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Dramatic increase of reactive VOC emission from ships at berth after implementing the fuel switch policy in the Pearl River Delta Emission Control Area

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Abstract. Limiting the fuel sulfur content (FSC) is a widely adopted approach to reduce ship emissions of sulfur dioxide (SO_2) and particulate matters (PM) particularly in emission control areas (ECA), but its impact on the emission of volatile organic compounds (VOCs) is still not well understood. In this study, emissions from ships at berth in Guangzhou, south China, were characterized before and after implementing the fuel switch policy with a FSC limit of 0.5% in the Pearl River Delta ECA in south China. After implementing the fuel switch policy, the emission factors (EFs) of SO_2 and $PM_{2.5}$ for coastal vessels dropped by 78% and 56% on average, respectively; the EFs of non-methane hydrocarbons (NMHCs), however, reached 1807 ± 1746 mg/kg, about 15 times that of 118 ± 56.1 mg/kg before implementing the new policy. This dramatic increase in the emission of NMHCs might be largely due to the replacement of high-sulfur residual fuel oil with low-sulfur diesel or heavy oils, which are typically more rich in short-chain hydrocarbons. Moreover, reactive alkenes overtook alkanes to become the dominant group among NMHCs and low carbon number NMHCs, such as ethylene, propene and isobutane, became the dominant species after the new policy. As a result of the largely elevated EFs of reactive alkenes and aromatics after the new policy, for per kilogram of fuel burned, emitted NMHCs had nearly 29 times larger ozone formation potentials (OFPs) and about 2 times higher secondary organic aerosol formation potentials (SOAFPs). Unlike coastal vessels, river vessels in the region used diesel fuels all along and were not affected by the fuel switch policy, but their EFs of NMHCs were even 90% larger than that of coastal vessels after implementing the new policy, with about 120% larger fuel-based OFPs and 70-140% larger SOAFPs. The results from this study suggest that while the fuel switch policy could effectively reduce SO_2 and PM emissions and thus help combat PM2.5 pollution, it would also lead to greater emissions of reactive VOCs, that may threatens ozone pollution control in the harbor cities. This change for coastal or ocean-going vessels, along with the large amounts of reactive VOCs from river vessels, raises regulatory concerns for ship emissions of reactive VOCs.

1 Introduction

World seaborne trade volumes are estimated to have accounted for over 80% of total world merchandise trade (UNCTAD, 2016). The controls on ship emissions, are however far less stringent than on land emission sources, and it is no surprise that ship engines are among the world's highest polluting combustion sources in terms of per ton of fuel consumed (Corbett and Fischbeck, 1997). As a large amount of marine ship emissions occur within 400 km of coastlines (Fu et al., 2017), ship emissions would give rise to air pollution in coastal areas, and thus contribute substantially to environmental burden of disease (Corbett et al., 2007; Lv et al., 2018; Feng et al., 2019; Ramacher et al., 2019; Wang et al., 2019a). Therefore, global efforts have been made to regulate and prevent health risks from ship emissions particularly in harbor cities.

An important intervention policy by the International Maritime Organization (IMO) for reducing ship emissions is the designation of emission control areas (ECA) where more stringent limit of fuel sulfur content (FSC) is implemented (IMO, 2017). This ECA approach has brought about significant improvements in ambient air quality for coastal areas (Lack et al., 2011; Tao et al., 2013; Contini et al., 2015; Zetterdahl et al., 2016). In the North Sea regions, for example, the new policy restricting FSC below 1.5% since 2007 resulted in reduction rates of 42%, 38% and 20%, respectively, for ambient

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concentrations of sulfur dioxide (SO_2), sulphate aerosols and ammonium aerosols that were related to ship emissions (Matthias et al., 2010); monitoring in U.S. coastal states revealed significant reductions in ambient $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) from residual fuel oil (RFO) combustion due to marine vessel fuel sulfur regulations in the North American Emissions Control Area (NA-ECA) (Kotchenruther, 2017); in the Marmara Sea and the Turkish Straits, ship emission of SO_2, $PM_{2.5}$ and PM_{10} (particulate matter with an aerodynamic diameter less than 10 μm) were projected to reduce by 95%, 67% and 67%, respectively, if FSC were restricted below 0.1% (Viana et al., 2015). Consequently, with the increasingly stringent control over land-based emission sources, limiting ship emissions has gradually stood out as an effective measure to combat air pollution in coastal zones.

Intervention measures on ship emission, however, are mostly targeted on SO_2 and PM, and much less attention has been paid to other pollutants from ship emissions, such as nitrogen oxides (NO_x) and volatile organic compounds (VOCs), although they are also important precursors to ozone and secondary aerosols (Chameides et al., 1992; Odum et al., 1997; Atkinson, 2000; O'Dowd et al., 2002). Cooper et al. (1996) found that many reactive VOCs, like ethylene, propylene and isobutylene, were present in emission from passenger ferries in the Skagerak-Kattegatt-öresund region; Agrawal et al. (2008) reported emissions of VOCs including carbonyls, 1, 3-butadiene, aromatics and n-alkanes from the main engine, auxiliary engine and boiler of a Suezmax class vessel; Agrawal et al. (2010) and Murphy et al. (2009) further calculated their emission factors based on shipboard platform measurements and aircraft-based measurements for the main engine of a PanaMax Class container ship. Very recently, Huang et al. (2018a) tested a Handysize-class bulk carrier under at-berth, maneuvering and cruising condition, and found single-ring aromatics accounted for 50-74% of VOCs with toluene as the most abundant species; Xiao et al. (2018) tested 20 ships at berth in the Jingtang Port in north China and found that alkanes and aromatics instead dominated in the VOCs emissions. As a matter of fact, previous studies have already demonstrated that ship emissions were able to impact the ambient ozone formation in coastal cities (Wang et al., 2019b). Meanwhile, ship emissions could contribute substantially to NO_x in the oceans and coastal areas (Song et al., 2010; Tagaris et al., 2017). So, even for lowering ambient ozone levels, there is a growing concern about ship emissions of ozone precursors, including NO_x and VOCs.

China hosts many of the world's busiest ports, sharing about 10% of global ship emissions (Fu et al., 2017). To reduce ship emissions, China has also designated three ECAs, namely the Pearl River Delta (PRD), the Yangtze River Delta and the Bohai Rim, where ships are required to gradually switch to fuels with a FSC limit of 0.5% from January 1, 2017 to December 31, 2019. As estmiated by Liu et al. (2018), this fuel switch policy could lower atmosheric concentrations of SO_2 and $PM_{2.5}$ by 9.5% and 2.7%, respectively, in the coastal region of the PRD in south China. A recent field observation campaign in Jingtang port also reveal that, due to the implementation of the fuel switch policy, ambient levels of SO_2 dropped from 165.5 ppb to 67.4 ppb while particulate vanadium (V), a marker of ship PM emission (Agrawal et al., 2009; Pey et al., 2013; Perez et al., 2016; Tao et al., 2017), decreased drastically from 309.9 ng/m^3 to 9.1ng/m^3 (Zhang et al., 2019). However, it is still unknown whether the fuel switch policy will bring about changes in ship emissions of VOCs.

For ships at berth, their main engines are shut down and auxiliary engines become the only emission source. As a ship is usually at berth for one day or more and the place where its auxiliary engine discharges pollutants is usually closer to densely

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populated areas, so emissions from ship at berth could have a larger impact on coastal areas (Cooper et al., 2003). In the present study, we conducted shipboard platform measurements of air pollutants emitted from coastal vessels at berth in Guangzhou Port in the PRD region in south China in 2017 and 2018 after implementing the fuel switch policy, and compared the results with those from a similar campaign previously conducted also by us in 2015 and 2016 before implementing the fuel switch policy. Apart from emissions of pollutants like $PM_{2.5}$ and SO_2, in this study we will put our focus on emissions of VOCs and aim to investigate changes in composition profiles and emission factors of VOCs from ships at berth and to assess the potential influence on the formation of ozone (O_3) and secondary organic aerosol (SOA) due to the fuel switch policy. Besides, river vessels, which commonly use diesel oil as fuel and did not need to implement the fuel switch policy at the moment, were also tested in 2017 in comparison with the coastal vessels that had implemented the policy.

2 Experimental section

2.1 Study area

Guangzhou Port is located in the estuary of the Pearl River and the center of the PRD region, adjacent to Hong Kong and Macao (Fig. 1). In 2017, cargo throughput of Guangzhou Port reached 590 million tons, ranking the fifth in China and the sixth in the world; and the container throughput in Guangzhou port reached 20.37 million TEU, ranking the fifth in China and the seventh in the world (China Port Press, 2018). In 2013, Guangzhou Port was estimated to contribute near 40% ship emissions of SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$ and VOC from nine port groups in the PRD bay area (Li et al., 2016a).

2.2 Test ships and fuel types

As required, FSC for ships at berth should be lower than 0.5% since 1 January 2017. In the PRD, measures are even more stringent that ships at berth should use diesel oil that conforms to Chinese national standard GB252-2015 (Standards Press of China, 2015). Table 1 presents the basic information of 11 tested ships, among which ships C and D were tested both before and after the implementation of the fuel switch policy. According to the classification of ships as by Li et al. (2016a), ships H, I, J and K were river vessels, which were not regulated because they already used diesel oil as fuel before implementing the fuel switch policy, and others were coastal vessels and none ocean-going ships were tested in this study.

2.3 Portable emission measurement system

The ship exhaust sampling system is composed of flue gas dilution system, flue gas analyzer, particulate matter sampler and air sampler (Figure 2). The ship exhaust first enters the Dekati® ejector dilutor (DI-1000, Dekati Ltd., Finland) from the sampling nozzle, spilt into four ways after diluted with clean air: one for air sampling by canisters and Teflon bags after passing through a filter; the other two for collecting $PM_{2.5}$ samples with 47mm Teflon filters (Whateman, Mainstone, UK) and 47mm quartz fiber filters (Whateman, Mainstone, UK), respectively, after the diluted exhaust was mixed well in a stay cabin, and then passing through a $PM_{2.5}$ cutting head; the last is the vent. Before dilution, trace gases in the ship exhaust was directly

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measured by a flue gas analyzer (F-550, WOHLER, Germany), and air sample was also collected simultaneously by canisters and Teflon bags. The dilution ratios of the flue gas dilution system were then can be more accurately calculated by comparing CO_2 concentrations in samples before and after the dilution. In addition, 500ml fuel oil being used by each ship was collected in brown glass bottles for determining its carbon and sulfur contents, and analyzing C_{11}-C_{36} hydrocarbon species. Non-methane hydrocarbons (NMHCs) in air samples collected in canisters and Teflon bags were analyzed by using a Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled to an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). More details about the analysis were described elsewhere (Zhang et al., 2013; 2015); CO_2/CO concentrations were analyzed by gas chromatography (Agilent 6980GC, USA) with a flame ionization detector and a packed column (5A molecular sieve, 60/80 mesh, 3 m × 1/8 in.) (Liu et al., 2015). The particulate samples collected by quartz filters were analyzed by a DRI Model 2015 multi-wavelength thermal/elemental carbon (OC/EC) analyzer (Li et al., 2018). The carbon contents of ship fuels were analyzed by an elemental analyzer (Vario EL III, Elementar, Germany), and the sulfur contents were analyzed by the conversion to sulfate with an Oxygen Bomb Combustion (IKA AOD1, IKA, Germany) followed by determination of sulfate with an Ion Chromatography (883 Basic IC plus, Metrohm, Switzerland) (Li et al., 2016b). C_{11}-C_{36} hydrocarbons in fuels were analyzed with an Agilent 7890/5975C gas chromatography/mass spectrometer detector (GC/MSD) equipped with a HP-5MS capillary column (30 m in length, 0.25 mm I.D., 0.25 μm film thickness) (Yu et al., 2018) after dissolving 50μl fuel oil in 1ml n-hexane and removing the insoluble compositions through filtration.

2.4 Calculations of emission factors

Emission factors (EFs) were calculated by carbon balance approach, which assumes that the carbon in fuel is transformed into the carbon in CO_2, CO, PM and VOCs, the EF of CO_2 is determined as following (Liu et al., 2014):

$$EF_{CO2}=\frac{C_F \cdot \Delta[CO_2]}{\Delta C_{CO2}+\Delta C_{CO}+\Delta C_{PM}+\Delta C_{VOCs}}, \quad (1)$$

where EF_{CO2} is the emission factor of CO_2 in grams per kilogram of fuel burned (g kg^{-1}); C_F is the mass fraction of carbon in fuel (g kg^{-1}); $\Delta[CO_2]$ is the incremental concentrations of CO_2; ΔC_{CO2}, ΔC_{CO}, ΔC_{PM}, ΔC_{VOCs} represent the carbon mass concentrations of CO_2, CO, PM and VOCs after subtracting their background concentrations.

The EF of a pollutant *i* is calculated by:

$$EF_i=\frac{\Delta[i]}{\Delta[CO_2]}\times EF_{CO2}, \quad (2)$$

where $\Delta[i]$ is the incremental concentrations of pollutant *i*.

According to the standard method ISO 8178-1, the sulfur in fuel is assuming to be fully transformed into SO_2, so we use Eq. (3) to calculate the EF of SO_2 (Zhang et al., 2018a):

$$EF_{SO2}=S\%\times\frac{64}{32}\times10^3, \quad (3)$$

where EF_{SO2} is the EF of SO_2 in g kg^{-1}, and S% represents FSC.

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3 Results and discussion

3.1 Changes in EFs for ships at berth

The FSC for the tested coastal vessels on average decreased from 2.2 ±0.5% before to 0.4 ±0.5% after implementing the fuel switch policy, though there are some ships, like ship G, violating the regulation with FSC still above the limit of 0.5% (Table 1). As a matter of fact, the ship fuel had transferred from residual fuel oil to diesel oil or heavy oil (Fig S1), and the compositions of fuels used by the coastal vessels tended to have more low-carbon number hydrocarbons as demonstrated by their total ion chromatograms (Fig S2). This change in fuel compositions may also explain why the mass percentages of <C6 VOCs (VOCs with carbon numbers below 6) in total VOCs in ship exhaust increased from 8.5%-27.3% to 44.4%-86.6% after implementing the fuel switch policy(Fig S3).

As shown in Table 2, the EFs for SO_2, which are independent of the combustion system (Corbett et al., 1999), decreased by 78.0% from 44.0 ±10.5 g kg^{-1} to 9.66 ±7.97 g kg^{-1} on average. Fuel-based EFs for CO_2, CO, NO_x, NMHCs, $PM_{2.5}$, OC and EC, however, are much more complicated as they are not only related to properties of the fuels, but also heavily influenced by performance of combustion system. The comparison before and after implementing the fuel switch policy is also challenged by the fact that the tested coastal vessels during the two campaigns are not the same ones and that we have tested a very limit number of ships. Nevertheless, ships C and D had been tested both before and after the new policy and we can make a comparison for them. The EF of CO_2 for ships C and D slightly increased from 3025 g kg^{-1} and 3069 g kg^{-1} before to 3131 g kg^{-1} and 3196 g kg^{-1} after the new policy; the EF of CO for ship C increased from 3.80 g kg^{-1} to 6.16 g kg^{-1}, but that for ship D decreased from 14.6 g kg^{-1} to 6.41 g kg^{-1}; the EF of NOx for ship C slightly decreased from 19.9 g kg^{-1} to 19.0 g kg^{-1}, while that for ship D decreased from 51.5 g kg^{-1} to 31.1 g kg^{-1}.

Like EFs of SO_2, the EFs of $PM_{2.5}$ also decreased significantly after the new policy. For example, EFs of $PM_{2.5}$ for ship C decreased by 45.6% from 1.02 g kg^{-1} to 0.56 g kg^{-1} and that for ship D decreased by 64.5% from 2.44 g kg^{-1} to 0.87 g kg^{-1}; similar to that of $PM_{2.5}$, the EFs of OC and EC for ship C decreased by 28.7% and 56.1%, and that for ship D decreased by 60.5% and 63.0%, respectively. Therefore, after implementing the new policy, the changes in EFs of CO_2, CO and NO_x were not significant for coastal vessels, but the EFs of SO_2, $PM_{2.5}$ and carbonaceous aerosols did become lower.

Compared to SO_2 or other pollutants, NMHCs from coastal vessels showed more dramatic changes in their EFs. As showed in Table 2, EFs of NMHCs ranged 60.7-197mg kg^{-1} with an average of 118 ±56.1 mg kg^{-1} before, and they ranged 292-5251mg kg^{-1} with an average of 1807 ±1746 mg kg^{-1} after implementing the fuel switch policy. For ships C and D that were tested both before and after the new policy, the EF of NMHCs for ship C increased about 6 times from 106 mg kg^{-1} to 706 mg kg^{-1}, and that for ship D also increased about 4 times from 60.7 mg kg^{-1} to 292 mg kg^{-1}. This great change in our study was consistent with that based on shipboard platform measurements by Copper et al. (2003), who also found the EFs of hydrocarbons from passenger ferry at berth increased from 0.29-0.57 g kg^{-1} to 1.71 g kg^{-1} after replacing the residual oil (FSC=0.53%) marine gasoil (FSC=0.09%) (Table 3).

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There are only a few previous studies available about air pollutants from coastal vessels at berth (Table 3). The ranges for EFs of CO_2, PM, TVOC, SO_2 in our study similar to those reported by Cooper et al. (2003), but our EFs of CO were much higher and our EFs of NO_x instead were much lower.

River vessels sail in inland rivers and many studies had investigated the emission from river vessels under crusing condition (Fu et al., 2013; Peng et al., 2016; Zhang et al., 2016), but no studies are available about their emissions at berth. In this study, river vessels used diesel as fuel, and they were not affected by the fuel switch policy. As showed in Table 3, for the tested river vessels (ships H, I, J and K), the EFs of CO_2 (3014 ±99.0g ₭g^{-1}) and NO_x (28.1 ±24.5 g ₭g^{-1}) were close to those for coastal vessels; the EF of CO (77.9 ±62.5 g ₭g^{-1}), however, was nearly 4 times larger than that of coastal vessels after implementing the fuel switch policy, and also larger than that reported for engineering vessel and research vessels under crusing condition with the maximum of 30.2 g ₭g^{-1} (Zhang et al., 2016); their EF of SO_2 was as low as 0.69 ±0.36 g ₭g^{-1}, while the EF of NMHCs was as high as 3.36 ±2.77 g ₭g^{-1}, 85.6% larger than that for coastal vessels after implementing the policy, but fell in the range for research vessels (1.24-4.18 g ₭g^{-1}) as reported by Zhang et al. (2016).

3.2 EFs of grouped and individual NMHCs

There are very sparse data about the EFs of grouped and individual NMHCs (Cooper et al., 1996; Murphy et al., 2010; Agrawal et al., 2008; 2010), especially for ship emissions at berth. In this study, 68 species of NMHCs, including 29 alkanes, 21 alkenes, 1 alkyne and 17 aromatics, were determined. As showed in Fig. 3 and Table 4, for coastal vessels before implementing the fuel switch policy, alkanes dominated the emissions among NMHCs with a share of 49.4 ±24.1% and an EF of 66.0 ±48.3 mg kg^{-1}, while aromatics and alkenes accounted for 27.9 ±12.3% and 21.9 ±11.9% of NMHCs with EFs of 29.2 ±8.6 mg kg^{-1} and 21.9 ± 4.5 mg kg^{-1}, respectively. However, there were dramatic changes in the compositions of NMHCs after implementing the fuel switch policy. Alkenes overtook alkanes to become the most abundant group with a share of 43.1% ± 12.8% and an EF of 924.6 ±1314.9 mg kg^{-1}, followed by alkanes (33.0 ±17.5%, 339.2 ±176.6 mg kg^{-1}) and aromatics (16.1 ±4.1%, 247.3 ±236.4 mg kg^{-1}).

As for EFs of individual NMHCs, the top 25 species remain unchanged after the implementation of the fuel switch policy, but their rankings have changed (Table S1). As showed in Fig. 4 and Table 4, n-undecane and n-dodecane were still among the dominant species, although their percentages decreased a lot. Their EFs did not change as much, which were 22.5 ±18.2 mg kg^{-1} and 21.5 ±17.1 mg kg^{-1} before and 22.5 ±24.6 mg kg^{-1} and 32.1 ±62.1 mg kg^{-1}, after the new policy, respectively. Instead, EF of isobutane increased from 0.06 ±0.07 mg kg^{-1} to 94.3 ±62.2 mg kg^{-1}. Striking increase in EFs was also observed for alkenes. Ethylene overtook 1-hexene to become the most abundant alkene, with its EF increasing from 2.8 mg kg^{-1} to 602 mg kg^{-1} on average. Propene, with the EF of 5.5 ±1.5 mg kg^{-1} before the fuel switch policy, had the second largest EF of 198 ±260 mg kg^{-1} after the fuel switch, an increase of over 30 times. 1-Hexene, which ranked the first among alkenes with the EF of 5.9 ±3.8 mg kg^{-1} before the fuel switch policy, also increased by 1.9 times to 17.3 ±19.4 mg kg^{-1}. The mass percentages of acetylene, the only alkynes detected, increased from 0.9 ±0.6% to 7.5 ±7.6%, with its EF rose from 0.9 ±0.6 mg kg^{-1} to 328.7 ±605.4 mg kg^{-1}. Benzene and toluene were dominant aromatic species before and after the new policy. Their EFs increased

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from 11.9 ±4.6 mg kg^{-1} and 6.0 ±1.2 mg kg^{-1} before to 116.5 ±200.8 mg kg^{-1} and 33.3 ±42.5 mg kg^{-1} after implementing the policy, respectively.

The composition of NMHCs from river vessels were similar to that of coastal vessels after implementing the fuel switch policy. As showed in Fig. 3 and Table S1, alkenes also dominated the emission of NMHCs with a share of 45.1 ±5.9%, while aromatics and alkenes accounted for 33.7 ±4.8% and 14.3 ±4.1%, respectively. For individual NMHCs, the most abundant species also were ethylene, isobutene, propene, acetylene, n-decane and benzene. However, the EFs of NMHCs for river vessels were 1.9 times that of coastal vessels after implementing the fuel switch policy (Table 2), suggesting that VOCs emissions from river vessels might played an important role as their emission are closer to populated areas and thus should be regulated.

Very recently both Xiao et al. (2018) and Huang et al. (2018a) had carried out VOCs emission tests on ships at berth in China's ECA. Xiao et al. (2018) reported that aromatics and alkanes dominated the VOCs emission from ships at berth. Furthermore, the most abundant alkane species were n-heptane, methylcyclohexane, n-octane, n-nonane, n-decane and n-undecane, and benzene and toluene contributed 9% of the VOCs emissions; Huang et al. (2018a) also investigated the VOCs emission from ship at berth, but aromatics had a share up to 70.9%, while alkenes only accounted for 6.7%. The variety of the ship fuels might be one of the key reasons for the big differences in compositions of VOC emissions among the available studies. The new policy only restricted the FSC below 0.5%, so many types of fuels could be used in ships, as can be seen from the four types of diesels by the tested ships (Fig. S1). Nonetheless, engine designs, performance and loads during sampling might also lead to the differences (Cooper et al., 1996).

3.3 Ozone and SOA formation potentials

3.3.1 OFPs of VOCs from ship exhausts

Ozone Formation Potentials (OFPs) is the approach that uses maximum incremental reactivity (MIR) to represent the maximum contribution of VOCs to near-surface ozone formation under optimal conditions (Carter, 2009). With ships emission data in this study, the normalized ozone reactivity, (R_{O3}, g O_3 g^{-1} VOCs) and OFPs (g O_3 kg^{-1} Fuel) can be calculated as:

$$R_{O3}=\sum_i w_i \times (MIR)_i \,, \quad (4)$$

$$OFPs=\sum_i EF_i \times (MIR)_i \,, \quad (5)$$

where w_i is the mass percentage of total VOCs emissions for *i* species.

As described in Fig. 5, the R_{O3} of tested coastal vessels increased by nearly 70% from 3.19 ±0.82 g O_3 g^{-1} VOCs to 5.41 ± 0.69 g O_3 g^{-1} VOCs. The main reason for the rise of R_{O3} is that shares of highly reactive alkenes (like ethylene and propene) increased among the VOCs emitted, and the contribution percentages of alkenes to R_{O3} increased from 56.4% ±13.3% to 75.7% ±13.3%. OFPs increased 28.7 times from 0.35 ±0.11 g O_3 kg^{-1} Fuel to 10.37 ±13.55 g O_3 kg^{-1} Fuel.

For river vessels, its average R_{O3} was 5.55 g O_3 g^{-1} VOCs, which was closed to that of coastal vessels after implementing the fuel switch policy, but their average OFPs (22.98 ±16.59 g O_3 kg^{-1} Fuel) was more than double that of coastal vessels. As

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showed in Fig. S4, the R_{O3} (4.22 g O_3 g^{-1} VOCs) reported by Huang et al. (2018a) for ship emission after implementing the fuel switch policy was about 20% lower than the R_{O3} (5.41 g O_3 g^{-1} VOCs) from this study, and the R_{O3} of 2.63 O_3 g^{-1} VOCs reported by Xiao et al. (2018) is even lower than the R_{O3} before implementing the policy in this study. These results also suggests that there is great diversity in ship-emitted VOCs even in different regions of China.

3.3.2 SOAFPs of VOCs from ship exhausts

Similarly, normalized secondary organic aerosols (SOA) and SOA formation potentials (SOAFPs) can also be calculated as:

$$R_{SOA} = \sum_i w_i \times Y_i \,, \quad (6)$$

$$SOAFPs = \sum_i EF_i \times Y_i \,, \quad (7)$$

where R_{SOA} is the normalized SOA reactivity (g SOA g^{-1} VOCs); Y_i is the SOA yield of VOC species *i*. Like Zhang et al. (2018), we could calculate the SOAFPs under high-NO_x and low-NO_x conditions (Ng et al., 2007). However, we should be cautious to interpret the results because intermediate volatile organic compounds (IVOCs) were not measured in this study, and this may lead to underestimate SOA yields (Huang et al., 2018b; Lou et al., 2019).

As showed in Fig. 5, under high-NO_x conditions, R_{SOA} decreased by ~75% from 0.29 ± 0.11 g SOA g^{-1} VOCs to 0.07 ± 0.08 g SOA g^{-1} VOCs, while under low-NO_x conditions R_{SOA} also decreased by 66.5% from 0.31 ± 0.09 g SOA g^{-1} VOCs to 0.11 ± 0.09 g SOA g^{-1} VOCs. This decline in R_{SOA} was resulted from the decrease in mass percentages of aromatics and alkanes, which have higher SOA yields than alkenes (Ng et al., 2007; Lim and Ziemann, 2009; Loza et al., 2014). However, with the dramatically increased EFs of VOCs, under high-NO_x conditions SOAFPs increased 1.6 times from 0.04 ± 0.03 g SOA kg^{-1} Fuel to 0.10 ± 0.09 g SOA kg^{-1} Fuel, and under low-NO_x conditions SOAFPs increased 2.5 times from 0.04 ± 0.03 g SOA kg^{-1} Fuel to 0.14 ± 0.11 g SOA kg^{-1} Fuel.

In particular, the R_{SOA} for ship F (Fig. S4) was significantly higher largely due to a higher fraction (11.5%) of n-dodecane, which has the highest SOA yield among the NMHCs. For river vessels, the R_{SOA} was the lowest in test ships, with the value of 0.04 ± 0.02 g SOA g^{-1} VOCs under high-NO_x conditions and 0.07 ± 0.03 g SOA g^{-1} VOCs under low-NO_x conditions. However, their SOAFPs was 0.17 ± 0.13 g SOA kg^{-1} Fuel under high-NO_x conditions and 0.32 ± 0.27 g SOA kg^{-1} Fuel under low-NO_x conditions, which were instead the largest due to much higher EFs.

As showed in Fig. S4, Huang et al. (2018a) reported R_{SOA} of 0.08 g SOA g^{-1} VOCs under high-NO_x conditions and 0.23 g SOA g^{-1} VOCs under low-NO_x conditions. The higher R_{SOA} are related to the higher fractions of aromatics in the VOC emissions. Xiao et al. (2018) also reported an average R_{SOA} of 0.02 g SOA g^{-1} VOCs under high-NO_x conditions, which was even lower than the R_{SOA} for river vessels in our study.

3.4 Conclusions

Ships emission control is primarily targeted on PM-related pollution and designating ECA with fuel switch policy is a widely adopted approach to combat air pollution in harbor cities. In the present study, we measured emissions from coastal vessels at berth in Guangzhou Port in the PRD region, one the three ECAs newly established since 2017, and preliminarily investigated

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the changes in emissions caused by the fuel switch policy, and further compared the results with that measured for river vessels unaffected by the new policy.

As reported by previous studies, our study also demonstrated that after implementing the fuel switch policy, the EFs of both SO_2 and $PM_{2.5}$ for coastal vessels decreased, as evidenced by the fact that the EFs of SO_2 reduced by ~78.0% and the EFs of $PM_{2.5}$ reduced by ~55.5% on average. However, the EF of VOCs increased about 14 times from 118 ± 56.1 mg/kg to 1807 ± 1746 mg/kg. Moreover, the compositions of VOCs emitted from the coastal vessels also changed greatly. The mass percentages of alkenes increased from 8.5%-27.3% to 44.4%-86.6%. The sharp increase of EFs, as well as elevated fractions of more reactive species, resulted in much higher OFPs for VOCs emitted per kilogram fuel burned, which sharply increased about 29 times from 0.35 ± 0.11 g O_3 kg^{-1} Fuel to 10.37 ± 13.55g O_3 kg^{-1} Fuel. The SOAFPs also increased by over 50% although their R_{SOA} reduced by 66.5%-74.8%.

For river vessels unaffected by the fuel switch policy, the EFs of NMHCs were measured as high as 3358 ± 2771 mg kg^{-1}, nearly doubled those for coastal vessels after implementing the new policy, with OFPs and SOAFPs also about 2 times of their counterparts for coastal vessels after implementing the policy.

In summary, our tests in the Guangzhou port demonstrated that for coastal vessels at berth, the fuel switch from high-sulfur residual fuel oil to low-sulfur diesel or heavy oil did bring about largely decreased emissions of SO_2 and $PM_{2.5}$ and therefore would benefit PM pollution control. However, the new policy raised another concern for the dramatic increase in emissions of reactive VOCs from coastal vessels. This phenomenon is also reinforced by the fact that river vessels, which use diesel oils all along and thus not affected by the fuel switch policy, also had much higher emissions of reactive VOCs. This larger emission of reactive VOCs would probably worsen the ozone pollution and SOA formation in the harbor cities, how to further lower the emission of reactive VOCs from ocean-going, coastal and river vessels is another regulatory and technological concern.

Data availability

The data used in this publication are available to the community and can be accessed by request to the corresponding author.

Author contributions

ZFW performed data analysis with contributions from YLZ and XMW. JJH, XLH, XY and WQY helped sampling. HZC and YJW helped project coordinating and data interpretation. RQZ, MZ, HF and ZZ helped sample analysis.

Competing interests

The authors declare that they have no conflict of interest.

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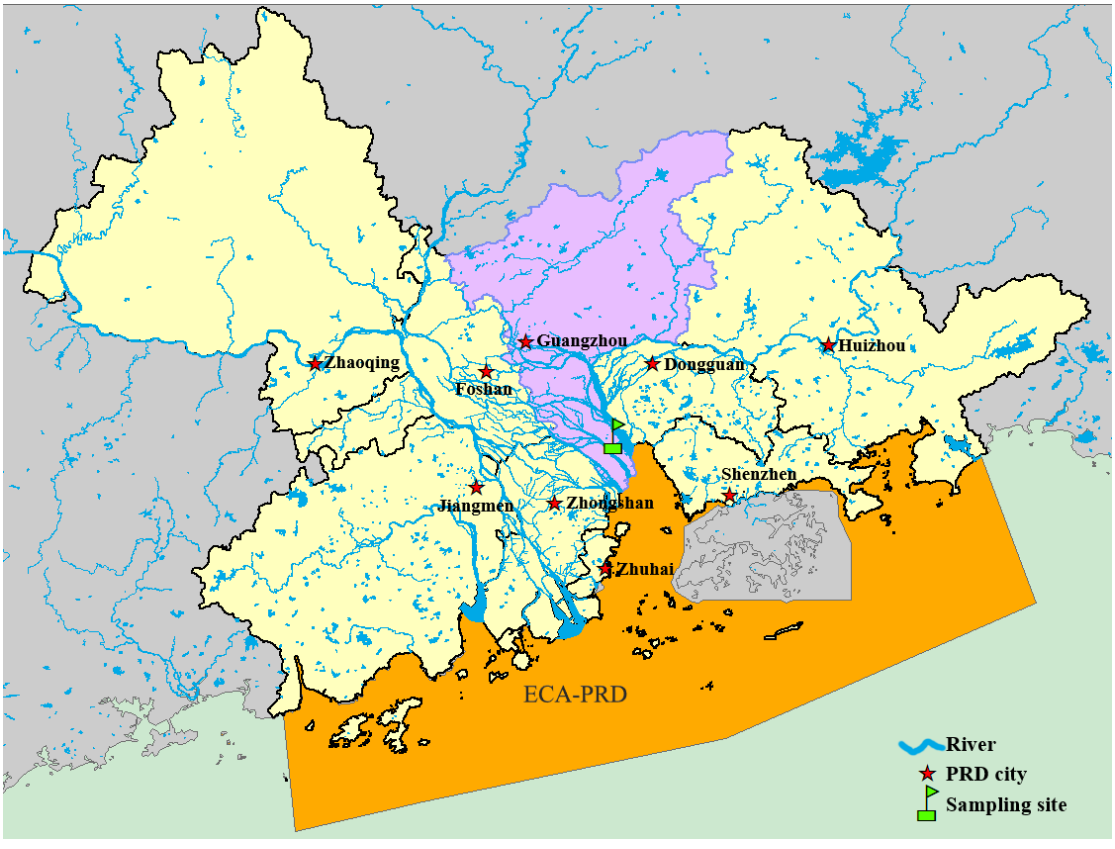

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479 Figure 1. The realm of ECA-PRD and the sampling site.

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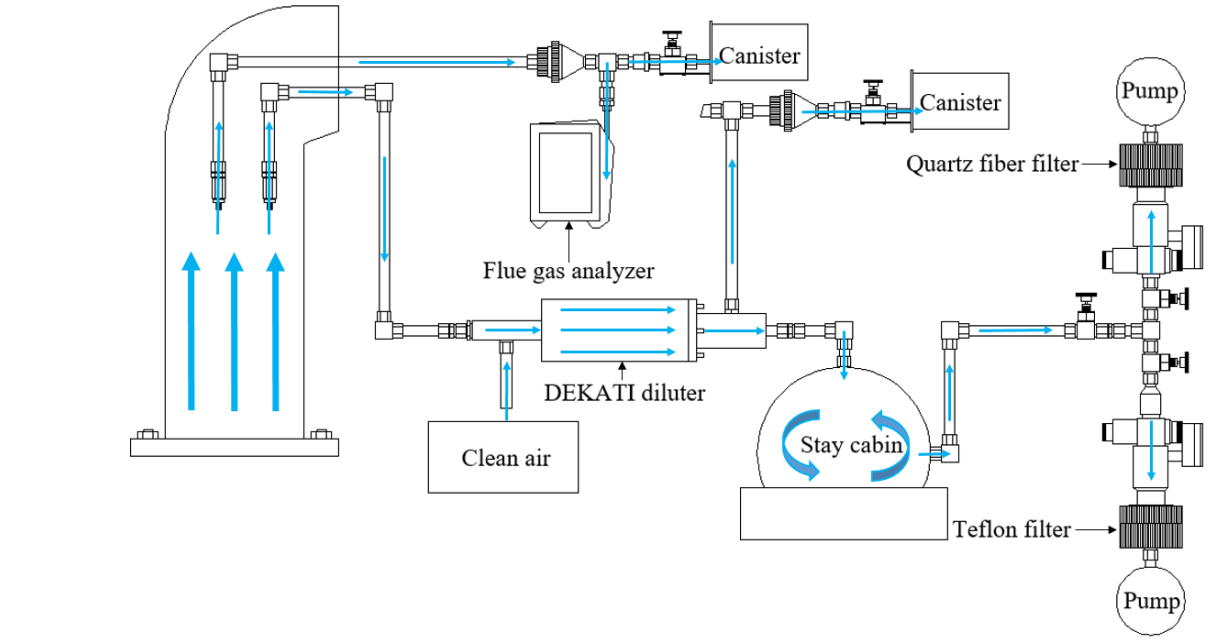

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481 Figure 2. Schematic diagrams of sampling setup

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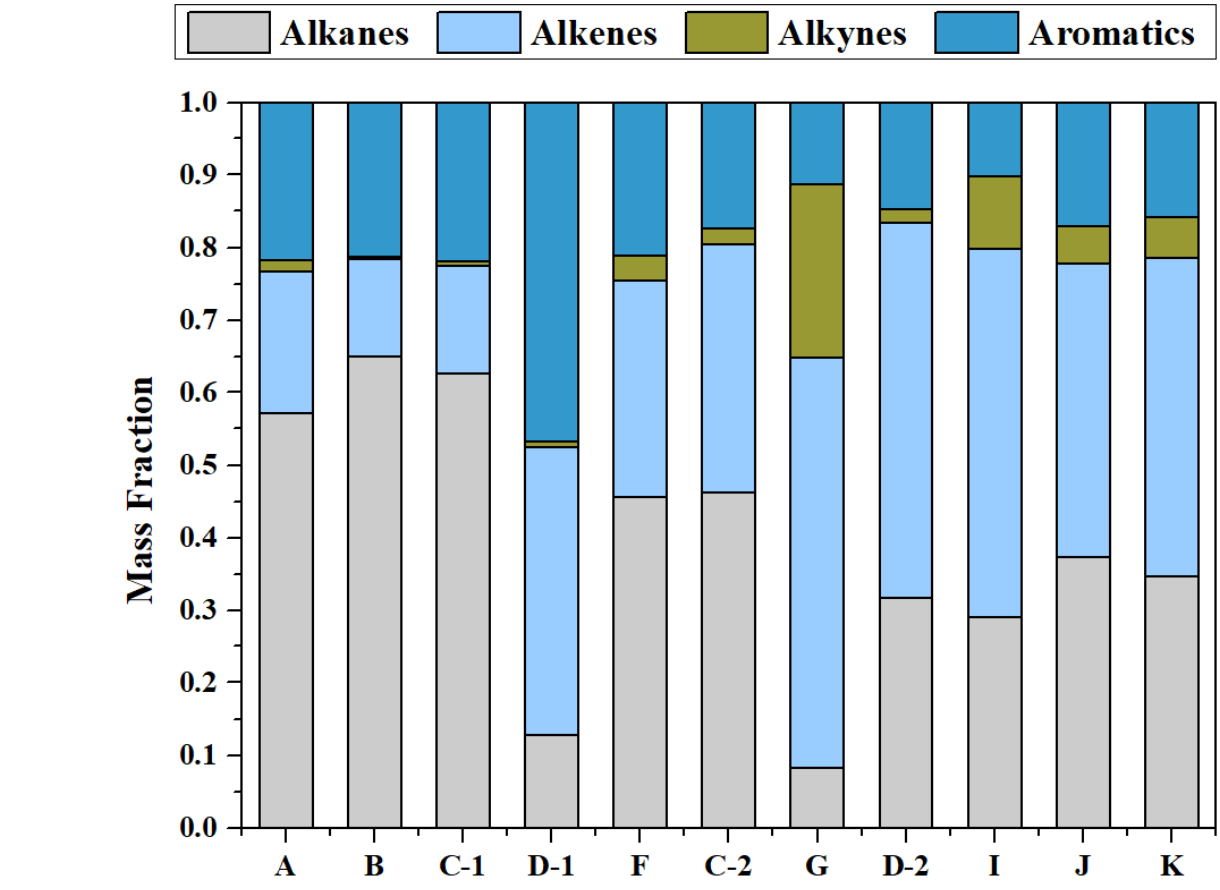

Figure 3. VOCs grouping according to their functional group. A, B, C-1 and D-1 are costal vessels tested before implementing the fuel switch policy, F, G, C-2 and D-2 are coastal vessels tested after implementing the fuel switch policy, and I, J and K are river vessels tested.

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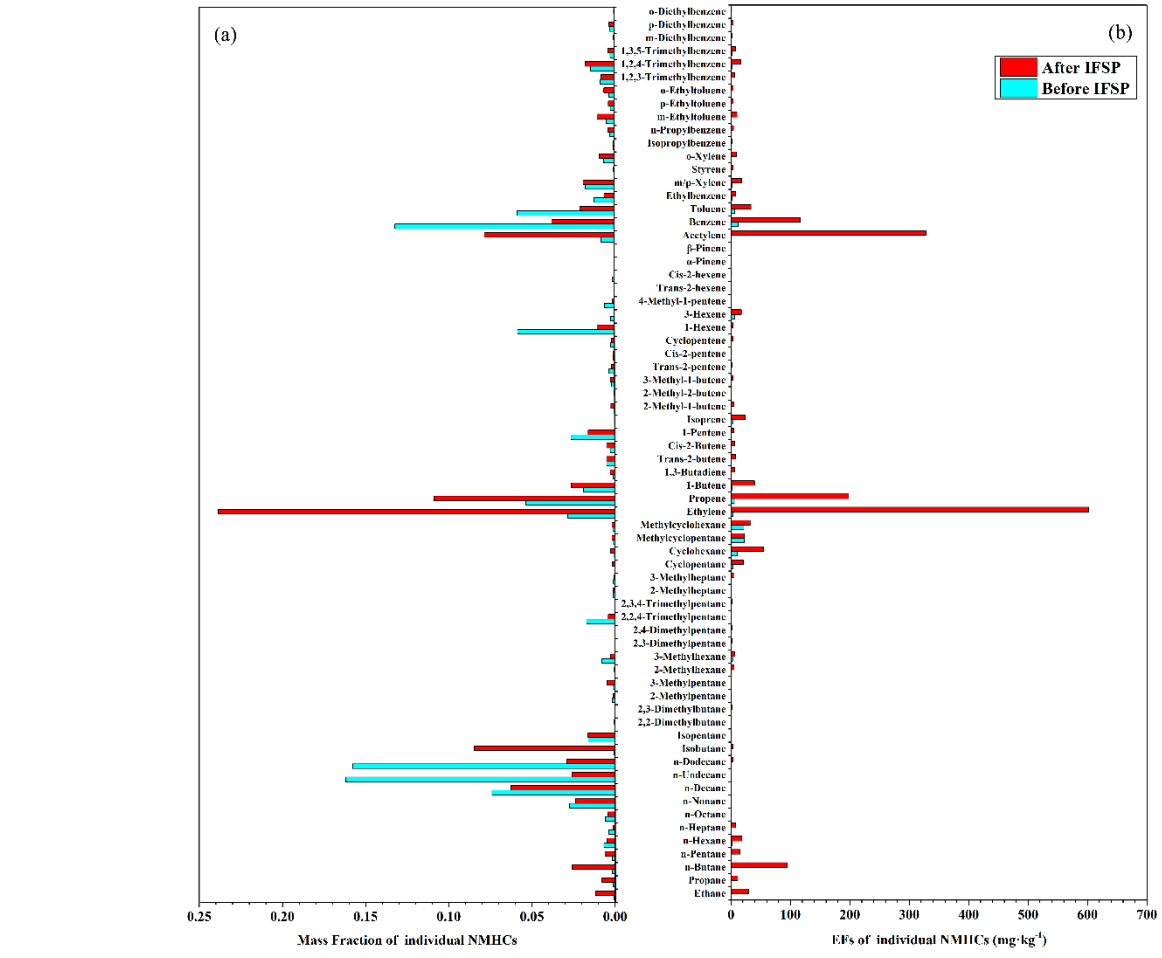

Figure 4. Comparison of VOCs emission factors before and after implementing the fuel switch policy (IFSP) for coastal vessels.

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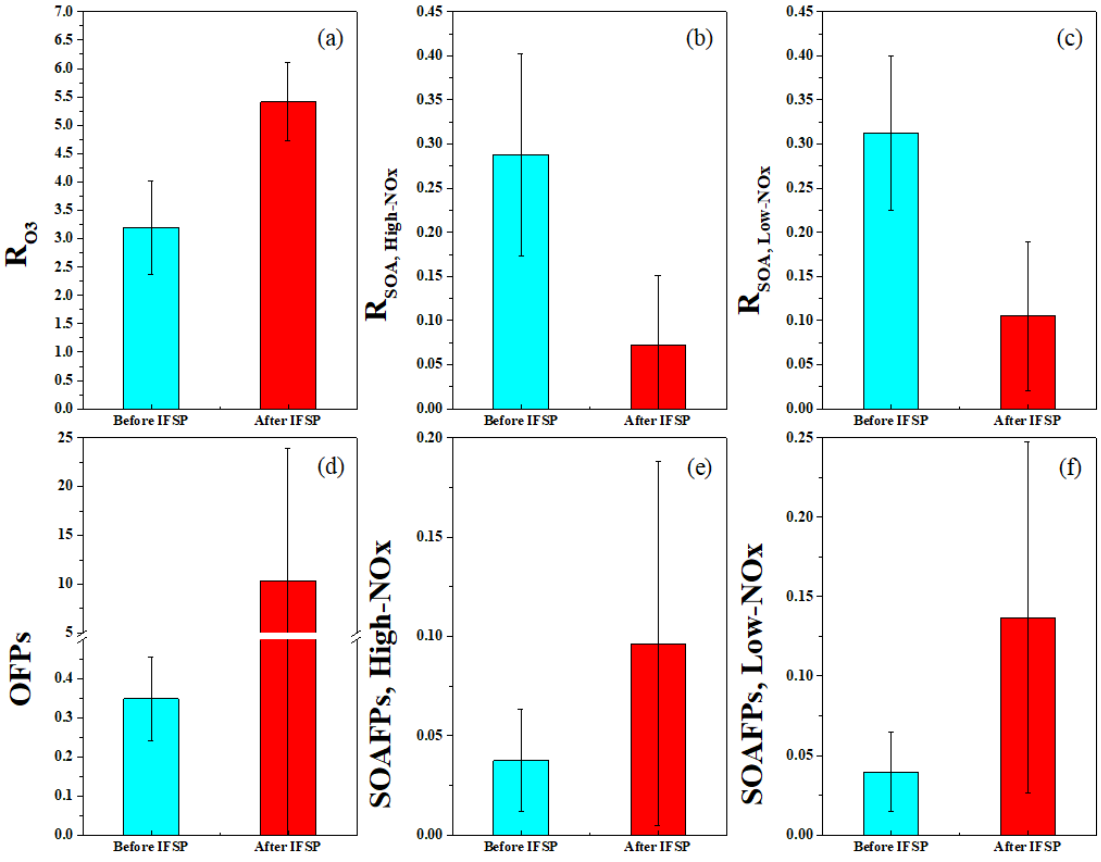

Figure 5. The changes in R_{O3} (g O_3 g^{-1} VOCs), R_{SOA} (g SOA g^{-1} VOCs), OFPs (g O_3 kg^{-1} Fuel) and SOAFPs (g SOA kg^{-1} Fuel) for coastal vessels before and IFSP.

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491 Table 1. The basic information of test vessels.

NO	Test date	Ship types	Gross tonnage (t)	Vessel age (yr)	Auxiliary engine		Fuel types		
					Power (kW)	Amount	Types	C/%	S/%
Coastal vessels (before implementing the fuel switch policy)									
A	2015.12.17	container vessel	47917	3	1760	2	residual oil	84.9	1.60
					1320	1			
B	2016.08.19	container vessel	41482	8	2045	3	residual oil	82.9	2.90
C-1	2016.08.19	container vessel	49437	4	1760	2	residual oil	82.7	2.10
					1320	1			
D-1	2016.11.15	bulk carrier	38384	3	660	3	residual oil	84.4	2.20
Coastal vessels (after implementing the fuel switch policy)									
E	2017.03.29	bulk carrier	8376	8	200	2	diesel oil	86.6	0.68
F	2017.12.22	bulk carrier	10716	10	200	3	diesel oil	86.6	0.13
C-2	2018.04.21	container vessel	49437	6	1760	2	diesel oil	85.8	<0.01
					1320	1			
G	2018.05.03	container vessel	25719	19	500	3	heavy oil (low-sulfur)	86.5	1.14
D-2	2018.05.06	bulk carrier	38384	4	660	3	heavy oil (low-sulfur)	87.5	0.47
River vessels									
H	2017.03.29	dry cargo carrier	2445	9	144	2	diesel oil	86.0	0.06
					76	1			
I	2017.09.27	container vessel	1862	7	73.5	2	diesel oil	86.0	0.03
J	2017.09.27	container vessel	1357	15	58	2	diesel oil	86.1	0.03
K	2017.09.27	container vessel	1420	10	58.5	2	diesel oil	85.9	0.02

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493 Table 2. The emission factors for test vessels (in unit of g ~~k~~g^{-1} fuel).

Ships	CO_2	CO	SO_2	NO_x	NMHCs	OC	EC	$PM_{2.5}$
Coastal vessels (before implementing the fuel switch policy)								
A	3097	8.03	32.0	61.7	0.11	0.59	0.15	2.30
B	3029	5.33	58.0	29.1	0.20	0.29	0.05	1.46
C-1	3025	3.80	42.0	19.9	0.11	0.22	0.07	1.02
D-1	3069	14.6	44.0	51.5	0.06	0.16	0.61	2.44
Coastal vessels (after implementing the fuel switch policy)								
E	3120	24.2	13.5	56.6	1.68	1.41	2.08	8.46
F	3156	5.50	2.52	13.0	1.11	0.55	1.41	2.17
C-2	3130	6.16	0.06	19.0	0.71	0.16	0.29	0.56
G	3079	41.0	22.8	19.2	5.25	2.05	1.49	5.90
D-2	3196	6.41	9.40	31.1	0.29	0.07	0.22	0.87
River vessels								
H	3087	26.2	1.20	25.0	0.81	0.74	5.21	12.5
I	3120	24.2	13.5	56.6	1.68	1.41	2.08	8.46
I	3055	59.6	0.52	13.3	1.40	-	-	-
J	2865	171	0.68	9.77	6.93	-	-	-
K	3050	55.0	0.36	64.4	4.29	-	-	-

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Table 3. Fuel-based average EFs (g kg^{-1}) from this study in comparison with those reported previously.

Ships	FSC	Condition	CO_2	CO	PM	TVOC	SO_2	NO_x
Coastal vessels or ocean-going vessels								
Coastal vessels-Before IFSP[a,e]	>0.5%	At berth	3055	7.93	1.81	0.12	44.0	40.6
Coastal vessels-After IFSP[a,e]	<0.5%	At berth	3136	16.7	3.59	1.81	9.66	27.8
Passenger ferry-α[b]	0.08%	At berth	3080-3297	2.69-4.58	0.99-2.12	0.57-0.99	1.56-1.65	70.3-90.6
Passenger ferry-β-1[b]	0.53%	At berth	3121-3284	4.34-6.99	1.96	0.29-0.57	10.2-11.0	54.4-71.6
Passenger ferry-β-2[b]	0.09%	At berth	3200	-	1.29	1.71	1.67	84.2
Passenger ferry-γ[b]	1.20%	At berth	3125-3226	1.50-2.60	1.37-2.00	0.87-1.14	23.7-24.1	64.7-84.7
Car/truck carrier[b]	0.23%	At berth	3237-3251	4.31-4.59	0.80-0.89	0.89-1.08	4.68	45.0-46.4
Container/ro-ro[b]	2.20%	At berth	3199-3212	3.55-4.17	2.49-3.10	0.79-0.88	44.0-44.2	59.4-70.4
Chemical tanker[b]	0.06%	At berth	3159	3.22-3.41	0.65-0.75	1.36-1.40	1.21	81.8-83.6
PanaMax Class Container[c]	3.01%	Cruising	2805	1.32	10.9	-	52.40	89.9
River vessels								
River vessels[a]	<0.5%	At berth	3134	77.9	12.5	3.36	0.69	28.1
Engineering vessel[d]	0.08%	Cruising	3071	30.2	9.40	23.7	1.60	115
Research vessel-α[d]	0.05%	Cruising	3153	6.93	0.72	1.24	0.92	35.7
Research vessel-β[d]	0.13%	Cruising	3151	9.20	0.16	4.18	2.60	31.6

[a]This study; [b]Cooper et al. (2003); [c]Agrawal et al. (2010); [d]Zhang et al. (2016); [e]implementing the fuel switch policy; [f]Zhang et al., (2018) with a coefficient of 0.22 kg/kWh to convert g/kWh to g/kg.

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498 Table 4. Emission factors (mg kg^{-1}) of NMHCs for test vessels.

Species	Coastal vessels (before IFSP[e])				Coastal vessels (after IFSP)				River vessels		
	A	B	C-1	D-1	F	C-2	G	D-2	I	J	K
Ethane	0.1	0.1	0.1	0.1	8.8	5.6	99.0	3.4	17.4	59.4	31.6
Propane	0.1	0.1	0.1	0.1	14.6	3.6	24.5	2.7	2.4	9.0	7.5
n-Butane	0.3	0.1	0.4	0.0	5.6	20.7	15.4	19.3	0.6	2.1	149.3
n-Hexane	0.4	1.7	1.0	0.4	5.0	1.4	2.8	3.6	0.3	3.6	0.6
n-Octane	0.8	1.0	0.7	0.3	9.6	4.5	1.2	0.7	4.9	57.7	26.3
n-Nonane	4.6	4.5	4.1	0.3	43.0	37.3	1.4	0.9	20.5	199.6	144.5
n-Decane	2.4	23.2	15.2	0.8	117.3	97.9	2.2	1.7	32.8	300.5	247.5
n-Undecane	21.0	45.7	22.9	0.3	45.6	42.8	0.7	0.7	24.7	195.9	179.9
n-Dodecane	26.8	42.5	15.5	1.3	127.2	1.0	0.2	0.1	0.7	6.8	57.6
Isobutane	0.2	0.04	0.04	ND	88.5	73.3	180.0	35.2	252.1	1336.5	459.1
Isopentane	2.2	1.1	2.0	1.2	14.5	14.1	35.6	7.6	23.6	171.3	73.4
3-Methylhexane	0.8	1.0	1.5	0.3	3.1	1.4	15.6	1.0	7.0	36.8	35.0
TM224PE[a]	ND	4.1	1.3	2.2	2.8	4.0	18.0	1.4	9.0	73.5	32.8
Other alkanes	1.8	3.0	1.8	0.6	21.2	18.4	34.6	14.4	11.1	129.0	43.2
Sum of alkanes	61.5	128.3	66.5	7.8	506.8	326.2	431.1	92.7	407.1	2581.9	1488.4
Ethylene	2.9	3.2	2.2	3.1	170.5	96.7	2062.7	79.3	401.8	1155.1	1125.2
Propene	7.1	6.3	3.7	4.9	82.8	71.1	595.2	42.8	201.1	969.5	378.3
1-Butene	2.1	0.6	2.6	1.7	23.9	21.1	102.7	10.1	32.0	149.0	105.6
Trans-2-butene	0.6	0.4	0.5	0.5	3.9	5.5	17.6	1.7	5.7	34.0	21.0
1-Pentene	4.1	2.0	1.2	2.9	17.3	14.7	57.9	5.2	24.7	143.1	80.4
1-Hexene	2.5	10.3	2.8	8.1	7.9	11.1	46.6	3.5	18.0	127.1	68.9
M4PE1ENE[b]	0.7	1.1	0.3	0.7	1.4	1.5	10.4	0.6	3.0	26.4	12.6
Other alkenes	1.1	2.7	2.4	2.2	23.1	19.9	82.5	7.2	26.1	206.0	96.8
Sum of alkenes	21.1	26.5	15.8	24.0	330.8	241.6	2975.6	150.4	712.5	2810.3	1888.8
Acetylene	1.8	0.7	0.6	0.5	38.5	15.4	1255.1	5.6	139.1	355.5	241.8
Benzene	9.6	11.6	7.9	18.6	18.3	13.0	423.7	10.9	46.6	191.7	129.5
Toluene	5.4	7.6	4.8	6.3	15.7	7.8	98.2	11.7	22.1	131.3	75.5
Ethylbenzene	1.1	2.5	1.8	0.7	7.4	5.3	13.1	3.0	6.3	61.5	28.2
m/p-Xylene	1.8	3.5	1.7	1.3	24.1	19.4	20.4	7.0	11.5	129.1	57.4
o-Xylene	0.6	1.5	0.7	0.5	14.1	10.1	9.3	2.9	6.3	69.1	31.6
m-Ethyltoluene	0.7	1.5	0.5	0.2	24.8	11.4	2.0	1.4	8.4	100.0	75.9
o-Ethyltoluene	0.3	1.2	0.6	0.1	16.8	6.1	1.7	0.9	5.0	54.2	28.9
TM123B[c]	1.1	2.4	1.1	0.2	19.7	9.5	2.2	0.8	5.5	71.1	43.9
TM124B[d]	1.0	5.3	2.1	0.2	44.1	18.3	3.3	1.6	15.2	167.8	99.7
Other aromatics	1.7	4.6	2.2	0.3	49.1	21.6	15.5	2.8	15.5	206.2	105.2
Sum of aromatics	23.3	41.8	23.2	28.4	234.0	122.6	589.5	43.0	142.5	1182.0	675.7

499 [a]2,2,4-Trimethylpentane; [b]4-Methyl-1-pentene; [c]1,2,3-Trimethylbenzene; [d]1,2,4-Trimethylbenzene.