BOREAL ENVIRONMENT RESEARCH 11: 295–309 ISSN 1239-6095
Helsinki 30 August 2006

Monitoring of black carbon and size-segregated particle number concentrations at 9-m and 65-m distances from a major road in Helsinki

Tuomo A. Pakkanen[1)], Timo Mäkelä[1)], Risto E. Hillamo[1)], Annele Virtanen[2)], Topi Rönkkö[2)], Jorma Keskinen[2)], Liisa Pirjola[3)4)], Heikki Parviainen[3)], Tareq Hussein[4)] and Kaarle Hämeri[4)5)]

[1)] *Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland*
[2)] *Tampere University of Technology, Institute of Physics, Aerosol Physics Laboratory, P.O. Box 692, FI-33101 Tampere, Finland*
[3)] *Helsinki Polytechnic, Department of Technology, P.O. Box 4020, FI-00099 Helsinki, Finland*
[4)] *University of Helsinki, Department of Physical Sciences, P.O. Box 64, FI-00014 University of Helsinki, Finland*
[5)] *Finnish Institute of Occupational Health, Topeliuksenkatu 41, FI-00250 Helsinki, Finland*

Received 29 June 2005, accepted 8 Dec. 2005 (Editor in charge of this article: Veli-Matti Kerminen)

Pakkanen, T. A., Mäkelä, T., Hillamo, R. E., Virtanen, A., Rönkkö, T., Keskinen, J., Pirjola, L., Parviainen, H., Hussein, T. & Hämeri, K. 2006: Monitoring of black carbon and size-segregated particle number concentrations at 9-m and 65-m distances from a major road in Helsinki. *Boreal Env. Res.* 11: 295–309.

In February and August 2003, black carbon (BC) and size-segregated particle number concentrations were monitored simultaneously at 9-m and 65-m distances from a major road in Helsinki, Finland, using aethalometers and electrical low-pressure impactors, respectively. During weekdays in winter, the average total particle number concentrations in the diameter range 0.007–1 μm increased during morning rush hours from the nighttime values of 17 000 and 12 000 cm^{-3} to 190 000 and 130 000 cm^{-3} at the 9-m and 65-m stations, respectively. The corresponding BC concentrations increased from 730 and 430 ng m^{-3} to 2800 and 1550 ng m^{-3}. Compared with those in winter, the average rush-hour particle number concentrations were much lower in summer, the likely reason being enhanced nucleation in cold winter conditions. BC concentrations were slightly higher during summer than during winter. Number size distributions measured at the 9-m and 65-m distances and at a background site had similar modal characteristics with the highest peak occurring below 0.03 μm. Despite the different wind conditions in winter and summer, concentrations of total particle number and BC decreased similarly between the 9-m and 65-m stations, the likely principal mechanism being mixing with background air. The strong diurnal variation in concentrations during the weekdays, together with the large concentration difference between the 9-m and 65-m distances, suggests that local traffic was the main source of the measured pollutants, especially during rush hours at the 9-m site. In winter, the decrease in the particle number concentrations from the 9-m site to the 65-m site was most pronounced for the smallest exhaust particles. During an episodic pollution event in winter there were indications of condensational growth of 0.007–0.03 μm particles, which increased the number concentration of 0.03–0.06 μm particles at the 65-m site.

Introduction

Several studies have shown that atmospheric particles have adverse health effects, and that fine particles seem to be more dangerous than the coarse ones (Schwartz *et al*. 1996, Wichmann and Peters 2000). In urban areas vehicle exhaust aerosol is an important contributor to atmospheric particle mass concentrations (Gillies and Gertler 2000) and especially to particle number concentrations (Buzorius *et al*. 1999, Kim *et al*. 2002, Laakso *et al*. 2003). Most of the vehicle exhaust aerosol particles are in the ultrafine size range (aerodynamic particle diameter < 0.1 μm), and therefore, on average, urban ultrafine particles (Berner *et al*. 1996, Pakkanen *et al*. 2001, Kim *et al*. 2002, Phares *et al*. 2003, Reponen *et al*. 2003) and exhaust particles (Kerminen *et al*. 1997, Cadle *et al*. 1999, Sakurai *et al*. 2003, Wang *et al*. 2003) have quite similar characteristics in their chemical composition: mostly carbonaceous material and minor amounts of species such as sulphate, nitrate, ammonium and potassium (Berner *et al*. 1996, Hughes *et al*. 1998, Pakkanen *et al*. 2001, Rhoads *et al*. 2003, Mathis *et al*. 2004, Smith *et al*. 2004), and various metals (Bérubé *et al*. 1999, Pakkanen *et al*. 2001, Harrison *et al*. 2003). Ultrafine particles, NO, CO and black carbon (BC) are emitted by vehicles, which often leads to high correlations between the concentrations of these pollutants at sites exposed to traffic (Wåhlin *et al*. 2001a, 2001b, Kim *et al*. 2002, Zhu *et al*. 2002, Ketzel *et al*. 2003, 2004, Noble *et al*. 2003). In some studies high ultrafine particle number concentrations have been related to nucleation of specific gaseous compounds during favourable conditions (Woo *et al*. 2001, Charron and Harrison 2003).

In several cities the average particle number concentrations at urban background sites are in the range of about 10^4–3×10^4 cm^{-3} (Buzorius *et al*. 1999, Ruuskanen *et al*. 2001, Wehner *et al*. 2002, Tuch *et al*. 2003, Stanier *et al*. 2004), or slightly lower (Ketzel *et al*. 2004). At urban traffic sites the nighttime concentrations rise quickly during the early morning, and hourly-average particle number concentrations of about 10^5–2×10^5 cm^{-3} are frequently measured during the rush hours (Shi *et al*. 1999, 2001, Ruellan and Cachier 2001, Wehner *et al*. 2002). Traffic emissions have been studied also in tunnels, on-road, and near rural or semi-urban major roads (Bukowiecki *et al*. 2002, Zhu *et al*. 2002, Reponen *et al*. 2003, Sturm *et al*. 2003, Vogt *et al*. 2003, Janhäll *et al*. 2004, Kittelson *et al*. 2004, Nanzetta and Holmén 2004).

Measurements at different sites (Shi *et al*. 1999, Wehner *et al*. 2002, Zhu *et al*. 2002) have shown that the influence of traffic emissions on ambient particle number concentrations decreases with increasing distance from the source, but the degree of the observed concentration decline is highly variable. For instance, Hitchings *et al*. (2000) observed that at 100–150 m distance from the road the total particle number concentration was about half of that measured in the vicinity of the road, when the wind was blowing from the road to the measuring sites. For winds blowing parallel to the road directions, the reduction to half of the concentration occurred at about 50–100 m distance. In Helsinki, Pirjola *et al*. (2006) derived equations for the concentration curves at distances of 0–140 m from the roadside, when the wind was from the road to the measurement sites: during morning rush hours, when moving 65 m from the roadside the average concentration reduced to 39% in winter and to 35% in summer. It is believed that the large variability in different studies can be partly explained by reasons such as different lower cut-off sizes of the measurement instruments, variable weather conditions and variable background versus source contributions. Usually, the main mechanism responsible for the decline of particle number concentrations with the distance from the source has been suggested to be dilution with the background air (Shi *et al*. 1999, Vignati *et al*. 1999, Väkevä *et al*. 2000, Pohjola *et al*. 2003, Ketzel and Berkowicz 2004). The importance of coagulation increases at major traffic sites where particle number concentrations of several hundreds of thousands cm^{-3} are observed (Sturm *et al*. 2003, Jacobson and Seinfeld 2004, Kerminen *et al*. 2004).

Particle number size distributions measured at traffic sites indicate that during rush hours a large majority of particles (about 70%–90%) are in the ultrafine size range (particle diameter < 0.1 μm) and even below about 0.03–0.05 μm (Shi *et*

al. 1999, Charron and Harrison 2003). Measurements made in Germany in urban background sites showed that there was an increasing trend in the fraction of ultrafine particles between 1993 (81%) and 1999 (90%) (Pitz *et al*. 2001). During daytime and rush hours, particle number size distributions show typically one or two modes centred at about 15–40 nm (Shi *et al*. 1999, Wåhlin *et al*. 2001b, Wehner *et al*. 2002, Ketzel *et al*. 2003, 2004). With increasing distance from the source (road traffic) the particle size usually shows larger modal diameters (Shi *et al*. 1999, Wehner *et al*. 2002, Ketzel *et al*. 2004).

Due to the large seasonal temperature differences, it is of interest to study the behaviour of traffic exhaust particles in winter and summer in high-latitude northern areas. One of the few studies including periods of low winter time temperatures was made in Helsinki in 1999–2000 by Hussein *et al*. (2002), who observed that at a semi-urban site average total particle number concentrations were considerably higher during winter as compared with those in summer. The aim of this work was to study the concentration variations of traffic-related black carbon and size-segregated particle number concentrations near a major road in winter and in summer, as well as the processes occurring during dilution. In connection with the LIPIKA project (Rönkkö *et al*. 2004), the results of this study will be compared with vehicle emission measurements made in a laboratory, inside a tunnel and under on-road conditions.

Material and methods

Measurement stations and measurement periods

During 10–26 February and 11–28 August 2003, measurements were performed simultaneously at 9-m and 65-m distances from the edge of the Itäväylä road in Helsinki, about six kilometers to the east of the city center. On weekdays the traffic on this road constitutes about 45 000 vehicles, of which about 2000 are heavy duty diesel vehicles and about 8700 are diesel passenger cars or diesel vans. The sampling heights were 5.7 m above the ground. In addition, a mobile laboratory, the "Sniffer", installed in a van (Pirjola *et al*. 2004), was measuring during most days around the measurement stations and at a background site about 600 m northwest of the stations. However, these "Sniffer measurements" were usually performed during the rush hours and they took only 5–15 minutes at each position. Background monitoring mostly occurred before and after the morning and afternoon rush hours. There is a slight downhill from the Itäväylä road to the 9-m station (about 0.3 m) and further to the 65-m station (about 1.7 m below the road level). About 35 m to the north of the 65-m station there is a factory that occasionally emitted particles and disturbed measurements (Fig. 1).

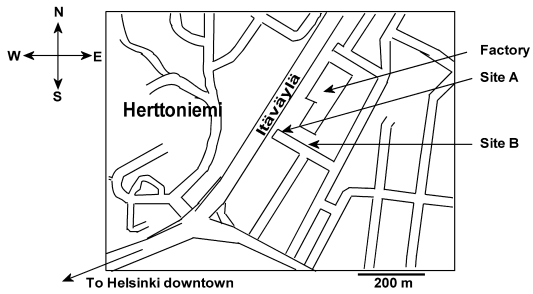

Fig. 1. The location of the 9-m (**A**) and 65-m (**B**) sampling sites.

Measurement instruments

Both measurement stations were equipped with electrical low-pressure impactors (ELPI, Keskinen *et al*. 1992), condensation particle counters (CPC) and aethalometers (Hansen *et al*. 1982). As shown below, the agreement between parallel ELPI and CPC measurements was good, and therefore CPC data is discussed only in connection to this comparison. The ELPI at the 9-m site measured particle number concentrations in the size fractions of about 0.030–0.063, 0.063–0.109, 0.109–0.173, 0.173–0.267, 0.267–0.407, 0.407–0.655 and 0.655–1.02 μm. The ELPI at the 65-m site measured nearly identical size ranges. In order to measure particle number in the size range of about 0.007–0.030 μm, both ELPIs were equipped with an additional filter stage (Marjamäki *et al*. 2002). The ELPI flow rate was 10 liters per minute and aluminium foils

greased with Apiezon L were used as collection substrates. The number size distribution readings were obtained in a resolution of five seconds, and the data was then calculated as one-minute and one-hour averages.

In ELPI number distribution calculations a particle density of 1 g cm^{-3} was assumed. McMurry *et al*. (2002) found that the density of ~0.1 μm urban aerosol particles in Atlanta, United States, varied between about 1.4 and 1.7 g cm^{-3}. For 0.3 μm particles they found two density categories: one with densities of ~0.4 g cm^{-3} and the other with densities of ~1.6 g cm^{-3}. They related the lower density values to traffic-related soot particles and the higher density values to atmospheric particles. On the other hand, Park *et al*. (2003) found that the density of diesel soot particles vary as a function of particle size. According to their study the density of 0.1 μm particles is approximately 0.8 g cm^{-3}. The density decreases as a function of particle size and for 0.2 μm particles it is ~ 0.5 g cm^{-3}. The aerosol particle population at a road side consists of a mixture of traffic-related particles and urban background particles. It is thus reasonable to assume that the average density of particles is in the range 0.5–2 g cm^{-3}. If the real particle density is 2 g cm^{-3} and a unit density is assumed in ELPI concentration calculations, the resulting concentration is approximately half of the true concentration. If the real density is 0.5 g cm^{-3}, the resulting ELPI concentration is approximately double compared to the true concentration.

In summer, both CPCs were of the model TSI 3025, but in winter there was a TSI model 3010 at the 65-m site and model 3025 at the 9-m site. Due to high concentration peaks, dilution was needed for the CPCs in winter and summer at both stations. The dilution, checked every day, was about 3–4 fold, and in all cases it was arranged by mixing filtered dilution air (about 3–4.5 liters per minute) with the sample (about 1.5–2 liters per minute). The TSI 3025 instruments measured particles having aerodynamic diameter > 3 nm, and the TSI 3010 measured particles larger than about 10 nm.

Slightly different aethalometers (Hansen *et al*. 1982) were used to measure black carbon (BC). In winter and summer there was a Magee Scientific AE1 at the 9-m station, sampling 5 litres per minute, while at the 65-m station there was a Magee Scientific AE2 (9 liters per minute) in winter and a Magee Scientific AE3 instrument (11 liters per minute) in summer. In the winter campaign a time resolution of one minute was used, whereas in the summer the aethalometers at 9-m and 65-m distances measured at one-minute and two-minute resolution, respectively. All aethalometers utilised absorption at 880 nm. High concentrations allowed the use of short measurement times, but otherwise the original calibration and setup of the manufacturer was used for all aethalometer instruments.

The Sniffer was equipped with several different instruments (Pirjola *et al*. 2004), but only the ELPI-results are considered here. The fine particle size fractions were nearly identical to those in the other ELPIs: 0.007–0.029 (filter stage), 0.029–0.056, 0.056–0.094, 0.094–0.158, 0.158–0.266, 0.266–0.388, 0.388–0.621 and 0.621–0.960 μm. The one-second data obtained from the ELPI was converted to one-minute and one-hour average data.

At the 9-m site, a Vaisala weather station, placed at a height of about 10 m, provided one-minute average data on wind speed (ws), wind direction (wdir), temperature (T) and relative humidity (RH).

Quality control and quality assurance

Earlier studies have shown the good performance of ELPI instruments. For instance, Shi *et al*. (1999) found an excellent agreement between the data measured using ELPI and SMPS instruments for particles larger than 0.03 μm aerodynamic diameter. In this work, the parallel ELPI and CPC measurements agreed fairly well, as presented later.

Before the winter campaign, the three ELPIs were tested in parallel in a laboratory and the agreement was within about ±7%. For the summer campaign the performance of the three ELPIs were compared at the 65-m station both before and after the campaign, and the agreement was again about ±7%. During the winter campaign ELPI measurements suffered from problems with the computers and data logging,

and therefore parallel data was obtained for both stations only for 19, 20, 21, 24, 25 and 26 February. The air intake of the Sniffer was 2.4 m above the ground and hence Sniffer's ELPI data is utilised only for the urban background air measurements made about 600 m to the northwest of the sampling sites. It is noted that due to the relatively wide size range measured by the ELPI filter stage (0.007–0.030 μm), the overall uncertainty is larger for this size range than for other size ranges. The uncertainties in filter stage number concentration depend on the shape of the particle number size distribution and particle density. If the peak of the nucleation mode is close to the geometric mean diameter of the filter stage (i.e. close to value 0.014 μm) and the particle density is close to 1 g cm^{-3}, the error in the measured particle number concentration is small. According to Pirjola *et al*. (2004, 2006), the peak size of nucleation mode at the Itäväylä road was close to 0.02 μm during the campaigns. In this case, assuming that the density is close to unit density, the filter-stage overestimates the number concentration by 20%–40% (Marjamäki *et al*. 2002). However, assuming that particle density and peak size do not change much near the road, the filter stage concentrations can be compared between different distances without additional uncertainties.

For the aethalometers the original calibration of the manufacturer was used. Comparisons between the instruments, made before the campaigns, showed an agreement of about ±5% in measured BC concentrations. Similar to the ELPI instruments, there were occasions when aethalometers did not provide data. In some cases the automatic tape advancer of the instrument did not work properly, and sometimes the external computers used for data logging had problems, possibly due to instability of the electricity supply.

Weather conditions

The hourly-average temperature varied between –15 and +5 °C during the winter campaign and between 8 and 23 °C during the summer campaign. In winter there was about half a meter of snow on the ground. In summer most nights were calm with practically no wind, which raised nighttime particle number and BC concentrations. In winter there was no wind in the morning of 21 February, and concentrations of both particle number and BC were high. In winter the wind direction was most of the time from the Itäväylä road to the measurement stations, whereas in summer the wind direction was variable.

Results and discussion

Number of particles in winter and summer 2003, measured by the ELPIs

Comparison of the parallel ELPI and CPC concentrations

During the summer campaign, average ELPI to CPC concentration ratios were 1.21 and 0.95 at the 9-m and 65-m stations, respectively. The diurnal variation of the hourly-average ELPI to CPC concentration ratio was quite similar at the 9-m and 65-m sites, although the ratio was consistently higher at the 9-m site (Fig. 2). As compared with those at nighttime, the measured ratios were higher during daytime at both distances. The CPC 3010 has a more limited measurement range and therefore, despite the dilution of samples, the upper concentration limit was often exceeded. Thus the ELPI-CPC comparison was not made for the 65-m site in winter. In winter at the 9-m site, the average ELPI to CPC number concentration ratio was 1.40 and had a diurnal behavior similar to that in summer, i.e. the ratios were higher during daytime than during night. By taking into account that the dilution made for the CPC measurements causes additional uncertainty, the overall agreement between parallel CPC and ELPI instruments can be considered good. As a result, only the ELPI and BC data will be discussed below.

Particle number concentrations

Total particle number concentrations followed each other relatively well at the 9-m and 65-m stations during both seasons (Fig. 3). The diurnal variation of the total particle number concentra-

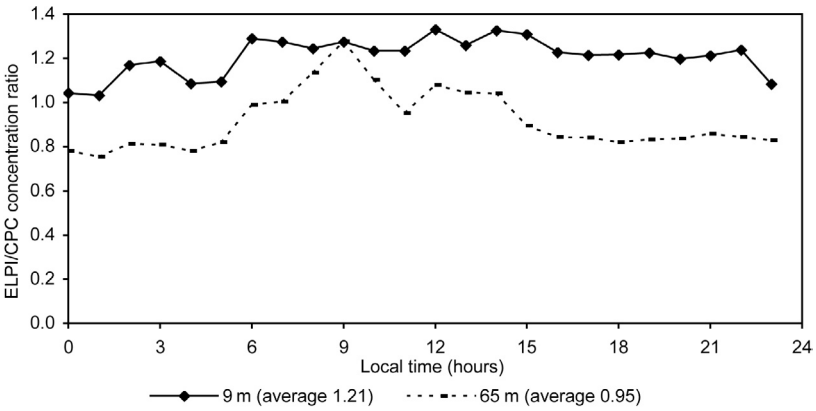

Fig. 2. Average diurnal variation of total particle number concentration ratios between the ELPI and CPC measurements in summer.

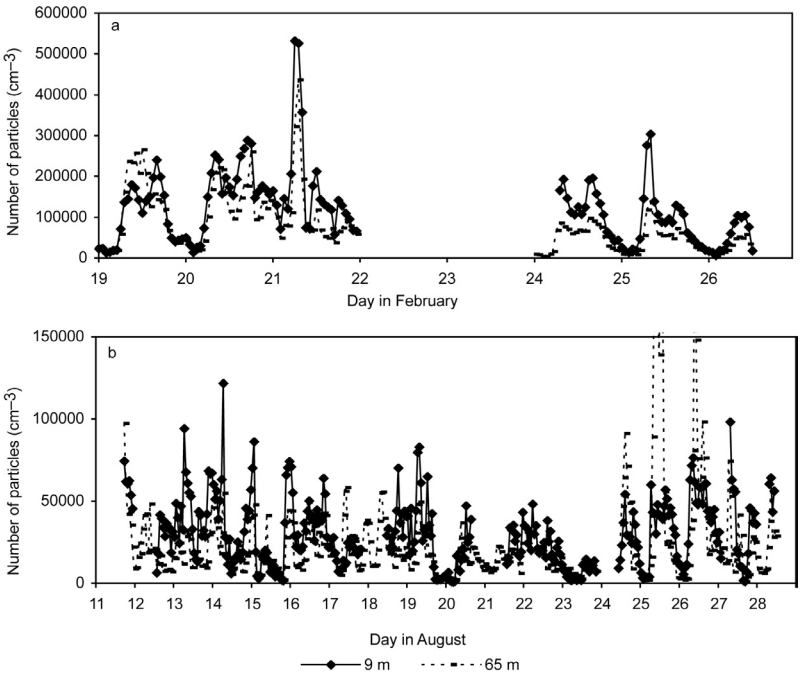

Fig. 3. Time series of hourly-average total particle number concentration in the diameter range 0.007–1 μm during the (**a**) winter and (**b**) summer campaigns. In summer the highest value was 230 000 cm^{-3}.

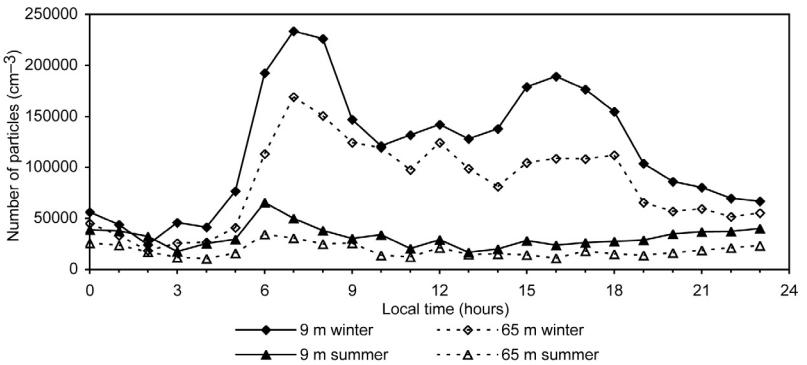

Fig. 4. Average diurnal variation of the total number concentration during the weekdays (25–26 August not included).

tion was not very strong in summer (Fig. 4), which was partly due to low wind speeds during the nights. In winter the total particle number concentration increased, on average, quickly

during the morning rush hours to high values of 190 000 and 130 000 cm^{-3} at the 9-m and 65-m distances, respectively (Table 1 and Fig. 4). Note that the high concentrations measured on 21 February are not included in Table 1. The average background particle number concentrations for the time period 07:00–09:00, measured by the Sniffer, were 25 000 and 8300 cm^{-3} during the winter and summer, respectively. The traffic was busier during the morning rush hours than in the afternoon. The day-to-day variations in concentrations were not very strong, although several people had a winter holiday week during the first week of the winter campaign. Note that several pairs of hourly concentration values were excluded from the averages (*see* footnotes in Table 1). In summer this exclusion did not change much the overall averages because both high and low concentration pairs were excluded. Saturdays and Sundays occurred on 15, 16, 22, and 23 February, and on 16, 17, 23, and 24 August. Unfortunately, for the winter there is no number concentration data for weekends. The morning and afternoon rush hour peaks were observed for most days, even though the afternoon peak was not always seen in summer due to the prevailing wind direction at those times. The nearby factory suffered occasionally from technical problems, especially during the summer campaign. Hence the high maximum concentrations observed at the 65-m site on 24–26 August were likely due to emissions from this factory since the wind was from north-northwest.

The high winter concentrations observed by us (Table 1) are comparable to those observed at higher temperatures in large cities such as Paris (Ruellan and Cachier 2001) and Birmingham (Shi *et al.* 2001). At our site in winter, about 90% of particles were detected on the filter stage which, as discussed above, has a larger uncertainty. One reason for the high winter concentrations is that on 19–26 February the wind brought traffic emissions straight to the measurement sites, whereas in August the traffic emissions were often carried to the northern side of the road away from the stations. During the time period 19–26 February, the temperatures varied between –5 and +5 °C being below zero during 21–26 February. In summer nights the temperature varied between 8 and 17 °C and during summer days it varied mostly between 13 and 21 °C. Hence, another likely reason for the much higher concentrations for winter was the low winter time temperature that may have enhanced the nucleation of various condensable traffic exhaust gases, as suggested earlier by Hussein *et al.* (2002). The relatively high nighttime particle number concentrations in summer can be explained by low wind speeds.

Table 1. Average particle number and BC concentrations over the night (N, 02:00–04:00), morning rush hours (MR, 07:00–09:00) and whole day (24 h) for weekdays and weekends in winter and summer. Average background values for the particle number concentration during morning rush hours was 25 000 cm^{-3} in winter and 8300 cm^{-3} in summer.

	Winter				Summer			
	Weekdays		Weekend		Weekdays		Weekend	
	9 m	65 m	9 m	65 m	9 m	65 m	9 m	65 m
Particle number concentration (cm^{-3})								
N	17000*	12000*	–	–	23900&	13000&	24400&	12700&
MR	190000*	130000*	–	–	59000&	36600&	20600&	12400&
24 h	120000	85000	–	–	35400&	18800&	25900&	16600&
BC concentration (ng m^{-3})								
N	730*	430*	1300	860	1200	620	2590	1130
MR	2800*	1550*	820	530	4550	2920	1180	460
24 h	2250	1330	1200	740	2700	1470	2150	970

* excluding 21 February.

& excluding hourly averages for concentration pairs with higher value at the 65-m distance.

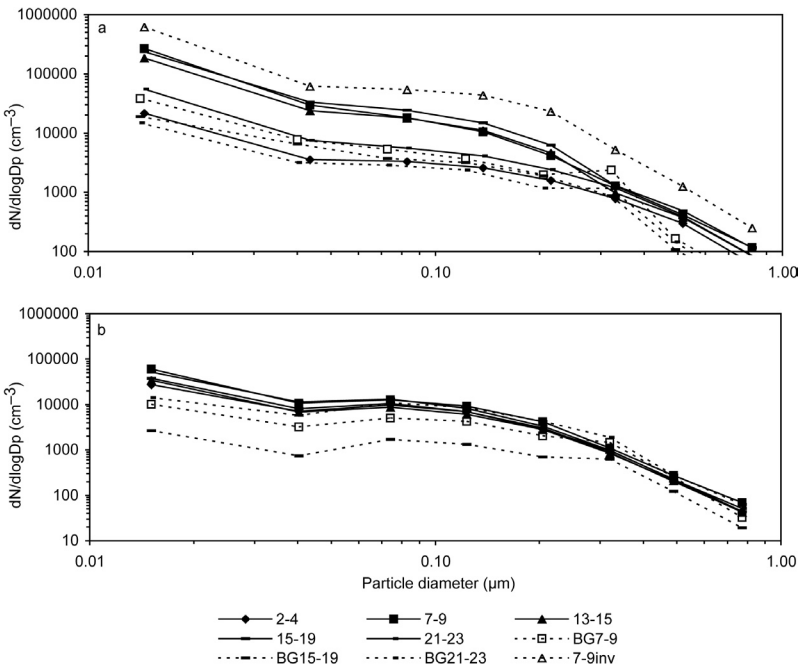

Fig. 5. Average number size distributions at the 9-m site during selected time periods for weekdays in (**a**) winter and (**b**) summer. The considered time periods are: nighttime (02:00–04:00), morning rush hour (07:00–09:00), daytime (13:00–15:00), afternoon rush hour (15:00–19:00) and evening (21:00–23:00). The dashed lines represent the average size distribution measured 07:00–09:00 during the inversion episode of 21 February (7-9inv), and median size distributions measured at the background site (BG) during morning rush hour, evening rush hour and evening hours (*see* above).

Particle number size distributions

It should be noted here that, as mentioned earlier, the particle density affects the particle number concentration measured by the ELPI, as well as the shape of the measured particle number distribution if the density varies as a function of particle size. This is a topic for further studies. As a matter of fact, the density dependence of the particle size distribution gives an interesting opportunity to study the particle densities as described by Ristimäki *et al*. (2002) and Virtanen *et al*. (2004a, 2004b).

The median background size distributions, estimated roughly from Fig. 5a and b, seem to be tri-modal with rather constant geometric mean diameters. The mode that had the smallest mean diameter and largest number of particles was located somewhere below about 0.03 μm. The fine structure of the size distributions below 0.03 μm could not be investigated in this study. The mean diameters of the two other modes at the background site seemed to be roughly at about 0.08–0.1 μm and 0.3–0.5 μm. Daily total background particle number concentrations varied between about 10 000 and 15 000 cm^{-3} during the winter and between about 5000 and 10 000 cm^{-3} during the summer. In winter the number concentrations in the background air were similar to those observed on the Itäväylä road during the night. In summer, concentrations of particles smaller than about 0.3 μm were lower in the background air compared with air measured on the Itäväylä road. The seasonal difference in nighttime concentrations between the Itäväylä road and background air can partly be explained by the very low wind speeds during summer nights, which obviously increased concentrations near the roads. The low nighttime wind speeds seemed to affect the summer time background concentrations in a way that in the late evening (21:00–23:00) concentrations were higher than those during the morning rush hours. It is noted, however, that the evening measurements were made largely on 18 August when the concentrations were higher than usual. The median background size distribution during 15:00–19:00 in summer had very low concentrations, largely due to the measurements made on 25 August when the wind carried cleaner air from north–northwest.

During both seasons, the shapes of the particle number size distributions were nearly identical at the two stations, but the particle number concentrations were lower at the 65-m station as compared with those at the 9-m station (Fig. 5).

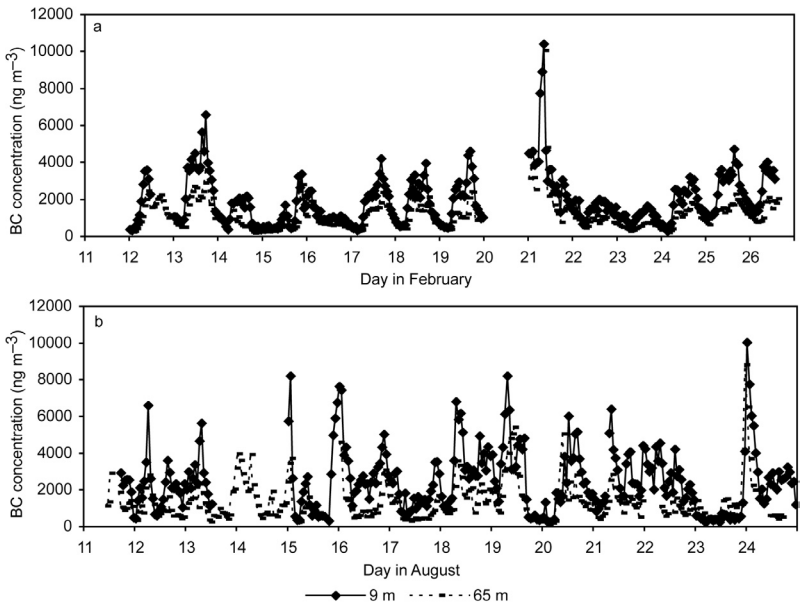

Fig. 6. Time series for hourly average BC concentrations during the (**a**) winter and (**b**) summer campaigns.

It should be noted that in order to make the comparison reliable, only the periods with existing data from both stations were considered in Fig. 5 and Table 1. The size distributions measured at the 9-m and 65-m distances from the road showed mode structures very similar to those measured at the background site (*see* above). The average size distributions representing various time periods of a day were nearly identical in the size-range of about 0.3–1 μm. This underlines the importance of long-range transport and indicates that local sources were less important for particle number concentrations in this size range. The situation is very different for particles smaller than about 0.3 μm. During the morning rush hours in winter, the average number concentration of 0.007–0.03 μm particles was eleven fold and that of 0.03–0.06 μm particles eight fold as compared with respective number concentrations during the nighttime. This demonstrates the importance of local traffic for ultrafine particles. In summer the average size distributions varied very little over the course of the day (Fig. 5b). This was probably due to the low wind speeds during the nights, higher wind speeds during the daytime, and the relatively common occurrence of south easterly–south westerly wind directions. Ketzel *et al*. (2003) reported that in May–November in Copenhagen, the influence of the traffic source was strongest at the 0.02–0.03 μm size range during daytime and evening hours. We believe that the situation is fairly similar in Helsinki in summer. In winter on average 78%–91% of the particles were observed on the filter stage (0.007–0.03 μm), whereas in summer the corresponding fraction was clearly lower (66%–79%). The difference between winter and summer is probably due to the low winter temperatures that enhance nucleation. The fraction of particles on the filter stage was highest during rush hours and daytime and lowest during the night. The fractions were larger at the 9-m station compared with the 65-m station.

Concentrations of BC in $PM_{2.5}$ particles in winter and summer 2003

The time series of hourly-average BC concentrations are presented in Fig. 6 and some average concentrations in Table 1 (21 February excluded from 02:00–04:00 and 07:00–09:00). The overall average BC concentrations, including weekdays and weekends, were 1900 and 1160 ng m^{-3} in the winter and 2500 and 1360 ng m^{-3} in the summer, at the 9-m and 65-m stations, respectively, when parallel data from both stations was considered. The values measured at the 65-m station are close to the average BC concentration of 1380 ng m^{-3} measured at another site in Helsinki in

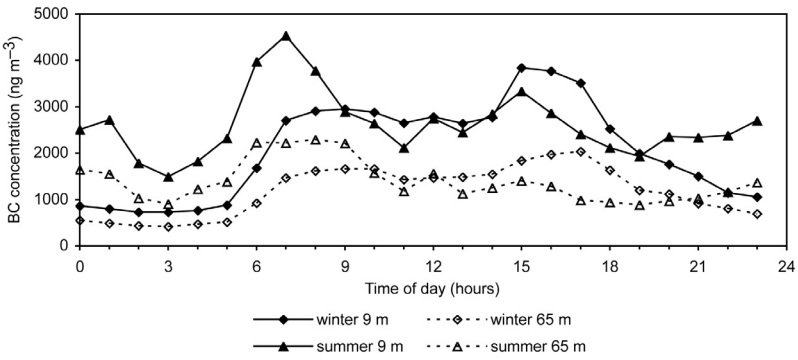

Fig. 7. Diurnal variation of average hourly BC concentrations for weekdays (21 February not included).

1996–1997 (Pakkanen *et al*. 2000). The diurnal variation of the BC concentration for weekdays was clear in both winter and summer (Fig. 7). The concentration peaks during morning and afternoon rush hours and the much lower nighttime concentrations indicate that local traffic was the most important source of BC. In summer the hourly-average wind speeds were low (often 0.2–0.5 m s^{-1}) during the night, which is reflected in relatively high BC concentrations in summer nights. As compared with those for weekday nights, BC concentrations were even higher for summer weekend nights when there was more traffic.

Decrease of particle number and BC concentrations between 9-m and 65-m distances

Dilution of particles emitted into the atmosphere by a certain source includes mixing of the emitted different-size particles with a certain background particle size distribution (Ketzel and Berkowicz 2004). A large down-wind dilution can be expected for particle sizes having high source to background concentration ratios. On the contrary, if the source to background ratio is low, the concentrations should stay close to the background level at all distances around the source. Earlier studies suggest that the high road-side particle number concentrations caused by local traffic decrease close to the background values at highly variable distances from the source: for example Zhu *et al*. (2002) reported a distance of about 300 m and Reponen *et al*. (2003) of about 200–400 m. In Brisbane, Australia, Morawska *et al*. (1999) did not see a statistically significant decrease in the particle number concentration with the distance from the road, except very close (about 15 m) to the road.

In this work, there was road construction work going on about 20–70 m to the south/west of the 65-m station during the summer campaign. This is reflected in the data as occasional high peak concentrations at the 65-m station during southerly/westerly winds. However, due to the short duration of these peaks, only a few hourly-average concentrations were elevated to a greater extent. The abnormal values occurred usually during certain periods when the wind carried emissions from the factory or from the construction site (summer only) to the sampling site(s). In spite of variations in wind and other weather conditions, the average 9-m to 65-m concentration ratios of particle number and BC were relatively similar to each other and between the summer and winter (Fig. 8). The average concentration ratios, including all the data pairs, were in winter 1.63 (standard deviation 0.5) and 1.76 (0.4) for number and BC, respectively, and 1.58 (0.9) and 2.28 (0.9) in summer. After excluding the likely outliers (concentration ratios < 1 and > 4), the average ratios remained close to the above values, except for the particle number concentration ratio in summer that increased up to 1.86. As compared with those in winter, the relations between the 9-m and 65-m concentrations were more scattered with higher standard deviations in summer, which is consistent with the more variable weather conditions during the summer campaign. In summer, the particle number concentration ratios < 1 were caused by emissions from the nearby factory. Compared with those in winter, the 9-m to 65-m ratios of hourly-average BC concentrations were higher

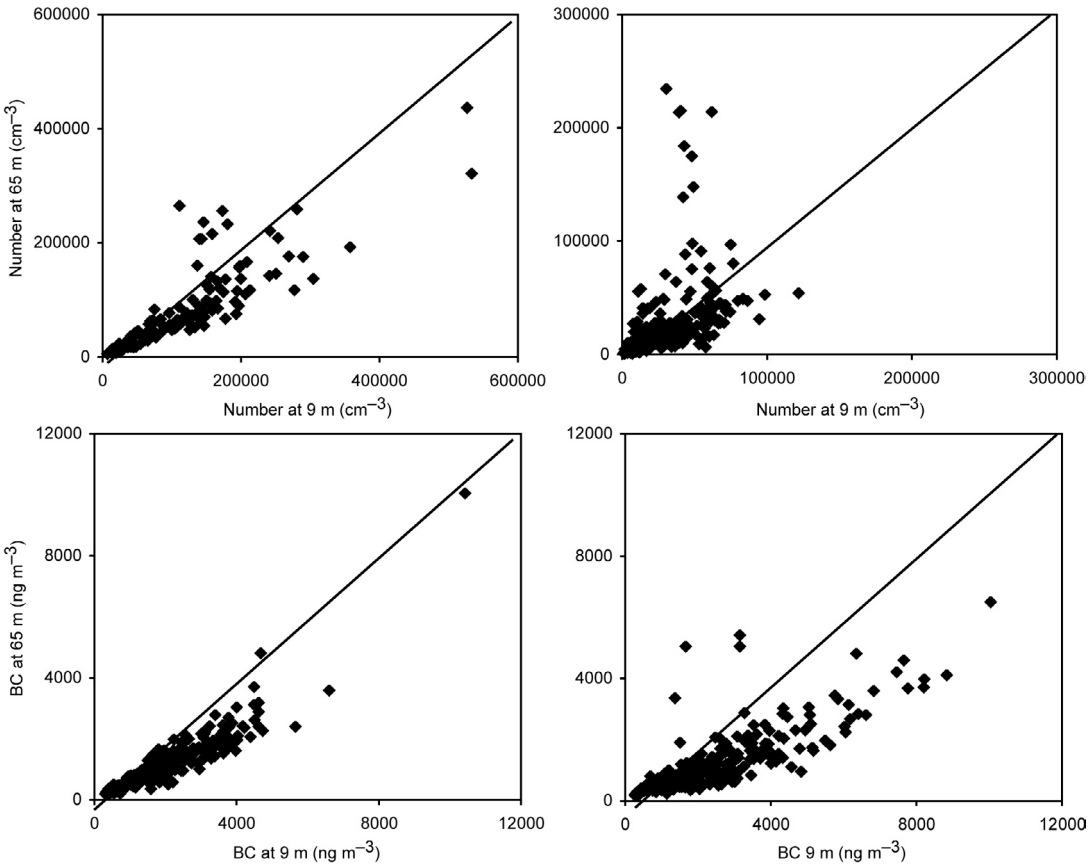

Fig. 8. Relation of hourly-average total particle number concentrations between the 9-m and 65-m stations during (**a**) winter and (**b**) summer, and the corresponding relations of black carbon (BC) concentrations during (**c**) winter and (**d**) summer.

in summer. High concentration ratios occurred sometimes when there was weak southerly wind preventing transportation of the traffic emissions to the 65-m site, but allowing the traffic turbulence to affect the 9-m site. It is noted that some of these high ratios were excluded according to the above definition of outliers. Our results are in agreement with the observations of Zhu *et al.* (2002), who found that in Los Angeles dilution was similar for particle number and BC (and in addition also for CO).

During winter and summer, the 9-m to 65-m ratio of the particle number concentration was different for different particle size fractions, and on average the ratios were higher in summer (Fig. 9). In summer the ratio was especially high for the 0.66–1.02 μm size range, likely due to road dust from the Itäväylä road. During the winter campaign usually the smallest particles (diameter 0.007–0.03 μm) had the largest 9-m to 65-m concentration ratios, while 0.5-1 μm particles had the lowest concentration ratios (slightly > 1). A clear exception to this pattern was the 0.03–0.06 μm size range, for which the concentration ratio was unexpectedly low as compared with that for the neighbouring size ranges, especially during the inversion situation (dashed lines in Fig. 9) of 21 February. The lower ratios for this size range can be partly explained by the fact that background air typically has a concentration peak at about 0.03–0.06 μm (Ketzel *et al.* 2003). According to the time scale studies of Kerminen *et al.* (2004), Ketzel and Berkowicz (2004) and Zhang *et al.* (2004), the principal processes modifying the number and size of freshly-emitted combustion aerosols in the atmosphere are mixing with the background air and condensation/evaporation.

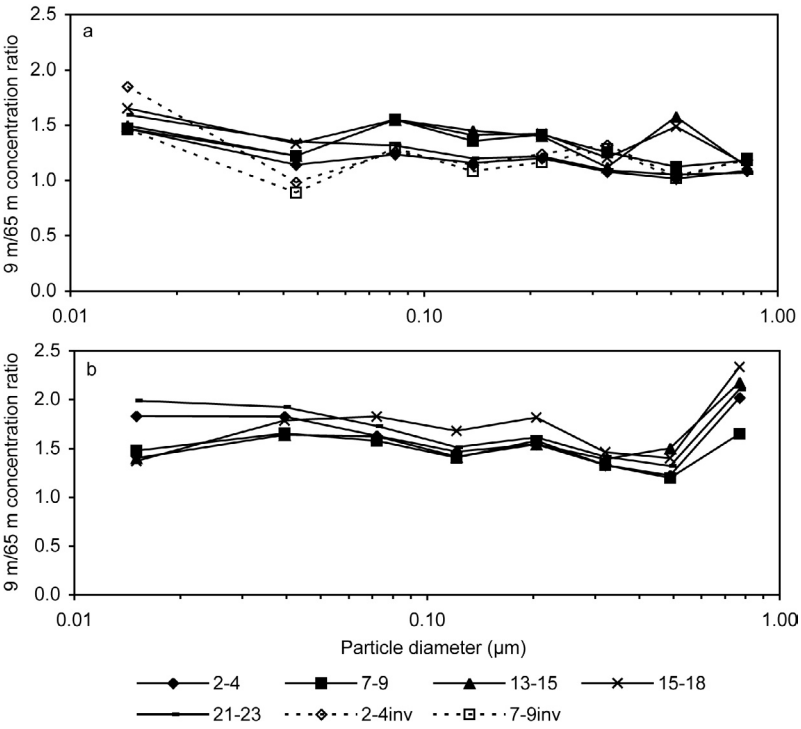

Fig. 9. Average 9-m to 65-m particle number concentration ratios for different size fractions during various times of day in (**a**) winter and (**b**) summer. The 2-4inv and 7-9inv for winter (dashed lines) represent the inversion situation on 21 February.

Hence the low 9-m to 65-m concentration ratios for 0.03–0.06 μm particles could be explained by condensation together with the high concentration difference between 0.007–0.03 μm and 0.03–0.06 μm particles. Kerminen *et al*. (2004) suggested that also self-coagulation (coagulation of approximately similar-size particles with each other) becomes important when the particle number concentration is very high and extended time for coagulation is available. In the morning of 21 February the particle number concentration was very high and there was no wind, so self-coagulation may have been important on this day. Overall, most of the details in Fig. 9 can be explained by the fact that long-range transport is usually important in the size range of about 0.2–0.7 μm, while local traffic exhaust contains particles smaller than about 0.1 μm and local road dust particles have sizes close to about 1 μm.

Summary and conclusions

In winter and summer 2003, black carbon (BC) and size-segregated particle number concentrations were measured simultaneously at 9-m and 65-m distances from a major road. In addition, a mobile laboratory measured occasionally particle number concentrations at a background site. On average, the total particle number concentration was much higher during the winter, whereas average BC concentrations were slightly higher during the summer. Both components showed a strong diurnal variation during weekdays, with lower nighttime concentrations and much higher concentrations during rush hours and daytime. Average concentrations were highest at the 9-m station and lowest at the background site. This suggests strongly that at the 9-m distance, most of the high rush-hour concentrations can be explained by the local traffic, and that even at the 65-m distance local traffic is a major source. The number size distributions measured at the 9-m and 65-m distances from the road and at the background site were relatively similar: the dominant mode was somewhere below about 0.03 μm, and the mean diameters of the two other modes were at about 0.08–0.1 μm and 0.3–0.5 μm. In winter, on average 78%–91% of particles were in the size range 0.007–0.03 μm during different times of the day, whereas in

summer this fraction varied between 66% and 79%. Usually the lowest fractions occurred at night and the highest ones during morning rush hours. The fraction of particles in the size range 0.007–0.03 μm was higher at the 9-m station as compared with that at the 65-m station.

In spite of the variable weather conditions, total particle number and BC concentrations decreased similarly from the 9-m to the 65-m distance in winter and summer. The average 9-m to 65-m concentration ratios for both BC and total particle number varied between about 1.6 and 2.2, which corresponds to a concentration decrease of about 38%–55% between these measurement sites. However, taken roughly, the concentration decrease was lower for larger particle sizes, with the exception that in winter the number of 0.03–0.06 μm particles decreased clearly less efficiently than the neighbouring particle size-classes. It is suggested that the concentration differences between the stations are explained principally by mixing with the background air. Taking the large concentration difference between the number of 0.007–0.03 μm and 0.03–0.06 μm particles, the seemingly less efficient decrease of the number of 0.03–0.06 μm particles during winter can be explained by condensational growth, where a subgroup of 0.007–0.03 μm particles shifts to sizes greater than 0.03 μm. The results of this study can be utilised in planning the emission reduction strategies and in estimating the population exposure to traffic emissions.

Acknowledgements: The authors thank the National Technology Agency (TEKES) and the Ministry of Trade and Communications for their financial support. This work was made in the framework of the European COST Action 633: Particulate Matter, Properties Related to Health Effects.

References

Berner A., Sidla S., Galambos Z., Kruisz C., Hitzenberger R., ten Brink H.M. & Kos G.P.A. 1996. Modal character of atmospheric black carbon size distributions. *J. Geophys. Res.* 101: 19559–19565.

Bérubé K.A., Jones T.P., Williamson B.J., Winters C., Morgan A.J. & Richards R.J. 1999. Physicochemical characterisation of diesel particles: factors for assessing biological activity. *Atmos. Environ.* 33: 1599–1614.

Bukowiecki N., Kittelson D.B., Watts W.F., Burtscher H., Weingartner E. & Baltensperger U. 2002. Real-time characterization of ultrafine and accumulation mode particles in ambient combustion aerosols. *J. Aerosol Sci.* 33: 1139–1154.

Buzorius G., Hämeri K., Pekkanen J. & Kulmala M. 1999. Spatial variation of aerosol number concentration in Helsinki city. *Atmos. Environ.* 33: 553–565.

Cadle S.H., Mulawa P.A., Hunsanger E.C., Nelson K., Ragazzi R.A., Barrett R., Gallagher G.L., Lawson D.R., Knapp K.T. & Snow R. 1999. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. *Environ. Sci. Technol.* 33: 2328–2339.

Charron A. & Harrison R.M. 2003. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere. *Atmos. Environ.* 37: 4109–4119.

Gillies J.A. & Gertler A.W. 2000. Comparison and evaluation of chemically speciated mobile source $PM_{2.5}$ particulate matter profiles. *J. Air & Waste Manage. Assoc.* 50: 1459–1480.

Hansen A.D.A., Rosen H. & Novakov T. 1982. Real-time measurement of the absorption coefficient of aerosol particles. *Appl. Opt.* 21: 3060–3062.

Harrison R.M., Tilling R., Romero M.S.C., Harrad S. & Jarvis K. 2003. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. *Atmos. Environ.* 37: 2391–2402.

Hitchins J., Morawska L., Wolff R. & Gilbert D. 2000. Concentration of submicrometer particles from vehicle emission near a major road. *Atmos. Environ.* 34: 51–59.

Hughes L.S., Cass G.R., Gone J., Ames M. & Olmez I. 1998. Physical and chemical characterization of atmospheric ultrafine particles in the Los Angeles area. *Environ. Sci. Technol.* 32: 1153–1161.

Hussein T., Hämeri K. & Kulmala M. 2002. Long-term indoor-outdoor aerosol measurement in Helsinki, Finland. *Boreal Env. Res.* 7: 141–150.

Jacobson M.Z. & Seinfeld J.H. 2004. Evolution of nanoparticle size and mixing state near the point of emission. *Atmos. Environ.* 38: 1839–1850.

Janhäll S., Jonsson Å.M., Molnar P., Svensson E.A. & Hallquist M. 2004. Size resolved traffic emission factors of submicrometer particles. *Atmos. Environ.* 38: 4331–4340.

Kerminen V.-M., Lehtinen K.E.J., Anttila T. & Kulmala M. 2004. Dynamics of atmospheric nucleation mode particles: a timescale analysis. *Tellus* 56B: 135–146.

Kerminen V.-M., Mäkelä T., Ojanen C., Hillamo R., Vilhunen J., Rantanen L., Havers N., von Bohlen A. & Klockow D. 1997. Characterization of the particulate phase in the exhaust from a diesel car. *Environ. Sci. Technol.* 31: 1883–1889.

Keskinen J., Pietarinen K. & Lehtimäki M. 1992. Electrical low pressure impactor. *J. Aerosol Sci.* 23: 353–360.

Ketzel M. & Berkowicz R. 2004. Modelling the fate of ultrafine particles from exhaust pipe to rural background: an analysis of time scales for dilution, coagulation and deposition. *Atmos. Environ.* 38: 2639–2652.

Ketzel M., Wåhlin P., Berkowicz R. & Palmgren F. 2003. Particle and trace gas emission factors under urban driv-

ing conditions in Copenhagen based on street and roof-level observations. *Atmos. Environ.* 37: 2735–2749.

Ketzel M., Wåhlin P., Kristensson A., Swietlicki E., Berkowicz R., Nielsen O.J. & Palmgren F. 2004. Particle size distribution and particle mass measurements at urban, near-city and rural level in the Copenhagen area and Southern Sweden. *Atmos. Chem. Phys.* 4: 281–292.

Kim S., Shen S., Sioutas C., Zhu Y. & Hinds C. 2002. Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles Basin. *J. Air & Waste Manage. Assoc.* 52: 297–307.

Kittelson D.B., Watts W.F. & Johnson J.P. 2004. Nanoparticle emissions on Minnesota highways. *Atmos. Environ.* 38: 9–19.

Laakso L., Hussein T., Aarnio P., Komppula M., Hiltunen V., Viisanen Y. & Kulmala M. 2003. Diurnal and annual characteristics of particle mass and number concentrations in urban, rural and Arctic environments in Finland. *Atmos. Environ.* 37: 2629–2641.

Marjamäki M., Ntziachristos L., Virtanen A., Ristimäki J., Keskinen J., Moisio M., Palonen M. & Lappi M. 2002. Electrical Filter Stage for the ELPI. *SAE Technical Paper Series* 2002-01-0055.

Mathis U., Kaegi R., Mohr M. & Zenobi R. 2004. TEM analysis of volatile nanoparticles from particle trap equipped diesel and direct-injection spark-ignition vehicles. *Atmos. Environ.* 38: 4347–4355.

McMurry P., Wang X., Park K. & Ehara K. 2002. The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density. *Aerosol Sci. Technol.* 36: 227–238.

Morawska L., Thomas S., Gilbert D., Greenaway C. & Rijnders E. 1999. A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road. *Atmos. Environ.* 33: 1261–1274.

Nanzetta M.K. & Holmén B.A. 2004. Roadside particle number distributions and relationships between number concentrations, meteorology, and traffic along a northern California freeway. *J. Air & Waste Manage. Assoc.* 54: 540–554.

Noble C.A., Mukerjee S., Gonzales M., Rodes C.E., Lawless P.A., Natarajan S., Myers E.A., Norris G.A., Smith L., Özkaynak H. & Neas L.M. 2003. Continuous measurement of fine and ultrafine particulate matter, criteria pollutants and meteorological conditions in urban El Paso, Texas. *Atmos. Environ.* 37: 827–840.

Pakkanen T., Kerminen V.-M., Ojanen C., Hillamo R., Aarnio P. & Koskentalo T. 2000. Atmospheric black carbon in Helsinki. *Atmos. Environ.* 34: 1497–1506.

Pakkanen T.A., Kerminen V.-M., Korhonen C.H., Hillamo R.E., Aarnio P., Koskentalo T. & Maenhaut W. 2001. Urban and rural ultrafine ($PM_{0.1}$) particles in the Helsinki Area. *Atmos. Environ.* 35: 4593–4607.

Park K., Cao F., Kittelson D. & McMurry P. 2003. Relationship between particle mass and mobility for diesel exhaust particles. *Environ. Sci. Technol.* 37: 577–583.

Phares D.J., Rhoads K.P., Johnston M.V. & Wexler A.S. 2003. Size-resolved ultrafine particle composition analysis 2. Houston. *J. Geophys. Res.* 108(D7), 8420, doi:10.1029/2001JD001212.

Pirjola L., Paasonen P., Pfeiffer D., Hussein T., Hämeri K., Koskentalo T., Virtanen A., Rönkkö T., Keskinen J. & Pakkanen T. 2006. Dispersion of particles and trace gases nearby a city highway: mobile laboratory measurements in Finland. *Atmos. Environ.* [In press].

Pirjola L., Parviainen H., Hussein T., Valli A., Hämeri K., Aalto P., Virtanen A., Keskinen J., Pakkanen T.A., Mäkelä T. & Hillamo R.E. 2004. "Sniffer" — a novel tool for chasing vehicles and measuring traffic pollutants. *Atmos. Environ.* 38: 3625–3635.

Pitz M., Kreyling W.G., Hölscher B., Cyrys J., Wichmann H.E. & Heinrich J. 2001. Change of the ambient particle size distribution in East Germany between 1993 and 1999. *Atmos. Environ.* 35: 4357–4366.

Pohjola M., Pirjola L., Kukkonen J. & Kulmala M. 2003. Modelling of the influence of aerosol processes for the dispersion of vehicular exhaust plumes in street environment. *Atmos. Environ.* 37: 339–351.

Reponen T., Grinshpun S.A., Trakumas S., Martuzevicius D., Wang Z.-M., LeMasters G., Lockey J.E. & Biswas P. 2003. Concentration gradient patterns of aerosol particles near interstate highways in the Greater Cincinnati airshed. *J. Environ. Monitoring* 5: 1–7.

Rhoads K.P., Phares D.J., Wexler A.S. & Johnston M.V. 2003. Size-resolved ultrafine particle analysis, 1. Atlanta. *J. Geophys. Res.* 108(D7), 8418, doi:10.1029/2001JD001211.

Ristimäki J., Virtanen A., Marjamäki M., Rostedt A. & Keskinen J. 2002. On-line measurement of size distribution and effective density of submicron aerosol particles. *J. Aerosol Sci.* 33: 1541–1557.

Rönkkö T., Virtanen A., Keskinen J., Pakkanen T., Mäkelä T., Hillamo R., Pirjola L., Lappi M., Hämeri K. & Hussein T. 2004. Dynamometer versus real-life nanoparticle emissions of vehicles — project LIPIKA. *J. Aerosol Sci.*, Abstracts of European Aerosol Conference, Budapest, Hungary, 6–10 Sep. 2004, S1035–S1036.

Ruellan S. & Cachier H. 2001. Characterisation of fresh particulate vehicular exhausts near a Paris high flow road. *Atmos. Environ.* 35: 453–468.

Ruuskanen J., Tuch T., Ten Brink H., Peters A., Khystov A., Mirme A., Kos G.P.A., Brunekreef B., Wichmann H.E., Buzorius G., Vallius M., Kreyling W.G. & Pekkanen J. 2001. Concentrations of ultrafine, fine and $PM_{2.5}$ particles in three European cities. *Atmos. Environ.* 35: 3729–3738.

Sakurai H., Tobias H.J., Park K., Zarling D., Docherty K.S., Kittelson D.B., McMurry P.H. & Ziemann P.J. 2003. On-line measurements of diesel nanoparticle composition and volatility. *Atmos. Environ.* 37: 1199–1210.

Schwartz J., Dockery D.W. & Neas L.M. 1996. Is daily mortality associated specifically with fine particles? *J. Air & Waste Manage. Assoc.* 46: 927–939.

Shi J.P., Khan A.A. & Harrison R.M. 1999. Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *Sci. Total Environ.* 235: 51–64.

Shi J.P., Evans D.E., Khan A.A. & Harrison R.M. 2001. Sources and concentration of nanoparticles (< 10 nm diameter) in the urban atmosphere. *Atmos. Environ.* 35: 1193–1202.

Smith J.N., Moore K.F., McMurry P.H. & Eisele F.L. 2004.

Atmospheric measurements of sub-20nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry. *Aerosol Sci. Technol.* 38: 100–110.

Stanier C.O., Khlystov A.Y. & Pandis S.N. 2004. Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS). *Atmos. Environ.* 38: 3275–3284.

Sturm P.J., Baltensperger U., Bacher M., Lechner B., Hausberger S., Heiden B., Imhof D., Weingartner E., Prevot A.S.H., Kurtenbach R. & Wiesen P. 2003. Roadside measurements of particulate matter size distribution. *Atmos. Environ.* 37: 5273–5281.

Tuch T.M., Wehner B., Pitz M., Cyrys J., Heinrich J., Kreyling W.G., Wichmann H.E. & Wiedensohler A. 2003. Long-term measurements of size-segregated ambient aerosol in two German cities located 100 km apart. *Atmos. Environ.* 37: 4687–4700.

Väkevä M., Hämeri K., Puhakka T., Nilsson E.D., Hohti H. & Mäkelä J.M. 2000. Effects of meteorological processes on aerosol particle size distribution in an urban background area. *J. Geophys. Res.* 105: 9807–9821.

Vignati E., Berkowicz R., Palmgren F., Lyck E. & Hummelshoj P. 1999. Transformation of size distributions of emitted particles in streets. *Sci. Total Environ.* 235: 37–49.

Virtanen A., Ristimäki J. & Keskinen J. 2004a. New method to define the effective density and fractal dimension of agglomerate particles. *Aerosol Sci. Technol.* 38: 437–446.

Virtanen A., Ritimäki J., Vaaraslahti K. & Keskinen J. 2004b. Effect of engine load on diesel soot particles. *Environ. Sci. Technol.* 38: 2551–2556.

Vogt R., Scheer V., Casati R. & Benter T. 2003. On-road measurement of particle emission in the exhaust plume of a diesel passenger car. *Environ. Sci. Technol.* 37: 4070–4076.

Wåhlin P., Palmgren F. & van Dingenen R. 2001a. Experimental studies of ultrafine particles in streets and the relationship to traffic. *Atmos. Environ.* 35: 63–69.

Wåhlin P., Palmgren F., van Dingenen R. & Raes F. 2001b. Pronounced decrease of ambient particle number emissions from diesel traffic in Denmark after reduction of the sulphur content in diesel fuel. *Atmos. Environ.* 35: 3549–3552.

Wang Y.-F., Huang K.-L., Li C.-T., Mi H.-H., Luo J.-H. & Tsai P.-J. 2003. Emissions of fuel metals content from a diesel vehicle engine. *Atmos. Environ.* 37: 4637–4643.

Wehner B., Birmili W., Gnauk T. & Wiedensohler A. 2002. Particle number size distributions in a street canyon and their transformations into the urban-air background: measurements and a simple model study. *Atmos. Environ.* 36: 2215–2223.

Wichmann H.-E. & Peters A. 2000. Epidemiological evidence of the effects of ultrafine particle exposure. *Philosophical Transactions of the Royal Society London A* 358: 2751–2769.

Woo K.S., Chen D.R., Pui D.Y.H. & McMurry P.H. 2001. Measurement of Atlanta aerosol size distributions: observations of particle events. *Aerosol Sci. Technol.* 34: 75–87.

Zhang K.M., Wexler A.S., Zhu Y.F., Hinds W.C. & Sioutas C. 2004. Evolution of particle number distribution near roadways. Part II: the "road-to-ambient" process. *Atmos. Environ.* 38: 6655–6665.

Zhu Y., Hinds W.C., Kim S., Shen S. & Sioutas C. 2002. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. *Atmos. Environ.* 36: 4323–4335.