

Dear reviewer,

We appreciate your comments and time on this manuscript, and we found the comments very helpful for us to improve the presentation of our data and interpretation. Besides most of your concerns about the "more robust sample-to-sample comparisons and statistics," we prepared the following analysis in the text and SI.

Indeed, the complex processes need to be carefully considered. Figures in supportive information illustrate the characteristics of the overall chemical composition of PM<sub>2.5</sub>, meteorological conditions, and near-surface wind speed and wind direction to provide a whole picture of the study. By following the requirement of the reviewer, we performed a comparison of formula numbers between all 52 samples, and we found that the diversity of results of FT-ICR MS was "stable and typical," as shown in Figure 1 in the reply. Based on the information, we are confident that the samples used in this manuscript can give a snapshot of the organic aerosol evolution in the region. Certainly, the analysis can cause uncertainties due to the limited amount of samples, and we discuss the limitations of the work in Atmospheric Implication to avoid possible misguidance. In addition, we have added the "case study" statement in the title.

For the specific comment, we have also prepared a point-to-point response to the comment, and the corresponding changes in the manuscript are also marked in the revision. We hope our efforts can meet your standard for publication. Again, all authors are thankful for the comments.

### **Reviewer 1**

My major concern with this paper is that it seems like one day of samples (four in total collected over one day) was used as a representative set for the entire field campaign (described at lines 96 and 139). The paper then proceeds to compare morning, afternoon, night, and overnight time periods with respect to various molecular features, but without more than one sample per time period, it is impossible to know whether any of

the trends that are discussed are meaningful. With highly variable emissions, oxidation conditions, and influx of air parcels carrying a wide range of fresh and oxidized species from different sources/oxidation conditions themselves, more data is needed to make reasonable conclusions about atmospheric processing given the extremely complex processes that the manuscript is trying to describe. Unfortunately I think this paper should be rejected in its current form and re-submitted upon inclusion of several more samples. It looks like 52 samples were collected over several weeks, so I'd like to see some of those incorporated into this analysis for more robust sample-to-sample comparisons and statistics. This work has the potential to yield very interesting results about the evolution of high molecular weight organic compounds, and I hope with more data we can learn more about their atmospheric chemistry.

Introduction:

Line 38: do you mean "due to the condensation of semivolatile vapors onto primary OA"? This part of the sentence is unclear.

**Response:**

Thanks for the suggestion. We have revised the sentence into (line 37):

"The condensation of semivolatile vapors that are more oxidized onto primary OA can lead to the evolution of OA during their atmospheric lives (Jimenez et al., 2009), and the evolution can also be caused by heterogeneous processes in aerosol phase (Ervens et al., 2011)."

Line 43: Suggest defining HULIS prior to using the acronym.

**Response:**

We have apprehended the definition of HULIS

Line 43: "Humic-like substances (HULIS)."

Line 46: I would consider phrasing this as "can generate nitrogen- and oxygen-

containing organics" for clarity.

**Response:**

We have changed it (lines 46-47): "...can generate nitrogen- and oxygen-containing organics"

Line 57: I would suggest adding a caveat here, e.g., "as a class of potentially light-absorbing..." since these properties depend heavily on chemical structure.

**Response:**

Accepted and changed (line 58).

Line 63: Suggest defining HUMIC before using the acronym.

**Response:**

Thank you, we have defined it in line 43.

Line 66: Suggest defining ESI before using acronym.

**Response:**

"ESI" has been defined as "electrospray ionization (line 68)".

Line 69: Do you mean "fatty acid"?

**Response:**

Thanks for the reminder. "Fat" is not a scientific term; we have revised it into fatty acid (lines 70-71).

Line 73: Perhaps could say "other nitrogen-containing functional groups" for clarity.

**Response:**

Revised as suggested (line 74).

Line 77-78: The sampling period labels are a bit confusing here but they make more sense in the Methods section when you describe which time of day they correspond to. Perhaps you can say "samples were collected for ## hours across the diel cycle" here

for clarity.

**Response:**

We have rephrased the sentence to:

“In this study, ambient PM<sub>2.5</sub> samples were collected for 5.5 hours for four samples in a daily cycle (lines 78-81).”

Materials and methods:

Line 95: Capital "T" missing in "total".

**Response:**

Corrected.

Line 96: Are you only considering 1 day's worth of samples for FT-ICR MS analysis? I strongly suggest using more than 1 day's worth of data here. A 52-sample dataset is strong; why weren't more days included here? Over how many days were those samples collected? This information is in Figure S1 but you should mention it in the main text.

**Response:**

Indeed, the inter-comparison between the results of different FT-ICR MS is consuming. We will emphasize that our study is mostly a case study and carefully laid out the limitations of this study in the Atmospheric Implication part.

By following the requirement of the reviewer, we performed a comparison between samples, and we found that the diversity of results of FT-ICR MS was "stable and typical," as shown in Figure 1 in this response.

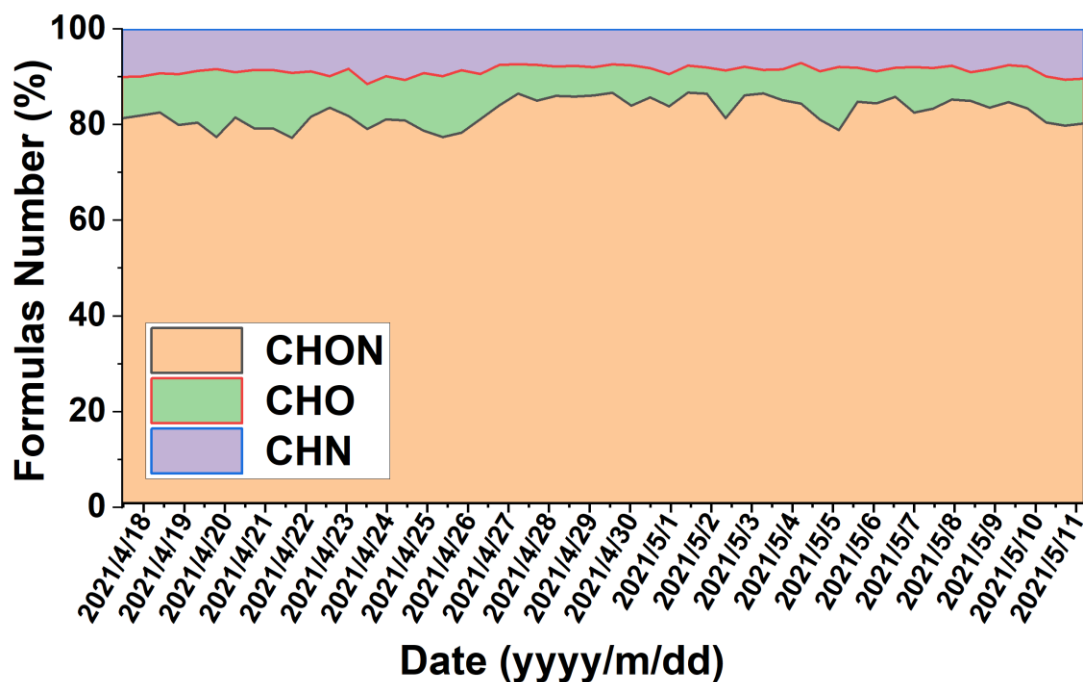


Figure 1 Ratios of formula numbers among the sampling period

The information in SI was added in Section 3.1 (Line 143), and the Figure 1 was also included in SI.

Line 102: Should be "sonication" instead of supersonic. Also, how many punches did you combine together? "The punches from the same collection time were immersed" sounds like you combined punches for extraction. If you use "ACN" later in the paragraph, please define it here.

**Response:**

We have revised "supersonic" to "sonication" in the corresponding sentence. The definition of ACN (Acetonitrile) has been added to the sentence (line 105).

Line 107: Can you clarify whether your acetonitrile extracts were then mixed with methanol for ESI analysis? If so, how do you know the concentration since these are field samples?

**Response:**

The sentence has been rephrased to:

“The mixture of acetonitrile extract was vaporized to dry. Then, the dry extract was reconstituted with water, and methanol was added proportionally in the water solution before FT-ICR MS analysis (lines 109-111).”

Line 115: I would like to see more description of this calibration procedure. Is this done in post-processing?

**Response:**

We have apprehended the following sentences into the SI:

The mass spectrometer was initially calibrated using sodium formate and then recalibrated with a known mass series in natural organic matter (Suwannee River fulvic acids), which contains a relatively high abundance of CHO formulae, providing a mass accuracy of 0.2 ppm or higher throughout the mass range of interest (line 20 in SI).

Line 121: All acronyms need to be defined (KMD, AI are new).

**Response:**

Sorry that we have moved the definition into SI. We have added the full description of them in the revision.

"Kendrick mass defect (KMD) were calculated according to Stenson et al." has been added at lines 123. The definition of AI is also apprehended (line 125).

Osc part: did you include only CHO species here, or are N and S included too? N and S can have different possible oxidation states and are not straightforward to include here unless you know the functional group they're present in (which you might). If you included them, I'd like to see more discussion on your approach. If you did not include them, I'd like to see more discussion on the impacts of leaving them out, given how important they are to your overall distribution (CHN and CHON especially, not really S since you mentioned you did not see it).

**Response:**

When calculating Osc, the two elements, Nitrogen and Oxygen, were considered. In

positive ESI mode, the valence of N was considered as -3. Also, S element was not considered because no S-containing molecules were detected in the sample in positive ESI mode. Therefore, we didn't put S into OSc calculation in CHN and CHON groups.

We have added this part of the explanation to the revision (lines 136-138).

### **Results and discussion:**

Line 136: Should be "sampling period" not "sampling site".

#### **Response:**

We have changed it (line 146).

Line 137: Typo, should be "especially".

#### **Response:**

Corrected (line 146).

Line 139: Emissions will change throughout your sampling period, as well as air parcel histories (as shown by your wind rose with air coming in from all directions). 1) Which meteorological conditions are you referring to and do you have data to show us that displays how stable they were during sampling? I do not think it is valid to select one day of samples and draw conclusions from that one day, given the immense expected variability in emissions locally, as well as air coming in from other locations, and possibly varying chemical conditions locally/regionally as well. Why was only one sample selected here? This weakens the paper and limits the conclusions you can make. If only one day's worth is available for analysis, I think the paper needs to be re-framed as a case study, with the limitations of having only one day very clearly laid out.

#### **Response:**

We thank the reviewer for this valuable question.

The representativity is the most important thing we have considered during the

preparation of this manuscript. As shown in Figure 2, wind direction and wind speed shifted in a typical diurnal cycle that varied in all directions. The windrose in Figure 1 is similar to Figure S1.

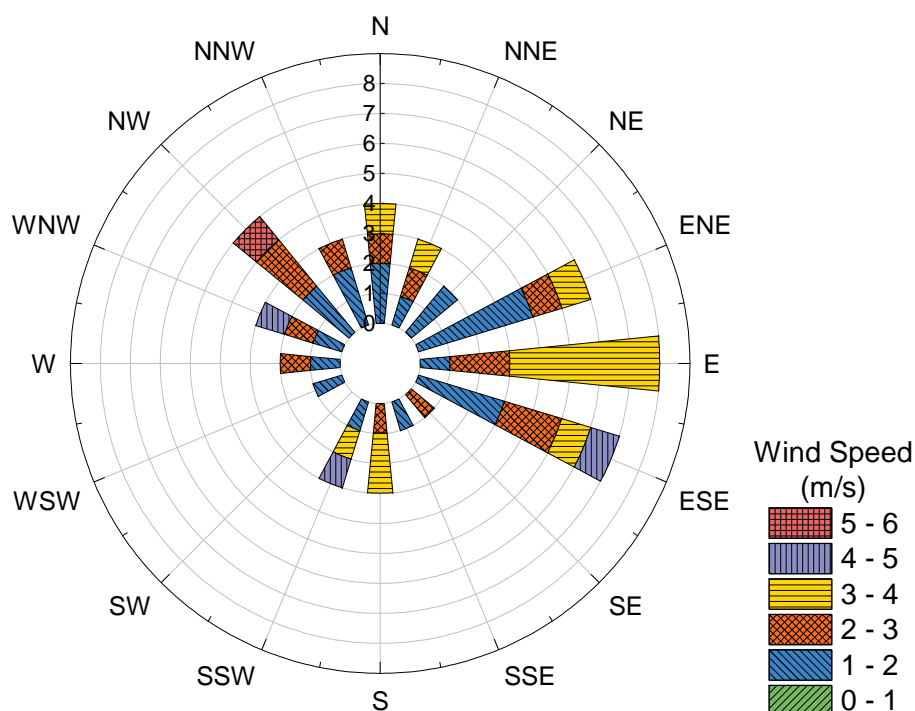


Figure 2. Windrose plot of the sampling day

Following the suggestion from the reviewer, we also performed an inter-comparison between different samples (Figure 1, provided above). We found that the proportion of CHO, CHON, and CHON remained stable, and the average of parameters of samples were close to the period statistics. Therefore, we are confident that the chosen day (20<sup>th</sup> April) can represent the chemical nature of the organic species during sampling periods.

We have added the following part in Atmospheric Implications:

“It is noticeable that there were some limits on this work. Under the variable emission, atmospheric process, and long-distance transport of organic aerosols, the samples can give a snapshot the evolution in the region, and the analysis can cause uncertainties.



Therefore, this work can be treated as a case study.” (Section 4)

Line 141-145: If this is based on just one day, it is challenging to draw meaningful conclusions/trends from any of these data. Comments from here on out don't address the data trends themselves since it is difficult to interpret these trends without more samples.

**Response:**

We provided enough evidence to convince the reviewer.

Line 160: Could you comment on how ionization efficiency might be impacting these statements?

**Response:**

The ionization efficiency is related to the molecular structure. In positive ion ESI mode, basic nitrogen compounds such as ammonia or pyridine compounds are easily ionized. Besides, ketone and ester groups can also be ionized. At the same concentration, the higher the ionization efficiency, the easier the compounds are ionized. Among the above compounds, ammonia has the highest ionization efficiency, followed by pyridine and, finally, ketone or ester. However, the ionization efficiency is also affected by other molecular structures, such as the steric hindrance due to the position of the side chain. So, in this study, most of the compounds detected are CHN or CHNO compounds.

Line 184: I noticed that here you talk about number frequency instead of intensity. It would be good to be consistent throughout your paper or explain why you are discussing different frequencies at different times.

**Response:**

The two terms, number frequency and relative intensity of formula were used with different conditions. This study uses number frequency to describe the complexity and diversity of organics among PM<sub>2.5</sub> samples. The normalized intensity can be used to evaluate the relative changes between different PM<sub>2.5</sub> samples. Therefore, we used both terms in different part of the description and discussion.

Line 186: I'd like to see more description of the meteorological conditions during sampling so we can get a better idea for what kind of photochemical conditions existed.

**Response:**

The summary of meteorological conditions is shown in the following Table 1.

Table 1. Summary of meteorological conditions

Temperature (°C)	Dew point (°C)	Pressure (hPa)	Wind direction (° )	Wind speed (m/s)
14.1	8.7	1018.1	70.4	2.2

It was in a typical spring photochemical condition.

Line 210: Are these necessarily POA of #O is 1-2? Could they be SOA after 1-2 generations of oxidation?

**Response:**

We agree with the reviewer that the OA of #O 1-2 can partially be SOA after oxidation. Our statement was mainly based on the local emission pattern that coal and traffic from heavy-duty diesel vehicles that was only allowed to inter the urban areas at Night.

Then we have changed the statement into:

"The batch of primary OA and less-oxidized SOA was also observed, such as CHO compounds with carbon atoms between 45–50, DBE between 5–10, and O atoms between 0 and 2." (lines 220-221)

Line 245: As mentioned above, did you account for N in these OSc calculations, as it can have different oxidation states depending on the functional group structure? Since you see so much CHON, I suggest discussing how you included it or why you excluded it and what impacts that might have on your results.

**Response:**

When calculating the OSc of CHON-like compounds, the oxidation state of N is also

taken into account, and N valence was -3.

In general, I found the figures interesting but containing a very large amount of data without much guidance to readers about which parts we should focus on. Many of the panels looked very similar at least without zooming in on interesting regions or circling parts that we should pay attention to. I suggest adding some information to help guide readers through these panels and to help point out differences between panels that we should focus on.

**Response:**

Thanks very much for the suggestion. Indeed, we have a very complex data matrix to interpret. In the revision, combined with the suggestions from reviewers, we also improved the presentation of data for readability.

SI:

Lines 25-29: Are there references for these constraints?

**Response:**

The following references have been added in the SI:

He, C., Zhang, Y., Li, Y., Zhuo, X., Li, Y., Zhang, C., Shi, Q., 2020. In-House Standard Method for Molecular Characterization of Dissolved Organic Matter by FT-ICR Mass Spectrometry. ACS Omega 5(20), 11730-11736.

Kujawinski, E.B., Behn, M.D., 2006. Automated analysis of electrospray ionization fourier transform ion cyclotron resonance mass spectra of natural organic matter. Anal. Chem. 78(13), 4363-4373.

Lines 30-36: Are there references for these compound class attributions?

**Response:**

The following references have been added in SI:

Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I.G.N.A., Schnetger, B., Niggemann, J., Simon, M., Dittmar, T., 2014. Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochim. Cosmochim. Acta* 140(1), 418-434.

Antony, R., Grannas, A.M., Willoughby, A.S., Sleighter, R.L., Thamban, M., Hatcher, P.G., 2014. Origin and sources of dissolved organic matter in snow on the East Antarctic ice sheet. *Environ. Sci. Technol.* 48(11), 6151-6159.

## References

Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I.G.N.A., Schnetger, B., Niggemann, J., Simon, M., Dittmar, T., 2014. Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochim. Cosmochim. Acta* 140(1), 418-434.

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