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Modal characteristics of particulate matter in urban atmospheric aerosols

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Abstract

As part of an urban aerosol study, elemental mass size distributions and atmospheric mass concentrations of particulate matter (PM) were experimentally determined at four different locations in Budapest, Hungary, comprising an urban background site (KFKI campus), two downtown sites (Lágymányos campus and Széna Square) and a road tunnel (Castle District Tunnel, CD Tunnel). The analytical results available were utilized in the present work to derive size distributions of PM. Mass, surface area and particle number size distributions of PM for the accumulation and coarse modes, the total distributions, and the modal parameters are presented and discussed. The aerosol mass is always found predominantly in the coarse mode, and the ratio of the masses for the coarse and accumulation modes has an increasing tendency with the aerosol mass concentration. Fraction PM_{10} contributes 83, 82, 69 and 69% of the total suspended particulate in the order of the sampling sites: KFKI campus, Lágymányos campus, Széna Square and CD Tunnel, respectively, while $PM_{2.5}$ makes up 55, 62, 40 and 34% of PM_{10}, respectively. Mass concentration of $PM_{0.1}$ fraction is only between 1.5 and 2.1% of the $PM_{2.5}$. The coarse and accumulation modes cross each other between 1.0 and 1.6 μm aerodynamic diameter, which is significantly smaller than the 50% cut-off value prescribed for the $PM_{2.5}$ samplers. It is the accumulation mode that represents the main surface area at all urban environments. The distributions of PM derived in the present paper are required for further studies.

Keywords: Size distributions; Modal parameters; Total suspended particulate; PM_{10}; $PM_{2.5}$; Urban aerosol; Cascade impactors

1. Introduction

Size distribution is one of the basic properties of atmospheric aerosols because it usually has direct relationships with the origin, chemical composition, atmospheric residence time, optical properties of particles, their chemical and physical processes in the atmosphere, bioavailability, environmental effects, and deposition in the human respiratory system. Consequently, a vast number of studies all over the world has been devoted to measuring the size distributions in very diverse environments [1,2]. The mass size distributions of elements, main inorganic or organic ionic species or other carbonaceous species (elemental and organic carbon in particular) in the diameter range usually above 0.1 μm aerodynamic diameter (AD)

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can primarily be obtained by collecting size-segregated aerosol samples, and analyzing them by different chemical methods. However, in some cases, it is not the chemical-specific (mass) size distributions that is of interest but the size distributions of particulate matter (PM) are required instead. Studies dealing with deposition of aerosols in the human respiratory system, with reactions of gases at the surface of aerosol particles are examples of such cases [3,4]. All of the mass, surface area and particle number distributions are needed also to evaluate aerosol dynamics including formation of new particles and new particulate mass, and also to estimate particle deposition. Besides that the fluxes from gas phase to aerosol phase can be estimated using the concept of condensational sink [5].

Epidemiological studies show statistical and positive association between different indicators of aerosol particles and increased human morbidity and mortality [6–8]. Atmospheric mass concentration of PM is one, though possibly the simplest, and therefore, the most accessible of these indicators. Air quality standards for PM are hence currently expressed in terms of mass concentration. Nevertheless, the standards (used to) deal with total suspended particulate (TSP, because of practical reasons, particles actually with a diameter less than approximately 50 μm AD) or are restricted more often to certain size fractions, i.e., to aerosol particles with a diameter $\leqslant$2.5 μm AD ($PM_{2.5}$ fraction) and/or $\leqslant$10 μm AD (PM_{10} fraction) [9]. It is thus also important to derive and investigate the mass size distribution of PM from the point of view of the size-based particulate standards and guidelines for air quality.

To address the needs for a comprehensive characterization of airborne PM and its environmental fate and effects in the area of Budapest, capital of Hungary, and to assess the human exposure to potentially toxic air pollutants, a research project was initiated [10]. As part of this programme, mass (m), surface area (s) and particle number (n) size distributions for the accumulation and coarse modes, and the corresponding total distributions in the particle diameter (d_p) interval of 0.1–10 μm AD (required for further studies) were derived from experimentally determined data. The main objectives of this work are to present and discuss the size distributions and their modal parameters for different urban environments, and to provide a detailed analysis of the modal characteristics.

2. Experimental methods

The aerosol samples were collected by cascade impactors (CIs) and stacked filter units (SFUs). The former device was a Battelle-type single-orifice PIXE International CI with seven impaction stages and a backup filter stage. The cut-off diameters for 50% collection efficiency of the impaction stages are 16, 8, 4, 2, 1, 0.5 and 0.25 μm AD; for the filter stage, it is considered to be at 0.125 μm AD. The other sampling device was a Gent-type SFU. Collection of the aerosol particles is achieved by sequential filtration through two polycarbonate membrane filters placed in series. Upstream of the filters is a pre-impaction stage. The aerosol particles are separated by the SFU into a coarse (approximately 10–2 μm AD, PM_{coarse}) and a fine ($<$2 μm AD, PM_{fine} or in another notation $PM_{2.0}$) size fraction. Construction, operation and quality control of the sampling devices were described recently [10–13].

Collection of the aerosol samples was performed in the non-heating season on semi-consecutive workdays in April–May 1999 at four urban sites in Budapest, a city with almost 2 million inhabitants. The sampling sites represent an urban background (campus of the Central Research Institute for Physics, KFKI campus), two downtown sites (Eötvös University's campus at Lágymányos, and Széna Square), and a road tunnel (Castle District Tunnel, CD Tunnel). The KFKI campus is situated on the border of the town in upwind direction. One of the downtown sites (Lágymányos campus) has, in addition to its downtown location, a good overall airshed circulation and ventilation, while another downtown site (Széna Square) has a more closed downtown character. The road tunnel is 350 m long, approximately 9 m wide and varies from 8 to 11 m in height. It comprises altogether two-lane traffic of passenger cars, light-duty vehicles and buses. Typical total vehicle circulation in both directions was 1780/h during the sample collec-

tions, and the vehicle fleet comprised 86% passenger cars, 8% light-duty trucks, vans and jeeps, 2% busses and heavy-duty trucks, 2% two-stroke engines and 2% of other vehicles (mainly motorcycles). The two types of aerosol samplers were installed with their intake facing down, side by side at a distance of approximately 20 cm from each other at approximately 1.8, 39, 4.5 and 1.7 m above the ground for the sampling sites mentioned. The locations given can be characterised by gradually increasing aerosol mass concentration. The mean atmospheric concentrations for the coarse inorganic aerosol species at the Lágymányos campus, Széna Square and the tunnel are higher than at the urban background level by average factors of 2.6 ± 1.1, 3.8 ± 2.1 and 65 ± 33, respectively. Similar comparisons of the sampling locations for the fine size fraction yield factors of 2.0 ± 1.1 and 2.0 ± 1.0 and 7 ± 4, respectively [10].

Three daily SFU filter pairs were collected at each residential sampling site, while two SFU filter pairs were taken within the tunnel in mornings. A total number of 6 daily CI samples were collected at the KFKI campus, 5 daily CI samples were taken at the Lágymányos campus, and 5 CI samples were collected within the tunnel in morning periods. At Széna Square, 10 CI samples were collected over daylight (daytime) and 11 over night. The typical volume for the SFU samples was approximately 19 m^3 for the daily collections, and 3–5 m^3 within the tunnel. The typical sampled volume for the daily CI samples was approximately 1.5 m^3; for the CI samples collected over daylight and night, it was 0.8 and 0.6 m^3, respectively, and approximately 0.1 m^3 air was sampled within the tunnel. For each sample type, field blank samples were also taken at the sites.

Collection of the aerosol samples was complemented with meteorological observations. During the whole sampling period, the weather was stable, slowly warming with daily ambient temperature (from 11 to 21 °C) and pressure (from 948 to 1008 hPa) in accordance with the typical seasonal parameters without any extreme meteorological situation [14]. The daily average horizontal wind speed and relative humidity ranged from 5.2 to 15 m/s, and 48 to 76%, respectively. Rain showers during the actual collection of the samples occurred only twice.

The coarse and fine filters were weighed before and after the sampling using a microbalance with a sensitivity of 1 μg to obtain the particulate mass as part of an analytical protocol [10]. The filters were pre-equilibrated in a room with stabilized temperature (24–26 °C) and relative humidity (20–25%) before the actual weighing. The CI samples were analyzed by particle-induced X-ray emission spectrometry for up to 29 elements, i.e., Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ba and Pb [13,15] at the Ghent University. The analyses were performed without any sample treatment. Quality assurance of the analytical procedure was performed via concentration ratios of elements that were also measured by instrumental neutron activation analysis. The last method was validated by the NIST Standard Reference Material 1648: urban PM. Agreement within 5–7% was found for those elements (e.g. K, Ca, Ti, Mn, Fe and Zn) that were determined with a good precision by both analytical methods. Detailed description and discussion of the analytical protocol and quality control were presented elsewhere [13,16].

3. Data reduction

Elemental mass size distributions were derived from the CI samples. Mass median aerodynamic diameters (MMADs) and geometric standard deviations (s_g) were fitted by one or two lognormal functions [17]. When applying two functions, the fitting was performed to all size distributions of a particular data set (sampling site) in one fitting session, and the width parameters of the functions were shared within the session. The individual MMADs and geometric standard deviations of an element derived from the fitting were averaged for the four sampling sites. The coarse- and accumulation-mode MMADs and geometric standard deviations of the most abundant coarse and fine elements, i.e., of Mg, Al, Si, Ca and Fe, and of S, Cl, Cu, Zn and Pb, respectively were further averaged, and then utilized as experimentally determined representative values. The mass size

distributions of PM were computed as two lognormal functions:

$$\frac{dm}{d(\log d_p)} = \frac{m_A}{\sqrt{2\pi}\log s_{gA}} \times \exp\left(-\frac{(\log d_p - \log \mathrm{MMAD}_A)^2}{2\log^2 s_{gA}}\right) + \frac{m_C}{\sqrt{2\pi}\log s_{gC}} \times \exp\left(-\frac{(\log d_p - \log \mathrm{MMAD}_C)^2}{2\log^2 s_{gC}}\right), \quad (1)$$

minimizing the differences between all pairs of optimized and experimentally determined MMADs, geometric standard deviations, PM_{fine} and PM_{coarse} values by the least square method. In Eq. (1), m is the total particle mass concentration, and the subscripts A and C indicate the accumulation and coarse modes, respectively. This is considered to be an adequate approximation, since only accumulation and coarse modes were observed in the mass size distributions even for the traffic situations, when fresh motor vehicle emissions could contribute to the presence of a mode in the nuclear range [18]. The mass size distributions of PM obtained were further converted to particle number size distributions assuming unit density (since the experimental distributions were expressed in AD) and smooth spherical particles, and, finally, surface area size distributions were calculated. Note that the mass size distributions of PM in $\mu g/m^3$ are identical to the volume size distributions of PM in $\mu m^3/cm^3$ in this representation.

4. Results and discussion

Mean atmospheric concentrations of PM as measured by gravimetry of the SFU filters were expressed for standard temperature and pressure (STP, 273 K and 1013 hPa), and are summarized in Table 1. The mass, surface area and particle number size distributions for the four sampling locations are displayed in Figs. 1–4. Integrated mass, surface area and particle number of the

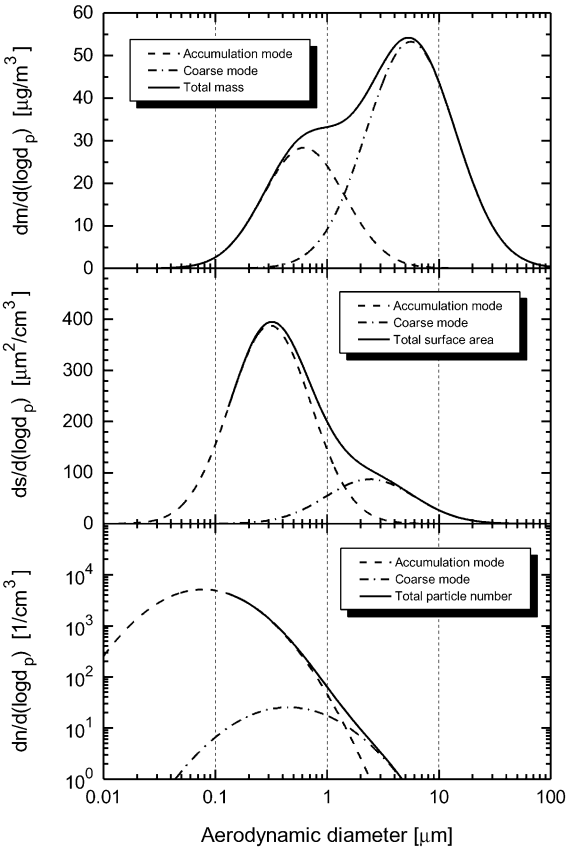

Fig. 1. Mass, surface area and particle number size distributions of PM for the coarse and accumulation modes, and the total distributions at the urban background site (KFKI campus) in Budapest.

Table 1
Mean atmospheric mass concentrations and standard deviations in $\mu g/m^3$ STP for PM as measured in the coarse and fine size fraction of the SFU samples collected at the KFKI campus (urban background), Lágymányos campus (downtown), Széna Square (downtown) and within the CD Tunnel

Size fraction	KFKI campus	Lágymányos campus	Széna Square	CD Tunnel
Coarse	35 ± 17	34 ± 15	41 ± 14	430 ± 170
Fine	30 ± 18	45 ± 22	28 ± 11	149 ± 56

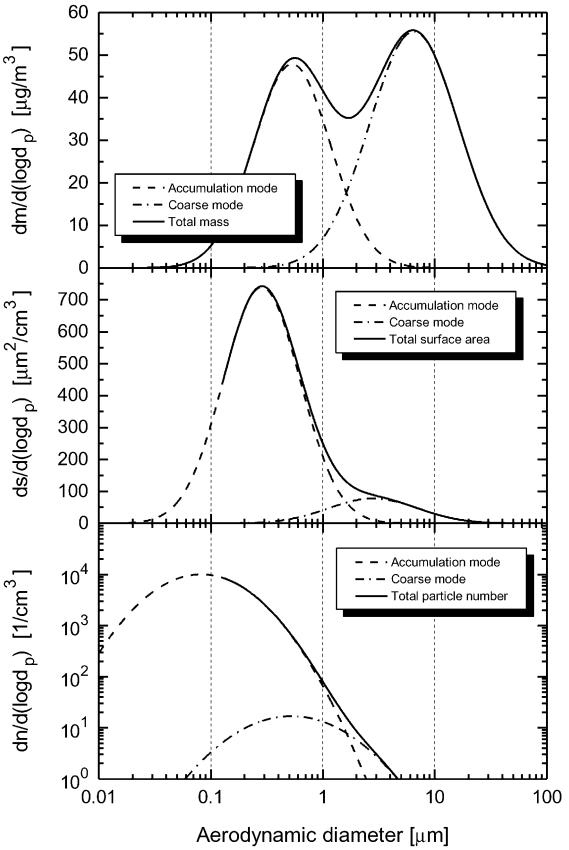

Fig. 2. Mass, surface area and particle number size distributions of PM for the coarse and accumulation modes, and the total distributions at a downtown site (Lágymányos campus) in Budapest.

coarse and accumulation modes are shown in Table 2 together with the median aerodynamic diameters and geometric standard deviations.

By comparing the mass size distributions for the different sampling locations, it can be seen that the aerosol mass is always found prominently in the coarse mode. This suggest that much of the airborne PM is mechanically derived and likely consists of local crustal and building material, and of resuspended road and soil dust due to transportation and other mechanical or construction activities. It has to be added, however, that the resuspended surface dust can naturally be associated with the fine particles that were deposited on the ground surface previously through deposition processes, and, therefore, the typical antropogenic (volatile) elements can appear in the coarse mode in polluted environments [13]. The mass of the accumulation mode is also significant at all sampling locations. Its relatively large value at the Lágymányos campus is most likely due to the 39-m sampling height above the ground, and to the shorter atmospheric residence times of the coarse particles. The relative intensity of the two modes vary considerably. The ratio of the masses for the coarse and accumulation modes has an increasing tendency with the aerosol mass concentration, so in the order of the sampling sites: KFKI campus, Lágymányos campus, Széna Square and CD Tunnel. It is most likely due to local road and soil

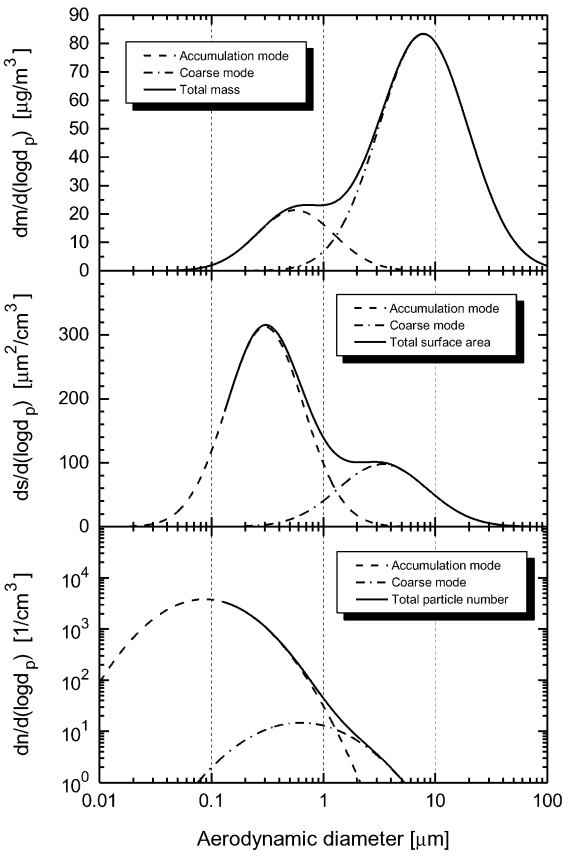

Fig. 3. Mass, surface area and particle number size distributions of PM for the coarse and accumulation modes, and the total distributions at a downtown site (Széna Square) in Budapest.

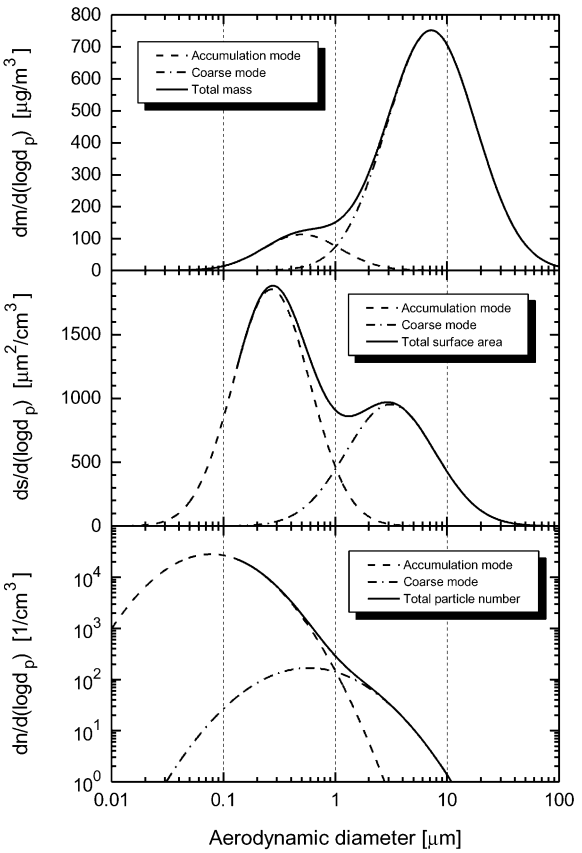

Fig. 4. Mass, surface area and particle number size distributions of PM for the coarse and accumulation modes, and the total distributions within a road tunnel (CD Tunnel) in Budapest.

dust resuspension, which is increasing evidently toward the city center. The shape of our mass size distributions agrees well with the volume/mass size distributions derived from particle number measurements for urban-influenced aerosols, but is different from traffic-influenced aerosols. The locations of the two modes are also similar to those encountered in the literature, but they seem to be shifted slightly toward larger diameters when comparing them exclusively to corresponding values for urban-influenced aerosol [18]. The two modes cross each other between 1.0 and 1.6 μm AD. At the 50% cut-off value prescribed for the $PM_{2.5}$ samplers, the mass size distributions can already be quite steep (cf. Fig. 3 and Fig. 4), hence, a small shift in the cut-point can have a relatively large influence on the collected mass or on the analytical results obtained later on.

Fraction PM_{10} contributes 83, 82, 69 and 69% to TSP in the order of the sampling sites indicated above. At the same time, $PM_{2.5}$ makes up 55, 62, 40 and 34% of PM_{10} in the order of the sampling sites indicated, respectively, while it only accounts for 45, 51, 28 and 24% of TSP, respectively. It is also worth mentioning that the mass concentration of $PM_{0.1}$ fraction is only between 1.5 and 2.1% of the $PM_{2.5}$, which means 0.5–1 μg/m^3 STP for residential sites similarly to values observed in other cities [19]. The contributions above exhibit significant seasonal variation (which is related to the residential space heating), and depends on the actual time and location (on source types and their intensity). A range of quite different $PM_{2.5}/PM_{10}$ ratios were, therefore, observed for different cities, e.g. some 60% for the center and urban background of London [20], approximately 50% for a set of cities in the Netherlands [21] and several urban areas in Canada [22]. The aerosol mass concentration in downtown Budapest (Széna Square) seems to be predominantly associated with the coarse particles during the non-heating season. For a set of very similar samples collected in a larger number at one of the downtown (Széna Square) in 1996, a correlation coefficient between TSP and PM_{10} of 0.60 ($n=33$) was derived, while it was larger, i.e., 0.78 ($n=33$) between TSP and PM_{coarse} [10].

The surface area of the accumulation mode is larger at all sampling locations than that of the coarse mode despite the fact that the coarse-mode mass is increased almost four times more than the accumulation-mode mass when comparing the tunnel to the urban background. So, it is the accumulation mode that represents the main surface area. It can be important since particulate surface area is one of the parameters that has been correlated with the observed adverse health effects of inhaled atmospheric particulates [23]. Combined effects of the potentially toxic or carcinogenic chemical composition (e.g. high abundance of some transition and heavy metals, acids or organic constituents absorbed) and the large surface area (as well as of some other properties) of the

Table 2
Total mass, surface area and particle number of PM in the coarse and accumulation modes in $\mu g/m^3$, $\mu m^2/cm^3$ and $1/cm^3$, respectively at STP, and the corresponding median aerodynamic diameters (MAD) in μm AD, collected at the KFKI campus (urban background), Lágymányos campus (downtown), Széna Square (downtown) and within the CD Tunnel (road tunnel)

Size mode	KFKI campus	Lágymányos campus	Széna Square	CD tunnel
Coarse particulate mass	53	56	83	751
Fine particulate mass	26	41	18	97
Coarse mass MAD	5.6	6.5	7.8	7.2
Fine mass MAD	0.62	0.53	0.56	0.50
Coarse particulate surface area	87	78	97	950
Fine particulate surface area	350	630	270	1600
Coarse surface area MAD	2.4	3.0	3.5	3.1
Fine surface area MAD	0.31	0.29	0.30	0.28
Coarse particle number	25	17	15	168
Fine particle number	4655	8640	3272	24 316
Coarse particle number MAD	0.48	0.56	0.65	0.59
Fine particle number MAD	0.08	0.08	0.08	0.08

The geometric standard deviations, valid for all three size distributions, for the coarse and accumulation modes are 2.5 and 2.1 μm AD, respectively.

accumulation mode can multiply the harmful effect of these particles on the human welfare.

With regard to the particle number concentrations, their value except for the tunnel correspond to those typically observed for urban aerosols. It has to be noted that the particle number size distributions, being derived from the mass distributions, are likely to underestimate the number concentrations below 0.1 μm AD. Contribution of particles from the nucleation mode to the total particulate mass can be neglected but they are present in a rather large number [18]. This is the reason why the total surface area and particle number size distributions (solid lines) are not plotted below the smaller cut-off diameter of the CI used, so below 0.125 μm AD in Figs. 1–4.

5. Conclusions

Important changes in the physical and chemical characteristics of air pollution have been observed and qualitatively determined in (highly) developed countries [24]. It was observed that the previous heavy air pollution by coarse aerosol particles (dust and smoke) decreased substantially in the cities mainly due to improved dust abatement and burning technologies, and to air-cleaning equipment of modern industrial sources, while fine and ultrafine aerosol particles penetrate into the atmospheric environment. With regard to the aerosol air pollution in Budapest, the aerosol mass in the non-heating season is still found predominantly in the coarse fraction (and mode). Ratio of the masses for the coarse and fine fractions (F/C ratio) as obtained from the SFU filters are 0.9 ± 0.7, 1.2 ± 0.8, 0.6 ± 0.2 and 0.35 ± 0.09 in the order of the sampling sites KFKI campus, Lágymányos campus, Széna Square and CD Tunnel, respectively. In addition, the F/C ratios have a clear tendency to decrease with increasing aerosol mass concentration. Fraction $PM_{2.5}$ makes up 55, 62, 40 and 34% of PM_{10}, respectively for the sampling site mentioned above. Hence, the downtown is more polluted with coarse aerosol species than the urban background, but the concentration levels exhibit significant spatial and temporal variability.

The diversity in the size distributions for the different locations can also have a considerable impact on the penetration and deposition of the aerosol particles in different parts of the human respiratory system, which is dealt with in separate papers [4,13].

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