

1 **Micro-scale (μg) radiocarbon analysis of water-soluble organic carbon in aerosol samples**

2 Yan-lin Zhang^{1,2,3*}, Jun-wen Liu⁴, Gary A. Salazar^{1,3}, Jun Li⁴, Peter Zotter², Gan Zhang⁴, Rong-rong Shen⁵,
3 Klaus Schäfer⁵, Jürgen Schnelle-Kreis⁶, André S.H. Prévôt² and Sönke Szidat^{1,3*}

4 ¹Department of Chemistry and Biochemistry, University of Bern, 3012 Berne, Switzerland

5 ²Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), 5232 Villigen-PSI, Switzerland

6 ³Oeschger Centre for Climate Change Research, University of Bern, 3012 Berne, Switzerland

7 ⁴State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of
8 Sciences, 510640 Guangzhou, China

9 ⁵Institute of Meteorology and Climate Research (IMK-IFU), Karlsruhe Institute of Technology (KIT),
10 82467, Garmisch-Partenkirchen, Germany

11 ⁶Helmholtz Zentrum München, German Research Center for Environmental Health (GmbH), Joint Mass
12 Spectrometry Centre, Cooperation Group Comprehensive Molecular Analytics, 85764 Neuherberg, Germany

13 *Correspondence to soenke.szidat@dcb.unibe.ch (S. Szidat); dryanlinzhang@gmail.com (Y. L. Zhang)

14

15 **Accepted version**

16

17 **Published in**

18 **Atmospheric Environment 97 (2014) 1-5**

19 **<http://dx.doi.org/10.1016/j.atmosenv.2014.07.059>**

20

21 **Abstract**

22 Radiocarbon (^{14}C) measurement of water-soluble organic carbon (WSOC) in ambient aerosols
23 is a quantitative tool for unambiguously distinguishing fossil and non-fossil sources. In this study, a
24 fast and reliable method for measuring ^{14}C in micro-scale (μg) WSOC aerosol samples is successfully
25 developed, which includes three steps: (1) extraction (2) freeze drying, and (3) online ^{14}C analysis of
26 CO_2 from WSOC combustion. Procedure blanks are carefully assessed by measuring high-purity
27 water and reference materials. Accurate ^{14}C results could be obtained for WSOC with only $10\ \mu\text{g C}$,
28 and thus the potential applications are substantially broadened because much less filter material is
29 needed compared to previous reported methods. This method is applied to aerosols samples collected
30 during winter from Switzerland and China. The results demonstrate that non-fossil sources are
31 important if not dominant contributors of WSOC. These non-fossil components are consistently
32 enriched in WSOC compared to bulk OC and water-insoluble OC for all samples, due to high water
33 solubility of primary and secondary biomass burning aerosols. However, the presence of fossil WSOC
34 is still considerable indicating a substantial contribution of secondary OC (SOC) formed from
35 precursors emitted by fossil emissions. Larger fossil contributions to WSOC is found in China than
36 in Switzerland and previously reported values in Europe, USA and South Asia, which may be
37 attributed to higher fossil-derived SOC formation in China.

38 **Keywords:** Aerosols, Radiocarbon ^{14}C , Water-soluble organic carbon, Source

39

40 **1 Introduction**

41 The water-soluble organic carbon (WSOC) component is a major fraction of atmospheric
42 aerosols with contributions from 20 up to 80 % of the total organic matter (Pöschl, 2005; Kirillova et
43 al., 2010). Due to its hydrophilic nature, WSOC can play an important role on Earth's climate by
44 altering the hygroscopic properties of aerosols and increasing cloud condensation nuclei (CCN)
45 activity (Asa-Awuku et al., 2011). As a major fraction of fine atmospheric aerosols, WSOC also has
46 an adverse impact on human health leading to cardiovascular and respiratory problems (Mills et al.,
47 2009). WSOC can be emitted as primary organic carbon (POC) especially during biomass combustion
48 (Mayol-Bracero et al., 2002) or produced as secondary organic carbon (SOC) by oxidation of gaseous
49 precursors emitted from various sources including fossil (e.g. coal combustion and vehicle emissions)
50 and non-fossil (e.g. biogenic, cooking and biomass burning) sources (Kirillova et al., 2010). In
51 general, SOC constituents are more water-soluble compared to POC (Kondo et al., 2007), and thus
52 WSOC can be used as a tracer for SOC in the absence of biomass burning (Weber et al., 2007).

53 The relative contribution from different emission sources (fossil vs. non-fossil) to WSOC is still
54 poorly constrained. Radiocarbon (^{14}C) analysis of sub-fractions of aerosols such as organic carbon
55 (OC), elemental carbon (EC) and WSOC provide a powerful tool for unambiguously determining
56 fossil and non-fossil sources of carbonaceous particles (Szidat, 2009; Zhang et al., 2012). However,
57 analytical techniques for measuring ^{14}C content in WSOC often require carbon amounts of $>250\ \mu\text{g}$
58 C extracted from aerosol samples (Kirillova et al., 2010; Wozniak et al., 2011), limiting this
59 application due to available material especially for low-loaded aerosol filter samples.

60 Here, we present a new method for ^{14}C measurements of WSOC, including three steps: (1)
61 extraction (2) freeze drying, and (3) online ^{14}C analysis of CO_2 from WSOC combustion. The
62 presented method is designed to meet the requirements for fast and easy handling of small samples
63 ($>10\ \mu\text{gC}$) by omitting the graphitization step for ^{14}C measurement. Graphitization step is often
64 laborious and thus lowers the possible number of analyzed samples. In addition, this step may
65 potentially contribute to contaminations and/or isotope fractionation which is especially problematic
66 for small samples. Both well-defined WSOC reference materials and WSOC extracted from ambient
67 aerosols from two case studies in China and Switzerland are used to assess the procedure blanks and
68 prove the feasibility of the suggested method. ^{14}C measurement in OC and its sub-fractions: WSOC
69 and water-insoluble OC (WINSOC) from both studies will also be discussed.

70 **2 Experimental**

71 **2.1 Reference materials and ambient samples**

72 The reference materials used in this study include oxalic acid II (NIST-HOx2, i.e. SRM 4990 C),
73 sucrose (IAEA-C6) and potassium hydrogen phthalate (Sigma-Aldrich). Solutions containing carbon
74 concentration in the range of 2–4 gC/l are prepared by diluting reference materials in ultrapure water
75 with low TOC impurity in 20 ml glass vials (prebaked at 500–550 °C for 4 hours). The atmospheric
76 samples used in this study are collected with high-volume samplers for 24 hours on quartz-fiber filters
77 during various field campaigns (Table 1). After sampling, all filters were wrapped in aluminum foil,
78 packed in air-tight polyethylene bags and stored at -18°C for later off-line analyses.

79 **2.2 Preparation of WSOC for ^{14}C measurement**

80 The analytical method of WSOC extraction from aerosol was described previously (Zhang et al.,
81 2012; Zhang et al., 2014). Under a laminar flow box, 16-mm-diameter discs are punched out of the
82 aerosol filters, sandwiched between two Teflon O-rings (OD: 25 mm, ID:14 mm) and placed with the
83 loaded side upwards on a 25-mm-diameter polycarbonate filter holder and topped by a polycarbonate

84 syringe body. 10 ml ultrapure water with low TOC impurity is then passed through the filter without
85 a pump and the water extracts are recovered in the 20 ml PFA vials (Savillex). The filter punches is
86 then delicately removed and placed for 3-4 h in a desiccator for drying. The water-extracted filter is
87 wrapped in aluminum foil, packed into a sealed plastic bag and stored in the freezer (-18°C) until
88 analysis. The solutions are pre-frozen at -20 °C at least for 5 hours before they are dehydrated to
89 dryness in freeze dryer with low-carbon background (Alpha 2-4 LSC, Christ, Germany) at -10 to 0 °C
90 for about 24 hours. The residue material is re-dissolved three times in 50 µl of ultrapure water each
91 and transferred into 200 µl tin capsules (Elementar, Germany) or into 250 µl boat-like quartz vessels
92 that were pre-baked at 850 °C for 4 h. Finally, samples are heated in the oven at 60 °C until complete
93 dryness before online or offline ¹⁴C measurement. WSOC solutions with known carbon concentration
94 from reference materials and procedure blank (ultrapure water) are prepared in the same way as
95 described above but with pre-baked quartz filters (850 °C for 4 h) without aerosol loading. The
96 experimental schematic diagram is summarized in the Supplemental Materials as Figure S1. The
97 detailed method of carbon amount determination in different carbonaceous fractions is also described
98 in the Supplemental Materials.

99 **2.3 ¹⁴C measurement of WSOC isolates**

100 The ¹⁴C measurement is conducted by the accelerator mass spectrometer MICADAS equipped
101 with a gas ion source to omit the graphitization step, allowing measuring ¹⁴C directly in CO₂ from 2
102 to 100 µg C (Wacker et al., 2013; Szidat et al., 2014). Before ¹⁴C analysis, WSOC has to be converted
103 to CO₂, which can be either combusted in an OC/EC analyzer (Model4L, Sunset Laboratory Inc, USA)
104 (Zhang et al., 2012) or Elemental Analyzer (EA, Model Vario Micro, Elementar, Germany), which
105 will be denoted as offline and online combustion approaches, respectively. ¹⁴C measurements could
106 be easily adapted to CO₂ produced from both approaches using the versatile gas interface coupled
107 with the MICADAS (Wacker et al., 2013). For the offline method, the CO₂ resulting from combustion
108 of WSOC in the quartz vessels with the OC/EC analyzer is trapped cryogenically and sealed in glass
109 ampoules in a dedicated vacuum system, so-called THEODORE (Szidat et al., 2004a). These glass
110 ampoules are cracked inside of the gas interface of the MICADAS to release CO₂ and the gas amount
111 is determined manometrically, diluted to 5% in helium and introduced continuously into the gas ion
112 source of the MICADAS for ¹⁴C measurement. For the online combustion, oxidation of the purified
113 water extracts is directly carried out in the EA as a combustion unit (up to 1050°C) in which samples
114 are oxidized to CO₂ and purified. The resulting CO₂ is directly trapped on X13 zeolite molecular sieve
115 (sodium aluminosilicate) in the gas interface at room temperature, which is later thermally released

116 by heating to 450 °C and is then measured in the same way as described before for the offline method
117 (Ruff et al., 2010).

118 ¹⁴C results are reported as fraction of modern (f_M), the fraction of the measured ¹⁴C/¹²C ratio
119 related to the ¹⁴C/¹²C ratio of the reference year 1950 (Stuiver, 1977). Blank correction of f_M is also
120 included which will be explained below. Due to excess ¹⁴C from nuclear bomb tests performed in the
121 1950s and 1960s, f_M values have to be converted to fraction of non-fossil (f_{NF}) (Zhang et al., 2012):

$$122 \quad f_{NF} = f_M / f_{M,ref} \quad (\text{Eq. 1})$$

123 $f_{M,ref}$ is a reference value of f_M for contemporary carbon sources including biogenic and biomass
124 burning emissions, which can be estimated according to the contemporary atmospheric CO₂ f_M (Levin
125 et al., 2010) and a tree growth model (Mohn et al., 2008), respectively. As a result, $f_{M,ref}$ values of
126 1.11 ± 0.05 and 1.10 ± 0.05 are used for WSOC samples collected in 2008/2009 and 2010/2011,
127 respectively.

128 **3 Results**

129 **3.1 Method evaluation**

130 The contribution of the procedural blank to the total measured concentration and f_M values can be
131 determined by mass balance represented by the following equation, which is modified from (Cao et
132 al., 2013):

$$133 \quad f_{M,corr} = (f_{M,meas} * m_{meas} - f_{M,bk} * m_{bk}) / (m_{meas} - m_{bk}) \quad (\text{Eq. 2})$$

134 where $f_{M,corr}$ is the blank-corrected f_M , and $f_{M,meas}$ and $f_{M,bk}$ are the measured f_M for samples and blanks,
135 respectively. m_{meas} and m_{bk} denote the carbon mass of the samples and blanks, respectively.

136 The mass of the procedure blank is on average $0.98 \pm 0.31 \mu\text{g}$ ($n=5$), which is directly determined
137 by the Sunset OC/EC analyzer. The f_M of the procedure blank cannot be directly measured as the
138 carbon amount of the blank is too low compared to minimum requirement of carbon amount ($\sim 3 \mu\text{gC}$)
139 for a reliable ¹⁴C measurement with MICADAS. Instead, the $f_{M,bk}$ can be calculated by the difference
140 from the expected f_M of the reference materials with their known values. As shown in Figure 1, the
141 f_M values of the ¹⁴C-free material (potassium hydrogen phthalate) increase with decreasing sample
142 size. This is expected when a constant contribution from a modern contamination is introduced in
143 ¹⁴C-free samples during sample preparation. As described above, the f_M values of this contamination
144 or procedure blank can be estimated with Eq 2 and was found to be 1.08 ± 0.34 (with $m_{bk} = 0.98 \pm 0.31$

145 μg , see above). Thus, a blank correction following Eq. 2 has to be applied to all samples to account
146 for procedure blank contributions. A further validation of this influence on f_M was carried out by
147 measuring two modern standards such as IAEA-C6 and NIST-HOx2 (see Figure 1b). The blank-
148 corrected f_M values of both materials are indistinguishable from the nominal values (t-test, $p < 0.05$).
149 The results presented in Figure 1 show that without such a correction the ^{14}C results would be biased.
150 The extent of bias depends on the size and ^{14}C -level of the samples. A sensitive test is carried out
151 with sample size ranging from 2 to 100 μg with three assumed f_M values (i.e. 0, 0.5 and 1) (Figure
152 2a). There is only a small bias (up to 7%) for the “modern” samples ($f_M=1.0$) even for very small
153 samples, while the bias can be $>10\%$ when the carbon amount is $<7 \mu\text{g}$ and $<12 \mu\text{g}$, for samples with
154 $f_M=0.5$ and $f_M=0$, respectively. However, the uncertainty of the blank-corrected f_M (derived from an
155 error propagation of Eq. 2) is increased compared to the original ^{14}C measurement uncertainty due to
156 contributions of the uncertainties from all components in Eq. 2 (Figure 2b). For samples larger than
157 10 μgC , the uncertainty of f_M is smaller than 6% for the full range of values between 0 and 1. This
158 uncertainty is smaller than the combined uncertainty of f_{NF} which includes uncertainties from carbon
159 mass determination and bomb-peak correction (see Sec. 3.4). Therefore, we conclude that at least 10
160 μgC are needed to get accurate ^{14}C results with acceptable uncertainties.

161 The average recovery of reference materials is $93 \pm 9 \%$ ($n=13$), $50 \pm 3 \%$ ($n=4$) and $97 \pm 3 \%$ ($n=6$)
162 for potassium hydrogen phthalate, NIST-HOx2 (oxalic acid) and IAEA-C6 (sucrose), respectively,
163 which is comparable to those reported by Kirillova et al. (2010). The lowest recovery is found for
164 oxalic acid, which was shown to be one of the smallest and very volatile molecules in ambient WSOC
165 (Kirillova et al., 2010; Seinfeld and Pandis, 2012). However, a higher recovery (ranging from 75%-
166 95%) is found for WSOC extracted from ambient samples, which is similar to those reported by
167 (Yang et al., 2003). Therefore, unrecovered fraction may not influence ^{14}C content in WSOC
168 significantly. A great agreement is found between the measured and calculated ^{14}C in WSOC, which
169 validates it (see below), although further studies are needed to measure ^{14}C directly for low molecular
170 weight compounds.

171 The comparability of the ^{14}C results of WSOC obtained with the offline and online method (see
172 chapter 2.3) is tested by measuring reference materials and ambient samples ($n=9$, see next chapter)
173 are measured with both methods showing No significant difference ($p < 0.05$) between the two
174 methods (Figure 3).

175 For comparison, ^{14}C content in water insoluble OC (WINSOC) and WSOC was either directly
176 measured and/or estimated by isotopic mass balance as follows:

177
$$f_{\text{NF}}(\text{OC}) = f_{\text{WSOC}} \times f_{\text{NF}}(\text{WSOC}) + (1 - f_{\text{WSOC}}) \times f_{\text{NF}}(\text{WINSOC}) \text{ (Eq. 3)}$$

178 where f_{WSOC} is the WSOC to OC fraction. Although ^{14}C results of WSOC and WINSOC have
179 been reported in literature before (Szidat et al., 2004b; Wozniak et al., 2012a; Wozniak et al., 2012b;
180 Kirillova et al., 2013; Zhang et al., 2013; Zhang et al., 2014), none of them has performed ^{14}C
181 measurement directly on both fractions. Here, no significant difference ($n=5$, $p<0.05$) was observed
182 between directly measured and indirectly calculated $f_{\text{NF}}(\text{WSOC})$ values indicating that both
183 approaches are feasible.

184 3.2 Case studies in Switzerland and China

185 In this study, ^{14}C measurements of WSOC extracts (ranging from 20 – 80 μgC) is performed for
186 aerosol samples collected during winter at Bern and Moleno, Switzerland, as well as at Guangzhou
187 and Beijing, China. As shown in Table 1, f_{NF} -values are 0.81-0.92 for Bern and Moleno (Switzerland)
188 indicating a dominant contribution from non-fossil sources to WSOC during the winter, mainly from
189 wood burning (Zotter et al., in preparation). A major fraction of primary biomass-burning OC is water
190 soluble, and the water solubility of OC can even be increased due to SOC formation and/or
191 heterogeneous oxidation. Such high non-fossil contributions to WSOC for winter aerosols have also
192 been reported at other sites in Europe, such as Zurich ($77\pm 18\%$) (Zhang et al., 2013) and Gothenburg,
193 Sweden (0.85 ± 0.09) (Szidat et al., 2009). Nevertheless, fossil contributions are also considerable,
194 accounting for 8-19% of WSOC, which is likely attributed to fossil-derived SOC given that primary
195 OC from vehicle emissions are less oxidized and thus less water soluble (Kondo et al., 2007).

196 f_{NF} values in Beijing and Guangzhou are 0.45-0.72, demonstrating that non-fossil sources are
197 still important if not dominant contributors of WSOC, although these contributions are lower than for
198 Switzerland due to higher fossil emissions from vehicles and coal-combustion in China. The larger
199 fossil-fuel fraction in WSOC found in China (21% and 51% for Guangzhou and Beijing, respectively)
200 compared to Switzerland (11% and 14% for Bern and Moleno, respectively) is most likely due to
201 enhanced fossil-derived SOC formation. The higher fossil contribution to WSOC in Beijing
202 compared to Guangzhou could be due to enhanced coal consumption for heating activities, since the
203 temperature is much lower in Beijing than in Guangzhou during winter. Non-fossil contributions to
204 WSOC in these two urban sites of China are lower than those reported in South Asia including rural
205 sites of Hanimaadhoo, Maldives ($81\pm 4\%$) and Sinhagad, India ($76\pm 4\%$) (Kirillova et al., 2013)
206 as well as an urban site in Delhi, India ($79\pm 4\%$) (Kirillova et al., 2014b). There are only a few
207 studies reporting ^{14}C measurements of WSOC in urban sites of China. For example, non-fossil
208 contribution to WSOC aerosols from Xi'an (an industrial city in western China) during later-fall is

209 ~70% (Pavuluri et al., 2013) and this contribution is substantially higher at a background site on the
210 Hainan Island in the southernmost province of China (77%±11%) (Zhang et al., 2014). Very recently,
211 ¹⁴C measurement of aerosol samples collected at a receptor station in the Southeast Yellow Sea for
212 the outflow from northern China shows that the WSOC in the Chinese outflow composes of 50%-70%
213 non-fossil carbon (Kirillova et al., 2014a), which is comparable to our findings in this study.

214 The non-fossil fraction is found to be always higher in WSOC compared to total OC and
215 WINSOC (p<0.01), which is consistent with previous findings that biomass burning OC from both
216 primary and secondary emissions are highly water-soluble (Sullivan et al., 2006; Pavuluri et al., 2013).
217 The non-fossil enrichment of WSOC compared to WINSOC ranges from 18% to 64%. This
218 enrichment has also been reported earlier in Europe (Szidat et al., 2009; Zhang et al., 2013), the USA
219 (Wozniak et al., 2012b) and Asia (Kirillova et al., 2013; Pavuluri et al., 2013). In contrast, fossil
220 contributions to WINSOC are larger compared to WSOC (p<0.01), suggesting a large fraction of
221 fossil OC is insoluble due to hydrophobic properties of particles from fossil sources.

222 **References**

- 223 Agarwal, S., Aggarwal, S. G., Okuzawa, K., and Kawamura, K.: Size distributions of dicarboxylic
224 acids, ketoacids, alpha-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in
225 atmospheric particles over Northern Japan: implication for long-range transport of Siberian
226 biomass burning and East Asian polluted aerosols, *Atmos. Chem. Phys.*, 10, 5839-5858,
227 2010.
- 228 Asa-Awuku, A., Moore, R. H., Nenes, A., Bahreini, R., Holloway, J. S., Brock, C. A., Middlebrook,
229 A. M., Ryerson, T. B., Jimenez, J. L., DeCarlo, P. F., Hecobian, A., Weber, R. J., Stickel,
230 R., Tanner, D. J., and Huey, L. G.: Airborne cloud condensation nuclei measurements
231 during the 2006 Texas Air Quality Study, *J. Geophys. Res.*, 116, 2011.
- 232 Cao, F., Zhang, Y.-L., Szidat, S., Zapf, A., Wacker, L., and Schwikowski, M.: Microgram level
233 radiocarbon determination of carbonaceous particles in firn samples: pre-treatment and
234 OC/EC separation, *Radiocarbon*, 55, 383-390 2013.
- 235 Fahrni, S. M., Wacker, L., Synal, H. A., and Szidat, S.: Improving a gas ion source for ¹⁴C AMS,
236 *Nucl. Instr. and Meth. in Phys. Res. B.*, 294, 320-327, 2013.
- 237 Kirillova, E. N., Sheesley, R. J., Andersson, A., and Gustafsson, O.: Natural abundance ¹³C and ¹⁴C
238 analysis of water-soluble organic carbon in atmospheric aerosols, *Anal. Chem.*, 82, 7973-
239 7978, 2010.

240 Kirillova, E. N., Andersson, A., Sheesley, R. J., Kruså, M., Praveen, P. S., Budhavant, K., Safai, P.
241 D., Rao, P. S. P., and Gustafsson, Ö.: ^{13}C and ^{14}C -based study of sources and atmospheric
242 processing of water-soluble organic carbon (WSOC) in South Asian aerosols, *J. Geophys.*
243 *Res.*, 118, 614-626, 2013.

244 Kirillova, E. N., Andersson, A., Han, J., Lee, M., and Gustafsson, O.: Sources and light absorption
245 of water-soluble organic carbon aerosols in the outflow from northern China, *Atmos. Chem.*
246 *Phys.*, 14, 1413-1422, 2014a.

247 Kirillova, E. N., Andersson, A., Tiwari, S., Srivastava, A. K., Bisht, D. S., and Gustafsson, Ö.:
248 Water-soluble organic carbon aerosols during a full New Delhi winter: Isotope-based source
249 apportionment and optical properties, *J. Geophys. Res.*, 119, 2013JD020041, 2014b.

250 Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and
251 Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo, *J. Geophys.*
252 *Res.*, 112, 2007.

253 Levin, I., Naegler, T., Kromer, B., Diehl, M., Francey, R. J., Gomez-Pelaez, A. J., Steele, L. P.,
254 Wagenbach, D., Weller, R., and Worthy, D. E.: Observations and modelling of the global
255 distribution and long-term trend of atmospheric $^{14}\text{CO}_2$, *Tellus B*, 62, 26-46, 2010.

256 Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini,
257 M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning
258 aerosols over Amazonia - 2. Apportionment of the chemical composition and importance of
259 the polyacidic fraction, *J. Geophys. Res.*, 107, D8091, 2002.

260 Mills, N. L., Donaldson, K., Hadoke, P. W., Boon, N. A., MacNee, W., Cassee, F. R., Sandstrom,
261 T., Blomberg, A., and Newby, D. E.: Adverse cardiovascular effects of air pollution, *Nature*
262 *Clinical Practice Cardiovascular Medicine*, 6, 36-44, 2009.

263 Mohn, J., Szidat, S., Fellner, J., Rechberger, H., Quartier, R., Buchmann, B., and Emmenegger, L.:
264 Determination of biogenic and fossil CO_2 emitted by waste incineration based on $^{14}\text{CO}_2$ and
265 mass balances, *Bioresour. Technol.*, 99, 6471-6479, 2008.

266 Pavuluri, C. M., Kawamura, K., Uchida, M., Kondo, M., and Fu, P. Q.: Enhanced modern carbon
267 and biogenic organic tracers in Northeast Asian aerosols during spring/summer, *J. Geophys.*
268 *Res.*, 118, 2362-2371, 2013.

269 Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects, *Angew.*
270 *Chem., Int. Ed.*, 44, 7520-7540, 2005.

271 Ruff, M., Fahrni, S., Gaggeler, H. W., Hajdas, I., Suter, M., Synal, H. A., Szidat, S., and Wacker,
272 L.: On-Line Radiocarbon Measurements of Small Samples Using Elemental Analyzer and
273 Micadas Gas Ion Source, *Radiocarbon*, 52, 1645-1656, 2010.

274 Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate
275 change, John Wiley & Sons, 2012.

276 Stuiver, M.: Discussion: Reporting of ^{14}C data, Radiocarbon, 19, 355-363, 1977.

277 Sullivan, A. P., Peltier, R. E., Brock, C. A., de Gouw, J. A., Holloway, J. S., Warneke, C., Wollny,
278 A. G., and Weber, R. J.: Airborne measurements of carbonaceous aerosol soluble in water
279 over northeastern United States: Method development and an investigation into water-
280 soluble organic carbon sources, J. Geophys. Res., 111, D23S46, 2006.

281 Szidat, S., Jenk, T. M., Gäggeler, H. W., Synal, H.-A., Hajdas, I., Bonani, G., and Saurer, M.:
282 THEODORE, a two-step heating system for the EC/OC determination of radiocarbon (^{14}C)
283 in the environment, Nucl. Instr. and Meth. in Phys. Res. B., 223-224, 829-836, 2004a.

284 Szidat, S., Jenk, T. M., Gäggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., Kalberer, M.,
285 Samburova, V., Wacker, L., Saurer, M., Schwikowski, M., and Hajdas, I.: Source
286 apportionment of aerosols by ^{14}C measurements in different carbonaceous particle fractions,
287 Radiocarbon, 46, 475-484, 2004b.

288 Szidat, S.: Sources of Asian haze, Science, 323, 470-471, 2009.

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

292 Szidat, S., Salazar, G. A., Vogel, E., Battaglia, M., Wacker, L., Synal, H.-A., and Türler, A.: ^{14}C
293 Analysis and Sample Preparation at the New Bern Laboratory for the Analysis of
294 Radiocarbon with AMS (LARA), Radiocarbon, 56, 561-566, 2014.

295 Wacker, L., Fahrni, S. M., Hajdas, I., Molnar, M., Synal, H. A., Szidat, S., and Zhang, Y. L.: A
296 versatile gas interface for routine radiocarbon analysis with a gas ion source, Nucl. Instrum.
297 Meth. B, 294, 315-319, 2013.

298 Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke,
299 C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic
300 aerosol formation in the anthropogenic-influenced southeastern United States, J. Geophys.
301 Res., 112, D13302, 2007.

302 Wozniak, A. S., Bauer, J. E., and Dickhut, R. M.: Fossil and contemporary aerosol particulate
303 organic carbon in the eastern United States: Implications for deposition and inputs to
304 watersheds, Global Biogeochem. Cycles, 25, 2011.

305 Wozniak, A. S., Bauer, J. E., and Dickhut, R. M.: Characteristics of water-soluble organic carbon
306 associated with aerosol particles in the eastern United States, Atmos. Environ., 46, 181-188,
307 2012a.

308 Wozniak, A. S., Bauer, J. E., Dickhut, R. M., Xu, L., and McNichol, A. P.: Isotopic characterization
309 of aerosol organic carbon components over the eastern United States, *J. Geophys. Res.*, 117,
310 D13303, 2012b.

311 Yang, H., Li, Q. F., and Yu, J. Z.: Comparison of two methods for the determination of water-
312 soluble organic carbon in atmospheric particles, *Atmos. Environ.*, 37, 865-870, 2003.

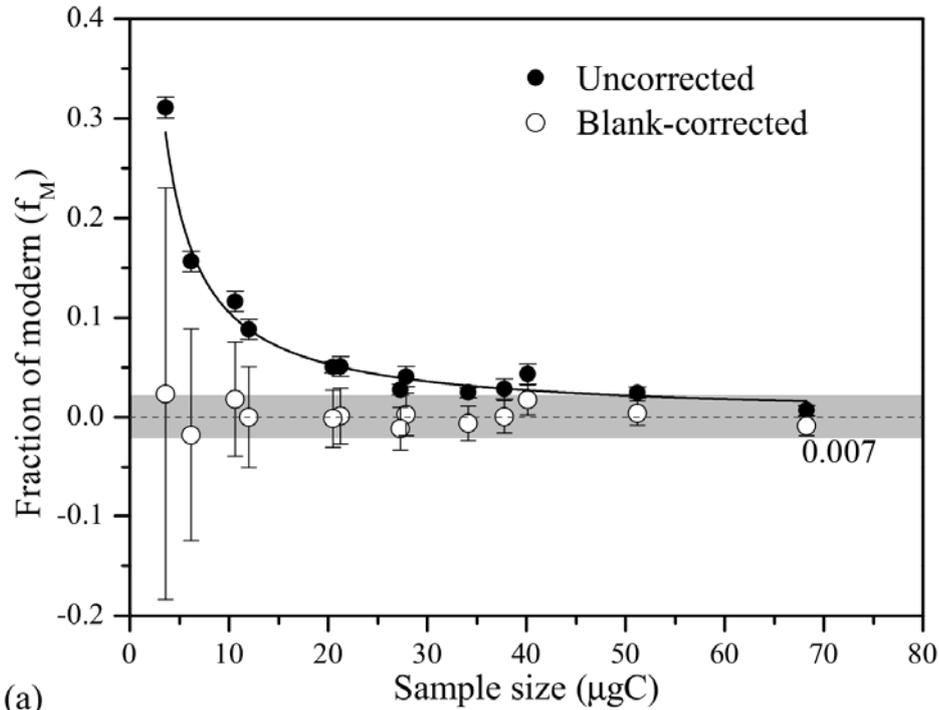
313 Zhang, Y.-L., Li, J., Zhang, G., Zotter, P., Huang, R.-J., Tang, J.-H., Wacker, L., Prévôt, A. S. H.,
314 and Szidat, S.: Radiocarbon-based source apportionment of carbonaceous aerosols at a
315 regional background site on hainan Island, South China, *Environ. Sci. Technol.*, 48, 2651-
316 2659, 2014.

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

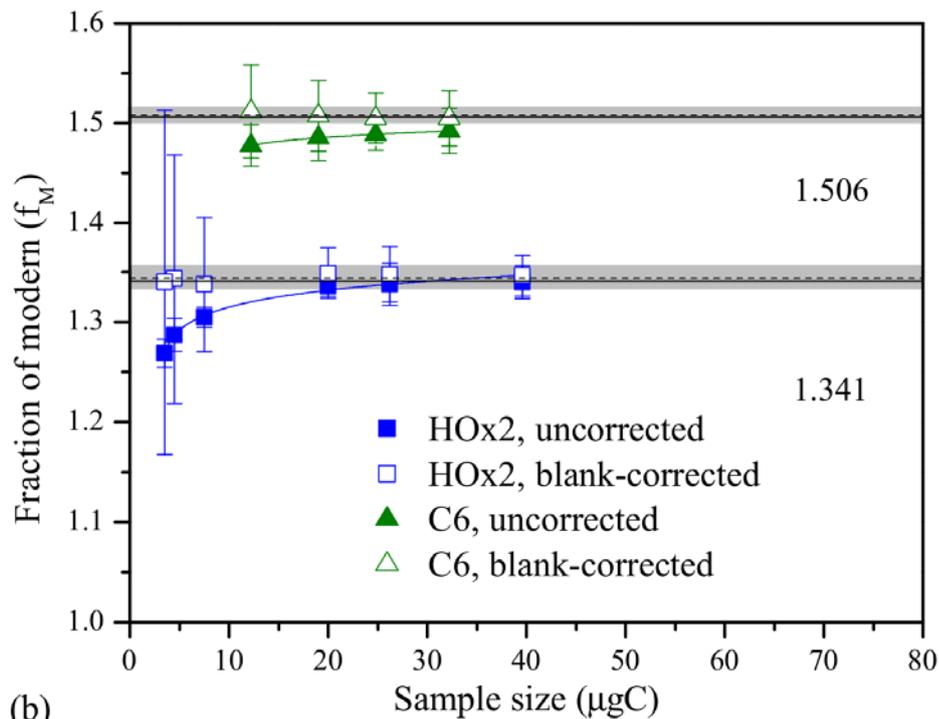
321 Zhang, Y. L., Zotter, P., Perron, N., Prévôt, A. S. H., Wacker, L., and Szidat, S.: Fossil and non-
322 fossil sources of different carbonaceous fractions in fine and coarse particles by radiocarbon
323 measurement, *Radiocarbon*, 55, 1510-1520, 2013.

324 Zotter, P., El-Haddad, I., Zhang, Y., Hayes, P. L., Zhang, X., Lin, Y.-H., Wacker, L., Schnelle-
325 Kreis, J., Abbaszade, G., Zimmermann, R., Surratt, J. D., Weber, R., Jimenez, J. L., Szidat,
326 S., Baltensperger, U., and Prévôt, A. S. H.: Diurnal cycle of fossil and non-fossil carbon
327 using radiocarbon analyses during CalNex, *J. Geophys. Res.*, 119, 6818-6835,
328 2013JD021114, 2014.

329



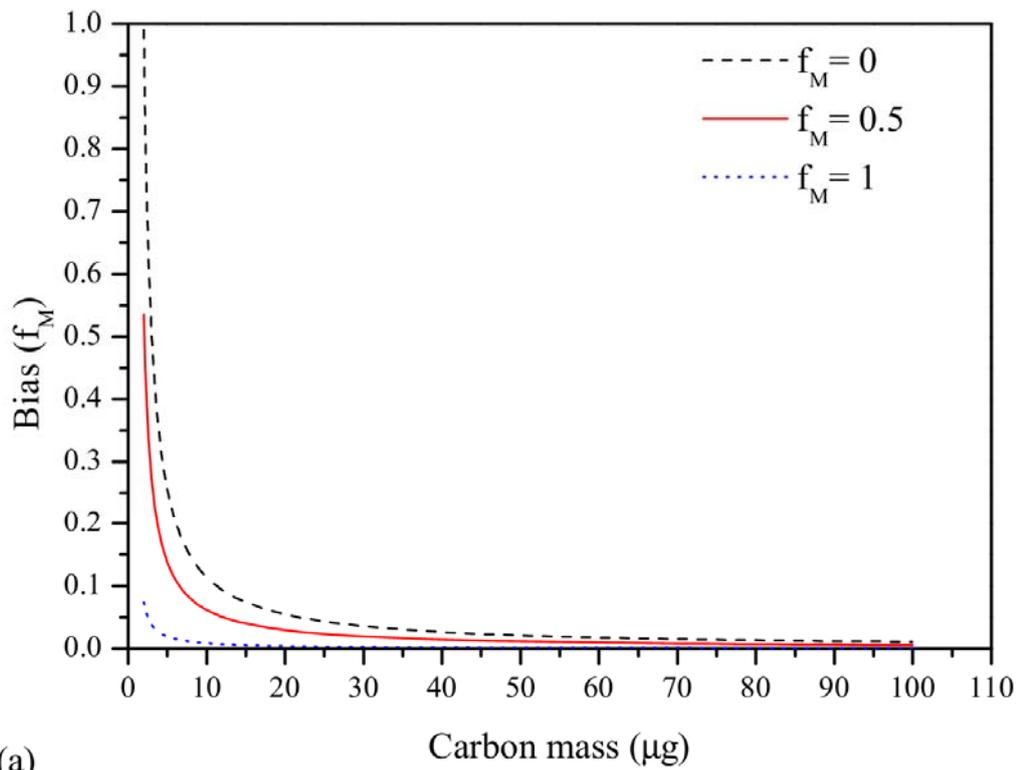
(a)



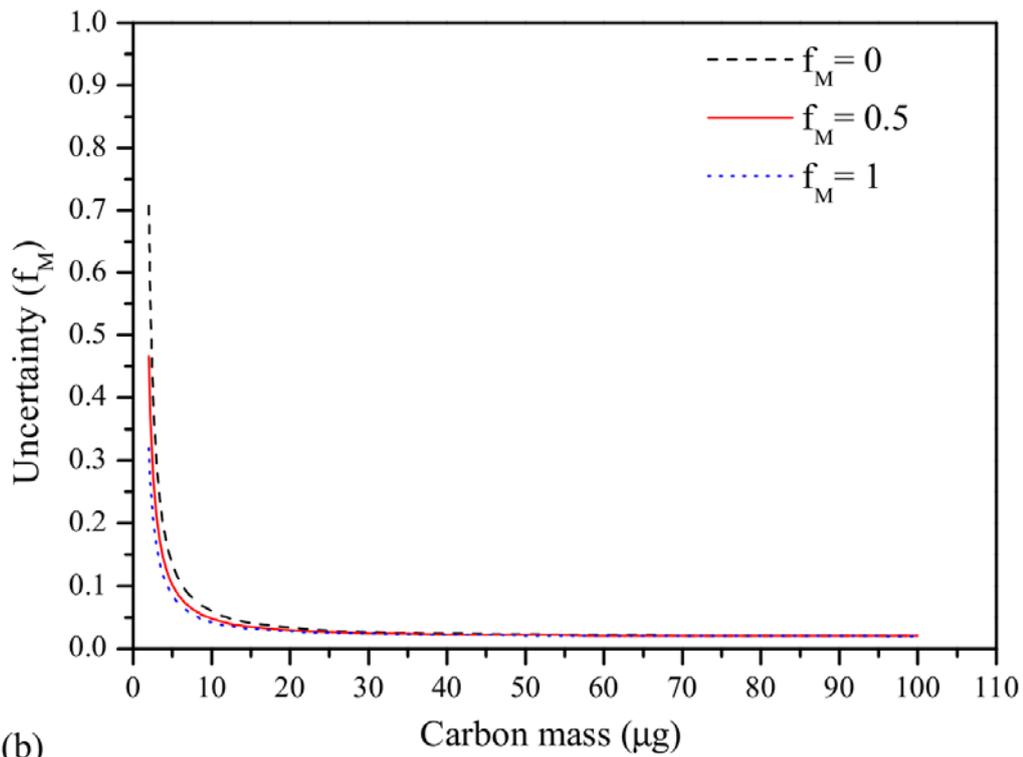
(b)

331

332 **Figure 1.** Fraction of modern (f_M) of fossil reference material (potassium hydrogen phthalate) (a) and
 333 “modern” reference materials including NIST-HOx2 and IAEA-C6 (b) against the sample size.
 334 Horizontal dotted lines and shaded areas represent mean of blank-corrected f_M and 2 sigma deviations,
 335 respectively. The unprocessed or nominal f_M values (solid lines) are also given as reference (numbers
 336 in the Figure).



(a)

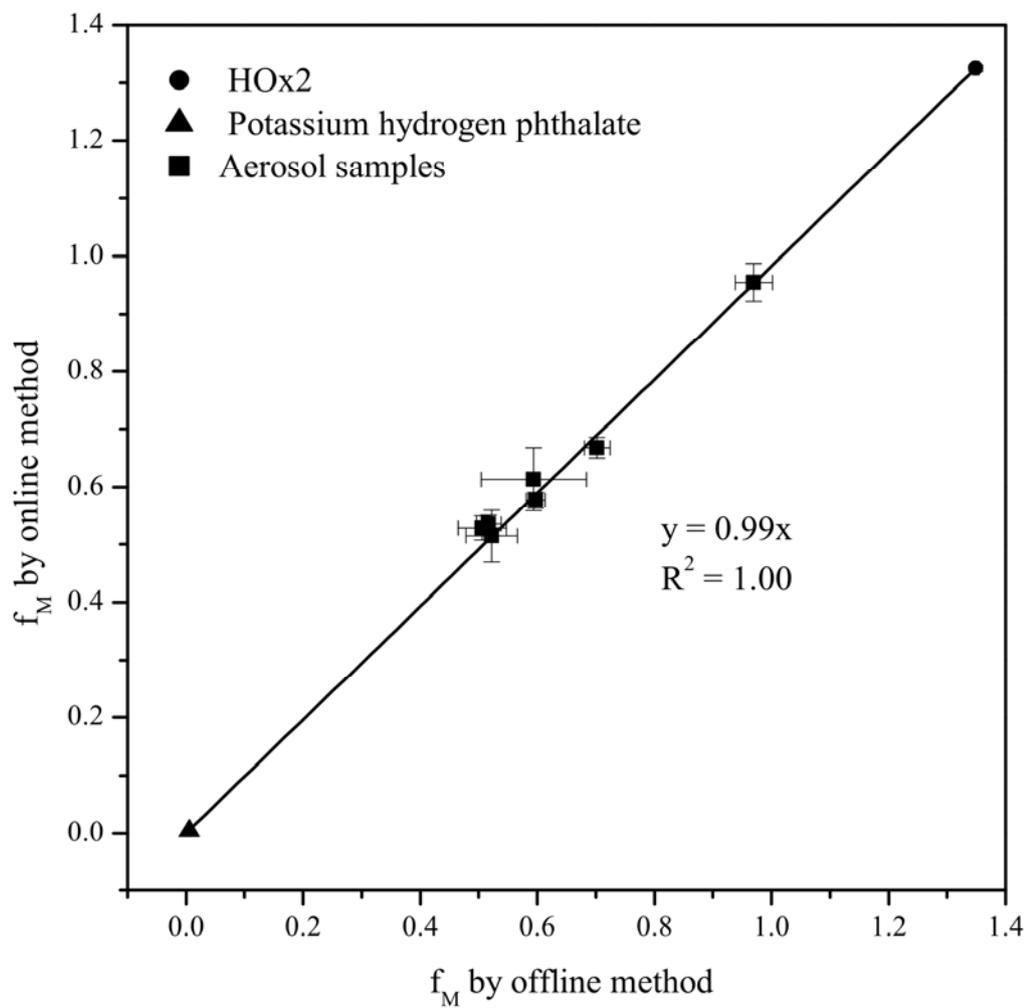


(b)

337

338 **Figure 2.** Sensitivity analysis of the bias of fraction of modern (f_M) without blank correction (a) and
 339 uncertainty of blank-corrected f_M depending on the sample size for different f_M values of the samples.

340



341

342 **Figure 3.** Comparison of ¹⁴C measurement of WSOC extracts by the online and offline methods.

343

344 **Table 1.** Blank-corrected fraction of modern (f_M) and fraction of non-fossil (f_{NF}) of WSOC, as well as WSOC/OC ratio, f_{NF} values of
 345 OC and WINSOC of aerosols samples collected at Bern and Moleno, Switzerland, as well as Beijing and Guangzhou, China.

Sample site and characteristic	PM size-cut	Data	WSOC/OC	f_M (WSOC)	f_{NF} (WSOC)	f_{NF} (OC)	f_{NF} (WINSOC)	f_{NF} (WSOC)*
Bern, urban kerbside, winter 2009	PM10	14-Jan-09	0.47	1.01±0.02	0.92±0.05	0.78±0.04	0.66±0.04*	
		3-Feb-09	0.30	0.95±0.02	0.86±0.05	0.70±0.04	0.63±0.04*	
Moleno, Alpine valley, highway nearby, winter 2008	PM10	30-Jan-08	0.50	0.97±0.01	0.89±0.05	0.79±0.05	0.68±0.04	0.91±0.05
		23-Feb-08	0.57	0.95±0.01	0.87±0.05	0.77±0.04	0.67±0.04	0.91±0.05
		25-Feb-08	0.55	0.90±0.02	0.81±0.05	0.79±0.05	0.64±0.04	0.84±0.05
Beijing, urban site, winter 2011	PM4.3	1-Dec-11	0.48	0.49±0.01	0.45±0.05	0.43±0.03	0.38±0.03	0.49±0.05
		15-Feb-11	0.51	0.49±0.01	0.45±0.05	0.36±0.03	0.32±0.03	0.41±0.05
Guangzhou, urban site, winter 2011	PM10	15-Dec-11	0.42	0.79±0.01	0.72±0.05	0.55±0.03	0.44±0.04*	
		16-Dec-11	0.44	0.79±0.01	0.71±0.05	0.58±0.03	0.47±0.04*	

346 * Indirectly calculated by Eq. 3 (see text for details).

347

348