1 **Real-world emission characteristics of VOCs from typical cargo ships and their**

2 **potential contributions to SOA and O$_3$ under low-sulfur fuel policies**

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32   **Abstract**

33   Mandatory use of low-sulfur fuel according to global sulfur limit regulation has

34   reduced the emissions of SO_2 and PM significantly on ships, while it also leads to very

35   large uncertainty on volatile organic compounds (VOCs) emission. Therefore, on-board

36   test of VOCs from 9 typical cargo ships with low-sulfur fuels in China were carried out

37   in this study. Results showed that emission factor of VOCs (EF_{VOCs}) varied largely from

38   0.09 to 3.01 g kg^{-1} fuel, with domestic coastal cargo ships (CCSs) had the highest level,

39   followed by inland cargo ships (ICSs) and ocean-going vessels (OGVs). The switch of

40   fuels from heavy fuel oil (HFO) to diesel increased EF_{VOCs} by 48% on average, which

41   enhanced both O_3 and secondary organic aerosol (SOA) formation potentials, especially

42   for OGVs. Besides, the use of low-sulfur fuels for OGVs also lead to significant

43   increase of naphthalene emission. These indicated the implementation of globally ultra-

44   low-sulfur oil policy in the near future needs to be optimized. Moreover, aromatics were

45   the most important common contributors to O_3 and SOA in ship exhausts, which need

46   to be controlled with priority. It was also found that benzene, toluene, and ethylbenzene

47   ratio of 0.5:0.3:0.2 on average could be considered as a diagnostic characteristic to

48   distinguish ship emission from other emission sources.

49   **Keywords:** cargo ships, low-sulfur fuel, VOCs, ozone, secondary organic aerosol

50   **1. Introduction**

51   Maritime transport accounts for more than 80% of global trade by volume (United

52   Nations Conference on Trade and Development, 2020), leading to significant

53   environmental and health effects (Corbett et al., 2007;Liu et al., 2016;Wang et al.,

54   2021a). As a non-ignorable anthropogenic emission source of air pollutants, shipping

55   emission has caused more and more attentions in recent decades. However, most of the

56   previous studies focus on primary pollutants, such as SO_2, NO_x, CO_x, HC, particulate

57   matter (PM) and its components, particulate number (PN), etc. (Zhang et al.,

58 2022b;Santos et al., 2022;Zhou et al., 2019b;Chu-Van et al., 2017;Reda et al.,

59 2015;Buffaloe et al., 2014;Beecken et al., 2014;Moldanova et al., 2013;Fu et al.,

60 2013;Moldanova et al., 2009;Lack et al., 2009;Lack et al., 2008). Only few studies

61 estimate the influence of ship exhaust on secondary photochemical oxidation products,

62 such as O_3 and secondary organic aerosol (SOA), and concern their relative precursors

63 (Jonson et al., 2009;Song et al., 2010;Lang et al., 2017;Wu et al., 2019;Wang et al.,

64 2019;Wu et al., 2020). Results from these limited studies show that the ozone formation

65 potential (OFP) and secondary organic aerosol formation potential (SOAFP) of

66 shipping emissions are much greater than from on-road vehicles due to their higher

67 VOCs emission factors and normalized reactivities (Wu et al., 2019;Wu et al., 2020).

68 Therefore, the neglection of secondary pollutants such as O_3 and SOA would vastly

69 underestimate the actual influence of shipping emissions on environment air.

70 Volatile organic compounds (VOCs) are typical O_3 and SOA precursors. Generally

71 speaking, alkanes, alkenes, aromatics and carbonyls with carbon number > 6 in VOCs

72 can form SOA (Grosjean, 1992;Grosjean and Seinfeld, 1989). While O_3 is formed from

73 the photochemical interactions of volatile organic VOCs and oxides of nitrogen (NO_x),

74 with alkenes having the highest Maximum Incremental Reactivity (MIR), followed by

75 aromatics and OVOCs (Carter, 1994). Typical aromatics, alkenes, and alkanes are the

76 most concerned VOCs from diesel exhausts. For example, Previous studies find that

77 aromatics and alkanes contribute most to SOAFP from diesel exhaust, with single-ring

78 aromatics such as toluene, benzene and xylene et al. are the most contributors (Gentner

79 et al., 2012;Che et al., 2023). Wang et al. (2020) point out that naphthalene, butene,

80 toluene, benzene, and dodecane et al. are the most contributors to OFP from exhausts

81 of diesel trucks. Besides, OVOCs such as formaldehyde, acetaldehyde, and

82 benzaldehyde also have high ozone formation potentials (Yao et al., 2015;Wang et al.,

83 2020). Even though concentrations of $PM_{2.5}$ decreased rapidly in recent years, O_3

84 presented continuous upward trends in most of China (Lu et al., 2020). More and more

85 strict limitations of VOCs have been applied to the main sources such as industrial

86 emission, vehicle exhaust etc., while VOCs from shipping haven't gained much

87 attention. Most of previous studies just give the characteristics of total non-methane

88 hydrocarbons (NMHCs) from ships, but not specific VOC species (Cooper, 2003;Zhang

89 et al., 2016a). Only few studies have reported the VOCs emission factors (EFs) and

90 their composition from specific type of ships under specific operating conditions (Wu

91 et al., 2020;Wang et al., 2020;Wu et al., 2019;Xiao et al., 2018;Zetterdahl et al.,

92 2016;Huang et al., 2018b;Cooper et al., 1996). The limited measured VOCs data cannot

93 reflect the actual situation of shipping emissions. More on-board VOCs measurement

94 for typical ships with representative fuels under different operating conditions need to

95 be carried out, especially after the implementation of low-sulfur fuel policies.

96   According to the International Maritime Organization (IMO), the maximum fuel

97 sulfur content has been set to be 0.5% (m/m) worldwide by 2020, and 0.1% (m/m) in

98 emission control areas (ECAs). The Chinese government also has set the coastal ECAs

99 that require the sulfur content of 0.5% (m/m) since 2019, and 0.1% (m/m) in inland

100 ECAs since 2020 (Ministry of Transport of the People's Republic of China, 2018). The

101 use of ultra-low sulfur fuel (< 0.1% (m/m)) globally is an inevitable trend in the near

102 future. Fuel quality could affect the pollutants from ship exhausts significantly. For

103 example, a large amount of PM, SO_2 and NO_x have been reduced since the

104 implementation of ship emission control policies (Weng et al., 2022;Wang et al.,

105 2021b;Zhang et al., 2019;Viana et al., 2015;Repka et al., 2021). While it also reveals

106 that the switching of high-sulfur content fuels (sulfur content ≥0.5%) to low-sulfur

107 content fuels (0.1%< sulfur content <0.5%) leads to significant uncertainties of VOCs

108 emissions from the results of previous studies. For example, Wu et al. (2019) show that

109 the reduction in EF of VOCs (EF_{VOCs}) is 67% when switching from high-sulfur content

110 heavy fuel oil (HFO) to low-sulfur content marine diesel oil for a container ship. While

111 another study finds that after limiting fuel sulfur content, the EF_{VOCs} are approximately

112 15 times that of before implementation of the fuel switch policy (IFSP) from ships at

113 berth in Guangzhou, China. This leads to nearly 29 times greater OFP and

114   approximately 2 times greater SOAFP than those before IFSP (Wu et al., 2020). Huang

115   et al. (2018) also presented similar results of larger SOAFP when switch fuel from high-

116   sulfur content HFO to diesel oil for a large cargo vessel. It seems the low-sulfur fuel

117   regulation has different effects on VOCs emission for different types of ships. Therefore,

118   it is essential to figure out the actual emission of VOCs as well as formation potentials

119   of SOA and O_3 under the condition of low-sulfur fuel regulations. This will greatly

120   reduce the uncertainties in VOCs inventory estimation and provide basic data for the

121   formulation of optimal emission control policies of ships after considering

122   comprehensive impacts on various pollutants.

123   By the end of 2022, China had 121,900 water transport vessels (Ministry of

124   Transport of the People's Republic of China, 2022), 15 ports in China were listed among

125   the top 20 ports in the world for cargo throughput, and 7 container ports were listed

126   among the largest 10 container ports in the world. The large amount of active ships in

127   China has resulted in serious impact on ambient air and human health, particularly in

128   coastal, inland and port areas (Huang et al., 2022;Zhang et al., 2017;Liu et al., 2016).

129   Research reveals that most of the pollutants are from cargo-transport ships compared

130   with other types of ships (Wan et al., 2020). Clarifying the EF of VOCs, profiles,

131   influence factors, and their contribution to O_3 and SOA formation potentials of the

132   typical cargo ships are the basis to estimate the VOCs inventory and to establish proper

133   control measures. Besides, it is also a very important breakthrough point to further

134   improve the ambient air quality in port and nearshore areas by controlling the VOCs

135   emission from ship exhaust.

136   Therefore, on-board test of exhaust pollutants from 9 typical cargo ships in China,

137   including 2 coastal cargo ships (CCSs), 3 ocean-going vessels (OGVs) and 4 inland

138   cargo ships (ICSs) were carried out in this study. VOCs samples from different types of

139   engines with different fuels under actual operating conditions were collected and 106

140   VOC species were analyzed. Based on the data, the following factors were evaluated

141   and discussed in this study: (1) fuel-based emission factor of VOCs (EF_{VOCs}) and their

142 components, (2) influence factors, (3) profiles of VOCs, (4) O_3 and SOA formation

143 potentials.

2. Materials and methods

2.1 Test ships and fuels

146   VOCs samples from 9 different ships were collected in this study, including 2

147 coastal cargo ships, 3 ocean-going vessels, and 4 inland cargo ships in Yangtze River.

148 The detailed technical parameters of the sampling ships are shown in Table 1. Different

149 types of cargo ships had different technical parameters in China. For example, the

150 engine powers of coastal cargo ships varied largely, with about 57% are equipped with

151 engines of more than 500 kW. Of the other left coastal cargo ships, 17% of which are

152 ranging from 150 kW to 250 kW. Therefore, one large coastal cargo ship with main

153 engine power of 1470 kW and another small coastal cargo ship with main engine power

154 of 178 kW were selected here. Coastal cargo ships typically transport cargos among

155 different coastal ports, with one to several days per voyage. The main operating modes

156 are cruise (~75% engine load), maneuvering (low and variable engine loads), and idling.

157   Ocean-going vessels usually have large tonnages with large power main engines.

158 Statistical AIS data show that engines with power of 4 kW to 10 kW account for the

159 largest proportion (~25%) of the total OGVs in China, followed by 2 kW to 4 kW (~23%)

160 and 10 kW to 20 kW (~20%). Besides, newly built OGVs have a tendency to have larger

161 and larger engine powers. Hence, three ocean-going vessels with different engine

162 powers ranging from 13.5 kW to 15.7 kW were tested in this study. They are designed

163 for transporting goods across borders, usually with several months per voyage. The

164 main operating mode is cruise in the open ocean. While during the processes of in and

165 out of the port, the engines of OGVs typically active in maneuvering mode with relative

166 lower and variable engine loads, which could have great influence on the nearshore

167 environment due to higher emission levels of pollutants.

168   Most inland cargo vessels are generally equipped with high-speed small main

169 engines of power within 1000 kW (~70%). Among them, the vast majority are below

170   500 kw. Therefore, four typical inland cargo ships of engine power between 138 kW

171   and 300 kW were chosen in this study. The inland cargo vessels typically active among

172   different inland ports or coastal ports near inland rivers, with several hours to several

173   days per voyage. Affected by the complicated water conditions of inland rivers, cruise

174   and maneuvering are the most important operating modes for inland cargo ships.

175   In brief, the measured ships in this study could represent the typical cargo ships in

176   China to a certain extent. It's worth noting that the ocean-going vessels were newly

177   constructed ships, while the inland cargo ships had older engines (6 to14 years)

178   compared with other types of ships (less than 10 years).

179   Besides, most large cargo ships are equipped with both main engine and auxiliary

180   engine. The main engine provides navigation power, and the engine loads vary greatly

181   with the different operating modes. While the auxiliary engine mainly provides

182   domestic electricity or heating on board, and the engine load is relatively stable with

183   about 75% load. Small cargo ships are equipped only with main engines, such as the

184   tested inland cargo ships and small coastal cargo ships in this study.

185

186

Table 1 Technical parameters of the sampling ships

Ship ID	Type	Tonnage (kt)	Main engine	Auxiliary engine	Ship age (year)	Implementation standard of fuel
CCS1	Coastal cargo ship	9.17	4-stroke, 1470 kW, 850 rpm	4-stroke, 182 kW, 1500 rpm	3	S<0.5% (m/m)
CCS2	Coastal cargo ship	0.30	4-stroke, 178 kW, 1500 rpm	-	10	S<0.5% (m/m)
OGV1	Ocean-going vessel	180	2-stroke, 15748 kW, 75 rpm	4-stroke, 1280 kW, 900 rpm	0	S<0.5% (m/m)
OGV2	Ocean-going vessel	110	2-stroke, 13500 kW, 91.1 rpm	4-stroke, 900 kW, 900 rpm	0	S<0.5% (m/m)
OGV3	Ocean-going vessel	210	2-stroke, 15745 kW, 75rpm	4-stroke, 1180 kW, 900 rpm	0	S<0.5% (m/m)
ICS1	Inland cargo ship	0.90	4-stroke, 255 kW, 1000 rpm	-	14	S<0.1% (m/m)
ICS2	Inland cargo ship	0.98	4-stroke, 300 kW, 1000 rpm	-	12	S<0.1% (m/m)
ICS3	Inland cargo ship	0.80	4-stroke, 145 kW, 1000 rpm	-	6	S<0.1% (m/m)
ICS4	Inland cargo ship	0.39	4-stroke, 138 kW, 1500 rpm	-	10	S<0.1% (m/m)

187

188   Characteristics of HFO and diesel oil used for the test ships in this study are shown

189   in Table S1. In order to meet the requirements of diesel engines of non-road mobile

190   machinery of China, regular diesel (0#) was used for all inland cargo ships here. Results

191   showed that the sulfur contents of all the fuels were no more than 0.5% (m/m), which

192   were within both current ship emission control standards of China and IMO. As typical

193   tracers of high-sulfur content HFO, nickel and vanadium content levels and their ratios

194   were still higher but not distinguishable enough in low-sulfur content HFO compared

195   with diesel oil, which further evidence that it needed to be cautious when they were

196   used as tracers of ship emissions under current low-sulfur regulation. While it should

197   be noted that much higher levels of calcium and zinc were detected in lubricating oils

198   of OGVs.

199   **2.2 Sampling system and samples**

200   A portable dilution sampling system was used in this campaign, whose

201   components and principles were described elsewhere (Zhang et al., 2018). Briefly, two

202   separate sampling pipes were placed into the exhaust stacks (about 1.5 m deep of the

203   exhaust outlet) to route emissions from the main engine and auxiliary engine to

204   sampling system on the highest deck of ship, respectively. Then, the probe of a flue gas

205   analyzer (Testo 350, testo, Germany) was placed into the sampling pipe to test the

206   gaseous matters directly to get online data (CO_2, O_2, CO, NO, NO_2, SO_2). Another

207   probe was used to extract the flue gas for the diluted system. The dilution ratios ranged

208   between 1-10 in this study. VOCs samples were collected by summa canister from both

209   main engines and auxiliary engines of all the ships listed in Table 1. The sampling time

210   was 20-30 minutes for each sample according to actual operating condition.

211   A total of 48 VOCs samples were obtained for the test ships, involving different

212   engine types with different fuels under different operating modes (seen Table S2 for

213   detailed information). For the coastal/inland cargo ships, all samples were collected

214   based on actual operating modes (about one to several days from one trip). While for

215   ocean going vessels, samples from much more operating modes could be obtained

216   thanks to the testing of the newly constructed ships (about one week from one trip).

217   **2.3 Chemical and data analysis**

218   As shown in Table S3, a total of 106 volatile organic compounds were detected in

219   this study according to USEPA TO15-1999, including 11 oxygenated volatile organic

220   compounds (OVOCs), 17 aromatics, 29 alkanes, 11 alkenes, 35 halohydrocarbons and

221   4 other species. These measured VOCs species were typical concerned VOCs and could

222   be considered as main VOC components referring to relative studies (Huang et al.

223   2018;Wu et al. 2020;Araizaga, Mancilla and Mendoza 2013), and could reflect the

224   emission conditions of ship exhaust. As shown in formulas (1) and (2), carbon balance

225   method was used to calculate the EF_{VOCs}, which was also introduced in our previous

226   study (Zhang et al., 2016a).

227   $$EF_x = \frac{\triangle X}{\triangle CO_2} \cdot \frac{M_X}{M_{CO_2}} \cdot EF_{CO_2} \tag{1}$$

228   where EF_x is the EF for VOC species X (g/kg fuel), $\triangle X$ and $\triangle CO_2$ represent

229   the concentrations of X and CO_2 with the background concentrations subtracted (mol

230   m^{-3}), M_X represents the molecular weight of species X (g mol^{-1}), M_{CO_2} is the

231   molecular weight of CO_2 (44 g mol^{-1}), and EF_{CO_2} is the EF for CO_2 (g (kg fuel)$^{-1}$).

232   $$EF_{CO_2} = \frac{C_F}{c(C_{CO}) + c(C_{CO_2}) + c(C_{PM}) + c(C_{HC})} \cdot c^*(CO_2) \cdot M_{CO_2} \tag{2}$$

233   where C_F represents the mass of carbon in 1 kg diesel fuel (g C (kg fuel)$^{-1}$), $c(C_{CO})$,

234   $c(C_{CO_2})$, $c(C_{PM})$, and $c(C_{HC})$ represent the mass concentrations of carbon as CO,

235   CO_2, PM, and HC (g C m^{-3}), respectively, in the flue gas, and $c^*(CO_2)$ is the molar

236   concentration of CO_2 (mol m^{-3}).

237   Detailed calculation processes of normalized ozone reactivity (R_{O_3}, g O_3 g^{-1}

238   VOCs), OFP (g O_3 kg^{-1} fuel), normalized secondary organic aerosols reactivity (R_{SOA},

239   mg SOA g^{-1} VOCs) and SOA formation potential (SOAFP, mg SOA kg^{-1} fuel) are given

240   as follows:

241   Normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs) and OFP (g O_3 kg^{-1} fuel) were

242   calculated using the maximum incremental reactivity (MIR) coefficient method (Carter,

243   2010a), which represents the maximum contribution of VOC species to the near-surface

244   O_3 concentration under optimal conditions. The equations are as follows:

245        $R_{O_3} = \sum_i(\omega_i \times \mathrm{MIR}_i)$ (3)

246   where ω_i is the mass percentage of the total VOC emissions for species i, MIR_i

247   is the MIR coefficient for VOC species i, which was referenced from Carter (2010b),

248   seen in Table S3 for details.

249        $OFP = \sum_i(MIR_i \times [VOC]_i)$ (4)

250   where OFP is the ozone formation potential (g kg^{-1} fuel), $[VOC]_i$ is the emission

251   factor for VOC species i (g kg^{-1} fuel).

252   The same as O_3, normalized secondary organic aerosols reactivity (R$_{SOA}$, mg SOA

253   g^{-1} VOCs) and SOA formation potential (SOAFP, mg SOA kg^{-1} fuel) were also

254   calculated, whose equations are as follows:

255        $R_{SOA} = \sum_i(\omega_i \times Y_i)$ (5)

256        $SOAFP = \sum_i(EF_i \times Y_i)$ (6)

257   where Y_i is the SOA yield for VOC species i (seen in Table S4 for details). Both

258   SOAFP of VOCs under high-NO$_x$ and low-NO$_x$ conditions were calculated.

259   **2.4 Quality assurance and quality control**

260   Rigorous quality assurance and quality controls were conducted during the whole

261   experiment. Ambient air blanks were analyzed in the same way as mentioned above to

262   determine background concentration. The VOCs concentrations of each sample were

263   obtained by subtracted ambient air blank results. Duplicate samples as well as standard

264   gas were examined after analyzing a batch of 10 samples to ensure that the error was

265   within 5%.

266   **3. Results and discussion**

267   **3.1 Emission factors and components of VOCs**

268   EF$_{VOCs}$ for the test ships are shown in Fig.1 and Table S5. In order to calculate the

269   EF$_{VOCs}$ and investigate their influence factors, EFs of other gaseous pollutants such as

270   CO_2, CO, NO, NO_2 were also given and discussed briefly. For CO_2, the emission factors

271   ranged from 2622 to 3185 g kg^{-1} fuel that influenced by both fuel type and operating

272   mode. CO showed opposite trend with CO_2, varying from 0.62 to 180 g kg^{-1} fuel,

273   reflecting the condition of combustion efficiency. The EF_{NO_x} ranged from 6.26 to 92.8

274   g kg^{-1} fuel, with 60% to 99% of whom were NO, which inferred the condition of

275   combustion temperature in cylinder.

276   Results showed that the EF_{VOCs} for all the test ships presented wide differences,

277   which were ranging from 0.09 to 3.01 g kg^{-1} fuel. Ship type, engine type, operating

278   mode and fuel type could influence the EF_{VOCs} that would be discussed in more detail

279   in Section 3.2. Briefly, higher VOCs had been observed both in low-load and high-load

280   operating modes such as maneuvering and idling, while in medium-load operating

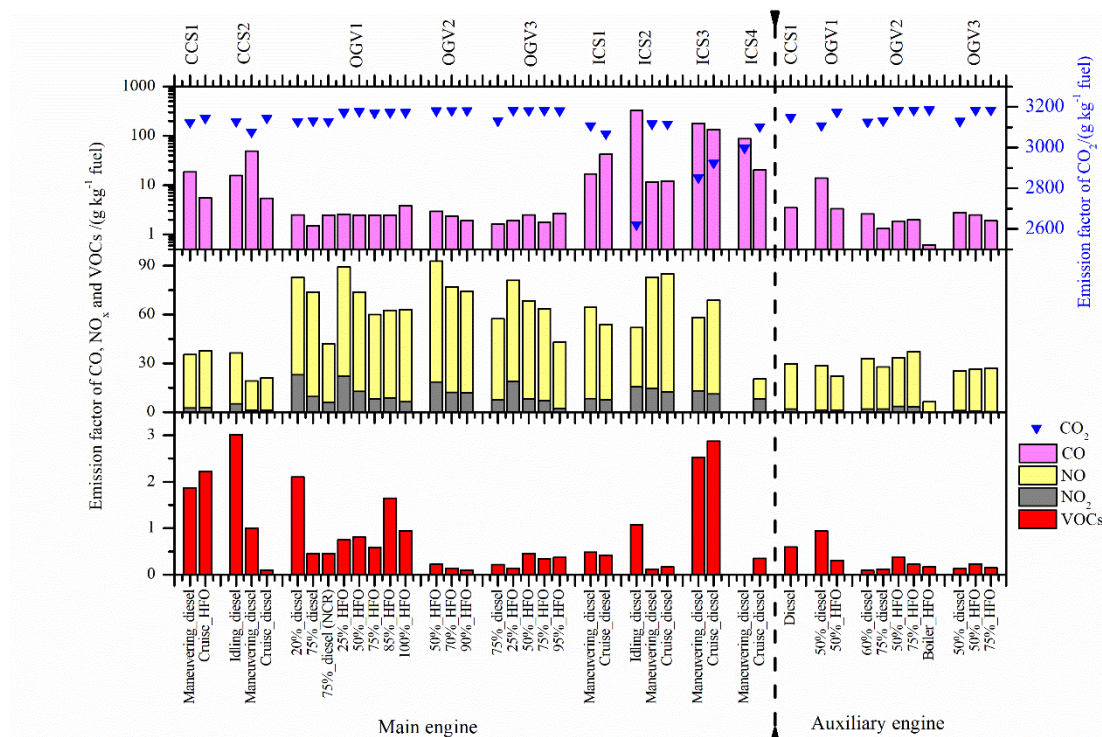
281   modes, the EF_{VOCs} presented lower levels (detailed result was also shown in Fig. 3 (a)).

282   Main engines presented obviously higher EFs levels than auxiliary engines (Fig. 3 (c)

283   for details). And CCSs and ICSs had relatively higher EFs compared with OGVs (Fig.

284   3 (d) for details). It was worth noting that when the fuels were switched from HFO to

285   marine diesel oil for OGVs, increasing trends were presented for EF_{VOCs} in this study.

286   While the CCSs showed the opposite trend with a slight decrease for EF_{VOCs}.

287

288   Figure 1 Emission factors of gaseous pollutants under all operating conditions for the

289   test ships

290   Average EF_{VOCs} emitted from ships in this study were also compared with those

291   reported in other studies (Table 2). Altogether, the measured EF_{VOCs} varied largely from

292   0.02 to 23.7 g kg^{-1} fuel for all the test ships. Complex factors could lead to the large

293   uncertainty, such as the different detected VOC species in different studies, different

294   engine types and fuel qualities. This also indicated that the uncertainty should be

295   noticed when EF_{VOCs} were used as basic data to calculate emission inventory or estimate

296   other environmental influence. The test ships in this study presented comparable EF_{VOCs}

297   level with other studies. It seemed that OGVs with large engines typically showed lower

298   EF_{VOCs} levels no matter what types of fuels were used compared with river ships and

299   costal ships. Moreover, compared with on-road vehicles with diesel fuel (Zhou et al.,

300   2019a), VOCs emitted from non-road engines, such as ship, agricultural machinery and

301   construction machinery, had much higher levels (Huang et al., 2018a;Hua et al.,

302   2019;Zhou et al., 2022), which should be paid more attention, especially in the case of

303   more and more strict limitations of VOCs have been applied to on-road vehicles.

Table 2 EFs of VOCs from ships in this study and previous studies

Ship type	Sulfur content (%)	Operating mode	EF of VOCs (g kg^{-1} fuel)	Number of detected VOCs species	Data sources
Coastal cargo ship / Ocean going vessel					
CCS (main-HFO)	0.39	Cruise	2.24	106	This study
CCS (main-diesel)	<0.05	Actual operating conditions	1.59	106	This study
CCS (auxiliary-diesel)	<0.05	Actual operating conditions	0.60	106	This study
OGV (main-HFO)	0.43-0.50	Actual operating conditions	0.52	106	This study
OGV (main-diesel)	<0.05	Actual operating conditions	0.82	106	This study
OGV (auxiliary-HFO)	0.43-0.50	Actual operating conditions	0.25	106	This study
OGV (auxiliary-diesel)	<0.05	Actual operating conditions	0.33	106	This study
Coastal cargo ship (high sulfur oil)	>0.5	At berth	0.12	68	(Wu et al., 2020)
Coastal cargo ship (low sulfur oil)	<0.5	At berth	1.81	68	(Wu et al., 2020)
Ocean going vessel (HFO)	2.07	Actual operating conditions	0.48 [a]	57	(Wu et al., 2019)
Ocean going vessel (diesel)	0.12	Actual operating conditions	0.06-0.18 [a]	57	(Wu et al., 2019)
Bulk carrier (HFO)	1.12	Actual operating conditions (main engine)	0.019-0.133	86	(Huang et al., 2018b)
Bulk carrier (diesel)	<0.5	At berth (main engine)/auxiliary engine	0.25-0.72	86	(Huang et al., 2018b)
Container ship	1.6-2.9	At berth	0.09-0.17	57	(Huang et al., 2017)
Passenger ferry α	0.08	At berth	0.57-0.99	-	(Cooper, 2003)
Passenger ferry β-1	0.53	At berth	0.29-0.57	-	(Cooper, 2003)
Passenger ferry β-2	0.09	At berth	1.71	-	(Cooper, 2003)
Passenger ferry γ	1.20	At berth	0.87-1.14	-	(Cooper, 2003)
Car/truck carrier	0.23	At berth	0.89-1.08	-	(Cooper, 2003)
Container/ro-ro	2.20	At berth	0.79-0.88	-	(Cooper, 2003)
Chemical tanker	0.06	At berth	1.36-1.40	-	(Cooper, 2003)
Passenger ferry (gas oil)	0.06	Actual operating conditions	0.875[b]	-	(Cooper et al., 1996)
Passenger ferry (fuel oil)	0.48	Actual operating conditions	0.135[b]	-	(Cooper et al., 1996)
River ship					
Inland cargo ship (diesel)	<0.05	Actual operating conditions	0.94	106	This study
River vessels	<0.5	At berth	3.36	68	(Wu et al., 2020)

River cargo ships	<0.5	Actual operating conditions	1.46	121	(Wang et al., 2020)
River speedboat	<0.5	Actual operating conditions	0.44	121	(Wang et al., 2020)
Engineering vessel	0.08	Actual operating conditions	23.7	-	(Zhang et al., 2016a)
Research vessel α	0.05	Actual operating conditions	1.24	-	(Zhang et al., 2016a)
Research vessel β	0.13	Actual operating conditions	4.18	-	(Zhang et al., 2016a)

305   a, the EFs values were estimated based on Fig.2. b, the EFs were calculated by assuming that the fuel consumption rate for the test ships was 200 g fuel kWh^{-1}

306

307   Components and mass fractions of VOCs from the test ships are shown in Fig. 2

308   and Fig. S1. OVOCs and aromatics were the main components of the detected VOC

309   species, accounting for 9.38% - 88.0% and 5.38% - 74.0% of total VOCs, respectively.

310   Alkanes also accounted for non-ignorable fractions, which were ranging from 0.2% to

311   57.2%. While alkenes, halohydrocarbons and other quantified species only contributed

312   small fractions of the total VOCs. The results in this study were consistent with that of

313   Huang et al. (2018) about a large ocean-going bulk carrier, but showed different VOCs

314   components with that of Wu et al. (2019) for a coastal container ship and Wu et al.

315   (2020) for auxiliary engines at berth. The different detected VOCs species in different

316   studies played an important role for the differences, while the fuel type and its chemical

317   composition might also have considerable impacts.

318   The main VOCs components of OVOCs, aromatics, alkanes and alkenes presented

319   different variation patterns under different operating modes, fuel types, and engine

320   types due to their different formation mechanisms (Fig. 2). For example, OVOCs from

321   diesel engines are typically from the oxidation of small molecular weight yet

322   uncomplete combustion hydrocarbons (Hao et al., 2014;Pan, 2008), therefore,

323   operating mode and engine type could influence the EF levels obviously, but not fuel

324   type. The direct emission of unburned fuel components and pyrosynthesis (formation

325   of aromatics by regeneration of fragmented radical species) are the two main formation

326   processes of PAHs (Radischat et al., 2015). EFs of aromatics showed relatively higher

327   levels in medium operating modes compared with other modes in this study. One main

328   reason was that the higher temperature in medium operating modes promoted the

329   polymerization, resulting in the processes of dehydrogenation and PAH formation

330   (Zhang et al., 2021), which exceeded the direct emission of unburned fuel components

331   (Radischat et al., 2015). Alkanes are mainly from the incomplete combustion of fuels,

332   therefore, alkanes from diesel fuel presented higher EFs than HFO because of the higher

333   aliphatic compounds in diesel fuel (Liu et al., 2022;Sippula et al., 2014). While alkenes

334   emitted from diesel engine are always related to the pyrolysis process of the fuel

combustion in the cylinder (Alotaibi et al., 2018;Zhang et al., 2022a). As a result, in high operating modes of more than 90% engine loads, it had higher EF$_{alkenes}$ levels in this study due to the pyrolysis process under higher temperature and incomplete combustion because of the less air to fuel ratios in the cylinder.

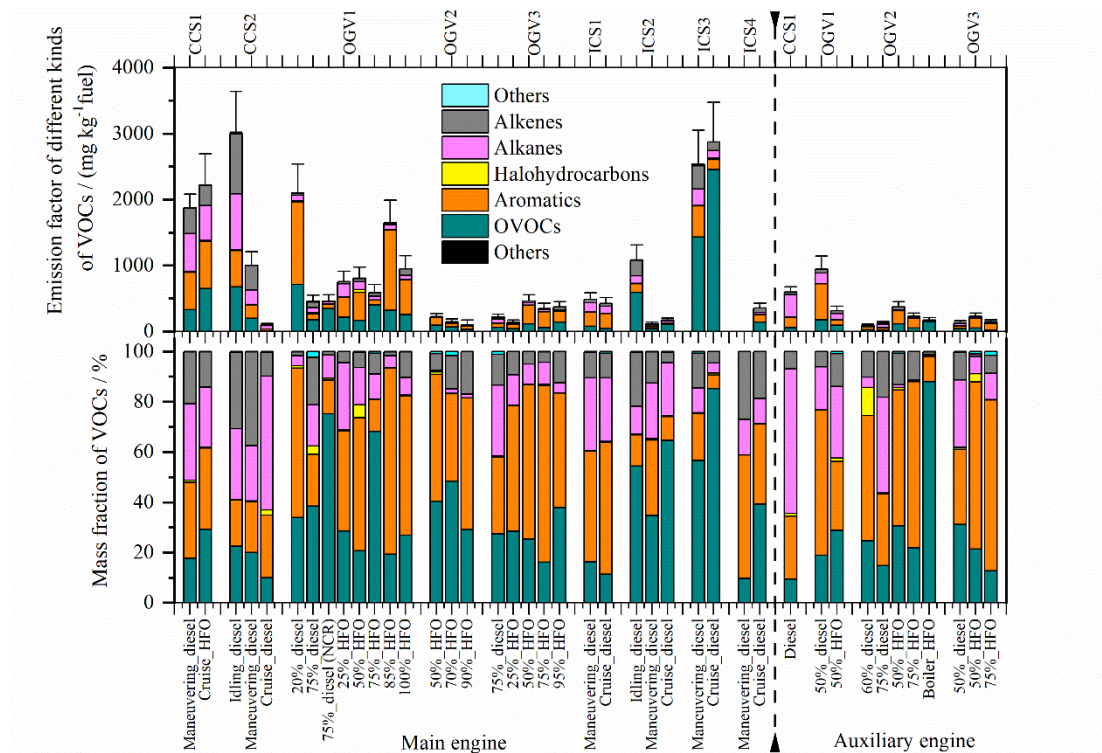



Figure 2 EFs of VOC components and their mass fractions

3.2 Influence factor analysis

It was mentioned above that influence factors such as operating condition, engine type, ship type and fuel type could affect the emission level and component of VOCs from ship exhaust. Box-whisker plots of VOC emission factors under these different drivers are presented in Fig. 3. As shown in Fig. 3 (a), engine load could affect the VOCs emission significantly. EF$_{VOCs}$ had the lowest level when the engines were operating in medium loads, and the highest in low loads. This was consistent with the results of VOCs emission reported by previous studies such as Huang et al. (2018), Wu et al. (2019) and Radischat et al. (2015), which were also shown in Fig. S2. The combustion condition in the cylinder could be responsible for the variation of VOCs emission, which meant incomplete combustion was one principal reason for the high

352 VOCs emission.

353   Engine type is also one significant influence factor of VOCs emission. The engines

354 were classified into three types in this study according to their engine speed, including

355 low-speed engines (LSE, rated speed < 100 rpm), medium-speed engines (MSE, 100

356 rpm ≤ rated speed < 1000 rpm) and high-speed engines (HSE, rated speed ≥ 1000 rpm).

357 It could be seen from Fig. 3 (b) that with the increase of engine speed, the EF_{VOCs}

358 showed an increasing trend. This could be explained by that compared with HSEs, LSEs

359 with high engine power usually had higher combustion efficiencies that led to lower

360 levels of VOCs emission (Zhang et al., 2018).

361   The EF_{VOCs} between main engines and auxiliary engines also varied obviously.

362 The average EF_{VOCs} from the main engines was 2.3 times that of auxiliary engines in

363 this study (seen in Fig. 3 (c)). Similar result was also reported by Liu et al. (2022) about

364 the intermediate volatile organic compounds (IVOCs) emission for the same test OGVs.

365 Even though the auxiliary engines were mainly high-speed or medium-speed engines

366 that had higher VOCs emissions mentioned above. Owing to the much lower VOCs

367 emission in medium loads that the auxiliary engines have been using, it could be

368 inferred that the impact of operating condition exceeded that of the engine type to VOCs

369 emission.

370   As seen in Fig. 3 (d), the EF_{VOCs} varied obviously under different types of ships,

371 with CCSs having the highest levels and OGVs the lowest. This could be explained by

372 the combined influence of operating condition and engine type as mentioned above.

373 Firstly, as shown in Fig. 3 (b), high-speed and medium-speed engines were equipped

374 for the CCSs, they could lead to higher EFVOCs compared with low-speed engines that

375 equipped for OGVs. Besides, the unstable operating conditions of SSCs and ICSs, such

376 as maneuvering and low-load, also promoted the emission of VOCs (Radischat et al.,

377 2015). Therefore, it could be indicated that coastal areas with high population density

378 need get more attention due to the higher VOCs emissions from CCSs and ICSs.

379   As mentioned before, fuel type could influence the EF_{VOCs} significantly (Wu et al.,

380 2019;Wu et al., 2020), which also would be one of the most important influence factors

381 in the future under the background of increasingly strict ship oil policy. Under the

382 condition of low-sulfur content fuels in China, the average EF_{VOCs} were 592 mg kg^{-1}

383 fuel and 878 mg kg^{-1} fuel for diesel and HFO in this study, respectively (seen in Fig. 3

384 (e)). In addition to the direct emission of unburned fuel components, VOCs also could

385 be emitted from the pyrosynthesis process of the fuel in the cylinder (Radischat et al.,

386 2015). In order to explore the relationship between chemical composition of low-sulfur

387 content fuel and VOCs emission, n-alkanes, b-alkanes and aromatics in the fuels from

388 OGVs were tested (Liu et al., 2022) (seen in Table S6 for details). Obviously, diesel had

389 higher content of n-alkanes and b-alkanes than HFO, and aromatics were the opposite.

390 It could be seen from Fig. S3 that both the $EF_{Alkanes}$, $EF_{Alkenes}$ and $EF_{halohydrocarbons}$ from

391 ships with diesel presented higher levels compared with that of HFO. $EF_{Aromatics}$ and

392 other components showed the opposite trends. While no obvious difference of EF_{OVOCs}

393 was observed between diesel and HFO. Emission characteristics of VOC main

394 components were basically consistent with fuel composition in this study. It could be

395 provided that the composition of fuel did have significant impact on VOC emissions.

396   To further explore the impact of sulfur content of fuel on VOCs emissions, EF_{VOCs}

397 of low-sulfur content fuel (<0.5% m/m) and high-sulfur content fuel (≥0.5% m/m) in

398 this study and previous studies were summarized in Fig. 3 (f). The average EF_{VOCs} from

399 low-sulfur content fuel was significantly higher than that of high-sulfur content fuel,

400 with almost 3.4 times. This indicated that when the fuels were switched from high sulfur

401 to low sulfur, there was dramatic increase in VOCs emissions. Low-sulfur content fuels

402 are usually produced in three ways, including blending technique that use light low-

403 sulfur oils mixed with heavy high-sulfur oils, heavy oil hydrogenation technology that

404 remove sulfur through hydrogenation of high-sulfur residual oil, and biological

405 desulfurization technology that use microbial enzymes catalyze and oxidate the organic

406 sulfur in oil, convert it into water-soluble sulfide and then remove (Kuimov et al., 2016).

407 Among these, blended low-sulfur oils are the most widely used oils (Zhang, 2019;Han

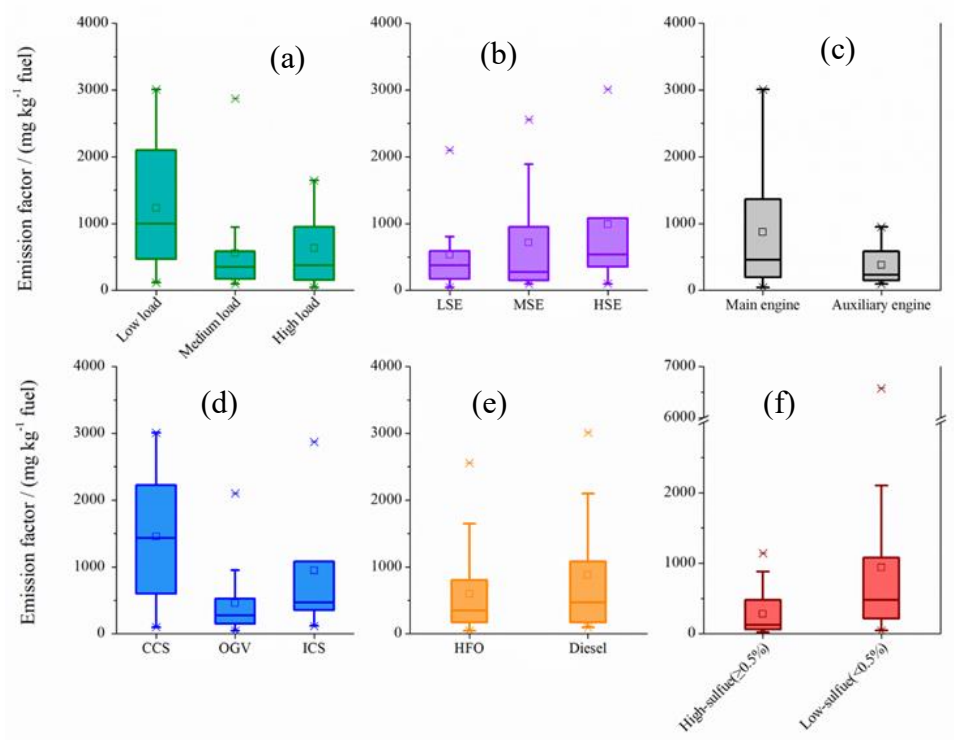
408 et al., 2022). Except for light low-sulfur oils mixed during the production of low-sulfur

409 oils, other non-petroleum refined oils, such as coal tar and chemical waste are also

410 added. Consequently, emission factors as well as the composition of VOCs have

411 changed significantly. Since low-sulfur content fuels (<0.5% m/m) have been using

412 worldwide since 2020, and 0.1% (m/m) in ECAs since 2015, it would imply that the

413 impact of fuel type on VOCs emissions needed to be given sufficient attention.

414

415 Figure 3 Box-whisker plots of VOC emission factors under different influence factors

416 **3.3 Profiles and diagnostic characteristics of VOCs**

417 3.3.1 Profiles of VOCs

418 Fig. 4 presents the mass fractions of VOCs (except halohydrocarbons,

419 tetrahydrofuran, carbon disulfide, and 1,4-dioxaneand due to their very small mass

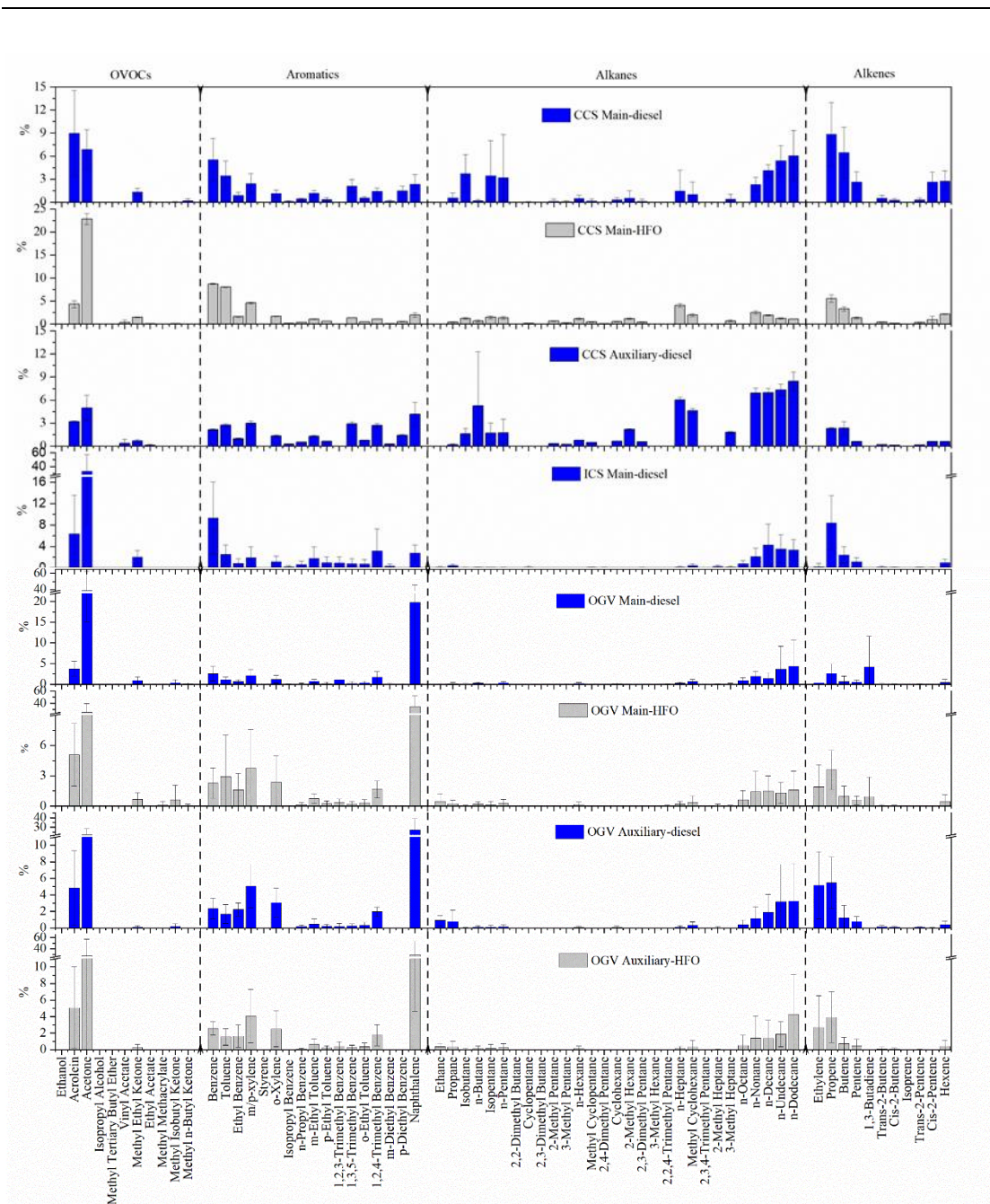
420 fractions (0.55%-3.06% of total VOCs)) from the three types of test ships (CCS, OGV

421 and ICS) under different engine types (main engine and auxiliary engine) and fuels

422 (HFO and diesel). Detailed mass fractions of all the test VOC species in this study were

423 also given in Table S7. As shown in Fig. 4, the profiles of VOCs showed obvious

424 differences. To be specific, the most abundant VOC species were acetone and acrolein

in OVOCs, propene and butene in alkenes, n-Nonane, n-Decane, n-Undecane, n-Dodecane in alkanes for almost all the test ships. As for aromatics, the OGVs showed big differences compared with other types of ships that had large amounts of naphthalene, while benzene, toluene and m/p-xylene were the highest content aromatic substances for other ships. Previous studies about OGVs showed the similar high naphthalene and acetone contents in the exhaust when use low-sulfur fuels (Agrawal et al., 2010;Huang et al., 2018b). Besides, high levels of formaldehyde and acetaldehyde were also found in exhausts from OGVs (Agrawal et al., 2010). Unfortunately, because of the limitation of testing methods, they were not measured in this study. Due to the high reactivity and the important role in formation of secondary organic aerosols, formaldehyde and acetaldehyde needs to get more attention from ship exhausts, especially for OGVs. In addition, a small scientific research ship (499 t, 5 years, high-speed engine, 0# diesel (0#)) was also tested in this study, whose VOCs profile was given in Fig. S4 for comparison. Obviously, the VOCs profile pattern was very similar with that of inland cargo ships with the same small high-speed engines and 0# diesel (0#) as fuel, indicating the significant impact of engine type and fuel type.

441

442 Figure 4 Mass fractions of individual VOCs from test ships under different engine types

443 and fuels (except halohydrocarbons, tetrahydrofuran, carbon disulfide, and 1,4-

444 dioxaneand due to their very small mass fractions)

445   The top 25 VOC species from the test cargo ships are presented in Table S8. It

446 could be seen that most of the top 25 VOC species emitted from exhausts were the same

447 but with different rankings for different engine types under different fuels. For example,

448 OVOCs, alkenes and aromatics were the most abundant VOC species for the main

449 engines of CCS and ICS, while alkanes were ranked as the highest content VOC species

450   for auxiliary engine. As mentioned above, naphthalene and acetone were the absolute

451   highest two VOC species for OGVs, followed by alkenes, OVOCs and aromatics from

452   exhausts of HFO fuel; but alkenes, OVOCs and alkanes from exhausts of diesel fuels.

453   This high naphthalene emission has also been shown in other studies (Radischat et al.,

454   2015;Huang et al., 2018c;Yeh et al., 2023). The unusually high naphthalene from OGVs

455   needed to be noted. Naphthalene was mainly formed during the pyrolyzation from

456   incomplete combustion and direct emission of unburned fuel components (Radischat et

457   al., 2015). A recent study reported that the addition of additives of naphthalene-based

458   lubricants to low-sulfur fuel during the blended fuel manufacturing process to improve

459   stability could lead to an increase in PAHs emission in exhaust, with naphthalene being

460   the main pollutant (Yeh et al., 2023). To further explore the extent to which the content

461   of naphthalene in fuel affects EFs of naphthalene in ship exhaust, several chemical

462   compositions such as alkanes and aromatic contents in fuels of the test OGVs were

463   measured and shown by Liu et al. (2022) (Seen in Table S6). Results showed that the

464   average naphthalene content in HFO was almost 30 times higher than that in diesel.

465   When the engine was operated in the same operating condition, higher $EF_{naphthalene}$ was

466   observed from HFO than diesel. Therefore, we infer that chemical component in fuel

467   does influence the emission of PAHs including naphthalene in the exhaust. Besides,

468   VOCs with lower molecular weights such as acetone and acrolein were the dominant

469   OVOCs compounds in this study. The main reason is probably as follows: OVOCs

470   compounds are typically derived from the oxidation of VOCs with incomplete

471   combustion (Hao et al., 2014), while VOCs with lower molecular weights have a higher

472   chance to be oxidized to form oxides than those with higher molecular weights which

473   are often broken up to VOCs with less carbon number during the oxidation process

474   (Wang et al., 2020).

475   Furthermore, characteristics of VOCs based on carbon number are also given and

476   discussed in this study. The detected VOC species were classified into 12 groupings,

477   from C1 to C12 (Fig. S5). Different types of ships with different fuels showed obvious

478 differences in components. For example, C3 VOCs were found to be the most important

479 species for all test ships, while C10 showed much higher mass fractions from OGVs

480 than other ships, which was caused by the high naphthalene content. The same as VOCs

481 profiles, ICSs and scientific research ships presented very similar VOCs mass fraction

482 distributions of the 12 groupings. Besides, except for the auxiliary engine of CCS with

483 diesel oil, the OGVs emitted comparatively higher high-carbon number (C7-C12)

484 components than low-carbon number (C1-C6) components.

485 3.3.2 Diagnostic characteristics of VOCs

486 Diagnostic ratios of pair species, such as toluene to benzene (T/B), ethylbenzene

487 to m,p-zylene (E/X), n-butane to isopentane (n-Bu/i-Bu) and isopentane to n-pentane

488 (i-P/n-P), are always used to identify potential emission sources (Zhang et al., 2016b;Li

489 et al., 2021;Song et al., 2018;Song et al., 2020). These ratios from ship exhausts in this

490 study are shown in Table S9. T/B was further analyzed here as it is the most wildly used

491 diagnostic ratio among them. It was reported in previous study that the T/B ratios were

492 <1 for biomass/biofuel/coal burning, 1 to 10 for vehicle emissions, and >1 for solvent

493 applications or industrial processes (Zhang et al., 2016b). In this study, the T/B ratios

494 varied between 0.29 and 1.28 from ship exhausts, which were overlapped with

495 biomass/biofuel/coal burning sources to some extent. However, it could be considered

496 to distinguish on-road diesel vehicles with a T/B ratio of 1.5 ± 0.8 (Wang et al.,

497 2013;Yao et al., 2015) and non-road diesel construction vessels with a T/B ratio of 1.4

498 ± 1.3. The results were similar with that of 0.45 - 0.57 from Wu et al. (2020) and 1.07

499 from Xiao et al. (2018), but significantly differed from that of 4.81 - 42.8 from Huang

500 et al.(2018c).

501 In order to overcome the overlapping effects of the T/B ratio among different

502 emission sources and better distinguish ship emissions from other emission sources, a

503 ternary diagram of the relative compositions of Benzene, Toluene, and Ethylbenzene

504 from ship exhausts in this study was presented in Fig. 5. The B:T:E ratios were

505 0.50:0.30:0.20 on average from the test ships, differed from that of 0.69:0.27:0.04 for

biomass /biofuel/coal burning, 0.06:0.59:0.35 for industrial emissions, and especially 0.31:0.59:0.10 for traffic emissions, respectively (Zhang et al., 2016b). Besides, most of the relative compositions of B, T, and E from ship exhausts in this study were relatively stable and mainly concentrated within certain area that was seldom overlapped with other emission sources in the ternary diagram. This indicated that the B: T: E ratios could be considered as a diagnostic characteristic to distinguish ship emission from other emission sources, especially the traffic emissions.

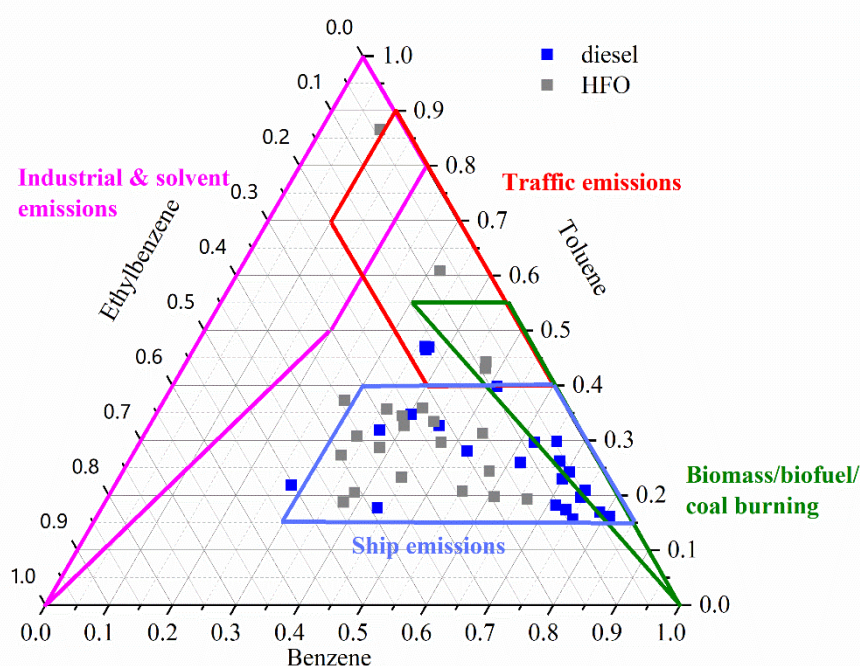



Figure 5 Relative proportions of benzene, toluene and ethylbenzene from the ship exhausts. B:T:E ratios from other sources were cited from Zhang et al. (2016b) that summarized 28 examples from biomass burning, 35 examples from biofuel burning, 17 examples from coal burning, 11 examples from diesel vehicle exhaust, 31 examples from gasoline vehicle exhaust, 24 examples from gasoline evaporation, 25 examples from roadside or tunnel tests, and 66 examples from industrial processes and solvent applications.

3.4 Ozone and SOA formation potential

3.4.1 Ozone formation potential

523 The normalized ozone reactivities (R_{O_3}) ranged between 2.95 and 4.60 g O_3 g^{-1}

524 VOCs for the test ships (presented in Fig. 6 and Table S10) in this study, meaning there

525 was diversity of ozone reactivities in VOCs from different ships, which was due to the

526 different shares of VOC species emitted from different ships with different fuels. The

527 R_{O_3} values were within the range of previous reported results estimated by Wu et al.

528 (2020) (2.62 to 5.41 g O_3 g^{-1} VOCs) and Wu et al. (2019) (approximately 4.5 to 6.0 g

529 O_3 g^{-1} VOCs), but showed different fragments of VOC species to R_{O_3}. The different

530 detected VOC species was also one inferred reason for the variation of R_{O_3} in different

531 studies. Aromatics and alkenes were the most significant contributors to R_{O_3} in this

532 study due to their high reactivities. Aromatics had relatively higher contributions for

533 the OGVs, and the CCSs and ICSs were more affected by alkenes, excepted for the

534 auxiliary engine with diesel oil of CCSs. Besides, it also can be seen from Fig. 6 (a)

535 that when the fuels were switched from diesel to HFO, more aromatics were contributed

536 to R_{O_3} because of the higher aromatic but lower aliphatic compounds in HFO (Sippula

537 et al., 2014). On the contrary, alkenes showed reverse trends with aromatics, which

538 were attributed to engine combustion and operation conditions of the test ships, as well

539 as the high content of alkenes in diesel fuel in China (Mo et al., 2016).

540 As described in Fig. 6 (b), the OFP varied significantly from 0.91 to 7.81 g O_3 kg^{-1}

541 fuel, with the main engines of CCSs presented the highest levels, but auxiliary engines

542 of OGVs the lowest, even though the R_{O_3} showed no such big differences among all

543 the test ships. The main reason was the huge variation of EF$_{VOCs}$, as well as the

544 difference in component of VOC species emitted from different ships with different

545 fuels. However, due to lack of measurements of OVOC species such as formaldehyde,

546 acetaldehyde, and benzaldehyde in this study, the presented OFPs were underestimated.

547 The same as R_{O_3}, aromatics and alkenes were the most significant contributors to OFP,

548 accounting for 28-61% and 20-50% of the total OFP, respectively. It's worth noting that

549 when the fuels were switched from HFO to diesel for the OGVs, there were obvious

550 increasing OFP trends. This was similar with result of Huang et al. (2018b) that HFO

551 had lower OFP compared with diesel fuel about an ocean-going vessel and Wu et al.

552 (2020) that after implementation of the fuel switch policy for ships at berth, OFP

553 increased from 0.35 to 10.37 g O_3 kg^{-1} fuel. However, the CCS had slightly higher OFP

554 value with HFO than diesel in this study. A previous study also reported that OFP from

555 HFO was ~3.3-fold higher than from burning diesel for a coastal container ship (Wu et

556 al., 2019). It seemed that when the fuels were switched from high sulfur to low sulfur,

557 there was obvious increase in OFP, especially for OGVs. While when the fuels were

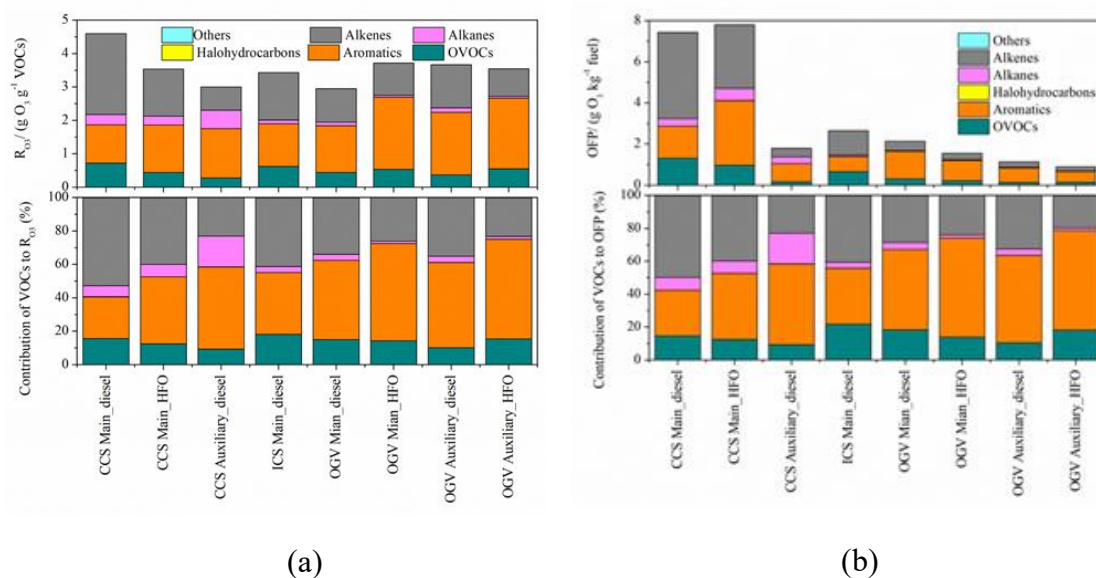
558 switched from low sulfur HFO to ultra-low sulfur diesel (sulfur content <0.1%), the

559 OFP would be also influenced by other factors, such as engine type, which needs to be

560 further explored by more on-board measurements. Besides, river ships and costal ships

561 had higher OFP than OGVs, and main engines had higher OFP than auxiliary engines,

562 which were consistent with previous study (Wu et al., 2020).

(a)   (b)

563

564 Figure 6 (a) The normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs) and contribution of

565 VOC species to R_{O_3}, (b) ozone formation potential (OFP, g O_3 kg^{-1} fuel) and

566 contribution of VOC species to OFP

567   3.4.2 SOA formation potential

568   The same as R_{O_3}, normalized SOA reactivities (R_{SOA}) under high-NO_x and low-

569 NO_x conditions were also estimated and presented in Fig. 7 (a), (b), and Table S10. The

570 R_{SOA} ranged from 63.2 to 134 mg SOA g^{-1} VOCs under high-NO_x condition and 137 to

312 mg SOA g^{-1} VOCs under low-NO$_x$ condition in this study, which were within the range of previous reported results (Wu et al., 2020;Huang et al., 2018b;Xiao et al., 2018;Wu et al., 2019), but at relatively higher levels compared with these studies. Unlike R_{O_3}, the R$_{SOA}$ showed relatively higher values for OGVs compared with CCSs and ICSs. The main reason for this was the content difference of heavy organic compounds in VOCs, such as higher proportion of naphthalene that has high SOA yield, which is also presented above in Table S4 and Fig. 4. Huang et al. (2018c) also showed the similar R$_{SOA}$ levels about a test OGV. Almost all the R$_{SOA}$ were contributed from aromatics and alkanes in this study. There were different variation trends of the total R$_{SOA}$ between different fuels for different types of ships, but obvious higher proportions of aromatics for ships with HFO than diesel fuel due to the higher aromatic contents in fuels, while alkanes were the opposite. Besides, the R$_{SOA}$ of ship exhausts in this study showed much higher levels compared with other traffic sources presented in previous study (Xiao et al., 2018), including diesel trucks and gasoline vehicles, which suggested that VOCs from ship exhaust deserved special attention.

The SOAFP in this study were ranging from 26.5 to 140 mg SOA kg^{-1} fuel and 71.5 to 303 mg SOA kg^{-1} fuel under high-NO$_x$ and low-NO$_x$ conditions, respectively (Fig. 7 (c) and (d)). The SOAFP values in this study were within the range of previous studies but showed relatively higher levels, which might be mainly caused by both the different detected VOCs species and the variation of VOCs EFs. Even though OGVs had relatively higher R$_{SOA}$ levels, due to the variation of EFs among the test ships, SOAFP showed different patterns with R$_{SOA}$. Main engines in this study had higher SOAFP values than auxiliary engines, no matter what type of fuel was used, indicating the important effect of engine type. The same as OFP, the switch of fuel from HFO to diesel could increase SOAFP for OGVs. Similar results were also found from Wu et al. (2020) that after IFSP, the SOAFP increased 1.6 times and 2.5 times under high-NO$_x$ and low-NO$_x$ conditions, and Huang et al. (2018b) that higher SOAFP was presented from diesel than from HFO. The CCSs showed opposite SOAFP variation trend with

599 OGVs, also similar with Wu et al. (2019) that SOAFP from HFO was 2.1-fold higher

600 than that of diesel. Moreover, the same as R_{SOA}, aromatics and alkanes were the most

601 significant contributors to SOAFP, and there were also obvious higher proportions of

602 aromatics to SOAFP for ships with HFO than diesel fuel. The main reason for this was

603 that EFs of aromatics from engines with HFO were higher than that of diesel fuel due

604 to the higher content of aromatics of HFO than diesel. It has been indicated that

605 intermediate VOCs (IVOCs) were significant SOA precursors with high yields

606 (Robinson et al., 2007;Tkacik et al., 2012). In another of our study, IVOCs from the test

607 OGVs were also detected, and the SOAFP of IVOCs from several selected conditions

608 (main engine and auxiliary engine of cruising loads, using MGO and HFO, respectively)

609 were calculated (Liu et al., 2022). Results showed that the SOAFP from IVOCs of the

610 main engine by using diesel and HFO were 540.5 and 482.1 mg SOA kg^{-1} fuel,

611 respectively, 542.2 and 451.3 mg SOA kg^{-1} fuel for auxiliary engine, respectively.

612 Obviously, the switch from low-sulfur fuel of HFO to ultra-low-sulfur fuel of diesel

613 could also increase the SOAFP from IVOCs. Even though SOAFP from VOCs were

614 lower than that of IVOCs, they were still not negligible, especially under low-sulfur

615 fuel policies.

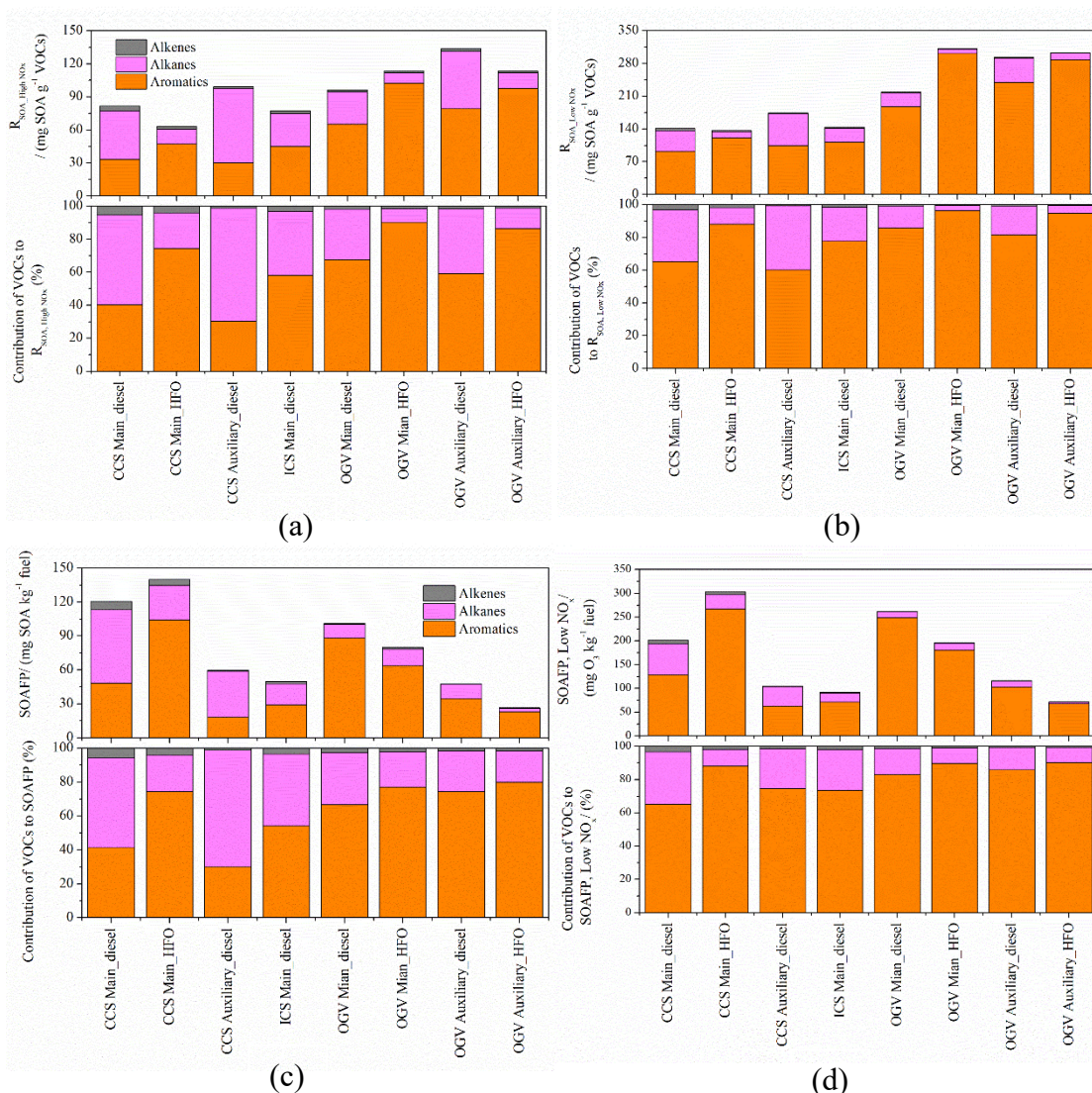



Figure 7 The normalized SOA reactivity (R_{SOA}, mg SOAg^{-1} VOCs) and contribution of VOC species to R_{SOA} under (a) high NO$_x$, (b) low NO$_x$; and the SOAFP (mg SOA kg^{-1} fuel) and contribution of VOC species to SOAFP under (c) high NO$_x$, (d) low NO$_x$

3.4.3 Top 20 contributing VOC species to OFP and SOAFP

Due to the significant contribution of VOCs to O$_3$ and SOA, it is essential to distinguish the most contributing VOC species for the formulation of emission reduction policies. Therefore, the top 20 contributing VOC species to OFP and SOAFP are presented in Table S11 and Table S12. Most of the listed VOC species to OFP and SOAFP among different engine types and fuels were the same but with different rankings. For example, propene was the most contributing VOC species to O$_3$ for the main engines of CCSs and ICSs, followed by acrolein, trimethyl benzene, butene etc.

628   While trimethyl benzene, propene and acrolein were ranking as the top VOCs species

629   to OFP for the auxiliary engine of CCSs. As for OGVs, naphthalene was the most

630   contributing VOC species to O_3, followed by propene, acrolein, 1,3-butadiene and

631   xylene etc. As shown in Table S12, the top VOCs species contributed to SOAFP were

632   benzene, naphthalene, n-dodecane, n-undecane and xylene etc. for all the test ships.

633   Naphthalene was undoubtedly the most contributing VOC species to SOAFP for OGVs.

634   In conclusion, it was obvious that as the important common contributors to both O_3 and

635   SOA, aromatics should be prioritized in control. Besides, VOCs species with high O_3

636   reactivities also need to be paid enough attention, such as alkenes, even though with

637   low emission factor levels.

638   **4. Conclusions and atmospheric implications**

639   Shipping emission is a non-ignorable anthropogenic emission source of air

640   pollutants, especially in coastal areas. Therefore, more and more strict emission control

641   regulations have been implemented globally. For example, the maximum fuel sulfur

642   content has been set to be 0.5% (m/m) worldwide by 2020, and 0.1% (m/m) in ECAs.

643   The Chinese government also has set the coastal ECAs that require the sulfur content

644   of 0.5% (m/m) since 2019, and 0.1% (m/m) in inland ECAs since 2020. The mandatory

645   use of low-sulfur fuels has reduced the emissions of SO_2 and PM significantly on ships,

646   while it also leads to very large uncertainty on VOCs emission. In view of this, on-

647   board test of VOCs from 9 typical cargo ships with low-sulfur fuels in China were

648   carried out in this study.

649   Results showed that EF_{VOCs} varied largely from 0.09 to 3.01 g kg^{-1} fuel, with

650   domestic coastal cargo ships (CCSs) had the highest levels and ocean-going vessels

651   (OGVs) the lowest. The test ships in this study presented comparable EF_{VOCs} level with

652   other studies. However, the measured EF_{VOCs} varied largely among different studies

653   due to complex reasons such as different detected VOC species, different engine types

654   and fuel qualities. OVOCs and aromatics were the main components of the detected

655   VOC species, followed by alkanes, while alkenes, halohydrocarbons and other

656 quantified species only contributed small fractions.

657   The emission level and component of VOCs from ship exhaust could be affected

658 by complex influence factors such as operating condition, engine type, ship type and

659 fuel type. For example, EF_{VOCs} had the lowest level when the engines were operating

660 in medium loads, and the highest in low loads. Besides, with the increase of engine

661 speed, the EF_{VOCs} showed an increasing trend. The average EF_{VOCs} from the main

662 engines was 2.3 times that of auxiliary engines in this study. Moreover, the EF_{VOCs}

663 varied obviously under different types of ships, with CCSs having the highest levels

664 and OGVs the lowest. It needs to be noted that fuel type could influence the emission

665 of EF_{VOCs} significantly. The switch of fuels from heavy fuel oil to diesel increased

666 EF_{VOCs} by 48% on average in this study. A bigger cause for concern is that from the

667 summarized results in this study and previous studies, the average EF_{VOCs} from low-

668 sulfur content fuel was significantly higher than that of high-sulfur content fuel, with

669 almost 3.4 times.

670   The most abundant VOC species were acetone and acrolein in OVOCs, propene

671 and butene in alkenes, n-Nonane, n-Decane, n-Undecane, n-Dodecane in alkanes for

672 almost all the test ships. As for aromatics, the OGVs showed big differences compared

673 with other types of ships that had large amounts of naphthalene due to the use of low-

674 sulfur fuels, while benzene, toluene and m/p-xylene were the highest content aromatic

675 substances for other ships. We also found that benzene, toluene, and ethylbenzene ratio

676 of 0.5:0.3:0.2 on average could be considered as a diagnostic characteristic to

677 distinguish ship emission from other emission sources.

678   The OFP in this study varied significantly from 0.91 to 7.81 g O_3 kg^{-1} fuel, with

679 the main engines of CCSs presented the highest levels, but auxiliary engines of OGVs

680 the lowest. The SOAFP in this study were ranging from 71.5 to 303 mg SOA kg^{-1} fuel

681 under low-NO_x conditions. Main engines in this study had higher SOAFP values than

682 auxiliary engines, no matter what type of fuel was used, indicating the important effect

683 of engine type. It's also worth noting that when the fuels were switched from high sulfur

684   to low sulfur, there was obvious increase in OFP and SOAFP, especially for OGVs.

685   Moreover, aromatics were the most important common contributors to O_3 and SOA in

686   ship exhausts, which need to be controlled with priority.

687   It could be concluded from this study and previous studies that either the switch

688   of high-sulfur HFO to low-sulfur HFO, or low-sulfur HFO to ultra-low-sulfur diesel,

689   VOCs emissions from OGVs increased significantly, which further promoted the

690   formation potential of O_3 and SOA, especially in coastal areas. Therefore, the

691   implementation of the ultra-low-sulfur oil policy in the near future is likely to further

692   increase the emission of VOCs, which needs to be optimized. Besides, the results herein

693   indicated that aromatics are absolutely the most important common contributors to OFP

694   and SOAFP, which need to be controlled with priority in ship exhausts. Since aromatics

695   are typically from the polymerization, improving engine combustion conditions of ship

696   engine is an effective way to reduce O_3 and SOA from ship exhausts, especially in

697   coastal and inland areas. Moreover, organic matters such as naphthalene from ship

698   exhausts with low-sulfur HFO should be explored and considered to be potential tracers

699   to identify ocean going ships from coastal and inland ships. Lastly, the EFs and profiles

700   of VOCs emitted from ship exhausts varied significantly, one important reason was that

701   the sample size of on-board measured VOCs was too small, in addition, the detection

702   methods and detected VOCs species differed greatly among different studies. Therefore,

703   much more on-board tests need to be implemented and standard VOCs detection

704   method as well as essential VOCs species should be clarified, especially under current

705   low-sulfur regulation.

706   **Author contributions**

707   FZ, YZ, CH, HW, YC and GW conceptualized and designed the study; BX, ZL,

708   CT, XW, YH, MC, and YC performed the measurements; FZ, RL, CW, YL, SZ, and

709   GW analyzed the data. FZ wrote the manuscript draft; All the authors reviewed, edited,

710   and contributed to the scientific discussion in the manuscript.

711   **Competing interests**

712   The contact author has declared that none of the authors has any competing

713 interests.

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