Response to Reviewers' Comments and Suggestions

Reviewer's Comments

Authors' responses and revisions

Comments from Referees

Author's response

Author's changes in manuscript

Comments:

This study attempts to elucidate sources of OC (WSOC, WINSOC) and EC using 14C and molecular organic tracers. Such methods have already been successfully applied in many regions around the world. This study found non-fossil fuel (NF) emissions were predominant in total carbon. Primary organic carbon was very important in North China. Given that the powerful property of radiocarbon in determining the sources of fossil and nonfossil and board implications present in this study, I recommend it for a publication in ACP after some revisions required below.

Source apportionment of POC (NF+FF) and SOC (NF+FF) is based on several assumptions, which should be carefully evaluated and clearly indicated in the paper. If POC and SOC numbers are shown in the abstract and conclusions, the authors should also point out assumptions and limitations in POC and SOC estimations in the abstract and conclusions as comments provided below.

Line 39: "dominant" is too strong to be used here.

Response and Revisions: Thank you for your suggestion. The "dominant" has been revised into "important."

Author's changes in manuscript: Carbonaceous aerosols are the important component of PM2.5 (~20–80%).

Line 46-49: to include coal combustion in fossil fuel emissions.

Response and Revisions: The "coal combustion" has been added into fossil fuel emissions.

Author's changes in manuscript:

Line 51: to add references?

Response and Revisions: The reference has been added.

Author's changes in manuscript:

Lines 52-56: the sentence should be reworded. a large fraction of SOA can be water insoluble as well.

Response and Revisions: Thank you for pointing out this. We have already changed "WINSOC better represents POC" into "a large fraction of WINSOC is from POC" (line 56)

Author's changes in manuscript:

Line 72-74: references related to recent studies in China should be included here.

Response and Revisions：The references regarding recent studies in China have been added in the revised manuscript.

Author's changes in manuscript:

Method part: sample numbers for all measurements should be clearly shown in the text and tables/Figure captions.

Response and Revisions：Thank you for your suggestion. The sample numbers for all measurements have already shown in the text and tables/Figure captions.

Author's changes in manuscript:

Line 107-108: more details should be provided.

Response and Revisions：More details have already been added into the revised manuscript (line 123-138). With regard to more detailed method development of 14C analysis of WINSOC and EC please see at http://pubs.acs.org/doi/abs/10.1021/es401250k?journalCode=esthag (Title: The use of levoglucosan and radiocarbon for source apportionment of PM2.5 carbonaceous aerosols at a background site in East China). In addition, detailed information of 14C analysis of WSOC, WINSOC and EC can be found at http://pubs.acs.org/doi/abs/10.1021/es503102w *(Title: Source Apportionment Using Radiocarbon and Organic Tracers for PM2.5 Carbonaceous Aerosols in Guangzhou, South China: Contrasting Local- and Regional-Scale Haze Events).*

Author's changes in manuscript:

Line 106: What are the uncertainties of fNF (and fM) in WSOC, WINSOC, OC and EC?

Response and Revisions：The uncertainties of fNF (and fM) in WSOC, WINSOC, OC and EC were up to 20%，20%，15% and 15%, respectively. (line 143-144)

Author's changes in manuscript:

Lines 138-140: should be removed because no evidence was provided.

Response and Revisions：Did you mean the sentence "The system blank F14C was 0.0036(SD=0.0001), which translated to a 14C age of around 45,000 years BP"? I think it was indeed necessary to explain the blank corrections.

Author's changes in manuscript:

Lines 150-170: please compare your data with published results (e.g. Beijing)? Why the biomass burning contribution to EC in Beijing was ~50%, which was much higher than those from other studies in the same city? Since only 2 samples were selected for each city, did these two samples can represent the winter? I suggest limitations should be pointed out clearly.

Response and Revisions：Thank you for your comments. The reasons for higher biomass burning contribution to EC in Beijing maybe attributed to ***(1) different method for isolation of OC and EC***

for 14C determination. *In this study, OC and EC separation was based on their different thermal behavior, which is different from other methods such as thermal-optical method. Our results were comparable with the same approach carried out in Beijing (~50%) (please see article at* http://pubs.acs.org/doi/abs/10.1021/es503102w*); and* ***(2) samples selection***. *We only selected two filter samples based on relatively lower and higher PM2.5 concentration for each site. The reasons for sample selection are 1) to see difference between haze and non-haze episode during winter campaign, and 2) limitations for 14C analysis such as OC/EC separation technique, the bulk samples required, and the high cost for 14C measurement. These selection choices may influence the final results to some extent. The limitation have already been added in the revised manuscript (line 189-192).*

Author's changes in manuscript:

171-175: to add comparisons with published results in China and also other sites in Asia.

Response and Revisions：Thank you for your suggestion. The comparisons have already been added into the revised manuscript (line 187-190).

Author's changes in manuscript:

Line 203: why 7.76 ± 1.47 ((OC/Lev) bb)? This can be estimated by ïijŽ OCBB=(OC/EC)BB *ECBB as well.

Response and Revisions：Yes, but here we have measured a good tracer of biomass burning emissions so we used (OC/Lev) bb for the estimation.

Author's changes in manuscript:

Line 206: SOC nf = OC nf - POC bb is not correct. Non-fossil source should at least include BB, SOC as well biogenic emissions and cooking.

Response and Revisions：Thank you for your comments. SOCnf may also include other non-fossil sources such as cooking and biogenic emissions, however, they should be limited during wintertime (e.g., <20%). Therefore, our estimates of SOC many generally represent an upper limit but this will not change our conclusion towards to the spatial distribution of SOC in China.

Author's changes in manuscript:

Line 208: POCf = WINSOC × (1-fc) is not correct. A large fraction WINSOC can be from secondary organic aerosol as well. So POCf is an upper limit of POCF. This should be carefully pointed out and discussed. And please add references after Eq 3-6.

Response and Revisions：Thank you for your comments. Yes, this is an upper limit of POCf. This sentence was added in the revised manuscript (line 259-260). Related articles on this model have already been added (line: 227-228).

Author's changes in manuscript:

Lines 236-246: Please discuss the possible biased in SOC estimations based on Eq 3-6.

Response and Revisions：We have already added the sentences "SOCf may be overestimated if a small fraction (e.g. <20%) WSOC is not secondary, so SOCf may be an upper limit. Meanwhile, SOCnf may also include other non-fossil sources such as cooking and biogenic emissions, however, they should be limited during wintertime (e.g., <20%). Therefore, our estimates of SOC many generally represent an upper limit but this will not change our conclusion towards to the spatial distribution of SOC in China." (line 259-264)

Author's changes in manuscript:

Line 227-230: How do you exclude contribution from residential coal combustion? I suggest removing the discussion if no other evidence can be found.

Response and Revisions：The sentence has already been revised into "The ratios of POCf to ECf (0.66–3.32) were within the emission ratios between coal combustion (2.7–6.1) (Zhang et al., 2008) and traffic exhausts fumes (0.5–1.3) (Zhou et al., 2014;He et al., 2008), indicating that coal combustion and traffic exhaust fumes were the major primary sources at all sites."

Author's changes in manuscript:

Reviewer: 2

Comments:

This manuscript applied a powerful radiocarbon source tracer to apportion fossil fuel and biomass/biofuel contributions to carbonaceous aerosols in ten cities of China. The method was well established. Although the sample numbers are limited for each city (two samples), the result contain new message for sources of organic carbon, elemental carbon, water soluble organic carbon, primary and secondary aerosols in Chinese cities. These carbonaceous aerosols are included as major concerns for climate changes and human health. The conclusion therefore is important for air pollution mitigation in China. Before publication on ACP, some technical improvements are suggested.

Line 46, "fossil fuels " changes to fossil fuel combustion.

Response and Revisions："fossil fuels" has already changed into "fossil fuel combustion."

Line 56, 2007b;Docherty et al., 2008;MayolâA˘ RBracero et al., 2002;Weber et al., 2007a); (Huang et al., 2014). Error.

Response and Revisions：Thank you for pointing out this. We have already made the correction in the revised manuscript (line 56-57).

Line 57, Several methods have been introduced to identify and quantify OC emission sources. Please show more methods for aerosol source apportionment; other methods like receptor models (PMF, CMB), and dispersion models.

Response and Revisions：Thank you for your suggestion. The references have already added in the revised manuscript (line 59-60).

Line 65 14C level (Szidat et al., 2009) Hence, 14C measurements can provide information about the. Full stop had been omitted.

Response and Revisions: Thank you for pointing out this. Full stop has already added in the revised manuscript.

Line 66: Numerous studies have been performed on the regional background of carbonaceous aerosols at urban sites. I prefer to change this sentence to: Numerous studies have been performed at urban sites to assess carbonaceous aerosol sources at the regional scale.

Response and Revisions: This sentence has been changed into "Numerous studies have been performed at urban sites to assess carbonaceous aerosol sources at the regional scale."

Line 68: contemporary carbon was the dominant pollutant in carbonaceous aerosols at a background site; The references should be cited for this conclusion at a background site (which one, it is better to detail the background site).

Response and Revisions: We have already added references and pointed out the detailed background sites in the revised manuscript (line 70-73).

while a significant difference was found among seasons at urban sites (Yang et al., 2005;Chen et al., 2013;Liu et al., 2013a;Zhang et al., 2014b;Liu et al., 2014a). This is a new/independent sentence which suggests seasonal variations at urban sites. The conjunction word "while" is not suitable since the seasonal variations have no clear relationship with the previous result from a background site.

Response and Revisions: We are sorry for the misunderstanding and thank you for your suggestion. We have already revised the sentence into "contemporary carbon was the dominant pollutant in carbonaceous aerosols at background sites such as Ningbo and Hainan stations (Liu et al., 2013a;Zhang et al., 2014b) while in urban sites where the relative carbon contributions have shown a significant seasonal difference."

Line 72: aerosols (Gelencsér et al., 2007;Ding et al., 72 2008;Lee et al., 2010;Yttri et al., 2011). It is better to add one or two latest references. The combination of organic tracer and radiocarbon diagnosing is the main advantage of this research. Therefore, it should have one or two latest literatures to support the hot topic of this method.

Response and Revisions: Thank you for pointing out this. We have already added new literatures in the revised manuscript (line 76-77).

Line 74: the beginning of the period of widespread hazes. Where? Probably it may be specified in China.

Response and Revisions: We are sorry for the misunderstanding and thank you for your suggestion. We have revised the sentence into "In this study, sampling was conducted in 10 typical Chinese cities during early winter when heavy haze pollution frequently occurs in this season."(line 78-79)

Line 75: carbon fractions such as WSOC, WINSOC and EC, along with water-soluble inorganic ions (F-, Cl-, SO42-, NO3-, NH4 , Na+, K+, Ca2+ and Mg2+) and anhydrosugars (levoglucosan, galactosan and mannosan). The details of water-soluble inorganic ions and anhydrosugars in

brackets should not be showed in the introduction, while they should appear in method or result.

Response and Revisions: Thank you for your suggestion. We have revised the sentence into "Carbonaceous aerosols, including different carbon fractions such as WSOC, WINSOC and EC, along with water-soluble inorganic ions and anhydrosugars, were analyzed in PM2.5 samples." The details of compounds have already shown in the method section.

The last paragraph of Introduction, authors may include some information for the advantage of the combination of radiocarbon and anhydrosugar tracer. In introduction, authors should clarify what are target sources for organic tracer.

Response and Revisions: Thank you for your suggestion. We have already added the sentence "In particular, anhydrosugars such as levoglucosan are used as a molecular marker to indicate biomass-burning emissions. The combination of 14C analysis and the concentration of levoglucosan has offered new insights into the detailed sources of carbonaceous aerosols" into the revised manuscript (line 81-84).

Fig.1, I suggest to include annual or winter aerosol optical depth to display the representative of the 10 cities for air pollution hotspots in China. Alternative, a literature for PM2.5 map in China may be helpful to show the relative high levels of the 10 cities. An example can be found in figure 1 of a publication: Light absorption enhancement of black carbon from urban haze in Northern China winter, Environ. Pollut., 221, 418-426, doi: http://dx.doi.org/10.1016/j.envpol.2016.12.004.

Response and Revisions: Thank you for your suggestion. We have already added new figure 1 into the revised manuscript.

I am interesting on the thermal and FID signal of the EC isolation of radiocarbon analysis of this method. This method is similar to CTO-375, but different from SWISS-4 (i.e. Zhang et al.) and NIOSH870 protocols.

Response and Revisions: These methods utilize the difference in thermal stability between OC and EC, which is different from the method of SWISS-S using thermal-optical approach. C14 signal in the EC fraction in this method was performed by evaporation of OC in a muffle furnace at 375°C in air with reaction time of 4h. More detailed method development of 14C analysis of WINSOC and EC please see at http://pubs.acs.org/doi/abs/10.1021/es401250k?journalCode=esthag (Title: The use of levoglucosan and radiocarbon for source apportionment of PM2.5 carbonaceous aerosols at a background site in East China). In addition, detailed information of 14C analysis of WSOC, WINSOC and EC can be found at http://pubs.acs.org/doi/abs/10.1021/es503102w *(Title: Source Apportionment Using Radiocarbon and Organic Tracers for PM2.5 Carbonaceous Aerosols in Guangzhou, South China: Contrasting Local- and Regional-Scale Haze Events).*

Line 308: PM2.5, OC and EC levels were highest in northern China, with maximum concentrations of 482 μg m-3, 75.9 μg m-3 and 19.3 μg m-3, respectively. Please show the detail site of these highest levels.

Response and Revisions: We have already added details in the revised manuscript. (line 329)

Line 309: OC and EC were the major components of PM2.5, accounting for 13 ± 8% and 2 ± 1%, of total PM2.5, respectively. This is not suitable conclusion of this study. Author did not analyze

several major chemicals such as sulfate, nitrate. I do agree that OC and EC are very important species of particulate matter, considering the health and climate impacts of the carbonaceous aerosols.

Response and Revisions：Thank you for pointing out this. The sentence has already been deleted.

Line 320: while SOC contributed more in cities in other regions of China. What is the meaning of other regions in China? Please specify the exact regions.

Response and Revisions：The sentence has already been revised into "while SOC contributed more in cities in other regions of China, such as Nanjing and Wuhan."

Line 321-322: however, the contribution of POC from both NF and NF increased significantly in these periods. This sentence should be corrected and improved.

Response and Revisions：This sentence has been changed into "however, the contribution of POC from both NF and FF increased significantly in these periods."

Final sentence: This indicates that synoptic conditions promote the accumulation of particles derived either from local or regional sources. This is not an informative conclusion for the scope of this research.

Response and Revisions：Thank you for your suggestion. We have deleted the sentence.

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

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Abstract

China experiences frequent and severe haze outbreaks from the beginning of winter. Carbonaceous aerosols are regarded as an essential factor in controlling the formation and evolution of haze episodes. To elucidate the carbon sources of air pollution, source apportionment was conducted using radiocarbon (^{14}C) and unique molecular organic tracers. Daily 24-hour $PM_{2.5}$ samples were collected continuously from October 2013 to November 2013 in 10 Chinese cities. The ^{14}C results indicated that non-fossil fuel (NF) emissions were predominant in total carbon (TC; average = 65 ± 7%). Approximately half of the EC was derived primarily from biomass burning (BB) (average = 46 ± 11%), while over half of the OC fraction comprised NF (average = 68 ± 7%). On average, the largest contributor to TC was NF-derived secondary OC (SOC_{nf}), which accounted for 46 ± 7% of

TC, followed by SOC derived from fossil fuels (FF) (SOC_f; 16 ± 3%), BB-derived primary OC (POC_{bb}; 13 ± 5%), POC derived from FF (POC_f; 12 ± 3%), EC derived from FF (EC_f; 7 ± 2%) and EC derived from BB (EC_{bb}; 6 ± 2%). The regional background carbonaceous aerosol composition was characterized by NF sources; POCs played a major role in northern China, while SOCs contributed more in other regions. However, during haze episodes, there were no dramatic changes in the carbon source or composition in the cities under study, but the contribution of POC from both FF and NF increased significantly.

1. Introduction

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

Carbonaceous aerosols are the ~~dominant~~important component of $PM_{2.5}$ (~20–80%) ~~(Rogge et al., 1993;He et al., 2004;Dan et al., 2004;Kanakidou et al., 2005)~~(Rogge et al., 1993;He et al., 2004;Dan et al., 2004;Kanakidou et al., 2005) and are regarded as essential for controlling the formation and evolution of haze episodes. Relatively high concentrations of carbonaceous aerosols have been

observed during typical haze days in northern, southern and central China ~~(Zhao et al., 2013;Deng et al., 2008;Zhang et al., 2014a)~~(Zhao et al., 2013;Deng et al., 2008;Zhang et al., 2014c). Generally, carbonaceous aerosols (total carbon, TC) can be divided into elemental carbon (EC) and organic carbon (OC) according to their different physical and chemical properties ~~(Krivácsy et al., 2001;Kleefeld et al., 2002)~~(Krivácsy et al., 2001;Kleefeld et al., 2002). EC is formed either from biomass burning (BB; e.g., wood fires, heating) or fossil ~~fuels~~fuel combustion (FF; e.g., vehicle or industry emissions such as coal combustion), and can be used as a tracer for primary combustion-generated OC because primary OC and EC are mostly emitted from the same sources ~~(Turpin and Huntzicker, 1995;Strader et al., 1999)~~(Turpin and Huntzicker, 1995;Strader et al., 1999). OC can be directly derived from primary emissions (primary OC; POC), or formed through oxidation of reactive organic gases followed by gas-to-particle conversion in the atmosphere (secondary OC; SOC~~).~~) (Choi et al., 2012;Subramanian et al., 2007). Moreover, further subcategories of OC exist, including water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WINSOC), which are distinguished on the basis of water-solubility; these may be essential for assessing the different sources of OC emissions during haze episodes, since WSOC is a proxy for SOC and BB OC, while a large fraction of WINSOC ~~better represents~~is from POC ~~(Weber et al., 2007b;Docherty et al., 2008;Mayol-Bracero et al., 2002;Weber et al., 2007a)~~(Weber et al., 2007b;Docherty et al., 2008;Mayol-Bracero et al., 2002;Weber et al., 2007a;Huang et al., 2014)~~; (Huang et al., 2014).~~.

Several methods have been introduced to identify and quantify OC emission sources, such as the use of organic molecular tracers ~~(Simoneit et al., 1999)~~(Simoneit et al., 1999), receptor models (PMF, CMB)(Singh et al., 2017;Bove et al., 2014;Marcazzan et al., 2003), and dispersion models (Colvile et al., 2003); however, their reliability is limited by their low atmospheric lifetimes, in turn due to

chemical reactivity and highly variable emission factors ~~(Fine et al., 2001, 2002, 2004;Gao et al., 2003;Hedberg et al., 2006;Robinson et al., 2006)~~(Fine et al., 2001, 2002, 2004;Gao et al., 2003;Hedberg et al., 2006;Robinson et al., 2006). Recently, radiocarbon (^{14}C) analysis has been used as a powerful tool for facilitating the direct differentiation of non-fossil fuel (NF) carbon sources from fossil fuel (FF) sources, because ^{14}C is completely absent from FF carbon (e.g., diesel and gasoline exhaust, coal combustion), whereas NF carbon (e.g., biomass burning, cooking and biogenic emissions) shows a high contemporary ^{14}C level ~~(Szidat et al., 2009)~~(Szidat et al., 2009). Hence, ^{14}C measurements can provide information about the contributions of FF, BB and biogenic emissions to carbonaceous aerosols. Numerous studies have been performed ~~on the regional~~at urban sites and background ~~of~~sites to assess carbonaceous ~~aerosols at urban sites; for~~aerosol sources. For example, contemporary carbon was the dominant pollutant in carbonaceous aerosols at a background ~~site; while a significant difference was found among seasons at urban sites~~ sites such as Ningbo and Hainan stations ~~(Yang et al., 2005;Chen et al., 2013;Liu et al., 2013a;Zhang et al., 2014b;Liu et al., 2014a)~~(Liu et al., 2013a;Zhang et al., 2014c)~~.~~. In urban, the relative carbon contributions have shown a significant seasonal difference (Yang et al., 2005;Chen et al., 2013;Liu et al., 2013b;Zhang et al., 2014a;Liu et al., 2014a;Zhang et al., 2017). A combination of ^{14}C analysis and organic tracer determination allows for more detailed source apportionment of carbonaceous aerosols ~~(Gelencsér et al., 2007;Ding et al., 2008;Lee et al., 2010;Yttri et al., 2011)~~(Gelencsér et al., 2007;Ding et al., 2008;Lee et al., 2010;Yttri et al., 2011;Zong et al., 2016;Liu et al., 2015;Zhang et al., 2014b).

In this study, sampling was conducted in 10 typical Chinese cities during early winter~~, i.e., at the beginning of the period of widespread hazes~~ when heavy haze pollution frequently occurs in this

season. Carbonaceous aerosols, including different carbon fractions such as WSOC, WINSOC and EC, along with water-soluble inorganic ions ~~(F^-, Cl^-, SO_4^{2-}, NO_3^-, NH_4^-, Na^+, K^+, Ca^{2+} and Mg^{2+}) and~~ and organic tracers (i.e. anhydrosugars~~ (levoglucosan, galactosan and mannosan),~~) were analyzed in $PM_{2.5}$ samples. ~~Source~~In particular, anhydrosugars such as levoglucosan are used as a molecular marker to indicate biomass-burning emissions. The combination of ^{14}C analysis and the concentration of levoglucosan has offered new insights into the detailed sources of carbonaceous aerosols. So, source apportionment of carbonaceous aerosols was performed using ~~^{14}C and organic tracers~~a source apportionment model based on the ^{14}C results and measured chemicals.

2. Materials and Methods

2.1 Aerosol sampling

Daily 24-hour $PM_{2.5}$ samples were collected continuously on the rooftops of institutes in 10 Chinese cities (Figure 1) from October 2013 to November 2013. In total, 292 aerosol samples, including 10 field blanks, were collected on pre-heated (450ºC for 5 h) quartz fiber filters (8 × 10 inches; Whatman, UK) using a high volume sampler with a flow rate of 0.3 m^3 min^{-1}. The filters were then wrapped in aluminum foil, packed into air-tight plastic bags, and stored at -20°C in a refrigerator until analysis. $PM_{2.5}$ mass concentrations were determined gravimetrically by state regulatory agencies. All samples were analyzed for OC and EC, and 20 samples, including two filters based on the $PM_{2.5}$ concentrations at each site, were selected for further chemical analysis. Details of the sampling information and meteorological parameters used during sampling are shown in the Supporting Information (SI).

2.2 Chemical analysis

OC and EC were obtained with an off-line carbon analyzer (Sunset Laboratory, Inc., USA) using

the thermo-optical transmittance method (NIOSH 870). Water-soluble inorganic ions (Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, SO_4^{2-} and NO_3^-) were analyzed with an ion chromatographer (83 _Basic IC Plus, Metrohm, Switzerland). Anhydrosugars (levoglucosan, galactosan and mannosan) were analyzed by gas chromatography-mass spectroscopy (GC-MS) (7890-5975; Agilent) using a capillary column (DB-5MS; 30m, 0.25 mm, 0.25μm). Analysis methods related to OC and EC, water-soluble inorganic ions ~~(Wang et al., 2012)~~(Wang et al., 2012) and anhydrosugars ~~(Liu et al., 2014a;Liu et al., 2014b)~~(Liu et al., 2014a;Liu et al., 2014b) were presented elsewhere and a detailed analytical procedure and method are available in the SI.

2.3 Separation of carbon species

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

2.4 Radiocarbon measurements

Isolation procedures for the ^{14}C measurements of WSOC, WINSOC and EC have been described previously ~~(Liu et al., 2016a; Liu et al., 2013a)~~(Liu et al., 2016b;Liu et al., 2013b). Two filters, based on the $PM_{2.5}$ concentrations at each site, were used for ^{14}C determination of WSOC, WINSOC and EC, to distinguish between FF and NF emissions. To obtain the WSOC, WINSOC and EC fractions from a single punch filter, a circular section of the punch filter was clamped in place between a filter support and a funnel and then 60 ml ultra-pure water was slowly passed through the

punch filter without a pump, allowing the WSOC to be extracted delicately. WSOC was quantified as the total dissolved organic carbon in solution using a total organic carbon (TOC) analyzer (Shimadzu TOC_VCPH, Japan) following the nonpurgeable organic carbon protocol. WSOC solution was freeze-dried to dryness at -40 °C. The WSOC residue was re-dissolved with ~500 µl of ultra-pure water and then transferred to a pre-combusted quartz tube, which was then placed in the freeze dryer. After that, the quartz tube was combusted at 850 °C. The remaining carbon on the filter was identified as WINSOC or EC by an OC/EC analyzer (Sunset, U.S.). After WSOC pretreatment and freeze-dried, OC is oxidized to CO_2 under a stream of pre-cleaned oxygen pure analytical grade O_2 (99.999%, 30 ml min^{-1}) during the pre-combustion step at 340 °C for 15 min. Before the OC is oxidized, the sample is first positioned in the 650 °C oven for about 45 s flash heating. This flash heating has the advantage of minimizing pre-combustion charring, since it reduces pyrolysis of OC. After the OC separation, the filters were removed from the system, placed into a muffle furnace at 375°C, and combusted for 4 h. The filters were then quickly introduced back into the system and oxidized under a stream of pure oxygen at 650°C for 10 min to analyze the EC fraction. Finally, the corresponding evolved CO_2 (WSOC, WINSOC, and EC) was cryo-trapped, quantified manometrically, sealed in a quartz tube and reduced to graphite at 600 °C using zinc with an iron (200 mg, Alfa Aesar, 1.5-3 mm, 99.99%) catalyst for accelerator mass spectrometry (AMS) target preparation. Approximately 200 µg of carbon was prepared for each carbon fraction.

All ^{14}C values were reported as the fraction of modern carbon (f_m) after correcting for fractionation with $\delta^{13}C$. The degree of uncertainty in the ^{14}C measurements was in the range of 0.2–0.6%. In this study, f_m was converted to the fraction of contemporary carbon (f_c), to eliminate the effects of nuclear

bomb tests through application of conversion factors of 1.10 ± 0.05 for EC and 1.06 ± 0.05 for 2013 OC data. Here, the f_m values of OC (OC = WSOC + WINSOC) and TC (TC = WSOC + WINSOC + EC) were calculated by isotopic mass balance. The uncertainties of f_{nf} (and f_m) in WSOC, WINSOC, OC and EC were up to 20% , 20% , 15% and 15%, respectively. The concentration in the field blank was negligible (0.37 ± 0.05 μg cm^{-2}; less than 5% carbon) and no field blank subtraction was made for ^{14}C determination. The system blank $F^{14}C$ was 0.0036(SD=0.0001), which translated to a ^{14}C age of around 45,000 years BP.

3. Results and Discussion

3.1 $PM_{2.5}$, OC and EC concentrations and spatial distribution

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

Northern China has high $PM_{2.5}$ concentrations. As shown in Table 1, the average $PM_{2.5}$ concentrations in Beijing (190 ± 79 μg m^{-3}), Xinxiang (245 ± 65 μg m^{-3}), Taiyuan (285 ± 84 μg m^{-}

469 ^{3}) and Lanzhou (212 ± 112 μg m^{-3}) were significantly higher than those in central and southern
470 China (from 85 μg m^{-3} in Guangzhou to 123 μg m^{-3} in Wuhan). Shanghai, in the eastern coastal
471 region, had the lowest average $PM_{2.5}$ concentration (67 ± 43 μg m^{-3}). The ratio of total organic matter
472 (TOM; 1.6 × OC + EC) to total fine particle mass ranged from 17.4% to 32.6%, except in Guiyang.
473 Cities in central and southern China, such as Chengdu, Wuhan, Nanjing, and Guangzhou, had a
474 higher ratio of TOM to $PM_{2.5}$ than other cities. Moreover, the OC/EC ratios in those cities were also
475 higher, with values ranging between 8.1 and 12. The spatial distribution pattern closely reflected
476 energy consumption and regional climate differences. ~~For example, there were more particle~~
477 ~~emissions from heating in northern China, and more secondary organic aerosols in southern and~~
478 ~~central China.~~ In particular, Guiyang, which is a developing city located on the Western plateau, had
479 a high level of $PM_{2.5}$ (227 ± 77 μg m^{-3}), comparable to that in northern China, but also had the lowest
480 levels of OC and EC. Moreover, the TOM to $PM_{2.5}$ ratio was only about 6.0%. This indicates that
481 there are different chemical sources in this developing city compared to megacities in China.

482 **3.2 Radiocarbon results: fraction of modern carbon (f_m)**

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

487 EC is only formed by primary emissions, which are inert in ambient air and originate either from
488 BB or FF combustion. In this study, about half of the EC was derived from BB in the 10 urban cities
489 (average 46 ± 11%; range: 24–71%), which represents a slightly higher proportion than that for the
490 same cities in winter and spring, but is similar to previous studies performed in cities in other

countries ~~(Szidat et al., 2009;~~(Szidat et al., 2009;Bernardoni et al., 2013~~;Liu et al., 2016b)~~;Liu et al., 2016a). However, this result differs from those obtained in remote regions dominated by BB (Barrett et al., 2015~~;Zhang et al., 2014b)~~;Zhang et al., 2014a)~~.~~. Compared with other studies in China, the measured biomass burning contributions to EC in Beijing are relatively higher than those in the same city during winter (Zhang et al., 2014b;Zhang et al., 2015b). This is due to the fact that different approach we used for OC/EC separation, and sample selection in this study (selected two filter samples based on relatively lower and higher PM2.5 concentration for each site) because of limitations for ^{14}C analysis (i.e. the bulk samples required and the high cost for ^{14}C measurement). However, the result is similar with those using the same approach (Liu et al., 2016c;Zong et al., 2016). Since limitations for A larger contribution of BB to EC was found in central and western China (i.e., Beijing, Lanzhou, Chengdu and Guiyang) (49~63%), where Guiyang had the largest proportion of BB in EC (63 ± 12%), followed by Beijing (50 ± 2.0%), Chengdu (50 ± 1.8%), Wuhan (48 ± 10%) and Nanjing (47 ± 5%); this shows that there are large amounts of BB emissions (e.g., from biofuel burning and outdoor fires) in western and central China during early winter. This phenomenon was also found in central China during the severe haze episode that occurred over China in January 2013, which suggests that these massive BB emissions were generated indoors (i.e., from domestic heating and cooking) and thus could not be detected by MODIS [*Liu et al.*, 2016b]. Guangzhou had the lowest proportion of BB in EC (32 ± 12%), suggesting that FF emissions (coal combustion and vehicle emissions) dominated in the Pearl Delta region. Similar to Guangzhou, Taiyuan and Xinxiang had lower proportions of BB in EC, of 36 ± 11% and 37 ± 1.7%, respectively. High proportions of BB in EC are due to extremely high levels of BB tracers (levoglucosan). In this study, levoglucosan concentrations were in the range 161 to 672 ng m^{-3} (377 ± 153 ng m^{-3}), and

were significantly correlated with EC concentrations in BB (r = 0.708, p=0.000).

Over half of the OC fraction was from NF sources at all sites (range: 54–82%), with an average NF source contribution of 68 ± 7~~%.~~%, comparable to previous study reported in four Chinese cities during 2013 winter (Xi'an, Beijing, Shanghai and Guangzhou were 63%, 42%, 51% and 65%, respectively)(Zhang et al. 2015a). Generally, the f_m spatial distribution of OC is similar to that of EC, with NF sources contributing more in central China. Here, OC was divided into WSOC and WINSOC, which has been separated with respect to fossil and NF sources. A large contribution of NF sources to WINSOC (64 ± 7%) was observed in this study, comparable to previous studies performed in urban areas of Europe, e.g., Gothenburg (55 ± 8%) and Zurich (70 ± 7%) ~~(Szidat et al., 2009;Zhang et al., 2013)~~(Szidat et al., 2009;Zhang et al., 2013). Moreover, the f_m values for WSOC (70 ± 8%) were slightly higher than those for WINSOC, which showed values comparable to those observed in European and American cities (~70−85%) ~~(Weber et al., 2007a;Szidat et al., 2009;Zhang et al., 2013)~~(Weber et al., 2007a;Szidat et al., 2009;Zhang et al., 2013). A higher f_m value indicated that, for WSOC, the contribution of NF emission sources was greater. WSOC is regarded as a mixture of SOC and BB-derived POC, whereas WINSOC is mainly composed of POC from FF combustion, BB and biogenic sources. In this study, the ratio of WSOC to OC increased significantly with an increase in the proportion of NF sources in OC (r = 0.531, p=0.016); this implies that POC from BB is more water-soluble, or that more NF-derived VOCs were involved in SOC formation.

3.3 Source apportionment of different carbon fractions

A source apportionment model for carbonaceous aerosols, including primary and secondary sources, was applied in this study using measured carbon fractions, anhydrosugars, and ^{14}C isotopic signals.

Detailed information on this model has been provided previously ~~(Liu et al., 2014a;Liu et al., 2016b)~~(Liu et al., 2014a;Liu et al., 2016a).

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

$$EC_f = EC \times (1-f_c) \quad [1]$$

$$EC_{bb} = EC \times f_c \quad [2]$$

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

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

According to the levoglucosan/mannosan (Lev/Man; 17.4 ± 5.9) and mannosan/galactosan (Man/Gal; 2.1 ± 0.3) ratios obtained in this study, 7.~~7 6~~76 ± 1.47 was adopted as the $(OC/Lev)_{bb}$ value [Liu et al., 2014].

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

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

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

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

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

Figure 2 shows the proportions of different carbon fractions, including EC_f, EC_{bb}, POC_{bb}, POC_f,

557 SOC_{nf} and SOC_f, in total carbon (TC) for the 10 urban cites during the sampling period. On average,
558 the largest contributor to TC was SOC_{nf}, accounting for 46 ± 7% of TC, followed by SOC_f (16 ±
559 3%), POC_{bb} (13 ± 5%), POC_f (12 ± 3%), EC_f (7 ± 2%) and EC_{bb} (6 ± 2%). The proportion of primary
560 sources (POC_{nf} + POC_f + EC_{nf} + EC_f) (average = 38 ± 9%; range: 25–56%) was lower than that of
561 secondary sources (SOC_{nf} + SOC_f) (average = 62 ± 9%; range: 35–83%), which underlines the
562 importance of SOC in carbonaceous pollution.

563 It should be noted that the model uncertainties in these contributions depended mainly on
564 correction factors, such as the $(POC/Lev)_{bb}$ emission ratios for wood burning, and on conversion
565 factors used for determining the f_c in ^{14}C analysis. Typical relative uncertainties were recently
566 estimated, using a similar modelling approach, at 20–25 % for SOC_{nf}, SOC_f, POC_{bb}, and POC_f, and
567 ~13% for EC_f, and EC_{bb} ~~(Zhang et al., 2015).~~(Zhang et al., 2015a). A large fraction WINSOC can
568 be from secondary organic aerosol as well. Hence POC_f is an upper limit of POC_f. SOC_f may be
569 overestimated if a small fraction (e.g. <20%) WSOC is not secondary, so SOC_f may be an upper
570 limit. Meanwhile, SOC_{nf} may also include other non-fossil sources such as cooking and biogenic
571 emissions, however, they should be limited during wintertime (e.g., <20%). Therefore, our estimates
572 of SOC many generally represent an upper limit but this will not change our conclusion towards to
573 the spatial distribution of SOC in China.

574 POC and EC aerosols are independent from atmospheric gas reaction conditions and thus directly
575 reflect the characteristics of local emission sources. The total proportions of EC_f and POC_f ranged
576 from 10–38%, with an average of 19 ± 9% for all sites. The total proportions of EC_f and POC_f in
577 northern and southern China were greater than in western central and eastern coastal China,
578 indicating a higher impact of FF on local air pollution in both regions. The ratios of POC_f to EC_f

(0.66–3.32) were ~~comparable to those derived directly from industrial~~within the emission ratios between coal combustion (2.7–6.1) ~~(Zhang et al., 2008)~~(Zhang et al., 2008) and traffic exhausts fumes (0.5–1.3) ~~(Zhou et al., 2014;He et al., 2008)~~(Zhou et al., 2014;He et al., 2008), indicating that ~~industrial~~ coal combustion and traffic exhaust fumes were the major primary sources at all sites. Beijing (2.6) and Xinxiang (3.3) were mainly dominated by coal combustion emissions. The total proportions of EC_{bb} and POC_{bb} ranged from 12–36%, with an average of 19 ± 8%. West central cities, such as Lanzhou, Chengdu, Guiyang, Nanjing and Wuhan, had large proportions of EC_{bb} and POC_{bb} (average = 23 ± 7%; range: 14–36%), which confirms the greater impact of BB on local air pollution in West central China; this should be considered when setting future limits for polluting corporations.

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

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

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

Theoretically, the aerosol composition at higher wind speeds should reflect regional background aerosol characteristics. Figure 3 shows the $PM_{2.5}$ chemical compositions of the stage for lower $PM_{2.5}$ concentration during sampling period. Here, due to the different conversion factors used to transform WINSOC to WINSOM (1.3), and WSOC to WSOM (2.1), OM calculations were based on the relative contributions of WSOC and WINSOC to OC. TOM is the sum of EC, WINSOM and WSOM. Generally, TOM contributions to $PM_{2.5}$ ranged from 21–38%, except in Guiyang where a value of 8% was observed. Moreover, OM was comprised mainly of NF emissions. In cities in northern China (Beijing, Xinxiang and Taiyuan), the contribution of WINSOM (both FF and NF) was greater, indicating that POC played a major role in regional air quality during this season. Simultaneously, the lower NO_3^-/SO_4^{2-} ratios also implied that POC from FFs might be derived predominantly from coal combustion. The 5-day back trajectory analysis showed that the air mass came from northern China, including regions such as Inner Mongolia and Hebei province, where the ambient temperature is always below 10°C during this season. It is very common for local rural residents to burn coal or biomass fuel to generate heat for their households. Therefore, coal and

biomass fuel combustion in northern China might be the major contributor to regional carbonaceous aerosols in northern China during this season. In other cities, WSOM levels in both FF and NF were much higher than those in WINSOM, showing the importance of SOC across China. However, NO_3^-/SO_4^{2-} ratios in Shanghai, Nanjing and Wuhan were much higher than in other areas. The back trajectory results showed that the air mass came from northern China or the Yangtze River Delta, implying that traffic exhaust emissions in those regions was more important for carbonaceous aerosol composition.

The chemical compositions of the higher $PM_{2.5}$ samples obtained in each city are shown in Figure 3. There were no dramatic changes in the carbon source or composition in any of the cities; however, the contribution of EC and WINSOM to both fossil and NF fuels increased significantly, along with the NO_3^-/SO_4^{2-} ratios, indicating the importance of POC from local regions. The back trajectory results showed that wind speeds were moderate and stable, and that synoptic conditions apparently promoted the accumulation of particles derived either from local or regional sources.

4. Conclusion

$PM_{2.5}$ samples were collected continuously from 10 Chinese urban cities during early winter 2013. $PM_{2.5}$, OC and EC levels were highest in northern China, with maximum concentrations of 482 μg m^{-3}~~,~~(Taiyuan, n=31), 75.9 μg m^{-3}(Taiyuan, n=31) and 19.3 μg m^{-3}~~,~~(Beijing, n=31), respectively. ~~OC and EC were the major components of $PM_{2.5}$, accounting for 13 ± 8% and 2 ± 1%, of total $PM_{2.5}$, respectively.~~ The ^{14}C results, for the lower and higher $PM_{2.5}$ concentration sample pairs obtained ~~at~~in each city, indicated that, overall, NF emissions constituted a significant proportion of TC (average = 65 ± 7%) at all sites, i.e., higher than FF sources. Furthermore, about half of the EC was derived primarily from BB (average = 46 ± 11%), and over half of the OC fraction came from NF

sources (average = 68 ± 7%). Source apportionment analysis was done using ^{14}C and unique molecular organic tracers. On average, the largest contributor to TC was SOC_{nf}, accounting for 46 ± 7% of TC, followed by SOC_f (16 ± 3%), POC_{bb} (13 ± 5%), POC_f (12 ± 3%), EC_f (7 ± 2%) and EC_{bb} (6 ± 2%). When relatively lower $PM_{2.5}$ concentrations were observed, OM was dominant in carbonaceous aerosols, mainly from NF. POC played a major role in regional air quality in the cities in northern China, while SOC contributed more in cities in other regions of China~~. There~~, such as Nanjing and Wuhan. During haze days, there were no dramatic changes in carbon sources or carbon compositions in the sampled cities ~~during haze days; however,~~, but the ~~contribution~~contributions of POC ~~from both NF and NF increased significantly in these periods. This indicates that synoptic conditions promote~~were relatively higher than the ~~accumulation of particles derived either from local or regional sources~~non-haze days.

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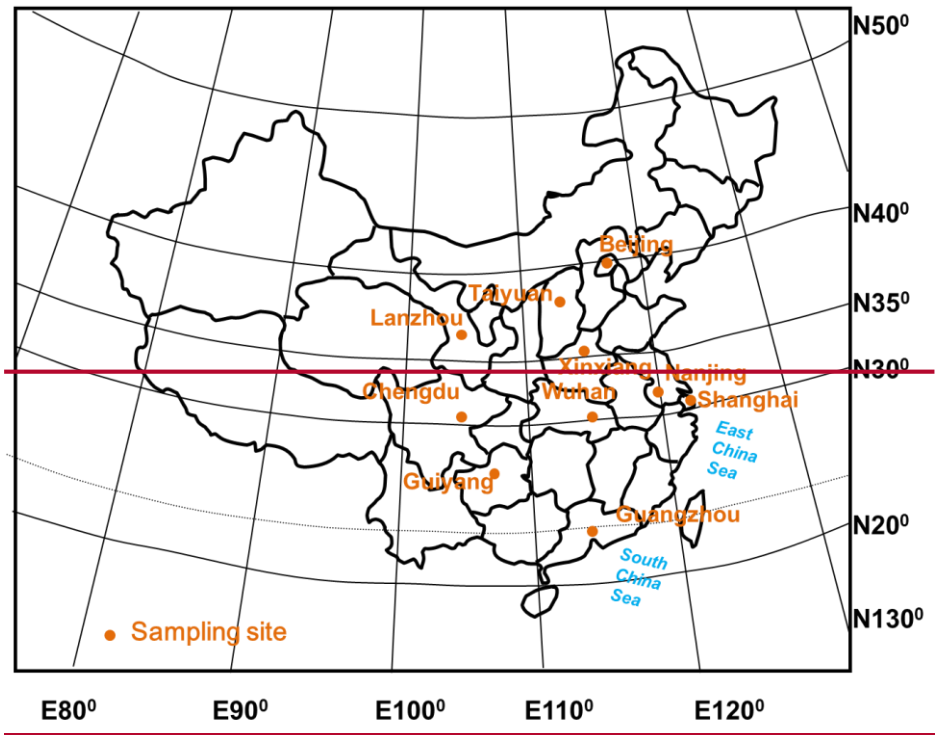
Table 1 The $PM_{2.5}$, OC and EC data used in this study (average ± standard deviation; μg m^{-3})

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 cites 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 μg m^{-3}, except for levoglucosan (Lev), galactosan (Gal) and mannosan (Man) (all ng m^{-3}).



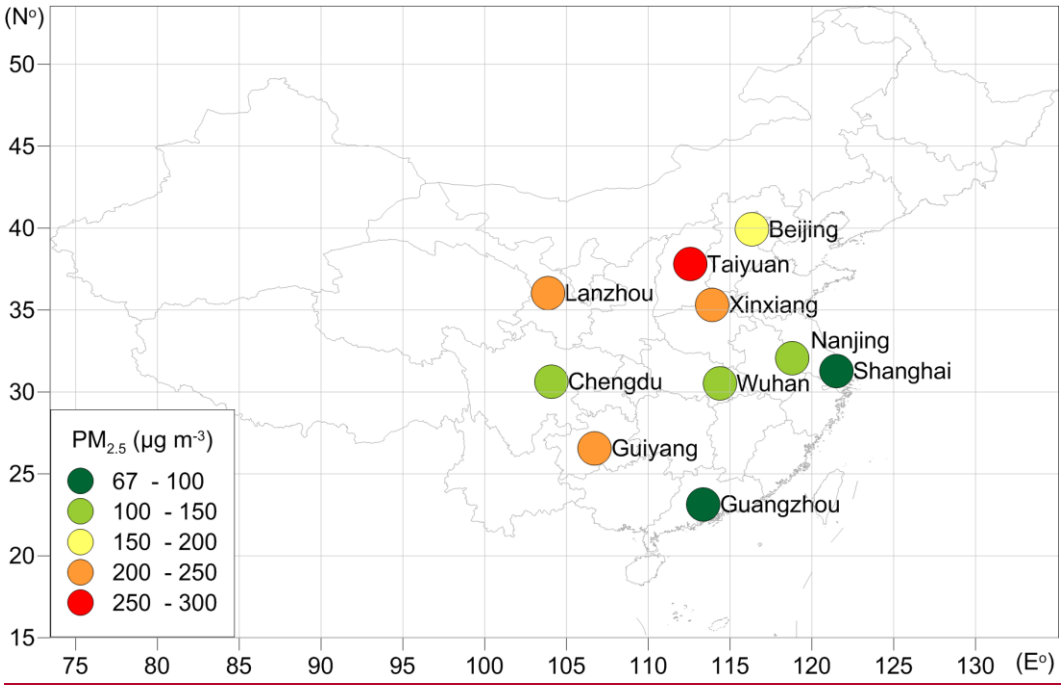


Figure 1. Geographic locations of the 10 Chinese sampling sites. The averages of monitored $PM_{2.5}$ concentrations (daily resolution, n = 31 for each site) during sampling campaign are shown in color plots.

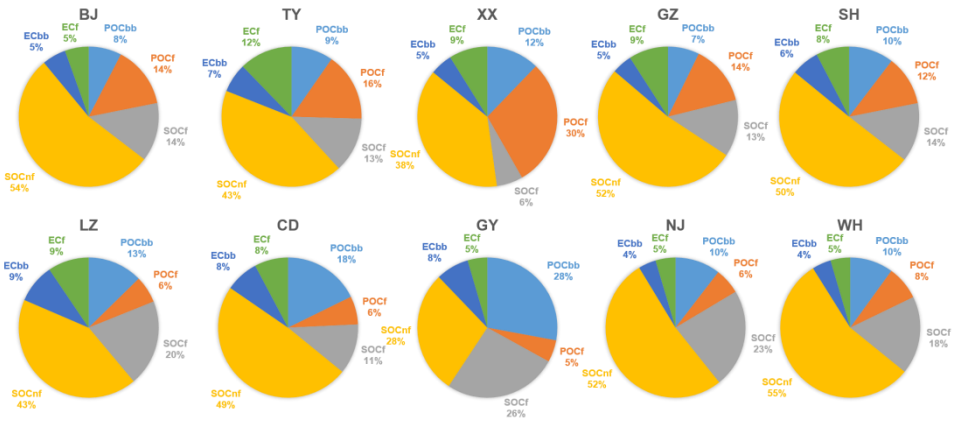


Figure 2. The proportions of different carbon fractions, including elemental carbon derived from fossil fuels (~~1EC~~$_f$EC$_f$), EC derived from burning biomass (EC$_{bb}$), BB-derived primary organic carbon (POC$_{bb}$), POC derived from FF (POC$_f$), non-FF secondary OC (SOC$_{nf}$) and SOC derived from FF (SOC$_f$) in total carbon (TC) for 10 urban cites during the sampling period.

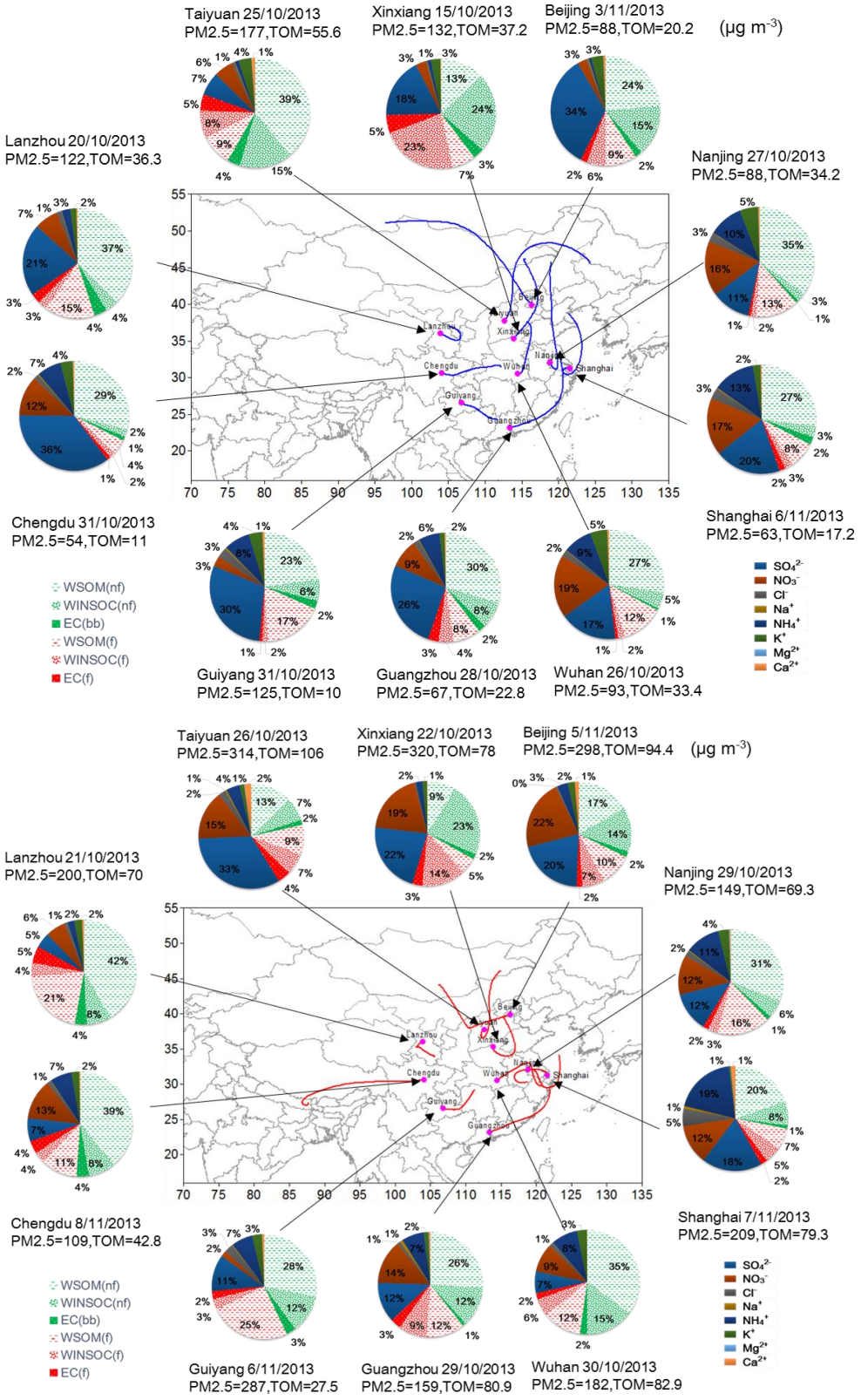


Figure 3. The chemical compositions of fine particles ($PM_{2.5}$) under non-haze (top) and haze (bottom) conditions during the sampling period.