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Changes in the SO_2 Level and $PM_{2.5}$ Components in Shanghai Driven by Implementing the Ship Emission Control Policy

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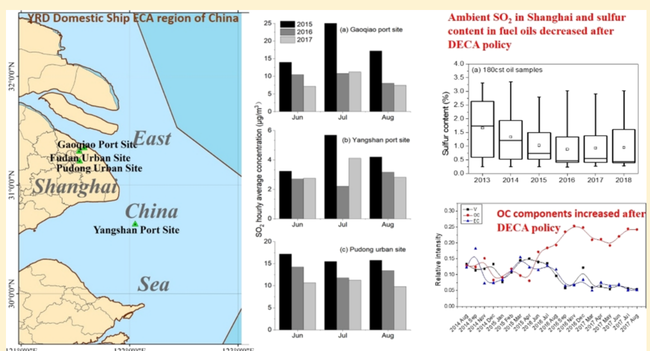
Supporting Information

ABSTRACT: This study aims to understand the effect of the Domestic Emission Control Area (DECA) policy on ambient SO_2 and particle components in Shanghai. Online single particle analysis and SO_2 measurements from 2015 to 2017 were compared to analyze the long-term variations before and after the DECA policy. Our study showed that there was a significant decrease in SO_2 by 27−55% after the implementation of the DECA policy. The number fraction of ship-emitted particles increased along with the increase in ship traffic activity, but the particles tended to contain lower-vanadium content. The elemental carbon component decreased, while the organic carbon components increased after switching oil. One thousand and ninety four ship fuel oil samples were collected. The oil sample analysis confirmed the ambient particle results; sulfur content decreased in domestic ship heavy fuel oils from 2013 to 2018; in the low sulfur fuel oils used after the DECA policy, vanadium was still highly correlated with sulfur as it was in high-sulfur fuels. Our results suggested that heavy fuel oil is still a major part of the low-sulfur ship oils in use. The multiple-component control including organic pollutants regarding low sulfur fuel oils may be necessary for preventing air pollution from ship emissions.



1. INTRODUCTION

Rapid development of the shipping industry has greatly advanced international trade and transportation. However, large quantities of exhaust gases and particles from the burning of ship fuels are emitted into the air, which can have a negative impact on human health and the climate.[1] The main air pollutants discharged by ships are sulfur dioxide, nitrogen oxides, and $PM_{2.5}$.[2] Air pollution caused by substantial shipping emissions, especially in the coastal areas, has attracted worldwide attention.[3−6] Automated identification system (AIS) of ships was used to establish the ship emission inventory.[7−10] Experimental measurements of ship emissions were combined with transport models to identify the sources of ship emissions and analyze their contribution to the impacts on air quality. Studies have showed that ship emissions could contribute 10−30% of $PM_{2.5}$ within 10 km of the coastal and riverine port areas like in Australian, China, and Europe.[7,11−13]

To reduce ship related air pollutants, the International Maritime Organization (IMO) has established emission control regulations through the international convention for the prevention of marine pollution by ships (MARPOL) and ship Emission Control Areas (ECA) have been defined and implemented worldwide.[14] Since 2011, four ECAs have been created: the Baltic Sea, the North Sea, the North American ECA (with 200 nautical miles), including most of US and Canadian coasts, and the US Caribbean ECA. Within the

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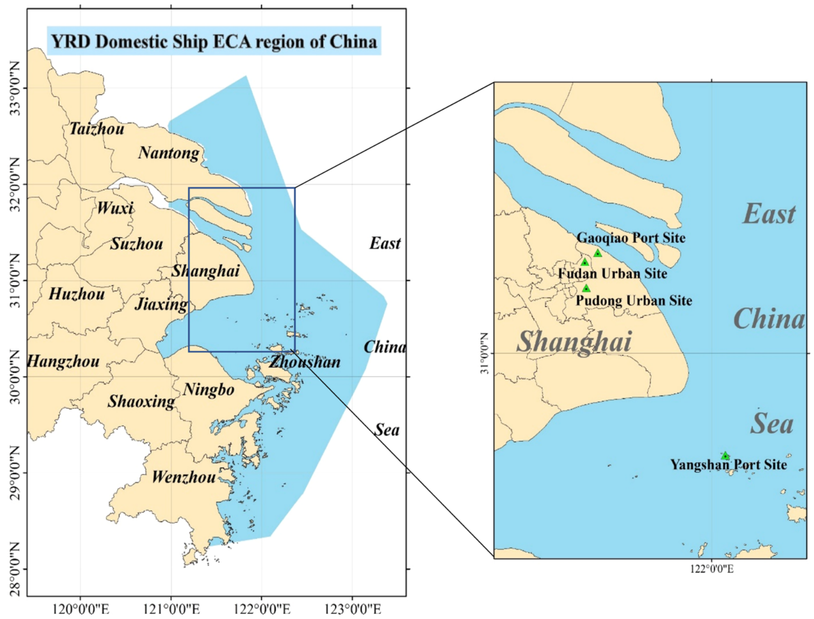

Figure 1. The Domestic Ship Emission Control Area (DECA) in Shanghai and the locations of the sampling sites.

ECAs, sulfur content in the ship fuel had to be reduced to 1% by August 2011, and then to 0.1% by January 2015.[15] Usually, low sulfur oil was obtained by the desulfurization of heavy fuel oils. However, it would be too expensive to produce the low sulfur oil with sulfur content below 0.1% through the desulfurization process. In fact, after January 2015, ships in ECAs virtually replaced high sulfur oil with light oils like marine gas oil (MGO) or the marine diesel oil (MDO) with sulfur under 0.1%.[16] It is expected that the use of low sulfur fuels (either low sulfur light oil or desulfurized heavy oil) will reduce marine sulfur dioxide emissions by more than 90% in ECAs.[17] In China, three Domestic Emission Control Areas (DECAs) were defined in 2015; implementation began in April, 2016 when ship berths were required to use fuel with a sulfur content less than or equal to 0.5%.

After the ECA or DECA policy were implemented, studies have been carried out to investigate how the use of low-sulfur fuels may have affected the atmospheric components in the port and nearby coastal areas. In California, the ship emission control in ports and along the coastlines, by requiring low-sulfur fuels oil in the main engine of ships, resulted in a 28–72% reduction in SO_2 concentrations and a 41% reduction in the emission of black carbon.[18,19] The European Union's low sulfur oil directive reduced ~50% of $PM_{2.5}$ emissions from ships in Venice, Italy, during 2007–2012.[17] In the Gulf of Mexico, switching to low-sulfur marine fuel achieved reductions in emissions of SO_x and $PM_{2.5}$ by 89 and 80%, respectively.[20] Studies also showed that SO_2 and $PM_{2.5}$ emissions decreased effectively in ECAs, but NO_x, which mainly depends on the engine temperature and combustion cycle, did not.[10,21] In Hebei, China, vanadium content in particles, which was used as a tracer of heavy oil burning by ships,[18,22–24] decreased along with the decrease of SO_2 after the implementation of low sulfur fuel policy.[25] However, the carbonaceous species in particles were not significantly influenced by fuel switching after DECAs in Bohai, China.[26]

The previous evaluations of the environmental impact of using low sulfur oil mostly focused on either short-term field measurements or the variation of a single pollutant level like SO_2. Few studies were done based on the long-term measurement of multiple atmospheric components. Furthermore, the ship fuel oil composition and the impact of ship traffic emissions on local air quality could vary among the individual port cities. It is critical and to provide a comprehensive evaluation of the environmental impact of ship emission control measures at representative port areas.

Shanghai port, located at the intersection of the East China Sea and the Yangtze River, is the largest container port in the world and the most important transition-hub port in China. Starting from April 1st, 2016, Shanghai port implemented the China DECA policy. In this work, we take Shanghai port as an example to assess the impact of the fuel oil change policy on the air quality of the coastal cities using a long-term field observation. A long-term survey covering 2015–2017 was conducted to reveal the changes in the atmospheric compositions of SO_2, sulfate, vanadium, and organic carbon (OC)/elemental carbon (EC) in urban and port sites in Shanghai before and after the DECA policy.

2. EXPERIMENTAL METHODS

2.1. Sampling Sites and Sampling Time. Experiments were carried in four observational sites including two urban sites and two port sites (as shown in Figure 1). Online single particle analysis was performed using single particle aerosol mass spectrometry (SPAMS) at a site at Fudan University campus. This site is a typical urban site located in an area with educational, commercial, and residential functions. The SPAMS sampling periods were April–September 2014, NovemberDecember 2014, February–April 2015, June–September 2016, November–December 2016, and March–August 2017 (see Table S1 for the sampling periods). Long-term (2015–2017) measurements of SO_2 and sulfate in $PM_{2.5}$ were carried out at the Pudong site, a coastal urban site located in a highly urbanized area near to Lujiazui CBD between the Huangpu River (about 2.5 km) and the coastal east China sea (20 km). Long-term measurement of SO_2 was also carried out at two port sites, the Gaoqiao and Yangshan sites. The Gaoqiao site is located at the mouth of the Yangtze River with

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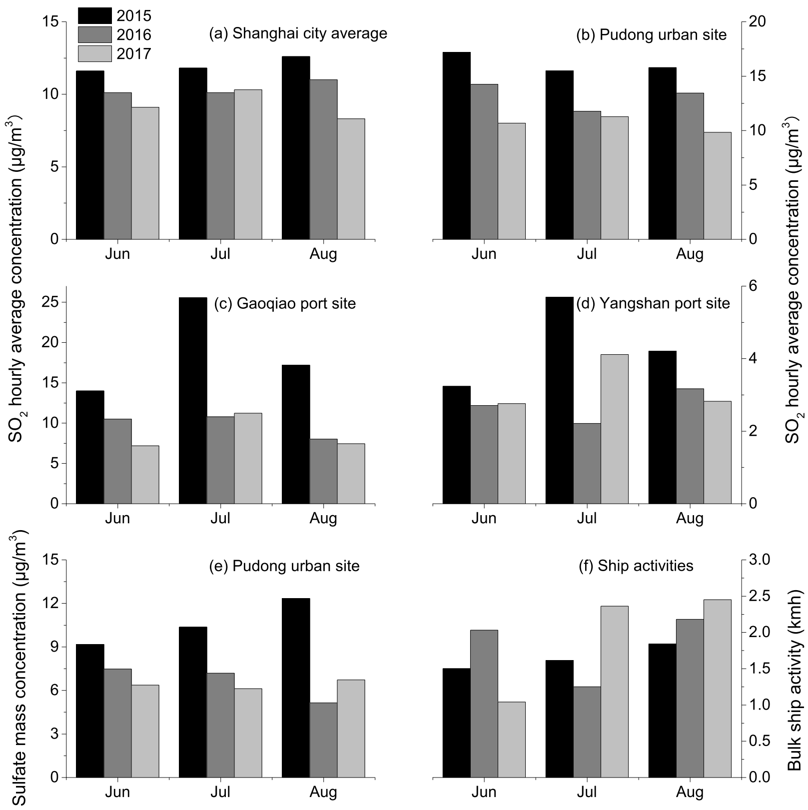

Figure 2. Monthly averaged SO_2 concentrations in (a) the Shanghai city average (released by Shanghai Environmental Monitoring Center), (b) Pudong urban site, (c) Gaoqiao port site, and (d) Yangshan port site; (e) monthly averaged sulfate mass concentration in $PM_{2.5}$ in the Pudong site; (f) monthly averaged bulk ship activities in the Shanghai port area.

high density of ship traffic lanes; the Yangshan site is located on an island with the deep water port hosting international container ships and is about 30 km from the Shanghai city. Three hours interval meteorological data during June to August in 2015–2017 at the Shanghai Baoshan meteorological station were used to analyze the dominant air flow in Shanghai in the summer season.

2.2. Measurements of SO_2 and Particulate Sulfate. Hourly concentrations of SO_2 at the Pudong urban site, Gaoqiao port site, and Yangshan port site were recorded using a Thermo 43i SO_2 analyzer. At the Pudong urban site, the concentrations of eight major water-soluble inorganic ions in $PM_{2.5}$ (Cl^-, NO^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were also measured by a Monitor for AeRosols and Gases (MARGA, model ADI 2080, Applikon Analytical B. B. Corp., The Netherlands).

2.3. Tracking Ship-Related Particle Emisisions Using SPAMS. A single particle aerosol mass spectrometer (Hexin Analytical Instrument Co., Ltd., China) was used to detect particles emitted from ships. The SPAMS first measures the size of a single aerosol particle in a size range of 200 nm to 2 μm. Then, it uses a 266 nm laser to disintegrate the particle and ionize its chemical compounds, of which mass-to-charge ratios (m/z) and concentration are determined by a bipolar time-of-flight mass spectrometer. Detailed information on the SPAMS has been described elsewhere.[27]

Particulates emitted from ships have unique compositions defined by soot, metal (i.e. vanadium, iron, and nickel), sulfate, and nitrate. Vanadium (V) is a good indicator of heavy fuel oil combustion from ships.[18,22–24] In the single particle mass spectra, particles with peak areas of m/z +51 [V^+] and m/z +67 $[VO]^+$ greater than 0.1% of the total peak area of the mass spectrum were considered to be particulate matter discharged by ships. In this work, a particle with a relative peak area of m/z +51 > 0.5% was defined as a high-vanadium (HV)-containing particle; a particle with a relative peak area of m/z +51 $\leq$ 0.5% (>0.1%) was regarded as a low-vanadium (LV)-containing particle.

In this study, we use the number fraction of V-containing particles (NF_V), obtained by dividing the V-containing particle number per hour by the corresponding total particle number, to indicate the contribution of ship emissions to the surrounding environment. We inferred the effect of oil change policy on ship emissions by observing the change in NF_V as well that in NF_{HV} and NF_{LV}. In addition, we performed a statistical analysis of the relative peak areas of V, OC, EC, and sulfate in the selected ship-emitted particles to determine the effect of the DECA on particle composition.

2.4. Analysis of the Ship Fuel Oil Sample. Coastal ships including the domestic and international ships usually burned heavy fuel oils with high sulfur and vanadium contents. To verify the composition change in the ship heavy oils used by the shipping industry after the DECA policy, sulfur and vanadium content of 1094 ship heavy fuel oil samples (collected from January 2013 to December 2018) were tested by using an inductively coupled plasma optical emission spectrometer (SPECTRO ARCOS SOP). The ship fuel oil was classified into different fuel oil grades, specifically 180 and 380cst by 50 °C kinematic viscosity [cst is the kinematic viscosity (1 cst = 1 mm^2/s)].[16] The heavy fuel oil samples included 489 180cst and 605 380cst samples. Generally, the 180cst oils were domestically produced and used by the

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domestic ships. The 380cst oils were bonded fuel oils used for the international ships.[28]

2.5. Estimation of Ship Activity and Ship Emission Inventory. The monthly ship traffic activity and the ship emissions for SO_2 in summer in 2015−2017 were estimated to show the general change in ship traffic sources in this region. The ship traffic activity was estimated using on automatic identification system (AIS) data (the methodology for calculating traffic activity is presented in Supporting Information text S1). The emission inventory was built using the AIS-based model developed by Fan et al.[11] and databases included Lloyd's register (now IHS-Fairplay)[29] and the China Classification Society (CCS) database. The maximum speed designed for ships was supplemented from Lloyd's database. The sulfur content of heavy fuel oil used by main engines was assumed to be 2.7% for international ships and as 1.5% for domestic ships.[30] The sulfur content in low sulfur oils required by the DECA was assumed to be 0.5% for heavy fuel oils for 2016 and 2017.

3. RESULTS AND DISCUSSION

3.1. Changes in Ambient SO_2 in Port and Urban Sites during 2015−2017. Ambient SO_2 can originate from multiple land-based and water area-based sources. In Shanghai, due to the favorable seaside wind direction in the summer monsoon season, wind roses showed that sampling periods from June to August were East and Southeast wind (as shown in Figure S2a−c). Shanghai was mostly influenced by shipping traffic emission with less impact from land-based emissions.[31] In this work, SO_2 data from the two port sites and the Pudong urban site in Shanghai in June−August each year during 2015−2017 were selected to assess the impact of the DECA on ambient SO_2 concentration (Figure 2). As a comparison, the average SO_2 concentrations of the Shanghai city (released by the Shanghai Environmental Monitoring Center) are also shown in Figure 2. From 2015 to 2017, the average 3 month SO_2 concentrations at the two port sites, the Gaoqiao site and Yangshan site, decreased by 55 and 27%, respectively. The Gaoqiao port, located in the cross section of the Yangtze River and the East China Sea, is influenced by high ship traffic activity and the berthing activity of domestic coastal ships in the port. The reduction in SO_2 at the Gaoqiao site after the DECA policy was more significant. The benefit from the low sulfur oil used during the berthing activity was also observed in the Yangshan site, although it is located at the island port with better meteorological conditions for dispersion. SO_2 at the Pudong site decreased from 16.1 in 2015 to 10.5 $\mu g/m^3$ in 2017 a 35% reduction higher than the average reduction observed in the Shanghai city (23%). Generally, reduction in SO_2 concentrations was more evident at the port site with a busy ship traffic and coastal urban sites than in the Shanghai city after implementation of the DECA policy. The measurements have shown that the DECA policy has had a positive impact by decreasing the SO_2 concentration in both the port and coastal urban area in Shanghai. The observed rates of reduction in SO_2 concentration were similar to the previous results in the Bohai Sea.[26]

Changes in the sulfate content of $PM_{2.5}$ at the Pudong site during 2015−2017 are also shown in Figure 2e. The concentration of sulfate in summer decreased substantially, with a reduction of 40%. Because the Pudong site is a coastal urban site, the implementation of the DECA policy resulted in the reduction of secondary aerosols by decreasing SO_2 emission in some degree.

The observed reduction in the concentrations of SO_2 and sulfate resulted from the combination of changes in both ship traffic activity and emission factors. The impact of changes in meteorological conditions was not considered in the current analysis. Theoretically, the implementation of the DECA policy could reduce SO_2 by about 80% by reducing the sulfur content (from 2.7 to 0.5%) in fuel oil as a reference.[11] However, there were variations in the actual ship traffic activities for different years. Since the passing-by ships travelling from the East China Sea to the Yangtze River would also have great impacts on the air quality of Shanghai, the bulk ship activity based on the AIS data of ships was estimated. As shown in Figure 2f, the bulk ship activity in the waters surrounding Shanghai increased by 7−10% between 2015 and 2017. Based on the ship AIS data, the monthly shipping emissions during June−August, 2015−2017 were estimated and were compared with the field measurement results of SO_2 and sulfate concentrations (as shown in Figure S1 in the Supporting Information). Generally, the variations in ship emissions agreed with the field measurement results. SO_2 emission in July around the Yangshan port had a sharp reduction in 2016 compared with 2015, then an increase in 2017, which agreed well with the observed SO_2 in the Yangshan site (Figures S1 and 2d).

3.2. Changes of the Compositions of Ship Emitted Particles before and after the DECA. Vanadium has been confirmed as a reliable tracer of ship heavy fuel oil in the previous studies.[22−24,31] In this study, ship-emitted particles were measured by SPAMS in the Fudan University site in Shanghai. During the sampling periods from June to August, vanadium containing particles dominantly came from coastal air flow with traffic emissions (Figure S2d). Average mass spectra for the V-containing, HV-containing, and LV-containing particles are shown in Figure S3. The number fraction of vanadium-containing particles (NF_V) sampled by SPAMS represents the relative contribution of ship emissions to the environment. During the sampling period, NF_V varied widely (<0.1−39.5%), but was mainly between 1 and 10% (Table S1), consistent with a previous study.[31] Before April 1, 2016, the mean value of NF_V was 1.4%. After April 1, 2016, the mean NF_V increased to 6.9%, as shown in Figure 3a. This increase was mainly caused by the significant increase of LV-containing particles. As shown in Figure 3c, NF_{LV} increased from 36% before the DECA to 54% after the DECA in all the V-containing particles, while NF_{HV} decreased sharply.

The variations in the vanadium content of particles emitted from ships reflected the combined changes of the ship traffic activity and ship fuel oils before and after the DECA policy. The increase in NF_V from 2014 to 2017 were mainly because of the following two key factors: (1) the rise in the ship traffic activity and (2) the continued use of heavy fuel oils in the Shanghai port. For the ship fuel oils factor, if light fuel oils, like diesel (with almost no vanadium) were dominant in the low sulfur ship oil market after the DECA policy, the V-containing particulates emitted from the ship should have been reduced. Instead, the NF_V was even higher than that before the DECA. Our observation suggested that the low sulfur heavy fuel oil might have been be the major type of low sulfur oils used after the DECA policy. The decreasing NF_{HV} against the increasing NF_{LV} implied that vanadium contents of the ship heavy fuel

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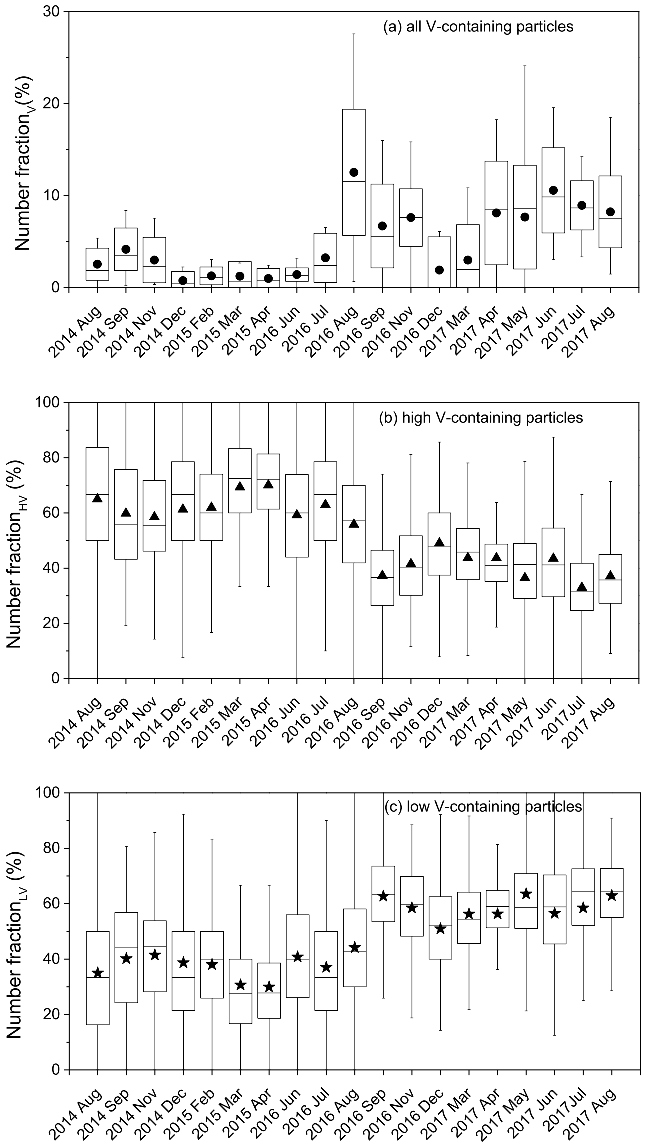

Figure 3. Box plots of the monthly averaged NF_V (a), the NF_{HV}, (b) and NF_{LV} (c) of all the sampling periods. The whiskers represent the 10th and 90th percentile. The two borders of the box display the 25th and 75th percentile. The band in each box denotes the median, and the dot or triangle or star represents the mean. The values for the 10th and 90th percentile for every sampling month are listed in Table S1.

oils decreased along with reduction in sulfur contents after the low-sulfur DECA policy.

Mass spectra of ship-emitted particles contained a series of OC and EC ion peaks. Some typical EC ($^{12}C^+$, $^{24}C_2^+$, $^{36}C_3^+$, $^{48}C_4^+$, and $^{60}C_5^+$) and OC ($^{27}C_2H_3^+$, $^{29}C_2H_5^+$, $^{37}C_3H^+$, $^{43}CH_3CO^+/CHNO^+$, $^{57}C_4H_9^+$, and $^{77}C_6H_5^+$) ions from single particle mass spectrometry were selected to represent the content of EC and OC, respectively. The relative intensities of V, EC, and OC peaks of all V-containing particles in the sampling periods are shown in Figure 4. The results showed that the relative intensity of V gradually decreased (12.2–6.4%) after the implementation of the DECA policy, consistent with the N_V change. The relative intensity of EC components had the same trend as that of V, decreasing from 11.5 to 6.7%. At the time, the mean relative intensity of OC components increased from 10.9 to 21.7%. The relative intensity of OC in

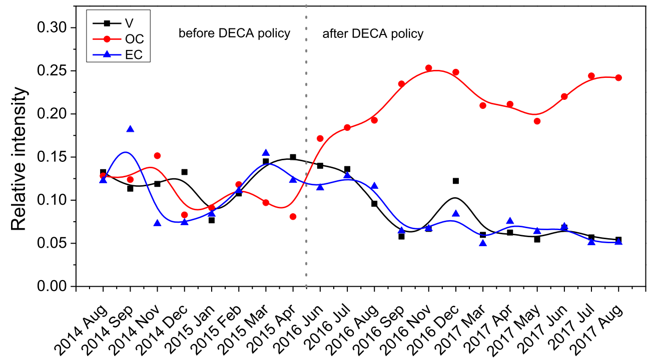

Figure 4. Temporal variations of V, EC, and OC signals in the mass spectra of all V-containing particles.

LV-particles increased dramatically from 13.9 to 24.8% (Figure S4). The variation in the LV-containing particles dominated the change in the total OC emitted from ships. The data suggest that the OC in the particles changed significantly in port areas in China because of the oil change policy.[32]

3.3. Composition Changes of Ship Heavy Fuel Oils during 2013–2018. The field measurements of particles in ship emissions presented in Section 3.2 implied that the low sulfur heavy fuel oil might be the major type of low sulfur oils used after the DECA policy in the Shanghai port. The consumption of ship fuel oils had been increasing from 2016 to 2018 in China, of which heavy fuel oils accounted for more than 60%.[33] Since heavy oil is much cheaper than light oil, heavy fuel oil with low sulfur content was chosen by most domestic coastal ships during berthing.[33] To explain the atmospheric observations and confirm the inference about the fuel oils, 1094 heavy fuel oil samples (included 489 180cst samples and 605 380cst samples) from 2013 to 2018 were collected and analyzed (Table S2).

The sulfur content in domestic 180cst heavy fuel oils decreased from 2013 to 2018 (Figure 5a). The average medium values of sulfur concentrations in 180cst oils was 1.23% before 2016 and was 0.49% after 2016. The reduction in sulfur content of 180cst oils suggested that the domestic coastal ships switched to low sulfur oils at the berth consistent with the requirement of the DECA policy. The sulfur contents in the bonded 380cst fuel oils were generally above 2.0% from 2013 to 2018 and did not decrease after the DECA policy (Figure 5b). To meet the DECA requirement, the international ships at the berth in the Shanghai port usually switch 380cst fuel oils to light oils such as the MGO oil or MDO diesel oil with sulfur content below 0.5%.[18−20] The changes in the fuel oil use after the DECA by both the domestic ships and the international ships explained the decrease in the ambient SO_2 concentration.

The elemental analysis of vanadium content was also performed for all the oil samples as shown in Figure 5. Vanadium in 180cst oils decreased from 39.5 ppm before the DECA to 12.7 ppm in weight after the DECA while no significant change was observed in the 380cst oil samples. After the DECA, vanadium still existed in the low sulfur 180cst oils but at lower concentration. This result is consistent with our observation of the decrease in HV-containing particles and increase in LV-containing particles after the DECA. It also confirmed that the dominant fuel oils used by ships sailing around the Shanghai port after the DECA were still heavy fuel oils.

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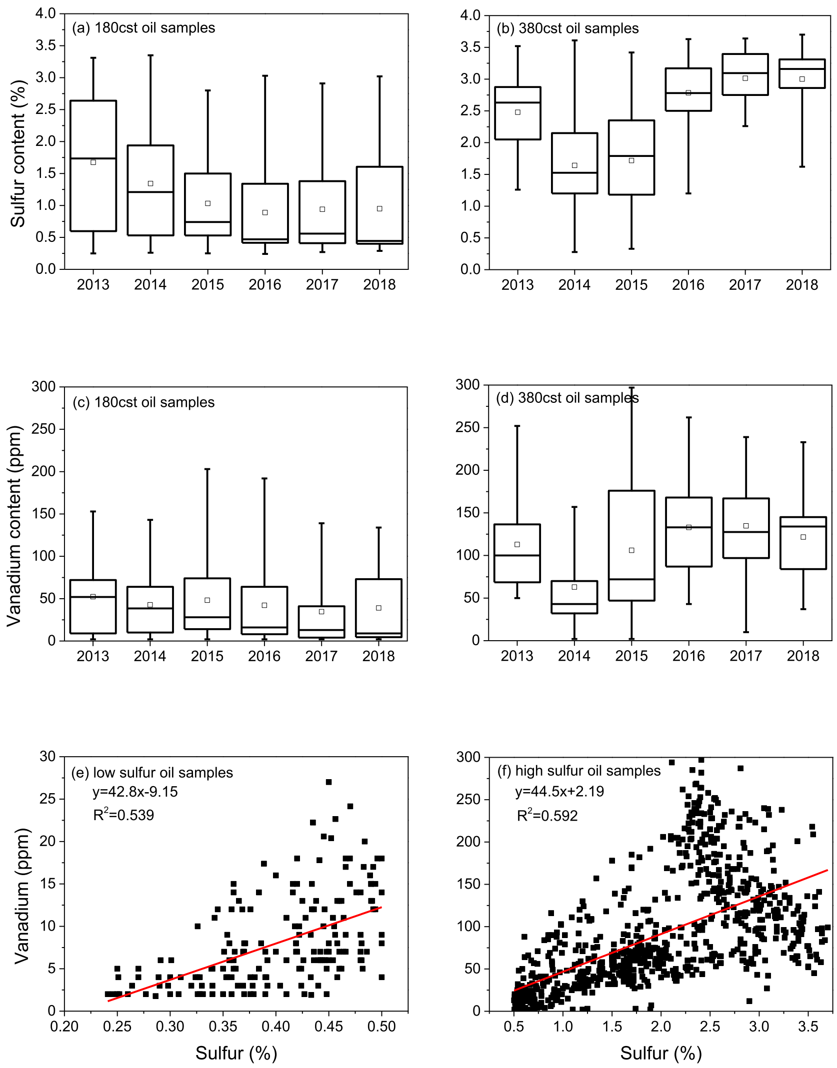

Figure 5. Annually averaged sulfur concentrations in 180cst (a) and 380cst (b) oil samples; annually averaged vanadium concentrations in 180cst (c) and 380cst (d) oil samples; correlations between sulfur and vanadium concentrations in low sulfur fuel oils (e) and high sulfur fuel oils (f).

The correlations between vanadium and sulfur contents in high sulfur oil samples ($S \geq 0.5\%$) and in low sulfur oil samples ($S < 0.5\%$) were calculated. Vanadium in fuel oils with a sulfur content below 0.5% still maintained good correlations as that in high sulfur oils. The slope of linear fitting (42.8) which represents the mass ratio of V and S in low sulfur fuel oil samples was similar with that in high sulfur oil samples (44.5). The highly correlated vanadium and sulfur contents in 180cst oil samples after the DECA in this study implied that these low sulfur oils might be produced by simply blending some nonsulfur materials into high sulfur heavy oils to dilute the sulfur concentration, rather than directly using more expensive low sulfur light oil (very low vanadium) or desulfurized heavy oil (high vanadium content). Although the non/low-sulfur blending materials used to produce low sulfur heavy fuel oil could be MDOs or MGO, other inexpensive nonoil materials might also be used.[33,34] Studies about emission factors for different ship fuel oils have shown that ship heavy fuel oils lead to much higher OC in emitted primary particles than MDOs; however, the variation of volatile organic compounds (VOCs) emitted from heavy fuel oil and diesel fuel oil use has shown different pattern and are not well known.[32,35−39] Therefore, given only the pure MDO or MGO is blended with the mother heavy fuel oil, the primary OC in particles will remain stable or decrease compared with the mother heavy fuel oil and the variation in the VOC due to oil switch would not be expected to cause evident secondary OC increase by ships. However, in our study, the OC in vanadium-containing particles increased measurably. Combined with the observation of an increase in the OC component in ship-emitted particles after the DECA policy, our study suggested that use of cheaper organic materials could account for the increase of OC. This suggestion was confirmed by the fact that the emission factors of some organics like toluene from low sulfur heavy fuel oil (42.7 ± 21.2 mg/kW h) were much higher than those from high sulfur heavy fuel oil (4.5 ± 7.2 mg/kW h).[40]

3.4. Policy Implication. This study observed that there was a significant reduction in ambient SO_2 concentration at both port sites and urban sites in Shanghai after the implementation of the Chinese DECA in the Shanghai port, despite increasing ship traffic activity. Vanadium and EC contents in particles emitted from ships also decreased. However, the OC content in ship-emitted particles increased after the DECA policy. Elemental analysis of 1094 heavy fuel oil samples from 2013 to 2018 confirmed our ambient observation. Both sulfur and vanadium contents in domestic

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180cst heavy fuel oils decreased after the DECA policy. The strong correlation between sulfur and vanadium concentrations in low sulfur oils revealed that the dominant fuel oils used by ships traveling around the Shanghai port after the DECA were still heavy fuel oils. The results finding higher OC components in particles following the DECA further suggested that some low sulfur heavy oils may have been produced by blending nonsulfur organic materials into high sulfur heavy oils. Currently, the main focus of the DECA fuel policy is the sulfur content in the fuel oil including no requirement for other fuel components. Given our findings, new emission factors from the burning of low sulfur oil after the implementation of the DECA policy should be evaluated systematically. More comprehensive fuel oil policy including multiple-component control is necessary for preventing air pollution from ship emissions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b03315.

Monthly shipping SO_2 emission; number of wind from different directions; average mass spectra; temporal variations of OC in LV particle; sampling periods of SPAMS; and quantity of 180cst and 380cst oil samples (PDF)

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Notes

The authors declare no competing financial interest.

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