

Changes in elemental composition and mass of atmospheric aerosol pollution between 1996 and 2002 in a Central European city

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Received 14 September 2005; received in revised form 10 November 2005; accepted 29 November 2005

Non-exhaust traffic emission particles and coarse-mode particles are increasing in Budapest, Hungary.

Abstract

Median atmospheric concentrations of Pb, Br, S, As, Se, and particulate matter (PM) decreased, and median concentrations of Sb, Cu, Zn, Fe, Ca, Cr and Ba increased in urban aerosol in downtown Budapest between 1996 and 2002. The changes in Pb and Br concentrations were unambiguously attributed to the phasing out of leaded gasoline. The increments were mainly related to and explained by non-exhaust vehicular emissions. The mechanical wear of asbestos-free brake linings of road vehicles contributed to the concentration of Cu and Sb on average by 69% and 66%, respectively in the PM₁₀ size fraction. Tire rubber abrasion was a major source for atmospheric Zn; on average, non-crustal sources accounted for 67% of Zn in the PM₁₀ size fraction. Contribution of the tire wear component to the PM₁₀ mass was estimated to be 6% at most, while its contribution to organic aerosol was of the order of 15%.

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Keywords: Urban aerosol; Road traffic; Non-exhaust vehicle emissions; Brake wear; Tire rubber wear

1. Introduction

Several Central and Eastern European countries changed their economy and political system in the beginning of the 1990s. In the period of transition, the economic productivity decreased (which also meant that emissions from industrial plants were usually reduced), and society experienced, quite suddenly, the achievements of the free market economy. In addition to the industrial recession, the structure of the economy changed; services and trade sector gained over heavy and chemical industry, some contemporary industrial and domestic (heating) technologies were adopted on a large scale, and the number of road vehicles and traffic densities increased. For instance, the number of passenger cars (including jeeps and microbuses) registered in Budapest combined with Pest

County, Hungary was about 800,000 in 1996 and 918,000 in 2002. Diesel-powered vehicles shared 8.5% of the national passenger car fleet in 1996, and 11.2% in 2002; the mean lifetime of passenger cars registered in Budapest was 10.6 years in 1996, and 9.6 years in 2002 (GKM, 1997, 2003). The changes affected the air quality—in particular in cities where road traffic belongs to the main emission sources of particulate matter (PM). Aerosol particles are emitted directly from the incomplete combustion of fossil fuel and from friction acting on individual components (mainly on brakes and tire rubber), or are produced indirectly through chemical reactions. The principal aerosol components emitted by unleaded gasoline and diesel-fueled vehicles are organic carbon (OC) and elemental carbon (EC). Abundances of sulfates and nitrates are also significant (up to several percents by mass); concentration of other elements in the exhaust aerosol is quite small (most being <1% by mass; US EPA, 2004). Relative abundance of the components varies with individual fuel type and exact composition (including lubricants and additives), as well as

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with details of combustion conditions and exhaust treatment (catalytic conversion). The wear rate of brake linings was estimated typically to be around 15 mg per vehicle-kilometer for passenger cars, while it increases for light- and heavy-duty vehicles to about 30 and 40 mg/km, respectively (Legret and Pagotto, 1999; Garg et al., 2000, and references cited therein). There is a large variety of compositions on the market consisting of four main components: fibers (semi-metallic, mineral, ceramic or aramid), binders/resins (modified phenol-formaldehyde), fillers (barium sulfate, antimony sulfide, metal oxides and alloys) and friction modifiers (graphite). Some fillers fulfill functions other than just occupying the space, e.g., heat conductivity or lubrication. On average, brake linings in use can contain about 25–30% K_2TiO_3 , 15–20% $BaSO_4$, 2–7% $Ca(OH)_2$, 5–10% graphite, 8–15% Cu, 2–7% Sb_2S_3 , 0.7–2.3% ZnO and ZrO_2 , 0.4–2% Pb in addition to bulk Fe, Si compounds, and organics (Hildemann et al., 1991; Dietl et al., 1997; Legret and Pagotto, 1999; Garg et al., 2000; Westerlund, 2001; Lough et al., 2005). Laboratory studies suggest that only about 30% by mass of the wear products is airborne, of which about 86% is contained in the PM10 size fraction (Garg et al., 2000). Wear products can accumulate on the wheel rims during braking and are thought to be emitted later from them, resulting in more-or-less steady and diffuse emission rates (Sternbeck et al., 2002). It was also recognized that the braking process produces temperatures at the lining/rotor interface to be high enough to melt and decompose many of the brake lining materials, which appear after condensation in the fine size fraction, and that the fibers present in the linings as fortifying components are usually decomposed during braking into non-fibrous material (Garg et al., 2000). As far as the tire tread wear is concerned, its rate is reported usually in the range of 10^1 – 10^2 mg/km per single vehicle for passenger cars and light-duty vehicles, while it is up to 10^3 mg/km for heavy-duty vehicles and buses (Pierson and Brachaczek, 1983; Rogge et al., 1993; Legret and Pagotto, 1999; Warner et al., 2002; and references cited therein). The broad interval can be explained by differences in tire and car construction, road surface properties, driving conditions, vehicle load, steering and traction wheels. The wear products are mainly emitted to the air as coarse particles since they are generated by rolling shear of the tire tread against the road surface (Lough et al., 2005; Kupiainen et al., 2005). Tire rubbers contain about 58% organics (polymers and high aromatics), 29% soot (e.g., carbon black) and 13% of inorganic material, mainly Zn, Ca, S, Fe, Al, Ti, K, Pb and Mg (Hildemann et al., 1991; Rogge et al., 1993; Legret and Pagotto, 1999). Zinc occurs in tire rubber of road vehicles typically in an amount of 1–3%, and it has often been used as marker element for tire wear (Pacyna, 1986; Rogge et al., 1993). Unfortunately, no other element than Zn is supplied into the ambient air in a major quantity by this component.

The criteria pollutants in the ambient air have been monitored in Budapest since the end of 1970s by national regulatory bodies. Regarding PM, it is the total suspended particulates that used to be monitored until about the middle of 2002 when the PM10 monitoring conception, regulation and

legislation of the European Union were adopted. Nevertheless, some research studies—performed systematically in intensive field campaigns during the spring since 1996—yielded more adequate data sets, i.e., concentrations and composition for size-resolved PM. The size fractions characterized included both PM10–2.0 and PM2.0 (occasionally PM2.5) size fractions for several downtown and urban background sites. The data sets available contain atmospheric concentrations for PM, elements (from Na to U), main ions (sulfate, nitrate and ammonium), black carbon (BC), occasionally OC and EC for the size fractions mentioned, infrequently concentrations for criteria gas pollutants (NO , NO_x , CO , SO_2 , and O_3), mass size distributions for PM and elements in the aerodynamic diameter (AD) range of about 0.05 to 10 μm , basic meteorological parameters, and sporadically vehicle circulation records. Since some of the sampling devices and methods used, as well as some of the analytical methods applied over the years have remained unchanged, the part of the comprehensive sets that was derived from them can be used for comparison purposes.

The objectives of the present paper are to investigate particulate air pollution in Budapest as representative of a Central European city within/after the transition, specifically to evaluate the changes in elemental composition and mass of the atmospheric aerosol in the downtown in the PM10–2.0 (coarse) and PM2.0 (fine) size fractions between 1996 and 2002, to explore the local variations in particulate air pollution, to identify the main sources of the constituents whose concentrations changed, to assess their contribution, and to look into the reasons of the alterations.

2. Methods

In the present paper, data sets for two downtown sites in Budapest were dealt with. One of the sites was at Széna Square (latitude $47^\circ 30.5' N$, longitude $19^\circ 01.7' E$, altitude 114 m above the mean sea level, a.s.l.) where the field campaign took place in spring 1996, 1998 and 1999. The samplers here were set up at a height of 4.5 m above the ground. The other site was at 5 Rákóczi Street (latitude $47^\circ 29.6' N$, longitude $19^\circ 03.6' E$, altitude 111 m a.s.l.) where the equipment was operated at a height of about 7.5 m above the street level in spring 2001 and 2002. The locations can be classified as kerbside sites according to the criteria proposed by the European Environmental Agency (Larssen and Kozakovic, 2003), and are very similar as far as both the downtown character and vehicle circulation intensity are concerned. Throughout the daytime period, the traffic exhibited a stop-and-start pattern at the sites. The number of vehicles that passed Rákóczi Street in front of the measuring location in 2002 was obtained on line from loop counting. The mean number of motor vehicles that passed in both directions per 15 min ranged from 86 to 766 with an overall mean of 513. There was tram transport powered via overhead copper cables on Széna Square, while there was no tram traffic along Rákóczi Street; the trams just crossed the street at several places—the closest tram line was at a distance of about 80 m from the sampling and measuring location.

Several filter samplers, impactors and in-situ instruments were deployed at the sites over the years. The Gent-type stacked filter unit (SFU) sampler (Maenhaut et al., 1994) with Nuclepore polycarbonate membrane filters was utilized in all campaigns. It operates at an airflow rate of 16.7 L/min, and separates the aerosol particles into a PM10–2.0 and a PM2.0 size fraction. At Széna Square, daily SFU samples were collected starting typically at 07:30 local daylight saving time (UTC + 2) in the morning, while at Rákóczi Street, the samples were collected separately over daylight period (from about 07:00 to 19:00) and night (from about 19:30 to 06:30). The total number of

SFU samples obtained was 33 in 1996, three in 1998 and 1999 each, and five in 2001, while 11 samples for daylight periods, and 12 samples for nights were obtained in 2002. Field blank samples were also taken. All samples were placed into plastic vials, and were stored in a refrigerator or freezer until the chemical analysis.

The polycarbonate filters were weighed before and after the sampling using a microbalance with a sensitivity of 1 µg to obtain the particulate mass. The samples were pre-equilibrated at a stabilized temperature (about 20 °C) and relative humidity (50%) before the actual weighing. Half of each polycarbonate filter was then analyzed by instrumental neutron activation analysis (INAA), and a quarter section of the same filter was analyzed by particle-induced X-ray emission spectrometry (PIXE; Maenhaut and Raemdonck, 1984; Salma and Zemplén-Papp, 1999, and references cited therein). The quality of the INAA analytical data was checked occasionally by the standard reference material NIST 1648 (urban particulate matter), and was continuously controlled on a sample by sample basis via concentration ratios of common elements that were measured by both INAA and PIXE with good precision (Salma et al., 1997). By combining INAA and PIXE data, atmospheric concentration for up to 46 elements from Na to U were derived. The polycarbonate filters were also analyzed for BC by a commercial smoke stain light reflectometer (Diffusion System, model 43) calibrated with other polycarbonate filters for which the BC loading had been determined (Andreae et al., 1984). The method may somewhat overestimate the actual concentration. Elemental carbon and OC in several size fractions were derived by thermal-optical transmission (TOT) analysis of quartz fiber filters collected in parallel with the SFU samples for 2002 (Birch and Cary, 1996)—which may be in contrast somewhat underestimated. Hence, the BC data derived from the smoke stain reflectometer were substantially larger than the EC data from the TOT method. The mean and standard deviation of the BC-to-EC concentration ratio was 2.8 ± 0.5 for the PM10 size fraction, which is in line with other comparisons (ten Brink et al., 2004). Nevertheless, the correlation coefficient between BC and EC was $R = 0.982$, which indicates that the BC data utilized in the present comparisons were coherent and can be used for examining trends in BC. Details of the field work, samples collected, and analytical methods applied, as well as data validation and the integral aerosol properties (i.e., atmospheric concentrations, crustal enrichment factors, PM2.0/PM10–2.0 concentration ratios, size distributions, temporal variations, and possible sources) were described and discussed in detail elsewhere (Salma et al., 2001a, 2002, 2004, 2005; Maenhaut et al., 2005).

3. Results and discussion

3.1. Changes in elemental and PM concentrations between 1996 and 2002

Primary data for the present comparisons were the atmospheric concentrations for aerosol constituents, and meteorological data for the period between 10 April and 17 May 1996, and for the period between 23 April and 5 May 2002 that were summarized in Table 1 of Salma et al. (2001a) and in Table 1 of Maenhaut et al. (2005), respectively. The analytical results for 1996 had been expressed at standard temperature and pressure, which were corrected for ambient conditions for the purpose of the present study. It is noted that median meteorological parameters recorded during the field campaigns in 1996 and 2002 agreed within 15%. This indicates that the general meteorological circumstances for the two spring periods were really similar. Occasionally, means of substantially shorter data series derived for some other years mentioned above were also utilized here as complementary values. The duration of the field campaigns in the study was limited in time, and consequently, the results and conclusions derived cannot be generalized for all seasons.

Table 1

Median atmospheric concentration in ng/m³ and median crustal enrichment factor (EF) for selected aerosol constituents in spring 2002, and the ratio of median EF in spring 2002 to that in spring 1996 (EF ratio) for the PM10–2.0 and PM2.0 size fractions in downtown Budapest

| Aerosol constituent | PM10–2.0 size fraction | | | PM2.0 size fraction | | |
|---------------------|------------------------|------|----------|---------------------|-------|----------|
| | Conc. | EF | EF ratio | Conc. | EF | EF ratio |
| BC | 1453 | 2.1 | 1.4 | 8204 | 76 | 1.4 |
| Na | 353 | 1.0 | 1.6 | 77 | 1.7 | 1.6 |
| Mg | 386 | 1.8 | 1.3 | 81 | 2.9 | 1.6 |
| S | 448 | 161 | 0.7 | 824 | 0.78 | 0.6 |
| Ca | 2334 | 5.6 | 1.3 | 262 | 5.3 | 1.4 |
| V | 1.92 | 1.4 | 0.9 | 0.93 | 4.3 | 0.5 |
| Cr | 7.3 | 6.6 | 1.7 | DL | — | — |
| Fe | 1504 | 3.1 | 1.3 | 427 | 6.2 | 1.6 |
| Co | 0.39 | 1.4 | 1.2 | 0.09 | 2.5 | 0.4 |
| Cu | 44 | 76 | 2.2 | 18 | 252 | 1.9 |
| Zn | 60 | 83 | 1.7 | 30 | 263 | 0.8 |
| As | 0.60 | 33 | 0.7 | 0.39 | 205 | 0.5 |
| Se | DL | — | — | 0.31 | 5632 | 0.5 |
| Br | 6.2 | 194 | 0.6 | 4.2 | 1391 | 0.3 |
| Sb | 10.0 | 5097 | 2.9 | 5.5 | 18892 | 2.7 |
| Ba | 40 | 9.5 | 1.7 | 14 | 19 | 1.7 |
| Pb | 11 | 96 | 0.4 | 16 | 801 | 0.3 |
| PM | 30360 | 2.9 | 0.9 | 20050 | 13 | 0.7 |

The EF value for BC is the concentration ratio to Al (instead of EF); DL stands for detection limit.

Nevertheless, since the weather parameters over the spring campaigns were stable and similar, it is believed and shown that the present study can supply adequate and valuable information even though the number of samples is limited.

The median PM10–2.0 and PM2.0 aerosol mass concentrations in spring 1996 were 48 and 26 µg/m³, respectively, while they were 30 and 20 µg/m³, respectively in spring 2002. Medians and means of atmospheric concentrations, of crustal enrichment factors (EFs) calculated relative to Mason's average crustal rock composition (Mason and Moore, 1982) with Al as the reference element for the PM10–2.0 and PM2.0 size fractions, and medians and means of PM2.0-to-PM10–2.0 concentration ratios were compared as ratio of the corresponding data for 2002 and 1996 (2002/1996 ratio). The ratios were found to be a simple but valuable tool for detecting the differences in the available number of data. The 2002/1996 ratio of the median concentrations for several elements and PM in both size fractions are displayed in Fig. 1a and b. It is seen that the median PM10–2.0 mass decreased by 25% over the period. The change was essentially due to lower level of the crustal component (road dust, see later), which was responsible for about 50% of the PM mass in 2002 (Maenhaut et al., 2005). Median concentration of some typical anthropogenic elements, i.e., Pb, As and Br exhibited significantly larger decrease than the PM. It is also to be realized that the median concentrations of typical geogenic elements, i.e., Al, Si, Sc, Ti, Sm, La and Th also decreased, and by a larger extent than the median PM did (the average 2002/1996 ratio of their medians was 0.62). This indicates a tendency that the crustal component (road dust) contributes decreasingly (though still very markedly) to the PM mass. At the same time, the median concentration of Sb, Cu, Zn, Cr and Ba

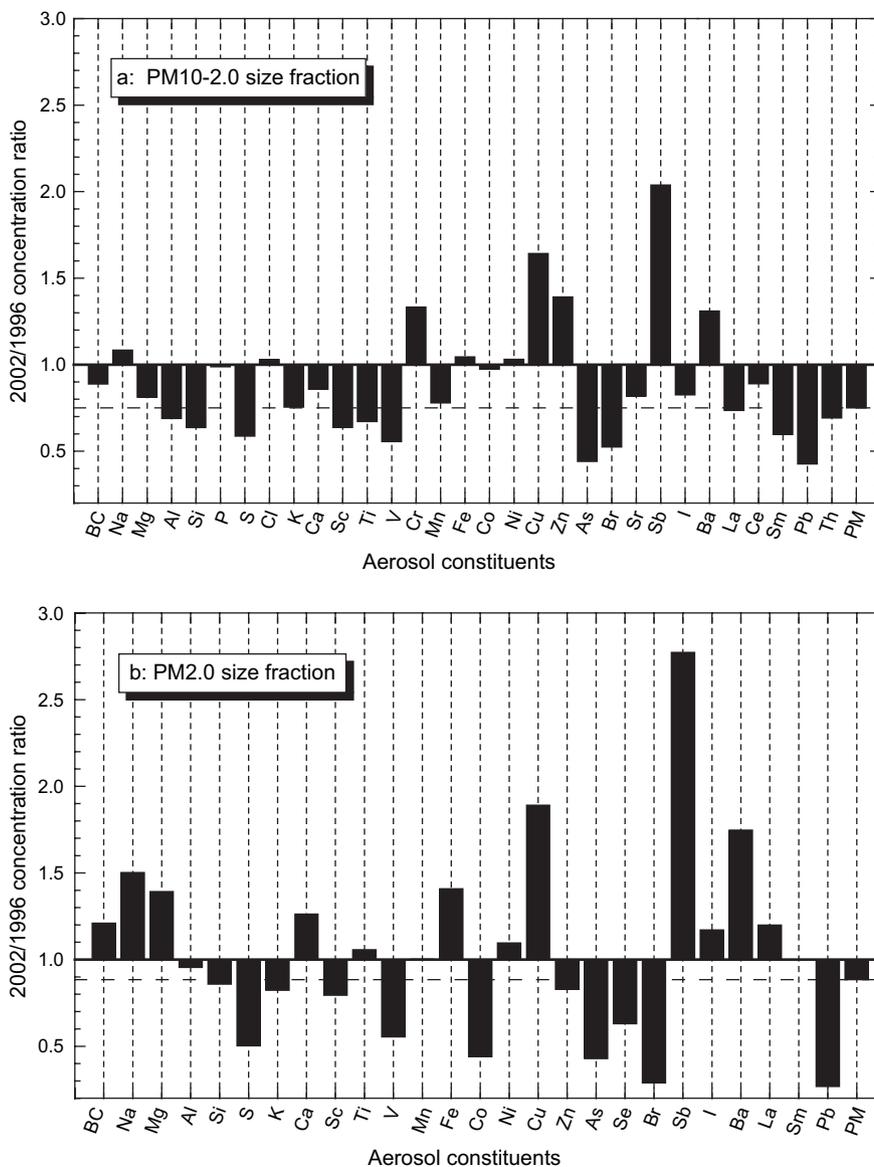


Fig. 1. Ratio of median atmospheric concentration in spring 2002 to that in spring 1996 for aerosol constituents and PM in the PM10–2.0 (panel a) and PM2.0 (panel b) size fractions in downtown Budapest. The dashed line indicates the change of the median aerosol mass.

showed very considerable increase. In the PM2.0 size fraction, the median PM mass decreased by 12%. Median concentrations of Pb, Br, As, Co, S, V and Se decreased markedly, while medians for Sb, Cu, Ba, Na, Mg, Fe, Ca and BC increased substantially. In both size fractions, but particularly in the coarse one, a larger number of constituents showed a decrease to a smaller extent, while a smaller number of constituents exhibited an increase to a larger extent. In general, the changes were relatively larger in the PM2.0 size fraction than in the PM10–2.0 size fraction. It is worth mentioning that the median atmospheric concentrations of Cu, Sb and Zn in the PM10–2.0 size fraction were about 35, 50 and 10 times, respectively larger for the downtown than for the urban background during the same spring time period in 2002. Similarly, the median concentration of BC in the PM2.0 size fraction was about 10 times larger for the downtown than for the urban background. All this indicates that their major

source type(s) are located in or near the city center, and that they are not really transported from outside the city. Median atmospheric concentration, median crustal EFs for 2002, and the 2002/1996 ratio of the median crustal EFs for the constituents that exhibited significant concentration change over the years in either or both size fractions are given in Table 1. The substantial changes in the median atmospheric concentrations were mostly confirmed by crustal EFs. For most elements in the PM10–2.0 size fraction including typical crustal elements (i.e., Mg, Si, Sc, Ti, Mn, Fe, Sr, La, Sm and Th), and K, Co, Ni and PM, the EFs did not change significantly which indicated that road and surface dust suspension and resuspension remained the major source for these constituents. (It is worth noting that the possible Al emissions from the wash coat made of alumina on the surface of catalytic converters in cars can be still considered to be negligible with respect to the dust sources.) As far as the EF for PM is concerned, it showed

that the contribution of crustal matter to the PM_{2.0} mass decreased substantially over the years.

Mean PM_{2.0}/PM_{10–2.0} concentration ratios were typically smaller than one, except for BC, S, As, I and Pb, which showed that most constituents were predominantly present in the PM_{10–2.0} size fraction. This is consistent with our earlier results for the downtown sites (Salma et al., 2001a). On average, the PM_{10–2.0} mass was larger than the PM_{2.0} mass in 2002 as well, which means that the particulate air pollution in downtown Budapest is still dominated by dust. At other kerbside sites in Europe, there was generally relatively less aerosol in the coarse size fraction (Putaud et al., 2004; Van Dingenen et al., 2004).

Platinum-group elements and Ce are of special interest in recent urban aerosol investigations because of their possible emissions from catalytic converters in cars. Particulate Pt was detected in both size fractions in the downtown over the period dealt with in 2001 only (Záray et al., 2004), so the data could not be compared. The mean concentration of Ce in the PM_{10–2.0} size fraction showed a slight tendency to decrease (see Fig. 1a) most likely due to the smaller contribution of the crustal component; thus, its mean crustal EF remained at about 1.7. The concentration of Ce in the PM_{2.0} size fraction was under the detection limit.

3.2. Daytime period and night differences in 2002

Mean values for concentrations and meteorological data representing the separate daytime periods and nights were also calculated, and their daytime/night (D/N) ratio was utilized to evaluate the possible sources of the constituents whose concentrations changed markedly. Atmospheric concentrations of air pollutants depend on the intensity of sources and sinks, and are largely driven by micrometeorology (e.g., boundary layer mixing height), and the thermodynamic conditions of the atmosphere (Marcazzan et al., 2002). Since the D/N ratio for the mean absolute temperature (in K) and pressure (in hPa) were about 1.015 and 1.000, respectively, the same (absolute) amount of pollutant is expected to result in a D/N concentration ratio of about 0.985 due solely to the difference in the sampled air volume. The D/N ratio of the mean concentrations for the selected aerosol constituents in both size fractions are displayed in Fig. 2a and b. In the PM_{10–2.0} size fraction, the D/N ratio for the aerosol mass was about 1.2, reflecting that particulate air pollution was more extensive over daytime periods than over nights, as expected. This points to the significance of the local dust mobilization and resuspension processes in downtown Budapest, and to the shorter atmospheric residence time for the coarse particles. The rather small D/N ratio for Ni indicates that it originated from sources that yielded larger concentrations over nights than over daytime periods. The elements S, Cu, Ca, Sb, Zn and Ba had markedly larger D/N mean ratio than the PM in the coarse size fraction, which suggests that their sources were strongly associated with daytime activities and processes. In the PM_{2.0} size fraction, the D/N ratios were generally closer to unity due mainly to the more uniform distribution of fine aerosol in time and

space than for coarse aerosol (Salma et al., 2001a), and to their significantly smaller deposition rates. As a consequence, the D/N mean ratio for the PM_{2.0} mass was 1.03 only. It is seen from Fig. 2b that sources of Ca, Cu, As, BC, Fe and Sb were more intensive over daytime periods, while concentrations of Ni, Se (and perhaps V and K), were larger overnight.

3.3. Sources of constituents whose concentration changed

In 1996, the main source of particulate Pb and Br in both size fractions was undoubtedly leaded gasoline (Salma et al., 2001b). Hence, changes in their atmospheric concentrations can certainly be attributed to phasing out of leaded gasoline in Hungary, which was completed on 1 April 1999. The measure already resulted in a drop of the concentrations in the downtown by a factor of 3–4 within some weeks, and the mean concentration levels have remained practically at the same value thereafter, as is demonstrated in Fig. 3a and b. The correlation matrix for some selected aerosol constituents in both size fractions is presented in Table 2. In 2002, the correlation coefficients between Pb and Br were insignificant, which means that they have distinct sources. Their correlations with NO, CO or fine BC were insignificant as well, which indicates that the major sources of Pb and Br do not include vehicular exhaust, or tire and brake wear emissions any more. Lead in the PM_{10–2.0} size fraction exhibited a strong correlation with typical crustal elements, thus it seems to be resuspended mainly from the surface dust. The median crustal EF for Pb in the PM_{10–2.0} size fraction was still large (see Table 1). The likely cause of the persistent Pb enrichment in roadway dust and soil are wheel weights made of antimonious lead (consisting of 95% Pb and 5% Sb) which are dropped from the wheels and are pulverized by traffic (Root, 2000), and deposition of Pb-containing fine particles on the ground surface followed by association with the dust particles present there (Salma et al., 2002; Kristensson et al., 2004). Application of the antimonious lead wheel weights was banned in the EU on 31 December 2005. In the PM_{2.0} size fraction, Pb had a large crustal EF, which suggests that its important sources include high-temperature source types like communal waste incineration, and perhaps some smaller contributions by exhaust from engine oil and unleaded gasoline.

The elements S, As and Se are typical markers for coal combustion (Pacyna, 1986; Pakkanen et al., 2003), and the decrease in their atmospheric concentrations can essentially and most likely be explained by less coal burning in the Budapest area. The correlation between S and As was stronger (but still medium) than between Se and the other two elements, which means that Se had other important sources, and that S originated also from other emissions besides coal burning, e.g., from diesel exhaust (Lough et al., 2005).

The largest concentration increase in both size fractions from 1996 to 2002 was observed for Sb and Cu. It is the mechanical surface wear, rubbing and friction of brake pad (disk brakes) and shoe (drum brakes) linings of vehicles that

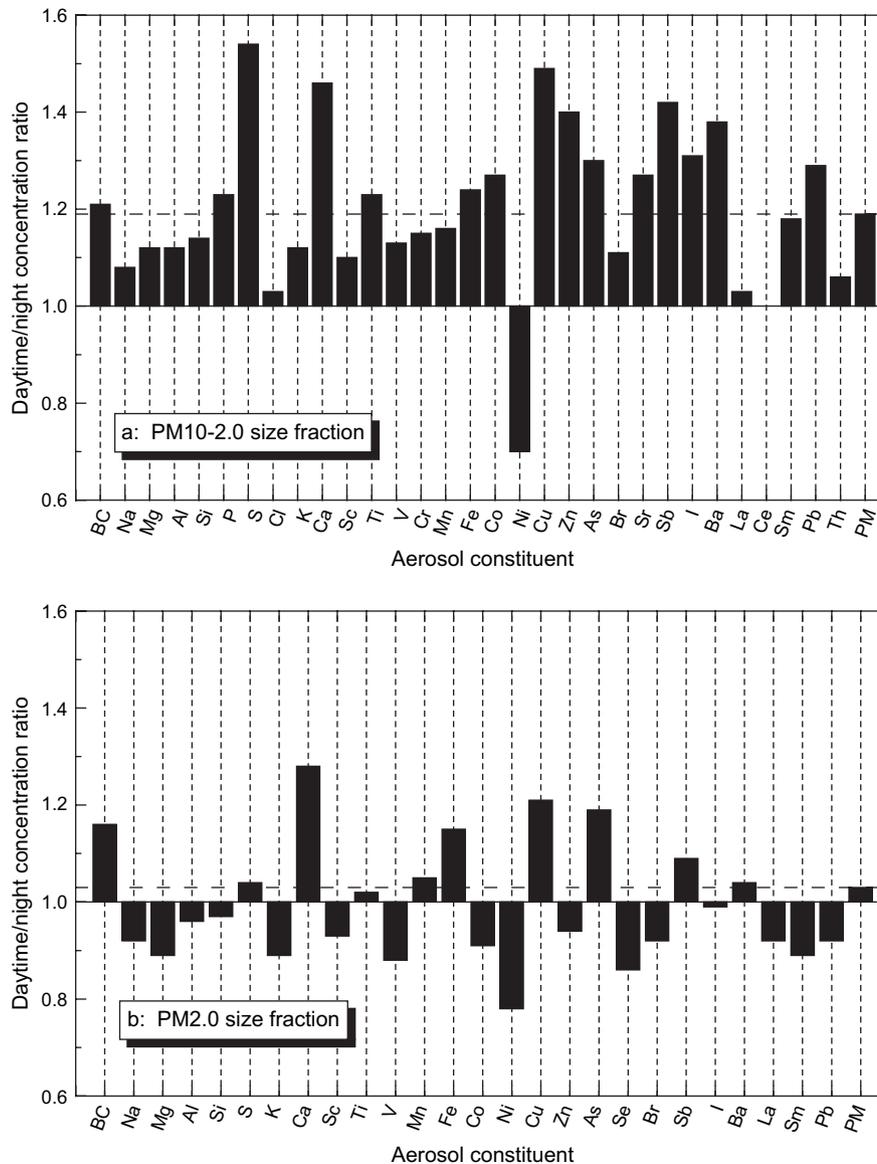


Fig. 2. Ratio of mean atmospheric concentration for daytime periods to that for nights for aerosol constituents and PM in the PM10–2.0 (panel a) and PM2.0 (panel b) size fractions in downtown Budapest in spring 2002. The dashed line indicates the change of the median aerosol mass.

emit these elements into the atmosphere (Garg et al., 2000; Weckwerth, 2001; Pakkanen et al., 2003). In the period studied, asbestos-free brake linings gradually spread across Hungary. An average Cu/Sb concentration ratio of 4.6 ± 1.2 was obtained directly for brake linings, 4.9 ± 1.7 for the coarse particles of the atmospheric aerosol in Cologne, Germany (Weckwerth, 2001), and 5.6 for German tunnels (Stechmann and Dannecker, 1990). In downtown Budapest, mean Cu/Sb ratios of 4.6 ± 1.0 for the PM10–2.0 size fraction, and 3.7 ± 0.2 for the PM2.0 size fraction were derived for the daytime periods in 2002, while for the nights, they were 4.1 ± 0.4 and 3.3 ± 0.7 for the PM10–2.0 and PM2.0 size fractions, respectively. It is worth mentioning that the Cu/Sb ratio for the PM10–2.0 size fraction is a remarkable characteristic of the brake wear since it is about two orders of magnitude smaller than that of 275 for the average crustal rock composition (Mason and Moore, 1982). The mean PM2.0/PM10–2.0

concentration ratio and standard deviation for Cu and Sb were 0.45 ± 0.14 and 0.52 ± 0.18 , which indicates that their main sources indeed include friction mechanisms. Detailed mass size distributions for Cu obtained in parallel with the SFU samples showed that on average, 85% of Cu mass was assigned to the coarse size mode (Salma et al., 2005), which reinforces the present source-type identification. Correlation between Cu and Sb in the PM10–2.0 size fraction was $R = 0.994$; and both of them were also correlated with Ca, Cr and Ba. They were also correlated, but to a lesser extent, with typical crustal elements (see Sc in Table 2 as example) and PM due to the resuspension from road and soil surfaces caused by mechanical and thermal turbulence induced by moving vehicles and exhaust gas (Salma et al., 2004). The correlation between Cu and Sb in the PM2.0 size fraction was still $R = 0.834$; and their correlation with BC, Ca, Fe and Ba was also strong. All this suggests that emissions from brake linings

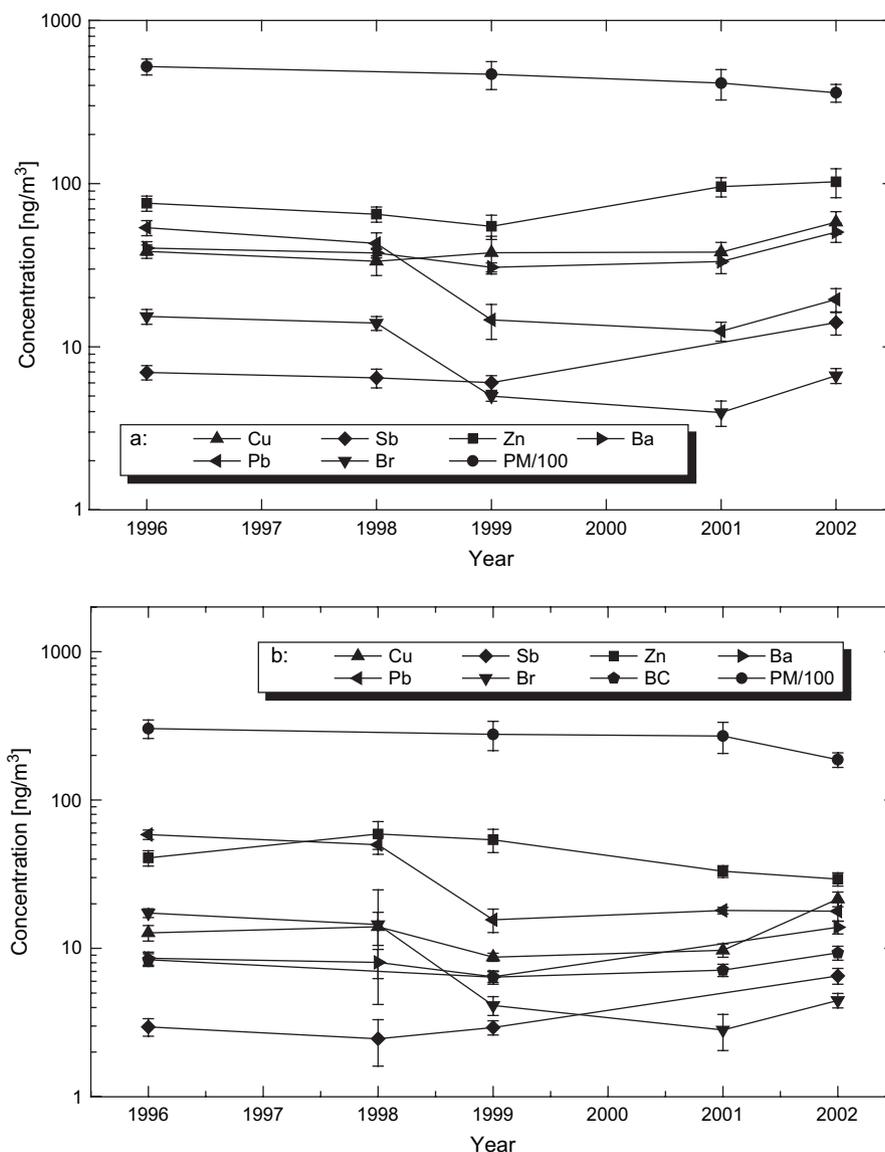


Fig. 3. Time trend for mean atmospheric concentration of some road-traffic-related constituents in the PM10–2.0 (panel a) and PM2.0 (panel b) size fractions in downtown Budapest in springs from 1996 to 2002. The error bars indicate one standard error.

were the major source of Cu and Sb in 2002 especially in the PM10–2.0 size fraction, and no other major component was involved. Due to its stabilizing properties, Sb is used in a number of alloys for motor bearings, and as flame retardant in the vulcanization of rubber (Dietl et al., 1997). Assuming that the brake wear and crustal matter components are the only significant sources of Cu and Sb in the PM10–2.0 size fraction in cities, the non-crustal coarse Cu and Sb concentrations (calculated from Cu, Sb and Al content in the PM and average crustal rock composition, Mason and Moore, 1982) can be attributed to the brake wear. Accordingly, the brake lining wear component made up on average $69 \pm 7\%$ of Cu and $66 \pm 9\%$ of Sb in the PM10 size fraction. This is consistent with our understanding of the main natural and anthropogenic emission sources of Cu and Sb (Pacyna, 1986). It is noted for comparison purposes that in 1996, the mean Cu/Sb ratio and standard deviation for the PM10–2.0 size fraction were 5.7 ± 0.9 , and the correlation coefficient was $R = 0.934$. Our results are

supported by elevated concentration levels of Cu and Sb close to major roads in soils, air and some plants (Dietl et al., 1997; Monaci et al., 2000; Dongarrà et al., 2003). Diesel soot also contains Sb (Weckwerth, 2001; Dongarrà et al., 2003), which contributes to the PM2.0 size fraction. Exhaust gas from gasoline combustion can account for up to 20% of Sb; other main sources are combustion fumes from petrol products, thermoelectric plants and refuse incinerators (Ondov et al., 1982; Pacyna, 1986).

It is inferred from the large crustal EFs for Zn (see Table 1) that it has other important anthropogenic emission sources besides road and soil dust dispersion and resuspension. Zinc showed a correlation coefficient of about 0.6 with Ca, Fe, Cu, Sb and Ba in both size fractions (cf. Table 2), and with the PM2.0-fraction BC. In the PM10–2.0 size fraction, it correlated with many more elements to a similar extent, while in the PM2.0 size fraction, the correlations listed were the only significant ones. It implies that the road traffic was a major

Table 2
Correlation (*R*) matrix for selected aerosol constituents in the PM₁₀–2.0 size fraction (upper diagonal triangle) and in the PM_{2.0} size fraction (lower diagonal triangle) in downtown Budapest during spring 2002

| Ca | Sc | Cr | Cu | Zn | Sb | Ba |
|--------|--------|-------|-------|--------|-------|-------|
| Ca | 0.913 | 0.885 | 0.908 | 0.646 | 0.901 | 0.948 |
| | Sc | 0.755 | 0.745 | 0.580 | 0.751 | 0.830 |
| BC | | Cr | 0.897 | 0.616 | 0.881 | 0.883 |
| –0.050 | S | | Cu | 0.689 | 0.994 | 0.984 |
| 0.895 | 0.047 | Ca | | Zn | 0.575 | 0.635 |
| 0.970 | –0.135 | 0.877 | Fe | | Sb | 0.980 |
| 0.203 | 0.777 | 0.235 | 0.106 | As | | Ba |
| 0.842 | –0.208 | 0.679 | 0.919 | –0.006 | Ba | |
| 0.605 | 0.318 | 0.665 | 0.546 | 0.581 | 0.341 | Pb |
| BC | S | Ca | Fe | As | Ba | Pb |

The statistical significance of the correlation is 0.95. Scandium was included with the PM₁₀–2.0 size fraction in order to examine the impact and behavior of resuspended crustal (surface) dust.

source for atmospheric Zn in the downtown. On average, non-crustal coarse Zn accounted for $67 \pm 12\%$ of Zn in the PM₁₀ size fraction. Its median PM_{2.0}/PM₁₀–2.0 concentration ratio was 0.43, and the fine-sized modes made up 41% of its total mass (Salma et al., 2005), which all point to the existence of other important sources for the fine particles. These could possibly be waste incineration, chemical industry and vehicle-exhaust emissions. Importance of the tire wear can be estimated roughly assuming that the non-crustal Zn in the PM₁₀–2.0 size fraction originated exclusively from the tire wear, and that the airborne tire wear products contained the same amount of Zn as the tire rubber tread, i.e., 2%. A mean contribution of the tire wear component to the PM₁₀ aerosol mass was found to be $5.6 \pm 2.7\%$ in that way. The value is to be regarded as an upper limit because resuspension of road dust particles that were associated with fine-mode Zn deposited to the surfaces previously could lower this contribution, similarly to some other components, e.g., corrosion of galvanized steel and Zn-containing paints, which can also emit coarse-mode Zn into the atmosphere. Nevertheless, our value agrees well with the corresponding estimates made by different methods and models in other studies (Rogge et al., 1993; Weckwerth, 2001; Kupiainen et al., 2005). The slightly larger contribution can also be caused by substantially worse road surface conditions in Budapest than in the other sites studied or test facilities. Similarly, assuming that the airborne tire rubber particles contain the same amount of organic matter as tire debris, i.e., of 58%, the mean contribution of the tire wear component to the organic aerosol (OA) was estimated to be of the order of $15 \pm 6\%$ in the PM₁₀ size fraction as an upper limit. A factor of 1.6 was used in the calculations to convert OC—that was derived by TOT from samples collected in parallel with the SFU samples in 2002—into OA (Birch and Cary, 1996; Salma et al., 2004). It has to be noted that the tire rubber particles can be electrically charged (Rogge et al., 1993), which means that some peculiarities can arise in their sampling (with regard to the collection efficiency, size separation or sampling losses).

Correlation analysis also suggested that Ca, Cr, Fe and Ba—in particular for the PM_{2.0} size fraction—can be related

to road traffic as well. These metals can originate from additives to common lubricants and technical fluids (e.g., crankcase or gear oil, greases, and brake fluids) and from worn parts that accumulate in the used lubricants (Pacyna, 1986; Pakkanen et al., 2003) in addition to their crustal and coal fly-ash sources. Time trends for some traffic-related constituents in both size fractions over the years considered are displayed in Fig. 3a and b.

4. Conclusions

Populated urban areas coincide with high traffic densities. Exhaust gas, soot, and worn-off products from tires and other mechanical parts of vehicles are sources with the largest emission rates from road traffic. With improved exhaust emission control technologies (and with forthcoming implementation of particle traps on new diesel vehicles), the non-exhaust particulate emissions increased (and are expected to increase further) in significance in particular when compared to other anthropogenic sources in cities. The aerosol constituents whose concentrations increased substantially in downtown Budapest since 1996 were mainly associated with the coarse size fraction having a shorter atmospheric residence time. Once deposited on the ground, they become part of a composite mixture from multiple source contributions usually dominated by crustal material, and significantly enriched in many elements that are emitted from anthropogenic sources. Road traffic resuspends the surface dust including the anthropogenic constituents, and creates diffuse emissions, and continual air pollution and exposure in cities. Based on the results and their relationships, it can be concluded that the coarse-mode Cu, Sb and Zn together with the fine-mode EC (or BC) and some particulate organic compounds seem to be appropriate markers for traffic-related emissions. The transition and heavy metals utilized in the present study as indicators of the increased emissions are important for health effects as well. Antimony, for instance, is a non-essential element with toxicological behavior similar to As. Antimony trioxide has been found to be carcinogenic to experimental animals in inhalation studies, and to cause direct lung damage following chronic inhalation. The greatest concern with regard to its carcinogenicity relates to the inhalation route. Chronic respiratory uptake of antimony-containing dusts leads to irritation of the respiratory tract and myocardial and liver damage (Agency for Toxic Substances and Disease Registry, 1992). Some water-soluble transition metals (e.g., Cr, Fe, Cu and Zn) leached from ambient filter extracts have been shown consistently to cause cell injury and inflammatory changes (albeit at higher concentrations) in vitro and in vivo (US EPA, 2004). The speciation and physico-chemical state of metals are also important for their behavior in the environment and availability to biota. The latex allergens or latex cross-reactive material present in sedimented PM derived from tire debris could be important factors in producing latex allergy and asthma symptoms in public (Miguel et al., 1996).

The present study demonstrates that non-exhaust traffic emissions and coarse-mode atmospheric particles have increasing importance on urban (local or regional) scale as far as both environment and health impacts are concerned and, therefore, it is believed that further co-ordinated investigations will be devoted to the subject.

Acknowledgements

Financial support by the Hungarian Scientific Research Fund (contr. T043348); by a bilateral project between Hungary and Flanders, and by the Belgian Federal Science Policy Office (contrs. EV/02/11A and BL/02/CR01) is appreciated. The study is a contribution to the European Science Fund COST Action 633 project.

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