

1 **Title: Gaseous and particulate pollutant emissions from ocean-going tankers in the context of**
2 **carbon reduction: main engine, auxiliary engine, and auxiliary boiler**

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12 **Abstract:** Ships are a major source of air pollution, which significantly impacts global health. In
13 this study, the gaseous and particulate emissions from the main engine, auxiliary engine, and
14 auxiliary boiler of a modern Tier III large ocean-going vessel fueled with marine gas oil and heavy
15 fuel oil have been investigated. Emissions of gaseous pollutants in the exhaust were measured online
16 and particulate samples were collected to determine detailed physical and chemical properties. The
17 results indicated that CO₂ and NO_x are the main gaseous pollutants, while organic carbon accounts
18 for the majority of particulate pollutants for the three devices. The element carbon emissions of the
19 auxiliary engine decreased with load increasing while those of the main engine maintained a level
20 of approximately 0.062 g/kWh. The black carbon emissions of the main and auxiliary engine
21 resulting from using marine gas oil were higher than heavy fuel oil. Consistent correlations among

22 pollutants were observed for the engines. Finally, the measured value of element carbon cannot be
23 utilized as a substitute for black carbon emissions due to the presence of light-absorbing organic
24 carbon in organic carbon.

25 **Keywords:** Marine diesel engine; Gaseous pollutants; Particle emissions; Heavy fuel oil; Marine
26 gas oil; Pearson correlation.

27

Abbreviations

AAE	Angstrom Absorption Exponent	MGO	marine gas oil
BC	black carbon	NDIR	non-dispersive infrared
DOC	diesel oxidation catalysts	NOx	nitrogen oxides
CLD	chemiluminescence detection method	OC	organic carbon
CO ₂	carbon dioxide	PAHs	polycyclic aromatic hydrocarbon
EC	elemental carbon	PM	particulate matter
ECAs	emission control areas	SCR	selective catalytic reduction
HFO	heavy fuel oil	SFOC	Specific Fuel Oil Consumption
HVO	Hydrotreated Vegetable Oils	SLCF	short-lived climate forcing
IMO	International Maritime Organization	SOx	sulfur oxides

28 1 Introduction

29 As the economy recovers, the role of the shipping industry in the global transport of goods has
30 become increasingly critical. Ship transportation accounts for over 80% of international trade

31 transportation [1]. However, ships' pollutants have also become an essential source of marine
32 pollution, especially in offshore areas. About 8% of sulfur oxides (SO_x), 15% of nitrogen oxides
33 (NO_x), and about 3% of the world's carbon dioxide (CO₂) come from ship emissions [2]. In addition
34 to the above-mentioned gas-phase pollutants, the emission of particulate matter from ships also
35 dramatically impacts the marine environment [3].

36 To reduce the emissions of ships, the International Maritime Organization (IMO) has set up
37 emission control areas (ECAs) in specific coastal regions. Only ships using fuels with a sulfur
38 content of less than 0.1% wt are allowed in the ECAs, while 0.5% wt sulfur content can be used
39 outside the ECAs [4]. As the shipping industry gradually transitions towards carbon reduction and
40 decarbonization, novel low-carbon and zero-carbon fuels are being implemented on ships. Due to
41 its lack of carbon atoms in its chemical structure, hydrogen exhibits high flammability, diffusivity,
42 and minimal carbon emissions. By precisely adjusting the nozzle diameter and spray cone angle,
43 the combustion performance and emission characteristics of hydrogen-diesel dual-fuel engines can
44 be effectively enhanced[5]. Furthermore, the utilization of hydrogen/biodiesel blended fuel can
45 further optimize both combustion performance and emission attributes of dual-fuel engines[6].
46 Additionally, Hydrotreated Vegetable Oils (HVO) offer a viable option for achieving short-term and
47 medium-term emission reductions as they can be used without necessitating changes to the engine
48 fuel system[7, 8]. Moreover, employing exhaust after-treatment technologies such as diesel
49 oxidation catalysts (DOC) along with selective catalytic reduction (SCR) techniques provides an
50 opportunity for additional pollutant emission reduction while meeting increasingly stringent
51 regulations[9]. Despite the gradual adoption of novel clean energy technologies in ocean-going

52 vessels, heavy fuel oil (HFO) remains the predominant fuel for ship diesel engines due to cost
53 considerations[10]. To meet the stringent emission regulations, ships using HFO are often required
54 to use exhaust aftertreatment technology to meet the needs of relevant regulations[11]. IMO has
55 only developed applicable regulations for SO_x and NO_x, while there are still no uniform regulations
56 on diesel particulate matter [12]. With the gradual improvement of the relevant rules on SO₂ and
57 NO_x, the particulate matter emissions from marine diesel engines have gradually attracted the
58 attention of all countries worldwide.

59 There are numerous factors that can impact ship emissions, such as the type of fuel used, and
60 the engine loading employed. Studies have shown that ship emissions are greatly affected by
61 changes in the load of marine diesel engines. The changes in load affect fuel combustion in the
62 cylinder, which in turn impacts the generation of emissions [13]. In addition, different operating
63 conditions of ships affect the load of engines. The diesel engine usually operates at a lower load
64 when the ship enters and leaves ports, while medium loads are typically used on high seas. When
65 entering and leaving the dock, ships' gaseous pollutants and particulate matter are significantly
66 higher than on high seas [14].

67 The fuel type is also an essential factor affecting diesel engine pollutant emissions [15]. HFO
68 has a high density and viscosity and contains high impurities, ash, and sulfur [16]. Therefore, when
69 using HFO, the emissions of gaseous pollutants and particulate matter in the ship will be higher than
70 when using Marine Gas Oil (MGO) [17]. Meanwhile, the emissions of particulate matter (PM) and
71 polycyclic aromatic hydrocarbons (PAHs) from HFO are higher than MGO, which increases the
72 impact of ship pollutants on human health [18].

73 The boilers which produce steam and hot water are also an essential source of ship emissions.
74 However, there are few regulations for boilers. When entering the ECAs and ports, the ships reduce
75 the emissions of the boilers by switching to MGO only.[19] The emissions of the boilers are low,
76 which accounts for less than 5% of ship emissions [20].

77 In summary, a substantial body of literature exists on ship emission characteristics. However,
78 these studies primarily focus on the emissions of engines utilizing a single fuel, with limited research
79 conducted on the emission disparities between different fuels. Furthermore, previous investigations
80 predominantly rely on bench experiments, and there are a few emission measurements from ships
81 during actual voyages. Additionally, there remains an inadequate understanding of the emission
82 characteristics exhibited by various burners installed on the same vessel. To gain deeper insights
83 into mechanisms governing pollutant formation, it is crucial to obtain more comprehensive emission
84 data that elucidates the influence of both fuel types and combustion devices.

85 In this paper, the emissions of pollutants from an ocean-going vessel utilizing HFO and MGO
86 have been investigated. Besides, the measurement of gaseous pollutants such as CO₂, NO_x, and
87 SO_x emitted by both the main engine and auxiliary engines during navigation was encompassed in
88 this study. Additionally, significant attention was given to examining particulate pollutants including
89 elemental carbon (EC), organic carbon (OC), and black carbon (BC). It is noteworthy that the
90 potential of OC/EC as a tracer for fuel sources and its impact on BC measurements was also
91 explored. For boilers, the primary focus was placed on analyzing their emissions of various
92 pollutants when using HFO. Furthermore, the correlations between different types of pollutants
93 were investigated.

94 2. Experimental process and methods

95 2.1 Engine and fuel properties

96 The study was conducted on an Aframax crude oil tanker, which has a deadweight capacity of
97 114000 tons. The total length and width of the vessel are 250 meters and 44 meters, respectively. In
98 addition, it is outfitted with a single main engine, along with three auxiliary engines and one boiler.

99 The main engine is a Tier III 6-cylinder MAN-6G60ME-C9.5-HPSCR two-stroke engine,
100 while the auxiliary engine is the DAIHATSU 6DE-20 medium-speed diesel four-stroke engine. The
101 engine parameters are listed in **Table 1**. Meanwhile, the information of the experimental devices is
102 shown in Table 2. The fuel consumption of the boiler is 131.5 kg/h. HFO 180 and MGO were used
103 for the test, their specific parameters are presented in Table 3.

104 **Table 1 Technical Parameters of the test engines**

	Main Engine	Auxiliary Engine
Engine type	Two-stroke engine	Four-stroke engine
No. of cyl	6	6
power (kW)	13500	900
speed (rpm)	91.1	900
bore (mm) × stroke (mm)	600 × 2790	205 × 300
Specific Fuel Oil Consumption (SFOC)	152 g/kWh+5%	
Dry weight (ton)	534	16

105

106

Table 2 the information of the experimental devices

Measured variable	Position	Sensor-device principle	Type	Accuracy
Fuel mass flow	Fuel line	Gravimetric meter	AVL / 733	± 0.12%
Temperature	Exhaust line	Thermocouple	TC direct	± 2.5 °C
NO _x , CO, SO ₂ , O ₂ , CO ₂	Exhaust line	CLA, NDIR, PMA	Horiba PG 350	±0.5% of the full-scale
BC	Exhaust line	Optical	AVL / 415SE	± 0.025 FSN
pressure	Exhaust line	Piezoresistive transducer	Kistler 4049	± 0.3% FS

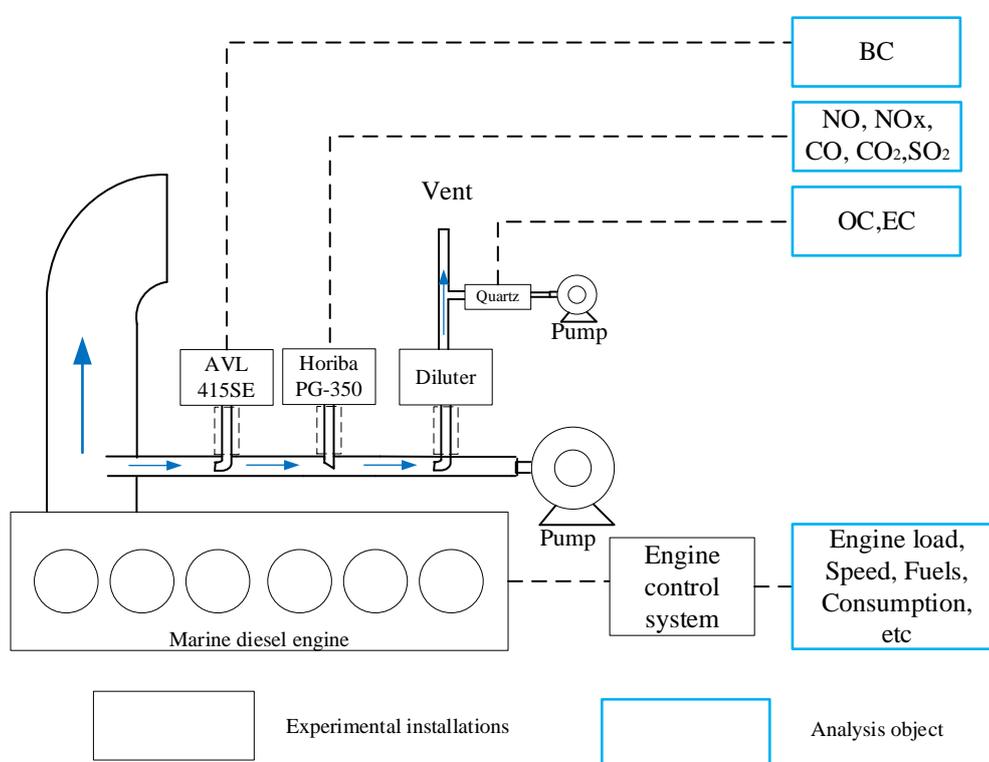
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Table 3 Tested fuel properties

	MGO	HFO 180
Water (%mass)	0	0.09
Kinematic viscosity (mm ² /s, 20°C)	4.72	152.3
Mechanical impurities (%)	0	0.132
Density (g/ml)	0.8343	0.979
Flashpoint (°C)	72.5 (101.3 kPa)	112 (101.3k Pa)
Gross calorific value (MJ/kg)	45.72	42.62
Net calorific value (MJ/kg)	42.71	40.28
Sulfur(mass%)	0.0229	0.432

108 2.2 Emissions Sampling and Analytical Methods

109 Due to practical limitations in conducting comprehensive condition testing during actual
110 navigation, experiments were conducted on the main engine within a load range of 25% to 90%,
111 adhering to ISO 8178-4 E3 test cycle. The auxiliary engine was operated within a load range of 25%
112 to 85%, following ISO 8178-4 D2 cycle.



113

114 **Figure 1 Schematic diagram of the sampling system**

115 Figure 1 illustrates the sampling system. To ensure the stability of exhaust gas, sampling
116 orifices were positioned at a distance approximately 6-10 times the diameter of the turbocharger.
117 The gaseous pollutant emissions from diesel engines were quantified using an exhaust gas
118 analyzer (Horiba, PG-350, Japan) employing the non-dispersive infrared (NDIR) spectroscopic
119 method and chemiluminescence detection method (CLD), respectively. The measured pollutants

120 included SO₂, CO₂, CO, and NO_x. Prior to measurement, the analyzer was calibrated for zero
121 point and total range using standard gases. BC measurements were conducted using AVL 415SE,
122 while PM carbon composition was collected utilizing a quartz membrane sampler. The exhaust
123 gas is diluted in the sampling tube through the diluter. The dilution rate is determined according
124 to the change in NO_x concentration before and after dilution to ensure that the dilution rate is
125 between 6-8.. The PM was then collected from the diluted exhaust gas utilizing a 47 nm quartz
126 filter membrane sampler with a duration of 30 minutes.

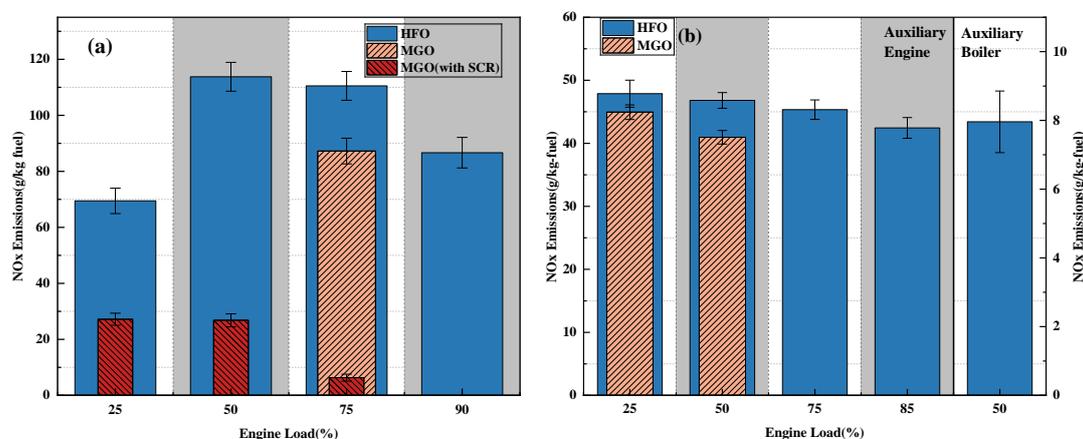
127 EC and OC were obtained from samples collected using quartz filter membranes. Prior to
128 sampling, the filter membranes were subjected to a 5-hour heating process at 500 °C in a muffle
129 furnace to eliminate moisture and carbon-containing pollutants. The quantification of EC and OC
130 was achieved by subjecting the samples to varying temperatures using a thermal/optical carbon
131 aerosol analyzer.

132 **Results and discussion**

133 **3.1. Gaseous emissions**

134 The NO_x emissions from various combustion devices in the tested vessel are depicted in Figure
135 2. Meanwhile the emission factor (g/kWh) of gaseous emissions are shown in Table 4. When
136 utilizing HFO, the main engine's NO_x emissions ranged from 69.74±3.7 g/kg fuel to 110.5±4.8 g/kg
137 fuel, while those of the auxiliary engine ranged from 42.4±1.7 g/kg fuel to 47.9±1.9 g/kg fuel. The
138 NO_x generated by diesel engines primarily originates from thermal NO_x formation, which
139 predominantly occurs in high-temperature regions and is influenced by temperature, excess air

140 coefficient, and residence time within the high-temperature zone [21]. Due to longer combustion
141 duration and higher excess air coefficient, two-stroke diesel engines exhibit higher levels of NOx
142 emissions compared to four-stroke auxiliary engines. In addition, fuel type is also an important
143 factor affecting NOx emissions. When burning HFO, NOx emissions are higher compared to MGO.
144 In contrast to HFO, MGO exhibits a shorter ignition delay due to its lower density and viscosity,
145 resulting in a reduced peak flame temperature and mitigated NOx formation [22]. Moreover, the
146 decreased nitrogen content in MGO contributes to the reduction of NOx emissions [23]. However,
147 a significant decrease in NOx emissions below 5 g/kWh has been achieved through the utilization
148 of SCR's catalytic oxidation process.



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Figure 2. (a–b): NOx emissions: (a) main engine, (b) auxiliary engine and boiler

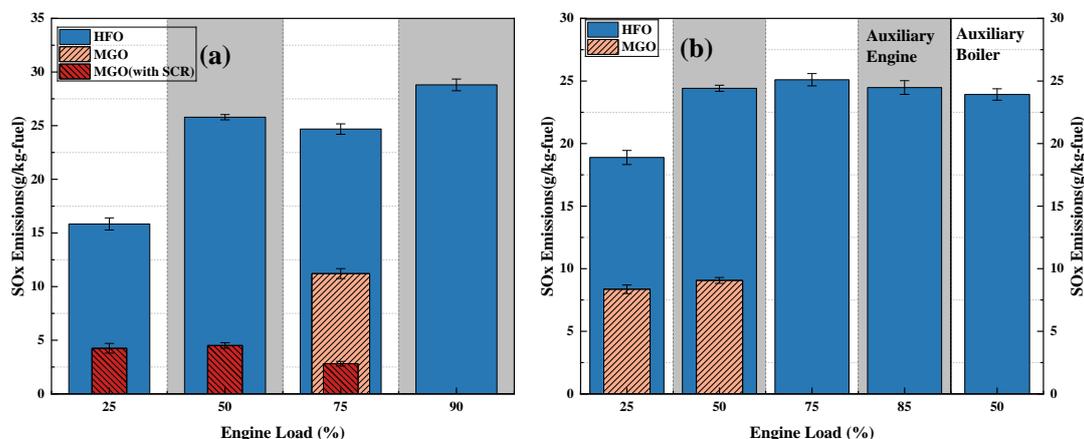


Figure 3. (a–b): SO₂ emissions: (a) main engine, (b) auxiliary engine and auxiliary engine.

The ship's SO₂ emissions primarily originate from fuel, with a minor contribution from lubricating oil [24]. In addition, the sulfur content of HFO surpasses that of MGO, which explains why the SO₂ emissions from MGO are lower than those from HFO [25].

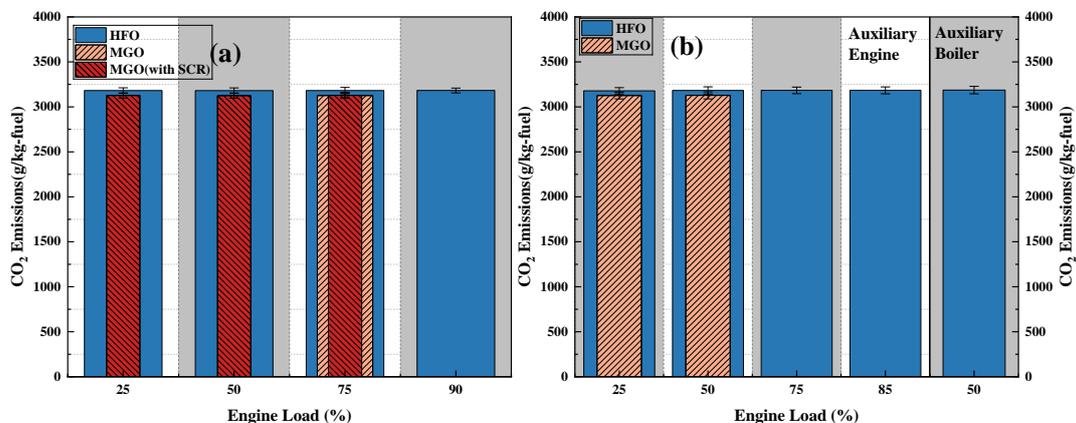


Figure 4. (a–b): CO₂ emissions: (a) main engine, (b) auxiliary engine and auxiliary boiler

Figure 4 illustrates the CO₂ emissions, which remain largely invariant to variations in load and engine type. Notably, the CO₂ emissions are marginally elevated when HFO is utilized in comparison to MGO. The CO₂ emissions of the boiler are approximately 3180 g/kg of fuel, which aligns with findings from previous studies [26].

162

Table 4 the Gaseous emissions (g/kWh) of main engine and auxiliary engine

	Fuel	Load	NO _x	NO ₂	NO	SO _x	CO ₂	CO	
Main Engine Emission Factors (g/kWh)	HFO	25%	12.35±0.77	6.36±0.44	5.99±0.14	2.55±0.09	550±6.07	0.41±0.25	
		50%	20.15±0.91	5.43±0.56	14.72±0.35	4.65±0.04	597±5.71	0.36±0.12	
		75%	20.01±0.90	3.97±0.29	16.04±0.56	4.17±0.09	560±6.20	0.40±0.11	
		90%	14.8±0.96	2.54±0.10	12.26±0.80	4.89±0.10	548±4.68	0.41±0.11	
	MGO	75%	13.81±0.75	3.28±0.25	10.52±0.42	1.93±0.78	507±4.18	0.84±0.21	
	MGO	25%	4.27±0.35	3.43±0.16	0.85±0.15	2.89±0.07	508±4.89	0.31±0.15	
	(with	50%	4.74±0.41	0.79±0.15	3.94±0.21	0.88±0.04	558±5.12	1.28±0.21	
	SCR)	75%	1.44±0.21	0.30±0.11	1.13±0.05	0.27±0.34	521±5.35	0.79±0.32	
	Auxiliary Engine Emission Factors (g/kWh)	HFO	25%	11.07±0.63	2.23±0.12	8.84±0.47	4.41±0.15	735.28±3.11	1.51±0.08
			50%	10.84±0.43	1.35±0.15	9.50±0.12	5.51±0.21	733.18±2.67	0.57±0.11
75%			10.17±0.27	1.31±0.07	8.86±0.23	5.64±0.11	719.43±2.82	0.58±0.08	
85%			9.77±0.34	1.43±0.09	8.34±0.17	5.64±0.18	716.19±2.44	0.55±0.03	
MGO		25%	10.71±0.33	0.9±0.18	9.81±0.14	2.01±0.14	743.66±5.11	0.77±0.02	
		50%	10.12±0.56	1.11±0.17	9.02±0.33	2.15±0.13	770.62±4.81	0.85±0.02	

163

3.2. Emission factors of carbonaceous matter at different operating loads

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The PM emitted by diesel engines primarily consists of OC, EC, and various metal salt

165

impurities [27]. Among these components, the dominant constituents of PM are carbonaceous

166

particles mainly composed of OC and EC.

167 The emissions of EC and organic carbon OC from both the main and auxiliary engines are
168 depicted in Figure 5. Regarding the main engine, OC accounts for the majority of carbonaceous
169 particle emissions at approximately 92-96%, while EC only contributes to around 4%-8%. It is
170 worth noting that multiple factors influence the formation of OC in engine emissions. However,
171 research has indicated that incomplete combustion of hydrocarbon molecules in fuel and leakage of
172 lubricating oil during sweeping are among the primary contributors to the generation of
173 carbonaceous particle emissions [28, 29]. With an increase in load, carbonaceous particle emissions
174 from HFO initially rise, reaching their peak at a load of 75%, followed by a decline. Compared to
175 HFO, MGO exhibits lower levels of carbonaceous particle emissions. Due to the high concentration
176 of hydrocarbon fuels in HFO, complete combustion becomes difficult during the combustion
177 process [30]. Consequently, unburned hydrocarbons gradually transform into OC within the exhaust
178 gas. Additionally, once an SCR system is employed, there is a significant reduction in both OC and
179 EC concentrations. This phenomenon can be attributed to the porous structure inherent in SCR
180 carriers which effectively intercept carbonaceous particles.

181 For the auxiliary engine, the proportion of EC in carbonaceous particles is higher compared to
182 that of the main engine, and the EC ratio exhibits different trends depending on the fuel type. From
183 Figure 5 (b), when using HFO, the proportion of EC is most prominent at low loads and gradually
184 decreases as the load increases. In addition, there is a higher proportion of EC at 25% engine load
185 compared to that at 50% load when using MGO. Moreover, the majority of carbonaceous particles
186 in the auxiliary boiler are composed of OC.

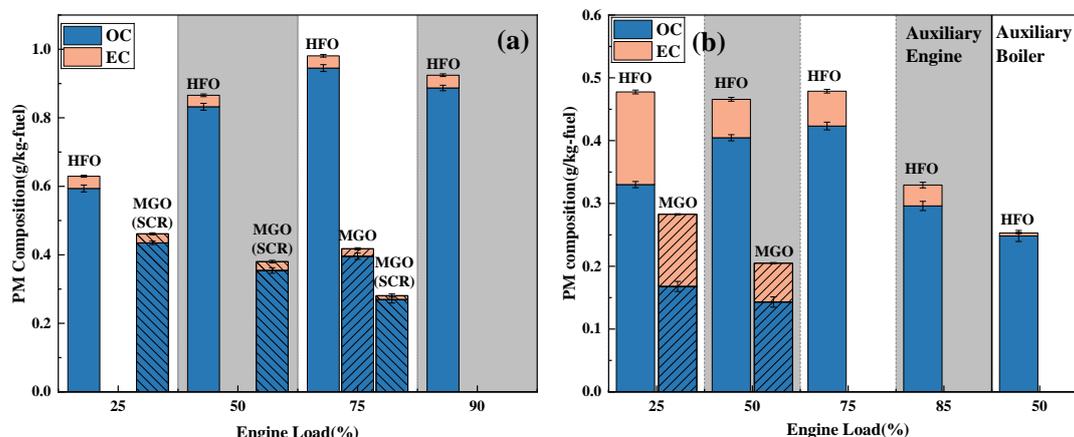
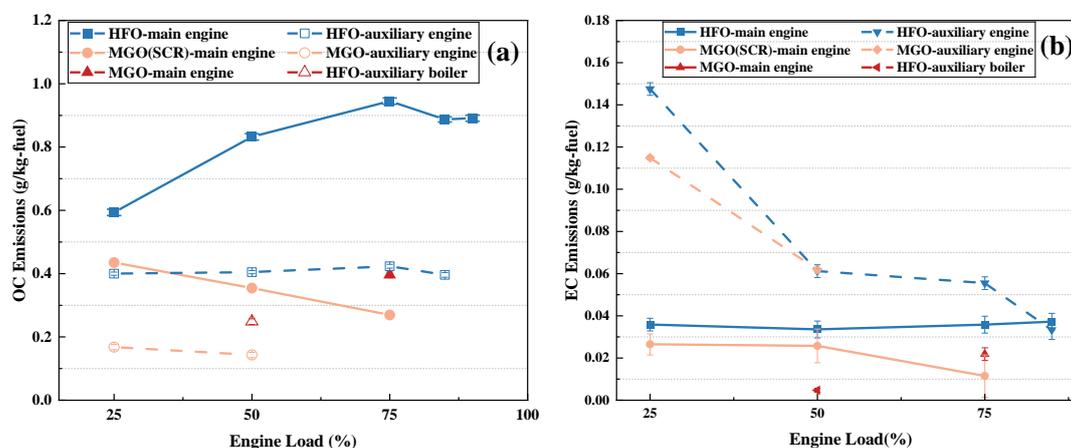


Figure 5. Carbonaceous particle emissions: (a) main engine, (b) auxiliary engine and auxiliary boiler

The emissions of OC and EC with engine loads are shown in Figure 6 (a). The emission of OC demonstrates a similar trend to the engine loads when different engines operate on the same fuel. Notably, the use of MGO effectively reduces OC emissions compared to HFO. When using HFO, OC emission exhibits an upward trend as the load increases from 25% to 75% and then a downward trend as the engine load continues to increase to 90%. Conversely, when MGO is used in the auxiliary engine, The OC emissions decrease with the increasing load. Moreover, SCR has proven to be highly effective in reducing OC emissions by 35%.

The EC emissions of the auxiliary engine are higher than those of the main engine, as shown in Figure 6 (b). This phenomenon can be attributed to the elevated fuel-air ratio of the two-stroke diesel engine, which reduces the formation of high-temperature and hypoxic regions within the cylinder. The EC emissions for the main engine remain at a level of approximately 0.035 ± 0.003 g/kg fuel when using HFO. As for the auxiliary engine, there is a decline in EC emissions as load increases for both fuel types. These findings align with previous research that demonstrated how higher engine loads lead to lower EC emissions due to improved combustion efficiencies [31].

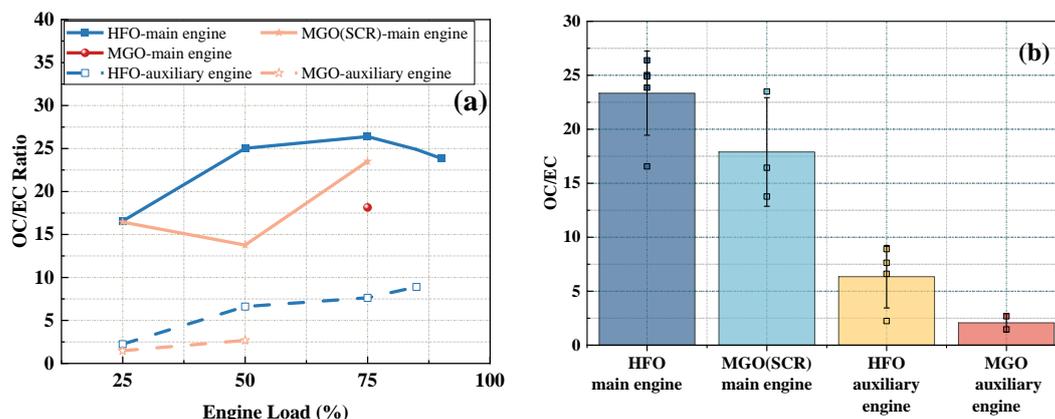
203 The differences in EC emissions between the two types of engines can be attributed to the
 204 inherent structural distinctions between two-stroke and four-stroke engines. As for the four-stroke
 205 engines, an increase in load results in higher in-cylinder temperature and excess air coefficient,
 206 consequently leading to a reduction in EC formation. Conversely, variations in excess air coefficient
 207 have minimal impact on EC generation for two-stroke engines. Furthermore, due to its moderate
 208 structure, SCR technology demonstrates a significant potential for reducing EC emissions.



209
 210 **Figure 6. EC and OC emissions: (a) main engine, (b) auxiliary engine and auxiliary boiler**

211 The OC/EC ratio is commonly employed in the analysis of atmospheric particulate matter
 212 sources to ascertain their origin and association with PM [32]. Notably, the OC/EC ratio exhibits a
 213 wide range of variation for marine diesel engines, as illustrated in Figure 7. For HFO, the average
 214 OC/EC is found to be 23.34 while that of the MGO is 17.9. In contrast, the OC/EC of the auxiliary
 215 engine for both fuel types is considerably lower ranging from 1.4 to 9. In this case, the average
 216 OC/EC value when using HFO and MGO is determined as 6.34 ± 2.89 and 2.07 ± 0.86 , respectively.
 217 The results further indicate that there exists a significant disparity between two-stroke and four-
 218 stroke engines regarding their respective levels of OC/EC emissions. Compared to the case when

219 MGO is used as fuel for the main engine without the SCR system, the OC/EC ratio after using the
220 SCR system increases due to a substantial reduction in EC concentration.



221

222

Figure 7. EC/OC ratio at different loads: (a) the main engine, (b) the auxiliary engine

223

There are significant variations in the OC/EC ratio among different sources. Typically, biomass

224

combustion yields a higher OC/EC ratio compared to fossil fuel combustion [33, 34]. Figure 8

225

illustrates the OC/EC ratio of carbonaceous particles from diverse sources [35, 36]. In this study,

226

the main engine exhibits the highest OC/EC ratio ranging from 13.8 to 25. The OC/EC ratio of

227

biomass burning is higher than that of road vehicles, while the auxiliary engine shows similar levels

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as road vehicles. The use of gasoline results in a higher OC/EC ratio compared to diesel. When

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biodiesel is used as fuel for two-stroke diesel engines, the OC/EC ratio significantly decreases

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compared to conventional fuels and becomes similar to that observed in four-stroke diesel engines

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using MGO.

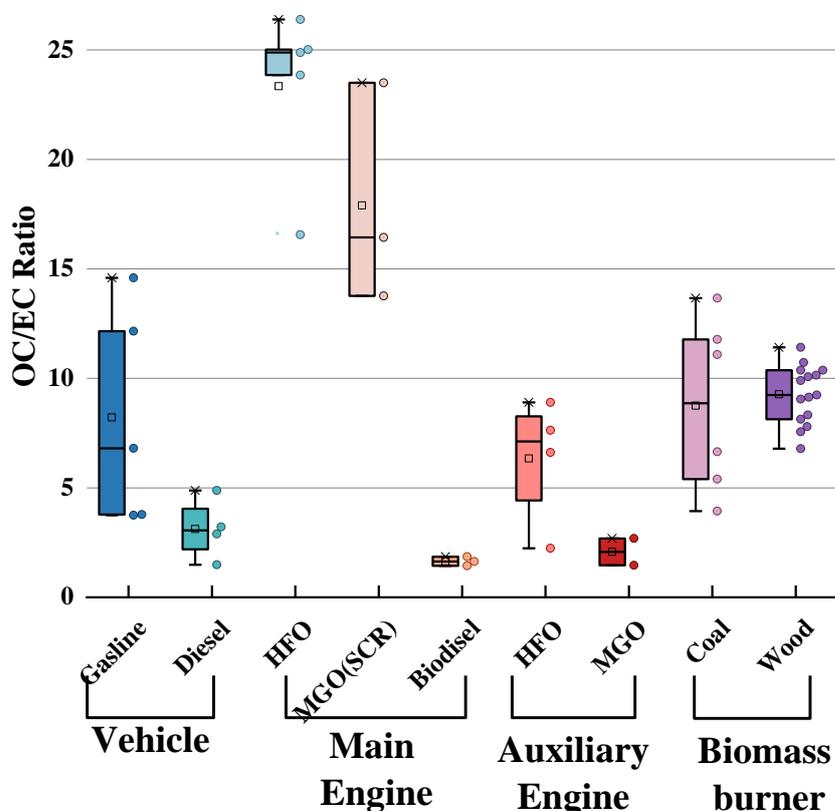


Figure 8. OC/EC ratio of carbonaceous particles from different sources

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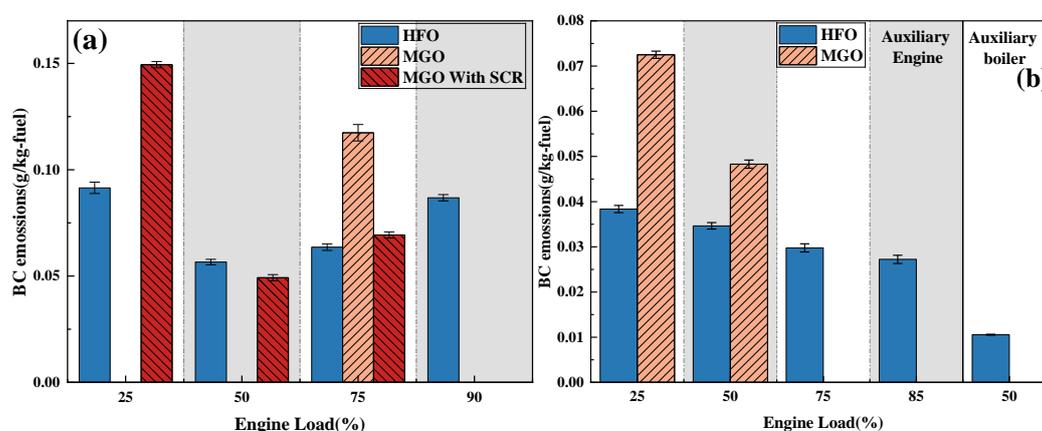
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234 BC exhibits strong absorption of visible light and is resistant to chemical migration. In contrast
235 to carbon dioxide and methane, BC is recognized as a significant short-lived climate forcing (SLCF)
236 substance, with its climate impact diminishing rapidly upon the cessation of emissions [37]. BC
237 released into the atmosphere absorbs light and radiates it back into the surrounding atmosphere,
238 thereby affecting the global climate. In particular, BC emissions north of the 40th parallel are
239 attributed to marine shipping activities, which are assumed to be a significant source contributor to
240 BC emissions in the Arctic [38]. The BC emissions of the main engine, the auxiliary engine, and the
241 auxiliary boiler are shown in Figure 9.

242

As the load increases, there is an initial decline followed by a subsequent rise in BC emissions.

243 At lower engine loads, the reduced cylinder temperature leads to a decrease in fuel thermal
244 efficiency and consequently results in the generation of unburned fuel and lubricating oil, which
245 significantly contributes to BC emissions. Additionally, the BC emissions from MGO surpass those
246 from HFO at 75% engine load. This phenomenon can be attributed to the presence of metallic
247 impurities and metals in HFO, which facilitate the combustion-induced oxidation of BC within the
248 cylinder [39]. However, the BC emissions for the auxiliary engine decrease with the load increase,
249 which is different from the main engine. This result is in line with the results of C. McCaffery et al
250 [40]. Furthermore, similar to the main engine, the auxiliary engine's BC emissions are higher when
251 using MGO compared to HFO.



252

253

Figure 9. BC emissions: (a) the main engine; (b) the auxiliary engine and the auxiliary boiler

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3.3. Effect of OC on EC and BC measurements

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It has been reported that EC emissions are commonly employed as a substitute for BC

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emissions to assess the ship's environmental impact [41]. However, there are some differences

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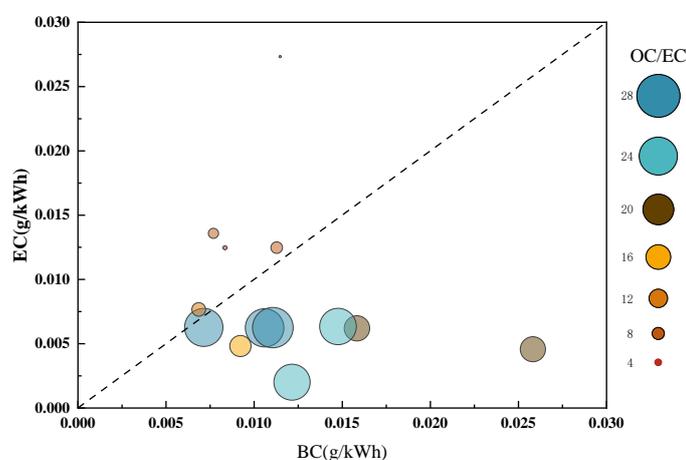
between the BC and the EC [42]. Additionally, OC will also have an impact on the measurement of

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BC, due to the BrC, which is a type of organic carbon that absorbs light. In this study, the relationship

259 between BC and EC exhibits a dynamic correction trend under different operating conditions. For
260 the main engine, the Pearson correlation coefficient of HFO is 0.3 (n=6), while that of MGO is 0.6
261 (n=5). In the case of the auxiliary engine, the Pearson correlation coefficient of the HFO is 0.1 (n=5),
262 lower than that of the main engine. However, due to insufficient data on auxiliary engines using
263 MGO, reliable correlation coefficients could not be obtained.

264 Due to the effect of BrC, there is a significant difference in BC emissions under the same EC
265 emissions, as shown in Figure 10. When the OC/EC ratio is bigger than 16, the BC/EC ratio is more
266 than 1. In contrast, the BC/EC ratio is less than 1 when the OC/EC ratio is smaller than 10. This is
267 because the AVL 415SE is a filter-based instrument, and is thus subject to the filter artifact which
268 would enhance the light absorption of BC and increase the reported BC value compared to the
269 instrument-average [43]. On the other hand, there is a large amount of tar BrC in OC, which is an
270 amorphous spherical carbon. It is composed of macromolecular substances predominantly
271 characterized by highly conjugated aromatic rings, such as polycyclic. The light absorption of BrC
272 in the short-wave range is significantly enhanced compared to small molecule organics, owing to
273 polyaromatic ring structure and a high degree of polymerization. In comparison to BC, BrC exhibits
274 higher Angstrom Absorption Exponent (AAE) values and a greater ratio of sp³ to sp² carbon bonds
275 [44].

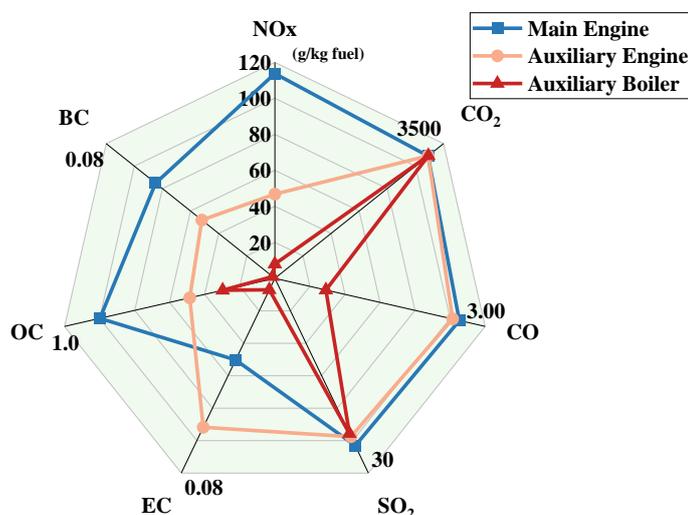


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277 **Figure 10. Relationship between emission factors of EC and BC with OC/EC ratios categorized by value.**

278 **3.4 Relationship between measured exhaust gases and particulate emissions**

279 The gaseous and particulate pollutant emissions based on fuel consumption at 50% load for
280 different diesel engines are shown in Figure 11. The emissions of CO₂, CO, and SO₂ remain
281 unaffected by the engine type, potentially due to their predominantly originating from the fuel in
282 the exhaust gas. In terms of NO_x emissions, the main engine exhibits the highest levels, followed
283 by the auxiliary engine, and then the auxiliary boiler. Thermal NO_x constitutes the primary
284 component of NO_x emissions from diesel engines, contributing up to 80%. The high NO_x emissions
285 of the main engine may be attributed to the elevated air coefficient and prolonged combustion
286 duration of two-stroke engines. The BC and OC show the same trend as the NO_x. Moreover, the
287 particulate pollutants emitted by diesel engines exhibit higher levels compared to those emitted by
288 auxiliary boilers. In addition, the main engine emits elevated levels of BC and OC in comparison to
289 the auxiliary engine, while demonstrating lower levels of EC.



290

291 **Figure 11. Gaseous and particulate pollutant emissions resulted from using HFO for different diesel engines**

292

at 50% load.

293

It is valuable to monitor the emissions of exhaust gases and conduct a comparative analysis

294

between their levels and the concentrations of particulate pollutants. However, due to space and cost

295

limitations, measuring all pollutants, particularly particulate pollutants, can be challenging. In

296

addition, gas pollutants are primarily detected using online methods that provide real-time emission

297

data, whereas offline methods are mostly used for detecting particulate pollutants. Therefore, the

298

relationship between different pollutants can be studied to predict the emission levels of related

299

pollutants, utilizing easily measurable pollutants as indicators. The major gas pollutants, including

300

CO, CO₂, NO, NO₂, and SO₂, are compared alongside the major particulate pollutants OC and EC.

301

The Pearson coefficient is used to determine the degree of correlation between the pollutant. The P-

302

value represents the probability of the correlation coefficient r being zero. A smaller p-value

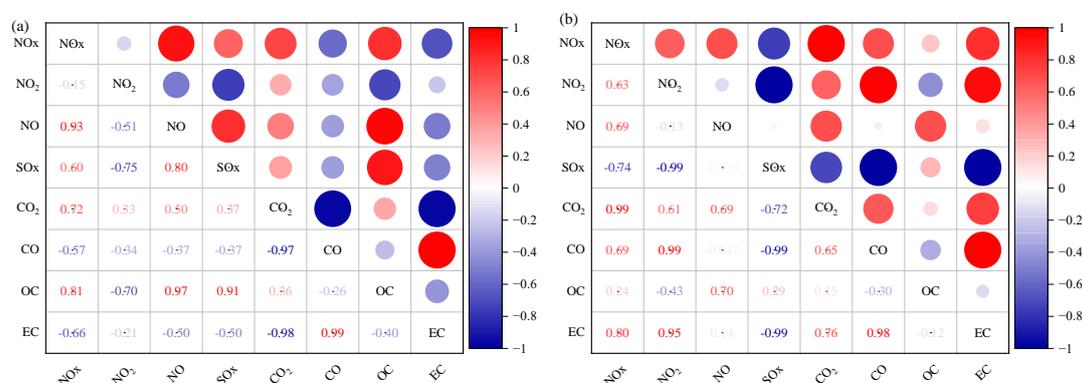
303

indicates a larger correlation coefficient r , indicating a stronger correlation [45].

304

The correlations between the gas pollutants and the particulate pollutants emitted by the main

305 engine and auxiliary engine are shown in Figure 12. Notably, there is a consistent trend in
 306 correlations for certain pollutants across both fuels. CO₂ exhibits a strong positive correlation with
 307 NO_x. And CO shows a strong positive correlation with EC. This is because both CO and EC are
 308 products of incomplete combustion. Since NO_x is mainly composed of NO, NO_x also has a
 309 significant positive correlation with NO.



310

311 **Figure 12 Correlations among gas and particulate pollutants: (a) main engine, (b)auxiliary engine**

312

313 4 Conclusions

314 In this study, the gaseous and particulate emissions originating from the main engine, auxiliary
 315 engine, and boiler of a Tier III ship powered by MGO and HFO have been investigated. The main
 316 conclusions are as follows:

317 (1) The type of fuels and engines significantly influenced pollutant emissions. Gaseous
 318 pollutants mainly consisted of CO₂ and NO_x, while OC accounted for the majority of particulate
 319 pollutants. For the main engine, the gaseous and particulate pollutants emitted by HFO were higher
 320 than those emitted by MGO, except for BC. Compared to MGO, utilizing HFO in the auxiliary

321 engine increased the emissions of OC and SO₂ but reduced the emissions of BC and EC. The
322 pollutants emitted from the boiler exhibited lower levels compared to those emitted by the engines,
323 except for CO, CO₂, and SO₂.

324 (2) When using HFO, OC emissions from both engines increased until reaching their peak at
325 75% load before declining. When using MGO, the SCR system effectively reduced OC and EC
326 emissions. Moreover, the PM emitted by the boiler was mainly composed of OC.

327 (3) The OC/EC ratio varied significantly among different sources. The OC/EC ratio of the main
328 engine exceeded 13, while that of the auxiliary engine ranged from 1.4 to 9. Both engines exhibited
329 higher OC/EC ratios when using HFO compared with MGO.

330 (4) The presence of light-absorbing organic carbon in OC led to a significant discrepancy
331 between the measured BC value and EC. An OC/EC ratio exceeding 16 yielded a BC/EC ratio
332 greater than 1, while a ratio below 10 resulted in a BC/EC ratio less than 1.

333 (5) The correlation of certain pollutants emitted by the main engine and auxiliary engine exhibited
334 consistent trends. CO₂ exhibits a strong positive correlation with NO_x. Moreover, CO shows a
335 positive correlation with EC.

336 The findings of this study can offer valuable data support for the effective regulation of gaseous
337 and particulate pollutant emissions from shipping, the further enhancement of marine fuel policies,
338 and a more precise evaluation of the environmental and climatic impacts resulting from ship
339 emissions within the context of climate change.

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