

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: 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**).

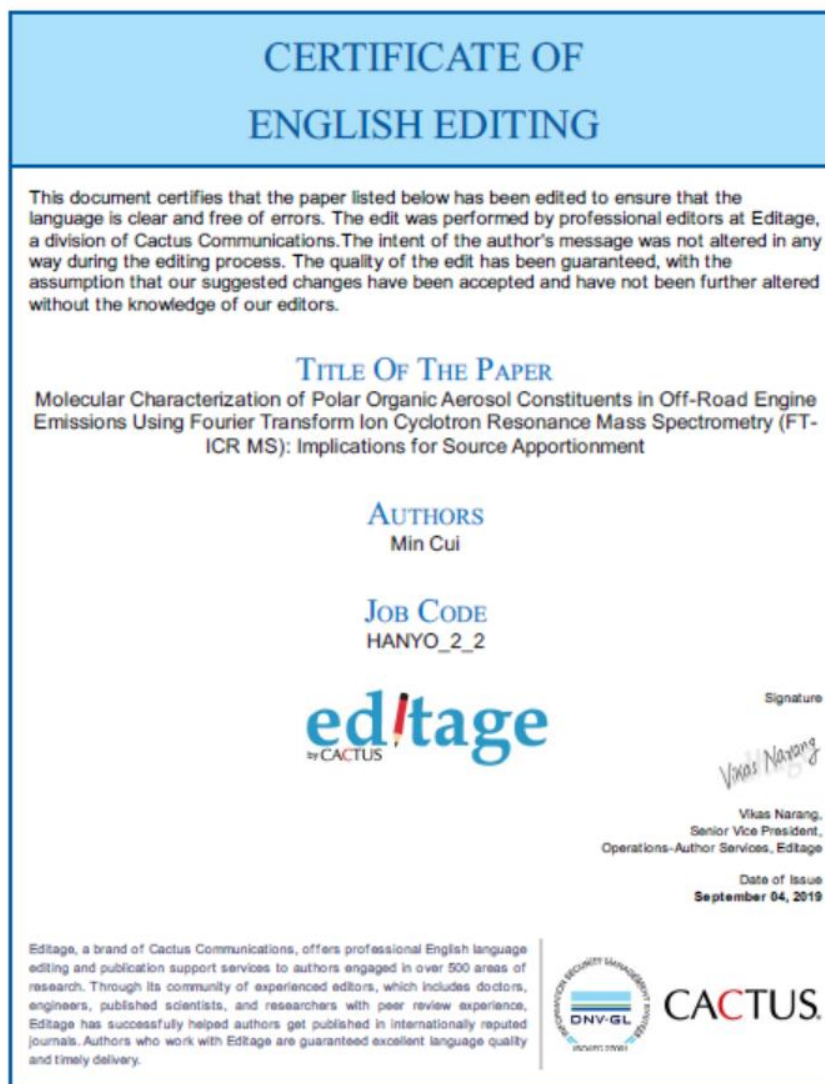


Figure R1 Certificate of english editing

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**).

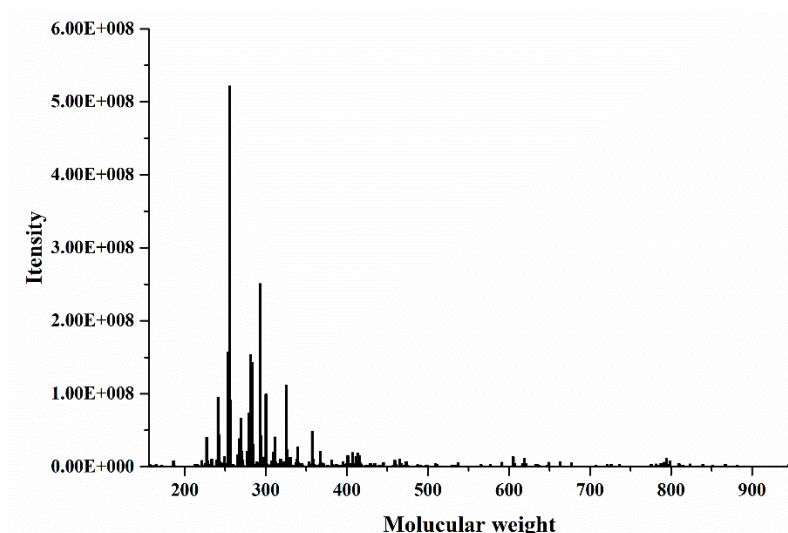


Figure R2 Intensity of detected peaks from blank sample

(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. I., 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](#)).

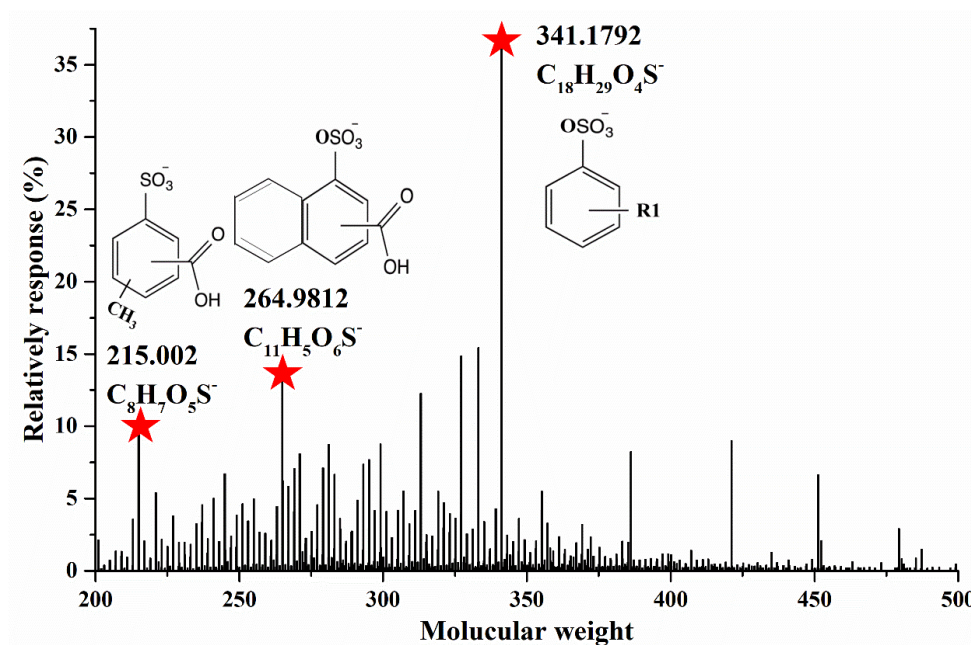


Figure S5 possible chemical structure of three of the most abundance peaks of S-containing compounds emitted from HFO-fueled vessels according to Riva et al., research.

“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.,

Villeneuve, 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 be 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	C16H31O5S⁻	335.1898	1	23.50	Excavator under moving	C5H3O13S2 ⁻	334.902	4	11.95
	C17H33O5S⁻	349.2054	1	22.42		C4H3O11S2 ⁻	290.9121	3	3.25
	C15H29O5S⁻	321.1741	1	22.07		C22H37O3S ⁻	381.2469	4	3.02
	C18H35O5S⁻	363.2211	1	19.07		C14H27O5S⁻	307.1585	1	2.69
	C14H27O5S⁻	307.1585	1	16.28		C15H29O5S⁻	321.1742	1	2.64
	C17H35O5S ⁻	351.2211	0	16.12		C16H31O5S⁻	335.1898	1	2.48
	C16H29O5S⁻	333.1741	2	14.63		C15H27O5S⁻	319.1585	2	2.37
	C17H31O5S⁻	347.1898	2	14.42		C18H29O4S⁻	341.1792	4	2.28
	C18H33O5S⁻	361.2054	2	14.39		C13H25O5S⁻	293.1428	1	2.07
Excavator under working	C15H27O5S⁻	319.1585	2	13.89	Diesel-fueled vessel	C16H29O5S⁻	333.1741	2	2.06
	C22H37O3S ⁻	381.2469	4	33.63		C12H25O5S ⁻	281.1428	0	22.20
	C24H41O3S ⁻	409.2782	4	14.90		C13H27O5S ⁻	295.1585	0	18.86
	C5H3O13S2 ⁻	334.902	4	11.85		C11H23O5S ⁻	267.1272	0	16.00
	C16H29O5S⁻	333.1741	2	8.43		C13H25O5S⁻	293.1428	1	15.57
	C15H27O5S⁻	319.1585	2	8.22		C15H29O5S⁻	321.1741	1	15.01
	C16H31O5S⁻	335.1898	1	7.89		C14H27O5S⁻	307.1585	1	14.75
	C17H31O5S⁻	347.1898	2	7.70		C12H23O5S⁻	279.1272	1	12.64
	C15H29O5S⁻	321.1741	1	7.58		C11H21O5S⁻	265.1115	1	11.14
	C17H33O5S⁻	349.2054	1	7.23		C16H31O5S⁻	335.1898	1	11.03
	C14H27O5S⁻	307.1585	1	6.77		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**).