Response to Referee #1

The authors thank Referee #1 for his/her detailed, extensive, expertise and valuable comments to further improve and clarify the MS. We have considered all recommendations, and made the appropriate alterations. Our specific responses to the comments are as follows.

Aspects requiring attention

1) source apportionment scheme description should be re-written to better clarify the information flow. Figure 3 has to be completely revised;

The apportionment scheme is now described more explicitly. We clarify all input data that are necessary for the apportionment and their actual entrance point into the scheme more systematically in both the text and Fig. 3. The arrows in Fig. 3 were originally selected in such way that they indicate the pathways and their major steps in the data treatment flow starting from the measured TC concentration toward the assessed end quantities of the five major carbonaceous species, i.e. EC_{FF} and OC_{FF}, EC_{BB} and OC_{BB}, and OC_{BIO}, which is considered helpful in overviewing the idea of the proposed new approach for readers, who are not very familiar with source apportionments.

2) indication on source apportionment uncertainties is mostly missing, some hints for their estimate should be added to the text; furthermore, possible role of secondary organic compounds on OC-BIO source apportionment needs further comments;

We added now a brief discussion on the model uncertainties and assessed their extent. We also completed the text with a comment on the possible role of secondary organics on OC_{BIO}.

3) assumptions needed for the application of the approach should be stated more clearly;

The assumptions are now formulated more explicitly. This was achieved within the modifications indicated in reply to comment Aspects requiring attention 1.

4) high time resolved measurements of carbonaceous fractions and aerosol absorption/extinction properties were performed in parallel to filter sampling, but they are rarely considered in data analysis. I suggest the authors to consider one of the following possibilities: a) completely remove the description of techniques and the introduction on paragraph 3; b) revise optical properties data (currently, data treatment is not adequate, see detailed comments) and exploit multi-wavelength measurements to attempt optical source apportionment approaches, i.e. Aethalometer model (Sandradewi et al., 2008 Environ. Sci. Technol. 42, 3316-3323 and following modifications) or Multi-Wavelength Absorption

Analyser model (Massabò et al., 2015. Atm. Environ, 108, 1-12). These models provide information on fossil fuel combustion/biomass burning contribution to carbonaceous aerosol basing on optical absorption measurements and thermal-optical OC/EC/TC. The information could support the results obtained by the 14C on TC and LVG source apportionment proposed in the paper.

The authors regret that they did not indicate to the handling editor and the potential referees at the submission stage that another MS, which deals with and evaluates the data from the on-line measurements obtained by the AE, PAS and DMPS in focus, is under preparation. This other MS will include the evaluation methods referred to by the Referee, thus the so-called Aethalometer model (the wavelength dependence of the optical absorption coefficient) for both the AE (Sandradewi et al., Environ. Sci. Technol., 42, 3316–3323, 2008; Sandradewi et al., Atmos. Environ., 42, 101–112, 2008; Favez et al., Atmos. Environ., 43, 3640–3644, 2009; Favez et al., Atmos. Chem. Phys., 10, 5295–5314, 2010) and PAS–DMPS (Ajtai et al., Atmos. Environ., 122, 313–320, 2015) data sets. In addition, a new approach of combining the PAS, DMPS (number size distribution) and AE (soot) data sets into one model is also planned. Comparing the results, advantages and limitations of the filter-based approach (in the present paper) and several optical-related source apportionment methods based on the on-line data sets will be one of the key points in this other MS. We decided to split the whole matter into two parts (with a natural division line between the collection of aerosol samples and on-line measurements) because we consider that their joint presentation 1) could be too lengthy and perhaps even too complex and likely could have a too broad scope, and therefore, 2) it would detract the attention from the new apportionment scheme proposed in the present MS, and 3) our goal is not to prepare a comparative MS on a selection of apportionment methods. We indicated now these additional arguments, motivations and aims very briefly in the text. Nevertheless, it seems plausible and advantageous to describe the experiments of the aerosol sample collection and measurement campaign together in order to have a more comprehensive overview on the aerosol campaign and resulting analytical data sets as a whole, and to assist the future MS to focus the attention specifically on modelling issues and data validation.

Major comments

1) page 4, par. 2.2: indication on minimum detection limits and uncertainty for the mentioned techniques are completely missing. Please, add such information (a table should be enough)

We included now into the text the determination limits of some measuring techniques where they were missing. We also indicated explicitly that the measured concentrations were at least several times larger than the determination limits due to the common levels that are present in the city centre and to the well-selected sampling/integration times, which also imply that the atmospheric variability and the uncertainties related to conversions (e.g. from OC and OM, or from LVG to OC_{BB}) can cause larger uncertainties that the analytical techniques themselves.

2) page 5, line 37. The authors used the same fm reference for modern material (1.08), independently on the source (BB or BIO). Usually in 14C source apportionment studies, two different values are chosen for BB (expected higher due to integrated signal) and BIO (which is expected to be in equilibrium with today atmospheric 14C/12C ratio. The approximation should be highlighted (see e.g. par 2.4 Minguillòn et al., 2011 cited by the authors)

Minguillòn et al. concluded that the differences in the f_C caused by the refined correction factor for biogenic emissions are generally small or negligible when compared to the method uncertainties. We added a similar comment and the related reference.

3) page 6, line 2: FDMS usually operates at 30 ◦ C. Any comment about possible mass losses (e.g. nitrate?)

We operated the FDMS-TEOM in an air conditioned cabin at a temperature of 21 °C. The FDMS instrumental extension of the TEOM system was developed specifically to account and correct for semi-volatile PM components (see page 5, line 42 – page 6, line 1 of the original MS). Its correct operation was confirmed several times earlier by comparing the filter-based $PM_{2.5}$ mass data (collected outside the BpART platform on Nuclepore filters at ambient air temperature) to the mean obtained from the on-line FDMS-TEOM data set averaged to the corresponding sampling time interval.

4) page 6, line 6 and 9-10. Basing on Drinovec et al. (2015), Atmos. Meas. Tech., 8, 1965–1979 (page 1970) I guess that 16.6 m2/g is the mass extinction (not absorption) coefficient: Aethalometer assumes proportionality between babs and batn through a proportionality factor C - Weingartner et al, (2003), J. Aerosol Sci., 34, 1445–1463. The mass absorption coefficient historically considered by Aethalometer @880 nm is 7.77 m2/g (Drinovec et al. (2015)). If a-priori assumption has to be applied to convert PAS measurements into BC concentration maintaining equivalence with what performed in the Aethalometer, then 7.77m2/g is the value to be extrapolated to 1064 nm for application to PAS measurements (please evaluate also the following comment).

We agree that the expression mass absorption coefficient used in the original MS is not completely the correct expression. It represents more a “specific attenuation parameter” or “mass attenuation cross section” (Hansen et al., J. Geophys. Res. 110, D18104, doi:10.1029/2005JD005776. 2005; Drinovec et al., Atmos. Meas. Tech., 8, 1965–1979, 2015) since it is related more to filter artefacts than the differences between the extinction and absorption coefficients in highly absorbing carbonaceous material. We changed the wording accordingly. The a-priori chosen conversion factor for deriving BC mass concentration from measured optical absorption strongly affects the results. The manufacturer suggested the conversion factor (before a posteriori data correction) of 16.6 m^2/g at a wavelength of 880 nm in earlier models of the AE (such as the AE16, AE22, and AE31). Nevertheless, a conversion factor of 7.77 m^2/g at the same wavelength was proposed for the new AE generation, which adopts automatically the dual spot method (Drinovec et al., Atmos. Meas. Tech., 8, 1965–1979, 2015). We appreciate this comment and modified the data in Tables 1 and 2, in Fig. 1, and related parts of the text at several places in accordance with this.

5) page 6, lines 18-23: the comparisons between optical EBC (from AE or PAS) and thermal EC are strongly affected by the assumption on absorption/extinction coefficients chosen a-priori. As such values are site/season/composition dependent, the parallel availability of optical (batn/babs) and thermal (EC) measurements could be better exploited to provide information on BC mass absorption coefficients in Budapest;

As argued in the answer to comment Aspects requiring attention 4, all the requested information is to be supplied in the MS which is under preparation and to which we refer now in a more direct way in the present paper.

6) page 7, line 37-38: in the cited works, SFUs are reported to have a cut-off diameter of 2 μm. Did the authors change e.g. nuclepore filter pore size or flow-rate to modify the size cut? Different cut-off size could partially justify differences, as well as the use of different instrumentation (i.e. SFU vs. TEOM) or the improvement of combustion technologies in the last 15 years, leading to smaller particles formation.

The Gent-type stacked filter unit (SFU) sampler was indeed designed and realised by one of the co-authors of the present paper (W. Maenhaut) for collecting PM size fractions with nominal aerodynamic diameter (AD) of 10–2 and <2 μm. The cut-point of 2 μm results from drawing air through the top (coarse) Nuclepore filter with 8 μm pore size at a face velocity of 16.6 L/min. The separation between the two size fractions is, however, not very sharp (which is in contrast with the steep impaction collection curve of inertial impactors used for collecting $PM_{2.5}$ or PM_{10}). Furthermore, according to P.K. Hopke, the cut-point between the two size fractions in the Gent SFU is rather at 2.2 μm than at 2 μm (P.K. Hopke, personal communication to W. Maenhaut). Thus, the cut-point of 2 μm is rather approximate. In many published papers, in which the Gent SFU was used, including many papers co-authored hy P.K. Hopke and some co-authored by W. Maenhaut (e.g., the paper by Putaud et al. (2010) to which reference is made in our manuscript) the cut-off value between the two size fractions was reported to be 2.5 μm.

In any case, several chemical species have a saddle point in their mass size distribution around the 2–2.5 μm diameter region, so that the difference between their masses in PM_2 and $PM_{2.5}$ is virtually negligible. We and the colleagues at the National Air Quality Network in Budapest observed a continuous shift in the mean PM_{fine}/PM_{coarse} mass ratio to larger values in central Budapest during the last 20 years with several collection devices and on-line instruments (e.g. Salma and Maenhaut, Environ. Pollut., 143, 479–488, 2006). This is likely related to some regulatory measures, improvement of combustion technologies and other changes after the economical transition in Hungary, and it does not seem to be influenced by the experimental or sampling method. We amended the text to express this tendency.

7) page 10, lines 9-15. Lignite contribution and its high LVG/MAN does not allow reliabile softwood/hardwood quantification. I suggest to completely remove this paragraph.

The sentences were removed as requested. (We think that this comment concerned page 11, line 9–15 of the original MS.)

8) page 11, line 27: "the fC values of the back filters were individually taken into account for the front filters". Please better explain the procedure for front filter correction.

The amounts of C on the front and back filters were first corrected to the sample preparation yield using the TC data of the OC/EC analysis with the laboratory TOT instrument, and then each amount of C-14 and C-12 on the back filter was subtracted from the corresponding isotope amounts on the front filter in order to obtain the corrected C-14 and C-12 amounts and their fraction. This sampling artefact seems to be particularly important for low-volume samplers. The correction method is now explained more explicitly.

9) page 12, line 5: from Bernardoni et al. (2013) I guess the mentioned value was obtained elsewhere (Bernardoni et al, 2011, Sci Total Environ, 409, 4788–4795)

We adopted one of the EC/OC ratios for wood burning from the cited paper (Bernardoni et al., J. Aerosol Sci., 56, 88–99, 2013, p. 95). Since the value was indeed obtained in an earlier study, we also cite now its original literature source, as requested.

10) page 12, figure 3 and lines 9-14: I don't think the chart correctly represents information flow described in the text. Chart information flow makes argue that factor f2 and f3 are needed to determine EC-BB and OC-BB from TC-C and OC-C. This interpretation would be nonsense, as no proportionality is expected between EC-BB and TC-C, as well as between OC-BB and OC-C (due to at least an independent source - BIO contributing to OC-C). Nevertheless, the text shows that the source apportionment follows a completely different path. If I correctly interpreted the text, it should be evidenced in the chart that input data are obtained from 14C

information (TC-C), and LVG (OC-BB and EC-BB thanks to emission ratios). f2 and f3 are then a by-product (by ratios or subtractions) of these quantities and do not have anything to do with "mass balance equations", opposite to what reported at line 10. Then, I guess from the text that EC-FF is derived as difference between total EC and EC-BB. EC-FF is then exploited to obtain the factor f4. I suggest to completely re-think the chart, including external inputs and their role in the source apportionment scheme. Arrows should start from input data and point to calculated quantities. Furthermore, corresponding text (lines 9-14, page 12) is quite obscure in its current form, and it should be re-written to better evidence the real information flow.

The related part is extensively rewritten, and Fig. 3 is also extended to express the calculation flow more precisely and according to the request of the Referee. See also the answer to Aspects requiring attention 1.

11) page 12, lines 14-17: I suggest to mention also a disadvantage of the proposed model compared to the direct determination of 14C in OC and EC fraction, mainly impacting on EC source apportionment: in the case of the proposed model, EC source apportionment requires assumption on wood burning LVG/EC emission ratio, whereas if 14C is directly measured in the EC fraction, the apportionment is straightforward.

A new paragraph dealing with these issues is now added to the text. We also ask to consider the closing remarks of the present Response.

12) page 13, line 25: "The importance of BB sources, FF combustion and biogenic sources for the PM2.5 mass". Please note that the model does not apportion the total contribution of these sources to PM2.5, but only the contribution of carbonaceous species emitted by these sources (e.g. high emissions of K+ from BB combustion are expected to impact on PM2.5, but they are - of course - completely neglected by this source apportionment approach). Their total relative impact to PM2.5 is for sure higher, and the proportions among them can be different.

We appreciate this comment, and a brief discussion is now added in the text.

13) page 13, line 31: please, add some considerations on estimated uncertainties related to the model.

The discussion is now added.

Page 14, line 16: please add considerations on the possible impact of secondary compounds related to BB emission on OC-BIO estimates

A brief extension on the effects of the secondary compounds related to the BB on the OC_{BIO} is now implemented.

14) page 14, line 19 and lines 26-27: at line 19 the authors find correlations between NOx (assumed as markers for traffic emissions) and EC-FF, whereas no significant correlation is found between NOx and OC-FF. I think this observation supports considerations 2 and 3 at

lines 26, 27. Nevertheless, an important role can be played also by secondary OC-FF, justifying disentanglement between primary species from FF combustion and OC-FF. It should also be noticed that to avoid effects due to different repartition of NO vs. NO2, NOx concentration should be better represented in ppb for the evaluation of more robust correlation coefficients.

A brief comment on the role of secondary OC_{FF} is now added. The concentration of NO_x was measured at some distance from the actual research station, and its 12-h mean concentration was utilised to calculate its correlation coefficients with the carbonaceous chemical species. This fact may play a larger limiting role than the repartitioning between NO and NO_2.

Minor comments

1) page 3, line 39: what is TEOM size-cut?

The upper size-cut for all aerosol sampling inlets (except for the DMPS which does not have any) was 2.5 μm. It is given on page 4, line 4–6 of the original MS.

2) page 4, line 8-9: don’t agree with the sentence. EUSAAR_2 was initially developed for background sites (see end of introduction in Cavalli et al., 2010 Atmos. Chem. Phys., 11, 10193–10203). Its application has effectively been extended to urban sites. Nevetheless, concerns were posed in the literature on its use in urban areas (e.g. Piazzalunga et al., Atmos. Chem. Phys., 11, 10193–10203, 2011)

The sentence was reformulated to include the issues raised by the Referee.

3) page 4, line 11: EUSAAR_2 protocol is longer than 15 minutes. Was it somewhat modified? Please, report, effective protocol

The overall sampling and analytical protocol took 3 hours. We modified the text to express this explicitly.

4) page 4, line 36: why did the authors use different thermal protocols for on-line and off-line instrumentation?

The thermal protocol for the laboratory OC/EC analyser was selected for comparative reasons (to preserve the possibility of the inter-comparison over years) since it has been also employed in our earlier studies in Budapest (page 4, lines 37–39). The related sentence was extended to make this reasoning more evident.

5) page 8, Table 2: I expected mean values for PM10 being the sum of mean values for PM2.5.and PM10-2.5. It is not so. Is it a time-averaging problem? Or can it be due to non-

parallel sampling (e.g. missing values in only one of the two samplers were considered in the average?)

The mean value of the on-line $PM_{2.5}$ mass derived for a specific sampling time interval was first added to the corresponding filter-based $PM_{10–2.5}$ mass on a sample-by-sample basis to obtain the PM_{10} mass data set, and then the overall mean value for the latter data was calculated. The mean value of the summed masses (thus the mean of the $PM_{2.5–10}$ + $PM_{2.5}$ data set) doesn't necessarily and exactly equal the sum of the mean mass values (thus the mean of the $PM_{2.5–10}$ data set + the mean of the $PM_{2.5}$ data set). The former data treatment is the correct method considering the dynamic character of atmospheric concentrations, uncertainties of the data, and the propagation law of errors. This was actually utilised in the MS.

6) page 9, line 3: LVG is not a substantial part of OC (as can be seen in figure 1). The observation can indicate an important contribution of LVG source (BB) also to other OC species.

The sentence was reformulated to express the relationship between the LVG and OC more precisely. The argument concerned the temporal relationship between them, and not their amounts.

7) page 9, figure 1: please plot EC and BC (if maintained) on a secondary axis to better allow appreciating modulations

The difference between EC_TOT and BC_PAS became more evident by adopting the new conversion factor for BC (see the answer to Major comment 4).

8) page 10, line 1: no % is needed in OC/EC ratio at the beginning of the line. Furthermore, I suggest to comment this datum which gives indication of strong secondary organic aerosol formation.

The typing mistake was corrected, and the comment was adopted.

9) page 11 line 29: the authors relate the need of sampling artefact correction to the total carbon load on a filter ("1 mg"), and not to the mass/area load. Can they justify this?

The sample preparation for and analytical data from the AMS apply to the total amount of C on the portion of the filter analysed, and not to the surface density. The sentence was extended to express this more precisely.

Finally, we think that the comments of the Referee helped us to improve the MS. We really appreciate this. We would also like to emphasize that the major message of the MS lies in the new pragmatic coupled radiocarbon-LVG apportionment scheme itself, which allows to assess the contribution of the major carbonaceous species with a reasonable uncertainty, and without coupling of thermal or separation methods with an AMS for rather small amounts of samples, which may not be accessible for many research groups.

Imre Salma
for all co-authors

Response to Referee #2

The authors thank Referee #2 for his/her detailed and valuable comments to further improve and clarify the MS. We have considered all recommendations, and made the appropriate alterations. Our specific responses to the comments are as follows.

Comments

1) Main added uncertainty to the classical method of radiocarbon analysis with the split of EC and OC before the analysis is included in predefined value of ECBB to OCBB ratio. Nevertheless, the authors do not comment uncertainty connected with this value at all. Moreover, although they found that one of the samples was probably contaminated by artificial 14C release, they omitted to discuss a possibility of such influence on the other samples.

A separate discussion part of the uncertainties connected with the apportionment method is now added to the text with a sensitivity calculation. We also like to indicate that the contamination occurred usually (and predominantly) for the back filters, and therefore, it may have an effect (be it limited) on the final uncertainty if it is not properly realised.

2) Finally, although the authors say that their OCBIO is in line with Simpson et al. (2007) the opposite is true due to different definition of fractions. The observed result was 0.17 μ g/m3 of OCBIO in K-puszta for winter (primary biogenic particles), which was roughly 0.2% of TC in PM10 and ca 20% of TC was attributed to non-fossil SOA. Therefore the reviewer suggests to call the last OC fraction same way (non-fossil SOA), also with regard to the text on page 12, line 44.

We decided finally to remove this part of the sentence to avoid discussions on primary and secondary particles, and indicated briefly the alternative attitude in the text.

3) The authors also spend quite a lot of space describing aethalometer and other on- line instrumentation results but they did not use an opportunity to test their method with aethalometer source apportionment method.

The authors regret that they did not indicate to the handling editor and the potential referees at the submission stage that another MS, which deals with and evaluates the data from the on-line measurements obtained by the AE, PAS and DMPS in focus, is under preparation. This other MS will include the evaluation methods referred to by the Referee, thus the so-called Aethalometer model (the wavelength dependence of the optical absorption coefficient) for both the AE (Sandradewi et al., Environ. Sci. Technol., 42, 3316–3323, 2008; Sandradewi et al., Atmos. Environ., 42, 101–112, 2008; Favez et al., Atmos. Environ., 43, 3640–3644, 2009; Favez et al., Atmos. Chem. Phys., 10, 5295–5314, 2010) and PAS–DMPS (Ajtai et al., Atmos. Environ., 122, 313–320, 2015) data sets. In addition, a new approach of combining the PAS, DMPS (number size distribution) and AE (soot) data sets into one model is also planned. Comparing the results, advantages and limitations of the filter-based approach (in the present paper) and several optical-related source apportionment methods based on the on-line data sets will be one of the key points of this other MS. We decided to split the whole matter into two parts (with a natural division line between the collection of aerosol samples and on-line measurements) because we consider that their joint presentation 1) could be too lengthy and perhaps even too complex and likely could have a too broad scope, and therefore, 2) it would detract the attention from the new apportionment scheme proposed in the present MS, and 3) our goal is not to prepare a comparative MS on a selection of apportionment methods. We indicated now these additional arguments, motivations and aims very briefly in the text. Nevertheless, it seems plausible and advantageous to describe the experiments of the aerosol sample collection and measurement campaign together in order to have a more comprehensive overview on the aerosol campaign and resulting analytical data sets as a whole, and to assist the future MS to focus the attention specifically on modelling issues and data validation.

4) page 4, lines 33-34: No blank uncertainty is given for mass on Nuclepore and quartz filters

The blank uncertainties are now added to the means. In an earlier study, the role and typical field blank uncertainties for Nuclepore, Teflon and quartz filters in the SFU sampler, which was also utilised in the present work, were determined from a larger number of sample sets, and they were discussed extensively (Salma et al., Atmos. Environ., 38, 27–36, 2004). It was concluded, for instance, that the uncertainty of the Nuclepore samples allows one to determine the PM mass more reliably than is the case with quartz fibre filters, and that the latter substrate is subject to several sampling and handling uncertainties. We refer now to this paper as well.

5) page 6, line 1-2: It seems unusual to combine online PM2.5 mass with offline filters (PM10-2.5) to construct PM10, especially when PM2.5 mass from filters is available even from the same filter pack. Moreover, fine fraction from Ghent SFU is rather PM2 than PM2.5 (Hopke et. al 1997) and therefore coarse fraction will be probably PM10-2 instead of PM10-2.5.

We decide to combine the $PM_{10-2.5}$ mass obtained from the Nuclepore filters with the corresponding mean on-line FDMS-TEOM $PM_{2.5}$ mass because the uncertainty for the $PM_{2.5}$ mass determined from the 12-h exposed fine quartz filters was considerably larger than that for the mean on-line data. See also the answer to comment 4, and the paper referred there. The Gent-type stacked filter unit (SFU) sampler was indeed designed and realised by one of the co-authors of the present paper (W. Maenhaut) for collecting PM size fractions with nominal aerodynamic diameter (AD) of 10–2 and <2 μm. The cut-point of 2 μm results from drawing air through the top (coarse) Nuclepore filter with 8 μm pore size at a face velocity of 16.6 L/min. The separation between the two size fractions is, however, not very sharp (which is in contrast with the steep impaction collection curve of inertial impactors used for collecting $PM_{2.5}$ or PM_{10}). Furthermore, according to P.K. Hopke, the cut-point between the two size fractions in the Gent SFU is rather at 2.2 μm than at 2 μm (P.K. Hopke, personal communication to W. Maenhaut). Thus, the cut-point of 2 μm is rather approximate. In many published papers, in which the Gent SFU was used, including many papers co-authored hy P.K. Hopke and some co-authored by W. Maenhaut (e.g., the paper by Putaud et al. (2010) to which reference is made in our manuscript), the cut-off value between the two size fraction was reported to be 2.5 μm. In any case, several chemical species have a saddle point in their mass size distribution around the 2–2.5 μm diameter region, so that the difference between their masses in PM_2 and $PM_{2.5}$ is virtually negligible.

6) page 6, line 7 and elsewhere: The term “data lines” should be probably “data points”

The data files recorded by the on-line instruments usually consist of many rows/lines of data. A row contains usually a date/time stamp in the first columns, and various other measured quantities (e.g. optical absorption coefficients at several wavelength, or mass concentration and reference mass concentration) in the following columns from which the final data of interest are calculated. By writing the expression data rows, we referred to this structure of the collected data file.

7) page 12, Fig 3.: The scheme is quite unclear, needs improvement.

The apportionment scheme is now described more explicitly. We clarify all input data that are necessary for the apportionment and their actual entrance point into the scheme more systematically in both the text and Fig. 3. The arrows in Fig. 3 were originally selected in such way that they indicate the pathways and their major steps in the data treatment flow starting from the measured TC concentration toward the assessed end quantities of the five major carbonaceous species, i.e. EC_{FF} and OC_{FF}, EC_{BB} and OC_{BB}, and OC_{BIO}, which is considered helpful in overviewing the idea of the proposed new approach for readers who are not very familiar with dedicated with source apportionment.

8) page 14, line 5: The term “tendentious” seems not properly used in the text several times (three times on this page), please check.

The term “tendentious” is removed from the text and it is replaced by other wording.

Imre Salma
for all co-authors

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 two weeks. The on-line instruments included a FDMS-TEOM, Aethalometer, photoacoustic spectrometer, 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 μg 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 for 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 soot (that is EC or BC) 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 be also 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.

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. Characterisation 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 can lead to larger concentrations of some groups of organic molecules and particulate matter (PM) mass on shorter (seasonal) time scales or as a tendency (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, it is 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, are quite straightforward, and, therefore, they are often the choice for source apportionment studies.

Biomass burning 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 larger 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 d (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 was 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, 2012a). 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 counts 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 y. 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 $>10^{7-8}$ y, during which the ^{14}C content decays and becomes negligible in FFs. 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, for 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 tendencies 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 on-line and off-line 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 on-line optical data sets (see Sect. 2.1), and their comparison to the present model.

2 Methods

2.1 Measurement and sample collection campaign

On-line 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 two weeks from Tuesday, 25–02–2014 to Tuesday, 10–03–2014. Calm weather situations were present all over the campaign; milder than ordinary winter air temperatures occurred, and there was no snow cover in the region at all.

The on-line 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) an Aethalometer (AE33, Magee Scientific, USA) for optical attenuation of aerosol samples collected on Teflon-coated glass fibre filter tape spots at seven wavelengths of 370, 470, 520, 590, 660, 880 and 950 nm; 4) a photoacoustic spectrometer (PAS) for the optical absorption coefficient (OAC) of particles in their dispersed state at four wavelengths of 266, 355, 532 and 1064 nm (Ajtai et al., 2010, 2015); 5) 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 6) a LI-840 CO_2 analyser with a single path, dual wavelength non-dispersive 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 also to urban areas. The time resolution (τ) of the AE33 and PAS instruments were 1 min and 18 s, respectively, and it was ca. 10 min for the FDMS-TEOM and DMPS systems. 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 τ=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 τ=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 τ=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 6:30 to 18:20 local time, UTC+1), and 14 exposed filter sets for the nights (from about 18:30 to 6:20) 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 hours. 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±7 μg 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 were 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 μg C cm^{-2}. The overall relative uncertainty of the TOT analysis was estimated to be 5%+0.2 μg 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±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±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., 2012a). 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 program 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 off-line combustion system, which was designed specifically for this purpose (Molnár et al., 2013). The samples were placed in test tubes together with 15 mg MnO_2 and 5 mg Ag wool reagents, and the tubes were evacuated to vacuum ($<5\times10^{-8}$ 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±0.1 μg 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 normalised 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 $^{14}C/^{12}C$ 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 $f_C=f_M/1.08$. 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 ($f_{FF}=1–f_C$).

The FDMS-TEOM resulted in ca. 2 thousand data rows during the aerosol campaign. 99% of the base mass concentrations were >5 μg 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 μg m^{-3} with a median of –3.3 μg 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 $PM_{2.5}$ mass derived by the FDMS-TEOM and the $PM_{10–2.5}$ mass obtained from the SFU sampler was considered as the PM_{10} mass. The AE33 measurements yielded ca. 20 thousand data rows. The instrument automatically adopts the dual spot method (Weingartner et al., 2003; Virkkula et al., 2007) for correcting the filter loading effect. The black carbon (BC_AE) concentrations were derived from the measurements at a wavelength of 880 nm by using a specific attenuation parameter of 7.77 m^2 g^{-1}. The PAS instrument measured the background for 6 min in each hour and the ambient aerosol in the rest of the time, which resulted in ca. 53 thousand data rows. The BC_PAS concentrations were derived from the measured OACs at a wavelength of 1064 nm by assuming an Ångström exponent of 1.00 in the dependency of the OAC on wavelength. The specific attenuation parameter of 7.77 m^2 g^{-1} used in the AE33 for 880 nm was extrapolated to the wavelength of 1064 nm at which value the PAS measures the BC. This yielded a value of 9.31 m^2 g^{-1}, which was utilised in the concentration calculations. The determination limit of the PAS method was estimated to be smaller than 0.5 μg m^{-3} (Ajtai et al., 2010). It is worth mentioning that the measured concentrations were above the determination limits at least several times due to the well-selected collection time for the samplers and integration times of the on-line instruments. This also implies that the atmospheric variability and the uncertainties related to conversions (e.g. from OC and OM or from LVG to OC_{BB}) can cause larger uncertainties that the analytical techniques themselves.

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 utilised for the modelling. Trajectories arriving at the receptor site at a height of 200, 500, 2300 m above the ground level at 6:00 and 18:00 local time were calculated.

3 Results and discussion

Data validation and its conclusions for the experimental methods are to be discussed in a separate article. It is just noted here that the concentration of soot (that is EC or BC) particles obtained by the different measuring methods were evaluated briefly by their correlation coefficients, mean concentration ratios and SDs for the 2×14 collection time periods (Table 1). The mean concentration ratio between the EC_RT-TOT and BC_PAS data was the closest to 1.00 (1.09), while the correlation coefficient between the EC_TOT and BC_AE data was the largest (r=0.923). The BC data derived from the AE were larger than both the EC_TOT and BC_PAS data by factors of 6.1 and 2.9, respectively. These relatively large differences can be explained by the limitation of the Aethalometer, namely that unknown multiple scattering of light in the filter causes a longer optical path, which results in overestimating the concentrations of soot particles, and which was also observed in several earlier studies

(Drinovec et al., 2015 and references therein). The enhancement factor is often between 2 and 6, and depends in a complex way on various parameters such as the filter material, amount of scattering particles embedded in the filter, the mixing state of absorbing and scattering particles, the face velocity of the sample air flow and RH. The EC concentration data obtained by the RT-OC/EC analyser (τ=3 h) were larger than those determined by laboratory OC/EC analyser, while the corresponding OC data were smaller. This is largely explained by the difference in thermal protocol used in the two instruments (Maenhaut et al., 2012b; Panteliadis et al., 2015); the more sophisticated instrumentation (e.g. detector) and larger amounts of TC in the laboratory OC/EC analyser may also have contributed. It has to be further noted that the time intervals for the RT-OC/EC data were not exactly the same as the sample collection periods. The EC_TOT data set (τ=12 h) was accepted to characterise the absolute concentration level of soot particles, the BC_PAS (τ=18 s) data were regarded to represent their temporal variability and partially, their absolute concentrations, while the BC_AE (τ=1 min) data set represented their relative changes in time (time variability). It is also mentioned that the MAC value used is not generally valid but can vary with aerosol composition, and morphology, origin and age of soot particles, which can further complicate the measurements.

Table 1. Correlation coefficients (upper diagonal triangle matrix) and mean concentration ratios with SD (lower diagonal triangle matrix) of EC measured by laboratory OC/EC analyser (EC_TOT), BC derived by AE33 (BC_AE) and by PAS (BC_PAS), and EC obtained by RT-OC/EC analyser (EC_RT-TOT). Averaging of the on-line data was performed for the sample collection time interval of the SFU sampler. The lower diagonal triangle matrix contains ratios of the concentration of the variable in the first column to the concentration of the variable in the first row.

Variable	EC_TOT	BC_AE	BC_PAS	EC_RT-TOT
EC_TOT	1.00	0.923	0.762	0.708
BC_AE	6.1±0.8	1.00	0.803	0.832
BC_PAS	2.1±0.21	0.34±0.05	1.00	0.677
EC_RT-TOT	2.1±0.6	0.45±0.07	1.09±0.31	1.00

3.1 Averages

The individual on-line concentrations and meteorological data were averaged for the 2×14 sampling time periods. Their ranges, overall medians, means with SDs are shown in Table 2 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 of 2000's years (Salma et al., 2004; Salma and Maenhaut, 2006). The EU 24-h health limit value for PM$_{10}$ mass of 50 µg m^{-3} was exceeded three times, on 25, 26 and 27 February (on the first three 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 in this time of the year were observed. The 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 herein; Maenhaut et al., 2012a). 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., 2012a), which indicates that BB preferably 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 µg 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 ng m^{-3}, and between 8.9 and 83 ng m^{-3}, respectively (Bauer et al., 2008), and their mean concentrations in Rehovot, Israel, in winter were 8.4 and 22 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 not necessarily has a direct relation with fungi levels (Burshtein et al., 2011).

Table 2. Range, median, 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, BC derived by AE33 (BC_AE) and by PAS (BC_PAS), 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). The averaging of the on-line data was performed for the sample collection time periods of the SFU sampler.

Variable	Unit	Min	Median	Max	Mean	SD
$PM_{2.5}$	μg m^{-3}	11	25	47	25	10
$PM_{10-2.5}$	μg m^{-3}	8.1	15.9	25	15.6	4.4
PM_{10}	μg m^{-3}	16	37	68	38	12
BC_AE	μg m^{-3}	3.0	6.0	12.7	6.6	2.1
BC_PAS	μg m^{-3}	1.01	2.0	3.7	1.97	0.35
EC_RT-TOT	μg m^{-3}	1.11	2.2	3.3	2.1	0.7
EC_TOT	μg m^{-3}	0.52	0.97	2.1	1.09	0.43
OC_RT-TOT	μg m^{-3}	2.0	3.7	6.8	3.8	1.4
OC_TOT	μg 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
$N\times10^{-3}$	cm^{-3}	4.1	8.9	17.1	9.3	3.2
UF$\times10^{-3}$	cm^{-3}	2.9	6.4	14.5	6.9	2.6
SO_2	μg m^{-3}	0.40	6.2	20	8.1	4.3
O_3	μg m^{-3}	2.3	15.8	58	18.4	13.7
NO_x	μg m^{-3}	19	83	474	96	62
NO	μg 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

There was some indication of larger $PM_{10-2.5}$ mass, total particle number concentration (*N)* and ultrafine (UF) concentration during daylight periods than for nights, while the $PM_{2.5}$ mass, $PM_{2.5}/PM_{10-2.5}$ mass ratio, OC and LVG exhibited larger values for nights than for daylight periods. The EC and BC data did not seem to show a clear diurnal variability. The mean contribution and SD of the $PM_{2.5}$ 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 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, by 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), by 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, BC_PAS 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 partially 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 could be 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. The pairwise correlation between EC and BC was significant (cf. Table 1). In addition, 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, and between N on one side and the PM_{10} mass, $PM_{2.5}$ mass, OC, EC, LVG on the other side were obtained. These suggest 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 can be atmospheric nucleation (Salma et al., 2014). It is also noted that the correlation coefficients between LVG on 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 effecting the fungal activity (Cox and Wathes, 1995). It was observed that fungi are more abundant when the RHs are high in both indoor and ambient air. We could not identify significant correlations in our data set between the RH on one side and ARL and MAL on the other side, which seems to be an attribute of the winter season.

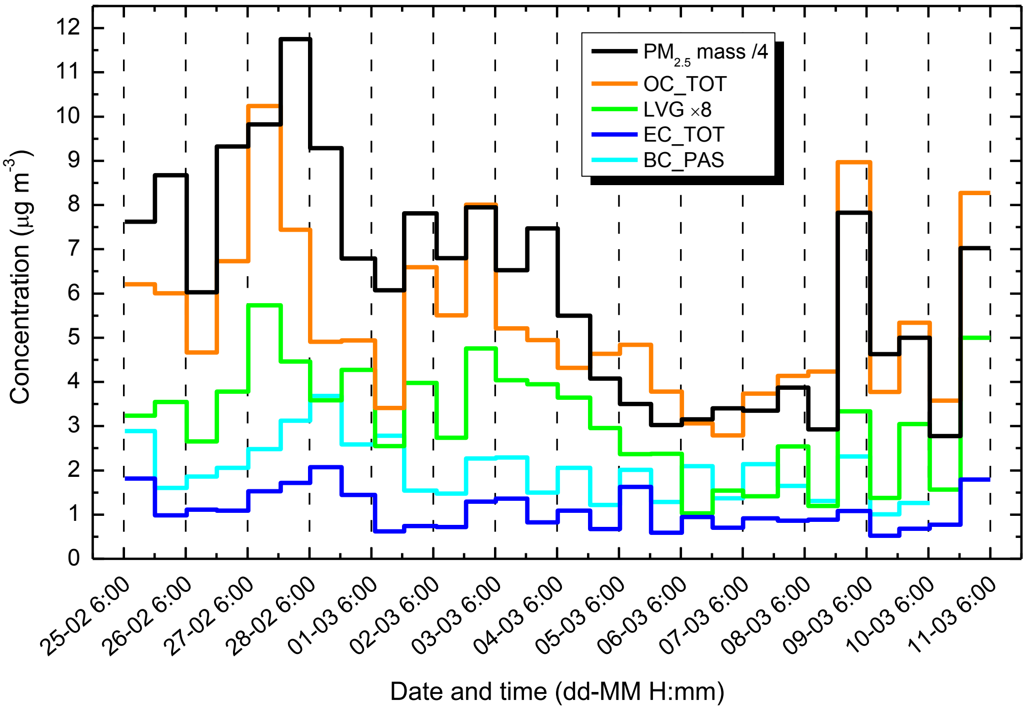


Figure 1. Temporal variability of the atmospheric concentrations for the PM$_{2.5}$ mass, EC and OC determined by the laboratory OC/EC TOT method (EC_TOT, OC_TOT, respectively), BC derived from PAS, and levoglucosan (LVG) for the sample collection periods of the 2×14 daylight times and nights.

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 utilised 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 of 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 µg m^{-3} with a median of 4.2 µg 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., 2012a). 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).

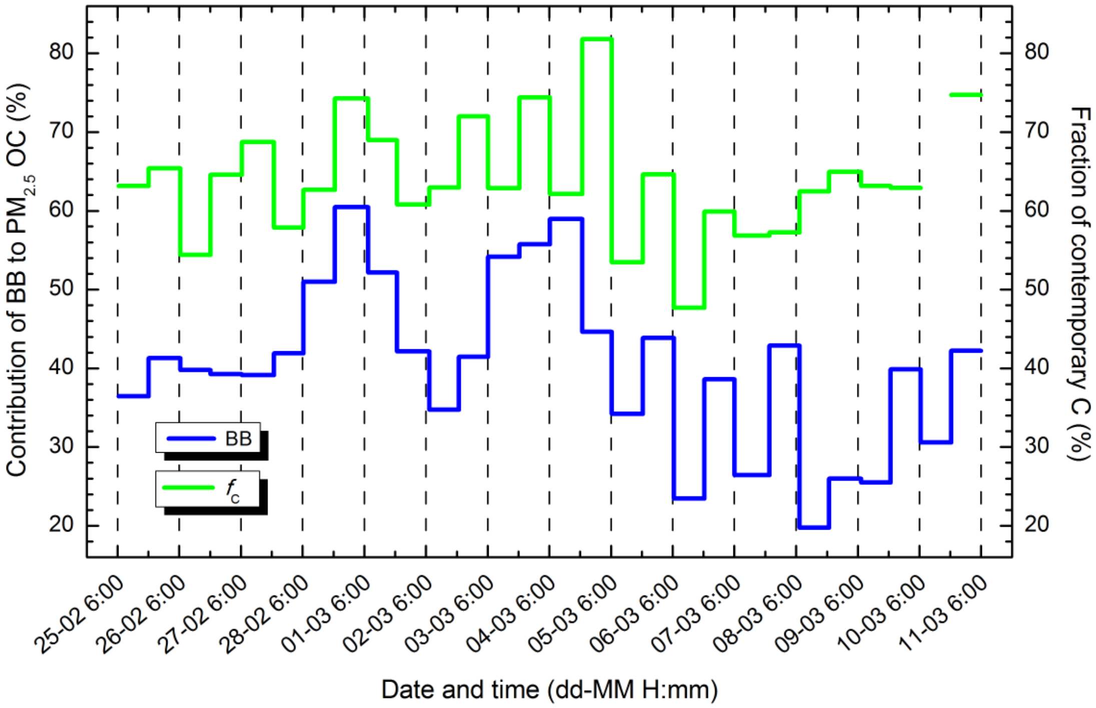


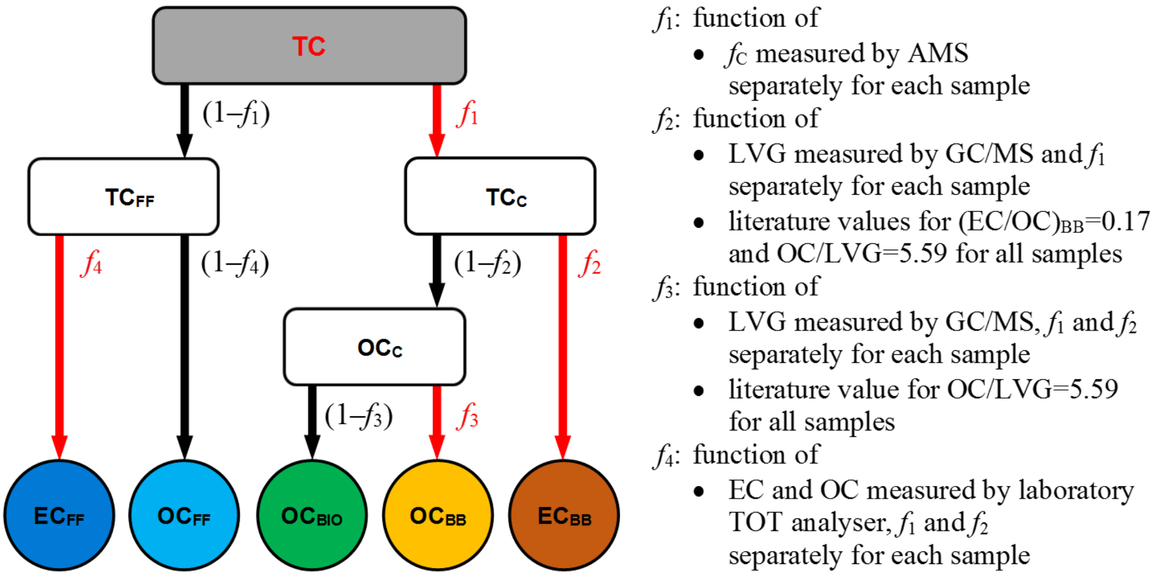
Figure 2. Temporal variability of the relative contribution of BB to the $PM_{2.5}$-fraction OC assessed by the levoglucosan marker method, and of the fraction of contemporary carbon (f_C) derived by the radiocarbon marker method.

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., 2012a). The typical ranges of the two ratios for different BB sources were overviewed by Maenhaut et al. (2012a). Softwood combustion typically yields a LVG/MAN ratio <4, while the same ratio for hardwood 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 utilised in Hungary; peat is not burned. The major form, 88% of the consumption expressed in tons of solid fuels utilised, 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, this all does not allow a reliable softwood/hardwood quantification. ~~Nevertheless, the mean LVG/MAN ratio was further utilised formally to calculate the share of softwood (ordinary spruce) burnt relative to the total amount hardwood burnt according to the relationship of %spruce=(14.8–LVG/MAN)/0.112 derived by Schmidl et al. (2008). The dependency was originally derived for the combustion of common hardwood (beech and oak) and softwood species (spruce and larch) in wood stoves in Austria. The individual LVG/MAN ratios were larger than 14.8 in half of our samples (in 14 cases), and the rest yielded a mean %spruce and SD of 20±13%. The relative uncertainty of the mean is rather large (69%). Moreover, considering the effect of the excluded data, the overall contribution of softwood burning would be even smaller, which seems too low for Hungary, and points again to the possible importance of lignite burning in the area.~~ It is worth mentioning that the calculation also raises the question whether the whole approach is justifiable for other regions or countries than 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 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 (cf. 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 utilised in the present study is summarised 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 relatively 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) utilised 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 utilised in the present calculation scheme. Thus, factor f_2 was determined from the a-priori known $(EC/OC)_{BB}$ 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 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, thus 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 utilised as primary input data in the scheme. They are also indicated in Fig. 3.



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.

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 SDs of $f_1=64\pm7\%$, $f_2=9.0\pm1.9\%$, $f_3=58\pm14\%$, $f_4=31\pm11\%$. 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., 2012a), 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 (cf. Table 3).

The mean relative contributions of the carbonaceous species to the TC with SDs 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 biomass burning 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 comparable 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)~~, and the estimate of the OC_{BIO} contribution during the winter season is also consistent with model calculations (Simpson et al., 2007)~~.

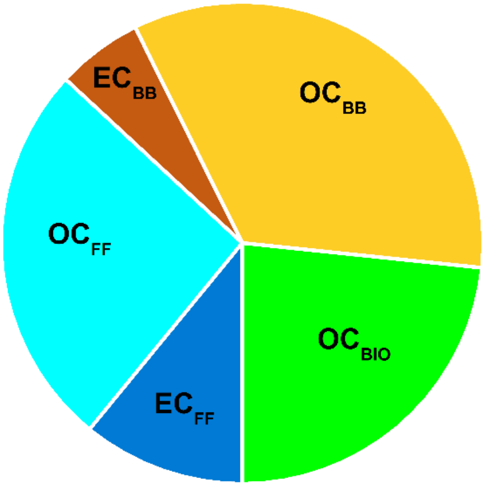


Figure 4. Median relative contributions of EC_{FF} (11.2%), OC_{FF} (27%), EC_{BB} (5.9%), OC_{BB} (34%) and OC_{BIO} (24%) to the total carbon with a median atmospheric concentration of 6.0 μg m^{-3} in the $PM_{2.5}$ size fraction in central Budapest.

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 SDs derived by averaging for all samples were 3.1±1.6% for the EC_{FF}, 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 largely similar to each other, 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 sulphate 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 PM2.5 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 3.

Table 3. 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

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 one side and OC_{FF} and OC_{BB} on the other side, 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 on one side with the three apportioned OC species on the other side showed only fluctuations. As far as the air temperature is concerned, only the dependency 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 dependency, 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 dependency 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 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, while POM from these sources also played an important role. At the same time, it cannot be excluded that secondary OC_{FF} could also partially play a role in disentangling primary species from FF combustion and OC_{FF}.

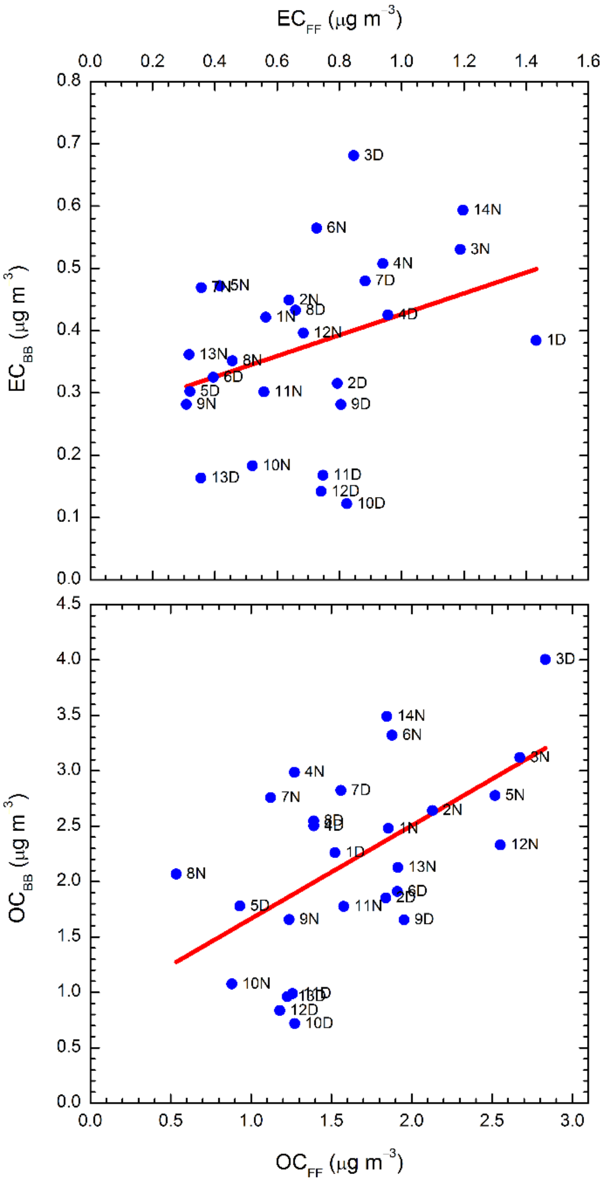


Figure 5. Scatter plots between apportioned atmospheric concentrations of EC_{FF} and EC_{BB}, and of OC_{FF} and OC_{BB} for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight time (D) or night (N)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

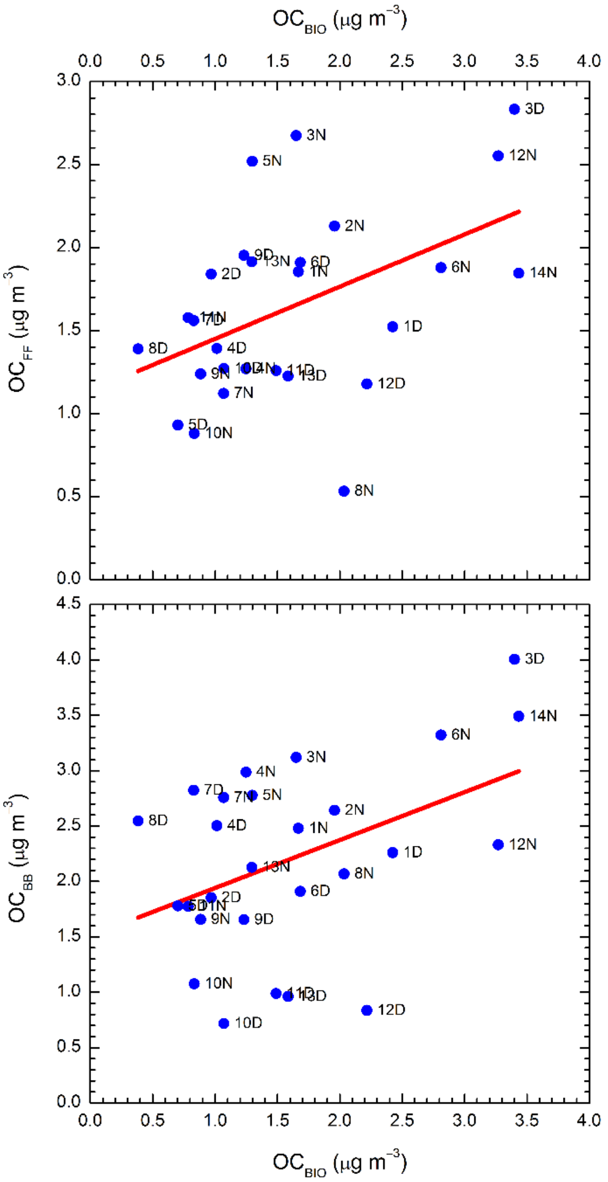


Figure 6. Scatter plots between apportioned atmospheric concentrations of OC_{BIO} and OC_{FF}, and of OC_{BIO} and OC_{BB}, for the $PM_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight time (D) or night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

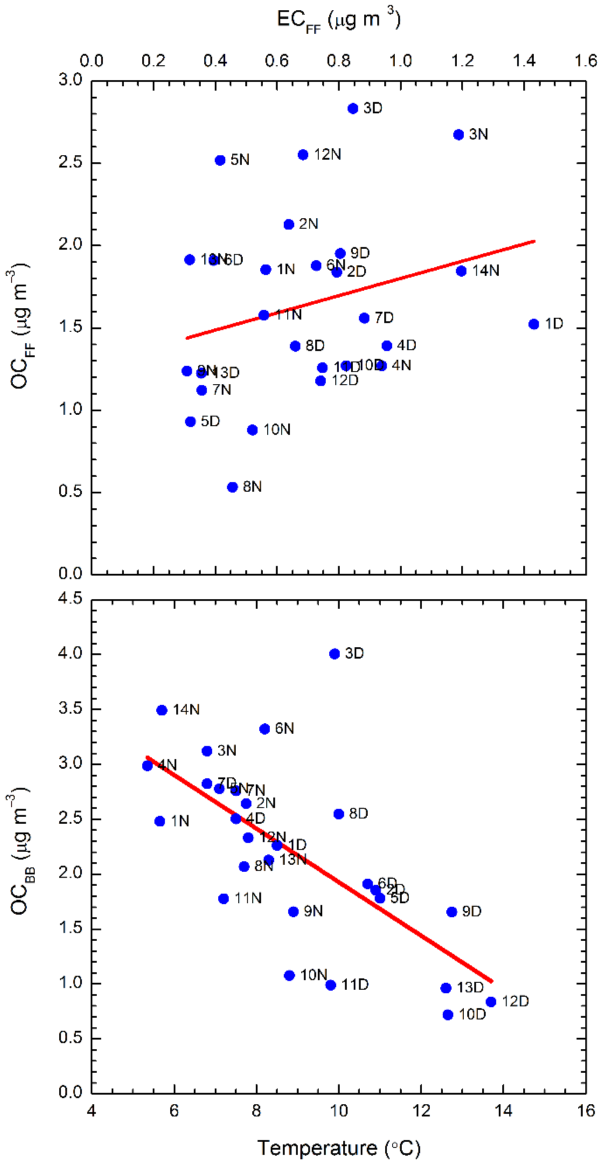


Figure 7. Scatter plots between apportioned atmospheric concentrations of EC$_{FF}$ and OC$_{BB}$, and of OC$_{BB}$ and air temperature (*T*) for the PM$_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The order number of the samples together with daylight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

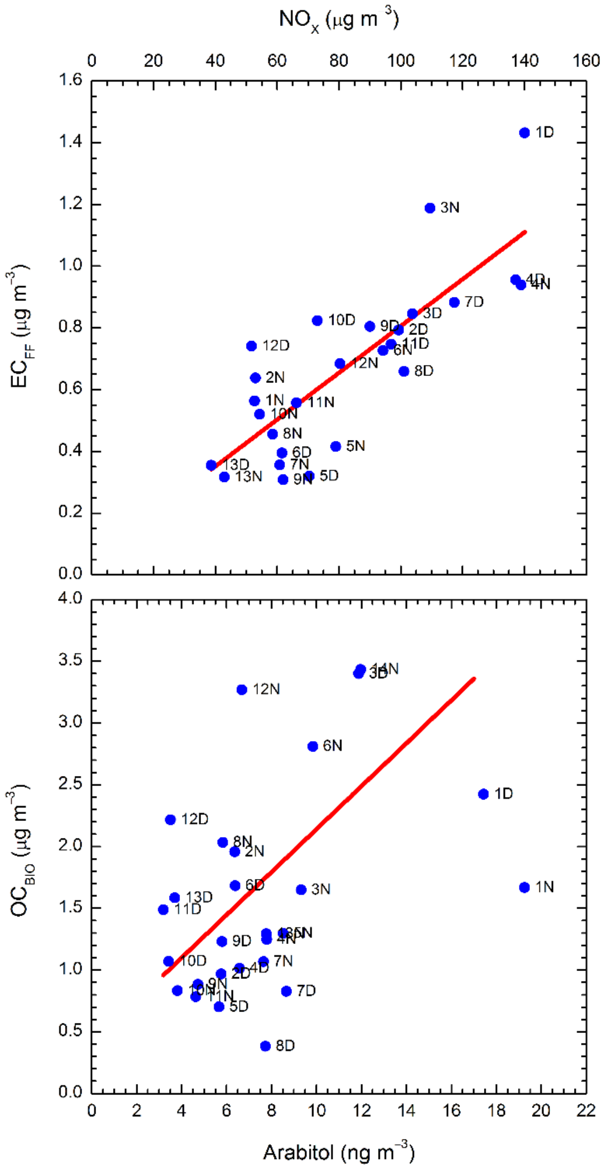


Figure 8. Scatter plots between atmospheric concentrations of NO$_x$ and apportioned EC$_{FF}$, and of arabitol and apportioned OC$_{BIO}$ for the PM$_{2.5}$ size fraction in central Budapest. The red lines represent a linear fit to the data. The data points 1D and 1N on the lower panel were excluded from the data set when fitting. The order number of the samples together with daylight time (D) or night (N) periods are indicated by labels next to the data points.

4 Conclusions

We showed here 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 driven vehicles, while most OC$_{FF}$ was attributed 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, realised 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 do contain 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 a rather 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 utilising 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 potentials to supply more detailed results and important information on emission and formation processes of carbonaceous chemical species. In this perspective research on a yearly time scale, the sample collection and analytical protocols need to be optimised jointly, and the conclusions reached in the present study are to serve as a basis for these dedicated plans.

5 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.

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References

Ajtai, T., Filep, Á., Schnaiter, M., Linke, C., Vragel, M., Bozóki, Z., Szabó, G., and Leisner, T.: A novel multi-wavelength photoacoustic spectrometer for the measurement of the UV-vis-NIR spectral absorption coefficient of atmospheric aerosols, J. Aerosol Sci., 41, 1020–1029, doi:10.1016/j.jaerosci.2010.07.008, 2010.

Ajtai, T., Utry, N., Pintér, M., Major, B., Bozóki, Z., and Szabó, G.: A method for segregating the optical absorption properties and the mass concentration of winter time urban aerosol, Atmos. Environ., 122, 313–320, 2015.

Bauer, H., Claeys, M., Vermeylen, R., Schueller, E., Weinke, G., Berger, A., and Puxbaum, H.: Arabitol and mannitol as tracers for the quantification of airborne fungal spores, Atmos. Environ., 3, 588–593, 2008.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., and Fermo, P.: PM_{10} source apportionment in Milan (Italy) using time-resolved data, Sci. Total Environ., 409, 4788–4795, 2011.

Bernardoni, V., Calzolai, G., Chiari, M., Fedi, M., Lucarelli, F., Nava, S., Piazzalunga, A., Riccobono, F., Taccetti, F., Valli, G., and Vecchi, R.: Radiocarbon analysis on organic and elemental carbon in aerosol samples and source apportionment at an urban site in Northern Italy, J. Aerosol Sci., 56, 88–99, 2013.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Technol., 25, 221–241, 1996.

Bonvalot, L., Tuna, T., Fagault, Y., Jaffrezo, J.-L., Jacob, V., Chevrier, F., and Bard, E.: Estimating contributions from biomass burning, fossil fuel combustion, and biogenic carbon to carbonaceous aerosols in the Valley of Chamonix: a dual approach based on radiocarbon and levoglucosan, Atmos. Chem. Phys., 16, 13753-13772, 2016.

Burr, G. S. and Jull, A. J. T.: Accelerator Mass Spectrometry for Radiocarbon Research, In: Encyclopedia of Mass Spectrometry, Gross, M. L. and Caprioli, R. (editors), Vol. 5, p. 656–669, Elsevier, Amsterdam, 2009.

Burshtein, N., Lang-Yona, N., and Rudich, Y.: Ergosterol, arabitol and mannitol as tracers for biological aerosols in the eastern Mediterranean, Atmos. Chem. Phys., 11, 829–839, 2011.

Caseiro, A. and Oliveira, C.: Variations in wood burning organic marker concentrations in the atmospheres of four European cities, J. Environ. Monit., 14, 2261–2269, 2012.

Caseiro, A., Bauer, H., Schmidl, C., Pio, C. A., and Puxbaum, H.: Wood burning impact on PM10 in three Austrian regions, Atmos. Environ., 43, 2186–2195, 2009.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, 2010.

Claeys, M., Kourtchev, I., Pashynska, V., Vas, G., Vermeylen, R., Wang,W., Cafmeyer, J., Chi, X., Artaxo, P., Andreae, M. O., and Maenhaut, W.: Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions, Atmos. Chem. Phys., 10, 9319–9331, 2010.

Cox, C. S. and Wathes, C. M. (editors): Bioaerosols Handbook, CRC Press, 1995.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, http://www.arl.noaa.gov/HYSPLIT.php, NOAA Air Resources Laboratory, College Park, MD, 2013.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The dual-spot Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, Atmos. Meas. Tech., 8, 1965–1979, 2015.

Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., and Fabiańska. M. J.: Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites, Atmos. Environ., 43, 2286–2295, 2009.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., and D'Anna, B.: Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France), Atmos. Chem. Phys., 10, 5295–5314, 2010.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States, Environ. Eng. Sci., 21, 387–409, 2004.

Fraser, M. P. and Lakshmanan, K.: Using levoglucosan as a molecular marker for the long range transport of biomass combustion aerosols, Environ. Sci. Technol., 34, 4560–4564, 2000.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier van der Gon, H., Facchini, M. C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J. G., Spracklen, D. V., Vignati, E., Wild, M., Williams, M. and Gilardoni, S.: Particulate matter, air quality and climate: lessons learned and future needs, Atmos. Chem. Phys., 15, 8217–8299, 2015.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenström, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined 14C – macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685–5700, 2011.

Gosselin, M. I., Rathnayake, C. M., Crawford, I., Pöhlker, C., Fröhlich-Nowoisky, J., Schmer, B., Després, V. R., Engling, G., Gallagher, M., Stone, E., Pöschl, U., and Huffman, J. A.: Fluorescent bioaerosol particle, molecular tracer, and fungal spore concentrations during dry and rainy periods in a semi-arid forest, Atmos. Chem. Phys., 16, 15165–15184, 2016.

Heal, M. R., Naysmith, Ph., Cook, G. T. Xu, S., Duran, T. R., and Harrison, R. M.: Application of ^{14}C analyses to source apportionment of carbonaceous $PM_{2.5}$ in the UK, Atmos. Environ., 45, 2341–2348, 2011.

Hennigan, C. J., Sullivan, A. P., Collett Jr. J. L., and Robinson, A. L.: Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, Geophys. Res. Lett., 37, L09806, doi:10.1029/2010GL043088, 2010.

Herich, H., Gianini, M. F. D., Piot, C., Močnik, G., Jaffrezo, J. L., Besombes, J. L., Prévôt, A. S. H., and Hueglin, C.: Overview of the impact of wood burning emissions on carbonaceous aerosols and PM in large parts of the Alpine region, Atmos. Environ., 89, 64–75, 2014.

Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of levoglucosan: A detailed laboratory and modelling study, Environ. Sci. Technol., 44, 694–699, 2010.

Iinuma, Y., Bruggemann, E., Gnauk, T., Muller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, J. Geophys. Res.-Atmos., 112, D08209, doi:10.1029/2006JD007120, 2007.

Kirchstetter, T. W., Corrigan, C. E., and Novakov, T.: Laboratory and field investigation of gaseous organic compounds onto quartz filters, Atmos. Environ., 35, 1663–1671, 2001.

Kontkanen, J., Paasonen, P., Aalto, J., Bäck, J., Rantala, P., Petäjä, T., and Kulmala, M.: Simple proxies for estimating the concentrations of monoterpenes and their oxidation products at a boreal forest site, Atmos. Chem. Phys., 16, 13291–13307, 2016.

Kourtchev, I., Hellebust, S., Bell, J. M., O'Connor, I. P., Healy, R. M., Allanic, A., Healy, D., Wenger, J. C., and Sodeau, J. R.: The use of polar organic compounds to estimate the contribution of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM2.5 in Cork Harbour, Ireland, Sci. Total Environ., 409, 2143–2155, 2011.

Locker, H. B.: The use of levoglucosan to assess the environmental impact of residential wood burning on air quality, Ph. D. Thesis, Dartmouth College, Hanover, 1988.

Maenhaut, W., François, F., and Cafmeyer, J.: The "Gent" stacked filter unit sampler for the collection of atmospheric aerosols in two size fractions: description and instructions for installation and use, in Applied Research on Air Pollution Using Nuclear-related Analytical Techniques, IAEA Report NAHRES-19, 249–263, Vienna, 1994.

Maenhaut, W., Raes, N., Chi, X., Cafmeyer, J., Wang, W., and Salma, I.: Chemical composition and mass closure for fine and coarse aerosols at a kerbside in Budapest, Hungary, in spring 2002, X-ray Spectrom., 34, 290–296, 2005.

Maenhaut, W., Vermeylen, R., Claeys, M., Vercauteren, J., Matheeussen, C., and Roekens, E.: Assessment of the contribution from wood burning to the PM_{10} aerosol in Flanders, Belgium, Sci. Total Environ., 437, 226–236, 2012a.

Maenhaut, W., Claeys, M., Vercauteren, J., and Roekens, E: Comparison of different operational parameters for thermal-optical EC/OC measurements of filter samples from Flanders, Belgium, Abstracts of the European Aerosol Conference 2012, Granada, Spain, 2-7 September 2012, Abstract 235, 2012b.

Minguillón, M. C., Perron, N., Querol, X., Szidat, S., Fahrni, S. M., Alastuey, A., Jimenez, J. L., Mohr, C., Ortega, A. M., Day, D. A., Lanz, V. A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J. F., Baltensperger, U., and Prévôt, A. S. H.: Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain, Atmos. Chem. Phys., 11, 12067–12084, 2011.

Molnár, M., Rinyu, L., Veres, M., Seiler, M., Wacker, L., and Synal, H.-A.: EnvironMICADAS: a mini ^{14}C AMS with enhanced gas ion source interface in the Hertelendi Laboratory of Environmental Studies, Hungary, Radiocarbon, 55, 338–344, 2013.

Nolte, C. G., Schauer, J. J., Cass, G. R., and Simoneit, B. R. T.: Highly polar organic compounds present in wood smoke and in the ambient atmosphere, Environ. Sci. Technol., 35, 1912–1919, 2001.

Panteliadis, P., Hafkenscheid, T., Cary, B., Diapouli, E., Fischer, A., Favez, O., Quincey, P., Viana, M., Hitzenberger, R., Vecchi, R., Saraga, D., Sciare. J., Jaffrezo, J. L., John, A., Schwarz, J., Giannoni, M., Novak, J., Karanasiou, A., Fermo, P., and Maenhaut, W.: ECOC comparison exercise with identical thermal protocols after temperature offset correction – instrument diagnostics by in-depth evaluation of operational parameters, Atmos. Meas. Tech., 8, 779–792, 2015.

Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., and Claeys, M.: Development of a gas chromatography/ion trap mass spectrometry method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols, Application to urban aerosols, J. Mass Spectrom., 37, 1249–125, 2002.

Piazzalunga, A., Belis, C., Bernardoni, V., Cazzuli, O., Fermo, P., Valli, G., and Vecchi, R.: Estimates of wood burning contribution to PM by the macro-tracer method using tailored emission factors, Atmos. Environ., 45, 6642–6649, 2011.

Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A.M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau, G., Maenhaut, W., Molnár, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European Aerosol Phenomenology - 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe, Atmos. Environ., 44, 1308–1320, 2010.

Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, J. Geophys. Res.-Atmos., 112, D23S05, doi:10.1029/2006JD008114, 2007.

Russell, L. M.: Aerosol organic-mass-to-organic-carbon ratio measurements, Environ. Sci. Technol., 37, 2982–2987, 2003.

Saarikoski, S., Sillanpaa, M., Sofiev, M., Timonen, H., Saarnio, K., Teinela, K., Karppinen, A., Kukkonen, J., and Hillamo, R.: Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessments, Atmos. Environ., 41, 3577–3589, 2007.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., and Hillamo, R.: Sources of organic carbon in fine particulate matter in northern European urban air, Atmos. Chem. Phys., 8, 6281–6295, 2008.

Saarnio, K., Niemi, J. V., Saarikoski, S., Aurela, M., Timonen, H., Teinilä, K., Myllynen, M., Frey, A., Lamberg, H., Jokiniemi, J., and Hillamo, R.: Using monosaccharide anhydrides to estimate the impact of wood combustion on fine particles in the Helsinki Metropolitan Area, Boreal Environ. Res., 17, 163–183, 2012.

Salma, I. and Maenhaut, W.: Changes in chemical composition and mass of atmospheric aerosol pollution between 1996 and 2002 in a Central European city, Environ. Pollut., 143, 479–488, 2006.

Salma, I., Maenhaut, W., Zemplén-Papp, É., and Záray, Gy.: Comprehensive characterisation of atmospheric aerosols in Budapest, Hungary: physicochemical properties of inorganic species, Atmos. Environ., 35, 4367–4378, 2001.

Salma, I., Chi, X., and Maenhaut, W.: Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary, Atmos. Environ., 38, 27–36, 2004.

Salma, I., Borsós, T., Weidinger, T., Aalto, P., Hussein, T., Dal Maso, M., and Kulmala, M.: Production, growth and properties of ultrafine atmospheric aerosol particles in an urban environment, Atmos. Chem. Phys., 11, 1339–1353, 2011.

Salma, I., Borsós, T., Németh, Z., Weidinger, T., Aalto, T., and Kulmala, M.: Comparative study of ultrafine atmospheric aerosol within a city, Atmos. Environ., 92, 154–161, 2014.

Salma, I., Németh, Z., Weidinger, T., Kovács, B., and Kristóf, G.: Measurement, growth types and shrinkage of newly formed aerosol particles at an urban research platform, Atmos. Chem. Phys., 16, 7837–7851, 2016.

Schmidl, C., Marr, L. L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., and Puxbaum, H.: Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions, Atmos. Environ., 42, 126–141, 2008.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmos. Environ., 33, 173–182, 1999.

Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P. M., Rogge, W. F., and Didyk, B. M.: Sugars-dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter, Environ. Sci. Technol., 38, 5939–5949, 2004.

~~Simpson, D., Yttri, K. E., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencsér, A., Pio, C., Puxbaum, H., and Legrand, M.: Modeling carbonaceous aerosol over Europe: Analysis of the CARBOSOL and EMEP EC/OC campaigns, J. Geophys. Res., 112, D23S14, doi:10.1029/2006JD008158, 2007.~~

Szidat, S., Jenk, T. M., Synal, H. A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C, J. Geophys. Res., 111, D07206. doi:10.1029/2005JD006590, 2006.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.-A., Hallquist, M., Shannigrahi, A. S., Yttri, K. E., Dye, C., and Simpson, D.: Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden, Atmos. Chem. Phys., 9, 1521–1535, 2009.

Turpin, B. J. and Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 602–610, 2001.

Viana, M., Chi, X., Maenhaut, W., Cafmeyer, J., Querol, X., Alastuey, A., Mikuška, P., and Večeřa, Z.: Influence of sampling artefacts on measured PM, OC, and EC levels in carbonaceous aerosols in an urban area, Aerosol Sci. Technol., 40, 107–117, 2006.

Virkkula, A., Mäkelä, T., Hillamo, R., Yli-Tuomi, T., Hirsikko, A., Hämeri, K., and Koponen, I. K.: A simple procedure for correcting loading effects of Aethalometer data, J. Air Waste Manage. Assoc., 57, 1214–1222, 2007.

Wacker, L., Bonani, G., Friedrich, M., Hajdas, I., Kromer, B., Némec, M., Ruff, M., Suter, M., Synal, H.-A., and Vockenhuber, C.: MICADAS: Routine and high-precision radiocarbon dating, Radiocarbon, 52, 252–262, 2010.

Weingartner, E., Saathof, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption of light by soot particles: determination of the absorption coefficient by means of Aethalometers, J. Aerosol Sci., 34, 1445–1463, 2003.

Yttri, K. E., Schnelle-Kreis, J., Maenhaut, W., Abbaszade, G., Alves, C., Bjerke, A., Bonnier, N., Bossi, R., Claeys, M., Dye, C., Evtyugina, M., García-Gacio, D., Hillamo, R., Hoffer, A., Hyder, M., Iinuma, Y., Jaffrezo, J.-L., Kasper-Giebl, A., Kiss, G., López-Mahia, P. L., Pio, C., Piot, C., Ramirez-Santa-Cruz, C., Sciare, J., Teinilä, K., Vermeylen, R., Vicente, A., and Zimmermann, R.: An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples, Atmos. Meas. Tech., 8, 125–147, 2015.

Zdráhal, Z., Oliveira, J., Vermeylen, R., Claeys, M., and Maenhaut, W.: Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations, Environ. Sci. Technol., 36, 747–753, 2002.

Zhang, T., Engling, G., Chan, Y. C., Zhang, Y. N., Zhang, Z. S., Lin, M., Sang, X. F., Li, Y. D., and Li, Y. S.: Contribution of fungal spores to particulate matter in a tropical rainforest, Environ. Res. Lett., 2, 024010, doi:10.1088/1748-9326/5/2/024010, 2010.

Zhang, Y. L., Perron, N., Ciobanu, V. G., Zotter, P., Minguillón, M. C., Wacker, L., Prévôt, A. S. H., Baltensperger, U., and Szidat, S.: On the isolation of OC and EC and the optimal strategy of radiocarbon-based source apportionment of carbonaceous aerosols, Atmos. Chem. Phys., 12, 10841–10856, 2012.