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Characterization of aerosol particle episodes in Finland caused by wildfires in Eastern Europe

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Abstract. We studied the sources, compositions and size distributions of aerosol particles during long-range transport (LRT) PM_{2.5} episodes which occurred on 12–15 August, 26–28 August and 5–6 September 2002 in Finland. Backward air mass trajectories, satellite detections of fire areas and dispersion modelling results indicate that emissions from wildfires in Russia and other Eastern European countries arrived in Finland during these episodes. Elemental analyses using scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalyses (EDX) showed that the proportions of S-rich particles and agglomerates (agglomeration was caused partly by the sampling method used) increased during the episodes, and they contained elevated fractions of K, indicating emissions from biomass burning. These aerosols were mixed with S-rich emissions from fossil fuel burning during transport since air masses came through polluted areas of Europe. Minor amounts of coarse Ca-rich particles were also brought by LRT during the episodes, and they probably originated from wildfires and/or from Estonian and Russian oil-shale-burning industrial areas. Ion chromatography analysis showed that concentrations of sulphate (SO₄²⁻), total nitrate (NO₃⁻+HNO₃(g)) and total ammonium (NH₄⁺+NH₃(g)) increased during the episodes, but the ratio of the total amount of these ions to PM₁₀ concentration decreased, indicating unusually high fractions of other chemical components. Particle number size distribution measurements with differential mobility particle sizer (DMPS) revealed that concentrations of particles 90–500 nm increased

during the episodes, while concentrations of particles smaller than 90 nm decreased. The reduction of the smallest particles was caused by suppressed new particle formation due to vapour and molecular cluster uptake of LRT particles. Our results show that emissions from wildfires in Russian and other Eastern European countries deteriorated air quality of very large areas, even at distances of over 1000 km from the fire areas.

1 Introduction

Large amounts of fine particles (PM_{2.5}) are emitted from various sources and transported long distances due to their slow removal from the atmosphere. Thus, in areas with low local emissions, the major proportion of the PM_{2.5} mass is usually long-range transported. Fine particles are associated with adverse health effects (Dockery and Pope, 1994; Laden et al., 2000; Pope et al., 2002; WHO, 2002, 2003), and no threshold concentration has been identified below which they have no impact on health (WHO, 2003).

The properties and sources of long-range transport (LRT) particles in Finland have been studied in conjunction with several short-term campaigns and long-term monitoring measurements. The emissions and mass concentrations of PM_{2.5} are generally quite low compared with more polluted regions of Europe (EMEP, 2001, 2002; Ruuskanen et al., 2001). Even in the urban areas of Helsinki, 50–70% of PM_{2.5} mass is caused by LRT (Vallius et al., 2003; Karppinen et al., 2004). In general, high concentrations of LRT PM_{2.5} mass and typical chemical components of LRT particles,

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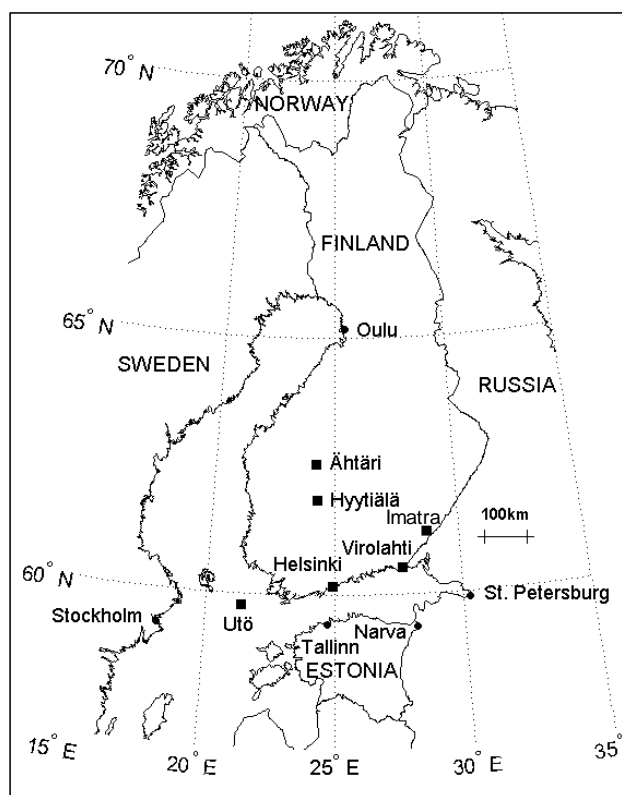


Fig. 1. Locations of the measurement and sampling sites (marked with squares).

such as sulphate and nitrate, are observed in Finland when air masses arrive from Eastern and Central Europe (Pakkanen et al., 2001; Ruoho-Airola et al., 2004). In northern Finland, the emissions from the Arctic Ocean and from the Kola Peninsula industrial areas in northern Russia also increase LRT particle mass concentrations (Virkkula et al., 1999; Yli-Tuomi et al., 2003). However, the sources and properties of aerosols during the strongest LRT periods are still poorly known in Finland, and only a few LRT episodes have been examined in detail to date. The main sources of these LRT episodes have been marine aerosols from the Atlantic Ocean (Tervahattu et al., 2002a, b), emissions from oil-shale burning industrial areas in Estonia and Russia (Tervahattu et al., 2004) and emissions from spring-time agricultural field burning and fossil fuel burning in Russia and other Eastern European countries (Niemi et al., 2004).

In this article, we describe three LRT $\text{PM}_{2.5}$ episodes that occurred in Finland in August and September 2002. We studied mass and number concentrations of PM as well as its chemical composition using bulk and individual particle methods. Backward air mass trajectories, fire satellite observations, dispersion modelling results and emission source data were also used to identify origin and to characterize the dispersion of LRT emissions. The main sources of the

episodes were emissions from forest and peat fires mixed with emissions from fossil fuel burning. A comparison with an earlier LRT $\text{PM}_{2.5}$ episode occurring during the spring-time agricultural field burning period (Niemi et al., 2004) was also carried out.

2 Materials and methods

We used several measurement and sampling sites in this study and their locations are shown in Fig. 1. Summary of the measurements and samplings performed at these sites is given in Table 1.

2.1 Meteorological and emission data

The meteorological conditions were derived from data collected by the Finnish Meteorological Institute at Kaisaniemi, Helsinki, and the Helsinki Metropolitan Area Council at Pasila, Helsinki. Backward air mass trajectories were produced using the vertical motion model in the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT4) model (Draxler and Rolph, 2003) with the Final Analyses (FNL) meteorological database at NOAA Air Resources Laboratory's web server (Rolph, 2003). For detection of fire areas, we used Web Fire Mapper (<http://maps.geog.umd.edu>), which is part of the MODerate-resolution Imaging Spectroradiometer (MODIS) Rapid Response System (Justice et al., 2002). The Navy Aerosol Analysis and Prediction System (NAAPS) model results were used to determine the distribution of smoke, dust and sulphate aerosols. Details of the model and model results are available at the internet pages (<http://www.nrlmry.navy.mil/aerosol/>) of the Naval Research Laboratory, Monterey, California. Using data of the European Monitoring and Evaluation Programme (EMEP), we searched for information on trace gas and particle emissions in the areas along the air mass routes (EMEP, 2001, 2002).

2.2 Particle mass and number size distributions

Particle mass and number size distributions are measured at a rural background station (SMEAR II) in Hyytiälä (Kulmala et al., 2001) by the University of Helsinki (Department of Physical Sciences). The particle mass fractions were measured with a Dekati PM_{10} 3-stage impactor with a backup filter. The duration of sample collection was 2–3 days. The inlet was located 2 m above ground level, and the flow rate was 29.2 L min^{-1} . The cut-off diameters (D_{50}) of the impactor stages were 10, 2.5 and $1 \mu\text{m}$. The collection substrates for impaction stages were polycarbonate membranes (Nuclepore 800 203, diameter 25 mm) with no holes, and the backup filter was made of Teflon (Gelman Teflo R2P J047, diameter 47 mm) with a diameter pore size of $2 \mu\text{m}$. The smearing of substrates to prevent particles from bouncing back from the substrates and the gravimetric analysis are described in

Table 1. Description of measurement and sampling sites for different analyses.

Location	Environment	Particle mass fraction measurement	Particle number size distribution measurements	Samples for ion chromatography measurements	Samples for SEM/EDX measurements
Hyytiälä	Rural background	Size fractions ^a	x		
Virolahti	Rural background	PM ₁₀		x	
Utö	Rural background			x	
Ähtäri	Rural background			x	
Helsinki at Kallio	Urban background	PM ₁₀ , PM _{2.5}			x
Helsinki at Luukki	Rural background	PM ₁₀			x
Imatra at Mansikkala	Urban	PM ₁₀			x

^a $D_p < 1 \mu\text{m}$, $1\text{--}2.5 \mu\text{m}$, $2.5\text{--}10 \mu\text{m}$ and $> 10 \mu\text{m}$

detail by Laakso et al. (2003). The PM₁₀ mass monitoring measurements performed in Virolahti, Helsinki (also PM_{2.5}), and in Imatra are briefly described in Sects. 2.3 and 2.4.

Particle number size distributions were measured in the diameter range between 3 and 500 nm using a twin differential mobility particle sizer (DMPS) in Hyytiälä. DMPS consists of a differential mobility analyser (DMA) and a condensation nucleus counter (CNC). It classifies particles into size classes depending on the electrical mobility of the particles. The different size classes are separated by changing the voltage difference inside the DMA. The size distribution of the sampled aerosol population is then determined in the CNC, which counts the number concentration of every size class. The twin DMPS system used consisted of two different DMPSs: the first classified particles from 3 to 10 nm and the second particles from 10 to 500 nm. Both systems used Hauke-type DMAs (Winklmayr et al., 1991) and a closed loop sheath flow arrangement (Jokinen and Mäkelä, 1997). The CNCs used were TSI Model 3025 and TSI Model 3010 in the first and second systems, respectively. Before the size characterization, the incoming aerosol was neutralized with a 2 mCi Krypton-85 beta source. The sampling height was 2 m above ground level. The time resolution was 10 min. The details of the DMPS sampling protocol are provided in Aalto et al. (2001).

2.3 Ion analyses

Rural background air quality is monitored at several measurement stations in Finland by the Finnish Meteorological Institute (FMI). We present ion measurement results from the EMEP stations in Ähtäri, Virolahti and Utö. Daily total suspended particle (TSP) samples were collected using open-faced 2-stage filter packs (NILU Products AS) containing cellulose filters (Whatman 40, diameter 47 mm). Sulphate (SO_4^{2-}), total nitrate ($\text{NO}_3^- + \text{HNO}_3(\text{g})$) and total ammonium ($\text{NH}_4^+ + \text{NH}_3(\text{g})$) were analysed with ion chromatography (IC, Dionne DX-500 and Waters). Details of the sampling and IC methods are described in Paatero et al. (2001). We also com-

pared the ion masses with the PM₁₀ masses measured in Virolahti. The PM₁₀ mass was monitored with Eberline FH 62 I-R (Eberline Instruments), which is based on β -attenuation.

2.4 SEM/EDX analyses

Air quality is monitored at several measurement stations in the Helsinki metropolitan area by the Helsinki Metropolitan Area Council, and in Imatra by the Environment Office of Imatra. We selected particle samples for individual particle analyses collected at Kallio and Luukki in the Helsinki area during all three episodes studied, and at Mansikkala in Imatra during the last episode. Particle samples were collected with Eberline FH 62 I-R samplers (Eberline Instruments) on fibreglass filter tape. In all, 17 particle samples (9 PM_{2.5} and 8 PM₁₀ samples) collected during the episodes (13, 27, and 28 August, 5 and 6 September 2002) and on reference days (8, 10, and 16 March, 18 and 22 August, 17 and 22 September 2002) were selected for the analyses.

The elemental compositions of individual particles and agglomerates were studied using scanning electron microscopy (SEM – ZEISS DSM 962) coupled with energy dispersive X-ray microanalyses (EDX – LINK ISIS with the ZAF-4 measurement program). The SEM/EDX samples were prepared by pressing a tape (Scotch Ruban Adhesive) attached to an aluminium plate onto the filter surface covered with particles. Then samples were coated with carbon (Agar SEM Carbon Coater) to make the sample surfaces conductive. The SEM/EDX was operated at accelerating voltage of 20 kV, and the counting time of the X-ray spectrum was 15 s. The elemental compositions of 100 randomly selected particles or agglomerates (minimum diameter 1 μm) were analysed from each sample. Submicron-sized particles had formed abundant large agglomerates during sampling and sample preparation for SEM/EDX analysis, enabling us to also obtain elemental information from the submicron size range by analysing these agglomerates. However, this agglomeration complicated detailed classification of fine particle types, and thus, only major differences in fine aerosols between episode

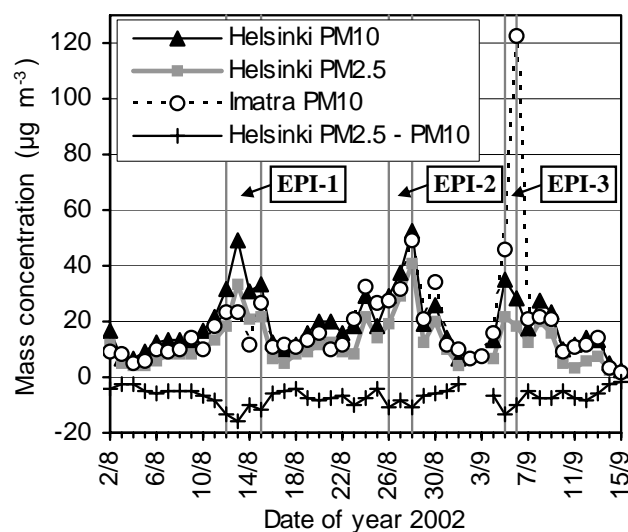


Fig. 2. Daily PM_{10} and $\text{PM}_{2.5}$ concentrations at Kallio in Helsinki and daily PM_{10} concentration at Mansikkala in Imatra on 2 August–15 September 2002. The three strong LRT episode periods (EPI-1, EPI-2 and EPI-3) are indicated with vertical lines. Note that the concentrations of coarse particles are depicted for figure clarity as the subtraction $\text{PM}_{2.5}-\text{PM}_{10}$ which gives negative values.

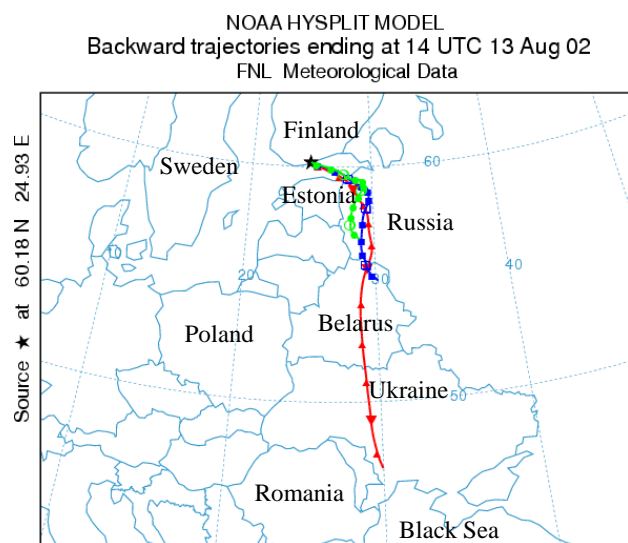


Fig. 3. Backward air mass trajectories (72 h) to Helsinki during the strongest stage of the EPI-1 (13 August 2002). Vertical heights at the start were 10 m (green circles), 100 m (blue squares) and 500 m (red triangles) above ground level.

and reference days could be observed. The relative elemental weight percentages (normalized to 100%) were calculated using ZAF-4 corrections for the following elements: Na, Mg, Al, Si, S, Cl, K, Ca, Ti and Fe. While the ZAF-corrected elemental results are semiquantitative, the accuracy is sufficient to identify different particle types and to compare differences

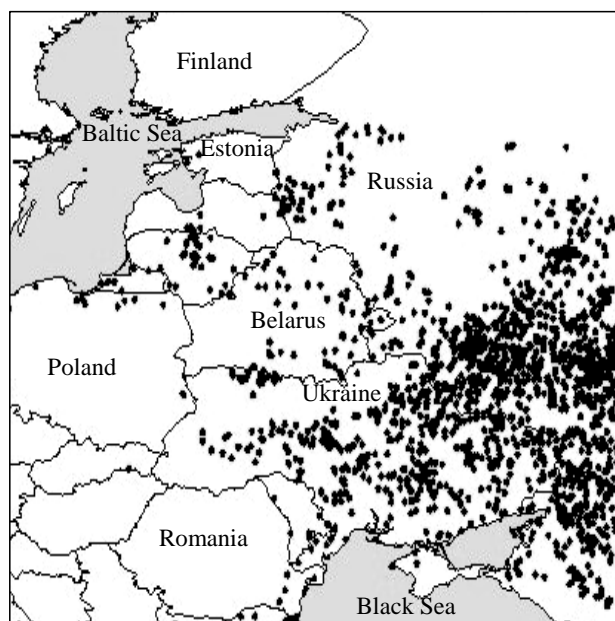


Fig. 4. MODIS fire detections in Eastern Europe during EPI-1 (10–15 August 2002).

in elemental ratios of the same particle type in different samples (Kupiainen et al., 2003; Niemi et al., 2004).

3 Results and discussion

3.1 General description of LRT episodes

PM_{10} and $\text{PM}_{2.5}$ concentrations rose to extraordinarily high levels in Finland during three periods in August and September 2002. We focus on the strongest periods of these episodes; the first episode (EPI-1) was on 12–15 August, the second (EPI-2) on 26–28 August and the third (EPI-3) on 5–6 September (Fig. 2). These episodes were also observed in Estonia and Sweden (Niemi et al., 2003; Räisänen et al., 2004). In Finland, the episodes were strongest in the south, but they were observed, albeit more weakly, over a wide area, including as far north as Oulu, 600 km from the southern coast of Finland. The maximum hourly PM_{10} concentrations in southern Finland during the episodes were $70\text{--}90\ \mu\text{g m}^{-3}$, whereas the typical values in this area are $\sim 15\text{--}20\ \mu\text{g m}^{-3}$ (Anttila et al., 2003). EPI-3 was especially strong in southeastern Finland, where the maximum hourly PM_{10} concentrations were $200\text{--}220\ \mu\text{g m}^{-3}$. Most of the particle mass was in the $\text{PM}_{2.5}$ size range, and $\text{PM}_{2.5}$ values observed during the episodes were multifold compared with long-term mean values. At Kallio in Helsinki, for example, the maximum hourly $\text{PM}_{2.5}$ values (maximum 24-h mean values in parentheses) were 45 (33), 54 (42) and 81 (29) $\mu\text{g m}^{-3}$ during EPI-1, EPI-2 and EPI-3, respectively, whereas the three-year (1999–2001) summer–autumn mean

Table 2. Mass and number size fractions in Hyytiälä during episodes (12–15 August, 26–27 August and 6–8 September 2002) and on reference days (2 August–15 September 2002, excluding episode days). Sample change time was 05:00 UTC. We also show three-year (1999–2001) mean summer-autumn values (Laakso et al., 2003) and values measured during an episode in March (17–19 March 2002) (Niemi et al., 2004).

	PM ₁	PM _{1–2.5}	PM _{2.5–10}	PM _{>10}	Nucl. (3–25 nm)	Aitken (25–90 nm)	Accum. (90–500 nm)	Total (3–500 nm)
	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\# \text{cm}^{-3}$	$\# \text{cm}^{-3}$	$\# \text{cm}^{-3}$	$\# \text{cm}^{-3}$
Reference days	5.3	1.2	1.2	0.6	489 *343	1138	591	2219 *2072
Episode days	15.9	3.7	2.3	0.7	226 *174	588	1067	1880 *1828
Summer-autumn mean (Laakso et al., 2003)	4.6	1.2	1.3	–	*365	1065	710	*2130
March episode (Niemi et al., 2004)	15.4	6.9	2.3	0.3	273 *211	955	2703	3924 *3867

* Denotes the concentration calculated with nucleation mode limits 10–25 nm, as in Laakso et al. (2003).

was only $7.9 \mu\text{g m}^{-3}$ (Laakso et al., 2003). The concentrations of coarse particles (low PM_{2.5}–PM₁₀ values in Fig. 2) also increased slightly during the episodes, especially during EPI-1.

August and the beginning of September 2002 were exceptionally warm and dry in Finland and in the neighbouring areas. For example, the monthly mean temperature at Kaisaniemi in Helsinki was 19.4°C in August, whereas the long-term (1971–2002) mean value was 15.8°C . The total monthly precipitation values were 6 and 5 mm in August and September, respectively, while the corresponding long-term (1971–2000) mean values were 78 and 66 mm. August 2002 was the warmest August and September 2002 the driest September of a 100-year period. During the episodes at Pasila in Helsinki the wind speed (hourly mean) was $2\text{--}6 \text{ m s}^{-1}$, relative humidity 40–90% and temperature $15\text{--}28^\circ\text{C}$.

The backward trajectories showed that air masses during EPI-1 arrived in Helsinki from eastern Estonia, Russia and Ukraine (Fig. 3). During EPI-2 the trajectories curved along a more western route, and air masses arrived in Helsinki from Russia via the Baltic Sea and the Baltic countries (Estonia, Latvia and Lithuania). EPI-3 was strongest in southeastern Finland, and air masses arrived over Virolahti and Imatra from the direction of Russia and eastern Estonia. The satellite observations of potential fire areas indicated that there were many wildfires in Russia, Ukraine, Belarus and the Baltic countries during the episodes. The number of fires near Finland was high before and during EPI-1 (Fig. 4). High emissions from large forest and peat fires led to accumulation of large smoke plumes over Eastern Europe (Goldammer, 2003). The NAAPS model results indicated that the strongest smoke plumes reached Finland during EPI-2 and especially during EPI-3 (Fig. 5).

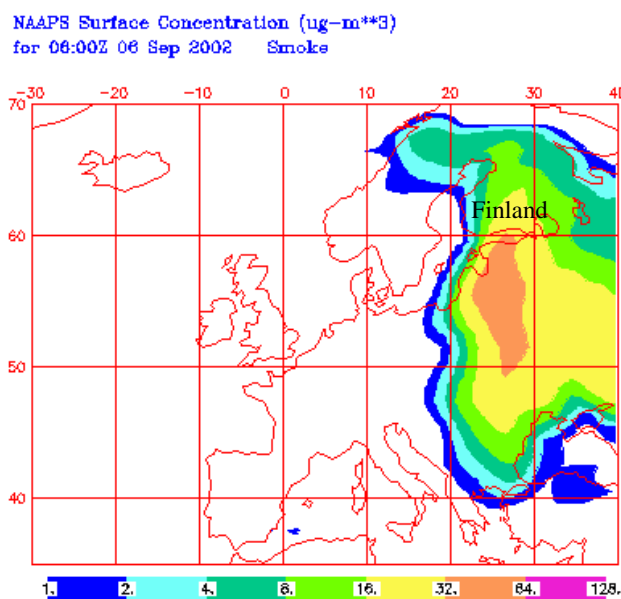


Fig. 5. NAAPS model results showing surface smoke concentrations for the strongest stage of EPI-3 (6 September 2002).

3.2 Particle mass and number size distributions

We compared the particle mass and number size fractions at the Hyytiälä measurement station during the three episodes (12–15 August, 26–27 August and 6–8 September 2002) with reference periods surrounding the episodes (2 August–15 September 2002) (Table 2). Because the sample collection times for mass concentration measurements were 2–3 days, we had to select slightly different periods for EPI-2 and EPI-3 in this section compared with other sections of this paper. Most of the particle mass was in the submicrometre

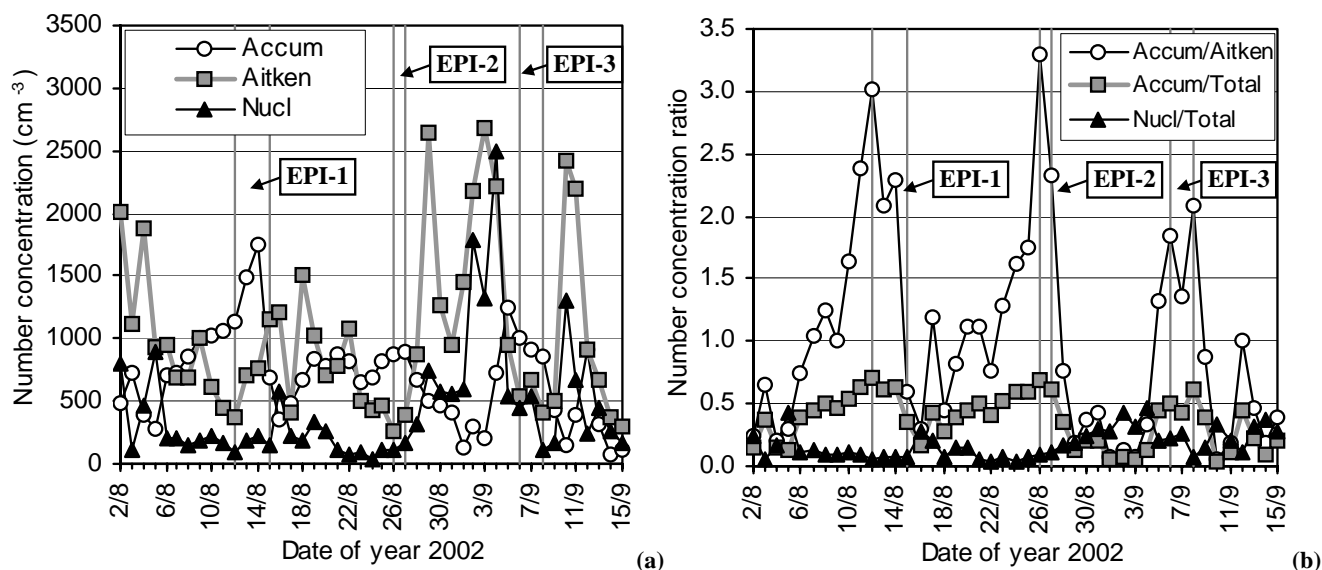


Fig. 6. (a) 24-h mean number concentrations of nucleation mode (Nucl, diameter 3–25 nm), Aitken mode (Aitken, 25–90 nm) and accumulation mode (Accum, 90–500 nm) particles, and (b) selected ratios of different modes and total amount (3–500 nm) of particles in Hyytiälä on 2 August–15 September 2002. Sample change time was 05:00 (UTC).

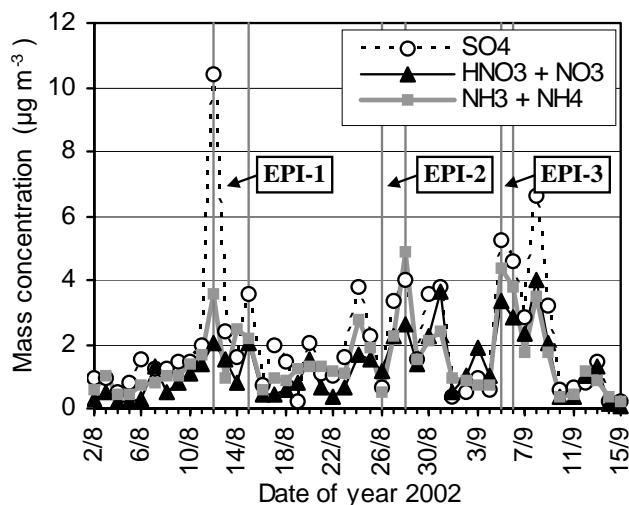


Fig. 7. 24-h mean total suspended particle (TSP) concentrations of SO_4^{2-} , total nitrate ($\text{NO}_3^- + \text{HNO}_3(\text{g})$) and total ammonium ($\text{NH}_4^+ + \text{NH}_3(\text{g})$) in Virolahti on 2 August–15 September 2002. Sample change time was 06:00 (UTC).

size range during all episodes as well as on reference days. During the episodes the particle mass increased on average by a factor of 3 for the size classes PM_{10} and $\text{PM}_{1-2.5}$ and by a factor of 2 for the size class $\text{PM}_{2.5-10}$, but for the size class exceeding PM_{10} the concentration remained at about reference levels. During the three episodes all of these PM concentrations were close to those observed during the LRT episode in March 2002, which originated from agricultural

field burning emissions mixed with fossil fuel burning emissions (Niemi et al., 2004).

The particle number concentration increased on average by a factor of 1.8 in the accumulation mode and decreased by a factor of 0.5 in the Aitken and nucleation modes (Table 2 and Fig. 6a). The decrease of the smallest particles was expected since small molecular clusters and particles are scavenged efficiently by a large number of bigger particles (see e.g. Mönkkönen et al., 2004). Abundant surface area of larger particles also consumes condensable vapours, preventing particle formation and growth. The total concentration of particles with a diameter less than 500 nm was fairly unaffected since the decrease in nucleation and Aitken mode concentrations was balanced by the increase in accumulation mode concentrations.

Figure 6b shows how big a fraction of particles smaller than 500 nm in diameter belong to accumulation and nucleation modes. The ratio of accumulation mode concentration to Aitken mode concentration (Accum/Aitken) is also shown. The Aitken mode particles can not be transported in the atmosphere as far as accumulation mode particles. The deposition efficiency of Aitken mode particles is high, they disappear by colliding and sticking to the accumulation mode particles, and they grow fast due to condensation of vapours (Seinfeld and Pandis, 1998, p. 100, 662, 971, 1020). Furthermore, the sources of Aitken mode particles are scarce in the areas around Hyytiälä. Thus, Aitken mode concentrations in Hyytiälä normally exceed those of the accumulation mode, and an Accum/Aitken ratio greater than one is typical of polluted air masses transported over long distances. High values (>1) of Accum/Aitken might thus be an indicator of

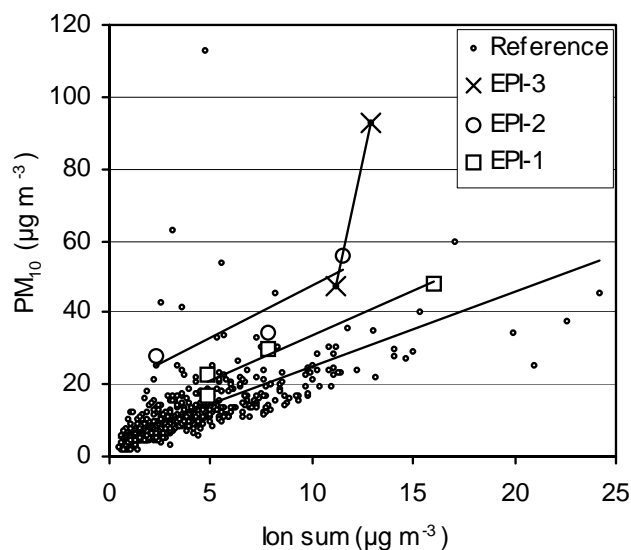


Fig. 8. Scatter plot and linear trend lines between 24-h mean ion sum and PM_{10} concentrations in Virolahti during EPI-1 (12–15 August 2002), EPI-2 (26–28 August 2002), EPI-3 (5–6 September 2002) and reference days (3 July 2002–31 December 2003).

different LRT episodes in general. This concept is also supported by the observations made during the LRT episode in March 2002.

3.3 Ion analyses

The 24-h mean TSP concentrations of sulphate, total nitrate and total ammonium increased strongly at the rural EMEP station of Virolahti during the episodes (Fig. 7). The ion sums (total amounts) of these chemical components were 8.2, 7.2 and 12.1 $\mu\text{g m}^{-3}$ during EPI-1, EPI-2 and EPI-3, respectively. The ion sums in Utö were about the same level as in Virolahti, whereas those in Ähtäri, a more northern station (see Fig. 1), were clearly lower (factor of 2/3). The values during the episodes were 3–4 times higher than those usually observed at these three stations at this time of the year (Leinonen, 2001).

We compared ion sums and PM_{10} concentrations measured in Virolahti during the episodes and the reference period (Fig. 8). The ion sum to PM_{10} ratios were lower than usual during the episodes; the means were 0.28, 0.18, 0.17 and 0.33 during EPI-1, EPI-2, EPI-3 and the reference period, respectively, and the differences between episodes and reference period were statistically significant ($p < 0.001$, One Sample T-test, SPSS 10.0 statistical program). This indicates that the particle matter during the episodes contained unusually high fractions of chemical components other than sulphate, nitrate and ammonium. The ion sum to PM_{10} ratio was especially low (0.14) during the peak stage of EPI-3 (6 September 2002), when the strongest smoke plume from wildfires reached southeastern Finland. Large emissions of

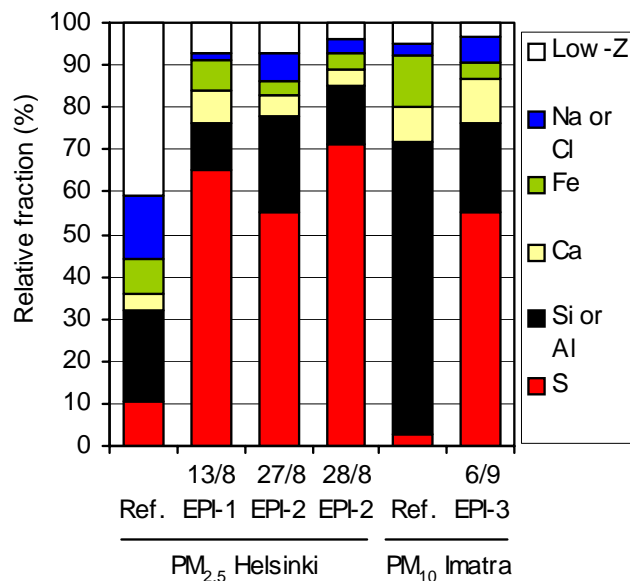


Fig. 9. Abundance of particle groups (%) in reference samples and episode samples collected at Kallio station in Helsinki during EPI-1 (13 August 2002) and EPI-2 (27 August and 28 August 2002), and at Mansikkala station in Imatra during EPI-3 (6 September 2002).

organic and black carbon and other chemical components from wildfires were probably the main reason for the reduction in the relative fraction of the ion sum during the episodes, as will be discussed below.

3.4 SEM/EDX analyses

We analysed the elemental composition of single particles and agglomerates with SEM/EDX from samples collected during the episodes and the reference days. The particles and agglomerates were classified into six different groups based on the most abundant element in each particle or agglomerate: (1) S, (2) Si or Al, (3) Ca, (4) Fe, (5) Na or Cl, (6) low-Z. Particles and agglomerates in the low-Z class contained only elements with an atomic number lower than 11 (Na), such as C, N and O, which could not be analysed quantitatively with the SEM/EDX used. We also classified particles and agglomerates with hierarchical cluster analysis (SPSS 10.0 statistical program) using Ward's method with squared Euclidean measures, which is well-suited to grouping different particle types (Bernard and Van Grieken, 1992). However, the elemental composition of the main fine particle group (S-rich) during the episodes proved to be so homogeneous (presumably partly due to agglomeration of particles during sampling) that we show only a few details of the clustering classification for coarse particles.

The amount of S-rich particles and agglomerates was extraordinarily high during the episodes (Fig. 9). The $PM_{2.5}$ samples of the urban background station at Kallio contained 65% and 71% S-rich particles and agglomerates during the

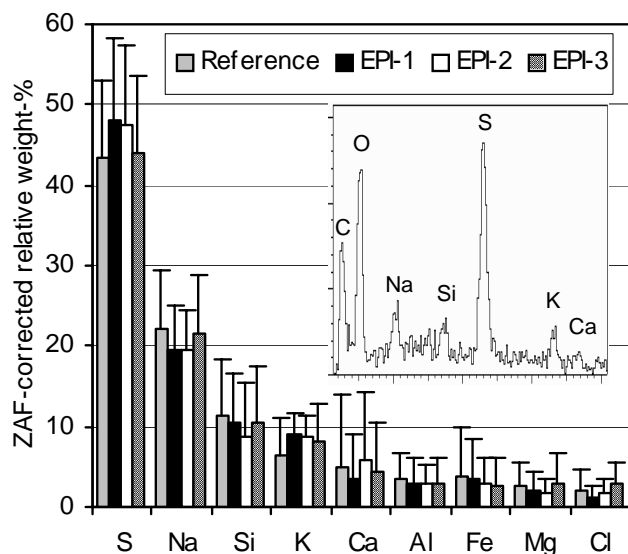


Fig. 10. Average weight percentages of selected elements in S-rich particles and agglomerates (typical SEM/EDX spectrum also shown) in PM_{2.5} samples collected at Kallio in Helsinki during EPI-1, EPI-2 and reference days, and in PM₁₀ samples collected in Helsinki and in Imatra during EPI-3. Error bars represent standard deviation (SD). Results are semiquantitative and weight percentages of selected elements are normalized to 100%.

peak days of EPI-1 and EPI-2, respectively, but only on average 10% (range 7–13%) during reference days. EPI-3 was clearly strongest in southeastern Finland, but unfortunately no PM_{2.5} samples were collected there during this period. We therefore studied PM₁₀ samples collected at urban station in Imatra. The fraction of S-rich particles and agglomerates was also very high (55%) during the peak day of EPI-3 in Imatra compared with the value (3%) for the reference day.

In addition to S, S-rich particles and agglomerates contained large amounts of C and O as well as some Na, Si and K (EDX spectra shown in Fig. 10). The presence of C was confirmed by analysing some S-rich particles and agglomerates directly on the gold-coated surface of (C-free) fibreglass filters. Particles and agglomerates also contained ammonium and nitrate (see IC results in previous section), but N could not be analysed with the EDX used. The fractions of other elements were usually quite low, but some of the particles and agglomerates contained also elevated concentrations of Ca.

The elemental ratios of S-rich particles and agglomerates in different samples were compared (Fig. 10). K was the only element for which the relative weight percentage had statistically significant ($p < 0.01$, Mann-Whitney U-test, SPSS 10.0 statistical program) differences between episode and reference samples. The relative weight percentages (sum of all analysed elements normalized to 100%) of K in S-rich particles and agglomerates were higher during all episodes (8.9% EPI-1, 8.9% EPI-2 and 8.2% EPI-3) than on reference days

(6.3%). The median S/K ratios of S-rich particles showed the same change; S/K ratios were lower during EPI-1 (5.5), EPI-2 (5.4) and EPI-3 (6.0) compared with reference days (7.8). The increased fraction of K is an indication of emissions from biomass burning (Andreae, 1983; Andreae et al., 1998). S-rich particles also contained some Na and Si, which may have originated partly from biomass burning but also from many other sources, e.g. marine aerosols, fossil fuel burning and refuse incineration (Watson et al., 2001; Ooki et al., 2002).

The relative weight percentages of K in S-rich particles did not rise (range 8.2–8.9%) as high as during the LRT PM_{2.5} episode in March 2002 (range 11.4–19.3%), which originated from agricultural field burning emissions mixed with fossil fuel burning emissions (Niemi et al., 2004). The median S/K ratios of S-rich particles were also higher during EPI-1 (5.5), EPI-2 (5.4) and EPI-3 (6.0) than during the March episode (range 2.1–5.2). Smouldering burning conditions are more dominant in boreal forest fires and peat fires than in grass, shrub or cereal waste fires, which mainly burn in flaming conditions (Echalar et al., 1995; Lavoue et al., 2000; Ortiz de Zárate et al., 2000; Soja et al., 2004). Thus, it seems likely that aerosols from forest and peat fires were less enriched with K than aerosols from agricultural field burning since the fraction of K is lower in the emissions from smouldering fires than in those from flaming fires (Echalar et al., 1995; Gaudichet et al., 1995; Robinson et al., 2004). Another reason for the relatively low proportion of K was probably the mixing of emissions from fossil fuel burning since air masses arrived from the regions of Eastern Europe with high S emissions (EMEP, 2001). However, the fraction of fossil fuel burning emissions in LRT particle mass was probably smaller during the wildfire episodes than in the March 2002 episode because the relative weight ratio of S in S-rich particles did not rise as high as during the peak stage of the March episode (61%) (Niemi et al., 2004).

The PM measurements in Helsinki showed that mass concentrations of coarse (PM_{2.5–10}) particles also increased slightly during the episodes (see Fig. 2). Since Si-Al-rich particles are usually clearly the dominating group of PM₁₀ particles in Helsinki and other Finnish cities (Haapala, 1999; Räisänen et al., 2004), we compared the relative fractions of the Si-Al-rich particle groups with the other groups. The ratio of Ca-rich to Si-Al-rich particle groups proved to be exceptionally high during all three episodes in Helsinki, and also in Imatra during EPI-3 (Table 3). The ratios were 0.24–0.53, which are 3–7 times higher than the values of the reference days and the long-term averages in Helsinki and Lappeenranta (Haapala, 1999; Räisänen et al., 2004).

The increased proportions of Ca-rich particles in PM₁₀ samples indicate that coarse Ca-rich particles were also brought by LRT during the episodes. Their mode and median sizes (geometric diameter) were 2 and 3 μm , respectively. The elemental combinations of Ca-rich particles were investigated with cluster analysis, and typical combinations

Table 3. Number ratio of particles in the Ca-rich particle group and in the Si-Al-rich particle group during episodes (13 August EPI-1, 28 August EPI-2 and 5–6 September 2002 EPI-3) and on reference days (Helsinki 22 August 2002 and Imatra 17 September 2002). We also show mean long-term values of the same ratio calculated from Haapala (1999) and from Räsänen et al. (2004).

Sampling location	EPI-1 Helsinki	EPI-2 Helsinki	EPI-3 Helsinki	EPI-3 Imatra	Reference Helsinki and Imatra	Haapala (1999) ^a Helsinki	Räsänen et al. (2004) ^b Lappeenranta
Number of analysed Ca-rich and Si-Al-rich particles	77	81	91	35	107	700	1270
Ratio of Ca-rich and Si-Al-rich groups (SD)	0.24	0.53	0.45	0.49	0.08	0.07 (0.07)	0.11 (0.07)

^a 18 samples collected between March and April 1998

^b 13 samples collected between March and June 2003; Lappeenranta is a small town located ~35 km southwest of Imatra

were Ca, Ca-S-(Si-Na), Ca-(S-Si-Al) and Ca-Mg-(Si) (minor elements in parentheses). The elemental combinations suggest that major components of Ca-rich particles might have been CaCO₃, CaSO₄ and CaMg(CO₃)₂.

Forest and peat fires were probably one of the major sources of Ca-rich particles during the episodes since Ca-rich particles are emitted from incomplete burning of biomass and most of their mass is in the coarse ($D_p > 1 \mu\text{m}$) size fraction (Allen and Miguel, 1995; Osan et al., 2002; Li et al., 2003; Pagels et al., 2003). Intensive fires also mobilize particles from the surfaces of plants and the ground (Allen and Miguel, 1995; Gaudichet et al., 1995; Pereira et al., 1996). The injection heights of particles from forest fires are in moderate surface fires usually ~2.3 km or less and in intensive crown fires ~5–12 km (Lavoue et al., 2000). The smallest particles of the coarse size fraction may therefore be transported from the wildfire areas to Finland.

Ca-rich particles are also emitted from many other sources, including fossil fuel burning and the cement and metal industries (Hoornaert et al., 1996; Lee and Pacyna, 1999). The trajectories indicated that air masses arrived in Helsinki during EPI-1 and in Imatra during EPI-3 via Estonian and Russian oil-shale-burning industrial areas located in Narva (see Figs. 1 and 3) and Slantsy (~25 km south of Narva). This area is one of the strongest particle sources in Northern Europe (EMEP, 2002), and the Ca content of emissions is high (Häsänen et al., 1997; Jalkanen et al., 2000; Tervahattu et al., 2004). These large emissions occasionally increase particle concentrations, even in southern Finland under suitable meteorological conditions (Jalkanen et al., 2000; Tervahattu et al., 2004). Thus, it is likely that Ca-rich particles may also have been transported from the regions of Narva and Slantsy to Helsinki during EPI-1 and to Imatra during EPI-3.

4 Summary and conclusions

Strong LRT PM_{2.5} episodes occurred on 12–15 August, 26–28 August and 5–6 September 2002 over large areas of Finland. Backward air mass trajectories, satellite detections of fire areas and dispersion modelling results indicate that emissions from wildfires in Russia and other Eastern European countries arrived in Finland during the episodes. The composition of individual particles and agglomerates was studied using scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalyses (EDX), and the bulk chemical concentrations of sulphate (SO₄²⁻), total nitrate (NO₃⁻ + HNO₃(g)) and total ammonium (NH₄⁺ + NH₃(g)) were studied using ion chromatography (IC). SEM/EDX analysis showed that the proportion of S-rich particles and agglomerates (agglomeration was caused partly by the sampling method used) increased strongly during the episodes and that the relative weight percentage (all analyzed elements normalized to 100%) of K was unusually high in these particles. Median S/K ratios, for instance, were clearly lower during EPI-1 (5.5), EPI-2 (5.4) and EPI-3 (6.0) than on reference days (7.8). The high proportion of K indicates emissions from biomass burning. These aerosols were mixed with S-rich emissions from fossil fuel burning during the transport since air masses came through polluted areas of Europe. Minor amounts of coarse Ca-rich particles were also long-range transported during the episodes, and they probably originated from wildfires and/or from Estonian and Russian oil-shale-burning industrial areas. The concentrations of sulphate, total nitrate and total ammonium increased during the episodes, but the ratio of total concentrations of these ions to PM₁₀ concentration decreased. This also confirms the presence of high amounts of particles originating from unusual (the above mentioned) emission sources. The composition of particles during the episodes was compared with an earlier LRT PM_{2.5} episode originating from spring-time agricultural field burning, and the relative fraction of K was lower during the wildfire episodes, probably due to the dominance

of smouldering burning conditions during boreal forest and peat fires.

The particle mass fractions were measured using a 3-stage impactor with a backup filter. Most of the LRT particle mass was in the submicrometre size fraction, and the mass of the submicrometre particles increased on an average by a factor of 3 during the episodes. The particle number size distributions were measured with differential mobility particle sizer (DMPS), and the number concentration of particles 90–500 nm increased by a factor of 1.8 during the episodes, but the concentrations of particles smaller than 90 nm were reduced. The reduction of the smallest particles was caused by suppressed new particle formation due to the small vapour and molecular cluster uptake of LRT particles. These results show how strongly the LRT of particles affect not only the fine particle mass but also the number size distributions of submicron particles. The high values (>1) of accumulation mode to Aitken mode number concentration ratios might be an indicator of different LRT episodes in general because Aitken mode particles can not be transported in the atmosphere as far as accumulation mode particles.

Our results show that the emissions from wildfires in Russian and other Eastern European substantially affected $PM_{2.5}$ concentrations over very large areas, even at distances of over 1000 km from the fire areas. The wildfire season in 2002 was exceptionally severe in Eastern Europe. However, the measurements by fire-monitoring satellites (<http://firemaps.geog.umd.edu>) and NAAPS model results (<http://www.nrlmry.navy.mil/aerosol/>) indicate that smoke from uncontrolled fires (and from agricultural field burning) is generally an important factor in the deterioration of air quality locally and occasionally even regionally in eastern and southern parts of Europe.

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