Characteristics of marine shipping emissions at berth: profiles for PM and VOCs

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Abstract. Emissions from ships at berth play an important role in the exposure of atmospheric pollutants to high density population in port areas, but these emissions have not been understood very well. In this study, volatile organic compounds (VOCs) and particle emissions from 20 container ships at berth were sampled and analyzed during the fuel switch period at Jingtang Port in Hebei Province, China. VOCs and particles were analyzed by gas chromatography-mass spectrometer (GC-MS) and the Single Particle Aerosol Mass Spectrometer (SPAMS), respectively. VOCs analysis showed that alkanes and aromatics, especially benzene, toluene and heavier compounds eg., n-heptane, n-octane, n-nonane, dominated the total identified species. Secondary organic aerosol yields and ozone forming potential were 0.017±0.007g SOA/g VOCs and 2.63±0.37g O₃/g VOCs, respectively. Both positive and negative ion mass spectra from individual ship were derived and intensity of specific ions could be quantified. Results showed that element carbon (35.74%), element carbon-organic carbon mixture (33.95%) and Na-rich particles (21.12%) were major classes with a total number fraction of 90.7%. Particles from ship auxiliary engines were in a size range of 0.2 to 2.5μm, with a peak occurring at around 0.4μm. The issue of vanadium as tracer element was discussed that V was not a proper tracer when using low sulfur content diesel oil. The average percentage of sulfate particles from shipping emissions before and after switching to marine diesel oil were 23.82% and 23.61% respectively. The total results provide robust evidences in port area air quality assessment and source apportionment.

1. Introduction

Emissions of multiple pollutants and greenhouse gases like NO_x, SO_2, particulate matters(PM) and CO_2 from ocean-going ships have been significant sources to global air pollution(Eyring et al., 2010;Corbett et al., 1999), of which the impacts were on a global scale and widely-spread. Along with the impacts on

5   air quality(Vutukuru and Dabdub, 2008) and climate change, health impacts were also revealed and researched by plenty of recent studies(Andersson et al., 2009;Corbett et al., 2007). There were about 60,000 cases of deaths due to cancer and cardiovascular diseases associated with ship exhausts worldwide(Tian et al., 2013). In East Asia, where 8 out of 10 top container ports were located, ship emissions caused premature deaths of between 14,500 to 37,500 in 2013, almost doubled comparing to

10   that in 2005(Liu et al., 2016).

Emission characteristics, including size distribution of particles, chemical compositions of particles and volatile organic compounds (VOCs), are with particular importance to understand the climate and health impacts of shipping. Plenty of studies on emission factors and chemical characteristics were conducted throughout China and western countries. In terms of domestic gaseous pollutants and PM emission

15   factors, CO, HC, NO_x and PM emission factors during maneuvering and cruising conditions from 7 in-use ships (4 container ships included) were tested by portable emission measurement system, illustrating the nucleation and accumulation mode of major PM (Peng et al., 2016), and in another case 3 offshore vessels were tested by on-board systems(Zhang et al., 2016). Black carbon in exhausts from 71 ships were analyzed in California(Buffaloe et al., 2013). Apart from those direct sampling of shipping exhausts,

20   plumes were sampled via aircraft 100km off the California coast(Chen, 2005) and in-port ambient PM measurements were also done in the Port of Dock using aerosol time-of-flight mass spectrometer(Healy et al., 2009). Chemical properties of PM in plumes of 1100 commercial ships were studied by time-of-flight aerosol mass spectrometer in Mexico Gulf(Lack et al., 2009). In summary, these listed studies generally focused on emission factors of typical gaseous pollutants and PM, and plume studies were

25   more relevant to the mixture of primary and secondary aerosol, result in insufficiency of directly-exhausted gas and PM studies. Another noticeable fact was that these studies on emission characteristics mostly explored the at-sea parts of shipping emissions, thus paying no adequate attention on specific at-berth conditions.

Based on the studies mentioned above, it could concluded that one of the major gaps in exploring

emission characteristics is to understand specific shipping emissions under at-berth mode. The significance of at-berth emissions was attributed to the fact that contribution of emissions under operation mode of 'at berth', mainly dominated by the auxiliary engine emissions, increased rapidly as the target areas shrank from global scale to the port regions. For global shipping emissions, the share of emissions

5   from auxiliary engines under at-berth mode was between 2-6%(Corbett and Koehler, 2003). When the domain was limited to a region-scale, eg. East Asia, the contribution of SO_2 and NO_x emissions at berth increased to 26%(Liu et al., 2016). When focusing on the national costal area, the shares continued growing to 28% and up(Fu et al., 2017). An in-port shipping emission inventory of Yangshan Port in China(Song, 2014) revealed that auxiliary engine exhausts contributed 40.5% and 43.3% to overall $PM_{2.5}$

10   and SO_x respectively. This is why the Fuel Switch at Berth regulation was proposed in 2011 and enforced in July 2015 in Hong Kong, then proposed in 2015 and enforced in 2017 in Main land China as the first step on marine fuel quality control. Yet no valid and comprehensive studies on chemical properties of auxiliary engine exhausts have been conducted in China, which owned 12 of 20 listed world's largest ports by 2010(Report, 2013). Consequently, the lack of studies on chemical characteristics of at-berth

15   emissions became a barrier to further analyze the mechanism of organic aerosol transition and toxicology of human health. Owing to the lack of these specific studies, it was more difficult to apply accurate at-berth data in evaluating health impact instead of using general average of shipping emission data without distinguishing both at-sea emission and at-berth emission.

Apart from the significance of at-berth emissions, another critical issue was the impact of different fuels

20   on shipping emission chemical characteristics. The main fuel types applied in ship main engines or auxiliary engines were mainly residential oil, heavy fuel or intermediate fuel oils (Hays et al., 2008) as well as marine diesel oil. Low-grade heavy fuel oil (HFO), known as bunker oil or residual oil, which usually had sulfur content of higher than 0.5% and metallic elements such as vanadium, nickel and copper, was commonly used in marine engines and was responsible for high level of PM and gaseous pollutants

25   such as SO_X(Agrawal et al., 2009). In contrast, marine diesel oil (MDO) was lighter and cleaner diesel with lower sulfur and metallic element content(Corbett and Winebrake, 2008). Aiming at reducing the emissions, More stringent limit on fuel sulfur content and switching to cleaner marine diesel fuels became a common trend(IMO, 2017). Various studies illustrated the distinction of using HFO and MDO in shipping emission chemical characteristics. For black carbon, using low sulfur content MDO could result

30   in a reduction of up to 80% of total BC emissions comparing to using HFO(Lack and Corbett, 2012).

Recent comparative study focused on HFO and MDO in Europe sulfate emission control area (SECA) and results showed that a decline of sulfur content from 0.48% to 0.092% lead to a reduction of 67% in PM mass and 80% in SO_2 emission(Zetterdahl et al., 2016). Another comprehensive study including PM, EC, heavy metals was made to make comparison between HFO and standardized diesel fuel (Streibel et al., 2017). Following the regulations of using low sulfur fuels implemented by western countries, China began to launch its own stepwise regulations associated with domestic emission control areas (DECAs) to minimize conventional pollutants from shipping emissions. Under the new regulation ships were required to use diesel with a lower sulfur content of below 0.5% at berth, corresponding to the vital role that at-berth emissions played in air quality. Fuel switch would lead to changes in chemical characteristics of ship-exhausted gas-phase VOCs and PM, which were closely relevant to ambient air quality in port areas and health impact on population. Nevertheless, previous comparative studies on different fuels tended to emphasize the diversity in total amount and emission factors, there lacked of studies revealing chemical characteristics caused by fuel switch especially in China.

In order to explore the chemical composition of VOCs and particulate matters (PM) from ship auxiliary engines, this research was located in a key port area and was designed to cover the primary period of new policy implementation: from December 27th, 2016 to January 15th, 2017 in Jingtang Port, which was among the pilot key ports where new regulation came into effect since January 1st, 2017. An amount of 20 container ships were sampled and measured for VOC and PM emissions from auxiliary engines in the mode of at-berth. Via the application of gas chromatography-mass spectrometer (GC-MS) and single particle aerosol mass spectrometer (SPAMS), this research conducted a comprehensive exploration in perspectives of VOC profiles, PM size distribution and typical ion mass spectra, which could act as fundamental to impact assessment of shipping emissions and source apportionment in key port regions.

2   Experimental and methods

2.1   Sampling methods and instruments

2.1.1   Information of sampling sites and ships

Ambient sampling site was located inside Jingtang Port area in Hebei Province, China. Instruments were settled inside a container on a flat ground close to the #28 Berth and on the east side was the channel that allowed ships sailing in and out of the berth. The information of 20 container ships included in this study

was collected via on-board inquiry and was listed in **Table 1**.

2.1.2 VOCs sampling and analysis by GC-MS

VOCs from ship at berth were sampled via Entech summa canisters with standard volume of 3.2L. When auxiliary engines were in operation, Teflon tubing with a length of 1m was stretched into the exhaust

5   pipe, with the other end linked to summa canister. The flow rate was kept constant by Entech CS1200ES passive canister sampler, which also filtered impurities like particles and ashes. The first patch of samples was regarded as preliminary tests in order to determine proper dilution factors and sampling time and flow rate. Sample dilution was conducted by Entech 4600 dynamic diluter with various dilution factor range from 10 to 80, depending on the original sample concentration. Agilent 5975C-7890A was

10   calibrated with standard gas and used for analyzing diluted VOC samples. A total of 93 VOC species were detected and mass percentage of single compound could be calculated according to sample inlet volume, dilution factor and calibration curve.

2.1.3   Particles sampling and analysis by SPAMS

Ship exhaust particles were collected directly from exhaust pipes of auxiliary engines on ships by Tedlar

15   bags and metal tubing designed specifically for particle sampling. The whole sampling process was achieved by a non-contact sampling box and air pump. Then samples were sent to the Single Particle Aerosol Mass Spectrometer from Hexin Analytical CO., Ltd(Li et al., 2011)as soon as possible to be analyzed. SPAMS shared common principle and mechanism with Aerosol Time-of-Flight Mass Spectrometer (ATOFMS). It was frequently applied in online measurement and analysis of single particle

20   aerosol from heavy diesel vehicle exhausts(Shields et al., 2007) and biomass burning(Bi et al., 2011;Xu et al., 2017).

Ambient particle sampling was conducted from December 27th, 2016 to January 15th, 2017, spanning about 20 days. Ambient particles were sampled and analyzed by SPAMS, with the inlet fixed at a height of 3.6m from the ground level.

25   2.2 Ion mass spectra identification and manual grouping

Ion mass spectra with positive and negative ion information were derived from SPAMS output as fundamental for further analysis. Both positive and negative ions were in an m/z range of 1-250. Based on ART-2a neural network algorithm(Song et al., 1999), single particles sharing similar mass spectral

signatures were further grouped into clusters. The whole algorithm process was operated on MATLAB 2011a, and a vigilance factor of 0.7 as well as a learning rate of 0.05 was set respectively with 20 iterations. Then further manual classification was demanded in order to merging particle clusters into expected types, depending on the target of research. Clusters that counted for top 95% of all particles would be

5   analyzed according to the method mentioned previously.

To identify each type of particles, ions with certain m/z value were used as markers(Fu et al., 2014). For element carbon (EC) particles, [C_n] signals were the most typical markers distributing in both positive and negative ion mass spectra. For organic carbon (OC) particles, ions with m/z=29, 37, 41, 43, 51, 61, 63,…represent $C_2H_3^+$, C_3H^+, $C_3H_5^+$, $C_4H_3^+$, ..., respectively. Meanwhile, there existed a status of EC ions

10   signals mixed with typical OC signals, which should be classified into EC-OC mixed particles (ECOC), and it was hard to accurately divide them into EC or OC types owing to the coexistence of EC and OC ion signals in single particle spectrum. ECOC particles were formed by EC or VOCs that had been oxidized in the air into OC attaching on the surface of the EC particles(Liu et al., 2003). Na^+ mostly came from sea salt while K^+ came from biomass burning as well as sea spray sources(Leeuw et al., 2011). V^+

15   and its oxidized ion VO^+ were considered as the symbol of ship exhaust for V existed in fuel like heavy fuel oils (HFO). Previous studies (Celo et al., 2015;Liu et al., 2017) frequently used V^+ and VO^+ to identify particles from ship exhausts, though they could be observed more rarely comparing to other large-quantity particles. Other metallic ions such as Fe^+ and Cu^+ could also be observed, and they had relatively small relative intensity, for the metal elements scarcely existed in atmosphere and fuels

20   combusted in powertrain systems. In most cases, particles with relative intensity of metallic ions higher than 0.05 and no other obvious high signals could be classified into metal rich particles.

3   Result and Discussion

3.1   VOCs speciation

Exhausts from a total of 20 ships have been sampled on board and all samples have been diluted to a

25   concentration of approximately 3-4 ppm in order to guarantee the validity and accuracy of GC-MS analysis. 93 species were detected for each ship sample. The sum of mass concentration of identified 93 species was defined as 1, thus normalizing the mass concentration of single species. 4 samples were excluded for their irregularity after 3-sigma test for all data. Then the remaining 16 samples were

averaged by percentage of mass concentration and then VOCs speciation profile was obtained for all 16 ships, which shared similarity in species mass concentration distribution. The histogram of VOC profile by mass percentage was shown in **Fig. 1** and top 32 species were listed in **Table 2**. Alkanes and aromatics dominated the total identified VOCs from ship auxiliary engine exhaust. N-heptane, methylcyclohexane,

5   n-octane, n-nonane, n-decane and n-undecane contributed considerably to alkane emissions, which indicated that alkanes with carbon number of more than 7 were more likely to be emitted from ship diesel engines compared with other mobile sources. Among aromatics benzene and toluene contributed approximately 9% to total VOCs emissions. This result was acceptably in consistence with study of Huang et al. on diesel emissions in Shanghai(Huang et al., 2015). In view of oxygenated VOCs and

10   haloalkane contents, acetone and CH_2Cl_2 exceeded benzene and toluene. However, there were considerable standard deviations in average oxygenated VOCs and haloalkanes mass proportion due to obvious ship-based difference and quantification inaccuracy of GC-MS for these two classes of compounds.

3.2   SOA Yields and OFP by VOCs from ship exhausts

15   Based on VOCs profile, SOA yields and ozone forming potential for ships were calculated. SOA yield value for individual precursor and definition of non-precursors were referenced from Gentner's study(Gentner et al., 2012). Here was a noticeable fact that intermediate VOCs (IVOCs) were not identified and quantified in this study, which may cause underestimation of the actual SOA yields. Also, VOC source profile of 3 types of diesel trucks (light-, middle- and heavy-duty truck respectively) (Yao

20   et al., 2015) and average profile for light-duty passenger gasoline vehicles were collected from previous research in China (Cao et al., 2015) to make comparison among them. Considering this comparison could provide insights to emission control strategy and fuel quality for different sectors in the same country, the comparison made among studies in China would make more sense. The results were presented in **Fig. 2**, and the average SOA yield for 16 ships measured was 0.017g SOA/g VOCs. As seen in Fig. 2,

25   conclusion can be drawn that in terms of SOA yields, ship-exhaust VOCs would generate more SOA than that of diesel trucks as well as gasoline vehicles. The main reason was the content difference of heavy organic compounds. Ship exhausts contained more heavy VOCs like alkanes and aromatics with carbon number of more than 9 than that of vehicles, among which aromatic contents like benzene, toluene and xylene were especially responsible for SOA yields. The unconsidered IVOCs tended to exist more

commonly in heavy fuels rather than diesel oil or gasoline.

Ozone forming potential showed different trend against SOA generation in that VOCs from ship exhausts had approximately equal OFP with diesel and gasoline vehicles. According to the calculating method of maximum increment reactivity (MIR)(Carter, 1994), lighter VOC had higher MIR scale, which meant

5 more contribution to ozone formation. VOCs from ship exhausts had relatively lower content of light hydrocarbons, thus lowering the overall ozone forming potential. The average OFP of ship emitted VOCs was 2.63g O_3/g VOCs. In conclusion, VOCs from ship exhausts might play a more important role in secondary organic aerosol formation in port area than diesel trucks and gasoline vehicles.

3.3 Overall particle characteristics by SPAMS

10 #### 3.3.1 Average ion mass spectra

Samples collected by Tedlar bags and glass bottles from 20 ships at berth were analyzed by SPAMS. Excluding some invalid samples with very few particles, the average ion mass spectra of both positive and negative ions expressed in relative area were obtained after SPAMS analysis and classification, as shown in **Fig. 3**. Individual ion mass spectra for each ship were shown in **Fig. 4**.

15 The average ion mass spectra presented overall characteristics of total 20 ships. For positive ion spectrum, it could be noticed that Na^+ signal was observed as the highest peak. Na^+ was recognized as symbolic ions from sea salt particles. It can be observed in the exhaust because the intake air of ships are full of sea salt. Another sort of abundant ions represented EC and OC, occurring in the form of C^+, C_2^+, C_3^+… as EC and C_3H^+, $C_2H_3^+$…as OC, respectively. It was easy to find that the relative signal area of EC ions

20 were higher and more widely distributed than OC ions, which was consistent with previous researches that fuel combustion produced more EC than OC particles. Though not as obvious as those abundant sorts above, the percentage of V^+ and VO^+ were relatively low but not negligible, which were commonly used to identify ship source particles.

For negative ion spectrum, the components were not as complex as positive. The highest peak was HSO_4^-

25 with m/z=-97, which exceeded 50% of the overall negative ion relative area. HSO_4^- was typical marker of sulfate particles, which were formed via secondary reaction in atmosphere. This part will be further discussed in following sections. EC signals such as C_2^-, C_3^-, and C_4^- could also be observed in negative spectrum. In addition, markers of nitrates with m/z=46 and 62 were NO_2^- and NO_3^-. Nitrates were

regarded as secondary particles that might come from the aging of primary particles emitted directly by fuel combustion or the transformation of gas-phase NO_2. The relative area of nitrate signals was much lower than HSO_4^-, illustrating that nitrate particles were not predominant in ship exhausts and not the main research goal in this study.

3.3.2 Manual grouping results

Based on single particle ion spectrum similarity and ART-2a neural network algorithm, particles from ship exhaust were further grouped into clusters of 175, among which the top 86 clusters covered 95%, with the rest defined as others. Clusters were set as OC, EC, ECOC, Na (Na-Rich), K (K-rich), V (V-rich), Cu (Cu-rich), Fe (Fe-rich), Mn (Mn-rich) and others, depending on the similarity and manual grouping. Method and criterion of the manual grouping mainly focused on positive ions. Particle grouping could be a fundamental access to accurate source apportionment of a target region.

After that a composition analysis was conducted and result was shown in **Fig. 5**. It was shown that EC and ECOC particles dominated with a proportion of 35.74% and 33.95%, while Na-rich particles ranked 3rd with percentage of 21.12%. Data of EC and ECOC indicated that carbon emitted by fuel combustion tended to product more EC and ECOC than purely OC particles. The amount and fraction of OC particles was remarkably lower than EC and ECOC with a factor of ~10. Meanwhile, OC tended to attach to EC particles and thus forming ECOC particles and increasing the fraction of ECOC particles. The explanation for high proportion of Na-rich particles was from sea spray sources. When engine works, air from above the sea is inhaled into engine and Na particles attached to the exhaust products after fuel combustion. In fact, part of ECOC and OC, EC particles still had high Na^+ ion signals. Only particles with relative area of Na^+ obviously higher than other positive ions were counted as Na-rich particles. The same rule also adapted to K-rich particles. Na^+ and K^+ were both widely spread among all particles. V-rich particles were likely to contain mixtures of ammonia sulfate or sulfuric acids(Divita et al., 1996), which could be proved by ion mass spectra. Particles with relatively high V^+/VO^+ signals occupied only 1.1% according to the classification criterion, which were contributed by a few numbers of ships. This will be discussed in following parts.

3.3.3 Size distribution

Particles with aerodynamic diameter ranging from 0.2μm to 2.5μm, covering the accumulation mode

(0.1μm to 1μm) and coarse mode (over 1μm)(Frick and Hoppel, 2010), were analyzed by SPAMS and

this size range has a significant correlation with PM$_{2.5}$ pollution, which should be evaluated seriously.

Size information of 257911 particles from 20 ships were derived from SPAMS and 19342 of them were

hit. It showed a skewed distribution with a peak appeared between 0.38μm and 0.44μm. This result

5 disagreed with the measurements conducted in Ireland using SMPS(Healy et al., 2009), in which particles

measured were mostly within the size range of 100nm. Moreover, bimodal distribution was not observed

for the reason of limited size range measurement of smaller than 2.5μm, while the coarse mode usually

occurred beyond that. The divergence might result from the difference of measuring instruments and

fuels. 95% of all particles with size information lay in 0.2μm-1.46μm, which implied that particles from

10 ship auxiliary engine exhaust could be classified into fine particles, contributing to the PM$_{2.5}$ in ambient

air. It is remarkable that the magnitude of size distribution in this study was consistent with some of the

test results by engines using different fuels. Most of the samples in this study were collected after January

1st, when new policy of forcing ships to switch to clean diesel fuel had taken effect. This could result in

the decline of particle aerodynamic diameter.

15 In order to further analyze the size distribution information of different sorts of grouped particles, **Fig. 6**

was drawn to reveal the proportion variation among different particles over size range. As OC particles

only occupied less than 5% of overall particles, they show no apparent trends and distributed dispersedly

in each section. It can be observed that in sections of larger than 1.30μm OC particles occasionally

"disappeared" in some bins, while they kept continuously between 0.2-1.30μm, which might indicated

20 that OC tended to concentrate in a relatively tiny size section. The rule of EC particle distribution was a

little similar to bimodal distribution, with the first peak settled in the section of 0-0.6μm. In the section

of 1.75μm to 2.5μm, it appeared to present another peak but not as obvious as the first one. Accordingly,

in section of 0.2-0.5μm, proportion of ECOC particles was lower than that in the section of over 0.5μm,

implying that ECOC tended to form larger particles comparing to EC. Another obvious fact was that K-

25 rich particles were more likely to present normal distribution in the range of 0.25μm to 1.0μm, which

was discrepant with size distribution of Na-rich particles. Na-rich particles distributed almost equally

among bins in 0.2-1.25μm, and proportion increased starting from 1.25μm. Metal contained particles

were observed between 0.25μm to 1.25μm, occupying much lower proportion comparing to other

massive sorts of particles. Metal contained in particles emitted by ship engine mainly came from

30 combustion of heavy fuel oil and were known to catalyze the oxidation of SO$_2$ and subsequence formation

of sulfuric acid or sulfate particles.

3.4 Whether vanadium can be used as tracers of ship fuel combustion in port area atmosphere?

3.4.1 Ion mass spectra difference between ships using different fuels

Owing to the fact that all samples were collected after January 1st, 2017, the regulated date of fuel switch,

5   it could not be judged by date whether ships had changed to diesel fuel. However, from the ion mass

spectra of individual ships it could be noticed that some of the ships had higher V intensity while others

not (Ni was also a certain element mostly from heavy fuel, but SPAMS seemed to perform less sensitivity

of Ni detection(Agrawal et al., 2009)), and there existed considerable difference in HSO$_4^-$ intensity. In

order to better distinguish ships using HFO and MDO, operation in MATLAB analysis was carried out.

10   Signals satisfied the intersection of conditions that intensity of peak m/z=51 and m/z=67 were higher

than 100 while m/z=37 lower than 100, could be recognized as vanadium-related signals, excluding the

possibility of counting OC signals for V signals. Ship13 and ship17 shared a similarity in both high V

and HSO$_4^-$ relative intensity, as shown in **Fig.** 7. Separate ion mass spectra of these two types were

derived respectively as shown in **Fig.** 8, in which ship13 and ship17 were defined as Type1 while the rest

15   as Type2.

Type1 ships included a total particle number of 30009 and among which 2633 were measured with ion

mass spectra. Type2 ships had a total number of 227902 and 23855 were measured. The average hit ratio

approximated 10%. In the ion mass spectra of Type1 ships, higher V$^+$ / VO$^+$ and HSO$_4^-$ signals of over

0.8 in relative intensity while Type2 ships had average HSO$_4^-$ relative intensity of 0.59 and no apparent

20   V$^+$/VO$^+$ signals. In addition, signal of m/z=-192 occurred in negative ions of Type1, which could

represent heavy EC signals relating to heavy oil combustion. Based on these features, it could be

concluded that Type1 represented ships using HFO and Type2 for MDO ships. Due to the relatively

fewer particles of HFO ships, there might be abnormity in low positive EC signals in ion mass spectra of

HFO ships. Nonetheless, major chemical PM characteristics of different fuel types could be observed

25   through ion mass spectra.

3.4.2 Comparison of vanadium intensity between shipping emissions and ambient data

Previous studies have illustrated that owing to the vanadium contents in heavy fuel, vanadium in ambient

atmosphere could be used as tracers indicating the heavy fuel combustion related to ship exhausts(Celo

and Dabek-Zlotorzynska, 2010). Field measurements in Shanghai Port in 2011 revealed that the V/Ni ratio could be applied to identification of shipping traffic emission(Zhao et al., 2013); domestic researches elsewhere focused on Bohai Rim in 2013 identified and quantified contribution of ship PM emission to ambient air quality using V as tracers(Zhang et al., 2014). Moreover, studies in Europe also

5 focused on metallic elements representing shipping-source particulate matters in atmosphere, which played crucial roles in ambient PM source apportionment analysis (Marco et al., 2011;Perez et al., 2016). As the new regulation came into effect and ships were demanded to use low sulfur diesel oil at berth, whether vanadium could still be used as tracers of ship emission to accomplish shipping source identification is worthy of exploration. Distinct from previous researches that mainly based on filter

10 analysis, this study provided an innovative perspective of spectrometry analysis.

Owing to the working principle of SPAMS, mass ratio of vanadium element to other symbolic elements could not be derived, and Ni as well as La showed no apparent signals in SPAMS spectra. The main methodology was to make comparison between the vanadium intensity of particles from ships to that of particles sampled in ambient atmosphere. If the vanadium intensity in ship exhausts is commonly lower

15 than that of the corresponding ambient data, then it is no longer a proper tracer for vanadium to identify ship exhaust sources. Calculation was performed using a method similar to the one mentioned previously. Due to the fact that sampled and particle numbers detected by SPAMS differ apparently among ships, we defined the ratio of total intensity to SPAMS detected particle number as vanadium-related intensity. The results of overall 20 ships sampled during January 4th to January 16th as well as the ambient vanadium

20 intensity is shown as **Fig. 9**.

Noticing that the ordinate was logarithmic, considerable distinction existed among ships in vanadium intensity. The intensities in the exhausts from 17ships were well below or comparable to corresponding ambient intensity, while ship2, ship13 and ship17 can be observed with apparently high vanadium intensity. This phenomenon might revealed the fact that after fuel substitution, vanadium from ship

25 exhausts at berth would not appear remarkably higher than that of the ambient in most cases. Another crucial evidence is the element analysis of 3 diesel samples collected during field measurements (shown in **Table 3**). None of the 3 diesel samples were vanadium detected, which showed significantly decrease from the literature data of 38.0-133.8mg/kg in previous studies using intermediate fuel oils(IFO) as shown in **Table 3**(Celo et al., 2015). From the aspect of vanadium "sources", it can be referred that if the

30 content of vanadium in fuel keeps declining, the role it plays will not be as significant as it used to be. It

will be much harder to detect the existence of vanadium in ambient atmosphere.

3.5   Sulfate particle contribution of ship exhausts to ambient particles

The primary goal of domestic ship emission control areas was to control SO_2 and sulfate emissions. The concrete demand for emission reduction was lowering sulfur content in fuel oil to a certain level, which

5   had been designed as lower than 0.5% by weight percentage. Based on these facts, it's meaningful to evaluate the impact of switching to clean diesel oil on ambient air quality. One of the effective methods was to extract ship-source sulfate particles out of overall ambient particles that were sampled by SPAMS and observe the change of ambient sulfate particle number as well as ship-source sulfate ratio over time. The first step was to identify and extract ship-source particles out of all that were sampled and analyzed

10   by SPAMS. The operation was based on information and properties of particles from ship exhausts, which had been analyzed and obtained from average ion mass spectra. Then by setting a certain similarity and using MATLAB, if the ion mass spectra of a particle shared similarity exceeding the setting value, it would be judged as particle from ship exhaust. The next was to extract sulfate particles out of ship-source and ambient, respectively. This step was accomplished by finding particles as sulfates with m/z=-97 and

15   -80, which represented HSO_4^- and SO_3^-, two typical markers of sulfates. The temporal profile (1 hour resolution) of ship-source and ambient particle number sampled by SPAMS between 18:00, December 27th and 18:00, January 15th was shown in **Fig. 10**, while the green line referred to the number fraction of ship-source to ambient sulfates. The red dashed line vertical to the time axis represented the time of 0:00 on January 1st when regulation of demanding clean diesel fuel to be switched came into effect.

20   By linear fitting for ship-source and ambient sulfate particle number, the correlation coefficients r=0.885, indicating that sulfate particles from ship and ambient had a strong correlation with each other. Meanwhile, it also can be seen from the change tendency that the change of sulfate particles in ambient air always kept synchronous with that of ship-source particles, proving the fact that ship-source sulfate particles had made relatively stable contribution to ambient sulfate particle concentration.

25   The analysis was divided into two sections by the time of January 1st, 2017. Before the time spot, it can be seen that around December 29th, both ambient and ship-source sulfate particles formed several peaks as well as the ship-source/ambient ratio. Peaks of ship sulfate particles were formed largely depending on ships sailing into or out of the berth, thus producing plumes sampled by SPAMS. In the following

days during December 29th to January 4th, evident decrease could be seen, especially around January 1st, which might due to switching to low sulfur diesel oil. Brief surveys had been conducted towards crew on board during measurement periods and it was informed that some of the ships had switched to low sulfur oil in advance of the regulated date. Between January 4th and January 6th a peak higher than others

5 could be observed, while the ratio kept even lower than around December 29th. The ship-source/ambient sulfate ratio reached peaks at 18:00 on January 9th and 16:00 on January 12th respectively, however, during these two time sections the quantity of measured particle numbers was apparently low, which could cause errors that were easy to be neglected.

Generally, the average ratio of ship source sulfate particles to ambient sulfate particles before and after

10 January 1st were 23.82% and 23.61%, respectively. In view of the data obtained from this method and measurements, using low sulfur fuel slightly bring down the contribution of ship source sulfate particles to atmospheric sulfates, though the numerical distinction was rather small. However, the fact that some ships had begun to use low sulfur fuel right before January 1st should be taken into consideration for the numerical results and further measurements as well as more solid data collection should be done to dig

15 out the accurate impact of new regulation.

4   Conclusions

Sampling of VOCs and particles from 20 ships at berth was conducted in winter Jingtang Port during the period of December 27th, 2016 to January 15th, 2017. Average VOC source profile of container ships was obtained, and SOA yields as well as ozone forming potential were calculated based on source profile.

20 Comparisons have been made to diesel and gasoline vehicles according to the source profile in previous researches. Secondary organic aerosol yields and ozone forming potential were 0.017 ± 0.007g SOA/g VOCs and 2.63 ± 0.37g O₃/g VOCs, respectively. Results showed that VOCs from ships tended to yield more secondary organic aerosol than diesel and gasoline vehicles, while ozone forming potential was comparable to them.

25 SPAMS sampling and analysis provided information of particle average ion mass spectra, manual grouping, total and specified group size distribution as well as impact of ship-source sulfate particles on ambient atmosphere. EC, ECOC and Na-rich particles were predominant sorts in overall particles, occupying over 90.7% of all particles. Size distribution indicated that most particles concentrated in the

range of 0.2-1.4μm, and different sorts of particles had various distribution patterns.

The issue of vanadium as tracer element was demonstrated and conclusion was drawn that after the fuel substitution, fuel vanadium contents had been significantly lowered and vanadium from ship auxiliary engine exhausts showed no obvious excess comparing to corresponding ambient data in most cases.

5 After identifying and extracting ship-source sulfate particles out of ambient sulfate particles during the whole sampling period, a temporal profile with resolution of 1hour was obtained. Comparing post-January 1st data to that of December, the ratio of ship-source sulfate particles to ambient sulfate particles presented a slight decrease from 23.82% to 23.61%. The reason why evident decrease was not observed may be the lack of solid data in December and that some ships had switched to low sulfur fuel in advance.

10 To better evaluate the impact of using low sulfur oil, more and further measurements and data were demanded.

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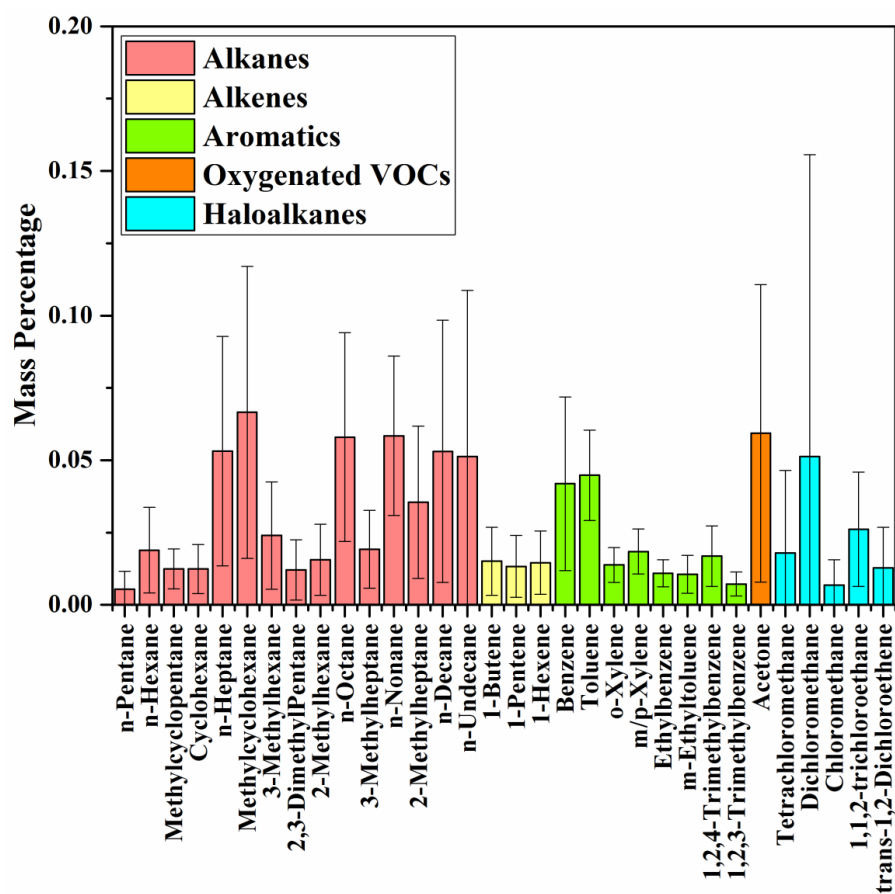

Figures

Figure 1: VOC source profile from ship auxiliary engine exhausts analyzed by GC-MS, 93 species

including PAMS and TO-15.

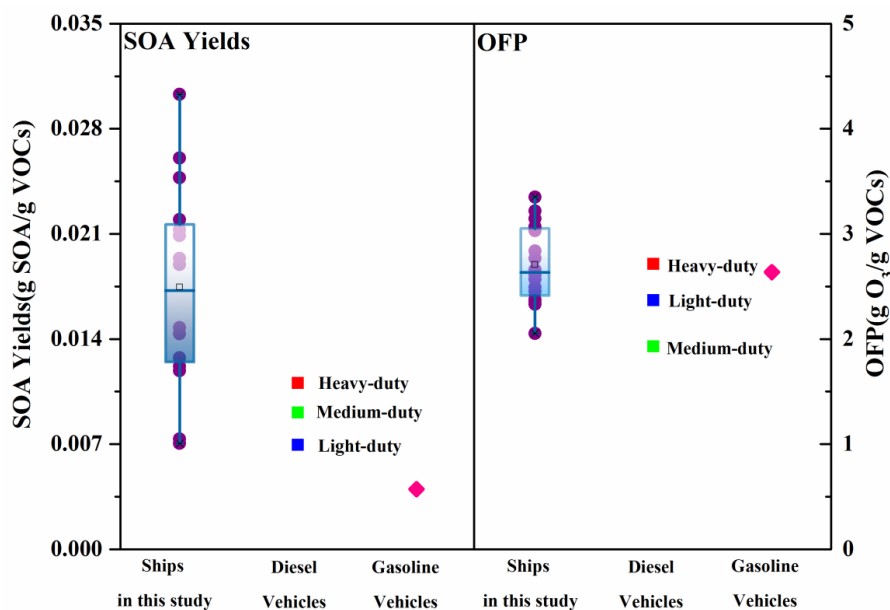



Figure 2: Comparison of SOA yields and ozone forming potential (OFP) calculated based on VOC source profile with VOC profile from previous study (Yao et al., 2015)

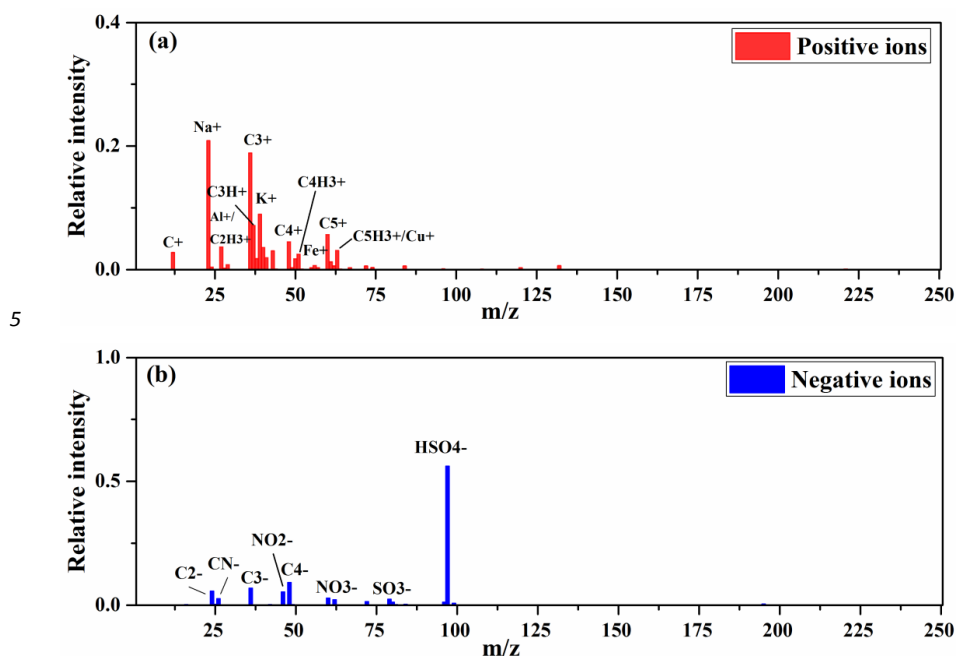



Figure 3: Average ion mass spectra derived from SPAMS of 20 samples of ship exhausts. Figure 3(a)

stands for the positive ions and (b) stands for the negative ions.

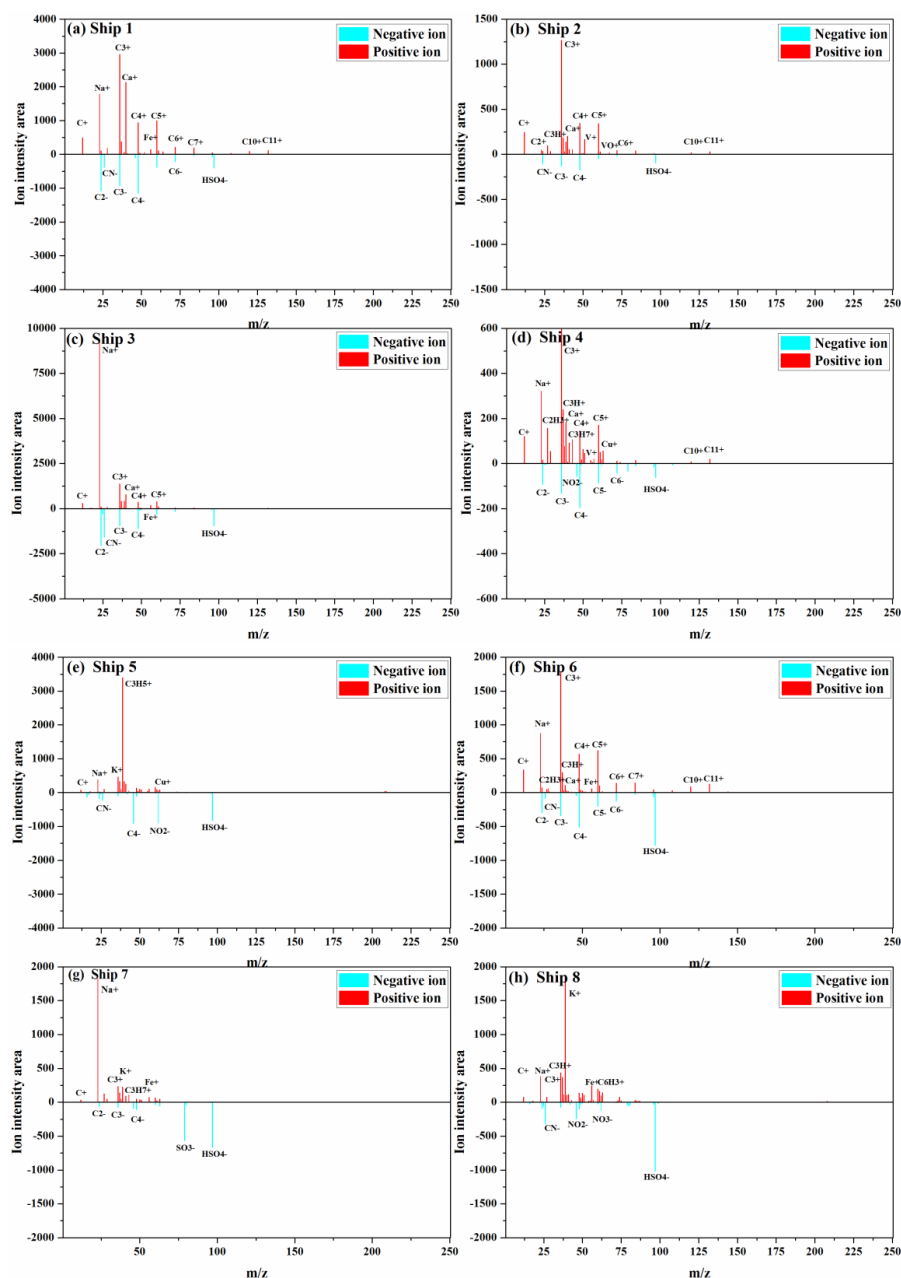
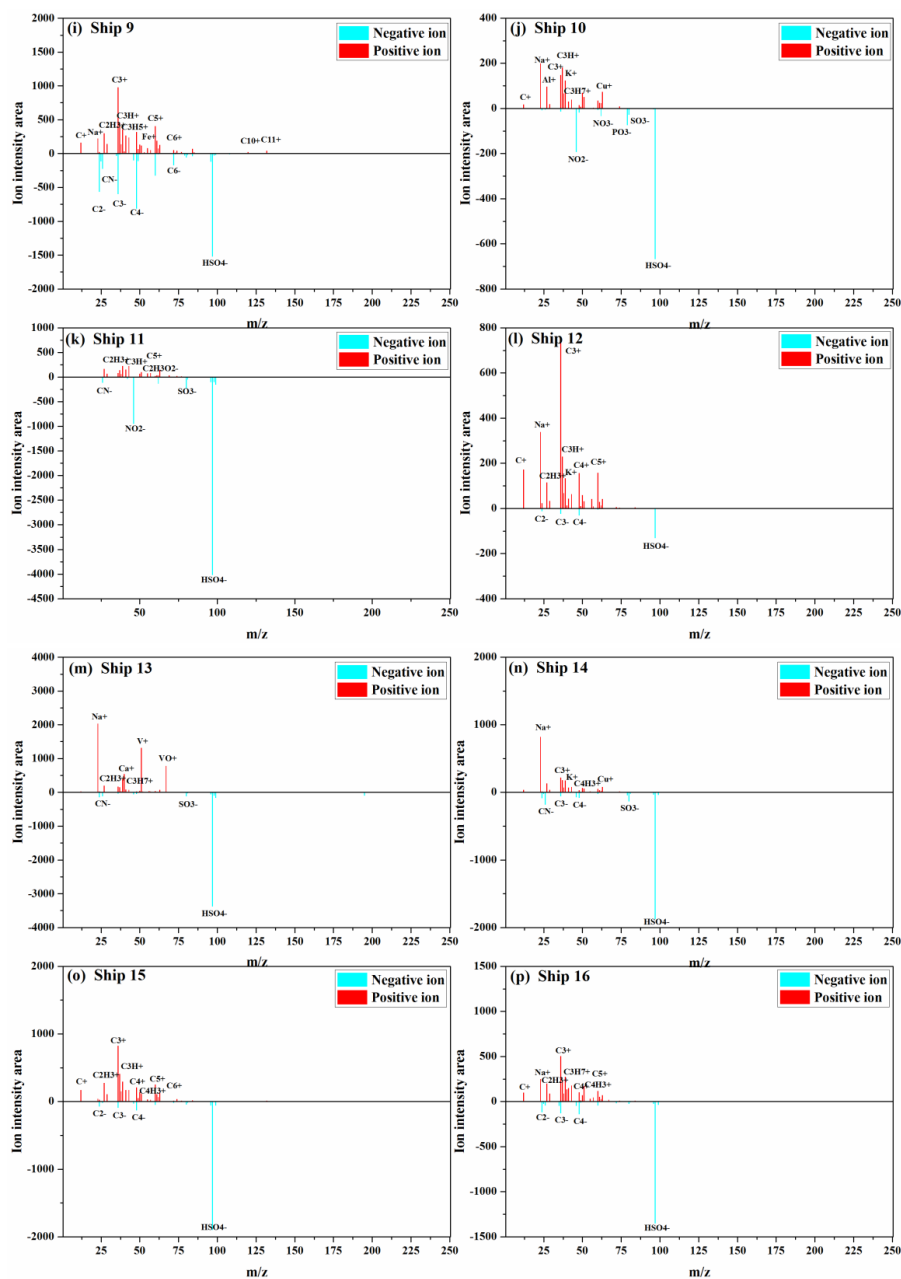
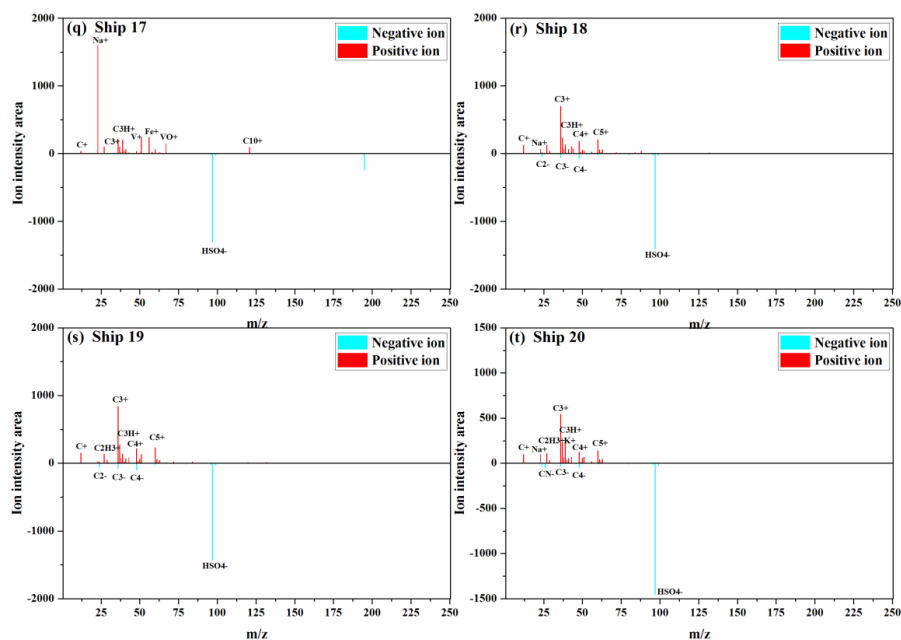
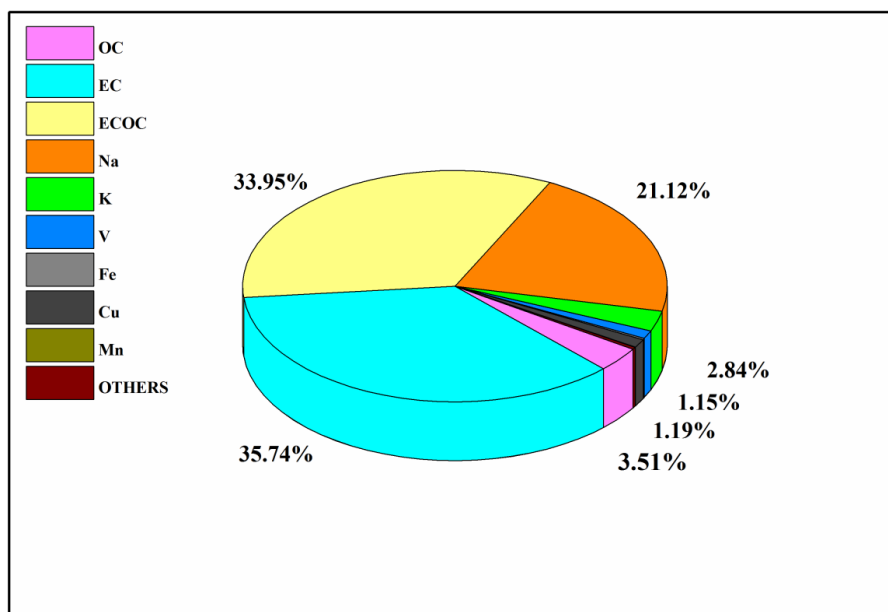



Figure 4: Individual ion mass spectra of 20 ships (a)-(t) including positive ions and negative ions.

5 **Figure 5:** Manual classification of ten types of particles from 20 samples and their proportion by numbers.

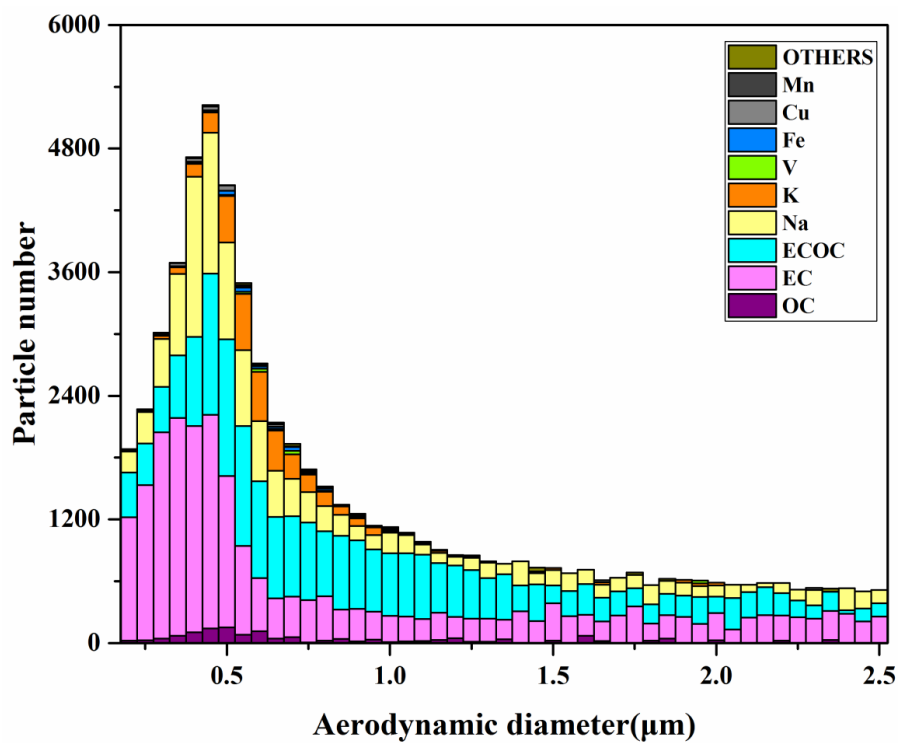



Figure 6: Size distribution of particles based on manual classification.

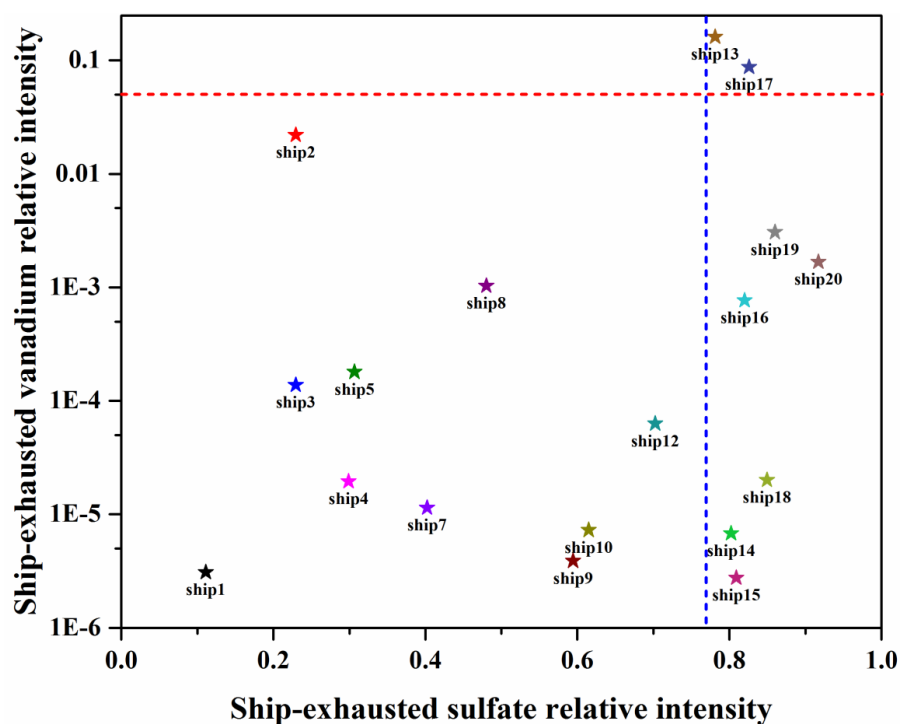



Figure 7: Vanadium and sulfate relative intensity of 20 ships

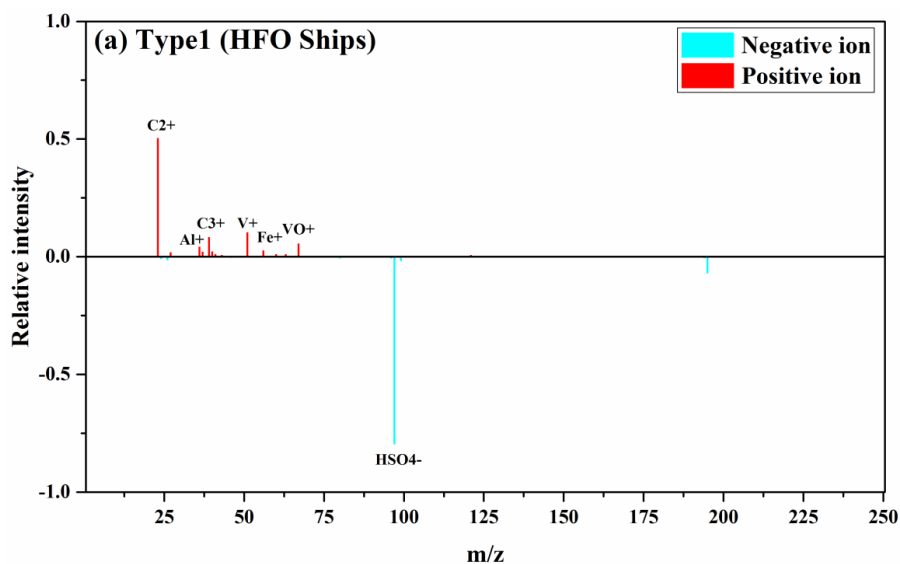
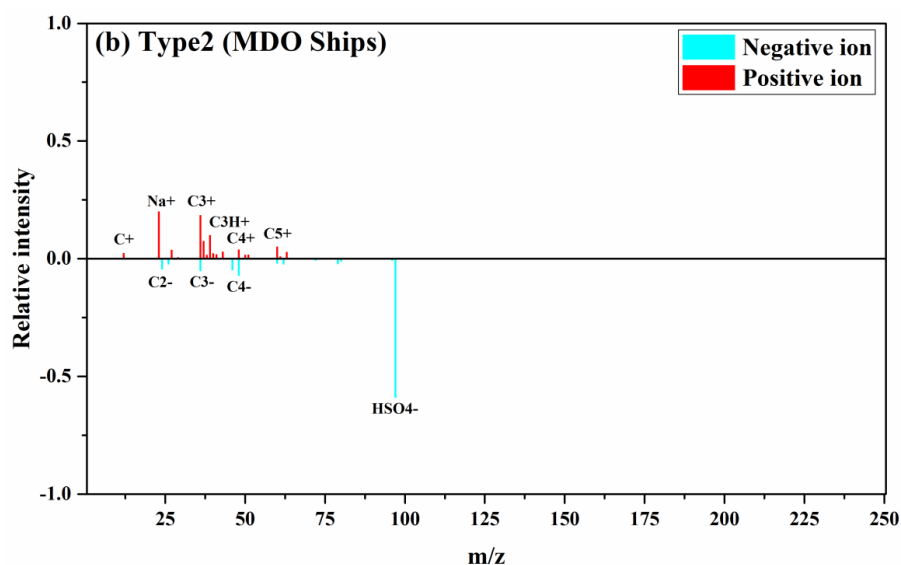
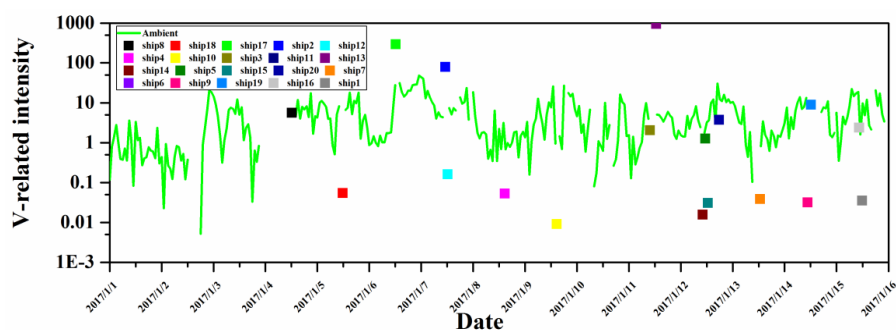



Figure 8: Ion mass spectra and grouping of 2 divided ship types based on fuel identification. (a) Type1 ships stands for ships using heavy fuel oil, and (b) Type2 ships stands for diesel ships.

5   **Figure 9:** Comparison of vanadium intensity of 20 individual ship particle samples to ambient particle samples from January 1st to January 16th.

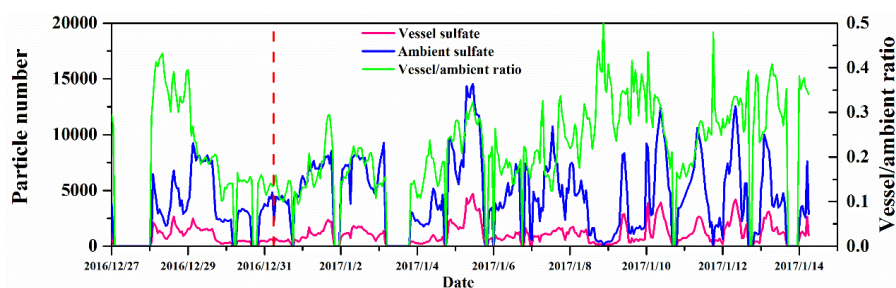



Figure 10: Hourly number average (number of particles sampled by SPAMS in one hour) of ship exhausted sulfate particle and ambient sulfate particles during the entire measurements.

Tables

<p align="center">Table 1: Brief information of 20 sampled ships</p>

Ship No.	Length*Width(m)	Model Year	Dead Weight Tonnage(t)	Auxiliary Engine Rated Power(kW)	Rated Speed(rpm)	Sulfur Content (%)
1	144*20.8	2015				
2	255.1*37.3	2013	49717	1760	900	
3	140*20	2006	12301.8	200	1500	0.08
4						
5	161*23					
6	147*9.8	2012		900	1000	0.09
7	98*15	2009		358.8	1500	
8						
9	124*11.6	2015	5420	600	1500	0.029
10	158.6*22.6	2014	18060	900	1500	0.095
11	132*19					
12				900		0.02
13	180*28	2014	28791			0.3
14	158.5*22.6	2015	11872	900	1000	0.07
15	140*19.8	2009	10685	220	1000	
16	255.1*37.3	2012	67040	600	1500	0.029
17	180*28	2014	27821			
18						
19	255.1*37.3	2013	66903	1320	900	
20						

Table 2: Top 32 VOC species mass percentage from 16 container ships

Compounds	Percentage	Standard deviation	Compounds	Percentage	Standard deviation
n-Pentane	0.536278	0.629109	1-Pentene	1.325768	1.070632
n-Hexane	1.891022	1.481339	1-Hexene	1.457199	1.094036
Methylcyclopentane	1.239405	0.691045	Benzene	4.190024	3.000858
Cyclohexane	1.241246	0.847235	Toluene	4.47936	1.565238
n-Heptane	5.313712	3.965797	o-Xylene	1.379276	0.603842
Methylcyclohexane	6.655522	5.044339	m/p-Xylene	1.84439	0.778013
3-Methylhexane	2.397949	1.855725	Ethylbenzene	1.091218	0.472748
2,3-DimethylPentane	1.206319	1.044379	m-Ethyltoluene	1.05578	0.652482
2-Methylhexane	1.559125	1.225618	1,2,4-Trimethylbenzene	1.684083	1.045932
n-Octane	5.798276	3.61007	1,2,3-Trimethylbenzene	0.718099	0.414425
3-Methylheptane	1.918903	1.344047	Acetone	5.92993	5.138703
n-Nonane	5.844313	2.757486	CCl_4	1.791729	2.854673
2-Methylheptane	3.546112	2.630706	CH_2Cl_2	5.132463	10.42498
n-Decane	5.305601	4.532773	CH_3Cl	0.681607	0.871668
n-Undecane	5.125647	5.741735	1,1,2-trichloroethane	2.610167	1.975113
1-Butene	1.507865	1.176521	trans-1,2-Dichloroethene	1.274261	1.402993

Table 3: Element analysis of 3 fuel samples and comparison with previous studies

			Celo et al., 2015			This study(Sampled on Jan 14th, 2017)	
Fuel		IFO380	IFO180	IFO60	MDO	MDO(ship 9)	MDO(ship 19)	MDO(unplanned ship)
15℃ density(kg·m^{-3})		988	973.7	957.6	854.3	848.2	853.1	846.3
w%	C	86.26	86.78	87.22	86.85	85.16	84.78	86.83
	H	11.26	10.7	11.05	12.97	13.07	13.21	13.15
	N	0.39	0.38	0.38	0.026	0.027	0.026	0.010
	S	2.7	2.21	1.22	0.119	0.38	0.080	0.065
mg·kg^{-1}	Fe	31.44	17.71	Not detected	Not detected	2.7	<1	<1
	V	133.8	102.4	38.0	Not detected	Not detected	Not detected	Not detected
	Ni	63.2	46.5	21.0	Not detected	Not detected	Not detected	Not detected
	Cu	29.51	23.63	Not detected	Not detected	Not detected	Not detected	Not detected

IFO: Intermediate Fuel Oil MDO: Marine Diesel Oil

Two of the fuel samples were from ship 9 and ship 19, and the sample marked as unplanned ship indicated

that this ship was not among the 20 ships included in this study.