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Comparative study of ultrafine atmospheric aerosol within a city

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HIGHLIGHTS

- Median particle number concentrations varied by a factor of 40 within a city.
- Diurnal N_{6-100} patterns were different for various urban sites.
- Median diameter of number size distributions decreased with anthropogenic impact.
- Nucleation strength factor was introduced to quantify the contribution of nucleation.

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ABSTRACT

Particle number size distributions in a mobility diameter range of 6–1000 nm and size-resolved number concentrations were determined with a time resolution of 10 min for a near-city background, city centre, street canyon and road tunnel environments in Budapest. Median N_{6-100} concentrations for the sites listed were 3.1×10^3, 9.3×10^3, 19.4×10^3 and 123×10^3 cm^{-3}, respectively. Contributions of the ultrafine (UF) particles (<100 nm) to the total particle number for all locations were rather large (up to 86%), and do not seem to vary substantially in time. Diurnal variations of the mean N_{6-100} concentrations had different patterns for both the various urban sites, and for workdays and weekends. Nucleation strength factor (NSF) was introduced for the first time to quantify the relative importance of new particle formation with respect to all sources of UF particles. During the daytime in summer, nucleation in the near-city background was a major production process of UF particles with a daily mean relative contribution of 42%. In the city centre and street canyon, the daily mean relative contributions of nucleation to the UF particles were 30% and 23%, respectively. Median particle diameters for the background, city centre, street canyon and road tunnel environments were 61, 42, 35 and 42 nm, respectively, so they were jointly influenced with the anthropogenic impact and aerosol ageing. Monthly mean frequency of new particle formation and growth events in the background seems somewhat larger, while it appears smaller for the street canyon in comparison to the city centre.

1. Introduction and objectives

Ultrafine (UF) atmospheric aerosol particles (with an electric mobility diameter <100 nm) are usually present in relatively large number concentrations (daily medians up to 10^4–10^5 cm^{-3}) and abundances (70–90% of all aerosol particles) in cities (Kulmala et al., 2004; Aalto et al., 2005; Putaud et al., 2010; Backman et al., 2012; Borsós et al., 2012). The particles are either emitted directly from high-temperature processes (such as automotive road traffic exhaust, industrial combustion processes, cooking and residential heating) or they are formed in the air by atmospheric nucleation. Importance of understanding the contribution of primary and secondary particles on regional and global spatial scales was recently outlined by Reddington et al. (2011).

Although studies are scarce, there is a body of evidence that UF particles represent specific and excess health risks relative to coarse or fine particles of the same or similar chemical composition (Oberdörster et al., 2005; JRC-EASAC, 2011). Their health effects are mainly caused by 1) the large number of insoluble particles deposited in the respiratory system, 2) their large surface area and 3) very small size. Clearance mechanisms of the respiratory system are only able to remove huge numbers of deposited particles with limitations, and the rest of particles contribute to releasing free radicals and causing inflammatory effects (Kreyling et al., 2006).

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The smallest UF particles can cross the cellular membrane of the respiratory epithelium, enter into the bloodstream or the cellular interstitial fluid. This modifies certain functions of the blood, and yields enhanced and systematic translocations of the deposited UF particles from the respiratory system to other organs including the liver, heart and nervous system, and can cause adverse health effects there (Oberdörster et al., 2005). The impacts are most severe on the elderly and people with compromised respiratory system such as the chronic obstructive pulmonary disease (Morawska et al., 2004; Geiser et al., 2005; Morawska, 2010). Ultrafine particles can impact the urban climate and heat island in city centres as well because they can grow to cloud condensation nuclei (CCN), and can influence the cloud formation and properties (Reddington et al., 2011). According to modelling studies, at least 50% of the CCN is related to the nucleation process on a global scale (Merikanto et al., 2009).

Several research studies were devoted to concentrations and physical properties of UF particles in cities (e.g., Väkevä et al., 2000; Woo et al., 2001; Wehner and Wiedensohler, 2003; Hussein et al., 2004; Aalto et al., 2005; Harrison and Jones, 2005; Stolzenburg et al., 2005; Jeong et al., 2006; Rodríguez et al., 2007; Avino et al., 2011; Salma et al., 2011a, 2011b; Dall'Osto et al., 2013). Methods to differentiate among the major production processes of particles were also proposed (Shi et al., 1999; Alam et al., 2003; Watson et al., 2006; Qian et al., 2007; Park et al., 2008; Costabile et al., 2009). There is, however, limited information available on the UF aerosol within a city. Despite that some properties or features of the UF aerosol are expected to differ in various urban environments. This is due to the relatively short residence time of most of these particles (Salma et al., 2011a), and the influential vicinity of their major production processes. Differences in the properties of UF particles could affect their impacts on public health and the environment. As far as mass size distributions are concerned, substantial differences in the distributions and some differences in the lung deposition for various urban sites within a city were indeed observed (Salma et al., 2002a, 2002b). The main objectives of this paper are to report average particle number concentrations, to interpret their temporal variation for some important size fractions and for derived properties such as nucleation strength factor; to determine representative and typical particle number size distributions for further modelling; and to discuss the frequency variation of new particle formation and growth events within a city.

2. Applied methods

2.1. Measuring methods

Aerosol particles were measured by a flow-switching type differential mobility particle sizer (DMPS, Aalto et al., 2001; Salma et al., 2011a) including a ^{241}Am neutraliser, a Nafion semi-permeable membrane drier, a 28-cm long Hauke-type differential mobility analyser and a butanol-based condensation particle counter (CPC, model 3775, TSI, USA). The system operates in an electric mobility diameter range from 6 to 1000 nm in 30 size channels at two sets of flows. In the first flow mode, 20 channels are measured (from 6 to 200 nm), while in the second flow mode, 10 channels are acquired (from 200 to 1000 nm). A shoulder around 200 nm often appears in the size distributions as an artefact caused by switching the flow and high voltage parameters. Its extent usually remains below 10% although it occurs as a systematic deviation. Fortunately, no major aerosol formation and transformation processes are exclusively confined to the diameter range affected. The diameters obtained refer to the dry state of particles since the DMPS operates in dried sample flow (with a typical relative humidity, RH $<$ 20%). The measurements were performed with a time resolution of approximately 10 min. The measuring system and method fulfil the recommendations of the international technical standards (Wiedensohler et al., 2012).

2.2. Measurement environments and time intervals

The measurements were performed in Budapest, Hungary. Its population is 2 million. The major pollution sources include vehicular road traffic, residential heating and household activities. Long-range transport of some pollutants also plays a role (Salma and Maenhaut, 2006). Contributions of passenger cars and buses to the vehicle fleet registered in Budapest and Pest County are 87% and 0.46%, respectively (OKJ, 2010). Diesel-powered vehicles shared 18.2% and 97% of the national passenger car and bus fleets, respectively. Unleaded petrol is exclusively sold for road vehicles, and the diesel fuel marketed for road vehicles contains S in a concentration $<$10 ppm. The experimental work was realised at four selected sites which represent different urban environments, i.e., a near-city background, a city centre, a street canyon and a road traffic microenvironment.

The measurements in the near-city background were performed at the KFKI Atomic Energy Research Institute (latitude 47° 29′ 12.5″ N, longitude 18° 57′ 17.7″ E, altitude 424 m above sea level, a.s.l.) continuously from 1 June to 10 August 2011. The site is situated within a woody campus on the western border of Budapest. It is expected to represent the air masses entering the city since the prevailing wind direction is NW. The measurements in the city centre were accomplished at the Eötvös University's campus at Lágymányos (latitude 47° 28′ 29.8″ N, longitude 19° 03′ 44.6″ E, altitude 114 m a.s.l.) continuously from 3 November 2008 to 2 November 2009 (Salma et al., 2011a). The site is situated in a distance of 80 m from the bank of the river Danube. The street canyon measurements were performed in a building of the Eötvös University located in the city centre (5 Rákóczi Street, latitude 47° 29′ 39.4″ N, longitude 19° 03′ 36.3″ E, altitude 111 m above a.s.l) continuously from 28 March to 31 May 2011. The street is approximately 2.0 km long, 25–40 m wide, and has a typical height of 25–30 m. The street belongs to regular long street canyons (Hunter et al., 1992). For this type of canyons, the bulk perpendicular air flow skims over the canyon and usually produces a single vortex within it, which favours air pollution build-up. The major ventilation occurs in longitudinal direction. The measurements in the traffic microenvironment were carried out in the Castle District Tunnel (latitude 47° 29′ 54.5″ N, longitude 19° 02′ 24.6″ E, altitude 106 m a.s.l. at its eastern gate) continuously from 12 to 26 July 2010 (Salma et al., 2011b). The tunnel has a single, straight bore with a length of 350 m, a width of 9.3 m, and it varies from 7.9 to 10.7 m in height. It is situated in the city centre, and is oriented perpendicular to the river Danube with its closer, eastern gate in a distance of approximately 130 m from the river bank. The tunnel comprises two-lane road traffic, and involves a pedestrian lane and a service curb along the sides. The tunnel has an elevation of 1.8% toward the western gate, which promotes passive ventilation. The air movement is enforced by ventilation without filtering from about 8:00 to 18:00 local time on workdays. Ambient air is drawn from the outer sideway spaces near the gates and above the bore by a mine ventilator through shafts, and it is delivered into the bore through a portal at a distance of 169 m from the eastern gate. The nominal ventilation rate is 1900 m^3 min^{-1}. Heavy-duty vehicles are not allowed to enter the tunnel. The measuring instrument was set up in a spare ventilation hall of the tunnel in a distance of 226 m from the eastern gate.

2.3. Data treatment

The measured data were mathematically inverted and were utilised to generate contour plots showing jointly the time variation in particle diameter and normalised particle number concentration (dN/dlog$d$). They were also used for calculating particle number concentrations in the diameter ranges from 6 to 1000 nm (N_{6-1000}), from 6 to 100 nm (N_{6-100}) and from 100 to 1000 nm ($N_{100-1000}$) with a time resolution of ca. 10 min. The N_{6-1000} and N_{6-100} concentrations represent well the total number of particles and UF particles, respectively (Salma et al., 2011a), while the $N_{100-1000}$ concentration contains aged particles expressing the regional aerosol population. The major portion of the N_{6-100} concentration (i.e., the Aitken mode) is essentially related to local processes due to the limited atmospheric residence time of these particles ($<10^0$ h), while the $N_{100-1000}$ concentration (the accumulation mode) expresses larger (regional) spatial and time scales because of much longer residence times of up to 10^1 d of these particles. Individual, 10-min data were utilised to calculate various concentration ratios, and these ratios were then averaged. Diurnal variations of the concentrations and their derived properties, averaged by the time of day separately for workdays and weekends (including the national holidays as well), and for nucleation and non-nucleation days (see later) were obtained. Local time (UTC+1 and daylight saving time, UTC+2) was chosen as the time scale because the daily routine activities of inhabitants in cities were firstly considered. To determine particle number size distributions representing longer time intervals, median normalised concentrations for each size channel were obtained from the measured 10-min data, and they were utilised for deriving median size distributions. The averaging was accomplished for the whole data sets, separately for workdays and weekends, as well as for nucleation and non-nucleation days. Number median mobility diameters (NMMDs) and geometric standard deviations (GSDs) were determined by the log-probability plot method. Classification of the days with and without evident new particle formation and growth event was performed according to a modified decision algorithm of Dal Maso et al. (2005), Salma et al. (2011a).

Inter-comparison of the data in this way is advantageous since the instrumentation was the same at all locations. At the same time, it also includes limitations since the time intervals were not overlapping, and the year-to-year variation can indeed play a role as further discussed in Sect. 4. As far as the comparisons of average concentrations for different time intervals of at least 2-month duration are concerned, it was demonstrated earlier (Salma et al., 2011a, Fig. 2) that there is no substantial and tendentious seasonal variation in the average particle number concentrations in Budapest. Similarly, small relative changes in the NMMDs for the Aitken and accumulation modes were only observed for different seasons (Hussein et al., 2004). These types of average properties can be compared for different seasons. Some other properties, such as mean diurnal variation of the particle number concentrations, exhibited some seasonal variation but these quantitative changes were different from the qualitative modifications related more to particular environment. Some further properties, such as nucleation frequency, showed evident seasonal variation and smaller dependence on the environment. These properties were only compared by careful selection of the corresponding data sets, e.g., on a month by month basis. These all justify the selected comparative treatment.

Table 1
Minimum, median and maximum of the daily median number concentrations of ultrafine particles in 10^3 cm^{-3} units, and the mean contribution of ultrafine particles to the total particle number with its standard deviation both in % for the near-city background, city centre, street canyon and road tunnel environments.

	Background	City centre	Street canyon	Road tunnel
Minimum	1.25	2.7	4.9	86
Median	3.1	9.3	19.4	123
Maximum	10.1	20	41	187
UF contribution	76	79	86	86
Std. deviation	9	6	3	5

3. Results and discussion

3.1. Average and extreme concentrations

Ranges and medians of the daily median N_{6-100} concentrations and their mean contribution to the total particle number with its standard deviation for the 4 urban environments are shown in Table 1. The order of the sites listed is characterised by increasing anthropogenic impact. It is seen that the range of the daily median concentrations for the background, city centre and street canyon stayed similarly within a factor of 7–8, while it only varied by a factor of 2 for the road tunnel. The city centre and street canyon exhibited larger median concentrations than for the background by factors of 3 and 6, respectively, while this value was 40 for the tunnel. The ratios for the open environments are somewhat larger but comparable to the earlier corresponding results for the PM_{10} mass concentration at the same locations (Salma et al., 2002a), while for the road tunnel, the median PM_{10} mass concentration was about 10 times larger than for the background in contrast to the factor of 40 for the UF particles. The largest measured (10-min) N_{6-100} concentrations recorded in the background, city centre, street canyon and road tunnel were 38×10^3, 75×10^3, 131×10^3 and 392×10^3 cm^{-3}, respectively.

Contributions of UF particles to the total particle number (Table 1) for the 4 locations are rather large, up to 86%, and do not seem to vary substantially in time. This is linked to the fact that large primary emissions and the new particle formation events mostly occur alternatively in Budapest, and that the combination of these two effects maintains a more or less constant ultrafine contribution (Salma et al., 2011a). The mean contributions slightly increase from site to site in the order of the locations mentioned, with a levelling off.

3.2. Diurnal variations

Mean diurnal variations of the N_{6-100} and $N_{100-1000}$ concentrations for the 4 environments averaged separately for workdays and weekends are shown in Fig. 1. In the background (Fig. 1a), the N_{6-100} concentrations for workdays and weekends vary similarly to each other. They both contain a single peak in the midday with a longer tail in the afternoon. The peak is connected to 1) atmospheric nucleation and consequent particle growth into and out of the UF size interval. It is also associated 2) with road traffic and nearby sources as their emissions become gradually and with a delay part of the near-city background, 3) with photochemical activity, 4) with effects of temperature (through volatilisation or re-evaporation, Dall'Osto et al., 2013) and mixing height/dynamics. A similar pattern was observed for UF particles at background sites previously (e.g., Moore et al., 2007). Mean value of the individual N_{6-100} concentration ratios for workdays and weekends was 1.24, which indicates the existence of the anthropogenic impact, and suggests that there must be relationship between the new particle formation and growth on one side and anthropogenic activities on the other side. The diurnal variations of the $N_{100-1000}$ concentrations for workdays and weekends are essentially constant and

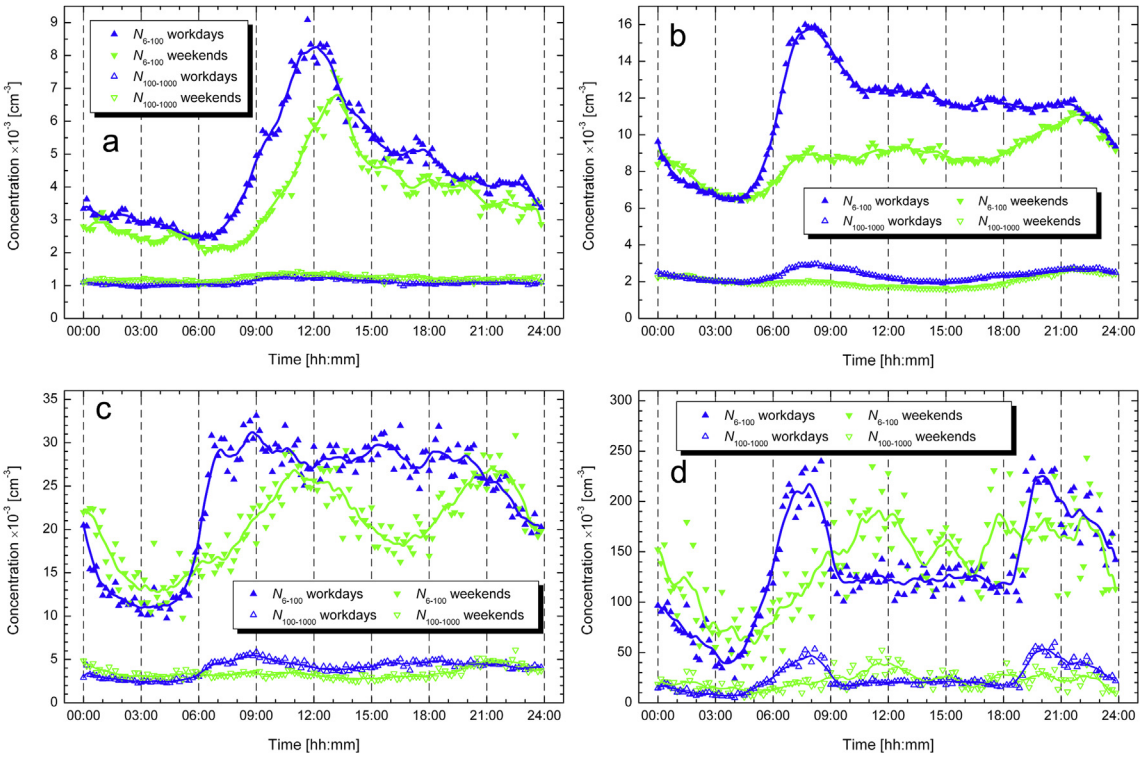

Fig. 1. Mean diurnal variations of N_{6-100} and $N_{100-1000}$ concentrations for the near-city background (a), city centre (b), street canyon (c) and road tunnel (d) environments averaged separately for workdays and weekends (including the national holidays). The curves were obtained by one-hour smoothing.

identical within the uncertainty interval indicating that the site can be indeed considered as a near-city background environment.

In the city centre (Fig. 1b), the mean diurnal variation of N_{6-100} concentration for workdays obviously resemble the typical activity pattern of inhabitants in cities, particularly of road traffic. It shows a major peak in the morning and a broader and smaller peak in the late evening. The first peak coincides with the intensive vehicle traffic, and it is caused by the direct emissions from vehicles. It is noted that the boundary layer mixing height is also increased during this interval because of increasing sun radiation. The second peak, however, occurs at about 21:00, thus markedly later than the afternoon rush hours, which usually happen in central Budapest between 16:30 and 18:30 (Borsós et al., 2012). Under strong anticyclonic conditions, evolution of the boundary layer mixing height and mixing intensity can decrease the concentration levels in the afternoons until sunset, and this can compensate the increased intensity of emissions. The evening peak is more influenced by local meteorology than by vehicular emissions. The effect of residential heating and combustion activities at evenings can also play a role. The diurnal behaviour obtained is consistent with the time variations in many other European cities (Hussein et al., 2004; Aalto et al., 2005; Moore et al., 2007; Avino et al., 2011; Borsós et al., 2012; Dall'Osto et al., 2013). In southern Europe, the effect of nucleation is more significant in the diurnal variations, while in central and northern parts, the UF particle concentrations follow more the traffic patterns (Reche et al., 2011). For weekends, the mean diurnal variation of the N_{6-100} concentration only contains a step-like increase and a relatively large evening peak. This is explained by the different daily activity patterns of citizens on workdays and weekends. Mean of the individual N_{6-100} concentration ratios for workdays and weekends was 1.26. As far as the $N_{100-1000}$ concentrations are concerned, their variation was rather small in comparison to the UF particles. On workdays, it only shows a very modest elevation from 6:00 to 10:00 (morning rush hours), which is mainly caused by emissions of larger particles and/or particle growth into this size range. The morning peak is missing for weekends but another small and broad elevation shows up from 20:00 to 22:00 instead. This can be related to the daily cycling of the local meteorological conditions.

In the street canyon (Fig. 1c), the mean diurnal variation of the N_{6-100} concentration for workdays shows a steep and substantial increase from 5:00 to 7:00, and it remains on the level of the maximum with fluctuations for the whole afternoon. The curve only starts decreasing after 20:00, which continues monotonically to 4:00. For weekends, the diurnal variation exhibits two broad peaks. The first of them reaches its maximum between 11:00 and 13:00 (so, substantially later than the corresponding concentration on workdays), which also results in a smaller slope of its increasing part. The maximum of the second peak is realised between 20:00 and 22:00. The concentrations from 0:00 to 5:00 are larger for weekends than for workdays. These all are explained by the features of road traffic. Mean of the individual N_{6-100} concentration ratios for workdays and weekends was 1.17. The mean diurnal $N_{100-1000}$ curves for workdays and weekends are rather similar to those for the city centre, with common explanations. The similarity indicates the existence of a continuous and overall urban background level (inside the city) for this size fraction.

In the road tunnel (Fig. 1d), the diurnal variation of N_{6-100} for workdays shows two peaks with maxima around 8:00 and 20:00. The first concentration increase is caused by increased vehicle flow in the morning rush hours. The concentration drop and the later jump result from switching on and off the ventilation facility around 8:00 and 18:00, respectively. The concentration level between them is maintained constant by the ventilation. The concentration decrease in the evening happens due to decreased traffic. On weekends, the diurnal variation of the N_{6-100}

concentration changes similarly to the traffic flow (Salma et al., 2011b) since the ventilation is not turned on at all. In this case, the road tunnel resembles an extreme street canyon, so the corresponding diurnal curves and their explanations are similar. Nevertheless, the evening peak is less evident due likely to the less direct effect of local meteorology. Mean value of the individual N_{6-100} concentration ratios for workdays and weekends was 1.03, so the lack of the ventilation on weekends hampers the effect of the smaller traffic. There was no new particle formation event and growth identified in the tunnel. The diurnal variations of the $N_{100-1000}$ concentrations reflect the temporal changes in the N_{6-100} concentrations in a smaller scale.

Mean diurnal variation of the N_{6-100} and $N_{100-1000}$ concentrations for the city centre averaged separately for the 4 seasons are shown in Fig. 2. There are some important similarities and differences among the corresponding curves. The concentration peak in the morning appears essentially at the same time in all seasons. It is almost exclusively linked to the emission intensity and timing of the morning rush hours. The peak increases for summer, spring, autumn and winter. This is related to the seasonal variation of local meteorological conditions. In spring, summer and autumn, the evening peak is well-separated from the morning peak with a deep and broad minimum between them. In winter, however, the concentration remained elevated between the two peaks due mainly to the smaller boundary layer mixing height. The position of the evening peak, however, varies in time. It occurs from 19:00 in winter to 22:00 in summer. The shift was partially caused by advancing clocks to the daylight saving time in the spring and autumn seasons but cannot explain its whole extent. The evening peak emphasises again that the role of local meteorology and its cycling in realising actual particle number concentrations. The curves also indicate a slight tendency for larger concentrations in winter with respect to summer.

3.3. Nucleation strength factor

The mean $N_{6-100}/N_{100-1000}$ concentration ratio averaged for nucleation days expresses the relative contribution of all emission sources and formation processes of UF particles relative to the regional aerosol. At the same time, a similar concentration ratio calculated for non-nucleation days expresses the relative contribution of all production processes of UF particles except for the nucleation relative to the regional aerosol. The ratio

$$\mathrm{NSF} = \frac{\left(N_{6-100}/N_{100-1000}\right)_{\text{nucleation days}}}{\left(N_{6-100}/N_{100-1000}\right)_{\text{non-nucleation days}}} \quad (1)$$

indicates the relative increment or contribution of nucleation to UF particles with respect to their all sources. It is introduced for the first time, and will be called the nucleation strength factor (NSF) in analogy of the enrichment factor utilised for mass concentrations of aerosol constituents. It was implicitly assumed in this reasoning that the major generation processes of particle number concentrations except for the nucleation are uniformly present on both nucleation and non-nucleation days. This is a reasonable assumption on a time scale of a month or longer. It was also presumed that the emission of particles larger than 100 nm over the time scale investigated can be neglected in comparison with the number concentration of UF particles. This is an ordinary situation in cities, which can be justified from the UF contributions to the total particle number in Table 1. If 1) NSF $\approx$ 1 then the relative contribution of nucleation to the UF particles with respect to other sources is negligible, 2) $1 <$ NSF < 2 then its relative contribution is significant or considerable, and 3) NSF>2 then the relative contribution of nucleation itself to the UF particles is larger than of any other production processes together.

Diurnal variations of the NSFs for the 3 environments (where nucleation was identified at all) are shown in Fig. 3. It can be seen that the curves exhibit a single peak with a longer tail on the decreasing side. The baselines of the peaks (the curves from 0:00 to 7:00) for the background and street canyon fluctuate around 1.00. This suggests that there is no difference between the UF contribution for nucleation days and for non-nucleation days in this time interval of the day. This confirms the basic assumption of the NSF discussed above. The pre-existing aerosol particles have small influence on nucleation events in these environments because they are usually present either in permanently low or steadily high concentrations, and because of further dispersion specialities of the street canyon. The baseline for the city centre is at a higher level with a mean and standard deviation of 1.24 ± 0.10, and it declines monotonically. The former observation means that either the pre-existing UF particles on nucleation days are in larger concentration than for non-nucleation days, which is unlikely, or the particle number concentration of the regional aerosol is smaller for nucleation days than for non-nucleation days. The latter option implies that nucleation events preferably take place on days characterised

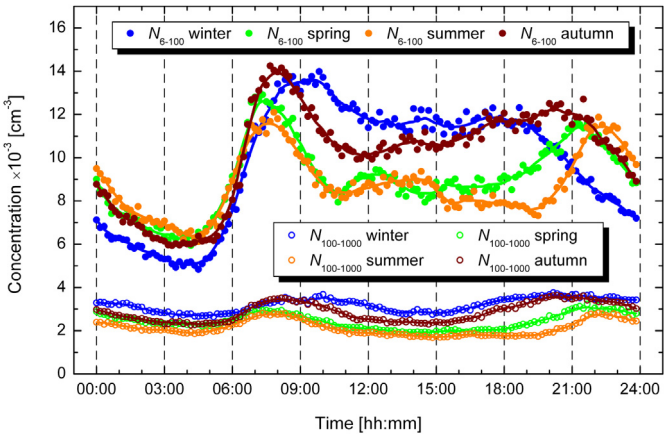

Fig. 2. Mean diurnal variations of N_{6-100} and $N_{100-1000}$ concentrations for the city centre averaged separately for winter, spring, summer and autumn. The curves were obtained by one-hour smoothing.

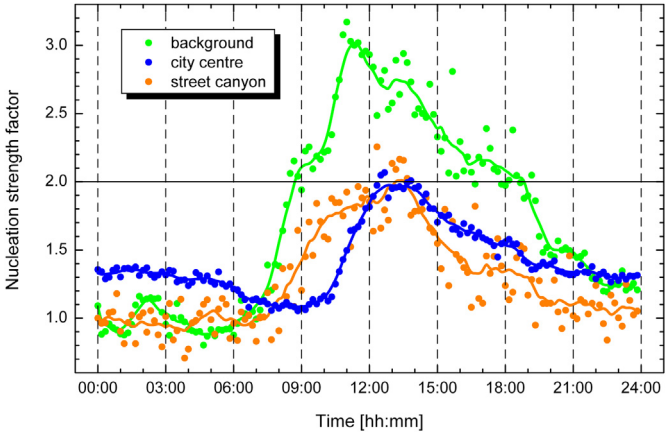

Fig. 3. Diurnal variations of nucleation strength factor for the near-city background, city centre and street canyon environments. The curves were obtained by one-hour smoothing. The horizontal line indicates the value at which nucleation becomes the major production source for ultrafine particles.

with smaller particle number concentrations. This can be confirmed directly from the experimental data, or from nucleation theories. As to the decrease of the baseline, it can be often visually experienced on the contour plots as well just before the banana curve starts. As far as the peak is concerned, it was created by new particle formation and growth processes. For the city centre, the peak starts increasing at 9:30, and the rising side is almost linear. For the background and street canyon, the increase starts earlier (at 7:30), and the rising side appears to be made of two straight lines. Their joinings seem to coincide with the start of rising for the city centre. The two parts of the rising side could be related to the fact that banana curves with double onset were not rare in the background. Double banana curves were reported earlier for a continental background site, and were explained as two superimposed nucleation events with the earlier event being of larger, regional origin and the later event being triggered by some local pollution, emission or air mass mixing phenomena (Hirsikko et al., 2013). Daily mean NSFs and standard deviations for the background, city centre and street canyon were 1.71 ± 0.69, 1.42 ± 0.26 and 1.29 ± 0.37, respectively. This means that the daily mean relative contribution of nucleation to UF particles relative to their all sources and formation processes were 42%, 30% and 23%, respectively. The relative importance of nucleation decreases with anthropogenic influence. If the averaging was, however, performed for the daylight time, mean values of 2.2 ± 0.5, 1.73 ± 0.18 and 1.63 ± 0.31, respectively were obtained. This implies that nucleation was the major process that produced 54% of UF particles in daylight time in the background in the studied season. The NSF for the central urban locations reached the value of 2 around 13:00 for few hours. This all implies that during these hours, the UF contribution of nucleation was similar to other production types – including traffic emissions – even in central parts. This emphasises the needs to study the health consequences of nucleation events in cities in addition to their (urban) climate relevance.

3.4. Size distributions

Fig. 4 shows median size distributions for the whole data sets (a) and those typical for nucleation event and consecutive particle growth (b). Some curves were scaled up to visualise better their shape. The particle number size distributions have rather dynamic feature since they reflect the continual and rapid changes in production, transformation and transport processes. Obtaining representative, i.e., average size distributions involves inherently disadvantages due to significant broadening of the Aitken and accumulation modes. It is seen in Fig. 4a that the averaging yielded a single peak. Deconvolution of the peak into the modes by fitting was not attempted because of theoretical limitations. Median diameters determined by the log-probability plot method are 61, 42, 35 and 42 nm for the background, city centre, street canyon and road tunnel environments, respectively. (The GSDs varied between 2.3 and 2.9.) The values are comparable with earlier atmospheric data (e.g., Hussein et al., 2004), and are in line with the median particle diameters ranging from 20 to 60 nm, and from 30 to 100 nm in gasoline and diesel engine exhausts, respectively (Harris and Maricq, 2001; Morawska et al., 2008). The NMMDs imply decreasing tendency with fresh vehicle emissions. The road tunnel is an exception since the size distributions are influenced by the ventilation facility introducing aged aerosol from the city background into the tunnel, which are larger in size than the freshly emitted particles (Salma et al., 2011b). The shoulder at 200 nm is an artefact (see Sect. 2.1.), and has a decreasing relative extent with particle number concentration. The NMMDs obtained from the median size distribution for workdays and weekends were equal to each other within the uncertainty interval. For nucleation days, the

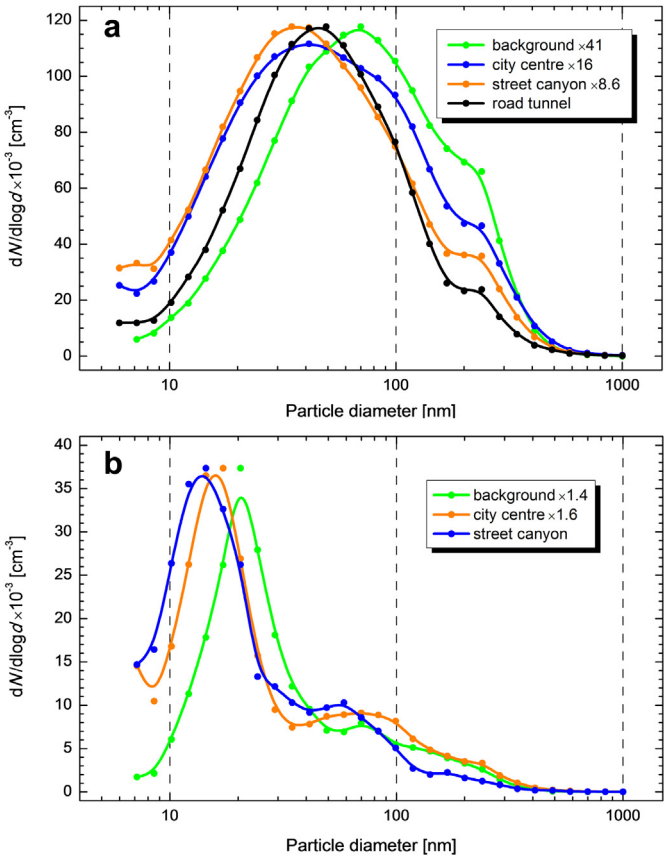

Fig. 4. Median particle number size distributions for the whole data sets for the near-city background, city centre, street canyon and road tunnel environments (a), and for class 1 nucleation events at a time of 1 h after the banana curve was registered (b) for the near-city background, city centre and street canyon environments. The curves were scaled to the maximum.

NMMDs were moderately smaller than for non-nucleation days for all environments. They were 51 vs. 67 nm, 38 vs. 45 nm, and 32 vs. 37 nm for the background, city centre and street canyon environments, respectively.

To derive typical size distributions for nucleation events, 10-min size distributions measured 1 h after the banana curve (of class 1 nucleation days, thus events with continuous and uninterrupted growth, see Sect. 2.3) were selected, and these individual distributions (7 data sets for the background, 31 for the city centre and 7 for the street canyon) were utilised to calculate median size distributions (Fig. 4b). Median diameters for the nucleation mode of 21, 13.7 and 15.8 nm, respectively were obtained. The values are comparable to earlier NMMDs in an urban area (Hussein et al., 2004).

3.5. Regional and urban nucleation events

New particle formation and growth events were identified in the background, city centre and street canyon environments, while no such phenomenon was observed in the road tunnel. The latter is explained by the lack of the sunlight and by rather large number concentrations of pre-existing aerosol particles. The banana curves in the background usually persisted for longer time, up to 27 h, than in the city centre. These represent regional nucleation events. There were nucleation events observed in the street canyon despite the large aerosol concentrations (Table 1) since the nucleation is realised by competing source and sink terms. There were essentially

two types of longitudinal airflows inside the street canyon: either from or toward the river Danube. This can lead to diverse and specific atmospheric conditions. In some cases, nucleation events were clearly recognisable during the daytime for several hours, when the wind only blew from the river, and the banana curves suddenly disappeared when the airflow changed to the opposite direction. The wind channel that is often formed above the river, brings cleaner regional air into the central part of the city, and dilutes the polluted air there (Salma et al., 2011a). According to numerical modelling, mixing two air parcels with different properties such as precursor concentrations, temperature and RH favours and enhances the nucleation (Nilsson and Kulmala, 1998; Kulmala et al., 2005). These events could be urban nucleation events confined to a certain territory only (Dall'Osto et al., 2013).

Monthly mean frequencies of the new particle formation and growth events for the 3 urban environments are shown in Fig. 5. It can be seen that the frequencies for the background seem somewhat larger, while the frequencies for the street canyon appear smaller than for the city centre. As far as the values in April are concerned, it was the maximum for the city centre, while it was substantially smaller for the street canyon. The difference can be caused by the closed character and smaller concentration of chemical species of biogenic origin in the street canyon than at the two other sites. The year-to-year variability naturally also influences the values.

4. Conclusions

Particle number concentrations increase substantially (by a factor of approximately 40 as far as daily medians are concerned) from a near-city background to a road tunnel within a city. In parallel with that, median particle diameters in the dry state decrease from 61 to 35 nm. Both changes should be jointly taken into consideration when assessing the health impacts of aerosol particle numbers on public via lung deposition modelling calculations. Similarly, the experimental sites for comparative studies among cities should be selected carefully to obtain comparable data.

In the beginning, atmospheric nucleation was identified and studied in clean terrestrial remote or rural environments, and nucleation in cities was considered to be an unfavourable process. It turned out later that nucleation is not at all a rare phenomenon in many cities. Moreover, it was quantified in the present study that nucleation is a very important production process of UF particle concentrations relative to other sources in urban environments. In the near-city background, atmospheric nucleation had the largest relative contribution (larger than the emission sources) for several hours in the daylight time in summer. Its relative contribution in summer/spring is considerable (up to 30%) even in central urban areas. Nucleation strength factor made it feasible to compare the importance of nucleation in various environments, and it can have further potentials in identifying the triggering or controlling conditions. New particle formation and consecutive growth can occur as regional type event; these can affect the whole city, or can be quenched in its certain, more polluted parts. In specific conditions, however, urban-type nucleations, which are restricted to some area of a city could also be realised. As a result, frequency of new particle formation events could vary somewhat within a city as well. The present results also demonstrate the potentials of time-resolved data sets. Long-term continuous measurements realised simultaneously at several locations are needed to further investigate and refine atmospheric nucleation and nucleated aerosol particles in cities because their role, properties (such as volatility and hygroscopicity) and effects are definitely of increasing importance.

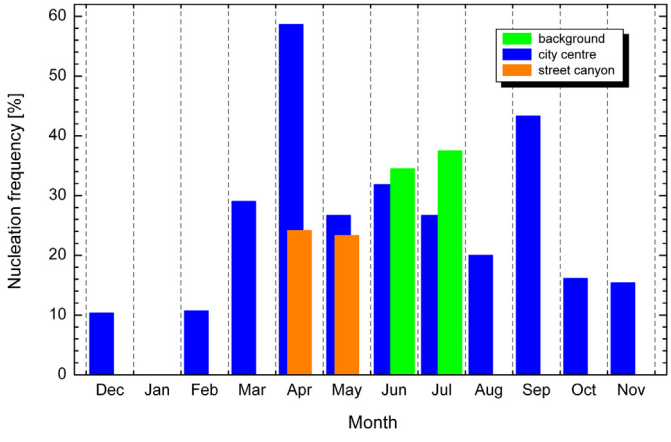

Fig. 5. Monthly mean nucleation frequencies for the near-city background, city centre and street canyon environments.

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