Authors' response to editor's remarks
ON MANUSCRIPT ACP-2018-737 – REFERRING TO MANUSCRIPT VERSION 03

(we present our responses in blue, original text in black. Between items of remarks & responses we inserted a separation line)

REFEREE #1: It is not clear how the components in particles such as vanadium were identified and quantified by the SPAMS. Detailed information is needed.
AUTHORS' RESPONSE: SPAMS identify particle composition, such as vanadium, in mass spectrometry method. In the ionization laser beam in SPAMS, the components in particles are ionized into ions carrying charge, then they are separated in the Time-of-Flight tube by atomic mass of the ion. Lighter ions, such as H+, transit fastest in TOF tube and produce peaks in shortest time. The 208Pb+ is heavier so that it reach the MS detector with longer time. This will result a spectrum sorted by ion atomic mass. Components of different atomic mass produce peaks in different position in mass spectrum. Vanadium in particles normally produce peaks at mass = 51V+ and 67 (VO+) and thus can be identified. This is the basics of MS and unnecessary to be included.
CHANGES IN MANUSCRIPT: None
EDITOR'S REMARK: The authors explain basic explanation of how a MS works, which indeed can be expected as basic knowledge. However, Referee #1 requests detailed information about the quantification of Vanadium concentrations. This needs to be added.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
We have added further descriptions on how vanadium particles were identified and quantified in SPAMS in section 2.3.

CHANGES IN MANUSCRIPT:
(Section 2.3, paragraph 2)
"Specific composition in particles, such as vanadium, is identified by their characteristic mass peaks in particle spectra. Particles producing vanadium peaks were labelled as vanadium particles. SPAMS quantifies their concentrations in a semi-quantitative manner through the number of detected particles in a specific duration of time. Considering that the aerosol flow was introduced into SPAMS at fixed flow rate (0.1L/min), the detected particle numbers (or particle detecting velocity) could be utilized as indication of ambient particle concentrations. In ambient sampling it was shown that the particle numbers in SPAMS were positively correlated with ambient $PM_{2.5}$ concentrations (R^2=0.69 in this study). In present study, we use particle detecting speed of vanadium containing particles as a metric of their concentrations. To derive ambient particle number concentrations from SPAMS particle numbers, we need to consider the efficiency issues of SPAMS on AFL transmission, laser detection and laser ionization(Wenzel et al., 2003)."

REFEREE #1: Page 5, lines 21-25: The discussion here is questionable. By looking at Figure 2, whenever ship plumes were captured, both NO and SO2/vanadium levels were high and correlated well. On what basis, the authors claimed the NOx in plumes reaching the site was aged? Using the NO/NO2 ratio in the plumes? Compared to the ratio measured in other countries and probably different type of ships? This is not convincing. Besides, NO2 is also emitted from shipping as a primary pollutant.
AUTHORS' RESPONSE: We have not tested NO/NO2 ratio in the exhaust because the observation was carried out in a station on land. The author also know that NO2, together with NO, is released as primary emissions. However their ratio, upon their emission into atmosphere, will subject to change quickly through the oxidation of NO into NO2 in the existence of ozone (O3), which is abundant in summer time. This was evidenced by the quickly reduced O3 level during plumes in Fig. 2 in manuscript. The referee seems to be doubtful about this reaction, which is the very basis that the NO-NO2-NOx analyzer is working on.
CHANGES IN MANUSCRIPT: *None*
EDITOR'S REMARK: I fully agree with Referee #1 who requests are more careful discussion. The measured

levels of NOx and the separation into NO and NO2 cannot be used to identify ageing of ship plumes. Since the authors do not know the level of chemical processing (depending on O3, meteorological conditions and atmospheric radiation) of ship exhaust in the marine boundary layer during transport to the sampling site, it seems to be more appropriate looking only at the sum parameter NOx. This suggestion is supported by the results presented in Table 1. Looking at NO there is no statistically significant difference between in-plume, non-plume and port average cases. An almost similar statement holds for NO2.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:

Thanks the editor's remark. We admit the editor and reviewer's opinion that other factors like atmospheric radiation could also influence NO and NO2 concentrations. In ultraviolet radiation in sunlight the NO2 disintegrate into NO and O atom. Meanwhile, the O atom and O2 molecules also form O3, which in turn could oxidize NO. These are cyclic reactions which will reach their equilibrium if no extra NO and NO2 is introduced. In fresh emitted plumes the NO-NO2-O3 equilibrium is interrupted, usually resulting reduction of O3 concentration, as observed in sites elsewhere (Alföldy et al., 2013;Merico et al., 2016).

Since editor and the reviewer #1 suggested that using of NO/NO_2 ratio is not careful enough, we have searched literatures on related topics and found that the NO2 ratio was used by several studies(Alföldy et al., 2013;Kurtenbach et al., 2016). The NO2 ratio is defined as the ratio between NO2 and the summed NOx (NO+NO2) parameter, which was the suggested parameter by the editor. We calculated the NO2 ratio during plumes periods in this study. This was done by firstly converting the gas concentrations to molar unit (conforming to existing studies), and then the NO and NO2 concentrations were calculated by subtracting the background levels during plumes, similar to the case of SO2. The distribution of the calculated NO2 ratio in this study is shown in Figure 1, where the NO2 ratios of a comparable study is plotted for comparison.

The distribution of the NO2 ratio in present study showed several modes. The largest mode occurred at about 0.2 (20%). This mode was also observed in the comparison study, which was recognized as fresh engine emissions of ships. The major difference between two studies is that a significant fraction of NO2 ratios occurred in larger values (> 0.4) in this study, which was not observed in (Alföldy et al., 2013). Initially the plumes of larger NO2 ratios were thought to be emitted by specific type of ships. After we correlating the NO2 ratio with ambient O3 levels, however, there exist obvious positive correlation between NO2 ratio and ambient O3 concentrations, as shown in right panel in Figure 2. The relation between NO2 ratio and O3 became more obvious in higher ambient O3 levels. It is noted that the correlations between NO2 ratio and other parameters including wind directions, ambient temperature, humidity were very weak. This result is indicating that the higher NO2 ratio of some plumes were not due to the emission characteristics of ships, but due to the transformation of NO to NO2 in the ambient, for if the higher NO2 ratio were caused by higher NO2 emission at their discharges and no ambient transformation occurred, then there will be no reason to observe the dependence of NO2 ratio on an ambient condition of O3. This could be an evidence of oxidation of primary NO by O3, therefore ship emitted NO had contributed to the depletion of ozone.

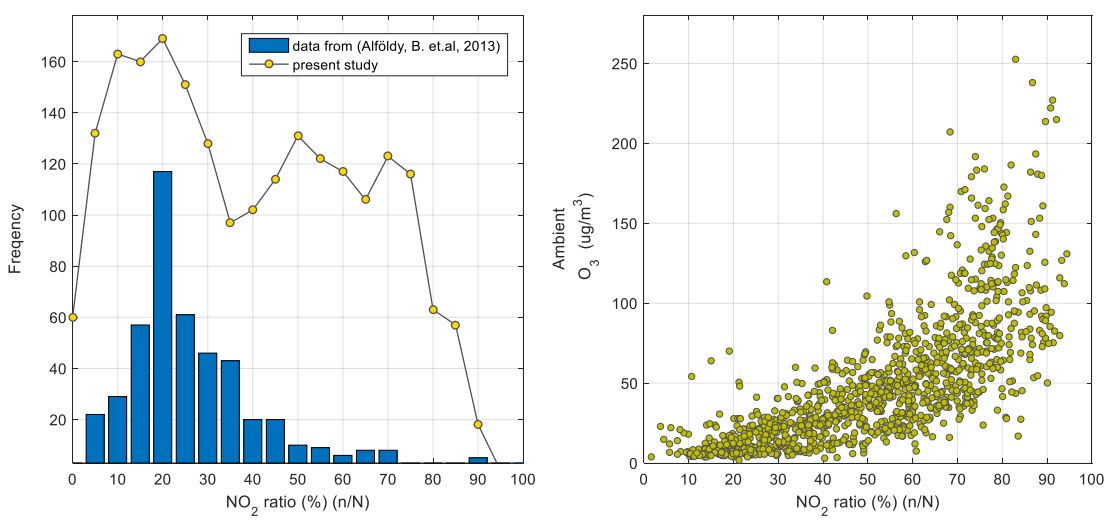

Figure 1. The NO_2 ratio distribution during plumes in this study and a similar study (left) and the plot of NO_2 ratio against ambient ozone concentration during plumes periods (right).

CHANGES IN MANUSCRIPT:

(Section 3.1, paragraph 5-6)

"In general the ozone concentrations in the port site were lower than Shanghai urban region by 13-33%. To inspect whether the O3 depletion was related to the oxidation of primary NO emissions in the port site, we calculated the NO2 ratios to analyse NOx composition in plumes. The NO2 ratio is defined as the ratio between NO2 and the NOx (NO+NO2), which was used by several relevant characterizations of ship emissions (Alföldy et al., 2013;Kurtenbach et al., 2016). Before the calculation of NO2 ratio we firstly converted NO and NO2 mass concentrations to molar unit, and then the background NO and NO2 levels were subtracted to make sure peaks were due to plumes. The distribution of the NO2 ratio in this study was shown in Figure 3, where the NO2 ratio distribution from ship plumes in another study was compared. The distribution of the NO2 ratios in present study showed several modes. The largest mode occurred at about 0.2 (20%). Obviously this mode was also present in the comparison study (Alföldy et al., 2013), which was recognized as fresh engine emissions from ships. A major difference between two studies is that significant fraction of NO2 ratios occurred in larger range (> 0.4) in present study, which was not observed in Alföldy et al., 2013. The larger NO2 ratios were once thought to be emitted from unidentified type of ships. When we correlated the NO2 ratio with ambient O3 concentrations, however, we found there was obvious positive correlation between them, as shown in right panel in Figure 3. This result suggests that the higher NO2 ratio of some plumes were not due to the emission characteristics of ships, but due to the transformation of NO to NO2 in the ambient, for if the NO2 ratio were higher at the discharges and no ambient transformation occurred, then there will be no reason to observe the dependence of NO2 ratio on an ambient condition of O3. This is an evidence that the primary NO emission (from ships or on-road traffics) had contributed to the O3 depletion in this area. ".

REFEREE #1: Given that shipping emission is a major source of PM2.5, it is odd that no PM2.5 peaks were found during the ship plumes in Figure 2. The reason provided by the authors is quite confused. Is it because ship emits sub-micron particles or because the malfunction of the PM2.5 monitor?

AUTHORS' RESPONSE: The authors have stated that PM2.5 peaks was not as apparent as that of SO2 and NOx in plumes, and have not states that no PM2.5 peaks were found. It should be made clear that only a short period of data was shown in Fig.2 only with the purpose of illustrating temporal variation in plumes. In the last question the referee is suspecting that PM2.5 analyzer was in malfunction. The author would like to illustrate another longer period of data in Figure R2 (shown below) and let the referee make his judgement. The sharp peaks of SO2 in Figure R2 could help to locate the plumes. If the PM2.5 instrument is in malfunction, how did the PM2.5 instrument happened to malfunction only in plumes? In another aspect, the SPAMS particle number concentration have shown good correlation with the PM2.5 measurement. How did the two instruments both malfunction? It sounds ridiculous.

CHANGES IN MANUSCRIPT: *None*

EDITOR'S REMARK: *The authors' response to the referee is not acceptable. Moreover, the entire discussion of the PM2.5 mass concentrations is confusing and inconsistent. Referee #1 simply requests are more consistent presentation of the PM2.5 case, which I do as well. We know from earlier observations that most of the PM emitted by ship engines is far smaller than 1.0 µm in diameter and will thus not contribute significantly to the PM2.5 mass concentration. This fact needs to be pointed out very clearly. In that respect the results presented in Table 1 are consistent but the explanation in the text is confusing and requires careful revision. In particular, the explanation announced on Page 7 line 21 of the annotated manuscript is either missing or well hidden.*

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:

We have removed relevant discussions on PM2.5 to Section 3.1, paragraph 7

CHANGES IN MANUSCRIPT:

(Section 3.1, paragraph 7)
"For particulate matter, the PM2.5 concentrations in port area were slightly lower than Shanghai city, although PNCv in plumes were times higher than non-plumes (Table 1). Longer period of PM2.5 data suggested the lower PM2.5 concentration is a general trend in this port site. This trend is not unique to the port regions because we observed it in other coastal area as well, which is readily observed in PM2.5 spatial distribution of Shanghai (Figure S4 in supplementary file). In the spatial distribution there was a general trend of decreasing PM2.5 concentrations from inner to coastal areas in Shanghai. This fact is assumed to be caused by the dispersion or advection of clean air from the sea. The primary PM in portside from ship emissions are mostly ultrafine particles, with mass emission factors much smaller than NOx and SO2 (Zhang et al., 2017). Therefore the primary PM from ships or other traffics could not contribute significantly to ambient PM mass concentrations. The vanadium particle number fractions in total particles in SPAMS were obviously larger (6.7 % on average) in portside than urban areas in Shanghai (1-2 %) (Liu et al., 2017)."

REFEREE #1: The reason for absent SO2 is contradictory to Figure 2. If the ships complied with the new regulations, why would you still see SO2 peaks in ship plumes? This kind of discussion is misleading.
AUTHORS' RESPONSE: As stated above, the cases the SO2 peaks were absent were rare and will not affect significantly the result of the study. The new regulation only confine the Sulfur content in fuel, not eliminate the Sulfur from the fuel.
CHANGES IN MANUSCRIPT: *None*
EDITOR'S REMARK: I fully agree with Referee #1. If the authors do (for 3% of the cases) not find a correlation between SO2 and V, how have these cases been treated? Where they excluded from the analysis? Clarification is requested.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
We are sorry to forget to make this clarifications when replying #2 Referee's related questions. In data analysis, the treatment of those cases were determined by checking the prevailing wind of that time. If the wind directions of that time was favorable, we will classify the plumes as from ship emissions, if not, they will be just excluded from analysis, because we are not sure about their real sources. The results in table I and table 2 were recalculated using this treatment when we prepared the manuscript version 3.

CHANGES IN MANUSCRIPT:
(Section 3.1, second paragraph, Line 8-9)
"To identify plumes, we excluded the possible industries influences by limiting the prevailing winds only to port directions."

REFEREE #1: It does not make sense to compare a site near sources with sites in a city without any detailed characteristics of the locations. It would be more meaningful to compare the ship emissions in this study with other similar studies conducted in Shanghai. In fact, there are a number of ship emission studies in this city.
AUTHORS' RESPONSE: The comment is not acceptable. We made comparison between air pollution level in a port site with that at the urban area of the same city, How did it make non sense? The referee had better suggest a study which he think make more sense.
CHANGES IN MANUSCRIPT: *None*
EDITOR'S REMARK: This response it not acceptable. It is not the duty of the referees to make the authors familiar with current literature! I fully support Referee #1 request for a comparison of the presented results with those from other studies in Shanghai port.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
We have added relevant discussions with results from similar study in Shanghai in section 3.1, paragraph

4.

CHANGES IN MANUSCRIPT:
(section 3.1, paragraph 4)
"Generally the concentrations of SO2 and NOx in the port site is 40~70% higher than Shanghai city (Table 1). The SO2 concentrations in non-plume periods were comparable with that in Shanghai city, irrespective of wind directions, therefore the non-plume SO2 can be recognized as background SO2 in this area. Contrastingly, the NOx concentrations showed obvious dependence on wind directions in non-plumes, whose concentrations were higher when inland wind prevails, suggesting the importance of land-based emissions to port in coastal areas. In a similar ambient observation at Yangshan port, (Zhao et al., 2013) obtained the average concentration of 29.4 and 63.7 μg/m3 for SO2 and NO2 respectively, higher than the present level of 15.6 μg/m3 (SO2), 53.2μg/m3 (NO2). Noting that the SO2 and NO2 were only intermittently measured for about 20 days in that study (May and August, 10 days each month). Therefore it is not feasible to make direct comparison. In plume period, the SO2 maximum hourly concentration in Yangshan (119.0 μg/m3) were close to present study (124 μg/m3); Due to land-based emissions, the NO2 maximum hourly concentration in Waigaoqiao port (260 μg/m3) is higher than Yangshan port (199.8 μg/m3)."

REFEREE #1: the explanation of low PM2.5 levels at the port site is not convincing at all. Why would other pollutants from shipping emissions be higher if this was caused by clean air?
AUTHORS' RESPONSE: The slight lower PM2.5 concentration at the port site is a fact. The author only postulated possible explanations.
CHANGES IN MANUSCRIPT: *None*
EDITOR'S REMARK: *The authors have to provide consistent explanations for their observations. There is no reason why PM2.5 should be influenced by clean air why gaseous pollutants will not. Another explanation is needed here.*

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
The lower PM2.5 concentrations in the port site than Shanghai city were not limited only to the port site. In air monitoring networks in Shanghai, we found the general trend that the coast sites have lower PM2.5 concentrations than the inner sites in west. In Figure 2 we prepared two maps showing the PM2.5 spatial distributions in Shanghai areas during the study period, and the year 2016. In either cases, the average PM2.5 concentrations in coastal areas in east were lower than the inner areas, which could only be explained by the clean air advection or dispersion from sea areas. The lower PM2.5 concentration in the port site was within this trend.
The higher NOx and SO2 levels were not conflicting the lower PM2.5 concentrations in port site, for the mass emission factors (EF) of NOx and SO2 from combustion sources (either on-road traffics or ships) is generally several times larger than that of PM. Many published EFs of PM, SO_2,NO_x support this. To quote as example, in china the measured EFs of NOx and SO2 from the main engines of ships, were 12.7-14.3 and 10.3-13.5 g/Kwh, respectively, while the EFs of PM were in 0.2-1.7 g/Kwh range (Zhang et al., 2017). The much less EFs of PM than gaseous pollutants were also applicable to auxiliary engines in ships and diesel trucks (Zavala et al., 2017). Obviously the insignificant primary PM emission in portside have not compensated the cleaning impacts from the sea, resulted lower $PM_{2.5}$ concentration than Shanghai city.
We added the PM2.5 spatial distribution maps into supplementary file, and moved this section to section 3.1, paragraph 7.

CHANGES IN MANUSCRIPT:
(Section 3.1, in paragraph 7)
"*For particulate matter, the PM2.5 concentrations in port area were slightly lower than Shanghai city, although PNCv in plumes were times higher than non-plumes (Table 1). Longer period of PM2.5 data suggested the lower PM2.5 concentration is a general trend in this port site. This trend is not unique to the port regions because we observed it in other coastal area as well, which is readily observed in PM2.5*

spatial distribution of Shanghai (Figure S4 in supplementary file). In the spatial distribution there was a general trend of decreasing PM2.5 concentrations from inner to coastal areas in Shanghai. This fact is assumed to be caused by the dispersion or advection of clean air from the sea. The primary PM in portside from ship emissions are mostly ultrafine particles, with mass emission factors much smaller than NOx and SO2 (Zhang et al., 2017). Therefore the primary PM from ships or other traffics could not contribute significantly to ambient PM mass concentrations. The vanadium particle number fractions in total particles in SPAMS were obviously larger (6.7 % on average) in portside than urban areas in Shanghai (1-2 %) (Liu et al., 2017)."

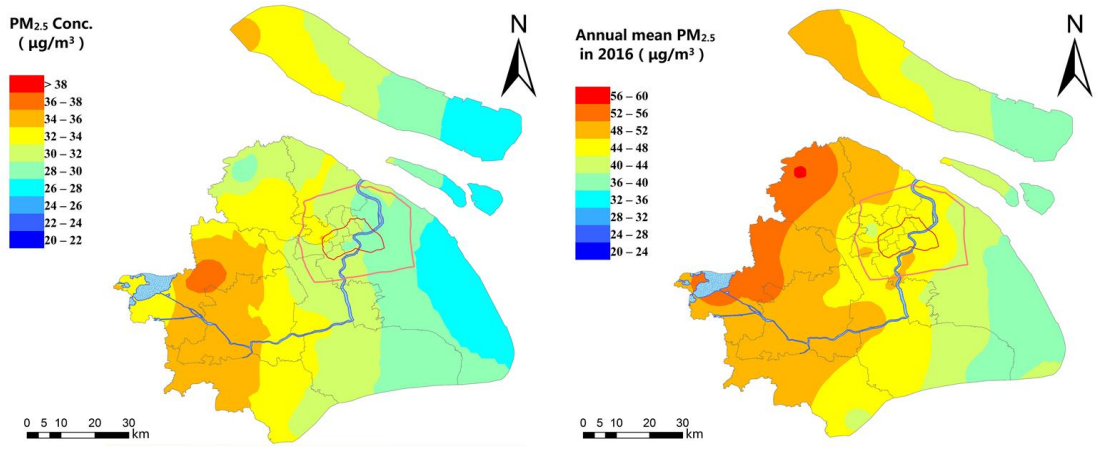

Figure 2. Spatial distributions of $PM_{2.5}$ in Shanghai area in the study period (left) and in 2016 (right).

Another remarks concerns Figure 6, which also shows the inconsistency of presentation of PM results. In the figure caption, the authors indicate that particle number concentrations are presented. In the figure itself, however, the y-axis title (left panel) indicates "Particles/hour". This is definitely not an adequate unit for particle number concentrations! Furthermore, the y-axis of the upper right panel indicates "Particle number", whereas the authors mean particle number concentration in units of cm-3. Both issues need to be clarified.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
We have revised the caption of figure 6 (now figure 7) to make its meaning clear.

CHANGES IN MANUSCRIPT:
(Figure 7 caption).
"Figure 7: Temporal trends of particle numbers detected per hour by SPAMS of four fresh vanadium particle types (Left panel); The upper right panel is the number-size distribution of the 4 types, with the y-axis representing particle numbers detected at each size bin in the entire study. The Lower right panel is obtained by normalizing the particles numbers of 4 types to give their relative contributions at each size."

MINOR ISSUES:
The company's name providing the instruments is THERMO SCIENTIFIC, not THERMAL SCIENTIFIC.
AUTHORS' RESPONSE TO REMARKS FROM EDITOR:
We have made this correction. Thanks.

CHANGES IN MANUSCRIPT:
(Section 2.2, first paragraph, Line 1-2)
"From Jun-21 to Sep-21, 2016, the portside gaseous pollutants NO-NO2-NOx, SO2, and O3 were monitored continuously with a suit of Thermo Scientific analyzers (NO-NO2-NOx, model 42i; SO2, model 43i; O3, 49i)."

Furthermore, another language editing is mandatory before publication.

AUTHORS' RESPONSE TO REMARKS FROM EDITOR:

We have made another language editing throughout the manuscript.

CHANGES IN MANUSCRIPT:

(see blue text in the revised manuscript).

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~~Atmospheric pollution from shipping and their contributions to air quality degradation in a port site in Shanghai~~

Atmospheric pollution from ships and their impacts on local air quality in a port site in Shanghai

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Abstract.

~~Growing shipping activities in port areas have generated negative impacts on climate, air quality and human health. To better evaluate the environmental impact of ship emissions, in the summer of 2016 ambient air quality measurement was carried out at Shanghai port, one of the busiest ports in the world. The concentrations of gaseous (NO, NO_2, SO_2, O_3) and particulate concentrations ($PM_{2.5}$), particle size distributions and chemical composition of individual ship emission particles were continuously monitored for 3 months. In online measurement the ship- emission plumes were clearly distinguishable of both gaseous and particulate matter, which have shown synchronized peaks during plumes. The SO_2 and vanadium particles numbers were found to correlate best with ship emissions in Shanghai port. Single particle mass spectra of fresh ship emission were identified based on the dominant peaks of sulfate, elemental carbon (EC) and indicative metals of V, Ni, Fe and Ca. Temporal trends and size distributions of major ship emission particle types were discussed. The sampled ship emission particles in the port site mainly concentrated in smaller size range where their number contributions are more apparent than their mass. For a costal port close to urban region, the land based emissions have generated important impacts to the portside air quality, especially for NO_x and $PM_{2.5}$. Quantitative estimation conducted in the present study show that in port region ship emissions contributed 36.4 % SO_2, 0.7 % NO, 5.1 % NO_2, 0.9 % O_3, 5.9 % $PM_{2.5}$, 49.5 % vanadium particles if land based emissions were included, and 57.2 % SO_2, 71.9 % NO, 30.4 % NO_2, 16.6 % O_3, 27.6 % $PM_{2.5}$, 77.0 % vanadium particles if land based emissions were excluded.~~

Growing shipping activities in port areas have generated negative impacts on climate, air quality and human health. To better evaluate the environmental impact of ship emissions, an experimental characterization of air pollutions from ships was conducted in Shanghai port in the summer of 2016. The ambient concentrations of gaseous (NO, NO_2, SO_2, O_3) and particulate

concentrations ($PM_{2.5}$), particle size distributions and chemical composition of individual particles from ship emission were continuously monitored for 3 months. Ship emission plumes were visible at the port site in terms of clear peaks of gaseous and particulate matter concentrations. The SO_2 and vanadium particles numbers were found to correlate best with ship emissions in Shanghai port. Single particle data showed that ship emission particles at the port site mainly concentrated in smaller size range (< 0.4 μm) where their number contributions were more important than their mass contributions to ambient PM. Composition of ship emission particles at the portside suggested they were mostly fresh particles, with their mass spectra dominated by peaks of sulfate, elemental carbon (EC), metallic composition of V, Ni, Fe and Ca, and very low nitrate signals. For some cases of plumes, the gaseous NO_x composition in plumes has the evidence of atmospheric transformation by ambient O_3, resulted ozone depletion in this area. Quantitative estimation in the present study show that in port region ship emissions contributed 36.4 % SO_2, 0.7 % NO, 5.1 % NO_2, -0.9 % O_3, 5.9 % $PM_{2.5}$, 49.5 % vanadium particles if land-based emissions were included, and 57.2 % SO_2, 71.9 % NO, 30.4 % NO_2, -16.6 % O_3, 27.6 % $PM_{2.5}$, 77.0 % vanadium particles if land-based emissions were excluded.

Keywords

Ship emission; Shanghai port; emission source contribution; SPAMS

1 Introduction

~~Ship emission constitutes an important source of gaseous and particulate pollution world wide. Growing shipping activities in recent years are attracting much attention to assess its impact on environment and health (Fuglestvedt et al., 2009). For emissions from sea-going vessels in pristine marine environment, it is found that ship emissions affect clouds properties along cruising route (Petzold et al., 2008;Coggon et al., 2012), which is directly relevant to earth radiation budget and climate issues. In portside or coastal regions, ship emissions generate negative impacts on the air quality at varied degrees (Donateo et al., 2014;Liu et al., 2017). With growing contributions of ship emissions to air pollution, its negative effects on human health of coastal residents is another subject that attracted attentions (Corbett et al., 2007).~~

Ship emissions constitute an important type of gaseous and particulate source in global scale. It has become important in recent years due to the increasing shipping activities. The annual ship emission of NO_x, SO_2 and $PM_{2.5}$ were estimated to be 2×10^7, 9.7×10^6, and 1.5×10^6 tons respectively (Johansson et al., 2017). The large emission intensities from ships have generated great burdens to regional and global environment (Fuglestvedt et al., 2009) and negative impacts to human health (Corbett et al., 2007). In marine environment, ships were found to be the dominant contributor to surface NO_2 and SO_2 concentrations (Dalsoren et al., 2009). Altered clouds properties were identified in these areas along ship cruising route by satellites (Petzold et al., 2008;Coggon et al., 2012), which could generate impacts to earth radiation budget and climate. For coastal or port regions, ship emissions have made significant contributions to atmospheric NO_x, SO_2 and PM in local environment (Donateo et al., 2014; Merico et al., 2017).

The typical fuel that ships burn is Residual Fuel Oil (RFO) with high sulfur content. Combustion of RFO in ship engines produces high concentration of gaseous and particulate pollutants including NO_x, SO_2, Elemental Carbon (EC), Organic Carbon (OC), sulfate and trace metals. Emission Factors of these pollutants from various ship types have been determined to develop emission inventories (Moldanova et al., 2013;Buffaloe et al., 2014;Cappa et al., 2014). In ambient measurement, however, the chemical and physical attributes of ship emissions are critical for identifying ship emission and assess their impacts (Murphy et al., 2009). Owing to more stringent regulations against ship emissions by restricting sulfur content in fuel, the detection of ship emissions relying only on individual tracers is unreliable because of the changing composition of RFO in different areas. To better identify ship emission in this context, multi-component characterizations including both gaseous and particulate are necessary in studies of field measurements (Xiao et al., 2018;Viana et al., 2009).

In Yangtze River Delta (YRD) region in China the shipping activities has increased significantly due to intensified international trades in recent years. The accompanying potential environmental and health problems from ship emissions in YRD are well recognized (Chen et al., 2018;Zhang et al., 2017;Fu et al., 2017). Global distributions of ship emission indicate that South and Eastern China Sea regions have the highest pollutants emission densities (Johansson et al., 2017). As shown in an emission inventory in China, shipping traffics emitted about 1.3 Tg SO_2, 1.9 Tg NO_x and 0.16 Tg PM in 2013, with NO_x and PM being equivalent to ~ 34 % and 29 % of total mobile vehicle emissions in China (Fu et al., 2017). To cope with severe air pollution caused by ship emissions, Shanghai government has initiated Domestic Emission Control Areas (DECA) in YRD. At present stage, according to YRD DECA regulations, the sulfur content of any fuel used on board while berthing at Shanghai port shall not exceed 0.5 % (m/m), except for the first hour after arrival and the last hour before departure, which has taken effect on April 1, 2016. This limitation level of sulphur is still higher than the implemented legislation in many harbors/ports in Europe and US (0.1%) (IMO, 2017). The DECA measure was currently implemented mainly in three major shipping areas including PRD, Pearl River Delta - PRD, and Bohai Rim region in China. Efficiency of the ECA measures has been tested in other places (Contini et al., 2015;Merico et al., 2017). It was shown that the control strategies in sulphur in fuel could generate synergetic reduction in both SO_2 and primary PM release from ships. The benefits of DECA measure in YRD were also suggested by the reduction of SO_2 concentration at several monitoring sites in port areas. There is a published study which dealt with the effectiveness of DECA in PRD region, estimating that the DECA measure could result average reduction of 9.54% SO_2 and 2.7% $PM_{2.5}$ in land areas (Liu et al., 2018).

An quantitative estimation of ship emission contribution to air quality is needed for better understanding of its environmental roles and controlling policies. In East Asia, an earlier emission inventory in Shanghai area estimated that the ship emissions were 58160, 51180, 6960 tons/year for NO_x, SO_2 and PM respectively in 2003 (Yang et al., 2007). Over the last decade Shanghai port throughput of goods has dramatically increased. In 2010, the total ship emissions of NO_X, SO_2 and $PM_{2.5}$ in YRD have grown to 7.1×10^5, 3.8×10^5 and 5.1×10^4 tons/year, respectively (Fan et al., 2016). A more recent study estimated that the primary $PM_{2.5}$ from ships ranged from 0.63 to 3.58 $\mu g/m^3$, accounting for 4.23 % of the total $PM_{2.5}$ in Shanghai Port (Zhao et al., 2013), based on a marine port measurement off coast of Shanghai. Such information of port in coastal areas is needed since their closer distance to the urban area of Shanghai city.

In the summer of 2016, an in-site sampling campaign focusing on ship emissions was performed at Shanghai Port. Gaseous and particulate matters concentrations were ~~online~~ monitored for 3 months to identify and characterize the ship emissions in Shanghai port areas. Based on the measurement data, quantitative assessment of the contribution of ship emissions to portside air quality was performed. Ship emission aerosol particles were characterized by a single particle aerosol mass spectrometer (SPAMS) which was deployed at the same site in parallel to the gaseous measurement. The SPAMS was utilized to identify ship emission aerosol composition and size with high temporal resolution, which is useful in detecting fast transient ship plumes, as demonstrated previously (Ault et al., 2010;Healy et al., 2009). In addition, the ship emission particle signatures obtained here is valuable in SPAMS source apportionment in future studies. The present study represents a comprehensive characterization of gaseous and particulate ship emissions in YRD and serves to provide essential scientific ~~supporting~~ information for future evidence-based ship emission control policies.

2 Experimental

2.1 Sampling site

The Waigaoqiao Port (31.337° N, 121.665° E) locates in the northeast of Shanghai city (~~Fig. 1~~ Figure 1) and is the largest port in China. The port has about 7 km of docks (3 km north section and 4 km south section). In 2016 the port has yearly traffic of 367 M-tons of goods and container volume of 37.13 million TEU (Twenty-foot Equivalent Unit). Ship categories in port consist of container vessel (62.4 %), tug (18.6 %), oil tanker (9.0 %), bulk (1.8 %), Ro-Ro (1.7 %) and other ships (6.5 %) (private data from authority). A power plant and a shipbuilding factory reside between the north and south section of port, which have their own docks. The portside air monitoring station locates on the south bank of Yangtze River, 400 m away from the nearest dock.

~~Gaseous and particulate matter instruments were installed within the station with the main sampling tube extending through the roof. The outlets of the main sampling tube was 1m above the station roof and 3.5m above the ground.~~ Gaseous and particulate monitor instruments were installed in the station room. The station was equipped with a main sampling tube extending through the roof. The outlets of the main sampling tube was 1m above the station roof and 3.5m above the ground. Ship emission plumes could influence the site in wind direction of about 300°-0°-120° sector (~~Fig. 1~~ Figure 1). In the summer season the prevailing wind direction of the site is southeast direction. In the supplementary file the wind rose during the sampling period is provided (~~Fig. S1~~ Figure S1). In ~55% of time the site was under the impact from port emissions. To the south and west of site there were intense road traffics of container trucks and the Shanghai outer ring. ~~Traffic emissions in south and west directions have important influences on air pollutions at the monitoring site when inland wind prevails.~~ Except emissions from ships in port directions, the site could also receive important influences from traffics when inland wind prevails.

2.2 Gaseous, $PM_{2.5}$ and peripheral measurement

~~The concentrations of gaseous NO-NO_2-NO_x, SO_2, and O_3 were measured continuously from Jun-21 to Sep-21, 2016. The gaseous pollutants were monitored by a suit of Thermal Scientific analyzers (NO-NO_2-NO_x, model 42i; SO_2, model 43i; O_3, 49i) installed in the monitor station. Calibration and checking of instruments were regularly performed by zero checks (through a zero-air generator) and span checks (through standard NO_2 and SO_2 gas of known concentrations; the O_3 standard was generated through a calibration photometer system); The $PM_{2.5}$ concentrations were monitored by oscillating microbalance method (Thermo TEOM 1405-F). Calibration of TEOM is not relied on standard, for the aerosol mass on a filter was monitored by the oscillation frequency change of the tapered element over specified time. The regular maintenance of TEOM includes the changing of filters before the filter loading approach 100%. The flow rate of TEOM was checked using a flowmeter. The lower detection limits of these instruments are: 0.4 μg/m^3 (NO, NO_2); 0.5 μg/m^3 (SO_2); 0.5 μg/m^3 (O_3); 1 μg/m^3 ($PM_{2.5}$). Weather conditions (temperature, humidity, pressure, wind speed and direction) were monitored by a mini-weather station installed on the rooftop of the station. The weather station sensor was about 1 m above the station roof and 3.5 m above the ground. Data from all the instruments and the monitor was managed in a customized database and set to 5 min resolution. Atmospheric pollutants concentrations in Shanghai city area, including gaseous pollutants and $PM_{2.5}$ concentrations, were monitored concurrently at 9 national air quality monitoring stations in 1h resolution. The averaged pollutants concentrations at these stations during the sampling period were included for comparison.~~

From Jun-21 to Sep-21, 2016, the portside gaseous pollutants NO-NO_2-NO_x, SO_2, and O_3 were monitored continuously with a suit of Thermo Scientific analyzers (NO-NO_2-NO_x, model 42i; SO_2, model 43i; O_3, 49i). Verification and calibration of the instruments were performed regularly by zero checks (through a zero air generator) and span checks (through standard NO_2 and SO_2 gas of known concentrations; the O_3 standard was generated through a calibration photometer system); The $PM_{2.5}$ concentrations were monitored by oscillating microbalance method (Thermo TEOM 1405-F). Calibration of TEOM was not relied on standard, for the aerosol mass on a filter was monitored by the oscillation frequency change of the tapered element over specified time. The regular maintenance of TEOM included the replacement of filters before their mass loadings approached 100%. The flow rate of TEOM was checked using a flowmeter. The lower detection limits of these instruments are: 0.4 μg/m^3 (NO, NO_2); 0.5 μg/m^3 (SO_2); 0.5 μg/m^3 (O_3); 1 μg/m^3 ($PM_{2.5}$). Weather conditions (temperature, humidity, pressure, wind speed and direction) were monitored by a mini-weather station installed on the rooftop of the station. The weather station sensor was installed about 1 m above the station roof and 3.5 m above the ground. Data from all the instruments and the weather monitor was managed in a customized database and were set to 5 min resolution. Atmospheric pollutants concentrations in Shanghai city area, including gaseous pollutants and $PM_{2.5}$ concentrations, were monitored concurrently at 9 national air quality monitoring stations in 1h resolution. The averaged pollutants concentrations at these stations during the same period were included for comparison.

2.3 Single particle aerosol mass spectrometer (SPAMS)

~~During the period from Jun 21 to Sep 21, 2016, a SPAMS (HeXin Analytical Instrument Co., Ltd., China) concurrently characterized single particle chemical composition and size of ambient aerosol in real time (Li et al., 2011). Operation principle of SPAMS is briefly described here. Ambient aerosol is drawn into SPAMS vacuum region through a critical orifice with limited aerosol flow. Aerosol particles then enter an aerodynamic focusing lens (AFL) where they are focused into a thin beam with transiting velocities as a function of particle aerodynamic size. In the SPAMS sizing region particles consecutively encounter two continuous laser beams (532 nm wavelength), reflect light and generate signals in two photomultiplier tubes. The time lag between two PMT signals is used to calculate particle velocity and to trigger the third laser (266 nm wavelength) at appropriate time to ionize the same particle. Chemical composition of ionized particle is measured by a dual polar time-of-flight mass spectrometer to record signal for both negative and positive ions. The time lags between two PMTs of PSL particles of known size are used to calibrate the aerodynamic size of ambient particles. Particle size, dual polar mass spectra, particle reflecting signals from two PMTs are saved for each particle. A $PM_{2.5}$ cyclone was placed at the outlet of sampling tube on the roof of the station to cut out particles larger than 2.5 μm before analysed by SPAMS.~~

From Jun-21 to Sep-21 in 2016, a SPAMS (HeXin Analytical Instrument Co., Ltd., China) was applied to characterized single particle composition and size of ambient aerosol at the port site (Li et al., 2011). Operation principle of SPAMS is briefly described. Ambient aerosol was drawn into SPAMS vacuum system through a critical orifice with limited aerosol flow. The particles then entered an aerodynamic focusing lens (AFL) where they were focused into thin beam, with transiting velocities in the vacuum as a function of their aerodynamic size. In SPAMS sizing region the particles consecutively encounter two continuous laser beams (532 nm wavelength), reflect light and generate signals in two photomultiplier tubes. The time lag between two PMT signals was used to calculate particle velocity and to trigger a ionizing laser pulse (266 nm wavelength) at appropriate time to ionize the same particle. Chemical composition of particles was determined by a dual polar time-of-flight mass spectrometer to record signals for both negative and positive ions. The time lags between two PMTs of PSL particles of known sizes were used to calibrate the aerodynamic size of ambient particles. Particle size, dual polar mass spectra, particle reflecting signals from two PMTs were saved for each particle. A $PM_{2.5}$ cyclone was placed at the outlet of sampling tube on the roof of the station to remove particles > 2.5 μm before analysed by SPAMS.

Specific composition in particles, such as vanadium, is identified by their characteristic mass peaks in particle spectra. Particles producing vanadium peaks were labelled as vanadium particles. SPAMS quantifies their concentrations in a semi-quantitative manner through the number of detected particles in specific duration of time. Considering that the aerosol flow was introduced into SPAMS at fixed flow rate (0.1L/min), the detected particle numbers (or particle detecting velocity) could be utilized as indication of ambient particle concentrations. In ambient sampling it was shown particle numbers in SPAMS were positively correlated with ambient $PM_{2.5}$ concentrations (R^2=0.69 in this study). In present study, we used particle detecting velocity of vanadium containing particles as the metric of their concentrations. To derive ambient particle number concentrations from

SPAMS particle numbers, we need to consider the efficiency issues of SPAMS on AFL transmission, laser detection and laser ionization (Wenzel et al., 2003).

2.4 SPAMS data analysis

~~The temporal resolution of SPAMS (seconds or minutes) makes it suitable to couple with online gaseous data to identify ship emissions. The quick fluctuations of gaseous concentrations, shifting of wind and the arrival of particle plumes, were well registered in SPAMS data. In addition, present study takes advantage of the power of SPAMS to identify individual ship emission particles based on particle fingerprint. Mass spectral patterns of ship emission particles were firstly identified and then were utilized to extract ship emission particles from single particle dataset. The temporal trends, size distribution, chemical composition, and wind rose of the extracted particles could be examined in further detail.~~

The temporal resolution of SPAMS (seconds or minutes) makes it suitable to couple with online gaseous data in identifying ship emissions. The fluctuations of gaseous concentrations, shifting of wind directions and the arrival of emission plumes, were well responded by SPAMS data. Additionally, present study took advantage of the ability of SPAMS to identify individual ship emission particles by their characteristic composition. Composition patterns of ship emission particles were identified firstly and were then applied to extract desired particles from all analysed particles. The temporal trends, size distribution, chemical composition, and wind roses of the extracted particles could be examined in further detail.

~~During sampling of 3 months a large amount of particles were chemically analysed by SPAMS (>2.3 million mass spectra). The identification of ship emission particles from 2.3 million total particles were based on a combined method of peak searching and algorithm clustering. Specifically, the SPAMS data are pre-analysed by visually inspecting of individual particle mass spectra to identify MS patterns during ship plumes. The concurrent SO_2 concentrations were utilized to locate ship emission plumes when sharp SO_2 peaks occurred, which is typical for RFO combustions (Murphy et al., 2009;Merico et al., 2016). Compared with non-plumes period, the most important indicating peaks occurred at V^+(51), VO^+(67), Fe^+(56), Ni^+(58) and serial peaks of elemental carbon at C_n^+(n=1,2,3…,12) in the positive mass spectrum (Ault et al., 2010;Healy et al., 2009;Ault et al., 2009). In this study the vanadium mass peaks (peak V^+(51) and VO^+(67))) were determined to be a prerequisite to indicate ship particles during plumes. Further notes on this particle identification method from ship emission are seen in the supplementary material. Peak searching method of criteria of m/z = 51 and 67 (i.e., only the existence of mass peak at 51 and 67, no peak area limitation) was firstly applied to search all possible candidates from all analysed particles. This search criterion is not too stringent because particles producing organic peaks at the same nominal mass (e.g. $C_4H_3^+$(51), $C_4H_3O^+$(67)) could interfere and may enter into searched clusters. Then the ART 2a algorithm (Song et al., 1999) was applied to the searched clusters to generate sub-clusters of particles (Vigilance=0.85; Learning=0.05; Iteration=20). By inspecting composition, size and wind rose patterns of sub-clusters, a small fraction of outlier particles from non-shipping emission sources were thus picked out and discarded.~~

During the sampling period of 3 months SPAMS generated a large particle set (>2.3 million particles were chemically analysed). To identify ship emission particles from all the analysed particles, we applied a combined method of peak searching

and algorithm clustering. Specifically, the individual particle mass spectra were visually inspected to get a general MS pattern during ship plumes. It is not feasible to inspect the large amount of spectra exhaustively. Instead, we used the concurrent SO_2 concentrations to locate ship emission plumes when sharp SO_2 peaks occurred, which is typical for RFO combustions (Murphy et al., 2009;Merico et al., 2016). Compared with non-plumes periods, the most indicative peaks during plumes occurred at V^+(51), VO^+(67), Fe^+(56), Ni^+(58) and serial peaks of elemental carbon at C_n^+(n=1,2,3…,12) in the positive mass spectrum (Ault et al., 2010;Healy et al., 2009;Ault et al., 2009). In this study the vanadium mass peaks (peak V^+(51) and VO^+(67))) were determined to be a prerequisite to indicate ship particles during plumes. Further notes on this particle identification method of ship emission particles were provided in supplementary file. We applied a rough searching with peak criteria of m/z = 51 and 67 (i.e., just the existence of mass peak at 51 and 67 with no peak area limitation) to search all possible candidates from the entire dataset. This particle criteria is not stringent because particles producing organic peaks at the same nominal mass (e.g. $C_4H_3^+$(51), $C_4H_3O^+$(67)) could interfere and may enter into searched clusters. Then the ART-2a algorithm (Song et al., 1999) was applied to the searched particles to generate sub-clusters of similar MS patterns (Vigilance=0.85; Learning=0.05; Iteration=20). By inspecting composition, size and wind rose patterns of sub-clusters, a small fraction of outlier particles from non-shipping emission sources were thus picked out and discarded.

2.5 Evaluation of ship emission contribution

The calculations method of ship emission contributions used in this study, which was originally developed by (Contini et al., 2011), is based on the extraction of ship emission plumes from background concentrations of pollutants :

$$\varepsilon_A = \frac{\Delta C_A F_{plm}}{C_A}$$

Where: ε_A, ship emission contributions of pollutants A; ΔC_A, the difference between average concentrations during plumes and non-plumes; F_{plm}, fraction of cases of plumes; C_A, the average concentration of pollutant A during reference period. The uncertainties of ε_A determined in this method could arise from several factors, such as the definition of port direction sector, the definition of plumes (the threshold level that discriminate plumes and the background), and pollutants and wind field measurements. This study ~~estimate~~ estimated the uncertainties by subjecting ε_A to ~~the~~ slight adjustment of the port directions by ±10° and pollutants threshold levels by 20% to inspect its variations. To conform to the original work (Contini et al., 2011), calm wind periods (wind speed < 0.5 m/s) were considered in the evaluation of uncertainties (either excluding or including calm wind periods).

3 Results and discussions

3.1 Identification and ~~statistics~~ description of ship emission plumes

~~In the vicinity of port, the measured ship-emitted pollutants often produce sharp peaks in relatively short period (Fig. 2). The sharp peaks are caused by ship emission plumes corresponding to shipping activities such as arrival, hoteling and departure,~~

~~which typically persist for a few (mostly 3-6) hours. The measured SO_2, NO, NO_2, O_3 and $PM_{2.5}$ concentrations during a typical period (Aug 27-29) are shown in Figure 2 to illustrate several cases. For comparison the averaged SO_2 concentration in Shanghai city and vanadium particle number concentration during the same period are included. It is clear that during plumes tracking period, the SO_2 concentration peaks were well correlated with vanadium particles number as detected by SPAMS. The synchronous peaks of gaseous and particulate matters during plumes was similarly observed elsewhere (Healy et al., 2009;Ault et al., 2010;Merico et al., 2016). Wind field during plumes also support they were actual emission plumes arrived at the site (Fig. 2).~~

In the vicinity of port, the ship emission pollutant concentrations often produce obvious peaks in relatively short period (Figure 2). These peaks were caused by ship emission plumes relating to shipping activities such as arrival, hoteling and departure, which typically persist for a few (mostly 3-6) hours. The ambient SO_2, NO, NO_2, O_3 and $PM_{2.5}$ concentrations during a typical period (Aug 27-29) were shown in Figure 2 to illustrate several plumes. For comparison the averaged SO_2 concentration in Shanghai city and vanadium particle number concentrations of the same period are provided. During plume periods, ambient SO_2 concentration peaks correlated well with vanadium particles numbers detected by SPAMS. The $PM_{2.5}$ peaks during plumes were not always unclear as in Figure 2. In supplementary file we present another period of $PM_{2.5}$, SO2 and vanadium particle concentrations to demonstrate stronger $PM_{2.5}$ peaks (Figure S3). The synchronized gaseous and particulate peaks in ship emission plumes was typically observed in port regions (Healy et al., 2009;Ault et al., 2010;Merico et al., 2016). These ship emission plumes were also consistent with the prevailing wind directions in plumes, as shown in Figure 2.

~~The measured gaseous and particulate matters demonstrated different characters during sampling period. In most cases of the non plume periods the portside SO_2 concentration matched well with the SO_2 in Shanghai city. This is a suggestion that a background SO_2 concentration of regional scale is underlying the measured concentration in portside, upon which the local SO_2 plumes were superimposing. As two typical combustion products, the NO and NO_2 concentrations also show corresponding elevated concentrations during plumes under favourable wind fields (Fig. 2). However, during the whole study NO and NO_2 are more importantly influenced by land based traffics (mostly from transportation diesel trucks) when the inland wind prevails. The ship emission NO_x plumes reached sampling site have been slightly aged. To understand the aging effect, when wind direction is in port sector (300° 0° 120°), the averaged NO/NO_2 ratio is 0.6 (mostly fall in 0.1~4.5 range), lower than typical ratio of 4 at ship exhaust (Alföldy et al., 2013) , suggesting the oxidation of primary NO into NO_2 had occurred for some time (1~50 min, based on wind speed measurement and transportation distance). This result is evidenced by the apparent consumption of O_3 in plumes as shown in Figure 2, commonly termed as titration effect between NO_x and O_3. The $PM_{2.5}$ mass concentration did not show as apparent response as that of SO_2 during ship emission plumes, despite that the typical vanadium particles had reached the site, as shown. The obscure response of $PM_{2.5}$ during ship plumes is explained by the finer particle sizes in relatively fresh ship emissions, as discussed subsequently.~~

~~Considering the facts described above, the present study defines ship plume periods by using SO_2 concentrations and vanadium particle number concentrations. For SO_2, a minimum threshold of Δ_{SO2} = SO_2(Port) – SO_2(Shanghai) > 5 ug/m^3 is applied to indicate ship plumes. For ship emission particles, the number concentration of vanadium particle is considered because in~~

~~some cases the SO_2 peaks are absent or obscure as typical fresh vanadium particles are indeed mount up quickly. The occurrence probability of this kind of event is low (3% in cases). The causes of this kind of events are two-fold: firstly, it is maybe due to the anchored ships burning low sulfur content oil (<0.5 % m/m) to comply with regulations in the port region, which came into force on April 1, 2016; secondly, it is also possible that the vanadium particles be emitted from industry sources such as petroleum refinery companies in this region. The wind directions when these events happened support both of the proposed causes. In this study the threshold of vanadium particle detection speed in ship plumes are set to C_V > 25 particles/hour. That is, ship plumes are defined as either Δ_{SO2} > 5μg/m^3 or C_V>25 particles/hour.~~

Considering these facts, present study defines ship plume periods using SO_2 concentrations and vanadium particle number concentrations. For SO_2, a minimum threshold of Δ_{SO2} = SO_2(Port) - SO_2(Shanghai) > 5 ug/m^3 was applied to indicate the arrival of ship plumes. Additionally, the number concentrations of vanadium particles (PNC_v) were considered because in some cases the SO_2 peaks were absent or obscure while typical fresh vanadium particles were increased. The occurrence probability of this kind of events was low (3% cases). This kind of events were possibly caused by the anchored ships burning low sulfur content oil (<0.5 % m/m) to comply with regulations in the port region, which has come into force on April 1, 2016; secondly, it cannot be excluded that vanadium particles be emitted from industry sources, such as petroleum refinery companies in this region. The wind directions during these events support both of the proposed causes. To identify plumes, we excluded the possible industries influences by limiting the prevailing winds only to port directions. Present study set the threshold of vanadium particles in ship plumes to PNC_v > 25 particles/hour. Therefore, ship plumes were identified as either Δ_{SO2} > 5μg/m^3 or PNC_v >25 particles/hour.

~~There were about 210 ship emission plumes captured during the sampling campaign. Table 1 summarizes the statistics on the concentrations of SO_2, NO, NO_2, O_3, $PM_{2.5}$ in port area and Shanghai city during the sampling period. Vanadium particles number concentrations are represented by particle detection speeds by SPAMS. It is stated that the SPAMS detection speed are positively correlated with particle number concentrations in ambient air, but should not be explained as absolute number concentrations without correction for SPAMS efficiency (Wenzel et al., 2003). Statistics are performed on pollution level in plume periods and in non-plumes. To separate influences from land sources (principally traffics), non-plume periods during wind from port direction are calculated in Table 1.~~

There were about 210 ship emission plumes captured during the entire period. Table 1 summarized the statistics of the SO_2, NO, NO_2, O_3, $PM_{2.5}$ concentrations in the port site and urban area in Shanghai during this study. Vanadium particles number concentrations were represented by particle detecting velocity by SPAMS. The SPAMS particle detecting velocity were positively correlated with particle concentrations in ambient atmosphere, but should not be explained as absolute number concentrations without correction for SPAMS efficiency (Wenzel et al., 2003). Statistics were performed on pollution concentration in plume and non-plumes periods. To separate influences from land-based sources, non-plume periods during winds from port direction were calculated in Table 1.

~~In general, the port site has concentrations of combustion products SO_2 and NO_x much higher than that in Shanghai city regions (Table 1). For SO_2 its concentrations in non-plumes were comparable with that in Shanghai city, regardless of wind direction, representing a background SO_2 level. However, NO_x concentrations in non-plumes from port sector wind were significantly lower than from land directions. This result suggests a larger ship emission contribution to portside SO_2 than to NO_x. For NO_x, due to the specific geographic proximity of Waigaoqiao port, its concentration was more importantly impacted by land-based traffics. In general the ozone concentrations in port were lower than Shanghai urban region by 13-33 %. The lower O_3 level around portside is consistent with higher SO_2 and NO_x concentrations in this area to consume O_3. For $PM_{2.5}$, its concentrations in port area are slightly lower than Shanghai city either in plume or non-plume periods, although vanadium particles concentrations in plumes were about 4 times higher than in non-plumes (Table 1). Longer period of $PM_{2.5}$ data at the same station supports the lower $PM_{2.5}$ concentration compared to Shanghai city, suggesting that it is a general trend at this port site. This is probably caused by the clean air advection from the sea and the wiping out effect of adjacent water surface through particle sedimentation. The vanadium particle detection probability, measured as the number fraction in total particles, is clearly larger (6.7 % on average) in portside than the urban area in Shanghai (1-2 %) (Liu et al., 2017).~~

Generally the concentrations of SO_2 and NO_x in the port site is 40~70% higher than Shanghai city (Table 1). The SO_2 concentrations in non-plume periods were comparable with that in Shanghai city, irrespective of wind directions, therefore the non-plume SO_2 can be recognized as background SO_2 in this area. Contrastingly, the NO_x concentrations showed obvious dependence on wind directions in non-plumes, whose concentrations were higher when inland wind prevails, suggesting the importance of land-based emissions to port in coastal areas. In a similar ambient observation at Yangshan port, (Zhao et al., 2013) obtained the average concentration of 29.4 and 63.7 $\mu g/m^3$ for SO_2 and NO_2 respectively, higher than the present level of 15.6 $\mu g/m^3$ (SO_2), 53.2$\mu g/m^3$ (NO_2). Noting that the SO_2 and NO_2 were only intermittently measured for about 20 days in that study (May and August, 10 days each month). Therefore it is not feasible to make direct comparison. In plume period, the SO_2 maximum hourly concentration in Yangshan (119.0 $\mu g/m^3$) were close to present study (124 $\mu g/m^3$); Due to land-based emissions, the NO_2 maximum hourly concentration in Waigaoqiao port (260 $\mu g/m^3$) is higher than Yangshan port (199.8 $\mu g/m^3$).

In general the ozone concentrations in the port site were lower than Shanghai urban region by 13-33%. To inspect whether the O_3 depletion was related to the oxidation of primary NO emissions in the port site, we calculated the NO_2 ratios to analyse NO_x composition in plumes. The NO_2 ratio is defined as the ratio between NO_2 and the NO_x ($NO+NO_2$), which was used by several relevant characterizations of ship emissions (Alföldy et al., 2013;Kurtenbach et al., 2016). Before the calculation of NO_2 ratio we firstly converted NO and NO_2 mass concentrations to molar unit, and then the background NO and NO_2 levels were subtracted to make sure peaks were due to plumes. The distribution of the NO_2 ratio in this study was shown in Figure 3, where the NO_2 ratio distribution from ship plumes in another study was compared.

The distribution of the NO_2 ratios in present study showed several modes. The largest mode occurred at about 0.2 (20%). Obviously this mode was also present in the comparison study (Alföldy et al., 2013), which was recognized as fresh engine emissions from ships. A major difference between two studies is that significant fraction of NO_2 ratios occurred in larger range

(> 0.4) in present study, which was not observed in Alföldy et al., 2013. The larger NO_2 ratios were once thought to be emitted from unidentified type of ships. When we correlated the NO_2 ratio with ambient O_3 concentrations, however, we found there was obvious positive correlation between them, as shown in right panel in Figure 3. This result suggests that the higher NO_2 ratio of some plumes were not due to the emission characteristics of ships, but due to the transformation of NO to NO_2 in the ambient, for if the NO_2 ratio were higher at the discharges and no ambient transformation occurred, then there will be no reason to observe the dependence of NO_2 ratio on an ambient condition of O_3. This is an evidence that the primary NO emission (from ships or on-road traffics) had contributed to the O_3 depletion in this area.

For particulate matter, the $PM_{2.5}$ concentrations in port area were slightly lower than Shanghai city, although PNC_v in plumes were times higher than non-plumes (Table 1). Longer period of $PM_{2.5}$ data suggested the lower $PM_{2.5}$ concentration is a general trend in this port site. This trend is not unique to the port regions because we observed it in other coastal area as well, which is readily observed in $PM_{2.5}$ spatial distribution of Shanghai (Figure S4 in supplementary file). In the spatial distribution there was a general trend of decreasing $PM_{2.5}$ concentrations from inner to coastal areas in Shanghai. This fact is assumed to be caused by the dispersion or advection of clean air from the sea. The portside primary PM from ship emissions are mostly ultrafine particles, with mass emission factors much smaller than NO_x and SO_2 (Zhang et al., 2017). Therefore the primary PM from ships or other traffics could not contribute significantly to ambient PM mass concentrations. The vanadium particle number fractions in total particles in SPAMS were obviously larger (6.7 % on average) in portside than urban areas in Shanghai (1-2 %) (Liu et al., 2017)

3.2 Particles properties from ship emission

3.2.1 Discrimination of fresh and background ship emission particles in port site

~~In single particle characterization techniques, fresh or 'pure' ship emission particles is separable from background or aged aerosol based on single particle signatures. The mass spectra of fresh and aged ship emission particles, wind roses and size distributions are shown in Figure 3, 4. It was observed that particles from ship emission plumes were characterized by the absence of or very low nitrate ($-62NO_3$ in negative spectra) signal in mass spectra, a pattern commonly found in combustion source characterizations (Spencer et al., 2006;Toner et al., 2006). In another respect, the temporal pattern, wind rose and size of nitrate containing vanadium particles were disproportionately distributed compared with fresh ones, which distinguished themselves as background ship emission particles (Healy et al., 2009;Ault et al., 2010) (Fig. 3). The dominant peaks in mass spectra of fresh ship emission particles are sulfate ($-97HSO_4^-$), EC (C_n^+/C_n^-, n are integers), and vanadium ($51V^+$, $67VO^+$) peaks, indicating the major components found in ship emission particles (Moldanova et al., 2013;Becagli et al., 2012;Murphy et al., 2009). Except for the nitrate peak ($-62NO_3^-$), other mass spectral patterns of background and fresh ship emission particles are similar (Fig. 3). Although organics is an important component of ship emission particles (Lack et al., 2009), the organic mass peaks in SPAMS spectra are insignificant compared with metal and EC peaks as shown in Fig. 3. The Lower OC signal is owing to the fact that SPAMS is not so sensitive to organics due to the low ionization efficiencies in laser ionization (Ulbrich~~

et al., 2009). However, an cluster of organic particles were indeed identified in ship plumes, although of minor detection probability, as discussed subsequently in 3.2.2.

Wind roses and size distributions of fresh and aged ship emission particles were also distinguishable. The fresh vanadium particles have wind rose pattern running parallel with the direction of riverbanks (300°-0°-120°). This is strong evidence that ships are the most predominant source of fresh vanadium particles in Shanghai port. Background vanadium particles, however, did not show any prominent source directions and displayed nearly uniform distributions in all directions. It is assumed that the aged vanadium particles are background particles which have undergone atmospheric processing in local or regional scale. The size distributions of vanadium particles as shown in Figure 4 indicates fresh vanadium particles with dominate particle numbers in smaller size range (<0.5 μm), compared with background ones. Although SPAMS detection efficiency declines in this size range due to the because of the smaller section to reflect laser light, significant number of ship emission particles were still detected in this size range. The explanation is that these particles are non-spherical fractal agglomerates, such as EC particles, having significantly larger cross sections to reflect laser light and be detected in SPAMS. The non-spherical fractal shape of fresh vanadium particles is seen with soot particle from fresh combustion sources. Similar observations were reported in other studies using single particle mass spectrometer in ultra-fine size range (Ault et al., 2010).

With single particle characterization, it is possible to separate fresh or 'pure' ship emission particles from aged types by particle signatures. The mass spectra, wind roses and size distributions of fresh and aged ship emission particles are displayed in Figure 4, 5. The dominant peaks in mass spectra of fresh ship emission particles include sulfate (-97HSO_4^-), EC (C_n^+/C_n^-, n are integers), and vanadium (51V^+, 67VO^+) peaks. These peaks were reflecting the major composition of fresh ship emission particles found by other techniques (Moldanova et al., 2013;Becagli et al., 2012;Murphy et al., 2009). Fresh ship emission particles produced very low or no nitrate (-62NO_3 in negative spectra) signal in mass spectra, as commonly observed in combustion source characterizations (Spencer et al., 2006;Toner et al., 2006). In aged particle type their nitrate signals were stronger than fresh type. Except for the nitrate related peaks (-46NO_2^-,62NO_3^-), other mass spectral patterns of fresh and aged ship emission particles were similar.

Through the discrimination of ship emission particles into two types, we have identified their different temporal pattern, wind rose and size distribution of ship emission particles in the portside (Figure 4). The temporal variation of fresh ship emission particles showed many peak shaped fluctuations, which was similar to and synchronized with SO_2 peaks well (Healy et al., 2009;Ault et al., 2010). However, the number concentrations of aged particles were generally much lower than fresh types (20% of the latter) and have shown more stable temporal concentrations than fresh vanadium particles. We also analysed the particle number concentrations of ship emission particles at different wind directions. The results were drawn as wind roses for each particle type in Figure 4. The differences between the wind roses of the two types were obvious. It is clear that fresh vanadium particles occurred almost entirely from port directions, and its wind rose ran nearly parallel with the direction of riverbanks (300°-0°-120°). This is a strong evidence that ships were the most predominant source of fresh vanadium particles in the port site. Aged vanadium particles, however, did not shown obvious favoured wind directions and distributed uniformly in all wind directions. Based on described characteristics of vanadium particles, present study assumed that the aged vanadium

particles were background particles which have undergone atmospheric processing in local or regional scale. The source of the background vanadium particles may be emitted from other places may not restricted in current port. The size distributions of fresh and background vanadium particles are shown in Figure 5. The fresh vanadium particles dominate particle numbers in smaller size range (< 0.4 μm) where aged or background particles contributed only minor fractions. Although SPAMS detection efficiency declines in this size range, a significant number of ship emission particles were still detected in this size range. The explanation is that this fraction of particles were non-spherical fractal agglomerates, whose cross sections was larger to reflect laser light and thus be detected in SPAMS. The non-spherical fractal shape of fresh vanadium particles was observed as soot particle from fresh combustion sources. Similar observations were reported in other studies using single particle mass spectrometer in ultra-fine size range (Ault et al., 2010).

3.2.2 Particle types in fresh ship emission plumes

~~The major particle types of fresh ship emission particles were identified after the separation of background particles. The composition, size distributions and emission characters were analysed to obtain the further information of these types, which will be helpful to in particle source identification in other sites. In general, the fresh vanadium particles could be grouped into 4 types based on their chemical composition: V-OC, V-EC, V-ECFe and V-Ash, and the average mass spectra are shown in Figure 5. The negative mass spectra of the four types were similar in that the SO4 peak were dominant in addition to other negative EC peaks, which is consistent with the elevated SO2 concentrations in plumes. The major chemical differences of the four particle types are in the positive mass spectra as depicted in Figure 5. In the positive mass spectra the V-OC type are characterized by the dominant organic peaks like $C_2H_3^+$, $C_2H_5^+$, $C_2H_3O^+$, with non or insignificant EC peaks. Generally the organics are ionized in low efficiencies in SPAMS. The rich organic signals of V-OC particles indicate that they are mainly composed of organics in engine exhaust plumes (Lack et al., 2009;Moldanova et al., 2013). The V-EC particles produce dominant EC peaks from C_1^+ to C_{13}^+ and metal peaks of V and Na, but without iron peaks Fe^+. This type is also the most abundant type of all vanadium particles. The V-ECFe type is similar to V-EC except for the addition of Fe^+ and Ca^+, Ni^+ peaks of lower frequencies. The V-Ash particles produce minor or no EC peaks except some metal peaks of V, Fe and Ni in positive spectra. These metals are used as lubricant additives or inherently present in RFO, therefore their presence in ship emission particles are expected and commonly found (Becagli et al., 2012;Moldanova et al., 2013).~~

After separation of background particles, we analysed the mass spectral signatures of fresh ship emission particles using ART-2a algorithm. These particles were grouped into 4 major types based on the similarity of their composition. Temporal variations, composition, size distributions and were analysed to obtain the further information of these types, which will be helpful in particle source identification in other sites. The 4 particle types were labelled as V-OC, V-EC, V-ECFe and V-Ash according to their characteristic composition, whose averaged mass spectra were shown in Figure 6. The negative mass spectra of the four types were similar in that the SO_4^- peak were dominant in addition to other negative EC peaks, which is consistent with the elevated SO_2 concentrations in plumes. The major differences of the four particle types were in the positive mass spectra as depicted in Figure 6. Generally the V-OC type were characterized by the dominant organic peaks including $C_2H_3^+$, $C_2H_5^+$,

$C_2H_3O^+$, with non or insignificant EC peaks. Generally the organics are ionized in low efficiencies in SPAMS (Ulbrich et al., 2009). The rich organic signals of V-OC particles indicate that they were mainly composed of organics in engine exhaust plumes (Lack et al., 2009;Moldanova et al., 2013). Due to the low ionization efficiency of organics, the particle numbers of V-OC in plumes was generally low compared with other types, which was inappropriately reflecting the dominance of organic compositions in ship emission particles (Lack et al., 2009). The V-EC particles produce dominant EC peaks from C_1^+ to C_{13}^+ and metal peaks of V and Na, but without iron peaks Fe^+. This type is also the most abundant type of all vanadium particles. The V-ECFe type is similar to V-EC type except for the addition of Fe^+ and Ca^+, Ni^+ peaks of lower occurrence frequencies. The V-Ash particles produced minor or no EC peaks except some metal peaks of V, Fe and Ni in positive spectra. These metals are used as lubricant additives or inherently present in RFO, therefore their presence in ship emission particles are expected and commonly found (Becagli et al., 2012;Moldanova et al., 2013).

~~Temporal concentrations and size distributions of these particle types are shown in Figure 6. Temporal number concentrations of these particle types displayed daily variations, with higher concentrations in daytime than night. The temporal concentrations of these particle types were poorly correlated (R^2<0.4), suggesting they were emitted differently. Since these particles were detected in a portside environment, they were assumed to be emitted by ships of different engine types or modes of operation. The V-OC particles, although having low ionization probabilities, were found to concentrate in specific cases of plumes. Since the information of individual ships is not yet available, it is therefore not attempted to link V-OC particle plumes to specific ship types directly in the present study. The V-OC particles concentrated in specific ship emission plumes and its' number concentration peaks were usually narrower (~ 1 hour) than the other particle types (3~5 hour). Sizes of V-OC particles were more uniformly distributed as compared with the other types (Fig. 6). Similar organic-rich particles were identified from ship exhaust by other technique (Moldanova et al., 2013).~~

Temporal concentrations and size distributions of these particle types are shown in Figure 7. Temporal concentrations of these particle types displayed daily variations, with higher concentrations in daytime than night. The temporal concentrations of these particle types were poorly correlated (R^2<0.4), suggesting they were emitted differently. Since these particles were detected in a portside environment, they were assumed to be emitted by ships of different engine types or modes of operation. The V-OC particles, although having low ionization probabilities, were found to concentrate in specific cases of plumes. Since the information of individual ships is not yet available, it is not possible to link V-OC particle plumes to specific ship types. The V-OC particles concentrated in specific ship emission plumes (Figure 7) and its' number concentration peaks were usually narrower (~ 1 hour) than the other particle types (3~5 hour). Sizes of V-OC particles were more uniformly distributed as compared with the other types (Figure 7). Similar organic-rich particles were identified from ship exhaust by other technique (Moldanova et al., 2013).

~~The V-EC particles dominated the particle numbers in ship plumes in this study. Compared with the other types their sizes enriched in smaller size ranges (< 0.5 μm), which is a typical character of soot particles from the combustion of RFO (Moldanova et al., 2013). The V-Ash particles, which is most probably the ash spheres from combustion process of inorganic constituents in RFO and lubricants, are mainly detected in larger size range (> 0.5 μm) (Fig. 6). SPAMS measure particle~~

~~aerodynamic size which is both determined by particle size and density. The larger densities of metal oxides or salts in V-Ash particles, as compared with soot agglomerates, is also making contributions in its size distribution. The origin of V-ECFe types were are probably the result of internal mixing between V-EC and V-Ash particles. Their size distribution is more similar to V-Ash type.~~

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3.3 Contributions of ship emission to ambient pollutants in port area

~~For a coastal port, the evaluation of ship emission to air quality needs to identify impacts from land-based emissions. Obviously these land-based emissions are making greater influences to portside air quality than a marine port far from coast (Zhao et al., 2013). To give an intuitive illustration, the averaged concentrations of SO_2, O_3, NO, NO_2, $PM_{2.5}$ and vanadium particle numbers in different wind directions are summarized in Figure 7. Concentrations of pollutants has demonstrated varied dependency on local wind conditions. It is evident that, for the coastal port site in this study, the NO_x and $PM_{2.5}$ concentrations, were highest during land direction wind prevails. As a contrast the SO2 concentrations and vanadium particle numbers were dominant only when winds from port sectors. The hotspots in wind rose of vanadium particle are most probably produced by individual docks along the riverside. The wind dependence of ozone concentrations is less apparent, except its' depletion in regions of high NO_x and SO_2 levels in wind roses, as previously explained. Obviously the port site was receiving very different pollution impacts from land emission and the ship emissions in port. Present study tries to separate land-based emission influences by limiting wind directions only in port directions. In the calculation of ship emission contribution, two reference periods were considered in this study: the entire study period (irrespective of wind) and only when the site was in downwind directions of port.~~

For a coastal port, the evaluation of ship emission to air quality needs to identify impacts from land-based emissions. Obviously these land-based emissions were making greater influences to portside air quality than a marine port far from coast (Zhao et al., 2013). To give an intuitive illustration, the averaged concentrations of SO_2, O_3, NO, NO_2, $PM_{2.5}$ and vanadium particle numbers in different wind directions were summarized in Figure 8. Concentrations of pollutants has demonstrated varied dependency on local wind conditions. It is evident that, for the coastal port site in this study, the NO_x and $PM_{2.5}$ concentrations were highest during inland direction wind prevails. Contrarily, the SO_2 concentrations and vanadium particle numbers were dominant only when winds from port sectors. The hotspots in wind rose of vanadium particle were most probably produced by individual docks along the riverside. The wind dependence of ozone concentrations was less apparent, except its' depletion

in regions of high NO_x and SO_2 levels in wind roses, as previously explained. Obviously the port site was receiving very different pollution impacts from land emission and the ship emissions in port. Present study tries to separate land-based emission influences by limiting wind directions only in port directions. In the calculation of ship emission contributions, two reference periods were considered in this study: the entire study period (irrespective of wind) and only when the site was in downwind directions of port.

~~Ship emission contributions of measured respective pollutants in two reference periods are summarized in Table 2. Results show that, if the land-based emissions were considered, the relative contributions from ship emission for SO_2 (36.4 %) were much higher than for NO (0.7 %), NO_2 (5.1 %), and $PM_{2.5}$ (5.9 %). The low contributions of NO_x are due to the inclusion of traffic emissions of stronger intensities in the land directions. The main sources of NOx in land directions was considered not far from the site because the average NOx levels in Shanghai city is lower than the port site, as evidenced in Table 1. In the port site the vanadium particle number concentrations (PNC_v) were dominantly contributed (49.5 %) by ship emissions. The PNCv contribution is a lower estimation considering that SPAMS detect particles less efficiently for smaller particles, where the vanadium particles tend to concentrate. Contributions of PNC_v in different particle size ranges were also calculated in table 2. In either of reference periods (excluding or including land-based emissions), ship emission contributions to PNC_v in smaller size range (0-0.4μm) are larger compared with PNC_v in larger size ranges (0.4-0.8 μm, 0.8-2.5μm).~~

Ship emission contributions of air pollutants in two reference periods are summarized in Table 2. Results show that, if the land-based emissions were considered, ship emission contributed 36.4 % SO_2 concentration in local air in port area, a much higher value than for NO (0.7 %), NO_2 (5.1 %), and $PM_{2.5}$ (5.9 %). The low contributions of NO_x were due to the inclusion of traffic emissions of stronger intensities from inland directions. The main sources of NO_x from inland directions was considered not far from the site because the average NO_x levels in Shanghai city is lower than the port site, as evidenced in Table 1. For vanadium particle number concentrations (PNC_v), ship emissions were the predominant source in present site (49.5 %). The PNCv contribution is a lower estimation considering that SPAMS detect particles less efficiently for smaller particles, where the vanadium particles tend to concentrate. Contributions of PNC_v in different particle size ranges were also calculated in table 2. In either of reference periods (excluding or including land-based emissions), ship emission contributions to PNC_v in smaller size range (0-0.4 μm) are larger compared with PNC_v in larger size ranges (0.4-0.8 μm, 0.8-2.5 μm).

~~The relative contributions of PNC_v from ship emission is apparently higher than $PM_{2.5}$ on mass concentration. Previous study showed that the direct $PM_{2.5}$ contribution from ship traffics lies within 1-8% range (Contini et al., 2011;Contini et al., 2015). Recent studies carried in Mediterranean region found that ship emission contributed 0.3-7.4% $PM_{2.5}$ concentrations in port areas (Merico et al., 2016). Ship emission studies in Europe and other regions was reviewed, and its concluded that shipping traffics contributions to $PM_{2.5}$ were in 1-14% range, with higher contributions with decreasing particle size (Viana et al., 2014). The calculated value of $PM_{2.5}$ in the present site is within the reported ranges. Recently (Merico et al., 2017) compared ship traffic atmospheric impacts using inventories, experimental data and modelling approaches in Adriatic-Ionian port areas, and found that ships contributed 0.5-7.4% $PM_{2.5}$ in these areas. The same study further found that ship traffics contribution to particle number concentrations (PNC) is 2-4 time larger than mass concentrations of $PM_{2.5}$. The PNC is not currently measured,~~

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~~In a study carried out at Yangshan marine port of Shanghai, the calculated $PM_{2.5}$ contribution (~4 %) is smaller than present study (5.9 %) (Zhao et al., 2013). In this study a different method was used to evaluate ship emissions, relying on vanadium concentrations to indicate ship emissions. Considering the methodology differences, it is deemed that the results from the two studies are similar within the uncertainty range (Table 2). A previous estimation in Shanghai area using inventories method showed that ship emissions contributed 9 % NO_x and 5.3 % $PM_{2.5}$ in Shanghai area (Zhang et al., 2017), generally agrees with this study in the condition of including land-based emissions (Table 2). However, for SO_2 the contribution in that estimation (12 %) is significantly smaller than the 36.4 % in this study. The high SO_2 levels in this study is a local character of the port site which is close to emission sources. After transported to the urban region the high SO_2 concentrations will dissipate and strength weakened. It is noted that, the synchronized SO_2 and vanadium particles plumes as observed in the port site, are observed in a much less frequency in a urban cite in Shanghai city where another SPAMS is monitoring. Estimation of ship emission impacts to the urban area will be the subject of future studies.~~

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observed in a much less frequency in a urban site in Shanghai city where another SPAMS is monitoring. Estimation of ship emission impacts to the urban area will be the subject of future studies.

~~By limiting the sampling with time windows to periods during winds from port sector, the influences of land-based emissions could be largely eliminated. As shown in table 2, by considering port sector wind, for all pollutants the ship emission contributions were magnified in amplitude. The most significant change occurs for gaseous NO_x, whose contributions from ship emission increased to levels larger or comparable with SO_2. Contributions obtained here can be compared with a similar study carried out in a European port (Merico et al., 2016). Gaseous emissions of NO, NO_2 and SO_2 were similar between these two studies, which is impressive considering the larger throughput of goods in Shanghai port. However, in an absolute sense, this study estimate that ship emissions contribute to 5.68 $\mu g/m^3$ SO_2, 3.00 $\mu g/m^3$ NO_x and 1.57 $\mu g/m^3$ $PM_{2.5}$ during the sampling period. These values are comparable or higher than the reported results in ports in other regions (Viana et al., 2014). For example, a previous study found that the ship-emitted particles contributed 0.8 $\mu g/m^3$ (primary particles) and 1.7 $\mu g/m^3$ (secondary particles) in Bay of Algeciras (Viana et al., 2009). Due to the adjacency of the site to port, the calculated $PM_{2.5}$ contribution could be largely deemed as primary for present site. The relative contributions of pollutants are partly compensated by the higher background pollution levels in this region.~~

By limiting the analysis just to period when the winds were from port directions, the influences of land-based emissions could be largely eliminated. As shown in table 2, for all pollutants the ship emission contributions were magnified considerably in amplitude. The most significant variation occurs for gaseous NO_x, whose contributions from ship emission increased to levels larger or comparable with SO_2. Contributions obtained here can be compared with a similar study carried out in a European port (Merico et al., 2016). Gaseous emissions of NO, NO_2 and SO_2 were similar between these two studies, which is impressive considering the larger throughput of goods in Shanghai port. However, in an absolute sense, this study estimate that ship emissions contribute to 5.68 $\mu g/m^3$ SO_2, 3.00 $\mu g/m^3$ NO_x and 1.57 $\mu g/m^3$ $PM_{2.5}$ during the sampling period. These values are comparable or higher than the reported results in ports in other regions (Viana et al., 2014). For example, a previous study found that the ship emitted particles contributed 0.8 $\mu g/m^3$ (primary particles) and 1.7 $\mu g/m^3$ (secondary particles) in Bay of Algeciras (Viana et al., 2009). Due to the adjacency of the site to port, the calculated $PM_{2.5}$ contribution could be largely deemed as primary for present site. The relative contributions of pollutants are partly compensated by the higher background pollution levels in this region.

4 Conclusions

~~In the summer of 2016, an experimental study was carried out to characterize and quantify ship emissions in the Shanghai port. Obvious ship emission plumes were detected in the port site through online measurement of gaseous and particulate matter. During plumes the SO_2 and vanadium particles concentrations has demonstrated well synchronized peaks, which could be reliably used to indicate the arrival of ship emission plumes. Statistics of pollutants during plumes show that the concentrations of SO_2 in plumes are about 3 times higher than the background concentrations. Except the plume periods, the SO_2~~

~~concentrations in port site varies with the background SO_2 level in regional scale. NO_x emissions from ships were also obvious during plumes, however, its' concentrations in port site are under much stronger influences from land emissions. For particulate matters, the primary ship emission produce dominant vanadium particle number concentrations (PNC_v) to the portside while its' contribution to the mass concentrations ($PM_{2.5}$) was less significant. Other pollutants O_3 was depleted by elevated primary NO_x and SO_2 emissions in port regions, resulting 11-33 % ozone consumption compared with urban region of Shanghai.~~

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~~Particle size distributions and chemical composition of individual ship emission particles were identified by single particle mass spectrometry at the same site. Similar as SO_2, the ship emission particles in portside could also be grouped into freshly emitted and background particle types. The mass spectra of fresh ship emission particles contain dominant peaks of EC, sulfate and trace metals (V, Ni, Fe and Ca). Size distribution of ship emission particles showed that they are tend to concentrate in smaller size range (< 0.5 μm), which is most probably composed of fractal black carbon agglomerates. Based on the different chemical composition of ship emission particles, ship emission particles during plumes could be grouped into four major types: V-OC, V-EC, V-ECFe and V-Ash. These particles were shown to reserve different temporal and size distribution trends.~~

Particle size distributions and chemical composition of individual ship emission particles were characterized through single particle mass spectrometry at the same site. Similar as SO_2, the ship emission particles in portside could also be grouped into freshly emitted and background particle types. The mass spectra of fresh ship emission particles contain dominant peaks of EC, sulfate and trace metals (V, Ni, Fe and Ca). Size distribution of ship emission particles showed that they are tend to concentrate in smaller size range (< 0.4 μm), which was most probably composed of fractal black carbon agglomerates. Based on the different chemical composition of ship emission particles, ship emission particles during plumes could be grouped into four major types: V-OC, V-EC, V-ECFe and V-Ash. These particles types were shown to have different temporal and size distribution trends, which was a manifestation of the complexity of ship emissions in a large, busy port.

~~Ship emission contributions to the air quality in Shanghai port area was quantified by extracting pollution concentrations during plume periods. The contributions of ship emissions were evaluated in two scenarios where the land based emission sources are either included or excluded. Results show that ship emission was a major contributor to the ambient SO_2 (5.68~~

~~μg/m^3, 36.4%) and vanadium particle concentrations (49.5%) in port side. NO_x contribution (3.00 μg/m^3, 5.8%) from shipping emissions was insignificant compared with emission from land-based sources, which was mainly from transportation sources. If land sources were excluded, shipping relative contributions of NO_x became comparable with that of SO_2. Due to the high NO_x and SO_2 levels in this area, significant fraction of ozone concentration was found to be depleted. Primary particles from ship emission were estimated to contribute to 5.9% (1.57 μg/m^3) $PM_{2.5}$ concentration during the sampling period. In the sense of particle number concentration (PNC), over 44% vanadium PNC in the port site were found to be contributed by ship emission. The vanadium PNC contribution from ship emission were found to increase with decreasing particle size, with 57% vanadium particles smaller than 0.4μm were found to sourced from ship emission. Since the size and mass of fresh exhaust particles are small, the mass concentration PM from exhaust pipes would be inappropriate to represent their real mass contribution after atmospheric aging. This study supports that particle number concentration (PNC) be included to fully characterize primary ship emitted particles.~~

The emission contributions from ships to local air quality in Shanghai port area was quantified by extracting pollutions during plume periods from background levels. Ship emissions contributions were evaluated in two scenarios where the land-based emission sources were either included or excluded. Results showed that ship emissions were a major contributor to the ambient SO_2 (5.68 μg/m^3, 36.4%) and vanadium particle concentrations (49.5%) in portside. NO_x contribution (3.00 μg/m^3, 5.8%) from shipping emissions was insignificant compared with emission from land-based sources, which was mainly from transportation sources. If land-based sources were excluded, shipping relative contributions of NO_x became comparable with that of SO_2. Due to the high NO_x and SO_2 levels in this area, a fraction of local ozone concentrations was found to be depleted. Primary particles from ship emission were estimated to contribute to 5.9% (1.57 μg/m^3) $PM_{2.5}$ concentration during the sampling period. For particle number concentration (PNC), over 44% vanadium particle numbers (PNC_v) in the port site were found to be contributed by ship emissions. The PNC_v contribution from ship emission were found to increase with decreasing particle size, with 57% vanadium particles smaller than 0.4 μm were found to be emitted from ship emission. Since the size and mass of fresh exhaust particles are small, the primary mass concentrations from ships would be inappropriate to represent their real mass contribution after atmospheric aging. This study supports that particle number concentration (PNC) be included in the characterization of primary emissions from ships.

Disclaimer

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Author contribution

Qingyan Fu, Xinning Wang and Yin Shen designed the experiment; Xinning Wang, Yin Shen and Jun Pan conducted the experiment; SPAMS data was analysed by Xinning Wang and Mei Li; Other data is analysed by Xinning Wang, Yan Zhang and Yanfen Lin; Manuscript is prepared by Xinning Wang, Qingyan Fu and Peter K.K. Louie.

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Figures

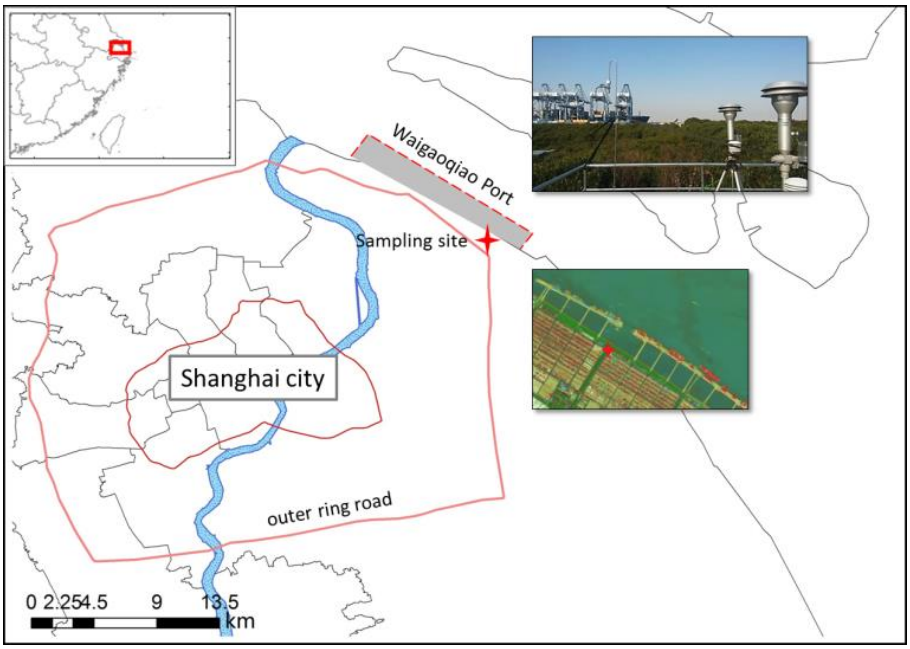


Figure 1: Map of sampling site in Shanghai port and surrounding areas. Port region is indicated by shaded area. The insets are the satellite image of the port site and a photo taken on the roof of monitoring station seeing in port direction.

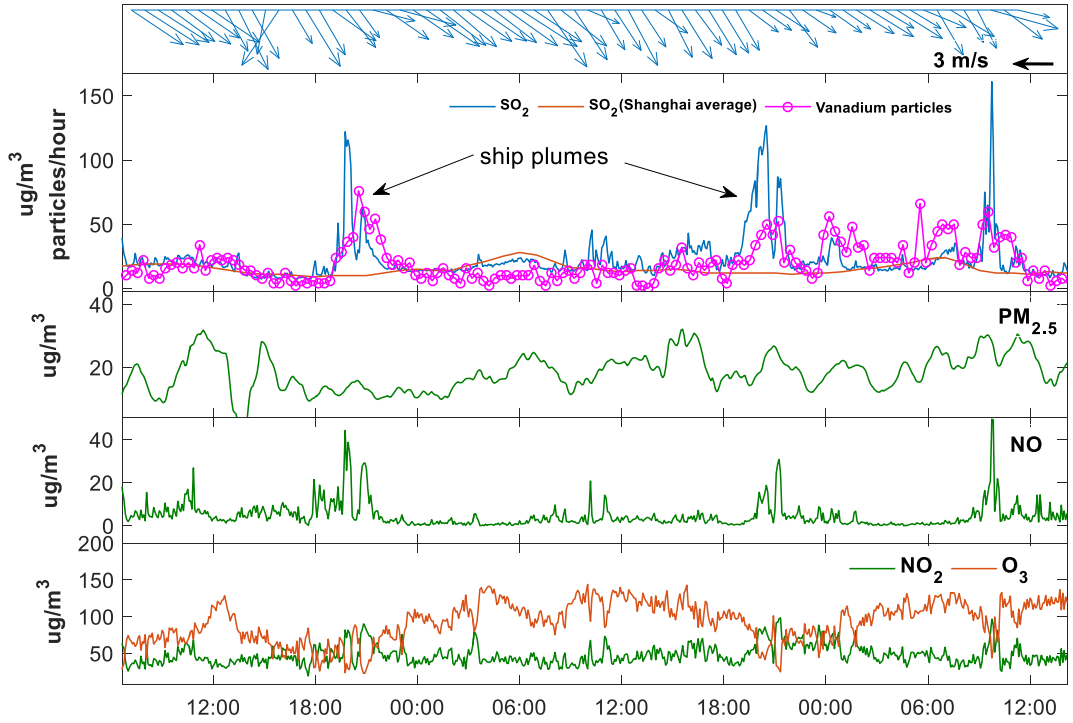


Figure 2: Temporal concentration of pollutants SO_2, NO, NO_2, O_3 and PM2.5 during 27-29 August 2016. Contemporary wind direction and speed, SO_2 concentration of Shanghai city and vanadium particles number concentration as detected by SPAMS are included as a reference.

5

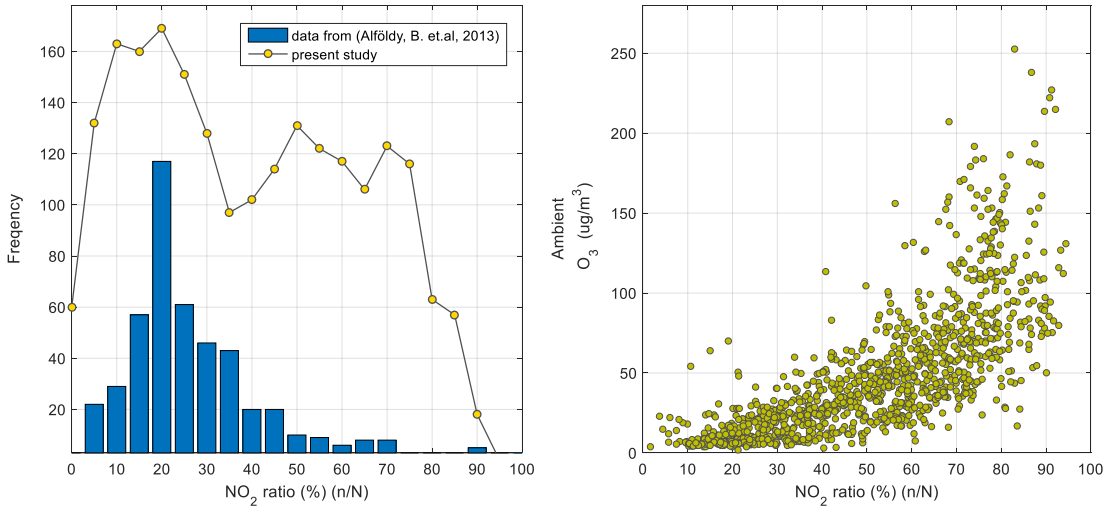


Figure 3. The NO_2 ratio distribution during plumes in this study and a similar study (left) and the plot of NO_2 ratio against ambient ozone concentrations during plume periods (right).

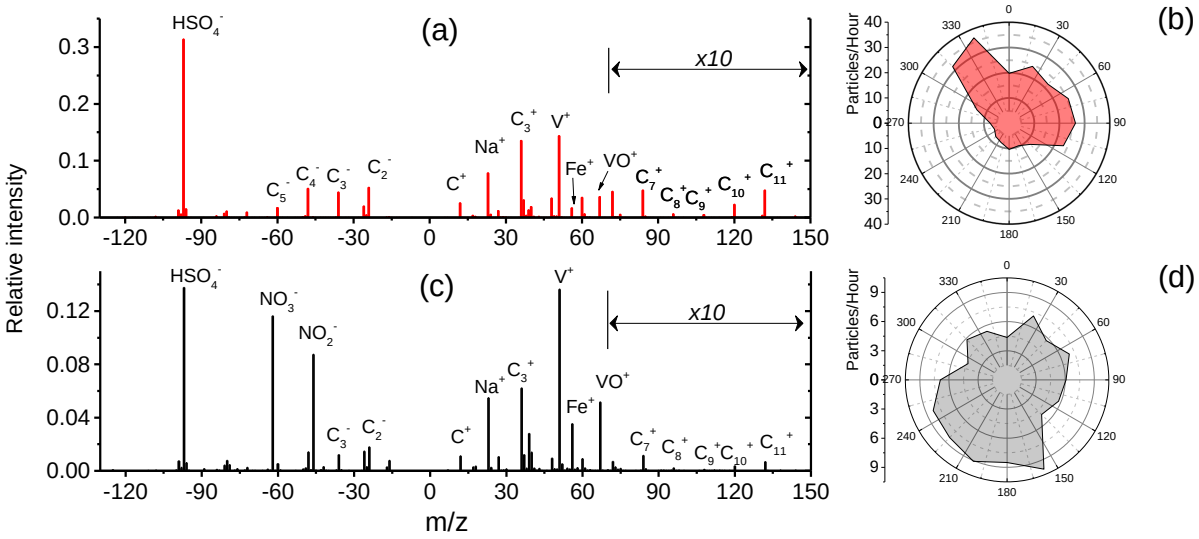


Figure ~~3~~ 4: Mean mass spectra of fresh and background ship emission particles in port (a, c) and the wind rose of particle number concentration (in measure of particle number per hour) of these two particle types (b, d). Peaks in mass range of 70-150 in (a) and (c) are magnified by 10 times.

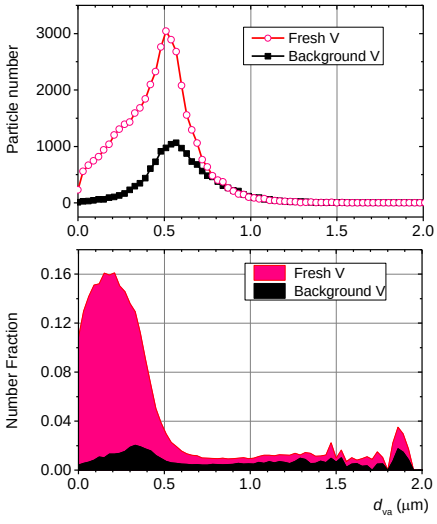


Figure ~~4~~ 5: Particle number size distribution of fresh and background ship emission particles by SPAMS (Upper). Size distribution of these fresh and background types of ship emission particles normalized by total particles at each size (Lower).

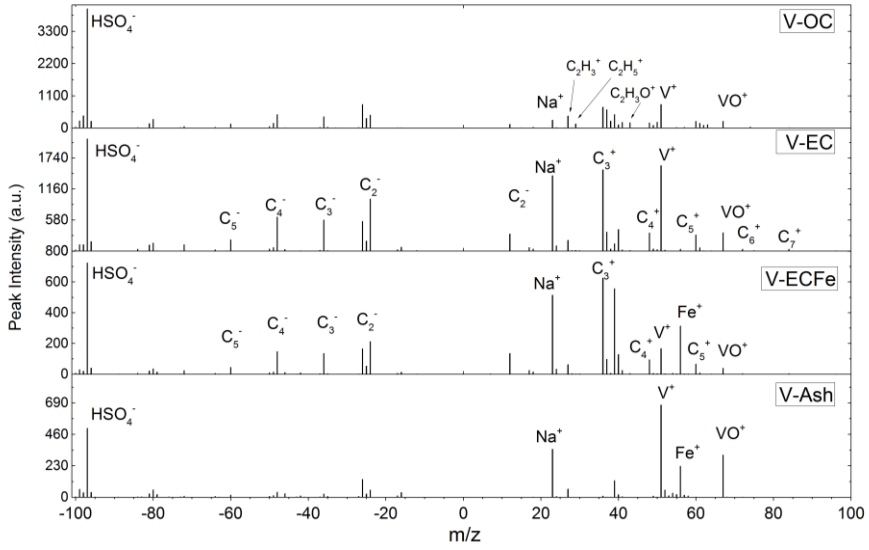
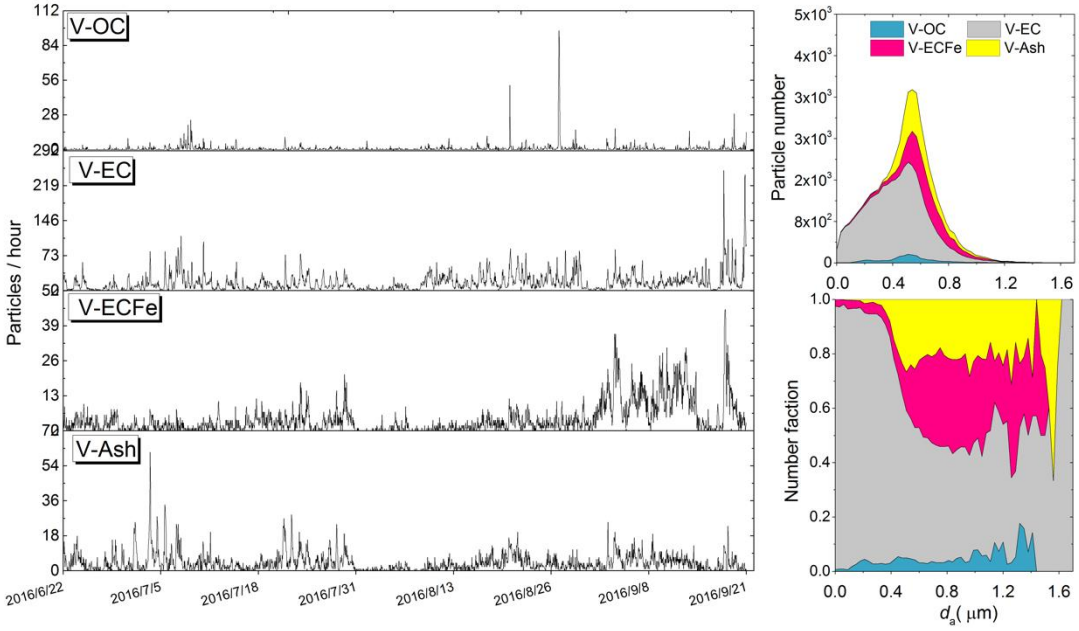


Figure ~~5~~ 6: Mean mass spectra of four major particle types from fresh ship emission.



~~**Figure 6: Temporal trend of number concentrations of four fresh vanadium particle types (Left panel); the number (upper right) and number fraction (lower right) of four vanadium particle types as a function of particle size.**~~

Figure 7: Temporal trends of particle numbers detected per hour by SPAMS of four fresh vanadium particle types (Left panel); The upper right panel is the number-size distribution of the 4 types, with the y-axis representing particle numbers detected at each size bin in the entire study. The Lower right panel is obtained by normalizing the particles numbers of 4 types to give their relative contributions at each size.

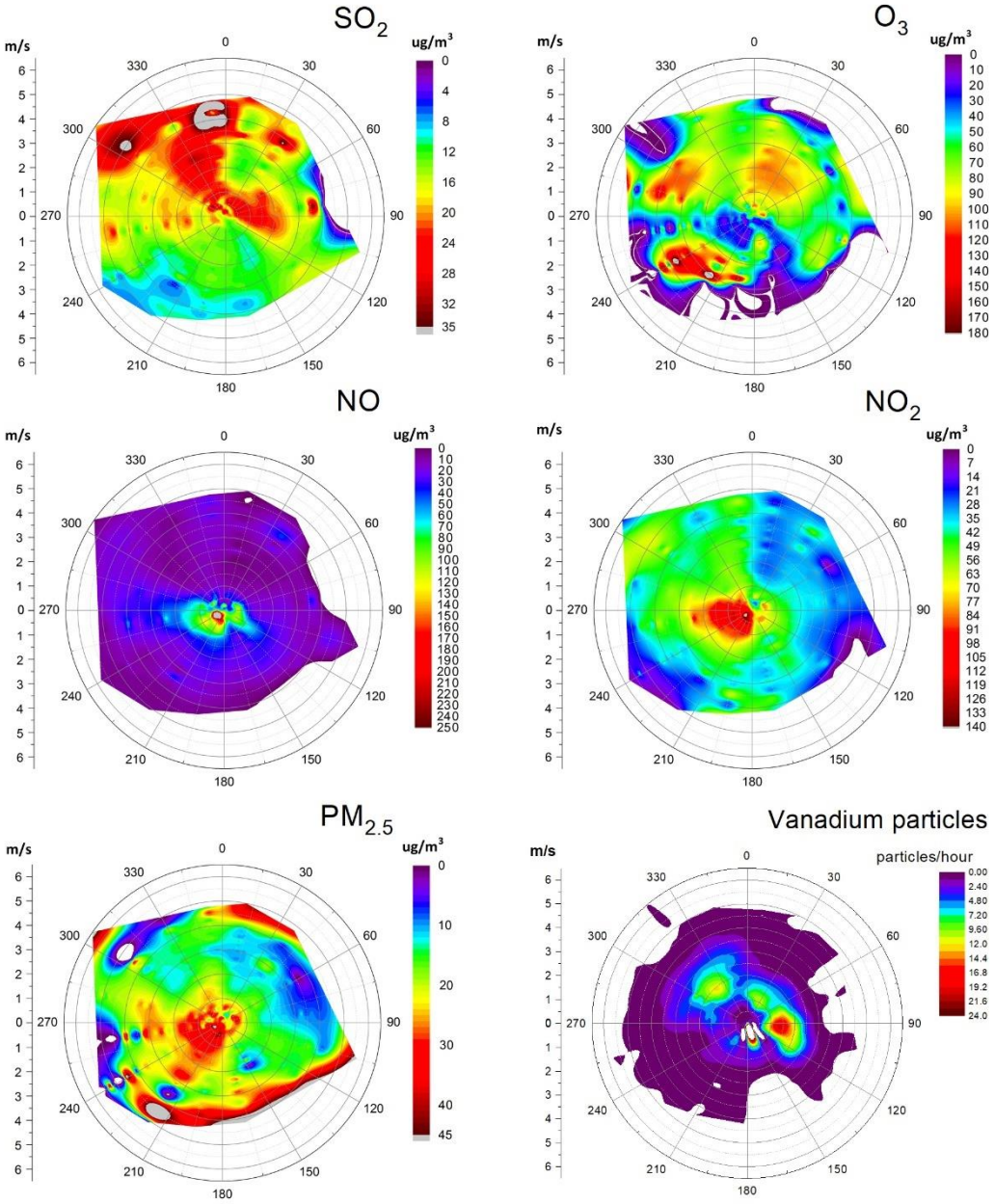


Figure ~~7~~ 8: Pollution roses of SO_2, NO, NO_2, O_3, $PM_{2.5}$ and vanadium particles during the whole study period. Vanadium particles wind rose is based on number concentration as measured by SPAMS.

Tables.

Table 1: Statistics of pollutants concentration level during the whole sampling period. Numbers are average concentration followed by 25th and 75th quantiles in brackets. Average pollution levels in Shanghai city during the same period are included as a comparison.

	In plume		Non-plume		Non-plume (port sector)		Port average		Shanghai average	
SO_2 ($\mu g/m^3$)	**28.3**	(17.6~31.8)	**9.9**	(8.1~11.6)	**10.2**	(8.2~12.1)	**15.6**	(8.7~16.8)	**10.8**	(9~12)
NO ($\mu g/m^3$)	**42.5**	(7.6~47.5)	**41.6**	(7.1~59.1)	**16.5**	(1.8~18.1)	**41.9**	(7.3~55.3)	**5.8**	(3~6)
NO_2 ($\mu g/m^3$)	**59.3**	(36.1~72.4)	**50.5**	(27.8~60.8)	**36.9**	(22.1~46.1)	**53.2**	(30.3~65.0)	**30.2**	(18~38)
O_3 ($\mu g/m^3$)	**53.1**	(19.3~77.8)	**54.6**	(15.4~84.7)	**71.3**	(45.4~97.6)	**54.1**	(16.9~82.7)	**81.1**	(40~107)
$PM_{2.5}$ ($\mu g/m^3$)	**30.2**	(14.8~39.6)	**25.1**	(12.8~32.5)	**19.6**	(11.6~23.2)	**26.7**	(13.2~34.1)	**31.4**	(16~43)
Vanadium particles (#/hour)	**47.6**	(31~55)	**10.9**	(5~17)	**12.3**	(7~19)	**22.8**	(7~29)	---	

Table 2: Contributions of ship emissions to ambient pollutants SO_2, NO, NO_2, O_3, $PM_{2.5}$ and vanadium particles in port area. Calculations are based on two situations: entire sampling period (all wind directions included) and only when site is in downwind direction of port emissions. Total lengths (in hours) of respective periods are given.

(%)		In port sector (excluding land-based emissions)		Entire period (including land-based emissions)	
		Average	range	Average	range
SO_2		57.2	(49.2, 64.8)	36.4	(29.2, 40.2)
NO		71.9	(57.0, 84.6)	0.7	(0.2, 1.7)
NO_2		30.4	(24.7, 34.6)	5.1	(3.7, 7.9)
O_3		-16.6	(-18.8, -13.4)	-0.9	(-2.8, -0.4)
$PM_{2.5}$		27.6	(22.5, 33.2)	5.9	(3.4, 9.6)
Vanadium particles*	(0-0.4 μm)	79.2	(73.9, 85.0)	57.1	(50.6, 64.0)
	(0.4-0.8 μm)	75.3	(68.1, 82.0)	44.7	(38.1, 52.3)
	(0.8-2.5 μm)	76.6	(70.4, 82.9)	47.0	(41.3, 52.9)
	(0-2.5 μm)	77.0	(70.6, 83.1)	49.5	(43.0, 56.7)

Length of sampling (in hours): Entire period: 2256; Port sector: 1136; In plume: 694;Non-plume: 1563; Non-plume (port sector): 625.
* Particle number contribution

Supplementary Material for acpd-2018-737:

~~"Atmospheric pollution from shipping and their contributions to air quality degradation in a port site in Shanghai"~~

"Atmospheric pollution from ships and their impacts on local air quality in a port site in Shanghai"

1. Wind rose of the port site during the study

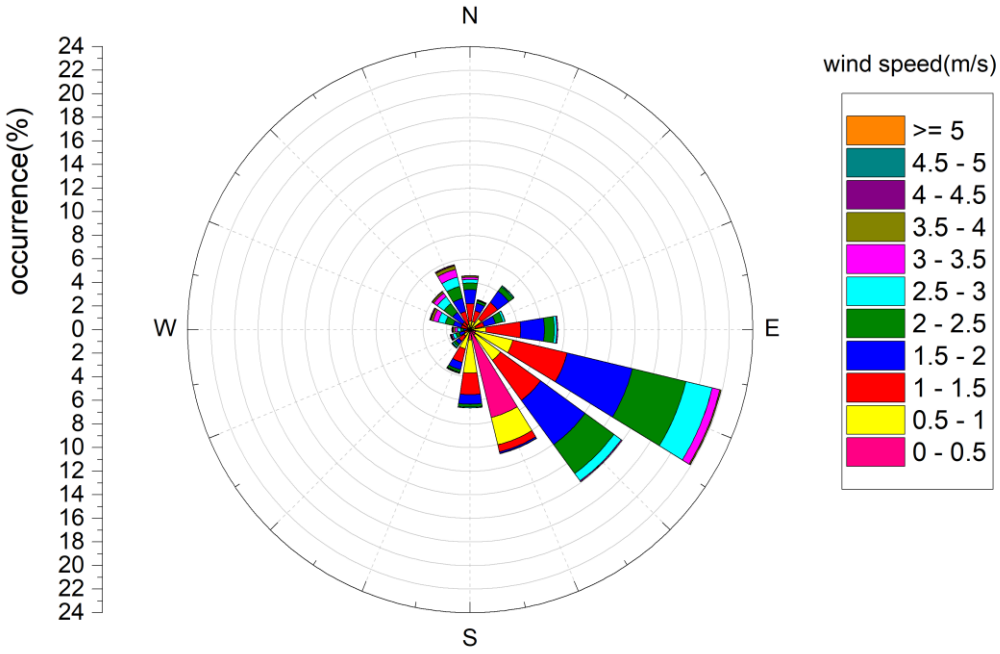


Figure S1. Portside wind rose during the study period.

2. *Explanation of identification method of ship emission particles*

The identification method relying on Vanadium signatures left a problem that this method lose some portion of shipping emission particles which produce no or insignificant Vanadium peaks (Xiao et al., 2018) . However, within the analyzing capability of SPAMS, Vanadium signatures are still the most reliable indicator of shipping emission particles in a real ambient condition. The present site in port area is both influenced by emission sources from the shipping activities and traffics on land. Single particle signature from diesel vehicles has displayed some similarity with shipping emission (especially for low Sulfur fuel oil, like MGO, IFO) because of the resemblance in chemical composition between them (Toner et al., 2008;Xiao et al., 2018). In this situation, to identify 'true' shipping emission particles from total particles will became difficult or even impossible if we discard the reliable clue of Vanadium. In this supplementary material we

illustrate the wind roses of several particle clusters of similar composition with the only major difference of Vanadium (Figure S1). From the figure it is clear that single particles with Vanadium is an ideal indication of shipping emission source from port directions, while the exclusion of Vanadium will only result an unwanted interferences of particles from land sources. Therefore, in present study the online single particle measurement, together with synchronous SO2 concentration, was utilized to indicate the occurrence of shipping emission plumes, not to dig out every shipping emission particles.

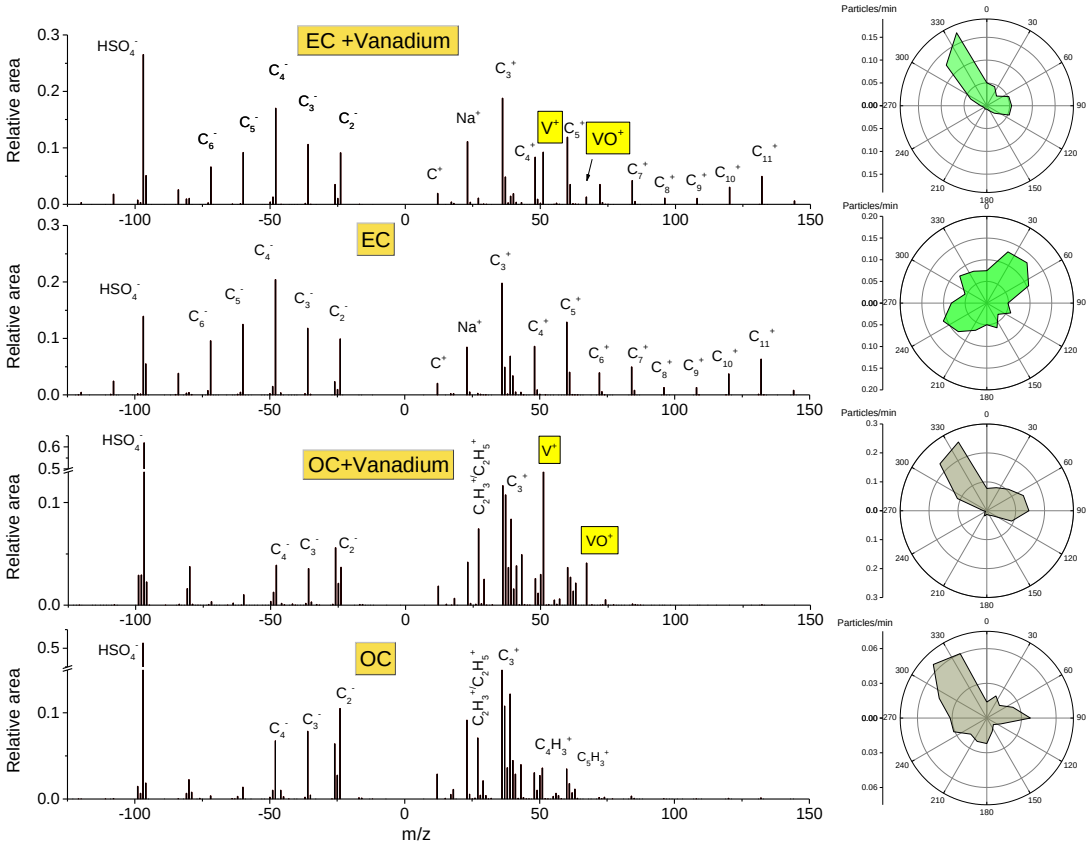


Figure S2. Mass spectra and wind roses of representative particle clusters with and without vanadium peaks.

3. *Temporal variation of $PM_{2.5}$, vanadium particles, SO_2 concentrations in the portside during a period from Jul-03 to Jul-06.*

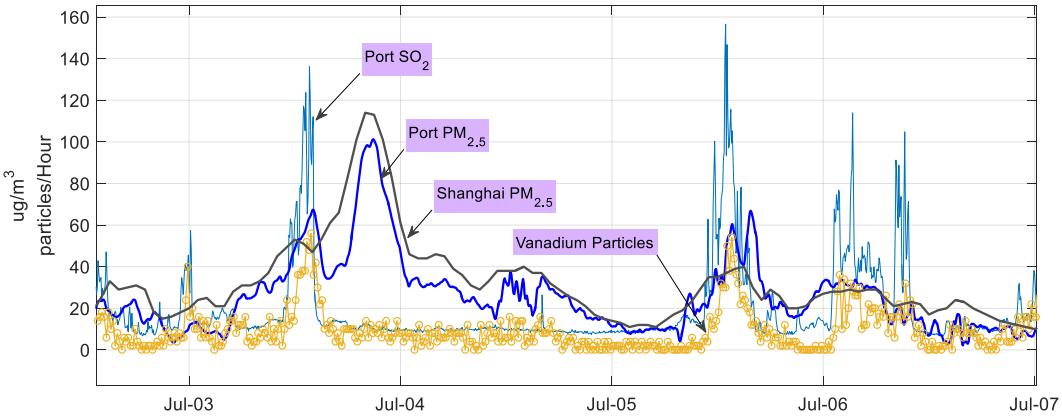


Figure S3. Temporal variations of SO_2, $PM_{2.5}$, vanadium particles numbers in port site and $PM_{2.5}$ in Shanghai city from Jul-03 to Jul-06.

4. Spatial distribution of $PM_{2.5}$ concentrations in Shanghai area

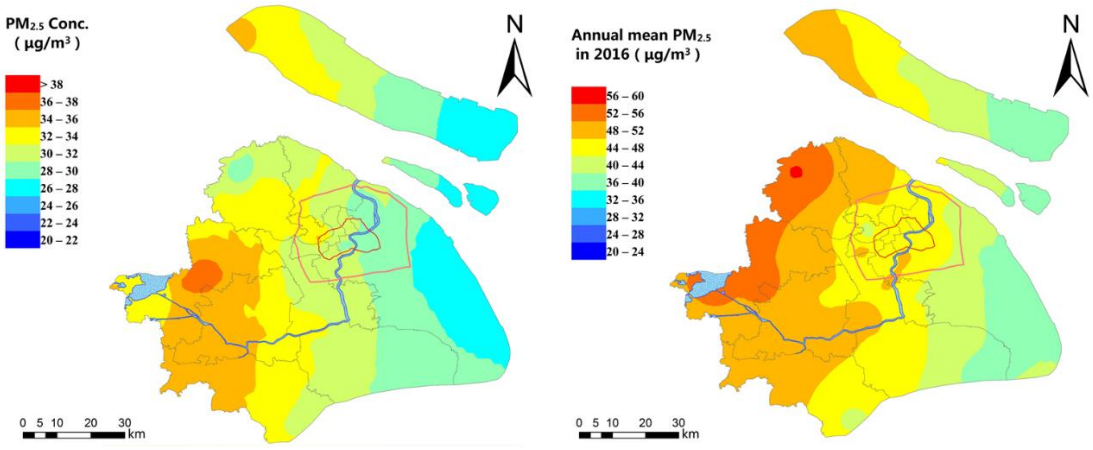


Figure S4. Spatial distributions of $PM_{2.5}$ in Shanghai area in the study period (left) and in 2016 (right).

References

Toner, S. M., Shields, L. G., Sodeman, D. A., and Prather, K. A.: Using mass spectral source signatures to apportion exhaust particles from gasoline and diesel powered vehicles in a freeway study using UF-ATOFMS, Atmospheric Environment, 42, 568-581, 10.1016/j.atmosenv.2007.08.005, 2008.

Xiao, Q., Li, M., Liu, H., Deng, F., Fu, M., Man, H., Jin, X., Liu, S., Lv, Z., and He, K.: Characteristics of marine shipping emissions at berth: profiles for PM and VOCs, Atmos. Chem. Phys. Discuss., 2018, 1-29, 10.5194/acp-2017-1132, 2018.