

Dear Editor,

we sincerely thank you very much for handling this manuscript. As the request, we have prepared a point-to-point response to all the questions from two reviewers. We hope this response will be satisfactory for both you and them. Again, thank you very much for your work, and we are very glad to contribute to the ACP journal for now and the future.

Introduction: I suggest making the fact that this is a case study of a small subset of samples very clear right away in the introduction to set the realistic scope of the work from the start. Maybe around line 84, “The molecular-level characterization of HMWOC was explored for a subset of four samples, one representing morning, afternoon, night, and midnight”.

Response: accepted and done (Line 83).

Methods: I apologize if I missed this, but were peaks from blank filters subtracted from the sampled filters? I see this was also asked by the other reviewer but I cannot see that it was addressed in the manuscript. I recommend very clearly stating your blank subtraction procedure in the text, as it is very difficult to interpret any of the results without understanding how you accounted for filter blanks or solvent blanks.

Response:

The following statement has been added in Section 2.2 (Lines 119-121)

“Extraction blanks and solvent blanks were prepared and analyzed to check for possible contamination. Contaminated peaks in these blanks were removed from organic aerosol samples.”

I thank the authors for including the extra SI figure (S4) to address my question about whether there were only a small # of samples included in the analysis and how representative those samples were. It is nice to see that the bulk composition of the aerosol remains consistent across samples. It does look like you have some nice data

from all 52 samples, from the data you put into Figure S4, so I would have loved to see more of it incorporated in the paper. Just because the bulk composition is similar across all 52 samples, it does not mean that you have the same distribution of species within each ion class (e.g., CHO, CHN, CHON), so I still would have loved to see more samples incorporated to the paper since the data do seem to exist and be somewhat processed already. However, I am fine with the current “case study” framing if only 4 samples can be fully incorporated.

Response:

We sincerely appreciate the understanding of the reviewer. Since we have a large data set which is 52 samples, we designed our research framework to dig the dataset. Later on, we would discuss the whole 52 samples of those high molecular weight compounds with their chemical nature, volatility, and source in different articles. Indeed, we will carefully treat the data quality.

Thanks for including the description of how you included N in your OSc calculations. Assuming only a valence of -3 would still introduce some error, especially for the CHON species that are not organonitrates or nitro groups. For CHON, I suggest adding a brief caveat that mentions the possible range of N valence states that could exist in CHON compounds (e.g., you could have a CHON species that's an amine + a carbonyl, rather than an oxidized N atom). Also, did you mean +3 instead of -3 if you have mostly ONO<sub>2</sub> or NO<sub>2</sub> groups?

Response:

Indeed, a valence of -3 of nitrogen can cause uncertainties. To our knowledge, the issue is quite complicated. Indeed, a complex amine compound with a carbonyl or carboxylic acid can also be a CHON molecule.

Reviewer response:

Thank you for your revisions and your comments. I recommend the following minor changes before acceptance.

1. Thank you for your comments and for the peak list. I understand many of your points in the response, however, I do not see corresponding changes to the manuscript that address them. Please revise the manuscript to address these concerns (either the main manuscript or the supplemental). If you feel that a concern does not warrant a change, please provide more justification for that. Specifically, please include information in the manuscript or in the supplemental that addresses:

A. How the isotopes were handled.

B. How the Na<sup>+</sup> ions were identified. I am especially interested in how decisions were made to between choices like formula with many nitrogen atoms compared to one that has fewer Nitrogen atoms and a Na<sup>+</sup> ion as an adduct.

C. How the blanks were handled.

D. What fraction of the peaks had a molecular formula assigned to them.

For this last point, I am asking what fraction of the total peak list you were able to assign molecular formulas to. This is often not 100% and it is helpful to know for future researchers because the list of peaks that is provided is often just the identified formulas.

Response:

A:

“The <sup>13</sup>C, <sup>18</sup>O and <sup>15</sup>N isotopic molecules were also assigned and analyzed when molecular formula assignment was performed.” has been added in *supportive information (Line 28)*.

B:

In the raw spectra, we manually compared the mass deviations of the Na-containing and H-containing peaks corresponding to the same molecular formula, which are very close to each other. In addition, we combined the distribution characteristics of the isotopic peaks to distinguish between many nitrogen atoms compared to one that has

fewer Nitrogen atoms and a Na<sup>+</sup> ion as an adduct.

“Considering that the number and relative abundance of [M+Na]<sup>+</sup> ions are lower than those of [M+H]<sup>+</sup> ions , only [M+H]<sup>+</sup> was counted and analyzed.” has been added in *supportive information (Line 30)*.

C:

“Extraction blanks and solvent blanks were prepared and analyzed to check for possible contamination. Contaminated peaks in these blanks were removed from organic aerosol samples.” has been added in Section 2.2 (Line 120)

D:

About 50% of mass peaks had a molecular formula assigned to them.

2. I am following up on the following comment in the response to review document:

On page 19: "the carboxylic acid functional group can be removed due to the reaction with acids such as HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, or be neutralized by NH<sub>3</sub> in the particle phase."

I am very confused by this statement. What chemical reactions are occurring between carboxylic acids and nitric or sulfuric acid? Do you have references for this chemistry? How would neutralization of the acid impact the measurements in this case? The only impact I can see is a change in solubility (possibly) but the carboxylic acid should still be present.

Author's Response:

We are sorry for the ambiguous interpretation of the result.

1. Reactions between nitric acid and carboxylic acid can form organonitrate. For example, Lim et al. (2016) reported organonitrate formation from the reactions between glyoxal and nitric acid in a chamber study. The reaction occurred on wet aerosols via HNO<sub>3</sub> In this work, we found a similar process can occur on large organic molecules in the aerosol phase.

2. Likewise, carboxylic acid can also react with sulfuric acid to form Organosulfate in the aerosol phase (Darer et al., 2011).

3. Carboxylic acid can react with ammonia to form ammonium salt or reduced N-containing particles like pyridine (Zarzana et al., 2012). This process might not impact the measurement but on the environment because the products commonly can absorb light to alter the optical properties of aerosols.

We have modified the following statement to clarify our purpose on this part (lines 291-295):

"...and the carboxylic functional group can be due to the reaction with acids such as HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to form organonitrate and organosulfates or be neutralized by NH<sub>3</sub> to form ammonium salt or reduced N-containing compounds in the particle phase (Lim et al., 2016; Darer et al., 2011; Zarzana et al., 2012). In previous studies, those processes were proven to occur in small carboxylic acids. In this work, we can observe a similar process on HMWOCs"

My new Reviewer's response: I recommend being more careful with the language here. I do not think the references that you are using are specifically showing this as a reaction that can occur with carboxylic acids. I do not disagree that this reaction may be possible, but saying that "those processes were proven to occur in small carboxylic acids" needs to be re-written if you are using those references.

Response:

we appreciate the caution of the reviewers. The description in this part was inappropriate. The formation of organonitrates and organosulfate was mainly from the reaction between HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> with alcohols or carbonyls. Carboxylic acid can be removed by reacting with free radicals, ammonia, or other base substances. Therefore, we have revised the part to:

The sentence has been revised to (Lines 292-294):

"...The sinking of carboxylic acids can be done by reacting with free radicals, ammonia, or other base substances to form oligomers, other carbonyl acids, reduced nitrogen-containing compounds, or salts (Ervens et al., 2011).

## References

Ervens, B., Turpin, B.J., Weber, R.J., 2011. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. *Atmos. Chem. Phys.* **11**, 11069-11102. <https://doi.org/10.5194/acp-11-11069-2011>.