Measurement report: Source apportionment of carbonaceous aerosol using dual-carbon isotopes (13C and 14C) and levoglucosan in three northern Chinese cities during 2018-2019

Summary:

The authors have conducted a yearlong study characterizing filter samples for elemental carbon, organic carbon, levoglucosan, 13C and 14C carbon isotopes in three major cities in Northeastern China. They conclude from the collected data that the Action Plan for Air Pollution Prevention Control implemented in 2013 was effective in reducing the use of fossil fuels. Overall, ambient measurements and the filter analysis they conducted was thorough, and are difficult to achieve. My only concern is the interpretation of the data and the conclusions drawn. More technical detail and deeper analysis will highlight the importance of this measurement data.

Response:

We are grateful to the reviewer for the time and effort on the manuscript. These comments are valuable for us to improve our paper. We made corrections to some data, and revised the corresponding results and conclusions of the source apportionment. Our responses to specific comments are given below.

Specific comments:

1. Levoglucosan is considered a marker for biomass burning, but it does have other sources. This should be taken into consideration in the analysis (Wu et al. First High-Resolution Emission Inventory of Levoglucosan for Biomass Burning and Non-Biomass Burning Sources in China, Environ Sci Technol, 55, 3, 1497-1507, 2021)

Response:

Thanks for your suggestions! We have reviewed the relevant references and corrected the concentration of Levoglucosan (Lev) from biomass burning.

“Recent studies indicated that Lev was degraded to some extent during atmospheric transportation, and about 25% of them came from other non-biomass

burning sources (Hoffmann et al, 2010; Wu et al., 2021). Therefore, correction of the biomass burning source lev (Lev_{bb}) is required before the source apportionment:

$$Lev_{bb} = \frac{Lev \times 0.75}{p} \quad (1)$$

where p (0.4–0.65) is the degradation rate of Lev, which has different characteristics in each seasons. For specific p value in each season, please refer to the research of Li et al. (2021b).”

2. Some references to consider/include in the variability of Δ 13 C of sources.

(1)Pugliese, S. C.; Vogel, F.; Murphy, J. G.; Moran, M.; Stroud, C.; Ren, S.; Zhang, J.; Zheng, Q.; Worthy, D.; Huang, L.; Broquet, G. Towards Understanding The Variability In Source Contribution Of Co2 Using High-Resolution Simulations Of Atmospheric Δ13Co2 Signatures In The Greater Toronto Area, Canada.

(2)Pugliese, S. C.; Murphy, J. G.; Vogel, F.; Worthy, D. Characterization Of The Δ 13 C Signatures Of Anthropogenic Co 2 Emissions In The Greater Toronto Area, Canada. Applied Geochemistry 2017, 83, 171 - 180.

Response:

Thanks for your suggestion! The first reference summarized the $\delta^{13}C$ values of various sources, and the second reference measured the $\delta^{13}C$ value of different fossil sources. Thus, the second reference was cited in the revised version as following.

“The $\delta^{13}C$ of aerosols derived from liquid fossil fuels (gasoline and diesel oil) was approximately −31 ‰ to −25 ‰ (Agnihotri et al., 2011; Huang et al., 2006; Lopez-Veneroni, 2009; Pugliese et al., 2017; Vardag et al., 2015; Widory, 2006). The $\delta^{13}C$ derived from coal combustion was relatively high, ranging from −25 ‰ to −21 ‰ (Agnihotri et al., 2011; Pugliese et al., 2017; Widory, 2006).”

3. Figure 1 could be emissions inventory map, highlighting the cities where measurements were taken. To compare what is accounted for and what the authors measure can be a valuable comparison.

Response:

Thank you for your suggestion! To better compare the ambient particulate pollution in the study region to other parts in China, we have revised **Figure 1** by adding the $PM_{2.5}$ concentrations for similar time periods across the country.

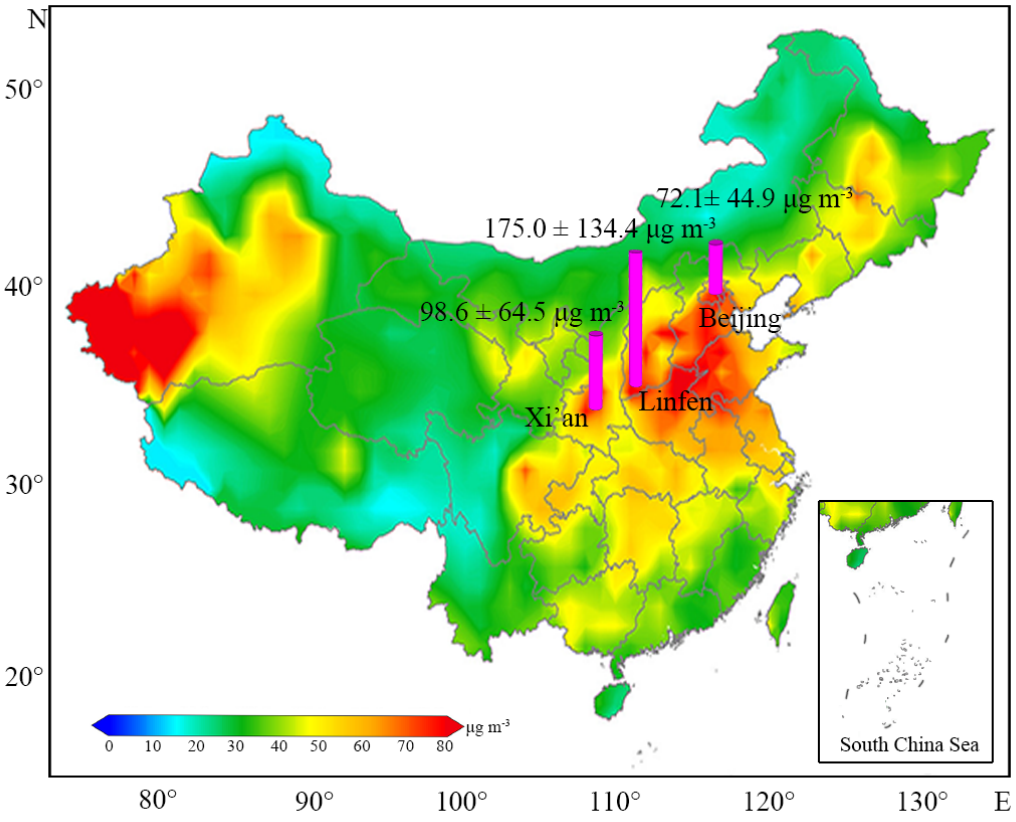

Fig. 1 Locations and $PM_{2.5}$ concentration of Beijing (BJ), Xi'an (XA), and Linfen (LF). The background map shows the distribution of $PM_{2.5}$ concentrations in most of China from 2015 to 2019 (Li et al., 2021a). The pink bars are the average $PM_{2.5}$ concentrations of the samples collected in this study during 2018 to 2019.

4. Were samples taken weekly? this wasn't clear.

Response:

Samples were not collected weekly. Samples from Beijing and Xi'an were collected on 4 fixed days (7^{th}, 14^{th}, 21^{st}, and 28^{th}) in a month, and samples from Linfen were collected on seven consecutive days in each season. We have revised the description in the manuscript.

"At BJ and XA, $PM_{2.5}$, samples were collected on the 7^{th}, 14^{th}, 21^{st}, and 28^{th} of

each month from April 28, 2018, to April 21, 2019. In LF, seven consecutive days in each season were selected for sample collection, and the sampling periods were concentrated in January, April, July, and October 2018. A total of 124 24-hour (10 a.m. to 10 a.m. on the following day) $PM_{2.5}$ samples and 4 field blanks were obtained."

5. More detail in the PM2.5 sampling setup is needed to describe the type of sample obtained. How was PM2.5 sampled specifically from ambient air (presumably in the presence of PM10 and larger particles)? Were there a denuder scrubbing out gasses (O3, VOCs, NOx, etc) that could react with or condense on the particles collected on the filter? If there was any chemistry happening on the filter, it would be difficult to interpret TC/OC since oxidant concentrations have also changed over the years.

Response:

Thanks for your comment! The sampler was equipped with a $PM_{2.5}$ impact collector, not with a denuder system, which was common in most carbonaceous studies (e.g. Cao et al., 2003; Park et al., 2018; Wang et al., 2015). Our samples were performed the chemical analysis immediately after the collection and weighing, not stored over years. We have supplemented the detailed description of sampling as follows:

"The sampler was equipped with an impact collector to collect the particles less than 2.5 μm in aerodynamic diameter."

6. This is a suggestion, not a needed comment. The use of the acronym AMS may be confusing since it's commonly used to describe the aerosol mass spectrometer. To abbreviate the accelerator mass spectrometer (AccMS? of ACLMS?)

Response:

Thanks for your suggestion! AMS is a special abbreviation for accelerator mass spectrometer, which has been widely used for several decades. Modification has not been made here, since aerosol mass spectrometer was not involved in this manuscript, and they would not be confused.

7. Minor clarification in line 203: what does MV stand for? I assume it means mV?

Response:

Thanks for your comment! The MV here is the voltage unit, and it is the abbreviation of Megavolt. We have changed it to the full name in the manuscript to avoid confusion.

"The graphite was pressed into an aluminum holder and measured using a 3 Megavolt AMS, with a precision of 3‰ (Zhou et al., 2006, 2007)."

8. Figure 3 it would be helpful to have 50% line to see when the dominant fraction shifts.

Response:

Thanks for your suggestion! We have added 50% lines to the Figure 3.

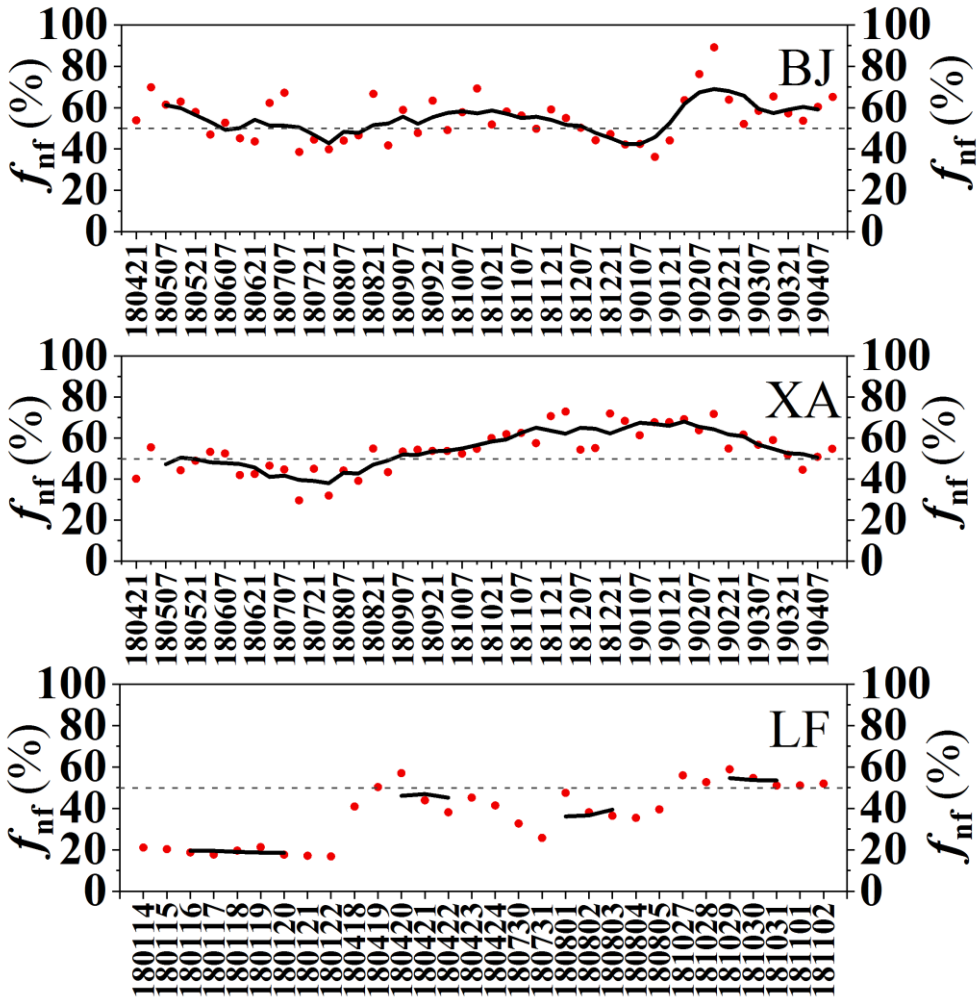

Fig. 3 Variations in proportion of non-fossil sources (f_{nf}) of carbonaceous aerosols at the sampling sites in Beijing (BJ), Xi'an (XA), and Linfen (LF). The red scatter dot represents the f_{nf} of each sample, and the black solid line represents the sliding average f_{nf} value of every five samples (date, "yymmdd").

9. In section 3.2, where there any reported data representing LF? is not, please highlight.

Response:

Thanks for your comment! Although LF has suffered from serious air pollution, it has received less attention because it is not a provincial capital city, so there is no reported data for comparison. We have added a description in the manuscript.

"Due to the less attention to LF, there is still a lack of related research of carbonaceous aerosols using radiocarbon in this city to compare."

10. Line 444: "topographic problems" can change to "due to the local topography"

Response:

Thanks for your suggestion! We have revised the corresponding description.

"However, when air masses circulated in the Guanzhong Basin due to the local topography or converged into the basin from multiple directions."

11. Figure 6 could have a cleaner x-axis, with datetime on a weekly scale.

Response:

Thanks for your suggestion! Since the samples were not collected weekly, we reduced the dates displayed in X-axis to make it more clearly.

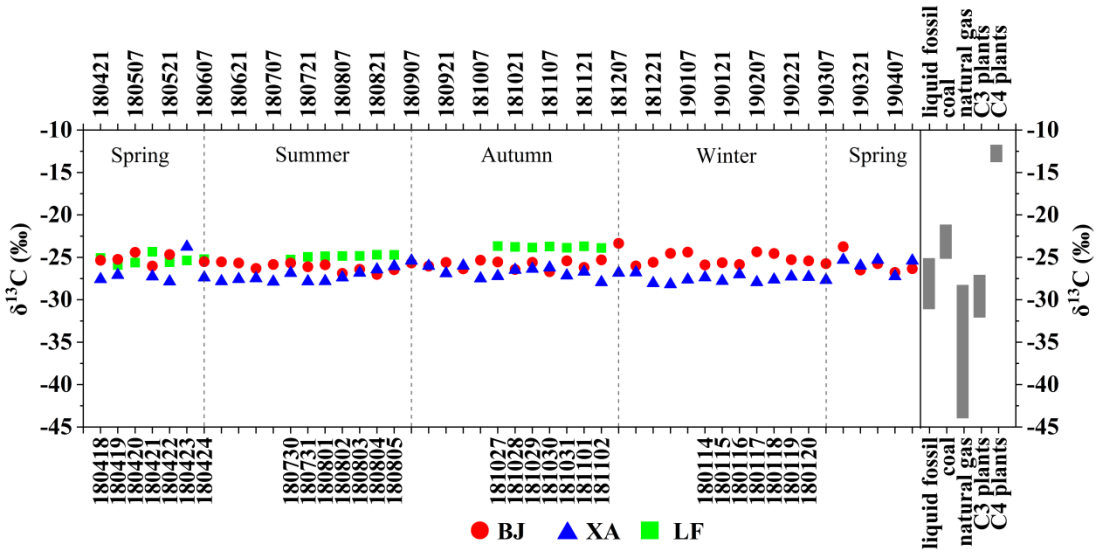

Fig. 6 $\delta^{13}C$ values of samples from Beijing (BJ), Xi'an (XA), and Linfen (LF), and comparison with the $\delta^{13}C$ distribution of various sources. The abscissa represents the sampling date (yymmdd). The labels of top axis represent the date of BJ and XA, and the bottom represents the date of LF. The gray box indicates the $\delta^{13}C$ of the main source (Agnihotri et al., 2011; Huang et al., 2006; Lopez-Veneroni, 2009; Martinelli et al., 2002; Moura et al., 2008; Pugliese et al., 2017; Smith & Epstein, 1971; Vardag et al., 2015; Widory, 2006).

12. Figure 7 isn't black/white friendly. Can you change just one variable (instead of a solid color) something with hashed lines?

Response:

Thanks for your suggestion! We have changed the legend to make them better distinguished.

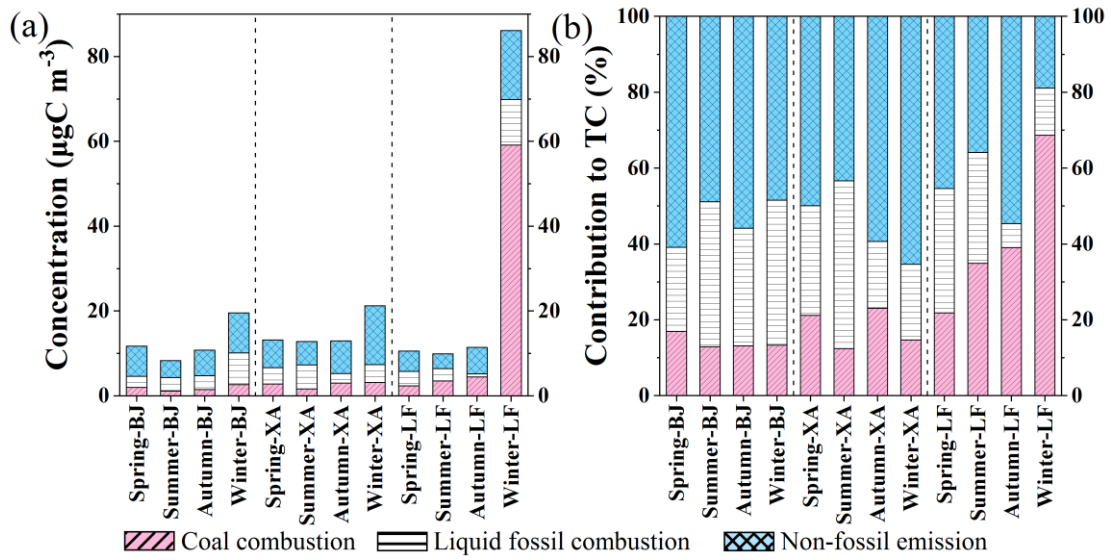

Fig. 7 Source apportionment of carbonaceous aerosols using radiocarbon (^{14}C) and stable carbon (^{13}C) isotopes at the sampling sites in Beijing (BJ), Xi'an (XA), and Linfen (LF) during different seasons. The blocks represent the concentrations and contributions of coal combustion, liquid fossil fuel, and non-fossil sources emissions, respectively.

13. Line 612-613: Was not clear the conclusion here since the distribution of allocated C sources for BJ in winter and summer appear the same. I think you meant Figure 9, since this discussion is about OCother.

Response:

Thanks for your comment! Figure 7 mentioned here was to explain that OC_{other} had similar seasonal characteristics with the carbonaceous concentrations from motor vehicle emissions. In this version, we have revised some sentences which were shown in bold as follows to make it more clearly. The description of the similar seasonal characteristic between OC_{other} and motor vehicle's contribution had been moved to the end of the paragraph.

"The OC_{other} contribution and concentration in XA were high in summer (35.2 ± 10.0%) and winter (5.4 ± 4.2 μgC m^{-3}), respectively. **We assume that this excess is mainly attributed to SOC formation from non-fossil and primary biogenic particles."**

“Furthermore, SOC formation from these non-fossil VOCs may be enhanced when they are mixed with other pollutants, such as VOCs and NO_x (Hoyle et al., 2011; Weber et al., 2007). Motor vehicles are one of the main anthropogenic sources of VOCs and NO_x (Barletta et al., 2005; Liu et al., 2008). **In Section 3.4, we found that the carbonaceous concentrations from motor vehicle emissions were high in XA during winter and summer (Fig. 7a), and the increasing of motor vehicle activities might partly explain the high concentration of OC_{other} during the two seasons.”**

Overall, to assess whether the government led Action plan to reduce pollution was effective is important and long-term sampling is needed. The authors are doing valuable research, they just have to extend their analysis more

Response:

Thanks for your suggestions and comments! This is greatly helpful for us to improve this and future research. The *Action Plan* had been supported to be effective in controlling air pollution from many long-term observations of $PM_{2.5}$ in China (Cao et al., 2018; Wang et al., 2010, 2012; Zhao et al., 2011). In future, related research will be carried out in more cities, and a long-term observation is also considered.

Reference

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