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

2 **potential contributions to SOA and O₃ 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 neglect 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

emission, vehicle exhaust etc., while VOCs from shipping haven't gained much attention. Most of previous studies just give the characteristics of total non-methane hydrocarbons (NMHCs) from ships, but not specific VOC species (Cooper, 2003;Zhang et al., 2016a). Only few studies have reported the VOCs emission factors (EFs) and their composition from specific type of ships under specific operating conditions (Wu et al., 2020;Wang et al., 2020;Wu et al., 2019;Xiao et al., 2018;Zetterdahl et al., 2016;Huang et al., 2018b;Cooper et al., 1996). The limited measured VOCs data cannot reflect the actual situation of shipping emissions. More on-board VOCs measurement for typical ships with representative fuels under different operating conditions need to be carried out, especially after the implementation of low-sulfur fuel policies.

According to the International Maritime Organization (IMO), the maximum fuel sulfur content has been set to be 0.5% (m/m) worldwide by 2020, and 0.1% (m/m) in emission control areas (ECAs). The Chinese government also has set the coastal ECAs that require the sulfur content of 0.5% (m/m) since 2019, and 0.1% (m/m) in inland ECAs since 2020 (Ministry of Transport of the People's Republic of China, 2018). The use of ultra-low sulfur fuel (< 0.1% (m/m)) globally is an inevitable trend in the near future. Fuel quality could affect the pollutants from ship exhausts significantly. For example, a large amount of PM, SO_2 and NO_x have been reduced since the implementation of ship emission control policies (Weng et al., 2022;Wang et al., 2021b;Zhang et al., 2019;Viana et al., 2015;Repka et al., 2021). While it also reveals that the switching of high-sulfur content fuels (sulfur content ≥0.5%) to low-sulfur content fuels (0.1%< sulfur content <0.5%) leads to significant uncertainties of VOCs emissions from the results of previous studies. For example, Wu et al. (2019) show that the reduction in EF of VOCs (EF_{VOCs}) is 67% when switching from high-sulfur content heavy fuel oil (HFO) to low-sulfur content marine diesel oil for a container ship. While another study finds that after limiting fuel sulfur content, the EF_{VOCs} are approximately 15 times that of before implementation of the fuel switch policy (IFSP) from ships at 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.

144   **2. Materials and methods**

145   **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       $EF_X = \frac{\triangle X}{\triangle CO_2} \cdot \frac{M_X}{M_{CO_2}} \cdot EF_{CO_2}$ (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       $EF_{CO_2} = \frac{C_F}{c(C_{CO})+c(C_{CO_2})+c(C_{PM})+c(C_{HC})} \cdot c^*(CO_2) \cdot M_{CO_2}$ (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

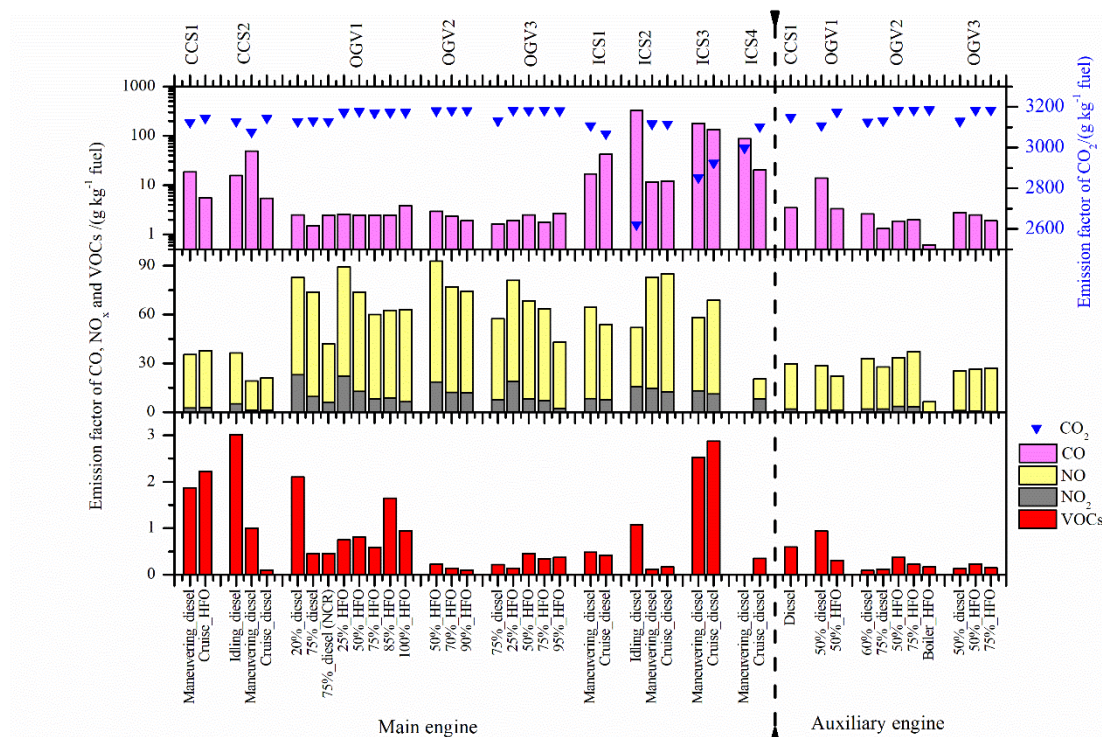
281 modes, the EF_{VOCs} presented lower levels (detailed result was also shown in Fig. 3 (a)).

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.

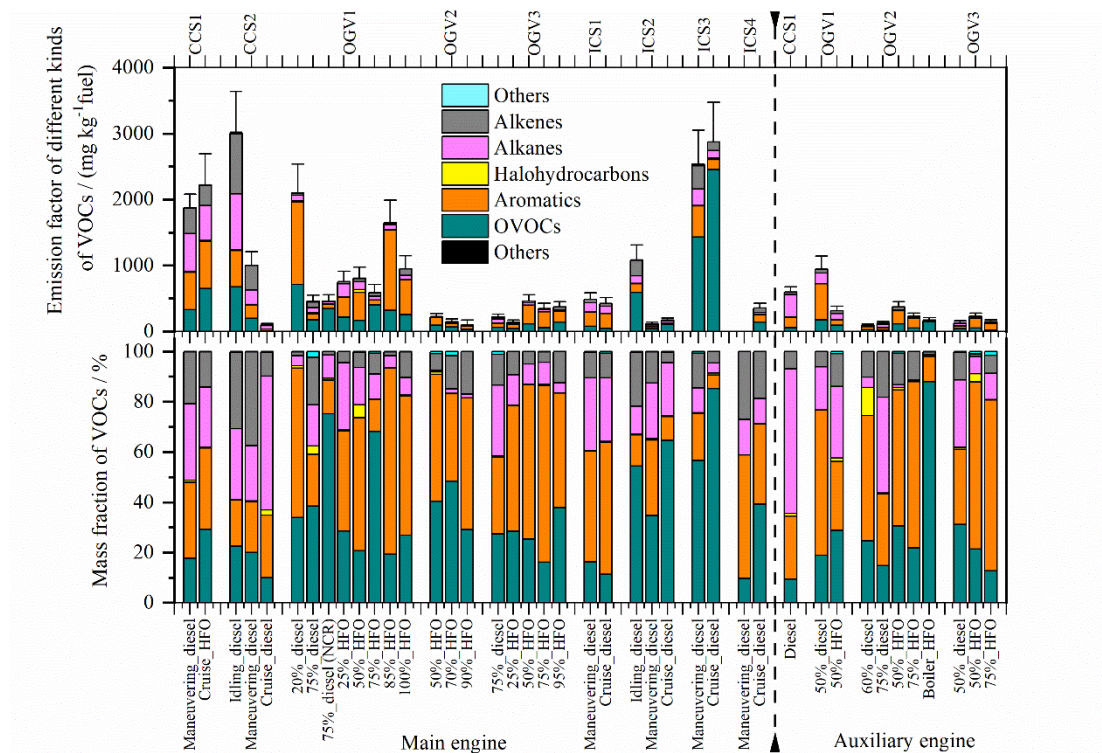



Figure 2 EFs of VOC components and their mass fractions

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

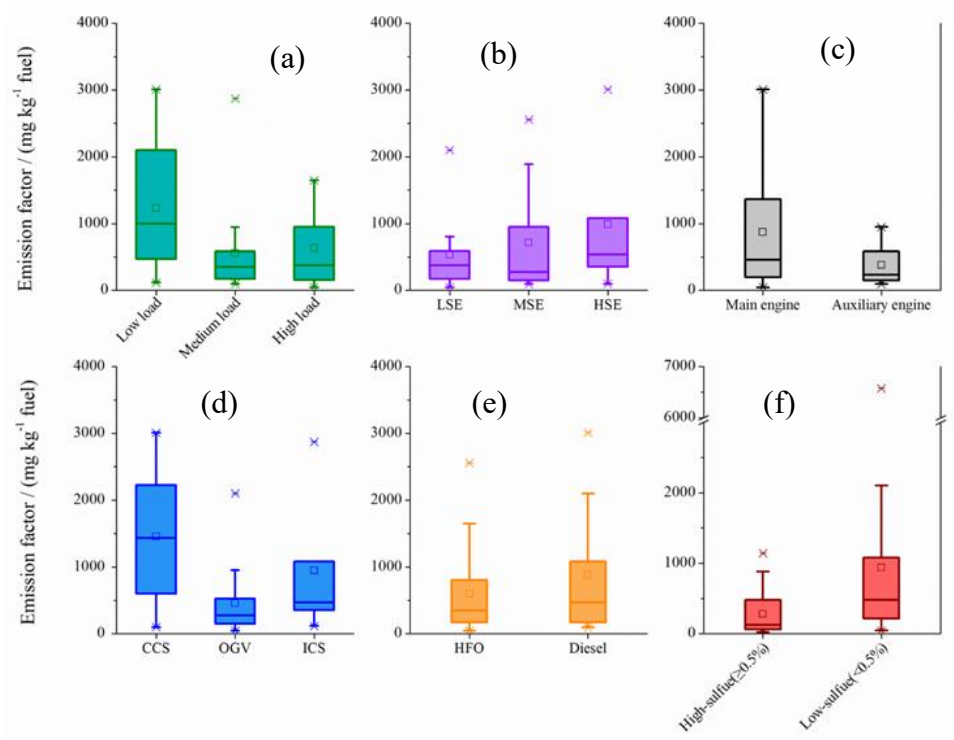
408 et al., 2022). Except for light low-sulfur oils mixed during the production of low-sulfur

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

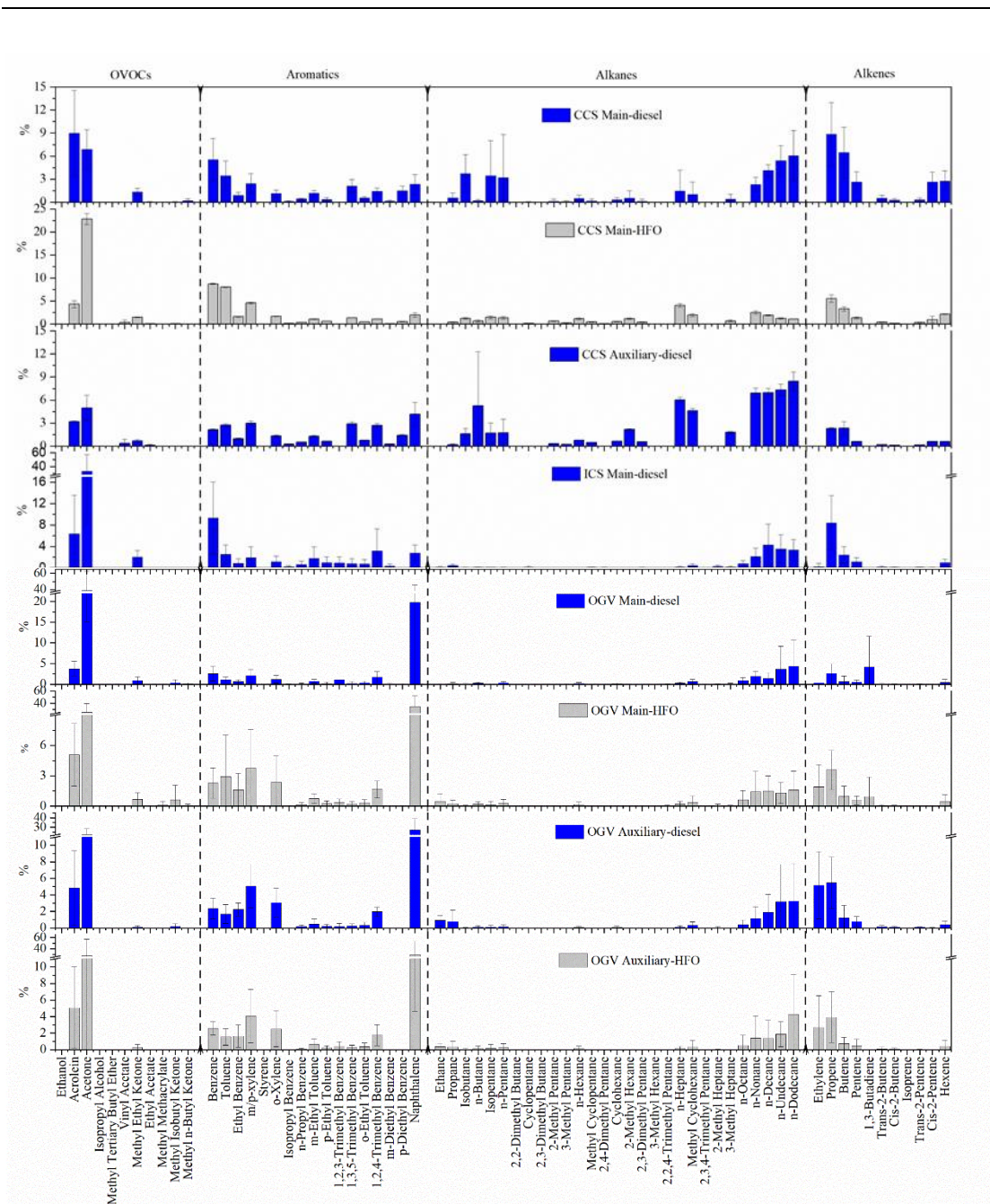
420 fractions (0.55%-3.06% of total VOCs)) from the three types of test ships (CCS, OGV

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) 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 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. While other VOC species were different from

452   different fuels for OGVs, such as high alkenes, OVOCs and aromatics from exhausts

453   of HFO fuel, but high alkenes, OVOCs and alkanes from exhausts of diesel fuels. This

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

455   2015;Huang et al., 2018c;Yeh et al., 2023). The unusually high naphthalene from OGVs

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

475   (Wang et al., 2020).

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

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

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

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

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

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

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

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

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

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

486  3.3.2 Diagnostic characteristics of VOCs

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

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

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

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

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

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

493 <1 for biomass/biofuel/coal burning, 1 to 10 for vehicle emissions, and >1 for solvent

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

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

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

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

498 2013;Yao et al., 2015) and non-road diesel construction vessels with a T/B ratio of 1.4

499 ± 1.3. The results were similar with that of 0.45 - 0.57 from Wu et al. (2020) and 1.07

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

501 et al.(2018c).

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

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

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

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

506 0.50:0.30:0.20 on average from the test ships, differed from that of 0.69:0.27:0.04 for

507 biomass /biofuel/coal burning, 0.06:0.59:0.35 for industrial emissions, and especially

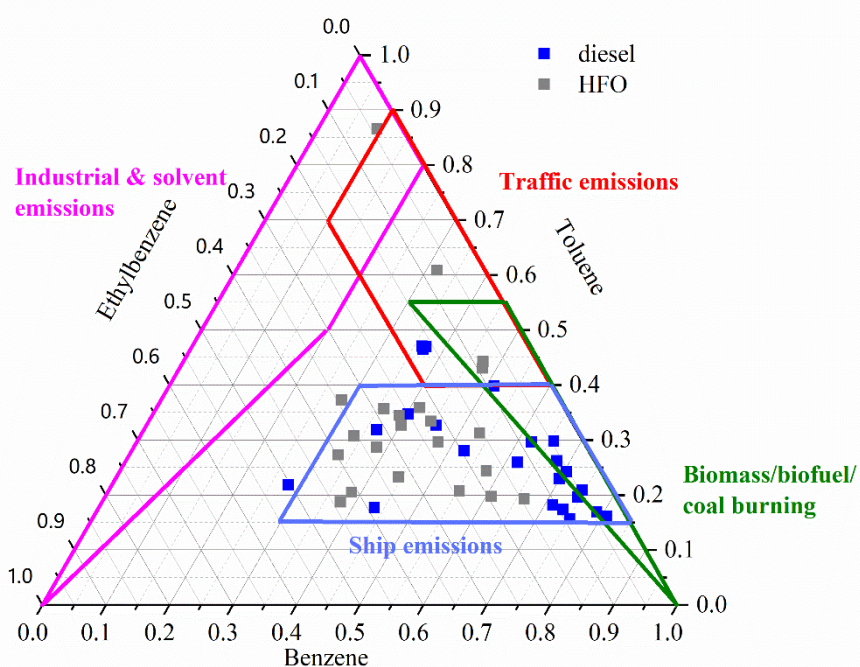
508 0.31:0.59:0.10 for traffic emissions, respectively (Zhang et al., 2016b). Besides, most

509 of the relative compositions of B, T, and E from ship exhausts in this study were

510 relatively stable and mainly concentrated within certain area that was seldom

511 overlapped with other emission sources in the ternary diagram. This indicated that the

512 B: T: E ratios could be considered as a diagnostic characteristic to distinguish ship

513 emission from other emission sources, especially the traffic emissions.

514

515 Figure 5 Relative proportions of benzene, toluene and ethylbenzene from the ship

516 exhausts. B:T:E ratios from other sources were cited from Zhang et al. (2016b) that

517 summarized 28 examples from biomass burning, 35 examples from biofuel burning, 17

518 examples from coal burning, 11 examples from diesel vehicle exhaust, 31 examples

519 from gasoline vehicle exhaust, 24 examples from gasoline evaporation, 25 examples

520 from roadside or tunnel tests, and 66 examples from industrial processes and solvent

521 applications.

3.4 Ozone and SOA formation potential

3.4.1 Ozone formation potential

The normalized ozone reactivities (R_{O_3}) ranged between 2.95 and 4.60 g O_3 g^{-1} VOCs for the test ships (presented in Fig. 6 and Table S10) in this study, meaning there was diversity of ozone reactivities in VOCs from different ships, which was due to the different shares of VOC species emitted from different ships with different fuels. The R_{O_3} values were within the range of previous reported results estimated by Wu et al. (2020) (2.62 to 5.41 g O_3 g^{-1} VOCs) and Wu et al. (2019) (approximately 4.5 to 6.0 g O_3 g^{-1} VOCs), but showed different fragments of VOC species to R_{O_3}. The different detected VOC species was also one inferred reason for the variation of R_{O_3} in different studies. Aromatics and alkenes were the most significant contributors to R_{O_3} in this study due to their high reactivities. Aromatics had relatively higher contributions for the OGVs, and the CCSs and ICSs were more affected by alkenes, excepted for the auxiliary engine with diesel oil of CCSs. Besides, it also can be seen from Fig. 6 (a) that when the fuels were switched from diesel to HFO, more aromatics were contributed to R_{O_3} because of the higher aromatic but lower aliphatic compounds in HFO (Sippula et al., 2014). On the contrary, alkenes showed reverse trends with aromatics, which were attributed to engine combustion and operation conditions of the test ships, as well as the high content of alkenes in diesel fuel in China (Mo et al., 2016).

As described in Fig. 6 (b), the OFP varied significantly from 0.91 to 7.81 g O_3 kg^{-1} fuel, with the main engines of CCSs presented the highest levels, but auxiliary engines of OGVs the lowest, even though the R_{O_3} showed no such big differences among all the test ships. The main reason was the huge variation of EF$_{VOCs}$, as well as the difference in component of VOC species emitted from different ships with different fuels. However, due to the missing of OVOC species such as formaldehyde, acetaldehyde, and benzaldehyde in this study, the presented OFPs were underestimated. The same as R_{O_3}, aromatics and alkenes were the most significant contributors to OFP, accounting for 28-61% and 20-50% of the total OFP, respectively. It's worth noting that

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(a)   (b)

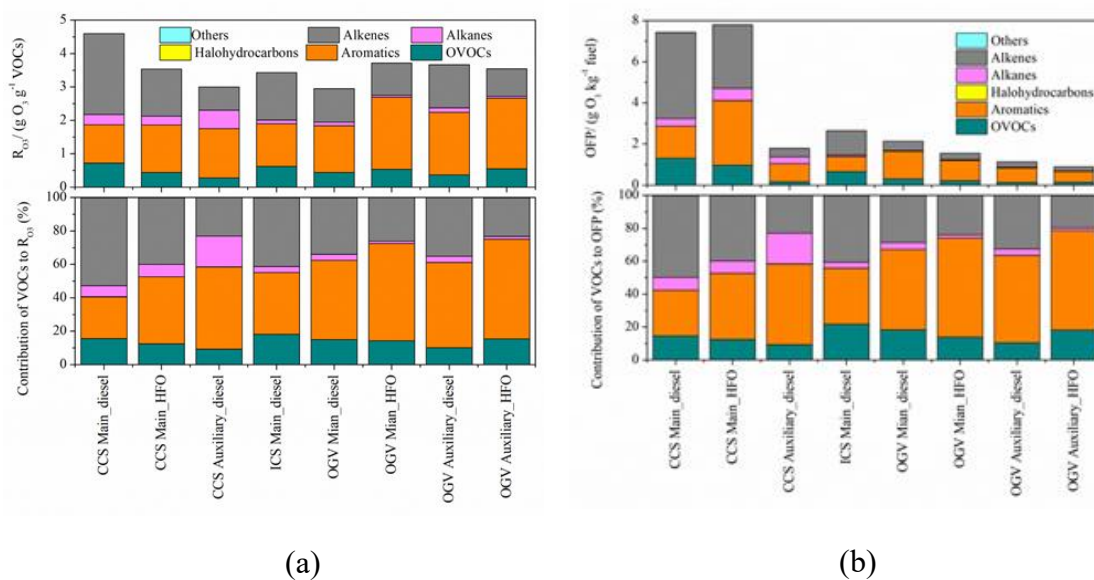



Figure 6 (a) The normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs) and contribution of

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

contribution of VOC species to OFP

3.4.2 SOA formation potential

The same as R_{O_3}, normalized SOA reactivities (R$_{SOA}$) under high-NO$_x$ and low-

570 NO$_x$ conditions were also estimated and presented in Fig. 7 (a), (b), and Table S10. The

571 R$_{SOA}$ ranged from 63.2 to 134 mg SOA g^{-1} VOCs under high-NO$_x$ condition and 137 to

572 312 mg SOA g^{-1} VOCs under low-NO$_x$ condition in this study, which were within the

573 range of previous reported results (Wu et al., 2020;Huang et al., 2018b;Xiao et al.,

574 2018;Wu et al., 2019), but at relatively higher levels compared with these studies.

575 Unlike R_{O_3}, the R$_{SOA}$ showed relatively higher values for OGVs compared with CCSs

576 and ICSs. The main reason for this was the content difference of heavy organic

577 compounds in VOCs, such as higher proportion of naphthalene that has high SOA yield,

578 which is also presented above in Table S4 and Fig. 4. Huang et al. (2018c) also showed

579 the similar R$_{SOA}$ levels about a test OGV. Almost all the R$_{SOA}$ were contributed from

580 aromatics and alkanes in this study. There were different variation trends of the total

581 R$_{SOA}$ between different fuels for different types of ships, but obvious higher proportions

582 of aromatics for ships with HFO than diesel fuel due to the higher aromatic contents in

583 fuels, while alkanes were the opposite. Besides, the R$_{SOA}$ of ship exhausts in this study

584 showed much higher levels compared with other traffic sources presented in previous

585 study (Xiao et al., 2018), including diesel trucks and gasoline vehicles, which suggested

586 that VOCs from ship exhaust deserved special attention.

587   The SOAFP in this study were ranging from 26.5 to 140 mg SOA kg^{-1} fuel and

588 71.5 to 303 mg SOA kg^{-1} fuel under high-NO$_x$ and low-NO$_x$ conditions, respectively

589 (Fig. 7 (c) and (d)). The SOAFP values in this study were within the range of previous

590 studies but showed relatively higher levels, which might be mainly caused by both the

591 different detected VOCs species and the variation of VOCs EFs. Even though OGVs

592 had relatively higher R$_{SOA}$ levels, due to the variation of EFs among the test ships,

593 SOAFP showed different patterns with R$_{SOA}$. Main engines in this study had higher

594 SOAFP values than auxiliary engines, no matter what type of fuel was used, indicating

595 the important effect of engine type. The same as OFP, the switch of fuel from HFO to

596 diesel could increase SOAFP for OGVs. Similar results were also found from Wu et al.

597 (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 OGVs, also similar with Wu et al. (2019) that SOAFP from HFO was 2.1-fold higher than that of diesel. Moreover, the same as R_{SOA}, aromatics and alkanes were the most significant contributors to SOAFP, and there were also obvious higher proportions of aromatics to SOAFP for ships with HFO than diesel fuel. The main reason for this was that EFs of aromatics from engines with HFO were higher than that of diesel fuel due to the higher content of aromatics of HFO than diesel. It has been indicated that intermediate VOCs (IVOCs) were significant SOA precursors with high yields (Robinson et al., 2007;Tkacik et al., 2012). In another of our study, IVOCs from the test OGVs were also detected, and the SOAFP of IVOCs from several selected conditions (main engine and auxiliary engine of cruising loads, using MGO and HFO, respectively) were calculated (Liu et al., 2022). Results showed that the SOAFP from IVOCs of the main engine by using diesel and HFO were 540.5 and 482.1 mg SOA kg^{-1} fuel, respectively, 542.2 and 451.3 mg SOA kg^{-1} fuel for auxiliary engine, respectively. Obviously, the switch from low-sulfur fuel of HFO to ultra-low-sulfur fuel of diesel could also increase the SOAFP from IVOCs. Even though SOAFP from VOCs were lower than that of IVOCs, they were still not negligible, especially under low-sulfur fuel policies.

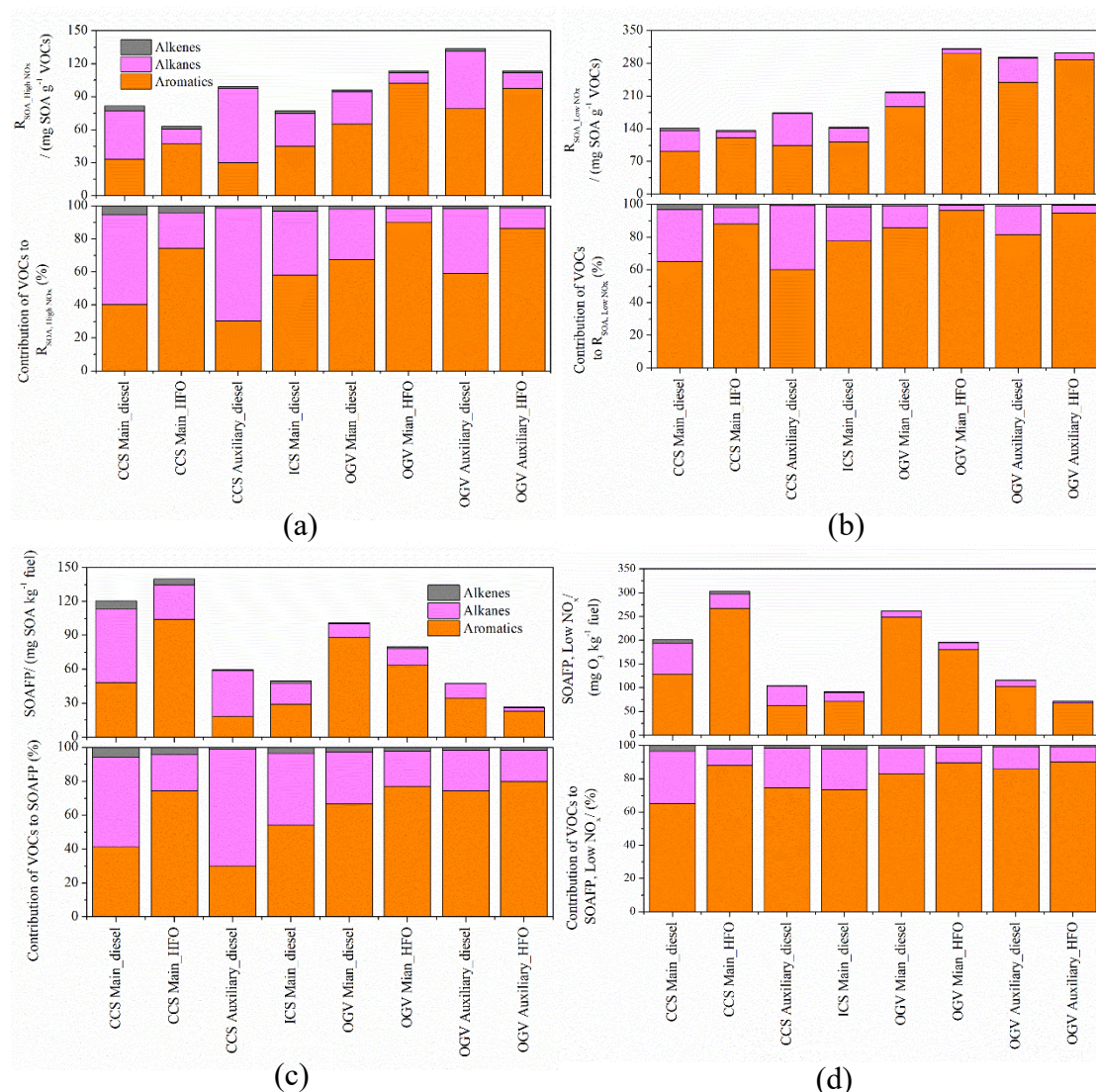



Figure 7 The normalized SOA reactivity (R_{SOA}, mg SOAg^{-1} VOCs) and contribution of VOC species to R_{SOA} under (a) high NO_x, (b) low NO_x; and the SOAFP (mg SOA kg^{-1} fuel) and contribution of VOC species to SOAFP under (c) high NO_x, (d) low NO_x

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.

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

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

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

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

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

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

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

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

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

638   low emission factor levels.

639   **4. Conclusions and atmospheric implications**

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

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

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

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

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

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

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

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

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

649   carried out in this study.

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

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

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

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

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

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

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

657   quantified species only contributed small fractions.

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

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

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

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

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

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

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

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

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

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

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

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

670   almost 3.4 times.

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

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

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

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

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

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

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

678   distinguish ship emission from other emission sources.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

706 low-sulfur regulation.

707 **Author contributions**

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

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

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

711 and contributed to the scientific discussion in the manuscript.

712 **Competing interests**

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

714 interests.

715 **Acknowledgements**

716 This study was supported by the National Natural Science Foundation of China

717 (42377096, 42130704 and 42077195), State Environmental Protection Key Laboratory

718 of Formation and Prevention of Urban Air Pollution Complex (No. 2021080547), and

719 the Ministry of Industry and Information Technology of China (No. MC-202019-C08).

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