Response to the Reviewers' comments

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

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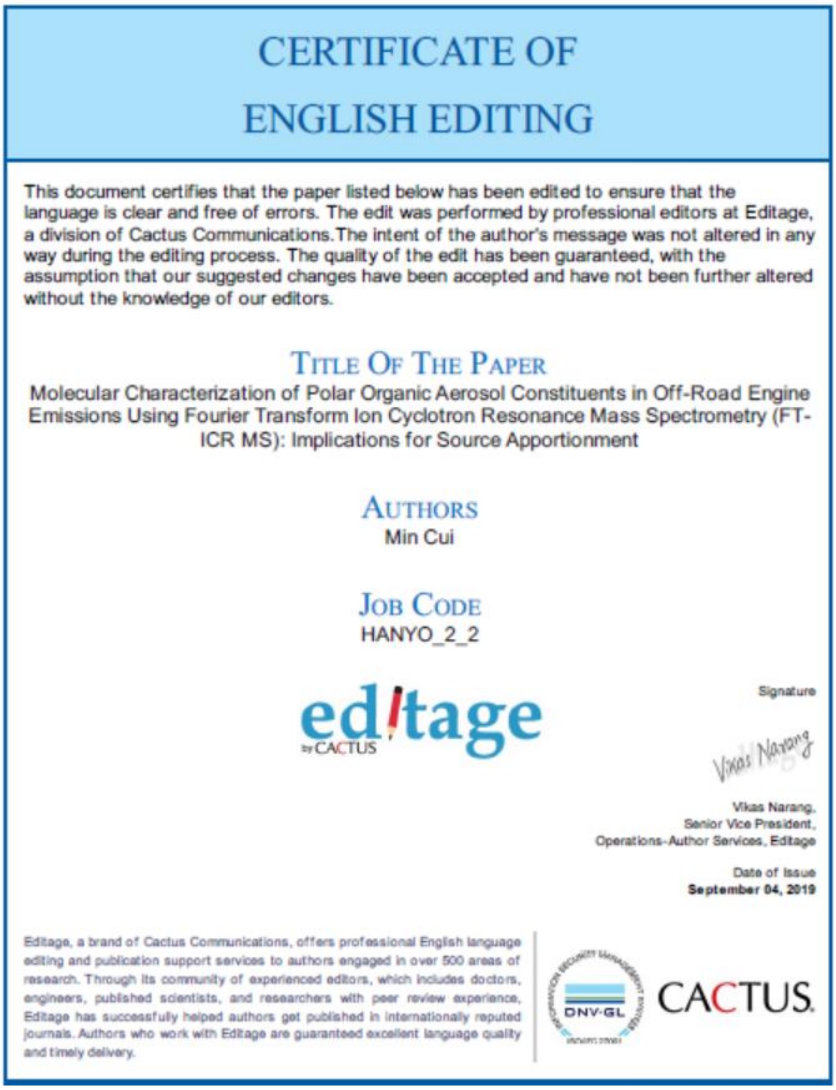
Thank you so much for your consideration! Also, the anonymous reviewer's comments are highly appreciated! So far, we have revised the manuscript accordingly. Our point-by-point responses (in black) to each reviewer's comments are listed below. And the modifications in the revised manuscript with marks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

Response to reviewer's 1

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

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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**).

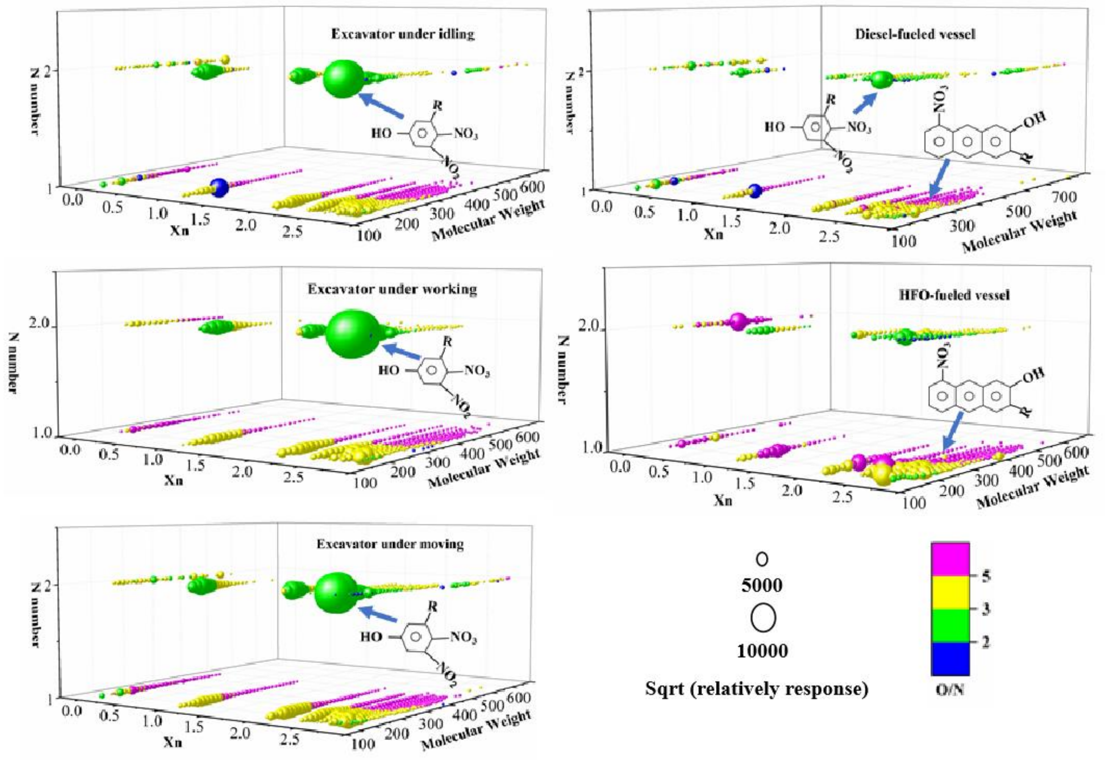


Figure 3 Molecular composition and possible structure of CHON for excavators under three modes and vessels using HFO and diesel

<u>Comment #10</u>: 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?

<u>**Response:**</u> 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**).

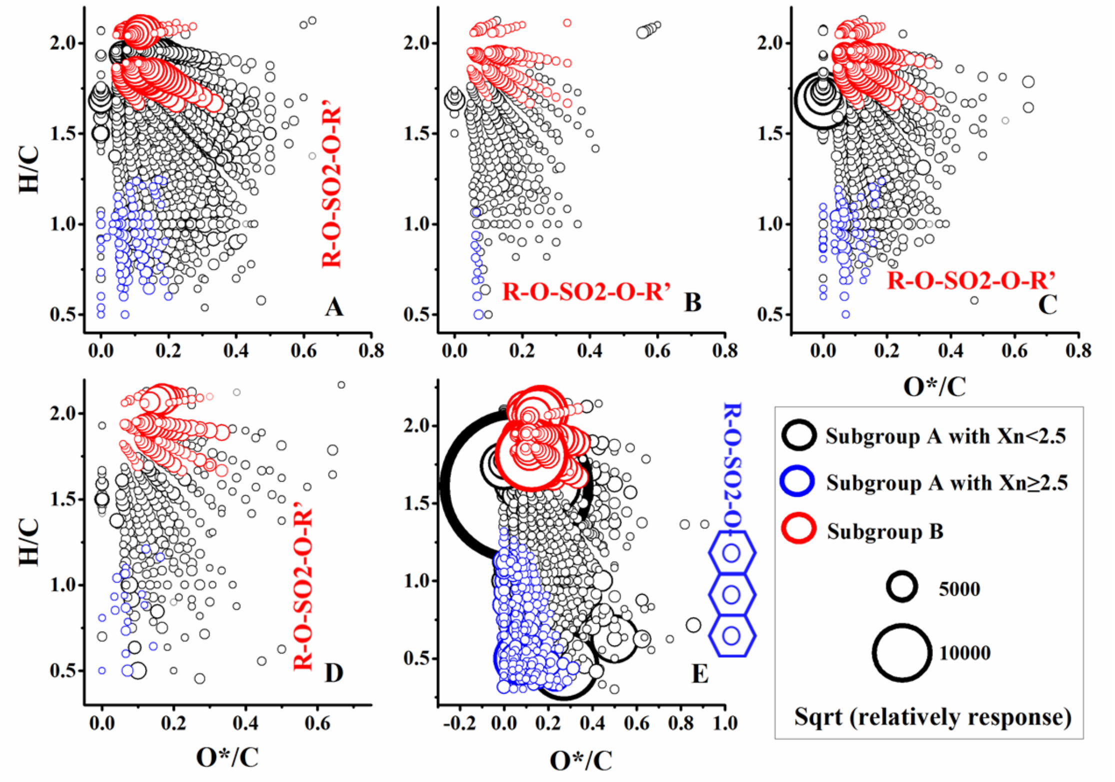


Figure 5 The ratios of O*/C vs H/C of CHOS and proportion of subgroup B and Xn>2.5 for off-road engines (A, B, C, D and E were the mass spectra for excavators under the idling, working, moving and vessels using diesel and HFO, respectively)

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**).

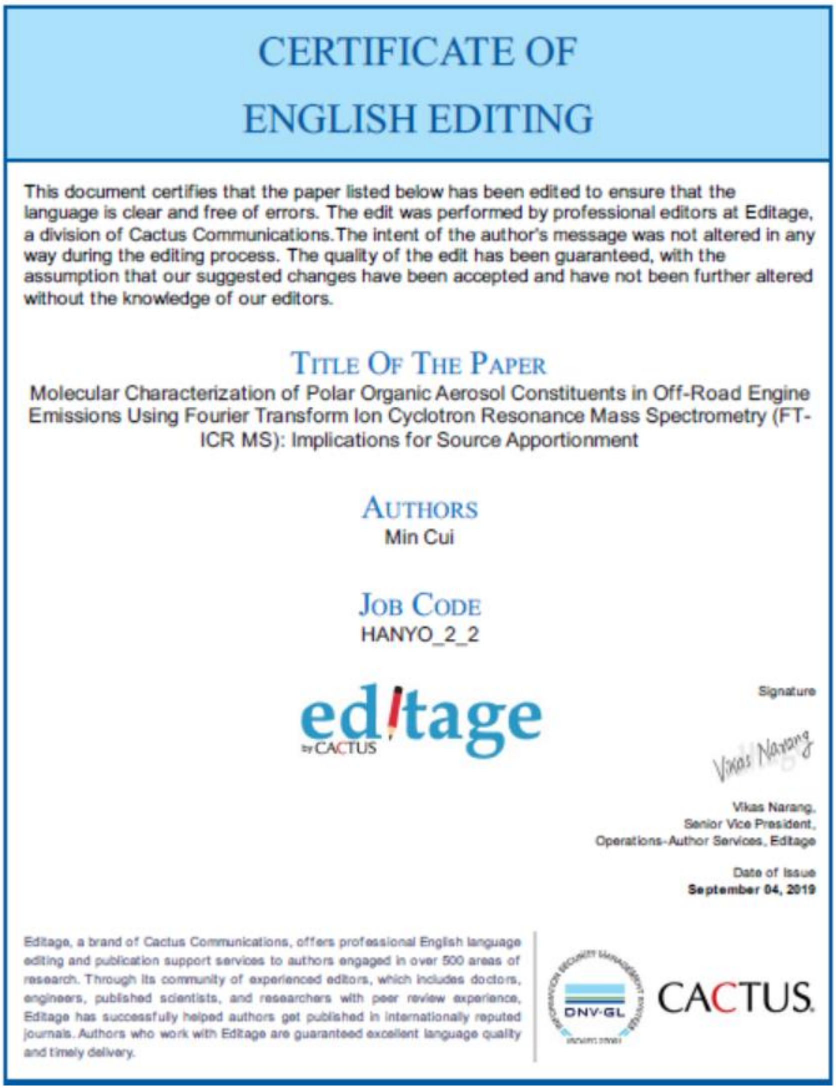
Comment #16: English and writing skills must be substantially improved. Otherwise, it will be impossible for this paper to be published on ACP.

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

Response to reviewer's 2

Comment #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.

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

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Comment#2: 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. 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 watersoluble, 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.

Response: Thanks for your constructive suggestion. We are completely in agreement with the reviewer's opinion that FT-ICR MS without chromatographic separation fails to recognize the isomers of POCs, and that an appropriate description of this limitation should be mentioned in the revised manuscript (**Page 6 lines 15-20**) to avoid misleading readers into thinking that this method is infallible. However, due to the high resolving power of FT-ICR MS, it is widely and successfully used to explore the chemical compositions of macromolecular polar organic compounds. Therefore, the chemical compositions and structures of POCs emitted from off-road engines were detected and deduced in this study by using FT-ICR MS and some empirical values.

Furthermore, it was reported that SPE methods for desalting could also remove a majority of the inorganic ions and low molecular weight organic compounds, such as some isoprene derived organosulfates and sugars. Thus, this limitation was also addressed in the revised manuscript (**Page 11 lines 8-11**).

"It should be noted that FT-ICR MS, without chromatographic separation, can only detect molecular formulas and molecular identification based on elemental composition alone. This is challenging because most complex molecules have several stable isomeric forms."

"A majority of inorganic ions (e.g. ammonium, sulfate, and nitrate) and low-molecular-weight organic compounds such as isoprene-derived organosulfates and sugars could be removed during SPE treatment (Gao et al. 2006, Lin et al. 2012, Surratt et al. 2007), which were not discussed in this research."

References:

[1] Gao, S., J. D. Surratt, E. M. Knipping, E. S. Edgerton, M. Shahgholi, J. H. Seinfeld, Characterization of polar organic components in fine aerosols in the southeastern United States: Identity, origin, and evolution. Journal of Geophysical Research, 2006, 111(D14)

[2] Lin, P., J. Z. Yu, G. Engling, M. Kalberer, Organosulfates in Humic-like Substance Fraction Isolated from Aerosols at Seven Locations in East Asia: A Study by Ultra-High-Resolution Mass Spectrometry. Environmental Science & Technology, 2012, 46(24): 13118-13127

[3] Surratt, J. D., M. Lewandowski, J. H. Offenberg, M. Jaoui, T. E. Kleindienst, E. O. Edney, J. H. Seinfeld, Effect of Acidity on Secondary Organic Aerosol Formation from Isoprene. Environ. Sci. Technol., 2007, 41: 5363-5369

Comment#3: 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?

Response: Thank you for your kindly input.

(1) The purpose of this research was to find the unique molecular composition of POCs to indicate off-road engine emissions, not to quantify the concentrations or calculate the emission factors of all the POCs emitted from off-road engines. Thus, POCs defined in this study were pure water extraction only (**Page 12 lines 9-12**), while the exact extraction efficiency for all of the polar organic matters was not considered. Consequently, some obviously unique tracers for off-road engines emission were discovered through POCs available in this research **(Page 27 lines 1-22; Page 28 lines 1-22; Page 29 lines 1-4)**. To avoid contamination throughout the duration of the analysis process, a blank sample was analyzed and the relative response of all peaks was calibrated by subtracting the response of peaks detected for blank filters (Only 300 peaks were detected in the blank sample, as shown in **Fig. R2**).

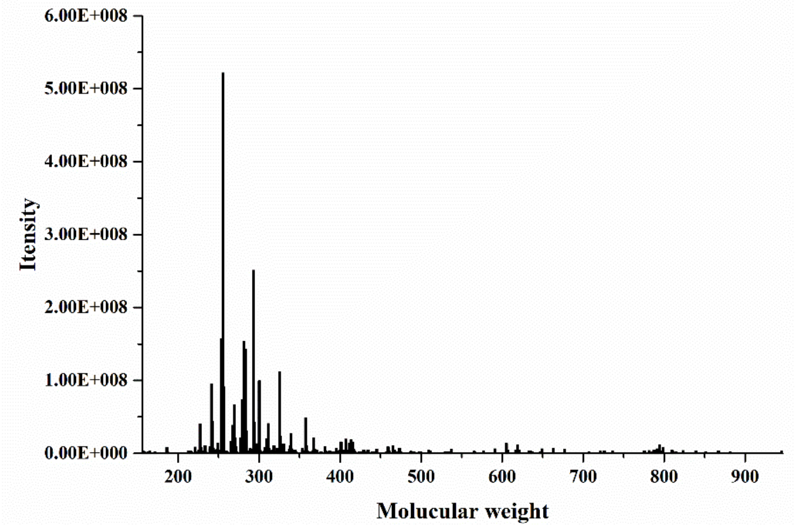
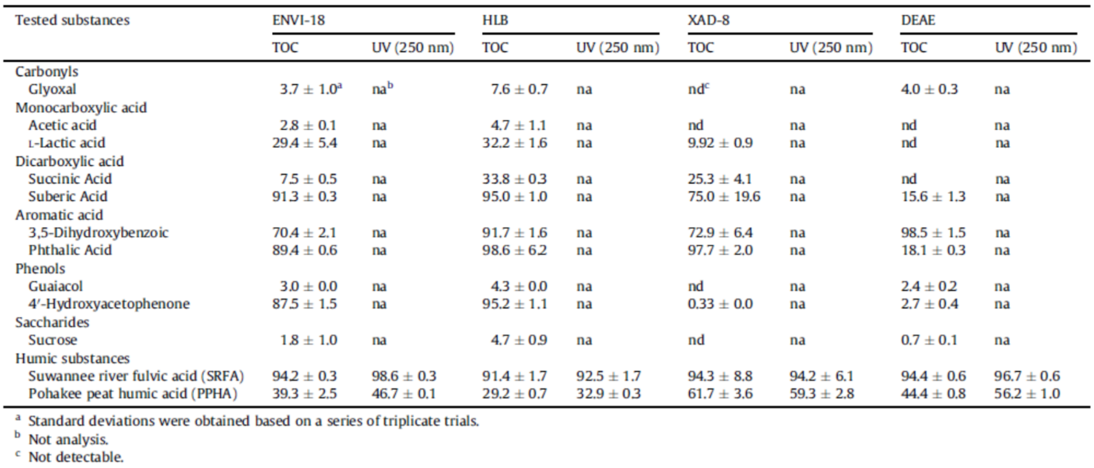


Figure R2 Intensity of detected peaks from blank sample

(2) Upon reviewing relevant references, it was found that approximately 60% water-soluble organic matters could be extracted by solid phase extraction (SPE) method with Oasis HLB columns (Varga et al., 2001). Furthermore, the extraction efficiencies of SPE with HLB columns for individual organic species varied sharply, from 4.3% for Guaiacol to 98.6% for phthalic acid (Fan et al., 2012).

Table R1 Recovery efficiencies for known organic compounds (from Fan et al., 2012)



Tested substances	ENVI-18		HLB		XAD-8		DEAE	
	TOC	UV (250 nm)	TOC	UV (250 nm)	TOC	UV (250 nm)	TOC	UV (250 nm)
Carbonyls								
Glyoxal	3.7 ± 1.0[a]	na[b]	7.6 ± 0.7	na	nd[c]	na	4.0 ± 0.3	na
Monocarboxylic acid								
Acetic acid	2.8 ± 0.1	na	4.7 ± 1.1	na	nd	na	nd	na
L-Lactic acid	29.4 ± 5.4	na	32.2 ± 1.6	na	9.92 ± 0.9	na	nd	na
Dicarboxylic acid								
Succinic Acid	7.5 ± 0.5	na	33.8 ± 0.3	na	25.3 ± 4.1	na	nd	na
Suberic Acid	91.3 ± 0.3	na	95.0 ± 1.0	na	75.0 ± 19.6	na	15.6 ± 1.3	na
Aromatic acid								
3,5-Dihydroxybenzoic	70.4 ± 2.1	na	91.7 ± 1.6	na	72.9 ± 6.4	na	98.5 ± 1.5	na
Phthalic Acid	89.4 ± 0.6	na	98.6 ± 6.2	na	97.7 ± 2.0	na	18.1 ± 0.3	na
Phenols								
Guaiacol	3.0 ± 0.0	na	4.3 ± 0.0	na	nd	na	2.4 ± 0.2	na
4′-Hydroxyacetophenone	87.5 ± 1.5	na	95.2 ± 1.1	na	0.33 ± 0.0	na	2.7 ± 0.4	na
Saccharides								
Sucrose	1.8 ± 1.0	na	4.7 ± 0.9	na	nd	na	0.7 ± 0.1	na
Humic substances								
Suwannee river fulvic acid (SRFA)	94.2 ± 0.3	98.6 ± 0.3	91.4 ± 1.7	92.5 ± 1.7	94.3 ± 8.8	94.2 ± 6.1	94.4 ± 0.6	96.7 ± 0.6
Pohakee peat humic acid (PPHA)	39.3 ± 2.5	46.7 ± 0.1	29.2 ± 0.7	32.9 ± 0.3	61.7 ± 3.6	59.3 ± 2.8	44.4 ± 0.8	56.2 ± 1.0

[a] Standard deviations were obtained based on a series of triplicate trials.
[b] Not analysis.
[c] Not detectable.

(3) Extraction by pure water was a common method to detect water-soluble POCs (Song et al., 2018; Wang et al., 2017). It was reported that only ultraviolet irradiation, electrolysis, or heating could promote OH radical formation and reaction with some organic matters (Li et al., 2019; Staudt et al., 2014). Ice bags were used throughout the ultrasound process to reduce the temperature, and we

believed that this way, certain oxidation products cannot be formed.

References:

[1] Fan, X., Song, J., Peng, P. a.: Comparison of isolation and quantification methods to measure humic-like substances (HULIS) in atmospheric particles. Atmospheric Environment. 60: 366-374, 2012

[2] Li, T., X. Zhang, C. Zhang, R. Li, J. Liu, P. Han, C. Fan, Thermodynamic and kinetic studies on OH-involved photo-decarboxylation mechanism for waste cooking oils to biofuels. Fuel, 2019, 254: 115665

[3] Song, J., M. Li, B. Jiang, S. Wei, X. Fan, P. a. Peng, Molecular Characterization of Water-Soluble Humic like Substances in Smoke Particles Emitted from Combustion of Biomass Materials and Coal Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Environmental Science & Technology, 2018, 52(5): 2575-2585

[4] Staudt, S., S. Kundu, H. J. Lehmler, X. He, T. Cui, Y. H. Lin, K. Kristensen, M. Glasius, X. Zhang, R. J. Weber, J. D. Surratt, E. A. Stone, Aromatic organosulfates in atmospheric aerosols: synthesis, characterization, and abundance. Atmos Environ (1994), 2014, 94: 366-373

[5] Varga, B. l., Kiss, G., Ganszky, I., Gelencser, A., Krivacsy, Z. n.: Isolation of water-soluble organic matter from atmospheric aerosol. Talanta, 55: 561-572, 2001

Comment#4: 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?

Response: We apologize for the lack of clarity in our statements. The details of filters selection and combination for each sample were elaborated in the revised manuscript (**Page 10 lines 9-17**).

"Due to the limitations of organic matter load in filters and cost-prohibitive analysis, the filters sampled from off-road engines with the same operation modes or fuel quality were combined together to characterize the comprehensive molecular compositions of POCs for off-road engines under different operation modes and fuel quality. As shown in **Table S1**, five samples (1, 2, 3, 4 and 5) were selected to conduct FT-ICR MS analysis, which represented vessels using heavy fuel oil, vessels using diesel, excavators under idling, moving, and working modes, respectively. Sample 1 was combined with 25% of the filter area from the two HFO-fueled vessels, namely YK and YF; Sample 2 was combined with 25% of filter area from two diesel-fueled vessels, namely GB1 and TB4; samples 3, 4, and 5 were combined with 50% of the filter areas from four excavators under idling, moving, and working modes, respectively, namely CAT320, CAT330B, CAT307 and PC60."

Comment#5: Experimental, Filter Collection Details:

What was the flowrate used for $PM_{2.5}$ sampling? Did you have denuders? If not, what potential positive artifacts occurred on your quartz filters when conducting the molecular composition analyses? Don't you expect some absorption of semivolatiles on these filters?

Response: The flowrate used for $PM_{2.5}$ sampling in this study was 10 L·min^{-1}. The denuders were not used in our study.

Schauer et al., (1999) compared the organic carbon mass emitted from medium-duty diesel trucks between denuder-based sampling technique and traditional filter-based sampling technique. They found that particulate organic carbon emission rate determined by the denuder-based sampling technique was found to be 35% lower than the organic carbon mass collected using a traditional filter-based sampling technique. This was concluded to be a result of a positive vapor-phase sorption artifact that affects the traditional filter sampling technique. It was reported that the quartz filter has a large surface area upon which adsorption of gaseous organics could occur, causing a positive artifact (Cheng et al., 2010). It was reported by Cheng et al., (2010) that in China, positive sampling artifact constituted 10% and 23% of the OC concentration determined by the bare quartz filter during winter and summer, respectively.

However, potential problems that arise from the usage of denuders include incomplete gas-phase removal, particle loss in the denuder tube, and semi-volatile compound off-gassing from particles when their corresponding gas phase components are removed in the denuder. It was reported that 5%-10% of the particles was lost in the denuders (Temime-Roussel et al., 2004). As a result, particle sampling in this study has ceased to use denuders.

References:

[1] Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., Tan, J. H., Du, Z. Y.: Improved measurement of carbonaceous aerosol in Beijing, China: intercomparison of sampling and thermal-optical analysis methods. Atmospheric Chemistry and Physics Discussions, 10(6): 15671-15712, 2010.

[2] Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. Environmental Science & Technology, 33(10): 1578-1587, 1999.

[3] Temime-Roussel, B.: Evaluation of an annular denuder tubes for atmospheric PAH partitioning studies—1: evaluation of the trapping efficiency of gaseous PAHs. Atmospheric Environment, 38(13): 1913-1924, 2004.

Comment#6: 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 (FTICR-MS): Implications for Source Apportionment

Response: We would like to thank the reviewer for their insightful suggestion. The title has been modified as per the suggestion.

Comment#7: 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.

Response: Thank you so much for your constructive suggestion. Upon comparing the sulfur-containing products observed in this study and Riva et al.'s study, it was interesting to find that some PAH-derived OS products generated in the lab also had significant response in field measurements. As shown in **Fig. S5**, three of the most abundant peaks of S-containing compounds emitted from HFO-fueled vessels were also observed in the lab from PAH oxidations in the presence of sulfate. This could add in deducing the possible chemical structure of the formulas observed by FT-ICR MS and discuss the formation path of S-containing compounds emitted from HFO-fueled vessels (**Page 22 lines 20-12; Page 23 lines 1-6**).

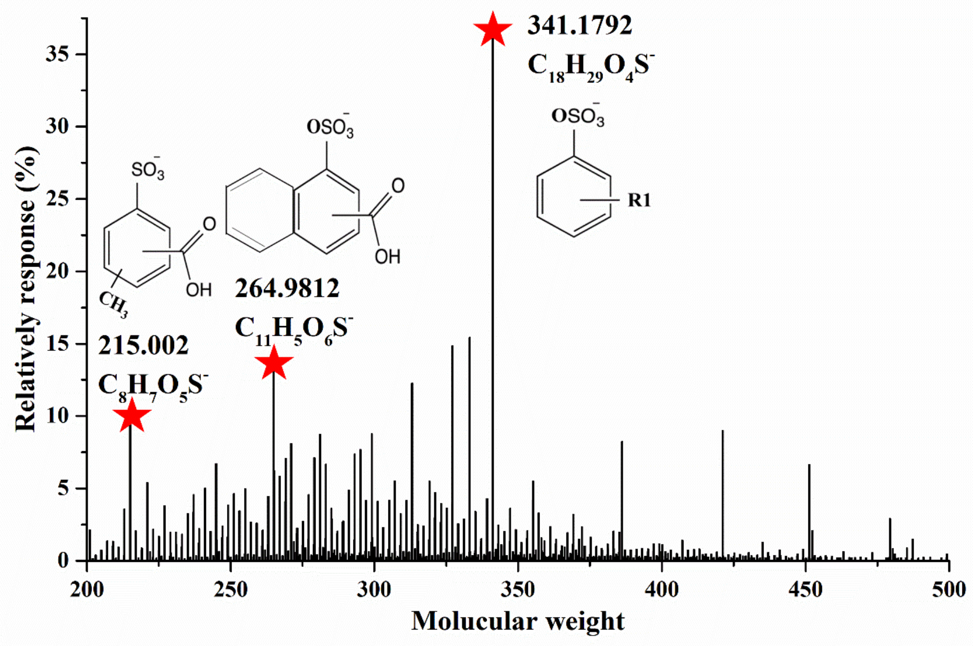


Figure S5 possible chemical structure of three of the most abundance peaks of S-containing compounds emitted from HFO-fueled vessels according to Riva et al., research.

"Thus, O5S1 and O4S1 may be organosulfates or sulfonates (Riva et al., 2015). Riva et al. (2015) 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. On comparing the sulfur-containing products observed in this study and the Riva et al. study, it was interesting to find that some PAH-derived OS products generated in the lab also have significant response in the field measurements. As shown as **Fig. S5**, three of the most abundance peaks ($C_8H_7O_5S^-$, $C_{11}H_5O_6S^-$ and $C_{18}H_{29}O_4S^-$) of S-containing compounds emitted from HFO-fueled vessels were also observed in the lab from PAH oxidations in the presence of sulfate."

Reference:

[1] Riva, M., Tomaz, S., Cui, T., Lin, Y. H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., Surratt, J. D.: Evidence for an unrecognized secondary anthropogenic source of organosulfates and sulfonates: gas-phase oxidation of polycyclic aromatic hydrocarbons in the presence of sulfate aerosol, Environ Sci Technol, 49(11): 6654-6664, 2015.

Comment#8: 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 interesting to know if you observed similar molecular formulas to that study.

Response: Thank you so much for your constructive suggestion. As shown in **Fig. S3**, the most abundant of CHOS compounds from excavators under three operation modes and diesel-fueled vessels were listed. It was interesting to find that the most abundant peaks of CHOS compounds observed in this study were also identified through the laboratory simulation study (Riva et al., 2016). The conclusions reported from Riva et al.'s study could provide a possible chemical reaction path to explain the chemical formula detected from off-road engine combustion. The formulas marked in bold red in **Table S3** were homologous to $C_{12}H_{23}O_5S^-$, which was reported to have been generated from dodecane oxidation by Riva et al.'s research, while the formulas in bold blue were likely formed from cycloalkanes (**Page 24 lines 1-8**)

Reference:

[1] Riva, M., Da Silva Barbosa, T., Lin, Y. H., Stone, E. A., Gold, A., Surratt, J. D.: Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes. Atmospheric Chemistry and Physics:1-39, 2016.

Table S3 The most abundant peaks of CHOS compounds emitted from excavators under three operation modes and diesel-fueled vessels.

	[M-H]$^-$	m/z	DBE	Relative response (%)		[M-H]$^-$	m/z	DBE	Relative response (%)
Excavator under idling	**$\mathrm{C16H31O5S}^-$**	335.1898	1	23.50	Excavator under moving	$\mathrm{C5H3O13S2}^-$	334.902	4	11.95
	$\mathrm{C17H33O5S}^-$	349.2054	1	22.42		$\mathrm{C4H3O11S2}^-$	290.9121	3	3.25
	$\mathrm{C15H29O5S}^-$	321.1741	1	22.07		$\mathrm{C22H37O3S}^-$	381.2469	4	3.02
	$\mathrm{C18H35O5S}^-$	363.2211	1	19.07		**$\mathrm{C14H27O5S}^-$**	307.1585	1	2.69
	$\mathrm{C14H27O5S}^-$	307.1585	1	16.28		**$\mathrm{C15H29O5S}^-$**	321.1742	1	2.64
	$\mathrm{C17H35O5S}^-$	351.2211	0	16.12		**$\mathrm{C16H31O5S}^-$**	335.1898	1	2.48
	$\mathrm{C16H29O5S}^-$	333.1741	2	14.63		**$\mathrm{C15H27O5S}^-$**	319.1585	2	2.37
	$\mathrm{C17H31O5S}^-$	347.1898	2	14.42		**$\mathrm{C18H29O4S}^-$**	341.1792	4	2.28
	$\mathrm{C18H33O5S}^-$	361.2054	2	14.39		**$\mathrm{C13H25O5S}^-$**	293.1428	1	2.07
	$\mathrm{C15H27O5S}^-$	319.1585	2	13.89		**$\mathrm{C16H29O5S}^-$**	333.1741	2	2.06
Excavator under working	$\mathrm{C22H37O3S}^-$	381.2469	4	33.63	Diesel-fueled vessel	$\mathrm{C12H25O5S}^-$	281.1428	0	22.20
	$\mathrm{C24H41O3S}^-$	409.2782	4	14.90		$\mathrm{C13H27O5S}^-$	295.1585	0	18.86
	$\mathrm{C5H3O13S2}^-$	334.902	4	11.85		$\mathrm{C11H23O5S}^-$	267.1272	0	16.00
	$\mathrm{C16H29O5S}^-$	333.1741	2	8.43		**$\mathrm{C13H25O5S}^-$**	293.1428	1	15.57
	$\mathrm{C15H27O5S}^-$	319.1585	2	8.22		**$\mathrm{C15H29O5S}^-$**	321.1741	1	15.01
	$\mathrm{C16H31O5S}^-$	335.1898	1	7.89		**$\mathrm{C14H27O5S}^-$**	307.1585	1	14.75
	$\mathrm{C17H31O5S}^-$	347.1898	2	7.70		**$\mathrm{C12H23O5S}^-$**	279.1272	1	12.64
	$\mathrm{C15H29O5S}^-$	321.1741	1	7.58		**$\mathrm{C11H21O5S}^-$**	265.1115	1	11.14
	$\mathrm{C17H33O5S}^-$	349.2054	1	7.23		**$\mathrm{C16H31O5S}^-$**	335.1898	1	11.03
	$\mathrm{C14H27O5S}^-$	307.1585	1	6.77		**$\mathrm{C10H19O5S}^-$**	251.0959	1	8.74

Comment#9: Abstract: The last sentence of the abstract needs to be completely re-worded. The current sentence is poorly worded and not easy to understand.

Response: We thank the reviewer for pointing out the lack of clarity. A professional language editing company has thoroughly polished and edited the revised manuscript..

Comment#10: I would change "polar organic matters (POM)" to polar organic compounds (POCs).

Response: Thanks for your suggestion. The "polar organic matters (POM)" has been changed into "polar organic compounds (POCs) through all of the revised manuscript.

Comment#11: 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 new aerosol marker compounds for non-road engines."

Response: Thanks. The sentence has been modified as reviewer suggestion (**Page 7 lines 15-17**).

Comment#12: Page 7, Line 5: Do you mean to say "plume" instead of "flume"?

Response: Thanks. "Flume" has been changed into "plume" (**Page 8 line 19**).

Comment#13: Experimental Section, Page 8, Line 14: Delete "continually"

Response: Thanks. "Continually" has been deleted (**Page 10 line 22**).

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~~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~~

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Abstract: The molecular compositions and structures of polar organic ~~matters~~ compounds (POCs~~M~~) in particles emitted from various vessels and excavators were characterized using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). ~~POM~~ POCs ~~was~~ were extracted ~~by~~ with purified water and ~~discussed~~ sorted by elemental composition ~~which was divided~~ into three groups~~, namely~~: CHO, CHON and S-containing compounds (CHONS and CHOS). The results show~~ed~~ that: (i) CHO (accounting for 49% of total ~~POM~~ POCs in terms of ~~relative~~ peak response) was the most abundant group for all tested off-road engines, followed by CHON (33%) and CHOS (35%) for diesel- and HFO (heavy fuel oil)-fueled off-road ~~equipment~~engines, respectively. (ii) The abundance and structure of the CHON group in water extracts were different in terms of engine type and load. The ~~fraction of~~ relative peak response of CHON was the highest for excavator emissions ~~under the~~in working mode, compared to ~~other modes (~~the idling and moving modes~~)~~. Furthermore, dinitrophenol and methyl dinitrophenol were the most abundant emission species for high-rated speed excavators ~~with high rated speed~~, while nitronaphthol and methyl nitronaphthol were more important for low-~~-~~rated speed vessels. (iii) The composition and structure of the S-containing compounds ~~was~~ were directly influenced by fuel oil characteristics (sulfur

content and aromatic ring), with ~~much~~ more condensed aromatic rings in the S-containing compounds observed ~~for~~ in HFO-fueled vessel~~s~~ emissions~~,~~. ~~while m~~More abundant aliphatic chains were observed ~~in emissions from~~ in diesel equipment emissions. Overall, higher fractions of condensed hydrocarbons and aromatic rings in POCs~~M~~ emitted from vessels using HFO cause~~d~~ strong optical absorption capacity. ~~And~~ D~~d~~ifferent structures ~~existing~~ in POCs~~M~~ could provide a direction ~~to~~ for qualitative and ~~quantities~~ quantitative analysis of~~the exact~~ organic compounds as tracers to distinguish ~~the~~ these emissions from diesel or HFO-~~—~~fueled off-road engines.

1. Introduction

A ~~R~~rapid~~ly~~ increase~~d~~ in the number of off-road engines (e.g. vessels and excavators) ~~have~~ has resulted in large quantities of pollutants emission, which have severe impacts on air quality, human health and climate change (Righi et al., 2011; Li et al., 2016; Liu et al., 2016; Wang et al., 2018; Zhang et al., 2018). ~~Only in China~~In China alone, the dead weight capacity of vessels increased from 51 million tons in 2000 to 266 million tons in 2016 (NBS 2017). It was reported that emissions from fishing boats ~~emission~~ accounted for 18.3% of total fine particulate matter (PM$_{2.5}$) emitted by on-road vehicles (Deng et al., 2017). Almost 14, 500-37, 500 premature deaths per year were caused by emissions from ocean-going vessels ~~emission~~ in East Asia (Liu et al., 2016). As reported by the US EPA, nearly 34% of elemental carbon (EC) emissions originated from off-road diesel vehicle emissions in the United States (USEPA 2015). Furthermore, ~~constructive~~ construction equipment, ~~one of the~~a typical off-road diesel vehicle~~s~~, emitted ~~abundance~~ abundant volatile organic matter (VOC). ~~which~~ VOC was considered ~~as~~ one of the most important ~~procedures~~ precursor of ~~dominant components of~~ HUmic-LIke Substances (HULIS)~~,~~ like organosulfates (Zhang et al., 2010; Tao et al., 2014).

~~The e~~Emission standards for ~~non~~off-road engines are ~~incomplete~~ not fully implemented in China, especially for ~~the~~ vessel emissions. ~~Nowadays~~Currently, stage 3 emission standard has been implemented for ~~non~~off-road diesel engines ~~from~~ since 2016, while stage 1 emission standard for emission from vessels ~~emission~~ will be implemented in 2020 (SEPA et al., 2015a, SEPA et al., 2016). Furthermore, the oil quality for ~~non~~off-road mobile sources ~~couldn’t~~ cannot be guaranteed. According to the standard of GB/T17411-2012, the sulfur content in oil ~~using~~ used for vessels could reach ~~to~~ 1-3.5%, which was 200-700 times higher than those for China IV diesel (SEPA et al., 2015b). There is a continued need ~~for~~ to apportion the contributions of off-road ~~equipment~~ engines to atmospheric $PM_{2.5}$. However, to the best of our knowledge, there is no unique tracer available to identify ~~and distinguish between~~ off-road engines ~~and on-road~~ combustion ~~engines~~ (Zhang et al., 2014; Liu et al., 2017). According to ~~the~~ published studies, Vanadium (V) was usually used to identify the contribution of $PM_{2.5}$ from ship emission. ~~But~~ However, it should be ~~noticed~~ noted that V emissions can also be attributed to industrial activities~~could also be emitted by industry activities~~. Therefore, overestimated/underestimated results of contributions from ship emissions to $PM_{2.5}$ in the atmosphere ~~could be gained by~~are obtained while using V as the only tracer (Zhang et al., 2014). Furthermore, some isomer ratios of polycyclic aromatic hydrocarbons were recommended as indicators of off-road engine~~s~~ emissions, but the huge variations of ~~those~~ these ratios in the atmosphere might ~~mislead~~ affect the ~~final~~ end results (Zhang et al., 2005; Cui et al., 2017). Thus, there is an ~~urgency~~ urgent need to explore ~~the~~ unique organic tracers.

Organic matter (OM) is one of the most important components in $PM_{2.5}$ emitted by ~~non~~off-road ~~mobiles~~vehicles, with the highest fraction accounting for up to approximately 70% in ship emissions (Cui et al., 2017). ~~Determining the characteristics of OM from different emission sources could help to reduce uncertainty in estimations of the relative contributions of different sources and improve our understanding of public health and climate effects.~~ However, ~~large portions~~substantial portions of OM emitted from off-road engine combustion, especially for ~~polar organic matter~~POCs, were ~~hardly~~ difficult to isolate and identify by traditional analytical instruments, and ~~were~~ still remain unknown. ~~Some traditional mass spectrometry is equipped with quadrupole, ion trap or time of flight, which has limited resolving power when comparing with the FT-ICR MS. For instance, large portions of unidentified organic matters were detected by Gas chromatography coupled with mass spectrometry (GC-MS), and only less than 20% of total OM could be resolved (Rogge et al., 1993; Schauer et al., 1999). It remains a challenge to quantify the high molecular weight and polar organic matter contents, which might have more significant effects on air quality, human health and climate change than those of resolved organic species (Feng et al., 2013; Fan et al., 2016).~~ For example, HULIS was reported to arise primarily from biomass burning and fossil fuel (coal and diesel) combustion. There is substantial literature that deals with the optical characterization and molecular composition of

HULIS emitted from biomass burning, an important source of BrC worldwide. However, the contribution of diesel combustion to BrC was also controversial (Zheng et al., 2013). A reason for these discrepant degrees of recognition between diverse sources was the similarity in chemical structure (nitrogen-containing bases and nitroaromatics) found between HULIS and the compounds emitted from biomass burning (Ren et al. 2018; Violaki and Mihalopoulos 2010). It may also be due to a lack of knowledge on characterization of POCs emitted from diesel vehicles, especially for off-road diesel vehicles.

FT-ICR MS ~~as one of the most~~is an advanced technique~~s~~ with a high mass resolution of 0.00001 ~~is~~ and is ~~always~~ commonly used to determine the organic matter composition at a molecular level in crude oil (Jiang et al., 2019). FT-ICR MS is usually coupled with ~~some~~ soft ionization techniques, such as electrospray (EST) and atmospheric pressure chemical ionization (APCI). They are used to analyze polar species and non-polar organic matters, respectively (Smith et al., 2009; Smit et al., 2015). It should be noted that FT-ICR MS, without chromatographic separation, can only detect molecular formulas and molecular identification based on elemental composition alone. This is challenging because most complex molecules have several stable isomeric forms (Laskin et al., 2009). However, some traditional mass spectrometry methods are equipped with quadrupole, ion trap, or time of flight, which have limited resolving power compared with the FT-ICR MS. Recently, ~~S~~some studies have successfully characterized the elemental components of polar organic ~~matter~~ compounds present in the atmosphere or emitted by different sources using FT-

ICR MS (Wozniak et al., 2008; Laskin et al., 2009; Smith et al. 2009; Yassine et al. 2014~~),~~ . ~~but~~ A few of them have been undertaken in China, especially for source~~s~~ emission (Lin et al., 2012; Jiang et al., 2016; Mo et al., 2018; Song et al., 2018). Song et al. (2018) reported that the most ~~abundance~~ abundant group of HULIS emitted from biomass burning and coal combustion was CHO, followed by CHON for biomass burning and CHOS for coal combustion. In contrast, Wang et al. (2018) observed that CHON was the dominant compound emitted from straw residue burning. In addition, the possible chemical structure of HULIS could be determined by FT-ICR MS. Tao et al. (2014) compared the molecular compositions of organosulfates in aerosols sampled in Shanghai and Los Angeles. They found that the organosulfates in Shanghai had a low degree of oxidation and unsaturation, indicating the presence of long aliphatic carbon chains. Smith et al. (2009) reported that organic aerosol emitted from biomass burning showed a clear trend of increasing saturation with increasing molecular weight and exhibited a significant CH_2-based homologous series.

This study aimed to detect chemical characterize polar organic aerosol constituents at the molecular level that are emitted from typical off-road engines by FT-ICR MS to provide new aerosol marker compounds for off-road engines~~This study aimed to detect the molecular characterization of polar organic matter emitted from typical nonoff-road engines by FT-ICR MS to provide a new direction to find biomarkers for nonoff-road engines~~. To this end, studies were conducted: 1) to identify the molecular composition of ~~polar organic matter~~POCs from excavators under three different operation modes; 2) to determine the molecular composition and possible structure of ~~polar organic~~

~~matter~~POCs from vessels using HFO and diesel, respectively; 3) to explore the key factors affecting the composition and structure of ~~polar organic matter~~POCs from HFO and diesel fueled off-road engines; 4) to ~~provide the direction to find the possible~~pave the way for the discovery of potential tracers for off-road engine~~s~~ emissions.

2. Materials and Methods

2.1 Sample collection

Four ships using HFO and diesel, and ~~as well as~~ four excavators covering different emission standards and powers were chosen as ~~being,~~ representative ~~of~~ off-road vehicles in China. Detailed information about the four ships and four excavators is ~~shown~~ presented in **Table 1**. Before conducting ~~the~~ field sampling, the original fuel was obtained directly from the fuel tank~~,~~ and sent to the testing company ~~to~~ for quality evaluation~~detect the fuel quality~~ (**Table 2**). For excavator emission sampling, three operation modes (idling, moving, and working) were selected~~ including the idling, moving and working modes~~, and sampling time was approximately half an hour for each mode. The flowrate of the $PM_{2.5}$ sampler was 10 L/min. Commercial equipment (MFD25, produced by Shanghai Besser ~~environmental~~ Environmental ~~protection~~ Protection ~~technology~~ Technology Co., Ltd.) was used for $PM_{2.5}$ sampling. The description of the particulate matter dilution and sampling system are presented~~ in full~~ in Xia's published study (Xia, 2017). In short, the exhaust ~~flume~~ plume was pumped into a retention chamber and $PM_{2.5}$ was intercepted by the four $PM_{2.5}$ samplers. One Teflon and three quartz filters (Φ=47 mm) were finally acquired and one of the quartz filters was used to determine the chemical composition of $PM_{2.5}$ for each excavator

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under the three operation modes. For vessel~~s~~ emissions, an on-board measurement system was used, as previously described (Cui et al., 2017; Deng et al., 2017). The on-board measurement system contains one dilution tunnel connected to two particulate samplers. Finally, particulate matter was collected on two quartz filters (Φ=~~-~~90 mm) for each vessel.

Table 1 Technical parameters of test off-road engines

Vehicle ID	Engine power (kW)	Type	Length × width (m)	Material	Age (years)	Rated speed (rpm)	Fuel type
YK	4440	vessel	116×18	Metal	11	173	HFO
YF	5820	Cargo vessel	139×20.8	Metal	16	141	HFO
GB1	91	Gillnet	20×4.3	Wooden	10	1500	Diesel
TB4	235	Trawler	24×5.2	Wooden	7	1310	Diesel
CAT320	106	Excavator	9.5*3.2	Metal	>11	1650	Diesel
CAT330B	165.5	Excavator	11.1*3.3	Metal	>11	1800	Diesel
CAT307	85	Excavator	6.1×2.3	Metal	9	2200	Diesel
PC60	40	Excavator	6.1*2.2	Metal	9	2100	Diesel

Table 2 Results of the fuel quality analysis

Engine ID	Carbon (C) %	Hydrogen (H) %	Oxygen (O) %	Nitrogen (N) %	Sulfur (S) %	Vanadium (V) mg/kg	Water Content MJ/kg	Kinematical viscosity (40℃) mm^2/s
YK	84.12	10.38	4.26	0.79	0.448	5	0.21	123.2
YF	80.54	10.05	8.23	0.78	2.46	19	8.98	410.2
GB1	85.96	12.76	<0.3	0.49	0.022	/	/	4.517
TB4	86.21	12.47	0.45	0.49	0.323	/	/	4.976
CAT320	86.38	11.5	2.00	0.05	0.019	<1	Trace	5.592
CAT330B	86.38	11.5	2.00	0.05	0.019	<1	Trace	5.592
CAT307	86.32	11.2	1.99	0.05	0.138	<1	Trace	5.420
PC60	85.88	12.1	1.85	0.04	0.034	<1	Trace	4.782

2.2 Chemical analysis

~~In this research, five combined samples for excavator under idling, working and moving and vessels using diesel and HFO were selected, respectively, from four~~

~~excavators (CAT320, CAT330B, CAT307 and PC60) under three modes, two diesel vessels (DB1 and DB2) and two HFO-fueled vessels (YK and YF) (**Table S1**). Then, different types of samples were subsequently extracted by water and 90%DCM+10%MeOH (DCM/MeOH), respectively and divided into 10 extraction samples. The extraction process was described as follows:~~

Due to the limitations of organic matter load in filters and cost-prohibitive analysis, the filters sampled from off-road engines with the same operation modes or fuel quality were combined together to characterize the comprehensive molecular compositions of POCs for off-road engines under different operation modes and fuel quality. As shown in Table S1, five samples (1, 2, 3, 4 and 5) were selected to conduct FT-ICR MS analysis, which represented vessels using heavy fuel oil, vessels using diesel, excavators under idling, moving, and working modes, respectively. Sample 1 was combined with 25% of the filter area from the two HFO-fueled vessels, namely YK and YF; Sample 2 was combined with 25% of filter area from two diesel-fueled vessels, namely GB1 and TB4; samples 3, 4, and 5 were combined with 50% of the filter areas from four excavators under idling, moving, and working modes, respectively, namely CAT320, CAT330B, CAT307 and PC60. The ~~P~~portions of filters (**Table S1**) were cut and combined for 40 ~~minutes~~ min, subjected to ultrasonic extraction with 40 mL ultrapure water, and then filtered using a 0.22 μm PTFE membrane (Jinteng, China). The extraction solvent was then divided into three portions. Two portions were used for measuring the concentrations of organic carbon and optical absorbance, as described in the Supporting Information part A and B. The third portion was processed ~~continually~~ to assess the chemical composition of POCs~~M~~ by FT-ICR MS. The remaining extraction filters were frozen and then dried to remove ultrapure water. The filters were then subjected to 40 min of ultrasonic extraction with 36 mL dichloromethane and 4 mL methanol. The extracted solvent was divided into three portions, and ~~then~~ these were processed in the same way as previously described for the ultrapure water extract.

Both samples extracted with water or organic solvents were processed by a solid phase extraction (SPE) method to remove ions, which disturbed the results of FT-ICR MS. A majority of inorganic ions (e.g. ammonium, sulfate, and nitrate) and low-molecular-weight organic compounds such as isoprene-derived organosulfates and sugars could be removed during SPE treatment (Gao et al. 2006, Lin et al. 2012, Surratt et al. 2007), which were not discussed in this research. The details of the solid phase extraction method ~~was~~ were presented ~~in~~ by Mo et al. (2018). Briefly, the pH value of water extracts was adjusted to 2.0 ~~by~~ using HCl, and then passed through an SPE cartridge (Oasis HLB, 30 μm, 60 mg/cartridge, Waters, USA). The adsorbed POCs~~M~~ ~~was~~ were eluted with 6 mL 2% (v/v) ammonia/methanol and dried ~~by~~ under a gentle stream of N_2. Finally, the POCs~~M~~ ~~was~~ were re-dissolved using 10 mL ultrapure water.

2.3 FT- ICR MS analysis

The molecular characterization of POCs~~M~~ was undertaken using negative-ion ESI FT-ICR MS (Bruker Daltonics GmbH, Bremen, Germany) with a 9.4-T refrigerated actively shielded superconducting magnet. Extracted solutions were injected at flow rate of 180 μL·h^{-1} through an Apollo II electrospray source. Emitter voltage, capillary column introduction voltage, and capillary column end voltage for negative-ion formation were 3.0 kV, 3.5 kV and -320 V, respectively. The scan range was m/z 100−900 with a resolution >450 000 at m/z = 319 with <0.4 ppm absolute mass error. During analysis, nitrogen-containing compounds were used as an internal calibration. Finally, the spectrum peaks with ratio of signal/noise higher than 10 were exported.

~~The formula~~ $\mathrm{C}c\mathrm{H}h\mathrm{O}o\mathrm{N}n\mathrm{S}s$ was used as a general formula~~.~~, since ~~Some~~ some criteria should be conformed to assign the possible formula (Wang et al., 2017). Briefly, all of the mathematically possible formulas for each ion were calculated with a mass tolerance of ±2 ppm. The H-to-C, N-to-C, O-to-C, and S-to-C ratios were limited to 0.3−3.0, 0−0.5, 0−3.0, and 0−2.0, respectively, in the ESI^- mode. Peak magnitude is not indicative of a compound's concentration in a sample due to inherent biases of SPE extractions and electrospray ionization efficiencies (Wozniak et al., 2008). Therefore, the relative responses of detected peaks are discussed here. Due to the common occurrence of contamination during ESI analysis (Smit et al., 2015), ~~T~~the relative response of all peaks was calibrated by subtracting the response of peaks detected for blank filters. The double bond equivalents (DBE) and aromaticity equivalents (Xc) were calculated as follows:

$$\mathrm{DBE}=1+1/2\,(2c-h+n) \qquad (1)$$

$$\mathrm{X}n\cancel{e}=(3*(\mathrm{DBE}-o-s)-2)/(\mathrm{DBE}-o-s) \qquad (2)$$

Where c, h, o, n, and s were the number of C~~、~~, H~~、~~, O~~、~~, N~~、~~, and S atoms in the corresponding formulas. It should be noted that the formula with DBE<0 or Xc<0 has been excluded (Wang et al., 2017).

3. Results and Discussion

3.1 General characteristics of POCs~~M~~ for off-road engines

In general, the range of detected peaks for excavators and vessels ~~were between~~had molecular weights ~~molecular weight of~~between 150-900 Da, but most of the intensive peaks occurred in the molecular weight range of 200-400 Da. ~~M~~The mass spectra for excavators in different operational modes and vessels using different oils were ~~different~~varied from each other. ~~There were~~The number of peaks for POCs were 4734, 3097, 4731, 4554 and 2818, ~~peaks~~ in excavator emissions under the idling, working, and moving modes, and vessel emissions using HFO and diesel, respectively. The average molecular weight of excavator emissions under the working mode and vessels using HFO were the lowest (322.6 ± 69.9 Da and 331.3 ± 72.9 Da respectively).

For excavators, CHO was the most abundant group of POCs~~M~~ in all three operation modes, accounting for 41%, 46% and 48% of all the formulas in terms of relative peaks response for the idling, working, and moving modes, respectively. S-containing compounds (~~i.e.~~ CHOS and CHONS) were most abundant in the idling mode, while the relative~~ly~~ peak response of the CHON group was highest under the working mode (**Fig. 1**). For vessels, CHO was the most abundant species group of POCs ~~M~~ for both, the vessel~~s~~ using diesel and the ones using HFO, accounting for 50~~%~~-60% of total peak intensity. However, CHOS accounted for almost 30% of total ion intensity for vessels using HFO, ~~and this was~~ higher than other off-road diesel engines. Furthermore, the chemical properties of POCs~~M~~ for vessels using HFO showed a larger degree of oxidation and unsaturation than other samples (**Table S2**). These differences in the composition of POCs~~M~~ might be attributable to variations in engine load, fuel supply, and air supply in different operation modes, which ~~were~~ are discussed ~~below~~later.

As discussed in supporting information (SI Part C), the chemical properties of extractions derived from water or DCM/MeOH were significantly different (**Fig. S1 and Fig. S2**). And through comparing the optical properties between water and DCM/MeOH extractions, it was found that the average mass absorption efficiency of water extracts was significantly higher than those for 90% DCM+10% MeOH extracts (**Fig. S3**). Thus, it was necessary to extract $PM_{2.5}$ by water to explore the emission characteristics of ~~polar organic matters~~POCs from off-road engines.

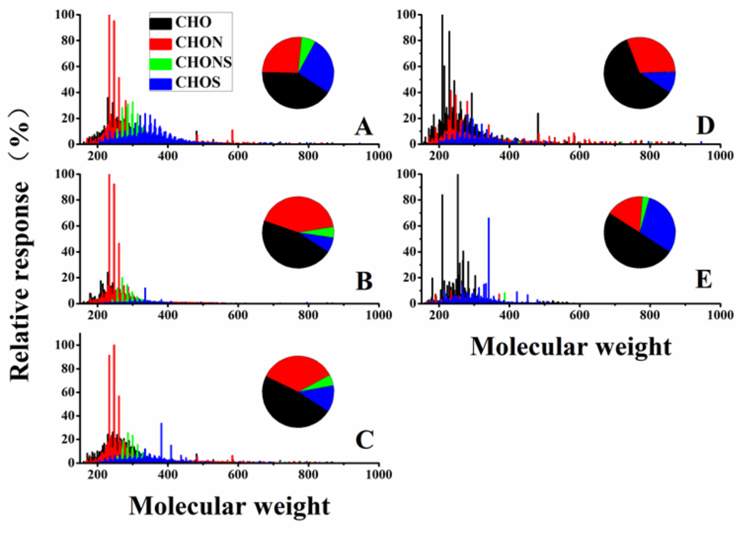

Figure 1 Mass ~~spectrum~~ spectra of POCs~~M~~ in water extractions for off-road diesel engines emissions. A, B, C, D and E were the mass spectra for excavators under idling, working, moving modes, and vessels using diesel and HFO, respectively

3.2 CHO compounds in POCs from off-road engines emission

The number of peaks for CHO compounds were 1746, 1287, ~~and~~ 1797, 1561, and

1318 ~~spectra peaks~~ for excavators in the idling, working and moving modes, and vessels~~respectively and 1561 and 1318 peaks for vessels~~ using HFO and diesel, respectively~~, were identified by FT-ICR MS~~. Considering the number of detected peaks for CHO compounds, the compositions of CHO group emitted from off-road engines were more complicated than those from ambient samples while being relatively comparable to those from other sources of emission~~s~~ (e.g. biomass: 1514-2296; ~~and~~ coal combustion: 918) (Lin et al., 2012; Jiang et al. 2016; Song et al. 2018).The average molecular weight of detected ions for CHO compounds for excavators in idling, working and moving and vessels using HFO and diesel ~~was~~ were 338 ± 96.7, 316 ± 84.6, 336 ± 96.6, 331 ± 72.9 and 357 ± 123 Da, respectively, which ~~was~~ were significantly higher than those emitted by coal and biomass burning (m/z=227-337 Da) (Song et al., 2018). Excavators under ~~the~~ working mode had higher engine loads and combustion temperatures than those in other operation modes. Thus, the lowest number of CHO group ions and smallest average molecular weight were found during the working mode compared to the idling and moving modes~~,~~. ~~which~~ This ~~indicated~~ indicated that long chain aliphatic hydrocarbons were liable to crack ~~during~~ under ~~high~~ elevate temperatures and ~~under~~ low air/fuel ratio conditions. This trend was consistent with the results of a previous study ~~results~~ (Wang et al., 2018) which found that low temperatures and oxygen-rich combustion would promote ~~the~~ a chain propagation reaction. Although the lipid contents of fossil fuel might be an important precursor of CHO compounds from off-road engines, different fractions of heteroatom and isomers could lead to significantly different structures for the CHO group (Hellier et al., 2017).

The highest ~~intensities~~ intensity peaks~~of~~ for CHO compounds for off-road diesel engines ~~was~~ were $C_9H_5O_6$ and $C_{13}H_9O_4$, while for vessels using HFO, the highest peaks were ~~for~~ $C_{10}H_5O_8$, $C_9H_5O_6$ and $C_{10}H_5O_9$.

The V~~v~~an Krevelen (VK) diagram (H/C versus O/C) was ~~usually~~ generally used to identify the structural properties of organic matter in FT-ICR MS research ~~due to~~as only the molecular formula was given (Wozniak et al., 2008; Lin et al., 2012). ~~Through~~ On comparing the ratios of H/C and O/C for CHO compounds for different off-road engines under three operational modes and using different fuel oils, we found that the CHO group for vessels using HFO had the highest degree of oxidation and unsaturation. Furthermore, the CHO group ~~under~~ in the working mode had a higher degree of oxidation and unsaturation than ~~under~~ in ~~the~~ idling and moving modes. As shown in **Fig. 2**, region 1 ~~likely~~ represented monocarboxylic acid, which was more abundant in both idling and moving modes than ~~those~~ 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). Most compounds detected in the CHO group for vessels using HFO were molecular species in region 2 with a high number of O atoms and a low ratio of H/C. This was consistent with the original structure of combustion HFO, which was defined as bottom residue oil, containing fewer aliphatic hydrocarbons than those for diesel (Wikipedia 2018). Furthermore, low engine speeds for vessels using HFO caused low temperature combustion which was prone to addition of O_2 to alkyl radicals and the subsequent formation of 6-member ring isomers (Sarathy et al., 2011;

Ranzi et al., 2015). The ratios of DBE/C can be used as an indicator for condensed aromatic ring structures (Hockaday et al., 2006; Lin et al. 2012; Yassine et al. 2014). When DBE/C was higher than 0.7, compounds were identified as soot-materials or oxidized polycyclic aromatic hydrocarbons (PAHs), ~~which was~~ an important class of light-~~-~~absorption organic ~~matters~~materials. The relative response of compounds with DBE/C>0.7 accounted for 3.2%, 6.5%, 3.1%, 26% and 8.3% of total ions for excavators under the idling, working and moving modes and vessels using HFO and diesel, respectively.

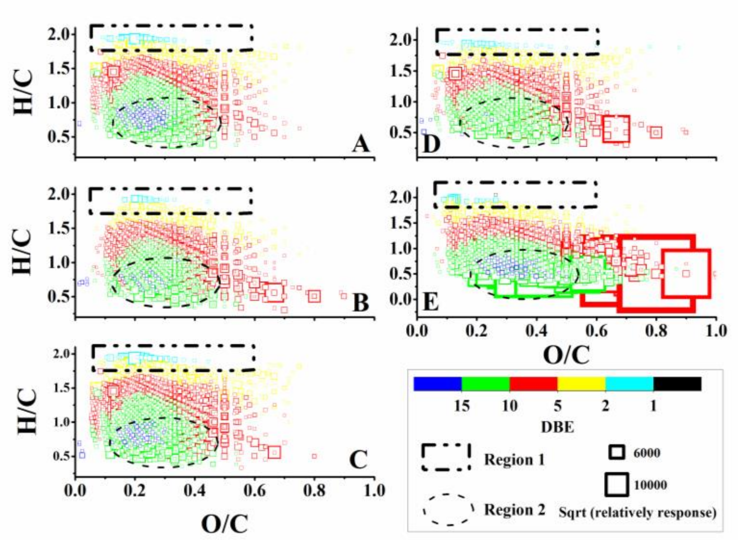

Figure 2 The V~~v~~an Krevelen (VK) diagrams of CHO compounds for off-road engines. (A, B, C, D and E were the mass spectra for excavators under idling, working, and moving modes and vessels using diesel and HFO, respectively)

3.3 CHON compounds in POCs from off-road engines emission

The peaks intensity percentage ~~relative response~~ ~~of~~ for the CHON group to ~~was~~total ions was the second largest ~~for~~ in POCs~~M~~ emitted from off-road diesel engines, except for ~~the fraction of CHON for~~ vessels using HFO (**Fig. 1**). The fraction of nitrogen oxide ~~was~~ declined with increasing length of the straight-chain alkyl (Hellier et al., 2017), which was consistent with the relative response of the CHON group for diesel and HFO fueled engine~~s~~ emissions. It was always considered that CHON mainly originated from biomass emission (18%-41%), while the percentage of peaks response for the CHON group to the total assigned ions measured from off-road diesel engines was comparable or slightly smaller than those emitted from biomass burning (Laskin et al., 2009; Wang et al., 2017; Song et al. 2018). As shown ~~from~~ by the average ratios of O/C and H/C for CHON group for vessels and excavators, the degree of oxidation and unsaturation of the CHON group for vessels ~~was~~ were higher than those for excavators (**Table S2**).

~~The relative response of~~ $C_{10}H_5O_5N_2$, $C_{11}H_7O_5N_2$, and $C_{12}H_9O_5N_2$ were the most abundant peaks in terms of ~~compounds~~ relative responses for the CHON group detected in diesel fueled excavators and vessel emissions, while $C_{10}H_4NO_6$, $C_9H_4NO_4$, and $C_{10}H_4NO_7$ were highest for vessels using HFO. Diesel-fueled off-road equipment and vessels using HFO were high-~~-~~rated speed and low-~~-~~rated speed engines, respectively (**Table 1**). This might be the main reason for the formation of 2 nitrogen atoms in the CHON group for high-~~-~~rated speed equipment, which results in higher combustion temperatures than those for low-~~-~~rated speed engines, thereby promoting nitrogen atom attachment. The higher oxygen content in vessel emissions using HFO might be attributable to the higher oxygen content and kinematical viscosity of the HFO (**Table 2**). The large value of kinematical viscosity in HFO was ~~caused by~~a result of the

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presence of a certain ~~amount~~number of aromatic hydrocarbons, fatty acids etc. which were difficult to combust and resulted in incomplete combustion (Örs et al., 2018).

For further discussion of probable chemical structures, the CHON group was divided into 23 subgroups, including OxN1 ($1 \leq x \leq 10$) and OyN2 ($2 \leq y \leq 14$) (**Fig. S4**). The distribution patterns of CHON subgroups for excavators under three operational modes were similar, with the highest relative response of N_2O_5, while NO_4-NO_5 were the highest group for vessel emissions in terms of relative response. The ratio of O/N higher than 3 is always indicative of the presence of nitro compounds ($-NO_2$) or some organic nitrates (with NO_3). Yassine et al. (2014) reported that DBE/C was only valuable to the aromaticity properties ~~for those~~of compounds with pure hydrocarbons. The aromaticity equivalent (Xc) has been proposed to evaluate the aromaticity of organic material with heteroatoms (e.g. N, S). When the value of Xc exceeds 2.5, aromatic structures are present within the compounds, while a value of Xc higher than 2.7, indicates the presence of condensed aromatic compounds (e.g. benzene core structure with Xc =2.5; pyrene core structure with Xc=2.83; ovalene core structure with Xc=2.92). ~~Analyses of the chemical structures for different off road engines revealed that CHON structures were different in excavators and vessels regardless of the operation mode and fuel oil used. Thus, only excavators under the working mode and vessels using HFO will be further discussed.~~

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As ~~mentioned~~mentioned,~~ in the previous,~~ the formulas in ~~the most abundance relative response of~~ CHON group with the most abundant relative responses for diesel-fueled excavators and vessels were~~As shown in **Fig. 3** ,~~ $C_{10}H_5N_2O_5$, $C_{11}H_7N_2O_5$, and $C_{12}H_9N_2O_5$, which ~~were~~compose the ~~biggest~~largest green ball in **Fig~~ure~~. 3** with Xn=2.5, indicating the presence of a benzene core structure ~~existing~~ in the com~~u~~pounds. Thus, it was most likely ~~was~~ ~~for excavators under three operational modes might be~~ dinitrophenol, and methyl dinitrophenol compounds. Likewise, $C_{10}H_4NO_6$, $C_9H_4NO_4$ and $C_{10}H_4NO_7$~~For vessel emissions,~~ comprise the largest yellow ball~~belong to the biggest yellow ball~~ in **Fig~~ure~~. 3** for HFO-fueled vessels, most of which have Xn>2.7 indicating the presence of condensed aromatic compounds~~existing~~. –N~~n~~itronaphthol~~,~~ and methyl nitronaphthol were the most ~~important~~ significant compounds~~(e.g. $C_{10}H_4NO_6$, $C_9H_4N_1O_4$ and $C_{10}H_4N_1O_7$)~~ arising from HFO-fueled ~~vessles~~vessel emissions, which have previously been reported ~~from~~ in vehicle~~s~~ emissions (Yassine et al., 2014; Tong et al., 2016). Furthermore, almost 55% of the CHON group had an O/N ratio higher than 5, and half of the CHON group had~~more~~ aromatic rings higher than 3 for HFO-fueled~~vessels using HFO~~. This was significantly higher than those for excavators and vessels using diesel. The reactivity and life span of these compounds should be considered to determine whether these chemicals could be used as tracers for off-road engines combustion. The same chemical structure discovered in the atmosphere ~~seemed as~~indicated that SOA could ~~be a~~provide valid evidence ~~to prove~~ that CHON with nitrophenol or nitronaphthol could exist in the atmosphere long enough ~~for enough time~~ to ~~detectability~~ be detected (Zhang et al., 2010).

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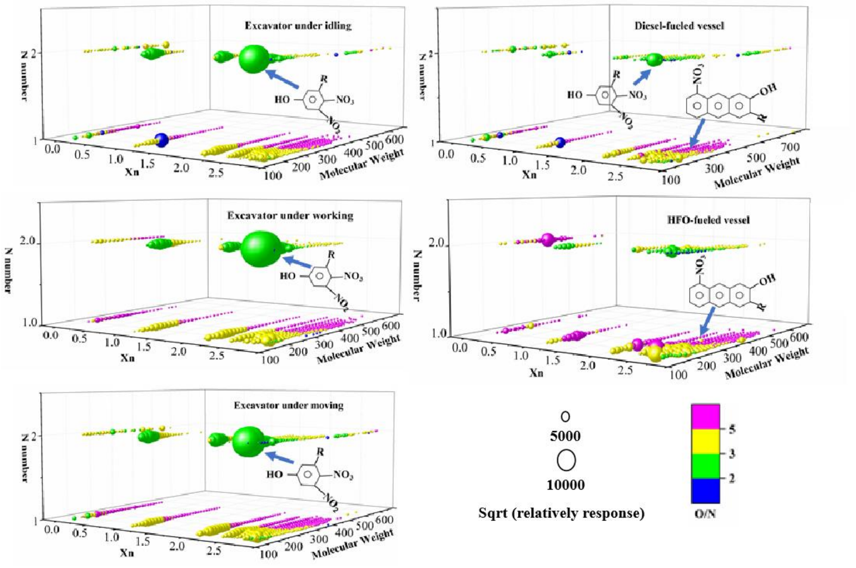

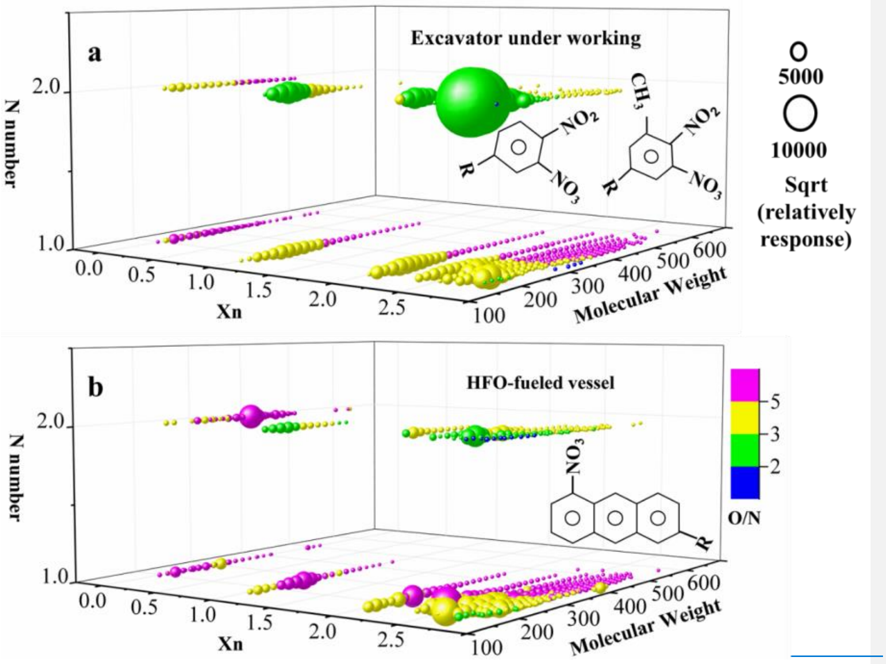

Figure 3 Molecular composition and possible structure of CHON for excavators under ~~the~~three ~~working~~ modes ~~(a)~~ and vessels using HFO and diesel~~(b)~~

3.4 S-containing compounds

The last group of POCs~~M~~ was S-containing organic compounds, including CHOS and CHONS. As shown in **Fig. 1** and **Table S2**, the percentage of ~~relative~~ peaks response ~~of~~ for S-containing species to total assigned peaks from vessels using HFO (35%) was higher than those from other vehicles, with 1, 3, 2 and 3 times more than those for excavators under idling, working, moving and vessels using diesel, respectively. However, the ~~relative response of the~~ CHONS group for excavators was significantly higher than those for vessel emissions in terms of relative ions intensity. The high fraction of peak responses for S-containing species from~~or~~ vessels using HFO ~~may~~ might be attributed to the high sulfur content in HFO. The maximum sulfur content in HFO ~~reported~~ detected in this study was 2.46%, which was significantly higher than those in diesel (**Table 2**). In addition, for excavators under the idling mode, the ~~sum~~ fraction of the relative response of S-containing compounds was 32.5%, while for the working and moving modes, they ~~was~~ were 11.6% and 17.1%, respectively.

~~In order to~~To facilitate further discussion, three ~~types of~~ subgroups for CHONS ($N_1O_5S_1$, $N_1O_6S_1$ and $N_1O_7S_1$) and eight ~~types of~~ subgroups for CHOS (O_3S_1, O_4S_1, O_5S_1, O_6S_1, O_6S_2, O_7S_1, O_7S_2 and other) were characterized (**Fig. 4**). Generally, O_4S_1 and O_5S_1 were the most abundant subgroups for all ~~of the~~ off-road engines. For example, $N_1O_5S_1$ was the most abundant subgroup for the working mode, accounting for 36.7% of S-containing compounds. When $O/S \geqslant 4$, this indicates that a sulfate group exists within the organic compounds. Thus, O_5S_1 and O_4S_1 may be organosulfates or sulfonates (Riva et al., 2015). Riva et al. (2015) found that sulfur-containing products from PAHs were possible, and might not be solely sulfates but also sulfonates, especially with O/S values of 4-5. On comparing the sulfur-containing products observed in this study and the Riva et al. study, it was interesting to find that some PAH-derived OS products generated in the lab also have significant response in the field measurements. As shown as **Fig. S5**, three of the most abundant peaks ($C_8H_7O_5S^-$, $C_{11}H_5O_6S^-$ and $C_{18}H_{29}O_4S^-$) of S-containing compounds emitted from HFO-fueled vessels were also observed in the lab from PAH oxidations in the presence of sulfate. Although the fraction of S-containing compounds for vessels using HFO was similar ~~with~~ to those for excavators under idling (**Fig. 1**), different structures of compounds existed between these two engines. The relative response of O_6S_2 and O_7S_2 for excavators under idling was considerably higher than those for vessels using HFO.

S-containing compounds for vessels were highly unsaturated with 8.03 for the average DBE value which was higher than those for excavators (6.77; **Table S2**). Furthermore, the fraction of compounds with Xc⩾2.5 accounted for 9.3%, 3.7% , 2.5%, 1.5% and 3.4% of the total S-containing compounds for vessels using HFO, diesel and excavators under idling, working and moving modes, respectively. Through a comparison of the average DBE value and fraction of compounds with Xc⩾2.5 between excavators and vessels, it was found that different structures were present in S-containing compounds. The most ~~of~~ abundant S-containing compounds emitted from off-road diesel engines ~~were~~ were aliphatic with long chains and sulfate fraction, which was consistent with the results ~~from~~ of Tao et al. (2014) who found that most of the CHOS group contained long aliphatic carbon chains and low degrees of unsaturation and oxidation in ambient air in Shanghai. ~~and t~~They suggested that most of these

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compounds were derived from diesel emission. It was interesting to find that the most abundant peaks of CHOS compounds observed in this study were also identified through the laboratory simulation study (Riva et al., 2016). The conclusions reported from Riva's study could provide a possible chemical reaction path to explain the chemical formula detected from off-road engine combustion. The formulas marked in bold red in **Table S3** were the homologous compounds with $C_{12}H_{23}O_5S^-$ which was reported to have been generated from dodecane oxidation by Riva et al.'s research, while the formulas in bold blue were likely formed from cycloalkanes. In contrast, the structures of S-containing compounds emitted from HFO fueled engines were liable to have condensed aromatic rings.

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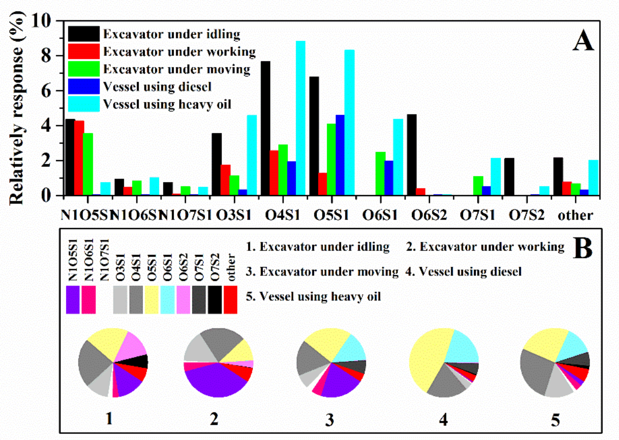

Figure 4 The distribution of subgroups of S-containing compounds for off-road engines

On an ~~A~~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 ~~important~~ impactful ~~species~~S-containing compounds emitted from off-road engines. ~~Because f~~For most CHOS compounds

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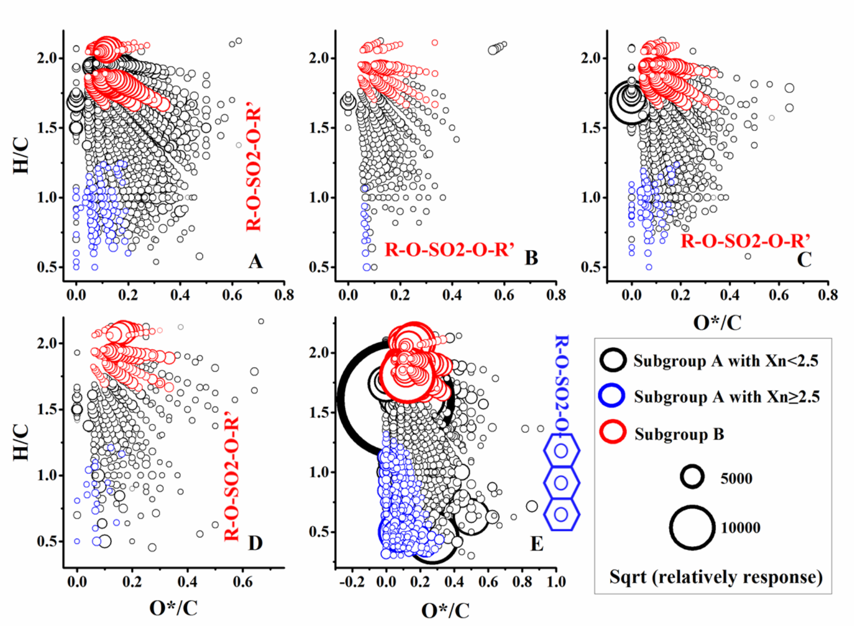
containing O/S ⩾ 4, O*(O*=~~(~~O - 3)~~)~~ was used to identify the oxidation of organic compounds by removing the effect of sulfate or sulfonates. The modified VK diagram (H/C and O*/C) was used to characterize the structure of CHOS compounds (**Fig. 5**). Some organosulfates or sulfonates with an aromatic ring (subgroup A~~) were reported that~~) could be produced by SOA precursors (e.g. α-pinene, β-pinene, monoterpenes) (Surratt et al., 2008). The most important precursors generating the subgroup A in this study might be the PAH-derived OS products in the presence of sulfate ~~the original primary compounds in combustion fuels, and not SOA precursors~~(Riva et al., 2015). However, there was another subgroup of organosulfates (subgroup B) emitted by diesel vehicles with long aliphatic carbon chains (Tao et al., 2014). Subgroup B of organosulfates was defined as C > 8, DBE < 3, and 3 < O < 7 (red cycles in **Fig. 5**) (Tao et al., 2014), while the remaining CHOS compounds could be considered as subgroup A (blue cycle represented subgroup A with Xn ⩾ 2.5 and the rest is contained within ~~be~~ the black circle). ~~Clearly t~~The fraction of subgroup B of CHOS compounds in off-road diesel engine emissions (average: 33.9%±6.64%) were significantly higher than those in HFO fueled vessel emissions (19.9%). For vessels using HFO, almost 10% of CHOS compounds (blue ~~color~~ in **Fig. 5**) were organosulfates with one or more aromatic rings, which was consistent with the quality of the HFO. ~~Similar with t~~The structures detected for CHON compounds for HFO-fueled vessels and~~,~~ the organosulfates with one or more aromatic rings were similarly ~~also~~ detectable in the atmosphere (Surratt et al., 2008).



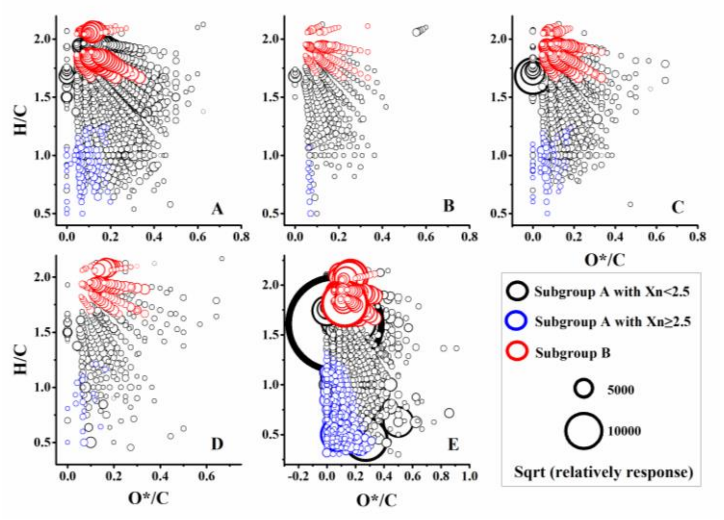


Figure 5 The ratios of O*/C vs H/C of CHOS and proportion of subgroup B and Xn>2.5 for off-road engines (A, B, C, D and E were the mass spectra for excavators under the idling, working, and moving modes and vessels using diesel and HFO, respectively)

4. Conclusions and environmental implications

CHO compounds were the most abundant species across all sources (biomass, coal, on-road vehicles and off-road vehicles) in terms of ions intensity, while the fractions of CHON and S-containing compounds were different from anthropogenic source emissions. Furthermore, the possible chemical structures of these compounds for diverse sources varied sharply.

For CHO compounds, the average DBE values from excavator and vessels emission were 8.38 ± 3.84 and 8.55 ± 3.77, which was higher than those emitted from crop burning (6.9) and coal combustion (7.48) (Song et al., 2018). The methoxyphenols ($C_9H_{14}O_4$, $C_{18}H_{28}O_8$, $C_{11}H_{20}O_5$, $C_{18}H_{22}O_7$, $C_9H_{12}O_4$) and fatty acids ($C_{16}H_{32}O_2$), derived from limonene and palmitic acid, were frequently observed in crop burning emissions. CHO compounds with high C numbers ($C_{20}H_{28}O_2$, $C_{20}H_{26}O_2$, $C_{20}H_{30}O_2$) were detected from wood burning. One benzene ring substituted with O-containing groups such as hydroxyl, methoxyl, and carboxyl ($C_8H_6O_4$, $C_{13}H_{18}O_4$ and $C_{12}H_{16}O_4$) were dominant in coal combustion. Overall, mono-aromatics dominated tunnel samples (Tong et al., 2016) and off-road diesel vessels. However, abundant condensed aromatic ring structures with high O numbers ($C_{10}H_5O_8$, $C_9H_5O_6$ and $C_{10}H_5O_9$) were found for HFO fueled vessels.

For CHON compounds, almost all sources were reported to emit nitrophenol compounds, while the substituted groups were slightly different due to different numbers of N and O atoms. The fraction of relative peak response of CHON compounds, an important light-absorbing substance, could reach half of the POCs from biomass burning emission. Methyl-nitrocatechols produced from the oxidation of cresol and N-bases composed of C, H, and N elements were considered as the biomarkers for biomass

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burning (Laskin et al., 2009; Wang et al., 2017). However, om comparing the signal intensity of nitroaromatics in ambient aerosol and fresh biomass burning smoke, Wang et al. (2017) found evidence to the contrary. Signal intensity was stronger in ambient aerosols than that in fresh biomass burning smoke, which indicated the existence of other sources or aging process. Recently, nitrophenol was also detected in tunnel samples indicating traffic sources. In this study, we found that dinitrophenol were abundant in non-road diesel vehicle emissions, while nitronaphthol with one or more methyl groups was dominant for HFO-fueled vessels emission.

Except for biomass burning, S-containing compounds were still an important group of organic matter for coal combustion, on-road vehicles, off-road diesel vehicles, HFO-fueled vessels, and in background sites, accounting for 48%, 17%, 8.9%, 33% and 32%, respectively, of total detected organic matters. Organosulfates and sulfonates were one of the most important HULIS, which were reported as the prominent S-containing compounds at background sites due to aging reactions of organics with H_2SO_4. For coal combustion, S-containing compounds had low DBE and $AI_{mod,w}$ values, which were probably considered as alkylbenzene rings substituted with one sulfate group. The specific structure of S-containing compounds was organosulfates or solfonates with condensed aromatic rings for HFO-fueled vessels, while more abundant organosulfates with aliphatic chains were observed in emissions from off-road diesel equipment. Likewise, the organosulfates with aliphatic long chains alkanes were observed in on-road traffic emissions due to its original oil structure (Jiang et al., 2016; Riva et al., 2016; Tao et al., 2014). These S-containing compounds with high aromaticity, or long

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chain alkanes, were frequently formed from secondary photochemical reactions between oxidation products of volatile and intermediate volatility organic compounds and acidified sulfate particle (Riva et al., 2015; 2016). Therefore, a high-abundance of S-containing compounds in the atmosphere might from secondary photochemical reactions and also be emitted directly from the combustion of off-road engines. ~~In this study, one of the advanced techniques, FT-ICR MS, was adopted to grasp the characterization of molecular composition of POM emitted from off-road engine combustion. Firstly, general characterizations of POM extracted by pure water were discussed. It was found that POM emitted from HFO vessels had highest degree of unsaturation and oxidation. Next, the detail characterizations of POM were discussed into three subgroups. CHO (accounting for 49% of total POM relative peak response) was the most abundant group for all tested off-road engines, followed by CHON (33%) and CHOS (35%) for diesel- and HFO-fueled off-road equipment, respectively. CHO compounds emitted by vessels using HFO had the highest degree of oxidation and unsaturation than the others, which majority were considered as soot materials or oxidized PAHs. For excavators, dinitrophenol, and methyl dinitrophenol have the highest intensity to CHON compounds, while nitronaphthol, and methyl nitronaphthol were the most important compounds for vessels. The most of S-containing compounds emitted from off-road diesel engines were along with long aliphatic carbon chains, but for HFO-fueled vessels, abundance of organosulfates were along with one or more aromatic rings. Comprehensive understanding of the molecular characteristics of POM from off-road engine emissions could provide further insight into the key chemical~~

~~factors causing different absorption properties between different sources of emissions and identify the possible tracers for off road engines combustion~~.

Author contribution. MC and CL contributed equally to this work. MC wrote the manuscript in close cooperation with CL and got helpful direction by YC, JL (Jun Li) and JZ. FZ, JL (Jia Li) and YM were responsible for sampling and chemical analysis. BJ, CY and MZ were familiar with data process of FT-ICR MS and mass absorption efficiency. ZX and GZ provided key contributions to article structure and logic.

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Competing interests. The authors declare that they have no conflict of interest.

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