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

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Abstract. Limiting fuel sulfur content (FSC) is a widely adopted approach for reducing ship emissions of sulfur dioxide (SO_2) and particulate matter (PM), particularly in emissions control areas (ECAs), but its impact on the emissions of volatile organic compounds (VOCs) is still not well understood. In this study, emissions from ships at berth in Guangzhou, southern China, were characterized before and after the implementation of the fuel switch policy (IFSP) with an FSC limit of 0.5% in the Pearl River Delta ECA. After IFSP, the emissions factors (EFs) of SO_2 and $PM_{2.5}$ for the coastal vessels decreased by 78% and 56% on average, respectively; however, the EFs of the VOCs were 1807 ± 1746 mg kg^{-1}, approximately 15 times that of 118 ± 56.1 mg kg^{-1} before IFSP. This dramatic increase in the emissions of the VOCs might have been largely due to the replacement of high-sulfur residual fuel oil with low-sulfur diesel or heavy oils, which are typically richer in short-chain hydrocarbons. Moreover, reactive alkenes surpassed alkanes to become the dominant group among the VOCs, and low carbon number VOCs, such as ethylene, propene and isobutane, became the dominant species after IFSP. As a result of the largely elevated EFs of the reactive alkenes and aromatics after IFSP, the emitted VOCs per kg of fuel burned had nearly 29 times greater ozone formation potential (OFP) and approximately 2 times greater secondary organic aerosol formation potential (SOAFP) than those before IFSP. Unlike the coastal vessels, the river vessels in the region used diesel fuels consistently and were not affected by the fuel switch policy, but the EFs of their VOCs were 90% greater than those of the coastal vessels after IFSP, with approximately 120% greater fuel-based OFP and 70-140% greater SOAFP. The results from this study suggest that while the fuel switch policy could effectively reduce SO_2 and PM emissions and thus help control $PM_{2.5}$ pollution, it also will lead to greater emissions of reactive VOCs, which may threaten ozone pollution control in harbor cities. This change for the coastal or ocean-going vessels, in addition to the large amounts of reactive VOCs from the river vessels, raises regulatory concerns for ship emissions of reactive VOCs.

1 Introduction

World seaborne trade volumes are estimated to account for over 80% of the total global merchandise trade (UNCTAD, 2016). The controls on ship emissions, however, are far less stringent than those on land emissions sources, and unsurprisingly, 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 can cause air pollution in coastal areas and thus contribute substantially to the 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 implemented to regulate and prevent health risks from ship emissions particularly in harbor cities.

An important intervention policy by the International Maritime Organization (IMO) to reduce ship emissions is the designation of emissions control areas (ECAs) where a more stringent limit of fuel sulfur content (FSC) is implemented (IMO, 2017). This ECA approach has resulted in 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 has resulted in reduction rates of 42%, 38% and 20% for ambient concentrations of sulfur dioxide (SO_2), sulphate aerosols and ammonium aerosols, respectively, which were related to ship emissions (Matthias et al., 2010); monitoring in U.S. coastal states has 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 emissions of SO_2, $PM_{2.5}$ and PM_{10} (particulate matter with an aerodynamic diameter less than 10 μm) were projected to be reduced by 95%, 67% and 67%, respectively, if FSC was restricted to below 0.1% (Viana et al., 2015). Consequently, with the increasingly stringent control over land-based emissions sources, limiting ship emissions has gradually stood out as an effective measure to control air pollution in coastal zones.

Intervention measures for ship emissions, however, are mostly targeted at 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, such as ethylene, propylene and isobutylene, were found in emissions 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 emissions factors based on shipboard platform measurements and aircraft-based measurements for the main engine of a PanaMax Class container ship. Recently, Huang et al. (2018a) tested a handysize-class bulk carrier under at-berth, maneuvering and cruising conditions, and found that single-ring aromatics accounted for 50-74% of the VOCs with toluene as the most abundant species. Xiao et al. (2018) tested 20 ships at berth in the Jingtang Port in northern China and found that alkanes and aromatics were dominant in the VOC emissions. Previous studies have already demonstrated that ship emissions impact ambient ozone formation in coastal cities (Wang et al., 2019b). In addition, ship emissions could contribute substantially to NO_x in the oceans and coastal areas (Song et al., 2010; Tagaris et al., 2017). Therefore, even in terms of for lowering ambient ozone levels, there is a growing concern about ship emissions as ozone precursors, including NO_x and VOCs.

China has many of the world's busiest ports, sharing approximately 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 have been required to gradually switch to fuels with an FSC limit of 0.5% from 1 January, 2017, to 31 December, 2019. As estimated by Liu et al. (2018), this fuel switch policy could lower atmospheric concentrations of SO_2 and $PM_{2.5}$ by 9.5% and 2.7%, respectively, in the coastal region of the PRD in southern China. A recent field observation campaign in Jingtang Port also demonstrated that due to the implementation of the fuel switch policy (IFSP), ambient levels of SO_2 dropped from 165.5 ppb to 67.4 ppb, while particulate vanadium (V), a marker of ship PM emissions (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 9.1 ng m^{-3} (Zhang et al., 2019). However, it is still unknown whether the fuel switch policy will result in changes in ship emissions of VOCs.

For ships at berth, their main engines are shut down, and auxiliary engines become the only emissions source. Because 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 populated areas, emissions from ships at berth could have a large 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 southern China in 2017 and 2018 after IFSP, and we compared the results with those from a similar campaign previously conducted by the authors in 2015 and 2016 before IFSP. Apart from the emissions of pollutants such as $PM_{2.5}$ and SO_2, in this study, we focus on emissions of VOCs and aim to investigate changes in composition profiles and emissions 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. In addition, river vessels, which commonly use diesel oil as fuel and did not need to implement the fuel switch policy, were also tested in 2017 for a 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 centre of the PRD region, adjacent to Hong Kong and Macao (Fig. 1). In 2017, cargo throughput of Guangzhou Port was 590 million tons, ranking fifth in China and sixth in the world, and the container throughput in Guangzhou Port was 20.37 million TEU, ranking fifth in China and seventh in the world (China Port Press, 2018). In 2013, Guangzhou Port was estimated to account for nearly 40% of ship emissions of SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$ and VOC from the nine port groups in the PRD bay area (Li et al., 2016a).

2.2 Test ships and fuel types

As required, the FSC for ships at berth should have been less than 0.5% since 1 January, 2017. In the PRD, measures are even more stringent in which 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 for the 11 tested ships (more information during sampling was presented in Table S1), among which ships C and D were tested both before and after IFSP. 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 have already used diesel oil as fuel before IFSP, and the others were coastal vessels. No ocean-going ships were tested in this study.

2.3 Ship exhaust sampling and laboratory analysis

The ship exhaust sampling system is composed of a flue gas dilution system, flue gas analyzer, particulate matter sampler and air sampler (Figure 2). The ship exhaust first entered the Dekati® ejector dilutor (DI-1000, Dekati Ltd., Finland) from the sampling nozzle and then was spilt into four parts after being diluted with clean air: one part was for air sampling with 2 L canisters and 4 L Teflon bags for 3-5 min after passing through a filter, two other parts were for collecting $PM_{2.5}$ samples with 47 mm Teflon filters (Whateman, Mainstone, UK) and 47 mm quartz fiber filters (Whateman, Mainstone, UK) at a flow of 16.7 L min^{-1} for 20-30 min, after the diluted exhaust was mixed well in a stay cabin, and then passing through a $PM_{2.5}$ separator, and the last part was the vent. Before dilution, the concentrations of CO_2, CO, SO_2 and NO_x in the ship exhaust were directly measured by a flue gas analyzer (F-550, WOHLER, Germany), while air samples were also collected simultaneously by a 2L canisters and a 4L Teflon bags. The dilution ratios of the flue gas dilution system were then more accurately calculated by comparing the CO_2 concentrations in the samples before and after the dilution. In addition, 500 ml of the fuel oil used by each ship was collected in brown glass bottles to determine its carbon and sulfur contents and to analyse the C_{11}-C_{36} hydrocarbon species.

VOCs in the air samples collected in the canisters and Teflon bags were analyzed by using a preconcentrator (Model 7100, Entech Instruments Inc., USA) coupled to an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). The calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 NMHCs including 15 AHs) and TO-14 standard mixture (39 compounds) from Spectra Gases Inc., NJ, USA to 0.5, 1, 5, 15 and 30 ppbv. More details about the analysis are described elsewhere (Zhang et al., 2013; 2015; Yang et al., 2018); Besides measured by the flue gas analyzer, the CO_2/CO concentrations were also 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 the 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 the determination of sulfate with an ion chromatography (883 Basic IC plus, Metrohm, Switzerland) (Li et al., 2016b). The C_{11}-C_{36} hydrocarbons in the 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 50 μl fuel oil in 1 ml n-hexane and removing the insoluble material through filtration.

2.4 Calculations of emission factors

The emissions factors (EFs) were calculated by a carbon balance approach, which assumed that the carbon in fuel was transformed into the carbon in CO_2, CO, PM and VOCs, and the EF of CO_2 was calculated as follows (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 emissions factor of CO_2 in unit of g kg^{-1}; C_F is the carbon content per kg of fuel (g kg^{-1}); $\Delta[CO_2]$ is the incremental concentrations of CO_2; ΔC_{CO2}, ΔC_{CO}, ΔC_{PM} and ΔC_{VOCs} represent the carbon mass concentrations of CO_2, CO, PM and VOCs, respectively, after subtracting their background concentrations.

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

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

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

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

$$EF_{SO2}=S\%\times\frac{64}{32}\times 10^3, \quad (3)$$

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

3 Results and discussion

3.1 Changes in EFs for ships at berth

The FSC for the tested coastal vessels decreased from 2.2 ± 0.5% on average before to 0.4 ± 0.5% after IFSP, although there were some ships, such as ship G, which violated the regulation with an FSC still above the limit of 0.5% (Table 1). In fact, the ship fuel was transferred from residual fuel oil to diesel oil or heavy oil (Fig S1), and the compositions of the fuels used by the coastal vessels tended to have more low-carbon number hydrocarbons, as demonstrated by their total ion chromatograms, than those of coastal vessels before IFSP (Fig S2).

As shown in Table 2, the EFs for SO_2, which were 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 ($NO+NO_2$), VOCs, $PM_{2.5}$, OC and EC, however, were more complex because they are not only related to the properties of the fuels but also heavily influenced by the performance of the combustion system. The comparison before and after IFSP was also challenged by the fact that the tested coastal vessels during the two campaigns were not the same and that we tested a limited number of ships. Nevertheless, ships C and D had been tested both before and after IFSP and we compared them. The EFs of CO_2 for ships C and D slightly increased from 3025 g kg^{-1} and 3069 g kg^{-1} to 3131 g kg^{-1} and 3196 g kg^{-1} after IFSP; 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 NO_x 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}.

Similar to the EFs of SO_2, the EFs of $PM_{2.5}$ also decreased significantly after IFSP. For example, the EFs of $PM_{2.5}$ for ship C decreased by 45.1% from 1.02 g kg^{-1} to 0.56 g kg^{-1} and that for ship D decreased by 64.3% from 2.44 g kg^{-1} to 0.87 g kg^{-1};

similar to that of $PM_{2.5}$, the EF of OC for ships C and D decreased by 28.7% and 60.5%, but no significance change occurred in the EF of EC. Therefore, after IFSP, the changes in the EFs of CO_2, CO, NO_x and EC were not significant for the coastal vessels, but the EFs of SO_2, $PM_{2.5}$ and OC decreased.

Compared to SO_2 or other pollutants, the VOCs from coastal vessels shown more dramatic changes in their EFs. As shown in Table 2, the EFs of the VOCs ranged from 60.7 mg kg^{-1} to 197 mg kg^{-1} with an average of 118 ± 56.1 mg kg^{-1} before IFSP, and they ranged from 292 mg kg^{-1} to 5251 mg kg^{-1} with an average of 1807 ± 1746 mg kg^{-1} after IFSP. For ships C and D that were tested both before and after IFSP, the EFs of the VOCs for ship C increased approximately 6 times from 106 mg kg^{-1} to 706 mg kg^{-1}, and that for ship D also increased approximately 4 times from 60.7 mg kg^{-1} to 292 mg kg^{-1}. This substantial change in our study was consistent with that based on shipboard platform measurements by Copper et al. (2003), who also found that the EFs of hydrocarbons from a 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%) with marine gasoil (FSC=0.09%) (Table 3).

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

River vessels sail in inland rivers and many studies have investigated the emissions from river vessels under cruising conditions (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 shown in Table 3, for the tested river vessels (ships H, I, J and K), the EFs of CO_2 (3014 ± 99.0 g kg^{-1}) and NO_x (28.1 ± 24.5 g kg^{-1}) were close to those for coastal vessels; the EF of CO (77.9 ± 62.5 g kg^{-1}), however, was nearly 4 times higher than that of coastal vessels after IFSP, and larger than that reported for engineering vessels and research vessels under cruising conditions with a maximum of 30.2 g kg^{-1} (Zhang et al., 2016); their EF of SO_2 was as low as 0.69 ± 0.36 g kg^{-1}, while the EF of the VOCs was as high as 3.36 ± 2.77 g kg^{-1}, 85.6% larger than that reported for coastal vessels after IFSP but within the range for research vessels (1.24-4.18 g kg^{-1}) as reported by Zhang et al. (2016).

3.2 EFs of grouped and individual VOCs

The data on the EFs of grouped and individual VOCs are sparse (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 VOCs, including 29 alkanes, 21 alkenes, 1 alkyne and 17 aromatics, were determined. As shown in Fig. 3 and Table 4, for coastal vessels before IFSP, alkanes dominated the emissions among the VOCs at 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 the VOCs 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 the VOCs after IFSP. Alkenes overtook alkanes to become the most abundant group at 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}). In addition, the mass percentages of <

C_6 VOCs (VOCs with carbon numbers below 6) in the total VOCs in ship exhaust increased from 8.5%-27.3% to 44.4%-86.6% after IFSP (Fig S3), which indicated more low carbon number VOCs were emitted from ships at berth.

For the EFs of the individual VOCs, the top 25 species remained unchanged after IFSP, but their rankings changed (Table S2). As shown in Fig. 4 and Table 4, n-undecane and n-dodecane were still among the dominant species, although their percentages decreased substantially. Their EFs did not change to the same degree and were 22.5 ± 18.2 mg kg^{-1} and 21.5 ± 17.1 mg kg^{-1} before IFSP and 22.5 ± 24.6 mg kg^{-1} and 32.1 ± 62.1 mg kg^{-1} after IFSP, respectively. In addition, the EF of isobutane increased from 0.06 ± 0.07 mg kg^{-1} to 94.3 ± 62.2 mg kg^{-1}. A 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 an EF of 5.5 ± 1.5 mg kg^{-1} before IFSP, had the second largest EF of 198 ± 260 mg kg^{-1} after IFSP, an increase of over 30 fold. The alkene 1-hexene, which ranked first among alkenes with an EF of 5.9 ± 3.8 mg kg^{-1} before IFSP, also increased 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 increasing from 0.9 ± 0.6 mg kg^{-1} to 328.7 ± 605.4 mg kg^{-1}. Benzene and toluene were the dominant aromatic species before and after IFSP. Their EFs increased from 11.9 ± 4.6 mg kg^{-1} and 6.0 ± 1.2 mg kg^{-1} to 116.5 ± 200.8 mg kg^{-1} and 33.3 ± 42.5 mg kg^{-1}, respectively, after IFSP.

The composition of the VOCs from the river vessels was similar to that of the coastal vessels after IFSP. As shown in Fig. 3 and Table S2, alkenes also were dominant in the emissions of the VOCs at 45.1 ± 5.9%, while aromatics and alkenes accounted for 33.7 ± 4.8% and 14.3 ± 4.1%, respectively. For the individual VOCs, the most abundant species were ethylene, isobutene, propene, acetylene, n-decane and benzene. However, the EFs of the VOCs for the river vessels were 1.9 times those of the coastal vessels after IFSP (Table 2), suggesting that VOCs emissions from the river vessels might have played an important role as their emissions are closer to populated areas and thus should be regulated.

Recently, both Xiao et al. (2018) and Huang et al. (2018a) carried out VOC emissions tests on ships at berth in China's ECA. Xiao et al. (2018) reported that aromatics and alkanes dominated the VOCs emissions from the 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 accounted for 9% of the VOCs emissions; Huang et al. (2018a) also investigated the VOC emissions from ships at berth, but aromatics accounted for up to 70.9% of those emissions, while alkenes only accounted for 6.7%. The variation in ship fuels might be one of the key reasons for the large differences in the compositions of the VOC emissions among the available studies. The fuel switch policy restricted only the FSC below 0.5%, so many types of fuels could be used in ships, as seen from the four types of diesels fuels used by the tested ships (Fig. S1). Nonetheless, engine designs, performance and loads during the sampling might have also led to the differences (Cooper et al., 1996).

3.3 Ozone and SOA formation potential

3.3.1 OFP of the VOCs from ship exhaust

Ozone formation potential (OFP) 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 emissions data in this study, the normalized ozone reactivity (R_{O3}, g O_3 g^{-1} VOCs) and OFP (g O_3 kg^{-1} fuel) were calculated as:

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

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

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

As described in Fig. 5, the R_{O3} of the tested coastal vessels increased by almost 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 increase in R_{O3} is that shares of highly reactive alkenes (such as 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%. OFP 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 the river vessels, their average R_{O3} was 5.55 g O_3 g^{-1} VOCs, which was close to that of the coastal vessels after IFSP, but their average OFP (22.98 ± 16.59 g O_3 kg^{-1} fuel) was more than double that of the coastal vessels. As shown in Fig. S4, the R_{O3} (4.22 g O_3 g^{-1} VOCs) reported by Huang et al. (2018a) for ship emissions after IFSP was approximately 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) was even lower than the R_{O3} before IFSP in this study. These results also suggest that there is great diversity in ship-emitted VOCs at berth, even in different regions of China.

3.3.2 SOAFP of the VOCs from ship exhaust

Similarly, normalized secondary organic aerosols reactivity (R_{SOA}, g SOA g^{-1} VOCs) and SOA formation potential (SOAFP, g SOA kg^{-1} fuel) can also be calculated as (Zhang et al., 2018a):

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

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

where Y_i is the SOA yield of VOC species *i*. We could calculate the SOAFP under high-NO_x and low-NO_x conditions (Ng et al., 2007). However, we should be cautious in interpreting the results because intermediate volatile organic compounds were not measured in this study, which may lead to underestimation of SOA yields (Huang et al., 2018b; Lou et al., 2019).

As shown in Fig. 5, for the coastal vessels, R_{SOA} decreased by ~75% from 0.288 ± 0.114 g SOA g^{-1} VOCs to 0.073 ± 0.079 g SOA g^{-1} VOCs under high-NO_x conditions, while R_{SOA} also decreased by 66.5% from 0.313 ± 0.088 g SOA g^{-1} VOCs to 0.105 ± 0.085 g SOA g^{-1} VOCs under low-NO_x conditions. This decline of R_{SOA} resulted from the decrease in mass percentages of aromatics and alkanes, which have higher SOA yields than those of alkenes (Ng et al., 2007; Lim and Ziemann, 2009; Loza et al., 2014). However, with the dramatically increased EFs of the VOCs, under high-NO_x conditions,

SOAFP increased 1.6 times from 0.037 ± 0.026 g SOA kg^{-1} fuel to 0.096 ± 0.092 g SOA kg^{-1} fuel, and under low-NO_x conditions, SOAFP increased 2.5 times from 0.040 ± 0.025 g SOA kg^{-1} fuel to 0.137 ± 0.111 g SOA kg^{-1} fuel.

In particular, the R_{SOA} for ship F (Fig. S4) was significantly higher than that of the other ships, largely due to a higher fraction (11.5%) of n-dodecane, which had the highest SOA yield among the VOCs. For the river vessels, the R_{SOA} was the lowest in the test ships, with a value of 0.037 ± 0.017 g SOA g^{-1} VOCs under high-NO_x conditions and 0.069 ± 0.026 g SOA g^{-1} VOCs under low-NO_x conditions. However, their SOAFP was 0.165 ± 0.131 g SOA kg^{-1} fuel under high-NO_x conditions and 0.322 ± 0.267 g SOA kg^{-1} fuel under low-NO_x conditions, which were the largest of the values due to their much higher EFs.

As shown in Fig. S4, based on the VOCs emissions from ship at berth reported in Huang et al. (2018a), we calculated a R_{SOA} of 0.080 g SOA g^{-1} VOCs under high-NO_x conditions and 0.228 g SOA g^{-1} VOCs under low-NO_x conditions for a coastal vessels also using low-sulfur fuels. This relatively higher R_{SOA} under low-NO_x conditions was related to the higher fractions of aromatics in the VOC emissions. Using another method in Gentner et al. (2012), Xiao et al. (2018) reported an average R_{SOA} of 0.017 g SOA g^{-1} VOCs under high-NO_x conditions, which was close to a R_{SOA} of 0.015 g SOA g^{-1} VOCs calculated by the same method for the coastal vessels after IFSP.

3.4 Conclusions

Ships emissions control is primarily targeted in terms of PM-related pollution, and designating ECA with a fuel switch policy is a widely adopted approach to control 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 of the three newly established ECAs since 2017, and we preliminarily investigated the changes in emissions caused by the fuel switch policy, and further compared the results with those measured for river vessels unaffected by the fuel switch policy.

As reported by previous studies, our study also demonstrated that after IFSP, the EFs of both SO_2 and $PM_{2.5}$ for the 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 the VOCs increased approximately 14 fold from 118 ± 56.1 mg kg^{-1} to 1807 ± 1746 mg kg^{-1}. Moreover, the compositions of the 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 in the EFs, as well as elevated fractions of the more reactive species, resulted in a much higher OFP for the VOCs than that of the other species, which sharply increased at approximately 29 fold from 0.35 ± 0.11 g O_3 kg^{-1} fuel to 10.37 ± 13.55g O_3 kg^{-1} fuel. The SOAFP also increased by over 50%, although the R_{SOA} was reduced by 66.5%-74.8%.

For the river vessels were not affected by the fuel switch policy, the EFs of the VOCs were measured at value as high as 3358 ± 2771 mg kg^{-1}, which was almost double those for the coastal vessels after IFSP, with the OFP and SOAFP also at approximately 2 times their counterparts for the coastal vessels after IFSP.

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 resulted in substantially decreased emissions of SO_2 and $PM_{2.5}$ and

therefore would benefit PM pollution control. However, the fuel switch policy raised another concern due to the dramatic increase in emissions of reactive VOCs from the coastal vessels. This phenomenon was also reinforced by the fact that river vessels, which had used diesel oils the entire time and thus were not affected by the fuel switch policy, also had high emissions of reactive VOCs. This high level of emissions of reactive VOCs probably worsen the ozone pollution and SOA formation in the harbor cities, and further lowering the emissions 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

YLZ and XMW designed the research. ZFW, YLZ and XMW wrote the paper. 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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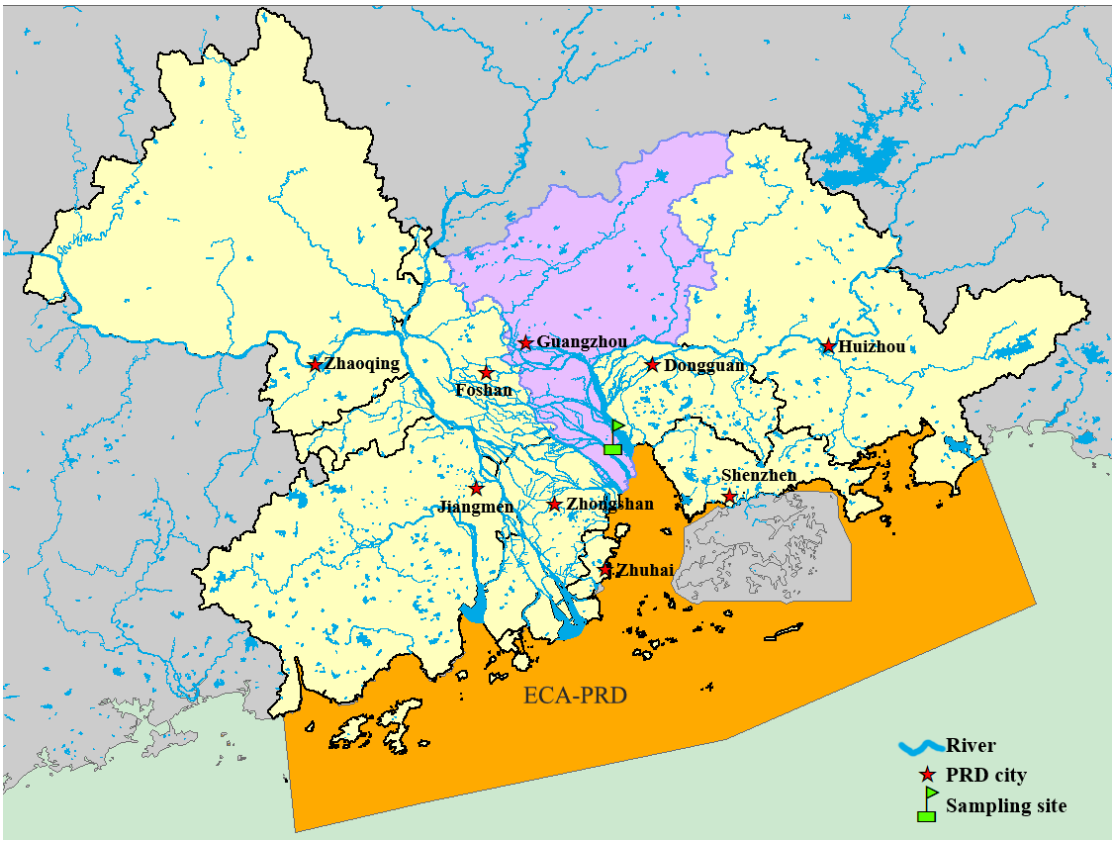
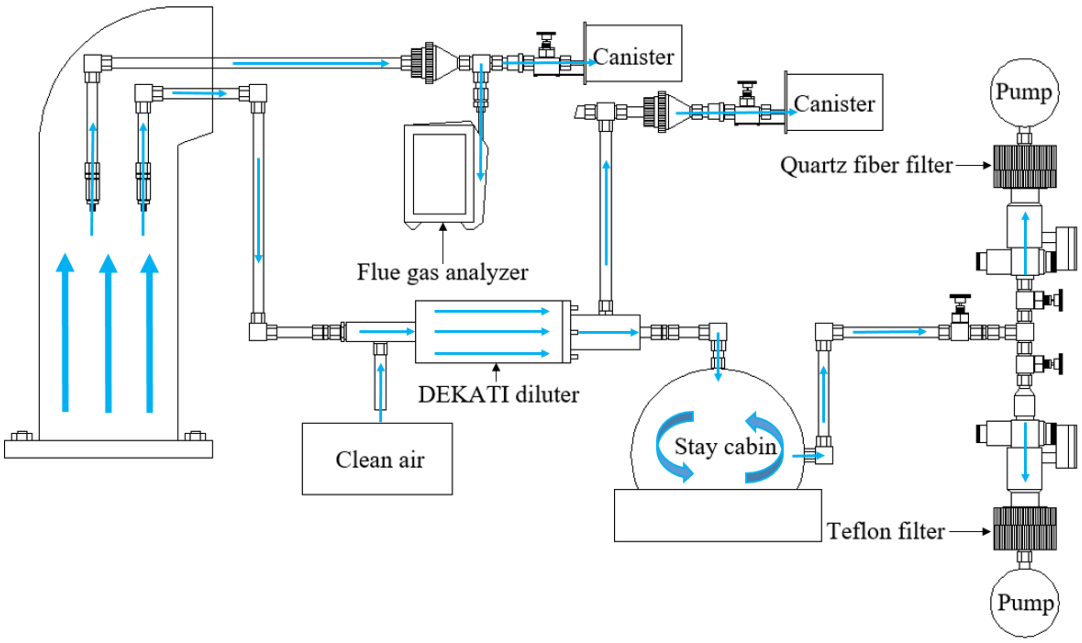


Figure 1. The realm of ECA-PRD and the sampling site.



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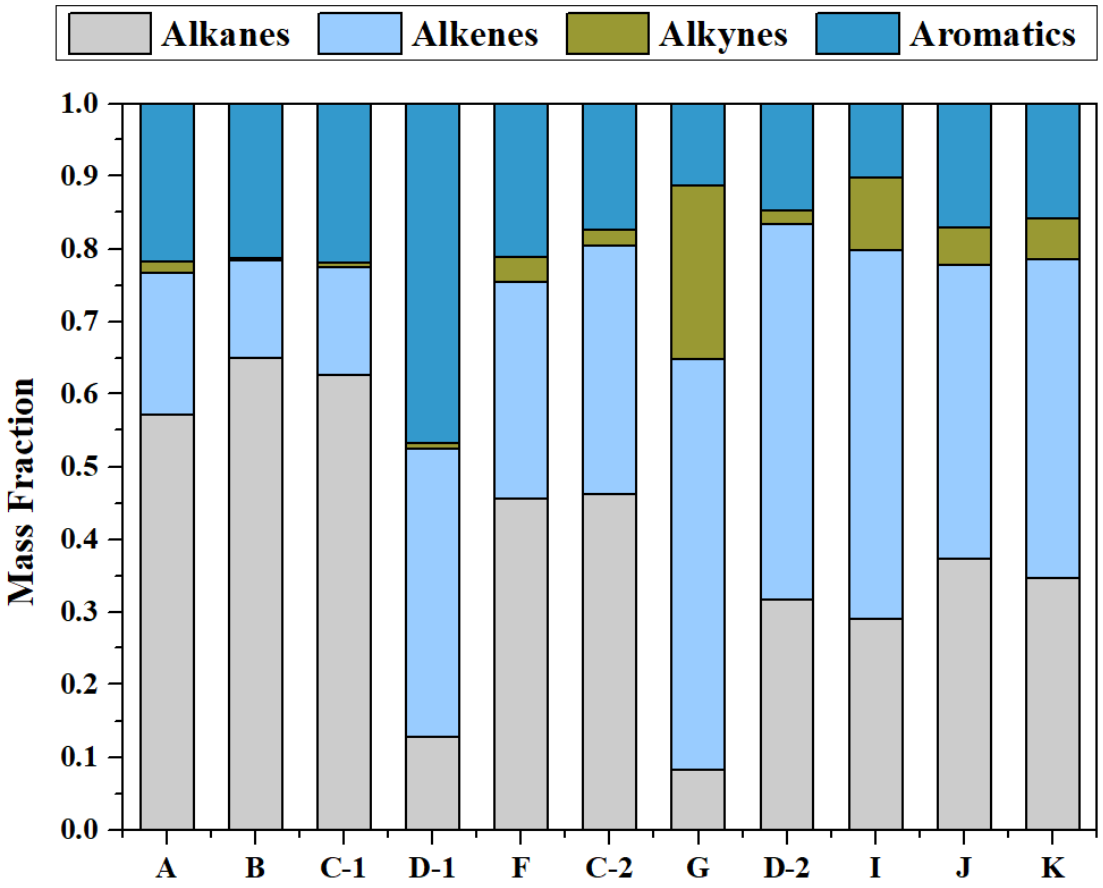
504 Figure 2. Schematic diagram of sampling setup.



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506 Figure 3. VOCs grouping according to their functional group. A, B, C-1 and D-1 are coastal vessels tested before IFSP, F, G,
507 C-2 and D-2 are coastal vessels tested after IFSP, and I, J and K are river vessels tested.

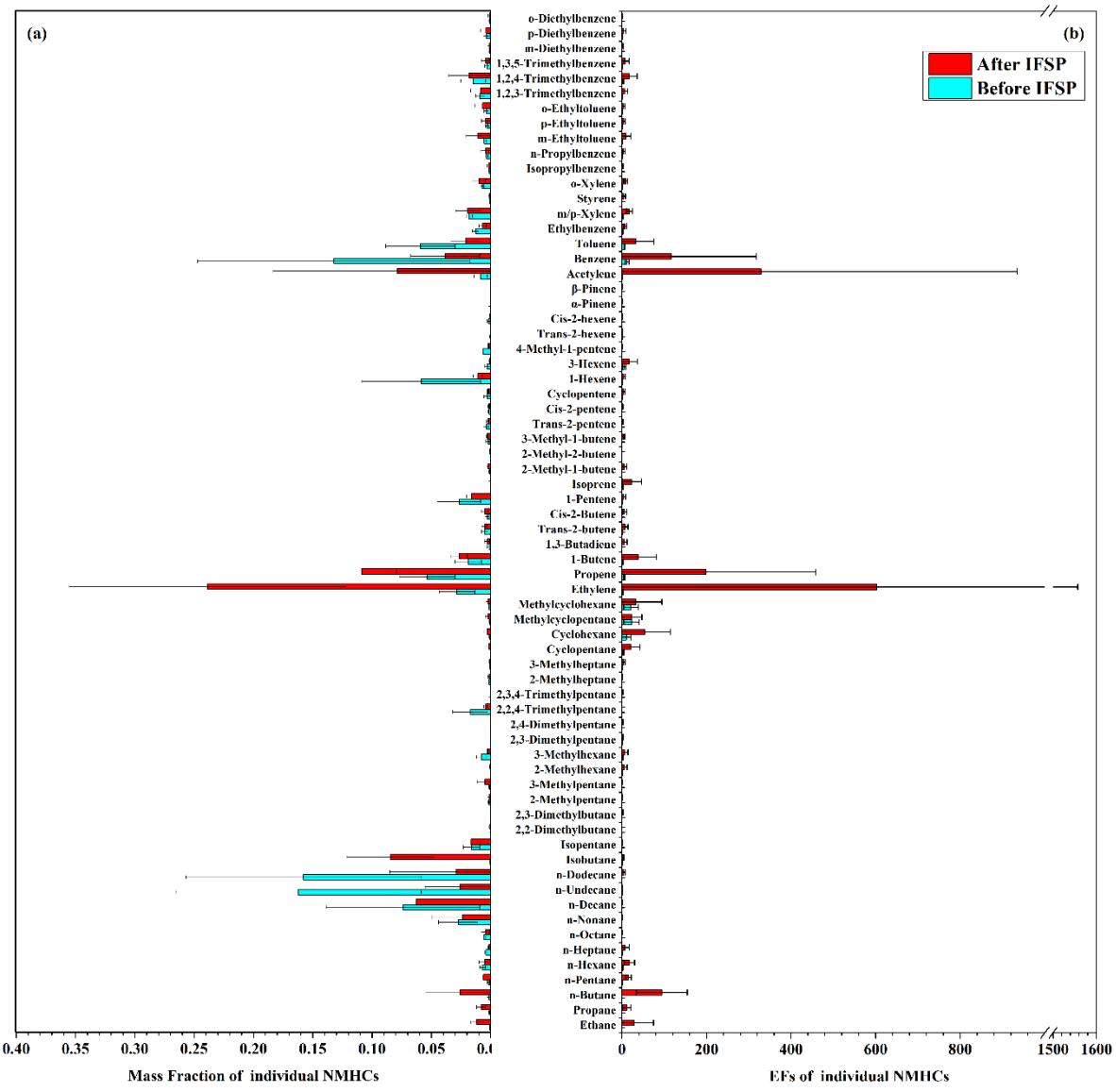
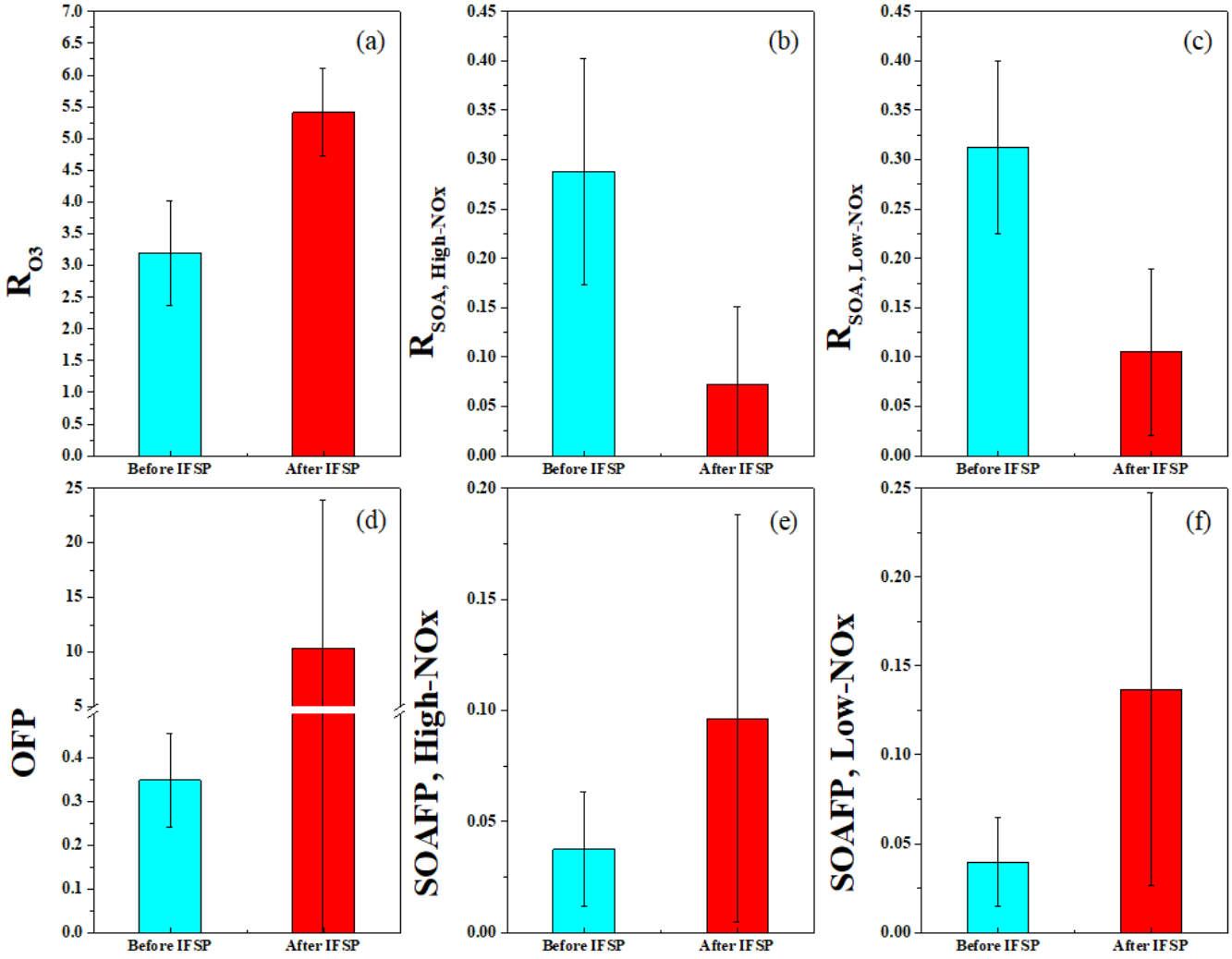


Figure 4. Comparison of VOCs emission factors before and after IFSP for coastal vessels.



510

511 Figure 5. The changes in R_{O3} (g O_3 g^{-1} VOCs), R_{SOA} (g SOA g^{-1} VOCs), OFP (g O_3 kg^{-1} fuel) and SOAFP (g SOA kg^{-1} fuel)

512 for coastal vessels before and after IFSP.

513 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 IFSP)									
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 IFSP)									
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

514

515 Table 2. The emission factors for test vessels (in unit of g kg^{-1}).

Ships	CO_2	CO	SO_2	NO_x	VOCs	OC	EC	$PM_{2.5}$
Coastal vessels (before IFSP)								
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 IFSP)								
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	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	-	-	-

516

517 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	VOCs	SO_2	NO_x
Coastal vessels or ocean-going vessels								
Coastal vessels-Before IFSP[a]	>0.5%	At berth	3055	7.93	1.81	0.12	44.0	40.6
Coastal vessels-After IFSP[a]	<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

518 [a]This study; [b]Cooper et al. (2003); [c]Agrawal et al. (2010); [d]Zhang et al. (2016); [e]Zhang et al., (2018b) with a coefficient of 0.22 kg kWh^{-1} to
519 convert g kWh^{-1} to g kg^{-1}.

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

Species	Coastal vessels (before IFSP)				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[e]	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

521 [a]2,2,4-Trimethylpentane; [b]4-Methyl-1-pentene; [c]1,2,3-Trimethylbenzene; [d]1,2,4-Trimethylbenzene; [e]Not detected.