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Real-world emission characteristics of VOCs from typical cargo ships and their potential contributions to SOA and O_3 under low-sulfur fuel policies

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Abstract

Mandatory use of low-sulfur fuel according to global sulfur limit regulation has reduced the emissions of SO_2 and PM significantly on ships, while it also leads to very large uncertainty on VOCs emission. Therefore, on-board test of VOCs from 9 typical cargo ships with low-sulfur fuels in China were carried out in this study. Results showed that emission factor of VOCs (EF_{VOCs}) varied largely from 0.09 to 3.01 g kg^{-1} fuel, with domestic coastal cargo ships (CCSs) had the highest levels and ocean-going vessels (OGVs) the lowest. The switch of fuels from heavy fuel oil (HFO) to diesel increased EF_{VOCs} by 48% on average, which enhanced both O_3 and secondary organic aerosol (SOA) formation potentials, especially for OGVs. Besides, the use of low-sulfur fuels for OGVs also lead to significant increase of naphthalene emission. These indicated the implementation of globally ultra-low-sulfur oil policy in the near future needs to be optimized. Moreover, aromatics were the most important common contributors to O_3 and SOA in ship exhausts, which need to be controlled with priority. It was also found that benzene, toluene, and ethylbenzene ratio of 0.5:0.3:0.2 on average could be considered as a diagnostic characteristic to distinguish ship emission from other emission sources.

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

1. Introduction

Maritime transport accounts for more than 80% of global trade by volume (United Nations Conference on Trade and Development, 2020), leading to significant environmental and health effects (Corbett et al., 2007;Liu et al., 2016;Wang et al., 2021a). As a non-ignorable anthropogenic emission source of air pollutants, shipping emission has caused more and more attentions in recent decades. However, most of the previous studies focus on primary pollutants, such as SO_2, NO_x, CO_x, HC, particulate matter (PM) and its components, particulate number (PN), etc. (Zhang et al.,

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2022b;Santos et al., 2022;Zhou et al., 2019b;Chu-Van et al., 2017;Reda et al., 2015;Buffaloe et al., 2014;Beecken et al., 2014;Moldanova et al., 2013;Fu et al., 2013;Moldanova et al., 2009;Lack et al., 2009;Lack et al., 2008). Only few studies estimate the influence of ship exhaust on secondary photochemical oxidation products, such as O_3 and secondary organic aerosol (SOA), and concern their relative precursors (Jonson et al., 2009;Song et al., 2010;Lang et al., 2017;Wu et al., 2019;Wang et al., 2019;Wu et al., 2020). Results from these limited studies show that the ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAFP) of shipping emissions are much greater than from on-road vehicles due to their higher VOCs emission factors and normalized reactivities (Wu et al., 2019;Wu et al., 2020). Therefore, the neglection of secondary pollutants such as O_3 and SOA would vastly underestimate the actual influence of shipping emissions on environment air.

Volatile organic compounds (VOCs) are typical O_3 and SOA precursors. Even though concentrations of $PM_{2.5}$ decreased rapidly in recent years, O_3 presented continuous upward trends in most of China (Lu et al., 2020). More and more 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. 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 approximately 2 times greater SOAFP than those before IFSP (Wu et al., 2020). Huang et al. (2018) also presented similar results of larger SOAFP when switch fuel from high-sulfur content HFO to diesel oil for a large cargo vessel. It seems the low-sulfur fuel regulation has different effects on VOCs emission for different types of ships. Therefore, it is essential to figure out the actual emission of VOCs as well as formation potentials of SOA and O_3 under the condition of low-sulfur fuel regulations. This will greatly reduce the uncertainties in VOCs inventory estimation and provide basic data for the formulation of optimal emission control policies of ships after considering comprehensive impacts on various pollutants.

By the end of 2022, China had 121,900 water transport vessels (Ministry of Transportation, 2022), 15 ports in China were listed among the top 20 ports in the world for cargo throughput, and 7 container ports were listed among the largest 10 container ports in the world. The large amount of active ships in China has resulted in serious

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impact on ambient air and human healthy, particularly in coastal, inland and port areas (Huang et al., 2022;Zhang et al., 2017;Liu et al., 2016). Researches reveal that most of the pollutants are from cargo-transport ships compared with other types of ships (Wan et al., 2020). Clarifying the EF of VOCs, profiles, influence factors, and their contribution to O_3 and SOA formation potentials of the typical cargo ships are the basis to estimate the VOCs inventory and to establish proper control measures. Besides, it is also a very important breakthrough point to further improve the ambient air quality in port and nearshore areas by controlling the VOCs emission from ship exhaust.

Therefore, on-board test of exhaust pollutants from 9 typical cargo ships in China, including 2 coastal cargo ships (CCSs), 3 ocean-going vessels (OGVs) and 4 inland cargo ships (ICSs) were carried out in this study. VOCs samples from different types of engines with different fuels under actual operating conditions were collected and 106 VOC species were analyzed. Based on the data, the following factors were valuated and discussed in this study: (1) fuel-based emission factor of VOCs (EF_{VOCs}) and their components, (2) influence factors, (3). profiles of VOCs, (4) O_3 and SOA formation potentials.

2. Materials and methods

2.1 Test ships and fuels

VOCs samples from 9 different ships were collected in this study, including 2 coastal cargo ships, 3 ocean-going vessels, and 4 inland cargo ships in Yangtze River. The technical parameters of the sampling ships are shown in Table 1. Different types of cargo ships had different technical parameters in China. For example, the tonnage of coastal cargo ships varied largely, therefore, one large tonnage ship and one small tonnage ship were selected here. Ocean-going vessels usually had large tonnages with large power main engines, hence, three ocean-going vessels with different tonnages were tested in this study. Most inland cargo vessels in Yangtze River were generally equipped with high-speed small main engines of power within 500 kW, therefore, four typical inland cargo ships of engine power between 138kW and 300 kW were chosen.

It's worth noting that the ocean-going vessels were newly constructed ships, while the inland cargo ships had older engines compared with other types of ships.

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)

Characteristics of HFO and diesel oil used for the test ships in this study are shown in Table S1. In order to meet the requirements of diesel engines of non-road mobile machinery of China, regular diesel (0#) was used for all inland cargo ships here. Results showed that the sulfur contents of all the fuels were no more than 0.5% (m/m), which were within both current ship emission control standards of China and IMO. As typical tracers of high-sulfur content HFO, nickel and vanadium content levels and their ratios were still higher but not distinguishable enough in low-sulfur content HFO compared with diesel oil, which further evidence that it needed to be cautious when they were used as tracers of ship emissions under current low-sulfur regulation. While it should be noted that much higher levels of calcium and zinc were detected in lubricating oils of OGVs.

2.2 Sampling system and samples

A portable dilution sampling system was used in this campaign, whose components and principles were described elsewhere (Zhang et al., 2018). Briefly, two separate sampling pipes were placed into the exhaust stacks (about 1.5 m deep of the exhaust outlet) to route emissions from the main engine and auxiliary engine to sampling system on the highest deck of ship, respectively. Then, the probe of a flue gas analyzer (Testo 350, testo, Germany) was placed into the sampling pipe to test the gaseous matters directly to get online data (CO_2, O_2, CO, NO, NO_2, SO_2). Another probe was used to extract the flue gas for the diluted system. The dilution ratios ranged between 1-10 in this study. Then particulate samplers and 8-Stage Anderson Cascade Impactor (TE-20-800, Tisch Environmental Inc, USA) were used to collect PM samples. I/OVOCs samples were obtained by automatic sampler to get IVOCs and OVOCs samples that had been reported in other study (Liu et al., 2022). VOCs samples that were mainly concerned in this study were collected directly by summa canister. The sampling time was 20-30 minutes for each sample according to actual operating condition.

A total of 48 VOCs samples were obtained for the test ships, involving different engine types with different fuels under different operating modes (seen Table S2 for the detailed information). For the coastal/inland cargo ships, all samples were collected based on actual operating modes (about one to several days from one trip). While for ocean going vessels, samples from much more operating modes could be obtained thanks to the testing of the newly constructed ships (about one week from one trip).

2.3 Chemical and data analysis

As shown in Table S3, a total of 106 volatile organic compounds were detected in this study according to USEPA TO15-1999, including 11 oxygenated volatile organic compounds (OVOCs), 17 aromatics, 29 alkanes, 11 alkenes, 35 halohydrocarbons and 4 other species. Carbon balance method was used to calculate the EF_{VOCs} that was introduced in our previous study (Zhang et al., 2016a). Detailed calculation processes of normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs), OFP (g O_3 kg^{-1} fuel), normalized secondary organic aerosols reactivity (R_{SOA}, mg SOA g^{-1} VOCs) and SOA formation potential (SOAFP, mg SOA kg^{-1} fuel) are given as follows:

Normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs) and OFP (g O_3 kg^{-1} fuel) were calculated using the maximum incremental (MIR) coefficient method (Carter, 2010a), which represents the maximum contribution of VOC species to the near-surface O_3 concentration under optimal conditions. The equations are as follows:

$$R_{O_3} = \sum_i (\omega_i \times \mathrm{MIR}_i) \quad (1)$$

where ω_i is the mass percentage of the total VOC emissions for species i, MIR_i is the MIR coefficient for VOC species i, which was referenced from Carter (2010b), seen in Table S3 for details.

$$OFP = \sum_i (MIR_i \times [VOC]_i) \quad (2)$$

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

The same as O_3, normalized secondary organic aerosols reactivity (R_{SOA}, mg SOA g^{-1} VOCs) and SOA formation potential (SOAFP, mg SOA kg^{-1} fuel) were also calculated, whose equations are as follows:

$$R_{SOA} = \sum_i (\omega_i \times \mathrm{Y}_i) \quad (3)$$

$$SOAFP = \sum_i (EF_i \times Y_i) \quad (4)$$

where Y_i is the SOA yield for VOC species i (seen in Table S4 for details). Both SOAFP of VOCs under high-NO_x and low-NO_x conditions were calculated.

2.4 Quality assurance and quality control

Rigorous quality assurance and quality control were conducted during the whole experiment. Ambient air blanks were analyzed in the same way as mentioned above to determine background concentration. The VOCs concentrations of each sample were obtained by subtracted ambient air blank results. Duplicate samples as well as standard gas were examined after analyzing a batch of 10 samples to ensure that the error was within 5%.

3. Results and discussion

3.1 Emission factors and components of VOCs

EF_{VOCs} for the test ships are shown in Fig.1 and Table S5. In order to calculate the EF_{VOCs} and investigate their influence factors, EFs of other gaseous pollutants such as CO_2, CO, NO, NO_2 were also given and discussed briefly. For CO_2, the emission factors ranged from 2622 to 3185 g kg^{-1} fuel that influenced by both fuel type and operating mode. CO showed opposite trend with CO_2, varying from 0.62 to 180 g kg^{-1} fuel, reflecting the condition of combustion efficiency. The EF_{NO_x} ranged from 6.26 to 92.8 g kg^{-1} fuel, with 60% to 99% of whom were NO, which inferred the condition of combustion temperature in cylinder.

Results showed that the EF_{VOCs} for all the test ships presented wide differences, which were ranging from 0.09 to 3.01 g kg^{-1} fuel. Ship type, engine type, operating mode and fuel type could influence the EF_{VOCs} that would be discussed in more detail in Section 3.2. Briefly, higher VOCs had been observed both in low-load and high-load operating modes such as maneuvering and idling, while in medium-load operating modes, the EF_{VOCs} presented lower levels (detailed result was also shown in Fig. 2 (a)). Main engines presented obviously higher EFs levels than auxiliary engines (Fig. 2 (c) for details). And CCSs and ICSs had relatively higher EFs compared with OGVs (Fig. 2 (d) for details). It was worth noting that when the fuels were switched from HFO to marine diesel oil for OGVs, increasing trends were presented for EF_{VOCs} in this study. While the CCSs showed the opposite trend with a slight decrease for EF_{VOCs}.

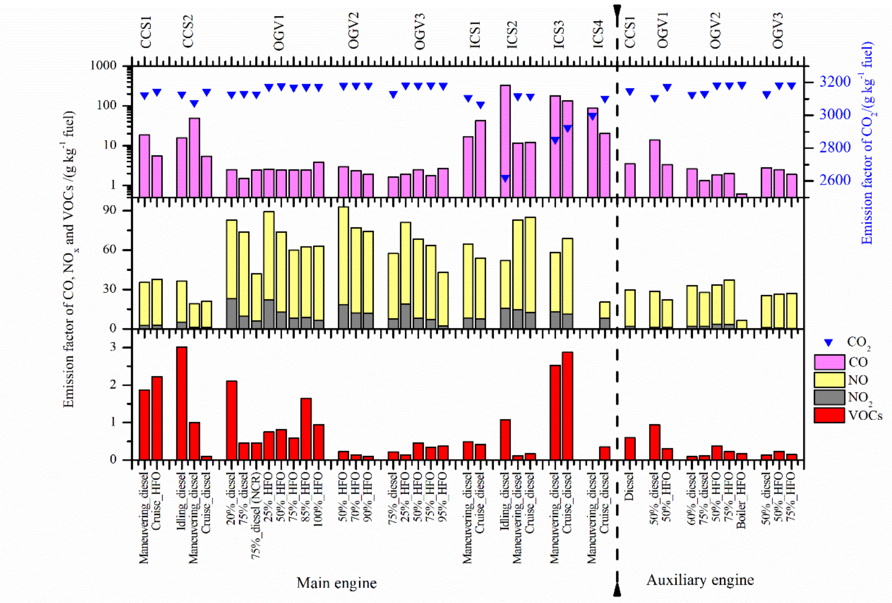

Figure 1 Emission factors of gaseous pollutants under all operating conditions for the test ships

Average EF_{VOCs} emitted from ships in this study were also compared with those reported in other studies (Table 2). Altogether, the measured EF_{VOCs} varied largely from 0.02 to 23.7 g kg^{-1} fuel for all the test ships. Complex factors could lead to the large uncertainty, such as the different detected VOC species in different studies, different engine types and fuel qualities. This also indicated that the uncertainty should be noticed when EF_{VOCs} were used as basic data to calculate emission inventory or estimate other environmental influence. The test ships in this study presented comparable EF_{VOCs} level with other studies. It seemed that OGVs with large engines typically showed lower EF_{VOCs} levels no matter what types of fuels were used compared with river ships and costal ships. Moreover, compared with on-road vehicles with diesel fuel (Zhou et al.,

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2019a), VOCs emitted from non-road engines, such as ship, agricultural machinery and construction machinery, had much higher levels (Huang et al., 2018a;Hua et al., 2019;Zhou et al., 2022), which should be paid more attention, especially in the case of 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)

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}

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Components and mass fractions of VOCs from the test ships are shown in Fig. S1 and Fig. S2. OVOCs and aromatics were the main components of the detected VOC species, accounting for 9.38% - 88.0% and 5.38% - 74.0% of total VOCs, respectively. Alkanes also accounted for non-ignorable fractions, which were ranging from 0.2% to 57.2%. While alkenes, halohydrocarbons and other quantified species only contributed small fractions of the total VOCs. The results in this study were consistent with that of Huang et al. (2018) about a large ocean-going bulk carrier, but showed different VOCs components with that of Wu et al. (2019) for a coastal container ship and Wu et al. (2020) for auxiliary engines at berth. The different detected VOCs species in different studies played an important role for the differences, while the fuel type and its chemical composition might also have considerable impacts.

The main VOCs components of OVOCs, aromatics, alkanes and alkenes presented different variation patterns under different operating modes, fuel types, and engine types due to their different formation mechanisms (Fig. S1). For example, OVOCs from diesel engines are typically from the oxidation of small molecular weight yet uncomplete combustion hydrocarbons (Hao et al., 2014;Pan, 2008), therefore, operating mode and engine type could influence the EF levels obviously, but not fuel type. The direct emission of unburned fuel components and pyrosynthesis (formation of aromatics by regeneration of fragmented radical species) are the two main formation processes of PAHs (Radischat et al., 2015). EFs of aromatics showed relatively higher levels in medium operating modes compared with other modes in this study. One main reason was that the higher temperature in medium operating modes promoted the polymerization, resulting in the processes of dehydrogenation and PAH formation (Zhang et al., 2021), which exceeded the direct emission of unburned fuel components (Radischat et al., 2015). Alkanes are mainly from the incomplete combustion of fuels, therefore, alkanes from diesel fuel presented higher EFs than HFO because of the higher aliphatic compounds in diesel fuel (Liu et al., 2022;Sippula et al., 2014). While alkenes 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.

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. 2. As shown in Fig. 2 (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 Wu et al. (2019) and Radischat et al. (2015). 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 VOCs emission.

Engine type is also one significant influence factor of VOCs emission. The engines were classified into three types in this study according to their engine speed, including low-speed engines (LSE, rated speed < 100 rpm), medium-speed engines (MSE, 100 rpm ≤ rated speed < 1000 rpm) and high-speed engines (HSE, rated speed ≥ 1000 rpm). It could be seen from Fig. 2 (b) that with the increase of engine speed, the EF_{VOCs} showed an increasing trend. This could be explained by that compared with HSEs, LSEs with high engine power usually had higher combustion efficiencies that led to lower levels of VOCs emission (Zhang et al., 2018).

The EF_{VOCs} between main engines and auxiliary engines also varied obviously. The average EF_{VOCs} from the main engines was 2.3 times that of auxiliary engines in this study (seen in Fig. 2 (c)). Similar result was also reported by Liu et al. (2022) about the IVOCs emission for the same test OGVs. Even though the auxiliary engines were mainly high-speed or medium-speed engines that had higher VOCs emissions mentioned above. Owing to the much lower VOCs emission in medium loads that the auxiliary engines have been using, it could be inferred that the impact of operating condition exceeded that of the engine type to VOCs emission.

As seen in Fig. 2 (d), the EF_{VOCs} varied obviously under different types of ships, with CCSs having the highest levels and OGVs the lowest. This could be explained by the combined influence of operating condition and engine type as mentioned above. Firstly, the CCSs equipped with high-speed or medium-speed engines emitted higher VOCs compared with OGVs that with low-speed engines. Besides, the unstable operating conditions of SSCs and ICSs, such as maneuvering and low-load, also promoted the emission of VOCs (Radischat et al., 2015). Therefore, it could be indicated that coastal areas with high population density need get more attention due to the higher VOCs emissions from CCSs and ICSs.

As mentioned before, fuel type could influence the emission of EF_{VOCs} significantly (Wu et al., 2019;Wu et al., 2020), which also would be one of the most important influence factors in the future under the background of increasingly strict ship oil policy. Under the condition of low-sulfur content fuels in China, the average EF_{VOCs} were 592 mg kg^{-1} fuel and 878 mg kg^{-1} fuel for diesel and HFO in this study, respectively (seen in Fig. 2 (e)). In addition to the direct emission of unburned fuel components, VOCs also could be emitted from the pyrosynthesis process of the fuel in the cylinder (Radischat et al., 2015). In order to explore the relationship between chemical composition of low-sulfur content fuel and VOCs emission, n-alkanes, b-alkanes and aromatics in the fuels from OGVs were tested (Liu et al., 2022) (seen in Table S6 for details). Obviously, diesel had higher content of n-alkanes and b-alkanes than HFO, and aromatics were the opposite. It could be seen from Fig. S3 that both the $EF_{Alkanes}$, $EF_{Alkenes}$ and $EF_{halohydrocarbons}$ from ships with diesel presented higher levels compared with that of HFO. $EF_{Aromatics}$ and other components showed the opposite trends. While no obvious difference of EF_{OVOCs} was observed between diesel and HFO. Emission characteristics of VOC main components were basically consistent with fuel composition in this study. It could be provided that the composition of fuel did have significant impact on VOC emissions.

To further explore the impact of sulfur content of fuel on VOCs emissions, EF_{VOCs} of low-sulfur content fuel (<0.5% m/m) and high-sulfur content fuel (≥0.5% m/m) in this study and previous studies were summarized in Fig. 2 (f). The average EF_{VOCs} from low-sulfur content fuel was significantly higher than that of high-sulfur content fuel, with almost 3.4 times. This indicated that when the fuels were switched from high sulfur to low sulfur, there was dramatic increase in VOCs emissions. Low-sulfur content fuels are usually produced in three ways, including blending technique that use light low-sulfur oils mixed with heavy high-sulfur oils, heavy oil hydrogenation technology that remove sulfur through hydrogenation of high-sulfur residual oil, and biological desulfurization technology that use microbial enzymes catalyze and oxidate the organic sulfur in oil, convert it into water-soluble sulfide and then remove (Kuimov et al., 2016). Among these, blended low-sulfur oils are the most widely used oils (Zhang, 2019;Han et al., 2022). Except for light low-sulfur oils mixed during the production of low-sulfur oils, other non-petroleum refined oils, such as coal tar and chemical waste are also added. Consequently, emission factors as well as the composition of VOCs have changed significantly. Since low-sulfur content fuels (<0.5% m/m) have been using worldwide since 2020, and 0.1% (m/m) in ECAs since 2015, it would imply that the impact of fuel type on VOCs emissions needed to be given sufficient attention.

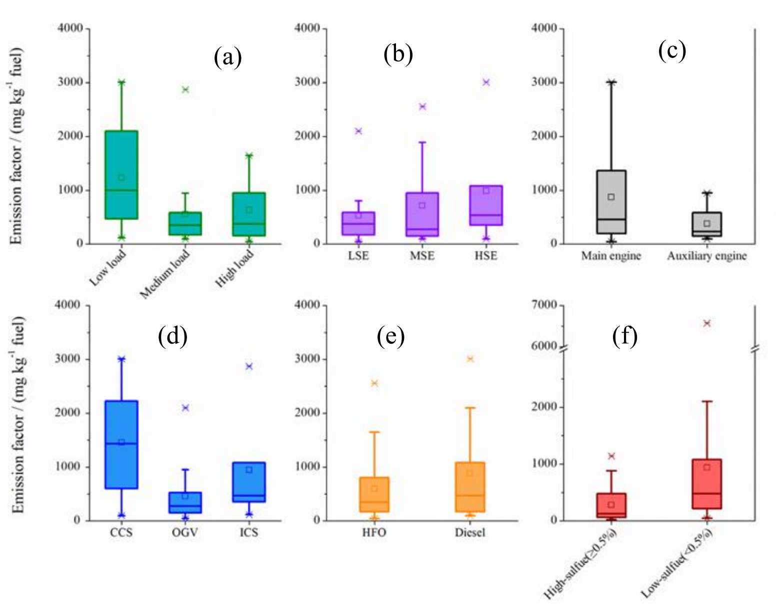

Figure 2 Box-whisker plots of VOC emission factors under different influence factors

3.3 Profiles and diagnostic characteristics of VOCs

3.3.1 Profiles of VOCs

Profiles of VOCs from the three types of test ships (CCS, OGV and ICS) under different engine types (main engine and auxiliary engine) and fuels (HFO and diesel) showed obvious differences (Fig. 3). 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

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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.

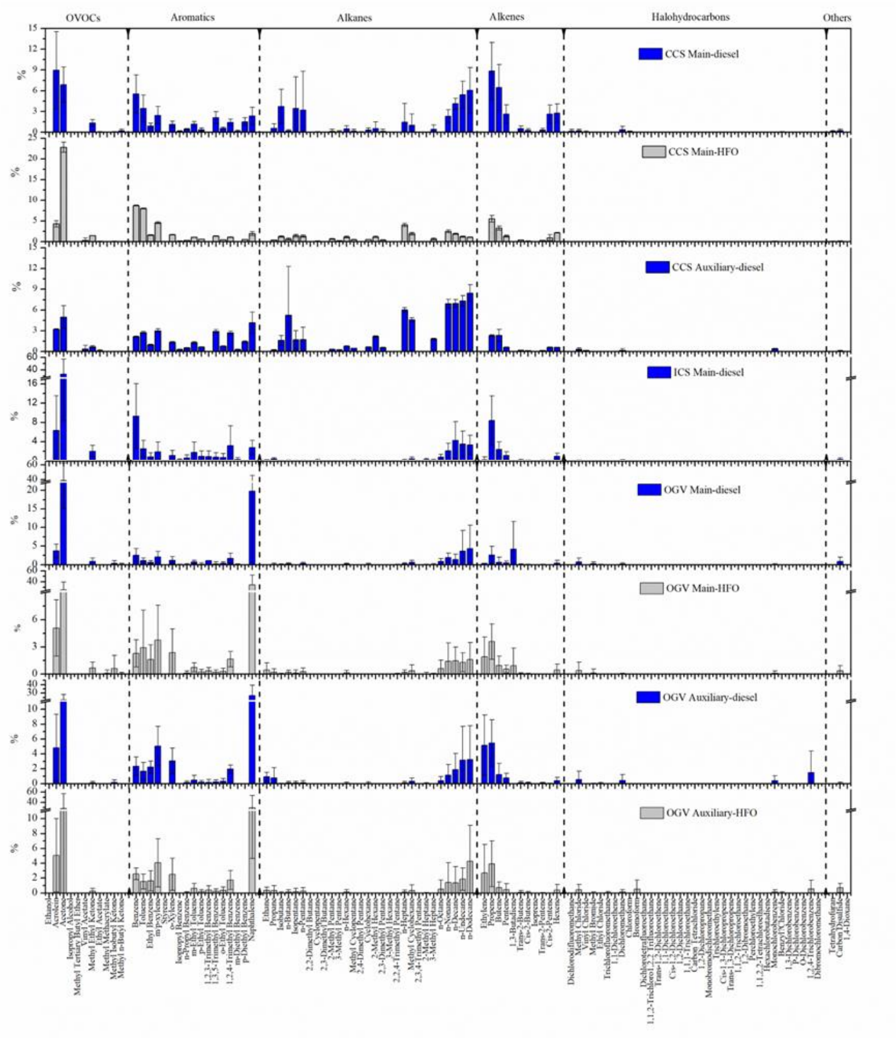

Figure 3 Profiles of VOCs from test ships under different engine types and fuels

The top 25 VOC species from the test cargo ships are presented in Table S7. It could be seen that most of the top 25 VOC species emitted from exhausts were the same but with different rankings for different engine types under different fuels. For example, OVOCs, alkenes and aromatics were the most abundant VOC species for the main engines of CCS and ICS, while alkanes were ranked as the highest content VOC species for auxiliary engine. As mentioned above, naphthalene and acetone were the absolute highest two VOC species for OGVs, followed by alkenes, OVOCs and aromatics from exhausts of HFO fuel, but alkenes, OVOCs and alkanes from exhausts of diesel fuels. This high naphthalene emission has also been shown in other studies (Radischat et al., 2015;Huang et al., 2018c;Yeh et al., 2023). The unusually high naphthalene from OGVs needed to be noted. Naphthalene was mainly formed during the pyrolyzation from incomplete combustion and direct emission of unburned fuel components (Radischat et al., 2015). A recent study reported that the addition of additives including naphthalene to low-sulfur fuel during the blended fuel manufacturing process to improve stability could lead to an increase in PAHs, especially naphthalene (Yeh et al., 2023). To further explore the extent to which the content of naphthalene in fuel affects EFs of naphthalene in ship exhaust, several chemical compositions such as alkanes and aromatic contents in fuels of the test OGVs were measured and shown by Liu et al. (2022) (Seen in Table S6). Results showed that the average naphthalene content in HFO was almost 30 times higher than that in diesel. When the engine was operated in the same operating condition, higher $EF_{\text{naphthalene}}$ was observed from HFO than diesel. Therefore, we infer that chemical component in fuel does influence the emission of PAHs including naphthalene in the exhaust. Besides, VOCs with lower molecular weights such as acetone and acrolein were the dominant OVOCs compounds in this study. The main reason is probably as follows: OVOCs compounds are typically derived from the oxidation of VOCs with incomplete combustion (Hao et al., 2014), while VOCs with lower molecular weights have a higher chance to be oxidized to form oxides than those with higher molecular weights which are often broken up to VOCs with less carbon number during the oxidation process (Wang et al., 2020).

Furthermore, characteristics of VOCs based on carbon number are also given and discussed in this study. The detected VOC species were classified into 12 groupings, from C1 to C12 (Fig. S5). Different types of ships with different fuels showed obvious differences in components. For example, C3 VOCs were found to be the most important species for all test ships, while C10 showed much higher mass fractions from OGVs than other ships, which was caused by the high naphthalene content. The same as VOCs profiles, ICSs and scientific research ships presented very similar VOCs mass fraction distributions of the 12 groupings. Besides, except for the auxiliary engine of CCS with diesel oil, the OGVs emitted comparatively higher high-carbon number (C7-C12) components than low-carbon number (C1-C6) components.

3.3.2 Diagnostic characteristics of VOCs

Diagnostic ratios of pair species, such as toluene to benzene (T/B), ethylbenzene to m,p-zylene (E/X), n-butane to isopentane (n-Bu/i-Bu) and isopentane to n-pentane (i-P/n-P), are always used to identify potential emission sources (Zhang et al., 2016b;Li et al., 2021;Song et al., 2018;Song et al., 2020). These ratios from ship exhausts in this study are shown in Table S8. T/B was further analyzed here as it is the most wildly used diagnostic ratio among them. It was reported in previous study that the T/B ratios were <1 for biomass/biofuel/coal burning, 1 to 10 for vehicle emissions, and >1 for solvent applications or industrial processes (Zhang et al., 2016b). In this study, the T/B ratios varied between 0.29 and 1.28 from ship exhausts, which were overlapped with biomass/biofuel/coal burning sources to some extent. However, it could be considered to distinguish on-road diesel vehicles with a T/B ratio of 1.5 ± 0.8 (Wang et al., 2013;Yao et al., 2015) and non-road diesel construction vessels with a T/B ratio of 1.4 ± 1.3. The results were similar with that of 0.45 - 0.57 from Wu et al. (2020) and 1.07 from Xiao et al. (2018), but significantly differed from that of 4.81 - 42.8 from Huang et al.(2018c).

In order to overcome the overlapping effects of the T/B ratio among different emission sources and better distinguish ship emissions from other emission sources, a ternary diagram of the relative compositions of Benzene, Toluene, and Ethylbenzene from ship exhausts in this study was presented in Fig. 4. The B:T:E ratios were 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.

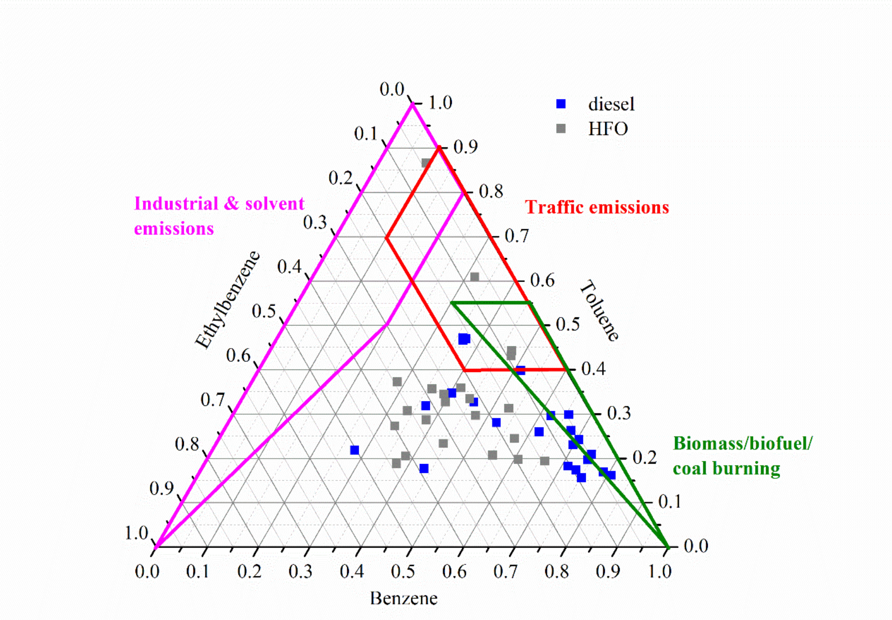

Figure 4 Relative proportions of benzene, toluene and ethylbenzene from the ship exhausts

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}

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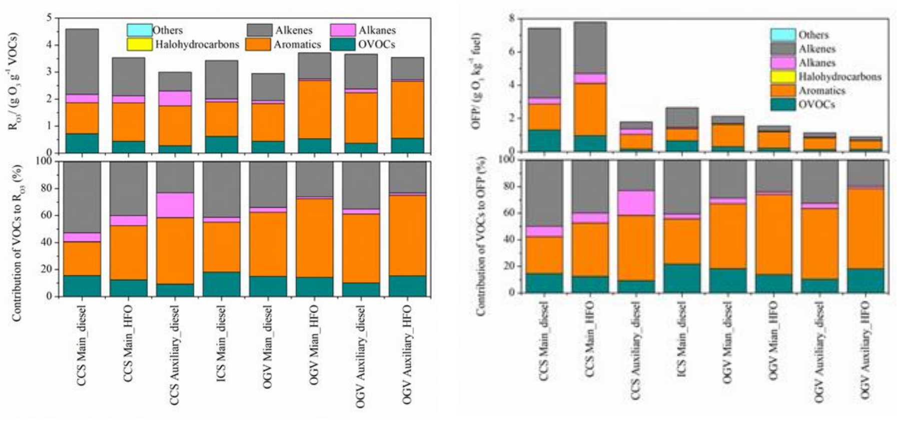
VOCs for the test ships (presented in Fig. 5 and Table S9) in this study, meaning there was diversity of ozone reactivities in VOCs from different ships, which was due to the different shares of VOC species emitted from different ships with different fuels. The R_{O_3} values were within the range of 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. 5 (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. 5 (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. 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)

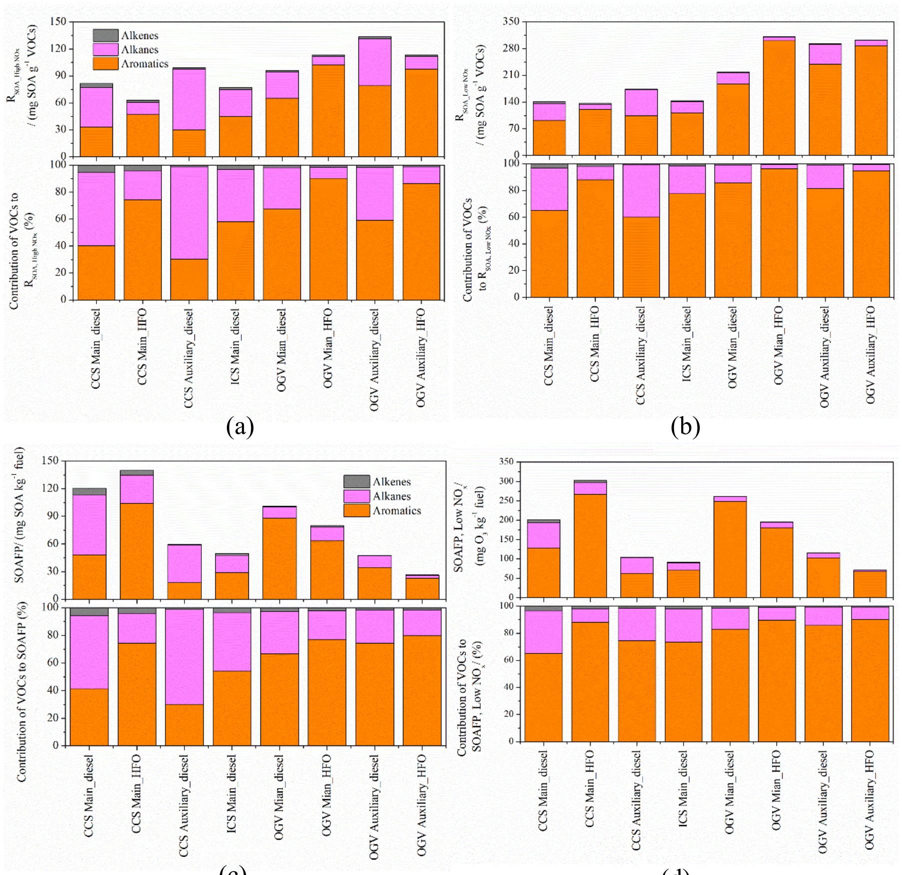
Figure 5 (a) The normalized ozone reactivity (R_{O_3}, g O_3 g^{-1} VOCs) and contribution of VOC species to R_{O_3}, (b) ozone formation potential (OFP, g O_3 kg^{-1} fuel) and contribution of VOC species to OFP

3.4.2 SOA formation potential

The same as R_{O_3}, normalized SOA reactivities (R_{SOA}) under high-NO_x and low-NO_x conditions were also estimated and presented in Fig. 6 (a), (b), and Table S9. The 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. 3. 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. 6 (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 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.



(a) (b)

(c) (d)

Figure 6 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 S10 and Table S11. 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.

While trimethyl benzene, propene and acrolein were ranking as the top VOCs species to OFP for the auxiliary engine of CCSs. As for OGVs, naphthalene was the most contributing VOC species to O_3, followed by propene, acrolein, 1,3-butadiene and xylene etc. As shown in Table S11, the top VOCs species contributed to SOAFP were benzene, naphthalene, n-dodecane, n-undecane and xylene etc. for all the test ships. Naphthalene was undoubtedly the most contributing VOC species to SOAFP for OGVs. In conclusion, it was obvious that as the important common contributors to both O_3 and SOA, aromatics should be prioritized in control. Besides, VOCs species with high O_3 reactivities also need to be paid enough attention, such as alkenes, even though with low emission factor levels.

4. Conclusions and atmospheric implications

Shipping emission is a non-ignorable anthropogenic emission source of air pollutants, especially in coastal areas. Therefore, more and more strict emission control regulations have been implemented globally. For example, the maximum fuel sulfur content has been set to be 0.5% (m/m) worldwide by 2020, and 0.1% (m/m) in 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. The mandatory use of low-sulfur fuels has reduced the emissions of SO_2 and PM significantly on ships, while it also leads to very large uncertainty on VOCs emission. In view of this, on-board test of VOCs from 9 typical cargo ships with low-sulfur fuels in China were carried out in this study.

Results showed that EF_{VOCs} varied largely from 0.09 to 3.01 g kg^{-1} fuel, with domestic coastal cargo ships (CCSs) had the highest levels and ocean-going vessels (OGVs) the lowest. The test ships in this study presented comparable EF_{VOCs} level with other studies. However, the measured EF_{VOCs} varied largely among different studies due to complex reasons such as different detected VOC species, different engine types and fuel qualities. OVOCs and aromatics were the main components of the detected VOC species, followed by alkanes, while alkenes, halohydrocarbons and other quantified species only contributed small fractions.

The emission level and component of VOCs from ship exhaust could be affected by complex influence factors such as operating condition, engine type, ship type and fuel type. For example, EF_{VOCs} had the lowest level when the engines were operating in medium loads, and the highest in low loads. Besides, with the increase of engine speed, the EF_{VOCs} showed an increasing trend. The average EF_{VOCs} from the main engines was 2.3 times that of auxiliary engines in this study. Moreover, the EF_{VOCs} varied obviously under different types of ships, with CCSs having the highest levels and OGVs the lowest. It needs to be noted that fuel type could influence the emission of EF_{VOCs} significantly. The switch of fuels from heavy fuel oil to diesel increased EF_{VOCs} by 48% on average in this study. A bigger cause for concern is that from the summarized results in this study and previous studies, the average EF_{VOCs} from low-sulfur content fuel was significantly higher than that of high-sulfur content fuel, with almost 3.4 times.

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 due to the use of low-sulfur fuels, while benzene, toluene and m/p-xylene were the highest content aromatic substances for other ships. We also found that benzene, toluene, and ethylbenzene ratio of 0.5:0.3:0.2 on average could be considered as a diagnostic characteristic to distinguish ship emission from other emission sources.

The OFP in this study 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. The SOAFP in this study were ranging from 71.5 to 303 mg SOA kg^{-1} fuel under low-NO_x conditions. 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. It's also worth noting that when the fuels were switched from high sulfur

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to low sulfur, there was obvious increase in OFP and SOAFP, especially for OGVs. Moreover, aromatics were the most important common contributors to O_3 and SOA in ship exhausts, which need to be controlled with priority.

It could be concluded from this study and previous studies that either the switch of high-sulfur HFO to low-sulfur HFO, or low-sulfur HFO to ultra-low-sulfur diesel, VOCs emissions from OGVs increased significantly, which further promoted the formation potential of O_3 and SOA, especially in coastal areas. Therefore, the implementation of the ultra-low-sulfur oil policy in the near future is likely to further increase the emission of VOCs, which needs to be optimized. Besides, the results herein indicated that aromatics are absolutely the most important common contributors to OFP and SOAFP, which need to be controlled with priority in ship exhausts. Since aromatics are typically from the polymerization, improving engine combustion conditions of ship engine is an effective way to reduce O_3 and SOA from ship exhausts, especially in coastal and inland areas. Moreover, organic matters such as naphthalene from ship exhausts with low-sulfur HFO should be explored and considered to be potential tracers to identify ocean going ships from coastal and inland ships. Lastly, the EFs and profiles of VOCs emitted from ship exhausts varied significantly, one important reason was that the sample size of on-board measured VOCs was too small, in addition, the detection methods and detected VOCs species differed greatly among different studies. Therefore, much more on-board tests need to be implemented and standard VOCs detection method as well as essential VOCs species should be clarified, especially under current low-sulfur regulation.

Author contributions

FZ, YZ, CH, HW, YC and GW conceptualized and designed the study; BX, ZL, CT, XW, YH, MC, and YC performed the measurements; FZ, RL, CW, YL, SZ, and GW analyzed the data. FZ wrote the manuscript draft; All the authors reviewed, edited, and contributed to the scientific discussion in the manuscript.

Competing interests

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

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