Comprehensive characterisation of atmospheric aerosols in Budapest, Hungary: physicochemical properties of inorganic species

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Abstract

As part of an air pollution project in Budapest, aerosol samples were collected by stacked filter units and cascade impactors at an urban background site, two downtown sites, and within a road tunnel in field campaigns conducted in 1996, 1998 and 1999. Some criteria pollutants were also measured at one of the downtown sites. The aerosol samples were analysed by one or more of the following methods: instrumental neutron activation analysis, particle-induced X-ray emission analysis, a light reflection technique, gravimetry, thermal profiling carbon analysis and capillary electrophoresis. The quantities measured or derived include atmospheric concentrations of elements (from Na to U), of particulate matter, of black and elemental carbon, and total carbonaceous fraction, of some ionic species (e.g., nitrate and sulphate) in the fine (< 2 μm equivalent aerodynamic diameter, EAD) or in both coarse (10–2 μm EAD) and fine size fractions, atmospheric concentrations of NO, NO_2, SO_2, CO and total suspended particulate matter, and meteorological parameters. The analytical results were used for characterisation of the concentration levels, elemental composition, time trends, enrichment of and relationships among the aerosol species in coarse and fine size fractions, for studying their fine-to-coarse concentration ratios, spatial and temporal variability, for determining detailed elemental mass size distributions, and for examining the extent of chemical mass closure. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Considerable air pollution occurs in large cities throughout the world (De Koning et al., 1986). It has a great impact on the local environment (e.g., on biosphere, buildings and materials) and visibility, and can even influence the surrounding rural areas. The pollution also affects many people inasmuch as these urban areas usually accommodate a large number of inhabitants. The coincidence of the concentrated pollu-tion sources, dense population and/or sometimes unfavourable geographical and climatic conditions may multiply its adverse effects in particular. Although the air pollution and smog problems are very complex, a small set of compounds has been identified as major contributors to the phenomenon. They are called criteria pollutants, and serve as indicators of the air quality in pollution control policy. The criteria pollutants usually include NO and NO_2, SO_2, CO, tropospheric O_3, total or size-fractionated suspended airborne particulate matter (PM). Research into the criteria pollutants and their synergism has revealed that it is the elevated levels of airborne particles that are mainly responsible for the increased health risks of inhabitants in large cities

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(Dockery et al., 1993; Reichhardt, 1995; Pope III et al., 1995). The atmospheric aerosols can be characterised from a number of viewpoints, i.e., by number or mass concentration, chemical (elemental, organic and ionic) composition, speciation, size distribution, morphology of the particles and by their source types. Many of these properties are, moreover, interdependent. In addition, the characteristics may display a pronounced variability in time and space due to the wide variety in formation, dynamic transformation, transportation and removal processes of the aerosols. The situation is particularly complicated in highly polluted (urban) airsheds.

To improve our knowledge on the air pollution in Budapest, Hungary, to address the needs for a comprehensive characterisation of airborne particulate matter and their effects and to assess human exposure to potentially toxic air pollutants, a research project was undertaken. The programme involves chemical characterisation of elemental, main ionic and organic composition of size-fractionated urban aerosols, source apportionment modelling calculations in two size fractions, and determination of detailed elemental mass size distributions together with deposition in the human respiratory system so that air pollution control measures could be implemented most effectively. The main objectives of the present paper are to report the properties of the inorganic species, to discuss their characteristics and behaviour, and to reveal the relationships among them.

2. Experimental

2.1. Sampling methods

Stacked filter units (SFUs) and cascade impactors (CIs) were employed for collecting size-fractionated aerosol samples. The former device was a Gent-type PM_{10} SFU (Maenhaut et al., 1994; Hopke et al., 1997). 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 equivalent aerodynamic diameter (EAD, for 20°C and 1013 hPa), and the first filter with the 8-μm 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 behaviour and the reproducibility were found to be very good (Hopke et al., 1997). The same sampling device

was used for collecting fine aerosol samples on quartz fibre filters as well. In this case, there is no change with regard to the first (coarse) Nuclepore filter, but the second (fine) Nuclepore filter in the cassette is replaced by a pre-heated (at 500°C for 5 h) Whatman QM-A quartz fibre filter, which is utilised for further chemical analysis. The other sampling 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 to 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 is used as impaction foil. The foils are coated with a thin adhesive layer of vaseline (for stages 7–2) or paraffin (stage 1) to minimise particle bounce-off from the impaction surfaces. Nuclepore polycarbonate membrane filter with a pore size of 0.4 μm is used as the backup filter. For the filter stage, the 50% collection efficiency is considered to be at 0.125 μm EAD. 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.

2.2. Sampling sites

Collection of the aerosol samples was performed at four urban receptor sites in Budapest, a Central European 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 (Wallén, 1977), this site was considered as the "urban background". The sampling devices were set up at approximately 1.8 m above the ground. 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. The third sampling site was located also 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 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. The fourth sampling site was 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, approximately 9 m wide, varies from 8 to 11 m in height, and comprises altogether 2-lane traffic of passenger cars, light-duty vehicles and buses. Traffic through the tunnel during the sampling in 1999 was recorded on videotapes for traffic characterisation. The typical total vehicle circulation in both directions was 1780 h^{-1}, and the vehicle composition approximated roughly the national ratios (Salma et al., 2000). The samplers were set up on the wall in the service curb/lane at approximately the halfway point of the length at a height of 1.7 m above the ground.

2.3. Field campaigns

The aerosol samples were collected in April–May 1996, June 1998 and April–June 1999 in non-heating seasons on semi-consecutive days. At the KFKI and Lágymányos campuses, daily SFU and CI samples were collected with planned and regular interruptions. At Széna Square, daily SFU samples were also taken with planned and regular interruptions, while separate CI samples were collected over daylight (typically from 7:30 to 21:30) and night (typically from 21:30 to 7:30) with planned and regular interruptions (Salma et al., 1998). In 1996, a simultaneous campaign was performed at the KFKI campus and Széna Square resulting in a total number of 33 SFU Nuclepore sample pairs at each sampling site. In 1998, three SFU Nuclepore sample pairs were collected at Széna Square and within the tunnel. In 1999, three SFU Nuclepore sample pairs and three quartz samples were collected at each residential sampling site, while two SFU Nuclepore sample pairs and two quartz samples were taken within the tunnel. As to CI samples, they were taken in 1999 only, and in parallel with the SFU samples. At the KFKI campus, a total number of six CI samples were collected, while five CI samples were taken at both Lágymányos campus and within the tunnel. At Széna Square, 10 CI samples were collected over daylight and 11 over night. The starting time for all daily SFU and CI collections was typically approximately 7:30 in the morning. The typical volume for the SFU samples was about 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 about 1.5 m^3, for the CI samples collected over daylight and night, it was 0.8 m^3 and 0.6 m^3, respectively, and about 0.1 m^3 air was sampled within the tunnel. Due to the sampling times chosen or to the planned and regular interruptions (which were evenly spread and typically only amounted to 10–15% of the total time), the filter clogging or CI overloading were not significant at any of the sampling sites. For each sample type, field blank samples were also taken at the sites. All samples were placed into plastic vials, and were stored in a refrigerator at a temperature of approximately 4°C.

The sampling campaigns conducted at Széna Square were complemented with simultaneous measurement of some criteria pollutants (i.e., NO, NO$_2$, SO$_2$, CO and total suspended particulate matter, TSP) by Monitor Labs equipment (Salma et al., 1998). All collections were coupled with meteorological observations including ambient temperature (T), pressure (Press) measurements, and at some sampling sites, horizontal wind speed (WS) and direction (WD), and relative humidity (RH) were recorded. During the sampling periods, the weather was in accordance with the typical seasonal parameters without extreme meteorological situations (Wallén, 1977). Rain during the actual collection of the samples only occurred occasionally as light shower.

2.4. Analytical methods

The coarse and fine Nuclepore filters were weighed before and after the sampling using a microbalance to obtain the particulate mass. The filters were pre-equilibrated in a room with stabilized temperature (24°C) and relative humidity (20–25%) before the actual weighing. Approximately half section of each Nuclepore filter was analysed by panoramic instrumental neutron activation analysis (INAA) at Budapest Research Reactor for up to 49 elements (Salma and Zemplén-Papp, 1999). The method was validated by the NIST Standard Reference Material 1648: urban particulate matter. Quarter section of each Nuclepore filter was also analysed by particle-induced X-ray emission spectrometry (PIXE) for up to 29 elements at the University of Gent (Maenhaut et al., 1981; Maenhaut and Raemdonck, 1984). The quality of the analytical data was continuously controlled on a sample by sample basis via concentration ratios of common elements that were measured by both INAA and PIXE (Salma et al., 1997). The Nuclepore filters were also analysed for black carbon (BC) by a commercial smoke stain light reflectometer (Diffusion System, model 43) calibrated with other Nuclepore filters for which the BC loading had been determined (Andreae et al., 1984). The CI samples were analysed by PIXE for up to 29 elements (Salma et al., 1994). The analyses above were performed without sample treatment. As to the quartz fibre filters, part of each of them was heated in a programmed way in oxygen in combination with sample pre-treatment (heating and aqueous extraction), and the evolved carbon dioxide was simultaneously recorded to resolve the carbon content into the total carbonaceous fraction (TC), elemental and more refractory organic carbon (EC) and water-soluble organic carbon (WSOC) by a TOC Astro 2100 solid module (Gelencsér et al., 2000) according to a procedure recommended by Cachier (1998). Another part of the quartz fibre filters was analysed by capillary electrophoresis (CE, Waters Quanta 4000 with fused silica capillary) for some

inorganic cations and anions, e.g., nitrate and sulphate (Krivácsy et al., 1997). All atmospheric concentrations were expressed at standard temperature and pressure (STP, 0°C and 1013 hPa).

3. Results and discussion

3.1. Atmospheric concentrations

The total number of species determined is 61. Medians of the atmospheric concentrations for some of the aerosol species in the coarse and fine size fractions, for the criteria pollutants and of the meteorological parameters derived for the two sets of 33 sample pairs collected at each of the KFKI campus (urban background) and Széna Square (downtown site) in 1996 are presented in Table 1. When the number of concentration data for a species was equal to or less than half of the total number of samples in the set, mean concentrations were calculated and are displayed in the table instead of the medians. It is worth mentioning that the national 24-h concentration limits for soot, TSP, NO_x, NO_2, SO_2, CO and Pb valid for the Budapest area are 50, 100, 150, 85, 150 $\mu g/m^3$, 5 mg/m^3 and 300 ng/m^3, respectively, (MSZ, 1990) expressed at 25°C and 1013 hPa. During the sampling period, TSP and NO_2 only exceeded the limits (in 12 and 3 occasions, respectively). In the downtown, the median TSP was found to be higher by approximately 25% than the sum of the median PMs for the coarse and fine size fractions (which is practically the PM_{10} fraction). As to the relationship between the mass concentrations of PM_{10} and fine size fraction (PM_2), the latter makes up only approximately 43% and 33% of the PM_{10} mass at the urban background and downtown, respectively, when medians are considered. The contribution exhibits significant seasonal variation (which is related to the residential space heating), and depends on the actual location. A range from 75% to 49% was, therefore, observed for different cities (Pinto et al., 1998; Mark et al., 1998; Van Putten et al., 1998; Dann and Brook, 1998). As far as correlation between TSP and PM_{10} for the downtown is concerned, a correlation coefficient of 0.60 was derived, while it was 0.78 between TSP and coarse PM thus larger but still not close to one. Hungary phased out of leaded gasoline from the market on 1 April 1999. Its consequences on the air quality and atmospheric concentrations of Br and Pb are dealt with in a separate article (Salma et al., 2000).

3.2. Crustal enrichment factors

Median enrichment factors (EFs) for some aerosol species in the coarse and fine size fractions collected in 1996, calculated relative to Mason's average crustal rock composition (Mason, 1966) with Al as reference element are shown in Figs. 1 and 2, respectively. For BC and PM, ratios to Al instead of EFs are shown in the figures. Most elements in the coarse size fraction have crustal EFs that are very close to one, thus suggesting that they are attributable mainly to soil and road dust dispersal and resuspension. Nevertheless, some elements, i.e., S, Cl, Cu, Zn, Ge, As, Se, Br, Mo, Ru, Sb, I, W, Au and Pb are significantly enriched. In the fine size fraction, S, Cl, Cu, Zn, Ge, As, Se, Br, Mo, Cd, Sb, I, W, Au, Hg and Pb have very high EFs, which suggests that they are mainly of anthropogenic origin. Interestingly, some of the enriched elements, i.e., S, V, Ge, As, Se, In, I, Cs and W have significantly higher EFs in the urban background than at the downtown suggesting that they are transported from outside the city. The EFs for the samples collected in 1999 and 1998 were not significantly different from the values obtained for 1996, expect for Cl, Br and Pb. The changes are to be related to the phase out of leaded gasoline (Salma et al., 2000).

3.3. Fine-to-coarse concentration ratios

Fine-to-coarse (F/C) concentration ratios were calculated on a sample by sample basis for 40 aerosol species and were averaged. The mean F/C ratios obtained for the samples collected in 1996 and 1999 were quite similar, expect for Cl, Br, W and Pb. Since the field campaign in 1999 included a larger number (four) of urban sampling sites, the mean F/C ratios are displayed for these samples. As can be seen in Fig. 3, the mean F/C ratios at the urban background site are typically below one, except for BC, S, K, V, Ni, Cu, Zn, As, In, Sb, I, Cs, W and Pb. This indicates that most elements are predominantly present in the coarse size fraction. The typical mineral dust elements like Al, Si, Ca, Ti and Fe have F/C ratios of approximately 0.2. Nevertheless, 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 (overall air pollution). For typical mineral dust elements and PM, the F/C ratios in the tunnel were decreased to 10–15% of the urban background value. 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.

3.4. Mass size distributions

Detailed elemental mass size distributions were obtained for 28 elements from the CI samples collected in 1999. The individual size distributions were averaged for 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

Table 1
Medians of atmospheric concentrations for some aerosol species in the coarse and fine size fractions, for the criteria pollutants and of the meteorological parameters at the KFKI campus (urban background) and Széna Square (downtown) in 1996. The units are ng/m^3 STP unless otherwise indicated

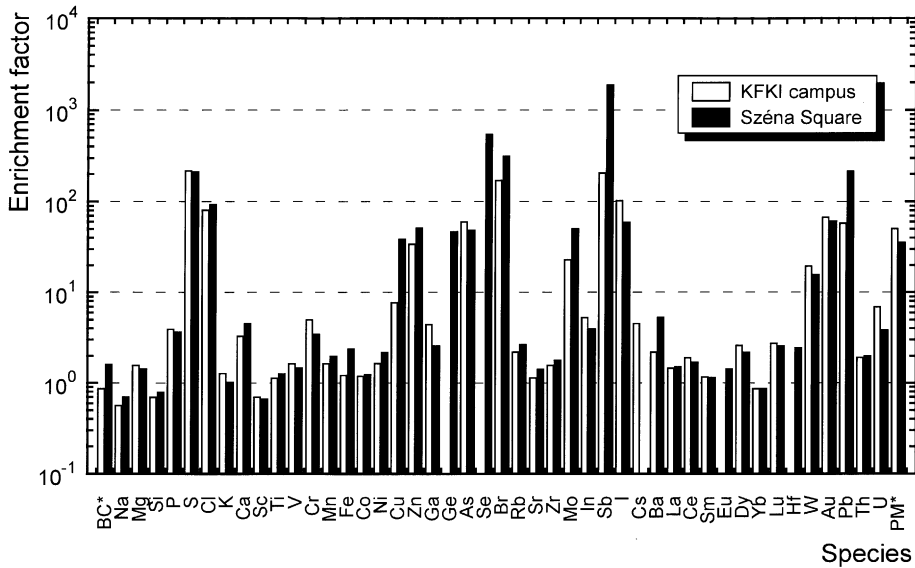| Species (unit)	Sampling site			
	KFKI campus (urban background) Size fraction		Széna Square (downtown) Size fraction	
	Coarse	Fine	Coarse	Fine
BC (μg/m^3 STP)	0.33	2.0	2.3	8.0
Na	93	56	338	56
Mg	166	34	518	63
Al	363	97	1413	125
Si	993	270	3820	385
P	28	<8	64	10[a]
S	278	2002	885	1791
Cl	52	20	181	23
K	155	160	459	155
Ca	611	115	2785	213
Sc	0.075	0.020	0.26	0.025
Ti	26	6.6	96	9.7
V	1.1	1.9	3.5	1.8
Cr	4.2[a]	2.3[a]	5.3	3.2
Mn	6.5	4.5	34	7.6
Fe	304	111	2004	339
Co	0.24[a]	0.13	0.47	0.24
Ni	0.62	0.86	2.4	0.86
Cu	1.9	2.3	34	11
Zn	11	22	61	32
Ga	0.35	0.12	0.48	0.17
As	0.46	1.2	1.4	1.4
Se	—	0.72	0.58[a]	0.52
Br	3.4[a]	5.5	13	16
Rb	2.0[a]	1.0[a]	4.1[a]	1.9[a]
Sr	2.1	1.3[a]	7.6	0.82
Zr	2.2[a]	—	3.0	1.5[a]
Mo	0.26[a]	0.27[a]	1.2	0.43
In	0.0049[a]	0.0041	0.0085[a]	0.0039
Sb	0.18	0.69	6.6	2.5
I	0.32	2.2	0.48	1.2
Cs	0.13[a]	0.13[a]	—	0.083[a]
Ba	4.7	2.9[a]	38	8.2
La	0.23	0.084	0.79	0.12
Ce	0.46	0.26	1.8	0.39[a]
Sm	0.037	0.010	0.12	0.013
W	0.21[a]	1.1[a]	0.31	0.23
Au	0.0018[a]	0.0017[a]	0.0031	0.0020[a]
Pb	3.7	19	42	52
Th	0.13[a]	—	0.21	—
U	0.11[a]	—	0.062	—
PM (μg/m^3 STP)	24	18	44	25
TSP (μg/m^3 STP)	—		88	
NO (μg/m^3 STP)	—		46	
NO$_2$ (μg/m^3 STP)	—		67	
SO$_2$ (μg/m^3 STP)	—		49	
CO (μg/m^3 STP)	—		2.3	
Press (hPa)	966		1002	
T (°C)	16		19	
WS (m/s)	—		1.4	
RH (%)	—		69	

[a] Means mean.

Fig. 1. Median crustal enrichment factors for the coarse aerosol size fraction at the KFKI campus (urban background) and Széna Square (downtown) in 1996. The values displayed for BC and PM are concentration ratios to Al instead of EFs.
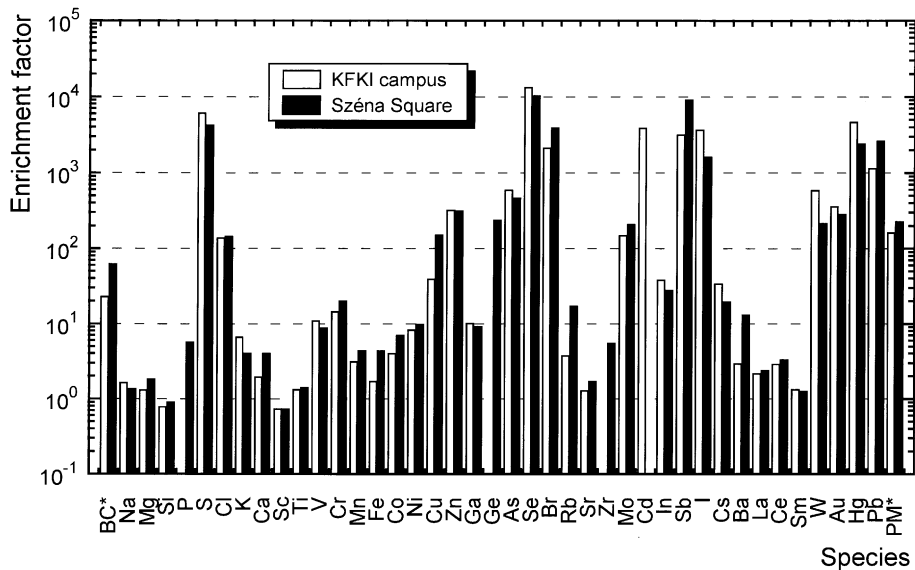

Fig. 2. Median crustal enrichment factors for the fine aerosol size fraction at the KFKI campus (urban background) and Széna Square (downtown) in 1996. The values displayed for BC and PM are concentration ratios to Al instead of EFs.

classified into two groups. Group 1 comprises Na, Mg, Al, Si, P, Ca, Ti, 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 (see below). Group 2 contains S, Cl, K, V, Cr, Mn, Ni, Cu, Zn, Ge, As, Se, Br, Rb and Pb. They either have a unimodal size distribution with their mass occurring primarily in the accumulation mode or exhibit clearly a bimodal size distribution at the urban background site. Significant mass in the fine particles points

Fig. 3. Mean fine-to-coarse concentration ratios and standard deviations for the aerosol species at the KFKI campus, Lágymányos campus, Széna Square and Castle District Tunnel in 1999.

to high-temperature sources (Milford and Davidson, 1985). When comparing the sampling sites, however, the mass size distributions show substantial differences. 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. Formation of the accumulation mode is not independent from the coarse particles (the opposite is generally assumed) but a strong association between the modes is observed instead. The average mass median aerodynamic diameters (MMADs) of the elements for the modes were presented and discussed earlier (Salma et al., 2001a). In short, typical MMADs for the coarse mode are from 5 to 8 μm EAD, and the MMADs are clearly shifted toward larger values with increasing aerosol mass concentration. This tendency is broken somewhat for the samples collected within the tunnel. The typical

average MMADs for the accumulation mode are between 0.5 and 0.6 μm EAD. In order to illustrate the tendencies in the size modes and MMADs mentioned, average size distributions of Cu are displayed in Fig. 4. If suitable foreign particles are present in sufficient quantity (above a critical surface concentration), the low volatility vapour formed from precursor gases by photochemical reactions in a polluted atmosphere will condense primarily on the existing particles when the temperature decreases. The diversity in the size distributions for different locations has a pronounced impact on the penetration of the aerosol particles and their deposition in the human respiratory system (Salma et al., 2001b). The conclusions above can also offer an argument for thinking over the applicability of the $PM_{2.5}$ ambient aerosol standard under general/extreme air pollution conditions.
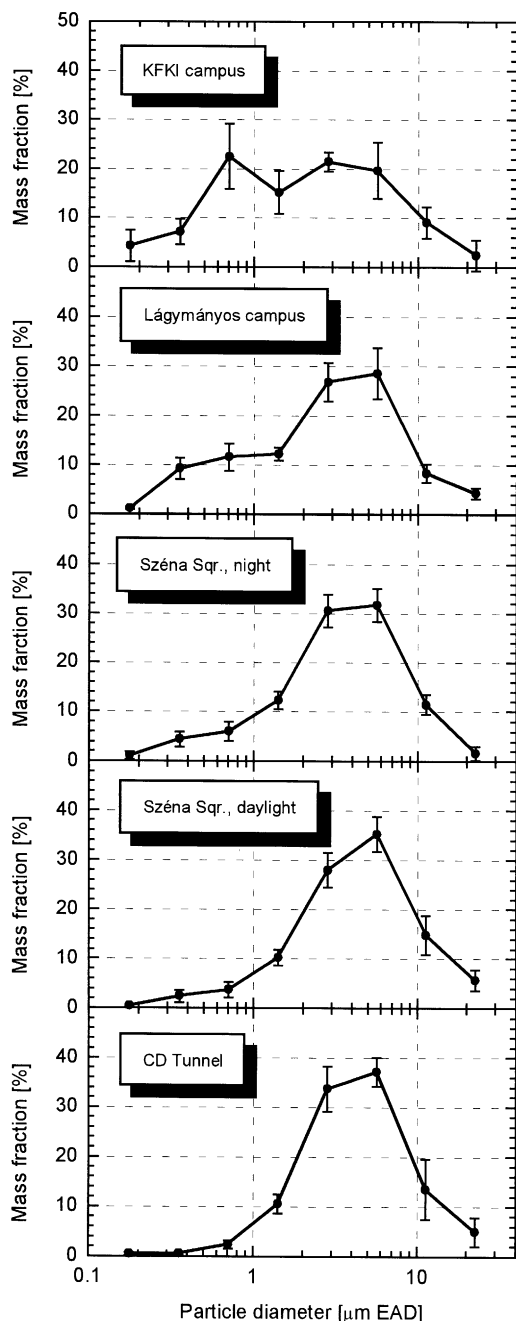
Fig. 4. Average mass size distributions of Cu for the data sets representing the KFKI campus, Lágymányos campus, Széna Square over night, Széna Square over daylight and Castle District Tunnel. The error bars indicate standard deviations.

3.5. Relationships among the sampling sites

For the coarse size fraction, all downtown-to-urban background concentration ratios for 1996 are above unity with an average ratio of 3.8 ± 1.5. For a few species, i.e., for Cu, Br, Sb and Ba, the difference is, however, one order of magnitude. For the fine size fraction, the downtown-to-urban background concentration ratios are also usually above unity with an average ratio of 1.7 ± 1.0. However, the concentrations of S, K, V, Ni, Se, In and I (and Hg too) in the urban background are, interestingly, equal to or even higher than at the downtown. On the other hand, concentrations of BC, Fe, Cu, Br, Sb, Ba and Pb at the downtown are markedly higher (by a factor of 2–3) than at the urban background. All this suggests that there may be an essential source for BC, Fe, Cu, Br, Sb, Ba and Pb in or near the city centre, and that the amount of fine S, K, V, Ni, Se, In and I transported into the city seems to be considerable. When comparing the four sampling sites in 1999, it is found that the mean atmospheric concentrations in the coarse size fraction for the 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. Thus, the average fine aerosol air pollution in Budapest is more uniform than the coarse one. In addition, no significant difference in the mean fine concentrations between the two downtown sites was observed despite the fact that the samplers at Lágymányos campus were set up at 35 m higher than at Széna Square. This conclusion agrees well with earlier observations made in Helsinki, Finland (Ojanen et al., 1998).

During the parallel field campaigns conducted in 1996, there were 27 days when aerosol samples were collected at both at the KFKI campus and Széna Square. It is, therefore, sensible to investigate the correlation between the daily atmospheric concentrations. For the fine size fraction, the highest correlation was observed for K (correlation coefficient, corr = 0.91) and S (corr = 0.89). The high correlation for S has to be attributed to the fact that this species is a secondary aerosol constituent which is formed from a fairly constant pool of precursor SO_2 gas with small diurnal and daily fluctuation. Atmospheric concentration of particulate S in the Budapest area is essentially controlled by the gas-to-particle conversion rate, the fine sulphate deposition velocity and meteorological conditions (fumigation, surface inversions). These processes must have similar effects on the S level at both sampling sites, and, at the same time, the local formation and generation of other particulate S species must be very limited. The other aerosol species measured are virtually all primary aerosol constituents. High correlation between the sampling sites was also obtained for Ga, As, Cs and Na (corr = 0.84) and for In, Al, Se, Sm (corr about 0.80). Most of them have also larger concentrations and/or crustal EFs at the urban

background than at the downtown. Interestingly, other elements (e.g., V, I and W) also having larger crustal EFs at the urban background than at the downtown, show insignificant correlation with a coefficient of about 0.50 or smaller. As to K, Na, Al and Sm, high correlations between the sampling sites for these elements were observed in the coarse size fraction as well, so the association between the sampling sites is not specific for the fine size fraction. Similarly, large correlation coefficients (about 0.80) were also derived for coarse Sc and La.

3.6. Chemical mass closure

The concentrations obtained by the chemical analyses were used for examining the extent of chemical mass closure, i.e., for assessing to what extent the gravimetrically measured particle mass could be reconstituted from the aerosol types (components) derived. For that purpose, the following aerosol types were considered: crustal matter, EC, ammonium sulphate, nitrate, lead/bromine and organic aerosol. The atmospheric concentration of the crustal matter was obtained as c(crustal matter) $= 1.16(1.90c(Al) + 2.15c(Si) + 1.41c(Ca) + 1.67c(Ti) + 2.09c(Fe))$, where $c(i)$ is the concentration of element i (Chan et al., 1997). It can be deduced from the comparison of mean S and sulphate concentrations that most of S (80–90%) is present as sulphate. For simplicity, $(NH_4)_2SO_4$ is assumed to be the main chemical form of the sulphate in the urban environments (Chan et al., 1997). Soluble nitrates were also included in the reconstituted aerosol mass, and are referred to as nitrate. The main source of Br and Pb were used to be leaded gasoline before 1999 (Salma et al., 2000), and, therefore, their total concentration referred as PbBr is utilised as indicator of the vehicular

emissions. Since the thermal method utilised for carbon analysis delivers the TC data in terms of mass of C, the data were multiplied by a factor of 1.4 typically used for the urban-type aerosol to convert the mass of C into the mass of the organic aerosol involving other (than C) atoms in the molecules as well (Turpin et al., 2000). Wood smoke is one of the other possible aerosol types. However, noncrustal K utilised generally as smoke indicator yielded negative values (as it is expected for low smoke activity sites) for the majority of the Nuclepore samples. Contribution of smoke to the PM was, therefore, considered to be negligible. Estimated amounts of the relevant aerosol types in the fine size fraction as average percentage of the mean particulate mass atmospheric concentration for the KFKI campus, Lágymányos campus, Széna Square and Castle District Tunnel are shown in Table 2. In addition to the aerosol types (or components) used for the chemical mass closure, contribution of some other components, i.e., of elements (from Na practically through U), BC and WSOC are also given in the lower part of the table for comparison. The gravimetric particulate mass for the four sampling sites is accounted for approximately 96%. 90%, 99% and 93% by the aerosol types (components) considered. The relative uncertainty of the mass fractions is estimated to be not more than 20%. The remaining unexplained part consists most likely of water and unaccounted species. However, considering that the gravimetric particulate mass was determined at 20–25% relative humidity, the water fraction is expected to be small. The major component at all sampling sites is the organic aerosol. Its contribution increases from the urban background to the tunnel, and it can be substantially more than half of the fine PM for the downtown sites and tunnel. Clearly, carbonaceous aerosols are now becoming equally or even more

Table 2
Average contribution of some aerosol types and other species in the fine size fraction as percentage of the mean gravimetric particulate mass atmospheric concentration for the KFKI campus, Lágymányos campus, Széna Square and Castle District Tunnel

Aerosol types or species	KFKI campus	Lágymányos campus	Széna Square	Castle District Tunnel
Crustal matter	7	5	7	5
Ammonium sulphate	33	24	19	2
Elemental carbon	8	4	6	12
Nitrate	6	3	6	<1
PbBr	<1	—	<1	—
Organic aerosol	43	54	61	74
Sum of the above	96	90	99	93
Elements (from Na through U)	14	11	10	2
Black carbon	9	11	23	25
Water-soluble organic carbon[a]	49	34	27	20

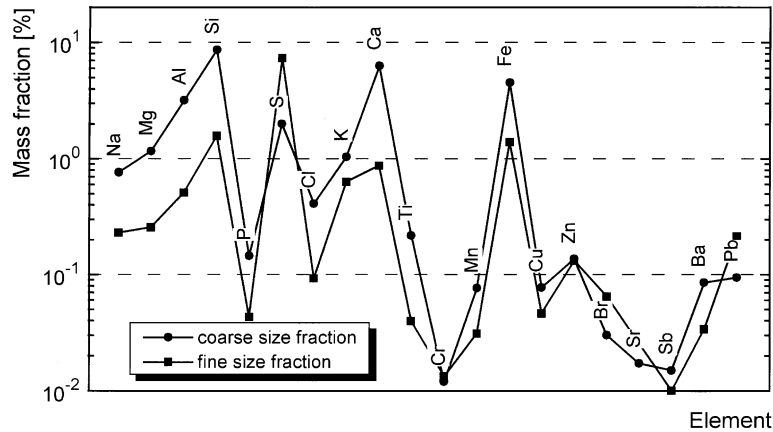[a] Expressed as percentage of the total carbonaceous fraction.

Fig. 5. Contribution of the median atmospheric concentrations of the elements to the median particulate mass in the coarse and fine size fractions for Széna Square (downtown). Data above 0.01% are only displayed.

important in industrialised countries than the inorganic species, e.g., the fine anthropogenic sulphate. In addition, nearly half of TC is water soluble on average in the urban background. This value is equal to that obtained for the continental background aerosol (Gelencsér et al., 2000). The mass fraction of WSOC, however, shows a decreasing tendency from the urban background to the tunnel. The second major component is ammonium sulphate (except for the tunnel), which contributes in a decreasing extent with increasing PM level. The crustal matter and EC constitute more or less equally, except for the tunnel where EC makes up approximately 12%. At the urban background, the concentrations of EC and BC are almost identical, at the other sites EC is always smaller than BC, as expected (Cachier, 1998). The difference between them increases with increasing aerosol mass concentration. Nitrate seems to be a minor component only. Contribution of PbBr is rather limited. All these also mean that the inorganic species dealt with in the present paper typically make up much less than half of the fine PM for the downtown sites and tunnel. As to the elements, contribution of their individual mass to the PM for the coarse and fine size fractions at one of the downtown sites as obtained from the means is displayed in Fig. 5. In both size fractions, only 20 elements contribute more than 0.01% to the PM. Of them, only a few species, i.e., coarse Si, Ca, Fe, Al, S, Mg and K, and fine S, Si and Fe constitute more than 1%.

For the coarse size fraction, less detailed information is available. Crustal matter accounts for approximately 20%, 30%, 53% and 67% of the PM for the urban background, two downtown sites and tunnel, respectively. Ammonium sulphate makes up 4–9% of the coarse PM at all sampling sites. Elements from Na practically through U contribute approximately 10%, 20–30% and 12% on average for the urban background,

downtown and tunnel, respectively. Black carbon makes up approximately 1%, 4% and 7% of the coarse PM for the same sampling sites, respectively.

4. Conclusions

During non-heating seasons, the atmospheric aerosol mass and most inorganic aerosol species are predominantly associated with coarse particles in the Budapest area. The downtown is on average approximately 3–4 times more polluted with coarse aerosol species than the urban background, but the concentration levels exhibit significant spatial and temporal variability. Most coarse-mode elements are attributable to soil erosion and (road) dust dispersion and resuspension processes. For the fine size fraction, several anthropogenic source types can be anticipated; some of them are located in or near the city centre, but there are a few fine aerosol species (S, K, As, V, Ni, Sc, ln, 1) that seem to be primarily transported from outside the city. The fine inorganic aerosol air pollution is spatially more uniform than the coarse one; on average, the whole downtown seems to be about 2 times more polluted than the urban background. The elemental mass size distributions of several typical anthropogenic elements exhibited very substantial differences between the various sampling sites. There was a clear tendency for the accumulation mode to be decreased and for the coarse mode to be increased with increasing aerosol mass concentration. With regard to the aerosol types, the inorganic components considered in the present paper make up less than half of the fine particulate matter at the downtown with ammonium sulphate being clearly the most abundant component of them. The organic aerosol is found to be the major aerosol component at all sampling sites, and its

contribution increases from the urban background to the downtown and road tunnel. In future work we will subject our data sets to receptor modelling and the results will also be related to air mass back trajectories and local meteorology.

Acknowledgements

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