

Characterization of urban particulate matter for a health-related study in southern Finland

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Particulate matter was physically and chemically characterized in November 2005–May 2006 concurrently with an epidemiological study among cardiac patients in Kotka, Finland. The daily $PM_{2.5}$ concentrations (campaign mean $10.6 \mu g m^{-3}$) typically displayed a similar pattern to that in Helsinki, suggesting that the air masses were well-mixed over a large area of southern Finland. There were occasionally increased short-term $PM_{2.5}$ and particle number concentrations, most likely due to emissions from local industrial sources. A strong relationship was detected between high particle number concentrations ($> 30\,000 cm^{-3}$) and north-easterly winds. $PM_{2.5}$, black carbon (BC) or nitrogen oxides (NO_x) did not show corresponding connection. The mean contribution of local traffic to BC and NO_x were estimated at 30% and 55%, respectively, during the campaign. The main chemical component of $PM_{2.5}$ was particulate organic matter ($37\% \pm 14\%$) followed by non-sea-salt sulphate ($26\% \pm 11\%$), whereas main component of $PM_{2.5-10}$ was soil-derived crustal material ($49\% \pm 11\%$).

Introduction

Epidemiological studies indicate that increased concentrations of atmospheric particles cause adverse health effects in urban populations. Still, it is uncertain which aerosol parameters, such as particle mass, particle number, surface area, particle size, chemical composition or water solubil-

ity, are the best indicators of harmfulness. There seems to be no threshold value for the mass or number concentration of particles in association with health effects. Daily mortality has been estimated to increase by 1% per each $10 \mu g m^{-3}$ increment of fine particles ($PM_{2.5}$; mass of particles smaller than $2.5 \mu m$ in aerodynamic diameter) measured at a central urban background site

(WHO 2005). The mortality estimate doubles and is about six-fold for the same increment as five-day mean and the mean of several years, respectively (Pope and Dockery 2006).

Urban fine particulate aerosol is a mixture that consists of primary particulate matter emitted directly from local sources and of secondary material formed in the atmosphere from gas-phase precursors. The origins of urban $PM_{2.5}$ include local combustion and non-combustion emissions from traffic (Yli-Tuomi *et al.* 2005), small-scale wood combustion (Karvosenoja *et al.* 2008), industrial sources and even vegetation in warm seasons (Szidat *et al.* 2004), as well as mixtures of similar emissions transformed during regional or long-range transport (LRT) of air masses. In Helsinki, Finland, 64%–76% of the atmospheric $PM_{2.5}$ has been estimated to be from LRT (Karppinen *et al.* 2004). One frequent source of LRT in the spring and summer in southern Finland are wildfire emissions typically originating from the Baltic countries, Belarus, Ukraine and western Russia (Niemi *et al.* 2004, 2005, 2009, Sillanpää *et al.* 2005, Saarikoski *et al.* 2007).

Spatial and temporal variations in particle number and mass concentrations, including chemical composition, were investigated at many different urban and rural sites (Putaud *et al.* 2004, Aalto *et al.* 2005, Sillanpää *et al.* 2006, Puustinen *et al.* 2007). However, the combination of health related studies with detailed aerosol measurements, allowing chemical mass closure, are uncommon (Happo *et al.* 2008, Jalava *et al.* 2008). Using receptor modelling in Helsinki, Lanki *et al.* (2006) showed that local traffic and oil combustion are more harmful sources of $PM_{2.5}$ to ischemic heart disease (IHD) patients than LRT or the soil source. Penttinen *et al.* (2006) reported similar results on the source-related effects of $PM_{2.5}$ on the respiratory health of asthmatic subjects in Helsinki.

In the multidisciplinary HIPPU study in Kotka, Finland, different online and offline physical and chemical measurement methods were used in connection to a six-month epidemiological panel and personal exposure study among ischemic heart disease patients and parallel high-volume particulate sampling for a toxicological cell study. This kind of highly integrated,

prospective study has not been done before in Finland and they are rare also elsewhere. However, a multidisciplinary retrospective analysis on urban air pollution and health had previously been made (Ghio 2004). It was well-motivated to investigate urban air particles and health also elsewhere in Finland than in Helsinki, because it is unclear, to what extent the $PM_{2.5}$ and particle number concentrations associated health outcomes in Helsinki, e.g. increased respiratory and stroke mortality (Kettunen *et al.* 2007, Halonen *et al.* 2009) as well as increased hospital emergency room visits for respiratory and cardiac causes (Halonen *et al.* 2008, 2009), could be generalized for other cities in southern Finland. In Helsinki, the local and regional emissions contributing to $PM_{2.5}$ have been estimated to originate mainly from traffic, residential wood combustion and oil combustion (Vallius *et al.* 2003, Saarikoski *et al.* 2008), because industrial emissions are very small, and the energy production and district heating are effectively maintained by large coal- and gas-fuelled plants with efficient emission control.

The principal objective of the present study was to chemically and physically characterize urban air particulate matter in Kotka, which is a city in southern Finland, where the local industries, the commercial harbours, and the transport sector were hypothesized to affect particle properties. A second objective was to compare in simultaneous measurements the contributions of local sources *vs.* regional transport and LRT to the particulate mixture in Kotka and Helsinki. The results from this work will be utilized in the analysis of the contributions of different sources to personal $PM_{2.5}$ exposure, to changes in inflammatory markers in patients' blood circulation, and to the toxicological properties of the urban air particulate samples. The results from the epidemiological and toxicological studies are not presented in this paper.

Material and methods

Sampling site and measurement period

The six-month field campaign was carried out between 14 November 2005 and 12 May 2006

in the city centre of Kotka, Finland (60°28'N, 26°56'E, 25 m a.s.l.) that is located on a small island, called Kotkansaari, on the northern coast of the Gulf of Finland, 130 km east of Helsinki. A transportable station for air quality monitoring and particulate sampling was placed in a central urban background location of Kotkansaari, on a schoolyard surrounded mainly by three-storey apartment buildings at a distance of 15–30 m. The nearest slow traffic road was situated 15 m away from the station. The distance of the major road with inbound traffic into the city was 1000 m west of the station. The sample intakes were about 5–6 m above the level of the nearest street.

The monitoring site was carefully selected to best represent the local environments (e.g. topography, micrometeorology) and local particle sources (e.g. car traffic, residential wood burning, energy plant for district heating, industries, harbours) in the vicinity of the homes of the cardiac patients participating in the six-month epidemiological panel study. All these subjects were living on Kotkansaari within a distance of less than two kilometres from the air-quality monitoring station.

The total particulate emissions from a variety of industrial activities, including energy production, and from traffic in Kotka in 2006 were estimated at 560 and 22 t a⁻¹, respectively (Kotka Environment Centre 2007). The main industrial activities in Kotka were a foundry and factories in connection to the production of paper, pulp, glass and glass fibre. The main point source in the area, a pulp mill, accounting for approximately 70% of the industrial primary particle mass emissions in the city (Kotka Environment Centre 2007), was 3 km north to north-east of the air-quality monitoring station. Other major local sources included the harbour activities. The main port (Mussalo), which is the largest container port in Finland, was in the sector south to south-west of the station at a distance of 4 km. The nearest harbour (City Terminal) was situated about 1 km north-east of the monitoring station. The total amount of goods traffic in all ports of the Kotka area was approximately 9 Mt in 2006. The population in Kotka was about 55 000 (2006).

In order to assess the contribution of the local industry to ambient particles in Kotka, the

campaign data were compared with the data collected in parallel in Helsinki. The monitoring site in Helsinki, SMEAR III station (60°12'N, 24°58'E, 26 m a.s.l.), was located at a distance of about 5 km north-east of Helsinki downtown. A major road with high levels of traffic (60 000 cars day⁻¹) was at a distance of less than 200 m from the station to the east. The estimated total annual particle emissions in Helsinki were in 2006 about 1000 t (Helsinki Metropolitan Area Council 2007). The main sources of the emissions were traffic (28%), energy production (33%), and domestic wood combustion for heating of houses and sauna stoves (29%).

High-time-resolution measurements

In Kotka, the PM_{2.5} mass and particle number concentrations were measured with high-time-resolution by using a β -attenuation particulate matter mass monitor (Eberline FH62-IR, Eberline Instruments Santa Fe, NM, USA) and a condensation particle counter (CPC; TSI Model 3022, Shoreview, MN, USA), respectively. The CPC used in this study could detect particles larger than 20 nm in diameter and the averaging time was one minute. The averaging time for PM_{2.5} measurement was 1 h.

Black carbon (BC) was measured with five-minute time resolution using an aethalometer (AE 42-2-HP-P3, Berkeley, CA, USA) with a flow rate of 16.7 l min⁻¹ (Hansen *et al.* 1982). The aethalometer was equipped with a cyclone removing particles larger than 2.5 μ m (aerodynamic diameter) from the sample air. Black carbon equivalent concentrations were calculated from the light absorption using a coefficient of 16.6 m² g⁻¹.

The NO_x (NO and NO₂) was measured with a chemiluminescence method (AC-30M Environnement S.A, Poissy, France). Data for the meteorological parameters in Kotka such as wind direction and speed, temperature, humidity, and pressure, were recorded in an automatic weather station, which was situated at a distance of 1.5 km south to south-east of the monitoring station. The route of arriving air masses was estimated using the NOAA HYSPLIT backward trajectory model (Draxler and Rolph 2003).

In Helsinki, the $PM_{2.5}$ mass, particle number, NO_x (NO and NO_2), and BC were measured with a tapered element oscillating microbalance (TEOM®, Thermo Fisher Scientific Inc. Waltham, MA, USA), a CPC (TSI Model 3022, Shoreview, MN, USA), a chemiluminescence analyzer (TEI 42S analyzer, Thermo Fisher Scientific Inc. Waltham, MA, USA) and an aethalometer (AE-16, Magee Scientific Company, Berkeley, CA, USA), respectively. The particle number size distribution was measured with twin Differential Mobility Particle Sizer (DMPS 3025 and 3010).

At both sites, the measurement period for NO , NO_2 and particle number concentration covers most of the time between 14 November 2005 and 12 May 2006. The measurement of $PM_{2.5}$ in Kotka and in Helsinki, and of BC in Helsinki started later, i.e. 15 December 2005, 27 January 2006, and 19 March 2006, respectively. The BC measurements in Kotka had a break between 20 January and 19 March 2006 due to technical failure.

Particle sampling

An EPA-WINS sampler (Peters *et al.* 2001) operated at a flow rate of 16.7 l min^{-1} was used to collect 24-h $PM_{2.5}$ samples on a daily basis. The particles were sampled on prewashed (methanol and deionised) polytetrafluoroethylene (PTFE) filters (diameter 47 mm, pore size $3 \mu\text{m}$, type FS, Millipore Ireland B.V., Carrigtwohill, Ireland). The total number of daily samples was 175.

Four-day (from Monday to Friday) Berner low-pressure impactor (BLPI: Berner and Lürzer 1980, Hillamo and Kauppinen 1991) samples were collected in parallel with three virtual impactors (VI; Loo and Cork 1988). The BLPI divides particles into 10 size fractions at a flow rate of 25 l min^{-1} . The aerodynamic 50% cut-off diameters of the BLPI stages are 7.5, 3.5, 1.8, 0.94, 0.53, 0.32, 0.16, 0.093, 0.067, and $0.035 \mu\text{m}$. Aluminium foil greased with Apiezon L vacuum grease was used as a collection substrate in the BLPI. The VI collected particles at a flow rate of 16.7 l min^{-1} in two size ranges: fine ($PM_{2.5}$, particle diameter $< 2.5 \mu\text{m}$) and coarse ($PM_{2.5-10}$, $2.5 \mu\text{m} < \text{particle diameter} < 10 \mu\text{m}$)

particles. The uppermost cut-off of coarse particles in the VI and BLPI was made with a PM_{10} inlet manufactured according to the design of Liu and Pui (1981). For comparison of the data with the $PM_{2.5}$ or $PM_{2.5-10}$ samples from the VI, the BLPI stages 1–7 ($0.035\text{--}1.8 \mu\text{m}$) and 8–10 ($1.8\text{--}10 \mu\text{m}$) were summed up and classified as fine and coarse particles, respectively. The prewashed PTFE filters (same type as in EPA-WINS) were used in two of the VI units whereas the third VI was loaded with two pre-cleaned (heated at 550°C for 4–5 hours) quartz fibre filters ($\varnothing 47 \text{ mm}$, Whatman QMA, Maidstone, UK). One of the VIs had a nylon ($\varnothing 47 \text{ mm}$ Nylasorb, $1.0 \mu\text{m}$, PALL, Ann Arbor, MI, USA) backup filter below the PTFE filter to collect HNO_3 , which is formed when semivolatile NH_4NO_3 collected on the aerosol filter evaporates and decomposes. A total of 78 (3×26) VI samples and 25 BLPI samples were collected.

Sub-micrometer particulate matter samples (particle diameter $< 1 \mu\text{m}$) were collected at the SMEAR-III station in Helsinki using two quartz fibre filters ($\varnothing 47 \text{ mm}$, Whatman Q-MA, Maidstone, UK) in series in a filter cassette system (Pall Life Sciences, Ann Arbor, MI, USA). The four upper stages of the Berner low-pressure impactor (BLPI; Berner and Lürzer 1980) were used to cut off the super-micrometer particles. The flow rate was 80 l min^{-1} . The PM_1 filter samples were collected during 2 February–12 May 2006. The sampling duration was mainly 24 h on working days and 72 h over the weekends. For particle size distribution determination, 14 Micro-orifice uniform deposit impactor (MOUDI: Marple *et al.* 1991, Timonen *et al.* 2008a) measurements were made during February–May 2006. The sampling time was mostly three days and the flow rate was 30 l min^{-1} .

Gravimetric and chemical analyses

The PTFE filters and aluminium foils were weighed on a Mettler M3 microbalance (Mettler Instrumente AG, Zurich, Switzerland) before and after sampling. The filters were allowed to stabilize inside a laminar flow bench for about 30 minutes before weighing. During the measurement period the temperature and relative humid-

ity in the weighing room varied in the range of 23.2 ± 0.6 °C and $18.2\% \pm 8.1\%$, respectively. Electrical discharger (Mettler Toledo, HAUG, Leinfelden-Achterdingen, Germany) and Po-210 (1U400 static master, NRD, Grand Island, NY, USA) radioactive source were used to eliminate electrostatic charges of the filters. The samples were stored in a freezer at -20 °C, until they were chemically analysed.

Organic (OC) and elemental carbon (EC) were analysed from quartz-fibre filters of the VI using a thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc. Tigard, OR, USA). The instrument uses a two-phase thermal method to separate organic and elemental carbon. During heating in the first phase, some of the organic carbon is pyrolysed and not evaporated from the filter. In the second phase, pyrolysed and elemental carbon are oxidized to volatile form. An optical correction was made to separate pyrolysed and elemental carbon (Viidanoja *et al.* 2002). In order to correct for a positive artefact caused by adsorption of gas phase organic material on quartz filters, two filters, one upon the other, were used in sample collection. The particulate organic carbon was calculated by subtracting the backup value (\sim gas phase organics) from the value of the front filter. The uncertainty of the TOA method was estimated to be 5% for OC and 15% for EC in concentrations above the quantification limit.

In addition to high-time-resolution aethalometer measurements, BC was analysed from the 24-h EPA-WINS samples by using a smoke stain reflectometer (SSR, Model M34D, Diffusion Systems, London, UK). The average reflectance of two measurements was converted into an absorption coefficient a by following the guidance in ISO9835 (1993). Finally, the absorption coefficient was converted into black carbon (BC) using the linear calibration equation obtained from a correlation analysis between filter blackness measurements and corresponding aethalometer readings (Hansen *et al.* 1984). Because of a contamination risk during the blackness measurements, only a half of each PTFE filter was used in the SSR measurement. The other half of the filter was used in ion chromatographic analyses.

A quarter or a half of the PTFE filters of EPA-WINS (24-h sample) and of the VI (4-day sample) and of the aluminium foils of the BLPI

(4-day sample) were analysed for selected ions by an ion chromatography (DX500, Dionex Corporation, Sunnyvale, CA, USA). The anions (Cl^- , NO_3^- , SO_4^{2-} , and oxalate) were analysed using an AS11 column and 1–20 mM sodium hydroxide eluent with a flow rate of 1.5 ml min^{-1} . Cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) were analysed using a CS12 column and 20 mM methanesulfonic acid eluent with a flow rate of 1.2 ml min^{-1} . The BLPI samples were extracted with 10 ml of deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA). A piece of a PTFE filter was first wetted with methanol (0.5 ml) to reduce the hydrophobic effect of the filter and then extracted with 9.5 ml of deionised water. Based on the test solutions, the uncertainty of the ion chromatographic analysis was estimated to be 5%–10% depending on the ion to be analysed.

Monosaccharide anhydrides (MAs = sum of levoglucosan, mannosan and galactosan) were analysed using a liquid chromatograph coupled to an ion trap mass spectrometer (LC-MS, Agilent Technologies SL, Santa Clara, CA, USA) (Dye and Yttri 2005). To separate different isomers of the MAs, two columns (Atlantis, 150 mm, Waters, Milford, MA, USA) one after the other were used at 7 °C. The eluent was deionised water (Milli-Q Gradient A10, Millipore, Billerica, MA, USA) with a flow rate of 0.1 ml min^{-1} . An electrospray ionization technique was used and the monitored ion was $m/z = 161$. Before analysis, a piece (1 cm^2) of the exposed quartz filter was extracted with a 2 ml of the mixture of tetrahydrofuran and deionised water (1:1) in ultrasonic bath for 30 min, and then the sample solutions were filtered (IC-Acrodisk 13 mm, $0.45 \mu\text{m}$, PALL, Ann Arbor, MI, USA). The uncertainty of the LC-MS method has been estimated at 20% (Saarikoski *et al.* 2007).

The concentrations of trace elements (Al, As, Br, Ca, Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Si, Sr, Ti, V and Zn) in the 4-day VI samples were determined by using an energy-dispersive X-ray fluorescence method (ED-XRF, Tracor Spectrace 5000: Spolnik *et al.* 2004). The accuracy and precision of this analytical method was estimated to be on the average of 14% and 4%, respectively (Sillanpää *et al.* 2005).

The concentrations of OC, EC, MA and ions were determined from the quartz filters of the

SMEAR-III station, using the analytical methods described above. The blank concentrations of sodium and calcium in the filter material of the PM_{10} samples were too high to allow determination of these ions typically existing mainly in the coarse particulate fraction.

Chemical mass closure

The chemical components of the particulate samples were divided into seven classes: ammonium (NH_4^+), nitrate (NO_3^-), non-sea-salt sulphate ($nss-SO_4^{2-}$), sea salt (SS), soil (SOIL), elemental carbon (EC) and particulate organic matter (POM) (Table 1). $nss-SO_4^{2-}$ and sea salt concentrations were calculated with the help of standard seawater composition (Brewer 1975) and assuming that all the sodium originates from the sea. The latter assumption is not entirely true for fine particles, because sodium is also emitted from some combustion sources. Thus, the value of SS in fine particles may be slightly overestimated. The measured OC concentrations were multiplied by a factor of 1.6 to obtain an estimate for total particulate organic matter (POM) mass concentration (Turpin and Lim 2001). Typical soil-related elements, Si, Al, Fe, Ca and K, appear predominantly as oxides in the atmosphere (Brook *et al.* 1997). The SOIL concentrations were calculated from the results of the ED-XRF-analyses (4-day VI samples).

The time resolution of fine particle mass ($PM_{2.5}$), ions and reflectance (BC) obtained from filter samples was 24 h. The 24-h OC concentration was estimated on the basis of the measured 4-day OC concentrations and 24-h oxalate concentrations. As the Pearson correlation coefficient between OC and oxalate was

very high (0.98, $n = 26$) and oxalate is one of the major compounds in secondary organic aerosol and in biomass combustion smoke, the 24-h OC concentration could be estimated relatively accurately for the chemical mass closure assessment. Daily fine particle SOIL concentrations were simply set equal to the 4-day SOIL results calculated from the trace metal analysis. The daily BC values were calculated from the high-time-resolution aethalometer readings and from the reflectance values of the 24-h EPA-WINS filters. The chemical mass closure of coarse particles was based on the 4-day VI and BLPI sample data.

The chemical mass closure of PM_{10} in Helsinki included ammonium, nitrate, sulphate, EC and POM. The soil and the sea-salt contributions to PM_{10} could not be calculated because of the high blank values of sodium and calcium in quartz filters as compared with the relatively small concentration of these ions in this particulate size range.

Quality control

The $PM_{2.5}$ concentration was measured by an automatic monitor (data calculated as 1-h average values) and using filter methods (24-h average with EPA-WINS and 4-day average with VI), and an approximate $PM_{2.5}$ concentration was obtained by summing up stages 1 to 7 of the BLPI (uppermost cut-off diameter $< 1.8 \mu m$; 4-day average value). The online method was based on β -attenuation and the others were based on gravimetric determinations. The correlation coefficients (0.95–0.98) and slopes (0.875–1.04) for different instruments showed that the $PM_{2.5}$ mass concentrations measured with the different

Table 1. Chemical components used in the mass closure assessment.

Component	Fine particles (24-h)	Coarse particles (4-day)
NH_4^+	$[NH_4^+]$	$[NH_4^+]$
NO_3^-	$[NO_3^-]$	$[NO_3^-]$
$nss-SO_4^{2-}$	$[SO_4^{2-}] - 0.246[Na^+]$	$[SO_4^{2-}] - 0.246[Na^+]$
SS	$3.248[Na^+]$	$3.248[Na^+]$
SOIL	$[Fe_2O_3] + [Al_2O_3] + [SiO_2] + [CaO] + [K_2O]$	$[Fe_2O_3] + [Al_2O_3] + [SiO_2] + [CaO] + [K_2O]$
EC	BC (aethalometer or reflectance)	[EC]
POM (1.6OC) ($\mu g m^{-3}$)	$1.6 \times (33.78[oxalate] + 0.46)$	$1.6[OC]$

techniques were highly comparable with each other. During the wildfire episode between 1 and 5 May 2006, the 4-day filter samples were overloaded, which reduced the flow rate and might have slightly changed the particle cut off diameter for some part of the sampling period.

Corresponding comparisons for the ions determined from the 24-h EPA-WINS and the 4-day VI and BLPI fine particle samples by ion chromatography were made and, with most of the ions, there was a relatively good agreement between the three datasets. For Na^+ , NH_4^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} and oxalate, the Pearson correlation coefficients and the slopes were 0.75–0.98 and 0.66–1.14, respectively. The deviations from each other were due to the sum of uncertainties in sampling, storage and analytical procedure. Fine particle calcium ion concentration seemed to be unreliable to measure. This was most likely due to a variable calcium concentration in blank filters and generally low calcium concentration in fine particulate samples, especially in PM_{10} .

Although there was a good correlation in fine particle nitrate between the three instruments, the backup filter concentration in VI showed that almost half of the nitrate (average 46%) had evaporated from the 4-day PTFE filters during particulate sampling. The 24-h EPA-WINS nitrate concentrations were on average 12% smaller than the total nitrate concentration (front + backup) in the 4-day VI- $\text{PM}_{2.5}$ samples. As the evaporated fine particle nitrate was measured only from the 4-day VI- $\text{PM}_{2.5}$ samples and the evaporation varied substantially (range of backup $\text{NO}_3^-/\text{total NO}_3^-$: 0.15–0.87), these results could not be utilized for the correction of nitrate in each 24-h sample.

The coarse particle sampling with one of the VI units was not operating correctly after maintenance service in the middle of the campaign, and these results had to be discarded. During that period the coarse particle ion concentrations were calculated from the BLPI (stages 8–10). According to comparison between the BLPI- $\text{PM}_{1.8-10}$ and the VI- $\text{PM}_{2.5-10}$ data, the ionic concentrations correlated ($n = 13$) reasonably well with each other. For coarse particle mass, Na^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-} , the Pearson correlation coefficients and the slopes between

the different instruments were 0.85–0.98 and 0.81–1.38, respectively. The correlation was relatively low for ammonium ($r = 0.64$), but its concentration in most coarse particle stages was below quantification level. Other coarse particle constituents (OC, EC and elements) were analysed from the two other VIs.

Due to a technical problem in the aethalometer, the BC data were not available between 20 January and 19 March. During that period the BC concentration was calculated from the smoke stain reflectometer analyses of the 24-h EPA-WINS $\text{PM}_{2.5}$ samples. The Pearson correlation coefficient between the 24-h BC concentrations (aethalometer) and the absorption coefficients (reflectometer) of the 24-h VI- $\text{PM}_{2.5}$ samples was 0.94.

Results and discussion

High-time-resolution measurements

The average concentrations of $\text{PM}_{2.5}$, BC, particle numbers and gaseous NO and NO_2 at the urban background stations in Kotka and Helsinki are summarised in Table 2.

$\text{PM}_{2.5}$ concentration and source apportionment

The average $\text{PM}_{2.5}$ concentration calculated from the 1-h values in Kotka was $10.6 \mu\text{g m}^{-3}$ for the period 15 December 2005–12 May 2006. For comparison, the average $\text{PM}_{2.5}$ value measured with TEOM® in Helsinki (27 January–12 May 2006) was $13.9 \mu\text{g m}^{-3}$ (Table 2). The annual average $\text{PM}_{2.5}$ concentrations in European cities have a 10-fold range ($4\text{--}40 \mu\text{g m}^{-3}$) as reviewed by Putaud *et al.* (2004), who also have shown that Nordic countries have the lowest mass concentrations.

The daily $\text{PM}_{2.5}$ concentrations were roughly on the same level and displayed a similar pattern in Kotka and Helsinki (Fig. 1a), which suggests that regional transport and LRT of well-mixed air masses had major contributions to particulate air pollution in southern Finland. The local sources of fine particles did not seem to have

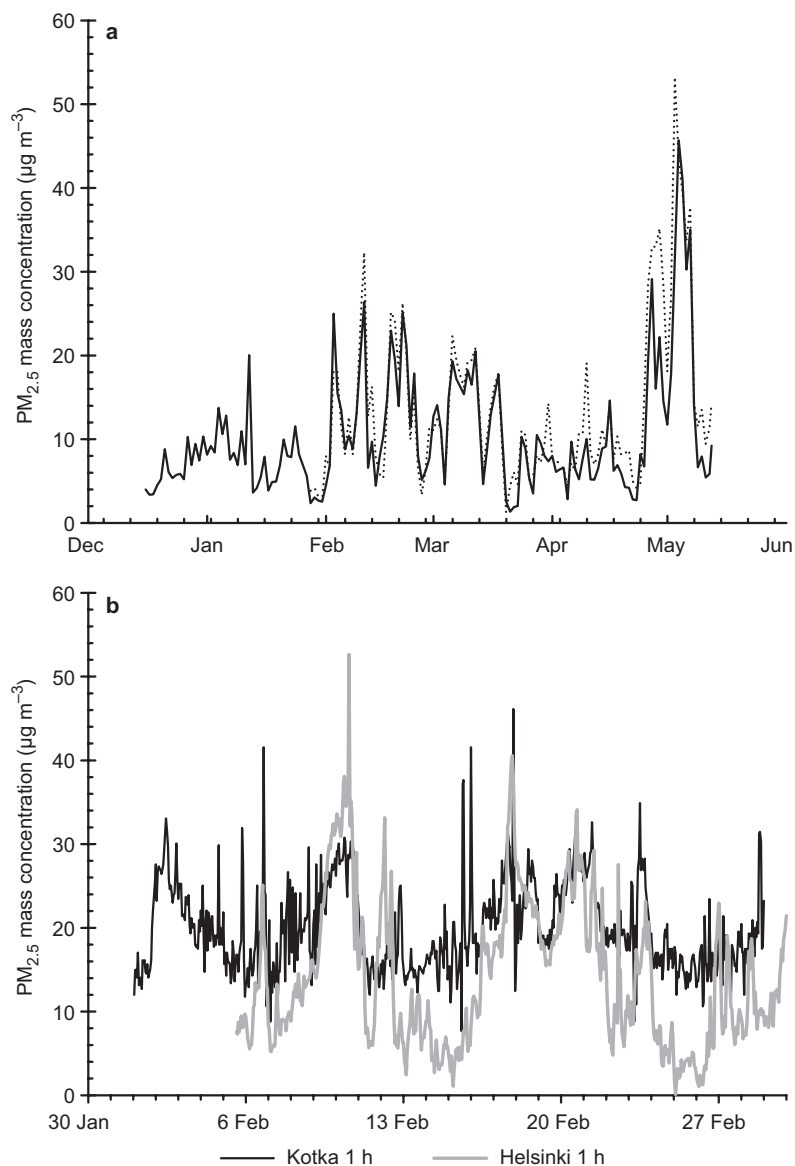


Fig. 1. (a) 24-h average PM_{2.5} concentrations in Kotka and in Helsinki during December 2005–May 2006. (b) An example of rapidly increased PM_{2.5} events during one month in Kotka.

Table 2. The campaign mean values of 1-h average PM_{2.5}, BC, NO and NO₂ ($\mu\text{g m}^{-3}$) and particle number (CPC, cm^{-3}) concentrations in Kotka and in Helsinki during 14 November 2005–12 May 2006 (PM_{2.5} from 15 December 2005). The PM_{2.5} and BC measurements started in Helsinki on 27 January and 19 March 2006, respectively. The values of parallel sampling periods are shown in parentheses. The lower particle size cut off for CPC in Kotka was 20 nm and in Helsinki 10 nm.

Kotka	<i>n</i>	Mean	SD	Helsinki	<i>n</i>	Mean	SD
PM _{2.5}	3531 (2487)	10.6 (11.8)	9.2	PM _{2.5}	2518	13.9 (13.9)	11.1
BC	2530 (1342)	0.75 (0.80)	0.64	BC	1342	1.40 (1.40)	2.05
NO	4802 (3699)	6.2 (6.5)	13.5	NO	3887	9.0 (10.1)	19.3
NO ₂	4713 (3612)	20.2 (21.7)	18.4	NO ₂	3886	26.3 (29.6)	18.0
CPC	3973 (3785)	7062 (6951)	7015	CPC	4097	12819 (12263)	10872

any remarkably different influences on the daily $PM_{2.5}$ concentrations in the two cities, but some short-lasting impacts differing from each other were found in the 1-h concentration (Fig. 1b). This good general agreement between the Kotka and Helsinki data is likely due to the fact, that both of the monitoring sites are located on the coast of the Gulf of Finland, and had obviously very similar diurnal mixing conditions.

In Kotka, the diurnal cycle of $PM_{2.5}$ was rather flat (not shown), which suggests LRT dominance over the local sources of fine particle emissions. Long lasting (> 24 h), elevated $PM_{2.5}$ concentrations ($\geq 20 \mu g m^{-3}$) were detected mostly when air masses, as estimated by backward trajectories (NOAA HYSPLIT MODEL), were coming from the Baltic countries, Belarus, Ukraine, Russia and other countries in eastern Europe.

Biomass combustion aerosol, originating from small-scale wood heaters of households, may be regionally significant in Finland especially during cold seasons (Saarikoski *et al.* 2008). The contribution of biomass burning to $PM_{2.5}$ in Kotka was derived from other studies. According to Puxbaum *et al.* (2007), the ratio of biomass combustion OC to levoglucosan varies a lot depending on the type of wood used and on the burning conditions. In this study, two ratios, 9.2 and 9.8, were used, as they are derived from a recent field measurement in Helsinki (Saarikoski *et al.* 2008) and from a recent laboratory study on the flue gas of a small masonry heater (Frey *et al.* 2009), respectively. Masonry heaters are commonly used as a secondary heating source in Finnish homes situating in urban areas. The ratio from the laboratory study was calculated from a combination of results, where total combustion consists of 75% normal and 25% smouldering combustion. The used ratios of biomass combustion OC to levoglucosan were assumed to be the most suitable ones for Finnish urban environments, but as a large range of values (1.9–23.5) has been presented in the literature (Puxbaum *et al.* 2007), the uncertainty in the current estimation may be large.

Our rough estimate showed that, in Kotka, approximately one quarter of the urban air POM originated from biomass burning, which equals 8%–9% (range 2%–18%) of the $PM_{2.5}$ mass. The estimation was done from 4-day VI- $PM_{2.5}$

samples collected during weekdays. The contribution of biomass burning to urban $PM_{2.5}$ may be even higher during weekends, when people spend more time at home and use more often their masonry heaters and sauna stoves. The wildfire episode originating from western Russia in the spring 2006 was excluded from this calculation.

As discussed earlier, the local emissions may have had only occasionally some temporary effects on the $PM_{2.5}$ concentration in Kotka. The maximal local contribution was estimated from cases ($n = 7$), where the $PM_{2.5}$ concentration increased rapidly in Kotka but was not elevated in Helsinki. The highest $PM_{2.5}$ concentration during such event was compared with the concentration preceding the event. Only cases, where this preceding $PM_{2.5}$ concentration was below the campaign mean, were processed. The local contribution to the $PM_{2.5}$ concentration during the events was estimated to be 65%–80%. No common factors such as wind direction or wind speed, or elevated NO_x , BC or particle number concentration were found to appear in parallel to these events.

Particle number concentrations

The particle number concentrations above 20 nm in size varied between 300 and 49 000 cm^{-3} in Kotka and the mean concentration was approximately 7000 cm^{-3} (Table 2). In urban background sites all over Europe, daily mean particle number concentrations ranging between 10^4 and 6×10^4 cm^{-3} have been recorded (Paatero *et al.* 2005). The particle numbers have a strongly inverse relationship with the distance to the nearest road with busy traffic (Pakkanen *et al.* 2006, Puustinen *et al.* 2007).

The difference between the number concentrations in Kotka and in Helsinki (Table 2) was at least partly due to the different cut-off size (Kotka 20 nm, Helsinki 10 nm), as the particle number size distribution data in Helsinki showed that on average 45% of the particles were below 20 nm in size and 33% of them were between 7 and 20 nm. According to Laakso *et al.* (2003), approximately 50% of the particles (size range 10–400 nm) in an urban background area of Helsinki in 1999–2001 were detected in the

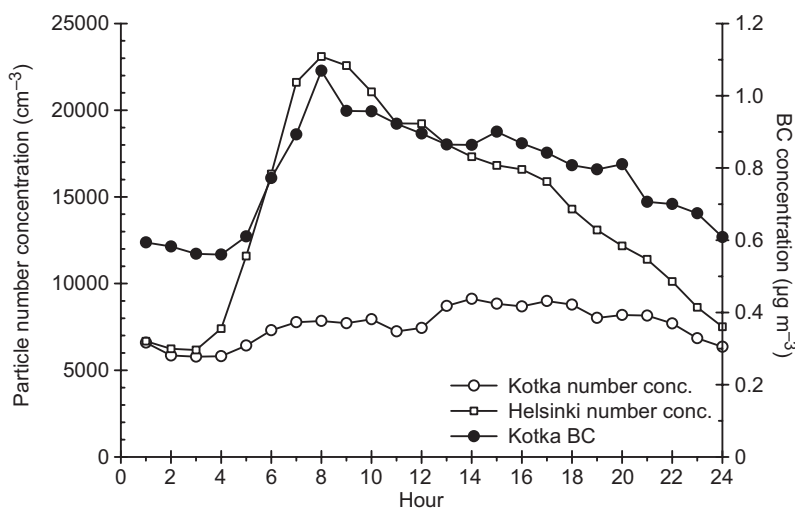


Fig. 2. Diurnal pattern of 1-h average black carbon (BC) ($\mu\text{g m}^{-3}$) and particle number (cm^{-3}) concentrations during weekdays in Kotka and in Helsinki during 14 November 2005–12 May 2006. The lower cut-off size of particles in Kotka was 20 nm and in Helsinki 10 nm.

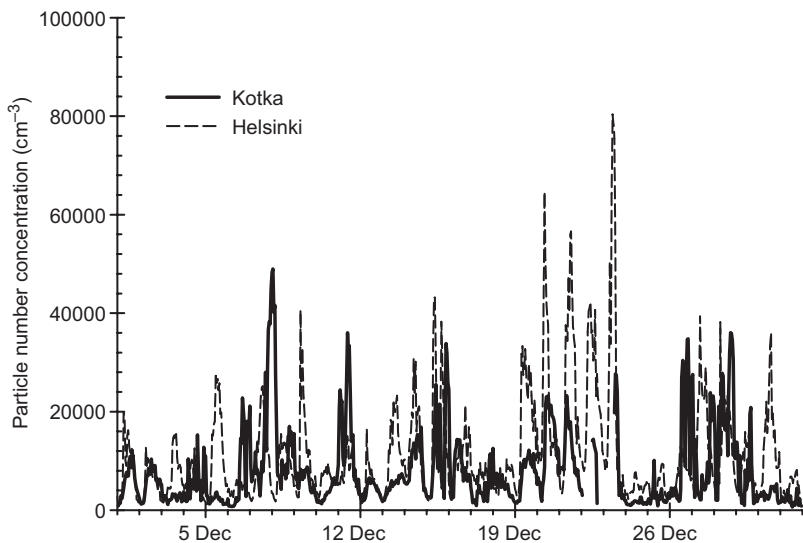
nucleation mode (10–25 nm). As car engines are an important source of the nucleation mode and also Aitken mode (30–90 nm) particles (Laakso *et al.* 2003), some of the traffic-related particles may not have been detected in Kotka. On the other hand, the centre of Kotka had generally much less traffic in vicinity to the monitoring site than the site in Helsinki.

The contribution of traffic to particle number concentration was studied in relation to diurnal variation. It turned out that the diurnal variation in Kotka was almost insignificant. The ratio of the highest diurnal mean value to the lowest diurnal mean value was only 1.3 during weekdays, while it was nearly 4 in Helsinki. The mean ratio in Helsinki lowered to approximately to 3, if particles below 20 nm were excluded, but still the diurnal variation clearly existed. Simultaneous measurement in the urban background station in Helsinki (SMEAR III) displayed a clear diurnal variation that followed the rush hours in traffic with the highest number concentrations between 07:00 and 09:00 (Fig. 2). A significant correlation of the diurnal variation in particle number with the traffic intensity was also detected in other urban sites (Morawska *et al.* 2002, Tuch *et al.* 2003, Ketzel *et al.* 2004, Stanier *et al.* 2004). One possible reason, why there was no obvious diurnal variation in particle number concentration in Kotka, is that the nucleation mode particles were not measured. On the other hand, other local sources may have played an important role in ultrafine particle emissions.

Other than traffic-related sources for particle number were studied from the cases, where air-pollution events were detected in Kotka but not in Helsinki. The limit concentration for a source event was chosen to be $18\,500\text{ cm}^{-3}$, which was twice the standard deviation plus the median concentration (Ziemba *et al.* 2006). Another criterion was that the event should last at least two or more hours. A set of 6–10 events, which fulfilled the criteria, were detected in December 2005 (Fig. 3). These events probably indicated a local emission source other than usual traffic and/or weather conditions with limited atmospheric mixing. It was expected that a local source would also increase black carbon and/or NO_x concentration, but there was no significant correlation of particle number concentration with BC or NO_x . Correspondingly, there were also no significant correlations with meteorological parameters such as temperature, relative humidity, wind speed or wind direction.

The association of 1-h average particle number concentration with the wind direction (N, NE, E, SE, S, SW, W and NW) was also investigated to estimate the influence of point sources such as factories or power plants (Table 3). The clearest correlation was detected between particle number concentrations over $30\,000\text{ cm}^{-3}$ and north-easterly winds. 70% of these elevated concentrations were measured when the wind was blowing from the north-east. The $\text{PM}_{2.5}$, NO_x or BC concentrations did not correlate with the highly elevated particle number concentrations.

Fig. 3. One-hour average particle number concentrations (cm^{-3}) in Kotka and in Helsinki during December 2005.



Also particle number concentrations above the daily mean ($10\,000\text{ cm}^{-3}$) were detected more frequently during northerly, north-easterly and easterly winds. Only few cases with particle number concentration over $20\,000\text{ cm}^{-3}$ were detected for wind direction from the south to the north-west.

The main local point source of industrial particle emissions, a sulphate pulp mill, was located 3 km north to north-east of the station. A more precise wind direction analysis showed that the pulp mill was not exactly in the location, wherefrom the highest particle number concentrations seemed to transport (wind direction 52.5° – 67.5°). There were two other sulphate pulp mills, one located 1.5 km and the other 13 km from the site in a sector of 45° – 90° . It

should be noticed that the wind direction and the particle measurements were not conducted at the same site, which means that small differences in wind direction may have occurred between the two sites.

Black carbon and NO_x concentrations

The main source of atmospheric BC in cities is fossil fuel combustion, especially combustion in diesel engines. BC consists of elemental carbon (EC) and highly polymerized organic matter. In many European cities, BC is strongly related to traffic and it is among the most important contributors to both $\text{PM}_{2.5}$ and PM_{10} (Pakkanen

Table 3. Numbers of cases (n) for selected particle number concentrations (cm^{-3}) in wind direction categories in Kotka. The calm weather conditions (wind speed below 1 m s^{-1}) accounted below 3% of the data and were included into calculations.

Wind direction	Particle number concentrations (cm^{-3})				Total n
	< 10000	10000–20000	20000–30000	> 30000	
N	187	75	21	1	284
NE	307	155	86	52	600
E	450	193	58	12	713
SE	286	50	22	8	366
S	315	24	6	0	345
SW	512	8	2	0	522
W	582	26	0	0	608
NW	470	65	1	0	536

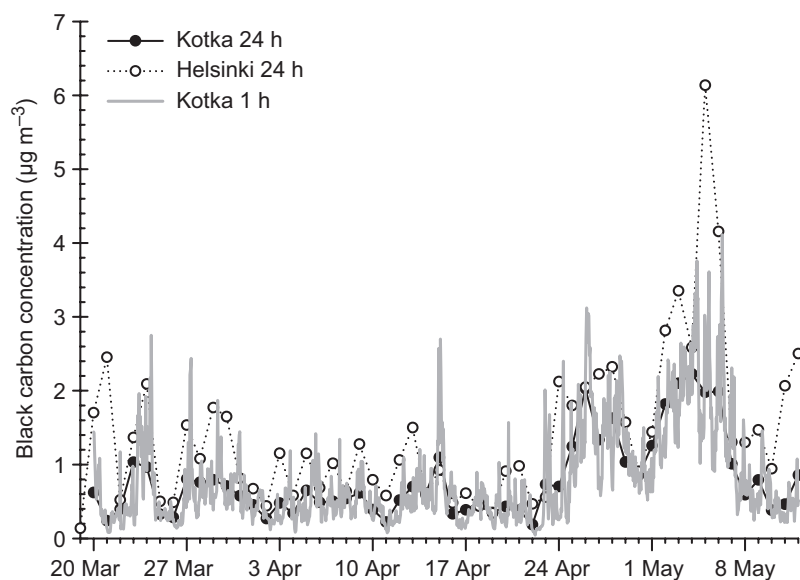


Fig. 4. Black carbon (BC) concentrations ($\mu\text{g m}^{-3}$) in Kotka and in Helsinki during 20 March–12 May 2006.

et al. 2000). In Kotka, the EC concentrations (4-day filter samples) and the BC concentrations (aethalometer and 24-h filter samples) correlated highly with each other (Pearson correlation coefficients 0.97 and 0.89, respectively). The campaign mean EC-to-BC ratio was 0.95. BC was moderately correlated with $\text{PM}_{2.5}$ ($r = 0.73$), while the correlation coefficients were smaller (range 0.37–0.66) with the other air quality parameters (NO , NO_2 and number concentration) measured on-line. A clear correlation was occasionally detected between the BC and the particle number concentrations, and between the BC and NO_x concentrations, indicating a common local source such as traffic.

The difference between the higher daytime average concentrations and the lower nighttime average concentrations in Kotka was not large (Fig. 2), which implies the influence of several BC sources. The 24-h-averaged time trends in BC in Helsinki and Kotka were occasionally similar to each other, indicating similar mixing conditions of local air pollution or some common fine particle sources in regional transport or LRT of air pollution (Fig. 4). Pakkanen *et al.* (2000) estimated that the long-range transported BC is on average about $0.4 \mu\text{g m}^{-3}$, which is assumed to represent the average regional background over southern Finland. A rough estimate can be done by assuming that the lowest diurnal value

in Kotka represents the background value with a minimal influence of local traffic and other local sources. In this study, the lowest value was $0.56 \mu\text{g m}^{-3}$ at 02:00 (all days included), which is consistent with the value reported by Pakkanen *et al.* (2000) before subtracting the estimated values of night time traffic and local sources (other than traffic). By subtracting the background concentration, which includes some night time traffic, from the campaign mean value, the contribution of local traffic to BC in Kotka can be estimated at about 30%.

The local traffic influence on BC concentrations was supported by the observations on NO and NO_2 , both showing clear diurnal variation. The highest NO_2 concentrations were detected during rush hours, and the morning values were generally higher than the afternoon values. NO was peaking one hour later and high concentrations were lasting longer. Subtraction of the minimum diurnal values from the campaign mean concentration, as done with BC, showed that contributions of local traffic to NO and NO_2 were approximately 60% and 50%, respectively.

Chemical mass closure

The chemical mass closures for 24-h $\text{PM}_{2.5}$ (campaign mean $9.7 \pm 6.6 \mu\text{g m}^{-3}$) and 4-day $\text{PM}_{2.5-10}$

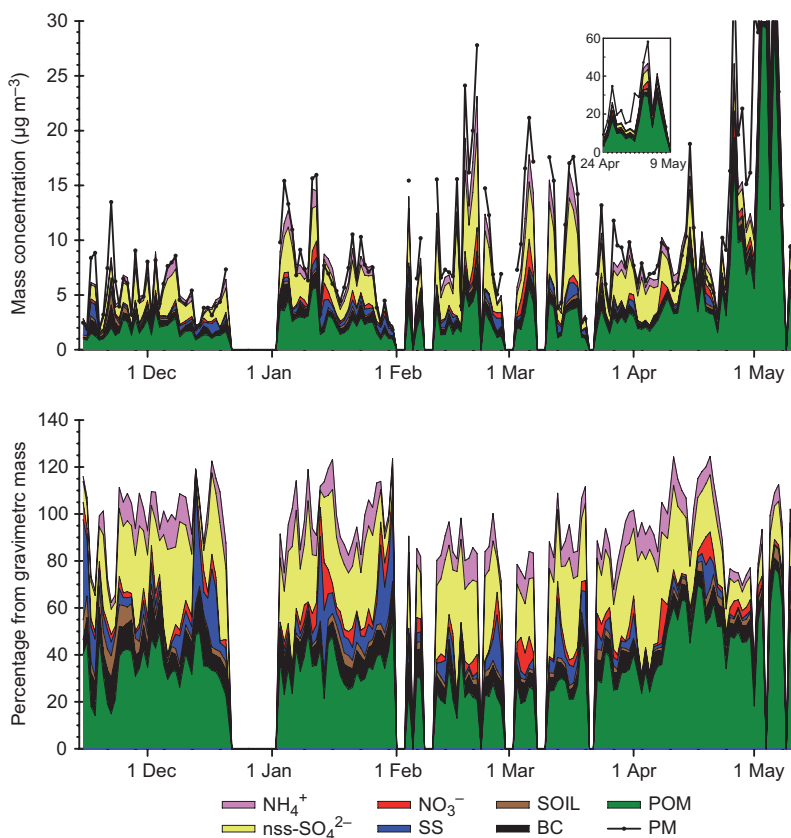


Fig. 5. Chemical mass closure of fine ($\text{PM}_{2.5}$) particle concentrations and the relative contribution (%) of different mass components in Kotka during 14 November 2005–12 May 2006. The sampling time was 24 h for $\text{PM}_{2.5}$.

(campaign mean $4.2 \pm 4.0 \mu\text{g m}^{-3}$) are summarised in Figs. 5 and 6, respectively. The identified aerosol components accounted on average for $95\% \pm 14\%$ of the $\text{PM}_{2.5}$ mass and $89\% \pm 21\%$ of the $\text{PM}_{2.5-10}$ mass.

Carbonaceous compounds

The 24-h POM was over half of the time, i.e. in 63% of the samples, the largest component of fine particles in Kotka and correlated highly with $\text{PM}_{2.5}$ concentration ($r = 0.86$). The average contribution of POM to $\text{PM}_{2.5}$ mass was $37\% \pm 14\%$. The POM concentration varied between 0.9 and $29.6 \mu\text{g m}^{-3}$ (average $3.6 \pm 4.1 \mu\text{g m}^{-3}$). The POM concentrations were typically below $9 \mu\text{g m}^{-3}$, except during the wildfire episode in spring 2006 (Fig. 5). Similar values (POM $1.0\text{--}25.1 \mu\text{g m}^{-3}$, 72-h PM_1 samples) were measured in Helsinki in spring 2006 (Timonen *et al.* 2008b). POM was also for 76% of the time the largest component

of PM_1 in December 2005–May 2006 in Helsinki. Diacids, mainly oxalic acid, and levoglucosan each comprised approximately 2% of POM (range 0.2%–3.5%) in Kotka.

The campaign mean BC contribution to $\text{PM}_{2.5}$ mass was $8\% \pm 3\%$ in 24-h sampling (Fig. 5). The contribution of BC to $\text{PM}_{2.5}$ with 1-h time resolution in Kotka varied from 1% to 64% (average 9%). The BC and $\text{PM}_{2.5}$ ratios with 1-h time resolution were calculated only for $\text{PM}_{2.5}$ values over $2 \mu\text{g m}^{-3}$. Values below that were considered as inaccurate. The highest ratios (over 20%) were measured mostly at $\text{PM}_{2.5}$ concentrations lower than the campaign mean, referring to local BC emissions and to limited mixing conditions. During LRT events both the $\text{PM}_{2.5}$ and the BC concentrations were increased.

The campaign mean of daily EC-to-POM ratios for $\text{PM}_{2.5}$ (0.27 ± 0.16) in Kotka was close to a typical value measured in urban background stations (Viana *et al.* 2006). The average contributions and concentrations of POM and EC

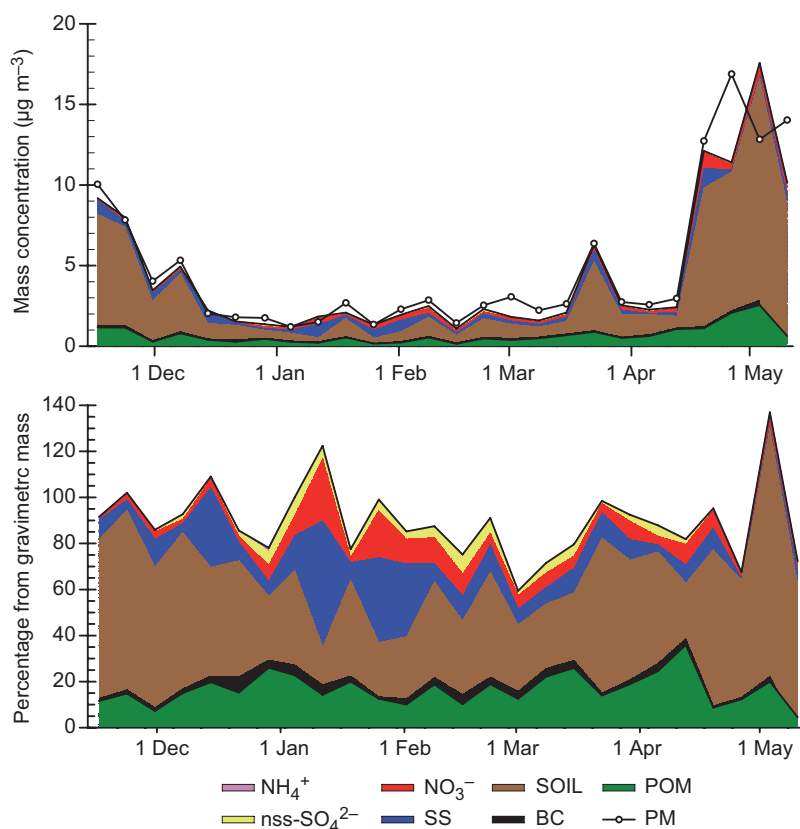


Fig. 6. Chemical mass closure of coarse ($PM_{2.5-10}$) particle concentrations and the relative contributions (%) of different mass components in Kotka during 14 November 2005–12 May 2006. The sampling time was 4 days for $PM_{2.5-10}$.

to coarse particle mass were $16\% \pm 6\%$ and $0.70 \pm 0.60 \mu\text{g m}^{-3}$ and $2\% \pm 1\%$ and $0.09 \pm 0.01 \mu\text{g m}^{-3}$, respectively.

Secondary inorganic compounds

The nss-SO_4^{2-} ($26\% \pm 11\%$) was a dominant secondary inorganic ion in $PM_{2.5}$ followed by ammonium ($8\% \pm 3\%$) and nitrate ($4\% \pm 3\%$) (Fig. 5). The mean 24-h average concentrations with standard deviations for nss-SO_4^{2-} , ammonium and nitrate were 2.4 ± 1.7 , 0.80 ± 0.63 and $0.40 \pm 0.47 \mu\text{g m}^{-3}$, respectively. In approximately 40% of the measurements, the contribution of nss-SO_4^{2-} to $PM_{2.5}$ mass was larger than that of POM. In Helsinki, the corresponding value was 30% in PM_{10} .

Equivalent concentrations of NH_4^+ and nss-SO_4^{2-} in Kotka showed equal amounts indicating that they were in the form of $(\text{NH}_4)_2\text{SO}_4$. The amount of NH_4NO_3 seemed to be very low, as no excess NH_4^+ was left after $(\text{NH}_4)_2\text{SO}_4$ formation.

However, some of the NH_4NO_3 may have evaporated during sample collection. The amount of evaporated nitrate was not measured for the 24-h samples. The ion charge equivalent ratio of analysed anions to cations was around unity (1.10 ± 0.22) indicating that the fine particles were close to neutral or slightly acidic.

The total contribution of secondary ions to 4-day $PM_{2.5-10}$ mass was $9\% \pm 6\%$, nitrate being the largest ($6\% \pm 1\%$) component, followed by nss-SO_4^{2-} ($3\% \pm 1\%$) (Fig. 6). The 4-day mean concentrations with standard deviations of nitrate and nss-SO_4^{2-} were 0.23 ± 0.20 and $0.11 \pm 0.03 \mu\text{g m}^{-3}$, respectively. The NH_4 concentrations were almost negligible. The equivalent calculation suggested that nitrate was mostly in the form of NaNO_3 .

Sea salt and soil material

Sea salt (SS) ($0.45 \pm 0.36 \mu\text{g m}^{-3}$) had mostly a moderate contribution to 24-h $PM_{2.5}$ ($7\% \pm 9\%$),

but occasionally there were days when the contribution was 20%–49% of the $PM_{2.5}$ mass (Fig. 5). During these events, the $PM_{2.5}$ concentrations ($1.8\text{--}7.8\ \mu\text{g m}^{-3}$) were below the average and the SS concentrations were twice ($0.96 \pm 0.42\ \mu\text{g m}^{-3}$) as high as the mean SS. According to backward trajectories, the air masses were coming mostly from the clean arctic areas such as the Norwegian or Arctic Seas. Some overestimation may be involved in these high contributions, because of the assumption that all the sodium is coming from the sea. A minor fraction of fine particulate sodium may also be emitted by combustion processes. However, the 4-day size distribution measurements showed that only a very small fraction of sodium was in the ultrafine size-range (Table 4), where combustion-related sodium particles are typically found. Also the number concentrations of particles or NO_x concentrations were not elevated during these days, as it would be expected if sodium originated from local pulp mills. The elevated sodium concentration may be partly explained by resuspended road salt that is spread over the main routes to prevent frost and ice forming on the road surface. On average, 70% of the sodium was in particles over $0.94\ \mu\text{m}$ in size (stages 7–10).

The mean SS contribution to 4-day $PM_{2.5-10}$ was 12%, but the range was wide (1%–44%) (Fig. 6). The SS concentrations in $PM_{2.5-10}$ varied between 0.08 and $1.21\ \mu\text{g m}^{-3}$ ($0.39 \pm 0.30\ \mu\text{g m}^{-3}$). Soil-derived material accounted for $3\% \pm 2\%$ and $49\% \pm 19\%$ of the $PM_{2.5}$ and $PM_{2.5-10}$ mass, respectively (Figs. 5 and 6). The

mean concentrations with standard deviation for soil material in fine and coarse particles were 0.34 ± 0.27 and $2.95 \pm 3.61\ \mu\text{g m}^{-3}$, respectively.

Trace metals

Trace metals, excluding the soil-related compounds, accounted together for less than 1% of the 4-day $PM_{2.5}$ and $PM_{2.5-10}$ mass. The average concentrations of Zn ($14 \pm 13\ \text{ng m}^{-3}$), V ($5.3 \pm 2.7\ \text{ng m}^{-3}$), Mn ($2.7 \pm 1.5\ \text{ng m}^{-3}$) and Pb ($5.5 \pm 3.3\ \text{ng m}^{-3}$) in $PM_{2.5}$ in Kotka were comparable to those reported by Pakkanen *et al.* (2001) for Helsinki. The concentrations of some other interesting species such as As, Cu and Ni were mainly below the quantification limit. Because of the long sampling time, no detailed source analysis was done.

Size distribution of PM mass and ions

The size distribution of particulate mass and ion content was categorized into three size classes: $0.035\text{--}0.16\ \mu\text{m}$, $0.16\text{--}1.8\ \mu\text{m}$ and $1.8\text{--}10\ \mu\text{m}$, which roughly represented the ultrafine, accumulation and coarse particles. The corresponding impactor stages were 1–3, 4–7 and 8–10. On the average, most of the mass was in the size range of $0.16\text{--}1.8\ \mu\text{m}$ ($59\% \pm 14\%$). The ultrafine and coarse particles had on average $10\% \pm 4\%$ and $31\% \pm 16\%$ of the mass, respectively. The main ions in ultrafine and accu-

Table 4. Size-segregated average (\pm SD) masses and ion concentrations (ng m^{-3}) and their relative contributions (%) in different size fractions of PM_{10} in Kotka ($n = 25$). D_p refers to particle diameter.

Component	Ultrafine $D_p < 0.16\ \mu\text{m}$ concentration ng m^{-3}	Accumulation $0.16 < D_p < 1.8\ \mu\text{m}$ concentration ng m^{-3}	Coarse $D_p > 1.8\ \mu\text{m}$ concentration ng m^{-3}	Ultrafine $D_p < 0.16\ \mu\text{m}$ contribution (%) to mass conc.	Accumulation $0.16 < D_p < 1.8\ \mu\text{m}$ contribution (%) to mass conc.	Coarse $D_p > 1.8\ \mu\text{m}$ contribution (%) to mass conc.
PM	1600 ± 1100	9600 ± 6700	5000 ± 3800	10 ± 4	59 ± 14	31 ± 16
SO_4^{2-}	201 ± 136	2435 ± 1847	120 ± 56	13 ± 6	27 ± 11	4 ± 3
NO_3^-	69 ± 72	478 ± 566	240 ± 206	4 ± 2	5 ± 3	6 ± 5
Cl^-	5 ± 2	37 ± 40	118 ± 113	0.4 ± 0.2	0.6 ± 1.1	3 ± 4
NH_4^+	84 ± 63	783 ± 554	10 ± 10	5 ± 2	8 ± 3	0.3 ± 0.2
Na^+	5 ± 4	124 ± 64	123 ± 92	0.4 ± 0.3	2 ± 2	4 ± 3
K^+	11 ± 9	81 ± 57	14 ± 9	0.7 ± 0.2	0.9 ± 0.3	0.3 ± 0.2
Mg^{2+}	1 ± 1	10 ± 5	16 ± 11	0.1 ± 0.1	0.1 ± 0.1	0.5 ± 0.4
Ca^{2+}	1 ± 1	26 ± 14	97 ± 68	0.1 ± 0.1	0.3 ± 0.1	2 ± 1

mulation particles were sulphate, followed by ammonium and nitrate (Table 4). Corresponding average values were measured with Micro-orifice uniform deposit impactor (MOUDI, Marple *et al.* 1991) in Helsinki during February–May, 2006 ($n = 14$). Sulphate, ammonium and nitrate covered $20\% \pm 11\%$, $9\% \pm 4\%$ and $6\% \pm 5\%$ from the mass in accumulation mode and $12\% \pm 7\%$, $7\% \pm 2\%$ and $4\% \pm 3\%$ in the ultrafine mode, respectively. The contribution of sulphate to particle mass in accumulation mode was higher in Kotka ($27\% \pm 11\%$) than in Helsinki ($20\% \pm 11\%$). However, the average mass concentrations of sulphate in Kotka ($2.4 \mu\text{g m}^{-3}$) and in Helsinki ($2.1 \mu\text{g m}^{-3}$) were about same in this particle size range. The difference in the ratio of sulphate to mass in accumulation particles was mainly due to the lower POM concentration in Kotka as compared with that in Helsinki.

Nitrate was most frequently the main water-soluble coarse particle component followed by sulphate and chloride. These three ions accounted together for 13% of the coarse particle mass. According to VI-samples ($\text{PM}_{2.5-10}$), half of the coarse mass was soil-related material. There were no major differences in the chemical components of coarse mode particles between Kotka and Helsinki.

Wildfire episode

The biomass smoke episode observed in April and May 2006 was exceptionally long compared to episodes in other recent years (Niemi *et al.* 2009), lasting for about 12 days (25 April–7 May). The wildfire episode increased substantially the mean spring (March–May) $\text{PM}_{2.5}$ concentration that was $11.8 \mu\text{g m}^{-3}$ with and $8.8 \mu\text{g m}^{-3}$ without the episode. The two highest 1-h $\text{PM}_{2.5}$ concentrations (4 May at 06:00 and 6 May at 07:00) were almost $90 \mu\text{g m}^{-3}$ and the highest 24-h value (3–4 May) was almost $60 \mu\text{g m}^{-3}$. The contribution of POM to $\text{PM}_{2.5}$ mass varied between 45% and 77% (average 56%) during the smoke episode, while the campaign mean contribution was slightly below 40%, when all the samples were included. This indicates that the POM concentrations increased substantially during the biomass smoke episode.

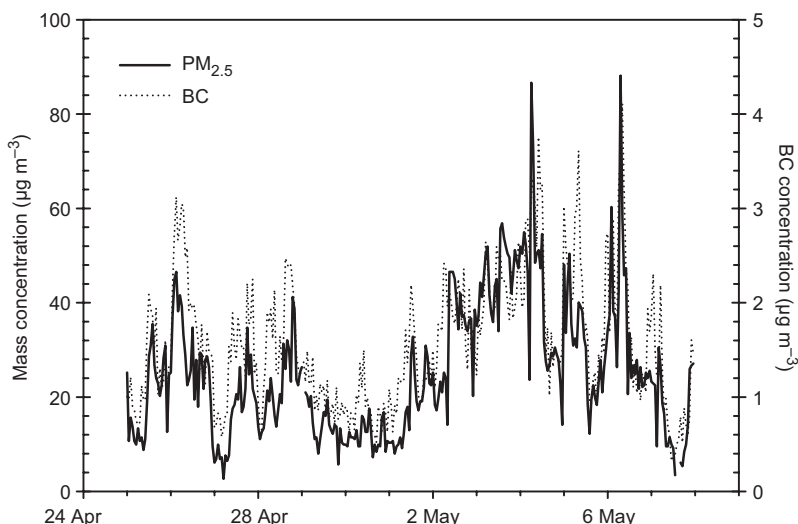
The concentrations of typical biomass combustion markers, levoglucosan and potassium, during the smoke episode were approximately three-fold, and that of oxalate over five-fold as compared with their campaign mean values. Potassium and oxalate have also other sources than biomass combustion, but when appearing together with increased levoglucosan concentration they are likely to originate from this source (Sillanpää *et al.* 2005). The BC concentration was 2-fold the campaign mean value during the episode, and the concentration time trend followed very closely that of $\text{PM}_{2.5}$ (Fig. 7). Also NO_2 had a somewhat similar trend to that of BC, but there was no significant correlation between NO and BC. The same wildfire smoke episode affected also Helsinki, where real-time chemical composition measurements and dispersion modelling were conducted by Saarikoski *et al.* (2007).

Summary and conclusions

This work is part of the HIPPU project, which contained central site ambient aerosol measurements in an industrial city of Kotka in southern Finland, together with simultaneous monitoring of personal air-pollution exposure and resultant systemic inflammation and cardiac effects in ischemic heart disease patients. The paper presents results from a 6-month field campaign with on-line ($\text{PM}_{2.5}$, BC, particle number, NO_2 and NO) aerosol measurements and off-line chemical characterization (mass, water-soluble ions, elemental carbon, organic carbon, trace metals, levoglucosan and reflectance). Comparison with simultaneous aerosol measurement data in Helsinki was made to assess the importance of regional emissions and long-range transport (LRT) of particulate pollution in relation to different local sources such as traffic, small-scale biomass combustion, industries, power and heat production, and harbours.

The campaign mean $\text{PM}_{2.5}$ concentration in Kotka was $10.6 \mu\text{g m}^{-3}$ and the main chemical component was particulate organic matter (POM: $1.6 \times$ organic carbon; $37\% \pm 14\%$), followed by non-sea-salt sulphate ($26\% \pm 11\%$). The main component of $\text{PM}_{2.5-10}$ mass (mean concentration $4.2 \mu\text{g m}^{-3}$) was soil-related mineral compounds

Fig. 7. $\text{PM}_{2.5}$ mass and black carbon (BC) concentrations in Kotka during the wildfire episode in spring 2006.



($49\% \pm 19\%$). Half of the PM_{10} mass was in the accumulation mode. During a spring episode of transnational wildfire smoke the concentrations of $\text{PM}_{2.5}$, POM, BC and typical biomass combustion tracers such as levoglucosan, potassium and oxalate were highly increased. At the same time, there was the maximal appearance of spring road-dust in $\text{PM}_{2.5-10}$.

Typical traffic-related measures such as particle number and black carbon (BC) concentrations showed that local traffic was occasionally but not continuously their major source. The contribution of local traffic to BC was estimated to be 30%, while those to NO and NO_2 were higher, 60% and 50%, respectively. In addition to traffic, the other typical particulate source in high latitude urban areas is small-scale biomass combustion. A quarter of POM was estimated to originate from biomass use, which equals to 8%–9% of the $\text{PM}_{2.5}$ mass.

High particle number concentrations (over $30\,000\text{ cm}^{-3}$) without $\text{PM}_{2.5}$, NO_x or BC involvement were clearly correlated with north-easterly winds, but no single source or explanation to that phenomenon could be identified. Several local point sources, including several large sulphate pulp mills, were located in that specific direction.

When compared with that in Helsinki, the mean $\text{PM}_{2.5}$ concentration during simultaneous measurements was 15% lower in Kotka, while the corresponding differences in mean BC, NO and NO_2 concentrations were –43%, –36% and

–27%, respectively. The 24-h average $\text{PM}_{2.5}$ concentrations showed similar patterns of variation in both cities, but the hourly $\text{PM}_{2.5}$ concentrations varied much less in Kotka. The variations in BC concentrations differed from each other in the two cities. In addition, the particle number concentrations did not show a clear diurnal variation in Kotka like they did in Helsinki.

Thus, LRT and regional emissions were the dominant sources of $\text{PM}_{2.5}$ in Kotka, although industrial activities (paper and pulp mills), power plants and busy harbours were located in the city, some of them even in vicinity to the sampling site. As LRT was the major source of $\text{PM}_{2.5}$ in Kotka, it will be possible to analyze the health effects related to this source in the patients of the concurrent health study more clearly than in Helsinki, where local traffic has always been a much more prominent source than presently in Kotka. Moreover, the effects on health of different LRT aerosol compositions can also be investigated, as there was a 12-day-long episode of transnational wildfire smoke during the present field campaign. The central suburban site of air quality monitoring and particulate sampling was highly representative of the local environments (e.g. topography, micrometeorology) and local particle sources (car traffic, residential wood burning, energy plant for district heating, industries, harbours) in vicinity to the homes of the cardiac patients, as all of them were living within two kilometres from the monitoring site.

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