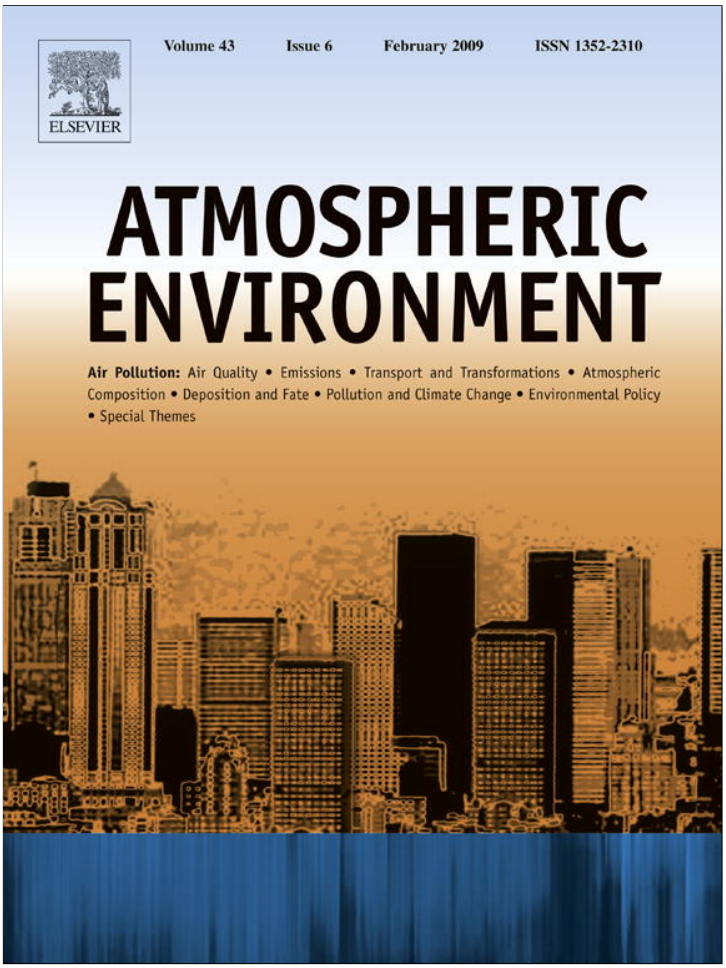

Atmospheric Environment 43 (2009) 1255–1264

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Long-range transport episodes of fine particles in southern Finland during 1999–2007

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ARTICLE INFO

Article history:
Received 25 February 2008
Received in revised form
19 November 2008
Accepted 20 November 2008

Keywords:
Long-range transport
Fine particles
Open biomass burning
Chemical tracers
Satellite remote sensing

ABSTRACT

The frequency, strength and sources of long-range transport (LRT) episodes of fine particles ($PM_{2.5}$) were studied in southern Finland using air quality monitoring results, backward air mass trajectories, remote sensing of fire hot spots, transport and dispersion modelling of smoke and chemical analysis of particle samples (black carbon, monosaccharide anhydrides, oxalate, succinate, malonate, SO_4^{2-}, NO_3^-, K^+ and NH_4^+). At an urban background site in Helsinki, the daily WHO guideline value (24-h $PM_{2.5}$ mean 25 μg m^{-3}) was exceeded during 1–7 LRT episodes per year in 1999–2007. The 24-h mean maximum concentrations varied between 25 and 49 μg m^{-3} during the episodes, which was 3–6 times higher than the local mean concentration (8.7 μg m^{-3}) in 1999–2007. The highest particle concentrations (max. 1-h mean 163 μg m^{-3}) and the longest episodes (max. 9 days) were mainly caused by the emissions from open biomass burning, especially during springs and late-summers in 2002 and 2006. During the period 2001–2007, the satellite remote sensing of active fire hot spots and transport and dispersion modelling of smoke indicated that approximately half of the episodes were caused partly by the emissions from wildfires and/or agricultural waste burning in fields in Eastern Europe, especially in Russia, Belarus and Ukraine. Other episodes were mainly caused by the LRT of ordinary anthropogenic pollutants, e.g. from energy production, traffic, industry and wood combustion. During those 'other episodes', air masses also arrived from Eastern Europe, including Poland. The highest concentrations of biomass-burning tracers, such as monosaccharide anhydrides (levoglucosan + mannosan + galactosan) and K^+, were observed during open biomass-burning episodes, but quite high values were also measured during some winter episodes due to wood combustion emissions. Our results indicate that open biomass burning in Eastern Europe causes high fine particle concentration peaks in large areas of Europe almost every year.

1. Introduction

The composition and mass concentrations of fine particles ($PM_{2.5}$) are substantially affected by long-range transport (LRT), especially in areas with low local emissions (EMEP, 2006; WHO, 2006). LRT can cause high $PM_{2.5}$ concentration peaks when air masses arrive during suitable meteorological conditions (no rain and weak mixing of air masses) from regions with high emissions of particles and/or their precursor gases. During LRT episodes, particles can cause detrimental health effects far from their emission sources, including rural background areas (WHO, 2006).

In Finland, anthropogenic emissions of fine particles and their precursor gases are low compared with the more polluted regions of Europe (EMEP, 2006). In general, atmospheric $PM_{2.5}$ concentrations are also low in Finland. For instance, the annual mean $PM_{2.5}$ concentrations are ~10–12 μg m^{-3} at urban traffic sites of Helsinki and only ~7–8 μg m^{-3} at a rural background site (Luukki) near Helsinki (Laakso et al., 2003; Myllynen et al., 2007). The new directive on ambient air quality and cleaner air for Europe (Directive, 2008/50/EC) sets annual limit value for $PM_{2.5}$ (25 μg m^{-3} to be met before year

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doi:10.1016/j.atmosenv.2008.11.022

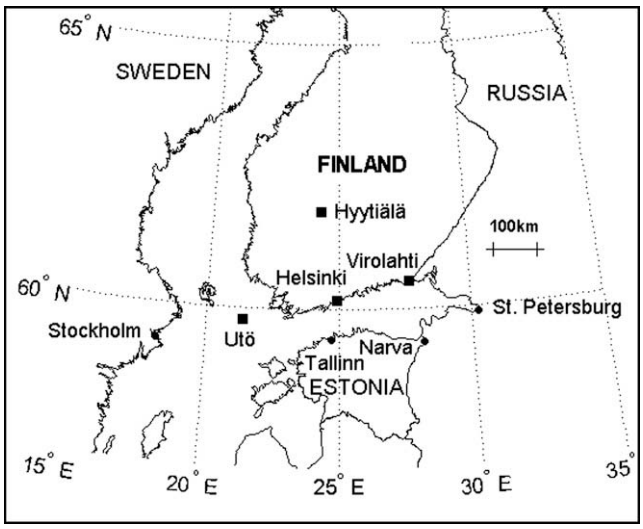

Fig. 1. Locations of the measurement and sampling sites (depicted with squares) in Finland.

2015) but the value is very high compared with the Finnish concentration levels. However, the daily particle concentrations in Finland vary substantially due to LRT. Even in the urban areas of Helsinki, 50–75% of the $PM_{2.5}$ mass originates from LRT (Karppinen et al., 2004; Vallius et al., 2003). During the strongest LRT pollution episodes, the 24-h mean particle mass concentrations multiply compared with the annual mean levels, and the WHO guideline value (25 μg m^{-3}) for 24-h $PM_{2.5}$ mean concentrations is exceeded over large areas of southern Finland (Niemi et al., 2004, 2005; Niemi, 2007; Saarikoski et al., 2007; Anttila et al., 2008).

The emission sources of fine particles during LRT episodes have been studied in detail during few LRT episodes in Finland. On 19–20 February 1998, an LRT episode peak was caused by sea salt from the Atlantic Ocean and by anthropogenic emissions from Western Europe (Tervahattu et al., 2002). During the years 2002, 2004 and 2006, emissions from wildfires and agricultural waste burning in fields together with other anthropogenic emissions in Eastern Europe caused several LRT episodes of fine particles in large areas over Finland (Niemi et al., 2004,2005,2006b; Saarikoski et al., 2007; Saarnio et al., 2006; Anttila et al., 2008). Although the above-mentioned episodes have been studied in detail, the long-term comprehensive view on LRT episodes has been missing so far in Finland.

In this work, the frequency, duration and strength of LRT episodes of fine particles in southern Finland were investigated in 1999–2007, using long-term air quality monitoring data. The potential source areas of particles and the presence of open biomass burning as a particle source were estimated during episodes in 2001–2007, based on backward air mass trajectories, satellite remote sensing of active fire hot spots and transport modelling of smoke. Several chemical components were analysed for source characterisation during the episodes in 2001–2005. To our knowledge, this is the first study that illustrates the long-term perspective on LRT fire smoke episodes in northern Europe.

2. Materials and methods

Aerosol measurements were performed at five background stations in Finland (Fig. 1). Kallio urban background station and Luukki rural station (~20 km northwest from Kallio) are located in Helsinki metropolitan area (population 1 million inhabitants and surface area 745 km^2). Hyytiälä, Virolahti and Utö stations are located in very sparsely populated rural areas. The measurements of each site are summarised in Table 1 and described in detail in next sections. The long-term monitoring results ($PM_{2.5}$ mass and inorganic ion concentrations) were used to detect LRT episodes and to describe their frequency, strength and duration. The chemical compositions of particle samples from Hyytiälä station were analysed with several methods for source characterisation of particles. Furthermore, trajectories, remote sensing of fire areas and transport modelling of smoke were used for sources characterisation.

2.1. Long-term monitoring of particle mass and ion concentrations

The longest continuous data series (1999–2007) of hourly $PM_{2.5}$ mass concentrations in Finland has been measured at Kallio urban background station in Helsinki. Long-term PM data sets are also available from Luukki regional background site; hourly PM_{10} concentrations were measured in 1999–2003 and $PM_{2.5}$ concentrations in 2004–2007. Both stations belong to the municipal air quality monitoring network maintained by the Helsinki Metropolitan Area Council. At rural background stations in Virolahti and Utö, hourly $PM_{2.5}$ concentrations were measured by the Finnish Meteorological Institute in July 2003–2007 and October 2003–2007, respectively. At all above-mentioned monitoring sites, particle mass concentrations were measured using β-ray attenuation monitors (Eberline FH 62 I-R, Eberline Instruments, GmbH, Germany) with PM_{10}- or $PM_{2.5}$-inlets.

The particle mass concentrations in different size fractions were measured with gravimetric method at Hyytiälä rural station (SMEAR II) in 1999–2007. The measurements were performed by the Department of Physical Sciences of the University of Helsinki. The particle samples were collected using a Dekati PM_{10} cascade impactor and with a backup filter. The sampling time was 2–3 days and the sample change time 6 am (UTC). The cut-off diameters (D_{50}) of the impactor stages were 10 and 2.5 μm between spring 1999 and autumn 2000. Since autumn 2000, third impaction stage with cut-off diameter of 1 μm was also used in the impactor. The collection substrates on impaction stages were polycarbonate membranes (Nuclepore 800 203, diameter 25 mm) with no holes.

Table 1
Summary of measurements at different background sites in Finland.

Analysed components and analysis method	Time resolution	Helsinki Kallio	Helsinki Luukki	Hyytiälä	Virolahti	Utö
		Urban	Rural	Rural	Rural	Rural
Long-term monitoring:						
$PM_{2.5}$ with β-ray attenuation analysis	1 h	1999–2007	1999–2007[a]		July 2003–2007	October 2003–2007
$PM_{2.5}$ and PM_1 with gravimetric analysis	2–3 days			1999–2007		
Selected ions with IC analysis[b]	1 day				1999–2005	1999–2005
PM_1 episode samples ($N = 24$):						
Several chemical components with SSR,IC and LC/MS analysis[c]	2–3 days			2001–2005		

[a] $PM_{2.5}$ was measured in 2004–2007 and PM_{10} in 1999–2003.
[b] SO_4^{2-}, (NO_3^-+HNO_3(g)) and (NH_4^+ + NH_3(g)) from TSP size class.
[c] Black carbon, sum of three monosaccharide anhydrides (∑MA = levoglucosan + galactosan + mannosan) and selected ions (K^+, NH_4^+, NO_3^-, SO_4^{2-}, oxalate, succinate and malonate).

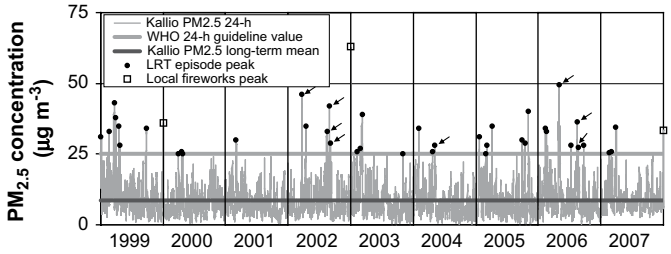

Fig. 2. 24-h moving average $PM_{2.5}$ concentrations at Kallio in Helsinki during 1999–2007. LRT episode peaks are depicted with black dots and local fireworks peaks with squares. Arrows depict eight episodes for which the source identification has been performed in previous studies (Niemi et al., 2004, 2005, 2006b; Saarikoski et al., 2007; Saarnio et al., 2006; Anttila et al., 2008).

The backup filter material was made of Teflon (Gelman Teflo R2P J047, diameter 47 mm) with 2 μm diameter pore size. The smearing of substrates to prevent particles from bouncing back from the substrates, and the gravimetric analysis are described in detail by Laakso et al. (2003).

The daily concentrations of sulphate (SO_4^{2-}), total nitrate ($NO_3^- + HNO_3(g)$) and total ammonium ($NH_4^+ + NH_3(g)$) are measured by the Finnish Meteorological Institute at several rural background stations in Finland. The results from Virolahti and Utö stations were used during 1999–2005. The total suspended particle (TSP) samples were collected using open-faced 2-stage filter packs (NILU Products AS) with cellulose filters (Whatman 40, diameter 47 mm). The sample change time was 6 am (UTC). The concentrations of above-mentioned chemical components were analysed with ion chromatographs (IC; Dionex DX-500 and Waters). The details of the sampling and IC methods are described by Paatero et al. (2001).

2.2. Fire smoke transport and trajectories

For investigation of fire areas, daily active fire hot spot detections were used from Web Fire Mapper (http://maps.geog.umd.edu), which is part of the MODerate-resolution Imaging Spectroradiometer (MODIS) Rapid Response System (Giglio, 2007). MODIS instruments are onboard Terra and Aqua satellites (Giglio, 2007). The Navy Aerosol Analysis and Prediction System (NAAPS) model results were used to determine the distribution of smoke aerosols from fires (model description and results available from the web pages of the Naval Research Laboratory, Monterey, CA, USA; http://www.nrlmry.navy.mil/aerosol/). The NAAPS surface smoke concentration maps are available four times per day (UTC 0, 6, 12 and 18). NAAPS uses surface smoke fluxes provided by the FLAMBE project (Reid et al., 2004) based on real-time MODIS fire counts to define the time and spatial dependence of the smoke injection. The method has proven useful in previous studies of long-range transport of smoke (e.g. Honrath et al., 2004).

The potential source areas of particles during the LRT episodes were investigated using backward air mass trajectories. Back trajectories were produced using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003) with the Final Analyses (FNL; years 1999–2006) and the Global Data Assimilation System (GDAS; year 2007) meteorological databases at the NOAA Air Resources Laboratory's web server (Rolph, 2003).

2.3. Episode samples and their chemical analyses

The particle samples for detailed chemical analyses were collected at Hyytiälä station using a Dekati PM_{10} cascade impactor and with a backup filter (see Section 2.1). The same samples were first used for gravimetric mass concentration measurements. After weighting, they were stored in freezer. PM_1 backup Teflon filter samples ($N = 24$) of selected LRT episodes in 2001–2005 were used for chemical analysis. The concentrations of the following chemical components were analysed: black carbon (BC), sum of three monosaccharide anhydrides ($\sum$MA = levoglucosan + galactosan + mannosan) and selected ions (K^+, NH_4^+, NO_3^-, SO_4^{2-}, oxalate, succinate and malonate).

BC was analysed from the Teflon filters by using a smoke stain reflectometer (SSR, Model M34D, Diffusion Systems, London, UK). The average reflectance of three measurements was converted into an adsorption coefficient (a) by following the guidance in 'International Standard ISO 9835: Ambient air – determination of a black smoke index' (1993). Finally, the adsorption coefficient was converted into black carbon (BC) by the linear calibration equation (BC = 1.8271a–0.0579, $R^2 = 0.7156$) obtained from a correlation analysis between five filter blackness measurements and corresponding aethalometer readings (Hansen et al., 1984). The uncertainty is in the order of 25%.

For $\sum$MA and ion analyses, one-third of the filter samples (diameter 47 mm) was extracted with deionised water (Millipore Alpha-Q) in an ultrasonic bath for 30 min. From the extract, $\sum$MA was analysed with a liquid chromatograph mass spectrometer (LC/MS; Agilent 1100 Series, Trap SL, Agilent Technologies, USA) and the ions were determined with two ICs (Dionex 500). Seven ions (K^+, NH_4^+, NO_3^-, SO_4^{2-}, oxalate, succinate and malonate) were obtained from the PM_1 samples, whereas other ions usually analysed by the IC (methanesulfonate, Cl^-, Na^+, Mg^{2+} and Ca^{2+}) could not be determined, either because of the high blanks in filters or because the concentrations were below their detection limits. The LC/MS and IC methods are described in detail in Saarikoski et al. (2007).

3. Results and discussion

The results and discussion is divided in to three sub-sections. First, the frequency and strength of LRT episodes are described. Then the air mass trajectories and fire smoke transport results are shown. Finally, the chemical composition of particles is presented to characterise aerosol sources and to verify smoke transport results.

3.1. Frequency and strength of LRT episodes in 1999–2007

During LRT episodes, the particle mass concentrations rise simultaneously to extraordinarily high levels at every monitoring station in Helsinki metropolitan area, including the urban background station in Kallio and rural background station in Luukki. In this work, the following concentration criterion was defined for the Kallio monitoring site as episodic (unusually) high concentration level: the 24-h $PM_{2.5}$ moving average concentration exceeded 25 $\mu g\,m^{-3}$, which is approximately three times higher than the long-term mean concentration (8.7 $\mu g\ m^{-3}$) during 1999–2007 (Fig. 2). At Luukki, the $PM_{2.5}$ concentration was only measured in 2004–2006 and PM_{10} in 1999–2003. Therefore, the concentration criteria for LRT episodes were defined separately for both periods; 24-h moving average $PM_{10} > 25\ \mu g\ m^{-3}$ during the 1999–2003 episodes and $PM_{2.5} > 20\ \mu g\ m^{-3}$ during the 2004–2006 episodes.

The air quality monitoring results from the Utö, Virolahti and Hyytiälä rural stations were used to double-check that the simultaneous high $PM_{2.5}$ peaks at Kallio and Luukki were mainly caused by LRT. During the LRT episodes, there had to be a clear $PM_{2.5}$ concentration peak and/or ion sum peak (sum concentration of sulphate, total nitrate and total ammonium) at Utö, Virolahti and/or Hyytiälä. The ion sum was used as a proxy variable for long-range transported aerosols (Karppinen et al., 2004) at Utö and Virolahti during 1999–2003 because $PM_{2.5}$ measurements were not started until summer 2003. The results from Luukki, Hyytiälä, Virolahti and Utö indicated (simultaneous $PM_{2.5}$ concentrations at Kallio,

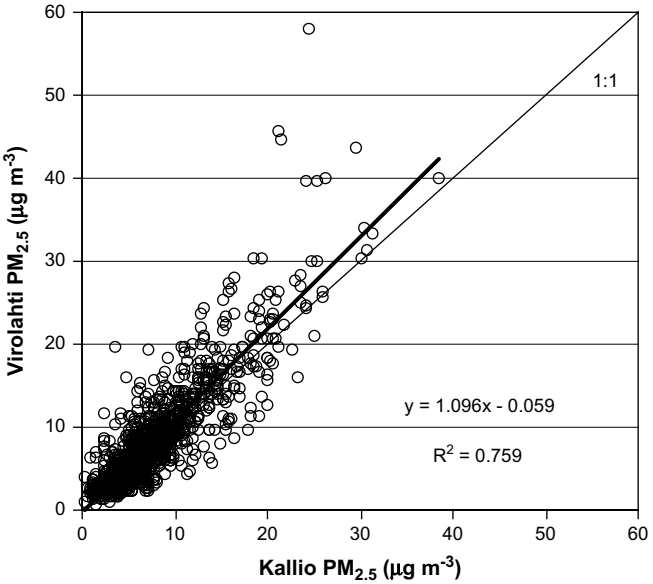

Fig. 3. Daily $PM_{2.5}$ concentrations at Kallio and Virolahti between 9 July 2003 and 31 December 2006.

Virolahti and Utö during 2004–2007 are shown as an example in Supporting information Fig. 1 and concentration diagrams for years 1999–2005 are available from Niemi et al., 2006a, pages 10–11) that episodic high 24-h moving average $PM_{2.5}$ peaks (>25 μg m^{-3}) at Kallio were mainly caused by LRT and that local emissions caused high peaks during New Year's Eve fireworks (squares in Fig. 2; 24-h mean max. 63 μg m^{-3} and 1-h mean max. 193 μg m^{-3}).

During the LRT episodes, the 24-h moving average $PM_{2.5}$ concentrations at Kallio varied between 25 and 49 μg m^{-3}, which were 3–6 times higher than the mean value (8.7 μg m^{-3}) during 1999–2007 (Fig. 2). Fig. 3 shows the scatter plot of daily $PM_{2.5}$ concentrations in Virolahti and Kallio between July 2003 and December 2006. The high correlation ($R = 0.87$) between stations shows that high $PM_{2.5}$ concentrations are usually observed over large areas of southern Finland during the episodes (see also Supporting information Fig. 1). The highest LRT episode peaks are often observed in southeastern Finland, close to the Russian border.

In Helsinki metropolitan area, the number of $PM_{2.5}$ LRT episodes varied between 1 and 7 y^{-1} in 1999–2007, the total number being 40 (black dots in Fig. 2; Table 2). On a monthly level, the LRT episodes occurred most often in February (#8), March (#7), April (#9), August (#4) and September (#4). The durations of individual LRT episodes varied between 0.1 and 8.7 d. Only the hours with 24-h $PM_{2.5}$ moving averages higher than 25 μg m^{-3} at Kallio were included in the duration, and thus weaker episode stages were excluded. The total mean duration of episodes was 0.6–15.0 d y^{-1} (average 6.0 d y^{-1}) (Fig. 4). The LRT episodes deteriorated air quality especially in 2002 and 2006, because the total durations of the episodes were quite long (total time 9.3 and 15.0 d, respectively) and the peak particle concentrations were high.

Table 2
Monthly number of LRT episodes in Helsinki metropolitan area during 1999–2007.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
1999	1	1	2	2					1				7
2000				3									3
2001			1										1
2002			1	1				2	1				5
2003		2	1							1			4
2004	1			1	1								3
2005	1	1	1	1					1	1	1		7
2006		2		1			1	2	1				7
2007		2	1										3
Total	3	8	7	9	1	0	1	4	4	2	1	0	40

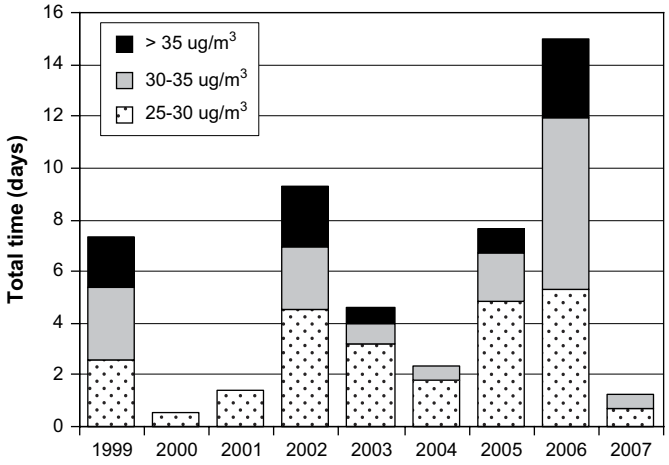

Fig. 4. Annual total duration and strength of LRT episodes in Helsinki metropolitan area during 1999–2007.

3.2. Fire smoke and air mass source areas during the episodes in 2001–2007

The presence of fires in Eastern Europe was investigated using daily MODIS active fire hot spot maps. Fig. 5a shows fire hot spots during an LRT episode at the end of March 2007 as an example. Fig. 5b demonstrates that abundant fires are observed in Eastern Europe close to Finland every year, especially in spring (~ between mid-March and early-May depending on year) and late summer (~ between August and September and also during October in the regions south from the rectangle). The number and exact timing of fires varied during different years, which is mainly caused by differences in meteorological conditions. Prolonged dry and hot periods (e.g. during summer 2002 and 2006) are favourable for fire ignition and burning. Agricultural waste burning in fields and wildfires in forests, peatlands and grasslands frequently occurs in Eastern Europe (FAO, 2001; Stohl et al., 2007; van der Werf et al., 2006). Most of the fires are caused by human activity, either intentionally or accidentally (FAO, 2001).

The dispersion of fire emissions is regulated by meteorological conditions. In this work, NAAPS model results were used to estimate which of the LRT episodes in Finland were caused at least partly by fire emissions in Eastern Europe. Fig. 5c shows a smoke transport map during the LRT episode in Finland at the end of March 2007 as an example (simultaneous Aqua/MODIS satellite image confirms smoke plumes, available from http://rapidfire.sci.gsfc.nasa.gov/real-time/2007088/; →UTC 10:15 image). The LRT of smoke was estimated for each episode and they were classified into three groups: abundant smoke (NAAPS surface smoke concentration maximum more than 4 μg m^{-3} in Helsinki), some smoke (NAAPS surface smoke 1–4 μg m^{-3}) and no smoke (Fig. 5d). These results indicate that abundant smoke from fires was long-range transported to Finland during 9 episodes and some smoke during 4 episodes in 2001–2007. LRT of fire smoke did not occur during 14 episodes. Thus, approximately half of the episodes were caused partly by aerosols from open biomass burning in Eastern Europe. Furthermore, $PM_{2.5}$ monitoring results in southern Finland and NAAPS smoke transport results indicate that weaker LRT smoke events occur every year (not shown, $PM_{2.5}$ did not exceed 25 μg m^{-3} episodic level selected). The verification of smoke transport results is presented in the next section for episodes in 2001–2005 using chemical tracers for biomass-burning aerosols. In

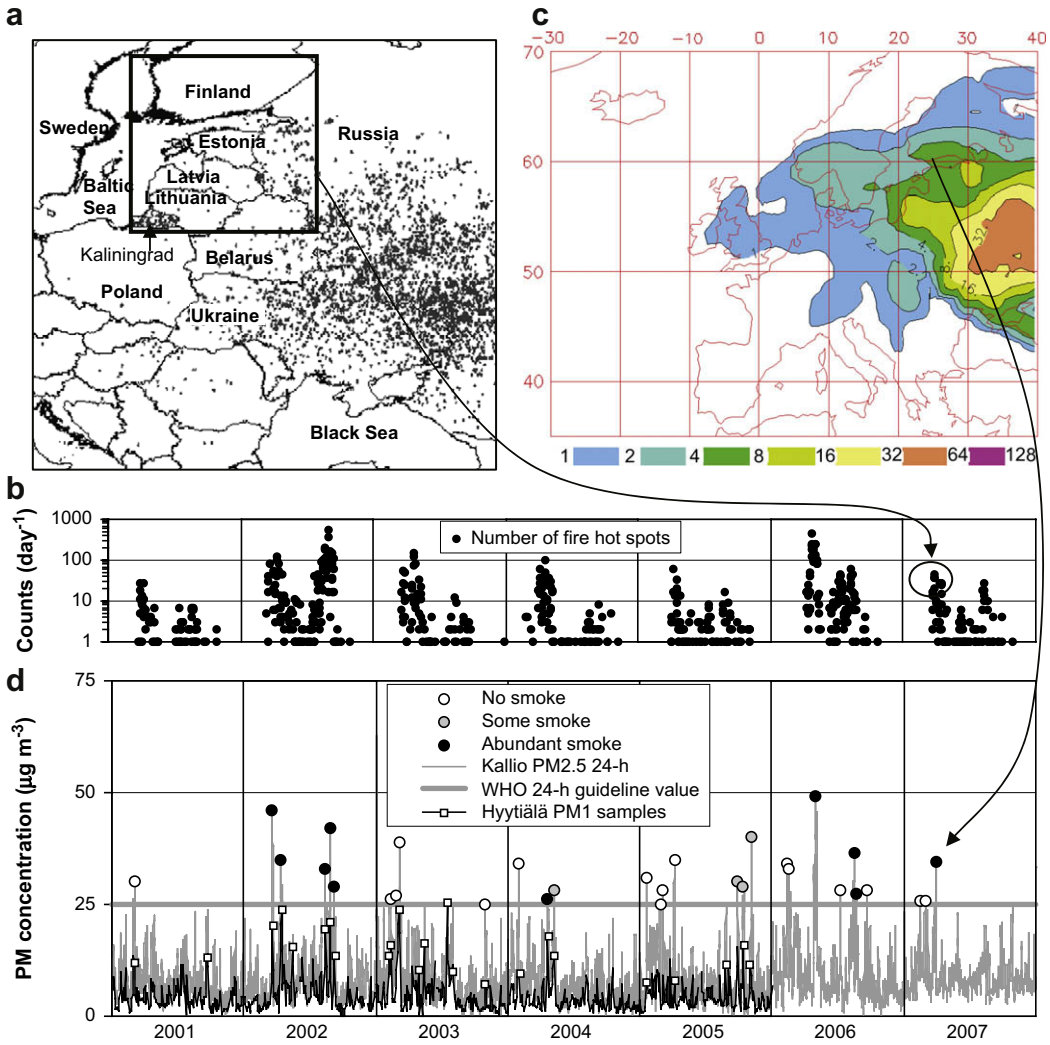

Fig. 5. (a) MODIS Aqua and Terra fire detections in Eastern Europe in March 26–30, 2007 (Web Fire Mapper); (b) daily MODIS Terra fire counts located in rectangle near Finland during 2001–2007; (c) NAAPS model results showing surface smoke concentrations ($\mu g\,m^{-3}$) in March 30, 2007 (UTC 06:00); (d) 24-h moving average $PM_{2.5}$ concentrations and different LRT episode types (no, some and abundant smoke) at Kallio in Helsinki in 2001–2007. Furthermore, 2–3 days PM_1 concentrations and sampling periods for chemical analysis in Hyytiälä in 2001–2005 are also shown.

2006, the high concentrations of biomass-burning tracers (e.g. levoglucosan) during fire smoke episodes were confirmed by Saarikoski et al. (2007) and Saarnio et al. (2006).

The total duration of episodes with some or abundant smoke was 26 days (mean 3.7 d y^{-1}, Fig. 6a) during 2001–2007 whereas the duration of episodes with no smoke was only 15 days (mean 2.1 d y^{-1}, Fig. 6b). The interannual variation was clearly higher for episodes with some or abundant fire smoke (0–10 d) than for episodes with no fire smoke (0–5 d). The most prolonged smoke plumes (episode duration 8.7 d) were observed at the turn of April–May 2006. During that episode, high particle concentrations were observed over very large areas, including Svalbard and the United Kingdom (Saarikoski et al., 2007; Stohl et al., 2007; Witham and Manning, 2007). The episode at the turn of August–September 2002 also caused elevated concentrations over large areas of Europe (Niemi et al., 2005; Witham and Manning, 2007). At the seasonal level (not shown here), the episodes with fire smoke occurred mostly in spring and late summer while the episodes with no fire smoke were most common during winter and early spring (January–March). The height of boundary layer is usually lowest during winter and spring, which enhances the accumulation of higher particle concentrations at surface level.

The highest daily mean concentration peaks ($PM_{2.5} > 35\ \mu g\,m^{-3}$) were observed usually during episodes with some or abundant smoke (total 6.3 d, Fig. 6a) and seldom during episodes without smoke (total 0.6 d, Fig. 6b). At the urban background station in Helsinki (Kallio), the highest 1-h mean value (163 $\mu g\,m^{-3}$) due to LRT was observed during an episode in August 2006, when a dense smoke plume arrived in southern Finland from Russian wildfires near the Finnish border.

The potential source areas of long-range transported particles were studied during all episodes using 72-h backward air mass trajectories with a starting height of 250 m above ground level, describing transport in the boundary layer. Trajectories were produced at 24-h intervals for each episode, including beginning and end time of episode. During the episodes with some or abundant smoke, air masses typically arrived from the following countries of Eastern Europe: Estonia, Latvia, Lithuania, Russia, Belarus and Ukraine (Fig. 7a). The largest fire emissions usually occurred in Russia (including Kaliningrad Oblast, see Fig. 5a as example) but numerous fires were also observed in Ukraine and Belarus, based on the emission estimates by van der Werf et al. (2006), monthly emission data with 1×1 degree resolution during 1999–2006 available from http://www.geo.vu.nl/users/gwerf/GFED.htm. During episodes without

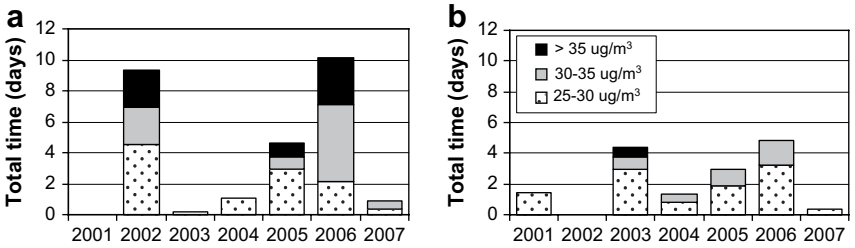

Fig. 6. Annual total duration and strength of LRT episodes in Helsinki metropolitan area during 2001–2007: (a) episodes with abundant or some LRT smoke and (b) episodes without LRT smoke.

LRT smoke, air masses mostly arrived from the same regions but also from more western countries such as Poland (Fig. 7b). These regions contain areas with high emissions from ordinary anthropogenic pollution sources (e.g. energy and industry plants, traffic and residential burning) (EMEP, 2006).

Most of the particle burden caused by LRT accumulates in Finland when 24-h $PM_{2.5}$ concentration is below the episodic level selected (~98.5% of time). Since the predominant wind direction in Finland is from the south-west, a significant proportion of long-range transported aerosols also originates from Western Europe (and from other directions) when the concentrations of fine particles are on ordinary or low level (WHO, 2006).

3.3. Composition of particles during episodes in 2001–2005

The chemical composition of particles was investigated during selected periods in 2001–2005 to characterise aerosol sources and to verify NAAPS smoke transport results. In Finland, the only long-term size-segregated sample series that was suitable for bulk chemical analysis has been collected at Hyytiälä rural station. In this work, PM_1 samples were used because most of the LRT particle mass usually belongs to submicron size fraction (Laakso et al., 2003; Niemi, 2007; Niemi et al., 2006a). The 2–3 days PM_1 concentrations and sampling periods (rectangles) are shown in Fig. 5d. The PM_1 episode peaks are clearly lower in Hyytiälä than in Helsinki due to the longer sampling periods (2–3 days average vs. 24-h moving average), to the smaller size fraction measured ($PM_{2.5}$ in Helsinki) and to the more distant location (~200 km north from Helsinki) from the more polluted regions of Europe. The total number of the LRT episodes in Helsinki metropolitan area was 20 during 2001–2005 but samples were not available from Hyytiälä during five episodes. To increase the sample number for chemical analysis, nine extra particle samples were analysed during weaker LRT periods. During those nine periods, LRT episode criteria were not exceeded in Helsinki metropolitan area (24-h $PM_{2.5}$ slightly lower than 25 μg m^{-3}). However, 2–3 days mean concentrations in all PM_1 samples ($N = 24$) were 2–5 times higher than the long-term mean (4.5 μg m^{-3}) at Hyytiälä in 2001–2005. During three of the nine extra periods (28–30 April 2003, 12–14 May 2003 and 24–26 August 2005), NAAPS smoke transport results indicated that fire smoke was long-range transported to Finland.

The results of chemical analyses are shown in Table 3. The episodes were classified into four groups based on NAAPS fire smoke results and season: (1) abundant smoke (NAAPS surface smoke concentration maximum more than 4 μg m^{-3} in Hyytiälä), (2) some smoke (NAAPS surface smoke 1–4 μg m^{-3}), (3) no smoke cold season (November–March), and (4) no smoke warm season (April–October). The most common chemical components analysed in all groups were SO_4^{2-} (mean proportion from PM_1 mass 16–33%), NH_4^+ (6.1–8.3%) and BC (4.1–6.3%). Organic matter has doubtless also been a major component in all episode samples, but organic carbon (OC) could not be analysed due to filter material used (Teflon). SO_4^{2-}, NH_4^+ and BC are typical components in polluted LRT air masses. The major anthropogenic source of S is fossil fuel burning. BC is emitted from both fossil fuel and biomass burning. Anthropogenic ammonium originates mainly from excretions of domestic animals, fields (especially due to use of synthetic nitrogen fertilizers) and biomass burning.

The proportions of other chemical components analysed were low in most samples (Table 3). Their mean percentages in the four episode type groups were 0.9–1.5% for NO_3^-, 0.1–0.5% for succinate, 0.2–0.3% for malonate, 0.7–1.3% for oxalate, 0.6–2.0% for K^+ and 0.2–1.0% for monosaccharide anhydrides (∑MA). Niemi et al. (2006a) analysed elemental ratios (Na, Mg, Al, Si, P, S, Cl, K, Ti and Fe) from the same samples with a scanning electron microscope (SEM) coupled with an energy dispersive X-ray microanalyser (EDX). Their results showed that, in addition to the above-mentioned chemical components, small amounts of mineral (Si-rich) particles were present in most samples and few samples contained also some biogenic particles during warm season episodes with or without fire smoke.

There were not very clear differences between episode types for the concentrations of most chemical components, excluding biomass-burning tracers (∑MA and K^+, next paragraph). However,

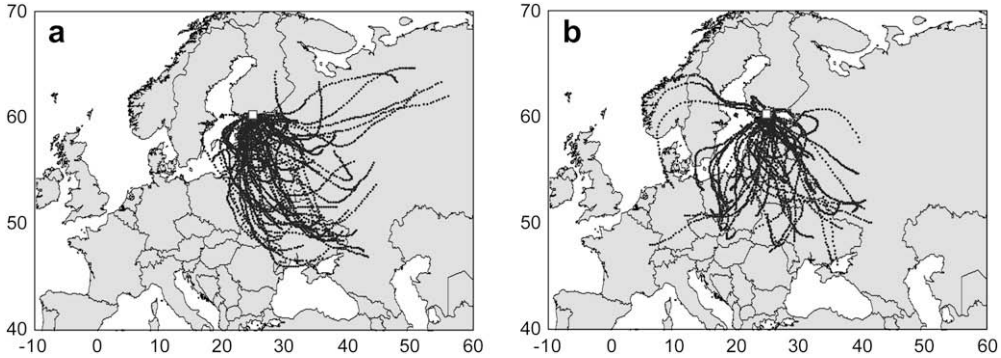

Fig. 7. Backward air mass trajectories (72 h) to Helsinki during LRT episodes in 2001–2007: (a) episodes with abundant or some LRT smoke and (b) episodes without LRT smoke.

Table 3
Concentrations of selected chemical components in PM_1 size fraction in Hyytiälä during LRT episode sampling periods.[a]

Episode type	Sampling time	PM_1 ($\mu g\,m^{-3}$)	BC ($ng\,m^{-3}$)	NO_3^- ($ng\,m^{-3}$)	SO_4^{2-} ($ng\,m^{-3}$)	NH_4^+ ($ng\,m^{-3}$)	Succinate ($ng\,m^{-3}$)	Malonate ($ng\,m^{-3}$)	Oxalate ($ng\,m^{-3}$)	K^+ ($ng\,m^{-3}$)	∑MA ($ng\,m^{-3}$)
NC	2–5.3.2001	12.0	731	29	3513	940	17	34	102	89	55
NW	17–19.9.2001	12.9	989	62	2696	883	66	43	159	198	39
AS	18–20.3.2002	20.4	**1305**	764	3410	1386	62	40	215	234	**260**
AS	12–15.4.2002	23.9	1208	347	4547	1631	57	51	268	463	155
NW	13–15.5.2002	15.5	502	96	2584	903	104	65	206	65	12
AS	12–14.8.2002	19.4	665	33	3230	1092	85	31	89	323	NA
SS	26–28.8.2002	21.0	721	63	2299	933	**154**	**104**	**393**	103	61
NW	6–9.9.2002	13.3	469	73	4438	1649	62	37	151	83	15
NC	5–7.2.2003	13.3	1248	196	4409	1460	12	18	123	153	120
NC	10–12.2.2003	15.8	779	12	6166	937	19	23	121	63	15
NC	5–7.3.2003	23.7	1143	11	**10,191**	**2089**	58	36	97	218	NA
SS	28–30.4.2003	10.5	751	369	1959	835	34	23	166	148	181
SS	12–14.5.2003	16.1	755	183	1482	552	33	26	155	223	83
NW	14.-16.7.2003	**25.2**	239	28	1528	513	145	59	112	37	0
NW	28–30.7.2003	9.9	357	20	2312	874	79	42	107	31	0
NW	29–31.10.2003	7.1	803	**826**	1613	793	12	14	75	118	79
NC	30.1–2.2.2004	9.6	716	208	2671	902	10	17	74	88	97
AS	19–21.4.2004	18.0	786	249	3339	1153	51	40	251	**598**	155
SS	5–7.5.2004	13.3	551	67	4112	1337	66	28	150	151	18
NC	17–19.1.2005	7.4	489	253	1576	676	0	0	49	68	110
NW	4–6.4.2005	8.0	389	193	1273	535	10	14	70	54	15
AS	24–26.8.2005	11.6	370	27	1554	546	46	25	93	227	NA
SS	12–14.10.2005	15.8	660	487	2365	1031	43	49	156	323	134
NC	31.10–2.11.2005	11.5	802	98	2002	772	14	18	68	136	106
Mean concentration											
Abundant smoke ($N = 5$)		18.7	867	284	3216	1162	60	37	183	369	190
Some smoke ($N = 5$)		15.3	688	234	2443	938	66	46	204	190	95
No smoke cool ($N = 7$)		13.3	844	115	4361	1111	19	21	91	116	84
No smoke warm ($N = 7$)		13.1	535	185	2349	879	68	39	126	84	23
Mean proportion from PM_1 (%)											
Abundant smoke ($N = 5$)			4.6	1.5	17	6.2	0.32	0.20	0.98	1.98	1.02
Some smoke ($N = 5$)			4.5	1.5	16	6.1	0.43	0.30	1.33	1.24	0.62
No smoke cool ($N = 7$)			6.3	0.9	33	8.3	0.14	0.16	0.68	0.87	0.63
No smoke warm ($N = 7$)			4.1	1.4	18	6.7	0.52	0.30	0.96	0.64	0.17

[a] Episodes are classified into four types based on the NAAPS fire smoke results and season: Abundant smoke (AS), Some smoke (SS), No smoke cool season (NC) and No smoke warm season (NW). Maximum values are marked with bold fonts. NA = not analysed.

the highest concentrations of SO_4^{2-} were observed during no smoke cool season episodes when the emissions from fossil fuel burning are highest from energy plants. BC concentrations were similarly high during the cool season but also during some episodes with abundant smoke. The concentrations of carboxylic acids (oxalate, succinate and malonate) were quite low during cool season due to slow secondary processes in the atmosphere and to low emissions from natural sources (Kerminen et al., 2000). The highest oxalate concentrations were observed during the smoke episodes because biomass burning is one of the major sources of oxalate. However, it is not a good quantitative tracer for LRT biomass-burning aerosols due to seasonal differences in secondary processes (Kerminen et al., 2000; Saarikoski et al., 2008). Furthermore, it also originates from the emissions of many other sources (e.g. from fossil fuel burning and biogenic sources, Chebbi and Carlier, 1996).

As expected, the highest relative differences between episode types were observed in monosaccharide anhydride and K^+ concentrations (Table 3) which are good tracers for biomass-burning aerosols (Andreae, 1983; Simoneit et al., 1999). ∑MA concentration means were 190, 95 84 and 23 ng m^{-3} for episodes with abundant smoke, some smoke, no smoke cool season and no smoke warm season, respectively. The corresponding values for K^+ were 369, 190, 116 and 84 ng m^{-3}.

The seasonal variation of ∑MA and K^+ concentrations and differences between episode types (data from Table 3) are illustrated in Fig. 8. The diagrams clearly show that biomass-burning aerosols had two major source types during different episodes: (1) high levels during cool season due to biomass burning in fireplaces and energy plants and (2) warm season peaks due to various open biomass-burning fires. The highest ∑MA peaks (maximum 2–3 days mean 260 ng m^{-3}) were caused by LRT of smoke from open biomass burning in Eastern Europe. The seasonal patterns of K^+ and ∑MA concentrations are somewhat similar but Pearson's correlation coefficient between their concentrations is quite low ($R = 0.59$, $p = 0.005$). There may be several reasons for the low correlation. The only source for ∑MA is the incomplete burning of cellulose (→levoglucosan) and hemicellulose (→galactosan and mannosan), which are the major components in plant biomass. Biomass burning is a major source of potassium but it also originates from other sources (e.g. fossil fuel burning, biogenic origins, sea salt and soil dust). The K^+ to ∑MA ratio in emissions is also quite variable, depending on the burning conditions and quality of biomass (Hedberg and Johansson, 2006; Iinuma et al., 2007). Sugar anhydrides are thought to be very stable in the atmosphere based on laboratory tests (Fraser and Lakshmanan, 2000). However, some recent studies have suggested that significant depletion of sugar anhydrides may occur during LRT due to photochemical oxidation, especially during warm and sunny season (Gao et al., 2003; Saarikoski et al., 2008; Saarnio et al., 2006).

These results on the seasonal pattern of ∑MA concentrations are qualitatively in line with measurements at several sites in Europe; high concentrations in winter and low in summer (Oliveira et al., 2007; Puxbaum et al., 2007; Yttri et al., 2007), excluding open fire episodes. However, ∑MA concentrations were lower (or similar) in Hyytiälä even during LRT episodes compared with the typical levels in urban sites (Oliveira et al., 2007; Saarnio et al., 2006; Yttri et al., 2007) or in more southern background sites in Europe (Puxbaum et al., 2007). For instance, the 24-h ∑MA

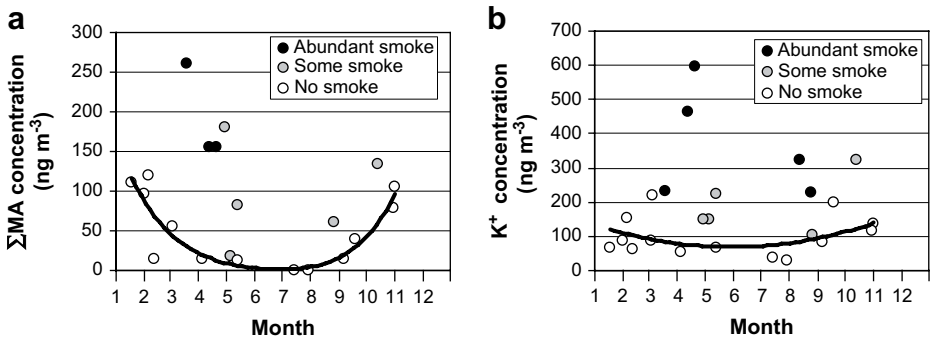

Fig. 8. Seasonal variation in (a) ∑MA and (b) K^+ concentrations in PM_1 samples from Hyytiälä during episodes in 2001–2005. Samples are classified into three groups: episodes with abundant, some and no smoke from open biomass burning. The trend curves illustrate seasonal cycles for episode samples with no smoke.

concentration in winter varied mainly in the range of 30–300 ng m^{-3} in urban background air in Helsinki and in the range of 50–500 ng m^{-3} in a suburban residential area with abundant local wood burning (Saarnio et al., 2006). In summer, ∑MA concentration remained under 50 ng m^{-3} in Helsinki, excluding the wildfire episodes (daily maximum ~600 ng m^{-3} during smoke episode in August 2006). Higher ∑MA concentrations in Helsinki metropolitan area are caused by local biomass combustion as well as by stronger impact of LRT.

3.4. Proportions of biomass-burning particles during episodes in 2001–2005

The ∑MA concentration can be used as a proxy variable to estimate the mass concentration of biomass aerosols in ambient air. However, this is a challenging task since the proportions of ∑MA from PM emissions are dependent on the quality of biomass burned, burning conditions and secondary processes during transport (previous section). In this work, the amount of primary particle mass from biomass burning was calculated using 5% as a coarse estimate for the proportion of ∑MA from primary PM_1 emissions (primary biomass burning PM_1 = ∑MA/0.05). This compromise estimate should fit quite well for the burning of birch (∑MA from $PM_{2.5}$ emissions ~3 to 10%, Frey et al., 2006; Hedberg and Johansson, 2006), which is the major tree species used in residential fireplaces and boilers in Finland. However, the percentage might be too low for the burning of conifers (e.g. ∑MA from PM_{10} for spruce ~15%, Schmidl et al., 2008). The estimate might be suitable or too high for grassland fires and for agricultural waste burning in fields (∑MA from $PM_{2.5}$ ~3 to 6%, Dhammapala et al., 2007; Hays et al., 2005, 2002) and suitable or too low for forest fires (∑MA from ~5 to 8% in $PM_{2.5}$ for forest fires in USA, Lee et al., 2005; Ward et al., 2006). In some of the above-mentioned studies, levoglucosan concentration was only measured, and ∑MA concentration was calculated using 1.33 as a conversion factor (∑MA = 1.33 × levoglucosan), based on other above-mentioned works.

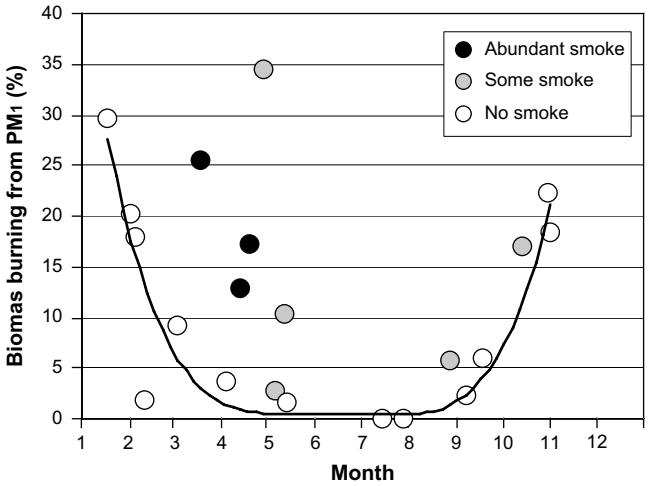

Fig. 9. Estimates for primary biomass-burning aerosol proportions in PM_1 episode samples from Hyytiälä during episodes in 2001–2005. The estimation method is explained in text. Samples are classified into three groups: episodes with abundant, some and no smoke from open biomass burning. The trend curves illustrate seasonal cycles for episode samples with no smoke.

The estimates for primary biomass-burning aerosol mean concentrations in PM_1 size fraction in Hyytiälä during episodes in 2001–2005 were 3.8, 1.9, 1.7 and 0.5 μg m^{-3} for episodes with abundant smoke, some smoke, no smoke cool season and no smoke warm season, respectively. The corresponding values for the proportions of primary biomass-burning particle from total PM_1 mass are 19, 14, 16 and 5%, respectively (Fig. 9). These results show that during most fire smoke episodes, NAAPS transport model results for surface smoke concentrations are in qualitative agreement with chemical results. Since some of the smoke episodes were short in duration, the concentrations and proportions of biomass-burning aerosols remained relatively low in the 2–3 days samples of Hyytiälä.

Some of the gas phase components (e.g. nitrogen oxides and semivolatile organic compounds) are conversed into the particle phase due to secondary processes in the atmosphere during transport. In this work, this increase in the mass concentrations of biomass-burning particles during LRT is neither included in NAAPS model results and nor in the estimate based on ∑MA concentrations. Thus, the total impact of biomass burning on the fine particle concentrations is probably larger than estimated in this work. In the future, it would be desirable to study the proportions of different emissions sources using more detailed chemical characterisation of aerosols and more detailed transport models with secondary chemistry algorithms.

4. Conclusions

The daily WHO guideline value (25 μg m^{-3}) for 24-h $PM_{2.5}$ mean concentration is usually exceeded in southern Finland several times per year due to LRT of pollutants from Eastern Europe. The strongest and longest LRT episodes are caused by emissions from open biomass burning, but emissions from ordinary anthropogenic sources (e.g. from energy production, traffic, industry and wood combustion) in Eastern Europe also cause significant episodes. Emissions from agricultural waste burning in fields and wildfires deteriorate air quality over very large areas, even at the distance

over 1000 km from the fire areas. Thus, the smoke from open biomass burning is an important factor in the deterioration of air quality in Eastern Europe and its vicinity during warm and dry periods in spring and late summer. In future, climate change may increase extreme meteorological conditions (e.g. dry heat waves) and smoke episodes, if more efficient fire prevention and suppression measures are not implemented.

Acknowledgements

We thank the Helsinki University Environmental Research Centre (HERC), the Finnish Cultural Foundation, the Academy of Finland (contract no. 201131), Maj and Tor Nessling Foundation (grant no. 2006167) and the Helsinki Metropolitan Area Council (YTV) for funding of the research. The support of the Office of Naval Research and the Naval Research Laboratory through program PE-0602435N is gratefully acknowledged. The NOAA Air Resources Laboratory (ARL) is acknowledged for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.html) used in this publication. The NASA Goddard Space Flight Centre (GSFC) and the University of Maryland (UMD) is acknowledged for the MODIS active fire detection results from the Web Fire Mapper (http://firemaps.geog.umd.edu/).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2008.11.022.

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