Response to Reviewers' Comments and Suggestions

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: "vehicle or industry emissions such as coal combustion"

Line 51: to add references?

Response and Revisions: The reference has been added.

Author's changes in manuscript: "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)"

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: "while a large fraction of WINSOC is from POC"

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: "A combination of 14C 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;Zong et al., 2016;Liu et al., 2015;Zhang et al., 2014b)"

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: "All samples were analyzed for OC and EC, and 20 samples, including two filters based on the PM2.5 concentrations at each site, were selected for further chemical analysis."

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: "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 CO2 under a stream of pre-cleaned oxygen pure analytical grade O2 (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."

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: "The uncertainties of fnf (and fm) in WSOC, WINSOC, OC and EC were up to 20%，20%，15% and 15%, respectively."

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

Response and Revisions：The sentence was removed.

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: "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 14C analysis (i.e. the bulk samples required and the high cost for 14C measurement). However, the result is similar with those using the same approach (Liu et al., 2016c;Zong et al., 2016)."

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: "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)."

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: "Typical relative uncertainties were recently estimated, using a similar modelling approach, at 20–25 % for SOCnf, SOCf, POCbb, and POCf, and ~13% for ECf, and ECbb (Zhang et al., 2015a). A large fraction WINSOC can be from secondary organic aerosol as well. Hence POCf is an upper limit of POCf. 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."

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.

Author's changes in manuscript: "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 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.

Author's changes in manuscript: "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."