Response to Reviewers' Comments and Suggestions - doi: 10.5194/acp-2016-97

Dear Editor,

We are thankful very much to you and the anonymous reviewers for the thoughtful comments and suggestions. We have revised this manuscript accordingly. Listed below are our point-by-point responses (blue) to each reviewer's comments (black). In addition, we would like to ask you if we can change the title of our paper as "Radiocarbon and PMF based source apportionment of $PM_{2.5}$ at a regional background site in North China: insight into the contribution of biomass burning" following the reviewers' comments?

Best regards,
Dr. Chongguo Tian

Reviewer 1

Air pollution from $PM_{2.5}$ is a major health and environmental concern in China. Accurate $PM_{2.5}$ source attribution is therefore critical for the development of successful air pollution control measures in the region. The study by Zong et al. investigates the sources of $PM_{2.5}$ at a background site in Northern China during the winter of 2014, utilizing different source apportionment techniques. By reporting detailed measurements of the elemental composition of $PM_{2.5}$ collected on 76 quartz filter samples, the manuscript provides interesting new data, which is further grouped into three source regions based on back trajectories analysis. In addition, radiocarbon measurements are used to apportion the carbonaceous fractions of the aerosols into fossil and biomass combustion contributions. These results are combined with a PMF model to derive the major sources of $PM_{2.5}$ in the region. While the combination of these different techniques is a very good approach for achieving accurate $PM_{2.5}$ source apportionment and can provide important insight into what is driving the elevated concentration in the region, there are several major problems in the reasoning, explanation and interpretation of the methods and the data reported in the manuscript.

Response and Revisions: Thanks very much for these comments. We have revised this manuscript accordingly. Please find our detailed responses below.

One concern is the use of only one station at a background location, to interpret sources of $PM_{2.5}$ over a very large area without any discussion of the possibility of local sources affecting the measurements. In one part of the manuscript the authors hypothesize that the elevated $PM_{2.5}$ at the sampling site are due to the proximity of sources (p.10, line 3-5). But later based on their cluster analysis they say only 11% of the air masses were from the Shandong Peninsula (p. 11 line 18).

Response and Revisions: Thanks for the comment. Background site is usually adopted to determine the regional-scale concentration burden and the source apportionment of aerosols (Moon et al., 2008; Sheesley et al., 2012; Waked et al., 2014; Yao et al., 2016; Yin et al., 2010). The sampling point in our study is a regional background site in North China, where no obvious emission source nearby. Besides, the back trajectory clusters indicated that more than half of the air masses (54%) during the sampling period were from the Beijing-Tianjin-Hebei region, followed by the air masses from the Mongolia (35%), and Shandong Peninsula (11%), suggesting the area air mass passed through in this paper included the whole North China. This proved the significance of our sampling site for the source apportionment of aerosol in North China in winter. Longkou city is on south side and is closest to the sampling site, so the emission from the city can be considered as the primary local sources. However, we found that only one trajectory in cluster 3 passed the urban area of Longkou, when measured $PM_{2.5}$ concentration was 95.3 $\mu g/m^3$. The level was lower than the average concentration in cluster 3 listed in Table 2, indicating minor contribution of local source emissions. So following the comment, we have deleted the description of "the elevated $PM_{2.5}$ at the sampling site was due to the proximity of sources" and added the corresponding content in the revised manuscript (page 10 line 27).

Further, measuring $PM_{2.5}$ concentrations based on filter mass is not accurate due to variability within the filter area. Each punch might weigh differently due to the inhomogeneity of the filter itself. There are no references about this technique being used anywhere else.

Response and Revisions: Thanks for the comment. The method that $PM_{2.5}$ mass collected on filters was very common and usually adopted for the $PM_{2.5}$ analysis in various studies (Huang et al., 2014; Kong et al., 2015; Liu et al., 2013; Zhang et al., 2015). In this study, before and after every sampling, the filters went through a 24h equilibration at 25±1℃ temperature and 50±2 % relative humidity and were gravimetrically measured using a temperature and relative humidity-controlled microbalance, such as reported in previous studies (Zhang et al., 2015; Kong et al., 2015; Huang et al., 2014; Liu et al., 2013). Besieds, each filter was weighed at least three times. Acceptable difference among the repetition was less than 10 μg for blank filters and 20 μg for sampled filters, which greatly ensured the precision of our results. According to the reviewer's suggestion, we have added aforementioned references in the revised manuscript (page 4 line 30).

Radiocarbon was only measured on two samples, each representing an air mass coming from a different region. One sample cannot capture any variability in sources and is not a true representative of regional sources. It is also not clear what the uncertainties in the results are and how they could affect the source apportionment. When using radiocarbon, it is particularly important to accurately represent the uncertainty in aerosol samples, as they are very small and usually have high degree of uncertainty, which needs to be considered when interpreting the results.

Response and Revisions: We appreciate the review's comment. It is difficult to capture variability of regional sources by a few samples. However, in order to better achieve our purpose using a few samples for ^{14}C analysis due to the extensive cost of the analysis, the representative capacity of all samples in the two clusters (cluster 1 and 3) was examined thoroughly. OC and EC concentration, and ratios of OC/PM$_{2.5}$ and EC/PM$_{2.5}$ of each sample were compared with that in the corresponding cluster by mean test. Finally, two combined samples (including four samples) were selected for ^{14}C measurement from a perfect synoptic process during the sampling period. We added these descriptions in the revised manuscript. In addition, the sizes of samples (M1 and M2) selected for ^{14}C analysis were described as follows. The carbon content of the WSOC, WIOC, EC in the combined sample M1 were 211.03, 209.12 and 283.86 μg, respectively, and these of M2 were 126.76, 182.59, and 200.10 μg, respectively. While the WSOC, WIOC in the blank samples only accounted for 1.94% and 1.15%, respectively, of the average value of M1 and M2. Furthermore, EC was not found in the blank samples. Thus, the blank interference for the f_m value of M1 and M2 in the ^{14}C measurement was very small (Liu et al., 2014), implying the uncentainties of ^{14}C measurement was minor in our study (page 6 line 26).

With respect to the back trajectory analysis and clustering, the manuscript did not provide enough detail to explain how this was performed and the model for the clustering. Also the authors did not include the reference, giving credit to the original HYSPLIT model development.

Response and Revisions: We appreciate the review's comment. Following the reviewer's suggestion, we have added a sentence "The HYSPLIT model is avaliable on the National Oceanic and Atmospheric Administration Air Resource Laboratory website (www. arl.noaa.gov/ready/hysplit4.html)." for the clarification of the model in the revised manuscript. We also rephrased a sentence to clarify the cluster analysis as: "Finally, a total of 152 trajectories were generated and these trajectories were bunched into three clusters by the toolkit of trajectory cluster analysis embedded in the model." in the revised manuscript (page 7 line 12-14).

In general, the manuscript was very hard to read and understand due to the language (and multiple typos and errors), which needs significant improvement. The title of the manuscript is also misleading, since the biomass-burning signal is not the main focus of the manuscript. The lack of appropriate citations makes it hard to track the accuracy and reliability of the statements and hypothesis throughout the manuscript and makes the interpretation of the results difficult. The details provided in the methods section are not enough to fully understand the analysis or to allow traceability or reproducibility of the results. The results and discussion section was hard to follow too due to the lack of structure within the text and paragraphs summarizing the result from the different experiments and drawing conclusions together.

Response and Revisions: Thanks for the comment. We have made every effort to polish our English and asked a native English speaker to take a proof reading of the final version of the revised manuscript. Inconsistent sentences have been corrected; Following the opinion of the reviewers, we have changed the title as "Radiocarbon and PMF based the source apportionment of regional $PM_{2.5}$ in North China: insight into the contribution of biomass burning "; Besides, many appropriate citations has been inserted into the revised manuscript, and some details of methods section were also added into manuscript; Some structure changes, such as segmenting some complicated section and adding detailed explain for the figures and tables, were conducted to make readers follow our results and discussion easier.

A list of specific comments and questions are provided below:

- Missing citations throughout the introduction

Response and Revisions: Thanks for the comment. According to the reviewer's suggestion, we have added some references(Cao et al., 2011; Chow and Watson, 2002; Ding et al., 2013; Pui et al., 2014; Sheesley et al., 2012; Szidat, 2009; Szidat et al., 2004) in the revised manuscript.

- Spaces missing p. 3 line 20; p. 4 line 10, p. 13 line 20, p. 27, line 22

Response and Revisions: Thanks for the comment. The missing spaces have been added in the revised manuscript.

- The introduction (and the rest of the manuscript) does not explain how ^{14}C provides information about fossil and modern sources.

Response and Revisions: Thanks for the comment. Following the reviewer's suggestion, we have added a sentence "The underlying principle of ^{14}C measurements is that the radioisotope has become extinct in fossil fuel carbon due to its age (half-life 5730 years), while its contemporary level in nonfossil carbon sources is relatively constant (Szidat, 2009; Szidat et al., 2004)." in the revised manuscript (page 3 line 28-31).

Page 5 line 9: Longkou district and Tianjin are not shown on map. Is Longkou the closest urban region and can it be considered a local source of urban emissions?

Response and Revisions: Thanks for the comment. Following the reviewer's suggestion, we have redrawn the Figure 1, and the locations of Longkou, Tianjin, Changdao and Chengde mentioned in the paper were labeled in the figure. As showed, Longkou city is closest to the sampling site, the emission from the city can be considered as primary local sources. The sentence has beed added in the revised manuscript (page 4 line 22-24). However, it should be noted that we found that only one trajectory during the sampling period passed the urban area of Longkou, when measured $PM_{2.5}$ concentration was 95.3 μg/m^3. The level was lower than the average concentration in cluster 3 listed in Table 2, indicating minor contribution of local source emissions (page 10 line 27).

Page 5, line 18: Why do the filters undergo a 24h equilibrium period at 25℃? Wouldn't that potentially introduce contamination with the filters absorbing volatile organic compounds during that period?

Response and Revisions: Thanks for the comment. The equilibrium condition and equilibrium period were selected according to the analytical standard of determination of atmospheric particles PM_{10} and $PM_{2.5}$ in ambient air by gravimetric method (HJ 618-2011, in Chinese) published by the Ministry of Environmental Protection of the People's Republic of China (http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/jcgfffbz/201109/t20110914_217272.htm). The method was extensively adopted in previous studies (Liu et al., 2013; Tao et al., 2014). Besides, blank samples were also conducted through the equilibrium process. Concentrations of OC in blank samples were < 3.5% of the average concentration for the total samples, indicating our samples were not contaminated throughout the whole analysis process (including equilibrium).

OC and EC page 6 lines 6-7: The DRI currently uses an updated protocol –IMPROVE_A (Chow et al., 2007). Which one was used for this manuscript? http://www.dri.edu/eaf-projects

Response and Revisions: We appreciate the review's comment. The citation has been corrected (Chow et al., 2007) in the revised manuscript (page 5 line 10).

Page 7, line 14: Radiocarbon methods are not cited properly (p. 7, line 14 Liu et al 2014 is not explaining the process) – correct citation is Zhang et al. 2015 (Env. Sci. & Tech) Radiocarbon-Based Source Apportionment of Carbonaceous Aerosols at a Regional Background Site on Hainan Island, South China

Response and Revisions: We appreciate the review's comment. The citation (Zhang et al., 2014) has been corrected in the revised manuscript (page 6 line 9).

Page 7 Line 16: which TOR protocol? (also acronym was not defined anywhere)

Response and Revisions: We appreciate the review's comment. It is thermal/optical reflectance (TOR), which has been defined in the revised manuscript (page 5 line 9).

Graphitization at CAS and AMS analysis – can you provide citation, sizes, black corrections?

Response and Revisions: Thanks for the comment. The citations (Wacker et al., 2013; Xu et al., 2007; Zhang et al., 2010) have been inserted into the text. On the other hand, the sizes of samples (M1 and M2) selected for ^{14}C analysis were described as follows. The carbon content of the WSOC, WIOC, EC in the combined sample M1 were 211.03, 209.12 and 283.86 μg, respectively, and these of M2 were 126.76, 182.59, and 200.10 μg, respectively. While the WSOC, WIOC in the blank samples only accounted for 1.94% and 1.15%, respectively, of the average value of M1 and M2. Furthermore, EC was not found in the blank samples. Thus, the blank interference for the f_m value of M1 and M2 in the 14C measurement was very small and was ignored in this study.

Page 8: HYSPLIT and EPA PMF v5.0 citations

Response and Revisions: Thanks for the comment. Following the reviewer's suggestion, we have added website, from which the software can be obtained, in the revised manuscript (page 7 line 12 and page 7 line 19).

Page 9, line 15 the text does not follow the order reported in Table 1 (notes on tables and figures will be provided at the end)

Response and Revisions: Thanks for the comment. The sequence of chemical species in Table 1 has been rearranged according to the description of the text.

Page 9, line 17 what is the uncertainty of the max $PM_{2.5}$ value? Also, there is no need to report significant digits, as the range is so large

Response and Revisions: We appreciate the review's comment. Following the reviewer's comments, the description about the maximum value has been deleted in the revised manuscript.

Page 10, line 2: It is not clear where Tuoji Island is and how it is relevant in the comparison.

Response and Revisions: Thanks for the comment. After careful consideration, the description about Tuoji Island in original draft may not be appropriate for our purpose. So the section about Tuoji has been deleted in the revised manuscript.

Page 10, line 8-9. Write chemical formula for sulfate, nitrate and ammonium and use them throughout the text. The lack of consistency with the names of the chemical elements and radiocarbon vs ^{14}C makes the text harder to read.

Response and Revisions: We appreciate the review's comment. Following the reviewer's suggestion, we replaced sulfate, nitrate, ammonium by their chemical formulas and radiocarbon by ^{14}C throughout the revised manuscript.

Page 10, line 20-1. There are major issues with the chemical elements here – The ones written out are not the correct elements!

Response and Revisions: Thanks for the comment. According the review's suggestion, the sentence has been rewritten as "The high contribution agreed with the regional scale emission of their precursors in the North China, as reported that the emission amounts of SO_2, NO_x and NH_3 were about 10, 5, and 5 times higher compared to OC in the region." in the revised manuscript (page 10 line 6).

Page 11, line 22: Mean test?

Response and Revisions: Thanks for the comment. Mean test is a statistical method, which can be used to determine if two sets of data are significantly different from each other. The analysis can be performed by SPSS software.

Break next section in paragraphs. It is very hard to read.

Response and Revisions: Thanks for the comment. This suggestion has been employed in the revised manuscript.

Page 12, second paragraph – write out chemical elements

Response and Revisions: Thanks for the comment. This suggestion has been employed in the revised manuscript.

Page 12, line 21. Cite the sources for sea salt composition

Response and Revisions: Thanks for the comment. This suggestion has been employed in the revised manuscript (page 11 line 24).

Page 13: It is really hard to follow and it might be helpful to break it up in a couple paragraphs

Response and Revisions: Thanks for the comment. This suggestion has been employed in the revised manuscript.

Page 14: It is not clear how the Enrichment Factor (EF) method works, if/how it has been applied in other studies and how reliable it is. Original citations are missing. More description is necessary. It will also be helpful to plot the EF calculated for all elements.

Response and Revisions: Thanks for the comment. The assistance of EF section for the source signals of aerosols in original draft may not be appropriate for our purpose. So after careful consideration, the section about EF has been deleted in the revised manuscript.

Page 14: Using OC/EC ratio and NO3/nss-SO4 a traces :

Response and Revisions: We appreciate the review's comment. The sentence has been changed as "The ratios of OC/EC and NO_3^-/nss-SO_4^{2-} were used as tracers to assess source signals of the three clusters." in the revised manuscript (page 12 line 25).

Lack of citations OC/EC p. 14 line 21

Response and Revisions: Thanks for the comment. Following the review's suggestion, a citation has been listed in the revised manuscript (page 12 line 28).

Mean test (p. 15 line 2)?

Response and Revisions: Thanks for the comment. As stated above, mean test is a statistical method, which can be used to determine if two sets of data are significantly different from each other. The analysis can be performed by SPSS software.

When calculating OC/EC ratios what is the uncertainty in the OC and EC and the ratio.

Response and Revisions: We appreciate the review's comment. Following the reviewer's suggestion, we assessed the uncertainty in OC, EC and their ratio based on results of eight pair replicate samples using the method of extreme difference. The results showed that the uncertainties of OC, EC and the ratio were 5.61%, 5.51% and 4.72%.

Lack of citations SO2 and NOx p. 15 line 7

Response and Revisions: Thanks for the comment. Following the review's suggestion, a citation has been listed in the revised manuscript (page 13 line 5).

Page 15, line18: Where is Chengde and how is it relevant?

Response and Revisions: We appreciate the review's comment. Chengde city has been displayed in the revised Figure 1. We mentioned the ratio of NO_3^-/nss-SO_4^{2-} in Chengde here in order to infer more obvious emission of stationary sources in the region where air masses of cluster 2 were passed.

Source app of carbonaceous $PM_{2.5}$ (pages 16-19)

Response and Revisions: Thanks for the comment. The description has been changed as "Source apportionment of carbonaceous $PM_{2.5}$".

The back trajectory analysis is not clear in the description of how the samples were combined. The figure does not help either.

Response and Revisions: Thanks for the comment. Following the reviewer's suggestion, we added one section about how the samples were combined in the method section of the revised manuscript. Besides, selecting reason and back trajectory analysis were also mentioned in this section (page 8 line 12- page 9 line 12).

Page 16 line 11 – 19 unclear and belong in the methods

Response and Revisions: We appreciate the review's comment. Following the suggestion, we have rewritten the description and changed it in the method section (page 8 line 22- page 9 line 12).

Page 18 line 2: What is the WSOC and WIOC concentration uncertainty? The reported numbers have two significant digits, but are the methods accurate enough to report concentrations of this precision?

Response and Revisions: Thanks for the suggestion. In this study, WSOC were directly measured by a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPH, Japan). WIOC was quantified by OC given by the TOR protocol subtracting WSOC. The uncertainties of WSOC were calculated by the method of extreme difference. The uncertainties of for M1 and M2 were 6.7% and 5.3%, respectively. The uncertainties of WIOC were calculated in this study according to the following equations: WIOC = sqrt ($OC^{\wedge 2}$ + $WSOC^{\wedge 2}$). The uncertainties of for M1 and M2 were 8.8% and 7.8%, respectively. According to the uncertainty analysis, we gave 2 digits for the data as shown in revised Table 3. We have mentioned this calculation method in our revised paper.

M1 and M2 are significantly different, but could this be due to high level of uncertainty in the measurement? Can it possibly be affected by local sources?

Response and Revisions: Thanks for the comment. According to the previous uncertainty analysis, the contemporary carbon fractions of OC were in the range from 0.5934 to 0.5936 for M1 and from 0.454 to 0.457 for M2, respectively. It suggests that the significant differences were attributed the source contribution, rather than the uncertainty of the measurement. The uncertainty of EC was less than that of OC, so the differences for EC were also attributed the source contribution. The local sources affected weakly the difference because the air masses didn't pass the local source region as shown in Figure 2.

Page 19, line 15: F_{peak} and Q are not defined

Response and Revisions: Thanks for the comment. The sentence has been rewritten as "After iterative testing from 5 to 15 factors for the model scenarios, we found the minimum deviation of the source apportionments of OC and EC between the results from ^{14}C measurement and a PMF model scenario with an F_{peak} value of 0 and the lowest Q values (6245)." (page 15 line 12)

Page 20, line 6: Citations missing

Response and Revisions: Thanks for the comment. The missing citations have been added in revised paper (page 15 line 22).

Page 24, line 3: PMF and ^{14}C results are compared within 3-4% precision, but it is likely the uncertainty is higher.

Response and Revisions: Thanks for the comment. PMF results were selected according to the minimum deviation between the results from PMF models and ^{14}C measurements. Besides, the uncertainties of ^{14}C measurement for OC and EC of the M1 were 6.8% and 3.8% (see Table 3), which were comparable with the difference between PMF and ^{14}C results. The minor uncertainty of ^{14}C measurements ensured its accuracy, thus the compare results of PMF and ^{14}C results could be trusted in this study.

Implications for PM alleviation – since it was mostly focused on biomass burning it seemed to not fully capture the scope of the work.

Response and Revisions: We appreciate the review’s comment. According to the source apportionment, coal combustion and vehicle emission were the primary contributors of $PM_{2.5}$ in the North China during winter. The two sources have been considered as the most leading emission sectors in the air pollution control program. While biomass burning, also an important emission, has been only considered slightly in the control program. Thus, biomass burning emission was highlighted in the manuscript and a section was conducted for the implications for PM alleviation from the aspect of biomass burning.

It would have been very helpful if there were a section in the manuscript where all the results were drawn together so the reader can logically conclude how the different techniques complemented each other and what the final result of the different analytical techniques was.

Response and Revisions: Thanks for the comment. Following the reviewer’s suggestion, we have added more description about the result analysis explanation in the revised manuscript. This would be convenient readers to grasp our key point in this study.

There are a lot of typos in the references.

Response and Revisions: Thanks for the comment. The typos in study have been corrected in revised manuscript.

Tables and Figures:

Table 1: It is not clear why the table is split in two and why the units are different. It would be much

easier to interpret the content if everything is aligned into 3 columns and the units are consistent.

Response and Revisions: Thanks for the comment. Following the reviewer's suggestion, we rearranged the contents as mentioned above. The table is split in two columns in order to show the data by different units. We retained the structure because it is able to show more information (page 31).

Table 2: Make into one page

Response and Revisions: Thanks for the comment. Table 2 has been made in one page (page 32).

Table 3: Uncertainty needs to be reported for each measurement

Response and Revisions: Thanks for the comment. The uncertainty has been reported in revised manuscript (page 33).

Table 4: Rows 1, 3, and 4 do not add up to a 100% when horizontally summed. The difference is minimal, but what is the reason for it? Also the significant digits are probably not necessary, based on the accuracy of the analysis.

Response and Revisions: Thanks for the comment. The difference was attributed to maintain the uniformity significance digit of the data. Following the suggestion, we gave two decimal places for all these data in the revised table (page 33).

Figure 1. Some locations that were mentioned in the text are not included in the figure.

Response and Revisions: Thanks for the comment. Figure 1 has been redrawn, and the locations mentioned in the manuscript have been added in the revised figure (page 34).

Figure 2. This is very difficult to follow, a more detailed description of what the figure is showing will be helpful

Response and Revisions: Thanks for the comment. More description has been added in the revised figure (page 35).

Figure 4. The figure caption should explain why the B&B and Fossil emissions from the PMF do not

add to a hundred in the bars. It is described in the text, but a note in the figure will make it much easier to understand.

Response and Revisions: Thanks for the suggestion. The explanation has been added in the revised figure (page 37).

Reviewer 2

In present study, a more reliable source apportionment of $PM_{2.5}$ on the regional scale in the North China in winter is provided using PMF simulation and the radiocarbon measurements. It is consistent work performed on a good level. It looks like the title of the paper does not relate the content of the paper well. It announces Biomass burning contribution to regional $PM_{2.5}$ during winter in general in the North China while the work was done only on one site. If one site represents the whole North China?

Response and Revisions: Thanks very much for these comments. Please find our detailed responses below.

1. It looks like the title of the paper does not relate the content of the paper well.

We appreciate the review's comment. As mentioned by the reviewer, the sources apportioned by the paper are not only biomass burning but also coal combustion, vehicle emission and so on. We use the title "Biomass burning contribution to regional $PM_{2.5}$ during winter in the North China" in order to highlight the important of biomass burning, which is often underestimated or ignored in some areas in China (Gao et al., 2016). However, we agree with the opinion of the reviewer, and change the title as "Radiocarbon and PMF based the source apportionment of regional $PM_{2.5}$ at a regional background site in North China: insight into the contribution of biomass burning ".

2. If one site represents the whole North China?

Thanks for the comment. Background site is usually adopted to determine the regional-scale concentration burden and the source apportionment of aerosols (Moon et al., 2008; Sheesley et al., 2012; Waked et al., 2014; Yao et al., 2016; Yin et al., 2010; Yttri et al., 2011). The sampling point in our study is a regional background site in North China, where no obvious emission source nearby. Besides, the back trajectory clusters indicated that more than half of the air masses (54%) during the sampling period were from the Beijing-Tianjin-Hebei region, followed by the air masses from the Mongolia (35%), and Shandong Peninsula (11%), suggesting the area air mass passed through in this paper included the whole North China. This proved the significance of our sampling site for the source apportionment of aerosol in North China in winter. Similar methods were applied frequently, for example, Liu conducted the source apportionment of carbonaceous aerosol in East China based on Ningbo, a background site in Zhejiang Province, China (Liu et al., 2013); Also, Zhang analyzed the carbon species in Mt. Jianfeng, a regional background site on Hainan Island, for the carbonaceous source in South China (Zhang et al., 2014).

Reference

Cao J-j, Chow JC, Tao J, Lee S-c, Watson JG, Ho K-f, et al. Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels. Atmospheric Environment 2011; 45: 1359-1363.

Chow JC, Watson JG. Review of PM2.5 and PM10 apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model. Energy & Fuels 2002; 16: 222-260.

Chow JC, Watson JG, Chen LWA, Chang MCO, Robinson NF, Trimble D, et al. The IMPROVE-A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database. Journal of the Air & Waste Management Association 2007; 57: 1014-1023.

Ding X, Wang X, Xie Z, Zhang Z, Sun L. Impacts of Siberian Biomass Burning on Organic Aerosols over the North Pacific Ocean and the Arctic: Primary and Secondary Organic Tracers. Environmental Science & Technology 2013; 47: 3149-3157.

Gao J, Peng X, Chen G, Xu J, Shi G-L, Zhang Y-C, et al. Insights into the chemical characterization and sources of PM2.5 in Beijing at a 1-h time resolution. Science of the Total Environment 2016; 542: 162-171.

Huang R-J, Zhang Y, Bozzetti C, Ho K-F, Cao J-J, Han Y, et al. High secondary aerosol contribution to particulate pollution during haze events in China. Nature 2014; 514: 218-222.

Kong SF, Li L, Li XX, Yin Y, Chen K, Liu DT, et al. The impacts of firework burning at the Chinese Spring Festival on air quality: insights of tracers, source evolution and aging processes. Atmospheric Chemistry and Physics 2015; 15: 2167-2184.

Liu D, Li J, Zhang Y, Xu Y, Liu X, Ding P, et al. The Use of Levoglucosan and Radiocarbon for Source Apportionment of PM2.5 Carbonaceous Aerosols at a Background Site in East China. Environmental Science & Technology 2013; 47: 10454-10461.

Liu J, Li J, Zhang Y, Liu D, Ding P, Shen C, et al. Source Apportionment Using Radiocarbon and Organic Tracers for PM2.5 Carbonaceous Aerosols in Guangzhou, South China: Contrasting Local- and Regional-Scale Haze Events. Environmental Science & Technology 2014; 48: 12002-12011.

Moon KJ, Han JS, Ghim YS, Kim YJ. Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia. Environment International 2008; 34: 654-664.

Pui DYH, Chen S-C, Zuo Z. PM2.5 in China: Measurements, sources, visibility and health effects, and mitigation. Particuology 2014; 13: 1-26.

Sheesley RJ, Kirillova E, Andersson A, Krusa M, Praveen PS, Budhavant K, et al. Year-round radiocarbon-based source apportionment of carbonaceous aerosols at two background sites in South Asia. Journal of Geophysical Research-Atmospheres 2012; 117.

Szidat S. ATMOSPHERE Sources of Asian Haze. Science 2009; 323: 470-471.

Szidat S, Jenk TM, Gaggeler HW, Synal HA, Fisseha R, Baltensperger U, et al. Radiocarbon (C-14)-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zurich, Switzerland. Atmospheric Environment 2004; 38: 4035-4044.

Tao J, Gao J, Zhang L, Zhang R, Che H, Zhang Z, et al. PM2.5 pollution in a megacity of southwest China: source apportionment and implication. Atmospheric Chemistry and Physics 2014; 14: 8679-8699.

Wacker L, Fahrni SM, Hajdas I, Molnar M, Synal HA, Szidat S, et al. A versatile gas interface for routine radiocarbon analysis with a gas ion source. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2013; 294: 315-319.

Waked A, Favez O, Alleman LY, Piot C, Petit JE, Delaunay T, et al. Source apportionment of PM10 in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization and including primary biogenic emissions. Atmospheric Chemistry and Physics 2014; 14: 3325-3346.

Xu X, Trumbore SE, Zheng S, Southon JR, McDuffee KE, Luttgen M, et al. Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2007; 259: 320-329.

Yao L, Yang L, Yuan Q, Yan C, Dong C, Meng C, et al. Sources apportionment of PM2.5 in a background site in the North China Plain. Science of the Total Environment 2016; 541: 590-598.

Yin J, Harrison RM, Chen Q, Rutter A, Schauer JJ. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. Atmospheric Environment 2010; 44: 841-851.

Yttri KE, Simpson D, Nojgaard JK, Kristensen K, Genberg J, Stenstrom K, et al. Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites. Atmospheric Chemistry and Physics 2011; 11: 13339-13357.

Zhang Y-L, Li J, Zhang G, Zotter P, Huang R-J, Tang J-H, et al. Radiocarbon-Based Source Apportionment of Carbonaceous Aerosols at a Regional Background Site on Hainan Island, South China. Environmental Science & Technology 2014; 48: 2651-2659.

Zhang YL, Huang RJ, El Haddad I, Ho KF, Cao JJ, Han Y, et al. Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013. Atmospheric Chemistry and Physics 2015; 15: 1299-1312.

Zhang YL, Liu D, Shen CD, Ding P, Zhang G. Development of a preparation system for the radiocarbon analysis of organic carbon in carbonaceous aerosols in China. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2010; 268: 2831-2834.

~~Biomass burning contribution to~~Radiocarbon and PMF based source apportionment of $PM_{2.5}$ at a regional ~~$PM_{2.5}$ during winter~~background site in ~~the~~ North China: insight into the contribution of biomass burning

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Abstract

Source apportionment of fine particles ($PM_{2.5}$) at a background site in ~~the~~ North China in the winter~~,~~ of 2014 was assessed ~~by~~via statistical analysis ~~on the chemical species grouped by the trajectory clusters~~, radiocarbon (^{14}C) measurement, and ~~the~~ Positive Matrix Factorization (PMF) modeling ~~linked with the ^{14}C measurement. During the sampling period,~~ . Results showed that the concentration of $PM_{2.5}$ was 77.6 ± 59.3 μg m^{-3}, ~~and the sulfate~~of which SO_4^{2-} concentration was the highest, followed by ~~nitrate,~~NO_3^-, organic carbon (OC), elemental carbon (EC) and ~~ammonium,~~NH_4^+, respectively. Demonstrated by ~~the~~ backward trajectory, more than half of ~~$PM_{2.5}$ was found~~the air mass during the sampling period was from the Beijing-Tianjin-Hebei (BTH) region, followed by ~~the~~ Mongolia and the Shandong Peninsula. ~~The cluster~~Cluster analysis of chemical species showed ~~that $PM_{2.5}$ from the Shandong Peninsula had~~ an obvious signal of biomass burning emission in the $PM_{2.5}$ from the Shandong Peninsula, while ~~that~~the $PM_{2.5}$ from the BTH region showed a vehicle emission pattern. ~~The~~This finding was further confirmed by the ~~radiocarbon~~^{14}C measurement of OC and EC in two merged samples selected from a successive synoptic process. The ^{14}C ~~measurement~~results indicated that biogenic and biomass burning emission contributed 59% and 52% to OC and EC concentrations, respectively, when air masses originated from the Shandong Peninsula, and the contributions fell to 46% and 38%, respectively, when the prevailing wind changed and came from the BTH region. ~~In addition,~~The minimum deviation of the source apportionments from PMF results and ^{14}C measurement was ~~used~~adopted as the optimal choice of the model exercises. Here, two minor overestimations with the same range (3%) suggested that the PMF results provided a reasonable source apportionment of regional $PM_{2.5}$ in ~~the North China during winter.~~this study. Based on the PMF results~~ above~~, eight main sources were identified~~,~~; of ~~which~~these, coal combustion, biomass burning, and vehicle ~~emissions~~emission were the largest contributors of $PM_{2.5}$, accounting for 29.6%, 19.3% and 15.8%, respectively. Compared with ~~the~~ overall source apportionment, the ~~contribution~~contributions of vehicle emission~~,~~, mineral dust and coal combustion, biomass burning increased ~~slightly~~ when air masses came from the BTH region, the ~~contribution of mineral dust and coal combustion rose obviously when air masses were from the~~ Mongolia~~ with high speed~~, and ~~biomass burning became the dominant contributor when air masses carried from~~ the Shandong Peninsula~~. As the largest contributor to $PM_{2.5}$ in winter of North China,~~, respectively. Since coal

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Keywords: Source apportionment, PMF, ^{14}C measurement, $PM_{2.5}$

1 Introduction

In recent years, air pollution has become a top environmental issue in China, and the main concern is ~~on the~~ fine particulate matter less than 2.5 micrometers in diameter ($PM_{2.5}$) ~~(Huang et al., 2014;Sheehan et al., 2014)~~(Huang et al., 2014; Sheehan et al., 2014). Fine particulate aerosols have a strong adverse effect on human health, visibility, and directly or indirectly affect weather and climate~~.~~ (Pui et al., 2014). The negative effects on ~~the~~ public health, including ~~the~~ damage to the respiratory and cardiovascular systems, the blood vessels of the brain, and the nervous system, have triggered both public alarm and official concern in China ~~(Kessler, 2014).~~(Kessler, 2014). In response to this great concern, the Chinese government has introduced the Action Plan for Air Pollution Prevention and Control (2013–17), which aims at marked improvements in ~~the~~ air quality ~~up to~~until 2017. In the plan, the ~~severest supervision~~most severe regulation for ~~the~~ improvement is a reduction of 25% in the annual average concentrations of $PM_{2.5}$ by 2017~~.~~ (Chinese-State-Council, 2013). It has been applied in ~~the~~ North China because the region has become the most severely polluted area in China, characterized by increasingly frequent haze events and regional ~~expansion~~expansions of extreme air pollution ~~in recent years~~ (~~Hu et al., 2015;Boynard et al., 2014;Quan et al., 2014~~Hu et al., 2015; Boynard et al., 2014).

~~Basically, the key point of reducing $PM_{2.5}$ concentrations is to control its sources. Reliable~~

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~~source identification and quantification are essential for the development of effective political abatement strategies. However, the sources of $PM_{2.5}$ typically emit a mixture of pollutants, including gas and particle phases, which would be mixed further in the atmosphere and can undergo chemical transformations prior to impacting on a specific receptor site, making it difficult to quantify the impacts. This encourages researchers to use more techniques to quantify the contribution of individual sources to $PM_{2.5}$ concentrations, such as the Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB), organic tracers, and stable carbon isotopes, etc. Whereas, these different approaches often result in source contributions that can differ in magnitude and/or are poorly correlated, and which one is more reliable cannot be determined (Balachandran et al., 2013). Recently, radiocarbon (^{14}C) measurement has been used as a powerful tool to quantify unambiguously the fossil and non-fossil contribution of carbonaceous aerosols in China (Liu et al., 2014;Zhang et al., 2015;Liu et al., 2013). The method provides a chance to make a more reliable source apportionment of $PM_{2.5}$ by linking with other methods although it focuses only on carbonaceous aerosols.~~

~~In present study, a more reliable source apportionment of $PM_{2.5}$ on the regional scale in the North China in winter was provided using PMF simulation, in which the source contribution of carbonaceous species was confirmed by the radiocarbon measurement. The effort is vital for the development of efficient mediation policies to achieve the improvement in air quality in the North China because the regional source apportionment cannot be replaced by that extensively focused in the metropolitan areas such as Beijing(Zhang et al., 2013), Tianjin(Gu et al., 2011), Jinan(Gu et al., 2014), and others within the North China. Thus, we collected continuously aerosol samples with high intensity on Qimu Island in winter to assess the source apportionment of $PM_{2.5}$. The objectives of this~~

~~study were (1) to determine the regional-scale concentration burden and the chemical composition of $PM_{2.5}$ in the North China, (2) to distinguish the source signals based on the chemical composition grouped according to the trajectory clusters, and 3) to assess the source apportionment of $PM_{2.5}$ using the PMF model linked with ^{14}C measurement.~~

The key point in reducing $PM_{2.5}$ concentrations is to control its sources. Reliable source identification and quantification are essential for the development of effective political abatement strategies (Balachandran et al., 2013). However, the sources of $PM_{2.5}$ typically emit a mixture of pollutants, including gas and particle phases, which mix further in the atmosphere and can undergo chemical transformations prior to impacting a specific receptor site, making it difficult to quantify the impacts (Balachandran et al., 2013). This encourages researchers to use more techniques to quantify the contribution of individual sources to $PM_{2.5}$ concentrations, such as the Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994), Chemical Mass Balance (CMB) (Chow and Watson, 2002), organic tracers (Ding et al., 2013), and stable carbon isotopes (Cao et al., 2011). However, these different approaches often result in source contributions that can differ in magnitude and/or are poorly correlated, and the most reliable one cannot be determined (Balachandran et al., 2013). Radiocarbon (^{14}C) measurements provide a powerful tool to unambiguously determine fossil and non-fossil sources of carbonaceous particles, and the method has been used in source apportionment of carbonaceous aerosols in China (Zhang et al., 2015; Liu et al., 2013; Liu et al., 2014). The underlying principle of ^{14}C measurements is that the radioisotope has become extinct in fossil fuel carbon due to its age (half-life 5730 years), while its contemporary level in non-fossil carbon sources is relatively constant (Szidat, 2009; Szidat et al., 2004). This method provides a chance to more reliably source apportion $PM_{2.5}$ by linking with other methods, although it focuses only on carbonaceous aerosols.

In the present study, a more reliable source apportionment of $PM_{2.5}$ at a regional background site in North China during winter was provided using PMF simulation, in which the source contribution of carbonaceous species was confirmed by the ^{14}C measurement. The effort is vital for the development of efficient mediation policies to achieve improvement in air quality in North China because regional source apportionment cannot be replaced by those extensively focused on the metropolitan areas such as Beijing (Zhang et al., 2013), Tianjin (Gu et al., 2011), Jinan (Gu et al., 2014), and others within North China. Thus, we collected continuous aerosol samples on Qimu Island during winter to apportion PM$_{2.5}$ sources. The objectives of this study are (1) to determine the concentration burden and the chemical composition of PM$_{2.5}$, (2) to distinguish the source signals based on the chemical composition grouped according to the trajectory clusters, and (3) to apportion PM$_{2.5}$ sources using the PMF model linked with ^{14}C measurement.

2 Materials and methods

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2.1 Sampling site and sample collection

The sampling campaign was conducted~~,~~ from January 3 ~~Jan~~ to February 11~~ Feb~~, 2014, at the Longkou Environmental Monitoring Station of the State Ocean Administration of China (37°41´N, 120°16´E~~)~~), on ~~the~~ Qimu Island. The island ~~is extended~~extends to the Bohai Sea ~~in the westward direction~~westwards, and is surrounded by sea on its other three sides, as shown in Fig. 1. ~~And the~~The sampling site is located ~~in about~~approximately 15 km northwest ~~from~~of the Longkou urban district and 300 km southeast ~~from~~of the Beijing-Tianjin-Hebei (BTH) region. ~~PM$_{2.5}$ at~~Longkou city is closest to the sampling site~~ exhibited largely a regional pollution signal during the sampling period, because the air masses were mainly carried from the BTH region~~, and ~~the Mongolia subjected by the East Asian winter monsoon as illustrated by the backward trajectories in Fig. 1, which will~~emissions from the city can be ~~elaborated later~~considered the primary local sources.

A total of 76 PM$_{2.5}$ samples were collected continuously on quartz fiber filters (Whatman, QM-A, 20.3 × 25.4 cm^{2}, heated at 450 °C for 6 h before use) using a Tisch high volume sampler at a flow rate of 1.13 m^{3} min^{-1} during the sampling period. The duration for each sample was 12 h, from 06:00–18:00 and from 18:00–06:00 (local time) the next day. Before and after each ~~sampling~~sample, quartz fiber filters ~~went through a~~were subjected to 24 h equilibration at 25~~±~~ ± 1 ^{o}C temperature and 50~~±~~ ± 2% relative humidity, and were then~~ were~~ analyzed gravimetrically using a Sartorius MC5 electronic microbalance~~.~~ (Zhang et al., 2015; Liu et al., 2013; Huang et al., 2014). Each filter was weighed at least three times. Acceptable difference among the repetitions was less than 10 μg for a blank filter and less than 20 μg for a sampled filter. After weighing, loaded filters were stored in a refrigerator at -20 °C until chemical analysis. ~~Also~~In addition, field blank filters were collected to subtract ~~the~~ possible contamination ~~that occurred~~occurring during or after sampling.

2.2 Chemical analysis

2.2.1 OC and EC

Organic carbon (OC) and elemental carbon (EC) were analyzed by a Desert Research Institute (DRI) Model 2001 Carbon analyzer (Atmoslytic Inc., Calabasas, CA) following the Interagency Monitoring of Protected Visual Environment (IMPROVE_A) thermal/optical reflectance (TOR) protocol ~~(Chow et al., 1993).~~(Chow et al., 2007). A punch of 0.544 cm^2 from each quartz filter was heated to produce four fractions (OC1, OC2, OC3 and OC4) in four temperature steps (140, 280, 480, 580 °C) under a non-oxidizing helium atmosphere and then in 2% O_2/98% He atmosphere at 580 °C (EC1), 740 °C (EC2), and 840 °C (EC3) for the EC fractions. At the same time, pyrolyzed organic carbon (POC) was produced in the inert atmosphere, which decreased the reflected light to correct for charred OC. The concentrations of OC and EC were obtained according to the IMPROVE protocol, OC = OC1 + OC2 + OC3 + OC4 + POC and EC = EC1 + EC2 +EC3 – POC. The detection limits of the method for OC and EC were 0.82 and 0.20 µg cm^{-2}, respectively. In addition, blank filters and replicate samples were examined simultaneously after analyzing a batch of 10 samples ~~in order~~ to obtain ~~their~~ inherent OC and EC concentrations on the ~~filter~~filters and to evaluate measurement accuracy, respectively. In this study, the contributions of OC and EC from blank filters were < 3.5 and 0.6% of their respective average concentrations. ~~Furthermore, comparison with average values from replicate analyses showed a good precision with relative deviations of 5.9%.~~The uncertainties of OC (5.6%) and EC (5.5%) were calculated from the replicate measurements.

2.2.2 Water-soluble ions and metal elements

Two ~~punches with~~ 47 mm diameter punches were cut off from each quartz fiber filter, one of which~~, one~~ was subjected to Milli-Q water extraction for ionic measurement, and the other ~~was~~underwent induced acid digestion for elemental measurement. The concentrations of water soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) were determined by ion chromatograph (Dionex ICS3000, Dionex Ltd., America) based on the analysis method ~~(Shahsavani et al., 2012).~~(Shahsavani et al., 2012). The concentrations of metal elements (including Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Cd and Pb) were estimated ~~on the basis of~~via inductively coupled plasma ~~coupled with~~ mass ~~spectrometer~~spectrometry (ICP-MS of ELAN DRCII type, Perkin Elmer Ltd., Hong Kong) following the previous method ~~(Wang et al., 2006).~~(Wang et al., 2006). The detection limit of water-soluble ions was 10 ng~~/~~ ml^{-1} with ~~the~~ error < 5%, and ~~1ml~~1 ml RbBr of 200 ppm was put in the solution as an internal standard before analysis. ~~Similarly, the~~The resolution of ICP-MS ranged from 0.3 to 3.0 amu with a detection limit ~~lower than~~≤ 0.01 ng/ml, and ~~the ~~error < 5%. ~~Element~~Five ppb elemental Indium (In) ~~of 5 ppb, as the internal standard, ~~was put in the solution before analysis~~.~~ as an internal standard.

2.2.3 ~~Radiocarbon~~^{14}C measurement

To achieve more ~~radiocarbon~~^{14}C information on carbonaceous fractions in $PM_{2.5}$, OC was split into water~~-~~-soluble organic carbon (WSOC) and water~~-~~-insoluble organic carbon (WIOC) fractions. WSOC was extracted from a punch filter by Milli-Q water as described in ~~previous study (Liu et al., 2014)~~a previous study (Zhang et al., 2014c), and was quantified as total dissolved organic carbon in solution by a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPH, Japan). WIOC was quantified by OC given by the TOR protocol subtracting WSOC. The uncertainties of WSOC calculated from four time measurements were 6.7% for M1 and 5.3% for M2, while the uncertainties of WIOC were 8.7% and 7.7%, in sequence, estimated by error propagation formulas.

^{14}C measurement of WSOC, WIOC and EC was performed using the OC/EC separation system ~~(Liu et al., 2014). Briefly, the extracted Milli-Q water was freeze-~~(Liu et al., 2014). Briefly, the extracted Milli-Q water was freeze-dried, and the residue was re-dissolved and transferred to a pre-combusted quartz tube. Then the quartz tube was combusted at 850 °C and WSOC was converted into CO_2. The extracted filters were isolated at 340 °C for 15 min for WIOC, after a flash heating of 650 °C for 45 s ~~for minimizing the~~to minimize charring. After~~ the~~ separation, the filters were heated at 375 °C for 4 h to remove ~~the ~~charring, and then oxidized under a stream of pure oxygen at 650 °C for 10 min to analyze the EC fraction. Finally, the corresponding evolving CO_2 (WSOC, ~~WINSOC~~WIOC and EC) was cryo-trapped and reduced to graphite at 600 °C for accelerator mass spectrometry (AMS) target preparation~~.~~ (Xu et al., 2007; Zhang et al., 2010; Wacker et al., 2013). The preparation of graphite targets for AMS analysis was performed using the graphitization line at the Guangzhou Institute of Geochemistry, CAS. The ratios of ^{14}C/^{12}C in the graphite samples were determined through a NEC compact AMS at Peking University. In this study, the isolated carbon amounts were typically in the range of 120-280 μg, depending on the samples. The WSOC and WIOC in the blank samples only accounted for 1.94% and 1.15%, respectively, of the average value of M1 and M2, and EC was not found in the blank samples. Thus, the blank interference for the fractions of modern carbon (f_m) of M1 and M2 in the ^{14}C measurement was very small and was ignored in this study. M1 and M2 are two combined samples for ^{14}C measurement, as elaborated later.

~~In order to compensate for the excess ^{14}C caused by the nuclear bomb testing in the 1950s and 1960s, the f_m given by AMS was further converted into the fraction of contemporary carbon (f_c). The f_c values in the samples were defined as $f_c = f_m/1.10$ for EC, $f_c = f_m/1.06$ for OC, and the fraction of fossil (f_f) was defined as $f_f = 1\text{-}f_c$ (Zong et al., 2015).~~

Finally, in order to compensate for the excess ^{14}C caused by nuclear bomb testing in the 1950s and 1960s, the f_m given by AMS was further converted into the fraction of contemporary carbon (f_c). The f_c values in the samples were defined as $f_c = f_m/1.10$ for EC, $f_c = f_m/1.06$ for OC, and the fraction of fossil (f_f) was defined as $f_f = 1 - f_c$ (Zong et al., 2015).

2.3 Data analysis methods

The hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model was used to generate 48-h backward trajectories with 12 h intervals. The HYSPLIT model is available on the National Oceanic and Atmospheric Administration Air Resource Laboratory website (www.arl.noaa.gov/ready/hysplit4.html). The trajectories were calculated for air masses starting from the sampling site at 500 m above ground level. ~~Finally, a~~A total of 152 trajectories were generated and these trajectories were bunched into three clusters~~.~~ by the clustering function in the HYSPLIT model. Air masses from the BTH region, the Mongolia and the Shandong Peninsula were defined as clusters from 1 to 3, respectively, as shown in Fig. 1. The observed chemical components of PM$_{2.5}$ ~~carried by~~from the three ~~air masses~~clusters were compared with each other to assess their potential sources.

~~PMF v5.0 provided by the US EPA was utilized to assess the source apportionment in this study.~~PMF v5.0 was utilized to apportion PM$_{2.5}$ sources, which is available at the US EPA website: www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses. PMF is a multivariate factor analysis tool, which assumes that concentrations at a receptor site are supported by ~~the~~ linear combinations of different source emissions. Thus, measured mass concentrations of selected species can be mostly expressed as ~~(Paatero et al., 2014)~~(Paatero et al., 2014):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

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where ~~x_{ij}~~ x_{ij} is the measured concentration of the ~~jth~~ j^{th} species in the ~~ith~~ i^{th} sample~~, f_{kj}~~, f_{kj} is the profile of ~~jth~~ j^{th} chemical species emitted by the ~~kth~~ k^{th} source~~, g_{ik}~~, g_{ik} is the amount of mass contributed by ~~kth~~ k^{th} source to the ~~ith~~ i^{th} sample, and ~~e_{ij}~~ e_{ij} is the residual for each samples/species. The ~~matrixes~~matrices of ~~g~~ g and ~~f~~ f are determined by minimizing an objective function ~~(Paatero et al., 2014)~~(Paatero et al., 2014).

~~After determination and interpretation of these factor profiles, source contributions identified by the model~~To further confirm $PM_{2.5}$ sources apportioned by the PMF model, the source contributions of OC and EC were examined by ^{14}C measurement. The modeled source contributions were merged into two groups according to fossil and contemporary carbon sources. Then the contribution ~~fraction~~fractions of fossil or contemporary carbon sources to OC and EC ~~was~~could be compared with the ~~results derived from~~ ^{14}C ~~analysis~~measurement for ~~the~~ specified ~~sample to confirm the model results.~~samples as:

$$R_{ij} = \sum_{k=1}^{n} g_{ik} f_{kj} \Big/ \sum_{k=1}^{p} g_{ik} f_{kj} \qquad (2)$$

~~Where R~~ where R is the contribution fraction, and ~~matrixes~~matrices of ~~g~~ g and ~~f~~ f are the same as in eqn(1). The ~~subscripts i~~ subscript i is a specified sample~~, j~~, j is ~~species of~~ OC or EC~~. n~~ species. n is the number of fossil or contemporary carbon sources, and ~~p~~ p is the number of all sources. The minimum deviation of $PM_{2.5}$ source contributions apportioned by the PMF exercises and ^{14}C measurements was used to determine the final model scenario. The model results were treated as providing a more reliable solution for the source apportionment.

2.4 Principle of samples selected for ^{14}C analysis

The comparison of OC and EC focused on cluster 1 and cluster 3 because most species of $PM_{2.5}$ in these two clusters were statistically greater than in cluster 2, as elaborated later. To better achieve the comparison using a few samples for ^{14}C analysis due to its extensive cost, the representative capacity of all samples in the two clusters was examined thoroughly. It is expected that PMF can better interpret those data close to the average condition of each chemical species, since the method utilizes error-minimizing estimates to decompose a matrix of sample data into two matrices under

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strict non-negativity constraints for the factors (Paatero et al., 2014). Therefore, OC and EC concentrations, and ratios of OC/$PM_{2.5}$ and EC/$PM_{2.5}$ of each sample, were compared with those in the corresponding cluster by mean test.

Finally, two combined samples were selected from a perfect synoptic process during the sampling period. The synoptic process occurred during January 16th and 18th, 2014. As shown in Fig. 2, the first half of air masses in the synoptic process were derived from the south and passed through the Shandong Peninsula (cluster 3) and the bottom half were from the north and passed over the BTH region (cluster 1). Thus, two samples collected continually from 06:00 to 18:00, January 16th and from 18:00 to 06:00 the next day in the first half of the synoptic process were merged into one sample (M1) for the ^{14}C analysis. Similarly, other two samples collected continually from 18:00 to 6:00, January 17th and from 06:00 to 18:00 in the next day were combined into the other sample (M2). M1 reflected the signal of air masses coming from the Shandong peninsula, while M2 showed the pattern of air masses from the BTH region. Mean test showed that except for a significant high ratio of EC/$PM_{2.5}$, the OC and EC concentrations and the OC/$PM_{2.5}$ ratio of M2 were negligibly different from cluster 1, at a 95% significance level, indicating its perfect representative capability for further carbonaceous analysis. However, M1 was not ideal because only ratios of OC/$PM_{2.5}$ and EC/$PM_{2.5}$ had no statistical difference, OC and EC concentrations were significantly higher than that in the cluster 3 at the same significance level. Even so, the samples were still considered for ^{14}C analysis because they were from a faultless synoptic process during the sampling period. Continuous samples were more dramatic than insular samples. In addition, the insignificant difference of the ratios of OC/$PM_{2.5}$ and EC/$PM_{2.5}$ assured the validity for $PM_{2.5}$ source assessment, which was more important than concentration in this study.

3 Results and discussion

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3.1 General characteristics of $PM_{2.5}$ and chemical components

Table 1 lists a statistical summary of the concentrations of $PM_{2.5}$, water-soluble ions, carbonaceous species and metal elements during the sampling period. ~~**3 Results and discussion**~~

~~**3.1 General characteristics of $PM_{2.5}$ and chemical components**~~

~~Table 1 lists a statistical summary of the concentrations of $PM_{2.5}$, water-soluble ions, carbonaceous species and metal elements during the sampling period.~~ As shown, the mean concentration of PM$_{2.5}$ was 77.6 ± 59.3 μg m^{-3}, ~~and the maximum value was 305 μg m^{-3}, ~~which ~~were~~was more than two~~ and eight~~ times higher than the grade I national standards (35 μg m^{-3}, Ministry of Environmental Protection of China: GB 3095-2012, www.zhb.gov.cn~~, 2012-02-29). Although the level of PM$_{2.5}$ concentration on Qimu Island was higher than the national standard, but it was much lower than that observed in winter in megacities of the North China, such as in Beijing (208 μg m^{-3} of PM$_{2.1}$ in 2013)(Tian et al., 2014) and Tianjin (221 μg m^{-3} in 2013)(Han et al., 2014). Besides, the concentration level was significantly higher than the result (42.4 μg m^{-3} in winter, 2012) measured at a national station for background atmospheric monitoring on Tuoji Island, located on the Bohai Strait (Wang et al., 2014). The obviously high concentration of PM$_{2.5}$ on Qimu Island was possibly attributed to the short distance between the sampling site and emission source on the Shandong Peninsula (see Fig. 1) and strong deposition of particles due to high precipitation over the Bohai Sea in the winter of 2012 (Zhang et al., 2014).~~

, 2012-02-29). Although the level of PM$_{2.5}$ concentration on Qimu Island was higher than the national standard, it was much lower than that observed in winter in the megacities of North China, such as in Beijing (208 μg m^{-3} of PM$_{2.1}$ in 2013) (Tian et al., 2014) and Tianjin (221 μg m^{-3} in 2013) (Han et al., 2014).

For~~ the~~ PM$_{2.5}$ components, water-soluble inorganic species (WSIS) were the dominant species, accounting for 37 ± 16 % of ~~the ~~PM$_{2.5}$ mass concentrations. Among the ~~ionic concentrations, sulfate~~ions, SO_4^{2-} ranked the highest with a mean concentration of 14.2 ± 18.0 μg m^{-3}, followed by ~~nitrate~~NO_3^- (11.9 ± 16.4 μg m^{-3}) and ~~ammonium~~NH_4^+ (3.11 ± 2.14 μg m^{-3}). The sum of the three secondary inorganic aerosols constituted the majority (81 ± 12 %) of the total WSIS concentrations. In addition, the average concentrations of OC and EC were 6.85 ± 4.81 and 4.90 ± 4.11 μg m^{-3}, accounting for 9.2 ± 2.1 % and 6.4 ± 1.8 % of the PM$_{2.5}$ concentrations, respectively. Total concentrations of analyzed metal elements were 665 ± 472 ng m^{-3}, accounting for 0.93 ± 0.50 % of the PM$_{2.5}$ mass concentration. Among the measured metal elements, the concentration of Fe (408 ± 285 ng m^{-3}) was the highest, followed by Zn (107 ± 142 ng m^{-3}), and Pb (88.4 ± 85.7 ng m^{-3}).

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The relative contribution of ~~sulfate, nitrate~~SO_4^{2-}, NO_3^-, and ~~ammonium~~NH_4^+ to the $PM_{2.5}$ at the sampling site was ~~obviously~~clearly higher than ~~that~~ in the cities, such as Beijing and Tianjin, within ~~the~~ North China, while the organic matter was ~~obviously~~clearly lower. The high ~~contribution agreed~~contributions of SO_4^{2-}, NO_3^-, and NH_4^+ agree with ~~the~~ regional scale ~~emission~~emissions of their precursors in ~~the~~ North China, as it has been reported that ~~the emission amounts of~~ SO_2, ~~NO_2~~NO_x, and NH_3 emissions were ~~about~~approximately 10, 5, and 5 times higher compared to OC in the region, respectively ~~(Zhao et al., 2012)~~(Zhao et al., 2012). ~~The~~This finding was also in agreement with ~~that~~results measured at Changdao Island ~~(Feng et al., 2012)~~(Feng et al., 2012). The island, located at the demarcation line between the Bohai Sea and the Yellow Sea, is a resort with little industry ~~at about~~approximately 7 km north ~~from~~of the Shandong Peninsula ~~(Feng et al., 2012)~~(Feng et al., 2012). ~~Measurement~~Measurements at the island ~~was treated~~were interpreted as ~~providing~~showing patterns of atmospheric outflow and regional pollution in North China ~~(Feng et al., 2012;Feng et al., 2007)~~(Feng et al., 2012; Feng et al., 2007). It suggested that our ~~measurement~~measurements also ~~provided~~provide a regional signal of $PM_{2.5}$ pollution in ~~the~~ North China. ~~Besides, sulfate~~Furthermore, SO_4^{2-} was the largest contributor of $PM_{2.5}$ ~~as aforementioned. The~~ , and the highest ~~contribution~~contributor is usually regarded as a regional pollution signal in winter. This is because ~~of the~~ during low temperature conditions in $PM_{2.5}$ source areas there is a lack of a fast conversion rate of SO_2 to ~~sulfate~~SO_4^{2-} in ~~cloud~~clouds or aerosol ~~droplet processes~~droplets and oxidation ~~reaction~~reactions via OH free ~~radical in low temperature condition in source areas (Hu et al., 2015). This also indicated that our measurement~~ radicals (Hu et al., 2015). Thus, our measurement largely reflected ~~largely~~ a pollution pattern on a regional scale, rather than just in source areas.

3.2 Source signals based on cluster analysis

As shown in Fig. 1, the 48-h back trajectory clusters ~~indicated~~indicate that more than half of the air masses (54%) during the sampling period were from the BTH region~~, defined as~~ (cluster 1~~,~~), followed by the air masses from ~~the~~ Mongolia (35%, cluster 2). Air masses of these two types traveled about 200 and 250 km, respectively, over the Bohai Sea before arriving at the sampling site. Thus, the atmospheric pollutants carried by the two ~~kind~~kinds of air masses were mixed well during ~~the~~ transport, ~~showing~~creating regional pollution signals. Only a small part of the air masses (11%) were from the Shandong Peninsula (cluster 3), ~~reflecting~~ potentially reflecting a mixed contribution

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of local and regional sources from south area of the sampling site. In addition, only one trajectory in cluster 3 passed the urban area of Longkou, when measured $PM_{2.5}$ concentration was 95.3 μg m^{-3}. This level was lower than the average of $PM_{2.5}$ concentrations in cluster 3, listed in Table 2, indicating minor contribution of local source emissions. To reveal the pollution patterns and source signals of $PM_{2.5}$ carried by air masses from the three different regions, chemical species of $PM_{2.5}$ were grouped according to the three trajectory clusters, as listed in Table 2.

Generally, mean test showed that the concentration levels ~~of $PM_{2.5}$~~ and ~~its~~ most abundant species types of $PM_{2.5}$ in ~~cluster~~clusters 1 and ~~cluster~~ 3 ~~were insignificant differences~~are both insignificantly different ($p > 0.05$) and statistically higher than ~~that~~ in cluster 2 ($p < 0.01$~~)~~), as shown in Table 2. The patterns ~~were~~observed are consistent with the spatial distributions of their emissions and concentrations in ~~the~~ North China; as reported ~~the~~, there are stronger ~~emission~~emissions and ~~the~~ more serious pollution in the BTH region and Shandong Province ~~compared with that~~than in Inner-Mongolia and Liaoning ~~(Zhao et al., 2012;Yang et al., 2011)~~(Zhao et al., 2012; Yang et al., 2011). ~~And~~ Compared with Shandong Peninsula, the pollution in BTH region may be more serious ~~in that~~because it ~~has~~travels much longer ~~distance from~~distances to the sampling site ~~compared with Shandong Peninsula, while their concentration levels of~~, yet $PM_{2.5}$ ~~were insignificant~~concentrations attributed to the two areas are insignificantly different. In addition, the mean wind speed of cluster 2 was 7.60 m s^{-1}, which was markedly higher than that of cluster 1 (4.79 m s^{-1}) and cluster 3 (4.86 m s^{-1}). ~~The wind~~Wind speeds were ~~yielded~~determined by ~~averaged~~averaging hourly moving ~~distance~~distances of ~~those~~ air masses during a 48 ~~hours~~h period. The higher wind speed of cluster 2 ~~resulted~~likely partly ~~in~~contributes to the lower $PM_{2.5}$ level at ~~the~~ sampling site, since ~~that~~ high wind speed could provide ~~a~~ favorable diffusion ~~condition~~conditions for atmospheric pollutants.

Some anomalies compared with previous discussion provided different source signals ~~among~~amongst the clusters. For instance, ~~the~~K^+ concentration ~~of K^+~~ was significantly higher in cluster 3 than ~~that~~ in cluster 1, while the titanium (Ti) concentration was obviously lower. This ~~reflected the relative~~reflects relatively high ~~emission~~emissions of K^+ in the Shandong Peninsula and Ti in the BTH region from both natural sources and anthropogenic activities. ~~In contrast~~Likewise, the concentration of Na^+ in cluster 2 was markedly higher than ~~that~~ in ~~cluster~~clusters 1 and ~~cluster~~ 3, showing the large contribution of sea salt particles generated by sea spray under high wind speed ~~in~~to cluster 2~~. It~~ $PM_{2.5}$ concentrations. This suggested that sea salt sources ~~could~~should not be ignored in this study, due ~~to that~~the proximity of the sampling site ~~was close~~ to the Bohai Sea.

Sea salt ~~emission is~~emissions are comprised of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2}~~$^{+}$.~~$^{+}$ (Ni et al., 2013). The amounts of ~~the~~different chemical species ~~from~~in sea salt ~~emission~~emissions can be ~~sustained with~~ determined from using Na^+ as the tracer of sea salt~~, so~~; the ~~amount~~amounts of these species from non~~-~~-sea salt (nss-) ~~emission~~emissions can be expressed as~~ nss-X = X– [Na$^+$] × a, ~~:

$$nss\text{-}x = x - [Na^+] \times a \qquad (3)$$

where~~ X ~~ x indicates the Cl^-, SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+} concentrations, and ~~a~~a is the typical equivalent concentration ratio of the corresponding species to Na~~$^{+}$, such as~~$^{+}$ in average seawater: Cl^-/Na^+ (1.80), SO_4^{2-}/Na^+ (0.25), K^+/Na^+ (0.036), Mg^{2+}/Na^+ (0.12) and Ca^{2+}/Na^+ (0.038) ~~in average seawater (Ni et al., 2013).~~(Ni et al., 2013). If the calculated concentration of ~~no~~ non-sea salt ~~(nss-)~~ chemical species is negative, then ~~there is~~ no ~~the species~~ excess ~~exists.~~species exist. According to the calculation, for corresponding total chemical concentration levels grouped in clusters from 1 to 3, nss-Cl^- accounted for 55 ± 29%, 19 ± 24% and 77 ± 10~~%;~~% of total Cl^-; nss-SO_4^{2-} accounted for 99 ± 2%, 95 ± 4% and 99 ± 0.3~~%;~~% of total SO_4^{2-}; nss-K^+ accounted for 98 ± 3%, 89 ± 9% and 99 ± 0.3~~%;~~% of total K^+; nss-Ca^{2+} accounted for 95 ± 4%, 91 ± 10% and 96 ± 3~~%, respectively. In this study, ~~% of total Ca^{2+}. Thus, marked contributions of nss-emission sources to ~~the~~ chemical concentrations at all three clusters were found~~ although the~~. However, these values ~~were possibly~~ may be underestimated, since total Na^+ ~~amount does~~concentrations do not necessarily originate from sea salt alone, but could partially come from dust and burning sources~~(Zhang et al., 2013). And~~ (Zhang et al., 2013). In addition, the loss of Cl^- particles due to a chloride depletion mechanism further ~~supported~~supports the underestimation of Cl^-. The contributions of nss-~~source~~sources were lower in cluster 2 than ~~that~~ in ~~cluster~~clusters 1 and 3, which was attributed to ~~the~~ high ~~emission~~emissions of sea spray ~~resulting from~~ coupled with high wind speed in cluster 2. Generally,

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K^+ is often used as a tracer for biomass burning. The high K^+ concentration and the largest contribution of nss-K^+ in cluster 3 indicated ~~obviously~~clearly high emissions associated closely with agricultural burning in the Shandong Peninsula. ~~The~~This finding agreed with the fact that Shandong is the largest producer of crop residues in ~~the~~ North China ~~(Zhao et al., 2012)~~(Zhao et al., 2012), and biomass burning is ~~one of the~~an important ~~sources~~source of inorganic and organic aerosols in the Bohai sea atmosphere ~~(Feng et al., 2012;Wang et al., 2014)~~(Feng et al., 2012; Wang et al., 2014). The contribution of nss-Mg^{2+} to total magnesium concentration was less than 4% for the all clusters, indicating the ~~specie~~species came mostly from sea salt emission. The mass ratio of Mg^{2+} to Na^+ was 0.07 ± 0.06, 0.06 ± 0.03 and 0.06 ± 0.03 for clusters from 1 to 3, respectively. The ~~ratio was~~ratios were less than 0.23, also demonstrating that Mg^{2+} mostly came from sea salt source ~~(Zhang et al., 2013).~~

~~Enrichment Factor (EF) method with an abundance element associated with crustal elements is often used to assess enrichment characteristics of various elements in $PM_{2.5}$. In the present study, Fe was used as the reference element for the assessment because other two major crustal elements (Si and Al) could not be measured due to the interference from the quartz fiber substrate of the samples. EF of each element was calculated relative to the average crustal rock composition of Fe: EF = $(X/Fe)_{Aerosol}/(X/Fe)_{Crust}$, where $(X/Fe)_{Aerosol}$ and $(X/Fe)_{Crust}$ were the ratios of mean concentration of target elements and Fe in $PM_{2.5}$ and continental crust, respectively. By convention, an EF value close to unity suggests that the element is dominantly contributed by natural soil dust or the contribution of anthropogenic sources is not significant, and the value much higher than 10 indicates that the element is predominantly originated from human activities, such as combustion, automobile, industrial emissions, agricultural activities and etc. (Shah et al., 2012). An EF with a range of 1 to 10 indicates a hybrid contribution from crustal and anthropogenic sources. Here, except for the EF of Ni (9.17 ± 5.11) in cluster 3, the average EF of Ti, Ni, Cu, Zn, As, Cd and Pb in all clusters was greater than 10, showing severe influence from anthropogenic activity. The average EF in the three clusters also reflected that Co had a strong nature source, and the other elements (V and Mn) in all three~~

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~~clusters and Ni in cluster 3 were supported from crustal dust and anthropogenic activities.~~(Zhang et al., 2013).

The ratios of OC/EC and NO_3^-/nss-SO_4^{2-} were used as tracers to assess source signals of the three clusters. ~~It has been found that low~~Low temperature burning, such as agricultural ~~residues~~residue burning, emits more OC compared with high temperature burning, e.g. vehicle exhaust. Thus, the ratio of OC to EC is often used to evaluate relative ~~contribution~~contributions of low and high temperature burning emission~~.~~ (Zhao et al., 2012). The OC/EC ratios were 1.41 ± 0.30, 1.47 ± 0.29 and 2.14 ± 0.50 for ~~the~~ clusters ~~from~~ 1 to 3, respectively. Mean test showed that the ~~ratios were insignificant~~ difference between cluster 1 and cluster 2 ratios were insignificant at a 95% confidence level, and ~~the~~both clusters 1 and 2 ratios ~~of two groups~~ were ~~statistical low~~statistically lower compared with that of cluster 3, at the same confidence level. This ~~suggested~~suggests that low temperature burning ~~emission~~clearly contributed ~~obviously~~to emission in cluster 3, while high temperature burning emission was more distinct in ~~cluster~~clusters 1 and 2. ~~Besides~~Furthermore, mobile sources, such as vehicles, exhaust more NO_x than SO_2, while stationary sources, such as coal-fired power plants, emit more SO_2 than NO_x~~. The~~ (Wang et al., 2005). These two precursors convert into ~~sulfate~~SO_4^{2-} and ~~nitrate~~NO_3^- in the atmosphere, and the two type sources show different ~~ratio~~ratios of NO_3^-/SO_4^{2-}~~ from the two type sources. Therefore, the~~. Hence, this ratio is often used as an indicator of the relative importance of mobile vs. stationary sources of sulfur and nitrogen in the atmosphere ~~(Liu et al., 2014;Zhao et al., 2013)~~(Zhao et al., 2013; Liu et al., 2014). In this study, after deducting the contribution of sea salt to ~~sulfate,~~SO_4^{2-}, the mean ratios of NO_3^-/nss-SO_4^{2-} were 0.96 ± 0.31, 0.47 ± 0.24 and 0.64 ± 0.14 for ~~cluster~~clusters 1 to 3, respectively. Mean test showed that the three cluster ratios ~~of the three clusters~~ exhibit significant ~~difference~~ differences from each other at a 95% confidence level. The ~~significant high~~highest ratio in cluster 1 ~~suggested~~suggests that amongst the three regions, mobile sources are the most important ~~contribution of mobile source~~contributors of in the BTH region~~ among the three regions, ,~~ followed by Shandong Peninsula (cluster 3). The ratio of NO_3^-/nss-SO_4^{2-} in cluster 1 was within the range of ~~that~~those found in large cities, such as Beijing (1.20), Tianjin (0.73), and Shijiazhuang (0.76), the capital of Hebei province ~~(Zhao et al., 2013)~~(Zhao et al., 2013), reflecting a hybrid contribution from the BTH region. The value in cluster 2 was slightly lower than that in winter in Chengde (0.55), one city located in the northern mountainous area of Hebei Province ~~(Zhao et al., 2013).~~(Zhao et al., 2013). It indicated more

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obvious contribution of stationary source emissions in ~~the following region,~~areas such as ~~the east area of~~eastern Inner Mongolia and the west part of Liaoning, than ~~that in~~from the BTH region and the Shandong Peninsula. These stationary source emissions are possibly associated ~~possibly~~ with coal combustion because of the lower ~~ration of~~ OC/EC ratio in cluster 2 ~~than that in~~compared to cluster 3.

3.3 Source apportionment of carbonaceous ~~aerosols in~~ $PM_{2.5}$

The cluster analysis clearly indicated that $PM_{2.5}$ ~~pollution on the Qimu Island was~~concentrations increased significantly ~~influenced by the high concentrations of $PM_{2.5}$ carried by the~~when air masses came from the BTH region and the Shandong Peninsula during the sampling period. The chemical species in $PM_{2.5}$ from the BTH region ~~had~~possessed more ~~remarked~~marked signals of high temperature burning and mobile ~~source~~sources, while ~~that~~those from the Shandong Peninsula had more obvious patterns of low temperature burning and stationary sources. ~~To further confirm the sources of $PM_{2.5}$, source apportionment of carbonaceous aerosols, as the main components of $PM_{2.5}$, was evaluated by ^{14}C measurement. In order to better achieve our purpose using a few samples for radiocarbon analysis due to the extensive cost of the analysis, two combined samples were collected from a perfect synoptic process during the sampling period. The selection was reasonable as elaborated below. The synoptic process occurred during 16th and 18th, January, 2014. As shown in Fig. 2, the first half air masses of the synoptic process were derived from the south and passed through the Shandong Peninsula (cluster 3) and the bottom half were from the north and passed over the BTH region (cluster 1). Thus, two samples collected continually from 06:00 to 18:00, 16th January and from 18:00 to 06:00 the next day in the first half of the synoptic process were merged into one sample (M1) for the radiocarbon analysis. Similarly, other two samples collected continually from 17th January 18:00 to 6:00 and from 06:00 to 18:00 in the next day were combined into the other sample (M2). The M1 reflected the signal of air masses coming from the Shandong peninsula, while~~

~~M2 showed the pattern of air masses from the BTH region.~~

~~Considering that the ^{14}C measurement will be linked with PMF result, the representative capacity of all samples in the two clusters was examined thoroughly. It is expected that PMF can better interpret those data close to the average condition of each chemical species since the method utilizes minimizing error estimates to decompose a matrix of sample data into two matrixes under strict non-negativity constraints for the factors (Paatero et al., 2014). Similarly, the expectation can be used to assess their ratio for different purposes. Therefore, OC and EC concentrations, and ratios of OC/PM$_{2.5}$ and EC/PM$_{2.5}$ of each sample were compared with that in the corresponding cluster by mean test. Results showed that except for a significant high ratio of EC/PM$_{2.5}$, the OC and EC concentrations and the OC/PM$_{2.5}$ ratio of M2 were insignificant difference with that in the cluster 1 at a 95% significant level, indicating its perfect representative capability for further carbonaceous analysis. However, the typical ability of M1 was slightly bad because only ratios of OC/PM$_{2.5}$ and EC/PM$_{2.5}$ were no statistical difference, OC and EC concentrations were significantly higher than that in the cluster 3 at the same significant level. Finally, the samples were still considered for radiocarbon analysis in that they were from the most faultless synoptic process during the whole sampling period. Such a result was more dramatic than that from two insular samples. In addition, the insignificant difference of the ratios of OC/PM$_{2.5}$ and EC/PM$_{2.5}$ assured the validity for PM$_{2.5}$ source assessment, which was more important than carbonaceous species in this study.~~

Table 3 lists the concentrations and contemporary carbon fractions of OC, WSOC, WIOC and EC of the two combined samples~~.~~, which were selected via a perfect synoptic process during the sampling period. The fraction of OC was yielded by the average ~~weighted~~weights of ~~concentration~~concentrations of WSOC and WIOC fractions. It can be expressed as~~ f_c~~:

f_c(OC~~)=[f_c~~) = [f_c(WSOC)×~~C~~c(WSOC)+~~f_c~~f_c(WIOC)×~~C~~c(WIOC)]/[~~C~~c(WSOC)+~~C~~c(WIOC~~)],~~)] (4)

where ~~f_c~~f_c(OC), ~~f_c~~f_c(WSOC) and ~~f_c~~f_c(WIOC) are the contemporary carbon fractions of OC, WSOC and WIOC, and ~~C~~c(WSOC)~~ ~~and ~~C~~c(WIOC) are the concentrations of WSOC and WIOC, respectively. Generally, WSOC is mainly associated with biomass burning and secondary formation ~~(Du et al., 2014)~~(Du et al., 2014), while OC directly emitted from the combustion of fossil fuel is mostly water insoluble ~~(Weber et al., 2007).~~(Weber et al., 2007). During the earlier stage of the

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synoptic process, the concentrations of WSOC and WIOC were 6.~~38~~4 μg m^{-3} and 6.~~32~~3 μg m^{-3}, respectively. ~~While~~Later on, the concentrations of the two carbonaceous fractions fell to 3.~~68~~7 μg m^{-3} and 5.~~30~~3 μg m^{-3}, respectively, after the shift of the dominant wind direction from southerly to northwesterly, as shown in Fig. 2. The fraction of WSOC to OC decreased from 50% to 41% and the WIOC fraction increased from 50% to 59% before and after the shift of the dominant wind~~. It~~ direction. This suggested that the contribution of fossil fuel combustion was more obvious in the BTH region than ~~that~~ in the Shandong Peninsula~~, and vice versa. The implication could be further confirmed by the radiocarbon analysis of the two samples~~. The contemporary carbon fractions of WSOC and WIOC decreased from 0.59 to 0.49 and from 0.60 to 0.43, respectively, which indicated a decrease ~~of~~in the impact of biogenic and biomass burning emission~~,~~ and an increase in contribution of ~~the~~ fossil fuel combustion to the two OC fractions after the shift of the prevailing wind. After the weighted average of the WSOC and WIOC fractions, the ~~f_c~~f_c(OC) values were 0.59 and 0.46 for the M1 and M2 samples, respectively. Together with ~~f_c~~f_c (EC), ~~it could be~~we determined that biogenic and biomass burning emission contributed 59% of OC and 52% of EC concentrations, respectively, when ~~the~~ air masses were from the Shandong Peninsula. After the change of wind ~~field~~direction, the contribution of biogenic and biomass burning emission fell to 46% for OC and 38% for EC, respectively, which suggested that fossil fuel combustion contributed a dominant portion ~~to~~of the carbonaceous aerosols from the BTH region.

The synoptic process ~~showed~~ clearly showed a shift of the dominant wind from southerly to northwesterly, namely from the Shandong Peninsula to the BTH region. ~~In the meanwhile~~Meanwhile, the pattern of biogenic and biomass burning emission ~~was~~became more and more weak, and the signal of fossil fuel combustion ~~was~~became more and more obvious. ~~It~~This was in agreement with ~~that discussed above.~~our previous discussion. For instance, ~~the emission~~emissions in the BTH region exhibited more signals of high temperature burning and vehicle ~~exhausts~~exhaust. It was characterized by the lower ratio of OC/EC (1.41 ± 0.30), the higher ratio of NO_3^-/nss-SO_4^{2-} (0.96 ± 0.31~~)~~), and the relatively lower concentration of nss-K^+ compared with ~~that~~those in the Shandong Peninsula (2.14 ± 0.50 for OC/EC ratio, 0.64 ± 0.14 for NO_3^-/nss-SO_4^{2-} ratio). The contribution of the biogenic and biomass burning emission to ~~the~~ carbonaceous ~~aerosol~~aerosols in the Shandong Peninsula was still significant, which has often been mentioned in previous studies (Feng et al., 2012; Zong et al., 2015; Wang et al., 2014), although there was great combustion of fossil fuel (e.g., coal) for not only

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industrial activity but also heating in winter.~~ The emission of biogenic and biomass burning in the Shandong Peninsula was often highlighted in previous studies (Feng et al., 2012;Zong et al., 2015;Wang et al., 2014).~~

3.~~3~~4 Source apportionment of $PM_{2.5}$

The EPA PMF 5.0 model ~~and the data sets~~was used together with a date set of 76×22 (76 samples with 22 species) ~~were conducted ~~to further quantitatively estimate the source ~~contribution~~contributions of $PM_{2.5}$. After iterative testing from 5 to 15 factors ~~for the~~in model ~~scenarios~~exercises, we found the minimum deviation of the source apportionments of OC and EC between the results from ~~radiocarbon~~^{14}C measurement and a PMF model scenario with an F_{peak} value of 0 and the lowest Q values~~. The comparison will be elaborated below. ~~ (6245).

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Based on ~~the ~~PMF modeling results, eight ~~main ~~source factors were identified, as shown in Fig. ~~3. Secondary inorganic aerosols, which were extensively identified in previous studies (Tao et al., 2014;Zhang et al., 2013), were apportioned into the primary source sectors in the present study. Because the results are more useful for guiding $PM_{2.5}$ source controls. The contributions of the eight sources to $PM_{2.5}$ were summarized in Table 4. The total and cluster fractional contributions (%) from each source were calculated based on the corresponding sample values simulated by the PMF modeling.~~

3. Traffic emission has attracted considerable concern in the megacities of China (e.g., Beijing and Shanghai) due to the remarkable growth of ~~vehicles~~vehicle numbers in China. ~~On~~In Beijing in 2012, on-road vehicles were estimated ~~as~~to be the largest local emission source and contributed 22% of $PM_{2.5}$, including primary and secondary fine particles~~, but~~ and excluding vehicle-induced road dust~~, in Beijing in 2012~~ ~~(Zhang et al., 2014c).~~(Zhang et al., 2014b). The first source factor was characterized by high loadings of NO_3^-, SO_4^{2-}, NH_4^+, OC, EC, Zn and Cu, which ~~encloses~~matched a vehicle emission profile~~.~~ (Zhang et al., 2013). Generally, ~~nitrate, sulfate,~~NO_3^-, SO_4^{2-}, OC and EC are mainly from engine exhaust ~~emission~~emissions, and ammonia is from vehicles equipped with three-way catalytic converters. Not only Zn and Cu, but also Pb and Cd are emitted directly bounded particles from exhaust ~~(Zhang et al., 2014c).~~(Zhang et al., 2014b). In addition, the high NO_3^-/SO_4^{2-}

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~~ratios~~ratio of 1.28 calculated by the PMF results ~~showed the pattern of~~suggested high temperature burning and vehicle ~~emission. And the~~ emissions. This source was the largest contributor ~~for~~of NO_3^-, which contributed 41% ~~of the chemical species of $PM_{2.5}$~~ during the sampling period. The contribution was higher than 31% of NO_x emitted by traffic sectors in ~~the~~ North China in 2003, ~~which~~an expected ~~an~~ increase of the contribution due to the rapid rise of vehicles in ~~the~~ North China in recent years ~~(Shi et al., 2014b)~~(Shi et al., 2014b). This factor was the prevalent anthropogenic $PM_{2.5}$ source in ~~the~~ North China, with an average contribution of 16% during the sampling period. The contribution was lower than that in Beijing ~~(Zhang et al., 2014c)~~(Zhang et al., 2014b), agreeing with the regional contribution characteristic in our study, rather than ones in large ~~city~~cities, where a large number of vehicles ~~were running~~run. The second factor consisted of mineral dust elements, such as Mn, Fe and Co, and chemical species from human activities, such as Zn and EC, showing a mixed pattern of natural and anthropogenic emissions. Vehicle emission is an important source of atmospheric ~~zinc~~Zn pollution because it can be emitted from direct exhaust, lubricating oil additives, ~~tyre~~tire and brake abrasion, wearing and corrosion from anticorrosion galvanized automobile sheet, and ~~reentrainment~~re-entrainment dust enriched with ~~zinc (Duan and Tan, 2013).~~Zn (Duan and Tan, 2013). Thus, the source factor was ~~treated~~identified as traffic dust under the relative high contribution of vehicle emission to $PM_{2.5}$ concentration.

The third source factor was ship emissions, typically characterized by high ~~proportion~~proportions of Ni and V, and a high V/Ni ratio ~~of V/Ni~~. High loading of ~~the~~these two metals is typically associated with ~~the emission~~emissions from residual oil, probably derived from shipping activities and some industrial processes ~~(Pey et al., 2013).~~(Pey et al., 2013). In addition, a V/Ni ratio of more than 0.7 is always considered ~~as~~ a sign of $PM_{2.5}$ influenced by shipping emissions ~~(Zhang et al., 2014a)~~(Zhang et al., 2014a). The average ~~ratios~~ratio of V/Ni from the measured data ~~were~~was 0.93 ± 0.46, indicating an obvious contribution of shipping emission. The average ratio of V/Ni calculated from the PMF source profile was 1.02, which was the second ~~high~~highest value ~~among that~~amongst those derived from the eight sources. ~~While the~~The highest value of 1.29 was for the mineral dust source, which ~~agrees~~agreed with a high ratio of 3.06 for soil background concentrations of the two metals in mainland China ~~(Pan et al., 2013).~~ (Pan et al., 2013).

The fourth factor showed high ~~loading~~loadings of Cu, Zn, As, Cd and Pb, which ~~was~~were treated as ~~mainly contributed by~~signals of industrial processes. ~~The emission~~Emissions from the iron

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and steel industry are possibly important ~~among~~amongst those industrial processes ~~based on~~for two ~~proofs~~reasons. One is that the sintering process in the iron and steel industries emits ~~lots~~large amounts of Pb, Hg, Zn and other heavy metal pollutants, and other processes such as ironmaking and steelmaking also emit fugitive dust containing high ~~concentration~~concentrations of heavy metals ~~(Duan and Tan, 2013)~~(Duan and Tan, 2013). The other reason is the huge scale of steel production ~~of steel~~ in ~~the~~ North China. ~~The national~~National statistical data shows that China produced ~~about~~approximately half ~~world~~the world's production of crude steel in 2014, and ~~the productions~~production in the BTH and Shandong were 25.3% and 7.8~~%~~%, respectively, of the total amount in China, respectively, which is available at the website (http://www.stats.gov.cn/tjsj/ndsj~~/.~~/). Thus, iron and steel industries are likely the main atmospheric sources of the metal elements~~.~~ in this study. In addition, the contribution of the source to ~~sulfate~~SO_4^{2-} was 12%, which ~~is~~was similar ~~with the value of 15% contribution~~to previously reported contributions of industrial processes to the amount of sulfur dioxide ~~as reported previously (Zhao et al., 2012)~~(15%) (Zhao et al., 2012).

The fifth source factor was biomass burning, characterized by high concentrations of K^+, OC, EC and NH_4^+, which have been used extensively as tracers of biomass-burning aerosols ~~(Zhou et al., 2015;Tao et al., 2014)~~(Zhou et al., 2015; Tao et al., 2014). The contribution of ~~the~~this source was significantly higher in cluster 3 than ~~that~~ in ~~cluster~~clusters 1 and ~~cluster~~ 2, as listed in Table 4. ~~It~~Results agreed with more biomass burning emission in the Shandong Peninsula, characterized by rich K^+ and the high OC/EC ratio. ~~Besides, the~~The average ratio of OC to EC from ~~the~~this source was also the highest (1.84) ~~among~~amongst the eight identified sources (0.23-1.84) calculated by the PMF modeling.

The sixth source factor was mineral dust, characterized typically by crustal elements, such as Ca^{2+}, Ti and Fe, which are ~~always~~often used as ~~the~~ markers of soil dust ~~(Zhang et al., 2013). The contribution of the source was obviously higher in cluster 2 than that in cluster 1 and 3, matching with the high wind speed in cluster 2. The average ratio of OC to EC (1.53) from the~~(Zhang et al., 2013). The contribution of this source was obviously higher in cluster 2 than that in clusters 1 and 3, corresponding to high wind speed in cluster 2. The average ratio of OC to EC (1.53) from this source was obviously higher than that (0.23) from vehicle dust, possibly suggesting that the source contributed more OC, mainly derived from biogenic dust, such as plant debris.

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~~The seventh source factor was characterized by high loading of Cl^-, Na^+, OC, EC, SO_4^{2-} Ni and As. Coal combustion is often showed by elevated Cl^- linked with high Na^+, OC and EC (Zhang et al., 2013). The source was the largest contributor of sulfate in the present study, matching with the inventory results in the North China (Zhao et al., 2012). Also, the source was the largest contributor of $PM_{2.5}$ as listed in Table 4, which was coherent with the fact that coal combustion is the predominant source of fine particle aerosols over China (Pui et al., 2014). As and Ni showing high loading in the factor was also used as the markers for coal-fired power plant emissions (Tan et al., 2016). The last source factor was sea salt, characterized by high loading of Na^+, Mg^{2+} and Cl^-, which are related to the primary sea salt aerosols produced by the mechanical disruption of the ocean surface. Similar to the second source (mineral dust), high wind speed in cluster 2 made the high contribution of the source in cluster 2 than that in cluster 1 and 3. In addition, the higher contribution fractions for Mg^{2+} than for Cl^- of the source were in agreement with that discussed above. The concentration ratios of Cl^-/Na^+ and Mg^{2+}/Na^+ calculated from the PMF source profile were 1.79 and 0.11, respectively, similar to the corresponding ratios of the species (1.80 and 0.12, respectively) in average seawater (Ni et al., 2013). The sea salt source contributed 2.53%, 15.2% and 1.93% of OC concentrations in cluster from 1 to 3, respectively, but nothing for EC in all the clusters. It indicated the source consisted of sea-spray organic aerosol, which was produced by marine biogenic activities (Wilson et al., 2015).~~

~~To obtain more reliable source apportionment, the source contribution to OC and EC derived from those PMF scenarios for the two specified samples (M1 and M2) was compared with the source apportionment indicated by the ^{14}C assessment. The model results with the minimum deviation were treated as providing a more reliable solution for the source assessment. For the final choice, the contributions of coal combustion, vehicle emission, industrial process and ship emissions derived from the PMF modeling to OC and EC were ranked as the fossil fuel combustion for the comparison.~~

~~Sea salt as marine biogenic source of OC was merged with biomass burning as contemporary carbon fractions. While mineral dust and vehicle dust were not taken into consideration for the classification because they originated from a hybrid sources of fossil and contemporary carbon emissions.~~The seventh source factor was characterized by high loadings of Cl^-, Na^+, OC, EC, SO_4^{2-} Ni and As. Coal combustion is often indicated by elevated Cl^- linked with high Na^+, OC and EC (Zhang et al., 2013). This source was the largest contributor of SO_4^{2-} in the present study, matching with the inventory results in North China (Zhao et al., 2012). In addition, this source was the largest contributor of $PM_{2.5}$, as listed in Table 4, which agreed with the fact that coal combustion is considered the predominant source of fine particle aerosols over China (Pui et al., 2014). High loadings of As and Ni in the factor was also used as a marker for coal-fired power plant emissions (Tan et al., 2016).

The last source factor was sea salt, characterized by high loading of Na^+, Mg^{2+} and Cl^-, which are related to the primary sea-salt aerosols produced by mechanical disruption of the ocean surface. Similarly to the second source (mineral dust), high wind speed in cluster 2 made the contribution of this source in cluster 2 higher than that in clusters 1 and 3. In addition, the higher contribution fractions of Mg^{2+} compared to Cl^- in this source were in agreement with our previous discussion. The concentration ratios of Cl^-/Na^+ and Mg^{2+}/Na^+ calculated from the PMF source profile were 1.79 and 0.11, respectively, similar to the corresponding ratios of the species (1.80 and 0.12, respectively) in average seawater (Ni et al., 2013). The sea salt source contributed 2.53%, 15.2% and 1.93% of OC concentrations in clusters 1 to 3, respectively, but provided no EC contribution in any of the clusters. This indicates the source consists of sea-spray organic aerosols, which were produced by marine biogenic activities (Wilson et al., 2015).

The contributions of the eight sources to $PM_{2.5}$ are summarized in Table 4. The total and cluster fractional contributions (%) from each source were calculated based on the corresponding sample values simulated by PMF modeling. Amongst~~ Fig. 4 shows the comparison of the PMF results and the ^{14}C measurement.~~

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~~In M1, the biogenic and biomass burning (B&B) emission identified by PMF modeling contributed 52% and 49% of OC and EC concentrations, which were 7 and 3 percent, respectively, below the respective fraction indicated by the radiocarbon measurement. Accordingly, the~~

~~contributions of fossil fuel combustion to OC and EC from the PMF result were the same fraction of 44%, which were 3 percent over and 4 percent below the corresponding values in the ^{14}C result. Similarly, in M2, the B&B emission contributed 41% and 33% to OC and EC in the PMF result, showing 4 and 5 percent below that in the ^{14}C result. The contribution of fossil fuel combustion to OC and EC in the PMF result was 52% and 65%, which were the same percent (3%) below and over the corresponding values in the ^{14}C result. In general, the source contributions merged from the PMF results were lower than that from the radiocarbon measurements. The underestimation may be attributed to the absence of considering the contribution of mineral dust and vehicle dust because of their hybrid sources of B&B and fossil fuel combustion. The largest difference was 7 percent, indicating a minor contribution of the two sources to carbonaceous species in PM$_{2.5}$. The substantial difference was the two overestimations with the same range (3%), one was the contribution of fossil fuel combustion to OC in the M1 and the other was the contribution of fossil fuel combustion to EC in the M2. The overestimation was attributed to classify irrelevantly B&B emission into fossil fuel combustion. In conclusion, the minor irrelevant classification suggested that the PMF results provided a reasonable source apportionment of regional PM$_{2.5}$ in the North China in winter.~~

~~As listed in Table 4, among~~ the eight sources identified by the PMF modeling, coal combustion, biomass burning and vehicle emissions were the largest contributors of PM$_{2.5}$, which accounted for 29.6%, 19.3% and 15.8%, respectively, during the sampling period. They were followed, in decreasing order, by mineral dust (12.8%), ship emissions (8.95%), sea salt (6.58%), traffic dust (4.24%) and industrial process (2.64%). Generally, the source apportionment profile of PM$_{2.5}$ in cluster 1 was similar to that during the whole sampling period, because the regional scale pollution ~~meantime~~mainly exhibited a pattern of atmospheric outflow of PM$_{2.5}$ from the BTH region in winter ~~(Feng et al., 2007;Feng et al., 2012)~~(Feng et al., 2007; Feng et al., 2012). A slight increase ~~of~~in the contribution of vehicle emission in cluster 1 ~~corresponded~~corresponds to the great concern ~~on the source~~about vehicle emission in megacities ~~of~~in China ~~(Zhang et al., 2014c). However, the source~~

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~~signals were obviously different from that in cluster 2 and 3. The strong northwesterly wind in the cluster 2 provided more large spatial scale signals of source apportionment of $PM_{2.5}$, which indicated~~(Zhang et al., 2014b). The source signals in cluster 2 were obviously different from that in clusters 1 and 3. The strong northwesterly wind in it provided more large scale spatial signals of $PM_{2.5}$ sources, indicating that coal combustion (37.7%) and mineral dust (26.8%) were the largest contributors in north areas of China in winter. The large scale $PM_{2.5}$ pattern linked ~~with~~to coal combustion agreed with the dominant position of coal consumption in Chinese energy structure~~ as reported that the~~; coal consumption accounted for 66% of primary energy in China in 2014 by the national bureau of statistics of China (available at http://www.stats.gov.cn/tjsj/ndsj/). ~~Except for~~Other than industrial ~~consumptions, an additional use of~~consumption, coal is additionally used for residential heating in ~~north~~northern areas of China during winter~~, which was extensively consumed~~. Although the household use of coal accounts for a small portion of total coal consumption in China, ~~the~~its release is still a major source of $PM_{2.5}$ in winter ~~(Cao et al., 2012) since those household stoves always run under a condition with lack or backward environmental protection equipment. The traffic emission concerned extensively in large cities contributed a minor part (3.57%) of $PM_{2.5}$ concentration on the large spatial scale because motor exhaust concentrates mainly in urban areas. In addition, Biomass~~(Cao et al., 2012), since household stoves usually run with no or outdated environmental protection equipment. Traffic emission, of much concern in large cities, only contributed a minor part (3.57%) of $PM_{2.5}$ concentrations on a large spatial scale because motor exhaust concentrates mainly in urban areas. In addition, biomass burning emission dominated the $PM_{2.5}$ pollution when air masses came from the Shandong Peninsula. The abundant emission from biomass burning was mainly attributed to ~~the~~ residential heating in the cold season.

The contributions of coal combustion, vehicle emission, industrial process, and ship emission derived from the PMF modeling of OC and EC were ranked as fossil fuel combustion for comparison. Sea salt as a marine biogenic source of OC was merged with biomass burning as contemporary carbon fractions. However, mineral dust and vehicle dust were not considered for this classification, because they originated from hybrid sources of fossil and contemporary carbon emissions. Fig. 4 shows the comparison of the PMF results and the ^{14}C measurement.

As described in section 2.4, M1 represents the air mass from Shandong peninsula, while M2 is on behalf of the air mass from BTH region. In M1, the biogenic and biomass burning emission identified by PMF modeling contributed 52% to OC and 49% to EC concentrations, which were 7 and 3 % below the fractions indicated by ^{14}C measurement, respectively,. The contributions of fossil fuel combustion to OC and EC from the PMF result were both 44%, which is 3 percent over and 4 percent below the corresponding values in the ^{14}C result. Similarly, in M2, the biogenic and biomass burning emission contributed 41% to OC and 33% to EC in the PMF result, 4 and 5 percent below the ^{14}C result, respectively. The contributions of fossil fuel combustion to OC and EC in the PMF result were 52% and 65%, respectively, which were the same percent (3%) below and over the corresponding values in the ^{14}C result. In general, the source contributions merged from the PMF results were lower than those from the ^{14}C measurement. This underestimation may be due to not considering the contributions of mineral dust and vehicle dust because of their hybrid sources. The largest difference between PMF and ^{14}C results was 7%, indicating a minor contribution of the two sources to carbonaceous species in $PM_{2.5}$. The substantial difference was the two overestimations with the same range (3%); one was the contribution of fossil fuel combustion to OC in M1 and the other was the contribution of fossil fuel combustion to EC in M2. The overestimation was attributed to irrelevantly classifying biogenic and biomass burning emission as fossil fuel combustion. In conclusion, the minor irrelevant classification suggested that the PMF result in this study provided a reasonable source apportionment of regional $PM_{2.5}$ in North China in winter.

4 Implications for PM alleviation

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According to ~~the~~ source apportionment results, coal combustion was the largest contributor of $PM_{2.5}$ in ~~the~~ North China during winter, and ~~the~~this source ~~posed~~imposed a larger spatial pattern of $PM_{2.5}$ pollution in ~~north~~northern areas of China compared with ~~the~~ North China. Therefore, to alleviate overall PM emissions, those generated by coal combustion should be ~~firstly abated. Also, the~~first targeted. The source has been identified as the ~~most~~ leading emission sector ~~with a goal of~~for controlling the annual $PM_{2.5}$ concentration in the air pollution control program. The contributions of traffic emission and biomass burning to $PM_{2.5}$ concentrations also ~~had an obviously~~formed a clear spatial pattern in ~~the~~ North China during winter. Vehicle emission contributed significantly to $PM_{2.5}$ in the BTH region, so ~~the~~for regulations this source should be ~~prior~~ considered ~~to control as~~ the second major emission sector ~~listed in the air pollution~~to control ~~program~~.

~~It~~ Biomass burning emission should be paid close attention to ~~the biomass burning emission due to its dominant contribution to the $PM_{2.5}$ burden in the Shandong Peninsula and~~ because the emission has been only lightly considered ~~slightly~~ in the control program. Indeed, the first national pollution source survey showed that Shandong province is the largest producer of crop stalks, with a production of 132 million tons in China in 2007 ~~(Compilation Committee of the first China pollution source census, 2011)~~(Compilation Committee of the first China pollution source census, 2011). Of ~~which~~these, about 20 million tons were produced in the Shandong Peninsula (including the cities of Weifang, Yantai, Weihai, Qingdao and Rizhao). ~~Approximate~~Approximately 40% of this production was used as household ~~fuels~~fuel for cooking and heating in ~~countryside of~~ the peninsula countryside. The fraction was significantly higher than ~~that~~ in western areas of the Shandong province, such as Zibo (9%) and Jinan (8%), and the fraction of open burning of crop residues in the peninsula (3%). ~~Besides, the~~The fraction of biomass open burning in the peninsula was also higher than the average fraction (1.5%) in Shandong province in 2007. Generally,~~ the~~ emissions from agricultural field burning are mainly concentrated in the harvest season and contribute significantly to regional haze and smog events in the region, which have attracted special concern ~~(Feng et al., 2012;Zong et al., 2015;Wang et al., 2014)~~(Feng et al., 2012; Zong et al., 2015; Wang et al., 2014). ~~But the~~Despite this, open burning emission has been considered only as a minor source sector in the control program. ~~Similarly, as an larger emitter, household~~Household emission of agricultural waste~~ is continuous~~, another larger source, are released continuously or semi-~~continuous~~continuously, and can also~~ can~~ induce PM$_{2.5}$ pollution on a regional scale, which has also been despised or ignored ~~(Zhang and Cao, 2015)~~(Zhang and Cao, 2015). ~~Although~~

Open burning is not fully controlled in China, although the government has enacted a series of regulations to prohibit field burning since the 1990s and ~~strengthens~~strengthened the force of ~~the~~its supervision recently~~, the open burning is not fully controlled in China.~~. The most basic reason ~~is that there is no~~for continued burning is the lack of a reasonable alternative to utilize or ~~handle the~~dispose of huge ~~production~~amounts of agricultural waste ~~per~~each year. ~~Under such a case, a part of~~In the current scenario, some agricultural wastes are collected and stored as fuel for household cooking and heating, and others are rapidly removed by open burning in ~~field~~fields for the next planting during harvest season. Although farmers know that such use and disposal of agricultural residues are ~~harm~~harmful to the environment~~. They~~, they still tend to use agricultural ~~waste~~wastes as household fuel and ~~remove them via burning~~burn wastes in ~~field~~fields, mainly due to the low ~~cost~~costs of the

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methods. A more permanent solution ~~is~~would be to find ~~the high~~higher economic value ~~of~~in agricultural wastes via development of renewable techniques. Indeed, agricultural ~~waste~~wastes can be utilized to produce ~~manifold~~many renewable ~~energy~~energies, such as biogas, feedstuffs, biochar, bioethanol, and bio-succinic acid~~, and so on~~. China has provided relevant energy regulations, ~~legislations~~legislation, and policy initiatives for rural renewable energy ~~(Li et al., 2015).~~(Li et al., 2015). The government has also ~~encourages~~encouraged and ~~sustains~~sustained the development of the renewable energy industry to increase the demand ~~of~~for raw feedstocks. Through these efforts, China has achieved some success in renewable development in rural areas, but ~~the~~these efforts are not an effective solution to the problem of surplus crop waste, because the ~~cost~~costs and ~~the benefit~~benefits cannot yet be offset. For instance, Zhangziying, a town located in the ~~east~~eastern area of the Daxing district of Beijing, has developed household biogas and straw gas since the 1980s, but ~~the~~in 2011 renewable energy only ~~occupied about~~made up approximately 10% of household energy consumption, ~~which was~~ much lower than the fraction of coal (30%) ~~in 2011(Li et al., 2015).~~(Li et al., 2015). Before the achievement of high economic value, except for the ban on crop straw burning, the government should compensate farmers to collect crop residues as feedstocks of renewable energy, rather than burning in ~~field~~fields or ~~household~~households ~~(Shi et al., 2014a).~~(Shi et al., 2014a). The revenue from the subsidy and ~~the~~ sale of crop residues ~~can support famer's~~could help alleviate economic burdens ~~for the~~on farmers, so they can use~~ of~~ clean energy, such as electricity, liquefied petroleum gas, biogas~~ and so on,~~, etc., for household consumption ~~(Kung and Zhang, 2015)~~(Kung and Zhang, 2015). ~~The~~These efforts will not only significantly improve air quality, but also make famers ~~to~~ learn the ~~convenient~~convenience of clean energy and wake from agricultural residue burning.

5 Conclusions

~~Source apportionment of wintertime $PM_{2.5}$ at a background site in the North China in 2014 was conducted by statistical analysis of the chemical species grouped according to the trajectory clusters, radiocarbon measurement of the carbonaceous species and the PMF modeling confirmed by the ^{14}C analysis.~~ During the sampling period, the ~~mean~~ average $PM_{2.5}$ concentration ~~of $PM_{2.5}$~~ was 77.6 ± 59.3 μg m^{-3}, and ~~sulfate concentrations were~~ SO_4^{2-} concentration was the highest of any constituent, with a mean of 14.2 ± 18.0 μg m^{-3}, followed by ~~nitrate~~NO_3^- (11.9 ± 16.4 μg m^{-3}), OC (6.85 ± 4.81 μg m^{-3}), EC (4.90 ± 4.11 μg m^{-3}~~)~~), and ~~ammonium~~NH_4^+ (3.11 ± 2.14 μg m^{-3}). The fractions of ~~sulfate,~~

~~nitrate~~SO_4^{2-}, NO_3^- and ~~ammonium~~NH_4^+ to $PM_{2.5}$ were obviously higher than ~~that~~those in ~~metropolis~~metropolises (e.g. Beijing and Tianjin) within ~~the~~ North China, while fractions of carbonaceous species ~~was~~were markedly lower~~, which~~; these showed regional pollution signals.

More than half of air masses during the sampling period were from the BTH region, followed by ~~the~~ air masses from ~~the~~ Mongolia (35%) and the Shandong Peninsula (11~~%) during the sampling period.~~

%). The concentrations of $PM_{2.5}$ and ~~its~~ most of the species carried by the air masses from the BTH region and the Shandong Peninsula were comparable ($p > 0.05$), and they ~~were~~occurred in statistically ~~higher~~greater concentrations than ~~that~~those carried by the air masses from ~~the~~ Mongolia ($p < 0.01$). ~~The patterns were attributed to the spatial distributions of their emissions and the high wind speed when air masses were from the Mongolia.~~ The $PM_{2.5}$ had an obvious signal of biomass burning emission, characterized by a high OC/EC ratio, low NO_3^-/nss-SO_4^{2-} ratio and high nss-K^+ concentration~~,~~ when air masses came from the Shandong Peninsula. ~~While~~In contrast, the $PM_{2.5}$ carried from the BTH region showed vehicle emission pattern, characterized by low OC/EC ratio, high NO_3^-/nss-SO_4^{2-} ratio and low nss-K^+ concentration. ~~The~~This finding was confirmed by the ~~radiocarbon~~ ^{14}C measurement of OC and EC in two merged samples ~~(One was collected when air masses were from the Shandong Peninsula and the other was air masses from the BTH region)~~ selected from a successive synoptic process. The ^{14}C measurement indicated that biogenic and biomass burning emission contributed 59% and 52% of OC and EC concentrations when air masses were from the Shandong Peninsula, and the contributions fell to 46% and 38~~% for OC and EC,~~%, respectively, when the prevailing wind changed and came from the BTH region.

Based on the PMF modeling ~~results~~result, eight main source factors were identified. The source contribution ~~to~~of OC and EC derived from PMF for the two specified samples was compared with that indicated by the ^{14}C assessment. Two minor overestimations with the same range (3%) showed the excellent capacity of the model~~ capacities~~, suggesting that the PMF ~~results~~result provided a reasonable source apportionment of regional $PM_{2.5}$ in the North China in winter. The PMF results indicated that coal combustion, biomass burning and vehicle emissions were the largest contributors of $PM_{2.5}$, ~~which account~~accounting for 29.6%, 19.3% and 15.8~~%,~~% of $PM_{2.5}$, respectively, during the sampling period. Compared with ~~the~~ overall source apportionment result, the contribution of vehicle

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emission increased slightly when air masses came from the BTH region, the fraction of mineral dust and coal combustion rose ~~obviously~~clearly when air masses with high speed were from ~~the~~ Mongolia, and biomass burning became the dominant contributor when air masses were from the Shandong Peninsula. Biomass burning emission was highlighted in the present study, because coal combustion and vehicle emission have already been considered as major emission factors in the government air pollution control program.

~~As the largest contributor of $PM_{2.5}$ in the North China in winter, coal combustion has been considered as the most leading emission sector to be controlled for improving the air quality. Vehicle emission contributed significantly the $PM_{2.5}$ levels in the BTH region, which has also been considered to control as the second major emission sector listed in the air pollution control program. Biomass burning emission was highlighted in the present study because of its dominant contribution to the $PM_{2.5}$ burden in Shandong Peninsula, which has been despised or ignored in the control program. To improve air quality, some suggests were provided to wake famers from agricultural residue burning in field and household.~~

Furthermore, the present study proposed that the minimum deviation between the results from PMF model and ^{14}C measurement could be used as a criterion to select a more reliable solution for source apportionment of $PM_{2.5}$. This method can be applied to CMB models or other isotopes (e.g. ^{13}C, ^{15}N and ^{35}S), which will help to improve scientific significance.

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Notes

The authors declare no competing financial interest.

Reference

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Balachandran, S., Chang, H. H., Pachon, J. E., Holmes, H. A., Mulholland, J. A., and Russell, A. G.: Bayesian-based ensemble source apportionment of $PM_{2.5}$, Environ. Sci. Technol., 47, 13511-13518, doi: 10.1021/es4020647, 2013.

Boynard, A., Clerbaux, C., Clarisse, L., Safieddine, S., Pommier, M., Van Damme, M., Bauduin, S., Oudot, C., Hadji-Lazaro, J., Hurtmans, D., and Coheur, P.-F.: First simultaneous space measurements of atmospheric pollutants in the boundary layer from IASI: A case study in the North China Plain, Geophys. Res. Lett., 41, 645-651, doi: 10.1002/2013gl058333, 2014.

Cao, J.-j., Chow, J. C., Tao, J., Lee, S.-c., Watson, J. G., Ho, K.-f., Wang, G.-h., Zhu, C.-s., and Han, Y.-m.: Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels, Atmos. Environ., 45, 1359-1363, doi: 10.1016/j.atmosenv.2010.10.056, 2011.

Cao, J.-J., Shen, Z.-X., Chow, J. C., Watson, J. G., Lee, S.-C., Tie, X.-X., Ho, K.-F., Wang, G.-H., and Han, Y.-M.: Winter and summer $PM_{2.5}$ chemical compositions in fourteen Chinese cities, J. Air Waste Manage. Assoc., 62, 1214-1226, doi: 10.1080/10962247.2012.701193, 2012.

Chinese-State-Council: Atmospheric Pollution Prevention and Control Action Plan, http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm (in Chinese), access: 12, September, 2013.

Chow, J. C., and Watson, J. G~~., Pritchett~~.: Review of $PM_{2.5}$ and PM_{10} apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model, Energy Fuels, 16, 222-260, doi: 10.1021/ef0101715, 2002.

Chow, J. C., Watson, J. G., Chen, L. ~~C., Pierson,~~ W. ~~R., Frazier, C.~~ A., ~~and Purcell, R. G~~Chang, M. C. O., Robinson, N. F., Trimble, D., and Kohl, S.: The ~~dri~~IMPROVE_A temperature protocol for thermal/optical ~~reflectance~~ carbon analysis~~ system: description, evaluation and applications in U.S.~~: Maintaining consistency with a long-term database, J. Air ~~quality studies, Atmos. Environ., 27, 1185-1201, 1993~~Waste Manage. Assoc., 57, 1014-1023, doi: 10.3155/1047-3289.57.9.1014, 2007.

Compilation~~-~~ Committee~~-~~ of~~-~~ the~~-~~ first~~-~~ China~~-~~ pollution~~-~~ source~~-~~ census: Dataset of the first China pollution source census, China Environmental Science Press, Beijing, 120 pp., 2011.

Ding, X., Wang, X., Xie, Z., Zhang, Z., and Sun, L.: Impacts of siberian biomass burning on organic aerosols over the north pacific ocean and the arctic: Primary and secondary organic tracers, Environ. Sci. Technol., 47, 3149-3157, doi: 10.1021/es3037093, 2013.

Du, Z., He, K., Cheng, Y., Duan, F., Ma, Y., Liu, J., Zhang, X., Zheng, M., and Weber, R.: A yearlong study of water-soluble organic carbon in Beijing I: Sources and its primary vs. secondary nature, Atmos. Environ., 92~~(0),~~, 514-521, doi: 10.1016/j.atmosenv.2014.04.060, 2014.

Duan, J., and Tan, J.: Atmospheric heavy metals and Arsenic in China: Situation, sources and control policies, Atmos. Environ., 74~~(0), 93-101, doi:10.1016/j.atmosenv.2013.03.031.~~, 93-101, doi: 10.1016/j.atmosenv.2013.03.031, 2013.

Feng, J., Guo, Z., Chan, C. K., and Fang, M.: Properties of organic matter in $PM_{2.5}$ at Changdao Island, China—A rural site in the transport path of the Asian continental outflow, Atmos. Environ., 41, 1924-1935, doi: 10.1016/j.atmosenv.2006.10.064, 2007.

Feng, J., Guo, Z. G., Zhang, T. R., Yao, X. H., Chan, C. K., and Fang, M.: Source and formation of secondary particulate matter in $PM_{2.5}$ in Asian continental outflow, J. Geophys. Res., 117, D03302, doi: 10.1029/2011jd016400, 2012.

Gu, J., Bai, Z., Li, W., Wu, L., Liu, A., Dong, H., and Xie, Y.: Chemical composition of $PM_{2.5}$ during winter in

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Tianjin, China, Particuology, 9, 215-221, ~~10.1016/j.partic.2011.03.001,~~doi: 10.1016/j.partic.2011.03.001, 2011.

Gu, J., Du, S., Han, D., Hou, L., Yi, J., Xu, J., Liu, G., Han, B., Yang, G., and Bai, Z.-P.: Major chemical compositions, possible sources, and mass closure analysis of $PM_{2.5}$ in Jinan, China, Air Qual. Atmos. Health, 7, 251-262, doi: 10.1007/s11869-013-0232-9, 2014.

Han, S.-q., Wu, J.-h., Zhang, Y.-f., Cai, Z.-y., Feng, Y.-c., Yao, Q., Li, X.-j., Liu, Y.-w., and Zhang, M.: Characteristics and formation mechanism of a winter haze~~–~~–fog episode in Tianjin, China, Atmos. Environ., 98, 323-330, doi: 10.1016/j.atmosenv.2014.08.078, 2014.

Hu, M., Guo, S., Peng, J.-f., and Wu, Z.-j.: Insight into characteristics and sources of $PM_{2.5}$ in the Beijing–Tianjin–Hebei region, China, ~~National Science Review,~~Natl. Sci. Rev., 2, 257-258, doi: 10.1093/nsr/nwv003, 2015.

Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., ~~El~~ Haddad, I. E., and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218~~–~~–222, doi: 10.1038/nature13774, 2014.

Kessler, R.: ~~PREVENTION~~Prevention: Air of danger, ~~Nature,~~ 509, S62-S63, doi: 10.1038/509S62a, 2014.

Kung, C.-C., and Zhang, N.: Renewable energy from pyrolysis using crops and agricultural residuals: An economic and environmental evaluation, Energy, 90, ~~1532-1544, 10.1016/j.energy.2015.06.114,~~Part 2, 1532-1544, doi: 10.1016/j.energy.2015.06.114, 2015.

Li, X., Lin, C., Wang, Y., Zhao, L., Duan, N., and Wu, X.: Analysis of rural household energy consumption and renewable energy systems in Zhangziying town of Beijing, Ecol. Modell~~,~~., 318, 184-193,

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~~10.1016/j.ecolmodel.2015.05.011,~~doi: 10.1016/j.ecolmodel.2015.05.011, 2015.

Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., Shen, C., Chen, Y., Tian, C., and Zhang, G.: The use of levoglucosan and radiocarbon for source apportionment of $PM_{2.5}$ carbonaceous aerosols at a background site in East China, Environ. Sci. Technol., 47, 10454-10461, doi: 10.1021/es401250k, 2013.

Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., Shen, K., He, Q., Ding, X., Wang, X., Chen, D., Szidat, S., and Zhang, G.: Source ~~Apportionment Using Radiocarbon~~apportionment using radiocarbon and ~~Organic Tracers~~organic tracers for $PM_{2.5}$ ~~Carbonaceous Aerosols~~carbonaceous aerosols in Guangzhou, South China: Contrasting ~~Local~~local- and ~~Regional-Scale Haze Events~~regional-scale haze events, Environ. Sci. Technol., 48, 12002-12011, doi: 10.1021/es503102w, 2014.

Ni, T., Li, P., Han, B., Bai, Z., Ding, X., Wang, Q., Huo, J., and Lu, B.: Spatial and Temporal Variation of Chemical Composition and Mass Closure of Ambient PM_{10} in Tianjin, China, Aerosol Air Qual. Res., 13, 1832-1846, doi: 10.4209/aaqr.2012.10.0283, 2013.

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111-126, doi: 10.1002/env.3170050203, 1994.

Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781-797, doi: 10.5194/amt-7-781-2014, 2014.

Pan, Y., Wang, Y., Sun, Y., Tian, S., and Cheng, M.: Size-resolved aerosol trace elements at a rural mountainous site in Northern China: Importance of regional transport, Sci. Total Environ., 461–462, 761-771, ~~10.1016/j.scitotenv.2013.04.065,~~doi: 10.1016/j.scitotenv.2013.04.065, 2013.

Pey, J., Pérez, N., Cortés, J., Alastuey, A., and Querol, X.: Chemical fingerprint and impact of shipping emissions over a western Mediterranean metropolis: Primary and aged contributions, Sci. Total Environ., 463~~-464, 497-507, 10.1016/j.scitotenv.2013.06.061,~~-464, 497-507, doi: 10.1016/j.scitotenv.2013.06.061,

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2013.

Pui, D. Y. H., Chen, S.-C., and Zuo, Z.: PM$_{2.5}$ in China: Measurements, sources, visibility and health effects, and mitigation, Particuology, 13, 1-26, ~~10.1016/j.partic.2013.11.001,~~doi: 10.1016/j.partic.2013.11.001, 2014.

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~~Quan, J., Tie, X., Zhang, Q., Liu, Q., Li, X., Gao, Y., and Zhao, D.: Characteristics of heavy aerosol pollution during the 2012-2013 winter in Beijing, China, Atmos. Environ., 88, 83-89, 10.1016/j.atmosenv.2014.01.058, 2014.~~

~~Shah, M. H., Shaheen, N., and Nazir, R.: Assessment of the trace elements level in urban atmospheric particulate matter and source apportionment in Islamabad, Pakistan, Atmos Pollut Res, 3, 39-45, 10.5094/apr.2012.003, 2012.~~

Shahsavani, A., Naddafi, K., Jaafarzadeh Haghighifard, N~~. J~~., Mesdaghinia, A., Yunesian, M., Nabizadeh, R., Arhami, M., Yarahmadi, M., Sowlat, M. H., Ghani, M., Jonidi Jafari, A~~. J~~., Alimohamadi, M., Motevalian, S. A., and Soleimani, Z.: Characterization of ionic composition of TSP and PM$_{10}$ during the Middle Eastern Dust (MED) storms in Ahvaz, Iran, Environ. Monit. Assess., 184, 6683-6692, doi: 10.1007/s10661-011-2451-6, 2012.

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Sheehan, P., Cheng, E., English, A., and Sun, F.: China's response to the air pollution shock, Nat. Clim. Change, 4, 306-309, doi: 10.1038/nclimate2197, 2014.

Shi, T., Liu, Y., Zhang, L., Hao, L., and Gao, Z.: Burning in agricultural landscapes: an emerging natural and human issue in China, ~~Landscape~~Landsc. Ecol., 29, 1785-1798, doi: 10.1007/s10980-014-0060-9, 2014a.

Shi, Y., Xia, Y.-f., Lu, B.-h., Liu, N., Zhang, L., Li, S.-j., and Li, W.: Emission inventory and trends of NOx for China, 2000–2020, J. Zheijang Univ.-Sci., 15, 454-464, doi: 10.1631/jzus.A1300379, 2014b.

Szidat, S., Jenk, T. M., Gäggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., Kalberer, M., Samburova, V., Reimann, S., Kasper-Giebl, A., and Hajdas, I.: Radiocarbon (^{14}C)-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zürich, Switzerland, Atmos. Environ., 38, 4035-4044, doi: 10.1016/j.atmosenv.2004.03.066, 2004.

Szidat, S.: Sources of Asian Haze, Science, 323, 470-471, doi: 10.1126/science.1169407, 2009.

Tan, J., Duan, J., Zhen, N., He, K., and Hao, J.: Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing, Atmos. Res., 167, 24-33, ~~10.1016/j.atmosres.2015.06.015,~~doi: 10.1016/j.atmosres.2015.06.015, 2016.

Tao, J., Gao, J., Zhang, L., Zhang, R., Che, H., Zhang, Z., Lin, Z., Jing, J., Cao, J., and Hsu, S. C.: $PM_{2.5}$ pollution in a megacity of southwest China: source apportionment and implication, Atmos. Chem. Phys., 14, 8679-8699, doi: 10.5194/acp-14-8679-2014, 2014.

Tian, S., Pan, Y., Liu, Z., Wen, T., and Wang, Y.: Size-resolved aerosol chemical analysis of extreme haze pollution events during early 2013 in urban Beijing, China, J. Hazard. Mater., 279, 452-460, doi: 10.1016/j.jhazmat.2014.07.023, 2014.

Wacker, L., Fahrni, S. M., Hajdas, I., Molnar, M., Synal, H. A., Szidat, S., and Zhang, Y. L.: A versatile gas interface for routine radiocarbon analysis with a gas ion source, Nucl. Instrum. Methods Phys. Res., Sect. B, 294, 315-319, doi: 10.1016/j.nimb.2012.02.009, 2013.

Wang, X., Bi, X., Sheng, G., and Fu, ~~H~~J.: Hospital indoor PM_{10}/$PM_{2.5}$ and associated trace elements in Guangzhou, China, Sci. Total Environ., 366, 124-135, doi: 10.1016/j.scitotenv.2005.09.004, 2006.

Wang, X., Chen, Y., Tian, C., Huang, G., Fang, Y., Zhang, F., Zong, Z., Li, J., and Zhang, G.: Impact of agricultural waste burning in the Shandong Peninsula on carbonaceous aerosols in the Bohai Rim, China, Sci. Total Environ., 481, 311-316, doi: 10.1016/j.scitotenv.2014.02.064, 2014.

Wang, Y., Zhuang, G. S., Tang, A. H., Yuan, H., Sun, Y. L., Chen, S. A., and Zheng, A. H.: The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing, Atmos. Environ., 39, 3771-3784, doi:

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10.1016/j.atmosenv.2005.03.013, 2005.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, J. Geophys. Res.~~–~~. Atmos., 112, D13302, doi: 10.1029/2007JD008408, 2007.

Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., Burrows, S. M., Carslaw, K. S., Huffman, J. A., Judd, C., Kilthau, W. P., Mason, R. H., McFiggans, G., Miller, L. A., Najera, J. J., Polishchuk, E., Rae, S., Schiller, C. L., Si, M., Temprado, J. V., Whale, T. F., Wong, J. P. S., Wurl, O., Yakobi-Hancock, J. D., Abbatt, J. P. D., Aller, J. Y., Bertram, A. K., Knopf, D. A., and Murray, B. J.: A marine biogenic source of atmospheric ice-nucleating particles, Nature, 525, 234-238, doi: 10.1038/nature14986, 2015.

Xu, X., Trumbore, S. E., Zheng, S., Southon, J. R., McDuffee, K. E., Luttgen, M., and Liu, J. C.: Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision, Nucl. Instrum. Methods Phys. Res., Sect. B, 259, 320-329, doi: 10.1016/j.nimb.2007.01.175, 2007.

Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., and Chen, G.: Characteristics of $PM_{2.5}$ speciation in representative megacities and across China, Atmos. Chem. Phys., 11, 5207-5219, doi: 10.5194/acp-11-5207-2011, 2011.

Zhang, F., Chen, Y., Tian, C., Wang, X., Huang, G., Fang, Y., and Zong, Z.: Identification and quantification of shipping emissions in Bohai Rim, China, Sci. Total Environ., 497–498, 570-577, ~~10.1016/j.scitotenv.2014.08.016, 2014~~doi: 10.1016/j.scitotenv.2014.08.016, 2014a.

Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM$_{2.5}$ in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, doi: 10.5194/acp-13-7053-2013, 2013.

Zhang, S., Wu, Y., Wu, X., Li, M., Ge, Y., Liang, B., Xu, Y., Zhou, Y., Liu, H., Fu, L., and Hao, J.: Historic and future trends of vehicle emissions in Beijing, 1998–2020: A policy assessment for the most stringent vehicle emission control program in China, Atmos. Environ., 89, 216-229, ~~10.1016/j.atmosenv.2013.12.002, 2014c~~doi: 10.1016/j.atmosenv.2013.12.002, 2014b.

Zhang, Y.-L., Li, J., Zhang, G., Zotter, P., Huang, R.-J., Tang, J.-H., Wacker, L., Prévôt, A. S. H., and Szidat, S.: Radiocarbon-based source apportionment of carbonaceous aerosols at a regional background site on Hainan Island, South China, Environ. Sci. Technol., 48, 2651-2659, doi: 10.1021/es4050852, 2014c.

Zhang, Y.-L., and Cao, F.: Is it time to tackle PM$_{2.5}$ air pollutions in China from biomass-burning emissions?, Environ. Pollut., 202, 217-219, ~~10.1016/j.envpol.2015.02.005,~~doi: 10.1016/j.envpol.2015.02.005, 2015.

Zhang, Y. L., Liu, D., Shen, C. D., Ding, P., and Zhang, G.: Development of a preparation system for the radiocarbon analysis of organic carbon in carbonaceous aerosols in China, Nucl. Instrum. Methods Phys. Res., Sect. B, 268, 2831-2834, doi: 10.1016/j.nimb.2010.06.032, 2010.

Zhang, Y. L., Huang, R. J., El Haddad, I., Ho, K. F., Cao, J. J., Han, Y., Zotter, P., Bozzetti, C., Daellenbach, K. R., Canonaco, F., Slowik, J. G., Salazar, G., Schwikowski, M., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Baltensperger, U., Prévôt, A. S. H., and Szidat, S.: Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013, Atmos. Chem. Phys., 15, 1299-1312, doi: 10.5194/acp-15-1299-2015, 2015.

Zhao, B., Wang, P., Ma, J. Z., Zhu, S., Pozzer, A., and Li, W.: A high-resolution emission inventory of primary pollutants for the Huabei region, China, Atmos. Chem. Phys., 12, 481-501, doi: 10.5194/acp-12-481-2012, 2012.

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Zhao, P. S., Dong, F., He, D., Zhao, X. J., Zhang, X. L., Zhang, W. Z., Yao, Q., and Liu, H. Y.: Characteristics of concentrations and chemical compositions for $PM_{2.5}$ in the region of Beijing, Tianjin, and Hebei, China, Atmos. Chem. Phys., 13, 4631-4644, doi: 10.5194/acp-13-4631-2013, 2013.

Zhou, Y., ~~Shuiyuan, C~~Cheng, S., Lang, J., Chen, D., Zhao, B., Liu, C., Xu, R., and Li, T.: A comprehensive ammonia emission inventory with high-resolution and its evaluation in the Beijing–Tianjin–Hebei (BTH) region, China, Atmos. Environ., 106, 305-317, ~~10.1016/j.atmosenv.2015.01.069,~~doi: 10.1016/j.atmosenv.2015.01.069, 2015.

Zong, Z., Chen, Y., Tian, C., Fang, Y., Wang, X., Huang, G., Zhang, F., Li, J., and Zhang, G.: Radiocarbon-based impact assessment of open biomass burning on regional carbonaceous aerosols in North China, Sci. Total Environ., 518–519, 1-7, ~~10.1016/j.scitotenv.2015.01.113,~~doi: 10.1016/j.scitotenv.2015.01.113, 2015.

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Table 1. Statistics of $PM_{2.5}$ chemical components on the Qimu Island during the sampling period

Species	Mean ± std. (μg m^{-3})	Range (μg m^{-3})	Species	Mean ± std (ng m^{-3})	Range (ng m^{-3})
$PM_{2.5}$	77.6 ± 59.3	12.7 – 305	~~Ti~~Fe	408 ± 285~~7.72 ± 7.34~~	~~0.01 – 30.~~7.12 – 1588
~~EC~~SO_4^{2-}	~~4.90 ± 4.11~~14.2 ± 18.0	~~0.80 – 19.6~~1.37 – 96.2	~~V~~Zn	107 ± 142~~3.90 ± 2.47~~	~~0.45 – 12.~~5.56 – 987
~~OC~~NO_3^-	~~6.85 ±~~ 11.9 ± 16.4~~.81~~	0.~~81 – 21.3~~27 – 87.1	~~Mn~~Pb	88.4 ± 85.7~~29.3 ± 28.0~~	3.02 – 412~~1.38 – 108~~
~~Cl^-~~NH_4^+	3.11 ± 2.~~06 ± 1.78~~14	0.61 – 10~~ – 8.90~~.1	~~Fe~~Mn	29.3 ± 28.0~~408 ± 285~~	1.38 – 108~~7.12 – 1588~~
~~NO_3~~Cl^-	~~11.9 ± 16.4~~2.06 ± 1.78	0.~~27 – 87.1~~10 – 8.90	~~Co~~Cu	9.08 ± 11.4~~0.24 ± 0.18~~	0.~~01 – 0.73~~03 – 77.7
~~SO_4^{2-}~~K^+	~~14.2 ± 18.~~0.96 ± 0.84	~~1.37 – 96.2~~0.07 – 3.95	~~Ni~~Ti	7.72 ± 7.34~~4.28 ± 2.30~~	0.01 – 30.7~~1.68 – 13.8~~
Na^+	0.43 ± 0.25	0.05 – 1.58	~~Cu~~As	6.61 ± 7.86~~9.08 ± 11.4~~	0.~~03 – 77.7~~67 – 43.4
~~NH_4~~Ca^{2+}	0.38 ± 0.22~~3.11 ± 2.14~~	0.~~61 – 10.~~07 – 1.32	~~Zn~~Ni	4.28 ± 2.30~~107 ± 142~~	1.68 – 13.8~~5.56 – 987~~
~~K~~Mg^{2+}	0.~~96~~03 ± 0.~~84~~03	0.~~07 – 3.95~~01 – 0.17	~~As~~V	3.90 ± 2.47~~6.61 ± 7.86~~	0.~~67 – 43.4~~45 – 12.5
~~Mg^{2+}~~OC	~~0.03 ± 0.03~~6.85 ± 4.81	0.~~01 – 0.17~~81 – 21.3	Cd	1.82 ± 4.06	0.04 – 25.9
~~Ca^{2+}~~EC	4.90 ± 4.11~~0.38 ± 0.22~~	0.~~07 – 1.32~~80 – 19.6	~~Pb~~Co	~~88.4 ± 85.7~~0.24 ± 0.18	0.01 – 0.73~~3.02 – 412~~

Table 2. Statistics of $PM_{2.5}$ chemical species in different clusters and significant level by mean test

Species (unit)	Mean ± standard deviation (range)			Significant level		
	Cluster1(n=42)	Cluster2(n=25)	Cluster3(n=9)	1&2	1&3	2&3
$PM_{2.5}$ (µg m^{-3})	93.0 ± 66.1 (24.5–305)	41.6 ±26.7 (12.7–143)	106±42.3 (50.3–193)	0.00	0.59	0.00
EC (µg m^{-3})	6.53 ± 4.66 (1.39–19.6)	2.50 ±1.84 (0.80–8.85)	3.94±1.49 (2.53–7.66)	0.00	0.11	0.05
OC (µg m^{-3})	8.58 ± 5.23 (1.45–21.3)	3.51 ±2.35 (0.81–11.4)	8.04±2.32 (5.25–13.5)	0.00	0.76	0.00
Cl^- (µg m^{-3})	2.37 ± 2.11 (0.10–8.90)	1.22 ±0.65 (0.20–2.85)	2.94±1.35 (1.42–5.53)	0.01	0.45	0.00
NO_3^- (µg m^{-3})	17.6 ± 19.6 (1.75–87.0)	2.75 ±4.25 (0.27–20.1)	10.6±6.09 (4.41–20.3)	0.00	0.30	0.00
SO_4^{2-} (µg m^{-3})	19.4 ± 21.8 (2.09–96.2)	4.55 ±4.06 (1.37–19.5)	16.4±8.74 (5.34–35.6)	0.00	0.69	0.00
Na^+ (µg m^{-3})	0.38 ± 0.24 (0.05–1.58)	0.55 ±0.26 (0.18–1.08)	0.31±0.06 (0.22–0.40)	0.01	0.41	0.01
NH_4^+ (µg m^{-3})	3.97 ± 2.29 (1.28–10.1)	1.53 ±0.98 (0.61–4.70)	3.52±0.96 (1.93–4.90)	0.00	0.57	0.00
K^+ (µg m^{-3})	1.11 ± 0.74 (0.28–3.10)	0.35 ±0.36 (0.07–1.69)	2.01±0.93 (0.78–3.95)	0.00	0.00	0.00
Mg^{2+} (µg m^{-3})	0.03 ± 0.03 (0.01–0.17)	0.03 ±0.02 (0.01–0.11)	0.02±0.01 (0.01–0.04)	0.66	0.41	0.13
Ca^{2+} (µg m^{-3})	0.37 ± 0.22 (0.11–1.32)	0.37 ±0.18 (0.07–0.74)	0.44±0.29 (0.09–0.97)	1.00	0.46	0.46
Ti (ng m^{-3})	6.96 ± 5.98 (0.35–25.9)	10.9 ±9.10 (0.01–30.7)	2.51±0.85 (1.16–3.58)	0.04	0.03	0.01
V (ng m^{-3})	4.68 ± 2.29 (0.76–11.3)	2.83 ±2.55 (0.45–12.4)	3.24±1.50 (2.05–7.12)	0.00	0.08	0.66
Mn (ng m^{-3})	33.8 ± 31.3 (1.97–108)	17.6 ±19.3 (1.38–95.4)	40.9±20.3 (9.14–69.8)	0.02	0.53	0.01
Fe (ng m^{-3})	404 ± 308 (7.12–1588)	375 ±263 (9.13–826)	521±188 (244–960)	0.70	0.29	0.15
Co (ng m^{-3})	0.26 ± 0.20 (0.01–0.73)	0.17 ±0.14 (0.01–0.48)	0.36±0.13 (0.10–0.59)	0.08	0.14	0.00
Ni (ng m^{-3})	4.85 ± 2.56 (1.68–13.8)	3.51 ±1.85 (1.68–6.79)	3.80±1.02 (2.45–5.84)	0.03	0.24	0.67
Cu (ng m^{-3})	11.6 ± 13.6 (0.72–77.7)	3.06 ±2.93 (0.03–8.99)	13.9±7.05 (3.90–26.4)	0.00	0.64	0.00
Zn (ng m^{-3})	146 ± 176 (9.92–987)	46.4 ±50.1 (5.56–208)	90.4±47.4 (24.2–201)	0.01	0.36	0.03
As (ng m^{-3})	9.03 ± 9.52 (1.11–43.4)	3.00 ±2.82 (0.67–14.0)	5.35±3.35 (2.25–13.6)	0.00	0.27	0.06
Cd (ng m^{-3})	2.70 ± 5.26 (0.11–25.9)	0.45 ±0.41 (0.04–1.29)	1.54±0.65 (0.49–2.66)	0.04	0.52	0.00
Pb (ng m^{-3})	110 ± 95.3 (5.30–412)	36.9 ±44.8 (3.02–176)	128±53.2 (45.4–215)	0.00	0.59	0.00

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Table 3. Concentration and contemporary carbon fraction of carbonaceous species in M1 and M2

	M1	M2		M1	M2
$PM_{2.5}$ (μg m^{-3})	159.2 ± 0.5	91.8 ± 0.5			
OC (μg m^{-3})	12.7 ± 0.7	~~8.98~~9.0 ± 0.5	~~f_c~~ f_c (OC)	0.59 ± 0.04	0.46 ± 0.04
WSOC (μg m^{-3})	6.~~38~~4 ± 0.4	3.~~68~~7 ± 0.2	~~f_c~~ f_c (WSOC)	0.59 ± 0.03	0.49 ± 0.03
WIOC (μg m^{-3})	6.~~32~~3 ± 0.6	5.~~30~~3 ± 0.4	~~f_c~~ f_c (WIOC)	0.60 ± 0.03	0.43 ± 0.03
EC (μg m^{-3})	8.~~58~~6 ± 0.5	5.~~81~~8 ± 0.3	~~f_c~~ f_c (EC)	0.52 ± 0.02	0.38 ± 0.01

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Table 4. Averages of fractional contributions (%) from eight sources identified by PMF model

	Vehicle emission	Traffic dust	Ship emission	Industrial process	Biomass burning	Mineral dust	Coal combustion	Sea salt
All	15.~~8~~83	4.24	8.95	2.64	19.~~3~~31	12.~~8~~81	29.~~6~~64	6.58
Cluster1	23.~~6~~64	4.89	8.79	3.64	19.~~6~~61	6.32	29.~~2~~16	3.96
Cluster2	3.57	3.60	9.34	1.19	4.88	26.~~8~~81	37.~~7~~66	~~13.0~~12.95
Cluster3	12.~~5~~46	3.08	8.67	1.96	52.~~7~~67	6.46	12.~~4~~38	2.32

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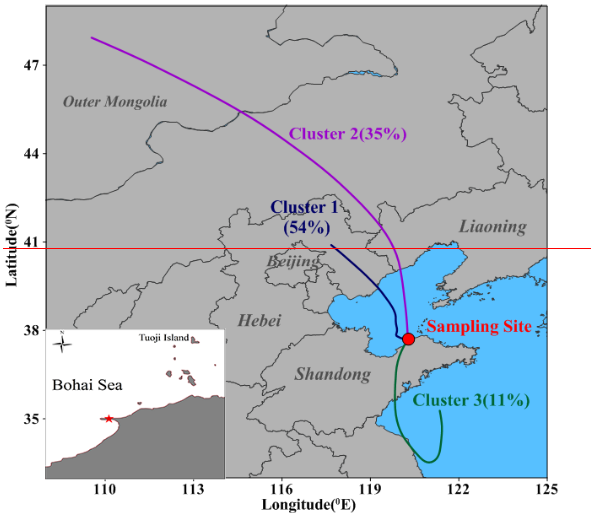
Outer Mongolia
Cluster 2(35%)
Cluster 1
(54%)
Liaoning
Beijing
Hebei
Sampling Site
Shandong
Cluster 3(11%)
Tuoji Island
Bohai Sea
47
44
41
38
35
Latitude(⁰N)
110
113
116
119
122
125
Longitude(⁰E)

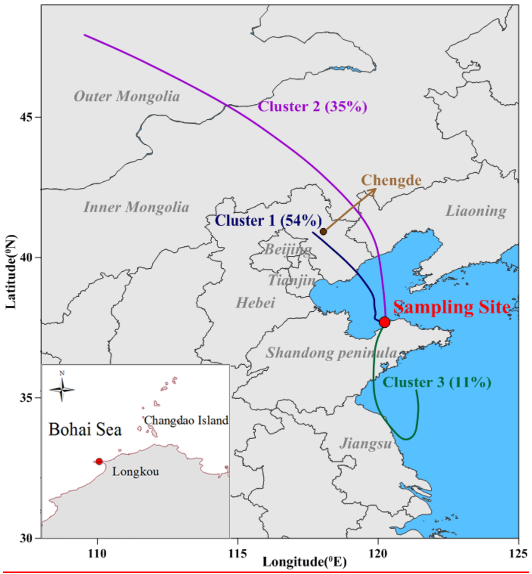

Figure 1. The sampling site and 48-h back trajectory clusters during the sampling period

Figure 2. 48-h back trajectories with 12 h intervals ~~during 16 ~~of the combined samples (M1 and M2) selected for ^{14}C analysis. M1 were collected continually from 06:00 to 18:00, 16th January~~, 2014.~~ and from 18:00 to 06:00 the next day, when the air masses were derived from the south and passed through the Shandong Peninsula; M2 were collected continually from 17th January 18:00 to 6:00 and from 06:00 to 18:00 in the next day, when the air masses come from the north and reflected the BTH pattern. (The digit in the figure is date and time with the format of YYYYMMDDHH, the time is local time~~)~~).

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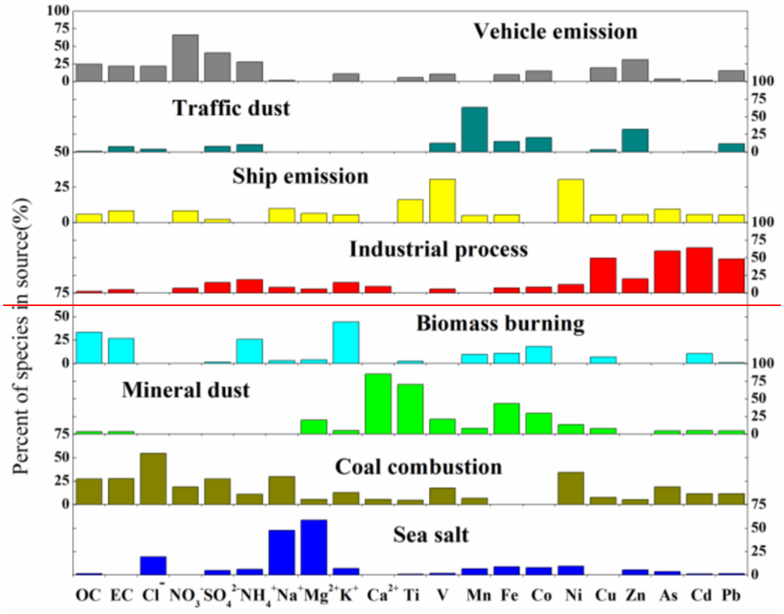

Vehicle emission
Traffic dust
Ship emission
Industrial process
Biomass burning
Mineral dust
Coal combustion
Sea salt
Percent of species in source(%)
100
75
50
25
0
OC
EC
Cl$^-$
NO$_3^-$
SO$_4^{2-}$
NH$_4^+$
Na$^+$
Mg^{2+}
K$^+$
Ca^{2+}
Ti
V
Mn
Fe
Co
Ni
Cu
Zn
As
Cd
Pb

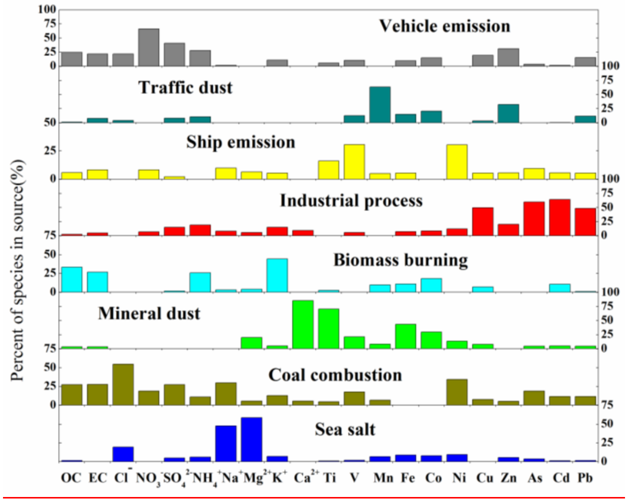
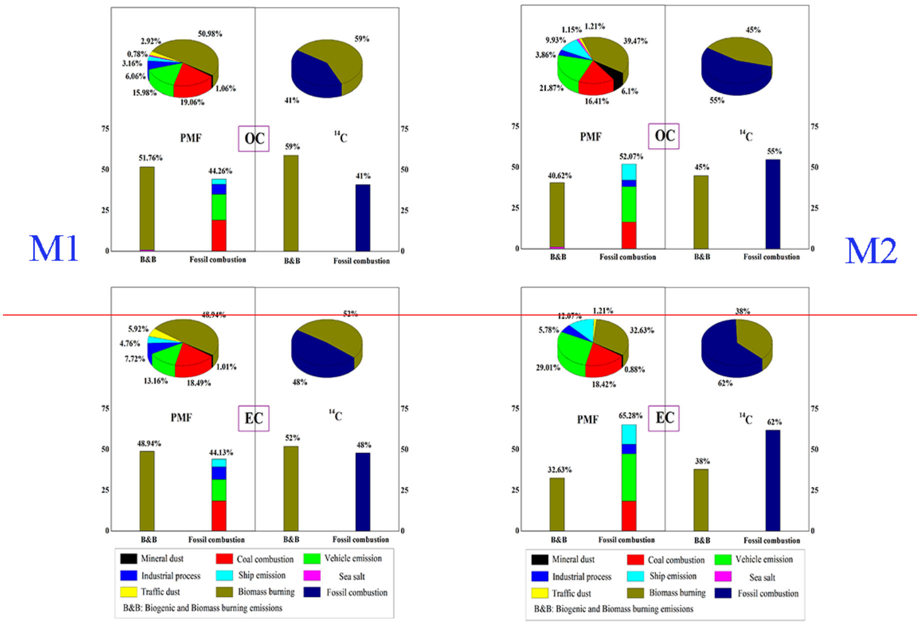


Figure 3. The contribution profiles of eight sources identified by PMF model



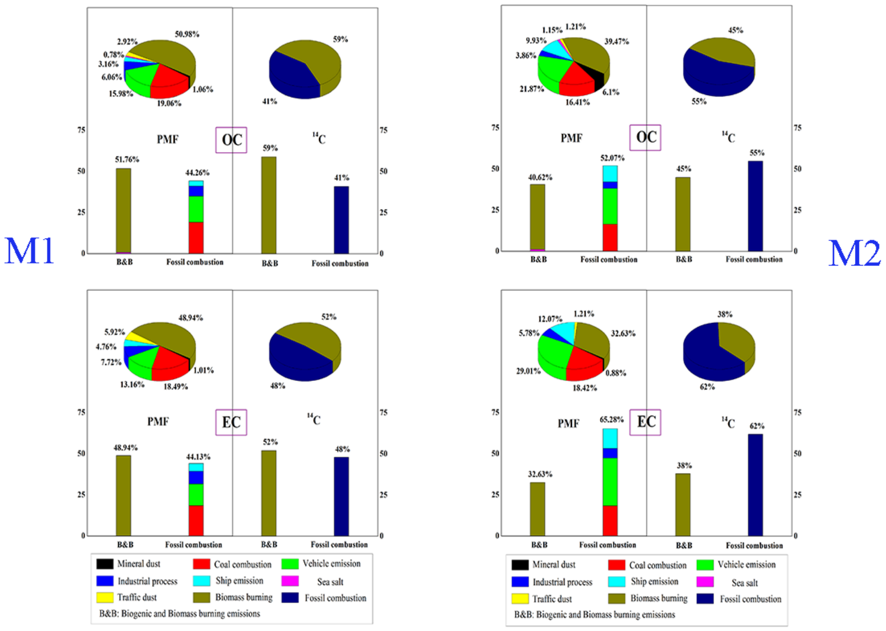


Figure 4. Comparison of source apportionment of OC and EC in the two specified samples (M1 and M2) from PMF and ^{14}C measurement. B&B ~~is~~refers to the source of biogenic and biomass burning. Note: the B&B and Fossil emissions from the PMF result do not add to a hundred in the bars because hybrid sources from B&B and fossil fuel combustion were not be considered in the comparison (mineral dust and vehicle dust).

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