

## Responses to comments of the reviewer #1

We appreciate the helpful comments and suggestions from the reviewer, which greatly improved the quality of our manuscript. The point-to-point responses to the comments are listed below in blue.

### **Responses to Reviewer #1:**

Reviewer #1 (Formal Review for Author (shown to author)):

The authors collected PM<sub>2.5</sub> filter samples diurnally in Tianjian and quantified organic molecular components in two seasons, winter 2016 and early summer 2017. They reported the organic compound levels and estimated the contributions from biomass burning, biogenic emissions and anthropogenic emissions, in view of primary and secondary sources. Although there are quite an amount of studies on source apportionments of PM<sub>2.5</sub> in northern China, their reports on aerosol organic compounds are relatively rare and valuable. The writing is easy to follow, while I suggest the authors to consider the following comments before the paper being published.

**Response:** We thank the reviewer for the valuable comments.

Major comments:

1、 It has been long realized that the major sources of OC in fine aerosols are combustion sources (fossil fuel combustion and biomass burning) and secondary oxidation, in comparison with coarse particles (PM<sub>10</sub> or TSP) where dusts and primary biological sources also matter. In the current study, biomass burning, anthropogenic sources (used as toluene and naphthalene SOC), and biogenic sources, as well as plant debris and fungal spore all together are contributing 25-35% of OC (Table 1, Figure 13). The readers may expect if the study could provide more information on the possible sources of the other 65-75%, i.e., the major fraction of OC.

**Response:** Organic molecular markers detected using GC/MS in this study mainly included aliphatic lipids (*n*-alkanes, fatty acids, *n*-alcohols), saccharides (anhydrosugars, primary saccharides, sugar alcohols), biogenic secondary organic aerosols (BSOA, including isoprene, monoterpene and  $\beta$ -caryophyllene SOAs) and toluene and naphthalene SOAs. We applied mannitol and glucose, isoprene,

monoterpene and  $\beta$ -caryophyllene to evaluate the contributions of primary and secondary biogenic sources to OC, and toluene and naphthalene were used to evaluate the contribution of anthropogenic sources to OC. In total, primary and secondary biogenic OC and anthropogenic OC contributed 25–35% to OC based on these tracers.

At present, there are more than 130 organic molecules that can be detected by GC/MS (Fu et al., 2008), such as phthalates, aromatic acids, polycyclic aromatic hydrocarbon, lignin and resin products, hopanes, complex compounds and some possibly existing molecules that are undiscovered now, which can also contribute to OC in PM<sub>2.5</sub>. These contributions of the estimated sources were underestimated based on the tracer method, and some uncertainties should be considered.

In addition, GC/MS is the widely used assay for small organic molecules. It has high temporal resolution and can provide detailed information of organic molecules. And it can quantify the concentrations of organic tracers, such as compounds analyzed in our study. However, GC/MS can only detect small molecules, which account for a small proportion of the total organic matter in the aerosols (Rogge et al., 1993). Other analytical techniques, such as FTICR-MS can detect more than 1000 organic compounds, including macromolecular polymers containing sulfur and nitrogen that are difficult to detect with conventional instruments. So the realization of full analysis of fine particles requires the combination of various analytical techniques (Zhang et al., 2017). Techniques for analyzing organic aerosols are listed in the Table S8. The discussions are shown in the revised manuscript on Pages 16 Lines 10-13 in part of 3.4.3. Table S8 is shown in supporting information.

Table S8. Techniques for analyzing organic aerosols (Ren et al., 2016)

Analysis targets	Techniques	References
OC, EC, WSOC	Thermal/optical reflectance, PILS-WSOC	El-Zanan et al., 2012
Organic molecules	HRMS, FTICR-MS	Kourtchev et al., 2016
Small organic molecules	GC/MS, GC/FID, GCXGC/MS, LC/MS, LC/MS/MS, TOF/MS	Kourtchev et al., 2016; Stenson et al., 2002
Organic monomer isotopes	GC-IRMS, EA-MICADAS	Cao et al., 2017
Functional group; Molecules	NMR, FT/IR	Foley et al., 2013; Russell et al., 2011
Online observation	AMS, HR-AMS, CIMS	Chen et al., 2016
Fluorescence	UV-APS, WIBS, EEM-FS	Pöhlker et al., 2012

2、 It is interesting that saccharides and sugar alcohols showed higher levels in winter than summer in PM<sub>2.5</sub> (Fig. 7, Fig. 9). The results imply that sugar alcohols are co-emitted during biomass burning, or co-transport (co-exist) with biomass burning aerosols (Table S3). This observational evidence where speculated in previous studies but not justified. Discussions from such a viewpoint could be interesting to the community.

Response: In Figure 7, it is obvious that the concentrations of levoglucosan (a specific tracer of biomass burning), saccharides and sugar alcohols were more abundant in winter than in summer. In addition, saccharides and sugar alcohols had high levels especially when the levoglucosan reached peaks in both seasons, implying that they may share the similar sources to some extent.

Thanks for the reviewer's good suggestion, we provided the fire maps in winter and summer during the sampling periods. Combining with wind direction (WD) to verify the contribution of biomass burning to sugar alcohols. Fire maps during the summer 2017 and winter 2016 in Tianjin are added in Figure S7 in supporting information.

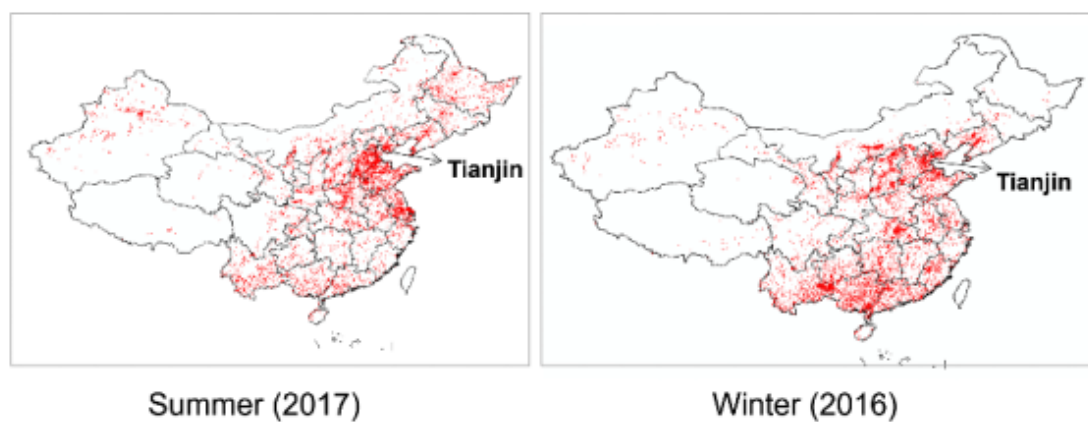


Figure S7: Fire maps during the summer 2017 and winter 2016 in Tianjin.

It can be seen clearly that there were large amounts of anthropogenic activities in winter (right in Figure S7). As we all know, the combustion of fossil fuels and biofuels were widely used for house heating in the winter 2016 in China. The biomass burning could contribute to levoglucosan and sugar alcohols. In summer, there were relatively dense fire spots distributed in the North China Plain (NCP) and some south agricultural provinces, such as Jiangsu, Anhui, Henan and Shandong (left in Figure S7). Fu et al. (2008) had reported that there were large-scale burning of wheat straw during May-

June across China. Meanwhile, the wind directions were mainly southerly during winter- and summer-time in Tianjin (Figure 2). Therefore, in addition to the contribution of local biomass burning, the southern wind carried a large number of biomass burning particulate matters from NCP and southern agricultural provinces into Tianjin, which could be the source of levoglucosan and sugar alcohols. Page 10, Lines 8-20.

Minor comments:

1、 P2, L22, 'due to' change to 'along with'?

Response: Following the suggestion, we have revised the sentence. “ Tianjin (39°N and 117°E), the largest coastal city of the NCP, located along the Haihe River and being adjacent to the Bohai Sea and East China Sea (Figure 1), has suffered severe haze pollution along with rapid economic and industrial developments during the past decades.” Page 2, Line 25.

2、 P2, L33, southerly wind mainly in summer, or throughout the year?

Response: The wind directions have been added, and southerly winds were mainly in winter and summer.

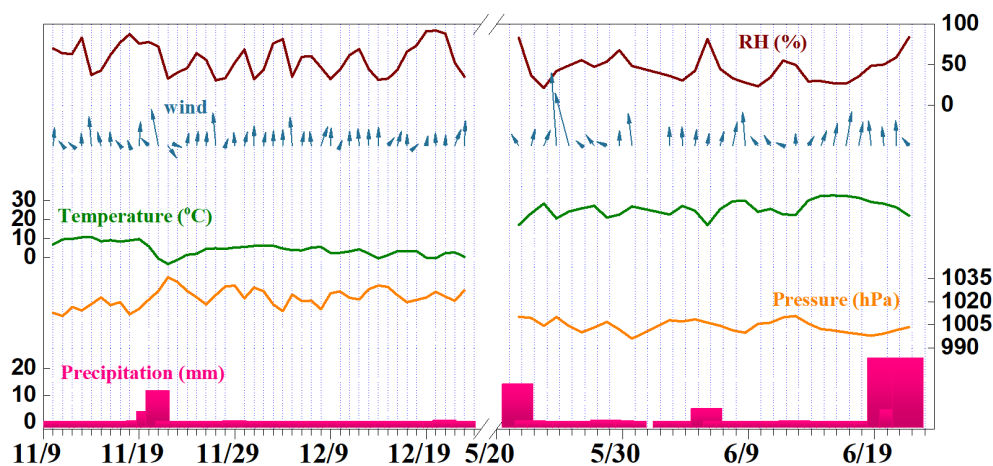


Figure 2: Daily variations in relative humidity (RH), wind direction (WD), temperature (T), pressure (P) and precipitation (Precip), The data were obtained from the automatic meteorological station at the sampling sites.

3、 Fig. 1, westerly winds prevail mainly in winter, better to add that. It is not necessary to add the location of Mt. Tai. It is better to add an insert figure, showing sampling location in an enlarged map of Tianjin.

Response: Thanks. We have provided clear information on the sampling site in Figure 1.

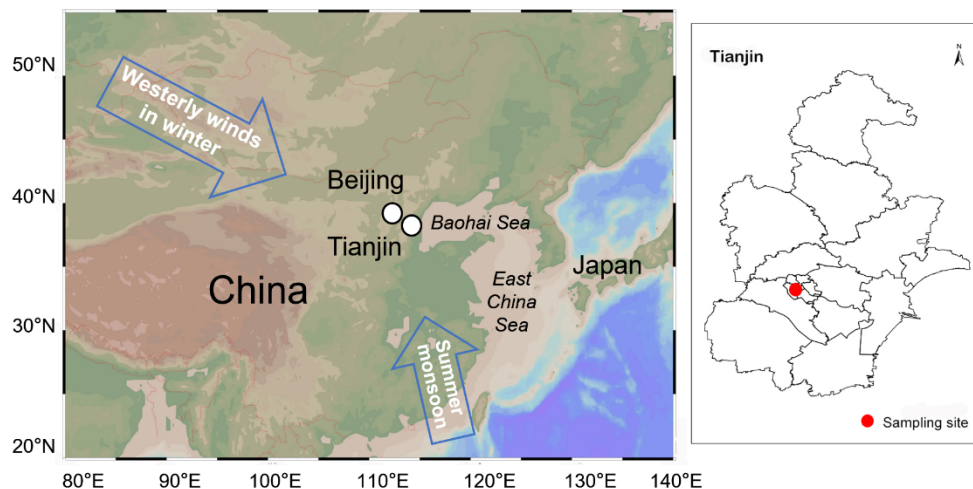


Figure 1: Map of showing the location of Tianjin city (left) and the sampling site (right) in Nankai district, Tianjin.

4、 P4, L29, how is  $PM_{2.5}$  mass measured? Such information is needed to readers. It is interesting to see co-varied  $PM_{2.5}$  and RH. What are the possibly reasons/implications?

Response: Following the suggestion, we have provided clear information on air quality data including AQI,  $PM_{2.5}$  and quality grade in Table S7 in supporting information.

The mass concentrations of  $PM_{2.5}$  were available from the website of China air quality online monitoring and analysis platform. And we have added the source of  $PM_{2.5}$  on Page 5, Lines 1-3.

5、 P5, L1, high concentrations that what level, any threshold?

Response: High concentrations represent the peaks relative to the sample concentrations in the surrounding days (see Page 5, Line 17).

6、 P5, L31-P6, L2, Table S2, it is not easy to understand how WNA (%) is calculated. As they account for only ~10%, What are the other 90%.

Response: Plant wax carbon number is expressed by the difference between a certain carbon number concentration and the average of its adjacent two carbon number concentrations:  $Wax C_n = C_n - [(C_{n+1} + C_{n-1})/2]$ , when the  $C_n < 0$ ,  $C_n = 0$ ; (n represents odd carbon number)

The % of Wax C<sub>n</sub> is the contribution of biogenic *n*-alkane that is derived from high plant waxes (Ren et al., 2016). The certain carbon we used to calculate contribution of plant wax were odd carbons from C<sub>25</sub> to C<sub>33</sub> (Kang et al., 2017; Ren et al., 2016). (%Wax C<sub>n</sub> = Wax C<sub>n</sub>/ΣC<sub>n</sub> × 100%)

In this study, plant wax *n*-alkanes only accounted for ~10%, and the large sources of *n*-alkanes maybe attributed to anthropogenic activities, such as biomass burning and fossil fuels, as mentioned in this study. Furthermore, there may also be some other sources that we need to further find afterwards (Page 6, Lines 15). The computational formula is provided in Table S2.

7、 P8, L11, 12, unify sugar alcohols and sugar polyols throughout the text.

Response: Thanks. We have corrected it as suggested in the revised manuscript.

8、 P11, L11, aerosols in Rishiri did not appear in Fu et al. 2010b.

Response: The data in Rishiri aerosols have not been unpublished, so we removed this information in the revision.

9、 P11, L26, give the full name of DHOPA as it appears for the first time.

Response: Thanks for the reviewer for pointing this mistake. We have corrected it on Page 12, Line 26.

10、 P12, L6, Fig.2, wind direction data could not be seen.

Response: We have corrected it in Figure 2.

11、 P12, L9-13, is there any direct evidence showing burnings in southern of the site in the same period?

Response: Yes. We've provided a fire spot map in Figure S7 in supporting information to show direct evidence of burnings in southern of the site.

12、 P12, L17-18, is that true that plastics will evaporate? Please add references.

Response: We have modified the sentence and added some references as follows: "...elevated temperature promotes the evaporation of phthalate esters from plastic products (Fujii et al., 2003; Wang et al., 2007)."

13、 P12, section 3.4.1, it is necessary to add methods to evaluate contributions of BB,

fungus spores and plant debris, etc., to OC.

Response: Thanks. The calculated methods for contributions of POC and SOC to OC were shown in the discussion. We have put this content in the method part (see Page 4, Lines 21-26).

14、 P13, L6, 'Table 12a-b, and 13' change to 'Figure 12a-b, and 13'.

Response: Thanks. We have corrected it as suggested in the revised manuscript (see Page 14, Line 19).

15、 P13, L6-10, fungus spore OC estimated by Zhu et al. (2016) is based on TSP samples. As these particles are quite large, they have large contributions to OC in their study. It is reasonable that fungus particles have small contributions to PM<sub>2.5</sub> samples.

Response: We agree that fungus spores and plant debris have large particle sizes and usually exist in coarse particles, while only some small fragments exist in fine particles with low content.

16、 P13, L16-17, it is necessary to add reference for the tracer mass fraction factors.

Response: We have added it as suggested on Page 4, Line 25.

17、 P14, L7-9, it would be better to add some reference about the possible plastic emissions if any.

Response: We have added references as suggested on Page 15, Line 23.

18、 Tables S3-4 were not referred in the text?

Response: Thanks. We have added it on Page 10, Lines 2-4.

## References:

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