Characteristics of Size-Fractionated Urban Aerosols and Trace Gases in Budapest[1]

Imre Salma,*,[2] Willy Maenhaut,† Éva Zemplén-Papp,‡ and János Bobvos§

*KFKI Atomic Energy Research Institute, PO Box 49, H-1525 Budapest, Hungary; †Institute for Nuclear Sciences, University of Gent, Proeftuinstraat 86, B-9000 Gent, Belgium; ‡Chemistry Section, Hungarian Academy of Sciences, PO Box 6, H-1361 Budapest, Hungary; and §Municipal Institute of State Public Health Officer Service, Váci út 174, H-1393 Budapest, Hungary

An air pollution study was conducted at two urban residential sites in Budapest from 9 April to 17 May 1996. Size-fractionated aerosol samples were simultaneously collected on a daily basis, and meteorological conditions were recorded at both sampling sites. Stacked filter units (SFUs) with an upper size inlet cutoff were used as sampling devices separating the urban aerosol into coarse [about 2- to 10-μm equivalent aerodynamic diameter (EAD)] and fine (<2 μm EAD) size fractions. In addition, atmospheric concentrations of some criteria pollutants, i.e., NO, NO$_2$, SO$_2$, CO, and total mass of the suspended particulate matter (TSP) were measured every half-hour at one of the sampling sites with commercial equipment. The SFU filters were weighed and analyzed by a light reflectance technique, particle-induced X-ray emission analysis, and instrumental neutron activation analysis. Atmospheric concentrations for 31 aerosol species have been obtained so far. The analytical results were used to characterize the levels and the multielemental composition of the urban aerosol at both sampling sites and for both size fractions, to investigate the atmospheric concentrations and diurnal variation of the criteria pollutants, and to compare the time trends of aerosols and trace gases. The present paper reports on the status of the air pollution study and gives a discussion of the results. © 1998 Academic Press

Key Words: size-fractionated urban aerosol; trace gases; criteria pollutants; particle-induced X-ray emission analysis; aerosol characteristics; air quality; Budapest.

INTRODUCTION

Budapest, with 1.89 million inhabitants, is the largest city of Hungary (*1*). There are several air pollution sources in the urban area including different industrial emissions, transportation, and domestic activities. So far, most of the monitoring of emissions, concentrations, and effects of air pollution has been directed toward the criteria pollutants, e.g., NO, NO$_2$, SO$_2$, CO, tropospheric O$_3$, and the suspended particulate matter (TSP). Figure 1 shows the trends in annual mean atmospheric concentration for NO$_2$, SO$_2$, CO, and TSP averaged over the data measured by eight automated monitor stations of the Municipal Institute of State Public Health Officer Service (ÁNTSz FI) located throughout Budapest for the last decade (*2*). Atmospheric concentrations of NO$_2$ and TSP increased by factors of about 3 and 2, respectively, between 1989 and 1991, whereas concentrations of SO$_2$ and CO generally showed a tendency to decrease and, during the period mentioned, decreased by factors of 2 and 1.7, respectively. As

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[2] To whom correspondence should be addressed. E-mail: salma@sunserv.kfki.hu. Fax: +36 1 395–92–93.
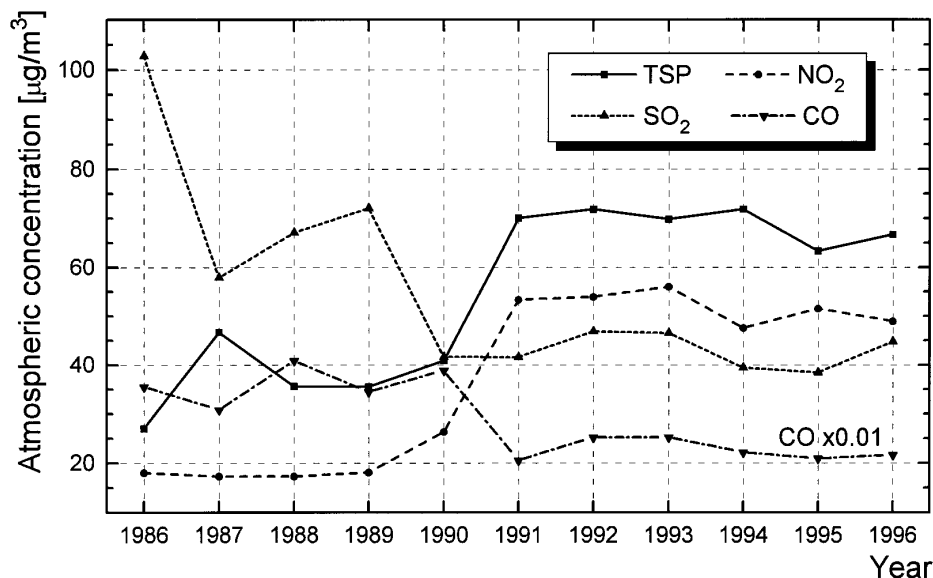
FIG. 1. Annual mean atmospheric concentrations of NO_2, SO_2, CO, and TSP as average of the data measured by eight automated monitor stations of ÁNTSz FI throughout Budapest for the period 1986 through 1996.

has already been realized (*3*), it is the elevated levels of airborne particles that are mainly responsible for the increased health risks of inhabitants in large cities. Although aerosol particles are already included in the regulatory work in Budapest, they are usually treated regardless of their size and are characterized by measuring their total mass. However, the ecological impact, health effects, as well as biogeochemical or other behavior of the aerosols are determined mainly by both their chemical composition and their size distribution. The mass size distribution of the atmospheric aerosol particles is generally multimodal (*4*). However, two separate and essentially independent size classes, a coarse mode and a fine mode, can clearly be distinguished in most aerosols. These two fractions differ strongly from each other in terms of sources and, consequently, in chemical composition and physical properties. The cutoff value of the equivalent aerodynamic diameter (EAD) dividing the two size fractions is about 2 μm. Therefore, collection and characterization of (at least) two different and well-defined size fractions are highly desirable in contemporary aerosol studies.

The elemental composition of the total atmospheric aerosols and the concentrations of S and N compounds at different receptor sites in Budapest and at regional background stations in Hungary have been studied (*5, 6*). To further improve our knowledge of the air pollution in Budapest, size-fractionated aerosol sampling was performed at two urban residential sites, and was complemented with simultaneous measurements of some criteria pollutants. The goals of the study are to characterize the atmospheric levels, multielemental composition, and time trends of the urban aerosol in separate fine and coarse size fractions; to investigate the atmospheric levels, diurnal variation, and time trends of criteria pollutants; and to compare these characteristics. Identifica-

tion of the major sources of aerosol fractions and trace gases and assessment of the relative contributions of these sources will eventually be accomplished by multivariate receptor modeling.

SAMPLE COLLECTION

The size-fractionated aerosol samples were collected with Gent-type stacked filter units (SFUs) (7). The SFU contains a preimpaction stage and two 47-mm-diameter Nuclepore polycarbonate filters with pore sizes of 8 μm (Apiezon-coated) and 0.4 μm, placed in series. At a flow rate of 15–16 liters/min, the preimpaction stage intercepts particles larger than about 10-μm EAD, and the first filter of 8-μm pore size has a 50% collection efficiency at about 2-μm EAD. Consequently, the aerosol particles are separated into coarse (about 10- to 2-μm EAD) and fine ($<$2-μm EAD) size fractions. Atmospheric concentrations of some criteria pollutants were measured with commercial equipment, i.e., Monitor Labs (ML) Models 8830 (IR absorption spectrometry for CO), 8841 (chemiluminescent analyzer for NO and for NO_2 with Molycon converter), 8850S (UV fluorescent analyzer for SO_2), 8810 (UV photometry for O_3), and FH62IN (β absorption on glass-fiber paper for the TSP). The sampling flow rate for the ML instruments was 0.5 liters/min, except for the TSP measurement where it was set to 1 m³/h. Relative uncertainty of the atmospheric concentrations obtained with the commercial equipment was estimated to be less than 10%.

The collection and measurement were conducted from 9 April until 17 May 1996. One of the two sampling locations was chosen downtown in a small park at Széna Square [latitude 47°30.6′ N, longitude 19°1.8′ E, altitude 115 m above sea level (as1)] at an automated monitor station of the Municipal Institute of State Public Health Officer Service. This site is affected by heavy traffic nearby. The SFU sampler was set up on the roof of the monitor station with its intake facing down at 4.5 m above the ground. Daily aerosol samples were taken with planned and regular interruptions. The starting time was typically about 7:30 in the morning, and the mean sampled volume was 18.6 m³. Besides the size-fractionated aerosol samples, atmospheric concentrations of NO, NO_2, SO_2, CO, and TSP and temperature, pressure, humidity, and wind speed and direction were measured and recorded every half-hour. Concentration of O_3, which is used in the present work for illustrative purposes only (see later and Fig. 3), was recorded not at Széna Square, but at another location with generally higher NO and NO_2 concentrations and similar diurnal variation and temporal characteristics. Median values for daily temperature, pressure, and humidity during the sampling were 18.9°C, 1003 hPa, and 68%, respectively. The weather was slowly warming with occasional rain showers during the sampling period. The prevailing wind direction in Budapest is northwest. The second sampling site was located 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 asl). Here, the SFU sampler was set up about 1.8 m above the ground. The starting time of collections at KFKI was typically about 6:30 in the morning, and the mean sampled volume was 21.9 m³. Local temperature and pressure data were also obtained as daily averages. A total of 33 samples and 4 field blanks were collected at each sampling site, and are stored in plastic Petri slide dishes. The field blanks are samples that were collected

by doing all the same manipulations and operations as for real samples, including even drawing air through them for about 1 min.

ANALYTICAL METHODS

The SFU filters were weighed using a microbalance to obtain the particulate mass (PM), and were analyzed by a light reflectance technique for black carbon (BC) (8).

A quarter section of each SFU filter was analyzed by particle-induced X-ray emission analysis (PIXE) at the University of Gent in Belgium. Particulars concerning the experimental setup and the analytical procedure for PIXE analysis of the SFU samples have already been described (9, 10). The filters were investigated by bombardment with a beam of protons of 2.4-MeV energy in a vacuum chamber. The beam area and beam current were 0.54 cm^2 and about 150 nA, respectively. The X-ray spectra were measured with a composite filter in front of the Si(Li) detector, and were typically accumulated for a preset charge of 60 μC. The spectra were fitted for 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 (in the fine fraction only), Br, Rb, Sr, Y (in the fine fraction only), Zr, Mo, Ba, Pb] with the computer program AXIL-84 (11). Elemental amounts were derived by using experimental calibration factors and field blank values, and, finally, atmospheric concentrations (in ng/m^3) were calculated. So far, no corrections for volatile (fine) particle loss or particle size effect were applied.

One-half of each SFU filter containing about 300 μg of particulate matter was pressed into a pellet with a diameter of 7 mm, and has been analyzed by instrumental neutron activation analysis (INAA). The methodology of INAA consists of two main
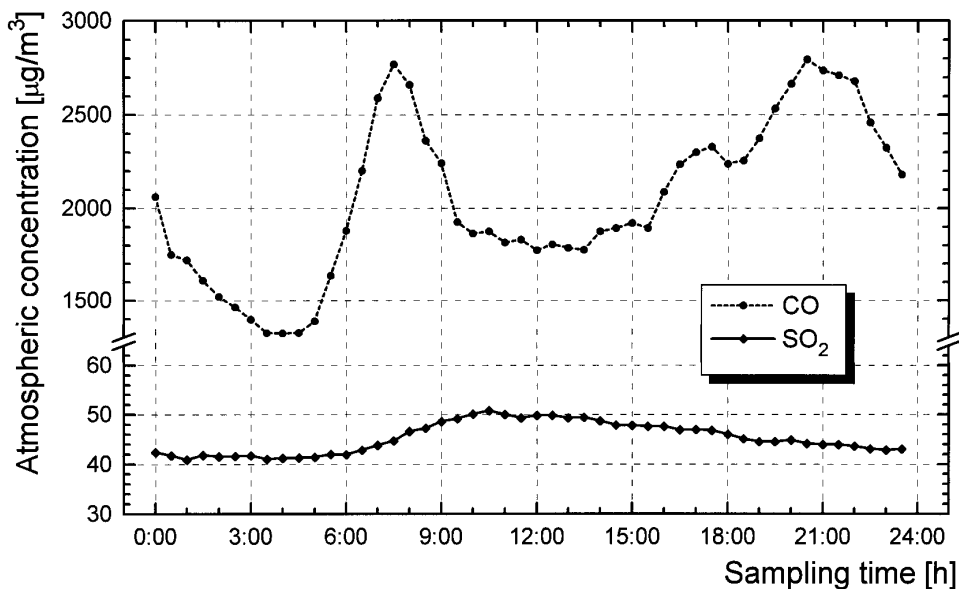

FIG. 2. Diurnal variation of the atmospheric concentrations of CO and SO$_2$ at Széna Square averaged over the sampling period 10 April to 17 May 1996 (38 days).

parts: a short- and a long-time irradiation with two consecutive γ spectrometric measurements after each. The short-time activation and measurements of all samples were completed, while the long-time activation and measurements of the series of the same pellets are in progress. Hence, the elemental amounts determined from these four measurements can only be combined later, and, therefore, this article focuses on the analytical results obtained by PIXE as far as the aerosol is concerned. (One-quarter of each filter was retained as a spare portion, and for possible analysis by further techniques.)

RESULTS AND DISCUSSION

Diurnal variations of the atmospheric concentrations of CO and SO_2, of NO, NO_2, and tropospheric O_3, and of TSP are presented in Figs. 2–4, respectively. The data points indicate half-hour concentration values averaged over the whole sampling period, i.e., from 10 April to 17 May (over 38 days). The diurnal variation of CO reflects typical city driving patterns. The concentration exhibits one maximum during the morning rush hours at about 7:30, and two maxima, a smaller maximum at about 17:00 and another broad one at about 20:00, in the evening. SO_2 data are rather constant, showing a slight elevation only at about 11:00. The data in Fig. 3 can be explained in terms of the simplified atmospheric nitrogen dioxide photolytic cycle (*12*). Concentration of NO rises as early-morning traffic emits its load of NO; it is soon oxidized to NO_2 leading to decreased concentrations of NO (a pronounced peak appears at 7:00) and to increased concentrations of NO_2. As the sun's intensity increases in the morning, atmospheric photochemical reactions take place, including
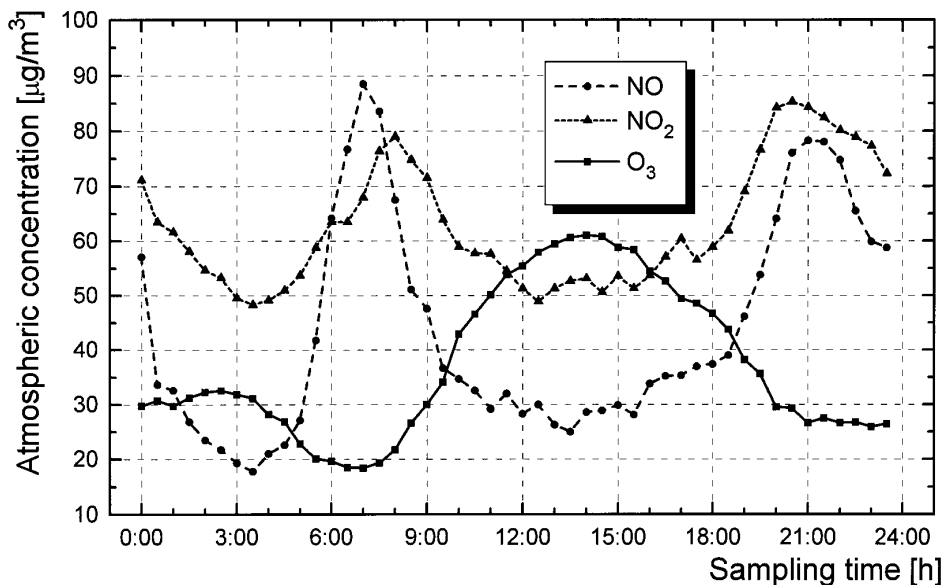

FIG. 3. Diurnal variation of the atmospheric concentrations of NO and NO_2 at Széna Square and O_3 averaged over the sampling period 10 April to 17 May 1996 (38 days).

photolysis of NO_2 and formation of O_3; thus, the concentration of NO_2 begins to drop (resulting in a peak at 8:00) while the concentration of O_3 rises. Ozone then can convert NO to NO_2, and it is so effective in this reaction that as long as O_3 is present, the NO concentration does not rise throughout the rest of the daylight even though there may be new NO emissions (*12*). In the evening, the cycle reverses. Figure 4 shows that concentration of TSP increases rapidly in the morning from about 5:30, reaches a value of about 100 $\mu g/m^3$ at 7:30, and remains at that level with small variations until late evening when it starts to decrease. Half-hour concentration data of TSP and CO averaged separately over the workdays (28 days) and holidays (10 days) within the sampling period are shown in Figs. 5 and 6, respectively. It can be seen that TSP values for workdays and holidays are quite similar during the night from 23:30 until about 4:00. For workdays, the concentration starts to increase 1.5 h earlier (at about 5:00) than for holidays, and reaches significantly higher values. In contrast, from 20:00 until 23:00, TSP data are much higher on holidays than on workdays. The trace gases (except for SO_2) exhibit differences between workdays and holidays similar to those for TSP, as illustrated by CO in Fig. 6. In addition to these differences, in the case of CO, the first peak in the afternoon that is present on workdays is absent on holidays. Ratios of the daily average of the half-hour concentration data averaged over the workdays to that over the holidays for NO, NO_2, SO_2, CO, and TSP are 1.4, 1.2, 1.0, 1.1, and 1.3, respectively. The ratio for CO is surprisingly close to 1, which can be explained by the huge peak in late evening on holidays (see Fig. 6). Summarizing, in the late evening from about 20:00 until 23:30 the air pollution at Széna Square is more serious during the weekends than during the workdays. Most
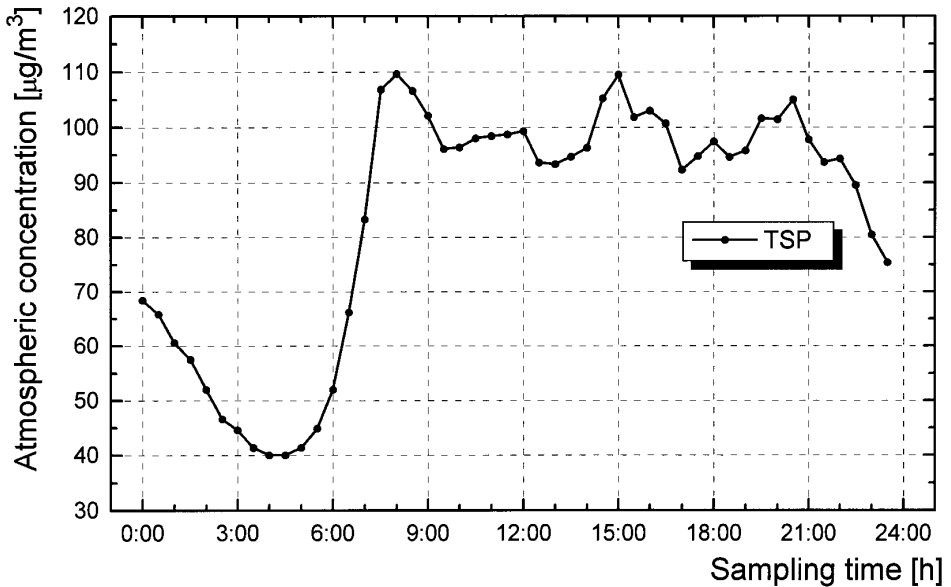

FIG. 4. Diurnal variation of the atmospheric concentration of TSP at Széna Square averaged over the sampling period 10 April to 17 May 1996 (38 days).
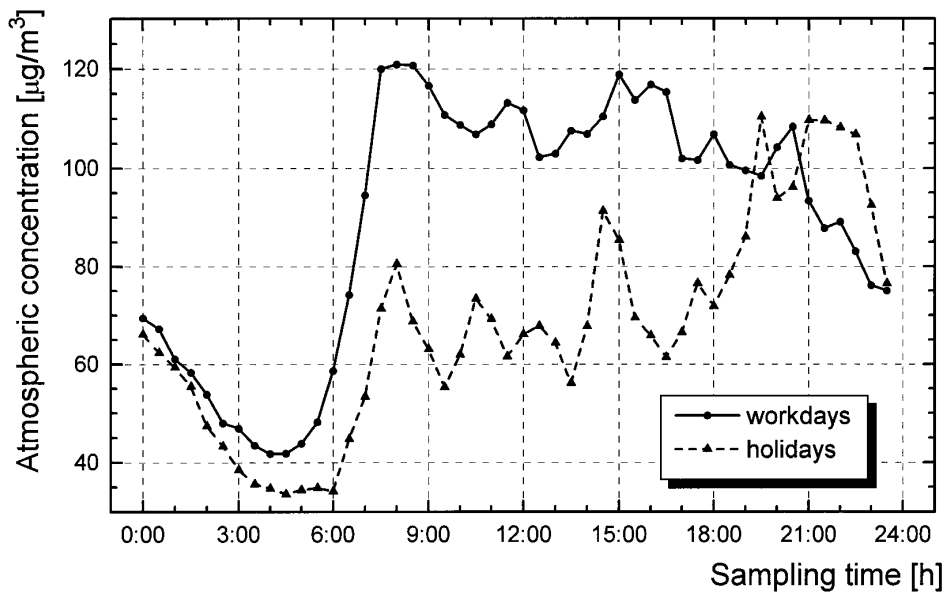
FIG. 5. Diurnal variation of the atmospheric concentration of TSP at Széna Square averaged separately over the workdays (28 days) and holidays (10 days).
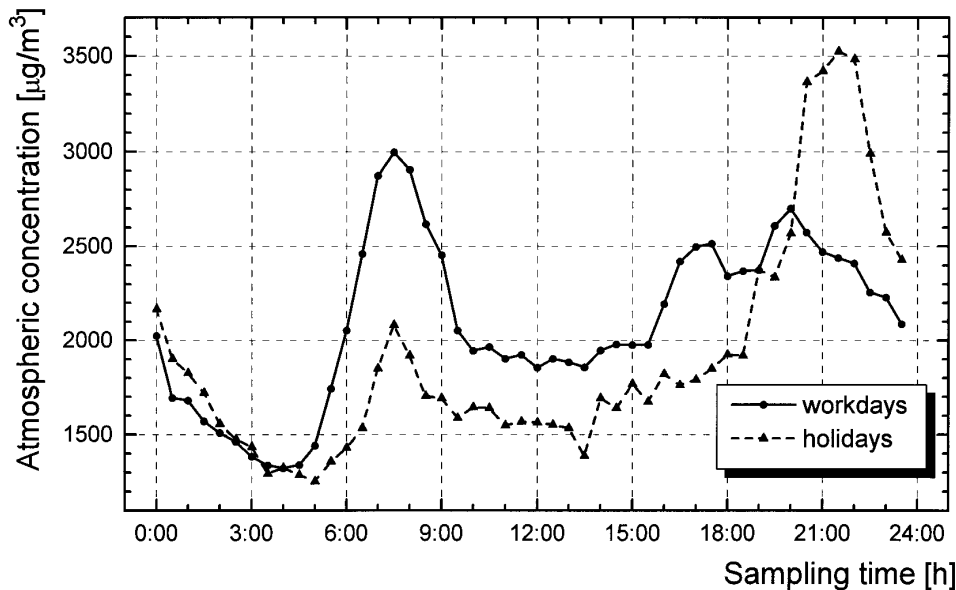

FIG. 6. Diurnal variation of the atmospheric concentration of CO at Széna Square averaged separately over the workdays (28 days) and holidays (10 days).

likely, it is related to vehicle circulation. Many people return in their cars from weekend houses and vacation to Budapest on holidays in the evening hours passing through the city center.

The daily average atmospheric concentrations for the measured criteria pollutants as a function of the sampling date (time trends over the sampling period) are presented in Fig. 7. Again, the concentration data for SO_2 are quite constant, while the other pollutants exhibit more variation. For these pollutants, a good correlation between the time trends can be found, indicating their possible common sources and, to some extent, the effect of the local meteorology. The median atmospheric concentrations for NO, NO_2, SO_2, CO, and TSP over the sampling period are 43, 62, 45 $\mu g/m^3$, 1.98 mg/m^3 and 81 $\mu g/m^3$, respectively.

The median atmospheric concentrations for 31 aerosol species in the coarse and fine aerosol fractions at Széna Square and KFKI campus are shown in Table 1. In the coarse fraction, all median concentration data for KFKI campus are lower than at Széna Square, and they differ by a typical factor of about 3–4. For a few species, i.e., Cu, Ge, Br, Ba, and Pb, the difference is about one order of magnitude, suggesting that in or near the city center, there may be an essential source for these elements. In the fine fraction, the concentration data for KFKI campus are also generally lower than at Széna Square, but the difference is much smaller; the downtown-to-suburban ratio is typically about 2. In some cases, i.e., for PM, S, K, V, Ni, As, and Se, the concentrations are almost equal to or higher at KFKI campus than at Széna Square. The similarities and differences in aerosol composition of the two sites are illustrated in Fig. 8, which shows median crustal rock enrichment factors (EFs), calculated
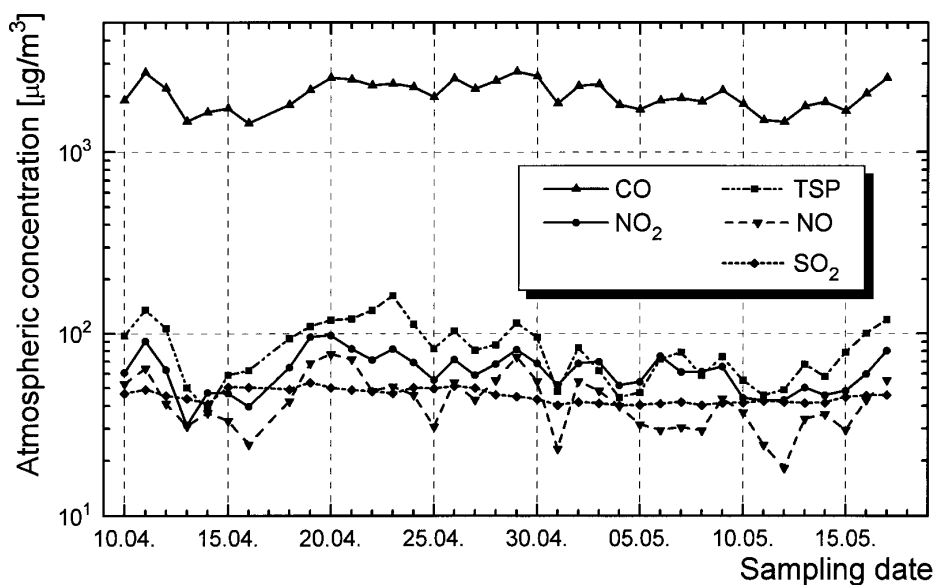

FIG. 7. Atmospheric concentrations as a function of sampling date (time trends) for NO, NO_2, SO_2, CO, and TSP at Széna Square from 10 April to 17 May 1996.

TABLE 1
Median Atmospheric Composition of the Coarse and Fine Aerosol Fractions (in ng/m^3)
at Széna Square and KFKI Campus

Aerosol species	Coarse size fraction		Fine size fraction	
	Széna Square	KFKI campus	Széna Square	KFKI campus
PM	41×10^3	20×10^3	24×10^3	17×10^3
BC	2100	300	7400	1780
Na	220	86	184	118
Mg	260	77	40	21
Al	850	250	97	68
Si	3300	790	340	210
P	53	22	5.6	0.72
S	760	210	1560	1600
Cl	120	32	13.3	9.2
K	380	120	134	126
Ca	2400	490	190	90
Ti	83	21	8.4	5.2
V	2.1	0.44	1.03	0.92
Cr	4.5	0.99	1.76	0.46
Mn	28	5.6	6.3	3.5
Fe	1700	240	300	87
Ni	2.1	0.48	0.79	0.67
Cu	29	1.54	9.8	1.81
Zn	50	8.2	29	17.4
Ga	1.45	0.26	0.20	0.11
Ge	0.74	0.04	0.09	0.04
As	1.42	0.54	0.43	0.96
Se	—	—	0.40	0.36
Br	9.3	0.84	8.3	2.3
Rb	1.23	0.48	0.38	0.26
Sr	6.4	1.60	0.90	0.36
Y	—	—	0.45	0.115
Zr	2.9	0.70	0.58	0.25
Mo	0.52	0.134	0.49	0.25
Ba	20	0.46	4.2	UL[a]
Pb	35	3.7	46	14.8

[a] Upper limit (26 upper limits in the set of 33 concentration data).

relative to Mason's average crustal rock (*13*) with Al as reference element. Most elements in the coarse fraction have EFs close to 1, suggesting that they are attributable mainly to soil (and road) dust dispersal and resuspension. (The small median EF for coarse Ba at KFKI campus can be explained by having 13 upper limits [detection limit (*14*)] in the concentration data. The mean EF for Ba is 1.27. Note that upper limit values were set equal to zero when calculating medians, but were left out when calculating means.) Nevertheless, some elements, i.e., S, Cl, Cu, Zn, As, Br, Mo, and Pb are significantly enriched. The same elements and Se exhibit large (10^2–10^4) EFs in the fine fraction, indicating their possible anthropogenic origin. For several elements, i.e., S, K, V, Ni, As, Se, and Rb, the fine fraction EFs are higher at KFKI campus
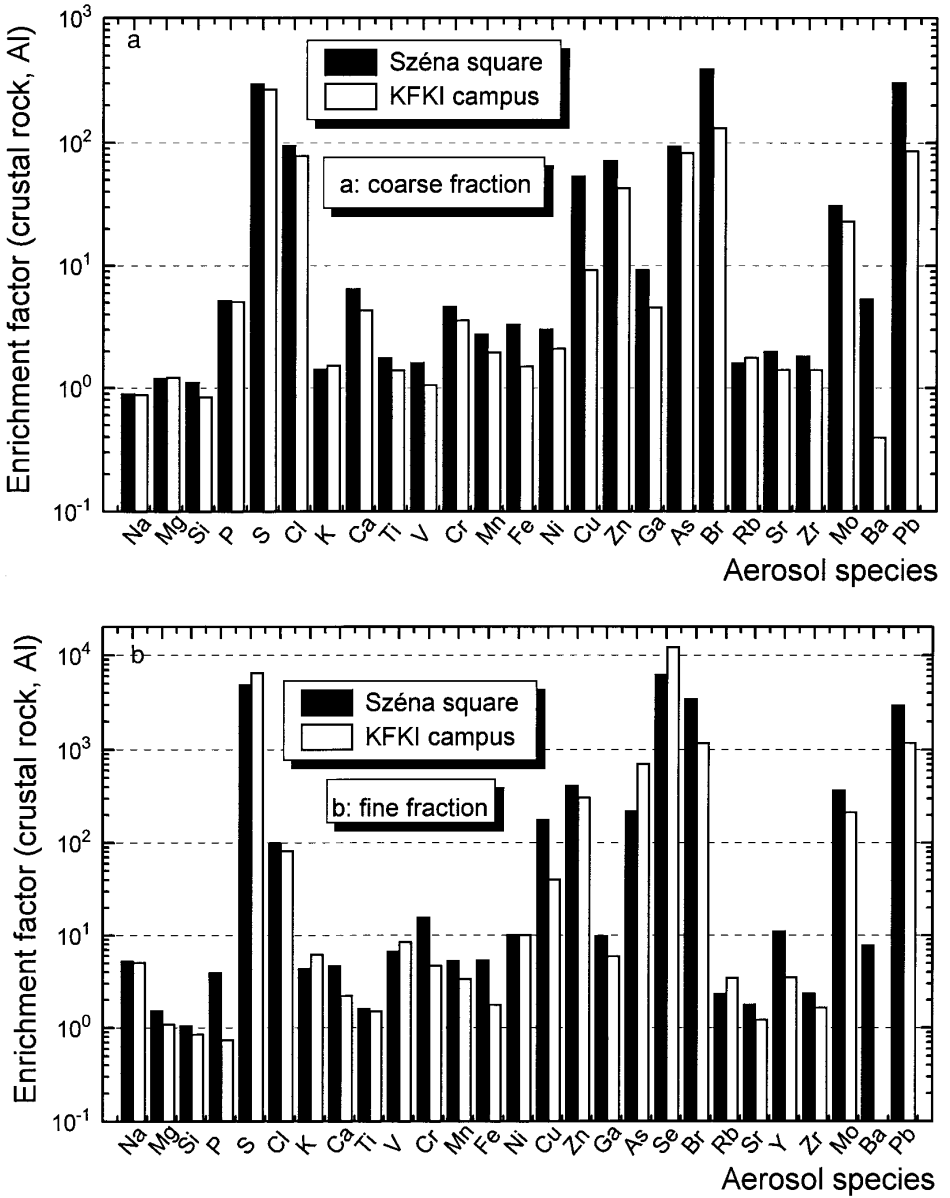
FIG. 8. Median crustal enrichment factors, calculated relative to Mason's crustal rock with Al as reference element, in the coarse (a) and fine (b) aerosol size fractions at Széna Square and KFKI campus.

than at Széna Square. But this is due to the fact that the concentration differences between the two sites are larger for Al (and the other crustal elements) than they are for the typical pollutant elements. The mean fine-to-coarse concentration ratios (F/C ratios) for both sampling sites are displayed in Fig. 9. The F/C ratios for Széna Square
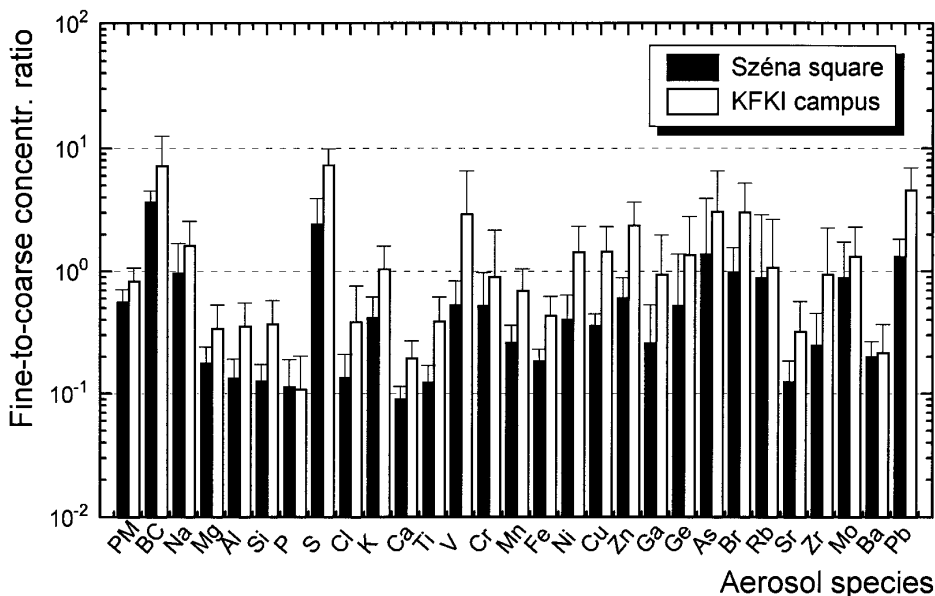
FIG. 9. Mean fine-to-coarse concentration ratios for 29 aerosol species at Széna Square and KFKI campus. Error bars indicate one standard deviation.

are typically below 1 (except for BC, S, As, and Pb), showing that the elements are present predominantly in the coarse aerosol fraction. For typical crustal elements such as Al, Si, Ca, Ti, Mn, Fe, and Sr, the F/C ratio is about 0.1. The F/C ratios for KFKI campus are larger than those for Széna Square (except for P, for which the two ratios are almost equal), and for many species, including BC, Na, S, K, V, Ni, Cu, Zn, Ge, As, Br, Rb, Mo, and Pb, the F/C ratio is even above 1. These elements are present mainly in smaller aerosol particles. Most likely, the differences in F/C ratios are due to the 309-m difference in altitude between the two sampling sites, to the wooded suburban character of the KFKI campus, and to the shorter atmospheric residence times of the coarse particles.

Figure 10 displays time trends for some typical crustal elements (i.e., Al, Si, Ca, Ti, Mn, and Fe) at Széna Square (a) and at KFKI campus (b). It is evident that the individual time trends show significant fluctuation with time. At each of the two sampling sites, the elements depicted appear highly correlated with each other, suggesting that a single dominant crustal component can be expected in multivariate receptor modeling. In contrast, when comparing the time trends from the two sites with each other, there seems to be little relationship between the crustal element data from both locations. Nevertheless, during certain periods, e.g., from 10 to 20 April, some correlation can be found. (Interestingly, unusually cold weather was observed after 10 April, which became milder with stormy winds after 15 April only, and a real, warm spring arrived after 20 April.) Time trends for Br, Pb, BC, and CO in the fine fraction (markers for internal combustion engine emissions) for Széna Square are shown in Fig. 11. As can be seen, there is quite a good correlation between Br, Pb,
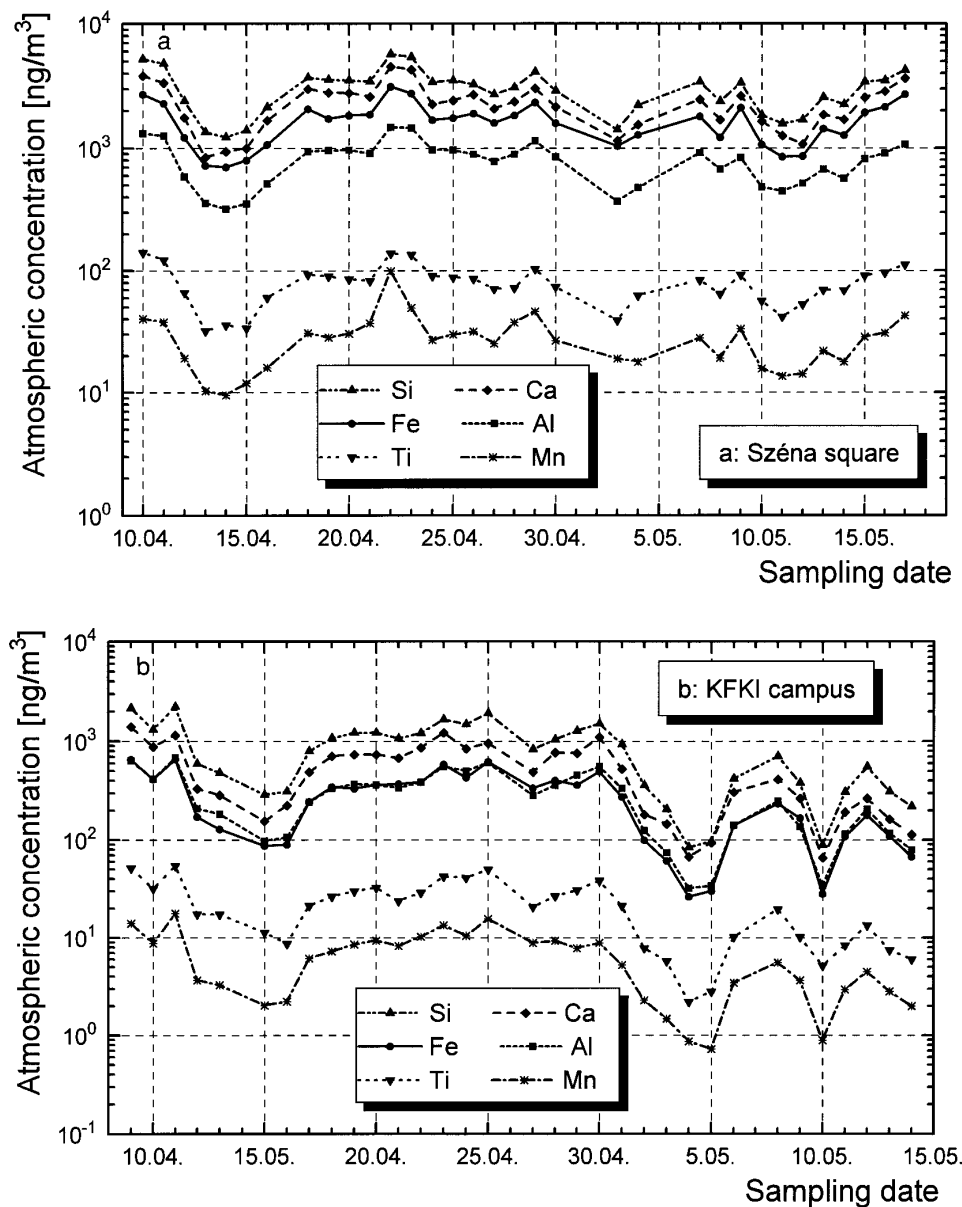
FIG. 10. Time trends for Al, Si, Ca, Ti, Mn, and Fe in the coarse aerosol size fraction at Széna Square (a) and KFKI campus (b).

and BC, but CO exhibits a somewhat different pattern than the three aerosol species. This might mean that there is another meaningful source of CO emissions besides transportation. The correlation coefficients between Br and Pb in the fine size fraction are 0.77 ($N = 33$) and 0.73 ($N = 33$) at Széna Square and KFKI campus, respectively,
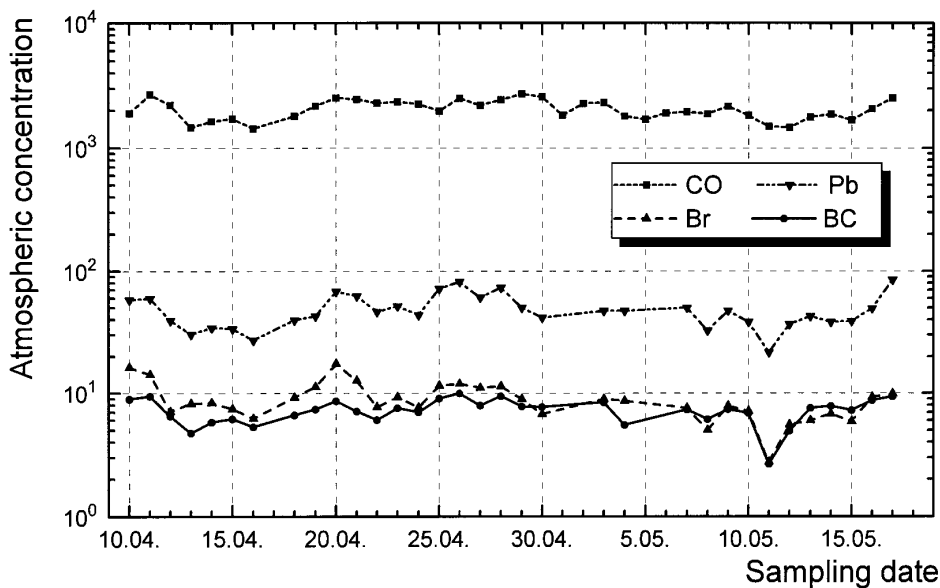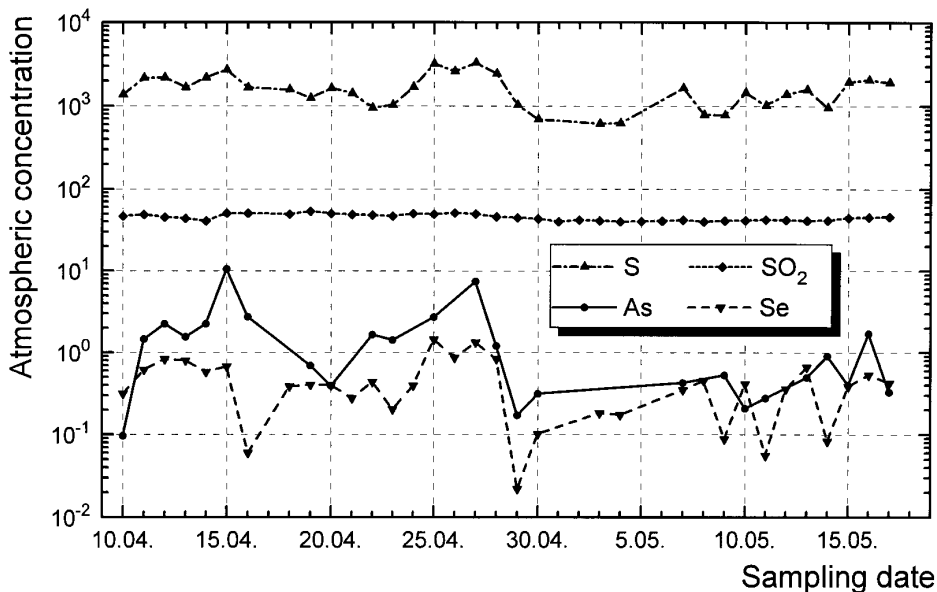
FIG. 11. Time trends for Br, Pb, and black carbon (BC) in the fine aerosol size fraction and for CO at Széna Square. (The concentration units are $\mu g/m^3$ for BC and CO and ng/m^3 for Br and Pb.)

while the mean fine Br/Pb concentration ratios (calculated on a sample-by-sample basis) are 0.19 ± 0.04 and 0.18 ± 0.07. Figure 12 presents time trends at Széna Square for species that are related to fossil fuel combustion. S, As, and Se exhibit significant fluctuation with time and tend to correlate with each other, but SO_2 shows completely discrepant behavior. Moreover, both the diurnal variability (cf. Fig. 2) and time trend fluctuation for SO_2 during the sampling period (cf. Fig. 7) are quite small, which seems to indicate that its dominant sources are more widespread and/or at a greater distance. The average annual variation of SO_2 in Budapest (and at the regional stations too) is, however, significant, and shows a minimum in summer. In 1980, the mean downtown atmospheric concentration for SO_2 in Budapest (though at different sites than in the present paper) over a long period was 147 $\mu g/m^3$, and the downtown-to-suburban concentration ratio was 2.3 (6). It was also concluded that there were correlations between the average SO_2 concentrations at different regional stations in Hungary. Similarly, in the present work, the fine fraction S data at Széna Square and at KFKI campus were highly correlated (with a correlation coefficient of 0.88, $N = 27$). In contrast, for the other aerosol species the correlation between the two sampling sites was weak or not significant. The high correlation for fine aerosol S has to be attributed to the fact that this species is a secondary aerosol constituent that is formed from a fairly constant pool of precursor SO_2 gas; its concentration in the Budapest area is essentially controlled by the gas-to-particle conversion rate, the fine sulfate deposition velocity, and meteorological conditions (fumigation, surface inversions). The other aerosol species measured are virtually all primary aerosol constituents. The lack of correlation for these species between two sites indicates that their sources are

FIG. 12. Time trends for S, As, and Se in the fine aerosol size fraction and for SO$_2$ at Széna Square. (The concentration units are μg/m^3 for SO$_2$ and ng/m^3 for the other species.)

local and that these sources exhibit different and variable intensity near each of the two sites. This is definitely the case for the coarse crustal aerosol component, but probably also for most of the typical anthropogenic elements. As a result, the spatial variability of the urban (aerosol) air pollution is considerable.

The crustal EFs and the differences in time trends for the various aerosol species suggest that several natural and anthropogenic components (dominant source types) can be anticipated in the coarse and fine fraction data sets, and that the urban aerosol in Budapest is a mixture of locally generated and transported aerosols. Identification of the various source types and assessment of their contribution to urban air pollution will be performed by multivariate receptor modeling after all INAA measurements are completed and the PIXE and INAA results have been combined into a final analytical data set. The relationships between the aerosol source types and the atmospheric trace gases and various meteorological parameters will then also be examined.

ACKNOWLEDGMENTS

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