

## ***Interactive comment on “Molecular Characterization of Polar Organic Matters in Off-road Engine Emissions Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS): New Direction to Find Biomarkers” by M. Cui et al.***

### **Anonymous Referee #2**

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#### Summary and Recommendation:

This study applied FR-ICR MS equipped with electrospray ionization (ESI) to chemically characterize polar organic compounds emitted from off-road engine combustion sources. The authors generated these emissions from engine types that appear to be relevant to China. The intentions of this study are very good, and will certainly be of interest to the readership of Atmospheric Chemistry and Physics. However, there

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are many shortcomings with the present manuscript that I will outline below in detail with my specific comments. In short, there are two major issues with this manuscript: (1) although the authors are likely not all native-English speakers, I found many portions of the text hard to follow or even distracting due to the poor English grammar or misspellings. In my technical (minor) comments below I outline some of them, but I don't feel the burden should be on reviewers to correct all of these mistakes; and (2) the chemical method (or approach) used to chemically characterize the polar organic aerosol constituents is flawed in how it was operated and this needs to be thoroughly addressed before I can recommend this manuscript for publication in ACP. Due to the nature of my specific comments below, I must recommend this manuscript be reconsidered after major revisions.

#### Specific Comments:

##### 1.) Lack of Chromatographic Separation Before ESI-MS Detection:

My biggest concern with this study is the lack of chromatographic separation before ESI-FT-ICR MS detection. Since chromatographic separation was not used, the authors were forced to utilize SPE to desalt the filter samples. The reason for this desalting step is that inorganic ions can cause unwanted adduct formations and ion suppression effects during ESI-MS analyses, both of which can lead to a misinterpretation of the "actual" chemical composition of polar organic aerosol constituents. Without chromatographic separation, such as reverse-phase liquid chromatography (RPLC) or hydrophilic interaction liquid chromatography (HILIC), it is difficult to resolve isomers from each other and also due to ion suppression/matrix effects that result from direct infusion (which was done here) quantitating is near impossible. Thus, the authors are forced to only report molecular formulas. So the qualitative results reported here is thus how many number of ions were detected with CHO, CHON, CHOS, and CHONS. Just because you may have a large number of a certain type of chemical class, doesn't necessarily translate into abundance of polar organic material. The authors imply that simply having ultra-high mass resolution is enough to justify the results from this study.

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I would argue this is only true if the complex organic matrix is chromatographically separated online before ESI-MS detection. ESI-MS is notoriously known to have major issues if this is not done.

Finally, one major issue with the SPE method as described here is you severely risk removing the most polar and water-soluble organic compounds that can't be retained by the Oasis HLB SPE cartridge. Previous field samples analyzed by both Gao et al. (JGR) and Surratt et al. (2007, ES&T) from the Seinfeld group at Caltech revealed that SPE caused isoprene-derived SOA constituents, which are very polar and water-soluble, to be completely removed during SPE treatment. As a result, the isoprene SOA constituents were not reported in Gao et al. (2006, JGR).

At minimum, the authors need to address these limitations either in the experimental method and/or in the results and discussion section.

2.) Experimental Section, Filter Extraction Method:

Were quality control tests conducted to ensure that organic aerosol constituents were effectively removed from the filter media during filter extraction? If not, this should likely be done and reported in a revised manuscript. Also, how much negative artifacts (or losses) do you expect occur during your filter extraction process? Also, by using water to extract the filters by sonication, do you worry that oxidants (e.g., OH radicals) are produced that can degrade your aerosol constituents or even transform them into unintended products?

3.) Experimental, Page 8, Lines 9-18:

How many quartz filters were combined for extraction for chemical analyses? Was it 5 filters collected from the same vessel and operating condition?

4.) Experimental, Filter Collection Details:

What was the flowrate used for PM<sub>2.5</sub> sampling? Did you have denuders? If not, what potential positive artifacts occurred on your quartz filters when conducting the

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molecular composition analyses? Don't you expect some absorption of semivolatiles on these filters?

5.) I would consider changing title to:

Molecular Characterization of Polar Organic Aerosol Constituents in Off-Road Engine Emissions Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS): Implications for Source Apportionment

6.) Page 19, Line 10:

The authors might want to look at Riva et al. (2015, ES&T) from the Surratt group. They found that sulfur-containing products from PAHs were possible, and may not be solely sulfates but also sulfonates, especially with O/S values of 4-5. It would be interesting to know if you observed any of these PAH-derived OS products that they generated in the lab from PAH oxidations in the presence of sulfate.

7.) Page 20, Lines 1-6:

Are the authors also familiar from work published by Riva et al. (2016, ACP) from the Surratt group on organosulfates from the oxidation of long-chain alkanes. It would be interesting to know if you observed similar molecular formulas to that study.

Minor (technical) Comments:

1.) Abstract: The last sentence of the abstract needs to be completely re-worded. The current sentence is poorly worded and not easy to understand.

2.) I would change "polar organic matters (POM)" to polar organic compounds (POCs).

3.) Introduction, Page 6, Lines 6-8:

Change this sentence to state:

"This study aimed to chemical characterize polar organic aerosol constituents at the molecular level that are emitted from typical non-road engines by FT-ICR MS to provide

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new aerosol marker compounds for non-road engines."

4.) Page 7, Line 5: Do you mean to say "plume" instead of "flume" ?

5.) Experimental Section, Page 8, Line 14: Delete "continually"

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