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Particle number, particle mass and NO_x emission factors at a highway and an urban street in Copenhagen

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Abstract. This paper presents measurements of traffic-generated gas and particle pollution at two sites, one near a major highway and one near a busy urban street in Copenhagen, Denmark. Both sites were equipped for a 4-week period with a set of two measurement stations, one close to the kerbside and one background station. Measurements were carried out from March to April 2008, investigating NO_x concentrations, submicrometer particle number size distribution (size range 10–700 nm), particle mass ($PM_{2.5}$, PM_{10}), and meteorological parameters. In this study we also estimate the emission factors for NO_x, particle number and particle mass using measured traffic volume and dilution rate calculated by the Operational Street Pollution Model (WinOSPM).

The mean concentrations of most of the measured pollutants are similar for the highway and the urban kerbside stations due to similar traffic density. The average concentrations of NO_x are $142 \, \mu g \, m^{-3}$ and $136 \, \mu g \, m^{-3}$ for the highway and the urban kerbside stations, respectively. These values are about 5 times higher compared to the corresponding background values. The average particle number concentration is $24\,900$ particles cm^{-3} and $27\,100$ particles cm^{-3} for the highway and the urban kerbside stations, respectively, and these values exceed those measured at the background stations by a factor of 3 to 5.

The temporal variation of the traffic contribution (difference of kerbside and background concentrations) is analysed for NO_x, particle number and mass, and it follows the traffic pattern at the urban and the highway sites. Emission factors for particle number are found to be quite similar at both sites, $(215\pm5) \, 10^{12}$ particles $veh^{-1} \, km^{-1}$ for the highway and $(187\pm3) \, 10^{12}$ particles $veh^{-1} \, km^{-1}$ for the urban site. Heavy duty vehicles (HDVs) are found to emit about 20 times more particles than light duty vehicles (LDVs), which is in good agreement with other published studies. Emission factors are also determined for individual particle modes identified in the size spectra. Average fleet emission factors for $PM_{2.5}$ at the highway and the urban site are $29 \, mg \, veh^{-1} \, km^{-1}$ and $46 \, mg \, veh^{-1} \, km^{-1}$, respectively. The estimated particle number and size spectra emission factors will provide valuable input for air quality and particle dispersion modelling near highways and in urban areas.

1 Introduction

Health effects appear to better correlate with submicrometer particle number concentration rather than particle mass concentration (Weichenthal et al., 2007; Su et al., 2006; Sioutas et al., 2005). Therefore, particle number size distribution measurements and emission factor determination have received growing attention.

Extensive measurement programs of urban and regional submicrometer particle number size distribution have been carried out at several locations worldwide. Vehicular emissions are one of the main sources of submicrometer particles in urban areas with dense and busy roadways (Hitchins et al., 2000; Morawska et al., 1999). Measurements have been conducted to estimate particle number emission factors under real-world conditions besides characterization and evaluation of vehicular particle pollution. There are studies stating fuel-based particle number emission factors (EF) (particles (kg fuel)$^{-1}$) (Kirchstetter et al., 1999; Yli-Tuomi et al., 2005;

Fig. 1. Location of the highway measurement stations. The black point in the overview map of Denmark indicates the position of the detailed map showing surrounding roads and the locations of the kerbside and background stations. (©Background map www.kms.dk).

Geller et al., 2005) and travel-based particle number emission factors (particles veh^{-1} km^{-1}) (Imhof et al., 2005; Kittelson et al., 2004). An important issue for emission factor estimation under real-world conditions is how to determine the dilution rate of investigated pollutants from the emission sources to the sampling site and several approaches are used in literature. Ketzel et al. (2003) used a dispersion model to calculate the dilution factor in a street canyon for NOx and particle number. Zhang et al. (2005) used CO emissions from vehicles on a highway as a tracer. In comparison, Jamriska and Morawska (2001) demonstrated a box model to calculate the emission rate of particle number considering the dilution rate as a function of wind direction and wind speed. This model was later been used by Morawska et al. (2005) to estimate vehicle number emission factors from on-road measurement. Harrison et al. (2006) used the ratio of roadside NO$_x$ concentrations to calculated total NO$_x$ emitted from the traffic fleet as the dilution rate, and they applied this method to estimate particle number emission factors in a congested urban street canyon where vehicle speeds vary greatly over short distances. Yli-Tuomi et al. (2005) studied the emissions from on-road vehicles in Finland at a city centre and at a highway and used the measured on-road concentrations to estimate the emission factors. Most of the above-mentioned studies are based on a short period of several hours or several days of measurements and the results are affected by individual meteorological conditions, except the study by Morawska et al. (2005) performed a measurement about 3 months.

In a previous Danish measurement campaign the traffic contribution was studied by analysing simultaneously street level and urban background measurements in Copenhagen (Ketzel et al., 2003). The information of traffic-related particle emissions from highways is still very scarce and for Danish highways there is no information available at all.

The objectives of this work are (1) to investigate the traffic contribution to air pollutants from a Danish highway and in particular to quantify emission factors of particle number in highway and urban street in Denmark and (2) to compare the emission factors from these two different roads with values from the literature. The particle number emission factors will further be processed to serve as input for air quality models.

2　Experimental

2.1　Sampling location and period

The highway measurement campaign was performed at the "Holbæk" Highway (route No. 21) 30 km east of Copenhagen, Denmark (Fig. 1) which has three lanes in each direction. This location was chosen due to its high traffic volume, the known representativeness of traffic pattern and fleet composition in Denmark and its orientation with respect to the main wind direction. The Danish Road Directorate operates an automatic traffic counting station right next to the highway kerbside monitoring station (measurement station No. 41). Three stations were installed during the campaign, two for the gas phase and particle pollutants and one for the meteorological parameters. As shown in Fig. 1, the highway kerbside station (Hw_Kb) (12°15′12″ E, 55°39′56″ N) was placed about 3 m north to the northern side of the highway. The highway background station (Hw_Bg) (12°15′05″ E, 55°39′49″ N) was placed about 200 m south of the southern side of the highway. There are two roads Roskildevej and Bondehøjvej nearby. The road Roskildevej has a traffic flow of 17 500 vehicles per day; however it is located more than 1 km south of the two stations and will influence both stations in a similar way and acts therefore as part of the general background. The road Bondehøjvej has very minor traffic (2400 veh. day^{-1}) and should not have any relevant contribution at our stations compared to the highway itself. The Hw_Bg station has a distance of about 200 m to Bondehøjvej, which is considered as far enough to avoid a direct influence. The meteorological station (12°15′04″ E, 55°39′49″ N) was placed next to the background station. The highway curves slightly at the measurement site which has to be taken into account when selecting the wind directions applicable for detailed analysis. For wind directions between 105° and 225° air masses observed at the background measurement station will in principle not be affected by air pollution from the highway. We chose this wind direction sector to investigate the traffic generated pollutants.

Two stations in the Copenhagen urban area were chosen for comparison. The urban kerbside station (Urb_Kb) is located at the H. C. Andersens Boulevard (HCAB, 12°34′16″ E, 55°40′28″ N) close to the town hall square and the urban background station (Urb_Bg) is located at the roof of H. C. Ørsted Institute at the height of 20 m (HCOE, 12°33′42″ E, 55°42′2″ N). There is the road Norre Alle close

Table 1. Selected instruments used during the highway campaign and at the urban sites in Copenhagen.

Measured parameter	Instrument/manufacturer	Time resolution	Intake height (m)			
			Hw-Ks	Hw-Bg	Urb-Ks	Urb-Bg
NO$_x$, NO, NO$_2$	API Chemiluminescent NO$_x$ Analyzer, Model 200A	1/2h	3.1	3.3	3.0	18
TEOM PM$_{2.5}$	Rupprecht & Patashnick Co., Inc., TEOM Particulate Mass Monitor Series 1400	1/2h	3.8	3.5	3.1	18
TEOM PM$_{10}$	Rupprecht & Patashnick Co., Inc., TEOM Particulate Mass Monitor Series 1400	1/2h	3.7	3.5	3.1	18
DMPS	Custom built type including TSI CPC 3010	3 min	3.4	3.3	3.1	18

to the urban background station, with traffic flow of about 36 000 vehicles per day. However, the station is located on the roof of a 20 m high building. Therefore, the direct influence of Norre Alle to the background station is limited. Previously conducted receptor analysis has shown, that the traffic contribution at the background station (originating from several sources not only Norre Alle) is only about 16%–18% compared to the kerbside station (Ketzel et al., 2003).These two stations are part of the Danish Air Quality Monitoring Programme (Kemp et al., 2008). The urban background station includes measurements of meteorological parameters.

The highway campaign took place from 8 March to 7 May 2008. The particle measurements at the highway kerbside station were operated only during the period of 23 March to 21 April 2008. The measurements at the urban stations are continuously running, however only data during the duration of the highway campaign are analysed here for comparison. A data set of 4 weeks was analysed in this work (24 March to 20 April 2008) when simultaneous measurements of all parameters from all four stations were available in good quality.

2.2 Instrumentation and quality assurance

The instrumentation used during the highway campaign and urban site measurements are listed in Table 1. All gas phase and particle compounds were measured by the same type of instruments at all of the four measurement stations. PM$_{10}$ (mass concentration of particles with aerodynamic diameter less than 10 μm) was not measured at urban sites during the campaign. The particle mass losses caused by evaporation of volatile compounds due to heating of the sampling air (50 °C) in the TEOM instrument (Tapered Element Oscillating Microbalance) are assumed to affect mainly the regional contribution of the aerosol (e.g. ammonium nitrate) and will lead to a similar reduction at the kerbside and background station as discussed in previous studies (Kemp et al., 2005; Palmgren et al., 2003). Therefore, the local contribution from the street (difference between kerbside and background) is assumed

to be unaffected by the evaporation losses and can be used for emission factor estimates. Meteorological parameters near the highway were measured using a Sonic Anemometer at 10 m height for wind speed (WS), wind direction (WD) relative humidity (RH), and temperature (T). Precipitation (preci) was also measured very close to the highway site. The urban background station is equipped with a meteorological station measuring wind speed, wind direction, relative humidity, temperature and solar radiation at the height of 10 m on the roof of a five-storey building.

At all stations, custom built Differential Mobility Particle Sizers (DMPS) were used. Each of them consist of a Differential Mobility Analyser (DMA) (Winklmayr et al., 1991) in combination with a Condensation Particle Counter (CPC) employing a re-circulating flow system (Jokinen and Mäkelä, 1997). The DMPS cover the size range 10 nm to 700 nm, and are equipped with a single Vienna type medium DMA and particles are counted using a TSI$^®$ Model 3010 CPC. The scanning time for each size spectrum is about 3 min, using alternating up-scans and down-scans. Corrections for reduced counting efficiency at lower sizes, multiple charging and particle sampling losses were made for all data according to the data inversion algorithm (Wiedensohler, 1988).

All DMAs used in the systems were built and calibrated (for the loss functions and broadening parameters of the transfer function) at the Lund University. The DMPS systems are inter-compared on a regular basis, showing very good agreement between the instruments, typically 5–15% difference in the total number concentrations. A comparison of the two used DMPS systems at the highway site for ambient air showed an agreement of ±15% in size-selected number concentration over the full size range. Averaged size spectra for half-hour time intervals were calculated and half-hour averages of the total particle number (PN), particle area (PA) and the particle volume (PV) were calculated and analyzed in relation to the trace gas and meteorological measurements.
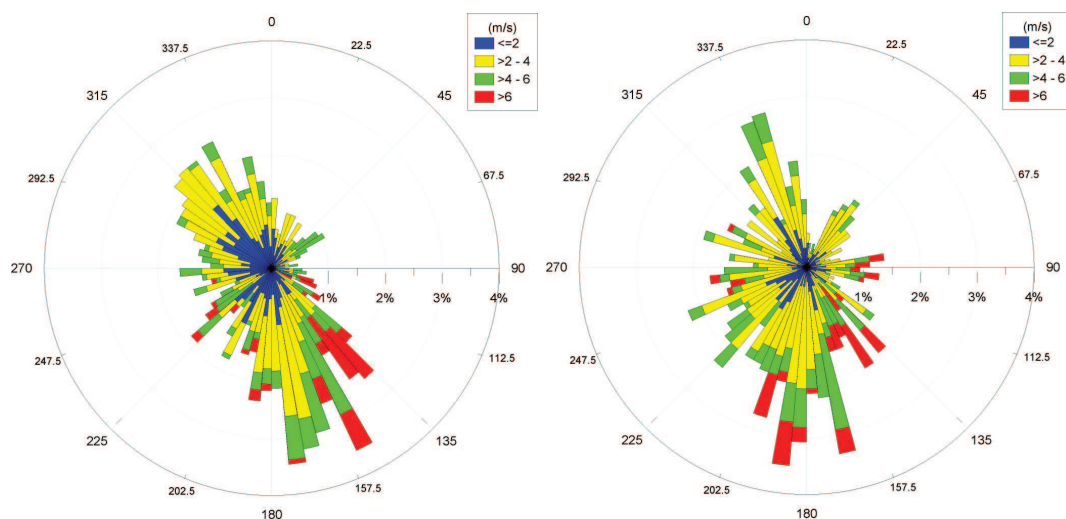
Fig. 2. Wind rose observed at the highway site (left) and the urban site (right).

Table 2. Statistical results of the meteorological parameters over the measurements period (SD: standard deviation).

Site		WS (m s^{-1})	T (°C)	RH (%)	Radiation (W m^{-2})	Precipitation (mm h^{-1})
Highway	mean	3.0	5.3	77.0	147.7	0.0
	median	2.6	5.7	79.8	30.9	0.0
	SD	1.7	3.0	13.7	200.1	0.1
	max	10.3	11.9	96.2	829.8	1.4
	min	0.2	−2.3	37.7	−0.3	0.0
Urban	mean	3.3	6.0	70.8	127.9	
	median	2.9	6.3	71.2	18.3	
	SD	1.6	2.8	11.5	180.8	
	max	8.9	13.6	91.8	751.4	
	min	0.6	−1.0	34.8	0.0	

3 Experimental results and discussion

3.1 Meteorological conditions

The meteorological parameters measured during the measurement period are summarized in Table 2. Precipitation was only measured near the highway site, and other parameters were measured at both the highway and the urban sites. The temperature values range from −1 °C to 13 °C with an average value of about 6 °C. The mean values of solar radiation and relative humidity are insignificantly higher at the highway site in comparison to the urban site. The wind rose shows a slightly different picture at both sites (Fig. 2). At the highway site the dominant wind is from south-east to northwest, the wind speed ranging from 0.2 m s^{-1} to 10.3 m s^{-1} with an average value of 3 m s^{-1}, and the wind speed is relatively higher when the wind direction is from south east. At the urban site, the dominant wind direction is also south east to north west, but with the wind blowing from the west more frequently. Here, the wind speed ranges from 0.6 m s^{-1} to 8.9 m s^{-1} with an average value of 3.2 m s^{-1}.

3.2 Diurnal pattern of traffic

Traffic volumes at the highway were measured automatically for 15 min time intervals. The traffic fleet is divided into three classes depending on the length of the vehicle: passenger cars (small vehicle less than 5.8 m), vans (medium vehicle between 5.8 m and 12.5 m), and trucks or buses (large vehicle larger than 12.5 m). The LDVs include cars and vans and the HDVs include trucks and buses. However, there are some limits to identify the type of vehicle by length. The average daily traffic intensity during the measurement campaign at the highway is 55 600 vehicles per day. The average diurnal variation of the total traffic volume and HDVs is shown in Fig. 3. During weekdays two peaks appear in the number of counted vehicles corresponding to the rush hours at 07:00–09:00 LT (local time) and 14:00–18:00 LT. The afternoon peak is slightly wider. The morning and afternoon peaks are dominated by passenger cars, and vans and HDVs have much less distinct morning and afternoon peaks. Considering the driving directions, the morning rush hour peak is linked to vehicles driving towards the city centre of Copenhagen, and the afternoon rush hour peak is linked to those coming from Copenhagen. The measured traffic speed is on average 110 km h^{-1}, and a bit lower for HDVs (90 km h^{-1}). In total, the traffic volume decreases about 35% in weekend, especially in the morning. On average the LDVs share is 92% of the total traffic volume, however, the percentages of LDVs and HDVs vary in time.

The diurnal variation of the traffic volume at the urban site (HCAB) was not monitored continuously but is measured by the Copenhagen municipality about once a year for 1–2 days and is assumed to follow a regular pattern (see upper right plot in Fig. 15). From other (partly automatic) traffic observations at other locations downtown Copenhagen we know that the traffic pattern is quiet stable and regular (Ketzel,

Table 3. Statistical parameters of the measured compounds (NO$_x$ is given in NO$_2$ mass units).

Pollutant	Unit	Site Location	Highway Nr. o.D.	Average	Ks/Bg ratio	Median	SD	CoV	Urban Nr. o.D.	Average	Ks/Bg ratio	Median	SD	CoV
NO$_x$	µg m^{-3}	Ks	1185	141.8	4.70	105.4	117.5	0.83	1312	136.1	4.80	111.1	97.0	0.71
NO$_x$	µg m^{-3}	Bg	1311	30.2		19.2	32.8	1.09	1313	28.3		22.1	22.0	0.78
PM$_{2.5}$	µg m^{-3}	Ks	1244	11.6	1.24	10.8	5.6	0.48	1163	14.0	1.40	13.2	6.3	0.45
PM$_{2.5}$	µg m^{-3}	Bg	1317	9.4		8.7	5.3	0.56	1163	10.0		9.4	5.1	0.51
PM$_{10}$	µg m^{-3}	Ks	1200	23.6	1.76	20.5	12.7	0.54						
PM$_{10}$	µg m^{-3}	Bg	1336	13.4		12.7	6.2	0.46						
PN	particles cm^{-3}	Ks	1342	24 862	3.60	18 915	19 984	0.80	1342	27 107	5.10	22 954	17 974	0.66
PA	µm^2 cm^{-3}	Ks	1342	325	1.64	291	185	0.57	1342	476	2.68	413	264	0.56
PV	µm^3 cm^{-3}	Ks	1342	10.5	1.32	9.1	6.2	0.59	1342	17.5	2.42	15.1	10.5	0.60
PN	particles cm^{-3}	Bg	1243	6904		5507	5185	0.75	1342	5311		4674	2801	0.53
PA	µm^2 cm^{-3}	Bg	1243	198		182	116	0.59	1342	178		151	103	0.58
PV	µm^3 cm^{-3}	Bg	1243	8.0		6.8	5.2	0.66	1342	7.2		5.6	5.0	0.68

SD: standard deviation; CoV: Coefficient of Variation=SD/Mean; Nr.o.D: Number of data points; Ks: kerbside; Bg: Background.

2004), thus these data were used for this study. The asynchronous measurements of traffic count and pollutant concentrations might affect the emission factor estimation, and a sensitivity test about the influence of vehicle count on emission factors is described in Sect. 4.5. The traffic exhibits a quite similar pattern compared to the highway site. The average daily traffic volume at HCAB is 60 000 vehicles per day. The LDVs share is about 95%. The average traffic speed is about 40–50 km h^{-1} for light duty vehicles and is expected to be lower for buses. During weekdays the rush hour peak extends over a shorter time interval compared to the highway site. A higher traffic volume is observed during the night at the urban site due to more activities near the city centre.

3.3 Average concentration levels and correlations of measured pollutants

The general statistics of the measured concentrations are summarized in Table 3 using the half hour average values during the selected 4 weeks when data are available. The mean values at the kerbside stations (highway and urban) are similar for most of the pollutants. The average NO$_x$ concentration is 142 µg cm^{-3} and 136 µg cm^{-3} for the highway and the urban kerbside stations, respectively, and they are about 5 times higher than the values measured at the background stations. The average of PN is 24 900 particles cm^{-3} and 27 100 particles cm^{-3} for the highway and the urban kerbside stations, respectively, and is about 3–5 times higher than the values measured at the background stations. The highway background values for NO$_x$ and PN are slightly higher than at the urban background, indicating that the highway background might be affected by the fresh highway emissions.

The correlation between the different compounds is calculated for the simultaneous data measured at the kerbside and background stations and the results are shown in Table 4. In general, NO$_x$ concentrations are well correlated
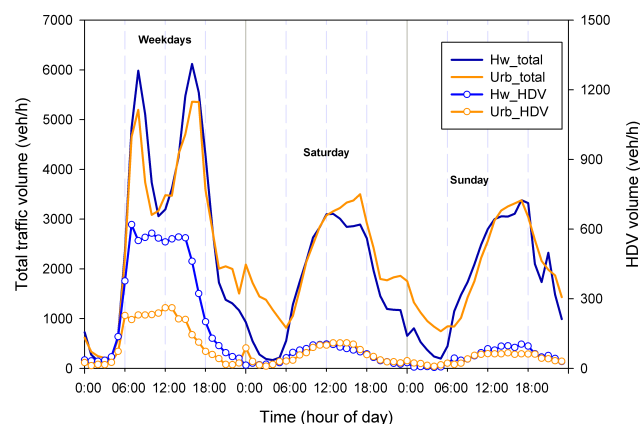

Fig. 3. Diurnal variation of the total traffic volume and HDVs volume at the highway (Hw) and the urban (Urb) sites at weekdays, Saturdays and Sundays.

with all other compounds indicating that traffic is the common source. The correlation coefficient is larger than 0.6 for particle volume and masses (PM$_{10}$ and PM$_{2.5}$) and larger than 0.9 for particle number. The correlations of NO$_x$ concentrations with other compounds at the highway site are slightly higher than those at the urban site, because traffic emissions are clearly dominating at the highway site. The bold faced correlation coefficients (below the diagonal in Table 4) are calculated from the time series of street increments (kerbside minus background). Switching to the street increments increases the correlations of NO$_x$ with particle area and particle volume at the highway and the urban sites from 0.84 to 0.92, 0.63 to 0.84 and from 0.86 to 0.91, 0.74 to 0.85, respectively. In addition, an increased correlation is found for PM$_{10}$ and PM$_{2.5}$ at the highway site. The subtraction removes the different time variation found in the background and isolates the traffic signal.
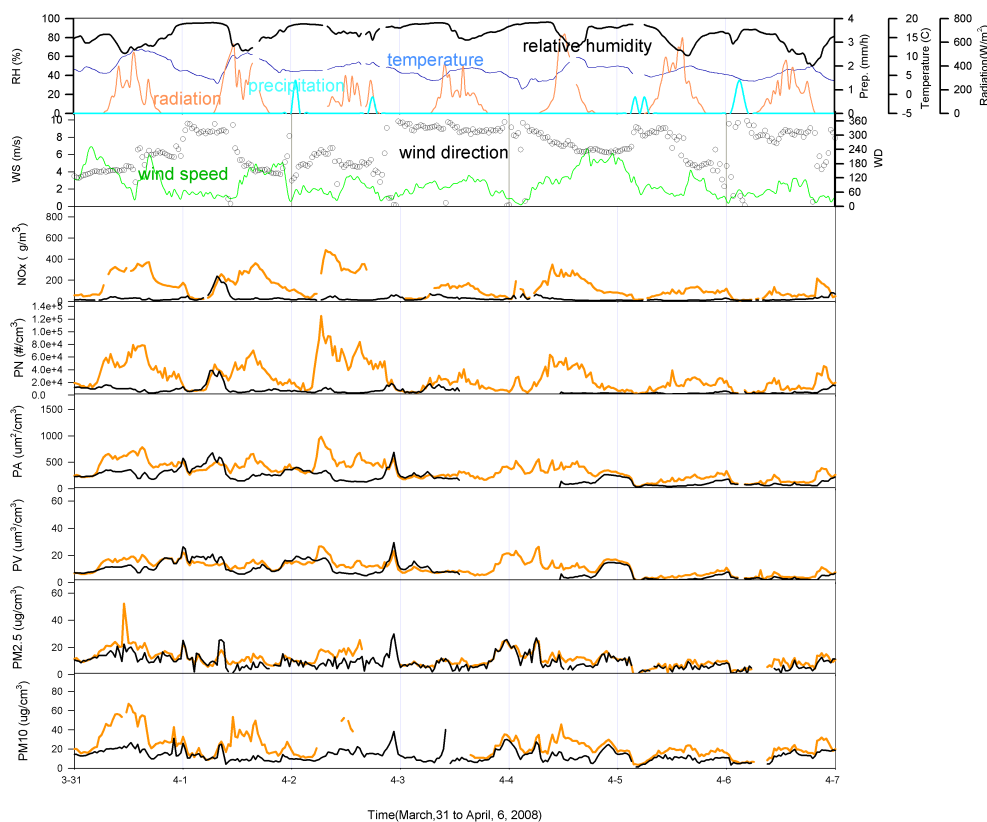
Fig. 4. Time series at the highway site for a selected period of one week from Monday, 31 March 2008 to Sunday, 6 April 2008. Measured pollutants at Hw_Kb (in orange) and Hw_Bg (in black), grid lines indicate midnight.

Table 4. Pearson Correlation Matrix for measured gas and particle compounds; above the diagonal for total concentrations measured at kerbside and under the diagonal (bold face) for the street increment (kerbside minus background). Left: for the highway site (number of data=1108) Right: for the urban site (number of data =956), particle number (PN), particle area (PA), particle volume (PV).

	Highway						Urban				
	NO$_x$	PN	PA	PV	PM$_{2.5}$	PM$_{10}$	NO$_x$	PN	PA	PV	PM$_{2.5}$
NO$_x$	1.00	0.94	0.84	0.63	0.64	0.76	1.00	0.92	0.86	0.74	0.62
PN	**0.93**	1.00	0.86	0.62	0.63	0.72	**0.92**	1.00	0.84	0.71	0.61
PA	**0.92**	**0.95**	1.00	0.92	0.83	0.75	**0.91**	**0.89**	1.00	0.96	0.78
PV	**0.84**	**0.85**	**0.96**	1.00	0.82	0.65	**0.85**	**0.82**	0.98	1.00	0.78
PM$_{2.5}$	**0.73**	**0.70**	**0.74**	**0.69**	1.00	0.77	**0.61**	**0.57**	**0.60**	**0.57**	1.00
PM$_{10}$	**0.80**	**0.73**	**0.73**	**0.66**	**0.69**	1.00					

3.4 Time series and diurnal pattern of measured pollutants

Examples of one week time series for various meteorological and pollution measurements are illustrated in Figs. 4 and 5 for the highway and the urban stations. Blank values in the plots are due to missing data because of technical problems of instruments or times of calibration.

The highway and urban background stations show similar pattern for daily variations especially at the kerbsides and the reduced concentrations at the weekend. At the urban kerbside station the pollutant concentrations are consistently higher during daytime hours compared to the urban background, since the pollution is accumulated at the urban site due to the presence of buildings. However, at the highway site there are also periods during daytime when the background and kerbside stations show similar pollutant concentrations. This is the case when the wind direction is close to north and the highway background site lies downwind of
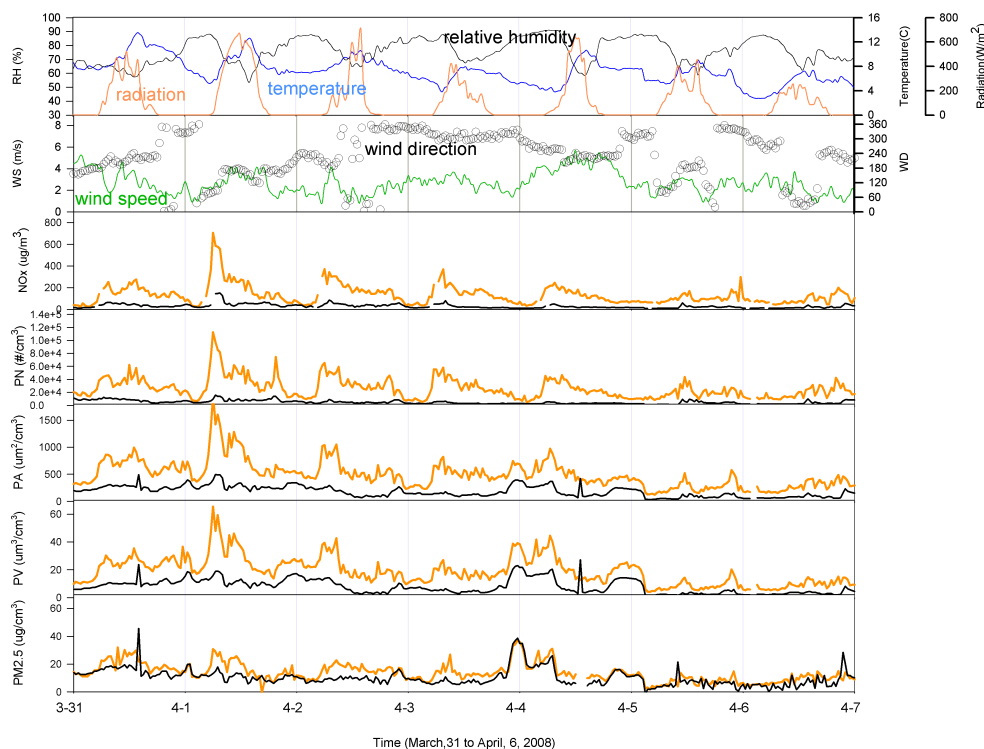
Fig. 5. Time series at the urban site for a selected period of one week from Monday, 31 March 2008 to Sunday, 6 April 2008. Measured pollutants at Urb_Kb (in orange) and Urb_Bg (in black), grid lines indicate midnight.

the highway. It is evident that the concentration is sensitive to the wind direction at both highway stations, for instance, on 2 April, when the wind is nearly constant blowing from the south, the kerbside concentrations are higher than those measured in the morning hours on 1 April and on 3 April with constant wind direction from north. Also the wind speed has influence on the concentrations. Higher wind speeds produce stronger turbulences and improve dilution resulting in lower concentration levels. This can be observed at the highway and urban sites on 4 April in comparison to other days. PA, PV and PM$_{2.5}$, PM$_{10}$ concentrations show a similar pattern at the kerbside and the background for each of the locations. For those compounds episodic behaviour is observed originating from non-local sources (long-range transported) e.g. on 4 April observed at all stations. NO$_x$ and PN are less affected by those episodes.

3.5 Particle size distribution

The following sections focus on the discussion of the measured average particle number and volume size distribution and its dependence on time of the day and wind direction.

3.5.1 Day-night profiles of particle number size distributions

The average particle number size distributions during daytime and night-time are presented in Fig. 7 for all four measurement stations and for weekdays and Sundays, respectively. One of the most obvious differences between highway and urban data is the different shape of the particle number size distribution. While the urban kerbside shows the typical maximum in the size distribution at about 23–30 nm, the size distribution at the highway peaks at about 10 nm, which is the lowest measured size. The number concentration during daytime of weekdays (left in Fig. 7) is higher than during night-time at all four measurement stations. At night-time the number decreases to almost half of the daytime concentrations in the size range of less than 100 nm at the kerbside stations and remains nearly constant at the background stations. This finding is most likely due to the lower traffic volume during night-time.

It is remarkable that the number concentration of particles in the range of 20–100 nm at Sundays is higher at night-time than at daytime (right in Fig. 7), showing the opposite trend with the traffic volume in Fig. 3. This phenomenon was also observed in a street canyon in Copenhagen in a previous study and was explained by the high share of taxis on weekends especially during night-time (Ketzel, 2003).
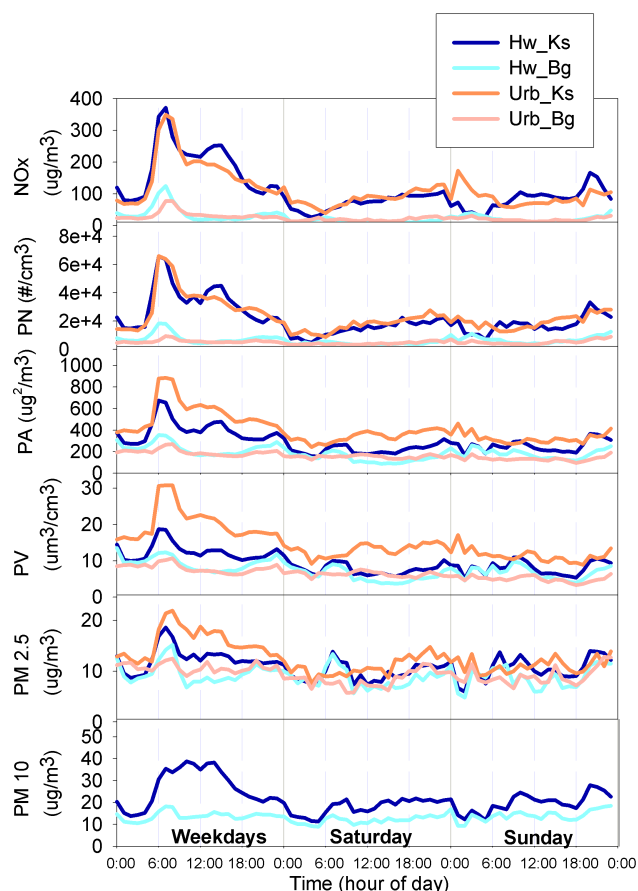
Fig. 6. Average diurnal variation of pollutants at the highway and the urban background and kerbside stations.

Furthermore, the higher atmospheric stability and lower wind speeds at night might play a role.

3.5.2 Average particle size distribution at weekdays and weekends

The average particle size distributions for weekdays and Sundays are shown in Fig. 8 as number and volume size distributions. The measurements obtained at the kerbside and the background stations are illustrated. Figure 8 shows that during weekdays the particle number concentration at the highway kerbside station rose to 60 000 particles cm^{-3} ($dN/d\log Dp$ unit) for sizes at about 10 nm. The shape of the curve indicates a maximum in the particle number concentration at about 10 nm or even smaller. This "nucleation" mode has been also observed by Giechaskiel et al. (2005) during a mobile laboratory chasing experiment on a high-speed track at about 100–120 km h^{-1}. Unfortunately the particles less than 10 nm is outside the size range of the measurements in this study. The particle number concentration at the urban kerbside station peaks at about 20 nm to 30 nm, which reaches 30 000 particles cm^{-3} ($dN/d\log Dp$ unit). The parti-

cle number concentrations at the two kerbside stations indicate a second mode at around 50–80 nm with a value at about 20 000–25 000 particles cm^{-3}. This mode is also observed at the background stations reaching its maximum with about 6000–7000 particles cm^{-3} corresponding to a regional background contribution.

The principle shape of the observed particle number concentration at the urban site is consistent with observations found in other urban areas (Bukowiecki et al., 2003; Wehner and Wiedensohler, 2003). Pirjola et al. (2006) reported that near a major highway the particle number size distributions showed 2–3 modes peaking at 14–23 nm (nucleation mode), 40–50 nm (soot mode) and 120–125 nm (accumulation mode). Zhang et al. (2004) found that particle number concentration peak appeared at smaller particle diameter when the samples were taken from closer to vehicular sources. They also found seasonal effects indicating higher ultrafine particle exposure levels in the winter even at distances further away from highways, and that the particle number concentration peaks shifts from 60 nm in summer to 10 nm in winter.

During Sundays (thin lines in Fig. 8) the particle number size distribution keeps the shape similar to those on weekdays, but with substantially lower concentrations at the two kerbside stations. This might indicate that the change of the vehicle composition (lower HDVs share) at the weekend is not reflected in a change in particle number size distribution. However, the particle number concentrations at the background stations do not decrease much from weekdays to Sundays.

The particle volume size distribution shows a completely different picture (right in Fig. 8). The accumulation mode is located at about 300–400 nm and dominates completely. The particle volume size distribution appears especially high at the urban kerbside station during weekdays. At the highway kerbside station, the maximum of the accumulation mode only reaches half of the concentrations compared to the urban kerbside station during weekdays, which indicates a higher traffic contribution at the particles probably due to non-exhaust emission.

3.5.3 Particle number size distribution decline near the highway

In this section we analyse a special situation at the highway site in order to investigate how the highway influence is detectable at the background station.

It is observed that the total particle number at the highway background station is elevated for northern wind direction (WD) (see Fig. 4). We investigate this phenomenon by selecting one downwind and one upwind case with relatively constant WD. Therefore, the particle number size distribution at the highway background station is compared to the highway kerbside station for those two cases. For northern WD, the highway background station is located downwind
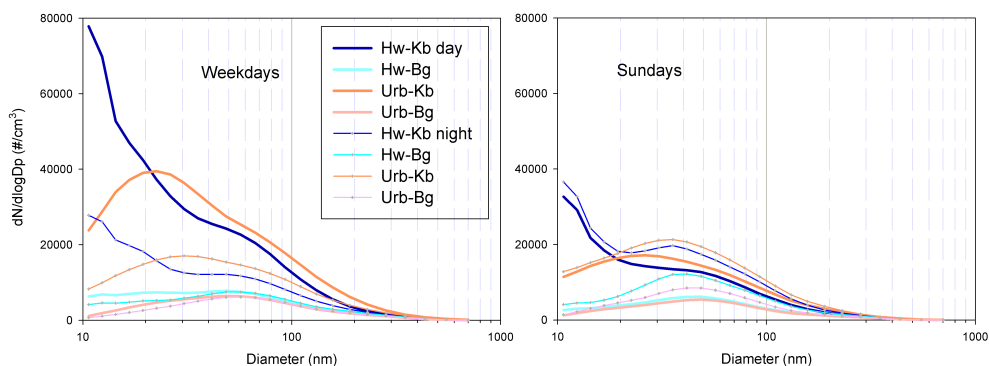
Fig. 7. Daytime (05:00 to 20:00) and night-time (21:00 to 04:00) variation of particle number size distributions during weekdays (left) and Sundays (right).
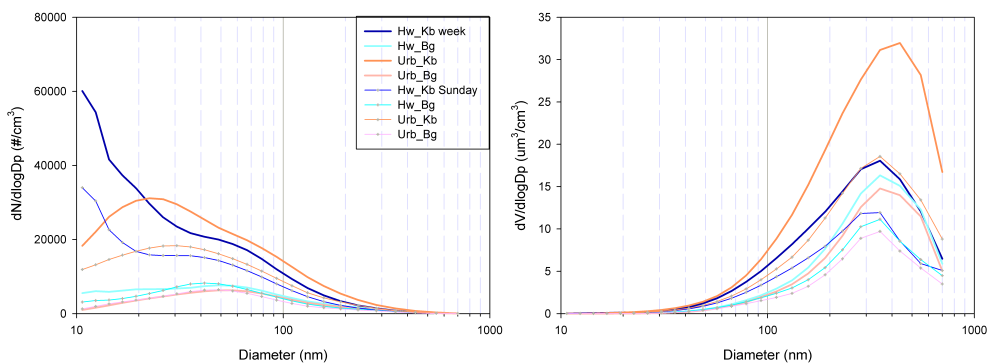

Fig. 8. Average particle number size distribution (left) and average particle volume size distribution (right) for weekdays and Sundays for all four measurement stations.

of the highway and for southern WD it is upwind. Figure 9 illustrates the effect of the WD on the particle number size distribution at the highway background station. The maximum of the nucleation mode for particle sizes less than 20 nm is observed when the WD is from north, but does not appear on the following day when the wind direction is from south. This shows that small vehicular exhaust particles with diameters less than 20 nm can still affect the particle number size distribution in a distance about 200 m away from the road. On the contrary, Zhu et al. (2002) found near a highway there were three modes with a mean geometric diameter of 12.6 nm, 27.3 nm and 65.3 nm, the smallest mode peaking with $1.6 \cdot 10^5$ cm^{-3} and disappearing at a distance of 90 m.

The particle number concentration decays by a factor of 5 to 10 in a distance of 200 m from the highway kerbside station indicated by Fig. 10. This gradient decrease of particle number concentration is also reported by other studies. Hitchins et al. (2000) found that the number concentration observed in a distance of 100 m to 150 m from the road was only half of the level measured in a distance of 15 m from the road. Pirjola et al. (2006) reported that the total particle number concentration decreased by 35–45% while the air mass was transported from the roadside to a distance of about 60–80 m from a highway.

3.6 Contribution of traffic generated pollutants

We define the difference of pollutant concentrations $\Delta C(t)$ between kerbside $C_{\text{kerbside}}(t)$ and background $C_{\text{background}}(t)$ as the "traffic contribution" in Eq. (3) as analyzed in this section and in Sect. 4. An urban street station is affected by 3 major source contributions: (1) contribution from the local street next to the station, (2) contribution from other local sources (e.g. other streets, train station, non-traffic sources) and (3) regional-long range transported pollution from outside the city. In this study, we assumed that the contributions from other local sources and regional-long range transported pollution for outside the city are similar at both kerbside and background stations ($C_{\text{kerbside}}(t)$ and $C_{\text{background}}(t)$). Thus, the basic idea with taking the difference in Eq. (3) is that the local street contribution is isolated. Additionally, at the highway site a selection of wind directions from 105° to 225° is applied when calculating the traffic contribution in order to assure that the background site is not influenced by the highway emissions. The contributions from nearby roads and regional-long range transport are also "neutralized" by taking the difference in Eq. (3).

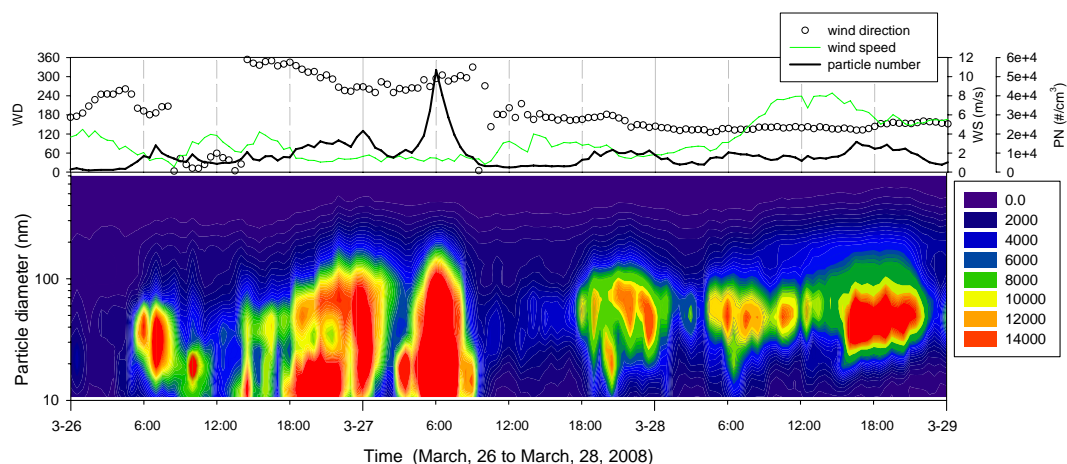$$\Delta C(t) = C_{\text{kerbside}}(t) - C_{\text{background}}(t) \qquad (1)$$

Fig. 9. Particle number size distribution at the highway background station upwind and downwind: case study from 26 (Wednesday) March to 28 (Friday) March 2008.
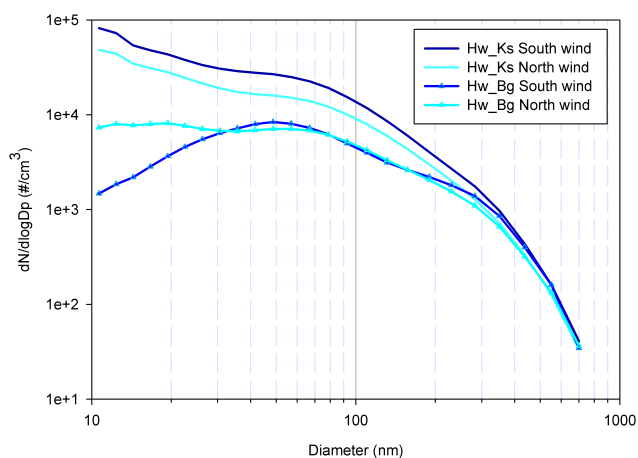

Fig. 10. Average particle number size distribution (using log scale) measured at the highway background and the highway kerbside stations for southern (105°−225°) and northern (225°−105°) wind direction (only weekdays included in the analysis).

3.6.1 Diurnal variation of the contribution of traffic emitted pollutants

In Fig. 11 the diurnal variation of the traffic contribution for various pollutants at weekdays, Saturdays and Sundays is shown. For weekdays, the average daily traffic contributions at the highway and urban site for NO$_x$ are 197 µg m^{-3} and 131 µg m^{-3}, respectively. For particle number they are 32 500 and 26 200 particles cm^{-3}, for particle volume 4.15 and 12.3 µm^3 cm^{-3}, and for PM$_{2.5}$ 3.8 and 5 µg m^{-3}. The traffic contribution is 8 µg m^{-3} for PM$_{10}$ that is only measured for the highway site during the campaign period. The diurnal patterns of NO$_x$ and particle number concentration are observed to be quite similar for the highway and the urban sites. At weekdays two peaks can be identified at rush hours,

at around 07:00 LT in the morning and at around 16:00 LT in the afternoon, corresponding well with the traffic volume pattern shown in Fig. 3. It is notable that the afternoon peaks are less distinct at the urban site which is associated to the scattered and lower traffic volume peak in the urban area during afternoons. The particle area (PA) and particle volume (PV) follow a similar pattern as the total particle number. However, the concentrations of PA and PV are lower at the highway site than at the urban site. The diurnal variation of PM$_{2.5}$ and PM$_{10}$ has a broad range of higher contributions during daytime with much less pronounced rush hour peaks. During weekends, the number of data points is significantly lower and a higher scatter is apparent in the diurnal curves. All pollutants appear with much lower concentrations in weekends compared to weekdays due to lower traffic volumes and less heavy duty vehicles. During the early morning hours on Sundays, NO$_x$ and particle number exhibit concentration maxima at the urban site due to the high share of taxis. These vehicles are mostly diesel-powered and equipped with oxidising catalytic converters. Similar findings have been reported in previous studies of traffic generated air pollution in Copenhagen (Wåhlin et al., 2001; Ketzel et al., 2003).

3.6.2 Lognormal fitting of particle number size distribution

The increments of particle number size distributions from kerbside to background at the highway and urban sites are further analyzed and fitted with lognormal curves. The averaged particle number size distribution and normalized particle number size distribution by NO$_x$ concentration are shown in Fig. 12. The normalization of the measured particle number size distribution to NO$_x$ results in a source profile independent from the dilution conditions, which could be used for estimating particle number emissions in numerical models. At the urban site, the normalized particle number size
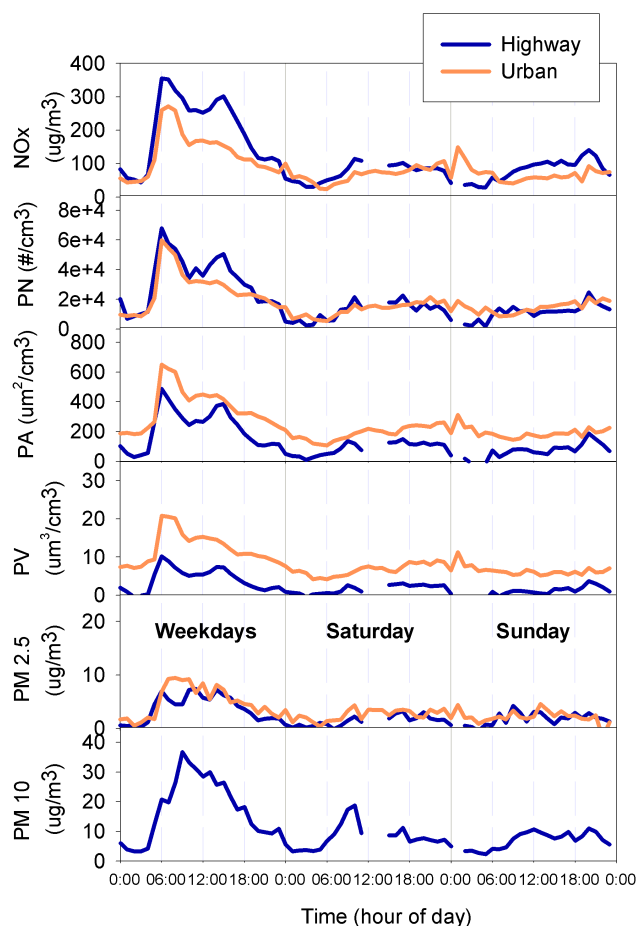
Fig. 11. Average diurnal variation of the traffic contribution (kerb-side minus background) at the highway site and the urban site during weekdays, Saturdays and Sundays. The gaps in the highway data originate from missing data due to the wind direction selection.

distribution is similar to the profile obtained in previous measurements at an urban street canyon station in Copenhagen (Ketzel et al., 2003).

The particle number size distribution measured at the urban site shows a nucleation mode with a maximum at about 20–30 nm and a "soot" mode at about 50–80 nm. The accumulation mode at around 200–300 nm is difficult to see in this number weighted plot and is therefore omitted in the fitting procedure, however, it is visible in the volume weighted plot in Fig. 8 or in Fig. 10. The concentration of nucleated particles is almost twice compared to the soot mode particles. Both modes are usually observed for aged aerosol and typically at rural and natural levels (Tunved et al., 2003; Berresheim et al., 2000). Kittelson (2004) found that traffic flow fluctuations induced variability in number concentration mainly for particles less than 50 nm in diameter. At the highway site, the nucleation mode dominates the particle number concentration and is shifted to much smaller sizes
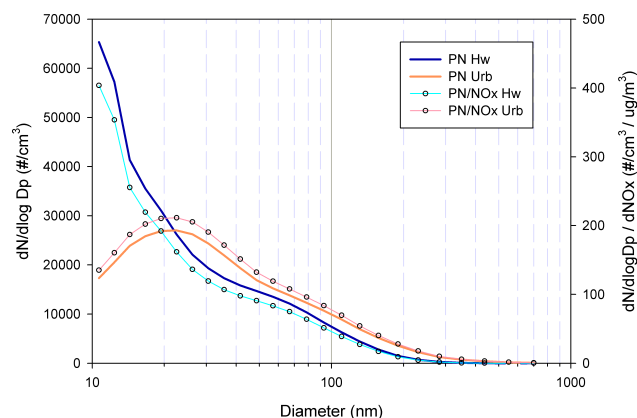

Fig. 12. Particle number size distribution of traffic contribution and normalized particle number size distribution (dN/d logDp to ΔNO$_x$, right scale) at the highway site (Hw) and the urban (Urb) site on weekdays.

(about 10 nm) compared to the urban site. The soot mode can also be identified at the highway although its concentration is slightly lower than at the urban site.

In order to further quantify the nucleation and soot modes, we used lognormal functions to fit the entire particle number size distribution. The distribution calculated for highway and urban traffic contribution can be represented by 3 lognormal modes, one nucleation mode at about 10 nm (named mode 1) representing small fresh nucleated particles, one nucleation mode around 17 nm (named mode 2) mainly containing nucleated particles by organic compounds or sulphuric acid and a soot mode around 60 nm (named mode 3) consisting of aggregates of less volatile carbonaceous material, (Kittelson, 1998). The mode 1 was added to estimate the concentration of small particles that are found at the highway close to the size range limit of the used instrument. Therefore the estimated values of this freshly nucleated particle fraction have a high uncertainty. The lognormal function used for mode parameterization here is given by the following equation:

$$dN/d\log Dp = \sum_1^{i=3} N_i \frac{e^{-(\log(Dp/\overline{Dp_i})^2/2\log(\sigma_i)^2)}}{\sqrt{2\pi}\log(\sigma_i)} \qquad (2)$$

where i is the number of modes, Dp (nm) the particle diameter, $\overline{Dp}$ (nm) the count median diameter (CMD), σ the standard deviation, and N (particles cm^{-3}) is the number concentration of particles in the individual mode.

The data at certain hours of the night-time (at 03:00 LT), morning and afternoon rush hours (at 07:00 LT and at 16:00 LT) (see the diurnal variation in Fig. 11) at all weekdays are used for the lognormal fit for the highway site and the urban site separately. The mode fitting parameters are listed in Table 5 and the results of lognormal functions are presented in Fig. 13. At the urban site, the particle number size distribution for the traffic contribution shows generally lower concentrations for the particles smaller than 30 nm.
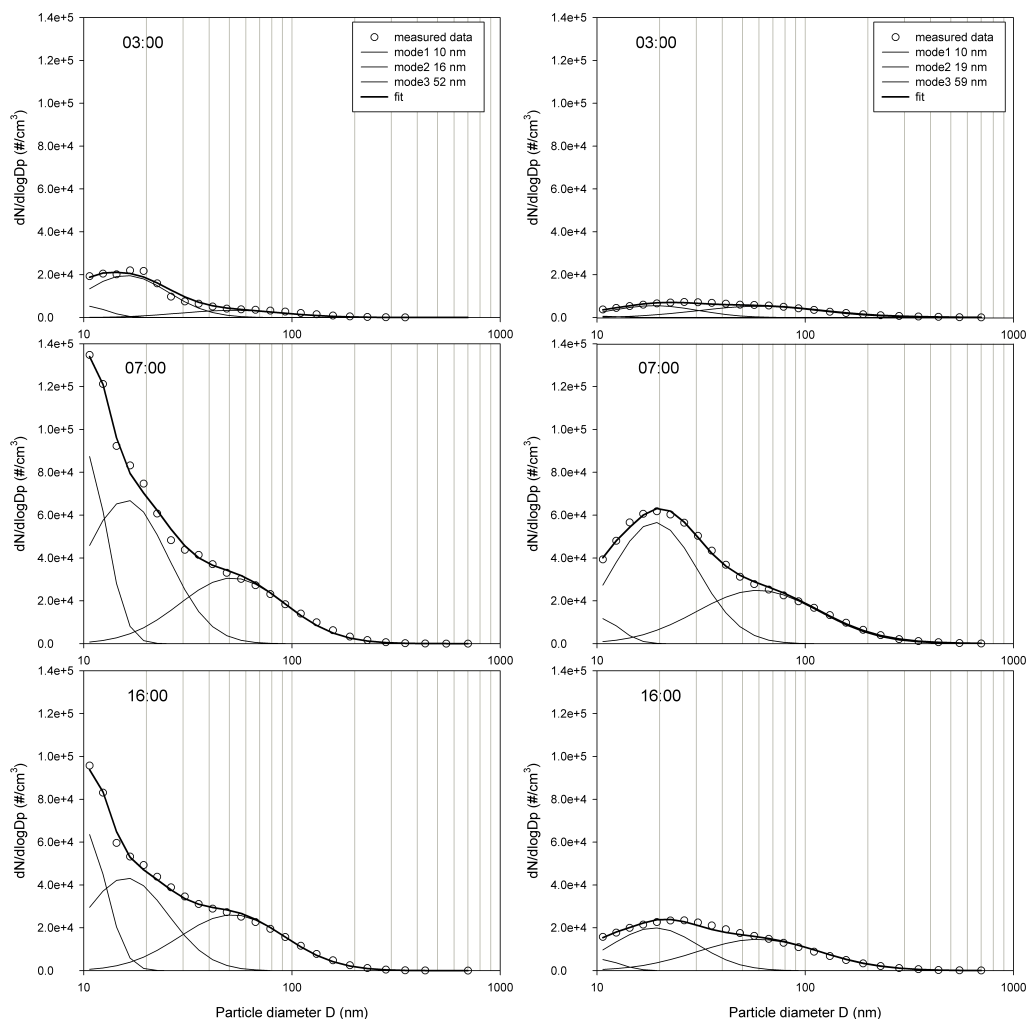
Fig. 13. Lognormal fit of particle number size distribution at the highway site (left) and the urban site (right), using averaged traffic contributed concentrations at 03:00 LT, 07:00 LT and 16:00 LT at weekdays.

Table 5. The parameters of three lognormal modes at the highway site and urban site as result of fitting the measured size distributions.

	Mode 1		Mode 2		Mode 3	
	CMD (nm)	σ	CMD (nm)	σ	CMD (nm)	σ
Highway	10	1.25	16	1.59	52	1.79
Urban	10	1.25	19	1.61	59	1.96

The number concentration in mode 2 located at about 19 nm at the urban site dominated during the morning rush hour (07:00 LT) and almost doubles the one in mode 3 located at about 59 nm at the urban site. During the afternoon rush hour, this number concentration in mode 2 decreases again only being little higher than that in mode 3. Mode 1 centred at 10 nm has only very small contribution at the urban

site independently of the time of the day. At the highway site, particles in mode 1 exhibit obviously high concentrations, especially at the rush hours, which is most likely due to higher traffic speed. Kittelson et al. (2004) found that high traffic speed favoured the formation of nucleation mode particles and lower speeds produced larger particles and larger aerosol volumes investigated by on-road travelling measurements. Near road measurements also show similar observations (Zhu et al., 2002). In our study, at both sites the particle number concentrations are higher during the morning rush hour than during the afternoon rush hour, though the traffic densities are quite similar (Fig. 3). The higher wind speed and more unstable atmospheric conditions generally observed in the afternoon, might facilitate the dilution of particles during the afternoon rush hour.

3.6.3 Correlation between NO$_x$, traffic volume and particle number size distribution

In this section we calculated the correlation between the time series of single size channels of the particle number size distribution with NO$_x$ concentrations for the highway and urban stations. In all cases the background was subtracted since only the traffic contribution is considered.

The Pearson correlation coefficient of the particle number in certain size ranges with NO$_x$ concentration and with traffic volume is shown in Fig. 14. The correlation coefficient is higher than 0.85 for diameters between 30 nm and 100 nm indicating that traffic is the dominating emission source for fine particles. For diameters less than 30 nm the correlation for measurements at the highway site is slightly lower. The weaker correlation for particles larger than 200 nm with NO$_x$ and traffic volume originates from the lower number of emitted particles in this size range. The traffic volume also shows a similar trend of correlation coefficient with respect to particle number. The correlation coefficient of traffic volume and particle number in our study shows similar pattern reported in other studies (Voigtlander et al., 2006; Kerminen et al., 2007). Voigtlander et al. (2006) reported for a street canyon in a medium-sized German city a correlation coefficient between passenger cars and particle number of 0.7–0.8 for the size range from 10 nm to 100 nm. Hussein et al. (2007) reported the correlation to be 0.8 for particles less than 100 nm. The high correlation coefficient of particle number for particles smaller than 200 nm in diameter with NO$_x$ concentration and traffic volume obtained in this study strongly supports the statement that NO$_x$ can be used as a tracer to estimate particle number size emission factors in this size range.

4 Vehicle Emission factors determination

4.1 Method

The emission factors (EFs) for NO$_x$ and particles are derived based on the above described traffic contribution (kerbside minus background concentrations) and the traffic data for the highway and urban street sites.

In this study, we assume that NO$_x$ and particles are diluted in the same way, and particle dynamic processes can be neglected in a first estimate since it is verified that dilution is the absolute dominating process of fine particles near roads (Zhang et al., 2004; Pohjola et al., 2003; Ketzel and Berkowicz, 2004).

The average vehicle emission factor (independent of the category) for the pollutant of species i, EFP$_i$, with units depending on i, (for example, particles veh^{-1} km^{-1},) is determined according to Eq. (3):

$$\text{EFP}_i = \frac{\Delta C_i(t) \cdot D(t)}{N_{\text{total}}(t)} \tag{3}$$
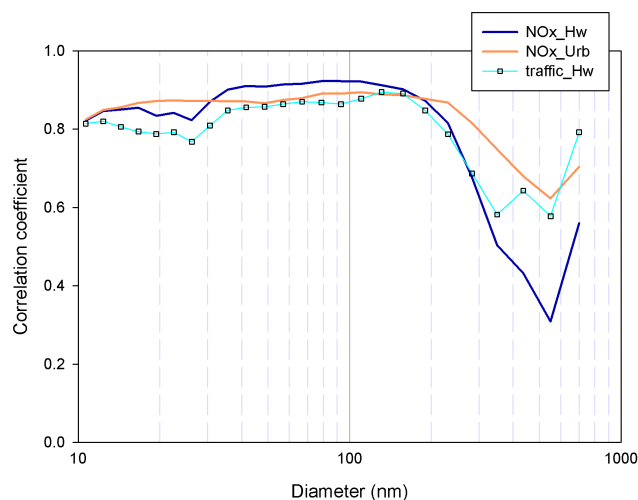

Fig. 14. Correlation coefficient for NO$_x$ contribution and particle number size distribution at the highway and urban sites, and correlation coefficient for traffic volume and particle number size distribution at the highway site.

Where $\Delta C_i(t)$ (particles cm^{-3}) is the concentration increment of species i, $D(t)$ (m^2 s^{-1}) the dilution rate at time t, and $N_{\text{total}}(t)$ (vehicle s^{-1}) the total number of vehicles passing at the measurement site per hour. The hourly dilution rate ($D(t)$) is calculated by the Danish Operational Street Pollution Model, WinOSPM, where wind speed, wind direction and traffic generated turbulence are considered (Berkowicz, 2000; Ketzel et al., 2003). This model based dilution rate $D(t)$ can be compared to the dilution rate ($D(t)$(m^2 s^{-1})) calculated from measured pollution data via Eq. (4):

$$D'(t) = \frac{\text{EF}_{\text{NO}_x} \cdot N_{\text{total}}(t)}{\Delta C_{\text{NO}_x}(t)} \tag{4}$$

where EF$_{\text{NO}_x}$ is the NO$_x$ emission factor calculated with the emission module of WinOSPM which implements the European COPERT 4 emission model (EEA, 2007) with the reported traffic situation in Sect. 3.2. The WinOSPM model is able to calculate for streets with variable building height or asymmetric streets. In this study WinOSPM is applied for both of the urban and highway stations. For the highway situation we compared $D'(t)$ and $D(t)$, which revealed reasonable good correlation with R^2 of 0.54. In this study we use $D(t)$ which shows less variation.

The emission factors for the highway and the urban street traffic situations are calculated for the two categories LDVs and HDVs. A more detailed disaggregation of emission factors into individual categories (i.e. passenger cars, taxi, delivery vans, trucks, buses) was not possible with the present dataset. The emission contribution for LDVs and HDVs was determined by multiple linear regression with following Eq. (5).

$$N_{\text{total}}(t) \cdot \text{EFP}_i = n_{\text{LDV}}(t) \cdot \text{EFP}_{i(\text{LDV})} + n_{\text{HDV}}(t) \cdot \text{EFP}_{i(\text{HDV})} + \varepsilon_i \tag{5}$$

where n_{LDV} and n_{HDV} are the numbers of LDVs and HDVs, ε_i the residual.

The Ordinary Least-Squares (OLS) approach is employed on a dataset of hourly average values of traffic and pollutant concentration data subdivided into weekdays, Saturdays and Sundays. The dataset was verified to hold the underlying assumptions of OLS estimation: 1) that Xs (n_{LDV} and n_{HDV}) are independent, 2) that Y ($N_{total}(t) \cdot EFP_i$) is linearly dependent on Xs, and 3) that Y and ε_i are normally and homogeneously distributed (Wilks, 2006). As a result, OLS produces estimators that are unbiased (i.e. expected to be equal to the true value) and efficient. Uncertainties in the traffic data e.g. the ratio of LDV and HDV will of course result in errors in the emission factors an estimate of the error is given in Sect. 4.5.

4.2 Emission factors for the mixed traffic fleet

Based on Eq. (3), we calculated the emission factors for the different compounds for weekdays, Saturdays and Sundays with the traffic contribution shown in Fig. 11. The weekly variation in emission factors are shown in Fig. 15 together with the traffic volume variation and the share of HDVs at both sites.

At the highway site, emission factors of NO_x, particle number, particle area and particle volume show some correlation with the variation of the HDVs share (See Fig. 15 left). On weekdays, two peaks are present one at early morning hours around 03:00 LT to 06:00 LT when the HDVs share is high ($\sim$25%), and one around 12:00 LT when the HDVs share is also high (18%). A third small peak appears around 21:00 LT. The early morning peaks are also seen at Saturdays and Sundays, but they are relatively smaller compared to the peaks on weekdays. On weekends, emission factors seem more fluctuating due to a smaller amount of data available for the calculation.

At the urban street site, the HDVs share is about half of the highway site (see Fig. 15 right). The emission factors of NO_x and particle number are also relatively lower at the urban site compared to the highway site. However, on the contrary, the emission factors of particle area and particle volume are much higher at the urban site compared to the highway site, which indicates that the emitted particles at the urban site are generally larger on average compared to the highway site. This might be caused by the higher driving speeds and engine load at the highway that influences the emissions of the engine and by a higher share of mechanical generated particles (brakes, re-suspension of road dust). During weekdays three peaks are found as for the highway data. By far the highest peak appears in the early morning. Klose et al. (2009) found a similar diurnal variation of the particle number emission factors in a German urban street with a pronounced peak at about 00:00 LT in the early morning. During the late evenings of Saturdays after 20:00 LT and until 05:00–06:00 LT in the next

morning the emission factors of NO_x and particles appear high even when the HDVs share is low. It might be due to diesel-powered taxis dominating the traffic and emitting higher numbers of particles. Jayaratne et al. (2005) concluded from recent studies that particle number emission factors of diesel vehicles are much higher than for petrol vehicles ranging around 1.0–$7.17 \cdot 10^{14}$ particles veh^{-1} km^{-1} and $1.74 \cdot 10^{11}$-$4.5 \cdot 10^{13}$ particles veh^{-1} km^{-1} for diesel and petrol driven vehicles, respectively.

The particle number emission factors for different modes are also presented at the bottom of Fig. 15. The emission factors of mode 2 and mode 3 closely follow the variation of total particle number emission factors at the highway and the urban sites. However, there are differences between the sum of the three modes (diameter > 10 nm) and the measured data. At the urban site, mode 1 only takes a tiny part of the total number concentrations as shown in Fig. 13, where the cut off at 10 nm only caused negligible losses. Thus, the emission factors for total particle number even show a slightly higher value than the sum of the emission factors for the three modes. At the highway site, mode 1 is much larger and includes a part of the total number concentration at sizes less than 10 nm. Therefore, the aggregated emission factor for the three modes is around 10% to 20% higher than the total number emission factor, which is estimated only for particles sizes larger that 10 nm.

4.3 Emission factors for HDVs and LDVs

Emission factors for the total vehicle fleet as well as differentiated into LDVs and HDVs are reported in Table 6. The half-hour average data set is used as input to estimate emission factors by performing multiple linear regression.

The NO_x emission factors for the total vehicle fleet are calculated (1.41 ± 0.03) g veh^{-1} km^{-1} (the coefficient and the stand error from OLS estimation only) at the highway site and (0.94 ± 0.02) g veh^{-1} km^{-1} at the urban site. These values are comparable to the NO_x emission factors calculated by the emission module of WinOSPM. The emission module of WinOSPM estimates 1.33 g veh^{-1} km^{-1} at the highway site (0.77 g veh^{-1} km^{-1} for the LDVs and 6.97 g veh^{-1} km^{-1} for the HDVs) and 0.95 g km^{-1} at the urban site (0.56 g veh^{-1} km^{-1} for the LDVs and 9.03 g veh^{-1} km^{-1} for the HDVs). The results show that the NO_x emission factor of LDVs increases with the vehicle speed that is $\sim$50 km h^{-1} at the urban site and $\sim$100 km h^{-1} at the highway site. However, the NO_x emission factor for HDVs decreases with the vehicle speed since the engines run more efficiently on highways compared to urban roads. The total NO_x emission factor is higher at the highway site, partly due to a higher share of HDVs (10.5% compared to 4.5% at urban site) and partly due to the higher emission factors for LDVs, which dominates the vehicle fleet. The NO_x emission factor ratio of HDVs to LDVs also increases from about 15 at the highway site to about 26 at the urban site.
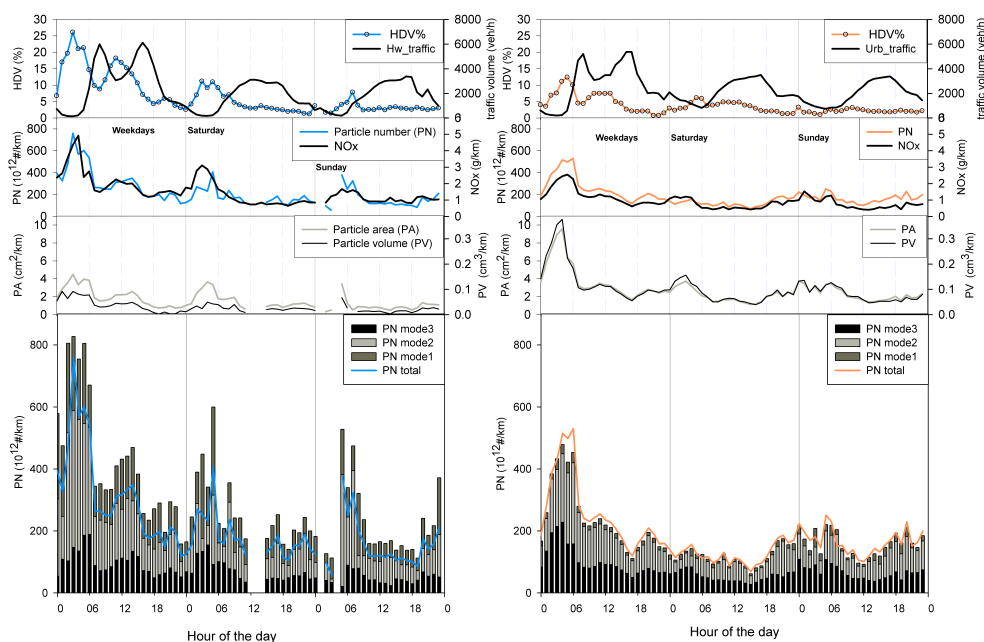
Fig. 15. Diurnal and weekly variation of traffic volume, HDVs share, emission factors of NO$_x$, particle number (PN), particle area (PA) and particle volume (PV) at the highway site (left) and the urban (right) site. Blanks at the highway site are due to missing data of wind directions at the highway site.

The average emission factors of particle number are slightly higher with (215 ± 5) 10^{12} particles veh^{-1} km^{-1} at the highway site compared to (187 ± 3) 10^{12} particles veh^{-1} km^{-1} at the urban site, due to the higher HDVs share at the highway. However the emission factors for LDVs and HDVs are slightly higher under the urban driving conditions. The emission factor ratios of HDVs to LDVs are about 22 at both sites for total particle number. We also find that this ratio differs from the emission factors of mode 2 and mode 3 and for both of the modes the ratio is slightly higher at the urban site (28, 24) than at the highway site (23, 19). Mode 1 (diameter=10 nm) gives this ratio to about 10 at both measurements sites with high uncertainty.

Table 7 summarizes the particle number emission factors separated for LDVs and HDVs from recent published field studies. The results are in a wide range. The results of Klose et al. (2009) are significantly higher than the other studies. Our results for both LDVs and HDVs show relatively low values and are still in agreement with the previous studies. The ratio of particle number emission factors of HDVs to particle number emission factors of LDVs varies in the range of 11 to 123. Our results are closer to the reported HDVs/LDVs ratios of 10–30 (Imhof et al., 2005) and 24 (Kirchstetter et al., 1999), but the study of Birmili et al. (2009) at a urban motorway in Berlin obtained much higher HDVs/LDVs ratios (123±28) . It is clear that particle number emission factors for the car fleet are depending on the traffic composition (e.g. LDVs/HDVs), driving conditions, the vehicle fleet in

the year of measurements (diesel share, share of Euro 1, 2, 3 etc.), the meteorological conditions, particle number measurements, etc. Therefore these parameters should be presented when comparing emission factors; however, it is not always easy to access this information in the literature.

To provide a comparison with other studies of the particle number emission factors for different particle fractions, the emission factors for different particle fractions PN$_{0.05}$ (diameter<50 nm), PN$_{0.05-0.1}$ (50 nm<diameter<100 nm) and PN$_{0.1}$ (diameter>100 nm) are also calculated. It is obvious that the emission factors of PN$_{0.05}$ that includes the major part of total particle number emissions are in good agreement with results reported by others (Imhof et al., 2006 and Yli-Tuomi et al., 2005). These authors also estimated emission factors of particle number in various size ranges under real-world conditions. Beddows and Harrison (2008) summarized the emission factors of those particle fractions (solid particle) and reported lower values than our results, especially for PN$_{0.05}$. It might be explained that near road particles less than 50 nm in diameter contain mostly volatile organic compounds and the concentration varies according to meteorological conditions and applied measurement technique (Charron and Harrison, 2003). PM$_{2.5}$ and PM$_{10}$ emission factors were also estimated. Emission factors for PM$_{2.5}$ for the mixed fleet at the highway and urban site are 29 mg veh^{-1} km^{-1} and 46 mg veh^{-1} km^{-1}, respectively. Emission factor of PM$_{10}$ for the mixed fleet at the highway is 131 mg veh^{-1} km^{-1}. They are comparable with the studies from UK (Jones and Harrison, 2006), but the values

Table 6. Calculated emission factors for various pollutants given for the mixed fleet and separated for LDVs and HDVs (per vehicle).

Parameter	Unit	EFP(total)	Std. error	EFP(LDVs)	Std. error	EFP(HDVs)	Std. error	HDVs/LDVs ratio
Highway								
NO$_x$	g km^{-1}	1.4	0.027	0.70	0.029	9.8	0.29	15
PN$_{total}$	10^{12} km^{-1}	215	5.3	81	6.9	1750	68	22
PN$_{mode1}$	10^{12} km^{-1}	98	3.2	54	5.8	595	56	11
PN$_{mode2}$	10^{12} km^{-1}	121	3.7	43	5.8	993	56	23
PN$_{mode3}$	10^{12} km^{-1}	76	1.9	31	2.6	575	25	19
PN$_{0.05}$	10^{12} km^{-1}	194	4.8	78	6.6	1486	64	19
PN$_{0.05-0.1}$	10^{12} km^{-1}	33	1.1	18	2.1	201	20	11
PN$_{0.1}$	10^{12} km^{-1}	6.8	0.39	3.5	0.76	44	7.4	12
PA	cm^2 km^{-1}	1.5	0.037	0.51	0.045	12.4	0.44	25
PV	cm^3 km^{-1}	0.029	0.001	0.01	0.001	0.25	0.011	25
PM$_{2.5}$	mg km^{-1}	29	1.0	11	2.0	233	18	21
PM$_{10}$	mg km^{-1}	131	4.0	44	7.0	1087	68	25
Urban								
NO$_x$	g km^{-1}	0.93	0.015	0.46	0.029	11.9	0.59	26
PN$_{total}$	10^{12} km^{-1}	187	3.1	101	6.2	2206	128	22
PN$_{mode1}$	10^{12} km^{-1}	31	1.4	23	3.0	208	62	9
PN$_{mode2}$	10^{12} km^{-1}	83	1.7	40	3.5	1088	73	28
PN$_{mode3}$	10^{12} km^{-1}	61	1.2	31	2.4	746	48	24
PN$_{0.05}$	10^{12} km^{-1}	101	2.4	39	4.8	1554	100	40
PN$_{0.05-0.1}$	10^{12} km^{-1}	47	1.4	34	3.1	335	64	10
PN$_{0.1}$	10^{12} km^{-1}	20.2	1.1	8.6	2.4	289.5	49.9	34
PA	cm^2 km^{-1}	2.5	0.037	1.4	0.073	27.8	1.5	20
PV	cm^3 km^{-1}	0.085	0.001	0.048	0.003	0.95	0.055	20
PM$_{2.5}$	mg km^{-1}	46	1.0	20	2.0	628	50	31

Table 7. Comparison of emission factors for particle number (LDVs and HDVs) reported from field studies.

reference	Road type	Speed LDV/HDV (km h^{-1})	EFP$_{(LDV)}$ (10^{12} particles veh^{-1} km^{-1})	EFP$_{(HDV)}$	Sizes (nm)	ratio HDVs/LDVs
Imhof et al., 2005	Motorway	120/85	690	7300	> 7	11
	Highway	85/75	320	6900	> 7	22
	Urban road	0–50/0–50	80	5500	> 7	69
Jones and Harrison, 2006	Urban road	0–40/0–40	58.4	636	11–437	11
Klose et al., 2009	Urban road	0–30/0–30	540	43 000	4–800	80
Birmili et al., 2009	Urban motorway	75–90	24	2960	10–500	123
This study	Highway	110/90	80.7	1750	10–700	22
	Urban road	0–50/0–50	100	2210	10–700	22

are significantly lower than the estimates for an American highway (Kirchstetter et al., 1999) of 43 mg veh^{-1} km^{-1} for LDVs and 987 mg veh^{-1} km^{-1} for HDVs. The road conditions, temperature and relative humidity also effect the PM$_{2.5}$ and PM$_{10}$ concentrations. Furthermore, road and brake dust, and tyre wear emissions also play important roles as non exhaust emissions in this context. It suggests that chemical composition analysis is further needed to characterize PM emissions in the vicinity of traffic roads in terms of the contribution of exhaust and non exhaust emissions.

4.4 Emission factors for size-resolved particle number

Figure 16 shows a comparison between emission factors of size-resolved particle number (particles veh^{-1} km^{-1}) from
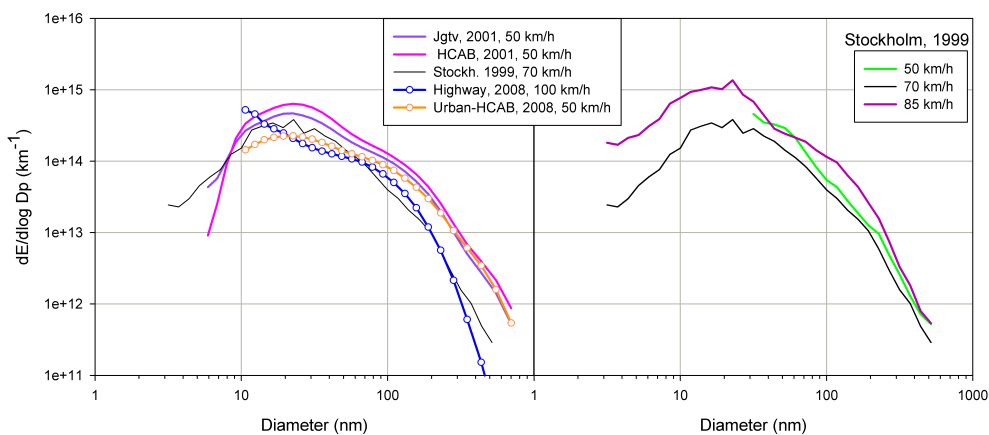
Fig. 16. Left: Comparison of the size-resolved emission factors for the average car fleet from this study (Highway and HCAB in 2008) with the size distribution measured at two streets in Copenhagen (Jgtv and HCAB in 2001; Ketzel et al., 2003) and in a road tunnel in Stockholm (in 1999, Kristensson et al., 2004). Right: Speed dependence of the emission factors in Stockholm, Sweden. For the speed 50 km·h^{-1} and particle sizes below 30 nm, the emission factor could not be estimated due to particle losses in the tunnel.

this study and kerbside measurements at Jagtvej (Jgtv) and H.C. Andersens Boulevard (HCAB) in Copenhagen (Ketzel et al., 2003), as well as, a tunnel study in Stockholm (Gidhagen et al., 2003; Kristensson et al., 2004). For all measurements, the size resolved particle number emission factors peak at about 10–30 nm in diameter, with an additional mode centred around 70–100 nm.

Particle number emission factors from HCAB distinctly decreased from 2001 to 2008 for particles less than 100 nm. This finding is consistent with the observed reduction of the ultrafine particles. Wåhlin (2009) reported that the average particle number concentration at a kerbside station (HCAB, the same location as our urban street site) has been reduced by 27% from the period 2002–2004 to the period 2005–2008, due to the transition to sulphur-free (<10 ppm) diesel fuel and petrol in Denmark from New Year 2005.

In our previous study we observed total particle emission factors for an average vehicle fleet (5% HDVs) of $\sim$300·10^{12} km^{-1} and $\sim$400·10^{12} km^{-1} at Jagtvej and HCAB (speed limit 50 km h^{-1}). This is slightly higher than our present study obtained at both the highway and urban sites. It should be noted that the DMA cut off size during this study was at 10 nm compared to 5.6 nm during the previous study. In the Swedish tunnel study the total particle emission factors for an average traffic fleet increased with increasing speed from $\sim$300·10^{12} particles veh^{-1} km^{-1} to $\sim$110·10^{13} particles veh^{-1} km^{-1} in the speed interval 70 km·h^{-1} to 85 km·h^{-1} due to higher engine load. Imhof et al. (2005) also reported an increase of emission factors for LDVs and HDVs with increasing travel speed at different sites. The results of this study do not reveal the speed dependence of total particle number emissions. Under urban driving conditions, the stop-and-go and frequent acceleration after traffic lights might increase the emission of submicrom-

eter particles, explaining our higher emission factors of particle number at the urban site compared to the highway site, especially for HDVs.

4.5 Sensitivity test for emission factors estimates based on traffic counts variations

It is obvious that the accuracy of the traffic count will affect the average emission factor and the HDV/LDV emission factor. Since the traffic flow at urban site was not simultaneously measured during the campaign and also the automatic counts at the highway site could be affected by misclassifications of the vehicle type we performed a sensitivity study to assess possible influence on the calculated emission factors.

The multi-linear regression equation (Eq. 5) was re-run to calculate the emission factors after altering the number of HDV (n_{HDV}) by 20%, either keeping $N_{total}(t)$ or n_{LDV} constant. This resulted in a change of the HDV emission factor of max. 17%. The average HDV share is 4.4%, 8.4% at urban and highway site respectively, therefore the emission factor of HDV at highway is slightly more sensitive compared to it at the urban site. The emission factor for LDV did not change significantly. This sensitivity tests shows that the relative error in the HDV emission factor is of similar size as an possible error in the estimated HDV traffic flow.

5 Conclusions

The evaluation and comparison of a four-week data set of measurements at a highway and an urban busy street including a kerbside station and a background station at both sites confirms that traffic is the main source to NO$_x$ and particle number at the kerbside measurement sites.

The measurement results show that observed concentrations of NO$_x$ and particle number are similar at the highway and urban kerbside stations, and these values exceed those measured at the background stations by a factor of 3 to 5. The influence of the highway traffic to the background station in 200 m distance is evident, since distinct high values of particle number concentrations of particles less than 20 nm in diameter were observed when the highway background station was located downwind of the highway.

The traffic contribution is analyzed as the increment of vehicular pollutant concentrations between the background stations and the kerbside stations at both the highway and the urban sites. NO$_x$ and particle number show similar behaviour with two peaks during rush hours. At evenings of weekends high values are observed only at the urban site due to additional weekend activities in the downtown area.

Emission factors were determined on the basis of the measured traffic contribution, car fleet and modelled dilution rate as $(215\pm5)10^{12}$ particles veh^{-1} km^{-1} for the highway and $(187\pm3)10^{12}$ particles veh^{-1} km^{-1} for the urban site. These values agree well with findings of other studies. HDVs are found to emit 10 to 40 times more particles in different modes than LDVs which is in good agreement with other published studies. The diurnal variation of all emission factors peak at 03:00 LT to 06:00 LT in the morning at weekdays at both sites and coincide with a high share of HDVs at this time. The weekends' late evening peak at the urban site is mostly due to the high number of taxis (mostly diesel-powered passenger cars) running in the downtown areas in the evening and during the night. The emission factors for size-resolved particle number for particles less than 100 nm is found to distinctly decrease compared to our previous study in 2001. This is most likely due to the transition to sulphur-free ($<$10 ppm) diesel fuel and petrol in Denmark from New Year 2005, reducing the traffic generated ultrafine particles.

Emission factors for PM$_{2.5}$ for the mixed fleet at the highway and urban site are 29 mg veh^{-1} km^{-1} and 46 mg km^{-1}, respectively. Emission factor of PM$_{10}$ for the mixed fleet at the highway is 131 mg veh^{-1} km^{-1}. The estimated particle number and size spectra emission factors will provide valuable input for air quality and particle dispersion modelling near highways and in urban areas.

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