Radiocarbon analysis on organic and elemental carbon in aerosol samples collected in Northern Italy and source apportionment.

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Abstract

This work aims at gaining information on the effects of different thermal treatments on radiocarbon measurements of organic (OC) and elemental (EC) carbon fractions in the atmospheric aerosol. Improvements to the traditional approaches for the determination of the fraction of modern carbon of OC and EC - $f_m(OC)$ and $f_m(EC)$ - are proposed.

$f_m(EC)$ determination is usually carried out after EC isolation using an oxygen step only. In this work, we show that the most refractory OC fraction cannot be efficiently removed by the oxygen treatment only without significantly affecting the EC recovery. Therefore, we propose to add a He step at high temperature to the oxygen treatment. Our tests demonstrate that adding a high temperature He step (final choice: 750 °C) to the oxygen treatment is effective in removing the refractory OC.

27 The direct determination of $f_m(OC)$ can be difficult because of possible OC pyrolysis during the

28 heating of an untreated sample. Therefore, we proposed to determine $f_m(OC)$ measuring either

29 the fraction of modern carbon of TC and EC or the fraction of modern carbon of water soluble

30 ($f_m(WSOC)$) and water insoluble ($f_m(WINSOC)$) organic carbon. Tests on the equivalence of the

31 approaches showed good agreement between them.

32 Our tests were carried out on samples collected in a heavy polluted area (Milan, Italy). $f_m(OC)$,

33 $f_m(EC)$, and $f_m(TC)$ results obtained in our tests were also used to attempt a preliminary source

34 apportionment in the area using ^{14}C measurements. EC resulted to be mainly fossil (85%), while

35 OC was dominated by modern contribution (64%).

36 As for the OC fraction, the fossil contribution was further separated into primary and secondary

37 contribution by OC/EC tracer method and 26% of fossil OC resulted to be of secondary origin.

38 Two approaches were tested for the evaluation of the wood burning contribution to OC. They

39 use radiocarbon or levoglucosan as tracers. Tailored emission factors were applied to obtain the

40 wood burning apportionment. Good agreement between the approaches was found and wood

41 burning primary contribution resulted to account for about 18 % of OC in Milan during

42 wintertime.

43 Secondary OC from biomass burning and the contribution from other urban sources were

44 tentatively identified following literature approaches, with the aim of identifying the biogenic

45 contribution to OC in the area, which was estimated to be about 18%.

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1. Introduction

58 Carbon is one of the main constituents of atmospheric aerosol. The study of carbonaceous

59 aerosol is important because of its adverse effects on health (Highwood and Kinnersley, 2006;

60 Mauderly and Chow, 2008; and therein cited literature), air quality (Turpin and Huntzicker,

61 1995; Putaud et al., 2004; Vecchi et al., 2009; among others), visibility (EPA, 1999; Watson,

62 2002; and therein cited literature), cultural heritage (Ghedini et al., 2000, Bonazza et al., 2005),

63 and Earth's radiation balance (Haywood and Boucher, 2000; Lohmann and Feichter, 2005; and

64 therein cited literature; IPCC, 2007; Pierce and Adams, 2009).

65 Large uncertainties still affect emission inventories of carbonaceous particles. Monks et al., 2009

66 reviewed global emission estimates: uncertainties up to factors 3.4 and 80 are reported for

67 primary and secondary carbonaceous particles, respectively. The highest uncertainties still

68 concern the natural emissions.

69 In this context, the development of analytical and modelling techniques aiming at the

70 identification of natural and anthropogenic contributions gains great importance. Moreover, the

71 possibility to separate fossil fuels and wood/biomass burning contributions by the anthropogenic

72 sources would help to develop more efficient abatement strategies and to estimate better the

73 effects of anthropogenic carbonaceous aerosol at global scale.

74 Total carbon (TC) in the atmospheric aerosol consists of two main fractions: elemental (EC) and

75 organic (OC) carbon. EC is produced by the incomplete combustion of fossil and biomass fuels

76 in an oxygen–poor environment (Chow et al., 2001). It is the most refractory carbon fraction and

77 it is the most efficient solar light absorber. OC consists in thousands of chemical constituents

78 belonging to many compound classes which make a complete characterisation extremely

3

79   difficult. Also carbonatic carbon can contribute to TC, but this component was not considered in

80   this work as previous studies reported that carbonate is negligible in PM10 at most European

81   areas. Exceptions are coastal sites in south Europe (ten Brink et al., 2004; Sillanpää et al., 2005;

82   Perrone et al., in press) or peculiar situations (Querol et al., 2009; Cuccia et al., 2011).

83   ^{14}C measurement on TC is a good tool for fossil/non fossil sources separation (Hildemann et al.,

84   1994; Currie, 2000 and therein cited literature). However, wood burning has to be considered

85   mainly of anthropogenic origin at mid-latitudes. Therefore, radiocarbon measurements on TC do

86   not allow the complete natural/anthropogenic contributions separation.

87   Recent literature works have attempted a natural/anthropogenic source apportionment, coupling

88   ^{14}C measurements on TC and the analysis of markers for modern sources (e.g. levoglucosan for

89   biomass burning, cellulose for the biogenic contribution, mannitol for fungal spores). In these

90   papers, markers concentration, emission ratios, and their uncertainties were used to estimate

91   possible ranges of source contributions by modelling techniques (Gelencer et al., 2007; May et

92   al., 2009; Gilardoni et al, 2011; Holden et al., 2011; Yttri et al., 2011a; Yttri et al., 2011b).

93   Szidat et al. (2006) proposed to perform radiocarbon measurements of OC and EC as they have

94   different sources. More in detail, ^{14}C measurements on OC and EC allow a distinction between

95   the two non-fossil sources (i.e. the wood/biomass burning and the biogenic source), provided

96   that the OC/EC emission ratio for wood/biomass burning is known. This model is limited by the

97   difficulty in the assessment of the secondary contribution from wood burning (Szidat et al.,

98   2009), as the OC/EC emission ratio measured at the source cannot correctly account for

99   secondary aerosol formation. Another drawback of radiocarbon measurements on carbon

100   fractions is the need to thermally separate OC and EC. Indeed, the analytical separation of OC

101   from EC using thermal protocols is ambiguous because part of the OC can change into EC (this

102   process is called pyrolysis or charring), especially in an oxygen–poor atmosphere and some of

103   the EC thermally evolves in presence of oxygen (Watson et al., 2005). It is also noteworthy that

104   water soluble organic carbon (WSOC) is particularly prone to pyrolysis (Novakov and Corrigan,

105   1995, Yu et al., 2002) and soluble inorganic compounds can catalyse EC pre-combustion

106   (Novakov and Corrigan, 1995; Chow et al., 2001; Yu et al., 2002; Wang et al., 2010). Therefore,

107   at the state of art EC and OC are operationally defined.

108   Radiocarbon measurements for the determination of the fraction of modern carbon (f_m, see

109   paragraph 2.3) must be carried out on each specific carbon fraction after a suitable isolation. EC

110   isolation is usually performed by sample pre-combustion at different temperature and time

111   duration in oxygen atmosphere, possibly after WSOC removal (Szidat et al., 2004a; Zencak et

112   al., 2007; Szidat et al., 2009; Andersson et al., 2011; among others). The residual sample is then

113   combusted for f_m(EC) determination. OC is generally measured on the carbon fraction evolved

114   during the sample combustion in oxygen at temperature lower than 340°C (Szidat et al., 2004a,

115   Zhang et al., 2010) to avoid possible contamination due to EC pre-combustion (Cachier et al.,

116   1989).

117   In this work, the effects of different thermal treatments for OC and EC separation on radiocarbon

118   measurements were explored. Off-line tests (quantification of the residual carbon fraction on the

119   filter after suitable thermal treatments) were performed aiming at a selection of possible thermal

120   protocols for the separation of carbon fractions. In this work an additional He step was added to

121   the pre-combustion step in oxygen – for the first time as far as we know –, in order to remove the

122   most refractory fraction of OC. Three protocols were selected to be further investigated by

123   f_m(OC) and f_m(EC) measurements. Improvements to the traditional approaches for f_m(OC) and

124   f_m(EC) determination were proposed and some tests were carried out on samples collected in a

125   heavy polluted area (Milan, Italy). Radiocarbon measurements were carried out using the

126   Tandem accelerator device at the INFN-LABEC laboratory (National Institute of Nuclear

127   Physics-Laboratory of Nuclear techniques for Cultural Heritage) in Florence. The f_m(OC),

128   f_m(EC), and f_m(TC) values obtained during our tests were also used to attempt a preliminary

129   source apportionment in the area.

130

2. Material and methods

2.1 Sampling

Samplings were carried out at an urban background station in Milan (Northern Italy). The station is placed at about 3 m a.g.l. in the University campus. Milan is the second largest town in Italy and is situated in the Po valley, one of the major pollution hot-spots in Europe.

PM10 samples were collected on Pall QAT-UP fibre filters (150 mm diameter) using a Digitel HV inlet operating at 500 l min^{-1}. Samplings were carried out during winter 2009-2010 (SC samples) and 2010-2011 (VI samples). Sampling time ranged from 18 to 36 hours to obtain suitable loadings on the filter depending on the tests to be carried out (see paragraph 2.3).

2.2. Carbon fractions quantification

Information about the TC, OC, and EC load on the filter as well as about the effect of the OC pyrolysis during the heating phase was obtained by thermal-optical transmittance analysis using a SUNSET instrument. The measurements were performed using the NIOSH5040 protocol (Birch and Cary, 1996). TC was determined on untreated samples, while EC was quantified by the analysis of water washed filter portions. Indeed, washing the filters was demonstrated to be a useful tool for a more reliable EC quantification as major interfering species are removed (Piazzalunga et al., 2011a). OC was calculated as the difference between TC and EC concentrations.

2.3. Radiocarbon analysis.

The samples for radiocarbon analysis were prepared in a sample preparation line suitably developed in the last years (Calzolai et al., 2011). Briefly, the sample was inserted in the home-made combustion oven, where thermal protocols suitable for the isolation of the selected carbon fraction were applied (see paragraph 3).

The CO_2 produced from the selected fraction is isolated from the other combustion products and

157   from the carrier gas. It is converted into a graphitic sample by a H_2 reduction reaction catalysed

158   by iron powder (Bosch reaction) (Vogel et al., 1984). The iron powder coated by graphite is then

159   pressed into capsules (hereinafter, iron powder, graphite and capsules will be referred to as

160   cathodes) to be inserted into the accelerator ion source for Accelerator Mass Spectrometry

161   (AMS) radiocarbon measurements. The accelerator facility is a 3 MV Tandetron accelerator by

162   High Voltage Engineering Europe (HVEE). A detailed description of the AMS system is given

163   in Fedi et al. (2007). This AMS system, equipped with a 846B sputtering ion source, is

164   optimized for the analysis of medium-size samples (~600 µg of carbon). Good results were

165   obtained with 450 µg C samples (Calzolai et al., 2011). In order to perform methodological ^{14}C

166   analyses on the EC fraction, which is generally present only in small quantities in the aerosol

167   samples, in this work, we necessarily reduced the sample size down to about 220 µg C. Cathodes

168   produced with such carbon quantities turned out to be affected by scarce graphite bead cohesion;

169   as a consequence, a relevant amount of the prepared samples gave no, or not reliable, result.

170   Work aiming at sample-holders and ion source modification for the analysis of smaller samples

171   is currently ongoing in our laboratory.

172   Following background subtraction, the measured ^{14}C/^{12}C ratios are corrected for isotopic

173   fractionation according to the ^{13}C/^{12}C ratios also measured in the accelerator. After normalisation

174   to the isotopic ratio measured for the HOxII standards (Mann, 1983), data were expressed as

175   fraction of modern carbon (f_m) in the sample, i.e. relative to the atmospheric radiocarbon

176   concentration in the reference year 1950 (Stuiver and Polach, 1977). ???Sicuri? A me lo 0.95

177   sembra di aver capito riporti al 1890…

178   The fraction of modern carbon is zero for fossil fuels, as a consequence of their long time of

179   formation compared to radiocarbon half-life time (5730±40 years); f_m should be 1 for modern

180   material. However, nuclear tests in the '50s increased the ^{14}C/^{12}C ratio in the atmosphere up to a

181   factor 2 in the early '60s. Values have been slowly decreasing since then and are now

182   approaching the 1 value: the trend of the ^{14}C content in the atmosphere can be found in Levin et

183 al. (2010). The ^{14}C excess in atmosphere led to the increase of ^{14}C/^{12}C ratio in biologic material

184 and it has to be accounted in the apportionment of modern sources (see paragraph 3.3).

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186 *2.4 Levoglucosan measurements*

187 Levoglucosan (1,6-anhydro-β-D-glucopyranose) is an anhydrosugar emitted by the cellulose

188 pyrolysis at T > 300°C (Simoneit, 1999) and it is commonly used as a tracer for wood burning. It

189 was analysed in our samples following the methodology reported in Piazzalunga et al. (2010).

190 *2.5 f_m(OC) and f_m(EC) determination*

191 f_m(EC) and f_m(OC) measurements can be biased by PyC formation. Moreover, it can occur that

192 highly refractory organic carbon does not evolve during the oxygen pre-combustion step, thus

193 being analysed with the EC fraction.

194 PyC formation may lead to the loss of a specific OC fraction (mainly WSOC) thus affecting

195 f_m(OC) determination. Therefore, the following indirect approaches were tested to determine

196 f_m(OC) starting from f_m measurements in other carbon fractions. The first approach (called A) is

197 based on the balance equation 1, which links the f_m(TC) to the f_m(OC) and f_m(EC):

198 $$f_m(TC) \cdot TC = f_m(EC) \cdot EC + f_m(OC) \cdot OC \qquad (1)$$

199 Using the equation 1, f_m(OC) can be determined provided that all the other terms are measured.

200 Another approach (called B) consists in determining f_m(OC) starting from f_m measurements on

201 WSOC and WINSOC. In this case, the balance equation 2 can be written as follows:

202 $$f_m(OC) \cdot OC = f_m(WSOC) \cdot WSOC + f_m(WINSOC) \cdot WINSOC \qquad (2)$$

203 The determination of f_m(OC) starting from equation 2 is proposed here for the first time. As

204 f_m(WINSOC) determination is less affected by possible loss of organic material due to pyrolysis,

205 it can be directly carried out on the carbon evolving in oxygen at a temperature lower than 340

206 °C. This temperature was indicated by Cachier et al., 1989 as the upper limit to avoid EC pre-

207 combustion in oxygen atmosphere.

208 WSOC is the carbon fraction removed by washing the filters and it can be represented as

209 WSOC=TC-TC_{ww}, where TC_{ww} is the total carbon measured on washed filters. Thus, f_m(WSOC)

210 can be determined by the balance equation 3:

$$f_m(WSOC) \cdot WSOC = f_m(TC) \cdot TC - f_m(TC_{ww}) \cdot TC_{ww} \qquad (3)$$

212 It is noteworthy that both TC radiocarbon measurements by AMS and TC quantification by

213 thermal evolution methods are much more robust and simpler than the determination on the EC-

214 OC fractions.

215 This approach is opposite to the one reported in literature works (Szidat et al. 2006), that

216 proposed to determine f_m(WSOC) starting from f_m(OC) and f_m(WINSOC) Nevertheless, as

217 previously mentioned, the direct f_m(OC) determination can be affected by pyrolysis problems.

218 Therefore, we preferred to apply equation 3 to obtain f_m(WSOC).

219 Filter washing is mandatory for the application of both approaches so that a suitable washing

220 procedure was set up (see paragraph 3.1).

221 The approach A requires f_m(EC) determination. Different thermal treatments aiming at EC

222 isolation were tested and details are reported in paragraph 3.2.1.

223 Three thermal protocols were chosen for further investigation. As it will be shown in paragraph

224 3.2.2, the equivalence of A and B approaches for f_m(OC) determination was tested and the effect

225 of the three selected protocols on the f_m(OC) and f_m(EC) determination was investigated.

226 In the end, the importance of the use of a He step for a better EC isolation was shown (paragraph

227 3.2.3).

228

229 **3. Results and Discussion**

230 *3.1 The filter washing procedure*

231 Tests for the choice of a washing procedure were carried out using ultra-pure MilliQ water by

232 Millipore (Resistivity > 18 MΩ·cm @ 25 °C). Before washing, the 150 mm quartz fibre filter

233 was cut into many circular portions (nota: si è cercato di usare "portion" per I 32mm e punch per

234 quelli da 1cm2) (32 mm diameter). Each portion was enclosed in two glass fibre filters - that

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were changed after each washing procedure to avoid contaminations - and placed in a filtration

assembly similar to the one presented in Yttri et al. (2009) that can be filled with known water

quantities for WSOC removal.

The reproducibility of the washing procedure was verified testing 5 water quantities in the range

1-13 ml cm^{-2}. Three 32 mm diameter portions were washed for all the tested water quantities.

One 1 cm^2 punch taken from each washed portion was analysed by the TOT method following

the NIOSH protocol. Reproducibility (standard deviation to the average value ratio on the three

punches) was better than 10% for TC, OC, and EC for all the tested water quantities.

Tests were also carried out to evaluate the existence of a water quantity minimising the pyrolysis

formation. Again, filters with different carbon contents (30-60 µg cm^{-2} TC) were cut into 32 mm

diameter portions. Each portion was washed using water quantities ranging from 1 to 14 ml cm^{-2}

(step: 1 ml cm^{-2}). After washing, 1 cm^2 punch from each portion was analysed by TOT focusing

on PyC quantification. Average results are shown in figure 1. It was noticed that a sudden

decrease of PyC concentration was registered with water quantities as low as 1 ml cm^{-2} and a

water amount of 5 ml cm^{-2} was enough to reduce PyC to negligible levels. Finally, our washing

procedure was set up at 7 ml cm^{-2} to account for cases in which heavy loaded filters have to be

analysed.
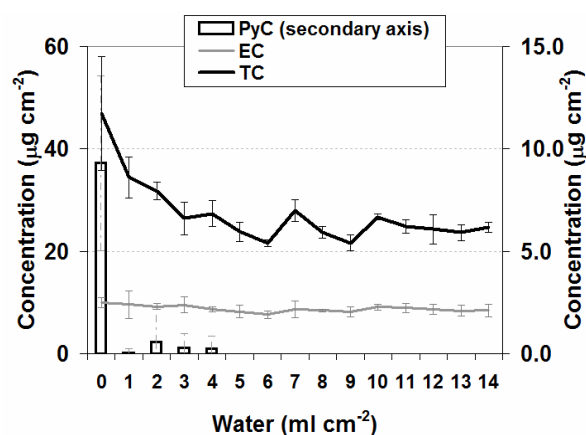
Figure 1: average PyC, EC, and TC measured on punches washed with different water quantities.

3.2 The selection of the thermal protocols

3.2.1 Off-line tests

257   A thermal protocol to isolate EC was developed in our laboratory with the goal of maximising

258   the OC evolution and the EC recovery. As ^{14}C measurements are very expensive and time-

259   consuming, off-line tests were carried out to identify a small set of protocols - three - to be

260   further investigated for f_m determination of OC and EC.

261   In figure 2 the scheme of the procedure for the selection of the EC isolation protocols to be

262   further tested is shown.

263   Briefly, two 1 cm^2 punches were cut from 32 mm washed portions. One was analysed by TOT to

264   quantify EC. The other was pre-combusted in a combustion oven identical to the one available

265   in the sample preparation line (Calzolai et al., 2011) using one of the thermal protocols under test

266   (see table 1). This pre-combusted portion was then analysed by TOT and the OC removal and the

267   EC recovery percentages were calculated comparing the results (named EC_{Ox}, OC_{Ox}, and TC_{Ox})

268   with those obtained on the washed but not pre-combusted punch (EC, OC_{ww}, and TC_{ww}).

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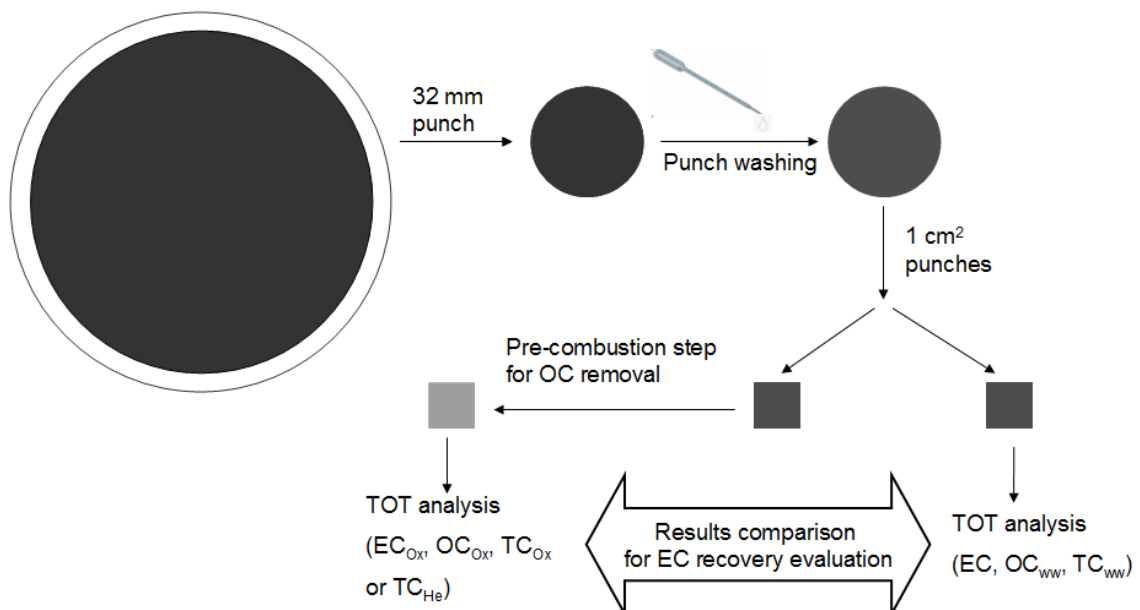
271   **Figure 2: scheme of the procedure for the off-line selection of EC isolation protocols**

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273   The off-line tests on washed punches were carried out in oxygen spanning temperatures in the

274 range 325-400°C and time duration between 20 and 120 min. Average results are reported in

275 table 1. Recovery variability can be up to 10%.

Protocol conditions in oxygen		Recovery after protocol application		
Combustion temperature (°C)	Combustion time (min)	OC_{Ox}/OC_{ww}	EC_{Ox}/EC	TC_{Ox}/TC_{ww}
400	90	9%	27%	14%
400	40	10%	39%	18%
400	20	12%	66%	26%
385	60	14%	58%	35%
385	30	18%	73%	44%
375	60	15%	64%	38%
375	**40**	**14%**	**75%**	**37%**
355	120	10%	63%	31%
355	95	12%	73%	45%
355	**75**	**14%**	**74%**	**39%**
340	95	14%	72%	45%
340	75	15%	74%	42%
325	**120**	**15%**	**79%**	**44%**

276

277 **Table 1: average recoveries obtained for the tested protocols in O₂. The protocols selected for further**

278 **investigations are evidenced in bold.**

279 The protocols selected for further investigations were those maximising the average EC recovery

280 (i.e. the ratio between EC_{Ox} and EC) and minimising OC residuals. Three protocols in oxygen

281 were selected: 325°C-120 min (LT, low temperature protocol in oxygen), 355°C-75 min (MT,

282 medium temperature protocol), and 375°C-40 min (HT, high temperature protocol). It is

283 noteworthy that protocols characterised by the oxygen step only do not remove all the OC

284 originally contained in the washed sample (about 10%-15% of the original OC remains on the

285 filter). This effect was observed even when temperature and time lengths were increased to

286 values causing significant EC losses (residual $EC_{Ox}/EC < 40\%$).

287 Therefore, a flash-heating in He atmosphere was added after the oxygen step - as far as we know

288 for the first time in this work - to remove the most refractory OC. The flash-heating step is based

289 on a rapid increase of the temperature in He atmosphere (about 1 min is needed); when the

290 chosen temperature (≥ 650 °C) is achieved, heating is stopped and the temperature rapidly

291 decreases (about 100 °C / min). The choice of the heating temperature in He was based on the

292 comparison between the total carbon on the filter after the He step. More in detail, the residual

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293   carbon on the filter after the He step (named TC_{He}, which is combusted for $f_m(EC)$

294   determination) has to be comparable to the EC quantified on the filter after the oxygen step only.

295   In this way, we assume that the He step allows the residual OC after the oxygen step to evolve

296   and prevents EC pre-combustion. On the contrary, if $TC_{He} > EC_{Ox}$ it would mean that the OC

297   evolution is not completed, while $TC_{He} < EC_{Ox}$ would indicate partial EC pre-combustion.

298   The temperature of the He step with a TC_{He}/EC ratio similar to the EC_{Ox}/EC one was 750°C for

299   LT and HT (see table 2). Considering that $TC_{He}/EC < EC_{Ox}/EC$ for MT, 750°C was chosen for

300   the He step for all the tested protocols. The protocols LT, MT, and HT followed by the He step

301   at 750 °C were further tested and called LT_{He}, MT_{He}, and HT_{He}, respectively.

Combustion temperature (°C)	Oxygen step Combustion time (min)	EC_{Ox}/EC (%)	TC_{He}/EC (%)		
			He-650°C	He-750°C	He-850°C
375	40	**75%**	90%	**77%**	57%
355	75	**74%**	76%	**66%**	63%
325	120	**79%**	87%	**80%**	73%

302

303   **Table 2: comparison between EC recovery after oxygen step and residual carbon after oxygen + He step at**

304   **different temperatures.**

305

306   *3.2.2 $f_m(OC)$ and $f_m(EC)$ determination using different approaches.*

307   First of all, the equivalence of the approaches A and B for $f_m(OC)$ determination (paragraph 2.5)

308   was verified.

309   For both A and B approaches, $f_m(TC)$ is carried out on the carbon evolving during combustion in

310   oxygen atmosphere for 20 minutes (Calzolai et al., 2011)

311   In the approach A, the LT_{He} protocol was applied to isolate EC isolation for $f_m(EC)$

312   determination. Indeed, LT_{He} gave the highest EC recovery (even if only slight differences among

313   the three protocols were registered). Obtaining high EC recovery is important to ensure that the

314   carbon analysed for ^{14}C content is representative of the whole considered fraction. After

315   isolation, residual EC is combusted in O_2 at 800°C for 20 minutes, i.e. with the same combustion

316 protocol as for $f_m(TC)$ determination.

317 To obtain $f_m(WINSOC)$ as required by the approach B, the CO_2 collected during the combustion

318 of the washed sample at 325°C – i.e. the same temperature used for the oxygen step in the EC

319 isolation process - for 20 minutes was analysed for ^{14}C.

320 Due to problems with the AMS analysis of small samples, the whole dataset necessary to

321 compare A and B approaches for $f_m(OC)$ determination (fraction of modern carbon for TC,

322 TC_{ww}, WINSOC, and EC) is available for two filters only. However, a good agreement (within

323 5%, see table 3) was found comparing the two approaches.

Sample	f_m (EC)	f_m (OC) (by A)	f_m (OC) (by B)	Δf_m (OC)
SC9_LT$_{He}$	0.231 (0.006)	0.716 (0.078)	0.734 (0.118)	-2%
SC17_LT$_{He}$	0.119 (0.006)	0.599 (0.063)	0.627 (0.105)	-4%
SC17_MT$_{He}$	0.089 (0.005)	0.608 (0.064)		-3%
SC17_HT$_{He}$	0.095 (0.006)	0.606 (0.064)		-3%

324 **Table 3: $f_m(EC)$, $f_m(OC)$ (by A and B approaches), and relative differences (Δf_m). Note that B approach for**

325 **$f_m(OC)$ determination does not depend on the protocol used for $f_m(EC)$ measurements. Uncertainties are**

326 **reported in parenthesis.**

327 It is noteworthy that uncertainties were more relevant (+40%) when $f_m(OC)$ was determined by

328 approach B using $f_m(WSOC)$ and $f_m(WINSOC)$. This is due to the higher number of calculations

329 involved and, consequently, to the strong influence of error propagation on differences.

330 Nevertheless, this approach allowed also $f_m(WSOC)$ and $f_m(WINSOC)$ determination, which can

331 be of interest for further source apportionment (e.g. fossil WINSOC from combustion, modern

332 WINSOC from primary biogenic particles, WSOC as tracers for oxygenated – often secondary -

333 compounds) (Pöschl et al., 2005, Szidat et al., 2009).

334 $f_m(EC)$ measured by LT_{He}, MT_{He}, and HT_{He} in the SC17 sample showed a good agreement within

335 few percent modern carbon·(see table 3). However, the LT_{He} result was higher than others, and

336 the values were not comparable within experimental uncertainties. Therefore, the LT_{He} protocol

337 was excluded in further investigation. As MT_{He} and HT_{He} results were comparable within

338 uncertainties, HT_{He} was finally selected as it had the shortest time duration.

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3.2.4 The effect of the He-750 °C step on f_m(EC) determination

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AMS measurements of fm(EC) using both HT and HT_{He} on the same washed sample were

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performed to test the He step effectiveness in removing residual OC after the oxygen step. The

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whole set of data was available for three samples. The results showed that the reduction of the

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measured f_m registered after EC isolation by HT_{He} compared to HT is significant (i.e. the values

344

are not comparable within the error bars, see figure 3). Therefore, the He step is effective in

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removing the residual OC present on the filter after the oxygen step only.

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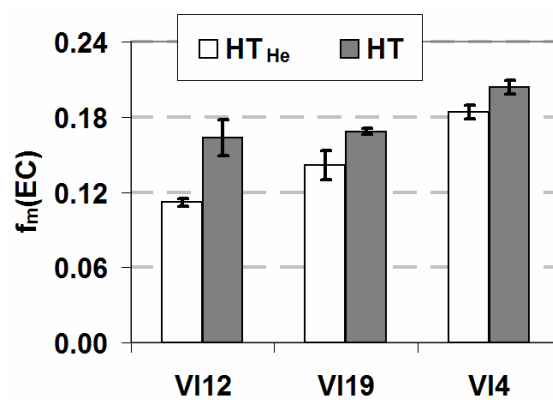
Figure 3: comparison between f_m(EC) determined after EC isolation by HT and HT_{He}

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3.3 Carbonaceous particles source apportionment

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The data on f_m(TC), f_m(EC), and f_m(OC) obtained during our tests were used to perform a

351

preliminary source apportionment.

352

The f_m(TC) was determined on 10 filters. It was in the range 0.48-0.65, indicating that modern

353

sources prevailed in Milan urban area during wintertime in most cases. Similar values had

354

already been found during wintertime at other urban sites in Europe (Szidat et al., 2006; Glasius

355

et al., 2011; Yttri et al., 2011b; Minguillón et al., 2011).

356

Radiocarbon measurements on EC and OC allowed a more detailed source apportionment.

357

As mentioned in paragraph 2.3, modern sources can have f_m >1 due to bomb excess. The

358

following values of f_m will be considered for source apportionment purposes:

359

15

360   a) fossil fuels: $f_{m, fossil}=0$

361   b) biogenic contribution: $f_{m, bio}=1.040 \pm 0.004$ obtained by long–term CO_2 series at

362   Schauinsland (Levin et al., 2008) in 2009-2010 (Levin, personal communication);

363   c) biomass burning contribution, $f_{m, wb}=1.083$ (Minguillón al., 2011) corresponding to

364   emissions from burning of 25-yr-old trees harvested in 2007–2008 as determined with a

365   tree-growth model as reported by Mohn et al. (2008).

366   EC contributions from fossil fuels (EC_{ff}) and from wood burning (EC_{wb}) combustion were

367   calculated as:

368
$$EC_{wb}=\frac{EC \cdot f_m(EC)}{f_{m,wb}} \qquad \text{and} \qquad EC_{ff}=EC-EC_{wb}$$

369   EC in our samples was mainly fossil (85% on average; range 78-90%), which is in agreement

370   with estimates at other European urban sites during the winter period (Szidat et al., 2009;

371   Minguillón et al., 2011).

372   As regards OC apportionment, two approaches were used to estimate OC by wood burning. They

373   were based on either radiocarbon or levoglucosan measurements and they required the

374   knowledge of source emission factors. The first approach (OC_{wb_1}) is based on EC_{wb}

375   determination by radiocarbon measurements: $OC_{wb\_1} = EC_{wb} \cdot (OC/EC)_{ER,wb}$. In the second

376   approach, OC_{wb_b} was determined by levoglucosan measurements on the same filters analysed

377   for radiocarbon as:

378                      $OC_{wb\_2}=$levoglucosan $(OC/levoglucosan)_{ER,wb}$.

379    $(OC/EC)_{ER,wb}$ and $(OC/levoglucosan)_{ER,wb}$ are the emission ratios for the wood burning source.

380   Large uncertainties still affect emission ratio values due to the dependence on the burnt wood

381   type and the used appliances. Different approaches can be applied to determine the most suitable

382   values in the investigated area. As an example, Minguillón et al., 2011 evaluated $(OC/EC)_{ER,wb}$

383   from literature values for agricultural fires and common biofuel species in the Mediterranean

384   burnt with similar combustion methods as those used in Spain. A similar approach is shown in

385   Piazzalunga et al. (2011b), where $(OC/EC)_{ER,wb}$ and $(OC/levoglucosan)_{ER,wb}$ were calculated

386   weighing literature data by wood consumption data for the Lombardy region. These weighed

387   emission factors were compared to ratios obtained by a PMF profile for the wood burning source

388   in the same area (Bernardoni et al., 2011) and good agreement between the approaches was

389   found for $(OC/EC)_{ER,wb}$ and $(OC/levoglucosan)_{ER,wb}$. However, the PMF approach was shown to

390   be more effective in real-world representation for what concerns levoglucosan to PM ratios.

391   Therefore, emission ratios (ER) derived by the PMF profile were used in this work for wood

392   burning: $(OC/EC)_{ER,wb} = 5.5 \pm 1.2$ and $(OC/levoglucosan)_{ER,wb} = 5.4 \pm 0.6$. Uncertainties on

393   emission ratios were calculated by uncertainties on the PMF source profile.

394   In figure 4, a comparison between OC_{wb_1} and OC_{wb_2} (normalised to OC) is shown. Agreement

395   within the experimental uncertainties was found for most of the samples and average values are

396   fully comparable ($18 \pm 5\%$ and $23 \pm 8\%$ for OC_{wb} determination by radiocarbon and levoglucosan

397   measurements, respectively). These results are similar to previous wood burning estimates

398   obtained in Milan during other winter periods by levoglucosan measurements (Piazzalunga et al.,

399   2011b).
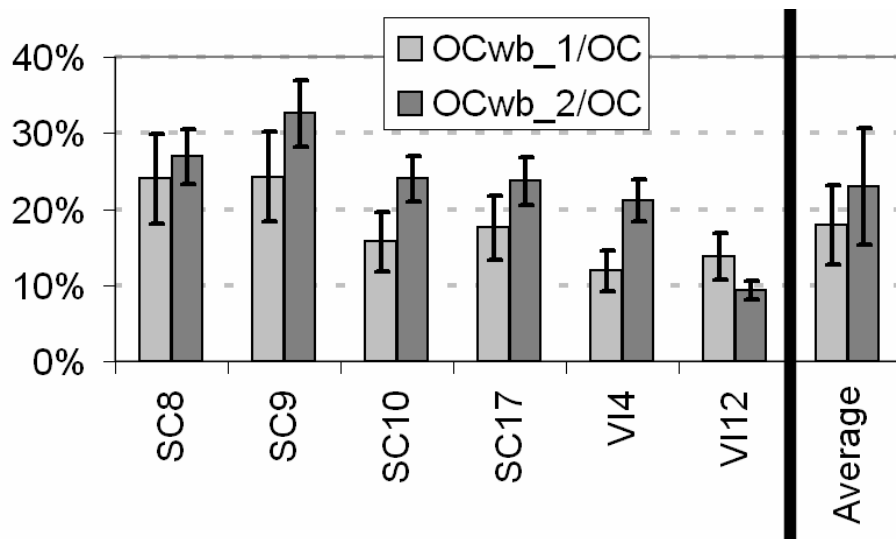
400

401   **Figure 4: comparison between OC_{wb} estimates obtained by radiocarbon and levoglucosan measurements**

402   The contribution to OC from other modern sources (primary or secondary biogenic contribution,

403   secondary particles from biomass burning or other urban non fossil contributions as tyre wear or

404   cooking) was estimated as:

17

405
$$OC_{\text{modern, other}} = \frac{OC \cdot f_m(OC) - OC_{wb\_1} \cdot f_{m,wb}}{f_{m,bio}} \; .$$

406    $OC_{\text{modern,other}}$ contributed for 39-50% to OC.

407   OC from fossil sources (OC_{ff}) was then assessed as $OC - OC_{wb} - OC_{\text{modern,other}}$ and was in the range

408   31-43% of OC. An evaluation of the fossil OC_{sec} ($OC_{sec,\,ff}$) was carried out joining the OC/EC

409   tracer method (Turpin and Huntzicker, 1995) and radiocarbon measurements. Primary fossil OC

410   was evaluated as $OC_{pri,\,ff} = 1.34 \cdot EC_{ff}$ (Giugliano et al., 2005; Bernardoni et al., 2011). Then,

411    $OC_{sec,ff}$ was calculated as $OC_{sec,ff} = OC_{ff} - OC_{pri,ff}$. The ratio $OC_{sec,ff} / OC_{ff}$ was 26% (variability

412    $\pm8\%$ absolute percent) on the radiocarbon dataset, which is similar to the contribution of fossil

413   oxygenated OC (OOC, surrogate of secondary OC) to the fossil OC determined coupling

414   Aerosol Mass Spectrometry results and radiocarbon measurements in Barcelona during

415   wintertime (35%, determined on PM1, Minguillón et al, 2011).

416   Literature approaches were followed trying to further apportion $OC_{\text{modern,other}}$ contributions.

417   Grieshop et al. (2009) reported that secondary organic aerosol (SOA) from wood burning can

418   reach similar levels as primary contribution. Assuming a comparable OM (organic matter) to OC

419   ratio for wood burning and secondary OOA (Lanz et al., 2008), the secondary contribution of

420   wood burning to OC ($OC_{sec,\,wb}$) was estimated to be comparable to OC_{wb} (i.e. about 18% of OC).

421   Another possible anthropogenic contribution to $OC_{\text{modern, other}}$ can be due to other urban non fossil

422   sources, e.g. cooking, brake lining dust, rubber in tire dust, re-suspended road dust (Hildemann

423   et al, 1994). Recent papers (Hodzic et al., 2010; Minguillón et al. 2011) estimated the

424   contribution from urban non fossil sources to OC ($OC_{urb,\,nf}$) to account for about 20% of the total

425   urban OC contribution ($OC_{urb,\,nf} + OC_{ff}$) as the average value given by Hildemann et al., 1994.

426   Applying this approach to our work, $OC_{urban,\,nf}$ can be tentatively estimated in about 9% of OC in

427   our samples.

428   Considering $OC_{sec,\,wb}$ and $OC_{urb,\,nf}$ contributions to $OC_{\text{modern,other}}$, the biogenic contribution to OC

429   (OC_{bio}) can be finally estimated to account for about 18% of OC in Milan urban area during

430   wintertime. Of course, this value is affected by great uncertainties, mainly related to the

431   problems in the evaluation of the other to components of $OC_{modern,other}$.

432   The estimated contributions of the discussed sources to OC and EC were merged to obtain the

433   average TC source apportionment shown in figure 5.
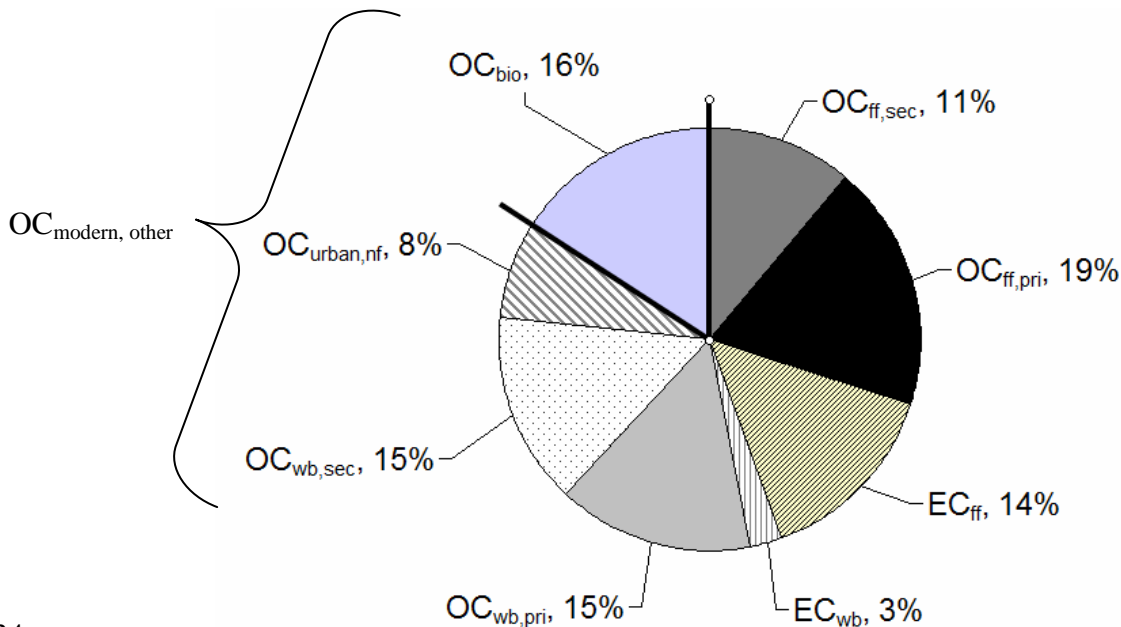
434

435   **Figure 5: TC source apportionment. The separation between anthropogenic and biogenic sources is evidenced**

436

437   **4. Conclusions**

438   In this work, tests for the choice of innovative approaches aiming at the improvement of $f_m(OC)$

439   and $f_m(EC)$ determination were carried out.

440   As for $f_m(OC)$, its direct determination is tricky due to pyrolysis. Therefore, two alternative

441   approaches were proposed. The first is based on $f_m(TC)$ and $f_m(EC)$ determination and the other

442   requires $f_m(TC)$, $f_m(TC_{ww})$, and $f_m(WINSOC)$ measurements. The first tests showed good

443   agreement between the approaches.

444   As for $f_m(EC)$, the addition of a He step at high temperature after the more traditional oxygen

445   pre-combustion was proposed to remove the refractory fraction of OC. Tests were carried out

446   aiming at the choice of the most suitable thermal treatment, focusing on maximising the OC

447   removal and EC recovery. The final choice was EC isolation by sample pre-combustion in

448   oxygen at 375°C for 40 min followed by a flash heating in He at 750 °C. The He step was

19

449 demonstrated to be effective in the removal of refractory OC, which might not evolve during the

450 oxygen step only.

451 The results obtained during the tests were also used to attempt a first source apportionment of

452 carbonaceous particles in Milan during wintertime. Modern sources slightly prevailed on fossil

453 fuel contributions to TC (57% fossil vs. 43% non fossil). When focusing on carbon fractions, OC

454 is dominated by modern contributions (64%), while EC is mainly of fossil fuel origin (85%).

455 Two approaches were compared to estimate the primary contribution from wood burning in the

456 area. The first was based on radiocarbon measurements and the second on levoglucosan

457 determination. The emission factors $(OC/EC)_{wb}$ and $(OC/levoglucosan)_{wb}$ used in this work were

458 derived by a PMF source profile. The good agreement between the determinations of $OC_{wb,pri}$ by

459 the two approaches confirms that such emission ratios are representative for the investigated

460 area. Primary wood burning contribution estimated by radiocarbon measurements was 18% of

461 OC on average.

462 The OC modern fraction which could not be ascribed to wood burning ($OC_{modern,other}$) was further

463 separated into other urban non fossil contributions and secondary contributions from wood

464 burning following literature approaches and by difference, the biogenic contribution in the area

465 was estimated to account for 16% of TC on average.

466

473

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