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Source apportionment of carbonaceous chemical species to fossil fuel combustion, biomass burning and biogenic emissions by a coupled radiocarbon–levoglucosan marker method

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Abstract. An intensive aerosol measurement and sample collection campaign was conducted in central Budapest in a mild winter for 2 weeks. The online instruments included an FDMS-TEOM, RT-OC/EC analyser, DMPS, gas pollutant analysers and meteorological sensors. The aerosol samples were collected on quartz fibre filters by a low-volume sampler using the tandem filter method. Elemental carbon (EC), organic carbon (OC), levoglucosan, mannosan, galactosan, arabitol and mannitol were determined, and radiocarbon analysis was performed on the aerosol samples. Median atmospheric concentrations of EC, OC and $PM_{2.5}$ mass were 0.97, 4.9 and 25 $\mu g\,m^{-3}$, respectively. The EC and organic matter (1.6 × OC) accounted for 4.8 and 37 %, respectively, of the $PM_{2.5}$ mass. Fossil fuel (FF) combustion represented 36 % of the total carbon (TC = EC + OC) in the $PM_{2.5}$ size fraction. Biomass burning (BB) was a major source (40 %) for the OC in the $PM_{2.5}$ size fraction, and a substantial source (11 %) for the PM_{10} mass. We propose and apply here a novel, straightforward, coupled radiocarbon–levoglucosan marker method for source apportionment of the major carbonaceous chemical species. The contributions of EC and OC from FF combustion (EC_{FF} and OC_{FF}) to the TC were 11.0 and 25 %, respectively, EC and OC from BB (EC_{BB} and OC_{BB}) were responsible for 5.8 and 34 %, respectively, of the TC, while the OC from biogenic sources (OC_{BIO}) made up 24 % of the TC. The overall relative uncertainty of the OC_{BIO} and OC_{BB} contributions was assessed to be up to 30 %, while the relative uncertainty for the other apportioned species is expected to be below 20 %. Evaluation of the apportioned atmospheric concentrations revealed some of their important properties and relationships among them. EC_{FF} and OC_{FF} were associated with different FF combustion sources. Most EC_{FF} was emitted by vehicular road traffic, while the contribution of non-vehicular sources such as domestic and industrial heating or cooking using gas, oil or coal to OC_{FF} was substantial. The mean contribution of BB to EC particles was smaller by a factor of approximately 2 than that of road traffic. The main formation processes of OC_{FF}, OC_{BB} and OC_{BIO} from volatile organic compounds were jointly influenced by a common factor, which is most likely the atmospheric photochemistry, while primary organic emissions can also be important. Technological improvements and control measures for various BB appliances, together with efficient education and training of their users, in particular on the admissible fuel types, offer an important potential for improving the air quality in Budapest, and likely in other cities as well.

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1 Introduction and objectives

Carbonaceous chemical species are abundant and important components of atmospheric aerosol particles in urban, rural and continental background environments from many aspects (e.g. Fuzzi et al., 2015, and references therein). They can affect the climate, air quality, visibility, human health, ecosystems and built environment on local, regional and sometimes even on larger (global) spatial scales. Their major source types include both primary emissions and secondary particle formation processes, which are related mainly to fossil fuel (FF) combustion, biomass burning (BB) and biogenic emissions. Characterization of particles from various sources and quantification of the contributions of the sources are necessary to understand the role and impacts of atmospheric aerosol in general and specifically in cities as well. Moreover, various forms of BB, in particular wood burning in household appliances for heating, cooking or pleasure, in boilers and industrial power plants are expected to rise in the coming years, which could lead to larger concentrations of some groups of organic molecules and particulate matter (PM) mass on shorter (seasonal) timescales or as a trend (Saarikoski et al., 2007; Gilardoni et al., 2011; Saarnio et al., 2012; Bernardoni et al., 2013; and references therein). The large number, complex character, spatial and temporal variability of the emission and formation sources of carbonaceous chemical species together with their dynamically changing transformation processes and atmospheric conditions make the quantification of the source types or their inventory-based source assessment challenging. There are, however, some receptor models, which facilitate the source apportionment on the basis of atmospheric concentrations and some model-derived properties. These include the source-specific marker methods, the so-called Aethalometer model (based on the wavelength dependence of the optical absorption coefficient, and thus not confined to the Aethalometer data only) and various multivariate models. The marker methods – such as the radiocarbon or levoglucosan methods – are advantageous from the point of view that they do not require many samples or extensive data sets and are quite straightforward; therefore, they are often the choice for source apportionment studies.

BB produces a large variety of organic molecules. Of them, three monosaccharide anhydrides, namely levoglucosan (LVG, 1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$; Simoneit et al., 1999) and its stereoisomers mannosan (MAN, 1,6-anhydro-β-D-mannopyranose) and galactosan (GAN, 1,6-anhydro-β-D-galactopyranose; Nolte et al., 2001) are abundant organic species in the aerosol phase. They are formed during pyrolysis of the bulk materials of wood such as cellulose and hemicellulose at temperatures higher than 300 °C (Caseiro et al., 2009). Levoglucosan, which is the most abundant of them (Simoneit et al., 1999), is considered reasonably stable in the atmosphere towards photolysis and acid-catalysed hydrolysis for at least 10 days (Locker, 1988; Fraser and Lakshmanan, 2000; Simoneit et al., 2004). Its lifetime can, however, be decreased by chemical reactions with OH radical in the aqueous phase under high relative humidities (Hennigan et al., 2010; Hoffmann et al., 2010). Such conditions can be important in tropical areas or for long-range-transported, aged smoke plumes in summer. Nevertheless, LVG has been regarded to be a conservative molecular marker in most studies on BB (Simoneit et al., 1999; Zdráhal et al., 2002; Puxbaum et al., 2007; Saarikoski et al., 2008; Szidat et al., 2009; Maenhaut et al., 2012). The ratios of the stereoisomers can provide information on the relative proportion of hardwood and softwood burning. Levoglucosan can, however, also be produced in the pyrolysis of lignite (Fabbri et al., 2009) and peat (Iinuma et al., 2007; Kourtchev et al., 2011), which can complicate the apportionment procedure.

There are additional organic markers that can be determined jointly with the monosaccharide anhydrides, and which can supply useful information on some bioaerosols. These are two sugar alcohols, namely arabitol (ARL, (2R,4R)-pentane-1,2,3,4,5-pentol, $C_5H_{12}O_5$) and mannitol (MAL, (2R,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol, $C_6H_{14}O_6$), which ordinarily originate from metabolic activity of fungi and bacteria (Bauer et al., 2008; Burshtein et al., 2011; Gosselin et al., 2016). Fungi are important microorganisms because they contribute substantially to the decomposition of organic material. Most fungi emit spores into the air. The fungal spores can irritate the respiratory system, cause allergies or infectious acute diseases, and chronic illnesses, in particular in indoor environments. Their presence in the air is commonly quantified by the spore count method, which provides their contribution in terms of particle number. The spores contain ARL and MAL as storage substances. Correlation between the fungal spore count and their concentration was verified in the PM_{10} size fraction (Bauer et al., 2008; Zhang et al., 2010). Mannitol is one of the common energy and carbon storage molecules produced by various organisms, including bacteria, yeasts, fungi, algae, lichens and many plants, but its major suspension into the air is often expected to be linked primarily to fungal spores under ordinary atmospheric conditions.

The radiocarbon method allows one to distinguish between the carbon originating from fossil and non-fossil (contemporary) sources by determining the isotopic ratios of C (Szidat et al., 2006, and references therein). Secondary neutrons generated by cosmic radiation in the upper atmosphere interact with atmospheric N and produce radioactive ^{14}C with a half-life and standard deviation (SD) of 5730 ± 40 years. This radionuclide is taken up by the living biosphere mainly via photosynthesis and the food chain, which results in a contemporary isotopic abundance of ^{14}C in the biomass. The FF formation in buried dead organisms detached from the atmospheric interactions takes $>10^{7-8}$ years, during which the ^{14}C content decays and becomes negligible in FF. The radiocarbon measurement results are usually expressed as the ^{14}C / ^{12}C isotope ratios in the samples relative to that for the unperturbed atmosphere in the reference year of 1950 (Burr and Jull, 2009). Source apportionments based solely on this method usually take advantage of the fact that elemental carbon (EC) is introduced into the atmosphere either from FF combustion or BB exclusively as primary particles. The apportionment is achieved by determining the C isotopic ratio specifically for EC (and organic carbon, OC) separated by different thermal treatment (and later also for other carbonaceous fractions such as water-soluble or water-insoluble OC) and combining this information with atmospheric concentrations and emission factors (e.g. Szidat et al., 2006, 2009; Minguillón et al., 2011; Zhang et al., 2012; Bernardoni et al., 2013).

In earlier studies in Budapest, the mean contribution of organic matter (OM, OM = 1.4 × OC, where 1.4 is the OM/OC mass conversion factor; see Sect. 2.2) to the $PM_{2.5}$ mass was 43 % for both a street canyon (kerbside) in the city centre and the near-city background (Salma et al., 2004; Maenhaut et al., 2005). Elemental carbon made up, on average, 14 % of the $PM_{2.5}$ mass in the street canyon, while its contribution in the near-city background was much smaller, 2.1 %. Source apportionment of C in Budapest has not been assessed so far. There has been an increasing and definite need to determine the trends in the concentration levels, abundances of the major carbonaceous species, and, in particular, to quantify the contribution and relevance of FF combustion, biogenic emissions and BB in cities all over Europe. These goals can be achieved by combining several online and offline measurement methods. For the source apportionment, we propose here a coupled straightforward approach based on both radiocarbon and LVG marker methods. The main objectives of the present paper are to demonstrate the potential of the analytical data set derived by several methods, which are based on different principles and which yield data with various time resolutions; to quantify the contributions of FF combustion, BB and biogenic sources by the coupled radiocarbon–LVG marker method for a winter season; to study the properties of and relationship among the apportioned carbonaceous species; to interpret their consequences on the air quality in Budapest as a central European city; and to discuss the details and potential of wood burning in the area. This paper is to be followed by another study, which will focus on the source apportionment methods based on several online optical data sets, and their comparison to the present model.

2 Methods

2.1 Measurement and sample collection campaign

Online aerosol measurements and collection of aerosol samples were performed at the Budapest platform for Aerosol Research and Training (BpART) facility in Budapest (Salma et al., 2016). The site represents a well-mixed, average atmospheric environment for the city centre. The sampling inlets and sensors were set up at heights between 12 and 13 m above the street level of the closest road. The aerosol campaign took place continuously for 2 weeks from Tuesday 25 February to Tuesday 10 March 2014. Calm weather situations were present throughout the campaign; milder than ordinary winter air temperatures occurred, and there was no snow cover in the region at all.

The online aerosol instruments included (1) a tapered element oscillating microbalance with a filter dynamics measurement system (FDMS-TEOM 1400a; Rupprecht and Patashnick, USA) for the PM mass; (2) a semi-continuous OC and EC analyser (RT-OC/EC analyser, Sunset Laboratory, USA); (3) a differential mobility particle sizer (DMPS; Salma et al., 2011) for measuring particle number size distribution in a diameter range of 6–1000 nm; and (4) a LI-840 CO_2 analyser with a single-path, dual-wavelength nondispersive infrared detection system (LI-COR, USA). The aerosol sampling inlets contained upper-size sharp-cut cyclones (URG, USA) with a 50 % efficiency at an aerodynamic diameter of 2.5 µm. Pallflex Tissuquartz filters (Pall, USA) were used in the RT-OC/EC analyser, and the EUSAAR2 thermal protocol (He gas: 200 °C for 120 s, 300 °C for 150 s, 450 °C for 180 s and 650 °C for 180 s; mixture of 2 % O_2 in He: 500 °C for 120 s, 550 °C for 120 s, 700 °C for 70 s and 850 °C for 80 s; Cavalli et al., 2010) was selected for the measurements. This protocol was initially developed for background sites, and was later extended to urban areas. The time resolution (τ) of the FDMS-TEOM and DMPS systems was ca. 10 min. The RT-OC/EC analyser typically collected samples for approximately 2 h 45 min, while the analysis took place for 15 min, which yielded measured data every 3 h. CO_2 was measured with $\tau = 1$ min. The concentration of some criteria pollutant gases was obtained from the closest measurement station of the National Air Quality Network in Budapest at a distance of 1.6 km from the BpART facility in the upwind prevailing wind direction. SO_2, O_3 and NO_x were determined by UV fluorescence (Ysselbach 43C), UV absorption (Ysselbach 49C) and chemiluminescence (Ysselbach 42C) methods, respectively, with $\tau = 1$ h. Basic meteorological data including air temperature outside and inside the BpART (T_{out} and T_{in}, respectively), relative humidity outside and inside the platform (RH_{out} and RH_{in}, respectively), global solar radiation (GRad), wind speed (WS) and wind direction (WD) were measured by an on-site meteorological station with $\tau = 10$ min.

The aerosol samples were collected by using a low-volume ($1\ m^3\ h^{-1}$), Gent-type stacked filter unit (SFU) sampler (Maenhaut et al., 1994). The collection device was loaded with a coarse Nuclepore filter in the first stage, and two, front and back Pallflex Tissuquartz quartz fibre filters directly on top of each other in the second stage. All three filters had a diameter of 47 mm. The quartz filters had the same manufacturer lot (batch) number to ensure their identical adsorption properties, and had been pre-baked at a temperature of 550 °C for 12 h prior to sampling to remove possible organic contaminants. The Nuclepore filters and front quartz filters collect $PM_{10-2.5}$ and $PM_{2.5}$ particles, respectively. A total of 14 exposed filter sets for the daylight periods (from about 06:30 to 18:20 local time, UTC+1), and 14 exposed filter sets for the nights (from about 18:30 to 06:20) together with two field blank sets were obtained. The filters were placed in polycarbonate Petri slide dishes, and were stored frozen until analysis.

2.2 Analyses of aerosol samples and data treatment

The PM mass concentrations were obtained by weighing each Nuclepore and front quartz filter twice before and twice after sampling on a microbalance with a sensitivity of 1 µg. The filters were pre-equilibrated before weighing at a temperature of ca. 20 °C and RH of 50 % for at least 24 h. The gravimetric data for the real exposed filters were corrected for the net PM mass using the field blank filters. The mean blank masses for the Nuclepore and front quartz filters corresponded to 4 ± 2 and $8 \pm 7\,\mu g\,m^{-3}$, respectively. Typical blank values with uncertainties for various filter types in the SFU collection device were determined earlier for a larger number of samples sets, and their role in calculating the mass concentrations was discussed (Salma et al., 2004). One or two punches with an area of $1.5\,cm^2$ of the quartz filters were analysed by the thermal–optical transmission (TOT) method (Birch and Cary, 1996) by a laboratory OC / EC analyser (Sunset Laboratory, USA) using the NIOSH2 thermal protocol (He gas: 310 °C for 60 s, 480 °C for 60 s, 615 °C for 60 s and 870 °C for 90 s; mixture of 2 % O_2 in He: 550 °C for 45 s, 625 °C for 45 s, 700 °C for 45 s, 775 °C for 45 s, 850 °C for 45 s and 870 °C for 120 s). This protocol was selected for comparative reasons since it had been also employed for our earlier studies in Budapest, and this choice facilitated the comparison of our present results to the earlier data as well (Salma et al., 2004; Maenhaut et al., 2005). All measured OC and EC data for the front filters were above the determination limit, which was approximately $0.6\,\mu g\,C\,cm^{-2}$. The overall relative uncertainty of the TOT analysis was estimated to be $5\,\% + 0.2\,\mu g\,C\,cm^{-2}$ for both OC and EC (Viana et al., 2006). The adsorptive sampling artefacts of the organic constituents were corrected by subtracting the concentration of OC for the back quartz filters from the corresponding OC data for the front quartz filters according to the tandem filter method (Kirchstetter et al., 2001, and references therein). The back / front concentration ratios for the blank-corrected data ranged from 1.7 to 48 % with a mean and SD of $22 \pm 13\,\%$. Elemental carbon was near or below the determination limit on the back quartz filters, with a mean back / front ratio and SD of $5.5 \pm 5.6\,\%$. For this reason, no correction for sampling artefact was adopted for EC. In order to convert the concentrations of OC into OM, the OC data were multiplied by an OM/OC conversion factor of 1.6, which was suggested for oxidizing urban environments (Turpin and Lim, 2001; Russell, 2003). It was estimated that the relative uncertainty associated with the conversion is approximately 30 % (Maenhaut et al., 2012). A filter section with an area of $1.7\,cm^2$ of each front quartz filter was also analysed for LVG, MAN, GAN, ARL and MAL by gas chromatography–mass spectrometry (GC/MS) after extraction and trimethylsilylation using a modified method of Pashynska et al. (2002). The extraction was now done with methanol. The recovery standard in the present work was methyl O-L-xylanopyranoside. The GC temperature programme was also slightly modified to the following: an initial temperature of 100 °C was maintained for 2 min, it was followed by a gradient of $3\,°C\,min^{-1}$ to 200 °C, with the latter kept constant for 2 min, then followed by a gradient of $30\,°C\,min^{-1}$ to 310 °C, after which this temperature was preserved for 2 min. The monosaccharide anhydrides and sugar alcohols were obtained above the determination limit (which was estimated to be approximately $0.1\,ng\,m^{-3}$) in all samples, while they were not measured on the back quartz filters.

Three-quarter sections of the front and back quartz filters were subjected to well-maintained C isotope analysis of the total carbon (TC = EC + OC) content by using accelerator mass spectrometry (AMS). The filter sections were treated in an offline combustion system, which was designed specifically for this purpose (Molnár et al., 2013). The samples were placed in test tubes together with 15 mg of MnO_2 and 5 mg of Ag wool reagents, and the tubes were evacuated to vacuum ($< 5 \times 10^{-8}$ bar). The carbonaceous compounds were oxidised quantitatively to CO_2 gas by the MnO_2 at a temperature of 550 °C for 3 days. The CO_2 gas was cryogenically separated from the other combustion gases and water vapour, and it was purified in a dedicated vacuum line. The amount of CO_2 was determined by using a high-precision pressure measurement. The sample preparation yield was calculated from the C mass derived by the pressure measurement and the uncorrected TC obtained from the laboratory OC / EC analyser. The CO_2 gas samples containing 20–150 µg C were introduced into a Mini Carbon Dating System spectrometer (Enviro-MICADAS, IonPlus, Switzerland) via its dedicated gas ion source interface with He carrier gas at a constant flow rate. The field blank filters were prepared identically to the front filters. In addition to the aerosol and field blank filters, several procedure blank samples were also prepared by filling the test tube with fossil CO_2 gas and by following an identical sample preparation treatment as for the filters in order to determine the analytical procedure blank value for the AMS data. Based on these experiments, a mean analytical procedure blank correction factor and SD of $1.0 \pm 0.1\,\mu g$ modern C (see below) per sample was obtained, and it was adopted for all aerosol filters. The ^{14}C / ^{12}C ratios were also corrected for isotopic fractionation by using the ^{13}C / ^{12}C ratios (Wacker et al., 2010) that were obtained simultaneously in the actual AMS measurements. The ^{14}C / ^{12}C isotopic ratios derived were also normalized to that of the oxalic acid II standard reference material (NIST 4990C, USA), and the measurement results were expressed as fraction of modern carbon (f_{M}), which denotes the $^{14}\mathrm{C}\,/\,^{12}\mathrm{C}$ ratio of the samples relative to that of the unperturbed atmosphere in the reference year of 1950 (Burr and Jull, 2009). As the majority of the currently combusted firewood was growing during the interval of atmospheric nuclear fusion bomb tests in the late 1950s and early 1960s, the aerosol particles originating from recent wood contain higher radiocarbon than corresponds to the present atmosphere by a mean factor of 1.08 for the Northern Hemisphere (Szidat et al., 2009; Heal et al., 2011). Thus, the fraction of contemporary carbon (f_{C}) was calculated as $f_{\mathrm{C}} = f_{\mathrm{M}}/1.08$. The same correction factor was also adopted for the TC from biogenic sources, although it is expected to show a somewhat smaller value due to its equilibrium with the recent atmospheric C isotope ratio. The differences in the f_{C} caused by the refined correction factor are ordinarily small when compared to the method uncertainties (Minguillón et al., 2011), and therefore this effect was neglected in the present study. Finally, the remaining fraction of the TC was regarded to be the fraction of fossil carbon ($f_{\mathrm{FF}} = 1 - f_{\mathrm{C}}$).

The FDMS-TEOM resulted in ca. 2000 data rows during the aerosol campaign; 99 % of the base mass concentrations were >5 $\mu\mathrm{g\,m^{-3}}$, which is the determination limit of the method. The reference mass concentration, which represents the correction for semi-volatile chemical species and water vapour, varied from -10.3 to $2.0\,\mu\mathrm{g\,m^{-3}}$ with a median of $-3.3\,\mu\mathrm{g\,m^{-3}}$. It corresponds to a median correction factor of 15 % in absolute value, which is in line with previous data. The sum of the $\mathrm{PM}_{2.5}$ mass derived by the FDMS-TEOM and the $\mathrm{PM}_{10-2.5}$ mass obtained from the SFU sampler was considered as the PM_{10} mass. The movement of the air masses was assessed by backward trajectories, which were generated by using the air parcel trajectory model HYSPLIT v4.9 with an option of vertical velocity mode (Draxler and Rolph, 2013). The Embedded Global Data Assimilation System meteorological database was utilized for the modelling. Trajectories arriving at the receptor site at a height of 200, 500 and 2300 m above the ground level at 06:00 and 18:00 local time were calculated.

3 Results and discussion

Further online data together with data validation and its conclusions for the experimental methods are to be discussed in a separate article.

3.1 Averages

The individual online concentrations and meteorological data were averaged for the 2×14 sampling time periods. Their ranges, overall medians, means and SD are shown in Table 1 together with the atmospheric concentrations of chemical species obtained from the SFU filters. The concentrations observed are consistent with those previously reported for urban environments in Europe (Putaud et al., 2010). The aerosol data are also in line with the decreasing tendency in the PM mass, OC and EC identified for the city centre of Budapest for the beginning years of the 2000s (Salma et al., 2004; Salma and Maenhaut, 2006). The EU 24 h health limit value for PM_{10} mass of $50\,\mu\mathrm{g\,m^{-3}}$ was exceeded three times, on 25, 26 and 27 February (the first 3 days of the campaign). The aerosol particle number and pollutant gas concentrations correspond to ordinary levels in central Budapest (Salma et al., 2016), and the meteorological data indicated calm weather situations without extremes, but milder air temperatures than typically present at this time of the year. The levels of monosaccharide anhydrides and sugar alcohols were determined in Budapest for the first time. The median concentrations of LVG, MAN and GAN are comparable to those in other urban sites in Europe in winter (Szidat et al., 2009, and references therein; Maenhaut et al., 2012). They exhibit a pronounced seasonal variation with a maximum in winter followed by autumn, spring and summer (Caseiro et al., 2009; Kourtchev et al., 2011; Maenhaut et al., 2012), which indicates that BB preferentially occurs in the coldest months. During winter in Europe, residential wood burning is the major source of LVG, and the observed concentrations are typically < $1\,\mu\mathrm{g\,m^{-3}}$ (Claeys et al., 2010; Caseiro and Oliveira, 2012; Herich et al., 2014; Yttri et al., 2015). Levoglucosan was the most abundant monosaccharide anhydride with a mean contribution and SD of 90 ± 1 %, followed by MAN and GAN with corresponding values of 6.3 ± 1.0 and 3.7 ± 0.4 %, respectively. The average concentrations of ARL and MAL were somewhat smaller than those reported for other locations. Arabitol and MAL in Vienna, Austria, during the autumn varied between 7 and $63\,\mathrm{ng\,m^{-3}}$, and between 8.9 and $83\,\mathrm{ng\,m^{-3}}$, respectively (Bauer et al., 2008), and their mean concentrations in Rehovot, Israel, in winter were 8.4 and $22\,\mathrm{ng\,m^{-3}}$, respectively (Burshtein et al., 2011). The differences can likely be explained by the variations in the types of fungus species, different climate, and vegetation. Arabitol and MAL usually show a considerable monthly variability with higher concentrations during autumn, and low levels during winter for ARL and summer for MAL. It was shown that an established biomarker for fungi (ergosterol) correlated with ARL and MAL only during spring and autumn. This correlation might be related to high levels of vegetation during spring blossoms and autumn decomposition, and does not necessarily have a direct relation with fungi levels (Burshtein et al., 2011).

There was some indication of larger $\mathrm{PM}_{10-2.5}$ mass, total particle number concentration (N) and ultrafine (UF) concentration during daylight periods than for nights, while the $\mathrm{PM}_{2.5}$ mass, $\mathrm{PM}_{2.5}\,/\,\mathrm{PM}_{10-2.5}$ mass ratio, OC and LVG exhibited larger values for nights than for daylight periods. The EC data did not seem to show a clear diurnal variability. The mean contribution and SD of the $\mathrm{PM}_{2.5}$ mass to the PM_{10} were 56 ± 11 % during the daylight times, while they were 63 ± 11 % during the nights. This is different from earlier

Table 1. Range, median and mean with SD of atmospheric concentrations for $PM_{2.5}$ mass obtained by FDMS-TEOM; $PM_{10-2.5}$ mass obtained from the SFU sampler; PM_{10} mass as the sum of the previous two on a sample-by-sample basis; EC and OC measured by RT-OC/EC TOT analyser (EC_RT-TOT and OC_RT-TOT, respectively) and laboratory OC / EC TOT method (EC_TOT and OC_TOT, respectively); levoglucosan; mannosan; galactosan; sum of the three monosaccharide anhydrides (ΣMAs); arabitol; mannitol; total aerosol particle number concentration (N); ultrafine particle number concentration (UF); SO_2, O_3, NO_x, NO and CO_2 concentrations; and air temperature and RH outside (T_{out}, RH_{out}, respectively) and inside (T_{in}, RH_{in}, respectively) the BpART research facility; and wind speed (WS). Averaging of the online data was performed for the sample collection time periods of the SFU sampler.

Variable	Unit	Min	Median	Max	Mean	SD
$PM_{2.5}$	$\mu g\,m^{-3}$	11	25	47	25	10
$PM_{10-2.5}$	$\mu g\,m^{-3}$	8.1	15.9	25	15.6	4.4
PM_{10}	$\mu g\,m^{-3}$	16	37	68	38	12
EC_RT-TOT	$\mu g\,m^{-3}$	1.11	2.2	3.3	2.1	0.7
EC_TOT	$\mu g\,m^{-3}$	0.52	0.97	2.1	1.09	0.43
OC_RT-TOT	$\mu g\,m^{-3}$	2.0	3.7	6.8	3.8	1.4
OC_TOT	$\mu g\,m^{-3}$	2.8	4.9	10.2	5.4	1.9
Levoglucosan	$ng\,m^{-3}$	129	393	717	387	153
Mannosan	$ng\,m^{-3}$	9.0	25	58	28	14
Galactosan	$ng\,m^{-3}$	4.3	16.1	33	16.0	7.2
ΣMAs	$ng\,m^{-3}$	143	443	807	431	173
Arabitol	$ng\,m^{-3}$	3.2	6.5	19.3	7.5	3.9
Mannitol	$ng\,m^{-3}$	1.56	3.4	19.9	4.7	3.9
$N \times 10^{-3}$	cm^{-3}	4.1	8.9	17.1	9.3	3.2
$UF \times 10^{-3}$	cm^{-3}	2.9	6.4	14.5	6.9	2.6
SO_2	$\mu g\,m^{-3}$	0.40	6.2	20	8.1	4.3
O_3	$\mu g\,m^{-3}$	2.3	15.8	58	18.4	13.7
NO_x	$\mu g\,m^{-3}$	19	83	474	96	62
NO	$\mu g\,m^{-3}$	2.4	23	222	31	30
CO_2	ppm(V)	446	456	485	456	8
T_{out}	°C	5.4	8.4	13.7	9.0	2.3
T_{in}	°C	18	20	24	20	1.4
RH_{out}	%	38	77	99	77	14
RH_{in}	%	17	36	46	35	5
WS	$m\,s^{-1}$	0.7	1.6	3.1	1.6	0.6

results when the share of the $PM_{10-2.5}$ mass was larger than that of the $PM_{2.5}$ (Salma et al., 2001, 2004; Salma and Maenhaut, 2006). The night-to-daylight period ratio for LVG was 1.41 for the median concentrations. These all can be associated with the diurnal pattern of major urban sources for these chemical species, with relatively short atmospheric residence time of both $PM_{10-2.5}$ particles and UF particles (the latter make up 75–90 % of N in Budapest; Salma et al., 2014), and relatively long atmospheric residence time for the $PM_{2.5}$ particles (which include soot particles, and likely provide a large mass fraction to the OC), and by diurnal cycling of some meteorological properties, in particular of GRad, planetary boundary layer height and atmospheric mixing intensity.

3.2 Temporal variability

The time series of the $PM_{2.5}$ mass, EC_TOT, OC_TOT and LVG are shown in Fig. 1 as an example. It was concluded previously that a direct coupling between the atmospheric concentration levels and the emission sources, mainly vehicular road traffic, can be identified in central Budapest; nevertheless, the local meteorology and extent of long-range transport of air masses have much more influence on the air quality than changes in the source intensity (Salma et al., 2004). This is reflected in the concentration variability in Fig. 1, and hence the correlations between the atmospheric concentrations could also be influenced by common effects of the local meteorology for shorter time intervals. Nevertheless, the calm weather situation usually present during the campaign limited this effect. There were close linear relationships between the PM_{10} mass and $PM_{2.5}$ mass ($r = 0.864$), between OC and LVG ($r = 0.809$) and between the $PM_{2.5}$ mass and LVG ($r = 0.807$). The latter two relationships indicate only that the LVG varies together with the OC and $PM_{2.5}$ mass. The correlation coefficient between the $PM_{2.5}$ mass and OC was somewhat lower ($r = 0.749$), which can imply differences in their major sources. No direct links between the $PM_{2.5}$ mass and EC, between OC and EC, between EC and LVG, or between N on the one hand and the PM_{10}

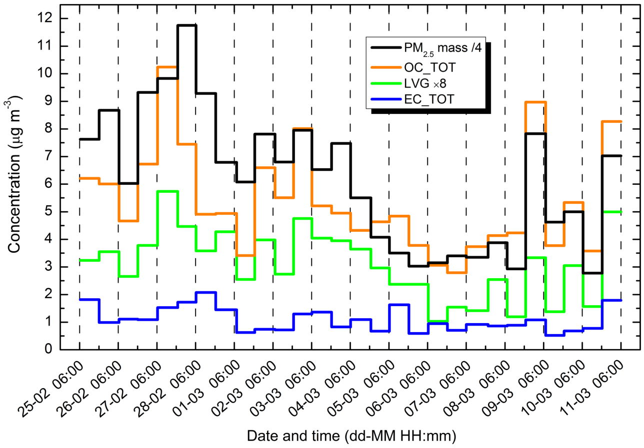


Figure 1. Temporal variability of the atmospheric concentrations for the $PM_{2.5}$ mass, EC and OC determined by the laboratory OC / EC TOT method (EC_TOT, OC_TOT, respectively) and levoglucosan (LVG) for the sample collection periods of the 2 × 14 daylight times and nights.

mass, $PM_{2.5}$ mass, OC, EC and LVG on the other were obtained. This suggests that the major sources of EC are different from BB. At the same time, soot particles contribute only partially to the total particle number, which points to an additional important source of particles even in the city centre. This may be atmospheric nucleation (Salma et al., 2014). It is also noted that the correlation coefficients between LVG on the one side and MAN ($r = 0.925$) and GAN ($r = 0.965$) on the other side were large, while the correlations of LVG with ARL and MAL were small ($r = 0.629$ and 0.204, respectively). The two sugar alcohols did not correlate ($r = 0.576$), which suggests that at least one of them had an additional substantial emission source other than fungi. This is consistent with an earlier observation according to which ARL and MAL were found to be highly correlated throughout the year, except for winter (Burshtein et al., 2011). Humidity was previously found to be a factor affecting the fungal activity (Cox and Wathes, 1995). It was observed that fungi are more abundant when the RH are high in both indoor and ambient air. We could not identify significant correlations in our data set between the RH on the one side and ARL and MAL on the other, which seems to be an attribute of the winter season.

3.3 Contributions

On average, EC (from the laboratory TOT method) accounted for 4.8 ± 2.1 % of the $PM_{2.5}$ mass. This is smaller than previously observed (14 ± 6 %) in a street canyon in central Budapest in spring, but it is larger than for the near-city background (2.1 ± 0.5 %; Salma et al., 2004; Maenhaut et al., 2005). Organic matter made up from 21 to 58 % of the $PM_{2.5}$ mass with a mean and SD of 37 ± 10 %. The mean contribution of EC to TC (both from the laboratory TOT method) with its SD was 17.1 ± 4.9 %, and the OC / EC concentration ratio varied from 2.4 to 8.9 with a mean and SD of 5.3 ± 1.7. The largest individual OC / EC ratios indicate time intervals when secondary organic aerosol (SOA) formation was substantial. This all means that the carbonaceous matter accounted for 42 ± 11 % of the $PM_{2.5}$ mass. The relatively large EC / TC ratio is typical for urban impacts (Salma et al., 2004).

Levoglucosan was utilized to estimate the amount of the PM mass and OC (from the laboratory TOT method) originating from BB. Several PM_{10} mass/LVG and OC / LVG conversion factors have been used in the literature; they were reviewed by Puxbaum et al. (2007). The conversion factor depends on the burning conditions and wood types. We adopted the factors of 10.7 for the PM_{10} mass from BB, and 5.59 for the $PM_{2.5}$-fraction OC from BB (OC_{BB}), which were suggested by Schmidl et al. (2008) for the mix of wood used in Austria. It was implicitly assumed that the amount of LVG in the coarse size fraction was negligible. This is a reasonable assumption since burning products are predominantly contained in fine particles. The uncertainty of the conversion was estimated to be approximately 30 %. The atmospheric concentration of PM_{10} mass originating from BB varied from 1.4 to 7.7 $\mu g\,m^{-3}$ with a median of 4.2 $\mu g\,m^{-3}$. The mean contribution of BB to the PM_{10} mass with SD was 11.1 ± 3.4 %. The contribution of OC_{BB} to the OC in the $PM_{2.5}$ size fraction ranged from 20 to 60 % with a mean and SD of 40 ± 11 % (Fig. 2). It can be concluded that BB represents a major source for $PM_{2.5}$ OC and a non-negligible source for the PM_{10} mass. It is mentioned for completeness that the correlation coefficient between LVG and T_{out} was $r = -0.677$. The weather was unusually mild in the Budapest area during the actual aerosol campaign, so the ordinary BB contributions in winter are expected to be larger than found in the current study. The present results and conclusions on BB are in line with other data from the Carpathian Basin and with various other locations in European cities (Caseiro et al., 2009; Piazzalunga et al., 2011; Maenhaut et al., 2012). Puxbaum et al. (2007) reported a BB contribution to OM of 28 % for the K-puszta station, which represents a rural background or regional site in the Carpathian Basin. As far as the measured monosaccharide anhydrides and sugar alcohols are concerned, their joint contribution to the OC was determined from their molecular formulae, which resulted in a mean and SD of 3.7 ± 0.9 %, and the corresponding values for ARL were 0.07 ± 0.03 % (see below).

The concentration ratio LVG / (MAN + .GAN) was proposed to differentiate between wood burning and other BB emissions, while the ratio LVG / MAN was applied to distinguish between hardwood and softwood burning emissions (Fine et al., 2004; Schmidl et al., 2008; Fabbri et al., 2009; Caseiro et al., 2009; Favez et al., 2010; Piazzalunga et al., 2011; Maenhaut et al., 2012). The typical ranges of the two ratios for different BB sources were overviewed by Maenhaut et al. (2012). Softwood combustion typically yields a LVG / MAN ratio <4, while the same ratio for hardwood

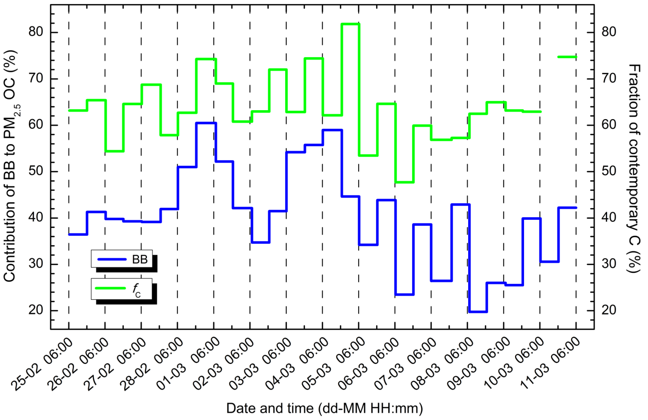


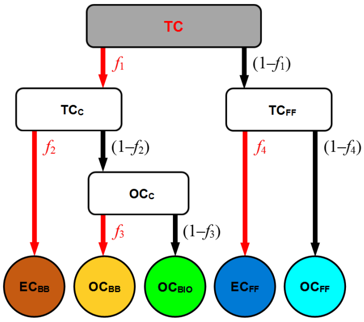
Figure 2. Temporal variability of the relative contribution of BB to the PM$_{2.5}$-fraction OC assessed by the levoglucosan marker method, and of the fraction of contemporary carbon (f_C) derived by the radiocarbon marker method.

emissions is 14–15. Emissions from lignite and peat burnings result in ratios of 54 and 8.6, respectively. Derivatives of crude oil, natural gas, coal and biomass are the major carbonaceous fuels utilized in Hungary; peat is not burned. The major form, 88 % of the consumption expressed in tons of solid fuels utilized, is lignite/brown coal. For our samples, the LVG / (MAN + GAN) ratios ranged from 6.3 to 11.0 with a mean and SD of 9.2 ± 1.2, while the LVG / MAN ratio varied from 9.8 to 18.5 with a mean and SD of 14.6 ± 2.4. The mean values are at the higher end of the intervals of the ordinary ratios, and may indicate that lignite burning provides a non-negligible contribution to the monosaccharide anhydrides. Unfortunately, all this does not lead us to a reliable softwood/hardwood quantification. The calculation also raises the question of whether the approach is justifiable for regions or countries other than that originally considered.

The C isotope analysis was performed on the TC content of both the front and back quartz filters. The uncorrected back / front filter ratio for TC determined by using the laboratory OC / EC analyser in the TOT mode varied from 12 to 51 % with a mean and SD of 29 ± 10 %, and the field blank filters contained 8.9 ± 3.4 µg TC in general. These indicate the importance of using the tandem filter correction method for TC (and OC) in aerosol samples collected by low-volume collection devices. These data also raise the issue of whether the back filters which contain adsorbed volatile organic compounds (VOCs) exhibit an identical ^{14}C / ^{12}C isotope ratio as the carbonaceous aerosol particles on the front filters. To investigate this, all back filters were analysed by the AMS method. The range and mean fraction of contemporary carbon with SD for the front filters were 59–83, 70 ± 7 %, respectively, while the same properties for the back filters were 28–122, 75 ± 24 %, respectively. As a conclusion, the f_C values of the back filters were individually taken into account for the front filters in the following way. The amounts of TC on the front and back filters were first corrected to the sample preparation yield using the TC data of the OC / EC analysis, and then each amount of ^{14}C and ^{12}C on the back filter was subtracted from the corresponding isotope amounts on the front filter in order to obtain the corrected amounts and their fraction. The correction factor varied in a range of 10–49 %, with a mean back-to-front ratio and SD of 25 ± 10 %, respectively. These imply that the tandem filter correction becomes necessary for the radiocarbon method on low-volume samples (if the TC is less than 1 mg on the portion of the filter analysed). The situation can be different for high-volume samplers. In addition, there was one individual correction value above 110 % for a back filter, which can be explained only by some anthropogenic ^{14}C sources, such as medical or other industrial release. The corrected f_C values are also shown in Fig. 2 as time series. The contribution of contemporary C to the TC varied from 48 to 82 % with a mean and SD of 64 ± 7 %. Radiocarbon data were obtained for Budapest for the first time. Interestingly, the correlation coefficient between LVG and f_C was modest, $r = 0.523$, which suggests that the contribution of OC from the other possible major source of modern carbon, i.e. biogenic sources, was substantial. Backward air mass trajectories showed that the fossil impact was larger for local air masses (sources), while an enhanced non-fossil fraction was generally observed for long-range-transported air masses.

3.4 Coupled source apportionment

The relative contributions of EC and OC to the TC derived directly from the measured atmospheric concentrations were combined with the results of the independent radiocarbon and LVG marker models regarding the fossil, contemporary (non-fossil) and BB sources in a coupled approach (see also Bonvalot et al., 2016) on a sample-by-sample basis. The novel source apportionment scheme of the TC into the contributions of EC and OC from FF combustion (EC$_{FF}$ and OC$_{FF}$, respectively), EC and OC from BB (EC$_{BB}$ and OC$_{BB}$, respectively), and OC from biogenic sources (OC$_{BIO}$) proposed and utilized in the present study is summarized in Fig. 3. It consists of pragmatic and effective attribution steps, which are expressed by multiplication factors. The factor f_1 was set to $f_1 = f_C$ of the actual sample. The modest correlation between LVG and EC (see Sect. 3.2) revealed that BB alone represents a less substantial source of EC relative to TC than the joint contributions of FF combustion and BB. For this reason, the relative contribution of EC$_{BB}$ was estimated by adopting the mean EC / OC values previously reported explicitly for BB. Szidat et al. (2006, and references therein) utilized a critically evaluated ratio of (EC / OC)$_{BB}$ = 16 ± 5 %, and Bernardoni et al. (2011, 2013) derived a ratio and SD of 18 ± 4 % for wood burning. Their mean value of (EC / OC)$_{BB}$ = 17 % was utilized in the present calculation scheme. Thus, factor f_2 was determined from the a priori known



f_1: function of
- f_C measured by AMS separately for each sample

f_2: function of
- LVG measured by GC/MS and f_1 separately for each sample
- literature values for $(EC/OC)_{BB}$=0.17 and OC/LVG=5.59 for all samples

f_3: function of
- LVG measured by GC/MS, f_1 and f_2 separately for each sample
- literature value for OC/LVG=5.59 for all samples

f_4: function of
- EC and OC measured by laboratory TOT analyser, f_1 and f_2 separately for each sample

Figure 3. Source apportionment scheme based on the coupled radiocarbon–levoglucosan marker method for the relative contributions of EC and OC from fossil fuel (FF) combustion, biomass burning (BB) and biogenic sources (BIO) to the total carbon (TC = EC + OC). The multiplication factors are further explained in the text. The subscript C indicates contemporary carbonaceous fraction. The red arrows specify the input of the primary multiplication factors into the apportionment scheme.

$(EC / OC)_{BB}$ and OC / LVG ratios and measured LVG concentration from the equation $f_1 \times f_2 \times TC/(5.59 \times LVG) = (EC / OC)_{BB}$, which yielded the multiplication factor $f_2 = 5.59 \times LVG \times (EC / OC)_{BB}/f_1/TC$. The LVG and TC data refer to the measured atmospheric concentrations for the actual sample, while the OC_{BB} / LVG ratio of 5.59 is discussed in Sect. 3.3 and also below. The relative contribution of BB to the contemporary OC was assessed by a multiplication factor $f_3 = 5.59 \times LVG/f_1/(1–f_2)/TC$, which was obtained from the equation $f_1 \times (1–f_2) \times f_3 \times TC = 5.59 \times LVG$. The remaining fraction of $(1–f_3)$ of the contemporary OC was considered as the relative contribution from biogenic sources. The TC from fossil sources was divided into the relative contribution of EC_{FF} in such a way that the weighted joint contributions of the EC from the FF combustion and BB become equal to the actual EC / TC ratio for the given sample – in other words, as the difference between the total EC and EC_{BB} from the equation $f_1 \times f_2+(1–f_1) \times f_4 = EC / TC$, which yielded the multiplication factor $f_4 = (EC / TC–f_1 \times f_2)/(1–f_1)$. In summary, the experimentally obtained values of TC, f_C, EC, OC and LVG derived for each sample, and general $(EC / OC)_{BB}$ and OC / LVG values, are utilized as primary input data in the scheme. These are indicated in Fig. 3.

The main advantage of this apportionment method is its pragmatic character and the fact that the required data are usually available in similar studies. Its main limitations include the $(EC / OC)_{BB}$ ratio for which the actual value can change with many factors, and the bias in the multiplication factors f_2 and f_3. The relative uncertainties of the individual measured data – which are typically below ca. 10 % – have an acceptable influence on the uncertainty of the apportioned species. The temporal variability of the final quantities likely becomes larger than their experimental uncertainty if several weeks of time intervals are considered. This is demonstrated in our mean factors averaged for all samples (for 2 weeks) and their SD of $f_1 = 64 \pm 7$, $f_2 = 9.0 \pm 1.9$, $f_3 = 58 \pm 14$, $f_4 = 31 \pm 11$ %. As far as the $(EC / OC)_{BB}$ ratio is concerned, it is expected that its actual value for an area approaches a more representative ratio with increasing time interval considered. Simple sensitivity calculations confirmed that it is the $(EC / OC)_{BB}$ ratio that has the largest effect on the uncertainty of the results, and they also revealed that it is the OC_{BIO} and OC_{BB} which are influenced the most by the input uncertainties. The overall relative uncertainty for them can be up to 25–30 %, while the relative uncertainty of the other apportioned species is expected to be below 20 %. Considering the uncertainties associated with other ordinary conversions in the field of carbonaceous aerosol species, e.g. of deriving OM from OC, which is estimated to be 30 % (Maenhaut et al., 2012), the model uncertainties of the apportionment species do not seem unusual, and are considered to be still acceptable. Moreover, the assessed uncertainties are comparable to the changes caused by typical atmospheric variability (see Table 2).

The mean relative contributions of the carbonaceous species to the TC with SD derived by averaging for all samples were 11.0 ± 4.2 % for EC_{FF}, 25 ± 6 % for OC_{FF}, 5.8 ± 1.4 % for EC_{BB}, 34 ± 8 % for OC_{BB} and 24 ± 9 % for OC_{BIO}. The latter contribution also includes the mean share of the primary organic aerosol emitted by fungi of ca. 0.02 %, which was assessed by using ARL (see Sect. 3.5 and Fig. 8). The relative contribution of fungal spores is rather small, which expectedly remains so for the PM_{10} size fraction as well, but it can have biological relevance due to its possible allergenic influence. The BB and FF combustion sources contributed similarly by 40 ± 10 and 36 ± 7 %, respectively, while the biogenic sources made up for 24 ± 9 % of the TC concentration. The median relative contributions are shown in Fig. 4. It has to be mentioned that the $(OC / LVG)_{BB}$ conversion factor is based on laboratory studies which mainly considered primary particles (emission products), although SOA from wood burning (or more exactly non-fossil SOA) can yield amounts that are important with respect to primary particles (Szidat et al., 2009). This can cause underestimation of the OC_{BB} contributions, and consequently, overestimation of the OC_{BIO} contributions. A further important uncertainty can arise from a variable OC / LVG conversion factor of 5.59 due to spatially and temporally changing burning conditions. The overall relative contributions are in very good agreement with other wintertime urban atmospheric studies (Szidat et al., 2009, and references therein; Minguillón et al., 2011; Bernardoni et al., 2013; Bonvalot et al., 2016).

The individual relative contributions of the carbonaceous species to the TC were converted to their share in the $PM_{2.5}$ mass as well. An OM/OC conversion factor of 1.6 was adopted in the calculations (see Sect. 2.2). The mean relative contributions to the $PM_{2.5}$ mass with SD derived by averaging for all samples were 3.1 ± 1.6 % for the EC_{FF},

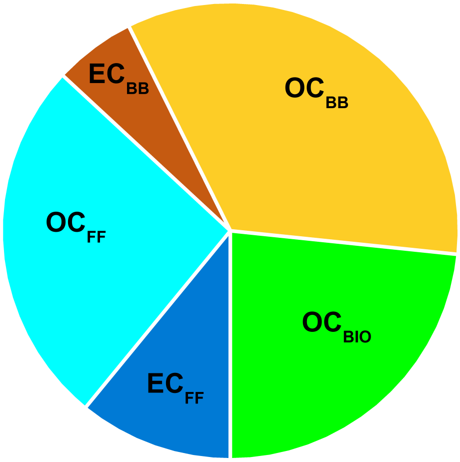


Figure 4. Median relative contributions of EC_{FF} (11.2 %), OC_{FF} (27 %), EC_{BB} (5.9 %), OC_{BB} (34 %) and OC_{BIO} (24 %) to the total carbon with a median atmospheric concentration of 6.0 µg m^{-3} in the $PM_{2.5}$ size fraction in central Budapest.

Table 2. Range, median, mean with standard deviation (SD) of the atmospheric concentrations for the apportioned EC and OC from FF combustion (EC_{FF} and OC_{FF}, respectively), EC and OC from BB (EC_{BB} and OC_{BB}, respectively), OC from biogenic sources (OC_{BIO}) and for the measured TC in µg m^{-3} for the $PM_{2.5}$ size fraction.

Species	Min	Median	Max	Mean	SD
EC_{FF}	0.31	0.68	1.43	0.69	0.29
OC_{FF}	0.53	1.52	2.8	1.60	0.59
EC_{BB}	0.122	0.38	0.68	0.37	0.14
OC_{BB}	0.72	2.3	4.0	2.2	0.8
OC_{BIO}	0.38	1.30	3.4	1.60	0.85
TC	3.5	6.0	11.8	6.5	2.1

11.1 ± 4.3 % for the OM_{FF}, 1.53 ± 0.40 % for the EC_{BB}, 14.4 ± 3.8 % for the OM_{BB} and 11.1 ± 6.1 % for the OM_{BIO}. The importance of BB sources, FF combustion and biogenic sources for the $PM_{2.5}$ mass was similar, namely approximately 15, 14 and 10 %, respectively, according to this apportionment model. We are aware that (1) high emissions of some pyrogenic inorganic species such as K, nitrate or sulfate are completely neglected by the present approach, and (2) the OM/OC conversion factor can also change for organic species from different source types. The latter ($PM_{2.5}$ mass) apportionment should, therefore, be considered as the first approximation only, and the contribution of BB to the $PM_{2.5}$ mass is likely underestimated. The relative contributions to the carbonaceous species and $PM_{2.5}$ mass are expected to also change substantially for various seasons or on an annual basis due to important changes or time patterns in heating, other human activities, formation pathways and biogenic emission strengths.

3.5 Apportioned carbonaceous species

The atmospheric concentrations of the apportioned carbonaceous chemical species and TC are shown in Table 2.

The properties and relationships among the apportioned carbonaceous species were investigated by pairwise correlations. Selected scatter plots are shown in Figs. 5–8. It can be seen that there was no meaningful linear relationship between EC_{FF} and EC_{BB} ($r = 0.340$, Fig. 5 upper panel) and between EC_{FF} and OC_{FF} ($r = 0.170$, Fig. 7 upper panel). All three apportioned OC species seem to show linear links with each other. The correlation coefficient between OC_{FF} and OC_{BB} was $r = 0.458$ (Fig. 5 lower panel), and they were $r = 0.431$ and 0.432 between OC_{BIO} on the one side and OC_{FF} and OC_{BB} on the other, respectively (Fig. 6). This suggests that the formation processes of OC species from anthropogenic VOCs and biogenic VOCs (BVOCs) were primarily influenced or controlled by a common factor, which is most likely the atmospheric photochemistry. This effect is, however, expected to occur in a complex way since the relationship of GRad with the three apportioned OC species showed only fluctuations. As far as the air temperature is concerned, only the dependence of OC_{BB} on T was arranged into a linear tendency ($r = -0.661$, Fig. 7 lower panel). Emission of BVOCs (e.g. monoterpenes) can be described by an exponential T dependence, thus $OC_{BIO} \propto BVOC \propto \exp(a \times T)$, where a is a constant (Kontkanen et al., 2016). Nevertheless, we could not identify any obvious link between T and $\log(OC_{BIO})$ or OC_{BIO} probably because of the narrow T range during the campaign, and because the transformation of BVOCs from the gaseous phase to the aerosol phase takes place in a complex system depending sensitively on many other multifactorial chemical and atmospheric conditions, which are not expressed obviously by pairwise correlations. The moderate pairwise correlations between the apportioned OC species also point to the relevance and role of primary organic matter (POM) from FF combustion, BB and biogenic sources, and to the effects of the secondary compounds related to BB emission on the likely overestimated contribution of the OC_{BIO}. At the same time, there was a strong linear relationship between NO_x – which is emitted for 60–70 % by road vehicles in Budapest – and EC_{FF} ($r = 0.823$, Fig. 8 upper panel), while the correlation coefficient between OC_{FF} and NO_x was not significant ($r = 0.037$). Arabitol, which expresses the primary emissions from fungi, and which possibly can be also related to somewhat more general biogenic activity, showed some dependence on the OC_{BIO} (Fig. 8 lower panel). By excluding the two data points (1D and 1N), which appear outliers, a correlation coefficient $r = 0.494$ was obtained. It has to be noted that primary biological emissions (including ARL) are mainly associated with the coarse size mode, while the $PM_{2.5}$ size fraction investigated in the present study overlaps only partially with it. Stronger links

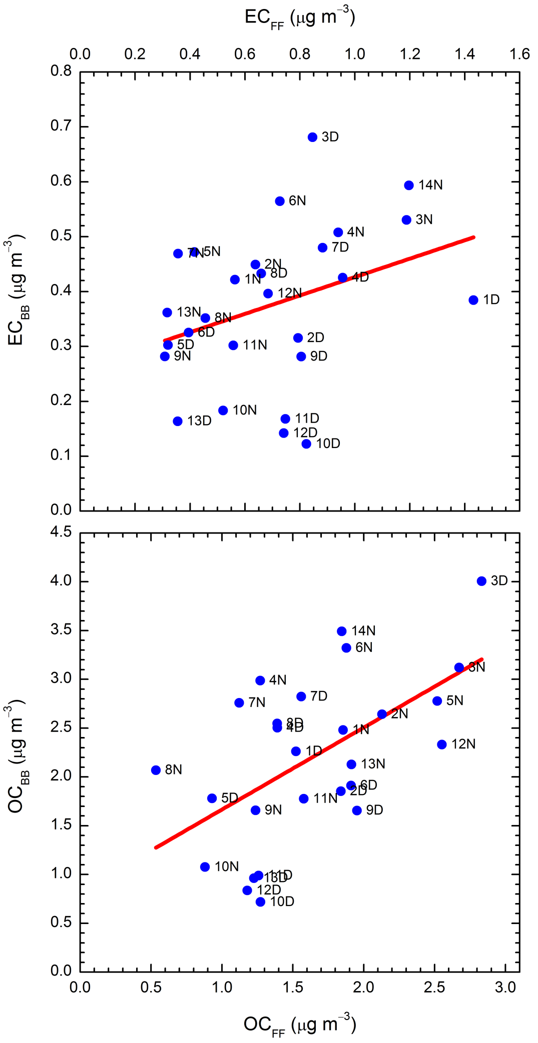


Figure 5. Scatter plots between apportioned atmospheric concentrations of EC_{FF} and EC_{BB}, and of OC_{FF} and OC_{BB} for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight time (D) or night (N) periods is indicated by labels next to the data points.

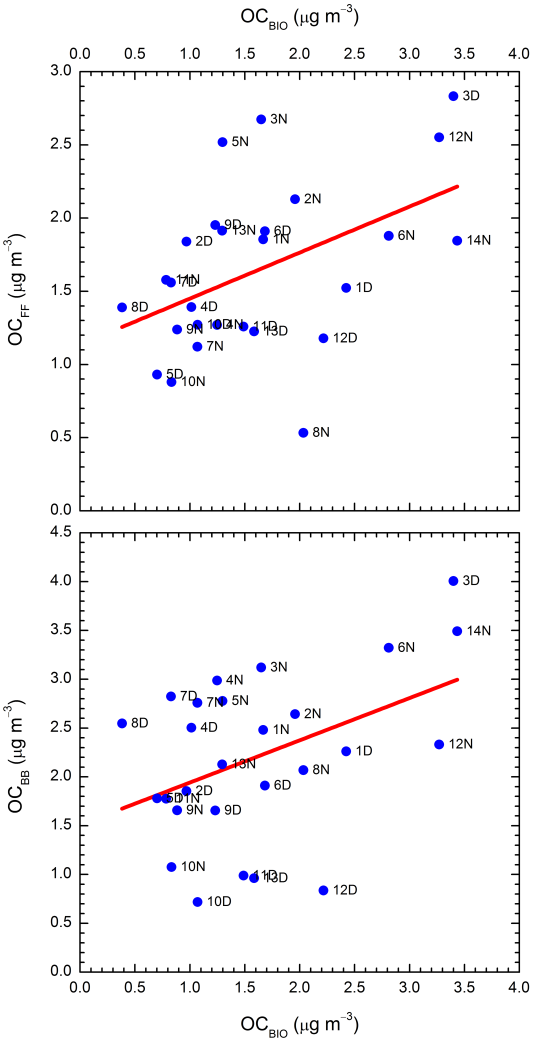


Figure 6. Scatter plots between apportioned atmospheric concentrations of OC_{BIO} and OC_{FF}, and of OC_{BIO} and OC_{BB}, for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight time (D) or night (N) periods is indicated by labels next to the data points.

between ARL and OC_{BIO} are expected to be obtained by considering ARL in coarse particles.

Our results altogether can be interpreted by concluding that (1) there were various substantial FF combustion sources active in the area which result in different EC / OC ratios; (2) EC_{FF} was mainly emitted by vehicular road traffic; (3) the contribution of non-vehicular fossil sources such as domestic and industrial heating or cooking using gas, oil or coal to OC_{FF} was substantial; (4) the mean contribution of BB to soot particles was smaller by a factor of approximately 2 than that of road traffic; and (5) formation of OC from fossil, BB and biogenic VOCs were jointly influenced by photochemistry, and POM from these sources may also be important. At the same time, it cannot be excluded that secondary OC_{FF} could also play a role in disentangling primary species from FF combustion and OC_{FF}.

4 Conclusions

We have shown that BB was responsible for 40 % of the carbonaceous matter (that is TC) in the $PM_{2.5}$ size fraction in central Budapest during a mild winter with no snow cover in the larger area, while FF combustion contributed by 37 %, and biogenic sources made up 24 %. EC_{FF} and OC_{FF} were associated with different FF combustion sources. Most emission of the former species was caused by road traffic, in particular diesel-fuelled vehicles, while most OC_{FF} was at-

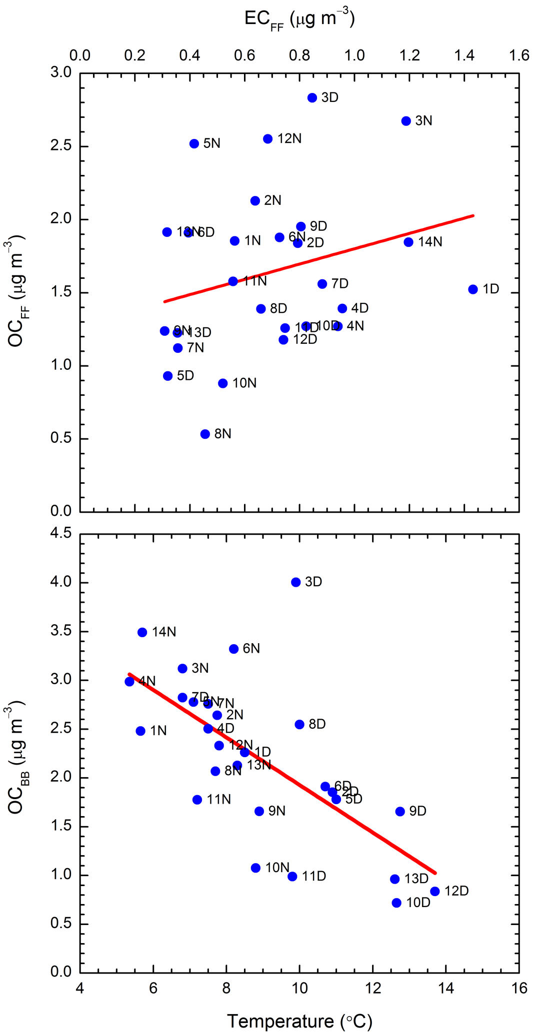


Figure 7. Scatter plots between apportioned atmospheric concentrations of EC_{FF} and OC_{BB}, and of OC_{BB} and air temperature (T) for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight time (D) or night (N) periods is indicated by labels next to the data points.

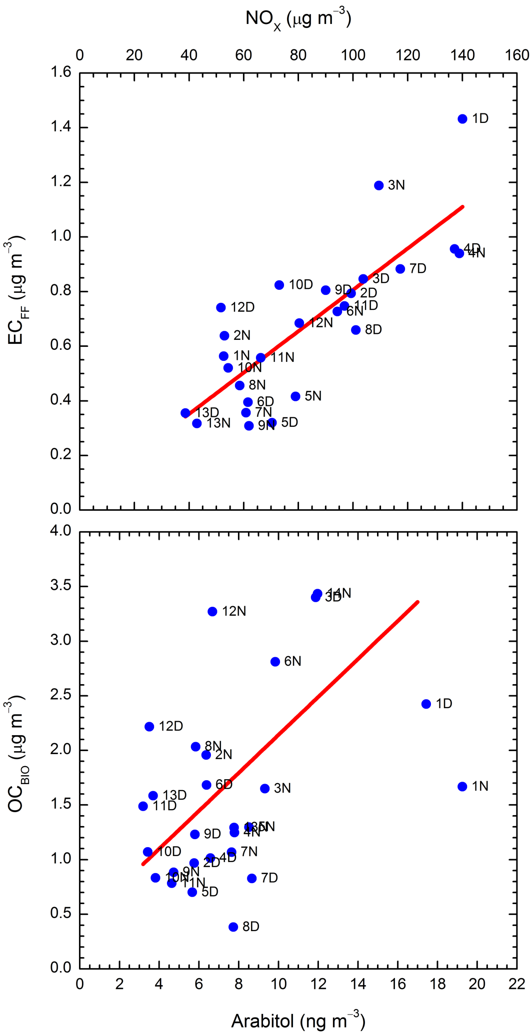


Figure 8. Scatter plots between atmospheric concentrations of NO_x and apportioned EC_{FF}, and of arabitol and apportioned OC_{BIO} for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The data points 1D and 1N on the lower panel were excluded from the data set when fitting. The order number of the samples together with daylight time (D) or night (N) periods is indicated by labels next to the data points.

tributed to other fossil source types. The main formation process of all three OC species (i.e. OC_{FF}, OC_{BB} and OC_{BIO}) from anthropogenic VOCs and BVOCs were influenced by a common factor, which is most likely the atmospheric photochemistry. This effect was, however, realized in a complex multifactorial way, and the role of POM was also important. The relative contribution of BB to the PM_{10} mass concentration was modest, approximately 11 %. The corresponding contributions are usually larger in many western and northern European cities. Our value seemingly indicates limited possibilities for implementing action plans for air quality improvements by controlling BB. Nevertheless, reducing soot and emissions from BB could result in a substantial decrease of up to about 40 % of the TC in the $PM_{2.5}$ size fraction. This chemical fraction and particle size range contains most of the potentially harmful, toxic and reactive organic compounds (e.g. polyaromatic hydrocarbons), intermediates or other particulate products from burning stained or processed wood. In addition, all and the most severe daily PM_{10} health limit exceedances in Budapest have occurred in winter when the contribution of BB is expected to be the largest, and when the BB takes place in many individual residences in the region during the same time interval, e.g. under cold weather conditions. Technological improvements and control measures for various (mostly household) appliances that burn biomass and wood, together with efficient education and training of their users, in particular on the admissible fuel types, offer important potential for improving the air quality in Budapest, and represent an important form of societal implications of atmospheric aerosols in cities in general.

Further improvements in the source apportionment can be achieved by utilizing the coupled radiocarbon–levoglucosan marker method on corresponding sets of different carbonaceous chemical fractions such as OC, EC, water-soluble OC and water-insoluble OC. This method possesses further potential to supply more detailed results and important information on emission and formation processes of carbonaceous chemical species. In this perspective research on a yearly timescale, the sample collection and analytical protocols need to be optimized jointly, and the conclusions reached in the present study are intended to serve as a basis for these dedicated plans.

Data availability. The observational data used in this paper are available at http://salma.web.elte.hu/BpArt of the Eötvös University, Hungary, or on request from the corresponding author.

Competing interests. The authors declare that they have no conflict of interest.

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