

Response to the comments

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Title: Size-segregated characteristics of OC, EC and organic matters in PM emitted
5 from different types of ships in China

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The constructive comments of the reviewers are highly appreciated. We have revised the manuscript accordingly. Our point-by-point responses (in black) to each comment are listed below. And the modifications in the revised manuscript are marked in red. Please see the manuscript for details.

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Reply to Referee 1#

I lack a discussion on the relevance of the study in a larger context. It should be elaborated upon from the viewpoint that the engines are relatively small, high speed marine engines, and only representative for smaller marine craft.

Response:

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The comment is well noted. Explanation about the studied vessels has been added in Section 2.1 according to the comment. Most of the studied vessels in this study were indeed with high-speed marine engines. However, YK was a large ocean-going low-speed engine ship with heavy fuel oil used, while DFH was a medium-speed engine ship with marine diesel used (See Table S1 for details). Hence, we considered that they
25 were representative of large/medium marine crafts in China to some extent.

Revision was made as follows (Lines 154-156, Section 2.1):

“Notably, most of the vessels had high-speed marine engines in this study, except for YK and DFH, which had low-speed engine and medium-speed engine, respectively.”

30 # I find that very little attention is given to the engine and combustion characteristics. It is stated that “Overall, fuel type, fuel quality, engine type might have higher influence on particle mass distributions from ships than the operating mode”, but it seems from Figure 1 that also operational mode is important for individual ships. Results on EC and OC at different engine loads are not discussed. It is necessary that
35 the authors also describe whether the presented results are average values from all samples from the tested engines. This would imply mixing of samples representative for different engine loads. #

Response:

Thanks for pointing out these. More parameters of the tested engines have been
40 added and shown in Table S1. The influence of combustion efficiency on the size distribution, organic formation, and PAHs distribution from different types of ships was briefly discussed in this manuscript in lines 248 to 256, lines 292 to 297, lines 385 to 388, etc. Since all the tests were onboard (in-situ) measurements, rather than the bed tests that could control all the conditions in this study, we could not draw absolute
45 conclusions about the engine and combustion characteristics here. Therefore, inferences caused by comprehensive influence factors were given and discussed in this study. Further study of a bed test for a low-speed HFO engine is in progress, from which we hope we can get more detailed and direct influence characteristics.

As for the size distributions of particles in different operation modes, we did not
50 obtain an absolute conclusion before because not all the ships showed consistent size distribution patterns in different operation modes. However, more coarse particles were indeed found in operating modes with higher engine loads. According to the comments of the reviewer, the sentence has been revised in lines 257 to 264 in the revised manuscript as follows: “The size-segregated particle mass distributions in different
55 operating modes were also compared in this study. The results showed that when the ships were operated with higher engine loads, there were more particles in coarse modes for most of the ships, which was similar to a previous study on mass distribution from measurements onboard of three ships (Fridell et al., 2008), but different from another

study on a marine engine that reported the particle mass distribution centered at 0.1-0.2 μm with much fewer coarse particles under at-berth condition compared to maneuvering and ocean-going conditions (Chu-Van et al., 2017).”

The conclusion has also been improved as “Overall, fuel type, fuel quality, engine type, and operating mode might have comprehensive influence on particle mass distributions from ships.” (Lines 269 to 271 in the revised manuscript).

Actually, emission factors and the ratios of OC and EC at different engine loads have been discussed in our previous studies (Zhang et al., 2016; 2018). In this study, we focused on the size-segregated OC and EC distributions. Therefore, no further discussion of OC and EC at different engine loads was given here. Besides, due to the relatively small sampling size of size-segregated samples under different engine loads, not all the operating conditions could be included in the onboard tests. Hence, no solid conclusion could be drawn. However, as we mentioned above, a bed test for a low-speed HFO engine is in progress under different engine loads (0%, 25%, 50%, 75%, and 90%). We hope that we could get detailed and robust results of OC and EC distributions at different engine loads from this bed test.

At last, we would like to clarify that the current results are obtained based on the average values of all samples from the tested engines. Relative contents have been added in lines 275 to 276 and lines 472 to 474 in the revised manuscript.

“Notably, OC and EC levels given in this study were the average values of all samples that were classified into these three types.”

“Same as OC and EC, the levels of PAHs and n-alkanes provided in this study were the average values of all samples that were classified into these three types.”

The abbreviations of ship types appear inconsistent and subjectively applied. Inconsistent in the sense that two types are named by installed power (high or low) and a third by fuel (HFO). Further, it is difficult to follow the specific ship name abbreviations. I suggest to use a different naming for ships that makes it easy to relate names to the relevant investigated category. An argumentation to support the cutoff in

engine power between the chosen categories is necessary. It is not apparent to me why it should matter whether the engine is on a fishing vessel, a research vessel or an engineering vessel etc. Rather, categories should be based on whether it is a 4-stroke cycle or 2-stroke cycle and the engine speed. To use “diesel” as a term for distillate marine fuels can be confusing since diesel is mainly referred to when discussing engine types rather than fuels (also heavy fuel oil is used in marine diesel engines). “Marine distillate oil” could replace “diesel” to avoid the confusion on whether a fuel or engine type is discussed. #

Response:

Thank you for pointing out these confusions. Firstly, according to the reviewer’s suggestion, we added the engine type (2-stroke or 4-stroke) in Table S1. YK was a 2-stroke low-speed engine ship, and the others were 4-stroke engine ships (1 medium-speed engine and 10 high-speed engines). Among the 4-stroke engine ships, fishing boats were classified as a special type, because they usually had much smaller engine power with older engine, and used non-standard diesel with much larger quantities (6 times the amount of water transport vessels in China) than other water transport vessels. Secondly, the fishing boats with engine power less than 300 kW could account for 75.6% of the total fishing boats in China, and the China registered ships with engine power less than 250 kW could account for 71.6% of the total registered ships in China. Therefore, combined with the studied ships, we considered 300 kW as a threshold between high engine power and low engine power in this study. Thirdly, fuel type is also a significant influence factor for the emitted pollutants. YK used typical heavy fuel oil as fuel, and the fishing boats used non-standard diesel as fuel, while the other ships used typical marine distillate oil as fuel. Therefore, after comprehensive consideration of the engine type, engine power and fuel type, we classified the studied ships into three categories in this study. We renamed the categories and abbreviations accordingly, namely, 4-stroke low-power diesel fishing boat (4-LDF), 4-stroke high-power marine-diesel vessel (4-HMV) and 2-stroke high-power heavy-fuel-oil vessel (2-HHV). All the abbreviations have been changed in the revised manuscript.

120 Finally, due to the fact that our research on shipping emissions was a complete series, including the emission factors and characteristics of gaseous pollutants, PM and its chemical composition, the influence factor, the organic matters, and the total emissions in our previously published papers (Zhang et al., 2016, 2018, 2019), we would like to retain the specific ship name abbreviations in this study for easy follow-up.

The “diesel” has been changed to “marine distillate oil” or “diesel fuel” in the revised manuscript according to the helpful comments.

125

The work includes a lot of literature references and reasoning about the particle number size distributions, which could possibly be cut down to make the manuscript more concise. No own results of PN is presented.

Response:

130 We thank the reviewer for his/her valuable comments. The contents and literature references in lines 217 to 222 in the original manuscript have been deleted. The reasoning about the particle number size distributions was also removed in lines 338 to 339 in the original manuscript. The description was also improved in lines 358 to 365 in the revised manuscript.

135 “In these processes, several factors can influence the size of the emitted particles: 1) surface growth involves the attachment of gas-phase species to the existing particles and results in increase of PM diameter and mass; 2) aggregation leads to chains and clusters of primary soot particles and an increase in particle size (to 10-100 nm in diameter) (Heywood, 1988); and 3) oxidation occurs during the formation and growth processes of the particles, resulting in the formation of gaseous species and reduction of soot particles and their precursors.”

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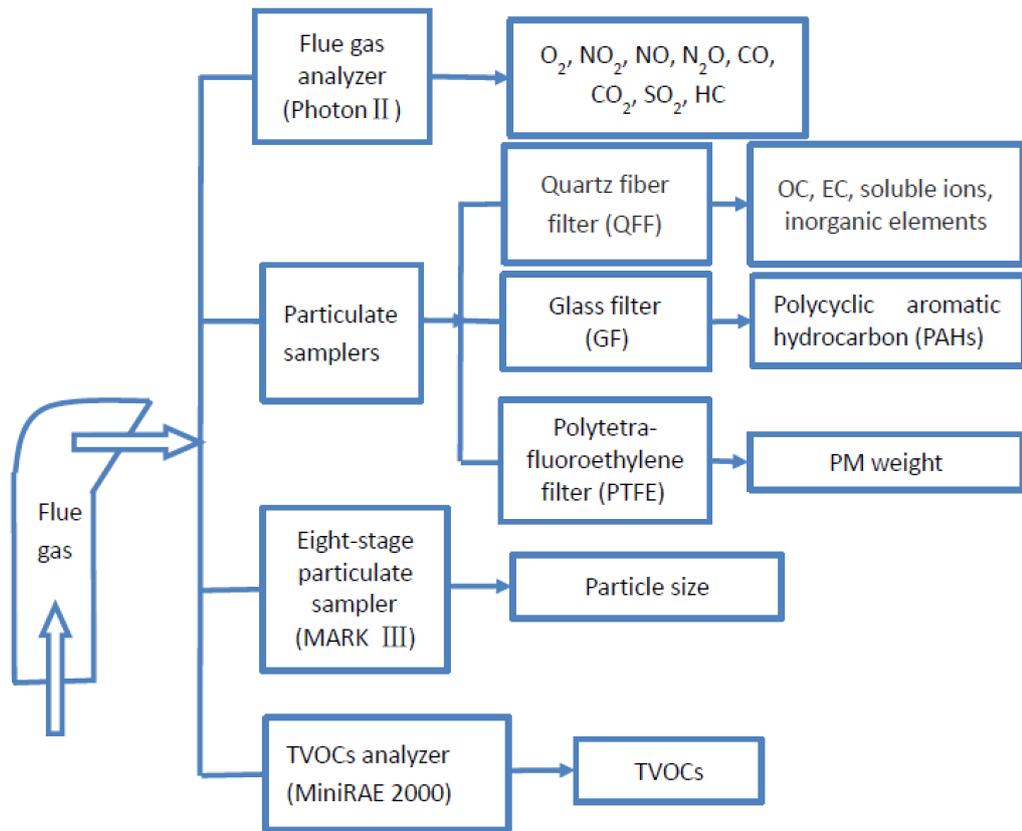
Influence of measurement methods can be very important. I strongly recommend that the sampling system, the dilution ratios and the fuels used are described at least in the supplementary material. I have not had a chance to review this.

145

Response:

Thanks for the comments. In this study, the size-segregated particle samples were collected directly from onboard tests through two sampling systems shown in the following Figures R1 and R2. It is noteworthy that these two sampling systems were carefully introduced in our previous studies (Zhang et al., 2016, 2018). Therefore, we did not put them in the supplementary material in this study. Please note, sampling system (I) was used for the high-power diesel vessels of HH, DFH, XYH, and sampling system (II) was used for the other vessels. The difference of the two sampling systems was that the sampling system (I) had no dilution system due to the limitation of the sampling system used in our early sampling period, and consequently all the particles were collected directly from the flue gas. Dilution ratios for all the tested ships ranged from 1.0 to 4.2 according to the actual sampling conditions, which were added in Table S3 in the supporting material. Moreover, the detailed parameters of all the fuels used for each tested vessel are given in Table S2. Some descriptions about the fuels were also added in lines 158-160 in Section 2.1.

“Marine distillate oil was used as the fuel of the high-power-diesel vessels. Non-standard marine distillate oil was used for the 4-stroke low-power diesel fishing boats, which was introduced in our previous study (Zhang et al., 2016), while heavy fuel oil was used for the tested HFO vessel in this study.”



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Figure R1 Sampling system (I) of the onboard test

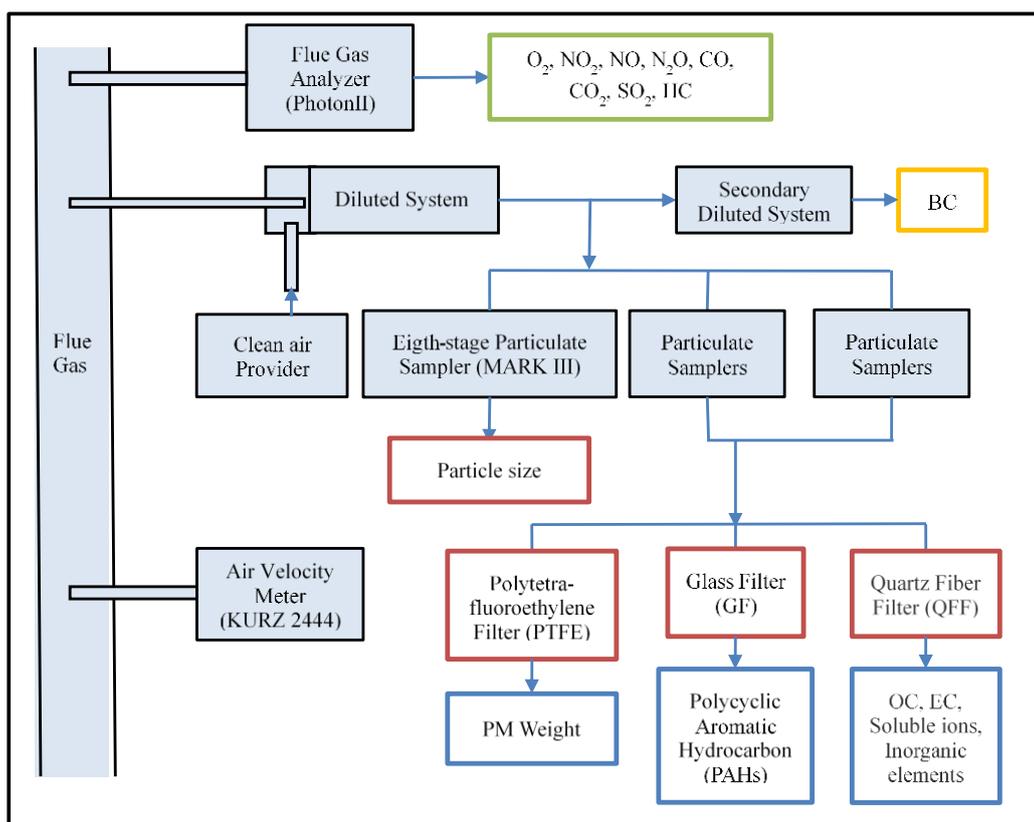


Figure R2 Sampling system (II) of the onboard test

170 # I find that in the results and discussion section it can be difficult to understand what is findings from this study, and what was previously known. E.g. page 16 lines 371-390 and page 21 line 501 to 505. I think this can be solved by changing the tense in the presentation. #

Response:

175 Sorry for the confusion. The tense was changed in some sentences, and some descriptions were improved in order to distinguish the findings of this study from previous studies. Revisions were shown in lines 371 to 390 and lines 499 to 504 in the revised manuscript.

180 “Soot particles are mainly formed through pyrolysis of diesel fuel and lubrication oil, and the organic fraction is formed through incomplete combustion of fuel and lubrication oil (Zetterdahl, 2016). Incomplete combustion of fuel and lubrication oil can significantly enhance the formation of fine particles, which might be the reason for the

185 higher OC to EC ratio in particles with $D_p < 0.43 \mu\text{m}$ in this study. This study also found that most EC contents were in the particles with $D_p < 1.1 \mu\text{m}$, coincident with the fact that soot is primarily in accumulation mode with particles of $0.1 < D_p < 1 \mu\text{m}$ (Kasper et al., 2007). Although OC was also concentrated in fine particles with $D_p < 1.1 \mu\text{m}$ (Section 3.1), its percentage was higher in particles with $D_p < 0.43 \mu\text{m}$, and lower in particles with $0.43 < D_p < 1.1 \mu\text{m}$, compared to the EC distribution. Therefore, OC to EC ratios were the lowest in particles with $0.43 < D_p < 1.1 \mu\text{m}$ for all the tested ships. For the
190 coarse particles in this study, though non-carbonous components were the dominant parts, OM increased after the cooling of the exhaust gas while content of EC and ash remained unchanged through adsorption of hydrocarbons and other volatile compounds (Zetterdahl, 2016), which enhanced the formation of coarse particles. Consequently, OC to EC ratios also showed high values in coarse particles with $D_p > 3.3 \mu\text{m}$. 2-HHV showed higher OC to EC ratio than the diesel fuel ships, which might be caused by the relatively lower combustion efficiency. Similarly, because 4-HMV ships had higher combustion efficiencies due to the higher fuel quality and better engine maintenance in this study, OC to EC ratios of 4-HMV showed the lowest levels.”

And,

200 “The relatively longer exhaust gas channel and higher temperature in the channel of 2-HHV enhanced the formation of new secondary nucleation-mode and/or accumulation-mode particles from gas-phase organic compounds, leading to higher proportions of organic matters in fine particles, which has been proved in a previous study (Kittelson, 1998).”

205

Reply to Referee 2#

1. # It's authors' duty to explain what's new in this paper compared to several other papers published by the same group, especially the one on Atmospheric Environment 2019. Both titles indicate similar contents. #

210 **Response:** Thanks for your comment. The paper published on Atmospheric Environment 2019 was focusing on the emission factors, profiles and characteristics of organic matters from the total particles emitted from ships. This information could provide some basic data for inventory estimation, source apportionment, and implication for source identification and health influence of ship emissions. However,
215 this manuscript is focusing on characteristics of OC, EC and organic matters from size-segregated particles. As shown in the manuscript, the proportions and characteristics of these compositions varied significantly in different particle sizes, which were worthy being analyzed carefully. This information could provide further knowledge of the composition of particles in different sizes, implication for particle formation
220 mechanism of ship exhaust, and also potential health impact, source apportionment of particles in different sizes. For example: the different profiles of chemical components in size-segregated particles implied that size-segregated chemical profiles should be considered when source apportionment was conducted. Furthermore, this study found more toxic organics such as PAHs in small particles emitted from fishing boats,
225 suggesting the necessity of more stringent control on this type of boats in China.

2. # The results were not organized in a clear way which made them very hard to follow. 1) For different particle size bins, what are the chemical component profiles? No figure gives a comprehensive component profile. Only the OC/EC percentages
230 compared among bins were provided. Authors failed to touch the whole picture of the "size-segregated characteristics", which should be the most important part of this study. For example, EC and OC were found very low for coarse PM. Then, which components are the major part for coarse PM? In addition, without a total mass analysis, it's impossible to judge the reliability of the sampling and analysis.

235 2) If the whole picture of size based chemical profile could be provided, then it's
OK to discuss the distribution for each component in different size bins. However,
this information is not very important compared with part 1). Currently, authors
spent too much pages on discussing this, including Fig. 2, 6 and etc. 3) All figures
were displayed in percentage or ratio. The mass of OC, EC, PAH or others should
240 be provided directly. Is it still necessary to provide so many figures if the mass could
be given? 4) Figure 1 is confusing. 'YK, GB1...' should be replaced with ship types,
e.g. 'HDPV'. #

Response:

The valuable comments are highly appreciated.

245 1) Unfortunately, we could not get the detailed chemical profiles of the size-segregated
particles in this manuscript. We only focused on OC, EC, organic matters of 16
priority PAHs, and n-alkanes in the particles. Other inorganic matters such as water-
soluble ions and metal elements were not analyzed because the sample volume was
too low of the particles in each size bin, especially in coarse particles. We inferred
250 that inorganic matters of ash and hydrated sulfates could be the dominant
component in coarse particles, which has been confirmed by a previous study
(Moldanová et al., 2009). The detailed chemical profiles of particles in different size
bins still need further investigation, which is also a target we are working on.
Besides, we compared the total PM concentrations between the two sampling
255 methods, namely the TSP sampling method and the Andersen sampling method.
The result showed that they had a Pearson correlation coefficient of 0.917, and the
correction was significant at the 0.05 level. As described in Sections 2.2, 2.3 and
2.4, all the sampling processes and chemical analysis were carried out according to
standard methods, which showed reliable quality assurance and quality control.
260 Therefore, we believed the sampling and analysis were reliable.

2) As explained above, we could not quantify the size-segregated inorganic matters in
this study. Instead, carbonaceous matters of OC, EC, PAHs and n-alkanes in the PM
were the focus in this study. Even though the detailed chemical profiles of size-

265 segregated PM were not able to give, the results were still meaningful for the
 implications of climate change, source apportionment, health influence, and
 formation mechanism of organic matters, as presented and discussed in this
 manuscript. We fully agree that the whole picture of size based chemical profile is
 very important and needs to be figured out correctly in the future.

270 3) Firstly, the emission factors of the total PM and size-resolved particle mass
 distributions are given in Figure 1 in the manuscript. It could be seen that the PM
 emission factors varied significantly among different ships, from 0.08 to 19.01 g
 (kg fuel)⁻¹. When the mass was distributed to different size bins, there were still
 large variations among the different types of ships (such as the OC and EC emission
 factors in different particle size bins shown in the following Figure R1). Due to the
 275 significant variations of the absolute mass/emission factor, it would be difficult to
 obtain the common pattern of the distributions and characteristics of OC, EC, and
 organic matters. Therefore, figures in percentage or ratio were displayed in this
 manuscript. Besides, since the distribution patterns of total OC, EC, PAHs and n-
 alkanes in different particle size bins are different, we consider that figures such as
 280 Figure 2 and Figure 6 are necessary in the manuscript.

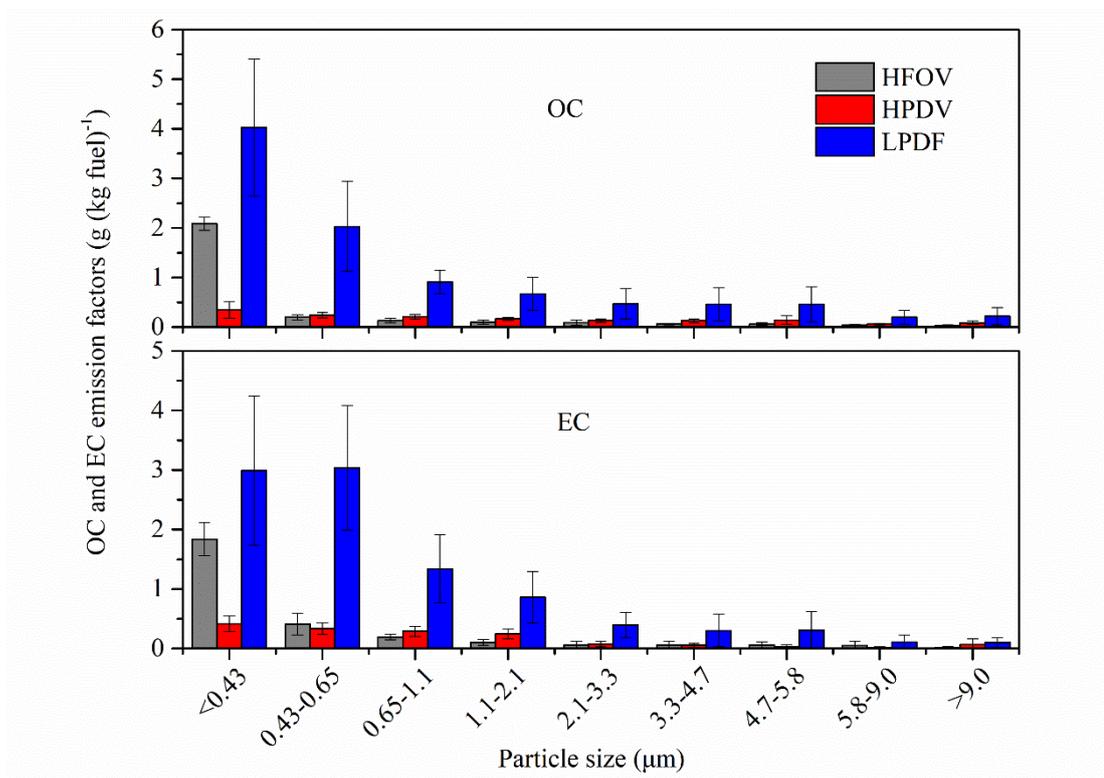
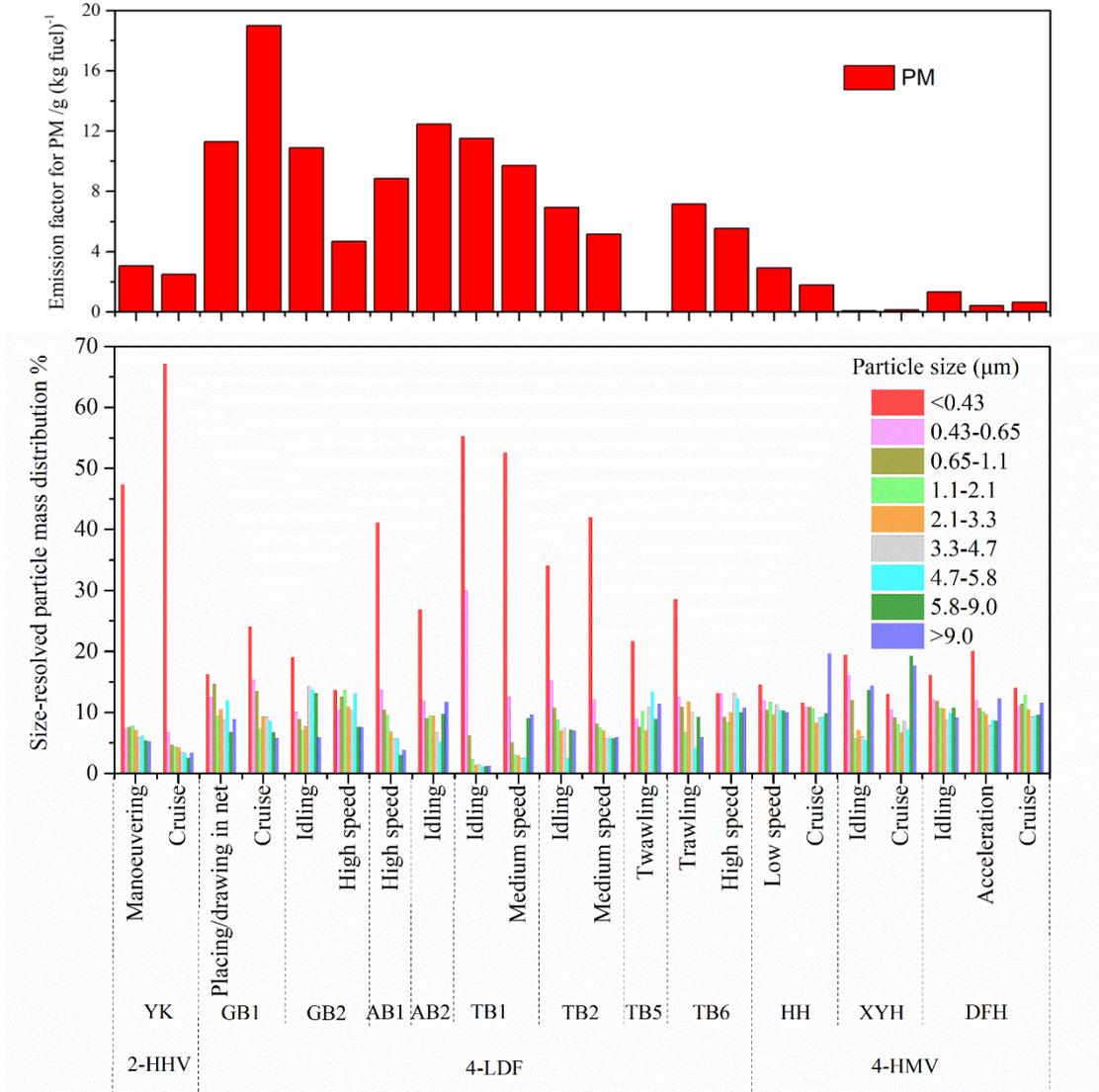


Figure R1 OC and EC emission factors in different particle size bins

4) Figure 1 has been improved in the revised manuscript, and 2-HHV, 4-HMV, and 4-LDF have been added in the figure (shown as follows).



285

Figure 1 Emission factor for total PM and size-resolved particle mass distributions with different modes for the 12 tested ships

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3. # Presentation quality in text also needs to be improved. 1) In abstract, line 30, 'in fine particles, OC and EC were the dominant components'. line 34, 'OC and EC have the lowest values for 0.43 to 1.1 μm '. Are they still dominant? 2) Line 34, What are the OC1, OC2 and OC3? 3) Line 214, how can 5% be called the large proportion? 4) line 282, HFOV vessels should be HFOV. and 'HPDV ships' should be 'HPDV'.

And this sentence is confusing. What's the meaning by 'HPDV accounted for 23%....'? Compared with what kind of ships? #

295

Response:

Thank you for pointing out these. OC and EC were indeed the dominant components in fine particles. In line 34, we meant that the OC to EC ratios had the lowest values for particles between 0.43 and 1.1 μm . They are not contradictory.

1) As explained in lines 392 to 397: OC and EC were tested according to the IMPROVE-A protocol in the thermal-optical carbon analysis. OC1, OC2, OC3, OC4, EC1, EC2, EC3, and pyrolysis carbon fragments were tested under different temperatures and conditions, which could be read directly from the result file (shown in the following Figure R2 as an example). Then OC and EC could be calculated according to the protocol. We analyzed the OC1 to EC3 fragments in this manuscript to help understand the different formation processes of particles.

305

		Peak Area	Carbon	
OC1	OC	94 mv-secs	0.17 ug C/cm2	.17 ug C/filter
OC2	OC	764 mv-secs	1.37 ug C/cm2	1.37 ug C/filter
OC3	OC	621 mv-secs	1.11 ug C/cm2	1.11 ug C/filter
OC4	OC	539 mv-secs	0.97 ug C/cm2	.97 ug C/filter
EC1	EC	388 mv-secs	0.70 ug C/cm2	.70 ug C/filter
EC2	EC	16 mv-secs	0.03 ug C/cm2	.03 ug C/filter
EC3	EC	0 mv-secs	0.00 ug C/cm2	.00 ug C/filter
LRPyMin	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter
LRPyMid	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter
LRPyMax	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter
LTPyMin	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter
LTPyMid	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter
LTPyMax	Py	0 mv-secs	.00 ug C/cm2	.00 ug C/filter

Figure R2 Example of test results for OC and EC fragments

2) Sorry for the confusion. “large proportions” has been changed to “non-ignorable proportions” in the revised manuscript in line 221.

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3) “HFOV vessels” has been revised to “2-HHV”, and “HPDV ships” has been changed to “4-HMV” in the revised manuscript in lines 285 to 290. The abbreviations of ship types have been changed to 4-stroke low-power diesel fishing boat (4-LDF), high-power-diesel vessel (4-HMV) and 2-stroke high-power heavy fuel oil vessel (2-HHV) (see Table S1 for details). This sentence has been improved as “For example, 4-HMV only accounted for 23% OC and 27% EC in particles with $D_p < 0.43 \mu\text{m}$ compared to 2-HHV which had 75% OC and 66% EC in particles

315

with $D_p < 0.43 \mu\text{m}$. This is in accordance with the characteristics of total PM mass distributions; that is, diesel fuel vessels had relatively smaller proportions of fine particles with $D_p < 0.43 \mu\text{m}$ and larger proportions of coarse mode particles than HFO ships.”

References:

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Size-segregated characteristics of OC, EC and organic matters in PM emitted from different types of ships in China

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Abstract

Studies of detailed chemical compositions in particles with different size ranges emitted from ships are in serious shortage. In this study, size-segregated distributions and characteristics of particle mass, organic carbon (OC), elemental carbon (EC), 16 EPA PAHs and 25 n-alkanes measured on board of 12 different vessels in China were given. The results showed that: (1) More than half of the total particle mass, OC, EC, PAHs and n-alkanes were concentrated in fine particles with aerodynamic diameter (D_p) < 1.1 μm for most of the tested ships, basically presenting downward distribution trends with the increase of particle size. However, different types of ships showed quite different particle size-dependent chemical compositions. (2) In fine particles, the OC and EC were the dominant components, while in coarse particles, OC and EC only accounted for very small proportions. With the increase of particle size, the OC to EC ratios first decreased and then increased, having the lowest values for particle sizes between 0.43 μm and 1.1 μm . (3) OC1, OC2 and OC3 were the dominant OC fragments for all the tested ships, while EC1 and EC2 were the main EC fragment for ships running on heavy fuel oil (HFO) and marine diesel fuel, respectively; Different OC and EC fragments presented different distributions in different particle sizes. (4) ~~4-stroke low-power diesel fishing boat (4-LDF)~~ ~~Low power diesel fishing boats (LPDF)~~ had much higher PAHs emission ratios than ~~4-stroke high-power marine-diesel vessel (4-HMV)~~ ~~high power diesel vessels (HPDV)~~ and ~~2-stroke high-power~~ heavy fuel oil vessel (~~HFOV2-HHV~~) in fine particles, and ~~HFOV2-HHV~~ had the lowest values. (5) PAHs and n-alkanes showed different profile patterns for different types of ships and also in different particle size bins, which meant that the particle size should be considered when source apportionment was conducted. It is also noteworthy from the results in this study that the smaller the particle size, the more toxic the particle was, especially for the fishing boats in China.

1. Introduction

Particulate matter (PM) emitted from ships have significant impacts on human health and air quality (Schröder et al., 2017; Liu et al., 2016; Oeder et al., 2015; Viana

et al., 2014). Ship emission is one of the most important sources of fine particulate matter (PM_{2.5}) in harbor or offshore areas. PM from both heavy fuel oil and marine diesel fuel shipping emissions shows strong biological effects on human lung cells (Oeder et al., 2015). A previous study indicated that shipping emissions in East Asia lead to 8,700-25,500 premature deaths per year due to PM_{2.5} (Liu et al., 2016). PM emitted from ships in harbor cities or areas accounts for non-ignorable proportions of primary PM_{2.5} (Gregoris et al., 2016; Zhao et al., 2013; Agrawal et al., 2009). This fraction can reach up to 17-30% if the contribution of shipping emissions to secondary particles is considered, too (Pandolfi et al., 2011; Liu et al., 2017). The chemical composition of PM emitted from ships is complex. Organic matter (OM), elemental carbon (EC) or black carbon (BC), water-soluble ions and heavy metals are the main components. In addition, PAHs in PM emitted from ships have drawn much attention due to their significantly negative impact on human health, as well as their diagnostic characteristics for source apportionment (Vieira de Souza and Corrêa, 2015; Pongpiachan et al., 2015; Alves et al., 2015). Ships are considered to be one of the most important sources for BC emissions in Arctic areas (Schröder et al., 2017; Quinn et al., 2011; Corbett et al., 2010) that could lead to the increase of ice melt due to its strong light absorbing properties. BC-containing aerosols in the Arctic can perturb the radiation balance with either a warming effect or a cooling effect on climate depending on the albedo of the underlying surface relative to the albedo of the BC haze itself (Quinn et al., 2011). Besides, as a key component of soot, BC is also considered to have substantial negative consequences for health. Furthermore, as important components, water-soluble ions such as SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻ and Na⁺ are routinely studied due to their unique emission characteristics in PM of ships, different from other sources (Sippula et al., 2014; Moldanová et al., 2013; Moldanová et al., 2009; Agrawal et al., 2008). Notably, heavy metals generally have high levels in PM emitted from ships compared to other sources. This especially holds for HFO fueled ships where metals like vanadium can be used as tracers (Moldanová et al., 2009; Agrawal et al., 2009). In addition, because a large number of particles emitted from ships are very small (<0.1

80 μm), which may have significant impacts on cloud formation (Fridell et al., 2008),
particle number concentrations particularly for ultrafine particles have gained more and
more attention in recent years.

The size-resolved number and mass distributions of particles emitted from ship
engines have been investigated for more than one decade due to their potential climate
85 impacts and influence on human health. Three measurement methods including engine
test, onboard test and plume tracking are usually reported in the literature. However,
most of the previous studies focused on the size-resolved particle number distributions
(Wu et al., 2018; Cappa et al., 2014; Beecken et al., 2014; Moldanová et al., 2013;
Juwono et al., 2013; Diesch et al., 2013; Alfoeldy et al., 2013; Winnes and Fridell, 2010;
90 Kasper et al., 2007; Cooper, 2003), which reported that the total particle number
concentrations were dominated by ultrafine particles (nucleation mode) or fine particles.
For example, the mean particle diameter was between 25 and 40 nm for a two-stroke
marine diesel engine (Kasper et al., 2007) and between 40 and 60 nm for a four-stroke
marine diesel engine measured on a test bench (Petzold et al., 2008). Unimodal
95 characteristics with the peak at 0.1 μm (Sinha et al., 2003; Fridell et al., 2008) or 40-50
nm (Chu-Van et al., 2017) or 30-40 nm (Winnes and Fridell, 2010) or even 10 nm
(Moldanová et al., 2013) were observed during onboard tests. Bimodal patterns were
found in plumes with maxima at 10-20 nm and 100 nm (Petzold et al., 2008), and 10
nm and 35 nm (Diesch et al., 2013), respectively. Particles with a marked nucleation
100 mode (10-100 nm) (Hobbs et al., 2000; Healy et al., 2009) and 58-131 nm (Juwono et
al., 2013) were also found in the plumes from different marine fuel oil commercial ships
and berthing bulk and container ships. It should be noted that the engine type and
operating mode could affect the particle number distribution (Juwono et al., 2013;
Cappa et al., 2014).

105 Few studies involved in size-resolved particle mass distributions emitted from
ships (Chu-Van et al., 2017; Moldanová et al., 2013; Murphy et al., 2009; Moldanová
et al., 2009; Fridell et al., 2008). Although most of the particles from ships were
concentrated in nucleation mode in terms of number concentration, the particle mass

was dominated by particles in the accumulation mode or even coarse mode. For
110 example, it was found that the mass distribution of hot-exhaust particles from a large
ship diesel engine had two main peaks: one in the accumulation mode at D_p around $0.5 \mu\text{m}$
and the other in the coarse mode at D_p around $7 \mu\text{m}$ (Moldanová et al., 2009).
Another earlier study also found that particles with a diameter of approximately $8 \mu\text{m}$
presented the largest mass peak in the mass spectrum for three tested ships (Fridell et
115 al., 2008). The size-resolved mass distribution of particles has not been fully studied.
One reason is that although the coarse particles account for non-ignorable proportions
of the total mass, they are relatively few in number concentration, which has not caught
much attention. Moreover, particles with size around $8 \mu\text{m}$ are usually not detected by
particle counters when the counting method is used to calculate the particle mass. Only
120 one study collected particles from ships using in-stack cascade impactor, which
revealed different mass distribution patterns from the particle counting method (Cooper,
2003). The result indicated that though the smaller particles ($<1 \mu\text{m}$) were dominant in
number concentration, they only accounted for 10-50% of the total mass (Cooper, 2003).
The counting method was simple but had drawback; namely, the mass could bias
125 towards larger particles.

A handful of studies on detailed chemical compositions of particles in different
sizes were conducted (Wu et al., 2018; Murphy et al., 2009). An aerosol mass
spectrometer (AMS) was used in a previous study to give organic carbon and sulfate
contents in ultrafine particles, but no black carbon and detailed molecular chemical
130 components could be monitored (Lu et al., 2006). In addition, in-stack ship-based
particle measurement was performed using micro-orifice uniform deposit impactor
(MOUDI) with off-line analysis. The results showed that freshly emitted particles from
ship exhaust comprised approximately 30% organic carbon and 70% sulfuric acid by
mass (Murphy et al., 2009). However, chemical compositions and their characteristics
135 in particles at different sizes emitted from ships are still unclear, especially for fine or
ultrafine particles. Only one study investigated detailed PAH speciation and total-BaP_{eq}
in size-segregated PM in the exhaust of a container ship with HFO and diesel oil (DO)

as fuel, and found that health risks increased with the decrease of particle size (Wu et al., 2018). Hence, it is urgent to gain detailed chemical compositions such as OC, EC and organic matters in size-segregated particles from different ships.

In this study, size-segregated particle samples from 12 different vessels were collected using an 8-stage cascade impactor. The mass, OC, EC, 16 EPA PAHs and 25 n-alkanes in particles of each size bin were detected. Size-segregated distributions and characteristics of mass, OC, EC and the detected organic matters were given. Potential health impact, source apportionment and particle formation mechanism of ship exhaust were also explored in this study.

2. Materials and methods

2.1 Tested vessels and fuels

Size-segregated particle samples on quartz filters from 12 different vessels were collected in this study, including one heavy fuel oil ocean-going vessel, eight fishing boats, one engineering ship, and two research ships. Their technical parameters are shown in Table S1. These vessels were classified into three types based on their engine type and fuel type, namely, low-power diesel fishing boat (LPDF4-LDF), high-power-diesel vessel (HPDV4-HMV) and 2-stroke high-power heavy fuel oil vessel (HFO vessel) (HFOV2-HHV) (see Table S1 for detail). Notably, most of the vessels are with had high-speed marine engines in this study, except for YK and DFH, which are had low-speed engine and medium-speed engine, respectively. The parameters of all the fuels used for each tested vessel are shown in Table S2. Marine distillate oil was used as the fuel of the high-power-diesel vessels. Non-standard marine distillate oil was used for the 4-stroke low-power diesel fishing boats, which was introduced in our previous study (Zhang et al., 2016); And while heavy fuel oil was used for the tested HFO vessel in this study. A total of 28 sets of size-segregated samples were obtained, shown in Table S3. The main operating modes of each vessel were chosen according to actual operating conditions. More information about the sampling systems and fuels used for the tested vessels can be found in our previous studies (Zhang et al., 2016; Zhang et al., 2018; Zhang et al., 2019). Notably,

the sampling system applied for the HFO vessel of YK was the same diluted system used for the fishing boats.

2.2 Sampling instrument

170 An 8-Stage Andersen Cascade Impactor (TE-20-800, Tisch Environmental Inc, USA) was used for particle collection. The flow rate was 28.3 liter per minute. The particles were separated into 9 size bins by the impactor, and the particle size range, sampling spot number/sampling area for each stage are shown in Table S4. The sampling duration for each sample varied from 10 to 30 minutes according to emission
175 conditions and dilution ratios (see Table S3 for detail).

2.3 Chemical analysis

The mass, organic carbon, element carbon, sixteen priority PAHs indicated by US EPA (the detailed information is shown in Table S5), and n-alkanes from C10 to C34 in each particle size bin were measured. The mass of the particles on each filter was
180 obtained by gravimetric method. OC and EC were measured with a 0.544 cm² punch aliquot of each filter sample by thermal optical reflectance (TOR) following the IMPROVE-A protocol with a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA). The measuring range of TOR was from 0.05 to 750 μg C cm⁻² with an error of less than 10%. The PAHs and n-alkanes were measured by
185 an optical-4 thermal desorption (TD) sample injection port coupled with an Agilent GC7890B/MS5977A (Agilent Technologies, Santa Clara, CA) system (Han et al., 2018). The detailed information of TD-GC/MS method for PAHs and n-alkanes was shown as follows.

Each of the collected Quartz filter samples was punched with an area of 5 mm in
190 diameter with a sampling spot as the center for PAHs and n-alkanes analysis. The filter was cut to small pieces and loaded into a TD glass tube. 1 μL deuterium marked compounds and 6-methyl benzene with concentrations of 10 ppm was injected into the tube as internal standards. The TD glass tube was then placed into the TD inject port, and was heated to 310 °C at a rate of 12 °C/min and thermally desorbed at 310 °C for
195 3 min. The desorbed organic compounds were trapped on the head of a GC-column

(DB-5MS: 5% diphenyl-95% dimethyl siloxane copolymer stationary phase, 0.25 mm i.d., 30 m length, and 0.25 mm thickness). The initial GC oven temperature was 60 °C and held for 4 min, then rose to 300 °C at a rate of 6 °C/min and was held at 300 °C for 8 min (Han et al., 2018). D8-Naphthalene, D10-acenaphthene, D10-phenanthrene, D12-chrysene, D12-perylene, D-C16, D-C20, D-C24, and D-C30 were used for the analytical recovery check. The detection limit for the TD-GC/MS method ranged from 0.2 pg mm⁻² (Ace) to 0.6 pg mm⁻² (Icdp).

2.4. Quality assurance/quality control

Rigorous quality assurance and control were conducted during the whole experiments. Filter blanks were analyzed in the same way as the above procedures to determine the background concentration. Duplicate samples as well as standard samples were examined after analyzing a batch of 10 samples to ensure that the error was within 5%. The average recoveries of the deuterium surrogates ranged from 84.3% to 101% in this study (shown in Table S6). The results of each sample were subtracted by the filter blank results. The final data reported in this study were not corrected by the recoveries.

3 Results and discussions

3.1 Total mass distributions in different particle size bins

Emission factors for the total PM and size-segregated particle mass distributions of all the 12 tested ships with different modes are shown in Fig. 1. The emission factor for PM was discussed in our previous studies (Zhang et al., 2016; Zhang et al., 2018; Zhang et al., 2019). In general, ~~4-stroke low-power diesel fishing boats~~~~low engine power fishing boats~~ had much higher PM emission factors than other types of ships, while ~~4-stroke high-power marine-diesel vessels~~~~high engine power diesel vessels~~ showed lower PM emission factors, especially for the ~~high-quality~~~~high-quality~~ fuel ships. Besides, low load operating modes showed higher PM emission factors for almost all the tested ships. In this study, we focused on the size-segregated particle mass distributions of the tested ships. It was found that more than half of the particle mass was concentrated in fine particles with $D_p < 1.1 \mu\text{m}$ (33-91%). However, there were still ~~non-ignorable~~~~large~~ proportions (5-53%) in coarse particles with $D_p > 3.3 \mu\text{m}$. The

225 findings were in line with the previous studies which reported that the mass
distributions of ship emissions were dominated by accumulation mode and/or coarse
mode particles (Moldanová et al., 2009, 2013; Murphy et al., 2009). ~~In contrast, the
total particle number concentrations were dominated by nucleation mode particles with
 $D_p < 0.1 \mu\text{m}$, while particles with $D_p > 0.5 \mu\text{m}$ showed very low number concentrations
that were often neglected in previous studies (Cappa et al., 2014; Beecken et al., 2014;
Moldanová et al., 2013; Juwono et al., 2013; Diesch et al., 2013; Alfoeldy et al., 2013;
Winnes and Fridell, 2010; Kasper et al., 2007).~~

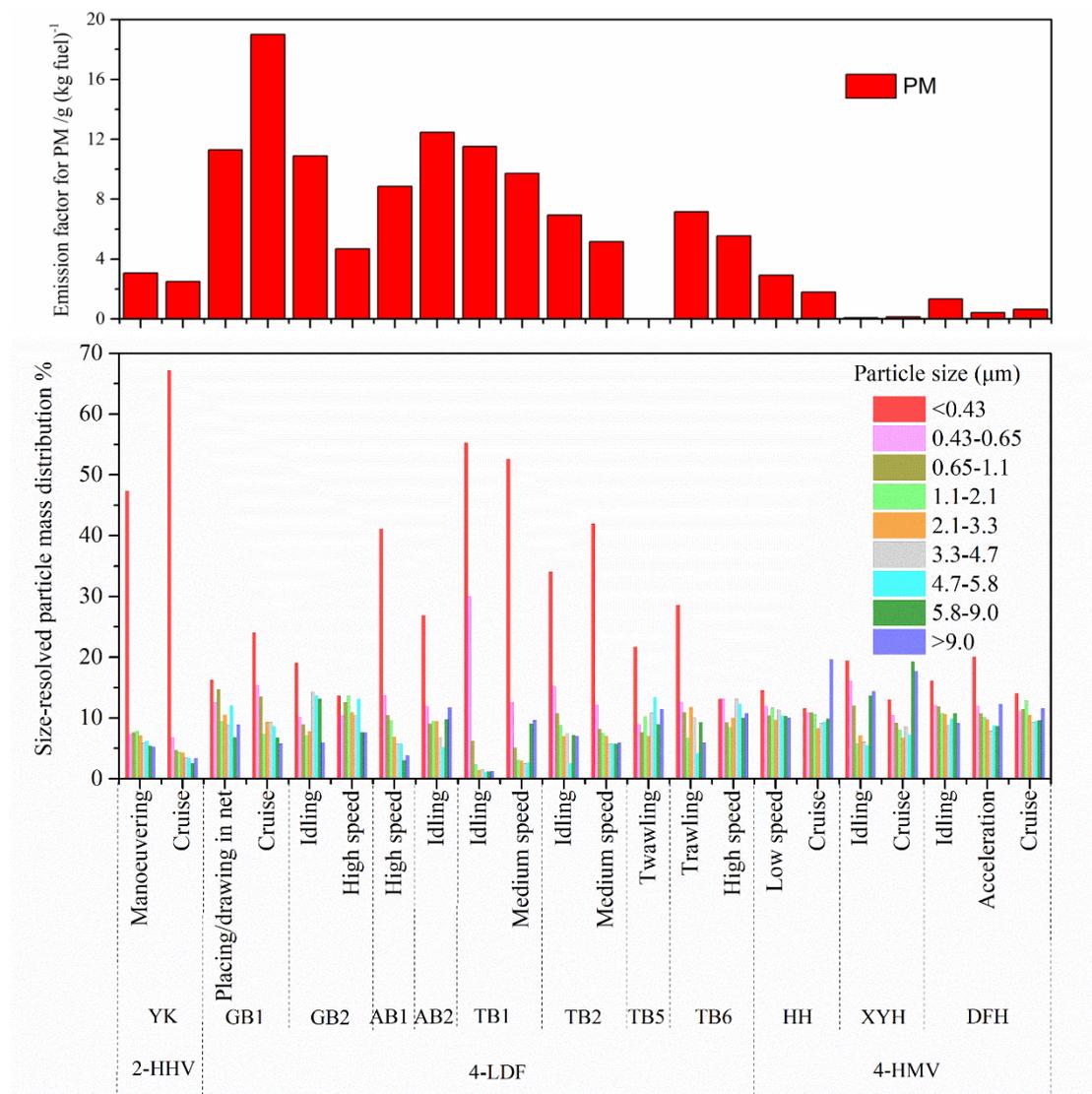


Figure 1 Emission factor for total PM and size-resolved particle mass distributions
with different modes for the 12 tested ships

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Different types of ships showed rather different size-segregated particle mass distributions. As shown in Fig. 1, the mass was concentrated on particles with $D_p < 0.43 \mu\text{m}$ for the HFO driven ship YK, coincident with the results of a previous study that found the particle mass peaked at around 50 nm for a HFO ship (Chu-Van et al., 2017), but inconsistent with a study on hot-exhaust particles from a HFO driven cargo vessel which revealed bimodal particle mass distribution with peaks at $\sim 7 \mu\text{m}$ and $\sim 0.5 \mu\text{m}$, attributed to the HFO combustion and the various nature and composition of the ship-exhaust particulates (Moldanová et al., 2009). In this study we found that ~~4-stroke high-power marine-diesel vessel~~ ~~high-power diesel vessels~~ had relatively smaller fractions of particle mass in the fine mode with $D_p < 0.43 \mu\text{m}$ but larger fractions in the coarse mode with $D_p > 5.8 \mu\text{m}$ than those of the HFO ship. This pattern was also consistent with the result of Fridell et al. (2008) who found a large peak at $\sim 10 \mu\text{m}$ from the emissions of large ~~diesel~~ ~~diesel fuel~~ engines. Furthermore, different fishing boats (GB1 to TB6 in Fig 1.) showed different size-segregated particle mass distributions in this study. It can be seen that lower engine power fishing boats had high percentages of fine particles with $D_p < 1.1 \mu\text{m}$, while higher engine power fishing boats showed high proportions of coarse particles. The different size-segregated particle mass distributions for different types of ships were likely caused by the quality of fuel and its combustion efficiency in the engines. For example, compared to ~~diesel fuel~~ ~~diesel oil~~, HFO contains high percentage of aromatics, which are known to contribute to nucleation mode particle formation (Zetterdahl et al., 2017). Moreover, incomplete combustion could enhance the formation of nucleation mode particles from the unburned fuel and lubrication oil (Zetterdahl et al., 2017). Hence, the relatively lower combustion efficiency of HFO ship led to higher proportions of fine particles than diesel-fueled ship. Moreover, the quality of fuel used for the same type of ships such as fishing boats varied largely in China, which might, at least to some extent, was also responsible for the different size distributions. Compared to higher engine power fishing boats, relatively lower combustion efficiencies of the lower engine power fishing boats resulted in higher proportions of fine particles (Zhang et al., 2018).

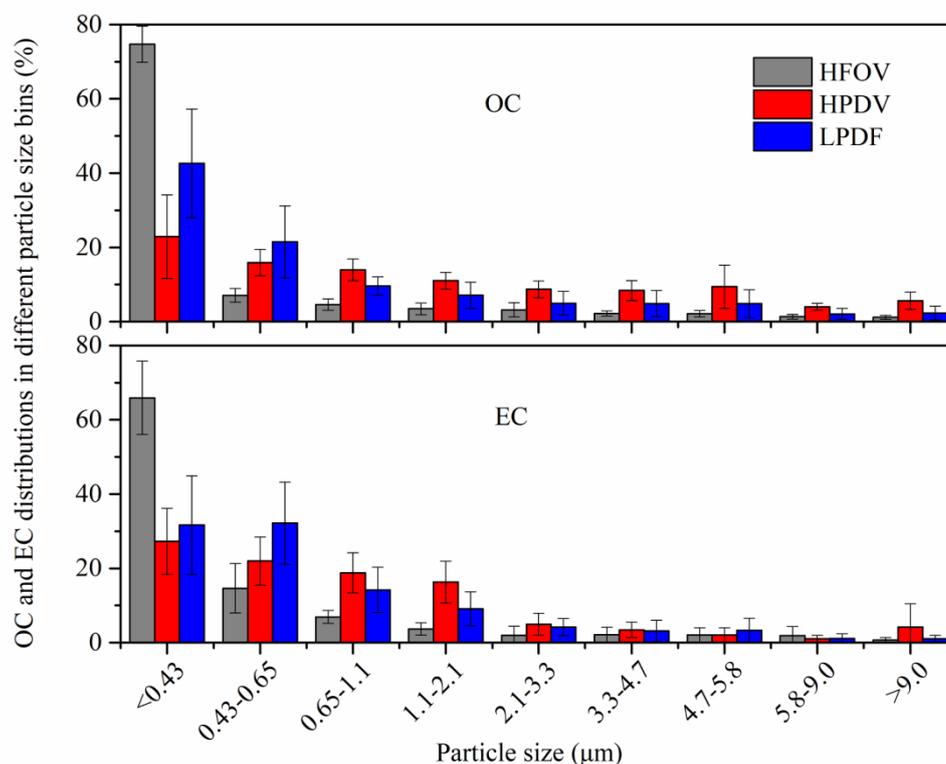
The size-segregated particle mass distributions in different operating modes were also compared in this study. ~~No obvious discrepancy was found for all the tested ships~~ The results showed that when the ships were operated with higher engine loads, there would be more particles distributed in coarse particles modes for most of the ships, which was similar to a previous study on mass distribution from measurements onboard of three ships (Fridell et al., 2008), but different from another study on a marine engine that reported the particle mass distribution centered at 0.1-0.2 μm with much fewer coarse particles under at-berth condition compared to maneuvering and ocean-going conditions (Chu-Van et al., 2017). The main reason was that the at-berth emission was calculated based on auxiliary engine but not the main engine by Chu-Van et al. (2017). Coincidentally, emissions from two auxiliary engines in the HFO driven ship YK and engineering ship HH were measured in this study (Fig. S1). Both showed high proportions of fine particles with $D_p < 0.43 \mu\text{m}$ and small percentages of coarse particles, similar to the findings of Chu-Van et al. (2017). Overall, fuel type, fuel quality, engine type, and operating mode might have higher comprehensive influence on particle mass distributions from ships ~~than the operating mode~~.

3.2 Characteristics of OC and EC in size-segregated particles

3.2.1 The OC and EC mass distributions in different particle size bins

Figure 2 and Table S7 present the total OC and EC mass distributions in different particle size bins for the three ship types. Notably, OC and EC value levels given in this study were the average values from of all samples that were classified into these three types. The OC and EC distributions in different particle size bins showed similar but distinguished characteristics compared to the PM mass distribution. All the tested ships presented similar trends, namely, the proportions of OC and EC decreased with the increase of particle size. About 53-86% of OC and 68-86% of EC were in the particles with $D_p < 1.1 \mu\text{m}$. Only very small percentages of OC and EC existed in the coarse particles. Among the three types of ships, HFOV2-HHV showed significantly higher OC and EC proportions in particles with $D_p < 0.43 \mu\text{m}$ (75% and 66%, respectively) than the other two types of ships operated with diesel fuel, while the OC and EC proportions

295 were lower in the other particle size bins of ~~HFOV2-HHV vessels~~ than those of the
 other two types of ships. For example, HPDV4-HMV ships only accounted for 23%
 OC and 27% EC in particles with $D_p < 0.43 \mu\text{m}$ compared with 2-HHV, which had
 75% OC and 66% EC in particles with $D_p < 0.43 \mu\text{m}$. ~~which were~~ This was –in
 accordance with the characteristics of total PM mass distributions; that is, ~~diesel~~
 300 fuel vessels had relatively smaller proportions of fine particles with $D_p < 0.43 \mu\text{m}$ and
 larger proportions of coarse mode particles than HFO ships. Notably, the proportion of
 EC in particle size bin of $0.43\text{-}0.65 \mu\text{m}$ had almost the same level as that in particle size
 bin of less than $0.43 \mu\text{m}$ for ~~LPDF4-LDF~~. The higher proportions of OC and EC in fine
 particles from the HFO driven vessel compared to the diesel fuel ships might be
 305 attributed to both the combustion efficiency and the use of HFO. Due to the large fuel
 to air ratio in the HFO engine (Kittelson et al., 1998), higher fractions of unburned fuel
 with heavier molecular weight as well as lubrication oil could more easily leak into the
 exhaust and raise the carbonaceous fractions (Hardy and Reitz, 2006). Besides, the
 incomplete combustion and the high content of aromatics in HFO both could enhance
 310 the formation of new nucleation mode particles (Zetterdahl et al., 2017), which would
 eventually promote a high fraction of fine mode carbonaceous particles.



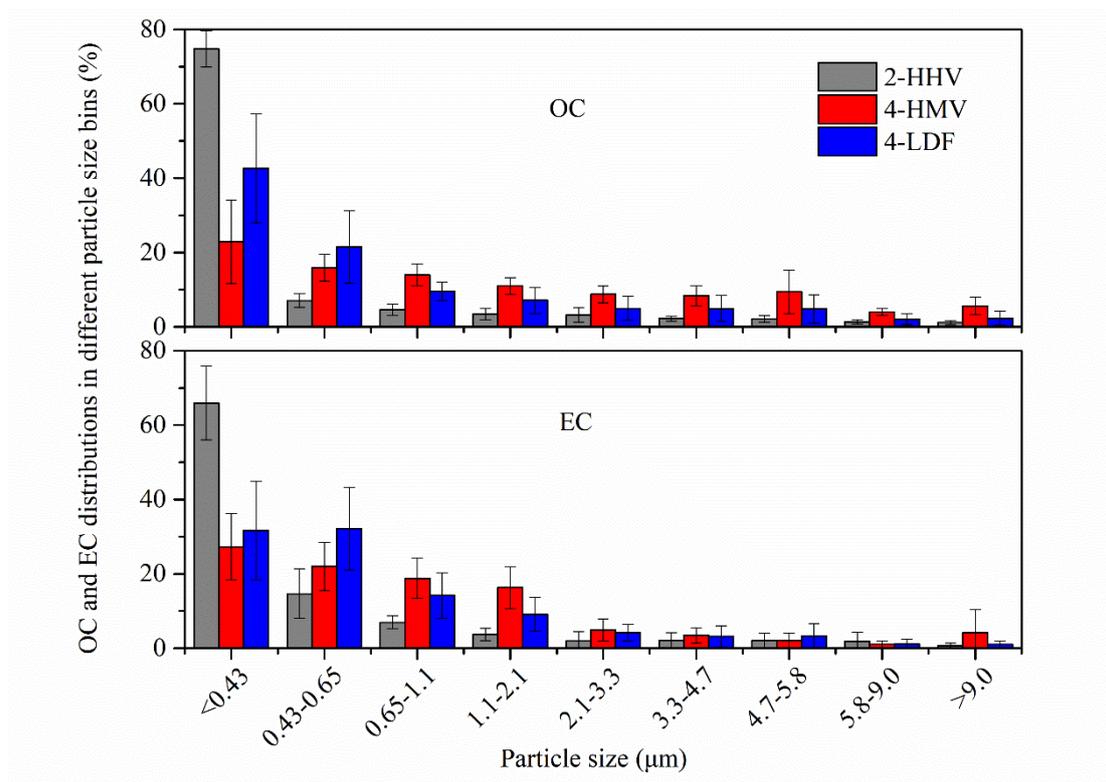


Figure 2 Total OC and EC distributions in different particle size bins

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3.2.2 OC and EC proportions in each particle size bin

In order to figure out the carbonaceous components in size-segregated particles, percentages of OC and EC in each particle size bin are given in Fig. 3. In general, both OC and EC proportions showed overall decreasing trends with the increase of particle sizes for all three types of ships. The OC+EC accounted for large proportions of the total particle mass in fine particles, between 40 and 65 % for particles smaller than 0.65 μm . However, OC+EC only explained small proportions in coarse particles, less than 15% for particles larger than 5.8 μm diameter, suggesting that most of the coarse particle mass was dominated by other non-carbonous components, such as ash and hydrated sulfates. The coarse particles could be seriously influenced by natural-based substances such as ash that was introduced into the cylinder by the air to maintain a certain-reliable equivalent ratio in the cylinder. This was confirmed in a previous study about the ship-exhaust particle composition based on transmission electron microscopy (TEM) study. Mineral/ash particles containing lime, calcite, vanadium oxide and nickel

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330 sulfide were also found to be dominant in coarse particles (Moldanová et al., 2009).

In addition, the differences of OC+EC proportion patterns among the three types of ships were large. OC+EC accounted for >60% in particles with $D_p < 0.65 \mu\text{m}$ for HFOV2-HHV, then decreased sharply to less than 30% in particles with $D_p > 0.65 \mu\text{m}$, and only explained ~10% in particles with $D_p > 9.0 \mu\text{m}$. The OC+EC for LPDF4-LDF showed similar trend to that for HFOV2-HHV, but had higher proportions in particles with D_p of 0.65-3.3 μm . In contrast, the OC+EC only accounted for ~40% in particles with $D_p < 1.1 \mu\text{m}$ for HPDV4-HMV, and decreased to less than 10% in particles with $D_p > 9.0 \mu\text{m}$. Because the OC and EC compositions in size-segregated particles from ships were not studied in the past, this study compared components of PM_{10} or hydrated sulfate and organic carbon in size-resolved particles with earlier studies. Diesch et al. (2013) found that organic matter (OM) was the most abundant component in PM_{10} , while EC contributed only 6% on average to PM_{10} . This result was similar to the composition of HFOV2-HHV emissions in this study but significantly different from that of the HPDV4-HMV and LPDF4-LDF, likely due to the different types of engine and fuel. Moreover, Healy et al. (2009) found that hydrated sulfate and organic carbon were the dominant components of size-resolved PM from ship plumes, while Murphy et al. (2009) reported that the fraction of unknown mass was much higher at small particle sizes, which were different from our results. The large discrepancies might be caused by the different sampling, analytical methods and the fuel quality. In addition, the unidentified components in each particle size bin should be clarified in the future, especially in coarse particles.

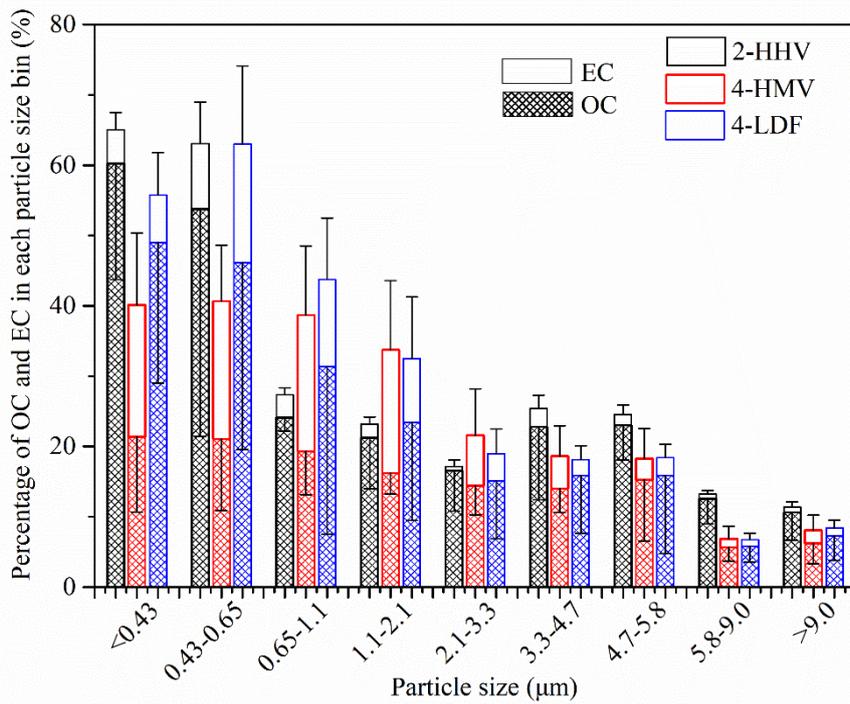
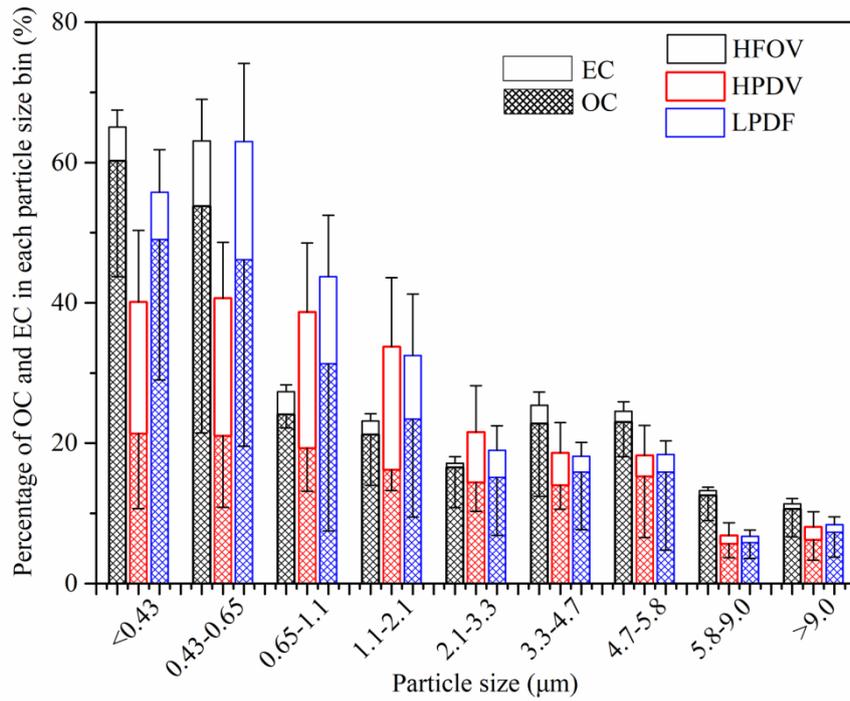


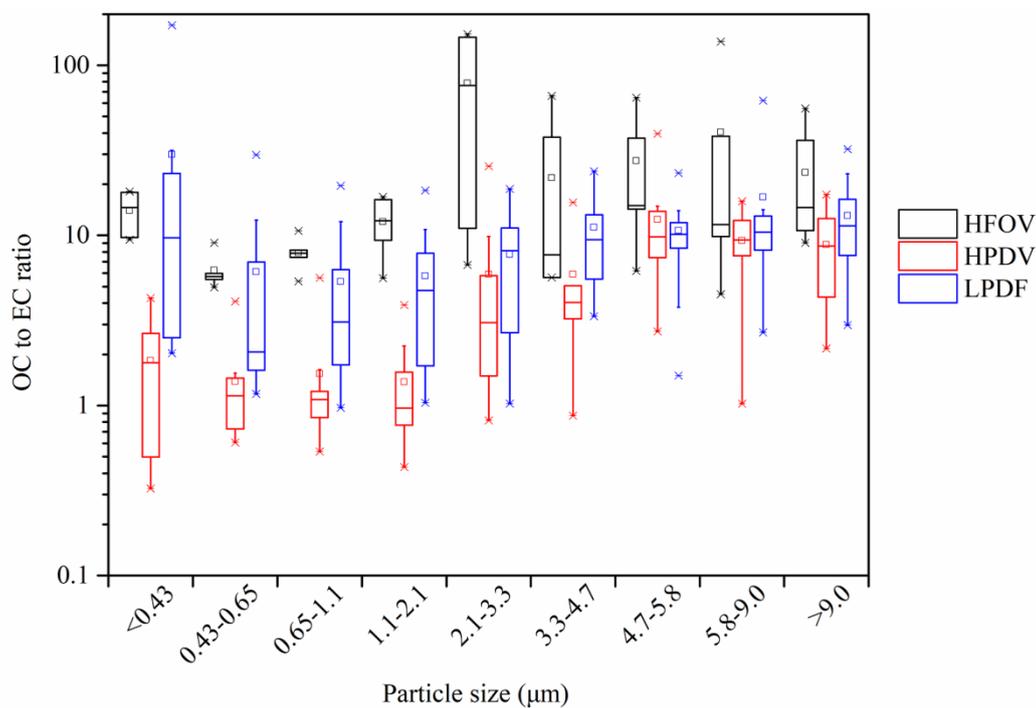
Figure 3 Percentage of OC and EC mass in each particle size bin

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The average proportions of OC were higher than EC in each individual particle size bin for all the tested ships. For better comparison, OC to EC ratios in all particle

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size bins are given for the three types of ships in Fig. 4. The OC/EC ratio of HFOV2-HHV in each particle size bin was the highest, followed by LPDF4-LDF and HPDV4-HMV. The OC/EC ratios in fine particles from HFOV2-HHV were more than 10, while they were less than 3 for 4-HMVHPDV. In addition, with the increase of particle size, the OC to EC ratios decreased first and then increased, with the lowest values in particle sizes of 0.43-1.1 μm . However, all the ships had similar median OC/EC ratios of ~ 10 in coarse particles with $D_p > 4.7 \mu\text{m}$.



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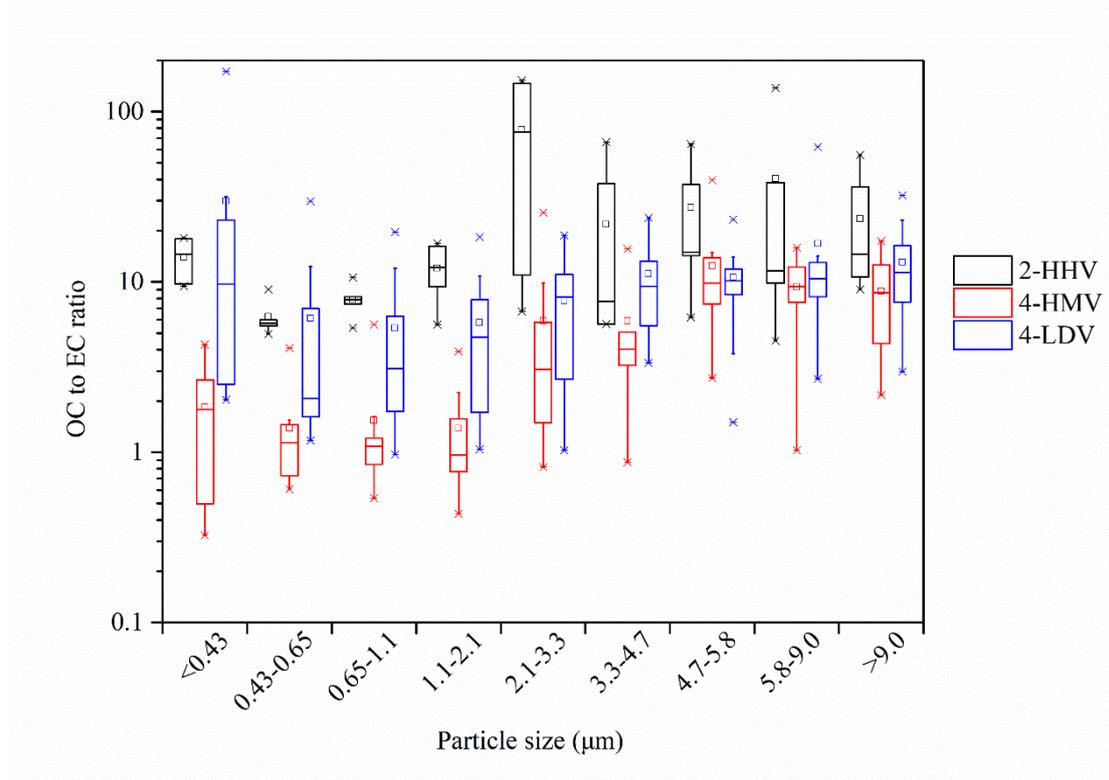


Figure 4 OC to EC ratio in different particle size bins

It is well known that particles emitted from diesel engines are formed through a complex process, starting with soot precursors generated from thermal decomposition of the large hydrocarbon molecules, through processes such as dehydrogenation, PAH formation, growth in molecular weight, particle inception, growth by surface reaction and coagulation, agglomeration and oxidation, etc. (Lighty et al., 2000). In these processes, several factors can influence the change-size of ~~particle number (PN) and diameter~~ the emitted particles: 1) coagulation reduces the PN through particle collision that forms new particle; surface growth involves the attachment of gas-phase species to the existing particles and results in no changes in PN but increase of PM diameter and mass; 2) aggregation leads to chains and clusters of primary soot particles and an increase in particle size (to 10-100 nm in diameter) (Heywood, 1988); and 3) oxidation occurs during the formation and growth processes of the particles, resulting in the formation of gaseous species and reduction of soot particles and their precursors. In addition, the exhaust gases continue to cool down and are diluted with air in the exhaust

gas channel. The decreased temperature has an impact on the condensation and adsorption of hydrocarbons and other volatile compounds, but not on the soot particles (Heywood, 1988). The volatile compounds in the exhaust gas channel may form new particles via transformation, nucleation, adsorption and condensation, depending on the conditions in the exhaust gas channel (Kittelson, 1998).

Soot particles ~~were~~are mainly formed through pyrolysis of diesel fuel and lubrication oil, and the organic fraction ~~was~~is formed through incomplete combustion of fuel and lubrication oil (Zetterdahl, 2016). Incomplete combustion of fuel and lubrication oil ~~could~~can significantly enhance the formation of fine particles, which might be the reason for the higher OC to EC ratio in particles with $D_p < 0.43 \mu\text{m}$ in this study. This study also found that most EC were in the particles with $D_p < 1.1 \mu\text{m}$, coincident with the fact that soot ~~was~~is primarily in accumulation mode with particles of $0.1 < D_p < 1 \mu\text{m}$ (Kasper et al., 2007). Although OC was also concentrated in fine particles with $D_p < 1.1 \mu\text{m}$ (Section 3.1), its percentage was higher in particles with $D_p < 0.43 \mu\text{m}$, and lower in particles with $0.43 < D_p < 1.1 \mu\text{m}$, compared to the EC distribution. Therefore, OC to EC ratios were the lowest in particles with $0.43 < D_p < 1.1 \mu\text{m}$ for all the tested ships. For the coarse particles in this study, though non-carbonous components were the dominant parts, OM increased after the cooling of the exhaust gas while content of EC and ash remained unchanged through adsorption of hydrocarbons and other volatile compounds (Zetterdahl, 2016), which enhanced the formation of coarse particles. Consequently, OC to EC ratios also showed high values in coarse particles with $D_p > 3.3 \mu\text{m}$. HFOV2-HHV showed higher OC to EC ratio than the diesel fuel ships, which might be caused by the relatively lower combustion efficiency. Similarly, because HPDV4-HMV ships had higher combustion efficiencies due to the higher fuel quality and better engine maintenance in this study, OC to EC ratios of HPDV4-HMV showed the lowest levels.

3.2.3 OC and EC fragments in size-segregated particles

According to the IMPROVE-A protocol used in the thermal-optical carbon analysis, fragments of OC (OC1, OC2, OC3, and OC4 fragments obtained in 120, 250,

450, and 550 °C in pure He atmosphere, respectively) and EC (EC1, EC2, and EC3 fragments obtained in 550, 700, and 840 °C in 98% He/2% O₂ atmosphere, respectively) were obtained and used to understand different formation processes (Sippula et al., 415 2014). In this study, percentages of OC and EC fragments in different particle size bins are shown in Fig. 5. Typically, OC1+OC2 were classified as volatile organic compounds while OC3+OC4 were categorized as refractory organic compounds. EC was divided into char and soot. EC1 was classified as char-EC and EC2+EC3 were classified as soot-EC (Han et al., 2018). OC1, OC2 and OC3 were the dominant OC fragments for 420 all the tested ships, while EC2 was the prevailing EC fragment for diesel fuel ships and EC1 was the main EC fragment for HFO ship. In comparison, OC1+OC2 in LPDF4-LDF ships accounted for higher percentages than other types of ships, especially OC1, while OC3+OC4 in HFOV2-HHV had more fractions than in LPDF4-LDF and HPDV4-HMV, revealing that more pyrolytic organic matters were emitted from 425 HFOV2-HHV ships.

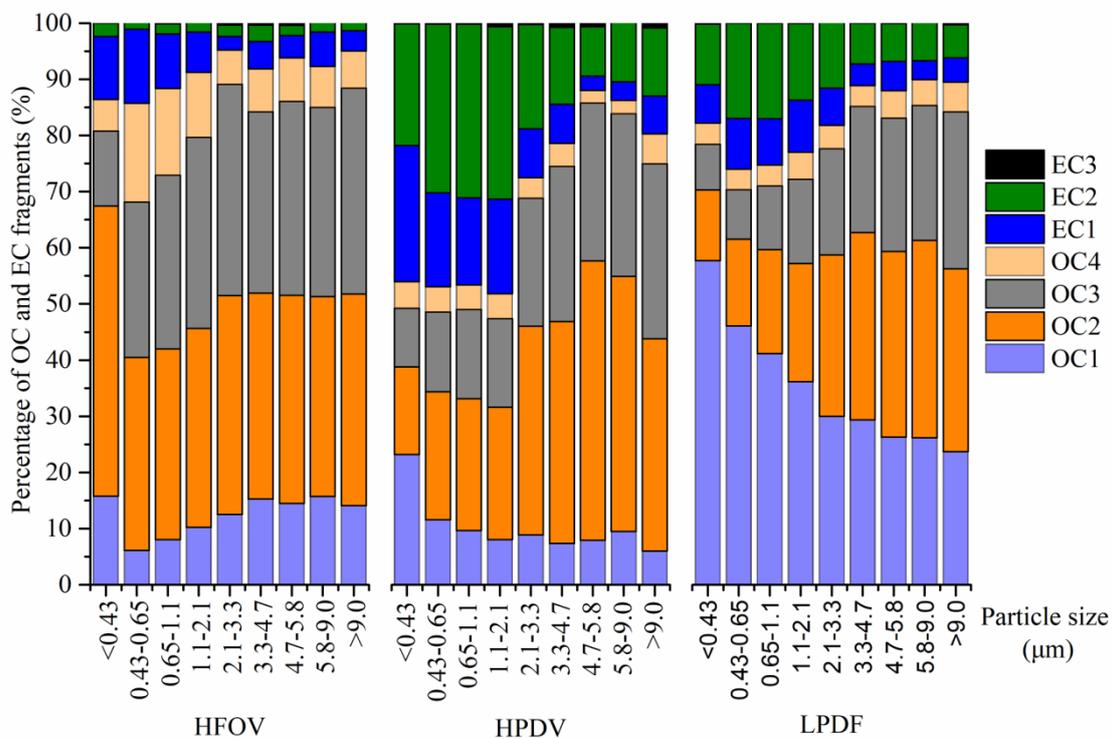
The results are consistent with a previous study which found that 37-57% of the OC were heavier OC fragments (OC3, OC4, and pyrolytic carbon) in PM emitted from heavy fuel oil ships, while the PM from diesel fuel ships was dominated by the most volatile OC1 and OC2 fragments (Sippula et al., 2014). Since OC was formed through 430 incomplete combustion of the fuel and lubrication oil, the different OC fragments in PM between HFO and ~~diesel~~diesel fuel ships (LPDF4-LDF and HPDV4-HMV) reflected the variations of the fuel composition. This result was coincident with the fact that heavy fuel oil has longer carbon chains than diesel fuel. For EC, the amount of soot particles emitted from cylinder depends on the difference between the formation rate and the oxidation rate during the expansion stroke (Zetterdahl, 2016). From Fig. 5 we 435 inferred that the 2-stroke ~~low-low~~-speed HFO engine (HFOV2-HHV) had higher oxidation rate than the 4-stroke medium/~~high-high~~-speed diesel engines (HPDV4-HMV and LPDF4-LDF), leading to lower soot-EC percentages.

The OC and EC fragments had different percentages in different size particles. On 440 one hand, OC1 in diesel fuel ships presented obvious decreasing trend with the increase

of particle size. However, though the highest proportion of OC1 was observed in particles with $D_p < 0.43 \mu\text{m}$ for HFOV2-HHV, there was an opposite variation trend of the other particle size bins to that of diesel fuel ships. Furthermore, for diesel fuel ships, both OC2 and OC3 had lower proportions in small particles and higher proportions in coarse particles. For HFOV2-HHV, OC2 accounted for the largest proportion in particles with $D_p < 0.43 \mu\text{m}$, whereas its proportion in other particle size bins was similar. In contrast, OC3 occupied the smallest proportion of HFOV2-HHV in particles with $D_p < 0.43 \mu\text{m}$, and was constant in other particle size bins. In addition, OC4 showed no significant variations among the particle size bins for all the tested ships. On the other hand, EC1 showed decreasing trends with the increase of particle size for all the tested ships, while EC2 had the highest proportions in particles with $0.65 < D_p < 1.1 \mu\text{m}$ for diesel fuel ships, with overall higher proportions in small particles and lower proportions in coarse particles. However, EC2 of HFOV2-HHV showed no significant variations. In addition, EC3 had very small proportions for all the tested ships and showed no significant variations with particle sizes.

It is known that particles in the nucleation mode consist of both solid particles and condensable organic and sulphur compounds that are usually formed during dilution and cooling of the exhaust gas (Kittelson, 1998). Hydrocarbons and carbon fragments are the main source of tiny particles from engines running under normal conditions with low-sulfur fuels (Kittelson, 1998). Besides, it has been proved that new particle formation via nucleation is more favorable than adsorption on existing particles if there is small surface area on which to adsorb when hydrocarbons transfer from gas phase to particle phase (Kittelson, 1998). Therefore, high volatile organic matter in nucleation mode particles might be the reason for higher proportions of OC1 in small particles. It is also known that the majority of accumulation-mode particles are solid agglomerates with adsorbed compounds (Kittelson, 1998). Due to the smaller relative surface areas of accumulation and coarse mode particles, fewer volatile organic matters can be adsorbed with the increase of particle size, leading to the decreased proportions of OC1. In addition, OC3 and OC4 stem from low volatile organic matters with large molecular

470 weights, which might be formed directly inside the cylinder under high temperature and pressure. The existence and formation of large size particles containing OC3 and OC4 have been proved in a previous study (Han et al., 2018). In this study, EC was primarily found in the accumulation mode. This is to some extent consistent with the findings of Kittelson (1998) that accumulation mode particles are mainly carbonaceous soot agglomerates formed directly by combustion, and those of Moldanová et al. (2009) that char and char-mineral particles were concentrated in a size range of 0.2-5 μm . Moreover, the decreased temperature in the exhaust gas channel has an impact on the condensation and adsorption of hydrocarbons and other volatile compounds during the coarse particle formation, but not on the soot particles (Heywood, 1988). As a result, EC fragments showed obvious decreasing trends with the increase of particle size in coarse-mode. The formation of OC and EC fragments could be influenced by many factors, such as engine condition (temperature, pressure), fuel type (fuel composition and structure), operating conditions, etc. (Tree and Svensson, 2007). However, detailed formation mechanism of OC and EC fragments in size-segregated particles still need to be further studied.



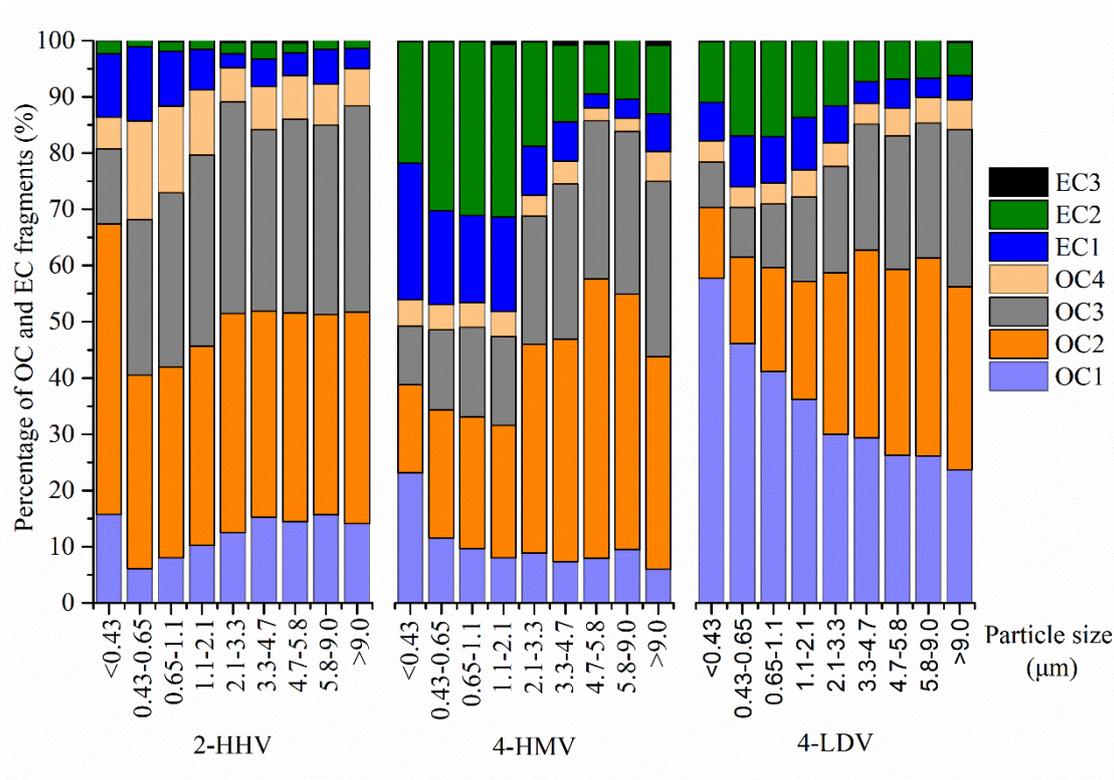


Figure 5 Percentage of OC and EC fragments in different particle size bins

3.3 Characteristics of PAHs and n-alkanes in size-segregated particles

3.3.1 Distributions of total PAHs and total n-alkanes in different particle size bins

The distributions of total PAHs and total n-alkanes in different size particles emitted from these three types of ships in China are shown in Fig. 6 and Table S8.

Notably, the same as OC and EC, the levels of PAHs and n-alkanes values given provided in this study were also the average values from of all samples that were

495 classified into these three types. Clearly, large proportions of identified organic

compounds were concentrated in fine particles. About 66.3% to 88.0% of PAHs were

in particles with $D_p < 1.1 \mu\text{m}$. The results are consistent with the finding of a previous

study that revealed >69% particle-PAH was associated with $\text{PM}_{2.5}$ emitted from

residential coal combustion (Shen et al., 2010). Similar observations were also reported

500 from indoor crop burning (Shen et al., 2011) and motorcycles (Yang et al., 2005). In

addition, a previous study about PM from a typical container ship has demonstrated that

the smaller the particles are, the greater their toxicity is (Wu et al., 2018). In comparison,

n-alkanes in fine particles with $D_p < 1.1 \mu\text{m}$ accounted for higher proportions than PAHs, with a range of 79.0~94.6%. Both PAHs and n-alkanes in particles with $D_p < 1.1 \mu\text{m}$ from [HFOV2-HHV](#) had the highest proportions among the three types of ships, and they were the lowest from [HPDV4-HMV](#). Thus, large proportions of PAHs (33.7%) and n-alkanes (21.0%) were still in particles with $D_p > 1 \mu\text{m}$ for [HPDV4-HMV](#), which were seldom reported in previous studies of ship engine exhausts.

It is well documented that incomplete combustion of fuel and lubrication oil was one of the major sources of organic compounds in PM and enhanced the new particle formation (Agrawal et al., 2010; Zetterdahl et al., 2017). Higher PAHs contents in heavy fuel oil and lower combustion efficiencies in 2-stroke lower-speed engines could lead to enhanced nucleation-mode particle formation, which could contain more PAHs and n-alkanes. In contrary, lower PAHs contents in diesel fuels of [HPDV4-HMV](#) ships, together with better maintenance of the engines, might lead to better combustion conditions and less nucleation-mode particle formation that had lower organic matter proportions. In addition, new particles could be formed in the exhaust gas channel through transformation of nucleation, adsorption and/or condensation. Therefore, the varied conditions in the exhaust gas channels caused the differences in organic matter proportions in coarse particles. The relatively longer exhaust gas channel and higher temperature in the channel of [HFOV2-HHV](#) enhanced the formation of new secondary nucleation-mode and/or accumulation-mode particles from gas-phase organic compounds, leading to higher proportions of organic matters in fine particles, [which has been proved in a previous study](#) (Kittelson, 1998).

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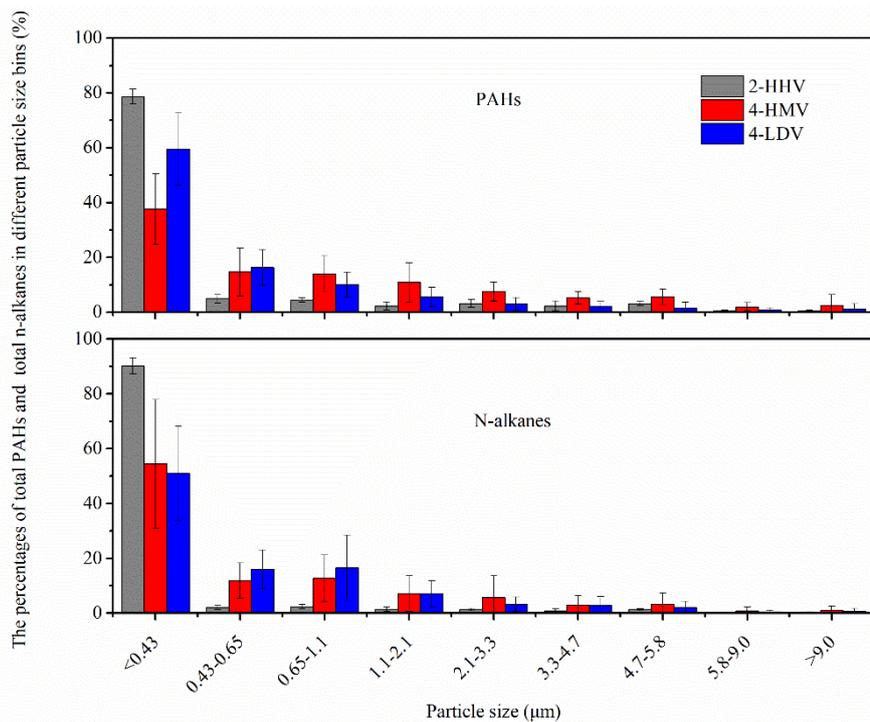
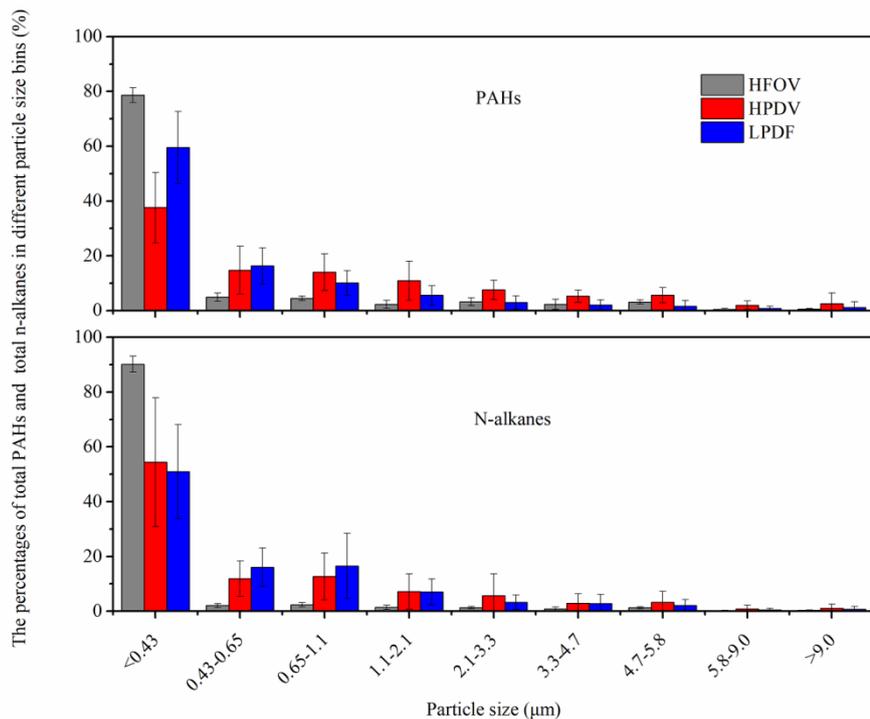


Figure 6 The distribution of total PAHs and total n-alkanes in different particle size bins (%)

530

3.3.2 Emission ratios of PAHs and n-alkanes in each particle size bin

In order to explore the variations of total PAHs and total n-alkanes in different size

particle bins, the emission ratio ($\mu\text{g (g}^{-1} \text{ PM)}$ and $\text{mg (g}^{-1} \text{ PM)}$) was defined and discussed in this study. It is calculated by dividing the total PAHs or n-alkanes mass ($\mu\text{g/mg}$) through the particle mass (g) in each particle size bin. The emission ratios of total PAHs and total n-alkanes in size-segregated particles are shown in Fig. 7. Obviously, the emission ratios of both PAHs and n-alkanes decreased with the increase of particle size, and they were more than two orders of magnitude higher in fine particles than in coarse particles. Namely, much more organic matter was contained in fine particles than in coarse particles. This is consistent with previous findings that nucleation-mode particles usually contain a large proportion of organic compounds (Kittelson, 1998; Moldanová et al., 2009).

Among the three types of ships, LPDF4-LDF had the highest PAHs emission ratios in fine particles with $D_p < 1.1 \mu\text{m}$, and the HFOV2-HHV had the lowest values. However, no significant difference of PAHs emission ratios was observed in particles with $D_p > 1.1 \mu\text{m}$ for all the tested ships ($p > 0.05$), so was for n-alkanes. In particular, the 4-stroke low-power diesel fuel fishing boats in China had not only high levels of PM emission factor, but also high proportion and emission ratio of organic matters in fine particles, implying their severe influence on human health and the environment.

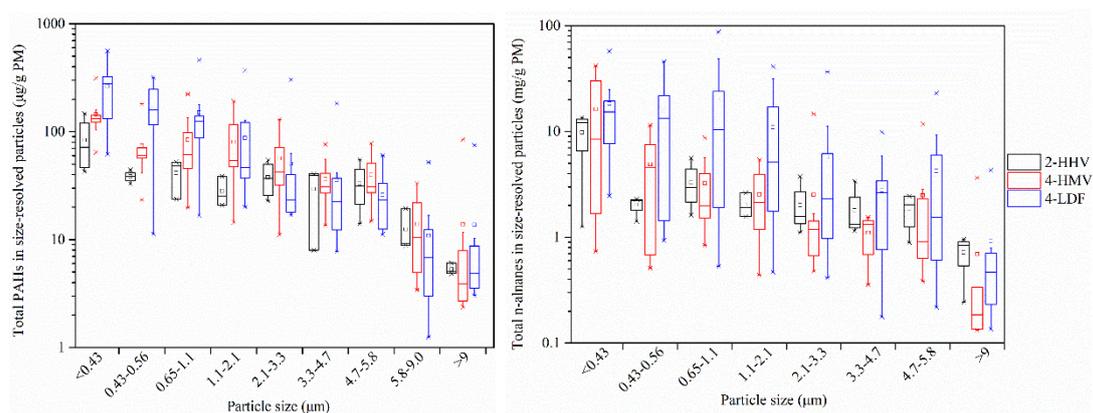
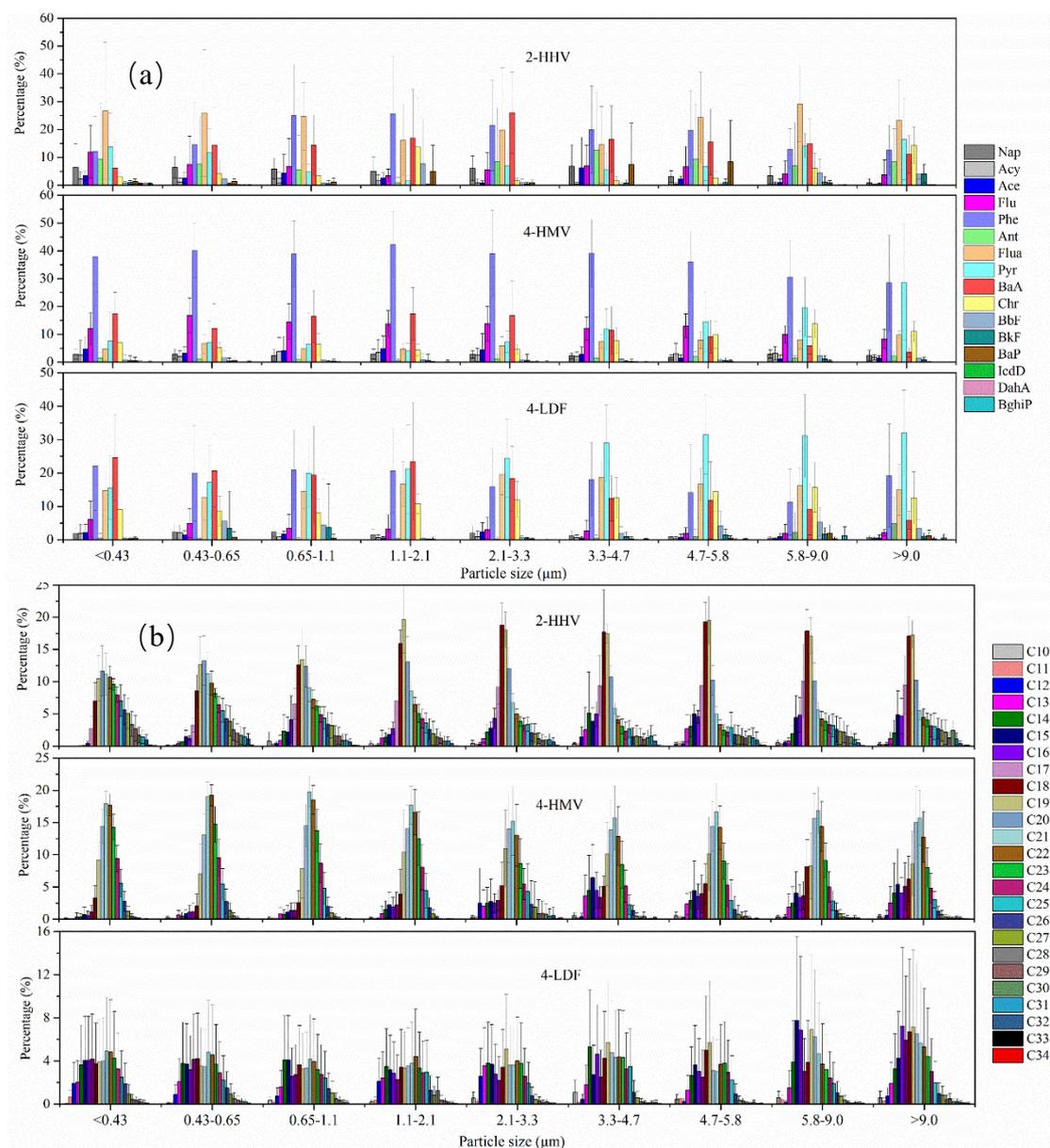


Figure 7 Emission ratios of total PAHs (in $\mu\text{g (g}^{-1} \text{ PM)}$) and n-alkanes (in $\text{mg (g}^{-1} \text{ PM)}$) in size-resolved particles

555 3.3.3 Profiles of speciated PAHs and n-alkanes in size-segregated particles

The speciated profiles of PAHs and n-alkanes in size-segregated particles emitted from the three types of ships are shown in Fig. 8. Phe, Flua, Pyr, BaA, Flu and Chr (full names and their abbreviations are shown in Table S5) were the most dominant PAHs, while their relative percentages in different types of ships and in different particle size bins varied. For HFOV2-HHV, the levels of Flua, Phe, BaA and Pyr were higher than other PAH species, while the profiles of PAHs in different particle sizes were similar. For HPDV4-HMV, Phe, Flu, BaA and Pyr were the main PAHs, with Phe having the highest proportions in all the particle size bins. Furthermore, the percentages of Phe and BaA were lower in coarse particles. This is in accordance with the fact that synthetic PAHs have higher concentrations in freshly formed particles (Pergal et al., 2013). However, the percentages of Pyr and Chr increased with the increase of particle size. For LPDF4-LDF, Pyr, BaA, Phe, Flua and Chr were the dominant components. The percentage of BaA decreased with the increase of particle size, whereas Pyr and Chr presented opposite trends. The various profiles of PAHs in different particle size bins indicated their different formation processes, which were likely related to the fuel quality, engine type and the condition in the exhaust gas channel (Lombaert et al., 2006). It should be noted that when diagnostic characteristics of PAHs in PM emitted from ships is used in source apportionment, particle size needs to be taken into consideration.



575 Figure 8 Speciated profiles of PAHs (a) and n-alkanes (b) in size-resolved particles

The ratio of high molecular weight (HMW) PAH (four to six rings) to low molecular weight (LMW) PAH (two and three rings) is shown in Fig. S2. The LPDF4-LDF had the highest HMW to LMW ratios (2.96-8.25), while the HPDV4-HMV had the lowest ratios (0.62-1.98). The results indicated that LPDF4-LDF and HFOV2-HHV had unfavorable combustion conditions compared to HPDV4-HMV, which is consistent with our previous conclusion. The HMW to LMW ratios were generally higher in fine particles and decreased with the increase of particle size, except for HFOV2-HHV

580

which still showed high ratios when particle size was larger than 5.8 μm . Since HMW
585 PAHs have high toxic equivalence (TEQ), the higher HMW/LMW PAHs ratios in fine
particles implied that small particles emitted from the three types of ships might be
more toxic than coarse particles. Furthermore, from our previous study the LPDF4-LDF
showed not only higher HMW to LMW ratios than other ships, but also much higher
~~emission~~ amount of total PAHs emission (Zhang et al., 2019), implying the necessity
590 of more stringent control on the emissions of particles from fishing boats in China.c

From Fig. 8, it can be seen that n-alkanes showed different percentage distributions
in different particle size bins from different types of ships. There were larger maximum
carbon numbers (C_{max}) in smaller size particles, such as C20/C21 for HFOV2-HHV,
C21/C22 for HPDV4-HMV and C21/C22 for LPDF4-LDF. However, with the increase
595 of particle size, the C_{max} of n-alkanes switched to C18/C19, C20/C21 and C18/C19 for
HFOV2-HHV, HPDV4-HMV and LPDF4-LDF, respectively. Similar to PAHs, when
diagnostic characteristics of n-alkanes in PM emitted from ships is used in source
apportionment, particle size needs to be taken into consideration.

4. Conclusions and implications

600 Particulate matters emitted from ships have gained more and more attention in
recent years due to their adverse impacts on human health and ambient air quality.
However, our knowledge on the abundance and chemical speciation in different particle
sizes are limited. In this study, size-segregated distributions and characteristics of mass,
OC, EC, 16 PAHs and 25 n-alkanes from 12 different vessels in China were presented.

605 This study found that over 50% of the total particle mass was explained by the
particles with $D_p < 1.1 \mu\text{m}$ for most of the tested ships. Specifically, the mass was
concentrated in particles with $D_p < 0.43 \mu\text{m}$ for HFOV2-HHV, and in particles with
 $D_p < 1.1 \mu\text{m}$ for lower power ~~diesel~~ diesel fuel fishing boats, while the mass was
accounted for higher percentages by coarse particles for higher power ~~diesel~~ diesel fuel
610 fishing boats and HPDV4-HMV.

Similar to the total particle mass distribution, about 53-86% of total OC and 68-
86% of total EC were in the particles with $D_p < 1.1 \mu\text{m}$, presenting downward trend with

the increase of particle size. The OC+EC accounted for major proportions of the total particle mass in fine particles. However, OC+EC only explained small proportions in
615 coarse particles, suggesting that most of the coarse particle mass was dominated by
other non-carbonous components. In addition, the OC to EC ratio of HFOV2-HHV in
each particle size bin was the highest, followed by LPDF4-LDF and HPDV4-HMV.
With the increase of particle size, the OC to EC ratios decreased first and then increased,
with the lowest values in particle sizes of 0.43-1.1 μm . Moreover, fragments of OC and
620 EC were obtained and used to understand different formation processes. OC1, OC2 and
OC3 were the dominant OC fragments for all the tested ships, while EC2 was the
prevailing EC fragment for diesel fuel ships and EC1 was the main EC fragment for
HFO ship. Different OC and EC fractions showed different distributions in different
particle size bins because of the different formation mechanisms.

625 16 PAHs and 25 n-alkanes in different particle bins were identified in this study.
Results showed that large proportions of the organic compounds were concentrated in
fine particles, with about 66.3 - 88.0% of PAHs and 79.0 - 94.6% of n-alkanes were in
particles with $D_p < 1.1 \mu\text{m}$. LPDF4-LDF had the highest PAHs and n-alkanes emission
ratios in fine particles with $D_p < 1.1 \mu\text{m}$, and the HFOV2-HHV had the lowest values,
630 but no significant differences were observed in particles with $D_p > 1.1 \mu\text{m}$. Results of the
speciated profiles of PAHs showed that Phe, Flua, Pyr, BaA, Flu and Chr were the most
dominant PAHs, while their relative percentages in different types of ships and in
different particle size bins varied. In addition, the HMW PAHs to LMW PAHs ratios
were generally higher in fine particles and decreased with the increase of particle size.
635 N-Alkanes also showed different percentage distributions in different particle size bins
from different types of ships. Moreover, there were larger C_{max} in smaller size particles,
but switched to smaller C_{max} with the increase of particle size for all the tested ships.

This study confirmed that the particle mass distributions in different size bins from
ships were significantly different from the particle number distributions, and different
640 types of ships had their own distinct mass distributions. The different profiles of
chemical components in size-segregated particles implied that size-segregated chemical

profiles should be considered when source apportionment was conducted. Furthermore, this study found more toxic organics such as PAHs in small particles emitted from fishing boats, suggesting the necessity of more stringent control on this type of boats in
645 China. In addition, detailed formation mechanisms of chemical composition in size-segregated particles need in-depth investigation. Finally, the large proportion of unidentified components in coarse particles still needs to be figured out. Due to the limitation of instrumental analysis, only very small proportion of specific organic compounds in each size particle bin were identified in this study, implying that
650 innovative analytical technology such as real-time measurements of particle-associated organic compounds using thermo-desorption aerosol gas-chromatograph approach should be urgently developed.

Data availability. The data used for this study can be obtained from fzhangtj@tongji.edu.cn upon request.

655 **Author contributions.** FZ did the sampling, led the writing and data analysis for the manuscript with significant contributions and comments from all co-authors. YC designed the field measurements and HG reviewed and edited the manuscript. VM, YZ, XY and JC contributed to the data analysis, the manuscript structure, and the writing of the text.

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

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