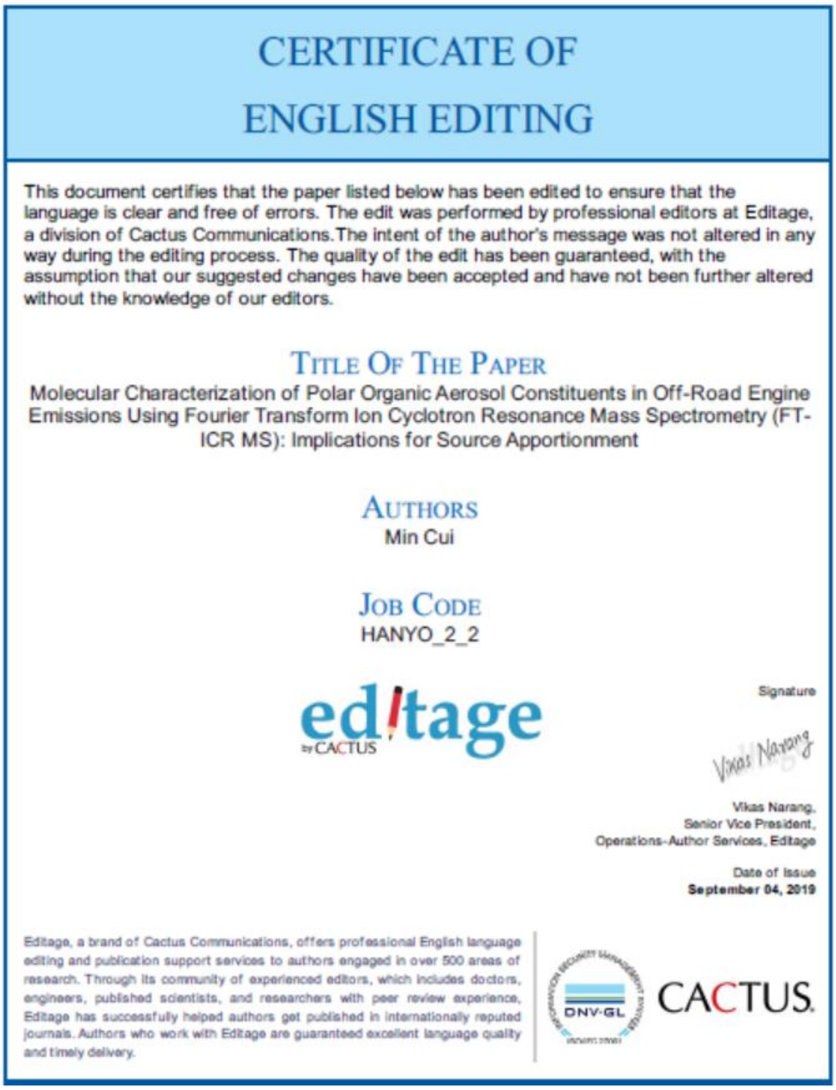
Thank you so much for your consideration! Also, the anonymous reviewer's comments are highly appreciated! So far, we have revised the manuscript accordingly. Our point-by-point responses (in black) to each reviewer's comments are listed below. And the modifications in the revised manuscript with marks are marked in blue. Please see the manuscript for details.

Comment #1: Firstly, the English should be substantially improved before I can comprehensively evaluate the quality and value of the paper. The ACPD language and writing skills in the present manuscript seriously hinder the transferring of knowledge to the readers, as well as the objective evaluation on the work. I would recommend the manuscript to be edited by an editing company.

Response: Thanks. A professional language editing company has thoroughly polished and edited the revised manuscript (**Fig. R1**).



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TITLE OF THE PAPER
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

AUTHORS
Min Cui

JOB CODE
HANYO_2_2

editage by CACTUS

Signature

Vikas Narang

Vikas Narang,
Senior Vice President,
Operations-Author Services, Editage

Date of Issue
September 04, 2019

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Figure R1 Certificate of english editing

Comment #2: The knowledge gaps illustrated comment in the introduction include (1) the unavailability of unique tracers for separating the on-road and off-road engine emissions; and (2) the challenge in detecting the large molecule and polar markers by the conventional GC-MS. However, I do not think the study filled the gaps sufficiently. How will the elemental compositions of off-road engine emissions contribute to the identification of these emissions in airborne particulate matters? Obviously, the molecular information of the tracers inferred in this study is inadequate. How about the differences in elemental compositions between the on-road and off-road engine emissions? Can the findings in this study be directly used in the concurrent source apportionment techniques, such as the filter based and AMS based source apportionment? In other words, there should be a section in this paper showing the implications of the study.

Response: We appreciate the reviewer's constructive suggestion. We recognize that the knowledge gaps illustrated in the introduction might not necessarily be filled with the results presented. Thus, some modifications and discussions were added in introduction and implications in the revised manuscript (**Page 4 lines 13-15; Page 5 lines 20-22; Page 6 lines 1-8; Page 23 lines 1-6; Page 27 lines 1-22; Page 28 lines 1-22; Page 29 lines 1-4**).

The purpose of this research was divided into two aspects in the revised introduction. One was to investigate the characterization of polar organic constituents at the molecular level to serve as molecular markers from off-road engines (**Page 4 lines 13-15**), which was sparsely reported in previous research. Meanwhile, the differences between the chemical characterization of polar organic matters (POCs) emitted from various sources were discussed in the revised implications (**Page 27 lines 1-22; Page 28 lines 1-22; Page 29 lines 1-4).** Moreover, we found that the organosulfates or sulfonates with condensed aromatic rings could be a unique tracer for heavy-oil fueled vessel emissions.

The other objective was to speculate the possible chemical structure of N-containing and S-containing organic compounds. These are considered one of the most important secondary organic aerosols (SOA) and HUmic-LIke Substances (HULIS) in the atmosphere to provide useful information to identify the significant role of off-road engine combustion in climate change or SOA formation (**Page 5 lines 20-22; Page 6 lines 1-8)**. By comparing the sulfur-containing products observed in this study and the chamber experiment, it was interesting to have found that some PAH-derived OS products generated in the lab also have significant response in field measurements **(Page 23 lines 1-6)**. We concluded that a high abundance of S-containing compounds in the atmosphere might come from secondary photochemical reactions as well as directly from the combustion of off-road engines.

Comment #3: Improve the English throughout the manuscript. Lines 13-15, page 3, line 1, page 4, lines 10-13, page 4. Too many grammatical errors, and I cannot list of them here.

Response: Thanks. A professional language editing company has thoroughly polished and edited the revised manuscript.

Comment #4: Methodology: How many samples were collected in total and in each scenario? How did you combine the samples? What was the purpose of combining the samples given the expected enough loading of PM for chemical analysis? How to consider the variations among the samples collected in the same scenarios? The representativeness of the samples should be discussed.

Response: As shown in **Table S1**, we selected four excavators, two diesel-fueled vessels, and two HFO-fueled vessels. For each excavator, we sampled from three operation modes. There were two important reasons to combine the samples. First, to get enough loading of organic matter. The second was that the analysis of FT-ICR MS samples was cost-prohibitive. We believed that combining samples from the same types of vehicles on the same operation modes could remove the random error, which could better represent the average emission status (**Page 10 lines 6-9**).

Comment #5: Off-road and non-road are alternatively used. Keep consistent throughout.

Response: Thank you. We have used “off-road” throughout the revised manuscript.

Comment #6: Lines 5-8, page 12: Do you mean Printer-friendly version the number of peaks for CHO compounds? The similarly inaccurate descriptions appeared many times in the manuscript, which need to be double checked and clarified.

Response: Thank you. We have checked the inaccurate descriptions, and modified them throughout the revised manuscript.

Comment #7: Lines 8-12, page 12: What are the ranges of number of peaks detected in biomass and coal combustions, and the references?

Response: Thank you. We have added the ranges of the number of peaks detected in biomass and coal in the revised manuscript, along with the references (**Page 15 lines 6-7**).

Comment #8: Lines 1-5, page 14: References must be provided to support the interpretations on the regions in Figure 2. 7. Lines 9-13, page 16: How does kinematical viscosity account for the high oxygen content in HFO-fueled vessel emissions?

Response: References have been provided to support the interpretations of the regions in **Fig. 2** in the revised manuscript (**Page 16 lines 13-16**). It was reported that the atomization of fuel drops was strongly attributed to their kinematic viscosity (Örs et al., 2018). High viscosity lead to poor atomization, which could cause incomplete combustion and result in an increased number of oxygen attachments onto the organic matter. Furthermore, high viscosity always accompanied high fatty acid compounds containing higher oxygen contents (Ramos et al., 2009).

"As shown in **Fig. 2**, region 1 represented monocarboxylic acid, which was more abundant in both idling and moving modes than in the working mode (Wozniak et al., 2008; Lin et al., 2012). Region 2 represented compounds with low ratios of H/C and O/C and DBE>10 which were commonly considered as condensed hydrocarbons (Wozniak et al., 2008; Lin et al., 2012)."

References:

[1] Wozniak, A. S., Bauer, J. E., Sleighter, R. L., Dickhut, R. M. and Hatcher, P. G.: Technical Note: Molecular characterization of aerosol-derived water-soluble organic carbon using

ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Atmospheric Chemistry and Physics, 8 (17): 5099-5111, 2008.

[2] Lin, P., Rincon, A. G., Kalberer, M. and Yu, J. Z.: Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, Environmental Science & Technology, 46 (14): 7454-7462, 2012.

[3] Örs, I., Sarıkoç, S., Atabani, A. E., Ünalan, S. and Akansu, S. O.: The effects on performance, combustion and emission characteristics of DICI engine fuelled with TiO_2 nanoparticles addition in diesel/biodiesel/n-butanol blends, Fuel, 234: 177-188, 2018.

[4] Ramos, M. J., C. M. Fernandez, A. Casas, L. Rodriguez and A. Perez. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour Technol 100(1): 261-268, 2009.

Comment #9: Lines 4-6, page 17. I do not get the point why the discussions only focus on the excavators under the working mode and vessels using HFO, given that the CHON structures were different even among the excavators as mentioned in Interactive the previous sentence.

Response: We are thankful for the reviewer's kind suggestion. The main structures of the CHON group from excavators under three operation modes and vessels using HFO and diesel were illustrated in **Fig. 3** in the revised manuscript. Although the fractions of the CHON group for excavators under different operation modes were different, the probable chemical structures were exactly the same, as shown in Figure 3. The meaning of the referred sentence might seem incorrect. Thus, the sentence has been deleted, and the structures of all the off-road engines were discussed in the revised manuscript (**Page 21 Figure 3**).

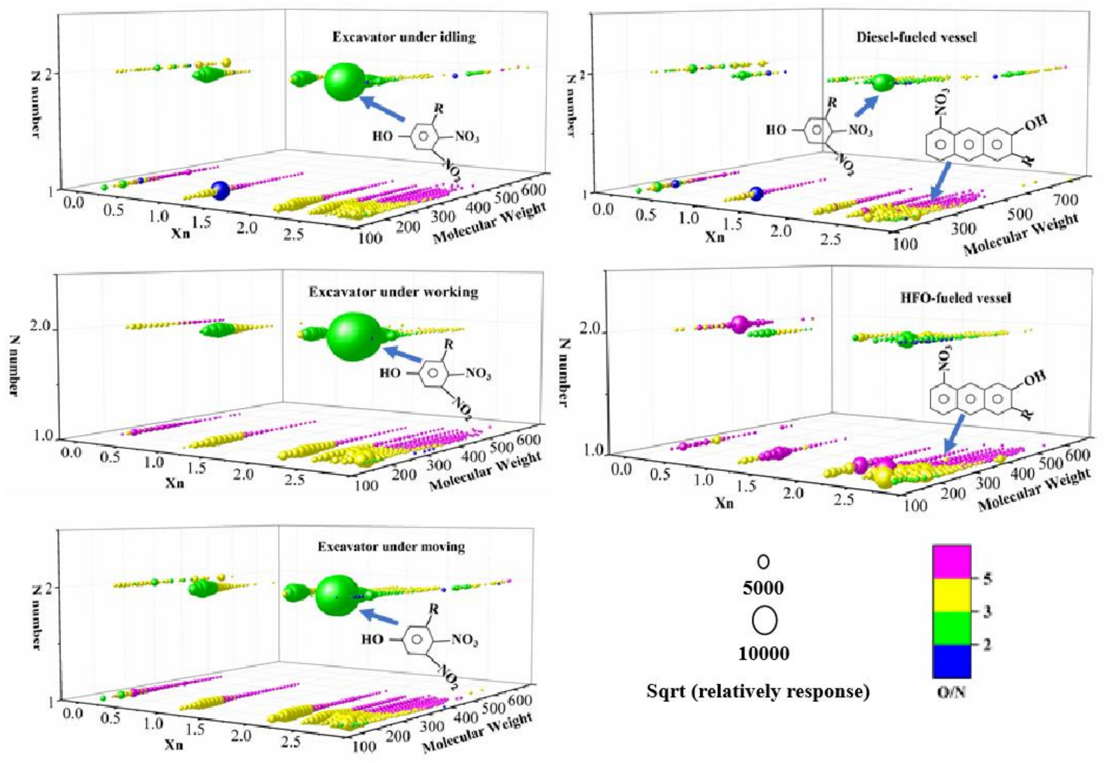

Figure 3 Molecular composition and possible structure of CHON for excavators under three modes and vessels using HFO and diesel

Comment #10: Lines 8-20, page 17: The inferences on the structures of CHON must be illustrated in more details. Was any of the proposed compounds ever reported in previous studies?

Response: Thank you for pointing this out. Detailed inferences on the structures of CHON were illustrated in the revised manuscript (**Page 19 lines 21-22; Page 20 lines 1-9**). The proposed compounds were also reported in previous research (Yassine et al., 2014; Tong et al., 2016).

"As mentioned, the most abundant relative responses of CHON group for diesel-fueled excavators and vessels were $C_{10}H_5N_2O_5$, $C_{11}H_7N_2O_5$, and C12H9N2O5, which compose the largest green ball in **Fig. 3** with Xn=2.5, indicating the presence of a benzene core structure in the compounds. Thus, it was most likely dinitrophenol, and methyl dinitrophenol compounds. Likewise, $C_{10}H_4NO_6$, $C_9H_4NO_4$ and $C_{10}H_4NO_7$

comprise the largest yellow ball in Fig. 3 for HFO-fueled vessels, most of which have Xn>2.7 indicating the presence of condensed aromatic compounds. Nitronaphthol and methyl nitronaphthol were the most significant compounds arising from HFO-fueled vessel emissions, which have previously been reported in vehicle emissions (Yassine et al., 2014; Tong et al., 2016)."

References:

[1] Yassine, M. M., Harir, M., Dabek-Zlotorzynska, E. and Schmitt-Kopplin, P.: Structural characterization of organic aerosol using Fourier transform ion cyclotron resonance mass spectrometry: Aromaticity equivalent approach, Rapid Communications in Mass Spectrometry, 28 (22): 2445-2454, 2014.

[2] Tong, H. J., Kourtchev, I., Pant, P., Keyte, I. J., O'Connor, I. P., Wenger, J. C., Pope, F. D., Harrison, R. M. and Kalberer, M.: Molecular composition of organic aerosols at urban background and road tunnel sites using ultra-high resolution mass spectrometry, Faraday Discussions, 189: 51-68, 2016.

Comment #11: Figure 3: I do not think the structures of dinitrophenol and methyl dinitrophenol have been correctly presented in Figure 3, same for nitronaphthol and methyl nitronaphthol. Please clarify.

Response: Thanks. The correct structures have been redrawn in **Fig. 3** in the revised manuscript (**Page 21 Figure 3**).

Comment #12: Lines 1-6, page 20. What are the bases that the conclusions can be drawn? For example, "The most of S-containing compounds emitted from off-road diesel engines were aliphatic with long chains and sulfate fraction".

Response: Thanks for your suggestion. The bases have been drawn in **Fig. 5** in the revised manuscript (**Page 26 Figure 5**).

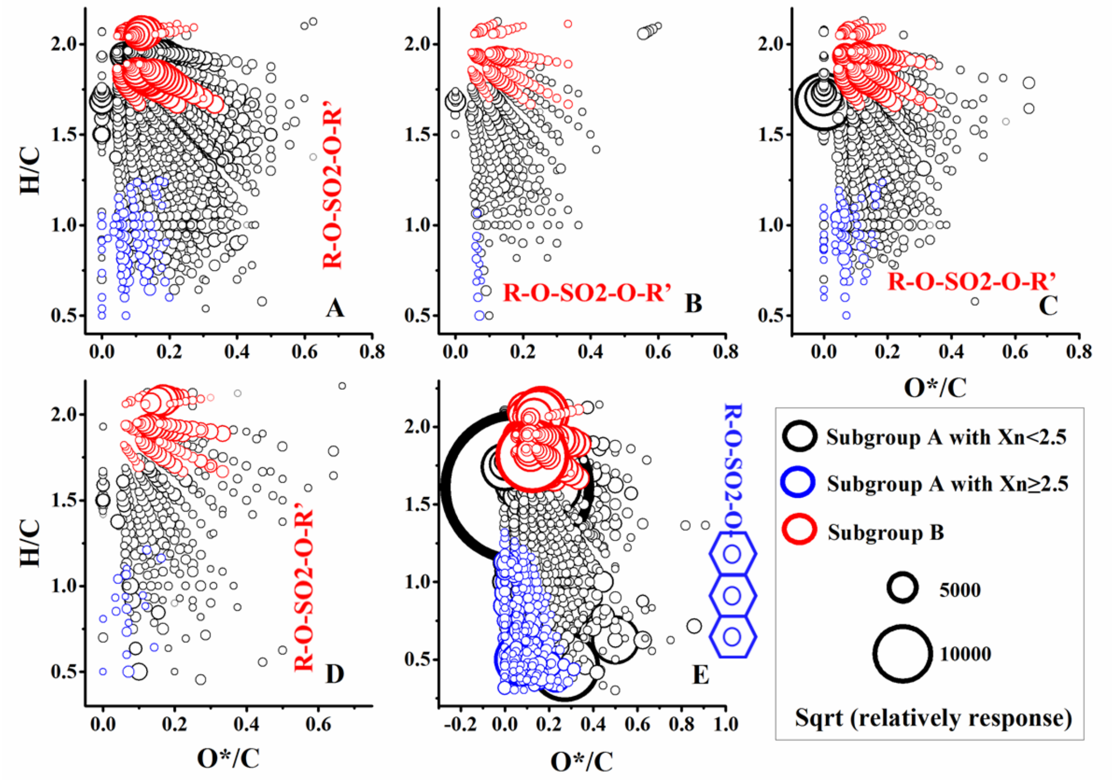

Figure 5 The ratios of O*/C vs H/C of CHOS and proportion of subgroup B and Xn>2.5 for off-road engines (A, B, C, D and E were the mass spectra for excavators under the idling, working, moving and vessels using diesel and HFO, respectively)

Comment #13: Lines 9-11, page 20: Descriptions should be more accurate. I suppose you mean that organic sulfates were the most important S-containing compounds emitted from off-road engines.

Response: Thanks for your kindly suggestion. The sentence has been modified in the revised manuscript (**Page 24 lines 14-16**).

"On an average, 88.5%±9.1% and 98.1%±0.22% of CHOS compounds for vessels and excavators respectively were with O/S⩾4, which indicated that organic sulfates or sulfonates were the most impactful S-containing compounds emitted from off-road engines."

Comment #14: Line 12, page 20: This expression "O*(O-3)" will mislead the readers. Change it to O* (O* = O - 3).

Response: Thanks for reminding. The suitable expression has been changed in the revised manuscript (**Page 25 line 1**).

Comment #15: As mentioned earlier, the implications of this study should be summarized and clearly demonstrated, rather than a simple summary of the findings.

Response: Thank you for your kindly suggestion. The implication of this study has been summarized in the revised manuscript (**Page 27 lines 1-22; Page 28 lines 1-22; Page 29 lines 1-4**).

Comment #16: English and writing skills must be substantially improved. Otherwise, it will be impossible for this paper to be published on ACP.

Response: Thanks. A professional language editing company has thoroughly polished and edited the revised manuscript.