Comparative study of elemental mass size distributions in urban atmospheric aerosol

Imre Salma[a,*], Willy Maenhaut[b], Gyula Záray[a]

[a]*L. Eötvös University, Department of Chemical Technology and Environmental Chemistry,*
H-1518 Budapest 112, P.O. Box 32, Hungary
[b]*Ghent University, Institute for Nuclear Sciences, B-9000 Gent, Proeftuinstraat 86, Belgium*

Abstract

Elemental mass size distributions in aerosols collected at four different urban sites with gradually increasing overall aerosol mass concentration are presented, compared and discussed in the present paper. The aerosol samples were collected with cascade impactor and stacked filter unit samplers, and were analyzed by particle-induced X-ray emission spectrometry and instrumental neutron activation analysis. Typical coarse-mode elements, i.e., Na, Mg, Al, Si, P, Ca, Ti, Fe, Ga, Sr, Zr, Mo and Ba, exhibited unimodal size distributions at all four urban locations studied, and the mass median aerodynamic diameters were increased with aerosol pollution level. Elements typically related to high-temperature or anthropogenic sources, i.e., S, Cl, K, V, Cr, Mn, Ni, Cu, Zn, Ge, As, Se, Br, Rb and Pb, either had a unimodal size distribution with most or their mass in the fine size fraction or clearly showed a bimodal size distribution at the urban background site. However, significant differences between the size distributions of four sampling sites were noted. There was a clear tendency for the accumulation mode to decrease and for the coarse mode to increase with increasing total aerosol mass concentration. A pronounced resuspension of the soil and roadway dust associated with the fine aerosol particles that were deposited on the ground surface previously, and the condensation process of volatile precursor gases on the already existing aerosol particles can explain the observed tendencies. The elemental mass size distributions derived for the polluted urban environments differ from those typically observed for industrial, combustion or automotive sources. A consequence of the diversity in the size distributions on the $PM_{2.5}$ speciation concept is also presented. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Size distributions; Urban aerosol; Cascade impactors; $PM_{2.5}$

---

* Corresponding author. Tel.: +36-1-209-0555.
E-mail address: salma@para.chem.elte.hu (I. Salma).

1. Introduction

Knowledge of the size distribution and chemical composition as a function of size are essential for determining the properties, behavior, atmospheric processes, effects and fate of aerosol particles. A vast number of detailed studies all over the world in very diverse environments has been devoted to measuring the size distributions of particle number, surface area, volume, aerosol mass, and the mass of inorganic and organic species or elements (Mészáros, 1999 and references therein). The differential size distributions exhibit fundamentally a multimodal character with several modes, typically: nucleation, accumulation and coarse modes (Whitby, 1978). Particles of the nucleation mode are predominantly smaller than 0.08 μm equivalent aerodynamic diameter (EAD) with a peak at about 0.01 μm EAD (Lundgren & Burton, 1995). The accumulation peak generally occurs below 1 μm EAD, while the coarse peak appears above 3 μm EAD with a typical size separation between the accumulation and coarse modes at about 2 μm EAD (Whitby, 1978). In addition, an ultrafine mode (with a maximum unambiguously below 0.01 μm EAD) was detected in very clean oceanic, coastal and Antarctic air, and in forested areas (Hoppel & Frick, 1991; Fitzgerald, 1991; Ito, 1993; Mäkelä et al., 1997; O'Dowd, Geever, Hill, Jennings, & Smith, 1998). Some authors report that the accumulation mode consists of two sub-modes, i.e., condensation (with a peak centered at about 0.2 μm EAD) and droplet mode (with a peak centered at about 0.7 μm EAD) under some conditions (Hering & Friedlander, 1982). Nevertheless, typical mass size distributions of many elements were found to be surprisingly uniform and consistent despite the wide variability in sampling locations and periods, and environmental conditions (Milford & Davidson, 1985).

With regard to the chemical composition, the volatile elements, which have predominantly anthropogenic or natural combustion sources, are associated with the accumulation mode. These aerosol particles, therefore, contain a higher concentration of potentially toxic components than the coarse ones (Kleeman & Cass, 1989). Moreover, bioavailability or environmental mobility of these components tend to also be greater than that of the elements of crustal origin (Chester, Lin, & Murphy, 1989). Epidemiological studies show statistical and positive association between different indicators of aerosol particles and increased human morbidity and mortality (Dockery et al., 1993; Reichhardt, 1995; Pope, Dockery, & Schwartz, 1995). Atmospheric mass concentration is one, though possibly the most simple, and therefore, the most accessible of these indicators. The United States Environmental Protection Agency revised its National Ambient Air Quality Standards for Particulate Matter in 1997 to adopt additional limits on the mass concentration of particles with diameters less than 2.5 μm EAD ($PM_{2.5}$) (US EPA, 1997). Some other countries followed up on this concept. There are, however, several uncertainties with regard to the effects on health and welfare of these particles. Some associations between particle concentrations and health turned out to be inconsistent, or plausible alternative explanations can be justified (Vedal, 1997; Gone, Olmez, & Ames, 2000). It has already been proposed that there are highly reactive free radicals or peroxides, or some other species of the particles that do not contribute significantly to the mass but which are responsible for the observed toxicity.

As part of an atmospheric aerosol project, a study was initiated to improve our knowledge on the mass size distributions of trace elements in urban aerosols, to intercompare the average size distributions obtained for different sampling sites in Budapest, Hungary, and to calculate the deposition of potentially toxic elements in the human respiratory system. Some results and

consequences of the study can contribute to our knowledge on elemental mass size distributions under polluted urban conditions, and are related to the $PM_{2.5}$ chemical speciation concept. The principal objective of the present paper is to outline and discuss these findings.

2. Experimental methods

2.1. Collection of aerosol samples

Two different types of sampling devices were employed for collecting aerosol samples, i.e., cascade impactors (CIs) and stacked filter units (SFUs). The former device was a Battelle-type single-orifice PIXE International cascade impactor operating at a nominal airflow rate of 1 l/min. It has seven impaction stages (numbered from 7 through 1) 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 EAD. Kimfol polycarbonate film with a thickness of 1.5 μm was used as impaction foil. The foils were coated with a thin adhesive layer of vaseline (for stages 7 through 2) or paraffin (stage 1) to minimize particle bounce-off from the impaction surfaces. Nuclepore polycarbonate membrane filter with a pore size of 0.4 μm was used as the backup filter. For the filter stage, the 50% collection efficiency was considered to be at 0.125 μm EAD. The other type of sampling device was a Gent-type PM_{10} SFU (Maenhaut, François, & Cafmeyer, 1994). Collection of the aerosol particles is achieved by sequential filtration through different filters. Two 47-mm diameter nuclepore polycarbonate filters with pore sizes of 8 μm (Apiezon-coated) and 0.4 μm are placed in a NILU type open face stacked filter cassette in series. Upstream of the filter cassette is a pre-impaction stage. The sampler is designed to operate at an airflow rate of 15–16 l/min. At this value, the pre-impaction stage intercepts particles larger than about 10 μm EAD (for 293 K and 1013 hPa), and the first filter with 8-μ*m* pore size has a 50% collection efficiency at about 2 μm EAD. Consequently, the aerosol particles are separated into a coarse (about 10–2 μm EAD) and a fine (< 2 μm EAD) size fraction. Performance of the SFU sampler was tested; the inlet behavior and the reproducibility were found to be very good (Hopke et al., 1997). 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.

Collection of the aerosol samples was performed in the non-heating season at four urban sites in Budapest, a city with almost 2 million inhabitants. One of the sampling locations was chosen on the western border of Budapest within the wooded campus of the Central Research Institute for Physics (KFKI, latitude 47°29.3′ N, longitude 18°57.3′ E, altitude 424 m above sea level, a.s.l.). Since the prevailing wind direction in Budapest is northwest, this sampling site was considered as the "urban background". The sampling devices were set up at about 1.8 m above the ground. Daily aerosol samples were collected here. A total of six CI samples and three SFU sample pairs were taken from 12 till 17 April 1999. The Eötvös University's campus at Lágymányos (latitude 47°28.5′ N, longitude 19°3.7′ E, altitude 144 m a.s.l.) was chosen as the second sampling site. The campus is situated on the bank of the river Danube. Despite its downtown location, it has good overall airshed circulation and ventilation. The samplers were installed on an observation mast at a height of 39 m above the street level. A total of five daily CI samples and three daily SFU sample pairs were taken on semi-consecutive workdays from

19 till 27 May 1999. The third sampling site was located in the downtown in a small park at Széna Square (latitude 47°30.6′ N, longitude 19°1.8′ E, altitude 115 m a.s.l.) at an automated air quality monitoring station of the Municipal Institute of the State Public Health Officer Service. This sampling site has a more closed downtown character, and is affected by heavy traffic nearby. The aerosol samplers were set up on the roof of the monitoring station at 4.5 m above the ground. Separate CI samples were collected here over daylight (from 7:30 through 21:30) and night (from 21:30 through 7:30) (Salma, Maenhaut, Zemplén-Papp, & Bobvos, 1998). A total of 10 daylight and 11 night CI samples were collected on semi-consecutive workdays from 19 April till 13 May 1999. As to the SFU filters, a total of three daily SFU sample pairs were collected. The fourth sampling site was downtown within the Castle District Tunnel (CD Tunnel, latitude 47°29.6′ N, longitude 19°2.5′ E, altitude of the entrance overlooking the Danube 105 m a.s.l.). The tunnel is 350 m long, about 9 m wide and varies from 8 to 11 m in height. It comprises altogether 2-lane traffic of passenger cars, light-duty vehicles and buses, and also involves one pedestrian lane and one service curb/lane along the two sides. The samplers were set up on the wall in the service curb/lane at about the halfway point of the length at a height of 1.7 m above the ground. Traffic through the tunnel during the sampling was recorded on videotapes for traffic characterization. The typical total vehicle circulation in both directions was 1780/h, 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). A total of five CI samples and two SFU sample pairs were collected within the tunnel for about 2 and 3 h, respectively, in the morning of 16 and 17 June 1999. The typical sampled volume for the daily CI samples was about $1.5 \, \text{m}^3$, for the CI samples collected over daylight and night, it was 0.8 and $0.6 \, \text{m}^3$, respectively, while about $0.1 \, \text{m}^3$ air was sampled within the tunnel. The typical volume for the SFU samples was about $19 \, \text{m}^3$ for the daily collections, and about $3 \, \text{m}^3$ within the tunnel. The filter clogging was not significant at any of the sampling sites. Some 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 very 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 situations. The daily average horizontal wind speed and relative humidity ranged from 5.2 to 15 m/s, and 48 to 76%, respectively, so that particle growth due to accumulation of moisture should have been limited (Hänel, 1976). Rain showers during the actual collection of the samples occurred only twice, on 17 April (sampling at KFKI campus), and during the second sampling day in the tunnel (17 June).

2.2. Elemental analysis

The CI samples were analyzed by particle-induced X-ray emission spectrometry (PIXE) 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 at the Ghent University (Maenhaut & Raemdonck, 1984; Salma, Maenhaut, Cafmeyer, Annegarn, & Andreae, 1994). The SFU samples were weighed before and after the sampling using a microbalance to obtain the particulate mass. The filters containing about 500–900 μg of particulate matter (PM) were analyzed by two bulk analytical methods, i.e., by panoramic instrumental neutron activation analysis (INAA) and PIXE. About

half-section of each filter was analyzed by INAA at Budapest Research Reactor for up to 49 elements (Salma & Zemplén-Papp, 1999). Quarter-section of each filter was also analyzed by PIXE for up to 29 elements (Salma et al., 1998). The analyses were performed without any sample treatment. The quality of the analytical data was continuously controlled by the PIXE/INAA concentration ratios for elements that were measured by both INAA and PIXE. Agreement within 5–7% was found for those elements (e.g., K, Ca, Mn, Fe and Zn) that were determined with a good precision by both analytical methods.

3. Results and discussion

3.1. Atmospheric concentrations

Atmospheric concentrations were derived by combining the independent analytical results obtained by INAA and PIXE for the SFU filters, and were expressed at standard temperature and pressure (STP, 273 K and 1013 hPa). Mean concentrations of some selected elements (for which size distributions were obtained, see later), and of PM in the coarse and fine size fractions collected at each sampling site are presented in Table 1. The sampling locations represent a wide concentration range. The concentrations show an unambiguous tendency to increase in the order of the sampling sites KFKI campus, Lágymányos campus, Széna Square and CD Tunnel, as expected. It was found that the mean atmospheric concentrations of the inorganic aerosol species in the coarse size fraction for the CD tunnel, Széna Square and Lágymányos campus are higher than at the urban background by average factors of 65 ± 33, 3.8 ± 2.1 and 2.6 ± 1.1, respectively. Similar comparisons of the sampling sites for the fine size fraction yield factors of 7 ± 4, 2.0 ± 1.0 and 2.0 ± 1.1, respectively (Salma, Maenhaut, Zemplén-Papp, & Záray, 2001a). The mean fine-to-coarse concentration ratios (F/C ratios) obtained from the filters for each sampling site are given in Table 2. The F/C ratios for the urban background site are typically below one except for S, K, V, Ni, Cu, Zn, As and Pb. This indicates that the elements were predominantly present in the coarse size fraction. However, the F/C ratios differ significantly between the four sampling sites. The ratios have a clear tendency to decrease monotonically with increasing aerosol mass concentration. The F/C ratios in the tunnel were decreased to 10–15% of the urban background value for typically coarse-mode elements and PM. For the typical anthropogenic elements, an even more serious change is observed; the F/C ratios were decreased to 2–5% of the urban background value. Some other physicochemical properties of the aerosol species, and the chemical mass closure were described elsewhere (Salma et al., 2001a).

3.2. Mass size distributions

Size distributions were obtained for 28 elements from the CI samples. Data of Nb were above detection limit for a few CI stages only. The individual size distributions were averaged for the five different data subsets, i.e., for the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and CD Tunnel. On the basis of the average size distributions, the elements can be classified into two groups. Group 1 comprises Na, Mg, Al, Si, P, Ca, Ti,

Table 1
Mean atmospheric concentrations and standard deviations in ng/m^3 STP of some selected elements and PM as measured in the coarse and fine size fraction of the SFU samples collected at the KFKI campus, Lágymányos campus, Széna Square and within the Castle District Tunnel

Element	Fraction	KFKI campus	Lágymányos campus	Széna Square	Castle District Tunnel
Na	coarse	125 ± 49	236 ± 35	293 ± 83	3078 ± 95
	fine	66 ± 43	100 ± 29	56 ± 21	76 ± 6
Mg	coarse	92 ± 39	257 ± 19	310 ± 91	6600 ± 278
	fine	26 ± 8	56 ± 7	33 ± 9	215 ± 29
Al	coarse	171 ± 19	680 ± 134	788 ± 120	15000 ± 300
	fine	37 ± 4	153 ± 17	69 ± 6	410 ± 9
Si	coarse	459 ± 40	1780 ± 301	2586 ± 507	45600 ± 912
	fine	104 ± 15	224 ± 35	285 ± 69	1419 ± 56
P	coarse	16 ± 3	36 ± 10	38 ± 10	898 ± 36
	fine	7 ± 2	< 5	9 ± 2	79 ± 22
S	coarse	134 ± 62	297 ± 56	326 ± 162	4982 ± 100
	fine	1276 ± 417	2185 ± 90	826 ± 68	992 ± 68
Cl	coarse	33 ± 3	84 ± 8	176 ± 46	1388 ± 28
	fine	20 ± 5	23 ± 7	73 ± 31	< 72
K	coarse	92 ± 7	232 ± 29	257 ± 75	5013 ± 100
	fine	102 ± 19	123 ± 11	96 ± 18	149 ± 36
Ca	coarse	358 ± 8	1437 ± 240	1847 ± 521	46380 ± 928
	fine	63 ± 3	142 ± 23	155 ± 22	1125 ± 36
Ti	coarse	10 ± 3	43 ± 8	91 ± 47	1449 ± 29
	fine	3.2 ± 0.3	6.2 ± 1.2	9 ± 8	35 ± 8
V	coarse	0.5 ± 0.3	1.70 ± 0.10	2.2 ± 0.8	29.5 ± 1.1
	fine	1.3 ± 0.9	1.7 ± 0.4	2.0 ± 1.6	1.65 ± 0.13
Cr	coarse	3.9 ± 1.0	4.9 ± 1.0	3.4 ± 1.0	78 ± 8
	fine	< 2	< 2	< 2	< 12
Mn	coarse	4.7 ± 1.4	15 ± 3	22 ± 4	339 ± 13
	fine	3.5 ± 1.1	6.5 ± 1.4	5 ± 2	21.6 ± 1.8
Fe	coarse	176 ± 38	807 ± 93	1675 ± 289	26770 ± 535
	fine	62 ± 5	187 ± 15	294 ± 45	1375 ± 41
Ni	coarse	0.8 ± 0.4	0.93 ± 0.12	1.7 ± 0.5	34 ± 3
	fine	1.2 ± 0.2	0.8 ± 0.3	1.2 ± 0.6	< 3
Cu	coarse	1.1 ± 0.3	10 ± 3	24 ± 6	912 ± 21
	fine	1.7 ± 0.5	8.7 ± 0.5	8.7 ± 1.7	70 ± 5
Zn	coarse	9 ± 3	30 ± 5	93 ± 14	887 ± 18
	fine	24 ± 2	34 ± 6	54 ± 17	89 ± 4
Ga	coarse	< 0.2	< 0.3	< 0.4	3.8 ± 0.7
	fine	< 0.2	0.11 ± 0.10	0.13 ± 0.08	< 0.4
Ge	coarse	< 0.2	0.61 ± 0.10	0.6 ± 0.2	16 ± 4
	fine	< 0.2	< 0.3	< 0.2	< 1
As	coarse	0.12 ± 0.02	0.40 ± 0.06	0.52 ± 0.11	6.7 ± 0.3
	fine	0.28 ± 0.19	0.79 ± 0.17	1.1 ± 0.4	0.51 ± 0.08
Se	coarse	—	—	—	—
	fine	0.36 ± 0.08	0.8 ± 0.2	0.48 ± 0.09	< 1

Table 1
(continued)

Br	coarse	< 3	< 3	4.3 ± 0.5	30 ± 2
	fine	3.6 ± 1.6	4.9 ± 1.1	4.1 ± 1.0	< 5
Rb	coarse	< 1	< 2	< 2	34 ± 11
	fine	< 0.6	< 0.8	< 0.7	< 4
Sr	coarse	1.0 ± 0.2	3.7 ± 0.9	4.9 ± 1.0	136 ± 13
	fine	< 0.5	0.73 ± 0.15	0.73 ± 0.12	< 3
Zr	coarse	< 0.8	3.9 ± 1.6	3.9 ± 1.0	97 ± 27
	fine	< 0.6	1.3 ± 0.3	< 0.7	< 5
Mo	coarse	0.49 ± 0.03	0.53 ± 0.07	1.83 ± 0.10	51 ± 4
	fine	0.39 ± 0.09	0.40 ± 0.09	0.65 ± 0.07	3.3 ± 0.6
Ba	coarse	< 32	15 ± 2	27 ± 3	628 ± 34
	fine	< 4	4.0 ± 1.3	6.4 ± 0.9	42 ± 7
Pb	coarse	4.8 ± 0.5	8.6 ± 1.3	13 ± 5	359 ± 47
	fine	9 ± 3	19 ± 2	16 ± 5	34 ± 7
PM	coarse	35000 ± 17000	34000 ± 15000	41000 ± 14000	430000 ± 170000
	fine	30000 ± 18000	45000 ± 22000	28000 ± 11000	149000 ± 56000

Table 2
Mean fine-to-coarse concentration ratios and standard deviations for some selected elements and PM as derived from the SFU samples collected at the KFKI campus, Lágymányos campus, Széna Square and within the Castle District Tunnel

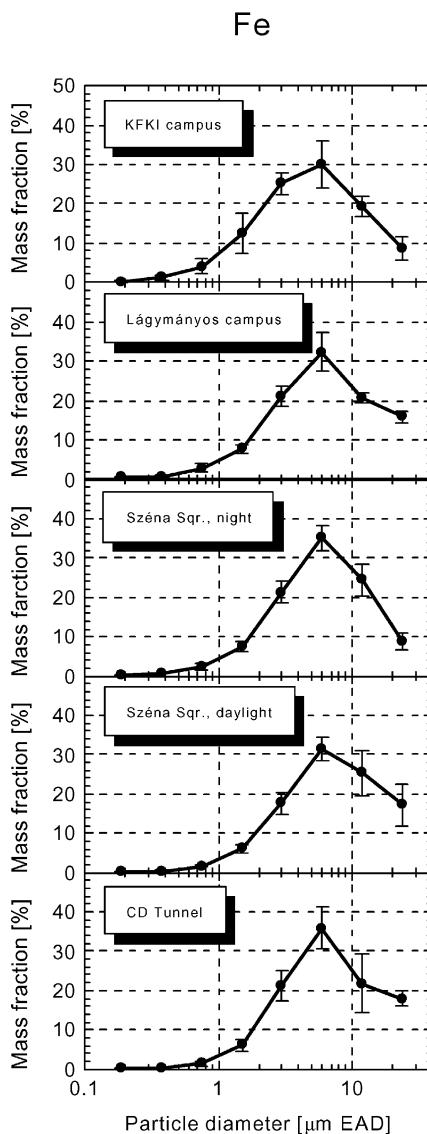| Element	KFKI campus	Lágymányos campus	Széna Square	Castle District Tunnel
Na	0.50 ± 0.15	0.46 ± 0.12	0.18 ± 0.08	0.03 ± 0.02
Mg	0.29 ± 0.04	0.22 ± 0.02	0.14 ± 0.03	0.03 ± 0.02
Al	0.22 ± 0.05	0.23 ± 0.05	0.09 ± 0.02	0.03 ± 0.01
Si	0.23 ± 0.05	0.13 ± 0.02	0.10 ± 0.03	0.03 ± 0.01
P	0.46 ± 0.05	—	0.21 ± 0.02	0.01 ± 0.01
S	9.5 ± 1.1	7.5 ± 1.2	2.5 ± 1.0	0.23 ± 0.02
Cl	0.70 ± 0.07	0.32 ± 0.08	0.32 ± 0.07	—
K	1.10 ± 0.12	0.54 ± 0.12	0.33 ± 0.07	0.04 ± 0.02
Ca	0.18 ± 0.02	0.10 ± 0.02	0.09 ± 0.02	0.03 ± 0.02
Ti	0.24 ± 0.10	0.14 ± 0.02	0.11 ± 0.03	0.03 ± 0.01
V	2.1 ± 0.5	1.0 ± 0.2	0.7 ± 0.4	0.06 ± 0.05
Mn	0.7 ± 0.2	0.44 ± 0.04	0.24 ± 0.08	0.05 ± 0.02
Fe	0.35 ± 0.03	0.23 ± 0.02	0.18 ± 0.04	0.05 ± 0.02
Ni	1.3 ± 0.5	0.8 ± 0.2	0.5 ± 0.2	—
Cu	1.5 ± 0.2	0.8 ± 0.2	0.4 ± 0.9	0.07 ± 0.03
Zn	3.0 ± 0.9	1.2 ± 0.06	0.6 ± 0.2	0.10 ± 0.03
As	2.4 ± 0.3	2.0 ± 0.7	1.5 ± 1.1	0.08 ± 0.03
Br	—	—	0.9 ± 0.2	—
Sr	—	0.22 ± 0.05	0.17 ± 0.02	—
Zr	—	0.4 ± 0.2	—	—
Mo	0.76 ± 0.15	0.71 ± 0.14	0.36 ± 0.05	0.08 ± 0.03
Ba	—	0.26 ± 0.07	0.24 ± 0.03	0.07 ± 0.03
Pb	2.0 ± 1.4	2.3 ± 0.5	1.2 ± 0.2	0.10 ± 0.04
PM	0.9 ± 0.7	1.2 ± 0.8	0.5 ± 0.2	0.35 ± 0.09

Fe

Fig. 1. Average mass size distributions of Fe for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.

Fe, Ga, Sr, Zr, Mo and Ba. All these elements have essentially a unimodal size distribution for all data sets with most of their mass in the coarse mode, and with little mass below 1 μm EAD. They are attributable to dispersion, and soil and road dust resuspension processes. There is little variation in the shape of the size distributions from one location to another. Average size distributions of Fe, as a representative example of this group, are plotted in Fig. 1. The data are plotted versus the geometric midpoints of the size ranges determined by the cut-off

Table 3
Mass median aerodynamic diameters in μm EAD as measured in the CI samples for the elements of group 1 averaged for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel[a]

Element	KFKI campus	Lágymányos campus	Széna Square over night	Széna Square oner daylight	Castle District Tunnel
Na	3.9	4.9	7.2	8.1	7.1
Mg	4.8	5.9	6.8	7.7	6.8
Al	5.5	6.5	7.2	8.0	6.7
Si	6.0	6.9	7.8	9.0	8.0
P	5.9	6.0	5.7	6.9	6.3
Ca	6.0	7.1	7.7	8.9	7.1
Ti	5.9	7.1	8.3	9.5	7.7
Fe	5.3	5.9	6.3	7.0	6.2
Ga	4.8	6.9	6.2	7.2	7.7
Sr	5.0	6.7	7.2	8.5	8.4
Zr	7.2	7.6	6.5	8.3	7.4
Mo	ns	ns	6.0	ns	3.6
Ba	5.0	4.5	4.5	5.0	4.9

[a]ns no significant data set available.

values of the collection stages. The lines connecting the experimental points are eye-guides only. The ordinate of the plot is the ratio of the elemental mass (m) in a given size range to the total elemental mass (m_T) on all stages (mass fraction) instead of the usually applied $m/m_T/\log(d_2/d_1)$ expression (relative mass in an unit size range), where d_1 and d_2 are the lower and upper EADs, respectively, of the given size range. For the CIs with logarithmically equidistant cut-off values used in this work, the difference only means a shift in the ordinates by a factor of $\log(2)$. The presentation was chosen to allow direct observation and visual judgment of the relative mass in the different parts of the distribution, or on the stages. Median mass aerodynamic diameters (MMADs) and geometric standard deviations were calculated by fitting a lognormal function to the individual size distributions. (The results agreed well with those obtained from the cumulative probability plots on logarithmically probability graph.) Typical geometric standard deviations obtained were about 2.5. With regard to the individual MMADs, they were averaged for the five different data sets, and the average values are summarized in Table 3. It can be seen that the typical MMADs are found from 5 through 8 μm EAD, and that the MMADs are clearly shifted toward larger values with increasing aerosol mass concentration. For the samples collected within the CD Tunnel, the trend breaks somewhat.

Group 2 contains S, Cl, K, V, Cr, Mn, Ni, Cu, Zn, Ge, As, Se, Br, Rb and Pb. Average size distributions of these elements are depicted in Figs. 2–5. (Distributions for Cu, and for Pb and Si were previously published (Salma et al., 2001a; Salma, Balásházy, Winkler-Heil, Hofmann, & Záray, 2001b).) They have a unimodal size distribution with their mass occurring primarily in the accumulation mode or clearly exhibit a bimodal size distribution at the urban background site, i.e., at the KFKI campus. In general, these elements and their common compounds are relatively volatile. Significant mass in the fine particles points to their high-temperature sources.
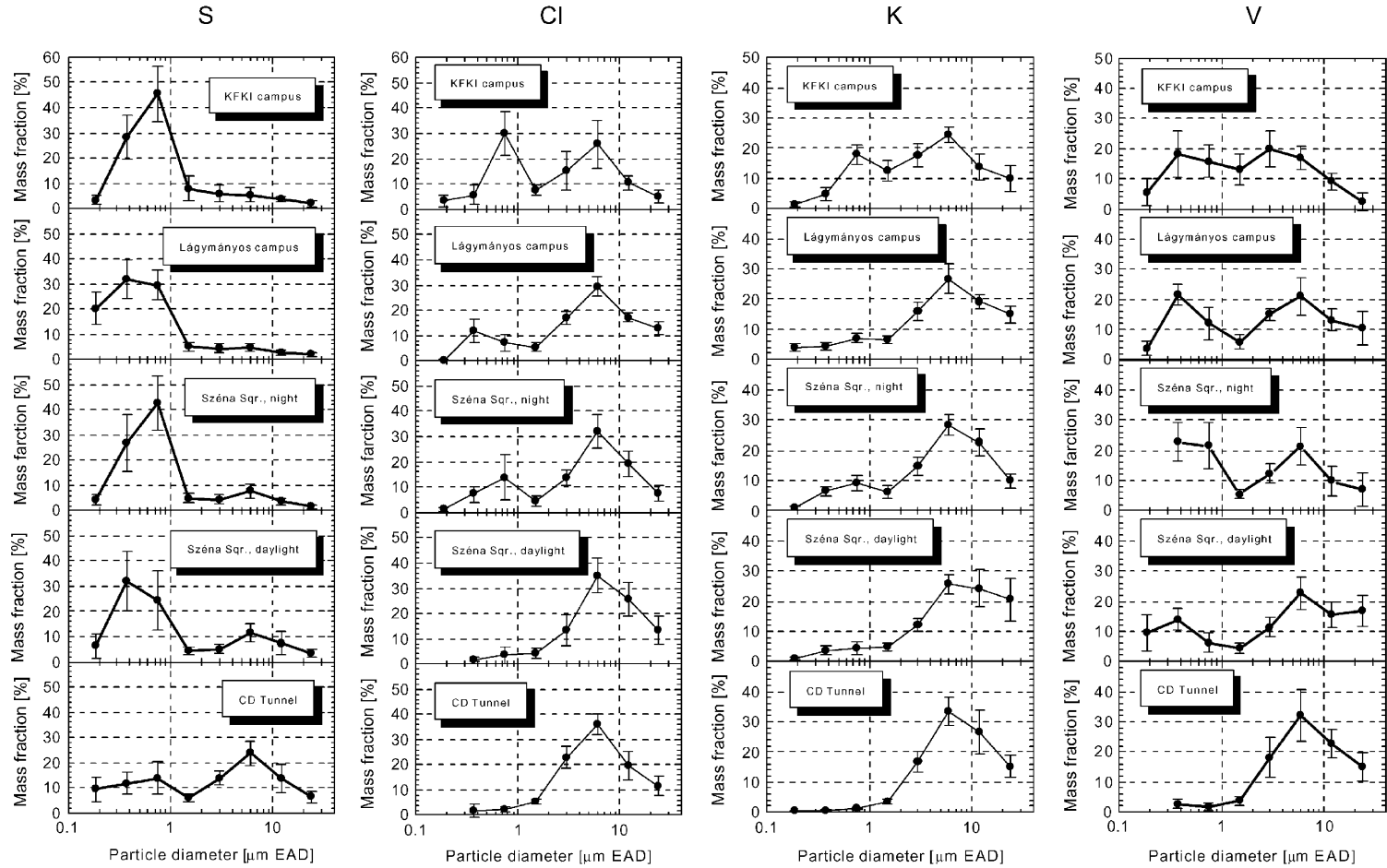
Fig. 2. Average mass size distributions of S, Cl, K and V for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.
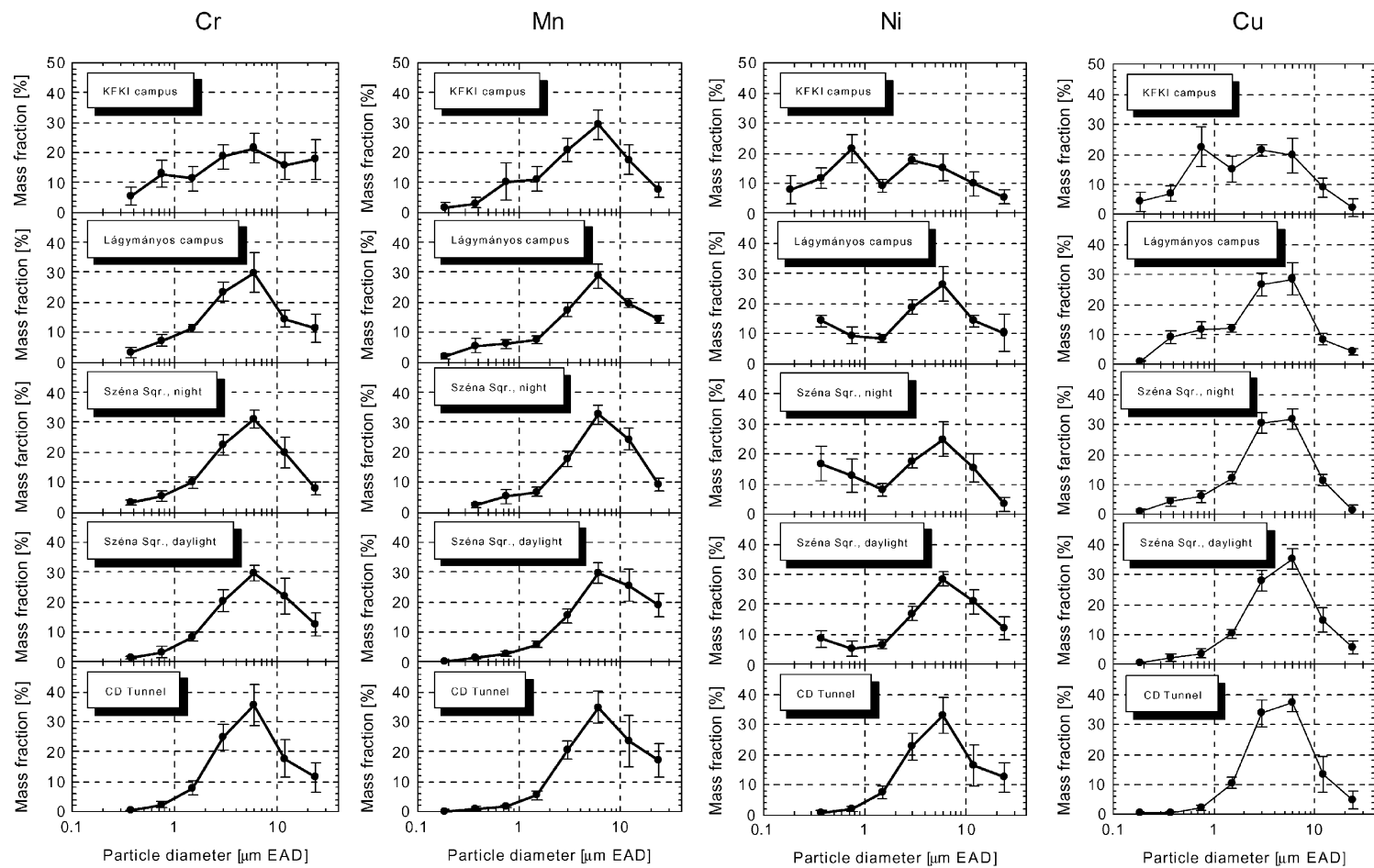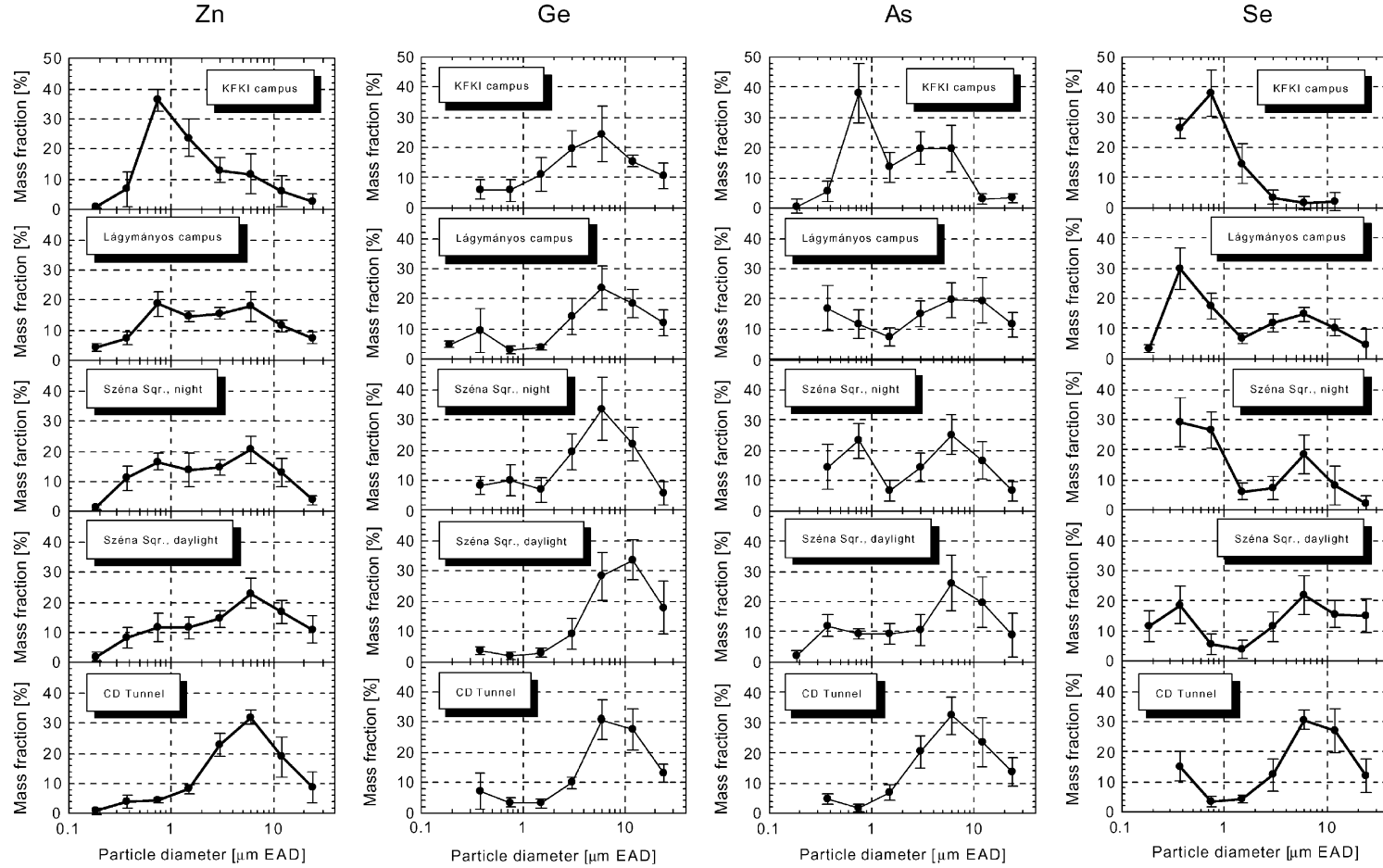
Fig. 3. Average mass size distributions of Cr, Mn, Ni and Cu for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.

Fig. 4. Average mass size distributions of Zn, Ge, As and Se for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.
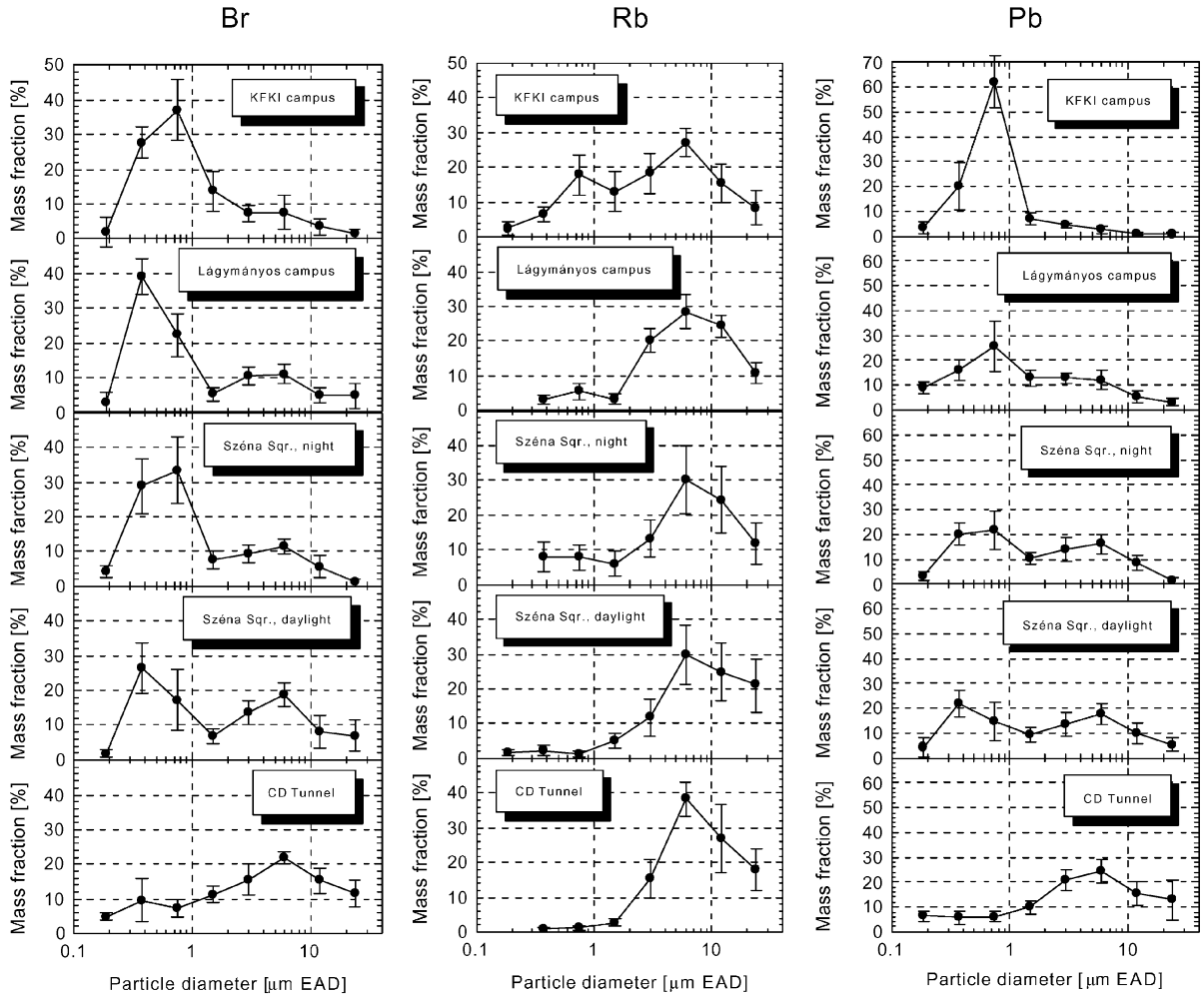
Fig. 5. Average mass size distributions of Br, Rb and Pb for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.

When comparing the sampling sites, however, the mass size distributions differ significantly from each other. Previous research has indicated that the size distributions are strongly affected by weather conditions (e.g., relative humidity or wind direction) and the solar radiation (photochemistry) (Väkevä et al., 2000). Normally, more aerosol particles are detected during daylight than at night, exhibiting a diurnal pattern, and the number of nucleation-mode particles is maximum during the afternoon (Haaf & Jaenicke, 1980). In the present study, in addition, there is an evident tendency for the accumulation mode to be decreased, and for the coarse mode to be increased with increasing overall aerosol mass concentration. In the CD Tunnel, all the elements, including typically anthropogenic ones, appear primarily in the coarse mode. This is consistent with the decreasing F/C ratios obtained from the SFU samples, and with the nearly constant

Table 4
Mass median aerodynamic diameters in μm EAD as measured in the CI samples for the elements of group 2 averaged for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel[a]

Element	Size mode	KFKI campus	Lágymányos campus	Széna Square over night	Széna Square over daylight	Castle District Tunnel
S	coarse	5.2	5.4	5.8	6.6	6.3
	accumulation	0.5	0.5	0.6	0.4	0.5
Cl	coarse	5.6	6.1	6.5	7.0	5.8
	accumulation	0.7	0.4	0.6	ns	ns
K	coarse	5.6	6.6	7.1	8.7	7.2
	accumulation	0.7	0.6	0.6	0.6	ns
V	coarse	3.8	5.5	5.7	7.0	6.7
	accumulation	0.4	0.4	0.6	0.3	ns
Cr	coarse	5.4	5.1	5.6	6.3	5.3
	accumulation	0.6	0.7	ns	ns	ns
Mn	coarse	5.9	6.4	6.7	7.2	6.5
	accumulation	0.7	0.4	ns	ns	ns
Ni	coarse	4.6	5.5	5.7	6.6	5.4
	accumulation	0.6	0.5	0.5	ns	ns
Cu	coarse	4.1	4.3	4.2	4.8	4.5
	accumulation	0.7	0.6	ns	ns	ns
Zn	coarse	5.0	5.7	6.1	6.7	5.7
	accumulation	0.9	0.7	0.7	0.7	0.6
Ge	coarse	5.4	6.6	6.8	9.9	8.1
	accumulation	ns	0.4	0.6	ns	ns
As	coarse	4.5	7.4	6.3	7.4	6.3
	accumulation	0.7	0.5	0.6	0.6	ns
Se	coarse	ns	5.4	6.2	7.0	7.9
	accumulation	0.6	0.5	0.6	0.3	ns
Br	coarse	5.4	4.1	5.4	5.4	6.0
	accumulation	0.6	0.4	0.6	0.4	0.4
Rb	coarse	5.4	6.7	7.4	8.0	7.1
	accumulation	0.7	0.6	ns	ns	ns
Pb	coarse	ns	5.1	4.8	5.0	5.2
	accumulation	0.6	0.6	0.6	0.5	ns

[a] ns not significant.

F/C ratios of the species (except for S and PM) in the tunnel. Individual MMADs and geometric standard deviations for the two modes were calculated by fitting two additive log-normal distributions to all size distributions of a particular data set in one fitting session. The width parameters of the functions were shared within a fitting session. Typical geometric standard deviation for the individual coarse and accumulation modes were about 2.5 and 2.2, respectively. It has to be noted that in a few cases, when the experimental data for the backup filter and/or for some impactor stages were below the detection limit, the fitting procedure lead to estimated uncertainties of 15–20% of the fitted value. The individual coarse- and accumulation-mode MMADs were averaged for the five different data sets, and are summarized in Table 4. The

typical average MMADs for the accumulation mode are between 0.5 and 0.6 µm EAD, and are almost constant (if not slightly decreasing with overall aerosol mass concentration) when comparing the sampling sites. The typical average MMADs for the coarse mode are of the order of 5 through 7 µm EAD, thus somewhat smaller than for those of group 1, but are again shifted clearly toward larger values with increasing aerosol mass concentration.

4. Interpretation and some consequences

The phenomenon described above does not seem to depend on the chemical properties of the elements involved. Its explanation should, therefore, be looked for in the aerosol generation and transformation processes that are determined primarily by physical properties. Human activities in cities produce fine particles, and at the same time, large amounts of dust from roadways or exposed soils are entrained into the atmosphere. In the environments impacted heavily by traffic, most of the coarse mode contains resuspended surface dust that is associated with the fine particles that were deposited on the ground surface previously through deposition processes, and, therefore, the typical antropogenic (volatile) elements appear in the coarse mode. In addition to that, the low volatility vapor formed from precursor gases by photochemical reactions in a polluted atmosphere can condense on the existing particles when the temperature decreases if suitable particles (condensation sink) are present. Surface plays the determining role in the control of such processes. In order to estimate the total surface area represented by the coarse and accumulation modes, mass size distributions for PM were derived utilizing the mean coarse and fine fraction particulate masses obtained gravimetrically from the SFU filters, and the coarse- and accumulation-mode MMADs and geometric standard deviations obtained by averaging the corresponding parameters 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. It has to be noted, however, that the size distributions of the major aerosol constituents like nitrate, organic and elemental carbon were not measured in the present work, and that the aerosol types (components) that are related to the elements determined, e.g., crustal matter and ammonium sulfate account only at most for about 40% of the gravimetrically determined fine PM (Salma et al., 2001a). The mass size distributions of PM were converted to number size distributions assuming unit density and smooth spherical particles, and, finally, surface area size distributions were calculated. The conversion was found to be adequate in the size range under the consideration (0.125–16 µm EAD). The total surface area of the coarse and accumulation modes are summarized in Table 5. It is the accumulation mode that represents the main surface area at all sampling sites. Nevertheless, condensation of the photochemical reaction products onto the surface of the coarse particles is thought to be also significant since the coarse-mode MMADs unambiguously increase with the overall aerosol pollution (see Table 3).

The elemental mass size distributions derived for the more polluted urban environments (in particular for the CD Tunnel) differ from those typically observed for industrial, combustion or automotive sources. As a consequence, consistency in the size distribution shapes assumed so far applies to typically coarse elements only. Under such conditions, formation of the accumulation mode appears to be not independent from the coarse particles but a strong association

Table 5
Estimated total surface area of the coarse- and accumulation-mode particles in $\mu m^2\, cm^{-3}$ for the aerosol collected at the KFKI campus, Lágymányos campus, Széna Square and within the Castle District Tunnel

Mode	KFKI campus	Lágymányos campus	Széna Square	Castle District Tunnel
Coarse	87	78	97	950
Fine	350	630	270	1600

between the modes is observed instead. Hence, generalizations on the basis of the elements that are typically related to the fine fraction could be misleading. When collecting $PM_{2.5}$ aerosol samples in rather polluted locations, like tunnels, it may happen for instance that only about 10–15% of the total mass of the typically fine-fraction and possibly toxic elements are gathered, and utilized for further chemical characterization. Moreover, a small shift in the 50% cut-point of a $PM_{2.5}$ sampler also has a relatively large influence on the collected mass or on the analytical results obtained later on, since the coarse mode can already be quite important at that cut-point (see Figs. 2–5, CD Tunnel). These conclusions offer a strong argument for thinking over the applicability of $PM_{2.5}$ ambient aerosol standard under extreme air pollution conditions. According to the present study, a joint PM_{coarse} and PM_{fine} standard seems to be more adequate in characterizing or monitoring the ambient aerosols under general conditions.

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 a separate paper (Salma et al., 2001b).

Acknowledgements

References

Chester, R., Lin, F. J., & Murphy, K. J. T. (1989). A three stage sequential leaching scheme for the characterisation of the sources and environmental mobility of trace metals in the marine aerosol. *Environmental Technology of Letters*, *10*, 887.
Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., & Speizer, F. E. (1993). An association between air pollution and mortality in six US cities. *New England Journal of Medicines*, *329*, 1753.

Fitzgerald, J. W. (1991). Marine aerosols: A review. *Atmospheric Environment*, *25A*, 533.

Gone, J. K., Olmez, I., & Ames, M. R. (2000). Size distribution and probable sources of trace elements in submicron atmospheric particulate material. *Journal of Radioanalytical Nuclear Chemistry*, *244*, 133.

Haaf, W., & Jaenicke, R. (1980). Accurate measurement of aerosol size distribution II: Construction of a new plate condenser electric mobility analyzer and first results. *Journal of Aerosol Science*, *8*, 447.

Hänel, G. (1976). The properties of atmospheric aerosol particles as function of the relative humidity at thermodynamic equilibrium with the surrounding moist air. *Advanced Geophysics*, *19*, 73.

Hering, S. V., & Friedlander, S. K. (1982). Origins of aerosol sulfur size distribution in the Los Angeles basin. *Atmospheric Environment*, *16*, 2647.

Hoppel, W. A., & Frick, G. M. (1991). Submicron aerosol size distributions measured over the tropical and south Pacific. *Atmospheric Environment*, *24A*, 645.

Hopke, Ph. K., Xie, Y., Raunemaa, T., Biegalsky, S., Landsberger, S., Maenhaut, W., Artaxo, P., & Cohen, D. (1997). Characterisation of the Gent Stacked Filter Unit PM_{10} sampler. *Aerosol Science and Technology*, *27*, 726.

Ito, T. (1993). Size distribution of Antarctic submicron aerosol. *Tellus*, *45B*, 145.

Kleeman, M. J., & Cass, G. R. (1989). Source contributions to the size and composition distribution of urban particulate air pollution. *Atmospheric Environment*, *32*, 2803.

Lundgren, D. A., & Burton, R. M. (1995). Effect of particle size distribution on the cut point between fine and coarse ambient mass fractions. *Inhalation Toxicology*, *7*, 131.

Maenhaut, W., Francois, F., & Cafmeyer, J. (1994). *The Gent stacked filter unit sampler for the collection of atmospheric aerosols in two size fractions, in applied research on air pollution using nuclear-related analytical techniques*. Report NAHRES-19, Vienna, Austria: International Atomic Energy Agency.

Maenhaut, W., & Raemdonck, H. (1984). Accurate calibration of a Si(Li) detector for PIXE analysis. *Nuclear Instruments and Methods*, *B1*, 123.

Mäkelä, J. M., Aalto, P., Jokinen, V., Pohja, T., Nissinen, A., Palmroth, S., Markkanen, T., Seitsonen, K., Lihavainen, H., & Kulmala, M. (1997). Observation of ultrafine aerosol particle formation and growth in boreal forest. *Geophysical Research Letters*, *24*, 1219.

Mészáros, E. (1999). *Fundamentals of atmospheric aerosol chemistry*. Budapest: Akadémiai Kiadó.

Milford, J. B., & Davidson, C. I. (1985). The size of particulate trace elements in the atmosphere-a review. *Journal of Air Pollution Control Association*, *35*, 1249.

O'Dowd, C. D., Geever, M., Hill, M. K., Jennings, S. G., & Smith, M. H. (1998). New particle formation: spatial scales and nucleation rates in the coastal environment. *Geophysical Research Letters*, *25*, 1661.

Pope, C. A., Dockery, D. W., & Schwartz, J. (1995). Review of epidemiological evidence of health effects of particulate air pollution. *Inhalation Toxicology*, *7*, 1.

Reichhardt, T. (1995). Weighing the health risk of airborne particulates. *Environmental Science and Technology*, *29*, 360.

Salma, I., Balásházy, I., Winkler-Heil, R., Hofmann, W., & Záray, Gy. (2001b). Effect of particle mass size distribution on the deposition of aerosols in the human respiratory system. *Journal of Aerosol Science* (in press).

Salma, I., Maenhaut, W., Cafmeyer, J., Annegarn, H. J., & Andreae, M. O. (1994). PIXE analysis of cascade impactor samples collected at the Kruger National Park, South Africa. *Nuclear Instruments and Methods*, *B, 85*, 849.

Salma, I., Maenhaut, W., Zemplén-Papp, É., & Bobvos, J. (1998). Characteristics of size-fractionated urban aerosols and trace gases in Budapest. *Microchemical Journal*, *58*, 291.

Salma, I., Maenhaut, Zemplén-Papp, É., & Záray, Gy. (2001a). Comprehensive characterisation of atmospheric aerosols in Budapest, Hungary: Physicochemical properties of inorganic species. *Atmospheric Environment*, *35*, 4367.

Salma, I., & Zemplén-Papp, É. (1999). Instrumental neutron activation analysis for studying size-fractionated aerosol samples. *Nuclear Instruments and Methods*, *A, 435*, 462.

United States Environmental Protection Agency (1997). 40 CFR, part 50, Federal Register *62*, 38761.

Väkevä, M., Hämeri, K., Puhakka, T., Nilsson, E. D., Hohti, H., & Mäkelä, J. M. (2000). Effects of meteorological processes on aerosol particle size distribution in an urban background area. *Journal of Geophysical Research*, *105*, 9807.

Vedal, S. (1997). 1997 critical review: Ambient particles and health. *Journal of Air Waste Management*, *47*, 551.

Whitby, K. T. (1978). The physical characteristics of sulfure aerosols. *Atmospheric Environment*, *12*, 135.