B.G. 2003. Adverse health effects from ambient air pollution in relation to residential wood combustion in modern society. *Scand. J. Work Environ. Health* 29: 251–260.

Caseiro A., Bauer H., Schmidl C., Pio C.A. & Puxbaum H. 2009. Wood burning impact on PM_{10} in three Austrian regions. *Atmos. Environ.* 43: 2186–2195.

Dye C. & 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.

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. & 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. & 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.

Fraser M.P. & 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. & 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.

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

Glasius M., Ketzel M., Wåhlin P., Bossi R., Stubkjær J., Hertel O. & Palmgren F. 2008. Characterization of particles from residential wood combustion and modelling of spatial variation in a low-strength emission area. *Atmos. Environ.* 42: 8686–8697.

Hedberg E., Johansson C., Johansson L., Swietlicki E. & 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.

Hennigan C.J., Sullivan A.P., Collett J.L.Jr. & Robinson A.L. 2010. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. *Geophys. Res. Lett.* 37, L09806, doi: 10.1029/2010GL043088.

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

694–699.

HSY 2010a. *Air quality in the Helsinki Metropolitan Area in 2009*. Helsinki Region Environmental Services Authority (HSY) Publications 2/2010. [In Finnish with English abstract].

HSY 2010b. *Helsinki Metropolitan Area climate report — emission trends in 2009*. Helsinki Region Environmental Services Authority (HSY) Publications 7/2010.

Iinuma Y., Brüggemann E., Gnauk T., Müller K., Andreae M.O., Helas G., Parmar R. & 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, doi: 10.1029/2006JD007120.

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

Karvosenoja N., Tainio M., Kupiainen K., Tuomisto J.T., Kukkonen J. & Johansson M. 2008. Evaluation of the emissions and uncertainties of $PM_{2.5}$ originated from vehicular traffic and domestic wood combustion in Finland. *Boreal Env. Res.* 13: 465–474.

Krecl P., Ström J. & Johansson C. 2007. Carbon content of atmospheric aerosols in a residential area during the wood combustion season in Sweden. *Atmos. Environ.* 41: 6974–6985.

Krecl P., Johansson C. & Ström J. 2010. Spatiotemporal variability of light-absorbing carbon concentration in a residential area impacted by woodsmoke. *J. Air Waste Manage. Assoc.* 60: 356–368.

Kuokka S., Teinilä K., Saarnio K., Aurela M., Sillanpää M., Hillamo R., Kerminen V.-M., Pyy K., Vartiainen E., Kulmala M., Skorokhod A.I., Elansky N.F. & 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.

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. & Jokiniemi J. 2011. Physicochemical characterization of fine particles from small-scale wood combustion. *Atmos. Environ.* 45: 7635–7643.

Lee T., Sullivan A.P., Mack L., Jimenez J.L., Kreidenweis S.M., Onasch T.B., Worsnop D.R., Malm W., Wold C.E., Hao W.M. & Collett J.L.Jr. 2010. Chemical smoke marker emissions during flaming and smoldering phases of laboratory open burning of wildland fuels. *Aerosol Sci. Technol.* 44: 9, i–v.

May B., Wagenbach D., Hammer S., Steier P., Puxbaum H. & Pio C. 2009. The anthropogenic influence on carbonaceous aerosol in the European background. *Tellus* 61B: 464–472.

McKendry P. 2002. Energy production from biomass (part 1): overview of biomass. *Biores. Technol.* 83: 37–46.

Medeiros P.M., Conte M.H., Weber J.C. & Simoneit B.R.T. 2006. Sugars as source indicators of biogenic organic carbon in aerosols collected above the Howland Experimental Forest, Maine. *Atmos. Environ.* 40: 1694–1705.

METLA 2010. *Finnish Statistical Yearbook of Forestry 2010*. Official Statistics of Finland. [In Finnish with English summary].

Mochida M., Kawamura K., Fu P. & Takemura T. 2010. Seasonal variation of levoglucosan over the western North Pacific and its assessment as a biomass-burning tracer. *Atmos. Environ.* 44: 3511–3418.

Naeher L.P., Brauer M., Lipsett M., Zelikoff J.T., Simpson C.D., Koenig J.Q. & Smith K.R. 2007. Woodsmoke health effects: a review. *Inhal. Toxicol.* 19: 67–106.

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

Pettersen R.C. 1984. The chemical composition of wood. *Adv. Chem. Ser.* 207: 57–126.

Puxbaum H., Caseiro A., Sánchez-Ochoa A., Kasper-Giebl A., Claeys M., Gelencsér A., Legrand M., Preunkert S. & 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, doi: 10.1029/2006JD008114.

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

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

Saarikoski S., Sillanpää M., Sofiev M., Timonen H., Saarnio K., Teinilä K., Karppinen A., Kukkonen J. & 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.

Saarnio K., Teinilä K., Aurela M., Timonen H. & Hillamo R. 2010b. 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.

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

Schmidl C., Bauer H., Dattler A., Hitzenberger R., Weissenboeck G., Marr I.L. & Puxbaum H. 2008a. Chemical characterisation of particle emissions from burning leaves. *Atmos. Environ.* 42: 9070–9079.

Schmidl C., Marr I.L., Caseiro A., Kotianová P., Berner A., Bauer H., Kasper-Giebl A. & Puxbaum H. 2008b.

Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmos. Environ.* 42: 126–141.

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

Schreuder A.B., Larson T.V., Sheppard L. & Claiborn C.S. 2006. Ambient woodsmoke and associated respiratory emergency department visits in Spokane, Washington. *Int. J. Occup. Environ. Health* 12: 147–153.

Shafizadeh F. 1984. The chemistry of pyrolysis and combustion. *Adv. Chem. Ser.* 207: 489–529.

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

Stohl A. & Wotawa G. 1995. A method for computing single trajectories representing boundary layer transport. *Atmos. Environ.* 29: 3235–3239.

Sullivan A.P., Frank N., Onstad G., Simpson C.D. & Collett J.L.Jr. 2011a. Application of high-performance anion-exchange chromatography–pulsed amperometric detection for measuring carbohydrates in routine daily filter samples collected by a national network: 1. Determination of the impact of biomass burning in the upper Midwest. *J. Geophys. Res.* 116, D08302, doi: 10.1029/2010JD014166.

Sullivan A.P., Frank N., Kenski D.M. & Collett J.L.Jr. 2011b. Application of high-performance anion-exchange chromatography–pulsed amperometric detection for measuring carbohydrates in routine daily filter samples collected by a national network: 2. Examination of sugar alcohols/polyols, sugars, and anhydrosugars in the upper Midwest. *J. Geophys. Res.* 116, D08303, doi: 10.1029/2010JD014169.

Szidat S., Ruff M., Perron N., Synal H.-A., Hallquist M., Shannigrahi A.S., Yttri K.E., Dye C. & Simpson D. 2009. Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden. *Atmos. Chem. Phys.* 9: 1521–1535.

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. & Jokiniemi J. 2008. Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. *Atmos. Environ.* 42: 7862–7873.

Turpin B.J. & 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.

Viidanoja J., Sillanpää M., Laakia J., Kerminen V.-M., Hillamo R., Aarnio P. & 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.

Waldén J., Hillamo R., Aurela M., Mäkelä T. & Laurila S. 2010. *Demonstration of the equivalence of $PM_{2.5}$ and PM_{10} measurement methods in Helsinki 2007–2008.* Studies 2010/3, Finnish Meteorological Institute, Helsinki.

Ward T.J., Hamilton R.F.Jr., Dixon R.W., Paulsen M. & Simpson C.D. 2006. Characterisation and evaluation of smoke tracers in PM: results from the 2003 Montana wildfire season. *Atmos. Environ.* 40: 7005–7017.

WHO 2006. *Air quality guidelines. Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide.* WHO Regional Office for Europe, Copenhagen.

Yttri K.E., Dye C., Slørdal L.H. & 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., Dye C., Braathen O.A., Simpson D. & Steinnes E. 2009. Carbonaceous aerosols in Norwegian urban areas. *Atmos. Chem. Phys.* 9: 2007–2020.

YTV 2009. *Air quality in the Helsinki Metropolitan Area in 2008.* Helsinki Metropolitan Area Council (YTV) publications 15/2009. [In Finnish with English abstract].