

Chemical composition and mass closure for fine and coarse aerosols at a kerbside in Budapest, Hungary, in spring 2002[†]

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A comprehensive chemical aerosol characterization was carried out at a kerbside in downtown Budapest in spring 2002. Several filter samplers were deployed in parallel for day and night collections, and a total of 23 parallel collections were made. All samples were analysed for the particulate mass (PM) by weighing. Depending on the sampler type and/or collection substrate, further analyses were performed for up to 46 elements by a combination of particle-induced x-ray emission (PIXE) spectrometry and instrumental neutron activation analysis (INAA), for major anions and cations by ion chromatography and for organic carbon and elemental carbon by a thermal–optical transmission technique. Some of the elements measured could clearly be associated with traffic-related sources, e.g. Cu and Sb were attributed to emissions from brake linings. Aerosol chemical mass closure calculations were made for the separate fine (<2 µm) and coarse (2–10 µm) size fractions and also for the PM₁₀ aerosol. For reconstituting the gravimetric PM, eight aerosol types were considered, and three aerosol types were deduced from the PIXE/INAA elemental data set. Organic matter and elemental carbon were the dominant aerosol types in the fine fraction; they explained on average 43 and 21%, respectively, of the fine PM. The coarse PM consisted mainly of crustal matter (49%) and organic matter (30%). The large contribution from crustal matter (road dust) to the coarse fraction is consistent with other data from kerbside sites in Europe. Copyright © 2005 John Wiley & Sons, Ltd.

INTRODUCTION

The study of atmospheric aerosols and their chemical composition as a function of size is needed for both scientific and policy reasons.^{1,2} Aerosols have an effect on human health and play a role in climate change. They have also a determining effect on visibility and contribute to the soiling of monuments. Atmospheric aerosols originate from a wide variety of natural and anthropogenic sources and data on their chemical composition are necessary for source identification and apportionment. Experimental data on aerosol particle size and composition are also needed for the testing and validation of numerical aerosol models, which are becoming tools to extrapolate monitoring data.¹ An important task in chemical aerosol characterization is

to measure the major aerosol components (aerosol types) and to examine to what extent the particulate mass can be explained by the measured components and thus aerosol chemical mass closure can be achieved. In the European aerosol phenomenology exercise, this task was attempted for various sites in Europe.² However, in that work data from Eastern Europe were lacking. Furthermore, for several sites, mass closure was not achieved because important components were not measured. Important components that need to be measured are organic matter, elemental carbon, sulfate, nitrate, ammonium, crustal material and sea salt. Determination of all these components in aerosol samples cannot be achieved with a single analytical technique. Instead, an array of techniques is required, including thermal analysis for organic and elemental carbon, ion chromatography for sulfate, nitrate and ammonium, and preferably a non-destructive multi-elemental technique, such as x-ray fluorescence (XRF) or particle-induced x-ray emission (PIXE), for evaluating the crustal component and sea salt. In this paper, we present results from a chemical aerosol characterization and mass closure study at a kerbside (street canyon) in Budapest, Hungary, in spring 2002. The study is a follow-up and complement to our earlier investigations of the chemical composition of size-fractionated aerosols at various sites in Budapest.^{3,4} A detailed discussion of the carbonaceous aerosol data for the current study has been presented elsewhere.⁵

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EXPERIMENTAL

The aerosol collections and measurements at the kerbside in Budapest took place at 5 Rákóczi Street, which is in the downtown in Pest (at 47°29'37"N, 19°03'38"E, 111 m above mean sea level). The equipment was installed on the first-floor balcony at a height of about 7.5 m above the street level. The street can be characterized by width, height and length parameters of 30, 25–30 and 600 m, respectively. Several filter samplers were deployed at the site. They included (1) a PM_{2.5} filter holder with two pre-fired Whatman QM-A quartz fibre filters in series [PM_{2.5}(Q)], (2) a PM₁₀ filter holder, also with two pre-fired Whatman QM-A filters [PM₁₀(Q)], (3) a Ghent PM₁₀ stacked filter unit (SFU) sampler,^{6,7} with coarse and fine Nuclepore polycarbonate filters (pore sizes 8 and 0.4 µm, respectively) in series [PM₁₀(NN)], and (4) a second Ghent PM₁₀ SFU sampler, with a coarse Nuclepore polycarbonate filter and a fine Pall Teflo filter (pore size 2 µm) [PM₁₀(NT)]. All filters had a diameter of 47 mm, and the four samplers operated at a flow-rate of 171 min⁻¹. The cut point (*d*₅₀ value) between the coarse and fine size fractions in the SFU sampler was 2 µm aerodynamic diameter (AD). Prior to use, the quartz fibre filters had been pre-heated for 24 h at 550 °C in order to remove organic contaminants. The purpose of the second quartz filter in the PM_{2.5}(Q) and PM₁₀(Q) filter holders was to assess artefacts [i.e. losses of semi-volatile compounds and/or adsorption of volatile organic compounds (VOCs)] in the collection of carbonaceous aerosols.⁸ The campaign started in the evening of 23 April 2002 and lasted until the morning of 5 May. Separate day and night collections were made with the four filter samplers, with the day samples starting at 7:00 am and ending at 7:30 pm, and the night samples starting at 7:30 pm and ending at 7:00 am the next day (all times are local time), and a total of 23 parallel collections were made.

The particulate mass (PM) was obtained from weighing each filter before and after sampling with a microbalance. The weighings were done at 20 °C and 50% relative humidity and the filters were pre-equilibrated under these conditions for at least 24 h. All quartz filters were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal–optical transmission (TOT) technique.⁹ The coarse and fine Nuclepore filters from PM₁₀(NN) were subjected to PIXE spectrometry and instrumental neutron activation analysis (INAA).^{10,11} The combination of these two techniques provided concentration data for up to 46 elements (from Na to Th). The filters from PM₁₀(NT) were analysed for major anions and cations by ion chromatography (IC).¹²

RESULTS AND DISCUSSION

Concentrations and artefacts

From the weights of the second quartz fibre filters in the PM_{2.5}(Q) and PM₁₀(Q) samplers, an attempt was made to assess the extent of the artefacts for PM. However, the uncertainty of the net weights was too large (30 µg) to draw any meaningful conclusions. The artefacts for OC and EC were assessed from the TOT analyses for the same samplers. The average second filter/first filter ratio and associated standard deviation for OC were 0.15 ± 0.02 and 0.10 ± 0.02

for PM_{2.5}(Q) and PM₁₀(Q), respectively. EC was insignificant on the second filter. The OC on the second quartz fibre filter was assumed to be mainly due to adsorption of VOCs (positive artefact), and it was subtracted from the OC on the first filter in order to arrive at artefact-free particulate OC data. Median concentrations of the fine, coarse and PM₁₀ mass concentration for several aerosol species and most elements measured are given in Table 1. Of the elements measured, only those which had concentrations in the coarse size range below detection limit in more than half of the samples are excluded from the table. For the PM₁₀ size range, the concentration ranges are also included in Table 1. The PM₁₀ aerosol mass concentrations are larger for PM₁₀(Q) than for PM₁₀(NN). The mean Q/NN mass ratio and associated standard deviation were 1.10 ± 0.16. That PM data from quartz fibre filters are larger than those from Nuclepore (or Teflon) filters is normally found in our studies (e.g. Ref. 12) and is mainly attributed to the adsorption of gaseous compounds by the quartz fibre filters.

Traffic-related sources of selected elements

The concentration data for the PM and the elements in Table 1 can be compared with those from our earlier studies in Budapest, where samples were collected with Ghent PM₁₀ SFU samplers. Data, as derived from SFU samples, for two sites in Budapest in April–May 1996 are presented in Table 1 in Ref. 3. One of the two sites in that study was Széna Square in downtown Buda (latitude 47°30.6'N, longitude 19°1.8'E, altitude 115 m above mean sea level). This site is at about 3 km to the NW of the Rákóczi Street site and is affected by heavy traffic nearby in about the same way. The median concentrations for the coarse and fine PM in spring 1996 at Széna Square were 45 and 25 µg m⁻³ compared with 30 and 20 µg m⁻³ in the present study. The 1.5 times larger value for the coarse PM at Széna Square is essentially due to higher levels of the crustal component (road dust), which was responsible for about 50% of the coarse PM (see below). For the typical crustal elements, such as Al, Si, Sc and Ti, the medians in the coarse size fraction are around 1.5–1.7 times larger in the 1996 Széna Square data set than in the current data set. For some typical anthropogenic elements, including S, As, Br and Pb, the medians in the 1996 Széna Square data set are a factor of ≥2 larger than in the current data set, for both the coarse and fine size fractions. The differences for Pb and Br (more than a factor of 3 in the fine size fraction) are certainly attributable to the use of leaded gasoline in 1996. Leaded gasoline was completely phased out on 1 April 1999 in Hungary and this resulted in 3–4 times lower levels of Pb and Br already in spring 1999 at Széna Square when compared with spring 1996.¹³ In contrast to virtually all other elements measured, for two typical anthropogenic elements, i.e. Cu and Sb, the medians are larger in the present study than in the 1996 Széna Square data set, i.e. 1.3 and 1.6 times larger, respectively, for the coarse size fraction and 1.7 and 2.2 times larger, respectively, for the fine size fraction. These two elements in urban aerosols are usually attributed to traffic, and in particular to emissions from brake linings.¹⁴ Weckwerth¹⁴ found that these emissions are mostly in coarse particles. He obtained an average Cu/Sb ratio of

Table 1. Median concentrations (ng m^{-3}) in the fine ($<2 \mu\text{m AD}$), coarse ($2\text{--}10 \mu\text{m AD}$) and PM_{10} size fractions (and concentration ranges for PM_{10}) at the Rákoczi Street site, Budapest, in the period 23 April–5 May 2002^a

| Species | Fine median | Coarse median | PM_{10} median | PM_{10} concentration range | |
|----------|-----------------|---------------|-------------------------|--------------------------------------|---------|
| | | | | Min. | Max. |
| PM(NN) | 20 000 | 30 000 | 48 000 | 17 600 | 98 000 |
| PM(Q) | | | 54 000 | 21 000 | 107 000 |
| OC(Q) | | | 10 600 | 4600 | 23 000 |
| EC(Q) | | | 3400 | 920 | 10 200 |
| Ammonium | 840 | 250 | 1050 | 197 | 3200 |
| Nitrate | 800 | 1440 | 2400 | 990 | 5100 |
| Sulfate | 1890 | 1300 | 4000 | 930 | 9300 |
| Na | 77 | 350 | 450 | 171 | 830 |
| Mg | 81 | 390 | 480 | 145 | 1010 |
| Al | 119 | 960 | 1060 | 210 | 2400 |
| Si | 290 | 2200 | 2600 | 580 | 5600 |
| P | DL ^b | 55 | 66 | 13.8 | 141 |
| S | 820 | 450 | 1660 | 470 | 2900 |
| Cl | DL | 168 | 193 | 50 | 560 |
| K | 125 | 310 | 420 | 146 | 940 |
| Ca | 260 | 2300 | 2600 | 580 | 5600 |
| Sc | 0.0188 | 0.164 | 0.181 | 0.042 | 0.45 |
| Ti | 9.0 | 62 | 73 | 15.2 | 151 |
| V | 0.93 | 1.92 | 2.9 | 0.87 | 6.4 |
| Cr | DL | 7.3 | 8.9 | 1.83 | 19.0 |
| Mn | 7.8 | 22 | 30 | 7.9 | 67 |
| Fe | 430 | 1500 | 1930 | 420 | 4800 |
| Co | 0.085 | 0.39 | 0.48 | 0.079 | 0.96 |
| Ni | 0.84 | 2.3 | 3.2 | DL | 10.7 |
| Cu | 18.4 | 45 | 61 | 13.0 | 270 |
| Zn | 30 | 60 | 84 | 24 | 560 |
| As | 0.39 | 0.60 | 1.40 | 0.198 | 8.5 |
| Se | 0.31 | 0.23 | 0.36 | DL | 1.48 |
| Br | 4.2 | 6.2 | 10.3 | 2.7 | 15.6 |
| Sr | DL | 5.0 | 5.0 | 1.58 | 14.9 |
| Zr | DL | 5.7 | 5.8 | DL | 29 |
| Mo | DL | 1.90 | 2.5 | DL | 10.7 |
| Sb | 5.5 | 10.5 | 16.6 | 3.9 | 49 |
| I | 0.97 | 0.37 | 1.53 | 0.68 | 5.8 |
| Cs | 0.032 | 0.085 | 0.103 | DL | 0.42 |
| Ba | 13.6 | 40 | 52 | 14.4 | 153 |
| La | 0.127 | 0.54 | 0.66 | 0.091 | 1.65 |
| Ce | DL | 0.60 | 0.60 | DL | 2.8 |
| Sm | 0.0114 | 0.072 | 0.082 | 0.024 | 0.21 |
| Eu | DL | 0.022 | 0.022 | DL | 0.065 |
| W | 0.156 | 0.36 | 0.58 | DL | 8.9 |
| Au | DL | 0.0061 | 0.0074 | DL | 0.110 |
| Pb | 16.3 | 11.7 | 24 | 8.0 | 270 |
| Th | DL | 0.134 | 0.137 | 0.042 | 0.36 |

^a Ions were obtained from $\text{PM}_{10}(\text{NT})$ and elements from $\text{PM}_{10}(\text{NN})$.

^b DL, detection limit.

4.9 ± 1.7 for coarse particles in urban aerosols in Cologne, Germany and 4.6 ± 1.2 for brake linings. The average Cu/Sb

ratio of 4.3 ± 0.8 for the coarse aerosol in the present work is remarkably similar to those data and, furthermore, both elements were mainly associated with the coarse size fraction (see also below), thus strongly suggesting that emissions from brake linings are also the major source of coarse Cu and Sb at the Rákoczi Street site.

In addition to Cu and Sb, also other elements, such as Fe, Zn and Ba, are often attributed to traffic in urban aerosols.¹⁵ The sources of these other elements could then be vehicle exhaust and/or vehicle brake wear, and either gasoline cars, diesel cars, buses or trucks could be principal sources. For example, Stechmann and Dannecker¹⁶ suggested that Ba and Fe originate especially from truck traffic. In our earlier study of Budapest aerosols,³ substantial concentration differences were observed for a number of elements for samples that were collected in parallel at Széna Square and at an urban background site (i.e. the KFKI campus). The difference was an order of magnitude for Cu, Br, Sb and Ba in the coarse size fraction and a factor of 2–3 for Fe, Cu, Br, Sb, Ba and Pb in the fine size fraction. This all points to traffic as a major source of these elements at Széna Square in that earlier study (1996). As indicated above, for two of those elements (Cu and Sb), traffic (and in particular brake linings) appears to be a major source in the present study. Although leaded gasoline was undoubtedly the main source of Pb and Br at Széna Square in 1996, it is hard to draw firm conclusions about their main sources on the basis of the (much smaller) concentration data observed in the present study.

With regard to the principal source of Fe and Ba at the Rákoczi Street site, for the coarse size fraction the median concentrations are similar to those observed at Széna Square, but for the fine size fraction somewhat larger medians are observed (the median for Ba is 1.66 times larger). One is tempted to conclude from this that traffic could be the major source for these two elements at the Rákoczi Street site. That there may indeed be other substantial (and most likely traffic-related) sources in addition to resuspended road dust and soil dust for these two elements is suggested by their crustal enrichments factors (EFs), calculated relative to Mason's average crustal rock¹⁷ with Al as reference element. In the coarse size fraction, median EFs of 3.1 and 9.5 were obtained for Fe and Ba, respectively, and in the fine size fraction, the median EFs were 6.2 and 19, respectively.

Fine to PM_{10} ratios

On the basis of the available data, average fine (PM_2 or $\text{PM}_{2.5}$) to PM_{10} ratios were calculated for the PM, OC, EC, ammonium, nitrate, sulfate and the various elements. The mean percentages of the PM_{10} mass in the fine size fraction are shown in Fig. 1, whereby for the elements, data are depicted for the same elements as retained for Table 1 (with the exception of Ce). The average fine/ PM_{10} ratios and associated standard deviations for PM were 0.53 ± 0.14 for $\text{PM}_{2.5}(\text{Q})/\text{PM}_{10}(\text{Q})$ and 0.38 ± 0.11 for $\text{PM}_2(\text{NN})/\text{PM}_{10}(\text{NN})$. Small fine/ PM_{10} ratios for PM were found during polluted time periods, when resuspension of local coarse road dust was important.⁵ Fig. 1 shows that OC, EC, ammonium, sulfate (and S), Se, I and W are mainly present in the fine size fraction. For As, Br, Mo, Au and Pb, about half of the PM_{10}

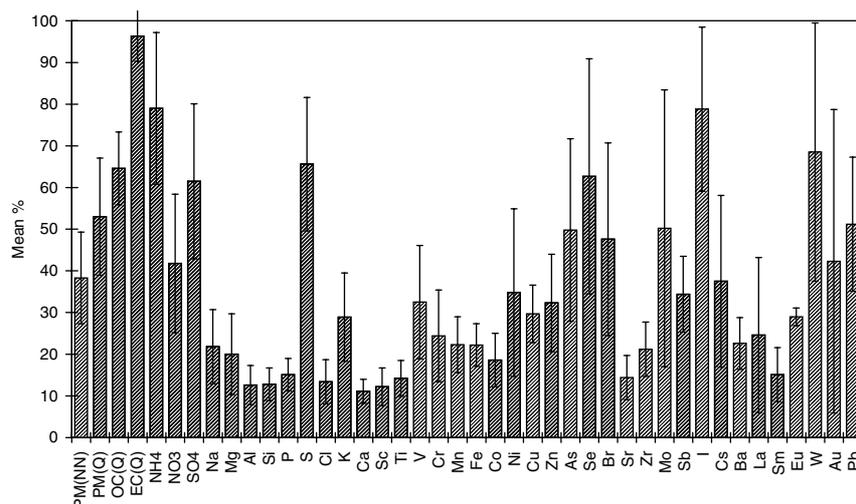


Figure 1. Mean percentage of the PM₁₀ mass in the fine (PM₂ or PM_{2.5}) size fraction and associated standard deviation for the PM, OC, EC, ammonium, nitrate, sulfate and various elements. Ions were obtained from PM₁₀(NT) and elements from PM₁₀(NN).

mass is, on average, in the PM₂ fraction. The crustal (Al, Si, Ca, Sc, Ti, Mn, Fe, Zr, La, Sm) and several other elements (e.g. Na, Mg, P, Cl) are predominantly associated with the coarse size fraction. Cu and Sb are also mainly associated with the coarse particles.

Our concentration data for the PM and several aerosol components and our fine to PM₁₀ ratios can be compared with those for other kerbside and urban sites, as obtained in the European aerosol phenomenology exercise.^{1,2} Van Dingenen *et al.*¹ reported for the PM₁₀ aerosol mass concentration yearly average medians of between 20 and 40 $\mu\text{g m}^{-3}$ at urban sites and of between 30 and 50 $\mu\text{g m}^{-3}$ at kerbsides. Our median of 48 $\mu\text{g m}^{-3}$ [as derived from the PM₁₀(NN) sampler] is thus at the higher end for kerbsides. The PM_{2.5}/PM₁₀ ratios at the various sites of the aerosol phenomenology exercise ranged from 0.57 to 0.85. The smallest ratios were obtained for kerbsides (i.e. in Barcelona and Bern) and were explained by the high proportion of resuspended (coarse) road dust at such sites. Our average PM_{2.5}/PM₁₀ ratio of 0.53 ± 0.14 for the Rákóczi Street site is even smaller than for the aerosol phenomenology sites and is consistent with the even larger proportion of resuspended (coarse) road dust at our site, as discussed in the next section.

Aerosol chemical mass closure

Aerosol chemical mass closure calculations were performed for the separate fine (PM₂) and coarse (2–10 $\mu\text{m AD}$) size fractions and also for the PM₁₀ aerosol, for each of the 23 parallel samplings. As gravimetric PM data we used the values from the PM₁₀(NN) collections. For reconstituting this gravimetric PM, eight aerosol types (or components) were considered: (1) organic aerosol, which was estimated by multiplying the corrected OC by a factor of 1.4;⁸ (2) EC; (3) ammonium; (4) nitrate; (5) sulfate; (6) sea salt, estimated as $\text{Cl} + 1.4486 \text{Na}$, where 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water;¹⁸ (7) crustal matter = $1.16 (1.90 \text{Al} + 2.15 \text{Si} + 1.41 \text{Ca} + 1.67 \text{Ti} + 2.09 \text{Fe})$, where the factor 1.16 is to compensate for the exclusion of MgO, Na₂O, K₂O and H₂O from the crustal mass calculation;¹⁹

and (8) other elements, which is the sum of the mass of all non-crustal/non-sea-salt elements measured by INAA and PIXE (S was excluded from this sum). The OC and EC data were obtained from the PM_{2.5}(Q) and PM₁₀(Q) samplers, applying a correction for converting from the PM_{2.5} to PM₂ size range. For OC, the PM_{2.5} data were multiplied by the $(\text{PM}_2/\text{PM}_{10})/(\text{PM}_{2.5}/\text{PM}_{10})$ ratio for the aerosol mass, which was on average 0.72; it was thus implicitly assumed that the size distribution for OC was similar to that of the PM, as is suggested by the similarity of the PM_{2.5}/PM₁₀ ratios for PM(Q) and OC(Q) (see Fig. 1). For EC, the PM_{2.5} data were simply multiplied by 0.9, since most of the EC is associated with fine particles [as also appears from the PM_{2.5}/PM₁₀ ratio for EC(Q); see Fig. 1]. Ammonium, nitrate and sulfate were obtained from the IC analyses of the PM₁₀(NT) samples, and the concentrations for the last three aerosol types (components) were derived from the INAA and PIXE results for the PM₁₀(NN) samples.

The average percentage attributions of the gravimetric PM to each of the eight aerosol types (components) are given in Table 2. The sums (in percent) of all included components are 104% and 94% for the fine and coarse size fractions,

Table 2. Average percentage attribution and associated standard deviation of the gravimetric aerosol mass (PM) to eight aerosol types (components) for the fine, coarse and PM₁₀ size ranges (based on 23 samplings)

| Component | Size fraction <2 $\mu\text{m AD}$ | Size fraction 2–10 $\mu\text{m AD}$ | PM ₁₀ size fraction |
|------------------|--------------------------------------|--|-----------------------------------|
| Organic matter | 43 \pm 10 | 30 \pm 6 | 34 \pm 5 |
| Elemental carbon | 21 \pm 11 | 1.7 \pm 0.8 | 8.1 \pm 2.3 |
| Ammonium | 5.7 \pm 3.0 | 0.8 \pm 0.6 | 2.9 \pm 1.8 |
| Nitrate | 5.8 \pm 3.2 | 4.7 \pm 2.0 | 5.2 \pm 2.3 |
| Sulfate | 13 \pm 6 | 4.4 \pm 2.0 | 8.0 \pm 3.7 |
| Sea salt | 0.9 \pm 0.6 | 2.4 \pm 1.3 | 1.8 \pm 0.9 |
| Crustal matter | 14 \pm 4 | 49 \pm 5 | 36 \pm 7 |
| Other elements | 0.5 \pm 0.2 | 0.6 \pm 0.3 | 0.6 \pm 0.2 |
| Sum | 104 \pm 15 | 94 \pm 8 | 96 \pm 6 |

respectively, and 96% for the PM₁₀ aerosol. Considering the uncertainties in estimating some of the components, especially organic matter (the multiplication factor of 1.4 for OC), the difference from 100% is probably not significant. It should also be noted that water was not included, except for that associated with crustal matter. Organic matter (43%) and EC (21%) are the major components in the fine size fraction, whereas crustal matter and organic matter are the dominant components in the coarse size fraction and for the PM₁₀ aerosol. The crustal matter undoubtedly consists mainly of resuspended road dust.

Time trends

The time trends for the PM and three selected aerosol components in the PM₁₀ size fraction are shown in Fig. 2. Crustal matter and organic aerosol, the two major components, are fairly well correlated with each other, as is expected for (primary) aerosol components that are associated with the same sources (i.e. traffic). Although a substantial fraction of the PM_{2.5} organic matter (OM) was found to be secondary organic aerosol (SOA), i.e. on average 37 (±18)% during the day and 46 (±16)% during the night,⁵ at least two-thirds of the PM₁₀ OM is, on average, expected to be of primary origin. That the PM is well correlated with the OM and crustal matter is simply a consequence of the fact that these two components together account for 70% of the PM₁₀ aerosol. In our study of the carbonaceous aerosol data from the Rákóczi Street site,⁵ we examined the relationships of the PM and carbonaceous aerosol concentrations with road traffic, local meteorology and long-range transport of air masses. It was concluded that a direct coupling between the atmospheric concentration levels and vehicle circulation could be identified within the urban canyon, but that, nevertheless, the local meteorology in particular and long-range transport of air masses had much more influence on the air quality than changes in the source intensity of road traffic. The first 5 days of the campaign were characterized by changeable, cloudy and wetter weather conditions which were finished by a cold front that passed over the city on 27 April. During the last 7 days, the weather was generally more stable, dry and warm, with a clear sky. It was disturbed by just one transition period when a fast-moving cold front with rain showers passed over the city during the night of 29 April,

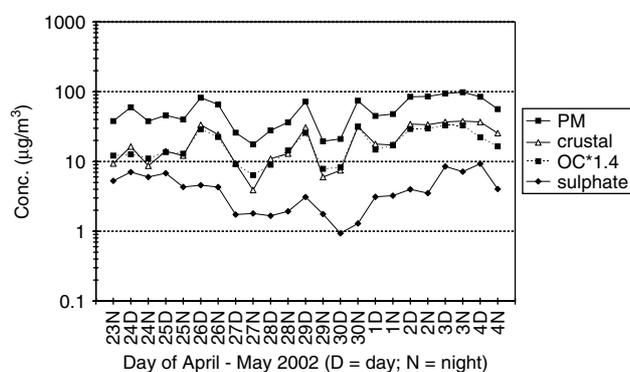


Figure 2. Time trends of the PM and three selected aerosol components in the PM₁₀ size fraction at the Rákóczi Street site in Budapest in spring 2002.

followed by a strong wind. As can be seen in Fig. 2, the atmospheric concentrations of the PM, organic matter and crustal matter in the first period were generally lower than in the second period. For sulfate a substantially different time trend is observed. This is consistent with the conclusion in our earlier study³ that this aerosol component is mainly transported from outside the city (and is therefore not related to traffic). In the first period of the campaign, the air masses originated mainly from Scandinavia or the North Atlantic, whereas in the second period, their source region shifted to southern Europe.⁵ The trajectories for the polluted last days of the campaign, when the highest levels of sulfate were noted, showed circulation above the Balkans for several days before the air masses reached Budapest.

Comparison with other studies

In our earlier study of Budapest aerosol,³ preliminary mass closure calculations were also carried out: they were only made for the fine (<2 µm AD) size fraction and were based on a very limited number of samples. For the Széna Square, it was found that the PM₂ aerosol consisted, on average, of 61% of organic aerosol, 6% of EC, 19% of ammonium sulfate, 6% of nitrate and 7% of crustal matter. These data are overall similar to those observed for the Rákóczi Street site (see Table 2), but in the present study a more than three times larger percentage was obtained for EC and that of crustal matter was twice as high. The median concentration data in Table 1 of our previous study can also be used to estimate the percentage contribution of the crustal component to the PM for both the fine and coarse size fractions in 1996 at Széna Square. This yields 9.7% of crustal matter for the fine PM and 50% of crustal matter for the coarse PM. Interestingly, the latter percentage is virtually identical with that observed for the coarse size fraction at the Rákóczi Street site.

Our aerosol chemical mass closure results can also be compared with those obtained for the kerbside sites of the European aerosol phenomenology exercise² (see Table 3). Organic matter and EC were the major contributors to the fine PM in that exercise, and this is also the case at our Budapest site. As far as the coarse and PM₁₀ aerosol are concerned, crustal matter (i.e. resuspended road dust) and organic matter are the major contributors to the PM for both the aerosol phenomenology sites and our Budapest site. In all three size fractions (fine, coarse and PM₁₀) organic aerosol and crustal matter are more pronounced at our Budapest site than at the aerosol phenomenology sites. At the latter sites, a substantial fraction of the PM remained unexplained, in particular for the coarse size fraction. The large contribution of crustal matter to the coarse aerosol at the Budapest site is consistent with the findings at other European kerbsides. Since this contribution is even larger at our site than at the other sites and since crustal matter is mainly associated with coarse particles, a smaller PM_{2.5}/PM₁₀ ratio is obtained at our site than elsewhere.

On average, about equal percentages of the PM₁₀ aerosol mass at our site are made up of organic aerosol and crustal matter, which both are essentially related to traffic, as was also concluded in the paper where the carbonaceous aerosol data from this study are discussed in detail.³

Table 3. Percentage contribution to the gravimetric aerosol mass (PM) from various aerosol types at kerbsides: comparison of results from the European aerosol phenomenology exercise² with data from the present study in Budapest

| Component | Fine ^a | | Coarse ^b | | PM ₁₀ | |
|------------------|-------------------|----------|---------------------|----------|------------------|----------|
| | Putaud | Budapest | Putaud | Budapest | Putaud | Budapest |
| Elemental carbon | 17 | 21 | 7 | 2 | 13 | 8 |
| Organic matter | 29 | 43 | 10 | 30 | 22 | 34 |
| Nitrate | 11 | 6 | 8 | 5 | 10 | 5 |
| Ammonium | 7 | 6 | 0 | 1 | 4 | 3 |
| Sulfate | 13 | 13 | 5 | 4 | 10 | 8 |
| Sea salt | 1 | 1 | 6 | 2 | 3 | 2 |
| Crustal matter | 8 | 14 | 37 | 49 | 19 | 36 |
| Unknown | 15 | -4 | 28 | 6 | 19 | 4 |

^a Fine indicates the size fraction <2.5 µm AD for Putaud *et al.*² and <2 µm AD for Budapest.

^b Coarse indicates the size fraction 2.5–10 µm AD for Putaud *et al.*² and 2–10 µm AD for Budapest.

CONCLUSIONS

A combination of different aerosol samplers, collection substrates and analytical techniques was used for arriving at a detailed elemental and chemical characterization of fine and coarse airborne particles in spring 2002 at a kerbside in Budapest. The concentrations of the fine and coarse PM and of the various elements resembled those obtained in spring 1996 at Széna Square in Budapest, which is 3 km from the site in the present study. For Pb and Br, substantially lower levels were found than in the earlier study because of the phasing out of leaded gasoline in Hungary. For other traffic-related elements, i.e. Cu and Sb, which were attributed to emissions from brake linings, substantially higher levels were noted in the current study than in the 1996 study.

The concentration data of the elements and species measured were used to examine the extent to which the gravimetrically PM could be reconstituted and thus aerosol chemical mass closure could be achieved. Such mass closure calculations were made for the fine, coarse and PM₁₀ size fractions. Crustal matter (i.e. resuspended road dust) and organic matter, which are both related to traffic, were the major components in the coarse and PM₁₀ aerosol.

The levels of the PM, the PM_{2.5}/PM₁₀ ratio and the large proportion of crustal matter in the coarse size fraction, as observed in this study, are consistent with observations from other kerbside sites in Europe. Several approaches can be used for obtaining the concentration of the crustal component, but the approach that was used in this work, and which uses data for the major crustal elements (i.e. Al, Si, Ca, Ti and Fe), is probably more accurate than that based on a single element (such as Al) or on measurement of the ash content. There are not many techniques that can provide accurate data for those five crustal elements in aerosol samples. PIXE, as used in this work, and XRF can deliver the required data and, of importance, the aerosol samples can be analysed non-destructively by PIXE and XRF. Many other techniques require dissolution of aerosol samples and of the crustal particles, and complete dissolution of the latter is difficult to achieve.

As at other kerbsides in Europe, around half of the PM₁₀ aerosol was made up of coarse particles at the Rákóczi Street site in spring 2002. The risk assessment of these coarse particles for human health suffers from inconsistent findings.²⁰ It is generally believed that fine (PM_{2.5}) particles constitute a much larger risk than the coarse particles. However, opposite findings have been obtained in some recent studies. For example, in a time-series study of air pollution, socioeconomic status and mortality in Vancouver, Canada, it was found that the daily mean coarse fraction (PM_{10-2.5}) was associated with increased cardiovascular mortality, whereas PM_{2.5} was not found to be an important predictor of mortality.²¹ In a study on the response of human alveolar macrophages to fine and coarse traffic-related urban aerosols in The Netherlands, it was found that coarse particles were more toxic than fine particles²² and that coarse particles decreased CD11b expression more than fine PM did.²³ Consequently, coarse particles and their characterization should not be neglected in studies of urban aerosols and of the effects of such aerosols on human health.

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