Responses to Reviewer’s Comments to

Zhang et al., “Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode in 2013”

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black color font. Our responses are in blue font. We have responded to all the referee comments and done the modifications accordingly.

Anonymous Referee #1

General comments:

This manuscript describes radiocarbon source apportionment of organic aerosols during winter-time smog episodes in China. Air quality is a big concern in Chinese cities and especially the sources and formation mechanisms of organic aerosol are still un-certain. Using radiocarbon for source apportionment of organic aerosols is a very useful method, because, unlike tracer ratios, the 14C signature of the sources is not changed by chemical transformations in the atmosphere.

The methods and results are described clearly. The results are very relevant, showing that winter haze episodes do not necessarily result from an increase of specific fossil or non-fossil sources, but from an accumulation of pollutants accompanied by strong formation of secondary organic aerosol.

Given these results, the manuscript could be made significantly stronger, if the authors would additionally investigate meteorological conditions and air mass histories and their potential role in the pollution episodes. If the conditions could be identified that favor the accumulation of pollutant and secondary organic aerosol formation, this would give important insight into the pollution episodes.

However, the presented results are sufficiently interesting and important to be published and therefore I recommend acceptance with minor revisions, detailed below.

Reply: We thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately. The primary objective is to study fossil versus non-fossil contribution to both the OC and EC during the moderately polluted days and heavily polluted days. As a result, we did not include intensive discussion on how meteorological conditions affect PM and SOA formation in current study. Actually, this kind of studies has already been reported in several other studies (Wehner et al., 2008; Zhang et al., 2014). In the revised MS, we add following sentence in Sec 3.1: “The higher PM2.5 mass, OC and EC observed during the polluted period was characterized by low wind speed but not significantly sensitive by the temperature and
relative humidity.” Concerning air mass back trajectory, we did not find any significant
dependence between PM2.5 (OC, EC) and air mass origins (see the response and Figure R2
below). Therefore, we decided not include air mass back trajectory analysis in this study.

Specific comments:

p2624, line 10ff: Is the uncertainty for \( \text{fm}(\text{OC}) \) based on the reproducibility of the
sunset OC/EC measurements and the uncertainties of the fraction modern? If, yes, please state
so explicitly. In principle the uncertainty of EC-OC determination is much larger than the
reproducibility derived from using one particular protocol. Inter-laboratory comparisons using
different protocols for EC-OC determination show much larger uncertainties, on the order of
30% for EC. Please discuss this and estimate a resulting uncertainty for \( \text{fm}(\text{OC}) \).

Reply: the uncertainty for \( \text{fm}(\text{OC}) \) (8%) was obtained from an error propagation and
include all the individual uncertainties of the \( \text{fM} \)(TC) (2%), \( \text{fM} \)(EC) (5%), TC (8%)and EC
(25%). The sentence is changed as “The uncertainty of \( \text{fM}(\text{OC}) \) estimated by this approach is
on average 8% obtained from an error propagation and include all the individual uncertainties
of the \( \text{fM}(\text{TC}) \) (2%), \( \text{fM}(\text{EC}) \) (5%), TC (8%) and EC (25%).” We would also like to emphasize
that the variability of EC concentrations between different protocols is substantially reduced,
if water-extracted filters are used (see Zhang et al., 2012 in MS).

p26272, line 7: What are the uncertainties given here (standard deviation, standard error
of the mean, propagated experimental uncertainties)?

Reply: it is standard deviation. The sentence is changed as “OCf contributions (mean±
standard deviation) to total OC were 37 ±3 %…”

p26272, line 11: You mean the variability between different cities? Because within each
city the fraction of OCf in OC still seems relatively constant

Reply: yes. The sentence is changed as “The large variability of the fraction of OCf to
total OC among the different cities…”

p26273, line 11: Please give a reference for the lev-to-K ratio in hardwood burning.

Reply: the reference is now added.

p26273, line 25: Please note that in the corresponding figure, OCother,nf is called OCbio

Reply: the figure is now changed.

p26273, line 27ff: In this sentence it is already assumed that OCother,nf is mainly
secondary aerosol. This is discussed in more detail later. Please state this more clearly here, or
maybe already on page 26267, line 5ff.

Reply: The sentences are changed as “Despite a large spread of \( \text{OC}_{\text{sec},f} \) and \( \text{OC}_{\text{other},nf} \), the
data conclusively shows that both contributions were always larger on the heavily than on the
moderately polluted days, highlighting the importance of fossil-derived SOC formation and
other non-fossil emissions excluding primary biomass burning sources. The increased
\( \text{OC}_{\text{other},nf} \) is likely due to enhanced SOC formation from biomass burning and other non-fossil
sources (see Sec. 3.3)."

p26274, line 22ff: Here you state very generally that SOC from non-fossil sources is mainly from biomass burning. However, this need not necessarily be true for SH and GZ, where temperatures during this time period are well above 0 degrees.

Reply: yes, the biogenic SOC could not be excluded for SH and GZ. The sentence is changed as “The dominating contribution of OC_{other, nr} is likely due to the increase of SOC formation from non-fossil sources mainly from biomass-burning emissions, although biogenic-derived SOC could not be excluded for SH and GZ where temperatures during the sampling period are above 0 degrees."

p26275, line 9: Do you mean here the fossil contribution to primary aerosol?

Reply: “fossil contribution” here means “fossil contribution to TC” which is now clarified.

P26276, line 10: Given that Huang et al., 2014 reached similar conclusions for total PM2.5, I think comparing the results and conclusions between these two studies, should go further than just comparison of the source apportionment methods. Please compare the results of this study to Huang et al., 2014 in more detail.

Reply: the primary objective of our study is to investigate sources and formation mechanisms of fine carbonaceous aerosols. The comparison between this study and Huang et al., 2014 is to evaluate the LHS model performance used in this study (see Sec2.5). We believe that both studies have already given sufficient but different information, so further comparison between 2 studies is not necessary.

P26276, line 25: A slope of 1.13 is usually not called a 13% offset. More often, the intercept of the regression line is called ‘offset’. In general, it is better not to force the regression line through 0, because the intercept also contains information. Please change this.

Reply: The term “offset” was changed to “deviation” in the text. As the intercept is statistically insignificant (see below in Fig. R1), we remained the figure as it was and added the sentence to the caption: “Note that the intercepts are insignificant for all three cases.”
This paper describes a source apportionment of the carbonaceous component of 24h samples of PM2.5 collected in four major cities in China in January 2013, when total PM2.5 concentrations reached very high levels (up to 100s g m⁻³). The source apportionment is principally based on the proportion fossil/non-fossil carbon in the TC, and in the OC and EC fractions, as determined from accelerator mass spectrometry (AMS) measurements of the amount of the radiocarbon isotope, ¹⁴C, in the carbon. These data were supplemented by measurements of the levoglucosan, mannosan and water-soluble K⁺ concentrations in the PM2.5 which provide additional information for the source apportionment of biomass burning.

Both the analytical and data-interpretation methodologies for this study follow very closely that of a number of previous studies, particularly in Europe, undertaking similar...
source apportionment of the carbonaceous aerosol. This has the advantage of use of methodology that has already been through the peer-reviewed literature. The novelty here is its application to PM2.5 samples in very large Chinese cities that have experienced PM2.5 levels up to an order of magnitude greater than in many European urban locations. Poor air quality in China is clearly a major cause for concern and it is important for all, particularly policy-makers, to have insight into the constituent components and sources of the PM2.5.

Key results from this study include the finding of substantial non-fossil contribution to OC (in common with similar studies globally) and the inference that a substantial fraction of this non-fossil OC is primary rather than secondary in nature. The authors also compared their source apportionments between the most heavily-polluted days and moderately polluted days and noted that despite the increase in absolute masses the proportion of secondary was even slightly higher.

The paper describes thorough experimental procedures and appropriate data analysis methodologies. The writing is generally fluent, although occasional grammar and comma punctuation usage requires amendments. I have a couple of points regarding scientific interpretation, and the remaining points are largely concerned with presentation. I recommend this paper as suitable for publication in ACP following attention to these issues and any other relevant issues raised by other reviewers.

Reply: we thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately.

(1) The authors could likely gain some greater insight into the origin of their various carbon fractions by undertaking an air-mass back-trajectory investigation for the days of their samples, particularly through a comparison of the high-pollution vs. moderate-pollution days.

Reply: the carbon faction is not dependent on air mass origins. The air mass back trajectory analysis (see Figure R2 below) shows the prevailing air masses are generally from the north during our measurement period which has already been reported by Huang et al. (2014). As a result, it is not included in the current study.
Figure R2: Air mass back trajectories of air arriving the measurement sites on each measurement day, calculated using the NOAA HYSPLIT model (Huang et al., 2014).

(2) The description and nomenclature of the divisors used in Equations (3) and (5) was not immediately clear to me, i.e. the terms $f_M(bb)$ and $f_M(nf)$ in the two equations respectively. I interpret these terms as being the values used to correct the $f_M(EC)$ and $f_M(OC)$ values to yield a fraction contemporary carbon in EC and OC, rather than the fraction modern carbon in EC and OC. In my opinion, the terminology $f_M(bb)$, and the phrase “a 14C reference value for biomass burning” do not make it clear that the reference value is the percent modern in EC emitted from burning contemporary carbon-containing fuel. Likewise, for lack of clarity in Equation (5). The application of these terms does not become clearer until the text in point #1 on P26267.

Reply: To make the Equation (3) clearer, the sentence is changed as “ECbb is calculated from the EC mass concentration, $f_M(EC)$ and a reference value of biomass-burning EC (i.e. fraction of modern in EC emitted from biomass burning sources, $f_M(bb)$)”.

To make the Equation (5) clearer, the sentence is changed as “Analogously, OC is divided into two sub-fractions, OC from fossil fuel (OCf) and non-fossil emissions (OCnf). To account for the thermonuclear weapon tests of the late 1950s and early 1960s, OCnf is calculated from the OC mass concentration, $f_M(OC)$ and a 14C reference value of non-fossil emissions (i.e. fraction of modern in OC emitted from non-fossil sources, $f_M(nf)$).”

Technical corrections:

Abstract: State the collection duration of each PM2.5 sample (24 h).

Reply: it is added.

Abstract: State the number of samples analysed for 14C, i.e. the number of sample values that underpin the mean and standard deviation of source apportionment pro-portions presented in the abstract.

Reply: it is added.
P26259, L6: Rephrase end of the sentence as “:::was conducted at the four major cities of Xian, Beijing, Shanghai and Guangzhou.” (The fact that the study was conducted in several large cities in China has already been stated in the previous sentence.)

Reply: it is corrected.

P26259, L7. Delete “An effective” and start the sentence directly as “Statistical analysis of:::” Remove the words “An effective” from in front of similar phrasing elsewhere in the paper where the Latin Hypercube technique is mentioned; it is a redundant adjective.

Reply: it is corrected.

P2659, L11: Rewrite as “across all sites.”

Reply: this is corrected.

P2659, L19: Delete “rather”.

Reply: this is corrected.

P2660, L1: Delete both the two commas.

Reply: this is corrected.

P2661, L9: Delete comma.

Reply: this is corrected.

P2621, L22: Please provide a quantitative indication of what is meant by “extremely high concentrations of PM2.5”

Reply: It is changed as “During January 2013, the severe problem of air pollution in China became a worldwide concern, as extremely high concentrations of 24-h PM2.5 (i.e. often >100 µm/m^3) were reported in several large cities affecting ~1.3 million km^2 and ~800 million people.”

P2663, L4: “Six filters were selected:::”

Reply: this is corrected.

P2665, L12: Sort out the formatting of the citation in this sentence.

Reply: this is corrected.

P2667, L21: Insert “for” to read “To correct for the:::”

Reply: this is corrected.

P2671, L16: Correct the sentence containing the phrase “:::with an equally enhancement:::” which doesn’t make grammatical sense.

Reply: the sentence is changed as “This finding suggests that the increase of EC_f and EC_bb emissions in the three cities on the heavily polluted days is likely due to an equal enhancement of fossil fuel and biomass-burning combustion emissions and the accumulation of these particulate pollutants.”

P2672, L13: Should this read the “ratio of ECf to OCF“?

Reply: this is corrected.

P2673, L6: Insert comma after “marker”
Anonymous Referee #3

The manuscript presents comprehensive and well-established methodology to reveal the sources of fine carbonaceous aerosols in China under conditions of heavy pollution episodes. The approach taken by the authors is not particularly innovative, it is put together from previous works, many of which are linked to the authors themselves. Nevertheless, it is worth publication since it deals with pollution levels not frequently encountered in other parts of the world, and applies methods that are adequate, up-to-date and well-proven in similar studies.

However, I have two major points that need to be addressed before publication in ACP

Reply: we thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately.

1) On Page 26266, as part of their own innovation, the authors introduce a \( p \) factor that is intended to split \( OC/EC \) primary emission factor between coal combustion and vehicular emission. \( p \) is simply defined as a percentage of coal combustion within total fossil fuel emission in China. Since the focus of this study is exclusively fine particulates, and coal combustion and tailpipe emission is well-known to produce fundamentally different size distributions, the use of this overly simplified \( p \) factor cannot be justified. This should either be omitted or estimated on the basis of relevant studies that take into account the size-resolved emission factors from both coal combustion and vehicular emission.

Reply: we agreed that the size distribution may differ in particles emitted from coal and tailpipe emission. However, it should be noted that the size of particles emitted from coal and tailpipe are mostly smaller than 2.5 \( \mu m \) (the particle size used in this study) (Huang et al., 2006; Zhang et al., 2012). As a result, the size distribution would not affect our results if we did not study fossil and non-fossil carbon in size-resolved particles (i.e. from 0.056 \( \mu m \) to 10
µm). In fact, a very large range of p (0-0.7) instead of simply p value was used in the study. In addition, when increasing the p value (i.e. from 0.35 to 0.70 for central p value) for Beijing, we found ECf, ECbb, OCbb and OCother, nf are independent of the choice of the p value (see Table S2 and Fig. S1), although the contribution of SOCf was decreased, but still underlining the importance of fossil-derived SOC. Moreover, the comparison of our study and Huang et al (2014) confirmed that our source apportionment model and input parameters were justified.

2) My other major concern is related to the assumption that OCsecondary becomes relatively more important in times of high levels of air pollutions. This issue is dis-cussed in details in many previous source apportionment papers, and is partly related to nomenclature. Can we consider enhanced particle-phase partitioning (condensation) of semi-volatile organic compounds at colder temperatures simply as an increase in secondary organic aerosol (SOA)? Traditional perception of SOA generally implies some photochemical transformations prior to aerosol partitioning, which may not be the case here, at least not for the entire mass increment that is declared to be OC-secondary. In my opinion, part of this apparent SOA is not SOA if we strictly follow the definitions of atmospheric chemistry. However, the methodology applied by the authors does not allow distinction to be made between simple condensation and photochemical transformations. Thus, at least a critical discussion of the issue needs to be added to the manuscript.

Reply: we agree that the condensation of semi-volatile organic compounds at colder temperatures may contribute to the explained SOA in source apportionment study. However, this contribution is very small compared to the real SOA enhancement because the temperatures during the heavily polluted days were not significant lower than those found on other days. So we do not believe that the increased SOA measured by our model is due to condensation of semi-volatile organic compounds. The condensation of semi-volatile organic aerosol generally may contribute with some extent to the measured SOA in winter but the increased SOA between the moderately and heavily polluted days is largely due to enhanced SOA formation. To make it clearer, the statement is added in Sec 3.3.1 “It should be also noted that the condensation of semi-volatile organic aerosols generally may contribute to some extent to the measured SOA in winter due to the colder temperature in the northern sites such as Beijing and Xian. However, the increased SOA between the MPD and HPD measured by the current method is mostly if not exclusively due to enhanced SOA formation since the temperatures during the moderately and heavily polluted days were not significantly different.”

References:


Zhang, R., Li, Q., and Zhang, R.: Meteorological conditions for the persistent severe fog and haze event over eastern China in January 2013, SCIENCE CHINA Earth Sciences, 57, 26-35, 2014.
Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode in 2013

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During winter 2013, extremely high concentrations (i.e. 4-20 times higher than the World Health Organization guideline) of PM2.5 (particulate matter with an aerodynamic diameter <2.5 μm) were reported found in four major cities in China including Xian, Beijing, Shanghai and Guangzhou. In this work, source apportionment of fine carbonaceous aerosols during this haze episode was conducted at four major cities in China including Xian, Beijing, Shanghai and Guangzhou. An effective statistical analysis of a combined dataset from elemental carbon (EC) and organic carbon (OC), $^{14}$C and biomass-burning marker measurements using Latin-hypercube sampling allowed a quantitative source apportionment of carbonaceous aerosols. Based on $^{14}$C measurement in EC fraction (6 samples each city), we found that fossil emissions from coal combustion and vehicle exhaust dominated EC with a mean contribution of 75±8% across all sites. The remaining 25±8% was exclusively attributed to biomass combustion, consistent with the measurements of biomass-burning markers such as anhydrosugars (levoglucosan and mannosan) and water-soluble potassium (K$^+$). With a combination of the levoglucosan-to-mannosan and levoglucosan-to-K$^+$ ratios, the major source of biomass burning in winter in China is suggested to be combustion of crop residues. The contribution of fossil sources to OC was highest in Beijing (58±5%) and decreased from Shanghai (49±2%) to Xian (38±3%) and Guangzhou (35±7%). Generally, a larger fraction of fossil OC was rather from secondary origins than primary sources for all sites. Non-fossil sources accounted on average for 55±10% and 48±9% of OC and TC, respectively, which suggests that non-fossil emissions were very important contributors of urban carbonaceous aerosols in China. The primary biomass-burning emissions accounted for 40±8%, 48±18%, 53±4% and 65±26% of non-fossil OC for Xian, Beijing, Shanghai and Guangzhou, respectively. Other non-fossil sources excluding primary biomass-burning were mainly attributed to formation of secondary organic carbon (SOC) from non-fossil precursors such as biomass-burning emissions. For each site, we also compared samples from moderately with heavily polluted days according to particulate matter mass. Despite a significant increase of absolute mass concentrations of primary emissions from both fossil and non-fossil sources; during the heavily polluted events, their relative contribution to TC was even decreased, whereas the portion of SOC was consistently increased at all sites. This observation indicates that SOC was an important fraction in the increment of carbonaceous aerosols during the haze episode in China.
1 Introduction

Driven by continuous urbanization and industrialization and a rapid growth in the number of motor vehicles and energy consumption, large-scale severe air pollution episodes often affect most cities in China. An increase in the number of haze days is expected to have an adverse impact on human health (Chan and Yao, 2008). Atmospheric fine particles such as PM2.5 (particulate matter with an aerodynamic diameter of below 2.5 μm) have been reported as an important air pollutant in China (Donkelaar et al., 2010; Yang et al., 2011; Cao et al., 2012; Huang et al., 2013; Zhao et al., 2013), and its burden is much higher than the 24h-mean of 25 μg/m³ suggested by the Air Quality Guidelines of the World Health Organization (WHO) (WHO, 2006).

Carbonaceous aerosols are a major fraction of PM2.5 contributing 20-50% of the total PM mass in China’s urban atmosphere (Cao et al., 2007). In addition to health and visibility effects, carbonaceous aerosols also influence the earth’s climate directly by scattering and absorbing solar radiation and indirectly by modifying cloud microphysics (Pöschl, 2005; IPCC, 2013). Carbonaceous aerosols can be classified into elemental carbon (EC) and organic carbon (OC). EC is exclusively emitted as primary aerosols from incomplete combustion of fossil fuels and biomass burning, whereas OC is a complex mixture of primary directly emitted OC particles (POC) and secondary OC (SOC) formed in-situ in the atmosphere via the oxidation of gas-phase precursors (Pöschl, 2005). POC and precursors of SOC may stem from a vast variety of sources from both anthropogenic (e.g. coal combustion, vehicle emissions and cooking) and natural sources (e.g. biogenic emissions) (Carlton et al., 2009). These sources change over time and space, which makes source apportionment difficult.

Several techniques have been applied to quantify the emission sources of carbonaceous aerosols. Radiocarbon ($^{14}$C) measurements provide a powerful tool for unambiguously determining fossil and non-fossil sources of carbonaceous particles, since $^{14}$C is completely depleted in fossil-fuel emissions due to its age (half-life 5730 years), whereas non-fossil carbon sources (e.g. biomass burning, cooking or biogenic emissions) show a contemporary $^{14}$C content (Szidat, 2009; Heal, 2014). Moreover, a better $^{14}$C-based source apportionment can be obtained, when $^{14}$C determinations are performed on OC and EC separately, since EC originates exclusively from combustion of biomass and fossil fuels (Szidat et al., 2006; Szidat, 2009; Bernardoni et al., 2013; Liu et al., 2013; Zhang et al., 2013). However, as both biogenic and biomass-burning OC contain $^{14}$C on the contemporary level, it is still difficult to quantify the contribution from these two sources to OC by $^{14}$C measurements alone. When these are combined with OC/EC and...
organic marker measurements, the primary and secondary origins of the fossil and non-fossil
toxic fractions can be identified (Szidat et al., 2006; Szidat et al., 2007; Szidat et al., 2009; Minguillón
et al., 2011; Yttri et al., 2011). In particular, levoglucosan, a thermal degradation product of
cellulose combustion, can be used as molecular marker to identify primary biomass-burning
emissions (Simoneit et al., 1999; Puxbaum et al., 2007; Viana et al., 2013).

During January 2013, the severe problem of air pollution in China became a worldwide
concern, as extremely high concentrations of 24-h PM2.5 (i.e. often >100 µm/m³) were reported
in several large cities affecting ~1.3 million km² and ~800 million people. To investigate sources
and formation mechanisms of fine carbonaceous aerosols from this high pollution episode across
China, an intensive field experiment was carried out in the four large cities Xian, Beijing,
Shanghai and Guangzhou, each of them located in different climatic regions, i.e. central-
northwest region, Beijing-Tianjin region, Yangtze Delta Region, and Pearl River Delta Region,
respectively. These measurements were used in conjunction with an effective statistical approach,
Latin-hypercube sampling (LHS) (Gelencsér et al., 2007), to elucidate the origins of the
carbonaceous aerosol during the haze event.

2 Methods

2.1 Sampling

Measurement sites are located in Xian, Beijing, Shanghai and Guangzhou, the representative
cities of the central-northwest region, Beijing-Tianjin region, Yangtze Delta Region, and Pearl
River Delta Region, respectively. In these regions, haze events frequently occur during winter,
when weather conditions trap pollutants over the plain. Detailed descriptions of the sampling sites
are given in Table 1. In each city, 24-hour integrated PM2.5 samples were collected on pre-baked
quartz filters using high-volume samplers at a flow rate of ~1.05 m³/min from 5 to 25 January
2013. The sampling sites are located within campuses of universities or at research centers, >100
m away from local sources, such as major roadways, industry or domestic sources. At each
sampling site, one field blank sample was collected and analyzed. The results reported here are
corrected for corresponding field blanks (Cao et al., 2013). All samples collected were stored at -
20 °C before analysis. The PM2.5 mass on each filter was gravimetrically measured using a
temperature and relative humidity controlled microbalance.
2.2 Thermal-optical carbon analysis

A 1.0 cm\(^2\) punch from the filter samples is taken for the analysis of the OC and EC mass concentrations by the EUSAAR_2 thermal-optical transmission protocol (Cavalli et al., 2010). The replicate analysis of samples (n = 6) showed a good analytical precision with relative standard deviations of 4.8%, 9.1%, and 5.0% for OC, EC and TC, respectively. The average field blank of OC was 2.0 ± 1.0 µg/cm\(^2\) (equivalent to ~0.5 µg/m\(^3\)), which was subtracted from the measured OC concentrations. A corresponding EC blank was not detectable.

2.3 \(^{14}\)C analysis of the carbonaceous fractions

Six filters were selected per sampling site for \(^{14}\)C analysis, three from days with a very high PM loading and three representing an average loading, which are described in Table S1 in the supplement. A thermo-optical OC/EC analyzer (Model4L, Sunset Laboratory Inc, USA) equipped with a non-dispersive infrared (NDIR) detector is used for the isolation of different carbon fractions for subsequent \(^{14}\)C measurements using a four-step thermo-optical protocol Swiss_4S. The method is described in detail elsewhere (Zhang et al., 2012). For EC isolation, filter samples are first treated by water extraction to remove water-soluble OC to minimize the positive artefact from OC charring to the \(^{14}\)C result of EC. To remove both non-refractory and refractory OC fractions, the water-extracted filters are then combusted or heated in the following 3 steps: step 1 in an oxidizing atmosphere (O\(_2\), 99.9995%) at 375 °C for 150s; step 2 in O\(_2\) at 475 °C for 180s; step 3 in helium, at 450 °C for 180s followed by at 650 °C for 180s. Finally, EC is isolated by the combustion of the remaining carbonaceous material at 760 °C within 150s in O\(_2\). This method is optimized to minimize a possible negative EC artifact due to losses of the least refractory EC in the OC removal steps prior to EC collection. In a recent study, we found that the aforementioned negative artefact due to premature EC loss during a harsh OC removal procedure (e.g. combustion of samples at 375 °C for 4 h or longer) before EC isolation potentially underestimates biomass-burning EC contribution by up to ~70%, if only small amounts of EC are recovered (Zhang et al., 2012). The EC recovery for \(^{14}\)C measurement in this work is 78±10%. A bias from underestimation of biomass burning EC caused by the EC loss of 22 ±10% is corrected using the approach described by Zhang et al. (2012). For TC samples, the filters are combusted using the whole Swiss_4S protocol without OC/EC separation. After the combustion/separation of the desired carbonaceous aerosol fractions (i.e. TC or EC), the resulting CO\(_2\) is trapped cryogenically and sealed in glass ampoules for \(^{14}\)C measurement, which is conducted by a tabletop accelerator mass spectrometry (AMS) system MICADAS using a gas ion source (Wacker...
et al., 2013) at the Laboratory for the Analysis of Radiocarbon with AMS (LARA), University of Bern, Switzerland (Szidat et al., 2014). $^{14}$C results are expressed as fractions of modern ($f_{M}$), i.e. the fraction of the $^{14}$C/$^{12}$C ratio of the sample related to the isotopic ratio of the reference year 1950 (Stuiver and Polach, 1977). This data is then corrected for $^{14}$C decay during the period between 1950 and 2013, i.e. the year of measurement. The uncertainties of $f_{M}(\text{EC})$ and $f_{M}(\text{TC})$ are <5% and <2%, respectively. $^{14}$C results in OC ($f_{M}(\text{OC})$) is not measured directly, but calculated by:

$$f_{M}(\text{OC}) = \frac{TC \times f_{M}(\text{TC}) - EC \times f_{M}(\text{EC})}{OC}$$

The uncertainty of $f_{M}(\text{OC})$ estimated by this approach is on average 8% obtained from an error propagation and include all the individual uncertainties of the $f_{M}(\text{TC})$ (2%), $f_{M}(\text{EC})$ (5%), TC (8%) and EC (25%). The uncertainty of $f_{M}(\text{OC})$ estimated by this approach is <5%. No blank corrections are made for determination of $^{14}$C, as the different carbonaceous fractions contributions from field blanks are all less than 2% and thus can be neglected.

### 2.4 Anhydrosugars and water-soluble potassium measurements

The anhydrosugars (levoglucosan and mannosan) are measured by a recently developed in-situ derivatization/thermal desorption gas-chromatography-mass spectrometry method (IDTD-GC-MS) (Schnelle-Kreis et al., 2005; Orasche et al., 2011). Briefly, the filter punches are placed into glass liners suitable for an automated thermal desorption unit. Isotope-labelled standard compounds are spiked onto the filter surface to account for matrix-influences for quantification. Derivatization is performed on the filter by adding of liquid reagent N methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA, Macherey-Nagel, Germany). During 16 min of desorption time, in addition an in-situ derivatization with gaseous MSTFA is carried out to quantitatively silylate polar organic compounds and optimize the automated desorption process. Derivatized and desorbed molecules are first trapped on a pre-column before separation by gas chromatography (BPX-5 capillary column, SGE, Australia). The detection and quantification of compounds is carried out on a Pegasus III time-of-flight mass spectrometer (TOF-MS) using the ChromaTOF software package (LECO, St. Joseph, MI).

Concentrations of water-soluble potassium ($K^+$) and other ions are analyzed with ion chromatography (850 Professional IC, Metrohm, Switzerland) after leaching of a 1.0 cm$^2$ punch of the filter samples with 50 g of ultrapure water (18.2 MΩ quality) for 30 min at 40°C in an ultrasonic bath.


2.5 Source apportionment methodology

Source apportionment results are obtained by an effective statistical approach known as Latin-hypercube sampling (LHS) using the dataset from the measured OC, EC, and levoglucosan mass concentrations, estimated emission ratios as well as $^{14}$C contents of OC and EC. The LHS methodology which is comparable to Monte Carlo simulation was first proposed by (Gelencsér et al., 2007) and later applied in many European sites (e.g. Szidat et al. (2009), Yttri et al. (2011), Gilardoni et al. (2011) and Genberg et al. (2011)). Briefly, central values with low and high limits are associated to all uncertain input parameters (Table 2). Due to the lack of information on the input factors, parameters are assigned equally between the low limit and the central value and between the central value and the high limit. All combinations of parameters are included in frequency distributions of possible solutions except those producing negative values. The approach used here is slightly modified compared to previous studies and briefly summarized in the following.

EC arises from biomass burning (EC$_{bb}$) and fossil-fuel combustion (EC$_{f}$):

$$EC = EC_f + EC_{bb}$$  \hspace{1cm} (2)

EC$_{bb}$ is calculated from the EC mass concentration, $f_M(EC)$ and a reference value of biomass-burning EC (i.e. fraction of modern in EC emitted from biomass-burning sources, $f_M(bb)$)EC$_{bb}$ is calculated from the EC mass concentration, $f_M(EC)$ and a $^{14}$C reference value of biomass burning ($f_M(bb)$):

$$EC_{bb} = EC \times \frac{f_M(EC)}{f_M(bb)}$$  \hspace{1cm} (3)

Analogously, OC is divided into two sub-fractions, OC from fossil fuel (OC$_{f}$) and non-fossil emissions (OC$_{nf}$). To account for the thermonuclear weapon tests of the late 1950s and early 1960s, OC$_{nf}$ is calculated from the OC mass concentration, $f_M(OC)$ and a $^{14}$C reference value of non-fossil emissions (i.e. fraction of modern in OC emitted from non-fossil sources, $f_M(nf)$), whereof the latter is calculated from the OC mass concentration, $f_M(OC)$ and a $^{14}$C reference value of non-fossil emissions ($f_M(nf)$):

$$OC = OC_f + OC_{nf}$$  \hspace{1cm} (4)

$$OC_{nf} = OC \times \frac{f_M(OC)}{f_M(nf)}$$  \hspace{1cm} (5)

In addition to this straightforward OC distinction, OC$_{f}$ and OC$_{nf}$ are semi-quantitatively classified into additional sub-fractions. On the one hand, OC$_{f}$ is split into primary and secondary OC from fossil sources, i.e. OC$_{pri,f}$ and OC$_{sec,f}$, respectively:

$$OC_f = OC_{pri,f} + OC_{sec,f}$$  \hspace{1cm} (6)
OC_{pri,f} is determined from EC_f and a primary OC/EC emission ratio for fossil-fuel combustion, i.e. \((OC/EC)_{pri,f}\):

\[
OC_{pri,f} = EC_f \times \left( \frac{OC}{EC} \right)_{pri,f}
\]  \(\text{(7)}\)

As fossil-fuel combustion in China is almost exclusively from coal combustion and vehicle emissions, \((OC/EC)_{pri,f}\) can be determined as:

\[
\left( \frac{OC}{EC} \right)_{pri,f} = p \times \left( \frac{OC}{EC} \right)_{pri,cc} + (1 - p) \times \left( \frac{OC}{EC} \right)_{pri,ve}
\]  \(\text{(8)}\)

where \(p\) is a percentage of coal combustion in total fossil emissions, and \((OC/EC)_{pri,cc}\) and \((OC/EC)_{pri,ve}\) a primary OC/EC ratio for coal combustion (cc) and vehicle emissions (ve), respectively.

This strategy can only be applied to OC_{nf} after some modification, as its primary OC/EC emission ratio is far too uncertain for a general split of non-fossil OC into of primary vs. secondary formation. Alternatively, OC_{nf} is subdivided into primary biomass burning (OC_{bb}) and all the other non-fossil sources (OC_{other,nf}):

\[
OC_{nf} = OC_{bb} + OC_{other,nf}
\]  \(\text{(9)}\)

OC_{other,nf} includes all the other non-fossil sources except OC_{bb}, thus mainly representing primary and secondary biogenic OC, urban non-fossil contributions (e.g. from cooking or frying) as well as SOC from biomass burning; due to cholesterol concentrations below the limit of detection in all samples, however, contributions of cooking and/or frying to OC_{other,nf} can be neglected. OC_{bb} is calculated by two alternative “marker-to-OC” methods using either EC_{bb} or levoglucosan (lev) as biomass-burning marker with corresponding primary marker-to-OC emission ratios (Eq. 9 and 10).

\[
OC_{bb} = \frac{EC_{bb}}{\left( \frac{EC}{OC} \right)_{bb}}
\]  \(\text{(10)}\)

\[
OC_{bb} = \frac{lev}{\left( \frac{OC}{OC} \right)_{bb}}
\]  \(\text{(11)}\)

The overlapping results of both calculations are considered as probable solutions for OC_{bb}.

The consistency of EC_{bb} and levoglucosan data is shown below in Figure 4.

Extensive discussion of the selection of the used input parameters can be found in earlier studies conducted in Europe (e.g. (Gelencsér et al., 2007), (Szidat et al., 2009), (Yttri et al., 2011), (Gilardoni et al., 2011), (Genberg et al., 2011)). However, due to different conditions in this study, the input values have to be adapted (Table 2):
I. To correct for the $^{14}$C bomb peak, the reference values of $f_{M}$ for biomass burning and non-fossil sources, i.e. $f_{M}(bb)$ and $f_{M}(nf)$, respectively, are adapted to the sampling year 2013. $f_{M}(bb)$ is estimated as 1.10 ± 0.05 using a tree growth model as described in (Mohn et al., 2008). The low limit of $f_{M}(nf)$ is 1.03, which is equal to the $f_{M}$ of CO$_2$ in the atmosphere (Levin et al., 2010), and the high limit of $f_{M}(nf)$ is set to $f_{M}(bb)$ with the central value as the average of both.

II. Literature data indicate that emission ratios depend on fuel types and combustion conditions as well as specific measurement techniques, e.g. for EC mass (Fine et al., 2004; Puxbaum et al., 2007). A range of 0.07-0.20 and 0.10-0.30 is used as the low-to-high values for the (lev/OC)$_{bb}$ and (EC/OC)$_{bb}$, respectively, covering most of the variation in the measurements and the range used in previous studies (e.g. Gelencsér et al. (2007); Genberg et al. (2011); Szidat et al. (2009); Yttri et al. (2011); Genberg et al. (2011)).

Zhang et al. (2007b) reported an average (lev/OC)$_{bb}$ ratio of 0.082 for the main types of Chinese cereal straw (rice, wheat, and corn) based on combustion chamber experiments. As cereal straw is one of the most abundant biomass burned in China, the above ratio (0.082) was used to estimate biomass-burning contribution to OC in Beijing (Zhang et al., 2008) and Hong Kong (Sang et al., 2011). However, this ratio is lower than that (0.14) obtained from the combustion of hardwood in fireplaces and stoves in the US (Fine et al., 2004), which was applied to estimate the contribution of biomass burning to OC at background sites in Europe (Gelencsér et al., 2007; Puxbaum et al., 2007; Schmidl et al., 2008). Considering both main biomass types (i.e. mainly cereal-straw, but also hard-wood burning) (see Sec. 3.2.3), the central value for (lev/OC)$_{bb}$ of 0.11 is used in this study. Based on emission factors for primary particulate emissions in China (Zhang et al., 2007), the central value for (EC/OC)$_{bb}$ is chosen as 0.22.

III. (EC/OC)$_{pri}$ is determined for emissions from traffic as 0.8-2.1 with the central value of 1.45, which is taken from composite profiles from tunnel experiments in Europe (Gelencsér et al., 2007) and the range of this ratio also covers many tunnel studies conducted in China (Huang et al., 2006; He et al., 2008). For (EC/OC)$_{pri}$, it ranges for emissions for coal burning in China from 0.32 to 0.62 depending on the share of briquette and chunk bituminous coal with central value of 0.44 for the average coal inventory (Zhi et al., 2008).

IV. In many urban sites such as Barcelona (Minguillón et al., 2011), Zurich (Szidat et al., 2006) and Pasadena (Zotter et al., 2014), EC was almost exclusively attributed to vehicle emissions. However, in China coal combustion is also considered to be an important source of EC.
contributor to EC emission in winter from both field studies (Cao et al., 2011b) and inventory estimations (Cao et al., 2011a). Recently, Huang et al. (2014) reported relative contribution from coal combustion to total fossil emissions (i.e. \( p \) in the Eq (8)) ranges from 0.16-0.80 in Chinese aerosols. In this study, \( p \) is assigned as 0-0.7 with the central value of 0.35. It should be noted that for the regions with negligible coal combustion, \( p \) can be directly assigned as 0 to simplify this approach. In such a case, \( (EC/OC)_{pri,f} \) is equal to \( (EC/OC)_{pri,ve} \).

To evaluate uncertainties of the quantification of source contributions, the LHS method is implemented to generate 3000 random sets of variables (Gelencsér et al., 2007). A few simulations producing negative solutions are excluded and the median value from the remaining simulations is considered as the best estimate (see Sec 3.2), and the 10th and 90th percentiles of the solutions are treated as uncertainties. These uncertainties typically amount to 13% and 10% for the separation of EC into EC_f and EC_bb as well as for OC into OC_f and OC_nf respectively. The uncertainties are higher for the further source apportionment of OC (on the average 25%, 20%, 20% and 25% for OC_pri,f, OC_sec,f, OC_bb and OC_other,nf, respectively). The \(^{14}C\) analysis performed on the EC fraction directly enables a more reliable quantification of fossil and biomass burning EC compared to those results obtained by many previous studies (e.g. Gelencser et al., 2007; Yttri et al., 2011; Genberg et al., 2011), in which \(^{14}C\) analysis were only conducted on TC samples alone. The results of the sensitivity analysis and the determination of the uncertainties will be discussed further in Sec. 3.2.4. The comparison of the \(^{14}C\) approach with other organic markers (see Sec 3.2.3) as well as with the source apportionment results from positive matrix factorization (Paatero and Tapper, 1994) using the multi-linear engine (ME-2) algorithm (Paatero and Hopke, 2009) (see Sec. 3.3.3) will provide additional measures to evaluate the model performance.

### 3 Results and discussions

#### 3.1 PM2.5 and carbonaceous aerosols mass concentrations

The whisker box plots (Figure 1) show the concentrations of PM2.5, OC and EC as well as EC to OC ratios (EC/OC) in the four Chinese cities. The average PM2.5 mass concentrations at the Xian, Beijing, Shanghai, and Guangzhou sampling sites during the sampling periods were 345±125 µg/m\(^3\), 158±81 µg/m\(^3\), 90±31 µg/m\(^3\), and 68±23 µg/m\(^3\), respectively. Despite large variations in the PM2.5 concentrations within each site, their concentrations were always higher in Xian and Beijing compared to those in Shanghai and Guangzhou, reflecting a poorer air quality
in Northern China. Extremely high PM2.5 concentrations were observed for several days during
the sampling period. The highest 24-h average PM2.5 value (134-517 µg/m^3) was 5-20 times
higher than the WHO guideline for 24-h PM2.5 (25 µg/m^3, (WHO, 2006)). Only 3% of PM2.5
mass values were below this guideline value, indicating a very high negative impact on human
health in all studied cities.

OC and EC concentrations showed similar spatial distributions as the PM2.5 mass in the
order: Xian>Beijing>Shanghai>Guangzhou. Given that average temperatures during the sampling
period were 10-20°C lower in Xian and Beijing than in Shanghai and Guangzhou, the high
concentrations of carbonaceous species in northern cities could be due to enhanced fuel
consumption for heating activities (Weilenmann et al., 2009; Nordin et al., 2013). The EC/OC
ratios were comparable for Xian, Shanghai and Guangzhou, but considerably lower at Beijing.

We also compared the data of OC, EC and EC/OC from heavily polluted days with
moderately polluted days, which were selected from the samples with the highest and average PM
loading, respectively (Table 3). ^14C measurements were also performed on these samples (Sect.
2.3), and a detailed source apportionment result will be presented in Sect. 3.2. The PM2.5, OC
and EC mass concentrations on heavily polluted days were mostly >2 times as high as those on
moderately polluted days at the four sites. On the heavily polluted days, the EC/OC ratios
significantly decreased by 29% and 43% in northern cities of Xian and Beijing, respectively,
whereas they slightly increased in Shanghai and Guangzhou by 13% and 16%, respectively. The
higher PM2.5 mass, OC and EC observed during the polluted period was characterized by low
wind speed but not significantly sensitive by the temperature and relative humidity.

3.2 Best estimate of source apportionment results

3.2.1 Fossil and biomass burning EC

Figure 2 shows the source apportionment results of EC. The concentration of EC from fossil-
fuel sources ($EC_f$) ranged from 0.61 to 16.8 µg/m^3, whereas the corresponding range for EC from
biomass burning ($EC_{bb}$) was 0.57 to 4.71 µg/m^3. $EC_f$ values were on average 3 times as high as
$EC_{bb}$, corresponding to a mean fraction of $EC_f$ to total EC of 0.75. The highest concentrations of
$EC_f$ and $EC_{bb}$ were observed in Xian, followed by Beijing and the two southern sites Shanghai
and Guangzhou.

Despite the wide range of EC concentrations, the fraction of $EC_f$ to total EC in Xian, Beijing
and Shanghai was fairly constant with average values of 78±3%, 76±4% and 79±4%,
respectively. This finding suggests that the increase of $EC_f$ and $EC_{bb}$ emissions in the three cities
on the heavily polluted days is likely due to an equal enhancement of fossil fuel and biomass-
burning combustion emissions and the accumulation of these particulate pollutants during winter
with an equally enhanced fossil fuel and biomass burning combustion emissions. At
Guangzhou, however, the EC<sub>f</sub> contribution was noticeably higher on the heavily (i.e. 80±2%)
compared to the moderately polluted days (i.e. 57±5%), indicating that the increase of the EC
concentrations was rather caused by additional fossil-fuel emissions than by biomass burning.
The measured fossil contributions to EC correspond to those previously reported at 3 city sites
and 2 regional sites in China (Chen et al., 2013), but are higher than for the Maldives (31±5%),
India (36±3%) (Gustafsson et al., 2009) and a background site on the South Chinese island
Hainan (25-56%) (Zhang et al., 2014a).

3.2.2 Fossil and non-fossil OC

The concentration of OC from fossil-fuel sources (OC<sub>f</sub>) ranged from 2.53 to 61.3 μg/m<sup>3</sup>,
whereas the corresponding range for OC from non-fossil sources (OC<sub>nf</sub>) was 0.8 to 42.7 μg/m<sup>3</sup>
(Figure 3). Similar to EC, the highest mean concentrations of OC<sub>f</sub> and OC<sub>nf</sub> were both observed at
Xian and Beijing. The mean concentration of OC<sub>nf</sub> was higher than that of EC<sub>f</sub> for all sites except
Beijing. OC<sub>f</sub> contributions (mean ± standard deviation) to total OC were 37±3%, 58±5%, 49±2%
and 35±8% in Xian, Beijing, Shanghai and Guangzhou, respectively, which was lower than the
Corresponding EC<sub>f</sub> fraction to EC for all samples (Figure 2). The high percentage of OC<sub>nf</sub>
demonstrates that even in densely populated and urbanized areas of China, non-fossil sources are
still a considerable and sometimes even a dominant contributor of OC, at least in winter. The
large variability of the fraction of OC<sub>f</sub> to total OC among the different cities furthermore
reflects complex sources and formation processes of OC<sub>f</sub>. In addition, the ratio of EC<sub>f</sub> and to OC<sub>f</sub>
(EC/OC<sub>f</sub>) in Beijing (0.24±0.10) was substantially lower than in Xian (0.53±0.15), Shanghai
(0.47±0.11) and Guangzhou (0.56±0.11), which will be discussed below.

3.2.3 Other biomass-burning markers

Figure 4 shows that levoglucosan (lev) and mannosan (man) concentrations significantly
Correlated with EC<sub>b</sub>. Their correlation coefficients were 0.87 and 0.92, respectively. In spite of
different concentration levels, no significant differences were observed in the slopes among
different cities for the different anhydrosugars or pollution levels. A possible explanation is that
the burning conditions and fuel type was rather consistent during the sampling period for the four
cities. Moreover, the regression slope (0.41±0.03) of levoglucosan and EC<sub>b</sub> obtained here was
similar to that (0.45) calculated by the ratio of the best estimates of lev/OC (0.10) and EC/OC
(0.22) using the LHS simulation (median values in Table 2), indicating that our assumption of
LHS input parameters is reasonable. The average lev-to-man ratio was 27.7 ± 8.47 (ranging from 16.4 to 45.9), which is at the higher end of the reported ratios for crop residue burning (ranging from 12.9 to 55.7 with a mean of 32.6 ± 19.1) and obviously higher than that from softwood 4.0 ± 1.0 (ranging from 2.5 to 5.8 with a mean of 4.0 ± 1.0) (Sang et al., 2013). However, the ratio is not significantly different from ratios reported for hardwood burning (ranging from 12.9 to 35.4 with a mean of 21.5 ± 8.3) (Sang et al., 2013).

Recently, Cheng et al. (2013) proposed that ratios of levoglucosan to another biomass burning marker, non-sea-salt-potassium (nss-K⁺ = K⁺ - 0.0355 × Na⁺, (Lai et al., 2007)), can be used to distinguish biomass burning from crop residue and wood. The average of lev-to-K⁺ in our study was 0.59±0.33 (ranging from 0.17 to 1.56 with only 2 samples >1), which is comparable to the ratios for wheat straw (0.10 ± 0.00), corn straw (0.21 ± 0.08) and rice straw grown in Asia (0.62 ± 0.32) (Cheng et al., 2013). These ratios are much lower than those ratios reported for hardwood (23.96 ± 1.82) (Cheng et al., 2013). With a combination of the lev-to-man and lev-to-K⁺ ratios, it can be concluded that the major source of biomass burning in winter of China is combustion of crop residues. In addition, non-sea-salt-potassium concentrations also show a very good correlation (R²=0.82) with EC_{bb} for the four cities. This also confirms that the variability of burning conditions and biomass types was rather small during winter 2013 in different regions of China.

### 3.2.4 Sensitivity analysis

Figure 5 shows the results of the sensitivity test for the average contribution of each source to TC for all sites. Each source is illustrated as a frequency distribution, from which the uncertainties of the source apportionment are deduced as given in Section 2.5. We found that EC_{bb} was always the smallest contributor (<10%), but was still non-negligible for all sites. The distributions of EC_{f} and EC_{bb} were much narrower than for the different OC sources due to the direct ¹³C determination of EC and the indirect calculation of the OC fractions. OC_{bb} and OC_{other,af} were the most uncertain contributors to TC due to the large variation of the input parameters for LHS calculations, i.e. (EC/OC)_{bb} and (lev/OC)_{bb}. Despite a large spread of OC_{sec,f} and OC_{other,af}, the data conclusively shows that both contributions were always larger on the heavily than on the moderately polluted days, highlighting the importance of fossil-derived SOC formation and other non-fossil emissions excluding primary biomass burning sources. The increased OC_{other,af} is likely due to enhanced SOC formation from biomass burning and other non-fossil sources (see Sec. 3.3). Despite a large spread of OC_{sec,f} and OC_{other,af}, the data conclusively shows that both contributions were always larger on the heavily than on the moderately polluted days, highlighting the importance of SOC formation from both fossil and non-fossil emissions.
3.3 The relevance of SOC for heavily polluted days

3.3.1 Further source apportionment of OC sources

As explained in Sec. 2.4, OC is apportioned into primary and secondary OC from fossil sources, whereas OC is subdivided into primary biomass-burning OC (OC) and the other non-fossil OC (OC). As shown in Figure 6, OC was generally more abundant than OC, suggesting that SOC is the predominant fraction of OC in Chinese cities during winter. The highest OC-to-OC ratio (with average of 4.2) was found in Beijing, indicating the largest SOC formation compared to the other three sites (average OC ratio of 1.3), which is in agreement with the higher OC/EC ratios (see Sect. 3.2.2). During heavily polluted days, OC ratios increased compared to moderately polluted days on average by 70% for four sites. This underlines that the episodes with bad air quality were mainly caused by additional SOC formation and accumulation of similar pollutants as for average winter conditions. The importance of fossil-derived SOC formation was also underlined by measurement in water-soluble OC during 2011 winter in Beijing and Guangzhou (Zhang et al., 2014b). Figure 6 shows that OCbb was higher than OCother on the moderately polluted days for all sites, while it changed to the contrary on the heavily polluted days. The excess of non-fossil OC concentration for the heavily polluted days was dominated by OCother, which was ~2.6 times as high as OCbb. The dominating contribution of OC is likely due to the increase of SOC formation from non-fossil sources mainly from biomass-burning emissions, although biogenic-derived SOC could not be excluded for SH and GZ where temperatures during the sampling period are above 0 degrees. The dominating contribution of OC is likely due to the increase of SOC formation from non-fossil sources (i.e. mainly from biomass-burning emissions). In conclusion, the source apportionment results of the excess carbonaceous aerosols consistently highlight the importance of SOC from both, fossil and non-fossil sources. It should be also noted that the condensation of semi-volatile organic aerosols generally may contribute to some extent to the measured SOA in winter due to the colder temperature in the northern sites such as Beijing and Xian. However, the increased SOA between the MPD and HPD measured by the current method is mostly if not exclusively due to enhanced SOA formation since the temperatures during the moderately and heavily polluted days were not significantly different (p≤0.05).

3.3.2 Relative contribution from OC and EC source categories to TC

The contributions of different OC and EC source categories to TC are shown in Table 4. Fossil sources (EC + OC + OC) account for an important contribution at all sites, which decreased from Beijing (60%) to Shanghai (56%), Xian (45%) and Guangzhou (43%). The larger
fossil contribution in Beijing can be explained by substantially higher \( \text{OC}_{\text{sec,f}} \) values, which were often >2 times as high as for the other three sites. However, no remarkable difference was found for the total primary fossil contribution (\( \text{EC}_T + \text{OC}_{\text{pri,f}} \)) between the heavily and the moderately polluted days. An exception of this tendency was observed for Guangzhou, in which the fossil contribution to TC increased by 36% during the polluted episodes. However, the contribution of \( \text{OC}_{\text{sec,f}} \) to TC was higher on the heavily polluted days than on the moderately polluted days for all sites, which indicates a significant contribution of fossil SOC to TC during winter haze or smog episodes in China.

Primary biomass-burning sources (\( \text{EC}_{\text{bb}} + \text{OC}_{\text{bb}} \)) were a large contributor to TC (on average 25%, 21%, 26% and 39% in Xian, Beijing, Shanghai and Guangzhou, respectively). However, the relative contribution of biomass burning decreased on average from ~28% to ~17% when comparing moderately with heavily polluted days. Therefore, primary biomass-burning emissions were not a major additional source during heavily polluted days.

A considerable fraction of TC originated from \( \text{OC}_{\text{other,af}} \) with a mean contribution of 21% for all sites. The presence of \( \text{OC}_{\text{other,af}} \) is unlikely attributed to primary or secondary biogenic particles as biogenic emissions are very low during winter at least in Northern China, although these can be enriched due to favoring condensation of SVOCs into the particle phase at colder temperatures. In combination with the observation of enhanced fossil SOC formation, we assume that this excess is mainly attributed to SOC formation from non-fossil, but non-biogenic precursors (i.e. mainly from biomass-burning emissions). Further, SOC formation from these non-fossil volatile organic compounds may be enhanced, when they are mixed with anthropogenic pollutants such as volatile organic compounds (VOCs) and NO\(_x\) (Weber et al., 2007; Hoyle et al., 2011).

As the \( \text{OC}_{\text{sec,f}} \) and \( \text{OC}_{\text{other,af}} \) contributions were always considerably higher on the most polluted days compared the moderately polluted days and the increase of primary sources (such as \( \text{EC}_{\text{bb}} \), \( \text{OC}_{\text{bb}} \) and \( \text{OC}_{\text{pri,f}} \)) was less prominent (see Figure 6), we conclude that the increment of TC on the heavily polluted days was mainly driven by the increase of SOC from both fossil fuel and non-fossil emissions. This is also underlined in Figure 6 by the composition of the excess for the heavily polluted days.

### 3.3.3 Comparison with multi-linear engine (ME-2) source apportionment

In a parallel study from the same sites and episodes (Huang et al., 2014), the multi-linear engine (ME-2) receptor model (Canacano et al., 2013) was used to estimate the OC contribution from different factors including coal, traffic, dust-related, cooking and secondary sources. This
model includes EC/OC, ions and organic marker compounds (polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (o-PAHs), resin acids, anhydrous sugars, lignin pyrolysis products and hopanes) in addition to high resolution Aerodyne aerosol mass spectra from offline analysis of nebulized water-extracts from filter samples by a high-resolution time-of-flight aerosol mass spectrometer, HR-ToF-AMS (Daellenbach et al., in preparation). For comparison with the results from this work, sources resolved by the ME-2 approach are further classified into the following basic classes: fossil primary OC (POC$_f$), non-fossil primary OC (POC$_nf$), fossil secondary OC (SOC$_f$) and non-fossil secondary OC (SOC$_nf$). Figure 7 shows a significant linear correlation between the two approaches ($p<0.01$, $n=24$, all samples are included), underscoring the proper choices of the selected source profiles in this study (i.e. inputs for LHS). A very good agreement between the two methods is found for SOC$_nf$, whereas an offset deviation of $\sim 13\%$ occurs for SOC$_f$ possibly due to uncertainties in both models. It is important to note that such a difference is not observed ($p=0.01$), if we exclude the data from Beijing. And SOC$_f$ may be overestimated, if we underestimate the contribution of coal combustion to fossil-fuel derived EC ($p$ in Eq. (8)) in Beijing. The findings of Huang et al. (2014) suggest that coal combustion is substantially higher in this city compared to the other sites. Increasing the value of $p$ by a factor of 2 (i.e. from 0.35 to 0.70) for Beijing decreases the contribution of SOC$_f$ to the benefit of POC$_f$, whereas the other components (EC$_b$, EC$_{bb}$, OC$_{bb}$, OC$_{other, nf}$) are independent of the choice of the $p$ value (see Tab. S2 and Fig. S1). This modification improves the agreement of SOC$_f$ between both approaches as shown in Fig. 7. Furthermore, it decreases the OC$_{sec}$-to-OC$_{pri}$ ratio of Beijing from 2.7 and 5.9 to 1.2 and 2.9 for the moderately and heavily polluted days MPD and HPD, respectively. As a consequence, these values become better comparable with those of the other cities, but still underline the importance of secondary aerosol formation during the heavily polluted days HPD.

4 Conclusions

Source apportionment of the carbonaceous aerosol in PM2.5 during a severe winter pollution episode of 2013 in China was conducted at four major cities including Xian, Beijing, Shanghai and Guangzhou. An effective 5 Statistical analysis of concentrations of OC and EC, anhydrosugars as well as $^{14}$C contents of OC and EC using Latin-hypercube sampling (LHS) allowed a quantitative estimation of six different sources. These sources included EC from combustion of biomass (EC$_{bb}$) and fossil fuels (EC$_f$), OC from fossil emissions including primary and secondary sources (i.e. OC$_{pri,f}$ and OC$_{sec,f}$ respectively) as well as OC from non-fossil sources including primary biomass burning and all the other non-fossil OC (i.e. OC$_{bb}$ and OC$_{other,nf}$ respectively). A sensitivity analysis of the LHS simulation showed the robustness of our results, as the uncertainty
of the different emission sources was usually below 20% of TC, which was mainly achieved by
the combination of different isotopic and molecular markers.

Fossil emissions predominated EC with a mean contribution of 75±8% at all sites. The
remaining 25±8% was attributed to biomass-burning sources, and the presence of the latter was
also confirmed by other biomass-burning markers such as levoglucosan and water-soluble
potassium. The fossil contribution to OC was lower than for EC and was highest in Beijing
(58±5%) and decreased in the order: Shanghai (49±2%) > Xian (38±3%) > Guangzhou (35±7%).

Conversely, non-fossil sources accounted on the average for 55±10% and 48±9% of OC and
TC, respectively. Air pollution from the neighboring rural regions may have contributed
substantially to non-fossil carbon of urban aerosols, as biofuel usage is more common for heating
and cooking in such regions during winter time in China. The average contribution of non-fossil
OC from OC$_{\text{lib}}$ was found to 40±8%, 48±18%, 53±4% and 65±26% for Xian, Beijing, Shanghai
and Guangzhou, respectively.

A considerable fraction of OC was identified as SOC. We found that OC$_{\text{soc,f}}$ dominated over
OC$_{\text{pri,f}}$ for all samples (i.e. portions of TC of 23±11% compared to 13±3%, respectively), strongly
implying importance of fossil-derived SOC to urban (often polluted) aerosols in China.
Furthermore, we classified the samples into 2 episodes, heavily polluted and moderately polluted
days, depending on PM mass. We found the relative OC$_{\text{other,f}}$ contributions tend to be higher on
the heavily polluted days at all sites, which were mainly attributed to enhanced SOC formation
from non-fossil precursors such as biomass-burning emissions. Even though a significant increase
of absolute mass concentrations of primary emissions (both fossil and non-fossil sources) was
found on the heavily compared to moderately polluted days, their relative contribution to TC was
even decreased, while SOC contributions from both fossil and non-fossil sources were
substantially increased. This finding was consistently observed for all sites, showing the
importance of SOC during severe haze events in China.

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Table 1. Sampling information.

<table>
<thead>
<tr>
<th>City</th>
<th>City description</th>
<th>Location</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xian (XA)</td>
<td>The largest city in Guanzhong city cluster</td>
<td>34.2°N, 108.9°E</td>
<td>-12 – -1</td>
</tr>
<tr>
<td>Northern China</td>
<td>(8.6 million)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beijing (BJ)</td>
<td>Capital of China, developed megacity in</td>
<td>39.9°N, 116.4°E</td>
<td>-9 – -1</td>
</tr>
<tr>
<td>Northern China</td>
<td>Beijing-Tianjin-Hebei city cluster (20.7 million)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shanghai (SH)</td>
<td>Industrial and commercial megacity in</td>
<td>31.3°N, 121.5°E</td>
<td>2 – 11</td>
</tr>
<tr>
<td>Southern China</td>
<td>Yangtze Delta Region city cluster (24 million)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guangzhou (GZ)</td>
<td>Industrial and commercial megacity in</td>
<td>23.1°N, 113.4°E</td>
<td>7 – 19</td>
</tr>
<tr>
<td>Southern China</td>
<td>Pearl River Delta Region city cluster (12.7 million)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Central values with low and high limits of input parameters for source apportionment using LHS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low</th>
<th>central</th>
<th>high</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC error factor$^a$</td>
<td>0.75</td>
<td>$^b$</td>
<td>1.25</td>
</tr>
<tr>
<td>$(\text{lev/OC})_{bb}$</td>
<td>0.07</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>$(\text{EC/OC})_{bb}$</td>
<td>0.10</td>
<td>0.22</td>
<td>0.30</td>
</tr>
<tr>
<td>$(\text{EC/OC})_{p,\text{lec}}$</td>
<td>0.32</td>
<td>0.44</td>
<td>0.62</td>
</tr>
<tr>
<td>$(\text{EC/OC})_{p,\text{ve}}$</td>
<td>0.8</td>
<td>$^b$</td>
<td>2.1</td>
</tr>
<tr>
<td>$p$</td>
<td>0</td>
<td>$^b$</td>
<td>0.7</td>
</tr>
<tr>
<td>$f_0(\text{bb})$</td>
<td>1.05</td>
<td>1.10</td>
<td>1.15</td>
</tr>
<tr>
<td>$f_0(\text{nf})$</td>
<td>1.03</td>
<td>$^b$</td>
<td>$^c$</td>
</tr>
</tbody>
</table>

$^a$ EC values multiplied by given factor.

$^b$ the average of low and high limits is used.

$^c$ $f_0(\text{nf})$ constrained to be $< f_0(\text{bb})$
Table 3. Averages and standard deviations of the mass concentrations (μg/m³) of PM2.5, OC and EC as well as EC/OC ratios and fractions of modern ($f_{\text{M}}$) of OC and EC for samples collected on moderately polluted days (MPD) (n=3 for each city) and heavily polluted days (HPD) (n=3 for each city) in Xian, Beijing, Shanghai and Guangzhou.

<table>
<thead>
<tr>
<th></th>
<th>PM2.5</th>
<th>OC</th>
<th>EC</th>
<th>EC/OC</th>
<th>$f_{\text{M}}$(OC)</th>
<th>$f_{\text{M}}$(EC)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Xian</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPD</td>
<td>136±27</td>
<td>24.6±6.3</td>
<td>7.2±1.9</td>
<td>0.30±0.07</td>
<td>0.67±0.04</td>
<td>0.25±0.03</td>
</tr>
<tr>
<td>HPD</td>
<td>479±25</td>
<td>94.2±6.8</td>
<td>19.8±0.9</td>
<td>0.21±0.02</td>
<td>0.66±0.02</td>
<td>0.24±0.02</td>
</tr>
<tr>
<td>HPD/MPD</td>
<td>3.5±0.7</td>
<td>3.8±1.0</td>
<td>2.7±0.7</td>
<td>0.71±0.17</td>
<td>0.99±0.06</td>
<td>0.98±0.16</td>
</tr>
<tr>
<td><strong>Beijing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPD</td>
<td>85±17</td>
<td>18.0±3.4</td>
<td>4.0±0.2</td>
<td>0.23±0.06</td>
<td>0.49±0.03</td>
<td>0.30±0.02</td>
</tr>
<tr>
<td>HPD</td>
<td>266±49</td>
<td>59.2±7.5</td>
<td>7.7±0.9</td>
<td>0.13±0.03</td>
<td>0.40±0.01</td>
<td>0.23±0.02</td>
</tr>
<tr>
<td>HPD/MPD</td>
<td>3.1±0.9</td>
<td>3.3±0.8</td>
<td>1.9±0.2</td>
<td>0.57±0.18</td>
<td>0.82±0.06</td>
<td>0.79±0.09</td>
</tr>
<tr>
<td><strong>Shanghai</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPD</td>
<td>59±10</td>
<td>6.2±1.0</td>
<td>1.9±0.1</td>
<td>0.31±0.04</td>
<td>0.55±0.03</td>
<td>0.21±0.02</td>
</tr>
<tr>
<td>HPD</td>
<td>131±3</td>
<td>15.6±0.5</td>
<td>4.2±0.3</td>
<td>0.27±0.02</td>
<td>0.54±0.01</td>
<td>0.24±0.04</td>
</tr>
<tr>
<td>HPD/MPD</td>
<td>2.2±0.4</td>
<td>2.5±0.4</td>
<td>2.2±0.2</td>
<td>0.87±0.12</td>
<td>0.99±0.06</td>
<td>1.13±0.22</td>
</tr>
<tr>
<td><strong>Guangzhou</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPD</td>
<td>38±14</td>
<td>5.4±2.3</td>
<td>1.6±0.5</td>
<td>0.31±0.04</td>
<td>0.75±0.05</td>
<td>0.48±0.05</td>
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<tr>
<td>HPD</td>
<td>96±6</td>
<td>23.3±2.2</td>
<td>6.1±0.4</td>
<td>0.26±0.01</td>
<td>0.62±0.01</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td>HPD/MPD</td>
<td>2.5±1.0</td>
<td>4.3±1.9</td>
<td>3.8±1.1</td>
<td>0.84±0.11</td>
<td>0.83±0.06</td>
<td>0.47±0.06</td>
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Table 4. Average TC concentration and relative contribution to TC from OC and EC source categories (see in Figure 6) for samples collected in Xian (XA), Beijing (BJ), Shanghai (SH) and Guangzhou (GZ) during the moderately polluted days (MPD) and the heavily polluted days (HPD). Distributions from Latin-hypercube sampling (LHS) are given as medians as well as the 10th and 90th percentiles (in parentheses). See Tab. S2 for an alternative solution for Beijing assuming a higher contribution of coal combustion as explained below in Section 3.3.3.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>TC μg/m³</th>
<th>ECᵣ</th>
<th>ECₘₐ</th>
<th>OCₚₑᵣ</th>
<th>OCₚₑₙ</th>
<th>OCₘₐ</th>
<th>OCₐₚₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>XA-MPD</td>
<td>31.8</td>
<td>18 (16-19)</td>
<td>5 (4-5)</td>
<td>16 (12-21)</td>
<td>12 (7-16)</td>
<td>25 (19-33)</td>
<td>24 (15-29)</td>
</tr>
<tr>
<td>XA-HPD</td>
<td>114.0</td>
<td>14 (12-15)</td>
<td>4 (3-4)</td>
<td>12 (10-16)</td>
<td>19 (15-22)</td>
<td>16 (13-20)</td>
<td>35 (30-38)</td>
</tr>
<tr>
<td>BJ-MPD</td>
<td>22.0</td>
<td>13 (12-15)</td>
<td>5 (4-5)</td>
<td>12 (9-16)</td>
<td>32 (27-35)</td>
<td>22 (17-29)</td>
<td>16 (8-20)</td>
</tr>
<tr>
<td>BJ-HPD</td>
<td>66.9</td>
<td>9 (8-10)</td>
<td>2 (2-3)</td>
<td>8 (6-11)</td>
<td>47 (44-49)</td>
<td>12 (9-17)</td>
<td>21 (16-23)</td>
</tr>
<tr>
<td>SH-MPD</td>
<td>8.1</td>
<td>19 (17-20)</td>
<td>5 (4-5)</td>
<td>17 (13-22)</td>
<td>21 (15-25)</td>
<td>23 (17-31)</td>
<td>16 (7-21)</td>
</tr>
<tr>
<td>GZ-MPD</td>
<td>7.0</td>
<td>13 (12-15)</td>
<td>10 (9-11)</td>
<td>12 (9-16)</td>
<td>11 (7-14)</td>
<td>45 (37-52)</td>
<td>9 (0-17)</td>
</tr>
<tr>
<td>GZ-HPD</td>
<td>29.4</td>
<td>17 (15-18)</td>
<td>4 (4-5)</td>
<td>15 (12-20)</td>
<td>18 (13-22)</td>
<td>20 (16-27)</td>
<td>26 (19-30)</td>
</tr>
</tbody>
</table>
Figure 1. Whisker-box plots of mass concentrations of PM2.5 (a), OC (b) and EC (c) as well as EC/OC ratios (d) for samples collected in Xian (XA), Beijing (BJ), Shanghai (SH) and Guangzhou (GZ) during the winter of 2013. The box represents the 25th (lower line), 50th (middle line) and 75th (top line) percentiles; the solid dots within the box represent the mean values; the end of the vertical bars represents the 10th (below the box) and 90th (above the box) percentiles.
Figure 2. Mass concentrations (μg/m³) of EC from biomass burning and fossil-fuel combustion (EC\textsubscript{bb} and EC\textsubscript{f}, respectively) as well as fractions of fossil EC to total EC for aerosols samples in Xian, Beijing, Shanghai and Guangzhou during moderately polluted days (MPD) and heavily polluted days (HPD). Note the different scaling for the northern and the southern cities.
Figure 3. Mass concentrations (μg/m^3) of OC from non-fossil and fossil emissions (OC_{nf} and OC_f, respectively) as well as fractions of fossil OC to total OC for samples collected in Xian, Beijing, Shanghai and Guangzhou during moderately polluted days (MPD) and heavily polluted days (HPD). Note the different scaling for the northern and the southern cities.
Figure 4. Scatter plots of concentrations of ECbb with levoglucosan (top), mannosan (middle) and non-sea-salt-potassium (nss-K+, bottom).
Figure 5. Latin-hypercube sampling (LHS) solutions of frequency distributions of the source contributions to TC from OC and EC source categories (see in Table 4) for samples collected in Xian (XA), Beijing (BJ), Shanghai (SH) and Guangzhou (GZ) during the moderately polluted days (MPD) and the heavily polluted days (HPD), respectively.
Figure 6. Average mass concentrations of OC and EC from different sources for samples collected in Xian (XA), Beijing (BJ), Shanghai (SH) and Guangzhou (GZ) during the moderately polluted days (MPD), heavily polluted days (HPD) and their corresponding excess (EX=HPD-MPD). Uncertainty bars represent 10 and 90 percentiles from LHS calculations. See Fig. S1 for an alternative solution for Beijing assuming a higher contribution of coal combustion as explained below in Section 3.3.3.
Figure 7. Comparison of secondary OC from fossil and non-fossil sources (i.e. SOC_f and SOC_nf, respectively) resolved by the $_{14}C$ and ME-2 approaches. The dashed line denotes a linear regression fit of SOC_f when excluding data from Beijing yielding an alternative regression slope marked with an asterisk (*). **Note that the intercepts are insignificant for all three cases.**