



1 **Sources of non-fossil fuel emissions in carbonaceous aerosols during early winter in Chinese**

2 **cities**

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13 **Abstract**

14 China experiences frequent and severe haze outbreaks from the beginning of winter.

15 Carbonaceous aerosols are regarded as an essential factor in controlling the formation and

16 evolution of haze episodes. To elucidate the carbon sources of air pollution, source apportionment

17 was conducted using radiocarbon (¹⁴C) and unique molecular organic tracers. Daily 24-hour PM_{2.5}

18 samples were collected continuously from October 2013 to November 2013 in 10 Chinese cities.

19 The ¹⁴C results indicated that non-fossil fuel (NF) emissions were predominant in total carbon (TC;

20 average = 65 ± 7%). Approximately half of the EC was derived primarily from biomass burning

21 (BB) (average = 46 ± 11%), while over half of the OC fraction comprised NF (average = 68 ± 7%).

22 On average, the largest contributor to TC was NF-derived secondary OC (SOC_{nf}), which

23 accounted for 46 ± 7% of TC, followed by SOC derived from fossil fuels (FF) (SOC_f; 16 ± 3%),

24 BB-derived primary OC (POC_{bb}; 13 ± 5%), POC derived from FF (POC_f; 12 ± 3%), EC derived

25 from FF (EC_f; 7 ± 2%) and EC derived from BB (EC_{bb}; 6 ± 2%). The regional background

26 carbonaceous aerosol composition was characterized by NF sources; POCs played a major role in



27 northern China, while SOCs contributed more in other regions. However, during haze episodes,
28 there were no dramatic changes in the carbon source or composition in the cities under study, but
29 the contribution of POC from both FF and NF increased significantly.

30

31 **1. Introduction**

32 Recently, a wide range of fine particle ($PM_{2.5}$) pollution has affected northern, central and
33 southern China, particularly on haze days, which has had significant effects on air quality,
34 atmospheric visibility and public health, and caused extensive public and scientific concern (Liu et
35 al., 2013a; Wang et al., 2014). Haze events in Chinese urban areas, especially in megacities, have
36 become a common phenomenon, appearing in every season, because of large and intensive
37 pollutant emissions and unfavorable meteorological conditions (He et al., 2014; Liu et al., 2013b).
38 Generally, heavy and serious haze pollution outbreaks start at the beginning of winter.

39 Carbonaceous aerosols are the dominant component of $PM_{2.5}$ (~20–80%) (Rogge et al.,
40 1993; He et al., 2004; Dan et al., 2004; Kanakidou et al., 2005) and are regarded as essential for
41 controlling the formation and evolution of haze episodes. Relatively high concentrations of
42 carbonaceous aerosols have been observed during typical haze days in northern, southern and
43 central China (Zhao et al., 2013; Deng et al., 2008; Zhang et al., 2014a). Generally, carbonaceous
44 aerosols (total carbon, TC) can be divided into elemental carbon (EC) and organic carbon (OC)
45 according to their different physical and chemical properties (Krivácsy et al., 2001; Kleefeld et al.,
46 2002). EC is formed either from biomass burning (BB; e.g., wood fires, heating) or fossil fuels
47 (FF; e.g., vehicle or industry emissions), and can be used as a tracer for primary
48 combustion-generated OC because primary OC and EC are mostly emitted from the same sources
49 (Turpin and Huntzicker, 1995; Strader et al., 1999). OC can be directly derived from primary



50 emissions (primary OC; POC), or formed through oxidation of reactive organic gases followed by
51 gas-to-particle conversion in the atmosphere (secondary OC; SOC). Moreover, further
52 subcategories of OC exist, including water-soluble organic carbon (WSOC) and water-insoluble
53 organic carbon (WINSOC), which are distinguished on the basis of water-solubility; these may be
54 essential for assessing the different sources of OC emissions during haze episodes, since WSOC is
55 a proxy for SOC and BB OC, while WINSOC better represents POC (Weber et al.,
56 2007b;Docherty et al., 2008;Mayol-Bracero et al., 2002;Weber et al., 2007a); (Huang et al., 2014).

57 Several methods have been introduced to identify and quantify OC emission sources, such as
58 the use of organic molecular tracers (Simoneit et al., 1999); however, their reliability is limited by
59 their low atmospheric lifetimes, in turn due to chemical reactivity and highly variable emission
60 factors (Fine et al., 2001, 2002, 2004;Gao et al., 2003;Hedberg et al., 2006;Robinson et al., 2006).
61 Recently, radiocarbon (^{14}C) analysis has been used as a powerful tool for facilitating the direct
62 differentiation of non-fossil fuel (NF) carbon sources from fossil fuel (FF) sources, because ^{14}C is
63 completely absent from FF carbon (e.g., diesel and gasoline exhaust, coal combustion), whereas
64 NF carbon (e.g., biomass burning, cooking and biogenic emissions) shows a high contemporary
65 ^{14}C level (Szidat et al., 2009) Hence, ^{14}C measurements can provide information about the
66 contributions of FF, BB and biogenic emissions to carbonaceous aerosols. Numerous studies have
67 been performed on the regional background of carbonaceous aerosols at urban sites; for example,
68 contemporary carbon was the dominant pollutant in carbonaceous aerosols at a background site;
69 while a significant difference was found among seasons at urban sites (Yang et al., 2005;Chen et
70 al., 2013;Liu et al., 2013a;Zhang et al., 2014b;Liu et al., 2014a). A combination of ^{14}C analysis
71 and organic tracer determination allows for more detailed source apportionment of carbonaceous



72 aerosols (Gelencsér et al., 2007; Ding et al., 2008; Lee et al., 2010; Yttri et al., 2011).

73 In this study, sampling was conducted in 10 typical Chinese cities during early winter, i.e., at
74 the beginning of the period of widespread hazes. Carbonaceous aerosols, including different
75 carbon fractions such as WSOC, WINSOC and EC, along with water-soluble inorganic ions (F^- ,
76 Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and anhydrosugars (levoglucosan, galactosan and
77 mannosan), were analyzed in $PM_{2.5}$ samples. Source apportionment of carbonaceous aerosols was
78 performed using ^{14}C and organic tracers.

79 **2. Materials and Methods**

80 **2.1 Aerosol sampling**

81 Daily 24-hour $PM_{2.5}$ samples were collected continuously on the rooftops of institutes in 10
82 Chinese cities (Figure 1) from October 2013 to November 2013. In total, 292 aerosol samples,
83 including 10 field blanks, were collected on pre-heated (450°C for 5 h) quartz fiber filters (8 × 10
84 inches; Whatman, UK) using a high volume sampler with a flow rate of 0.3 m³ min⁻¹. The filters
85 were then wrapped in aluminum foil, packed into air-tight plastic bags, and stored at -20°C in a
86 refrigerator until analysis. $PM_{2.5}$ mass concentrations were determined gravimetrically by state
87 regulatory agencies. Details of the sampling information and meteorological parameters used
88 during sampling are shown in the Supporting Information (SI).

89 **2.2 Chemical analysis**

90 OC and EC were obtained with an off-line carbon analyzer (Sunset Laboratory, Inc., USA) using
91 the thermo-optical transmittance method (NIOSH 870). Water-soluble inorganic ions (Na^+ , Cl^- ,
92 Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , SO_4^{2-} and NO_3^-) were analyzed with an ion chromatographer (83
93 Basic IC Plus, Metrohm, Switzerland). Anhydrosugars (levoglucosan, galactosan and mannosan)



94 were analyzed by gas chromatography-mass spectroscopy (GC-MS) (7890-5975; Agilent) using a
95 capillary column (DB-5MS; 30m, 0.25 mm, 0.25 μ m). Analysis methods related to OC and EC,
96 water-soluble inorganic ions (Wang et al., 2012) and anhydrosugars (Liu et al., 2014a;Liu et al.,
97 2014b) were presented elsewhere and a detailed analytical procedure and method are available in
98 the SI.

99 **2.3 Separation of carbon species**

100 A punched section of filtrate was cut and sandwiched in a filtration unit, then extracted with 100
101 mL ultra-pure water (18.2 M Ω). WSOC species were quantified using a total organic carbon (TOC)
102 analyzer (TOC-VCPH; Shimadzu, Japan). The punched filtrate was dried in a desiccator, wrapped
103 in aluminum foil and then stored in a refrigerator. WINSOC and EC were obtained from the
104 water-filtered sample with an off-line carbon analyzer (Sunset Laboratory, Inc.) using the
105 thermo-optical transmittance method (NIOSH 870).

106 **2.4 Radiocarbon measurements**

107 Isolation procedures for the ^{14}C measurements of WSOC, WINSOC and EC have been
108 described previously (Liu et al., 2016a; Liu et al., 2013a). Two filters, based on the PM_{2.5}
109 concentrations at each site, were used for ^{14}C determination of WSOC, WINSOC and EC, to
110 distinguish between FF and NF emissions. To obtain the WSOC, WINSOC and EC fractions from
111 a single punch filter, a circular section of the punch filter was clamped in place between a filter
112 support and a funnel and then 60 ml ultra-pure water was slowly passed through the punch filter
113 without a pump, allowing the WSOC to be extracted delicately. WSOC was quantified as the total
114 dissolved organic carbon in solution using a total organic carbon (TOC) analyzer (Shimadzu
115 TOC_VCPH, Japan) following the nonpurgeable organic carbon protocol. WSOC solution was



116 freeze-dried to dryness at $-40\text{ }^{\circ}\text{C}$. The WSOC residue was re-dissolved with $\sim 500\text{ }\mu\text{l}$ of ultra-pure
117 water and then transferred to a pre-combusted quartz tube, which was then placed in the freeze
118 dryer. After that, the quartz tube was combusted at $850\text{ }^{\circ}\text{C}$. The remaining carbon on the filter was
119 identified as WINSOC or EC by an OC/EC analyzer (Sunset, U.S.). After WSOC pretreatment and
120 freeze-dried, OC is oxidized to CO_2 under a stream of pre-cleaned oxygen pure analytical grade
121 O_2 (99.999%, 30 ml min^{-1}) during the pre-combustion step at $340\text{ }^{\circ}\text{C}$ for 15 min. Before the OC is
122 oxidized, the sample is first positioned in the $650\text{ }^{\circ}\text{C}$ oven for about 45 s flash heating. This flash
123 heating has the advantage of minimizing pre-combustion charring, since it reduces pyrolysis of
124 OC. After the OC separation, the filters were removed from the system, placed into a muffle
125 furnace at $375\text{ }^{\circ}\text{C}$, and combusted for 4 h. The filters were then quickly introduced back into the
126 system and oxidized under a stream of pure oxygen at $650\text{ }^{\circ}\text{C}$ for 10 min to analyze the EC
127 fraction. Finally, the corresponding evolved CO_2 (WSOC, WINSOC, and EC) was cryo-trapped,
128 quantified manometrically, sealed in a quartz tube and reduced to graphite at $600\text{ }^{\circ}\text{C}$ using zinc
129 with an iron (200 mg, Alfa Aesar, 1.5-3 mm, 99.99%) catalyst for accelerator mass spectrometry
130 (AMS) target preparation. Approximately $200\text{ }\mu\text{g}$ of carbon was prepared for each carbon fraction.
131 All ^{14}C values were reported as the fraction of modern carbon (f_m) after correcting for
132 fractionation with $\delta^{13}\text{C}$. The degree of uncertainty in the ^{14}C measurements was in the range of
133 $0.2\text{--}0.6\%$. In this study, f_m was converted to the fraction of contemporary carbon (f_c), to eliminate
134 the effects of nuclear bomb tests through application of conversion factors of 1.10 ± 0.05 for EC
135 and 1.06 ± 0.05 for 2013 OC data. Here, the f_m values of OC (OC = WSOC + WINSOC) and TC
136 (TC = WSOC + WINSOC + EC) were calculated by isotopic mass balance. The concentration in
137 the field blank was negligible ($0.37 \pm 0.05\text{ }\mu\text{g cm}^{-2}$; less than 5% carbon) and no field blank



138 subtraction was made for ^{14}C determination. The system blank F^{14}C was $0.0036(\text{SD}=0.0001)$,
139 which translated to a ^{14}C age of around 45,000 years BP.

140 **3. Results and Discussion**

141 **3.1 $\text{PM}_{2.5}$, OC and EC concentrations and spatial distribution**

142 $\text{PM}_{2.5}$ levels ranged from 21.9 to $482 \mu\text{g m}^{-3}$, with an average level of $178 \pm 103 \mu\text{g m}^{-3}$. A total of
143 98% and 81% of $\text{PM}_{2.5}$ exceeded the First Grade National Standard ($35 \mu\text{g m}^{-3}$) and Second Grade
144 National Standard ($75 \mu\text{g m}^{-3}$) of China, respectively, indicating relatively poor air quality during
145 sampling days. The OC and EC levels ranged from 0.99 to $75.9 \mu\text{g m}^{-3}$ (average = $22.8 \pm 15.3 \mu\text{g}$
146 m^{-3}) and 0.07 to $19.3 \mu\text{g m}^{-3}$ (average = $3.66 \pm 3.28 \mu\text{g m}^{-3}$), respectively; thus, OC and EC were
147 major components of $\text{PM}_{2.5}$, accounting for $13 \pm 8\%$ and $2 \pm 1\%$ of $\text{PM}_{2.5}$, respectively. The OC
148 and EC levels in this study were generally higher than those recorded previously in more
149 developed cities (e.g., New York, Los Angeles, Erfurt, Kosan) (Kam et al., 2012; Kim et al.,
150 2000; Gnauk et al., 2005; Rattigan et al., 2010), indicating severe carbonaceous pollution and
151 emphasizing the importance of restricting carbonaceous aerosols in China.

152 Northern China has high $\text{PM}_{2.5}$ concentrations. As shown in Table 1, the average $\text{PM}_{2.5}$
153 concentrations in Beijing ($190 \pm 79 \mu\text{g m}^{-3}$), Xinxiang ($245 \pm 65 \mu\text{g m}^{-3}$), Taiyuan ($285 \pm 84 \mu\text{g}$
154 m^{-3}) and Lanzhou ($212 \pm 112 \mu\text{g m}^{-3}$) were significantly higher than those in central and southern
155 China (from $85 \mu\text{g m}^{-3}$ in Guangzhou to $123 \mu\text{g m}^{-3}$ in Wuhan). Shanghai, in the eastern coastal
156 region, had the lowest average $\text{PM}_{2.5}$ concentration ($67 \pm 43 \mu\text{g m}^{-3}$). The ratio of total organic
157 matter (TOM; $1.6 \times \text{OC} + \text{EC}$) to total fine particle mass ranged from 17.4% to 32.6%, except in
158 Guiyang. Cities in central and southern China, such as Chengdu, Wuhan, Nanjing, and Guangzhou,
159 had a higher ratio of TOM to $\text{PM}_{2.5}$ than other cities. Moreover, the OC/EC ratios in those cities



160 were also higher, with values ranging between 8.1 and 12. The spatial distribution pattern closely
161 reflected energy consumption and regional climate differences. For example, there were more
162 particle emissions from heating in northern China, and more secondary organic aerosols in
163 southern and central China. In particular, Guiyang, which is a developing city located on the
164 Western plateau, had a high level of $PM_{2.5}$ ($227 \pm 77 \mu\text{g m}^{-3}$), comparable to that in northern China,
165 but also had the lowest levels of OC and EC. Moreover, the TOM to $PM_{2.5}$ ratio was only about
166 6.0%. This indicates that there are different chemical sources in this developing city compared to
167 megacities in China.

168 **3.2 Radiocarbon results: fraction of modern carbon (f_m)**

169 Table 2 shows the proportion (%) of NF sources in various carbon fractions. Overall, NF
170 emissions represented a more significant proportion of the TC (average = $65 \pm 7\%$; range:
171 50–79%), at all sites, than FF sources, which underscores the importance of NF sources to
172 carbonaceous aerosols during early winter in China.

173 EC is only formed by primary emissions, which are inert in ambient air and originate either
174 from BB or FF combustion. In this study, about half of the EC was derived from BB in the 10
175 urban cities (average $46 \pm 11\%$; range: 24–71%), which represents a slightly higher proportion
176 than that for the same cities in winter and spring, but is similar to previous studies performed in
177 cities in other countries (Szidat et al., 2009; Bernardoni et al., 2013; Liu et al., 2016b). However,
178 this result differs from those obtained in remote regions dominated by BB (Barrett et al.,
179 2015; Zhang et al., 2014b). A larger contribution of BB to EC was found in central and western
180 China (i.e., Beijing, Lanzhou, Chengdu and Guiyang) (49–63%), where Guiyang had the largest
181 proportion of BB in EC ($63 \pm 12\%$), followed by Beijing ($50 \pm 2.0\%$), Chengdu ($50 \pm 1.8\%$),



182 Wuhan ($48 \pm 10\%$) and Nanjing ($47 \pm 5\%$); this shows that there are large amounts of BB
183 emissions (e.g., from biofuel burning and outdoor fires) in western and central China during early
184 winter. This phenomenon was also found in central China during the severe haze episode that
185 occurred over China in January 2013, which suggests that these massive BB emissions were
186 generated indoors (i.e., from domestic heating and cooking) and thus could not be detected by
187 MODIS [Liu *et al.*, 2016b]. Guangzhou had the lowest proportion of BB in EC ($32 \pm 12\%$),
188 suggesting that FF emissions (coal combustion and vehicle emissions) dominated in the Pearl
189 Delta region. Similar to Guangzhou, Taiyuan and Xinxiang had lower proportions of BB in EC, of
190 $36 \pm 11\%$ and $37 \pm 1.7\%$, respectively. High proportions of BB in EC are due to extremely high
191 levels of BB tracers (levoglucosan). In this study, levoglucosan concentrations were in the range
192 161 to 672 ng m⁻³ (377 ± 153 ng m⁻³), and were significantly correlated with EC concentrations in
193 BB ($r = 0.708$, $p=0.000$).

194 Over half of the OC fraction was from NF sources at all sites (range: 54–82%), with an
195 average NF source contribution of $68 \pm 7\%$. Generally, the f_m spatial distribution of OC is similar
196 to that of EC, with NF sources contributing more in central China. Here, OC was divided into
197 WSOC and WINSOC, which has been separated with respect to fossil and NF sources. A large
198 contribution of NF sources to WINSOC ($64 \pm 7\%$) was observed in this study, comparable to
199 previous studies performed in urban areas of Europe, e.g., Gothenburg ($55 \pm 8\%$) and Zurich ($70 \pm$
200 7%) (Szidat *et al.*, 2009; Zhang *et al.*, 2013). Moreover, the f_m values for WSOC ($70 \pm 8\%$) were
201 slightly higher than those for WINSOC, which showed values comparable to those observed in
202 European and American cities (~ 70 – 85%) (Weber *et al.*, 2007a; Szidat *et al.*, 2009; Zhang *et al.*,
203 2013). A higher f_m value indicated that, for WSOC, the contribution of NF emission sources was



204 greater. WSOC is regarded as a mixture of SOC and BB-derived POC, whereas WINSOC is
205 mainly composed of POC from FF combustion, BB and biogenic sources. In this study, the ratio
206 of WSOC to OC increased significantly with an increase in the proportion of NF sources in OC (r
207 $= 0.531, p=0.016$); this implies that POC from BB is more water-soluble, or that more NF-derived
208 VOCs were involved in SOC formation.

209 3.3 Source apportionment of different carbon fractions

210 A source apportionment model for carbonaceous aerosols, including primary and secondary
211 sources, was applied in this study using measured carbon fractions, anhydrosugars, and ^{14}C
212 isotopic signals. Detailed information on this model has been provided previously (Liu et al.,
213 2014a; Liu et al., 2016b).

214 Briefly, EC from FF combustion (EC_f) and BB-derived EC (EC_{bb}) can be estimated using the
215 following respective equations:

$$216 \quad \text{EC}_f = \text{EC} \times (1 - f_c) \quad [1]$$

$$217 \quad \text{EC}_{bb} = \text{EC} \times f_c \quad [2]$$

218 Similar to EC, OC can be divided into FF OC (OC_f) and NF OC (OC_{nf}) based on ^{14}C
219 concentrations. OC_{nf} consists of BB-derived primary OC (POC_{bb}), NF-derived SOC (SOC_{nf}) and
220 biological primary carbon (BPC), such as spore and plant debris. BPC particles exist mainly in
221 coarse fractions ($> 2.5 \mu\text{m}$) and only account for $\sim 1\%$ of OC in $\text{PM}_{2.5}$ [Guo et al., 2012]. Thus, this
222 carbon fraction was ignored in the present study. POC_{bb} can be semi-quantitatively estimated from
223 Lev concentrations, due to its unique characteristic of originating from BB, as follows:

$$224 \quad \text{POC}_{bb} = \text{Lev} \times (\text{OC}/\text{Lev})_{bb} \quad [3]$$

225 According to the levoglucosan/mannosan (Lev/Man ; 17.4 ± 5.9) and mannosan/galactosan



226 (Man/Gal; 2.1 ± 0.3) ratios obtained in this study, 7.76 ± 1.47 was adopted as the $(OC/Lev)_{bb}$
227 value [Liu et al., 2014].

228 Thus, the SOC_{nf} fraction can be estimated through subtraction:

$$229 \quad SOC_{nf} = OC_{nf} - POC_{bb} \quad [4]$$

230 FF-derived POC and SOC can be estimated by the following respective equations:

$$231 \quad POC_f = WINSOC \times (1-f_c) \quad [5]$$

$$232 \quad SOC_f = WSOC \times (1-f_c) \quad [6]$$

233 Figure 2 shows the proportions of different carbon fractions, including EC_f , EC_{bb} , POC_{bb} , POC_f ,
234 SOC_{nf} and SOC_f , in total carbon (TC) for the 10 urban cites during the sampling period. On
235 average, the largest contributor to TC was SOC_{nf} , accounting for $46 \pm 7\%$ of TC, followed by
236 SOC_f ($16 \pm 3\%$), POC_{bb} ($13 \pm 5\%$), POC_f ($12 \pm 3\%$), EC_f ($7 \pm 2\%$) and EC_{bb} ($6 \pm 2\%$). The
237 proportion of primary sources ($POC_{nf} + POC_f + EC_{nf} + EC_f$) (average = $38 \pm 9\%$; range: 25–56%)
238 was lower than that of secondary sources ($SOC_{nf} + SOC_f$) (average = $62 \pm 9\%$; range: 35–83%),
239 which underlines the importance of SOC in carbonaceous pollution.

240 It should be noted that the model uncertainties in these contributions depended mainly on
241 correction factors, such as the $(POC/Lev)_{bb}$ emission ratios for wood burning, and on conversion
242 factors used for determining the f_c in ^{14}C analysis. Typical relative uncertainties were recently
243 estimated, using a similar modelling approach, at 20–25 % for SOC_{nf} , SOC_f , POC_{bb} , and POC_f ,
244 and ~13% for EC_f and EC_{bb} (Zhang et al., 2015).

245 POC and EC aerosols are independent from atmospheric gas reaction conditions and thus
246 directly reflect the characteristics of local emission sources. The total proportions of EC_f and POC_f
247 ranged from 10–38%, with an average of $19 \pm 9\%$ for all sites. The total proportions of EC_f and



248 POC_f in northern and southern China were greater than in western central and eastern coastal
249 China, indicating a higher impact of FF on local air pollution in both regions. The ratios of POC_f
250 to EC_f (0.66–3.32) were comparable to those derived directly from industrial coal combustion
251 (2.7–6.1) (Zhang et al., 2008) and traffic exhausts fumes (0.5–1.3) (Zhou et al., 2014; He et al.,
252 2008), indicating that industrial coal combustion and traffic exhaust fumes were the major primary
253 sources at all sites. Beijing (2.6) and Xinxiang (3.3) were mainly dominated by coal combustion
254 emissions. The total proportions of EC_{bb} and POC_{bb} ranged from 12–36%, with an average of $19 \pm$
255 8%. West central cities, such as Lanzhou, Chengdu, Guiyang, Nanjing and Wuhan, had large
256 proportions of EC_{bb} and POC_{bb} (average = $23 \pm 7\%$; range: 14–36%), which confirms the greater
257 impact of BB on local air pollution in West central China; this should be considered when setting
258 future limits for polluting corporations.

259 Total SOC in OC ranged from 42–84% (average = $72 \pm 10\%$) among the sites tested in this study,
260 which is similar to recent studies, conducted in the haze period in China of January 2013, which
261 used high-resolution aerosol mass spectrometry; i.e., 41–59% [Sun et al., 2014] and 44–71%
262 [Huang et al., 2014] obtained from online and offline measurements, respectively. There was no
263 significant difference in the SOC/OC ratio among the different regions in China studied herein,
264 except for Guiyang, which had a somewhat lower SOC/OC ratio. Moreover, SOC was comprised
265 predominantly of NF sources at all sites (67–89%), except at Guiyang with values of 42–53%,
266 which are similar to areas in developed countries with good air quality, such as Puy de Dôme,
267 France (86–88%) and Schauinsland, Germany (84–93%) [Gelencsér et al., 2007]. However, our
268 values were higher than those of previous studies conducted in China during other winter and
269 spring seasons, indicating the importance of NF to SOC in China during early winter.



270 3.4 Comparison of chemicals between samples by PM_{2.5} concentration

271 Two samples, one each with a low and high PM_{2.5} concentration, were obtained from all 10 study
272 sites (Figure S1) for ¹⁴C and inorganic ions analysis, to investigate the composition of
273 carbonaceous aerosols and evaluate the importance of FF and NF carbon in haze formation across
274 China in early winter. During sampling, the air masses generally moved in a northwesterly to
275 northeasterly direction to reach the site. The 5-day back trajectory analysis revealed relatively
276 lower concentrations of PM_{2.5} when the wind speed was higher, and relatively higher PM_{2.5} levels
277 when the wind speed was lower and more stable; synoptic conditions apparently promoted the
278 accumulation of particles (Figure 3).

279 Theoretically, the aerosol composition at higher wind speeds should reflect regional background
280 aerosol characteristics. Figure 3 shows the PM_{2.5} chemical compositions of the stage for lower
281 PM_{2.5} concentration during sampling period. Here, due to the different conversion factors used to
282 transform WINSOC to WINSOM (1.3), and WSOC to WSOM (2.1), OM calculations were based
283 on the relative contributions of WSOC and WINSOC to OC. TOM is the sum of EC, WINSOM
284 and WSOM. Generally, TOM contributions to PM_{2.5} ranged from 21–38%, except in Guiyang
285 where a value of 8% was observed. Moreover, OM was comprised mainly of NF emissions. In
286 cities in northern China (Beijing, Xinxiang and Taiyuan), the contribution of WINSOM (both FF
287 and NF) was greater, indicating that POC played a major role in regional air quality during this
288 season. Simultaneously, the lower NO₃⁻/SO₄²⁻ ratios also implied that POC from FFs might be
289 derived predominantly from coal combustion. The 5-day back trajectory analysis showed that the
290 air mass came from northern China, including regions such as Inner Mongolia and Hebei province,
291 where the ambient temperature is always below 10°C during this season. It is very common for



292 local rural residents to burn coal or biomass fuel to generate heat for their households. Therefore,
293 coal and biomass fuel combustion in northern China might be the major contributor to regional
294 carbonaceous aerosols in northern China during this season. In other cities, WSOM levels in both
295 FF and NF were much higher than those in WINSOM, showing the importance of SOC across
296 China. However, $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios in Shanghai, Nanjing and Wuhan were much higher than in
297 other areas. The back trajectory results showed that the air mass came from northern China or the
298 Yangtze River Delta, implying that traffic exhaust emissions in those regions was more important
299 for carbonaceous aerosol composition.

300 The chemical compositions of the higher $\text{PM}_{2.5}$ samples obtained in each city are shown in
301 Figure 3. There were no dramatic changes in the carbon source or composition in any of the cities;
302 however, the contribution of EC and WINSOM to both fossil and NF fuels increased significantly,
303 along with the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios, indicating the importance of POC from local regions. The back
304 trajectory results showed that wind speeds were moderate and stable, and that synoptic conditions
305 apparently promoted the accumulation of particles derived either from local or regional sources.

306 4. Conclusion

307 $\text{PM}_{2.5}$ samples were collected continuously from 10 Chinese urban cities during early winter
308 2013. $\text{PM}_{2.5}$, OC and EC levels were highest in northern China, with maximum concentrations of
309 $482 \mu\text{g m}^{-3}$, $75.9 \mu\text{g m}^{-3}$ and $19.3 \mu\text{g m}^{-3}$, respectively. OC and EC were the major components of
310 $\text{PM}_{2.5}$, accounting for $13 \pm 8\%$ and $2 \pm 1\%$, of total $\text{PM}_{2.5}$, respectively. The ^{14}C results, for the
311 lower and higher $\text{PM}_{2.5}$ concentration sample pairs obtained at each city, indicated that, overall,
312 NF emissions constituted a significant proportion of TC (average = $65 \pm 7\%$) at all sites, i.e.,
313 higher than FF sources. Furthermore, about half of the EC was derived primarily from BB



314 (average = $46 \pm 11\%$), and over half of the OC fraction came from NF sources (average = $68 \pm$
315 7%). Source apportionment analysis was done using ^{14}C and unique molecular organic tracers. On
316 average, the largest contributor to TC was SOC_{nf} , accounting for $46 \pm 7\%$ of TC, followed by
317 SOC_{f} ($16 \pm 3\%$), POC_{bb} ($13 \pm 5\%$), POC_{f} ($12 \pm 3\%$), EC_{f} ($7 \pm 2\%$) and EC_{bb} ($6 \pm 2\%$). When
318 relatively lower $\text{PM}_{2.5}$ concentrations were observed, OM was dominant in carbonaceous aerosols,
319 mainly from NF. POC played a major role in regional air quality in the cities in northern China,
320 while SOC contributed more in cities in other regions of China. There were no dramatic changes
321 in carbon sources or carbon compositions in the sampled cities during haze days; however, the
322 contribution of POC from both NF and NF increased significantly in these periods. This indicates
323 that synoptic conditions promote the accumulation of particles derived either from local or
324 regional sources.

325

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332

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Table 1 The PM_{2.5}, OC and EC data used in this study (average ± standard deviation; µg m⁻³)

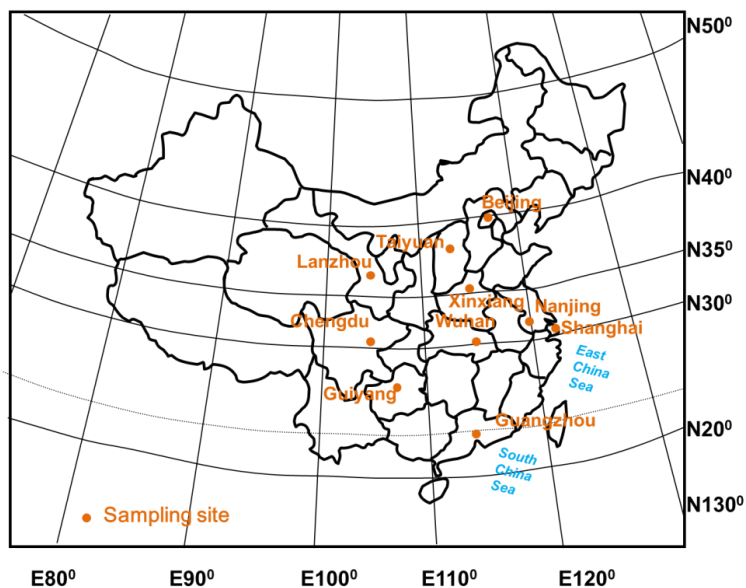
Sites	N	PM _{2.5}	OC	EC	OM/PM _{2.5} (%)	OC/EC
Beijing	31	189±79	26.5±12.5	3.6±1.8	24±4.6	7.7±1.8
Xinxiang	31	245±65	29.3±11.7	4.8±2.2	21±4.9	6.5±1.9
Taiyuan	31	285±84	37.3±15.5	7.8±2.8	23±4.4	4.9±1.5
Lanzhou	31	212±112	21.4±9.1	5.0±2.7	19±3.9	4.8±1.2
Guiyang	30	227±77	7.5±4.4	0.76±0.5	6.0±3.4	11±4.4
Chengdu	26	105±39	17.7±8.1	1.8±0.8	28±4.8	10±3.0
Wuhan	22	123±49	17.5±8.3	2.0±1.2	24±8.5	9.6±2.7
Guangzhou	28	85±32	17.4±9.9	2.3±1.8	33±11	8.1±2.4
Nanjing	19	111±50	18.8±8.7	1.6±0.6	28±9.3	12±3.8
Shanghai	27	68±43	7.2±9.0	1.0±0.9	17±8.5	7.4±3.0



Table 2 Proportion of modern carbon in WSOC, WINSOC, OC, EC, TC, and anhydrosugar, and ratio data for 10 urban cities in China for the period October 2013 to November 2013

	Start date	PM _{2.5}	WSOC	WINSOC	EC	f _m (WSOC)	f _m (WINSOC)	f _m (OC)	f _m (EC)	f _m (TC)	Lev	Lev/OC	Gal	Man
BJ1	11/3/2013	88	5.49	5.62	1.4	0.72	0.73	0.72	0.51	0.70	176	15.9	31.7	65.1
BJ2	11/5/2013	298	23.7	29.2	6.47	0.63	0.67	0.65	0.49	0.63	398	7.50	38.6	79.3
XX1	10/15/2013	132	4.71	17.7	4.30	0.65	0.51	0.54	0.38	0.51	553	24.7	29.3	52.1
XX2	10/22/2013	320	9.29	39.8	6.73	0.64	0.63	0.63	0.35	0.60	601	12.3	31.8	60.8
TY1	10/25/2013	177	15.9	12.5	5.90	0.81	0.66	0.74	0.44	0.69	518	18.2	28.4	56.4
TY2	10/26/2013	314	26.9	26.9	14.2	0.58	0.52	0.55	0.28	0.50	672	12.5	36.3	86.4
LZ1	10/20/2013	123	13.8	2.81	3.74	0.72	0.58	0.70	0.56	0.67	442	26.7	22.6	53.8
LZ2	10/23/2013	199	25.1	7.64	7.51	0.67	0.65	0.66	0.42	0.62	439	13.4	21.4	51.5
GY1	10/31/2013	125	3.74	1.18	0.64	0.57	0.81	0.63	0.71	0.64	247	50.1	16.4	35.5
GY2	11/6/2013	287	9.41	4.36	2.04	0.52	0.78	0.61	0.55	0.60	436	31.7	24.7	64.6
CD1	10/31/2013	53.8	4.40	0.86	0.63	0.87	0.55	0.82	0.51	0.79	198	37.6	13.2	21.2
CD2	11/8/2013	109	14.7	5.59	4.77	0.78	0.71	0.76	0.49	0.71	368	18.2	27.9	46.6
WH1	10/26/2013	73.2	13.0	3.59	1.40	0.69	0.71	0.69	0.42	0.67	344	20.7	15.1	32.0
WH2	10/30/2013	182	25.9	18.1	4.94	0.75	0.73	0.74	0.54	0.72	324	7.37	16.3	30.1
NJ1	10/27/2013	88.2	14.3	2.04	1.48	0.73	0.62	0.72	0.51	0.70	235	14.4	11.9	23.7
NJ2	10/29/2013	149	26.5	7.91	3.42	0.65	0.63	0.64	0.43	0.63	520	15.1	18.6	30.9
GZ1	10/28/2013	67.2	7.40	3.89	2.20	0.79	0.64	0.74	0.41	0.68	161	14.3	10.5	25.3
GZ2	10/29/2013	149	23.1	20.7	5.55	0.69	0.58	0.64	0.24	0.59	279	6.37	13.7	35.6
SH1	10/20/2013	63.2	6.39	1.70	1.58	0.78	0.57	0.73	0.56	0.71	165	20.4	9.77	19.7
SH2	10/23/2013	209	23.8	18.2	5.72	0.75	0.60	0.68	0.33	0.67	468	11.1	18.8	37.2

Note: all fractions are in $\mu\text{g m}^{-3}$, except for levoglucosan (Lev), galactosan (Gal) and mannosan (Man) (all ng m^{-3}).



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513 Figure 1. Geographic locations of the 10 Chinese sampling sites.

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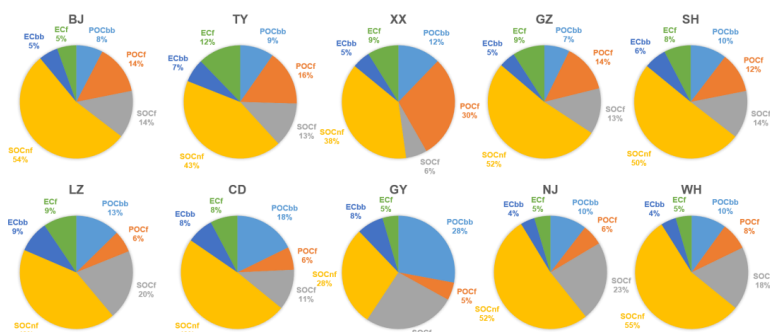
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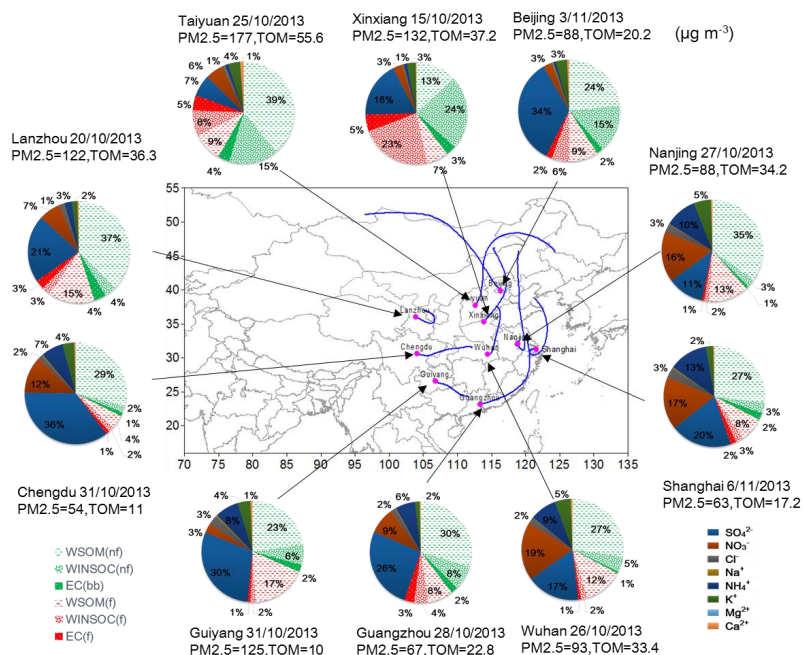
525 Figure 2. The proportions of different carbon fractions, including elemental carbon derived from
526 fossil fuels ($1EC_f$), EC derived from burning biomass (EC_{bb}), BB-derived primary organic carbon
527 (POC_{bb}), POC derived from FF (POC_f), non-FF secondary OC (SOC_{nf}) and SOC derived from FF
528 (SOC_f) in total carbon (TC) for 10 urban cites during the sampling period.

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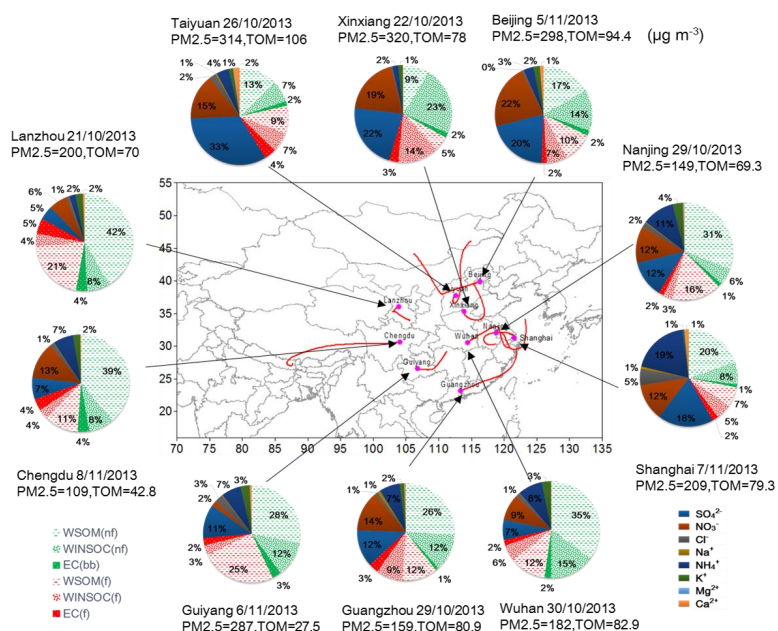


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534 Figure 3. The chemical compositions of fine particles (PM_{2.5}) under non-haze (top) and haze
 535 (bottom) conditions during the sampling period.

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538 both native speakers of English. For a certificate, please see:

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