

Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary

Imre Salma^{a,*}, Xuguang Chi^b, Willy Maenhaut^b

^a Department of Chemical Technology and Environmental Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary

^b Ghent University, Institute for Nuclear Sciences, B-9000 Ghent, Proeftuinstraat 86, Belgium

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Abstract

As part of an international research project, aerosol samples were collected by several filter-based devices on Nuclepore polycarbonate membrane, Teflon membrane and quartz fibre filters over separate daylight periods and nights, and on-line aerosol measurements were performed by TEOM and aethalometer within an urban canyon (kerbside) and at a near-city background site in Budapest, Hungary from 23 April–5 May 2002. Aerosol masses in PM_{2.0}, PM_{10–2.0}, PM_{2.5}, PM₁₀ size fractions and of TSP were determined gravimetrically; atmospheric concentrations of organic (OC) and elemental carbon (EC) for PM_{2.5} (or PM_{2.0}), PM₁₀ fractions and for TSP were measured by thermal–optical transmission method. Repeatability of the mass determination by Nuclepore filters seems to be 5–6%. Collections on Teflon filters yielded smaller mass on average by 8(±12)% than that for the Nuclepore filters. Quartz filters overestimated the PM₁₀ mass in comparison with the Nuclepore filters due primarily to sampling artefacts on average by 10(±16)% at the kerbside. Tandem filter set-ups were utilised for correcting the sampling artefacts for OC by subtraction method. At the kerbside, the aerosol mass was made up on average of 35(±4)% of organic matter (OM) in the PM₁₀ fraction, while the contribution of OM to the PM_{2.5} mass was 43(±9)%. At the background, OM also accounted for 43(±13)% of the PM_{2.0} mass. On average, EC made up 14(±6)%, 7(±2)% and 4.5(±1.1)% of the mass in the PM_{2.5}, PM₁₀ fractions and TSP, respectively, at the kerbside; while its contribution was only 2.1(±0.5)% in the PM_{2.0} fraction in the near-city background. Temporal variability for PM mass, OC and EC concentrations was related to 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 can be identified within the urban canyon, nevertheless, the local meteorology in particular and long-range transport of air masses have much more influence on the air quality than changes in the source intensity of road traffic. Concentration ratios of OC/EC were evaluated, and the amount of secondary organic aerosol (SOA) was estimated by using EC as tracer for the primary OC emissions. Mean contribution and standard deviation of the SOA to the OM in the PM_{2.5} size fraction at the kerbside over daylight periods and nights were of 37(±18) and 46(±16)%, respectively. © 2003 Elsevier Ltd. All rights reserved.

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1. Introduction

In urban environments, it is the road traffic that is recognised to be one of the major sources of particulate

air pollution (Fenger, 1999; Colvile et al., 2001). Aerosol particles are emitted directly from the incomplete combustion of liquid fossil fuel and from friction acting on individual components (as tires and breaks), or are produced indirectly through chemical reactions in the air invoked by the emissions. Particulate matter (PM) is also formed by the incomplete combustion of the fuel

*Corresponding author. Tel.: +36-1-209-0555.

E-mail address: salma@para.chem.elte.hu (I. Salma).

that contains engine oil. Another significant portion of PM related to the traffic is just resuspended by the mechanical and thermal turbulence induced by moving vehicles and exhaust gas from street and unexposed soil surfaces. The principal aerosol components emitted by unleaded gasoline and diesel fuelled vehicles are organic carbon (OC) and elemental carbon (EC) (Fraser et al., 1999). Abundances of sulphates 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, 2002). Relative abundance of the components varies with individual fuel type and exact composition (including lubricants and additives), as well as with details of combustion conditions and exhaust treatment (catalytic conversion). The emissions are released in close proximity to human receptors; moreover, dilution and dispersion of the pollutants are significantly reduced in most cities by the urban (street) canyon effect of buildings alongside the roads (Vardoulakis et al., 2003). Since people in cities spend large amount of time indoors (Kruize et al., 2003), the major impact of road traffic emissions on human health occurs mainly inside the buildings that line city streets. In these microenvironments, however, the indoor concentrations of pollutants are influenced largely by the outdoor ambient air quality.

Despite the evident significance of OC and EC in atmospheric and environmental processes (e.g., Seinfeld and Pandis, 1998; Molnár et al., 1999), our knowledge on their concentrations, sources and/or formation mechanisms, and health implications is quite poor, particularly, in comparison with the inorganic aerosol components (Jacobson et al., 2000; Turpin et al., 2000). It is mainly due to the very large number of individual organic compounds that can have complex and sometimes similar chemical structure to each other (Rogge et al., 1993; Saxena and Hildemann, 1996; Mazurek et al., 1997), to the artefacts associated with their collection (Turpin et al., 2000; Kirchstetter et al., 2001), and to the discrepancies with respect to distinguishing between OC and EC (Schmid et al., 2001; Chow et al., 2001). In the framework of an international research project dealing with urban carbonaceous aerosol, an intensive field campaign was organised to collect aerosol samples with several filter-based systems and impactors, and to perform on-line (in situ) aerosol measurements in Budapest, Hungary. In the present study, atmospheric concentrations for the aerosol mass derived from different filter media are evaluated, OC and EC concentrations obtained by tandem filter subtraction method are presented, discussed and utilised further for estimating the abundance of the organic matter (OM) and secondary organic aerosol (SOA) in urban environments, relationship of the atmospheric concentrations with road traffic, local meteorology and long-range transport of air masses are investigated and interpreted.

2. Methods

2.1. Field work

The field work took place in parallel at two sites in Budapest from 23 April–5 May 2002 in the non-heating season. The main site was set-up on the first-floor balcony at a height of about 7.5 m above the street level at 5, Rákoczi Street in downtown (World Geodetic System 1998, WGS98 coordinates: latitude 47°29'37"N, longitude 19°03'38" E, altitude 111 m above the mean sea level, msl), and it can be classified as kerbside according to the criteria proposed by the European Environmental Agency (EEA, Larssen and Kozakovic, 2003). It was located within an urban (street) canyon, that is characterised by a length of about 2.0 km, a width from 25 to 40 m, and a typical height of 25–30 m. The canyon is subdivided into three main parts by two boulevards crossing it; the field work took place in the middle section that is approximately 600 m long. Hence, the street itself and its middle section belong to regular long street canyons, for which the bulk (of the perpendicular) synoptic air flow skims only over the canyon and produces a single vortex within the canyon (Hunter et al., 1992). This provides generally little ventilation of the canyon and favours air pollution build-up.

Several filter samplers, impactors and on-line instruments were deployed at this site. Among the filter samplers were: (1) Gent-type stacked filter unit (SFU) sampler with coarse and fine Nuclepore polycarbonate membrane filters in series (Maenhaut et al., 1994; Hopke et al., 1997), (2) SFU sampler with coarse polycarbonate filter and fine Teflon membrane filter in series, (3) PM_{2.5} filter holder containing two quartz filters in series, (4) PM₁₀ filter holder containing two quartz filters in series, and (5) open-faced filter holder without any size-fractionating inlet containing two quartz filters in series (total filter holder). The SFU samplers have PM₁₀ inlets, and the cut-off value of the aerodynamic diameter (AD) between the coarse and fine size fractions is 2 µm at the nominal air flow rate of 171/min. Hence, they separate the aerosol into a PM_{10–2.0} and a PM_{2.0} size fraction. All aerosol samples were collected separately over daylight time (from about 7:00 through 19:00 local daylight saving time, UTC+2) and night (from about 19:30 through 6:30). A total of 11 samples for daylight periods, and 12 samples for nights together with 6 field blanks were collected by each sampling device. Use was also made of a tapered element oscillating microbalance (TEOM, Rupprecht and Patashnick, model 1400A) with the filter heated to 50°C in order to prevent moisturing, and of a tape aethalometer (Magee Scientific, model AE-14U) to measure in situ PM and black carbon (BC), respectively. Both instruments were equipped with a PM_{2.5} inlet, and operated with a time resolution of

5 min all over the field work. The number of vehicles passing the street in both directions was obtained also on line from counting devices mounted into the roadway for controlling traffic lights near the sampling site. At one end of the street canyon, criteria air pollutants and some meteorological parameters were measured at a height of about 3.5 m above the street by an official air quality monitor station. Some synoptic meteorological parameters (above roof-top) were also recorded at a height of about 40 m above the ground on a meteorological mast located in a distance of 1.9 km from the kerbside.

The second sampling site was located on the western border of the city within the wooded campus of the Central Research Institute for Physics (KFKI campus, WGS98 coordinates: latitude 47°29'27"N, longitude 18°57'10"E, altitude 432 m above msl), and it can be classified according to the EEA criteria as near-city background (Larssen and Kozakovic, 2003). Since the prevailing wind direction in Budapest is northwest (Wallén, 1977), this site also represents the background (baseline) for the whole city. SFUs described for the kerbside as Nos. 1 and 2, and SFU samplers with coarse polycarbonate membrane filter and quartz fibre filter in series were employed here. The sampling inlets were installed at approximately 1.8 m above the ground. Daily aerosol samples were collected starting at about 8:00 local time. In total 6 polycarbonate filter pairs, 10 polycarbonate/Teflon filter pairs, and 11 polycarbonate/quartz filter pairs together with 4 field blank filter pairs were obtained. All samplers mentioned above operated at an air flow rate of 16–17 l/min, except for the total filter holder which was utilised at a flow rate of 120 l/min. All filters had a diameter of 47 mm; the quartz filters (Whatman QM-A) had same manufacturer lot (batch) number to ensure similar vapour adsorption properties (Kirchstetter et al., 2001), and were pre-heated at 550°C for at least 12 h in order to remove organic impurities.

2.2. Analytical methods and data treatment

The samples were placed into polycarbonate Petri slide dishes; the quartz filters were frozen at –25°C during transport and storage, the others were stored at a temperature of 2–4°C. Aerosol mass was obtained from weighing each filter before and after sampling on a microbalance with a sensitivity of 1 µg. The samples were pre-equilibrated before weighing at a temperature of 20°C and relative humidity of 50% for at least 24 h. Possible static electricity on the Nuclepore filters was eliminated. A 1.5-cm² rectangular portion of each quartz filter was analysed for OC and EC by a thermal–optical transmission (TOT) method (Birch and Cary, 1996) using a carbon analyser (Sunset Lab, USA) at the Ghent University. The method and instrument were evaluated

in an intercomparison test on the analysis of carbonaceous aerosols, and their performance was classified among the best results of the compared methods (Schmid et al., 2001). In order to convert the measured amount of C into OM, the OC data should be multiplied with a factor that is an estimate of the average molecular mass per carbon atom for the organic aerosol. Factors between 1.2 and 1.4 correspond to mildly oxidised organic material (Turpin et al., 2000); some recent studies suggest that a factor of 1.6 ± 0.2 describes better the oxidising urban environment (Turpin and Lim, 2001). We adopted the latter factor. In the present paper, use is also made of some complementary atmospheric concentrations obtained by particle-induced X-ray emission analysis of Nuclepore filters (Maenhaut et al., 1981). For converting the transmittance data from the aethalometer into BC values, a mass absorption efficiency of 19 m²/g (given by the manufacturer) was adopted. The BC data were also subjected to an empirical correction in order to reduce the discontinuities (jumps) in the series of data experienced when the filter tape is moved from a loaded area to an unexposed one (Reid et al., 1998).

3. Results and discussion

3.1. Atmospheric concentrations

Ranges and medians of the atmospheric concentration for PM mass obtained from the SFU samplers, PM_{2.5} and PM₁₀ filter holders at the kerbside and background site are summarised in Table 1. As expected, the concentrations were increased in the order of the series: background, kerbside over nights and kerbside over daylight periods by factors of 1.4 and about 2, respectively, for the PM_{10–2.0} fraction. In the PM_{2.0} fraction, smaller differences between the locations were observed in accordance with our previous studies (Salma et al., 2001). It can be seen from Table 1 that medians for the PM₁₀ (and PM_{2.0}) fractions determined by various filters differ from each other. The mean ratios of the individual mass concentrations revealed systematic deviations. It was inferred from them that the repeatability of the PM_{10–2.0} mass measurement by the SFU sampler with Nuclepore filters was 5–6%. For the PM_{2.0} fraction, the mean concentration ratio of Teflon data to Nuclepore data and its standard deviation was 0.92 ± 0.12 . Similar comparison of the quartz data to the Nuclepore data at the background site resulted in a mean and standard deviation of 1.3 ± 0.3 ; while for the PM₁₀ fraction at the kerbside, they were 1.10 ± 0.16 . (It has to be noted that the mean value for the background was based on a limited number of ratios only.) The fact that the quartz fibre filters usually result in significantly larger PM values than Nuclepore and Teflon membrane

Table 1
Ranges and medians of PM mass in $\mu\text{g}/\text{m}^3$ at a kerbside and near-city background site in Budapest

Site, collection period and filter type	PM2.0		PM10–2.0		PM10	
	Range	Median	Range	Median	Range	Median
Kerbside, daylight periods						
Polycarbonate membrane	9–26	22	12–68	36	21–94	60
Teflon membrane	9–24	14	—	—	20–92	44
Quartz fibre	(8–52 ^a)	(26 ^a)	—	—	28–107 ^b	54 ^b
Kerbside, nights						
Polycarbonate membrane	10–25	20	8–74	26	18–98	44
Teflon membrane	10–22	16	—	—	16–94	42
Quartz fibre	(12–55 ^a)	(31 ^a)	—	—	21–105 ^b	53 ^b
Near-city background, days						
Polycarbonate membrane	9–17	13	9–24	19	19–41	32
Teflon membrane	6–18	12	—	—	15–41	28
Quartz fibre	5–26	15	—	—	18–50	34

^aFor PM2.5 fraction.

^bMeasured by PM10 filter holder.

filters was also found in several earlier studies (e.g., Kirchstetter et al., 2001; Maenhaut et al., 2001). It is attributed to the collection process itself, which on the one side, alters the gas-particle equilibrium of a number of condensable constituents of the aerosol (like semi-volatile organics), and on the other side, causes adsorption of some gaseous compounds (mainly volatile organics) by the collection substrate (Jacobson et al., 2000; Turpin et al., 2000). Depending on the sampled volume, chemical composition, ambient air temperature, surface area of the filter and air flow face velocity, this can lead to both negative (evaporative) and positive (adsorptive) biases (Kirchstetter et al., 2001). It is generally assumed that the positive sampling artefacts prevail in collections with quartz fibre filters (Turpin et al., 2000). Nevertheless, the masses derived from the second quartz filters of the PM2.5, PM10 and TSP filter holder devices were not significant. They were below the detection limit (that was approximately $30\mu\text{g}$ for the quartz filters, and about $5\mu\text{g}$ for the Nuclepore and Teflon filters) in approximately half of the cases; for the remaining real data, an “overestimated” mean and standard deviation of $(6\pm 5)\mu\text{g}/\text{m}^3$ was obtained for the PM2.5 and PM10 filter holders. For the total filter holder, it was only $(1.4\pm 0.9)\mu\text{g}/\text{m}^3$ due to the larger air flow rate than for the size-fractionating filter holders (120 l/min vs. 17 l/min). The individual PM2.0/PM10–2.0 mass ratios obtained from the SFU samplers with Nuclepore filters are shown in Fig. 1. The daily concentration for PM2.5 mass from TEOM varied between 11 and $49\mu\text{g}/\text{m}^3$ with a median of $25\mu\text{g}/\text{m}^3$. The mass was on average by $13(\pm 12)\%$ smaller than that derived from the PM2.5 filter holder primarily due

to the increased temperature applied to the TEOM filter (Ayers et al., 1999). Mass for TSP as obtained from the total filter holder over daylight periods and nights varied in the range 48–239 and 28–142 $\mu\text{g}/\text{m}^3$, respectively, with medians of 136 and 92 $\mu\text{g}/\text{m}^3$, respectively.

With regard to OC and EC determined on the tandem quartz filters, the mean ratio back filter/front filter for OC was $15(\pm 2)\%$ for the PM2.5, and $10(\pm 2)\%$ for the PM10 fraction. For the total filter holder, a mean ratio of $4.5(\pm 1.3)\%$ was obtained, which is smaller again than for the size-fractionating filter holders due to the larger air flow face velocity. EC was insignificant (below the detection limit of about $0.2\mu\text{g}/\text{cm}^2$) on the back filter for all three samplers. In order to arrive at “artefact-free” OC results, the OC data for the back quartz filter were subtracted from the OC values for the front quartz filter (tandem filter subtraction method, Kirchstetter et al., 2001). The magnitude of the evaporative artefacts remains still uncertain in this method, however and, therefore, the OC concentrations presented should be considered as lower limit values. Nevertheless, the correction method performs well in urban environments (Viidanoja et al., 2002). Ranges and medians of OC, EC and BC concentrations in different size fractions at the kerbside and background site are summarised in Table 2. It can be seen from it that there was virtually no difference for the OC, EC and BC data obtained from the fractionating devices between the daylight periods and nights. It suggests that the sampling site was close to the emission sources to allow any significant photochemical transformation of the fresh aerosol. Concentrations of OC for the kerbside were increased with regard to the background approximately in the

Table 2

Ranges and medians of OC, EC concentrations (both derived from quartz filters by TOT method) and BC concentrations (measured by aethalometer) in $\mu\text{g}/\text{m}^3$ in different size fractions at a kerbside and near-city background site in Budapest

Site, collection period and size fraction	OC		EC		BC	
	Range	Median	Range	Median	Range	Median
Kerbside, daylight periods						
PM2.5	3.5–14	6.8	1.8–11	3.4	1.4–8.3	2.9
PM10	5.9–24	11	1.6–10	3.6	—	—
TSP	8.3–44	24	1.7–8.1	4.7	—	—
Kerbside, nights						
PM2.5	3.6–15	6.9	0.9–8.3	3.2	0.7–6.8	3.0
PM10	4.6–23	11	0.9–8.3	3.3	—	—
TSP	5.5–28	19	1.1–9.0	4.3	—	—
Near-city background, days						
PM2.0 ^a	2.9–5.5	4.1	0.19–0.64	0.33	—	—

^a Measured by SFU with quartz fibre fine filter.

same manner as PM2.0 mass, while median EC as an indicator of air pollution in urban areas was an order of magnitude larger than in the background. At the kerbside, the aerosol mass consisted on average of 35(\pm 4)% of OM in the PM10 fraction regardless on the time of day (for PM10–PM2.5 fraction, the contribution was 27(\pm 9)%), while for the PM2.5 fraction, there seems to be somewhat larger difference between the daytime periods and nights. Organic aerosol accounted for 46(\pm 8)% and 41(\pm 9)% of the mass, respectively. At the background, 43(\pm 13)% of the PM2.0 mass consisted of OM similarly to the kerbside. On average, EC made up 14(\pm 6)%, 7(\pm 2)% and 4.5(\pm 1.1)% of PM in the PM2.5, PM10 fractions and TSP, respectively, at the kerbside; while its contribution was only 2.1(\pm 0.5)% in the PM2.0 fraction in the near-city background. For the kerbside, mean PM2.5/PM10 ratios and associated standard deviations for PM, OC and EC derived from the filter holders were 53(\pm 14)%, 65(\pm 9)% and 96(\pm 6)%, respectively. (The individual concentration ratios for OC are indicated in Fig. 1.) It is noted that the mean PM2.0/PM10 mass ratio and standard deviation obtained from the SFU sampler with Nuclepore filters was 38(\pm 11)%. At the kerbside, OC in the PM10 fraction made up 69(\pm 10)% of OC in the TSP (for mass, it was 59(\pm 11)%). The BC data derived from the aethalometer were generally smaller than the EC data from the TOT method; the mean BC/EC ratio and its standard deviation were 0.86 \pm 0.07; nevertheless, their correlation coefficient was 0.98. A common explanation for the relatively small ratio is that the mass absorption efficiency (19 m²/g) as used for the aethalometer is not generally valid but may vary with aerosol composition and morphology, and changes with origin and age of the soot particles (Liousse et al., 1993).

The atmospheric concentrations presented are consistent with those previously found in urban environments around the world; the carbon data are at the lower middle range of the values reported. Typical OC concentrations vary from a few to some tens of $\mu\text{g}/\text{m}^3$ (e.g., Castro et al., 1999; Ruellan and Cachier, 2001; Hitzinger and Tohno, 2001; Viidanoja et al., 2002) but much larger values were also reported for polluted atmospheres. EC (or BC) concentrations in urban areas usually vary from 1.5 to 20 $\mu\text{g}/\text{m}^3$; they can be much larger near high-traffic roads in cities (Ruellan and Cachier, 2001) but much smaller carbon concentrations were also observed (Griffin et al., 2002).

3.2. Temporal variability

Fig. 1 displays temporal variability as 15-min averages together with 6-h smoothed curves for PM2.5 mass and BC, and as mean values for OC, EC and PM10–2.0 mass over daylight periods and nights. The PM2.5 mass and BC on-line data exhibited large variability. Correlation coefficient between them was 0.90 indicating that their main source was common, which is road traffic. Vehicles not only emit fine particles but also resuspend considerable amount of dust from the road and soil surfaces, and, therefore, significant correlations (with coefficients typically larger than 0.8) of PM10–2.0 with PM2.5 (and PM2.0) mass, BC (and EC) were observed as well. However, temporal variability for vehicle circulation as displayed in Fig. 2 showed clear periodicity, and, therefore, its correlation with the atmospheric concentrations was not significant (coefficients were generally smaller than 0.3). (It is recognised that the longer atmospheric residence time of the aerosol species also contributes to the poor correlation between these species

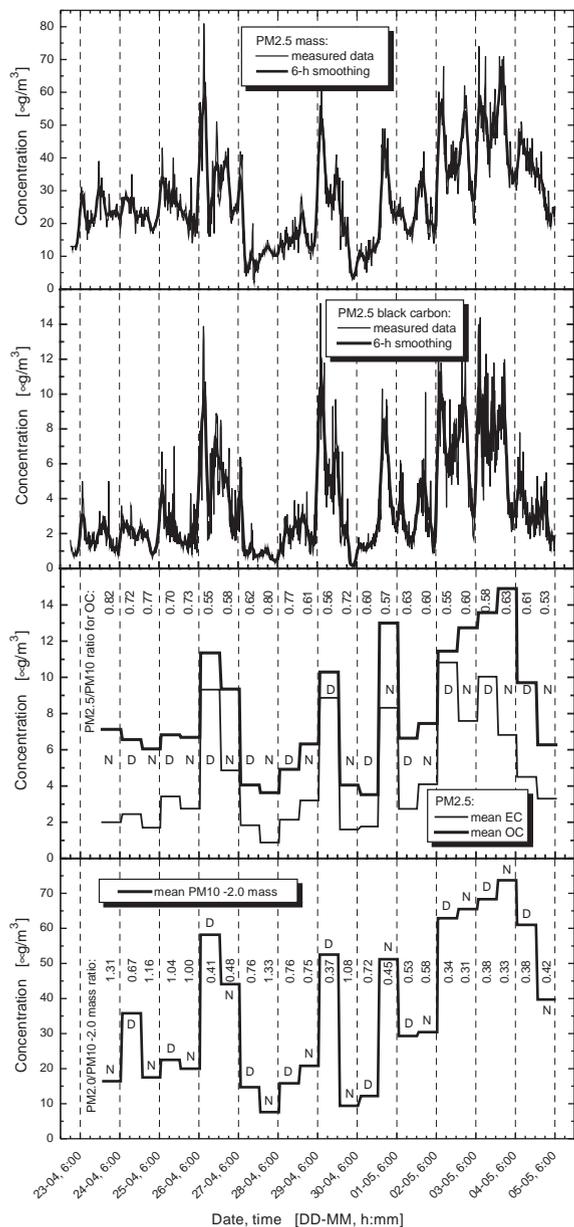


Fig. 1. Temporal variability as 15-min averages together with 6-h smoothed curves for PM2.5 mass and BC, and as mean concentrations for OC, EC and for PM10–2.0 mass over daylight periods and nights together with the PM2.5/PM10 concentration ratios for OC, and PM2.0/PM10–2.0 mass ratios at the kerbside. Daylight periods (D) and nights (N) of the field campaign are also indicated on the panels that show mean values.

and traffic.) On each day, two peaks—corresponding to the early morning and late afternoon rush hours—can be detected on the smoothed curve. The maximum and location of the daily peaks are very similar for workdays, and only differ from that for holidays. Effect of

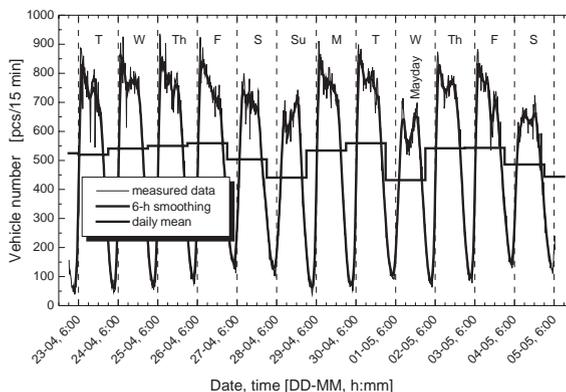


Fig. 2. Temporal variability for vehicle circulation as 15-min averages together with 6-h smoothed curves and daily mean values. Days of the week are also indicated.

the periodicity in traffic can be identified in the PM2.5 mass and BC temporal variability as well. They indeed exhibit two peaks each day in the corresponding time periods; nevertheless the absolute magnitude and relative intensity of the concentration peaks were very much different from day to day despite the constant mean traffic intensity on workdays, which is also depicted in Fig. 2. Hence, the large variation in the daily concentrations is caused by other effects than changes in the source intensity of road traffic, and their influence seems to be much more important. In order to investigate the effect of local meteorology and atmospheric dynamics, temporal variability for temperature measured in the synoptic air mass and within the urban canyon, solar radiation, synoptic horizontal wind speed (WS), and synoptic relative humidity together with precipitation is displayed in Fig. 3. It is worth mentioning that within the street canyon on average, the synoptic temperature increased by 2–3°C, the synoptic horizontal WS decreased to approximately 50%, and the synoptic relative humidity increased by 10–15%. The horizontal WS in the street canyon was typically below 1.7 m/s. It is seen that the field campaign can be divided into some periods from the meteorological point of view. The first 5 days were characterised by changing, cloudy and more wet weather conditions which were finished by a cold front that passed the city on 27 April. Over the last 7 days, the weather was generally more stable, dry and warm with clear sky. It was disturbed by just one transition period when a fast-moving front with rain showers passed the city over the night of 29 April with a strong wind after it. In the first period, the atmospheric concentrations were generally smaller than in the second period, and the mean values were changing irregularly from day to day but were usually larger for the daylight periods than for the nights. In the second period and, in particular, from 1

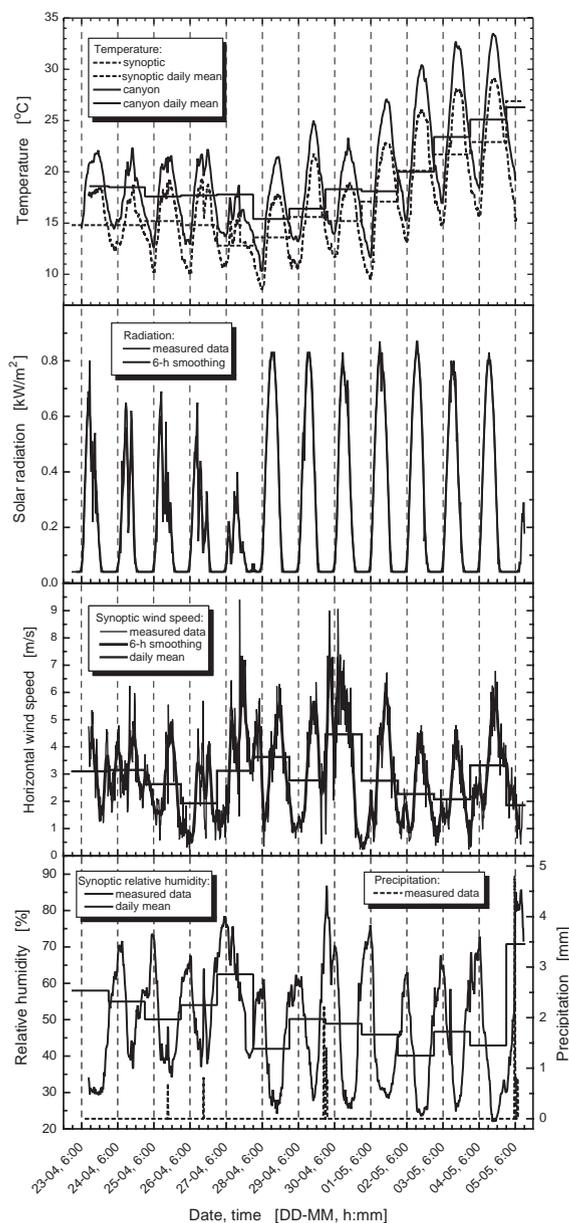


Fig. 3. Temporal variability for synoptic temperature and temperature measured within the street canyon together with daily means, for solar radiation, for synoptic horizontal WS with daily means, for relative humidity with daily means together with precipitation.

till 3 May when the synoptic wind was low, the atmospheric concentrations were generally larger and had increasing tendency. The build-up of the mean concentrations continued monotonically even from daylight period to night. High synoptic wind ($WS > 3.5 \text{ m/s}$) over the night of 29 and morning of 30 April coincided with small concentrations; the weather

front was associated with the smallest $\text{PM}_{2.5}$ mass, BC and OC concentrations. The precipitation that occurred on 25 April afternoon and on 26 April around noon decreased the aerosol concentration significantly though for short times (some hours) only, while the rainfall in combination with the front (on 29/30 April) caused better air quality for a longer period (almost a day). As shown in Fig. 1, the polluted time periods were characterised by small ratios as far as both $\text{PM}_{2.0}/\text{PM}_{10-2.0}$ mass ratios (0.3–0.4) and $\text{PM}_{2.5}/\text{PM}_{10}$ OC ratios (approximately 0.6) are concerned. It indicates that the local sources (especially resuspension) dominated. Smaller concentrations were associated with larger mass ratios (typically above 1) and OC ratios (typically between 0.7 and 0.8) indicating the effect of the long-range transport of air masses (Salma et al., 2001). Five-day three-dimensional isobaric backward trajectories were calculated using the program Hysplit4 for arrival levels of 800, 850 and 925 hPa and for arrival times of noon and midnight each day via Internet utilising FNL archive data (Hysplit, 2002). It was concluded from them that in the first period, the air masses originated mainly from Scandinavian or North Atlantic region, while in the second period the source region was shifted to Southern Europe. Trajectories for the polluted last days of the campaign showed circulation above the Balkans for several days before the air parcel reached Budapest.

3.3. Primary and SOA

Contribution of secondary (and primary) sources of OC (OC_{SEC}) to the OM was estimated simply by using EC as tracer for the primary OC emissions (Turpin and Huntzicker, 1995)

$$\text{OC}_{\text{SEC}} = \text{OC}_{\text{PM}_{2.5}} - \left(\frac{\text{OC}}{\text{EC}} \right)_{\text{PRIM}} \text{EC}. \quad (1)$$

It is supposed in this method that (1) primary OC and EC have the same source, and therefore, there is a representative OC/EC ratio for the primary aerosol ($(\text{OC}/\text{EC})_{\text{PRIM}}$), (2) EC is primary in origin. The requirements can be met in the $\text{PM}_{2.5}$ size fraction, since OC in the coarse (e.g., $\text{PM}_{10-2.0}$) fraction originates from other sources (e.g., pollen, spores, plant debris, tyre rubber and paved road dust) than EC. A weakness of the approach is that $(\text{OC}/\text{EC})_{\text{PRIM}}$ emission rates vary by source, and, therefore, the ratio is influenced by meteorology, time fluctuations in emissions, and local sources (e.g., vehicles, fireplaces, cooking operations, Seinfeld and Pandis, 1998). Under favourable meteorological conditions and close to the main primary source of OC, however, OC can sometimes be solely primary in origin. In many cases, $(\text{OC}/\text{EC})_{\text{PRIM}}$ was estimated from atmospheric concentrations assuming that either the lowest observed OC/EC

ratio represents the pure primary aerosol (Castro et al., 1999), or the data for the days when SOA formation could obviously be excluded were averaged (Strader et al., 1999). In these studies, $(OC/EC)_{\text{PRIM}}$ ratios between 1.1 and 2.9 were obtained. For pure primary aerosol from diesel engines, a ratio of 1.1 was measured (Kleeman et al., 2000). It has to be emphasised that the calculation approaches yield semi-quantitative information only because of the large uncertainties associated with them.

Range of the OC/EC ratios in the PM_{2.5} size fraction and their mean with standard deviation at the kerbside were 1.06–4.12, and 2.2 ± 0.7 , respectively. In the present study, temporal variability and relationships of OC/EC ratio with different meteorological parameters and atmospheric concentrations were examined in order to separate a reasonable subset of ratios for estimating the $(OC/EC)_{\text{PRIM}}$. The temporal variability for OC/EC ratio is presented in Fig. 4. Interestingly, it is seen that the nights exhibited generally larger values than the daylight periods due possibly to variation in the meteorology (especially in the boundary layer height), to ageing of organic aerosol, to the transport of SOA produced during the previous day to the receptor site, and partially due to night time chemistry (Seinfeld and Pandis, 1998; Griffin et al., 2002). The data for the sampling periods D4, D7, D10 and D11 (daylight times on 26 and 29 April, 2 and 3 May, respectively) exhibited the lowest ratios, and the values for the previous nights were also small. By examining the scatter plots of OC/EC ratios with the other variables and co-pollutants, it can be concluded that no obvious dependency of the OC/EC ratios on the mean ambient temperature, solar radiation, O₃, NO, fine-fraction S (used as indicator for sulphate, Salma et al., 2001) and CO mean concentrations could be identified. Nevertheless, the periods selected were associated with small fine S (hence sulphate) concentrations which possibly indicates the

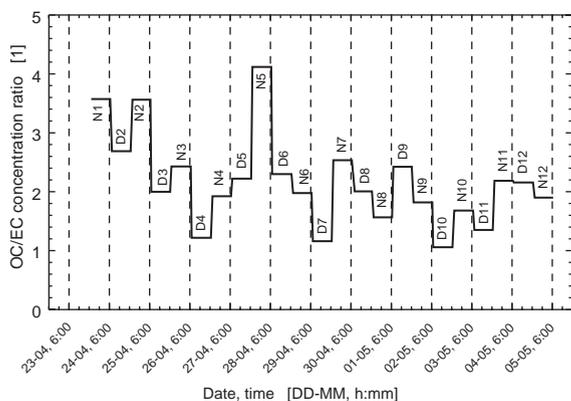


Fig. 4. Temporal variability for OC/EC concentration ratio at the kerbside. Daylight periods (D) and nights (N) of the field campaign are also indicated.

small portion of long-range transported SOA (since atmospheric oxidation of SO₂ to sulphate is slow, sulphate was considered here to be a tracer for the long-range transport), and with low levels of O₃ (the smallest daylight period O₃ concentrations over the whole campaign) which may indicate little local photochemical activity. Significant correlation of OC/EC ratios with synoptic horizontal WS over separate daylight times and nights, and with SO₂ were obtained; correlation coefficients were 0.88, 0.65 and 0.69, respectively. Scatter plot of OC/EC ratio and WS is shown in Fig. 5 as example. The periods selected were characterised by the lowest wind over the daylight periods, and by the largest SO₂ concentrations which both suggest that the local sources (firstly road traffic) dominated. In addition, the correlation coefficient between OC/EC ratio and EC was -0.78 , and EC concentrations were the largest for these four samples (indicating strong primary OM emissions). Based on the above arguments, the $(OC/EC)_{\text{PRIM}}$ ratio was estimated by the mean value of the four ratios selected, which was 1.20 ± 0.12 . (It is noted that the OC/EC ratios for the PM_{2.0} size fraction in the background varied from 9 to 16 with a mean and standard deviation of 12 ± 2 .) The OC_{SEC} data calculated for the kerbside were further utilised to derive the concentrations of SOA by applying the same conversion factor (of 1.6) as in calculating the OM mass from the OC values since there is no aggregate information available on the different chemical nature of

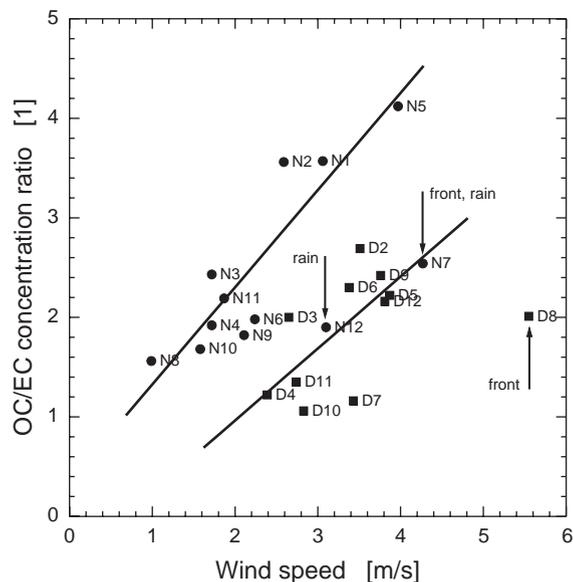


Fig. 5. Scatter plot of OC/EC ratio with the synoptic horizontal WS at the kerbside. Daylight periods (D) and nights (N) of the field campaign are also indicated. Data marked by arrows correspond to changing weather situations, and, therefore, were left out from the correlation calculation.

the SOA and OM (Griffin et al., 2002). Contributions of the SOA to the OM mass in the PM_{2.5} size fraction at the kerbside over daylight periods and nights were in the range 1–55% and 23–71%, respectively, with mean and standard deviation of 37(±18)% and 46(±16)%, respectively. Hence, primary OM dominated usually, but the SOA exceeded the primary contribution during some photochemical episodes. Finally, no significant correlation between the SOA and ambient temperature, horizontal WS, solar radiation, relative humidity, traffic intensity, EC, NO, CO, SO₂ and fine S concentrations could be observed; while the correlation coefficients of SOA and PM mass in all size fractions measured, O₃ and OC concentrations were about or above 0.7. This supports that formation of the SOA is advanced by oxidising of reactive organic gases by gas-phase reactions in the polluted urban atmospheres where partitioning to the aerosol phase takes place further from the emission sources of the (anthropogenic) precursor gases mainly via condensation on the available particles.

4. Conclusions

During an intensive aerosol collection and measuring campaign in the non-heating season, PM mass, OC and EC concentrations were determined for urban canyon and background environments. Their characteristics and temporal variability were investigated, and were linked to road traffic, local meteorology and long-range transport. Contribution of OM to PM was derived, and, finally, abundance of SOA was estimated. Based on the results and their relationships, it can be concluded that EC is an excellent surrogate for vehicle related emissions, and that there was a unambiguous connection between fine (or coarse) aerosol and road traffic but a clear and more important influence of local meteorological data and long-range transport of air masses (than of changes in source intensity) on the air quality was observed. We found that an important part of PM is generated by the turbulence created and influenced by road traffic, so this portion of emissions would not be decreased by reducing particulate emissions of vehicular exhaust. OC/EC ratios were characterised by sudden changes in time; variability of OC and EC was likely influenced by WS, mixing height and characteristics.

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