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Fossil fuel combustion, biomass burning and biogenic sources of fine carbonaceous aerosol in the Carpathian Basin

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Abstract. Fine-fraction aerosol samples were collected, air pollutants and meteorological properties were measured in-situ in regional background environment of the Carpathian Basin, a suburban area and central part of its largest city, Budapest in each season for 1 year-long time interval. The samples were analysed for $PM_{2.5}$ mass, organic carbon (OC), elemental carbon (EC), water-soluble OC (WSOC), radiocarbon, levoglucosan (LVG) and its stereoisomers, and some chemical elements. Carbonaceous aerosol species made up 36% of the $PM_{2.5}$ mass with a modest seasonal variation and with a slightly increasing tendency from the regional background to the city centre (from 32 to 39%). Coupled radiocarbon-LVG marker method was applied to apportion the total carbon (TC=OC+EC) into contributions of EC and OC from fossil fuel (FF) combustion (EC_{FF} and OC_{FF}, respectively), EC and OC from biomass burning (BB) (EC_{BB} and OC_{BB}, respectively) and OC from biogenic sources (OC_{BIO}). Fossil fuel combustion showed rather constant daily or seasonal mean contributions (of 35%) to the TC in the whole year in all atmospheric environments, while the daily contributions of BB and biogenic sources changed radically (from <2 up to 70–85%) over the seasons at all locations. In autumn, the three major sources contributed equally to the TC in all environments. In winter, it was the BB that was the major source with a share of 70% at all sites. The contributions from biogenic sources in winter were the smallest, although they were still non-negligible with an increasing share (from 5 to 8%) from the regional background to the urban sites. In spring, FF combustion and biogenic sources were the largest two contributors at all locations with typical shares of 45–50% each. In summer, biogenic sources became the major source type with a monotonically increasing tendency (from 56 to 72%) from the city centre to the regional background. The share of BB was hardly quantifiable in summer. The EC_{FF} made up more than 90% of EC in spring and summer, while in autumn and winter, the contributions of EC_{BB} were considerable. Biomass burning in winter and autumn offers the largest and considerable potentials for improving the air quality in cities as well as in rural areas of the Carpathian Basin.

1 Introduction and objectives

Carbonaceous aerosol constituents make up a major part (e.g. 20–60% in the continental mid-latitudes and up to 90% in tropical forests) of the $PM_{2.5}$ mass (Kanakidou et al., 2005; Fuzzi et al., 2015). Their largest emission or production source types are fossil fuel (FF) combustion, biomass burning (BB) and biogenic sources (Le Quéré et al., 2018). These processes also represent the highest source of certain important aerosol species such as soot and of some pollutant or greenhouse gases such as CO, NO_x, CO_2 and volatile organic compounds (VOCs) on global scale (Wiedinmyer et al., 2011; Tian et al., 2016). The sources produce both primary and secondary particles, and they are linked directly or indirectly to a variety of anthropogenic activities in many ways (Hallquist et al., 2009). The perturbations in atmospheric concentrations and chemical, physical and meteorological properties caused by these sources have important consequences on the Earth system. They include the radiation balance (Lohmann et al., 2000), cloud formation/properties, water cycling and other biogeochemical cycles (Andreae and Rosenfeld, 2008; Cecchini et al., 2017), atmospheric chemistry and nucleation (Fuzzi et al., 2015; Nozière et al., 2015; Kirkby et al., 2016), atmospheric transport/mixing (Rosenfeld et al., 2019), forest growth and agriculture production (Artaxo et al., 2009; Rap et al., 2015), ecosystems (Cirino et al., 2014), built environment and cultural heritage (Bonazza et al., 2005), and human health/wellbeing (Lelieveld and Pöschl, 2017; Burnett et al., 2018). Some particular sources, e.g. fuel wood or agricultural residue burnings are expected to be increased due to their role in decentralised and substitute energy production (Vicente and Alves, 2018). At the same time, their potential disadvantages and risk have been less recognised (Hays et al., 2003; Chen et al., 2017). It is, therefore, highly relevant to estimate the relative contribution of FF combustion, BB and biogenic sources to major carbonaceous aerosol species, namely to organic carbon (OC) and elemental carbon (EC).

Huge number, composite character, spatial and temporal variability of the sources together with the complex mixture and atmospheric transformation of their products make the quantification of these source types or their inventory-based source assessment challenging (Nozière et al., 2015). There are several methods to apportion the particulate matter (PM) mass or carbonaceous species among some or all major source types. They include source-specific marker methods (Fraser et al., 2000; Szidat et al., 2006, 2009; Minguillón et al., 2011; Zhang et al., 2012; Bernardoni et al., 2013), multi-wavelength optical methods (Sandradewi et al., 2008a, 2008b; Zotter et al., 2017; Forello et al., 2019) and various multivariate statistical

67   methods based on online or offline data (Hopke, 2016; Maenhaut et al., 2016).The latter

68   approaches are recently also combined with dedicated molecular tracers/fragments and mass

69   spectrometry or advanced optical techniques (Stefenelli et al., 2019). The marker methods are

70   advantageous from the point of view that they do not demand many samples or very extensive

71   data sets and that the required analytical data are ordinarily available in related studies. Among

72   the most frequently and successfully adopted two markers are radiocarbon (^{14}C, $T_{1/2}$=5730 y),

73   which is used for quantifying FF combustion and levoglucosan (LVG, monosaccharide

74   anhydride $C_6H_{10}O_5$), which is utilised for assessing BB. The latter molecule is often applied

75   together with its stereoisomers mannosan (MAN) and galactosan (GAN) since their

76   concentration ratios were connected to biomass type (e.g. hardwood or softwood; Fine et al.,

77   2004; Schmidl et al., 2008). Formation, modelling utilisation, atmospheric processes and

78   analytical determinations of these markers together with their advantages and limitations were

79   described, evaluated and discussed in detail earlier (e.g. Simoneit et al., 1999, 2004; Fraser and

80   Lakshmanan, 2000; Nolte et al., 2001; Pashynska et al., 2002; Zdráhal et al., 2002; Puxbaum

81   et al., 2007; Saarikoski et al., 2008; Caseiro et al., 2009; Fabbri et al., 2009; Szidat et al., 2006,

82   2009; Favez et al., 2010; Hennigan et al., 2010; Hoffmann et al., 2010; Kourtchev et al., 2011;

83   Piazzalunga et al., 2011; Maenhaut et al., 2012, 2016; Yttri et al., 2014). The coupled

84   radiocarbon-LVG marker method, introduced recently (Salma et al., 2017), is a combination

85   of the two approaches and it allows to apportion the TC (TC=OC+EC) among all major source

86   types, thus among the contributions of EC and OC from FF combustion (EC_{FF} and OC_{FF},

87   respectively), EC and OC from BB (EC_{BB} and OC_{BB}, respectively), and OC from biogenic

88   sources (OC_{BIO}).

89

90   Water-soluble OC (WSOC) is also an important carbonaceous aerosol species because it is

91   considered as an indicator of secondary organic aerosol (SOA) or carbonaceous particles after

92   atmospheric chemical aging (Claeys et al., 2010). It is related to more oxygenated chemical

93   species than freshly emitted or formed organic constituents, and this class of molecules is

94   expected to contribute substantially to cloud condensation nuclei (CCN) activity of particles

95   and represent potentially larger negative health effects of particulate mass deposited in the

96   human respiratory system due to its solubility (Hallquist et al., 2009; Fuzzi et al., 2015; Nozière

97   et al., 2015).

98

99   Despite their overall role together with the health, climate and environmental effects, there are

100   serious gaps in our knowledge on FF combustion, BB and biogenic sources – particularly on

101 the latter type in more polluted or urban areas. Information on the properties of the major

102 apportioned or secondary carbonaceous aerosol species and on their relationships with other

103 atmospheric quantities have been missing internationally on extended spatial scales as well as

104 on larger cities. The Carpathian Basin (also known as the Pannonian Basin) is the largest,

105 topographically well separated, orogenic basin in Europe (Salma et al., 2016b). Its land is

106 mostly used for intensive agriculture and farming, while larger forested areas with deciduous,

107 coniferous or mixed wood occur in the inner and bounding mountains. Weather situations

108 within the basin are generally uniform, which makes it advantageous for studying atmospheric

109 phenomena and processes. Budapest with 2.3 million inhabitants in the metropolitan area and

110 with its central geographical location is the largest and principal city in the basin. The mean

111 green space intensity – which indicates the healthy green coverage – for Budapest in 2015 was

112 estimated from Landsat satellite images to be approximately 50% with spatial variations from

113 19% in the city centre to 55% in the suburban zone (Tatai et al., 2017).

114

115 As part of a research project, we collected aerosol samples in the regional background

116 atmospheric environment of the Carpathian Basin, suburban area and city centre of Budapest

117 in each season for 1 year-long time interval and analysed them for various aerosol constituents,

118 which are required for source apportionment. The analytical results were complemented by

119 supporting air pollutant and meteorological data as well. The major objectives of the present

120 paper are to report the main findings of this research, to discuss the properties and contributions

121 of FF combustion, BB and biogenic sources and related atmospheric processes, to interpret the

122 relationships among various variables for different environmental types and seasons, and to

123 formulate some general conclusions on air quality of the region and city.

124 **2 Methods**

125 **2.1 Collection of aerosol samples and in-situ measurements**

126 The aerosol samples were collected at three sites in Hungary, in a rural background area and at

127 two urban sites in Budapest (Fig. 1). The samplings at the rural location were realised at K-

128 puszta station (N 46° 57' 56", E 19° 32' 42", 125 m above mean sea level, a.s.l.), which is

129 situated on the Great Hungarian Plain in a clearing within a mixed forest of coniferous and

130 deciduous trees (Salma et al., 2016a). The station is part of the European monitoring and

131 evaluation of the long-range transmission of air pollutants programme (EMEP network) and

132 represents the largest/main area (regional background) of the Carpathian Basin. One of the
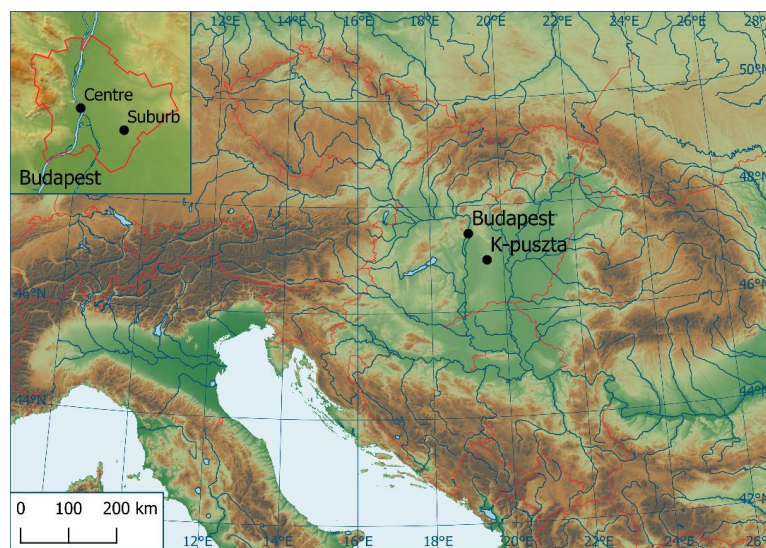
Figure 1. The Carpathian Basin with location of the sampling sites in Budapest (city centre and suburban area) and at K-puszta station (regional background).

urban sites was at an open suburban area of residential Budapest at the Marczell György Main Observatory of the Hungarian Meteorological Service (N 47° 25' 46", E 19°10' 54", 138 m a.s.l.). The collections at the other urban location were performed at the Budapest platform for Aerosol Research and Training (BpART) Laboratory of the Eötvös University (N 47° 28' 30", E 19° 03' 45", 115 m a.s.l.). The latter site is situated on the bank of the Danube and represents a well-mixed average atmosphere of the city centre (Salma et al., 2016a). Some details of the sampling campaign are summarised in Table 1.

The aerosol sampling was realised by three identical high-volume DHA-80 devices equipped with $PM_{2.5}$ inlets (Digitel, Switzerland). The collection substrates were quartz fibre filters with a diameter of 150 mm (QR-100, Advantec, Japan). Daily aerosol samples were taken starting at 00:00 LT (LT=UTC+1 or daylight-saving time UTC+2). The sampled air volumes were ca. 720 m^3. One field blank sample was also taken at each site and season. All filters were pre-heated at 500 °C for 24 h before the exposure and were stored in a freezer after the collections.

164 **Table 1.** Start and end dates of the sampling periods and number of aerosol samples collected in regional

165 background of the Carpathian Basin, suburban area and city centre of Budapest in different seasons.

166 Initials of the consecutive months allocated to the seasons are indicated in brackets.

167

Site type	Season/ Sample	Autumn (SON)	Winter (DJF)	Spring (MAM)	Summer (JJA)
Region	Period	18–31. 10. 2017	09–22. 01. 2018	17–30. 04. 2018	17–30. 07. 2018
	Number	14	14	14	14
Suburb	Period	18–31. 10. 2017	06–22. 01. 2018	17–30. 04. 2018	17. 07–01. 08. 2018
	Number	14	17	14	14
Centre	Period	18–27. 10. 2017	10–16. 01. 2018	17–23. 04. 2018	17–23. 07. 2018
	Number	7	7	7	7

168

169 Total particle number concentrations (N_{6-1000}) were derived from a differential mobility particle

170 sizer (DMPS) system with a time resolution of 8 min (Salma et al., 2019). The DMPS

171 measurements have been performed continuously and according to the recommendations of

172 international technical standards. Concentrations of criteria air pollutants, i.e. SO_2, NO/NO_x,

173 CO, O_3 and PM_{10} mass were obtained from regular stations of the National Air Quality

174 Network. For the regional background and suburban area, they were measured directly at the

175 sampling sites, while for the city centre, the pollutants were recorded in a distance of 4.5 km

176 in the upwind prevailing direction from the sampling site. The concentrations are measured by

177 UV fluorescence (Ysselbach 43C), chemiluminescence (Thermo 42C), IR absorption (Thermo

178 48i), UV absorption (Ysselbach 49C) and beta-ray attenuation methods (Thermo FH62-I-R),

179 respectively with a time resolution of 1 h. Local meteorological data including air temperature

180 (T), relative humidity (RH), wind speed (WS) and global solar electromagnetic radiation

181 (GRad) were acquired by standardised meteorological methods at the sites with a time

182 resolution of 10 min. According to our knowledge, there were no extensive agricultural burns

183 or wild fires in the basin during to the actual sampling time intervals, and the BB in the area is

184 expected to be dominated by biofuel utilisation.

185 **2.2 Analysis of aerosol samples**

186 The PM mass was determined by weighing each filter before and after the sampling on a

187 microbalance with a sensitivity of 1 μg. The exposed and blank filters were pre-equilibrated

188 before weighing at a T of 19–21°C and RH of 45–50% for at least 48 hours. The measured

189 mass data for the exposed filters were corrected for the field blank values. A few PM mass data

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190   were below the limit of quantitation (LOQ), which was approximately 6 µg m^{-3} or above but

191   very close to it.

192

193   One or two punches with an area of 1.0 or 1.5 cm^2 each of the filters were directly analysed by

194   thermal-optical transmission (TOT) method (Birch and Cary, 1996) using a laboratory OC/EC

195   analyser (Sunset Laboratory, USA) adopting the EUSAAR2 thermal protocol. The measured

196   OC data for the exposed filters were corrected for the field blank values, while the EC on the

197   blanks was negligible. All measured OC and EC data were above the LOQ, which was

198   approximately 0.09 µg m^{-3}.

199

200   One or two sections with an area of 2.5 cm^2 each of the filters were extracted in water, the

201   extracts were filtered, and the filtrates were analysed for WSOC by a Vario TOC cube analyser

202   (Elementar, Germany) in three repetitions with an injected volume of 1 ml each. The measured

203   WSOC data for the exposed filters were corrected for the field blank values. All measured

204   WSOC data were above the LOQ, which was ca. 0.08 µg m^{-3}.

205

206   A section with an area of 2 cm^2 of each filter was analysed for LVG, MAN and GAN by gas

207   chromatography/mass spectrometry (GC/MS) after trimethylsilylation (Blumberger et al.,

208   2019). The filter sections were extracted repeatedly by dichloromethane-methanol in an

209   ultrasonic bath. The extracts were filtered and spiked with an internal standard (IS) of methyl

210   β-L-arabinopyranoside. The trimethylsilylation was realised by hexamethyldisilazane as

211   silylating agent, pyridine as solvent and trifluoroacetic acid as catalyst at 70 °C. The prepared

212   samples were analysed by a Varian 4000 GC-MS/MS system (USA) with a GC/MS column of

213   SGE forte BPX-5 capillary (length×inner diameter 15 m×0.25 mm; film thickness 0.25 µm,

214   SGE, Australia). The quantification was carried out in the selected ion monitoring mode by

215   quantifier ions with mass-to-charge ratios of m/z=204 for LVG and of 217 for MAN, GAN and

216   IS. The LVG data for the exposed filters were corrected for blank values; while MAN and

217   GAN were not detected in the blanks. The LOQ for LVG and MAN was approximately 1.2 ng

218   m^{-3}, while it was approximately 0.5 ng m^{-3} for GAN. All LVG data were above the LOQ, while

219   the MAN and GAN could not be quantified in the summer samples.

220

221   Filters collected in parallel on seven overlapping days in each season were subjected to C

222   isotope analysis of the TC content by accelerator mass spectrometry (AMS) with an off-line

223   combustion system (Molnár et al., 2013; Janovics et al., 2018). Carbonaceous aerosol species

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224   on eighth section of each filter were oxidised quantitatively to CO_2 gas (Major et al., 2018).

225   This was later introduced into an IonPlus Enviro Mini Carbon Dating System spectrometer

226   (Switzerland) via its dedicated gas ion source interface. The measured results for the exposed

227   filters were corrected for the blank values. The $^{14}C/^{12}C$ ratios were also corrected for isotopic

228   fractionation by using the $^{13}C/^{12}C$ ratios (Wacker et al., 2010) that were obtained

229   simultaneously in the actual AMS measurements. The $^{14}C/^{12}C$ isotope ratios derived were also

230   normalised to that of the oxalic acid II 4990C standard reference material (NIST, USA), and

231   the measurement results were expressed as fraction of modern carbon (f_m), which denotes the

232    $^{14}C/^{12}C$ ratio of the samples relative to that of the unperturbed atmosphere in the reference year

233   of 1950 (Burr and Jull, 2009). Since majority of currently combusted fuel wood was growing

234   during the interval of atmospheric nuclear fusion bomb tests in the late 1950s and early 1960s,

235   the samples were corrected by a mean factor of 1.08 derived for the Northern Hemisphere

236   (Szidat et al., 2009; Heal et al., 2011). Thus, the fraction of contemporary carbon (f_c) was

237   calculated as $f_c=f_m/1.08$. The same correction factor was also adopted for the TC from biogenic

238   sources, although it is expected to show a somewhat smaller ^{14}C abundance. The differences

239   in the f_c caused by the refined correction factor are ordinarily small when compared to the

240   method uncertainties (Minguillón et al., 2011) and, therefore, this effect was neglected.

241

242   A quarter section of each filter was utilized to determine the K (as a possible inorganic tracer

243   for BB), Ni (as a possible tracer for residual oil combustion) and Pb (as a former tracer for

244   vehicles with gasoline engine) content of the aerosol samples by inductively coupled plasma

245   optical emission spectrometry using an iCAP7400 DUO instrument (Thermo Fischer

246   Scientific, Germany). The filter sections were extracted by microwave-assisted $HNO_3–H_2O_2$

247   digestion. The analytical results for the exposed filters were corrected for the blank values. The

248   LOQ values of the elements listed were approximately 0.02 µg m^{-3}, 0.4 and 0.5 ng m^{-3},

249   respectively, and most atmospheric concentration were above them.

250   **2.3 Data evaluation and modelling**

251   Concentrations of organic matter (OM) were derived from the OC data by a conversion factor

252   of 1.4 for the regional background and suburban area, and of 1.6 suggested for the city centres

253   (Turpin and Lim, 2001; Russell, 2003). It was estimated that the relative uncertainty associated

254   with the conversion is approximately 30% (Maenhaut et al., 2012). Whenever it was possible,

255   the comparisons of atmospheric concentration, other variables or their ratios with respect to

256   sites or seasons were accomplished by calculating first the ratios on a sample-by-sample or

257   day-by-day basis and then by averaging these individual ratios for the subset under

258   consideration.

259

260   The coupled radiocarbon-LVG marker method was utilised to apportion the TC among the

261   EC_{FF}, OC_{FF}, EC_{BB}, OC_{BB} and OC_{BIO} (Salma et al., 2017). The method consists of pragmatic

262   attribution steps, which are realised by multiplications with apportionment factors. The factors

263   are calculated for each sample from measured TC, f_c, EC, OC and LVG concentrations as

264   primary input data and from general, a priori known EC/OC ratio for BB [$(EC/OC)_{BB}$] and

265   OC/LVG ratio for BB [$(OC/LVG)_{BB}$]. They combined adaptation is related to subsequent and

266   step wise subtraction of contemporary TC, EC_{BB} and OC_{BB} from TC on the one hand, and of

267   EC_{FF} from fossil TC on the other hand. The apportionment factors are expressed as: $f_1=f_c$,

268    $f_2=(OC/LVG)_{BB} \times LVG \times (EC/OC)_{BB}/f_1/TC$, $f_3=(OC/LVG)_{BB} \times LVG/f_1/(1-f_2)/TC$ and $f_4=(EC/TC$

269    $-f_1 \times f_2)/(1-f_1)$ (Salma et al., 2017). For the $(EC/OC)_{BB}$ ratio, we implemented a mean of 17%

270   derived from a critically evaluated ratio and standard deviation (SD) of (16 ± 5)% (Szidat et al.,

271   2006) and from a ratio and SD of (18 ± 4)% (Bernardoni et al., 2011, 2013) obtained specifically

272   for wood burning. As far as the $(OC/LVG)_{BB}$ ratio is concerned, its actual value depends

273   predominantly on the wood types and burning conditions (Puxbaum et al., 2007). In the present

274   study, an $(OC/LVG)_{BB}$ ratio of 5.59 was adopted (Schmidl et al., 2008). The mean

275   apportionment factors separately for the different site types and seasons are summarised in

276   Table S1 in the Supplement. It is the OC_{BIO} and OC_{BB} which are most sensitively influenced

277   by the input uncertainties. Their relative uncertainty for some individual low concentrations

278   could be up to 40–50%, while it is expected to be approximately 30% or smaller for the other

279   carbonaceous species.

280   **3 Results and discussion**

281   General relationships that can exist among the atmospheric environments and seasons

282   including coupled meteorological and chemical processes need to be overviewed before

283   interpreting the spatial and temporal variability and tendencies in aerosol properties.

284   **3.1 Differences and similarities among atmospheric environments and seasons**

285   The median concentrations of SO_2, NO, NO_2 and PM_{10} mass over the sampling time intervals

286   were larger in the city centre than in the suburban area in all seasons (Table S2 in the

287   Supplement). This can mainly be explained by their anthropogenic sources in the city centre,

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288   mostly due to the increased intensity and density of road traffic. In contrast, the O_3 level was

289   substantially higher in the suburban area than in the city centre and considerably larger in the

290   regional background that in the suburban area. It tended to show a maximum in summer. This

291   behaviour is typical for large-scale O_3 formation mechanism. This all implies that there were

292   substantial differences in photochemical activity between the regional background and the

293   urban sites except for summer.

294

295   The meteorological data over the sampling time intervals are in accordance with ordinary

296   values and denote weather situations without extremes (Table S3 in the Supplement). The T

297   data indicate an urban heat island in central Budapest, particularly in winter and autumn. At

298   the regional site, there was snow cover with a thickness from 2 to 4 cm during the sample

299   collections in winter for approximately 4 days, while in the Budapest area, there was snow in

300   spots with a thickness of 1–2 cm for 2–3 days. The data suggest that there was somewhat milder

301   weather over the winter sample collections than usually present.

302

303   Time series of $PM_{2.5}$ mass, EC and WSOC over the sampling time intervals separately in the

304   different environments and seasons are shown in Figs. 2, 3 and 4, respectively. The former

305   variable represents the bulk fine PM; EC is a typical primary aerosol constituent, while WSOC

306   expresses the SOA. These species are rather different as far as their sources and properties are

307   concerned. Nevertheless, their concentrations often changed coherently at the locations with

308   the strongest link in winter. It can likely be explained by the common effects of regional

309   meteorology – particularly of boundary layer mixing height – in the Carpathian Basin

310   especially under anticyclonic weather situations. It seems that the daily evolution of the

311   regional meteorology and partially, the long-range transport of air masses often have higher

312   influence on the changes in atmospheric concentrations than the source intensities if the sources

313   are distributed over a large area (Salma et al., 2001, 2004). The strongest connection can be

314   related to cold air masses above the Carpathian Basin which generate a lasting T inversion layer

315   (the so-called cold pillow) and which restricts the vertical mixing and results in poor air quality

316   over extended areas of the basin in larger and smaller cities as well as in rural areas.
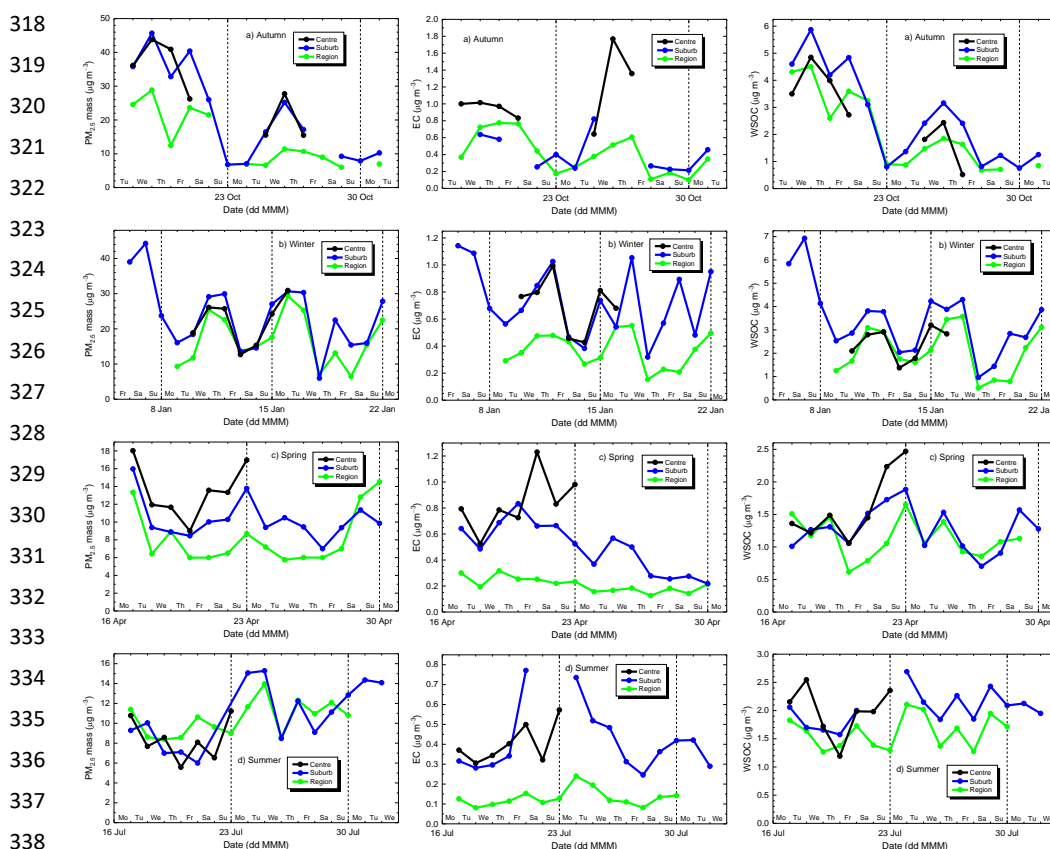
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Figure 2. Time variation of PM$_{2.5}$ mass for regional background in the Carpathian Basin, suburban area and city centre of Budapest during the aerosol sampling time intervals in different seasons (a–d).

Figure 3. Time variation of EC for regional background in the Carpathian Basin, suburban area and city centre of Budapest during the aerosol sampling time intervals in different seasons (a–d).

Figure 4. Time variation of WSOC for regional background in the Carpathian Basin, suburban area and city centre of Budapest during the aerosol sampling time intervals in different seasons (a–d).

3.2 Tendencies in aerosol concentrations

Median atmospheric concentrations of the measured aerosol constituents separately for the different environmental types and seasons are presented in Table 2. The concentrations are in line with or somewhat smaller than the corresponding results obtained in earlier studies at the same or similar locations usually for shorter time intervals (Salma and Maenhaut, 2006; Kiss et al., 2002; Salma et al., 2004, 2007, 2013, 2017; Ion et al., 2005; Maenhaut et al., 2005, 2008;

11

369   Puxbaum et al., 2007; Blumberger et al., 2019). The $PM_{2.5}$ mass and OC concentrations in the

370   city centre were larger by a mean factor of 1.6−1.7 than in the regional background, while they

371   were similar to the suburban data. Their winter values were usually the largest, and they

372   reached the minimum in summer or spring.

373

374   The concentrations of EC increased monotonically in the order of the environments: regional

375   background, suburban area and city centre location by typical factors of 2 and 3, respectively.

376   In the regional background, the EC data for autumn and winter were similar to each other and

377   they were the largest. In the suburban area, the EC data showed a maximum in winter and a

378   minimum in summer. In the city centre, the EC levels in autumn, winter and spring were similar

379   to each other, and they all showed a minimum in summer. These can be explained by larger

380   intensity of soot emissions from incomplete burning (road vehicles, residential heating and

381   cooking by solid fuel), which is a typical anthropogenic source, and which is associated with

382   seasonal variation (e.g. due to residential heating) as well as with constant sources (e.g. due to

383   traffic or cooking) over a year.

384

385   The WSOC showed maximum medians in winter at all sites. In autumn and summer, the urban

386   locations had similar concentrations to each other, while it was somewhat smaller in the

387   regional background. In winter, the suburban site exhibited the maximum median

388   concentration. This is explained by larger influence of BB in this environment and season and

389   by higher water solubility of its products (see later and Sects. 3.3 and 3.5). In spring, the

390   medians had a monotonically increasing tendency from the regional background to the city

391   centre.

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393 **Table 2.** Median atmospheric concentrations of $PM_{2.5}$ mass, elemental carbon (EC), organic carbon

394 (OC), water-soluble organic carbon (WSOC), levoglucosan (LVG), mannosan (MAN), galactosan

395 (GAN), fraction of contemporary total carbon (f_c), K, Ni, Pb and total aerosol particle number ($N_{6–1000}$)

396 for regional background in the Carpathian Basin, suburban area and city centre of Budapest in different

397 seasons.

398

Constituent	Site type	Autumn	Winter	Spring	Summer
$PM_{2.5}$ mass ($\mu g\ m^{-3}$)	Region	12.5	16.5	8.6	10.7
	Suburb	25	26	9.7	11.7
	Centre	28	24	13.3	8.2
EC ($\mu g\ m^{-3}$)	Region	0.37	0.36	0.20	0.122
	Suburb	0.45	0.68	0.51	0.35
	Centre	0.99	0.77	0.79	0.37
OC ($\mu g\ m^{-3}$)	Region	2.3	3.2	2.0	2.2
	Suburb	4.5	5.4	2.4	2.7
	Centre	6.6	4.6	2.8	2.6
WSOC ($\mu g\ m^{-3}$)	Region	1.63	2.0	1.08	1.66
	Suburb	2.4	3.8	1.27	2.0
	Centre	2.7	2.8	1.45	2.0
LVG ($\mu g\ m^{-3}$)	Region	0.172	0.40	0.0180	0.0081
	Suburb	0.44	0.71	0.040	0.0124
	Centre	0.38	0.48	0.036	0.0103
MAN ($ng\ m^{-3}$)	Region	19.2	18.5	2.6	<1.2
	Suburb	37	39	2.9	<1.2
	Centre	26	21	4.1	<1.2
GAN ($ng\ m^{-3}$)	Region	n.a.	10.6	1.20	<0.5
	Suburb	16.4	20	0.61	<0.5
	Centre	11.7	14.1	1.21	<0.5
f_c (%)	Region	69	75	61	74
	Suburb	66	74	48	60
	Centre	76	74	48	60
K ($\mu g\ m^{-3}$)	Region	0.182	0.23	0.088	0.081
	Suburb	0.22	0.25	0.097	0.075
	Centre	0.26	0.27	0.106	0.057
Ni ($ng\ m^{-3}$)	Region	0.75	0.68	1.21	1.12
	Suburb	0.88	0.78	1.24	1.09
	Centre	1.10	0.63	1.51	1.08
Pb ($ng\ m^{-3}$)	Region	3.8	3.0	3.2	2.8
	Suburb	5.8	6.8	4.1	3.5
	Centre	7.5	5.2	4.4	2.3
$N_{6–1000}$ ($10^3\ cm^{-3}$)	Region	3.9[†]	3.7[†]	4.8[†]	n.a.
	Suburb	n.a.	n.a.	n.a.	n.a.
	Centre	14.6	10.9	13.9	6.4

399 n.a.: not available; †: for $N_{6–800}$

400 The mean atmospheric concentrations of the monosaccharide anhydrides were decreasing in

401 the order of LVG, MAN and GAN. The concentrations of LVG were larger by ca. 1 order of

402 magnitude than for the joint concentrations of MAN and GAN. Their mean ratio was the largest

403 in winter and the smallest in autumn. This could be affected by the share of hardwood burnt in

404 different seasons (Fine et al., 2004; Schmidl et al., 2008; Maenhaut et al., 2012). The LVG

405 concentration did not vary monotonically with respect to the sites; it was larger in the city

406 centre by a factor of 1.7 than in the regional background and was smaller by approximately

407 20% than in the suburban area. This could be related to the spatial distribution of biofuel

408 utilisation mainly for residential heating and to atmospheric dispersion of their emission

409 products in the different environments.

410

411 As far as the contemporary C is concerned, there were three individual consecutive samples

412 collected in the city centre in autumn with significantly larger values than any other data in the

413 set. There are several applications of nuclide ^{14}C mostly in pharmaceutical/medical and

414 biological academy field in Budapest, which could release radiocarbon of anthropogenic origin

415 into the ambient air (in particular from labelled inorganic compounds such as $NaHCO_3$). These

416 three data were regarded to be outliers and were excluded from the further evaluation. The

417 centre/suburb f_c ratio in autumn, however, remained still somewhat higher (1.15) with respect

418 to the other seasons (for which the ratios were uniformly 1.00). This indicates that the

419 anthropogenic ^{14}C contamination could lightly affect the remaining analytical results as well.

420 Its consequences on the source apportionment are discussed in Sect. 3.5. In autumn and winter,

421 the mean centre/suburb, centre/region and suburb/region ratios were similar to each other (with

422 an overall mean and SD of 1.02±0.10) at all sites, while in spring and summer; they decreased

423 in the order of the ratios above with means and SDs of 1.04±0.20, 0.82±0.13 and 0.80±0.15,

424 respectively. These tendencies are governed by carbonaceous matter of different origin.

425

426 The concentrations of K in autumn, winter and spring increased monotonically for the regional

427 background, suburb area and city centre. They showed a maximum in winter. Its concentrations

428 were the smallest in summer and exhibited an opposite tendency as far as the location types are

429 concerned, thus they decreased monotonically for the sites listed above. The concentrations of

430 Ni were similar to each other without any evident tendency. Except for its concentrations in

431 spring, which seemed to be the largest. The concentration of Pb showed an increasing tendency

432 from the regional background to the urban sites. The present data are smaller than the median

433 levels of 16 ng m^{-3} in the city centre and of 9 ng m^{-3} in the near-city background measured in

434   spring 2002 after the phase out of leaded gasoline in Hungary in April 1999, and are in line

435   with its overall decreasing trend (Salma and Maenhaut, 2006; Salma et al., 2000).

436

437   The particle number concentrations in the city centre were 1 order of magnitude larger than in

438   the regional background. This is explained by the spatial distribution of their main sources and

439   by the relatively short atmospheric residence time of ultrafine particles (Salma et al., 2011).

440   The latter property also causes that there are larger variations in their atmospheric

441   concentrations, which implies that the present measurement (sampling) time intervals are not

442   long enough for reliable conclusions on tendencies.

3.3 Tendencies in concentration ratios

444   Mean values and SDs of some important concentration ratios separately for the different

445   environments and seasons are shown in Table 3. The $PM_{2.5}/PM_{10}$ mass ratio exhibited strong

446   seasonal dependency. In spring and summer, the PM_{10}–$PM_{2.5}$ fraction particles (coarse mode)

447   made up approximately 2/3 of the particulate mass, while in autumn and perhaps also in winter,

448   the $PM_{2.5}$ mass prevailed with a similar ratio. These imply and confirm that in spring and

449   summer, the suspension or resuspension of soil, crustal rock, mineral and roadside dust is

450   substantial in Budapest, while in autumn and winter, the aerosol mass levels are more

451   influenced by residential heating, cooking and road traffic (Salma and Maenhaut, 2006).

452

453   Contribution of the OM to the $PM_{2.5}$ mass for the regional background, suburban area and city

454   centre showed little seasonal variation with annual means and SDs of (31 ± 5)%, (32 ± 6)% and

455   (35 ± 7)%, respectively. These balanced contributions are in line with other European results

456   (Puxbaum et al., 2007; Putaud et al., 2010), and indicate a huge number, big variety and

457   spatially more-or-less equally distributed sources of OC in the Carpathian Basin. The mean

458   contributions of EC to the $PM_{2.5}$ mass were between 1 and 6%, with a minimum in the regional

459   background in summer. The contributions can change substantially in different

460   microenvironments within a city (e.g. 14% for a street canyon in central Budapest in spring;

461   Salma et al., 2004; Maenhaut et al., 2005). The carbonaceous particles (OM+EC) in the

462   regional background, suburban area and city centre made up (32 ± 5)%, (36 ± 7)% and (39 ± 7)%,

463   respectively of the $PM_{2.5}$ mass as annual means and SDs. Their seasonal means revealed limited

464   variability (except for the city centre, where it changed from 33% in winter to 48% in summer).

465   The TC/$PM_{2.5}$ mass ratios are given as auxiliary information to allow the recalculation of the

466   contributions to the TC shown in Fig. 5 to that to the $PM_{2.5}$ mass.

467

Table 3. Mean values and SDs for the $PM_{2.5}/PM_{10}$ mass, $OM/PM_{2.5}$ mass, $EC/PM_{2.5}$ mass, $TC/PM_{2.5}$ mass, WSOC/OC and OC/EC ratios for regional background in the Carpathian Basin, suburban area and city centre of Budapest in different seasons.

471

Ratio	Site type	Autumn	Winter	Spring	Summer
$PM_{2.5}/PM_{10}$ mass (%)	Region	64±10	n.a.	n.a.	n.a.
	Suburb	64±4	67±11	30±8	48±8
	Centre	67±9	56±14	32±4	33±7
$OM/PM_{2.5}$ mass (%)	Region	33±6	29±5	32±5	33±4
	Suburb	32±9	31±5	32±6	32±5
	Centre	36±5	30±3	30±4	36±5
$EC/PM_{2.5}$ mass (%)	Region	3.1±1.4	2.3±0.5	2.3±0.7	1.2±0.3
	Suburb	3.2±1.0	3.1±0.9	4.9±2.2	3.5±1.1
	Centre	4.3±2.4	3.3±0.6	6.4±1.7	4.6±0.9
$TC/PM_{2.5}$ mass (%)	Region	28±5	22±4	25±4	23±3
	Suburb	24±7	26±4	27±5	26±4
	Centre	27±5	22±3	28±5	29±10
WSOC/OC (%)	Region	64±11	58±7	54±9	72±5
	Suburb	55±16	64±6	53±7	76±6
	Centre	42±16	59±4	56±9	76±11
OC/EC	Region	8.8±3.2	9.0±1.4	11±3	18±4
	Suburb	8.4±3.5	7.3±1.5	5.4±2.0	7.3±1.6
	Centre	6.3±2.2	5.9±0.7	3.5±0.7	6.7±1.5

472

The mean WSOC/OC ratios in autumn showed a monotonically increasing tendency from the city centre to the regional background. This is just opposite to the atmospheric WSOC concentration (which decreased monotonically). In winter, the suburban area exhibited the maximum concentration. This can be explained by intensive BB in the area with respect to the other environments (Sect. 3.5) and with the fact that BB particles possess relatively high hygroscopicity (Swietlicki et al., 2008) and water solubility. In the remaining two seasons, the shares of the WSOC were similar to each other and varied without an obvious tendency. This can be linked to comparable and large photochemical activity in all environments in spring and summer (Sect. 3.1). The present ratios are in line with the values reported earlier for the corresponding locations (Kiss et al., 2002; Ion et al., 2005; Maenhaut et al., 2005, 2008; Viana et al., 2006; Puxbaum et al., 2007; Salma et al., 2007). It is noted that the determined OC (and WSOC) concentrations are somewhat method dependent; their ratios can change sensitively e.g. with the thermal protocol used in the OC/EC TOT analyser for samples containing large amounts of refractory C (Kuhlbusch et al., 2009; Pantheliadis et al., 2015).

16

487

488   The highest OC/EC ratios indicate the conditions under which the SOA formation is the largest.

489   The ratio had a maximum in the regional background in summer, which can be associated with

490   large photochemical activity and strong GRad. The ratios for the urban locations did not

491   indicate obvious seasonal tendencies. Formation, composition and properties of SOA and

492   atmospheric humic-like substances (HULIS) together with modelling the air mass transport

493   within the Carpathian Basin are to be dealt with in a separate paper after additional

494   investigations are completed.

495

496   Finally, it is noted for completeness that the annual mean LVG/MAN ratios and SDs for the

497   regional background, suburban area and city centre were 13.9±5.9, 14.3±6.2 and 14.7±5.8,

498   respectively, and that ca. 40% of all available individual ratios were larger than the limit of

499   14.8 derived by Schmidl et al. (2008). The latter value was obtained for the combustion of

500   common hardwood (beech and oak) and softwood species (spruce and larch) in domestic wood

501   stoves in Austria. This means for our samples and conditions, the relationship between the

502   softwood and hardwood burnt mentioned is not applicable because of several reasons, e.g. the

503   likely differences in fireplaces and fuel wood in Hungary and mid-European Alpine regions.

3.4 Apportioned carbonaceous species

505   Median atmospheric concentrations of the apportioned EC_{FF}, EC_{BB}, OC_{FF}, OC_{BB} and OC_{BIO}

506   aerosol constituents derived by the coupled radiocarbon-LVG model separately for the

507   different environments and seasons are summarised in Table 4. The present values are coherent

508   with the earlier median concentration from late winter/early spring of 2014 at the BpART

509   Laboratory (Salma et al., 2017) and with the results for the regional background (Gelencsér et

510   al., 2007; Puxbaum et al., 2007). The uncertainty of the individual apportioned data could be

511   larger than for the experimental results (e.g. TC) and, therefore, the substantial differences

512   among their means and their obvious tendencies are only interpreted.

513

514   The median concentrations of EC_{FF} were similar to each other in autumn, spring and summer,

515   and exhibited a minimum in winter. In all seasons, its concentrations in the urban environments

516   tended to be larger by a factor of 2–3 than in the regional background. The OC_{FF} concentrations

517   at the urban locations were similar to each other in all seasons, while they tended to be larger

518   than the regional values by a factor of 2–3 in autumn and summer. The EC_{BB} and OC_{BB}

519   concentrations showed a maximum in winter and a minimum in summer. The concentrations

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520 of OC_{BB} in the city centre seemed to be somewhat smaller than in the suburban area, while the

521 latter was larger by a factor of 2–3 than in the regional background in autumn and spring. The

522 concentrations of OC_{BIO} showed a monotonically decreasing tendency from autumn to

523 summer, spring and winter in all environments. The fluxes of BVOCs from plants strongly

524 depend on environmental conditions, age of leaves and vegetation, water and nutrient

525 availability, and it is also affected by the presence of some anthropogenic emissions.

526 Photochemical oxidation reactions of BVOCs, interactions among biogenic and anthropogenic

527 precursors and products, and aerosol formation yield considerations play a rather important

528 role in the process (McFiggans et al., 2019). The tendencies are further discussed after deriving

529 the contributions of the apportioned species to various quantities in Sect. 3.5.

530

531 **Table 4.** Median atmospheric concentration of apportioned elemental carbon from fossil fuel

532 combustion (EC_{FF}) and from biomass burning (EC_{BB}), of apportioned organic carbon from fossil fuel

533 combustion (OC_{FF}), from biomass burning (OC_{BB}) and from biogenic sources (OC_{BIO}) in µg m^{-3} for

534 regional background in the Carpathian Basin, suburban area and city centre of Budapest in different

535 seasons.

536

Constituent	Site type	Autumn	Winter	Spring	Summer
EC_{FF}	Region	0.35	0.057	0.23	0.12
	Suburb	0.35	0.10	0.57	0.32
	Centre	0.60	0.24	0.74	0.36
EC_{BB}	Region	0.19	0.34	0.020	0.0076
	Suburb	0.40	0.62	0.050	0.0083
	Centre	0.36	0.46	0.047	0.0095
OC_{FF}	Region	0.85	1.0	0.71	0.53
	Suburb	2.1	1.1	1.0	0.83
	Centre	1.5	1.2	1.0	0.81
OC_{BB}	Region	1.1	2.0	0.12	0.045
	Suburb	2.4	3.6	0.29	0.049
	Centre	2.1	2.7	0.27	0.056
OC_{BIO}	Region	2.0	0.22	1.3	1.8
	Suburb	2.3	0.36	1.2	1.8
	Centre	3.1	0.31	1.3	1.6

537

538 Pearson's coefficients of correlation between the variables were calculated to examine their

539 possible paired relationships. The results should be interpreted with caution since many data

540 sets are not (fully) independent from each other and can be biased by meteorological processes

541 (Sect. 3.1), can be coupled by their potential common sources or can be influenced jointly by

542 further factors/causes for them. Moreover, interactions among biogenic and anthropogenic

543 VOCs or among organic precursors with rather different SOA yields can significantly enhance

544 or suppress, respectively the SOA production (Hoyle et al., 2011; McFiggans et al., 2019).

545 Selected coefficients are shown in Table S4 in the Supplement for the annual data sets.

546 Potassium correlated with both carbonaceous species of BB origin at all locations, while its

547 coefficients with the other variables seemed insignificant. There was a linear relationship

548 between NO (which is emitted for 60–70% by road vehicles in Budapest) and OC_{FF}. The

549 relationships between T and the apportioned constituents indicated that BB was more intensive

550 under cold weather conditions, while the utilisation of FFs was more constant over the year

551 (campaign). The relationships approved the correct attribution of the apportioned species.

3.5 Contributions of major source types

553 It was the FF combustion that showed the most balanced and constant daily or seasonal mean

554 contributions to the TC over the whole year and at all sites. Its annual means and SDs for the

555 regional background, suburban area and city centre were (31±7)%, (36±12)% and (36±13)%,

556 respectively. In contrast, the daily mean contributions of BB and biogenic sources changed

557 radically over the seasons at all locations. For BB, the individual contributions for the

558 atmospheric environments listed above ranged from <2 to 73% (with a median of 10%), from

559 <2 to 73% (24%) and from <2 to 72% (19%), respectively. The analogous daily data for

560 biogenic sources spanned from <2 up to 88% (52%), from <2 to 70% (35%) and from <2 to

561 67% (39%), respectively.

562

563 Their seasonal mean contributions in forms of EC and OC to the TC separately for the different

564 environmental types are shown as circle chart diagrams in Figure 5. In autumn, the three major

565 source types contributed equally to the TC. In winter, it was the BB which was the major source

566 with a relative share of approximately 60% at all sites, and its contribution was the largest in

567 this season. The contributions of FF combustion in winter were similar to each other for all site

568 types with a typical share around 25%. The contributions of biogenic sources were the smallest

569 in this season, although they were still non-negligible. Their share showed an increasing

570 tendency from the regional background to the urban sites (from 5 to 8%), which could likely

571 be explained by larger temperatures (urban heat island) and less snow coverage in the city

572 centre (Sect. 3.1) than in its surroundings. In spring, FF combustion and biogenic sources were

573 the largest two contributors at all locations with typical shares of 45–50% each. The EC_{FF}

574 showed the largest contributions in spring, which were increased monotonically in the order of

575   the location type: region, suburb and centre. In summer, biogenic sources became the major

576   contributor with a monotonically increasing share from the centre to the region.
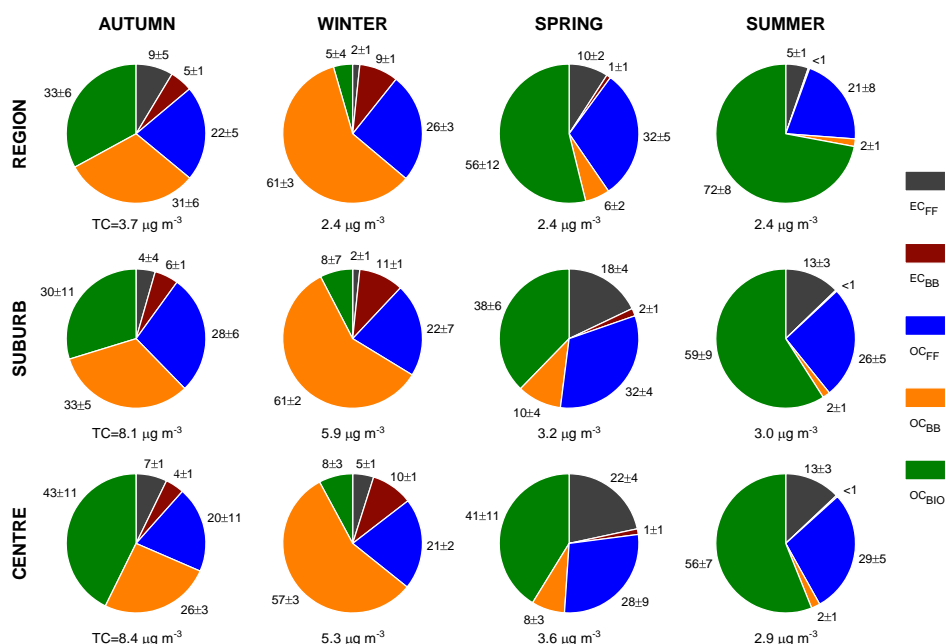
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Figure 5. Mean contributions with SDs of elemental carbon from fossil fuel combustion (EC_{FF}) and

595   from biomass burning (EC_{BB}), of organic carbon from fossil fuel combustion (OC_{FF}), from biomass

596   burning (OC_{BB}) and from biogenic sources (OC_{BIO}) to $PM_{2.5}$-fraction total carbon (TC) in % for regional

597   background in the Carpathian Basin, suburban area and city centre of Budapest and seasons. The median

598   atmospheric concentrations of TC are indicated under individual circle charts, while the corresponding

599   mean $TC/PM_{2.5}$ mass ratios are shown in Table 3.

600

601   Further conclusions can be derived by focusing on specific contributions of EC_{FF} and EC_{BB} to

602   EC, and of OC_{FF}, OC_{BB} and OC_{BIO} to OC (Figs. 6 and 7, respectively). Elemental carbon is

603   sometimes applied as a marker of automotive emissions mainly from diesel engines in cities of

604   the continental mid-latitude northern hemisphere. The present research indicates that in urban

605   ambient air in Central Europe, this assumption is, however, valid only in spring and summer

606   (when the share of the EC_{FF} was indeed larger than 90%). In autumn, the contributions of EC_{BB}

607   can be considerable (up to 40–60%) at urban sites, so they can be by no means negligible.

608   Furthermore, in winter, the relative mass of soot particles from BB can be even larger.

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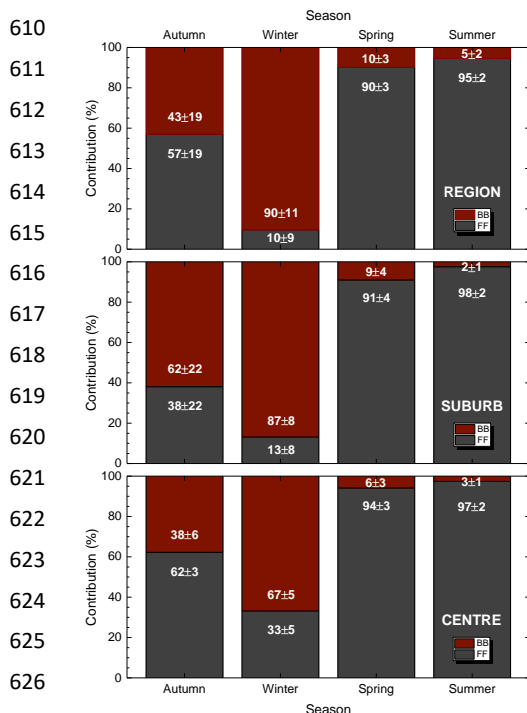
Figure 6. Seasonal distribution of mean contributions from FF combustion and BB with SDs to the PM$_{2.5}$-fraction EC for regional background in the Carpathian Basin, suburban area and city centre of Budapest. The corresponding median atmospheric concentrations of the EC are given in Table 2.
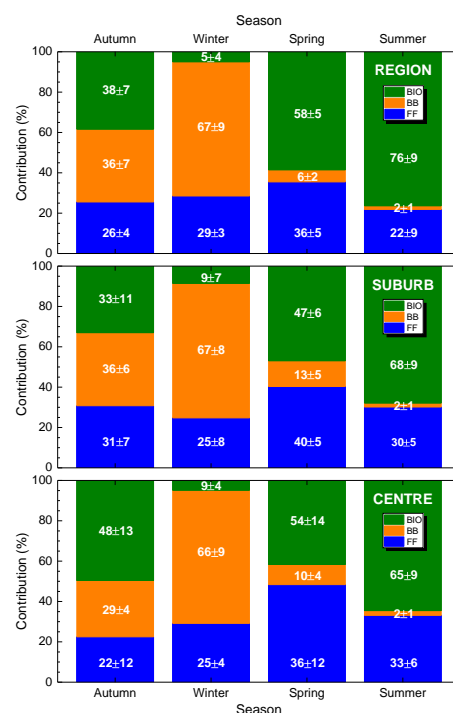
Figure 7. Seasonal distribution of mean contributions from FF combustion, BB and biogenic sources (BIO) with SDs to the PM$_{2.5}$-fraction OC for regional background in the Carpathian Basin, suburban area and city centre of Budapest. The corresponding median atmospheric concentrations of OC are given in Table 2.

It can be seen in Fig. 7 that the contributions from FF combustion to OC were fairly constant with a typical value of 25–35% and with an overall mean and SD of (30±8)% averaged for all atmospheric environments and seasons. In spring, some possible elevation could occur. Biomass burning was the major source of OC with a share of 67% in winter. Biogenic sources prevailed (with a share of 65–75%) in summer and made up about half of the OC in spring. The contributions from BB were hardly quantifiable in summer, while biogenic emissions were still considerable in winter, particularly at the urban sites. In autumn, the three major source types made up balanced (constant and similar) contributions in all environments. Closely looking, there could be a slight overestimation of biogenic sources and a related small

21

654 underestimation of FF combustion (see Fig. 3 in Salma et al., 2017) in the city centre (left lower

655 column in Fig. 7) due to possible atmospheric contamination by anthropogenic ^{14}C, which was

656 discussed in Sect. 3.2. It is mentioned that primary organic aerosol is not included in the model,

657 which could influence somewhat the overall contributions of the sources.

658 **3.6 Potentials for air quality**

659 To examine the potentials of the apportioned carbonaceous species for regulatory and

660 legislation purposes, the contributions of the main source types to the $PM_{2.5}$ mass were roughly

661 estimated. It was assumed that the OM/OC conversion factors for the aerosol particles

662 originating from FF combustion, BB and biogenic sources were equal to the conversion factor

663 for the bulk fine-fraction particles, thus 1.4 for the regional background and suburban area, and

664 1.6 for the city centre. The results obtained are summarised in Table S5 in the Supplement. The

665 separate contributions typically represent up to 1/5 or 1/4 of the PM mass as lower estimates

666 and are discussed in Sect. 4.

667

668 The contributions were also evaluated as function of the $PM_{2.5}$ mass concentration, which is a

669 key measure for air quality considerations. The plots for the seasonal mean contributions of

670 OC_{FF}, OC_{BB} and OC_{BIO} to the TC are shown in Fig. 8a–c, respectively. The contributions of

671 FF combustion (Fig. 8a) did not seem to depend substantially on the $PM_{2.5}$ mass level at any

672 of the locations, so FF exhibits a constant and steady-state importance over various air pollution

673 periods. The share of BB showed an increasing tendency with poor air quality (Fig. 8b). The

674 change rate (the slope of the fitted line, b) was larger for the regional background (b=6.7) and

675 smaller but similar to each other for the urban sites (b≈2.1). For biogenic emissions the trends

676 were just the opposite (Fig. 8c); their relative importance decreased by poorer air quality. The

677 tendency was similar again for the urban sites (b≈−1.5) and substantially larger for the regional

678 background (b=−6.9). The tendencies of the EC_{FF} and EC_{BB} were analogous. These results

679 together indicate that BB influences the air quality in the regional background very extensively

680 and it also has substantial effect on the air quality in the Budapest area, mainly in winter and

681 in autumn as well. The conclusions have importance in and consequences on the potentials for

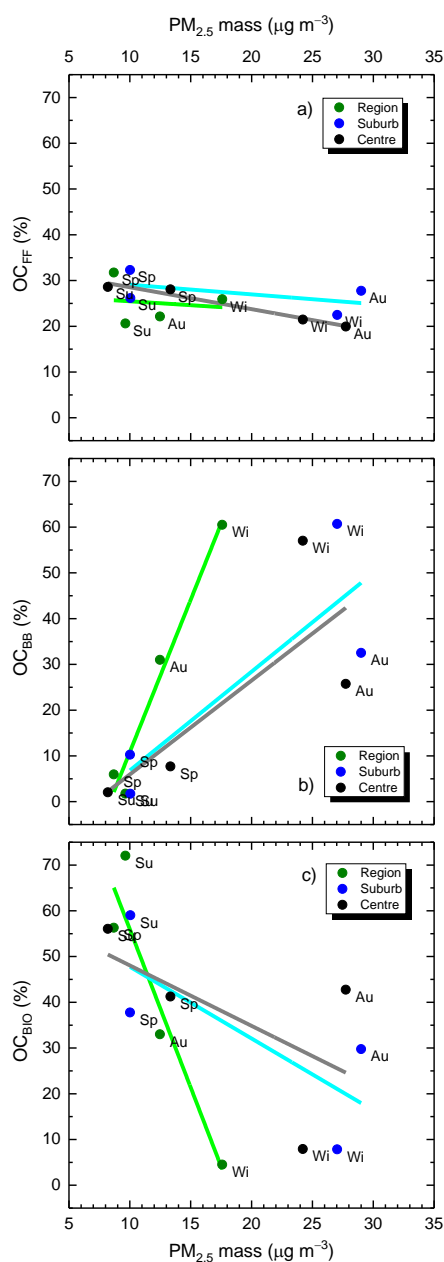682 improving the air quality further interpreted in Sect. 4.

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716 **Figure 8.** Seasonal mean contribution of apportioned OC_{FF} (a), OC_{BB} (b) and OC_{BIO} (c) to TC as

717 function of the seasonal median $PM_{2.5}$ mass concentration (surrogate or proximity value for the air

718 quality) for regional background in the Carpathian Basin, suburban area and city centre of Budapest.

719 The seasons are indicated by their two starting letters. The linear lines are to guide the eyes.

4 Conclusions

In the present study, the major carbonaceous aerosol species were apportioned among FF combustion, BB and biogenic sources in various types of atmospheric environments of interest in the Carpathian Basin in each season. The results and conclusions achieved were obtained from the first systematic complex research project as far as the spatial scale within the basin and time span (of 1 year) are concerned and represent valuable research contributions on a large area in Central Europe.

The carbonaceous particles made up from 30 to 48% of the $PM_{2.5}$ mass (as seasonal mean) depending on the environment and season. It is the BB in winter that represents the largest potential (with a mass share of >20%; Table S4 in the Supplement) for improving the air quality both in cities and on rural areas of the basin. It is worth mentioning that all air pollution (smog) alert episodes in Hungary were announced so far exclusively because of the PM_{10} mass limit exceedances and they all happened in winter. Possibilities in controlling various forms of BB for air quality improvements seem to be, therefore, rather relevant. In the present case for instance, there were 3, 8 and 8 days, respectively (19 days in total) in the subset of 4×7 days in the regional background, suburban area and city centre which daily mean values exceeded the EU annual $PM_{2.5}$ limit value of 25 µg m^{-3}. They all occurred in winter and autumn. If the BB sources (i.e. OC_{BB} and EC_{BB}) had decreased by half of their actual concentrations then the number of exceedance days would reduce to 2, 6 and 5, respectively (13 days in total), while a perfect fuel gas aftertreatment of the BB as a sources would result in the number of exceedances of 1, 4 and 5, respectively (10 days in total). In addition to carbonaceous particles, some adjunct inorganic constituents are also generated and, more importantly, soil or mineral dust and fly ash particles are also mobilised or blown up into the air due to the combustion or burning process itselfs. These, on the one hand, can further and substantially enhance the overall mass contributions and potentials of the high-temperature sources (including BB), and, on the other hand, may change somewhat their relative contributions.

Fossil fuel combustion is an abundant source of PM mass (with a share of >20%; Table S4 in the Supplement) only at urban sites in spring and summer. Resuspension or suspension of road and surface dust by moving vehicles can again represent a substantial auxiliary increment for FF contribution. Biogenic sources are normally considered as natural process or to be dominated by natural processes, and, therefore and strictly speaking, they are not associated

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753 with the issue of air pollution. It is expected that the unaccounted PM$_{2.5}$ mass contains

754 secondary inorganic aerosol particles mostly sulfates, nitrates and elements, and soil or

755 mineral/crustal rock dust particles as well (Salma et al., 2001), which should definitely be

756 revisited and taken into account in further source apportionment research.

757

758 Another challenge in health-related or air-quality-type assessment studies is to refine the

759 apportionment within the major source types with burning of plastics, domestic waste (garbage)

760 and household coal and fuel wood burning through identification of their appropriate tracers

761 and via quantification of various emission factors of their specific sources e.g. by advanced

762 hyphenated MS or optical methods combined with powerful statistical data treatment. These

763 additional combustion categories deserve more investigations since many of them seem to be

764 prevalent and of increasing volume in the studied geographical area, and they produce some

765 specific air pollutants or toxics which can represent serious risk for human health, wellbeing

766 and the environment.

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Discussions

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