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 composition and structure of polar organic matters (POM) in particles emitted from various vessels and excavators were characterized using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). POM was extracted by purified water and discussed by elemental composition which was divided

5   into three groups, namely CHO, CHON and S-containing compounds (CHONS and CHOS). The results showed that: (i) 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 (heavy fuel oil)-fueled off-road equipment, respectively. (ii) The abundance and structure of the CHON group in

10   water extracts were different in terms of engine type and load. The fraction of relative peak response of CHON was highest for excavator emissions under the working mode compared to other modes (idling and moving). Furthermore, dinitrophenol and methyl dinitrophenol were the most abundant emission species for excavators with high rated speed, while nitronaphthol and methyl nitronaphthol were more important for low rated

15   speed vessels. (iii) The composition and structure of S-containing compounds was directly influenced by fuel oil characteristics (sulfur content and aromatic ring), with much more condensed aromatic rings in S-containing compounds observed for HFO-fueled vessels, while more abundant aliphatic chains were observed in emissions from diesel equipment. Overall, higher fractions of condensed hydrocarbons and aromatic

20   rings in POM emitted from vessels using HFO caused strong optical absorption capacity. And different structures existing in POM could provide a direction to qualitative and quantities the exact organic compounds as tracers to distinguish the emission from

diesel or HFO - fueled off-road engines.

1. Introduction

Rapidly increased number of off-road engines (eg. Vessels and excavators) have 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, 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 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 ocean-going vessels emission in East Asia (Liu et al., 2016). As reported by US EPA, nearly 34% of elemental carbon (EC) emissions originated from off-road diesel vehicle emissions in the United States (USEPA 2015). Furthermore, constructive equipment, one of the typical off-road diesel vehicles, emitted abundance volatile organic matter which was considered as one of the most important procedures of dominant components of HUmic-LIke Substances (HULIS), like organosulfates (Zhang et al., 2010; Tao et al., 2014).

The emission standards for non-road engines are incomplete in China, especially for the vessel emissions. Nowadays, stage 3 emission standard has been implemented for non-road diesel engine from 2016, while stage 1 emission standard for vessels emission will be implemented in 2020 (SEPA et al., 2015a, SEPA et al., 2016). Furthermore, the oil quality for non-road mobile sources couldn't be guaranteed. According to the standard of GB/T17411-2012, the sulfur content in oil using 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 apportion the contribution of

off-road equipment 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

5 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 it should be noticed that V could also be emitted by industry

activities. Therefore, overestimate/underestimate results of contribution from ship

emission to $PM_{2.5}$ in atmosphere could be gained by using V as the only tracer (Zhang

10 et al., 2014). Furthermore, some isomer ratios of polycyclic aromatic hydrocarbons

were recommended as indicators of off-road engines emission, but the huge variations

of those ratios in the atmosphere might mislead the final results (Zhang et al., 2005; Cui

et al., 2017). Thus, there is an urgency need to explore the unique organic tracers.

Organic matter (OM) is one of the most important components in $PM_{2.5}$ emitted

15 by non-road mobiles, with the highest fraction accounting for up to approximately 70%

in ship emission (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 of OM, especially for polar organic matter,

20 were hardly 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,

5   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).

FT-ICR MS as one of the most advanced techniques with a high mass resolution of

0.00001 is always used to determine the organic matter at a molecular level in crude oil

(Jiang et al., 2019). FT-ICR MS usually coupled with some soft ionization techniques,

10   such as electrospray (EST) and atmospheric pressure chemical ionization (APCI) to

analyze polar species and non-polar organic matters, respectively (Smith et al., 2009;

Smit et al., 2015). Some studies have successfully characterized the elemental

components of polar organic matter in 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.

15   2014), but few of them have been undertaken in China, especially for sources 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 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

20   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 significant

5   CH_2-based homologous series.

This study aimed to detect the molecular characterization of polar organic matter emitted from typical non-road engines by FT-ICR MS to provide a new direction to find biomarkers for non-road engines. To this end, studies were conducted: 1) to identify the molecular composition of polar organic matter from excavators under different

10   operation modes; 2) to determine the molecular composition and possible structure of polar organic matter from vessels using HFO and diesel, respectively; 3) to explore the key factors affecting the composition and structure of polar organic matter from HFO and diesel fueled off-road engines; 4) to provide the direction to find the possible tracers for off-road engines emission.

15   **2. Materials and Methods**

2.1 Sample collection

Four ships using HFO and diesel 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

20   shown 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 detect the fuel quality (**Table 2**). For excavator emission sampling, three operation modes were selected

including the idling, moving and working modes, and sampling time was approximately

half an hour for each mode. Commercial equipment (MFD25, produced by Shanghai

Besser environmental protection technology Co., Ltd.) was used for PM$_{2.5}$ sampling.

The description of particulate matter dilution and sampling system are presented in full

5   in Xia (Xia 2017). In short, the exhaust flume 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 under three operation

modes. For vessels emission, an on-board measurement system was used, as previously

10   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 (year)	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

15   **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℃) mm²/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:

Portions of filters (**Table S1**) were cut and combined for 40 minutes ultrasonic extraction with 40 mL ultrapure water and 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 chemical composition of POM by FT-ICR MS. The remaining extraction filters were frozen and then dried to remove ultrapure water. The filters were then subject to 40 min of ultrasonic extraction with 36 mL dichloromethane and 4 mL methanol. The extracted solvent was divided into three portions, and then were processed same as previously described for the ultrapure water extract.

Both samples extracted with water or organic solvents were processed by a solid phase extraction method to remove ions, which disturbed the results of FT-ICR MS. The detail of the solid phase extraction method was presented in Mo et al. (2018). Briefly, the pH value of water extracts was adjusted to 2.0 by HCl, and then passed

5   through an SPE cartridge (Oasis HLB, 30 μm, 60 mg/cartridge, Waters, USA). The adsorbed POM was eluted with 6 mL 2% (v/v) ammonia/methanol and dried by a gentle stream of N_2. Finally, the POM was re-dissolved using 10 mL ultrapure water.

2.3 FT- ICR MS analysis

The molecular characterization of POM was undertaken using negative-ion ESI

10   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 $\mu L \cdot h^{-1}$ 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

15   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 $C_cH_hO_oN_nS_s$ was used as general formula. Some criteria should be conformed to assign the possible formula (Wang et al., 2017). Briefly, all of the

20   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 in the ESI⁻ mode. 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:

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

$$Xc=(3*(DBE-o-s)-2)/(DBE-o-s) \tag{2}$$

5 Where c, h, o, n, s were the number of C、H、O、N、and S atoms in the
corresponding formula. 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 POM for off-road engines

10 In general, the range of detected peaks for excavators and vessels were between
molecular weight of 150-900 Da, but most of the intensive peaks occurred in the
molecular weight range of 200-400 Da. Mass spectra for excavators in different
operational modes and vessels using different oils were different. There were 4734,
3097, 4731, 4554 and 2818 peaks in excavator emissions under the idling, working and

15 moving modes and vessel emission 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 POM in all three operation
modes, accounting for 41%, 46% and 48% of all the formulas for the idling, working

20 and moving modes. S-containing compounds (i.e. CHOS and CHONS) were most
abundant in the idling mode than in other operation modes, while the relatively peak
response of the CHON group was highest under the working mode than in other

operation modes (**Fig. 1**). For vessels, CHO was the most abundant species group of POM for both vessels using diesel and HFO, accounting for 50%-60% of total peak intensity. 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

5   properties of POM for vessels using HFO showed a larger degree of oxidation and unsaturation than other samples (**Table S2**). These differences in the composition of POM might be attributable to variations in engine load, fuel supply, and air supply in different operation modes, which were discussed in next parts.

As discussed in supporting information (SI Part C), the chemical properties of

10   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, 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

15   organic matters from off-road engines emission.
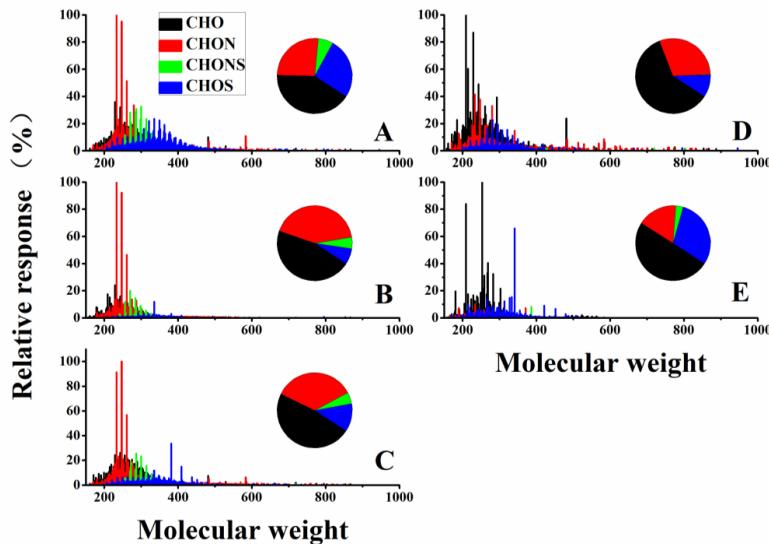
Figure 1 Mass spectrum of POM in water extractions for off-road diesel engines emissions. A, B, C, D and E were the mass spectra for excavators under idling, working, moving and vessels using diesel and HFO, respectively

3.2 CHO compounds in polar organic matters from non-road engines emission

1746, 1287 and 1797 spectra peaks for excavators in the idling, working and moving mode, respectively and 1561 and 1318 peaks for vessels using HFO and diesel, were identified by FT-ICR MS. Considering the number of detected peaks, the compositions of CHO group emitted from off-road engines were more complicated than those from ambient samples while relatively comparable to those from other sources of emissions (e.g. biomass and coal combustion) (Lin et al., 2012; Jiang et al. 2016; Song et al. 2018).The average molecular weight of detected ions for excavators in idling, working and moving and vessels using HFO and diesel was 338±96.7, 316±84.6 336±96.6, 331±72.9 and 357±123 Da, respectively, which was 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

5   the idling and moving modes, which indicated that long chain aliphatic hydrocarbons

were liable to crack during high temperatures and under low air/fuel ratio conditions.

This trend was consistent with a previous study results (Wang et al., 2018) which found

that low temperatures and oxygen-rich combustion would promote the chain

propagation reaction. Although the lipid contents of fossil fuel might be an important

10   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 of CHO compounds for off-road diesel engines was

$C_9H_5O_6$ 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 $C_{10}H_5O_9$.

15   The van Krevelen (VK) diagram (H/C versus O/C) was usually used to identify the

structural properties of organic matter in FT-ICR MS research due to only molecular

formula was given (Wozniak et al., 2008; Lin et al., 2012). Through comparing the

ratios of H/C and O/C 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

20   highest degree of oxidation and unsaturation. Furthermore, CHO group under the

working mode had a higher degree of oxidation and unsaturation than under 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. Region 2 represented compounds with low ratios of H/C and O/C and DBE>10 which were commonly considered as condensed hydrocarbons. Most compounds detected in the CHO group for vessels using HFO were molecular species

5 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 vessel using HFO caused low temperature combustion which was prone to addition of O_2 to alkyl radicals and the subsequent

10 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.

15 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.
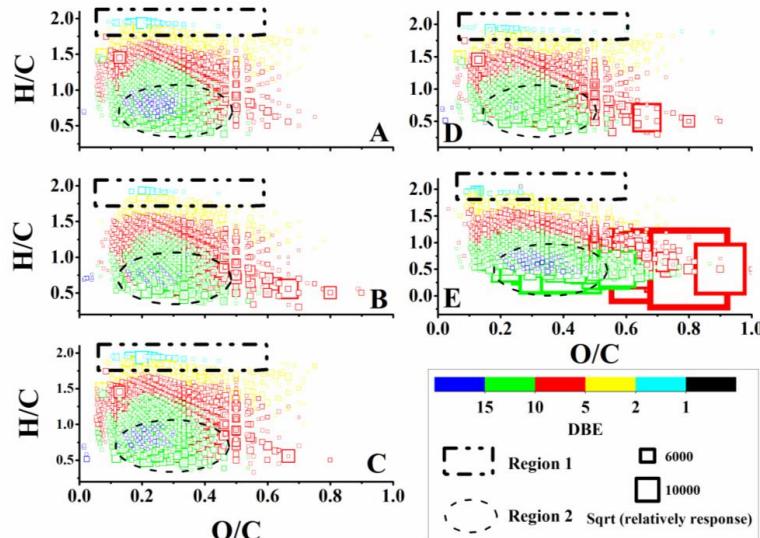
Figure 2 The van Krevelen (VK) diagrams of CHO compounds for off-road engines. (A, B, C, D

and E were the mass spectra for excavators under idling, working, moving and vessels using diesel

and HFO, respectively)

3.3 CHON compounds in polar organic matters from non-road engines emission

The relative response of CHON group was the second largest for POM 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 engines emissions. It was always considered

that CHON mainly originated from biomass emission (18%-41%), while the percentage

of CHON group 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 the average ratios of O/C and H/C for vessels and

excavators, the degree of oxidation and unsaturation of the CHON group for vessels

was 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 compounds 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

5 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

10 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 the presence of a certain amount 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

15 divided into 23 subgroups, including OxN1 (1≤x≤10) and OyN2 (2≤y≤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. The ratio of O/N higher than 3 is always indicative of the presence of nitro compounds (-NO_2) or some organic nitrates (with

20 NO_3). Yassine et al. (2014) reported that DBE/C was only valuable to the aromaticity properties for those 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

5   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.

As shown in **Fig. 3**, $C_{10}H_5N_2O_5$, $C_{11}H_7N_2O_5$ and $C_{12}H_9N_2O_5$ for excavators under three operational modes might be dinitrophenol, and methyl dinitrophenol. For vessel

10   emissions, nitronaphthol, and methyl nitronaphthol were the most important compounds (e.g. $C_{10}H_4NO_6$, $C_9H_4N_1O_4$ and $C_{10}H_4N_1O_7$), which have previously been reported from vehicles emission (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 vessels using HFO. This was

15   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 SOA could be a valid evidence to prove that CHON with nitrophenol or nitronaphthol could exist in the atmosphere for

20   enough time to detectability (Zhang et al., 2010).
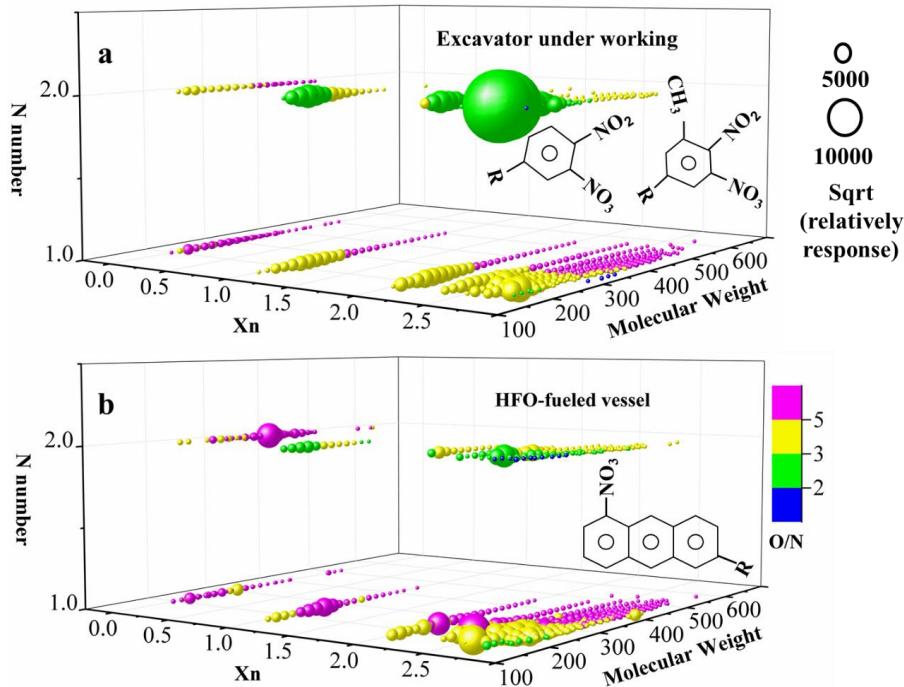
Figure 3 Molecular composition and possible structure of CHON for excavators under the working

mode (a) and vessels using HFO (b)

3.4 S-containing compounds in polar organic matters from non-road engines

emission

The last group of POM was S-containing organic compounds, including CHOS and

CHONS. As shown in **Fig. 1** and **Table S2**, the relative response of S-containing species

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. The high fraction

of S-containing species for vessels using HFO may be attributed to the high sulfur

content in HFO. The maximum sulfur content in HFO reported 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 of the relative response of S-containing compounds was 32.5%, while for the working and moving mode was 11.6% and 17.1%, respectively.

In order to facilitate further discussion, three types of subgroup for CHONS ($N_1O_5S_1$, $N_1O_6S_1$ and $N_1O_7S_1$) and eight types of subgroup 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 indicate that a sulfate group exists within the organic compounds. Thus, O_5S_1 and O_4S_1 may be organosulfates. Although the fraction of S-containing compounds for vessels using HFO was similar with 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$\geqslant$2.5 accounted for 9.3%, 3.7% , 2.5%, 1.5% and 3.4% of the total S-containing compounds for vessels using HFO, diesel and excavators under idling, working and moving, respectively. Through a comparison of the average DBE value and fraction of compounds with Xc$\geqslant$2.5 between excavators and vessels, it was found that different structures were present in S-containing compounds. The most of S-containing compounds emitted from off-road diesel engines

were aliphatic with long chains and sulfate fraction, which was consistent with the results from 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 they suggested that most of these compounds were derived from diesel

5   emission. In contrast, the structures of S-containing compounds emitted from HFO fueled engines were liable to have condensed aromatic rings.
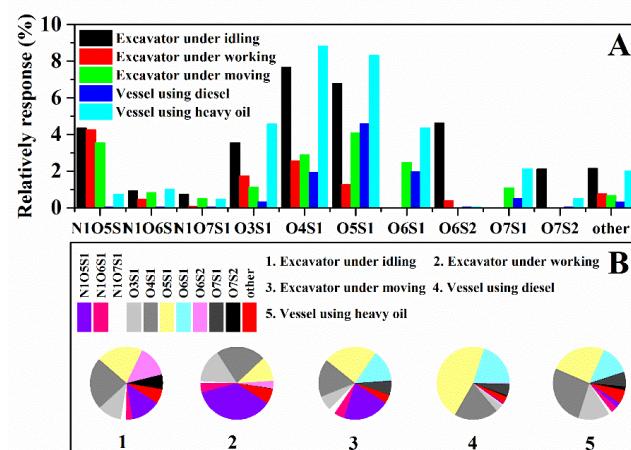
Figure 4 The distribution of subgroup of S-containing compounds for off-road engines

On Average, 88.5%±9.1% and 98.1%±0.22% of CHOS compounds for vessels and

10   excavators respectively were with O/S≥4, which indicated that organic sulfates were the most important species emitted from off-road engines. Because for most CHOS compounds containing O/S≥4, O*(O-3) was used to identify the oxidation of organic compounds by removing the effect of sulfate. The modified VK diagram (H/C and O*/C) was used to characterize the structure of CHOS compounds (**Fig. 5**). Some

15   organosulfates 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 original primary compounds in combustion fuels, and not SOA precursors. 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

5   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 black circle). Clearly the fraction of subgroup B of CHOS compounds in off-road diesel engine emissions (average: 33.9% ± 6.64%) were higher than those in HFO fueled vessel

10   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 the structures detected for CHON compounds for HFO-fueled vessels, the organosulfates with one or more aromatic rings were also detectable in the atmosphere (Surratt et al., 2008).
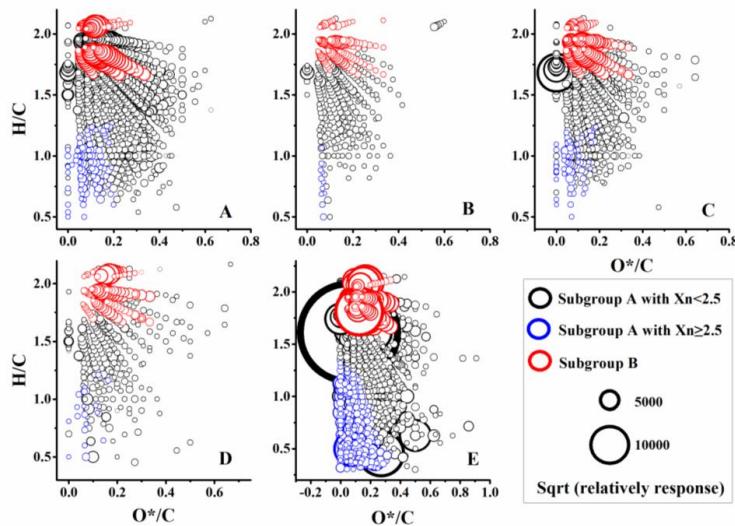
Figure 5 The ratios of O*/C vs H/C of CHOS and proportion of subgroup B and Xn>2.5 for off-road engines (A, B, C, D and E were the mass spectra for excavators under the idling, working, moving and vessels using diesel and HFO, respectively)

4. Conclusions

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

5   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.

10   **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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20   **Competing interests.** The authors declare that they have no conflict of interest.

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