Response to Referee's Comments on acpd-2018-737: " Ambient measurement of shipping emissions in Shanghai port areas"

The authors are pleased to submit our responses to the comments raised by the anonymous referee #2. The authors appreciate and are thankful to the referee's valuable comments and suggestions which help greatly to improve the quality of the manuscript. Each item of the raised comments is responded individually in following pages in the format of:

Referee's comments – Black;

The Authors' responses – Blue,

Author's changes in manuscript – *Red, italic*

Response to Referee #2

General comment: The paper regards an analysis of the impact of shipping to atmospheric pollutants measured in the area of Shanghai harbour (China). The approach used is based on the identification and characterization of ship plumes using high temporal resolution measurements of gaseous pollutants and of particles using a SPAMS. The work is interesting and allowed to investigate the typical spectra of particles released by ships as well as to evaluate statistically the contribution of shipping to local air quality. The work is suitable for the Journal and generally well written (even if minor spell check is required), however, some aspects are not completely clear (see my specific comments) and an additional effort in the discussion of size distributions of the impacts should be included. In conclusion, I believe that the paper should be considered for publication after a major revision.

Specific Comments:

1. Title. I think that it is not correct to speak of "measurements of shipping emissions" because emission factors or measurements of specific emission rates are not given. I would suggest to change the title to put in evidence the core of the work: contribution of shipping to atmospheric pollution.

Authors' Response:

Thanks for comment. The authors agree with the referee's opinion about the title of the paper. To reflect the core of this work more accurately, the title of this manuscript would be changed to "Atmospheric pollution from shipping and their contributions to air quality degradation in a port site in Shanghai".

changes in manuscript:

Page 1, Line 1-2:

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

2. Introduction. The adoption of a DECA (Domestic ECA) is quite interesting and it would be even more interesting if a more detailed discussion is included. For example, it would possible to comment on the efficacy of this measure in reducing the impact of shipping on local pollution levels. It is also worth to mention that a recent work (Contini et al., 2015 – Atmospheric Environment 102, 183-190) showed that application of "domestic" restrictions on the fuel quality could be effective in reducing not only local SO_2 concentrations but also primary emissions of

particles from ships. I believe that a discussion on this aspect would be appreciated by the readers.

Authors' Response:

We acknowledge the referee's suggestion to include a further discussion on DECA. In fact, the DECA strategy has not only been implemented in YRD region, but also in Pearl River Delta (PRD) and Bohai-Rim area, which constitute the three major shipping regions in China. According to monitored data at several sites adjacent to port area in YRD, there has been >20% reduction in ambient SO_2 concentration in the same period before and after the DECA measure, although part of the SO_2 reduction are attributable to emission control measures in coal burning in power plant, boilers, furnaces and domestic use in China. There is a published study which dealt with the effectiveness of DECA in PRD region, estimating that the DECA measure could result an average reduction of 9.54% in SO_2 and 2.7% in $PM_{2.5}$ in land areas (Liu et al., 2018).

changes in manuscript:

Page 2,Line 30 – Page 3, Line 4:

" 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 SO2 and primary PM release from ships. The benefits of DECA measure in YRD were also suggested by the reduction of SO2 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% SO2 and 2.7% PM2.5 in land areas (Liu et al., 2018)."

3. Sections 2.3 and 2.4. It is often mentioned the high temporal resolution of SPAMS measurements, I would suggest to explicitly report the numerical value.

Authors' Response:

SPAMS is a real time measurement and particles drawn into instrument and analyzed consecutively. Depending on the analysis objective, the temporal resolution of SPAMS can be set to several minutes and this value is adjustable.

changes in manuscript:

Page 5,Line 21-22:

" The temporal resolution of SPAMS (seconds or minutes) makes it suitable to couple with online gaseous data to identify ship emissions."

4. Page 6 (lines 1-5). V-particles measured without the presence of SO_2 peaks are interpreted as due to the use of low-sulphur content fuel, however, it would not be possible that they are coming from other industrial (or anthropic in general) sources? Some words on this should be included.

Authors' Response:

Thanks for the valuable suggestion. The authors have not considered the fact that vanadium could also be released from other sources as petroleum refinery and other industries. There is indeed petroleum company in adjacent regions and other industries, whose influences should be considered. According to the measurement data, however, the occurrence probability of

vanadium particles plume without SO_2 peak is certainly small (3% in cases), so that the interferences of industrial sources will not greatly affect the results in this paper. In another aspect, the determination of contribution of shipping emissions will exclude the industrial influences by confining the wind directions only from the port sector, so that the industrial interferences (from land directions) were set to a minimum.

changes in manuscript:

Page 7,Line 29-34:

" 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. "

5. Page 7, line 23. To speak at this level of BC is not really useful, likely authors mean EC.

Authors' Response:

Thanks for the penetrating comments. 'BC' is replaced by 'EC' in manuscript.

changes in manuscript:

Page 9,Line 25:

"such as EC particles, having significantly larger cross sections to reflect laser light and be detected in SPAMS "

6. Page 8, lines 2-3. This sentence is not clear and should be re-written. I believe that authors means that ultrafine particle concentrations could be a better metric compared to mass concentrations to investigate the impact of shipping to atmospheric aerosol.

Authors' Response:

This paragraph has been removed.

changes in manuscript:

this sentences has been removed.

7. Page 9, line 30. The approach based on this formula was originally developed in Contini et al (Journal of Environmental Management 92 (2011) 2119-2129) and successively used by other authors. I believe that it would be fair to mention this aspect.

Authors' Response:

This item of reference was replaced by the suggested one.

changes in manuscript:

Page 6,Line15-16:

"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 : "

8. Looking at the size distributions reported in figures 4 and 6, it appears that V particles are especially relevant for ultrafine particles, however this aspect is not deeply investigated on the evaluation of the impacts. It would be possible to use the approach discussed on page 9 to

investigate the size dependency of the impacts of shipping, eventually estimating the impacts for different size ranges. I believe that, if a sufficient statistics could be obtained, this will give very useful additional information compared to the impact on total particle number reported in Table 2.

Authors' Response:

Thanks for that suggestion. The authors agree with the advice to separate V particles into different size ranges and evaluate their impact individually. After inspection of V particle size distribution, the particle diameters will be grouped into three size ranges: <0.4μm;0.4-0.8μm;>0.8μm; Their impacts will be calculated and discussed as a function of size. The next version of manuscript, which will be submitted soon, will cover this topic together with discussions as suggested in 9# comment raised by the referee.

changes in manuscript:

Page 13,Line4-6:

" Contributions of PNCv 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 PNCv in smaller size range (0-0.4μm) are larger compared with PNCv in larger size ranges (0.4-0.8 μm, 0.8-2.5μm)."

9. Page 10, lines 13-23. The comparison with shipping impact measured in other ports is certainly interesting, however, it is done on relative impacts and not on absolute contributions due to shipping activities this means that it depends not only on ship traffic but also on the contributions of the other sources acting on the specific measurement site. This should be mentioned because it could explain some of the apparent discrepancy mentioned by the authors. In addition, I would suggest to expand the comparison to other ports analysed with the high temporal resolution approach (Merico et al Transportation Research Part D 50 (2017) 431–445) but also with other complementary approaches (see for example Viana et al 2014 Atmos. Environ. 90, 96–105).

Authors' Response:

The authors agree with that advices. We acknowledge that the pollution absolute contributions from shipping are also important. The discussions with other port will also include more relevant studies in the literatures. Absolute contributions of shipping emissions and relevant discussions will be embodied in the next version of manuscript which will soon be submitted.

changes in manuscript:

Page 13,Line7-17:

"The relative contributions of PNCv from ship emission is apparently higher than PM2.5 on mass concentration. Previous study showed that the direct PM2.5 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% PM2.5 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 PM2.5 were in 1-14% range, with higher contributions with decreasing particle size (Viana et al., 2014). The calculated value of PM2.5 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% PM2.5 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 PM2.5. The PNC is not currently measured, instead the size distributions, PNC contributions of vanadium particles in different sizes, as measured by SPAMS, apparently agrees with these previous work. "

Page 13,Line35-Page 14, Line 6:
"However, in an absolute sense, this study estimate that ship emissions contribute to 5.68 μg/m3 SO2, 3.00 μg/m3 NOx and 1.57 μg/m3 PM2.5 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 μg/m3 (primary particles) and 1.7 μg/m3 (secondary particles) in Bay of Algeciras (Viana et al., 2009). Due to the adjacency of the site to port, the calculated PM2.5 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."

10. Regarding the impacts reported in Table 2, it would be possible to estimate the uncertainties?

Authors' Response:

In the preparation of Table 2 we have considered the estimation of uncertainties, which is a conventional practice in scientific report. The uncertainties of calculation may stem from sources such as the identification of plumes, the definition of port sector directions and the gaseous and particulate measurement itself. Some of these sources are found difficult to define. To be consistent with the original study (Contini et al., 2011), the uncertainties in this work will be estimated by inspection variations in slight changes of wind direction and the elimination of data of low wind velocity (< 0.5 m/s). The uncertainties will be included in the next version of manuscript.

changes in manuscript:

Page 6,Line19-25:
"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 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)."

Page 27,Line5-10:
"

(%)	*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*	(0-0.4μm)	79.2	(73.9, 85.0)	57.1	(50.6, 64.0)
	(0.4-0.8μm)	75.3	(68.1, 82.0)	44.7	(38.1, 52.3)
	(0.8-2.5μm)	76.6	(70.4, 82.9)	47.0	(41.3, 52.9)
	(0-2.5μm)	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*

"

11. Page 11 line 5. This sentence is not clear. Authors likely mean that the impact of shipping is more relevant and clearly discernible on SO_2 and V particles compared to the other pollutant analysed. Could authors clarify?

Authors' Response:

Thanks for the advice. The original sentence would be revised.

changes in manuscript:

Page 15,Line8-9:

"During plumes the SO2 and vanadium particles concentrations has demonstrated well synchronized peaks, which could be reliably used to indicate the arrival of ship emission plumes."

12. In the supplementary material it is reported "…in present study the online single particle measurement was utilized to indicate the occurrence of shipping emission Plumes…" however in the main text was mentioned that both particles and SO2 concentrations were used. Please clarify this apparent contradiction.

Authors' Response:

Thanks for pointing out this unclarity. The intention behind the supplementary text is to give the reader a extended discussion on the identification method of ship emitted particles. As explained in supplementary text, the adoption of vanadium tracer could not guarantee that every single ship emitted particles in a plume be identified. From figure S1 it could be inferred that only a fraction of ship emitted particles in plumes are identified by vanadium peak criteria, because not every individual particles in a emission plume contain a detectable vanadium content.

The mentioned sentence "…in present study the online single particle measurement was utilized to indicate the occurrence of shipping emission plumes…" is emphasizing this fact and not really mean that only the vanadium particles were used to indicate the influence of plumes. Actually both of vanadium particles and SO_2 concentration were applied to identify plumes in data analysis process. In fact, the SO_2 concentration is critical to identify plumes in which few vanadium particles were present.

To prevent possible confusion, the original sentence is revised.

changes in manuscript:

Supplementary file: Page 2,Line26-28:

"in present study the online single particle measurement, together with synchronous SO2 concentration, was utilized to indicate the occurrence of shipping emission plumes"

Minor corrections

13. Page 1, line 15. Better “particle size distributions”.

Authors’ Response:

Suggestion accepted.

changes in manuscript:

Page 1,Line15:

“concentrations (PM2.5), particle size distributions and chemical composition of individual ship emission particles”

14. Page 1, line 28. Please eliminate the initial S.

Authors’ Response:

Suggestion accepted.

changes in manuscript:

Page 2,Line2:

“Ship emission constitutes an important source of gaseous and particulate pollution world wide”

15. Page 2, line 19. Subscript for SO_2. The same in page 4 (line 25).

Authors’ Response:

It has been corrected.

changes in manuscript:

Page 5,Line32:

“concurrent SO_2 concentrations were utilized to locate ship emission plumes when sharp SO2 peaks occurred”

16. Page 7, line 14. Better “different size distributions…”.

Authors’ Response:

Accepted.

changes in manuscript:

Page 9,Line14-15:

“Wind roses and size distributions of fresh and aged ship emission particles were also distinguishable.”

17. Page 8, line 12. Better “by the dominant”. In addition, I would remove etc, if necessary please mention explicitly.

Authors’ Response:

Suggestion accepted.

changes in manuscript:

Page 10,Line16-17:

“In the positive mass spectra the V-OC type are characterized by the dominant organic peaks like $C_2H_3^+$, $C_2H_5^+$, $C_2H_3O^+$,”.

18. Page 8, line please remove etc. as above.

Authors’ Response:

The ‘etc.’ is removed.

changes in manuscript:

Page 10,Line31-33:

"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."

19. Page 8, line 25. Better "is therefore not attempted…"

Authors' Response:

Accepted.

changes in manuscript:

Page 11,Line3:

"is not yet available, it is therefore not attempted to link V-OC particle plumes to specific ship types directly in the present"

20. Page 9, line 2. > 0.5 μm

Authors' Response:

Original letter replaced with the Latin letter 'μ'.

changes in manuscript:

Page 11,Line18-19:

"ash spheres from combustion process of inorganic constituents in RFO and lubricants, are mainly detected in larger size range (> 0.5 μm)"

21. Page 11, line 10 ozone without capital letter.

Authors' Response:

Accepted.

changes in manuscript:

Page 15,Line15:

"NO_x and SO_2 emissions in port regions, resulting 11-33 % ozone consumption compared with urban region of Shanghai."

Refereces

Contini, D., Gambaro, A., Belosi, F., De Pieri, S., Cairns, W. R. L., Donateo, A., Zanotto, E., and Citron, M.: The direct influence of ship traffic on atmospheric PM2.5, PM10 and PAH in Venice, Journal of Environmental Management, 92, 2119-2129, 10.1016/j.jenvman.2011.01.016, 2011.

Contini, D., Gambaro, A., Donateo, A., Cescon, P., Cesari, D., Merico, E., Belosi, F., and Citron, M.: Inter-annual trend of the primary contribution of ship emissions to PM2.5 concentrations in Venice (Italy): Efficiency of emissions mitigation strategies, Atmospheric Environment, 102, 183-190, 10.1016/j.atmosenv.2014.11.065, 2015.

IMO: Emission Control Areas (ECAs) designated under MARPOL Annex VI, 2017.

Liu, H., Jin, X., Wu, L., Wang, X., Fu, M., Lv, Z., Morawska, L., Huang, F., and He, K.: The impact of marine shipping and its DECA control on air quality in the Pearl River Delta, China, Science of The Total Environment, 625, 1476-1485, https://doi.org/10.1016/j.scitotenv.2018.01.033, 2018.

Merico, E., Gambaro, A., Argiriou, A., Alebic-Juretic, A., Barbaro, E., Cesari, D., Chasapidis, L.,

Dimopoulos, S., Dinoi, A., Donateo, A., Giannaros, C., Gregoris, E., Karagiannidis, A., Konstandopoulos, A. G., Ivosevic, T., Liora, N., Melas, D., Mifka, B., Orlic, I., Poupkou, A., Sarovic, K., Tsakis, A., Giua, R., Pastore, T., Nocioni, A., and Contini, D.: Atmospheric impact of ship traffic in four Adriatic-Ionian port-cities: Comparison and harmonization of different approaches, Transportation Research Part D-Transport and Environment, 50, 431-445, 10.1016/j.trd.2016.11.016, 2017.

Response to Referee's Comments on acpd-2018-737: " Ambient measurement of shipping emissions in Shanghai port areas"

The many items of comments raised by the referee #1 are responded individually as following. Text is present in the format of:
Referee's comments – Black;
The Authors' responses – Blue.
Changes in manuscript - *Red, Italic*

Response to Referee #1

This study conducted field measurements from June to September in 2016 at Shanghai port in order to understand the impact of ship emissions on the air quality in portside. Trace gases, PM2.5 and vanadium particle number concentrations were continuously monitored at the site. Ship plumes were clearly captured by the instruments. SO2 and vanadium particle number concentrations correlated well with ship plumes. Four types of ship plumes were identified based on the mass spectra of Single Particle AMS. The contributions of ship emissions to different air pollutants in the atmosphere and in the air masses from port directions were quantified. Given that Shanghai port is the largest port in the world, this study will add values to existing literature of ship emission studies. However, the manuscript is not well organized/written and has room to be improved. In addition, there are quite a lot of grammar errors and technical mistakes, which sometimes make the reviewer confused. Furthermore, some discussions and conclusions are lack of evidence. As such, this manuscript can be considered for publication after the following specific comments are well addressed.

Specific Comments:

Abstract:

Firstly, English needs editing by a native English speaking professional or company. For example, line 16: … that shipping emissions is a major….".

Response:

The language problems, as the author responded in reply to RC2, will be corrected in the next edition of manuscript. The author acknowledge the referee's effort.

Changes in manuscript:

Pages1 , Lines16 :

Original sentence removed

Secondly, there are also some technical mistakes. One example, lines 14-15: Gaseous (NO, NO2, SO2, O3) and particulate concentrations (PM2.5)… It should be "The concentrations of gaseous pollutants (NO…..) and fine particulate matters (PM2.5)…". Also, both shipping emission and ship emission are used throughout the manuscript which should be consistent. Another problem at lines 18-20, the subject is "Single particle mass spectra of fresh shipping emission" but the last words became "…and nitrate peaks in aged particles". This is really confusing the reviewer.

Response:

1. Original sentence revised as: "The concentrations of gaseous pollutants (NO, NO_2, SO_2, O_3) and fine particulate matters ($PM_{2.5}$), size distribution and chemical composition of ship emission

particles were continuously monitored for 3 months".

Changes in manuscript:

Pages 1 , Lines 14 -16 :

"The concentrations of gaseous (NO, NO2, SO2, O3) and particulate concentrations (PM2.5), particle size distributions and chemical composition of individual ship emission particles were continuously monitored for 3 months. "

2. Both of the "shipping emission" and "ship emission" are seen in literatures. This manuscript unify them to "ship emission".

Changes in manuscript:

All the "shipping emission" are changed to "ship emission"

3. The sentence will be "Single particle mass spectra of fresh shipping emission were identified based on the dominant peaks of Sulfate, EC and indicative metals of V, Ni, Fe and Ca".

Changes in manuscript:

Pages1 , Lines20-21 :

"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 "

Thirdly, the abstract should provide specific and detailed findings rather than common senses. The only specific finding described in the abstract is probably the last sentence. The others are all about common knowledge which is also applied to any other ports. What is the uniqueness of the study port?

Response:

Abstract section will be revised concentrating on the key findings and the uniqueness of present study. It will include aspects on fresh ship emission particle signatures, gaseous pollutants characters from ship emission and their contributions, size resolved ship emission particle contributions to portside and the importance of separation of land emissions.

Changes in manuscript:

Pages1 , Lines12-28 :

"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, NO2, SO2, O3) and particulate concentrations (PM2.5), 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 SO2 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 NOx and PM2.5. Quantitative estimation conducted in the present study show that in port region ship emissions contributed 36.4 % SO2, 0.7 % NO, 5.1 % NO2, -0.9 % O3, 5.9 % PM2.5, 49.5 % vanadium particles if land-based emissions were included, and 57.2 % SO2, 71.9 % NO, 30.4 % NO2, -16.6 % O3, 27.6 % PM2.5, 77.0 % vanadium particles if land-based emissions were excluded.

"

Introduction:

As there are too many grammar errors, I have made some comments and revisions on the manuscript. I will submit my comments with the manuscript.

Response:

All the grammatical errors will be corrected in next edition.

Changes in manuscript:

The grammar errors has been corrected throughout the manuscript.

Experimental:

It is not clear whether the sampling site is downwind location of the port or not, or whether the ship plumes could really arrive at the sampling site or not. The authors should provide more detailed description of the site. What were the prevailing winds during the sampling period and how to ensure the capture of ship plumes? There is also no information about the station. Is it a container or mobile vehicle? What is the height of the station if the outlet of the sampling tube was 3.5 m above the ground?

Response:

The referee seems to be suspicious about the possibility to detect ship emissions in port site. This question was answered by the many published studies in portside across the world (Healy et al., 2009;Ault et al., 2010;Contini et al., 2015;Merico et al., 2016).

For an online, continuous monitoring the prevailing wind notion is not useful because a prevailing wind direction does not imply wind will stay in that direction. They could shift to any directions during a long period of time. The monitoring site is certainly in the downwind direction of port when the wind is in 300°-0°-120° sector, which was clearly indicated in Fig. 1 in manuscript.

During the sampling period the prevailing wind is from southeast which is typical for summer season, as presented in Figure R1. Wind in other directions including port directions also occurred although with less frequency.

The station is on the south riverbank, as already stated in manuscript and illustrated clearly in Fig. 1 in original manuscript. The author could not understand how it is thought the station is on a container or mobile vehicle.

Changes in manuscript:

Pages3 , Lines 30- Page4 ,12:

"The Waigaoqiao Port (31.337° N, 121.665° E) locates in the northeast of Shanghai city (Fig. 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. Ship emission plumes could influence the site in wind direction of about 300°-0°-120° sector (Fig. 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). 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.

"

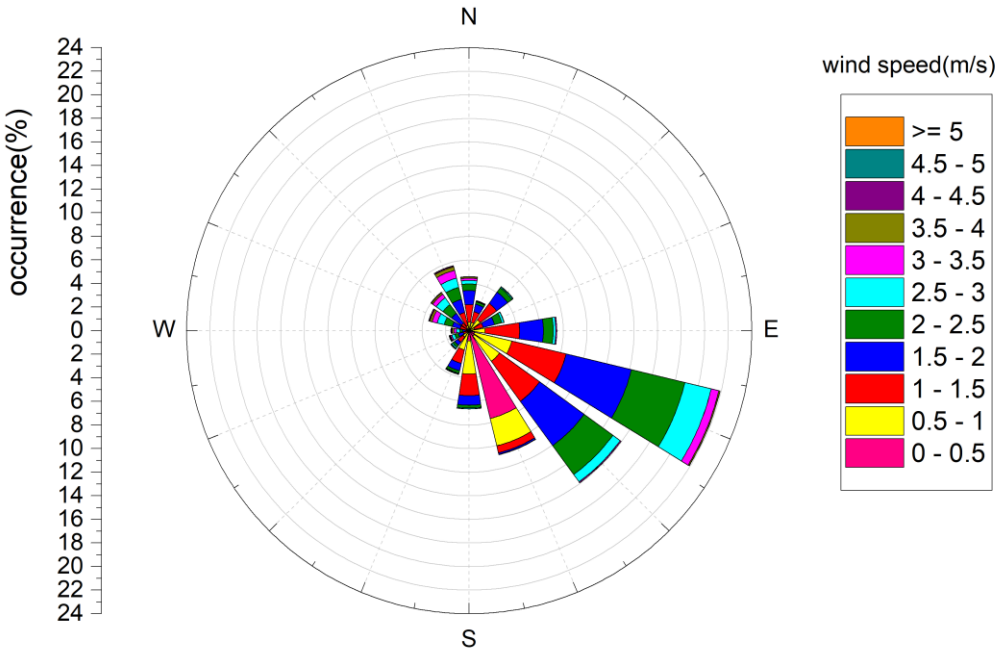

Figure R1. Portside wind rose during the study period.

Was the CO measured? Though it was claimed that calibration and maintenance of the instruments were regularly performed, brief QA/QC procedures and detection limits are still requested. Nothing was mentioned about the QA/QC of PM2.5 monitoring.

Response:

During the period the CO analyzer is not functional, so that the discussion on CO is not included in this study. The QA/QC procedures of NO-NO_2-NO_x, O_3, SO_2 and particulate $PM_{2.5}$ is under guidance of << Technical specifications for operation and quality control of ambient air quality continuous monitoring system for SO_2, NO_2, O_3 and CO >> and <<Technical specifications for operation and quality control of ambient air quality continuous monitoring system for Particulate matter (PM_{10}/$PM_{2.5}$)>> in China. QA/QC procedures in the national air quality monitoring stations are the same. Procedures and detection limits will be added.

Changes in manuscript:

Pages 4 , Lines 14-28 :

"The concentrations of gaseous NO-NO2-NOx, SO2, and O3 were measured continuously from Jun-21 to Sep-21, 2016. The gaseous pollutants were monitored by a suit of Thermal Scientific analyzers (NO-NO2-NOx, model 42i; SO2, model 43i; O3, 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 NO2 and SO2 gas of known concentrations; the O3 standard was generated through a calibration photometer system); The PM2.5 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/m3 (NO, NO2); 0.5 µg/m3 (SO2); 0.5 µg/m3 (O3); 1 µg/m3 (PM2.5). 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 PM2.5 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."

It is not clear how the components in particles such as vanadium were identified and quantified by the SPAMS. Detailed information is needed.

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

Data analysis: in the results, pollution and wind roses were presented while nothing is described about the method to draw pollution and wind roses, and how to explain the pollution and wind roses. In addition, the method of calculation of shipping contributions is improperly placed in the "Results" section, which should be described in the "Experimental".

Response:

Pollution roses are normal and frequently presented in literatures. The author has used the most normal method to draw a wind rose: firstly perform statistics (can either be minimum, maximum, counts, mean value, or any statistics) on relevant pollutant concentrations (e.g., number concentrations of vanadium particles) in every wind directions and then do the plot. If the wind

speed data is also included, then another frame of information appears and a map is obtained , which will produce Fig. 7 in original manuscript.

The explanation of wind roses is equally straightforward, in that it could demonstrate, in a intuitive manner, the direction of emission sources relevant to the observation site. The author will explaine wind roses within text in appropriate places in next edition.

The method to quantify the contribution from ship emission will be moved to 'Experimental' section.

Changes in manuscript:

Line 6, Line 14-25:

*"**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 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).

"

Page 5, line 3: what is ART-2a algorithm? This method was mentioned to be used to the searched clusters to generate sub-clusters of particles. However, no information at all about this method was provided.

Response:

The ART-2a is a classification algorithm conventionally adopted by SPAMS community to group similar particle based on the particle similarities. A reference on ART-2a algorithm will be added here in case that the reader want further information on the algorithm.

Changes in manuscript:

Line 6, Line 9-11:

"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)."

Results and discussions

Page 5, line 10: which typically persist for a few hours: can you tell us the specific hours in your study rather than vague value like this?

Response:

The specific value of hours is variant, most of them fall in range of 3-6 hours.

Changes in manuscript:

Page 6, Line 30:

"as arrival, hoteling and departure, which typically persist for a few (mostly 3-6) hours."

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.

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

Page 5, line 26-29: 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?

Response:

The authors have stated that $PM_{2.5}$ peaks was not as apparent as that of SO_2 and NO_x in plumes, and have not states that no $PM_{2.5}$ 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 $PM_{2.5}$ 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 SO_2 in Figure R2 could help to locate the plumes. If the $PM_{2.5}$ instrument is in malfunction, how did the $PM_{2.5}$ instrument happened to malfunction only in plumes? In another aspect, the SPAMS particle number concentration have shown good correlation with the $PM_{2.5}$ measurement. How did the two instruments both malfunction? It sounds ridiculous.

Changes in manuscript:

None

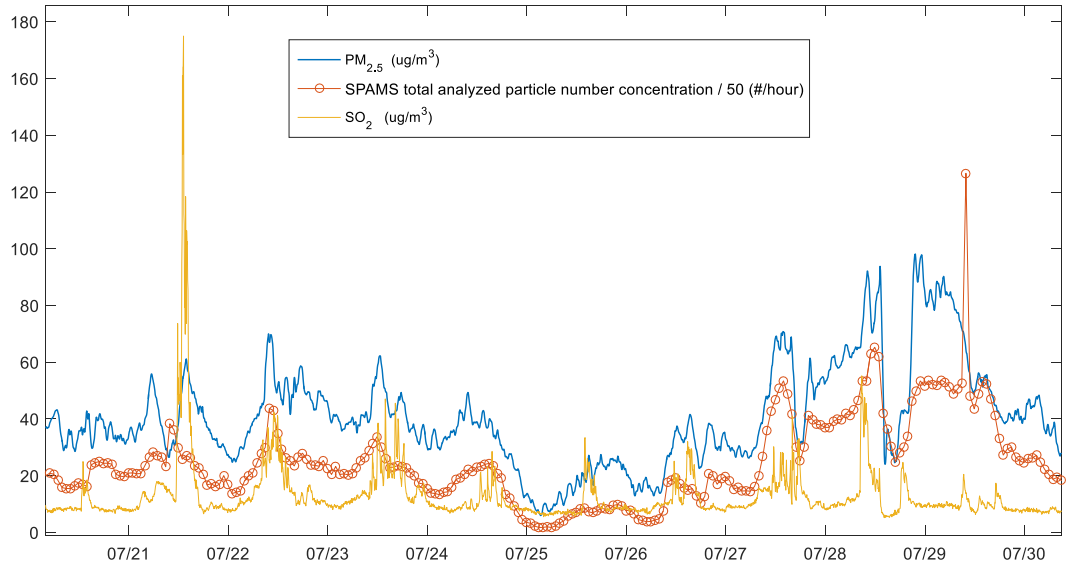

Figure R2. Temporal variations of $PM_{2.5}$, SO_2 concentrations and SPAMS analyzed particle number concentrations during Jul-20 to Jul-30 in this study.

Page 5, lines 31-32: what is the basis for the definition of ship plumes using the minimum threshold of delta SO2? In particular, the authors later claimed that in some cases the SO2 peaks were absent?

Response:

Very clear, frequent sharp peaks of SO_2 over the background SO_2 concentration is suggesting that they are emitted from adjacent combustion sources. Concurrent increases of vanadium particles suggest they are combusting Residual oil. Wind directions during plumes mainly in port directions suggest they are from ships. The cases the SO_2 peaks were absent were rare(3% cases), and will be explained in next edition of manuscript.

Changes in manuscript:

Page 7, Line 29-34:

"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."

Page 6, lines 2-3: 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.

Response:

As stated above, the cases the SO_2 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

Page 6, line 16: “This result suggests that shipping activities are the main source of SO2 plumes in port”. Please comment on the NOx emission from ships - is it not important, because of impacts of land-based traffics? But later in Page 10, lines 15-18, you claimed NO was higher than SO2 in fresh ship plumes.

Response:

The author think that NOx emission from the land-based traffic to the site is important considering all surrounding sources. The claim in Page 10, lines 15-18 was under the condition that land-based emission were excluded by considering the period when site was only under influence of port direction.

Changes in manuscript:

None

Page 6, line 18: 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.

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

Page 6, lines 21-24: 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?

Response:

The slight lower $PM_{2.5}$ concentration at the port site is a fact. The author only postulated possible explanations.

Changes in manuscript:

None

Page 6, line 27: the title reads awkward. Should it be "Particles in the background air and the ship plumes"?

Response:

The title is revised as: ” Discrimination of fresh and background ship emission particles in port site”.

Changes in manuscript:

Page 8, line 25:

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

Page 6, lines 28-31: These should be in "Experimental" section.

Response:

Will be revised.

Changes in manuscript:

This section has been removed

Pages 6-7: the first paragraph of section 3.2.1 is messy and lack of logic. It should be re-organized.

Response:

Not acceptable. The referee think it is messy and lack of logic if he is not familiar.

Changes in manuscript:

None

Page 7, line 13: The wind rose distribution….. in figure 3. This should be merged with the description of mass spectra for Figure 3 earlier. When it is first mentioned, you should describe all once.

Response: Is it a really publicly accepted rule in scientific paper?

Changes in manuscript:

This sentence has been removed.

The text will be considered for some reorganization.

Page 7, lines 16-17: "Background vanadium particles, … in all directions". This is not true in Fig 3(d).

Response:

Original text has stated "prominent" and "nearly".

Changes in manuscript:

None

Page 7, lines 20-21: There is no actual comparison at all. No idea about the particle size in background air, larger or smaller?

Response:

Revised as: " The size distributions of fresh vanadium particles were dominated by fine particles (< 0.5 um in diameter), as shown in Fig. 4. ".

Changes in manuscript:

Page 9, line 21-22

"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."

Page 7, line 22-23: "significant fine ship emission particles were still detected in fine size range". The terms have been randomly used everywhere. What do you mean fine ship emission particles? very non-professional description. It should be fine particles from ship emissions.

Response:

Will be uniformed to 'fine particles'.

Changes in manuscript:

The manuscript use " particles in smaller size range (<0.5 μm)" if appropriate.

Is this contradictory to your previous claim that PM2.5 in ship plumes is lower than that in urban air? In other word, the PM2.5 in background air could be more significant and be detected more significantly?

Response:

It should be noted that particles are measured by SPAMS in number concentrations, while $PM_{2.5}$ is measuring particle mass. The fine particles are only a fraction of $PM_{2.5}$ and not always correlated with $PM_{2.5}$. No contradictory identified.

Changes in manuscript:

None

Page 7, lines 24-27: These two sentences are repeated. the 2nd sentence contains grammar errors.

Response:

Revised as: "The non-spherical, fractal shape of fresh vanadium particles is consistent with the typical shapes from fresh combustion sources (Ault et al., 2010). ".

Changes in manuscript:

Page 9, Line 25-28.

"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)."

Page7, lines 28-30: these two sentences are not related. Lack of logic.

Response:

This discussion will be removed.

Changes in manuscript:

This section has been removed.

Page 7, line 30: "size distribution of fresh particles…". how do you define "fresh particles from ship exhaust" and "particles from ship emissions"?

Response:

Uniformed to "ship emission particles".

Changes in manuscript:

This term are unified to "ship emission particles"

Page 7, line 31:" …that the number concentration mainly concentrated in UF mode (<100 nm)". very poor English writing. It is non-professional at all.

Response:

This discussion will be removed.

Changes in manuscript:

This section has been removed.

Page 7, lines 32-33: No idea at all why PM2.5, NOx and SO2 were suddenly discussed here. This section is about SPAMS measurement data. Also, where showed that PM2.5 had less increase than NOx and SO2? Moreover, are you sure EF of PM are typically much lower than NOx and SO2 in all types of ships with different fuel?

Response:

This discussion will be removed.

Changes in manuscript:

This section has been removed.

Line 34: Do not understand if there is any connection with less significant increase in PM2.5 mass concentration.

Response:

Seen revisions proposed in last comment.

Changes in manuscript:

None

Page 8, lines 1-3: Terrible explanation. The authors lack basic knowledge.

Response:

The referee did not point out the what is the basic knowledge and how they are terrible. In discussion of aerosol mass and number concentrations, it is easy to understand that particle number multiplied the average mass of individual particles produce the total mass concentration. Consider the supposed two cases: An aerosol sample of low numbers of particles but with larger size, and an aerosol sample of larger particle numbers but small average size. The two case may generate the same mass concentration. However, the difference between the two cases is that the latter produce larger surface area which favors the secondary accumulation (secondary formation of nitrate, sulphate, organics) to particle surface. This is why the number concentration matters. Hope the explanation is less terrible to the referee.

Changes in manuscript:

Page 16, line 1-4

''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.''

Page 8, line 9: "The negative mass spectra" how? To me it should be negative m/z value for HSO4-. Mass spectra should not be negative. Please make it clearer. In addition, the whole sentence is confusing. "…other negative EC peaks…". Specifically what are they in the spectra?

Response:

The positive and negative mass spectra a common nomenclature in SPAMS literatures, and will not generate confusions. The EC peaks is already noted in 3.2.1 section when it appear the first time.

Changes in manuscript:

Page 5, line 14-15

"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."

Page 8, line 20: Firstly, this description is unclear. How could "chemical composition" suggest distinct physical properties"? Secondly, is Fig 6 about this? But it is clear that Fig 6 is about temporal pattern of particle number concentration.

Response:

The sentence is revised as "Temporal concentrations and size distributions of these particle types

are shown in Figure 6.".

Changes in manuscript:

Page 10, line 27

"Temporal concentrations and size distributions of these particle types are shown in Figure 6."

Page 8, lines 26-27: Did you scan it using TEM? If not, how do you know yours is the same as other studies?

Response:

The several sentences will be revised as: "In previous study an organic particle type was identified by TEM images of ship emission particles (Moldanova et al., 2013). This organic particle contain vanadium impurities, which agree with organic and vanadium signatures in mass spectra in Figure 5. During the incomplete combustion (e.g., starting up phase) the organic vapours in fuels will condense onto particles (ash, EC particles) in the cooler ambient environment, resulting uniform size distribution compared with other types (lower right panel in Figure 6). The V-OC type are more transient in that the peak width of its concentration peaks are normally narrower than other types (~1 hours contrasting to 3~5 hours of other types).";

Changes in manuscript:

Page 11, line 1-7:

"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)."

Page 8, lines 27-29: Again, you do not have evidence to say this - is the reason that the size distribution of V-OC is different from other types related to incomplete combustion?

Response:

This is an inference to explain the observed result. No existing study is found by author.

Changes in manuscript:

The discussion is removed.

Page 8, line 31: "…. suggesting they are principally emitted in specific phases of engine operations." Any references support this?

Response:

This item was omitted, as shown in previous comment.

Changes in manuscript:

The discussion is removed.

Page 8, line 33: "UF size…" I guess it means ultra-fine. If correct, what is the size range of ultra-fine particles?

Response:

It's size include < 400 nm (aerodynamic diameter) in this study. Next edition they will be uniformed

to “smaller size range (<0.5 um)”.

Changes in manuscript:

Terms will be uniformed to “smaller size range (<0.5 um)”.

Page 9, line 1: “….product of combustion of RFO (Moldanova et al., 2013).” But your measurement was conducted after the implementation of sulfur reduction regulations. This means the fuel used at berth is not RFO but clean fuel.

Response:

Clean fuel with S <0.5% will also produce Soot particles.

Changes in manuscript:

None

Line 2: are mainly detected in larger size range (> 0.5 um) (Fig. 6). The peak particle size for V-EC, V-ECFe and V-Ash looks similar in Fig. 6. How would you say this?

Response:

The size distribution shape of V-EC, V-ECFe and V-Ash types in upper-right panel is presented in absolute numbers. In smaller size range (< 0.5 µm) their number concentration all declined due to the decreased detection efficiencies of SPAMS in this size range. However, their relative contributions change as a function of size as shown in bottom-right panel.

Changes in manuscript:

None

Lines 3-5: This fits other types of particles as well. I don't understand why you said this here. This is basic knowledge.

Response:

The referee likes to speak “basic knowledge”. Is it really your basic knowledge if I have not present it?

Changes in manuscript:

None

Lines 5-6: “The origin of V-ECFe types are probably the result of internal mixing between V-EC and V-Ash particles”. Any possible reasons for this speculation?

Response:

This statement and the latter one has been removed.

Changes in manuscript:

The discussion is removed.

Line 7: how do you know or do you believe it?

Response:

See previous statement.

Changes in manuscript:

The discussion is removed.

Lines 9-18: The whole paragraph is nothing to do with your results but information about other

studies. This should be in "Introduction" section.

Response:

Will be moved to “introduction”.

Changes in manuscript:

It has been moved to “Introduction ” section

Lines 19-20: Very confused statement and unclear purpose.

Response:

Revised

Changes in manuscript:

Page 12, line 5-7:

“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).”

Lines 22-23: “… clearly showed that they are under the overwhelming influences of land emissions on the sampling site.” Why? How do we read the pollution roses in Fig 7? How do we know they were affected by other sources?

Response:

The information in wind roses in figure 7 is rather clear that the port site PM2.5, NOx are strongly influenced by land-based emissions, while the SO2, and ship emitted vanadium particles are under the major impact of ship emissions in port. The ozone wind rose indicates apparent depletions where NOx and SO2 are concentrated.

Changes in manuscript:

None

Lines 26-27: “Because the air pollution in this two conditions are so different,……” Which two conditions?

Response:

It is referring to periods when the site is influenced by land-based and port emissions.

Changes in manuscript:

Page12, line18-21:

“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.”

Page 9, lines 30-32 and page 10, lines 1-2: all these should be in “Experimental” section.

Response:

Will be moved to “Experimental” section.

Changes in manuscript:

It has been moved to “Experimental” section.

Page 10, lines 8-12: Quite confused discussion. Re-written.

Response:

This section will be removed

Changes in manuscript:

Discussions has been removed in manuscript.

Page 10, lines 15-17: Here you finally evidenced the major contribution of ship emissions to NOx. But if you went to section 3.1, you claimed that NOx were mainly from land traffics while ship contribution is not important. The two explanations are contradictory.

Response:

The referee have not understood the point. The mentioned situation is after the land-based emission have been ruled out. It is nothing surprising to found that, if the emission in Shanghai is removed, the activities in port region will certainly be the dominant source of both NO_x and SO_2.

Changes in manuscript:

None

Page 10, lines 19-20: Do you compare the absolute concentrations of these pollutants attributed to ship emissions in these two studies? This kind of comparison using percentage is very dangerous! I bet the total concentrations of these pollutants in these two studies are totally different.

Response:

The absolute contributions will be presented and discussed in next edition, together with suggestions raised by referee #2.

Changes in manuscript:

Page 13,Line7-17:

"The relative contributions of PNCv from ship emission is apparently higher than PM2.5 on mass concentration. Previous study showed that the direct PM2.5 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% PM2.5 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 PM2.5 were in 1-14% range, with higher contributions with decreasing particle size (Viana et al., 2014). The calculated value of PM2.5 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% PM2.5 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 PM2.5. The PNC is not currently measured, instead the size distributions, PNC contributions of vanadium particles in different sizes, as measured by SPAMS, apparently agrees with these previous work. "

Page 13,Line35-Page 14, Line 6:

"However, in an absolute sense, this study estimate that ship emissions contribute to 5.68 µg/m3 SO2, 3.00 µg/m3 NOx and 1.57 µg/m3 PM2.5 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 µg/m3 (primary particles) and 1.7 µg/m3 (secondary particles) in Bay of Algeciras (Viana et al., 2009). Due to the adjacency of the site to port, the calculated PM2.5 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."

Lines 24-25: Did you do t-test to say this? ~4% vs. 5.9% is similar to me. Importantly, compare absolute concentrations. The comparison based on percentage does not make sense and can mislead readers.

Response:

No t-test.

Changes in manuscript:

The same as previous change.

Conclusions

The conclusion section is poorly written. It must be re-organized and re-written.

Response:

Conclusion will be revised.

Changes in manuscript:

Page 15,line 6 - page line 16,line4:

"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 SO2 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 SO2 in plumes are about 3 times higher than the background concentrations. Except the plume periods, the SO2 concentrations in port site varies with the background SO2 level in regional scale. NOx 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 (PNCv) to the portside while its' contribution to the mass concentrations (PM2.5) was less significant. Other pollutants O3 was depleted by elevated primary NOx and SO2 emissions in port regions, resulting 11-33 % ozone consumption compared with urban region of Shanghai.

Particle size distributions and chemical composition of individual ship emission particles were identified by single particle mass spectrometry at the same site. Similar as SO2, 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.

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 SO2 (5.68 μg/m3, 36.4%) and vanadium particle concentrations (49.5%) in port side. NOx contribution (3.00 μg/m3, 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 NOx became comparable with that of SO2. Due to the high NOx and SO2 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/m3) PM2.5 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.

"

Ault, A. P., Gaston, C. J., Wang, Y., Dominguez, G., Thiemens, M. H., and Prather, K. A.: Characterization of the Single Particle Mixing State of Individual Ship Plume Events Measured at the Port of Los Angeles, Environmental Science & Technology, 44, 1954-1961, 10.1021/es902985h, 2010.

Contini, D., Gambaro, A., Donateo, A., Cescon, P., Cesari, D., Merico, E., Belosi, F., and Citron, M.: Inter-annual trend of the primary contribution of ship emissions to PM2.5 concentrations in Venice (Italy): Efficiency of emissions mitigation strategies, Atmospheric Environment, 102, 183-190, 10.1016/j.atmosenv.2014.11.065, 2015.

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

~~**Ambient measurement of shipping emissions in Shanghai port areas**~~

Xinning Wang[1], Yin Shen[1], Yanfen Lin[1], Jun Pan[1], Yan Zhang[2], Peter K.K. Louie[3], Mei Li[4], Qingyan Fu[1]

[1] Shanghai Environmental Monitoring Center, Shanghai 200030, P.R. China.
[2] Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, P.R. China.
[3] Hong Kong Environmental Protection Department, Hong Kong, P.R. China.
[4] Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou, 510632, China.

Correspondence to: Qingyan Fu (qingyanf@semc.gov.cn)

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~~ping~~ emissions, in the summer of 2016 ambient air quality measurement was carried out at Shanghai port, one of the busiest ports ~~port~~ in the world. The concentrations of gaseous (NO, NO_2, SO_2, O_3) and particulate concentrations ($PM_{2.5}$), particle size distributions ~~sizes~~ and chemical composition of individual ship~~ping~~ emission particles were continuously monitored for 3 months. ~~High temporal resolution data show that shipping emissions were is the major culprit of local air pollution problem~~. In online measurement the ship ~~Shipping~~ emission plumes were clearly distinguishable ~~observed~~ ~~using online measurement~~ ~~in port area~~ of both gaseous and particulate matter, which have shown synchronized peaks during plumes. The SO_2 and v~~V~~anadium particles numbers were found to correlate best with ship~~ping~~ emissions in Shanghai port. Single particle mass spectra of fresh ship~~ping~~ emission were identified based on the dominant peaks of sulfate ~~Sulfate~~, elemental carbon (EC) ~~EC~~ and indicative metals of V, Ni, Fe and Ca ~~and nitrate peaks in aged particles~~. Temporal trends and size distributions of major ship emission particle types were discussed. The sampled ship emission particles in the port site ~~from ship emission~~ mainly concentrated in smaller ~~ultra fine~~ 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 ~~Advanced measurement~~ conducted in the present study show that in port region ship~~ping~~ emissions contributed 36.4 % SO_2, 0.7 % NO, 5.1 % NO_2, -0.9 % O_3, 5.9 % $PM_{2.5}$, 49.5 % v~~V~~anadium 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 % v~~V~~anadium particles if land-based emissions were excluded.

Keywords

Ship~~ping~~ emission; Shanghai port; emission source contribution; SPAMS

1 Introduction

~~S~~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 ~~assessing~~ 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 ~~could have a~~ negative impacts on the air quality at varied ~~variant~~ degrees ~~in these areas or cities~~ (Donateo et al., 2014;Liu et al., 2017). With growing contributions of ship emissions to air pollution ~~air pollution from ship emissions~~, its negative effects on human health of coastal residents is another subject that attracted attentions ~~has been studied~~ (Corbett et al., 2007).

The typical fuel that ships burn is Residual Fuel Oil (RFO) with ~~usually has~~ high sulfur content. Combustion of RFO in ship engines produces high concentration of gaseous and particulate pollutants including NOx, 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 ~~toward~~ 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~~s~~ characterizations including both gaseous and particulate ~~measurements~~ are ~~found~~ necessary in studies of field measurements ~~ambient studies~~ (Xiao et al., 2018;Viana et al., 2009).

In Yangtze River Delta (YRD) region in China the shipping activities has increased ~~increase~~ significantly due to intensified international trades in recent years. The accompanying potential environmental and health problems from ship~~ping~~ 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 ~~SO2~~, 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~~ping~~ emissions, Shanghai government has initiated Domestic Emission Control Areas (DECA) in YRD ~~to control air pollution from shipping activities~~. At present stage, according to ~~by way of~~ 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. ~~More stringent regulations of sulfur content limitations of 0.5 % and eventually 0.1 % in DECA are in preparation.~~ 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. ~~Despite the high emissions level from ship traffics in YRD, ambient measurements on ship emissions in this area are very limited except studies on ship emission inventories or modeling (Liu et al., 2017;Zhang et al., 2017;Chen et al., 2018). In order to restrict constraint the uncertainties inherent to inventories or simulations studies it is essential to be validated that the validation is compared with the actual measurement data (Zhao et al., 2013).~~

In the summer of 2016, an in-site sampling campaign ~~experimental characterization~~ focusing on ship emissions was ~~were~~ performed at Shanghai Port. Gaseous and particulate matters concentrations were online monitored ~~achieved by online monitoring~~ 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 ~~from~~ ship emissions to ~~on~~ portside air quality was performed. Ship~~ping~~ 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 ~~were~~ 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 ~~an advanced~~ 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 ~~formulation~~.

2 Experimental

2.1 Sampling site

The Waigaoqiao Port (31.337° N, 121.665° E) locates in the northeast of Shanghai city (Fig. 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 ~~in-port~~ 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. Ship emission plumes could influence the site in wind direction of about 300°-0°-120° sector (Fig. 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). In ~55% of time the site was under the impact from port emissions. ~~The outlets of main sampling tube, fixed on the roof of the station were 3.5m above the ground~~. To the south and west of site there were ~~are~~ intense road traffics of container trucks ~~in surrounding regions~~ and the Shanghai outer ring. Traffic emissions in south and west directions have important influences on ~~to~~ air pollutions at the ~~in~~ monitoring site when inland wind prevails. ~~The impact of land traffic emission will be discussed in following sections.~~

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 $\mu g/m^3$ (NO, NO_2); 0.5 $\mu g/m^3$ (SO_2); 0.5 $\mu g/m^3$ (O_3); 1 $\mu g/m^3$ ($PM_{2.5}$). 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.

~~In-port gaseous concentrations of NO-NO_2-NO_x, SO_2, and O_3 were measured continuously from Jun-21 to Sep-21, 2016. The gaseous pollutant monitors are a suit of Thermal Scientific analyzers (NO-NO_2-NO_x, model 42i; SO_2, model 43i; O_3, 49i) installed in the monitoring station. Calibration and maintenance of instruments were regularly performed according to the requirement of relevant national standards in China. The $PM_{2.5}$ concentrations are monitored with the oscillating microbalance~~

~~method (Thermo TEOM 1405-F). Ambient conditions (temperature, humidity, pressure, wind speed and direction) are monitored by a meteorological monitor on the rooftop of the station, which is about 3.5m above the ground. Data from all instruments are set to 5 min resolution and is managed in a customized database. The pollution level in Shanghai city area, including gaseous and $PM_{2.5}$ concentrations, are monitored continuously by 9 national air quality monitoring stations. Pollutants averaged concentrations at these 9 stations during the same monitoring period were included as a reference.~~

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 ~~PMT~~. 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. ~~to obtain the $PM_{2.5}$ cut-point before detection by SPAMS.~~

2.4 SPAMS data analysis ~~Data analysis~~

The ~~high~~ temporal resolution of SPAMS (seconds or minutes) makes it ~~very~~ 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 ~~the high resolution measurement by~~ SPAMS data. In addition, present study takes advantage of the ~~unique~~ power of SPAMS to identify individual ship~~ping~~ emission particles based on particle fingerprint. Mass spectral patterns of ship~~ping~~ emission particles were firstly ~~first~~ identified and then were utilized to extract ship emission particles from single particle dataset ~~them out~~. The temporal trends, size distribution, chemical composition, and wind rose of the extracted ~~searched~~ particles could be examined in further detail.

During sampling of 3 months a large amount of particles were chemically analyzed by SPAMS (>2.3 million mass spectra). The identification of ship~~ping~~ emission particles from 2.3 million total particles were based on a combined method of peak searching and algorithm clustering ~~to achieve better performance~~. Specifically, the SPAMS data are pre-analyzed by visually inspecting of individual particle mass spectra to identify MS patterns ~~of shipping emission particles~~ during ship plumes. The concurrent SO_2 ~~SO2~~ 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~~. The obtained mass spectra of shipping emission particles are similar to as detected previously in other port regions~~ (Ault et al., 2010;Healy et al., 2009;Ault et al., 2009). In this study the v~~V~~anadium 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~~ping~~ 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 analyzed 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) ~~(Vigilance=0.85; Learning=0.05; Iteration=20)~~ 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.

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 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 of ship emission plumes

In the vicinity of port, the measured ship emitted ~~emission~~ pollutants ~~concentrations~~ often produce sharp peaks in relatively short period (Fig. 2). The sharp peaks are caused ~~produced~~ 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 ~~ship plumes~~. For comparison ~~purpose~~ the averaged SO_2 concentration in Shanghai city and v~~V~~anadium 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 v~~V~~anadium particles number ~~concentration~~ as detected by SPAMS. The synchronous peaks of gaseous and particulate matters during plumes was similarly observed elsewhere ~~This result is in good agreement with previous characterizations studies in portside~~ (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). ~~During the whole sampling period the Shanghai city SO_2 concentration matched very well with ambient SO_2 concentration in port area during non-plumes periods. This is also consistent with the observation data that pollution plumes arising from shipping emission superimpose on background and regional SO_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 ~~emissions~~ (mostly from transportation diesel trucks) when the inland wind prevails. The ship~~ping~~ 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 ~~have~~ 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 v~~V~~anadium particles had reached the site, as shown. The obscure response of $PM_{2.5}$ during ~~to~~ ship plumes is explained by the finer particle sizes in relatively fresh ship~~ping~~ emissions, as discussed subsequently. ~~in following section~~.

Considering the facts described above, ~~Taking into consideration of all the relevant factors~~, the present study defines ship plume periods by using ~~ways of~~ SO_2 concentrations and v~~V~~anadium 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~~ping~~ emission particles, the number concentration of v~~V~~anadium particle is considered because in some cases the SO_2 peaks are absent or obscure as typical fresh v~~V~~anadium 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. ~~This is probably caused by anchored ships using oil of low sSulfur contend (<0.5 % m/m) to comply with new regulations in Shanghai port, which came into force on~~

~~April 1, 2016~~. In this study the threshold of v~~V~~anadium particle detection speed in ship plumes are set to $C_V > 25$ particles/hour. That is, ship plumes are defined as either $\Delta_{SO2} > 5\mu g/m^3$ or $C_V > 25$ particles/hour.

There were ~~In total~~ about 210 ship~~ping~~ emission plumes ~~were~~ captured during the sampling campaign. Table 1 summarizes the statistics on the ~~pollutants~~ 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.

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 ~~are~~ 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 ~~are~~ significantly lower than from land directions. This result suggests a larger ship emission contribution to portside SO_2 than to NO_x. ~~that shipping activities are the main source of SO_2 plumes in port.~~ For NO_x, due to the specific geographic proximity of Waigaoqiao port, its concentration was more importantly impacted ~~is significantly influenced~~ by land-based traffics. In general the ozone concentrations in port were ~~are~~ 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 v~~V~~anadium particles concentrations in plumes were ~~are~~ 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 v~~V~~anadium particle detection probability, measured as the number fraction in total particles~~, as measured by SPAMS~~, is clearly larger (6.7 % on average) in portside than ~~in~~ the urban area in Shanghai (1-2 %) (Liu et al., 2017).

3.2 Particles properties from ship emission ~~Characterization of single particle properties from ship emissions~~

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

~~Particle size and chemical characterization from ship emission was performed by a SPAMS (Li et al., 2011) in parallel with gaseous measurement. The close proximity of the monitoring site to docks makes it possible to detect very fresh ship emission particles in addition to aged ones (Healy et al., 2009).~~ In ~~By using~~ single particle characterization techniques, fresh or 'pure' ship emission particles is separable ~~can be separated~~ 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 ~~the fresh ship emission particles in plumes are~~ 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 vVanadium 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 mass spectra of fresh ship emission particles and aged ones are shown in Figure 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 vVanadium ($51V^+$, $67VO^+$) peaks, indicating reflecting 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 OC is an important component composition 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 It maybe owing to the fact that SPAMS is not so sensitive to organics species due to the low ionization efficiencies in laser ionization (Ulbrich et al., 2009). However, there is an organic cluster of organic particles were indeed identified in ship plumes, although of minor detection probability number fractions, as discussed subsequently in 3.2.2. subsequent section.

The wind rose distribution of fresh and background vVanadium particles are shown in figure 3. It is clear that fresh and background vVanadium particles have different size distributions and wind rose patterns (Fig. 3, 4). Wind roses and size distributions of fresh and aged ship emission particles were also distinguishable. The fresh vVanadium particles have wind rose pattern which runs almost running parallel with the direction of with riverbanks (300°-0°-120°). This is strong evidence that ships are the most predominant source of fresh vanadium particles in Shanghai port. Background vVanadium particles, however, did not show any prominent source directions and displayed nearly uniform distributions concentrations in all directions. It is assumed It is reasonable to assume that the aged vVanadium particles are background particles which have undergone atmospheric processing in local or regional scale.

The size distributions of vVanadium particles as shown in Figure 4 indicates fresh vVanadium particles with dominate particle numbers in smaller size range (<0.5 μm um), compared with background ones. Although SPAMS detection efficiency declines in this smaller size range due to the because of the smaller section to reflect laser light, significant number of fine ship emission particles were still detected in this fine size range. The explanation is that these particles are non-spherical fractal agglomerates, such as EC BC particles, having significantly larger cross sections to reflect laser light and thus be detected in SPAMS. The non-spherical fractal shape of fresh vVanadium particles is seen consistent with soot typical particle shapes from fresh combustion sources. Similar observations were observed were also reported in other studies using single particle mass spectrometer in ultra-fine size range (Ault et al., 2010).

The size distribution agrees with the sizes of ship emission particles measured in other studies (Gonzalez et al., 2011;Merico et al., 2016). It is reported that for ship exhaust their particle number contributions are more considerable than their mass contributions (Donateo et al., 2014;Jonsson et al., 2011;Merico et al., 2016). Size distribution of fresh particles from ship exhaust shows that the number concentration mainly concentrated in UF mode (<100 nm) (Gonzalez et al., 2011;Moldanova et al., 2013). The less significant increase in $PM_{2.5}$ mass concentration than NO_x and SO_2 in plumes are due to, in one respect, that the emission factors of PM are typically much lower than NO_x and SO_2 (Agrawal et al., 2010;Moldanova et al., 2013),

~~and second, that the smaller size of fresh vanadium particles before secondary accumulation happens in the atmosphere (Moldanova et al., 2013). Considering that the secondary processing occurred on every particle, the particle number concentrations of fresh shipping emissions is more significance than their initial mass concentrations. The study suggests that particle number quantification is more appropriate in an accurate evaluation of primary ship emissions.~~

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. ~~After the separation of background ship emission particles, fresh vVanadium particles are isolated to represent fresh ship emission particles. Further analysis is performed to study their composition and emission characters, which will be helpful in particle source identification of SPAMS in future studies.~~ In general, the fresh v~~V~~anadium 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 negative mass spectra of the four types are common in the dominating SO_4^- peak in addition to other negative EC peaks in spectra, consistent with the high SO_2 concentration in ship emission 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. ~~Considering the low ionization probability of OC in laser ionization, this particle type is deemed to be mainly composed of condensed organics in engine exhaust plume~~ (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 v~~V~~anadium particles. The V-ECFe type is similar to ~~as~~ 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).

Temporal concentrations and size distributions of these particle types are shown in Figure 6. ~~The chemical composition and size distribution of these four types suggest they have distinct physical properties (Fig. 6).~~ Temporal number concentrations of these particle types displayed daily variations, with higher concentrations in daytime than night. ~~Temporal trends of these 4 types show that their concentrations display daily fluctuations, with higher concentrations in daytime than night nighttime~~. 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. ~~However, the inter-correlations among their concentrations are low (r^2 < 0.4), suggesting the~~

different emission process among them (variant engine types, operation modes, etc.). 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). The V-OC particle type probably corresponds to the amorphous organic particles in TEM images, usually having inner metallic impurities (Moldanova et al., 2013), as indicated by the metal peaks in mass spectrum. In incomplete combustion (e.g., starting up phase) the organic vapors in fuels will condense onto particles (ash, EC particles) in the cooler ambient environment, resulting uniform size distribution compared with other types (lower right panel in Figure 6). The V-OC type are more transient in that the peak width of its concentration peaks are normally narrower than other types (~1 hours contrasting to 3~5 hours of other types), suggesting they are principally emitted in specific phases of engine operations. 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-EC particles are the most abundant types found in ship plumes in this study. As mentioned earlier the enrichment of EC particles in UF size regions indicates the fractal agglomerates shapes typical of soot from engine, which is a common product of 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. It is reminded that the measured aerodynamic size by SPAMS is dependent both on particle physical diameter and particle densities. Therefore the larger size of V-Ash particles does not imply they are physically larger, because the ash spheres are mainly composed of metal oxides or salts of higher effective densities than EC. 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 as V-Ash type. , suggesting that the adhesion of fractal EC particles to ash spheres has not change the diameter of the latter significantly.

3.3 Contributions of ship emission to ambient pollutants in port area

Quantification of ship emissions impact on regional and local air quality is an important issue to assess its impact on environment (Donateo et al., 2014;Aulinger et al., 2016;Merico et al., 2016). 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 μg/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 of Shanghai city. In this study, the ambient measurement data in a coastal port is utilized to quantitatively assess the contribution of ship emissions to air quality, making current study more comparable with others.~~

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. ~~Due to its close proximity to urban region, the measurement site is under more important influences from land emissions than the marine port far from coastal area (Zhao et al., 2013). To give a more nuance illustration, the role of wind fields of portside on influencing the measured pollutants are shown for SO_2, O_3, NO, NO_2, $PM_{2.5}$ and vVanadium particle numbers (Fig. 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. ~~Wind roses of some pollutants (NO, NO_2 and $PM_{2.5}$) clearly showed that they are under the overwhelming influences of land emissions on the sampling site~~. As a contrast ~~On the contrary~~, the SO_2 concentrations and vVanadium particle numbers were ~~are~~ dominant only when winds from port sectors. The hotspots in wind rose of vVanadium particle are most probably produced by individual docks along the riverside. The wind dependence of ozone ~~Ozone~~ concentrations is less apparent, except its' ~~showing~~ 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. ~~Because the air pollution in this two conditions are so different, it is appropriate to separate land based emissions influences by limiting wind directions only to port directions. Therefore, in the present study two reference periods are considered in calculating shipping contributions: the entire study period (irrespective of wind) and only when the site is in downwind of port direction.~~

~~The calculations method of ship contributions is based on the extraction of ship emission plumes from background concentrations of pollutants (Merico et al., 2016):~~

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

~~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.~~

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).

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, instead the size distributions, PNC contributions of vanadium particles in different sizes, as measured by SPAMS, apparently agrees with these previous work.

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.

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 μg/m^3 SO_2, 3.00 μg/m^3 NO_x and 1.57 μg/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 μg/m^3 (primary particles) and 1.7 μg/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.

~~Shipping emission contributions of measured respective pollutants in two reference periods are summarized in Table 2. As shown in Table 2, Results show that shipping emission contribution for gaseous SO_2 (36.4 %) are much larger than for NO (0.7 %), NO_2 (5.1 %), and for $PM_{2.5}$ (5.9 %), if not considering the factor of wind direction (entire period). The low contributions of NO_x from shipping are due to the inclusion of land emissions (mostly traffics) of stronger intensities. However, 49.5 % vVanadium particles numbers are contributed from shipping emissions despite the inclusion of land emissions, suggesting the importance of number concentration from shipping emissions. It is worth noting that in the entire period calculations, the frequency of winds at respective directions during the sampling period influences the calculated contributions. The calculations in this way may somewhat overestimate ship emissions because of the prevailing southeast wind during summer in Shanghai. During the period when southeast winds are prevalent, adjacent coastal regions other than port area may experience more ship emissions.~~

~~By limiting the sampling with time windows to periods when winds from port sector, the influences of land emissions could be largely eliminated, in which a less biased estimations of shipping emission are obtained. As shown in table 2, by considering port sector wind, for all pollutants the ship emission contributions are magnified in amplitude. The most dramatic change occurs for gaseous NO_x, whose contributions from shipping upgraded to levels larger or comparable with SO_2. The larger contribution of primary NO than NO_2 and SO_2 indicates that the plumes are relatively fresh ones. Contributions obtained here can be compared with a very similar study carried out in a European port (Merico et al., 2016). Gaseous emissions of NO, NO_2 and SO_2 are similar between these two studies, which is an impressive result considering the much larger throughput of goods in Shanghai port. However, the main differences between two studies are the larger contributions from the shipping for O_3 depletion (16.6 % vs. 5 %) and $PM_{2.5}$ concentrations (27.6 % vs. 9 %) in Shanghai port. In that study particle number contributions from shipping emissions (<50 %) are smaller than this study as measured by SPAMS (77 %).~~

~~In the marine port study at Yangshan island of Shanghai, the calculated $PM_{2.5}$ contribution (~4 %) is smaller than present study (5.9 %) (Zhao et al., 2013). In the Zhao et al study a different method is used to evaluate ship emissions, relying on vVanadium concentrations to indicate ship emissions. Considering the methodology differences, it is deemed that the results from the two studies are similar if land based emission sources were included in Waigaoqiao port. 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. It is worth noting that~~

~~the high SO_2 contributions in this study only represent the port site which is close to emission sources. The detected pollutions in the port site are usually found to be fresh and with elevated concentrations. With transportations to the urban region their concentrations will dissipate and strength weakened. Quantifications of ship emission contributions in the urban regions will be the subject of future studies and beyond the scope of the present study.~~

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.

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.

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 $\mu g/m^3$, 36.4%) and vanadium particle concentrations (49.5%) in port side. NO_x contribution (3.00 $\mu g/m^3$, 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 $\mu g/m^3$) $PM_{2.5}$ 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 gaseous and particulate emissions from shipping emissions are measured in Shanghai port to study their emission characters. Pollutants from ship emission in port often result sharp peaks of concentrations during plumes passing the site. Of the measured pollutants (SO_2, NO, NO_2, O_3, $PM_{2.5}$ and vVanadium particles), SO_2 and vVanadium particles show the best responds to ship emission plumes. Using the SO_2 and vVanadium particles concentration as indicators, ship emission plumes can be successfully identified from background atmosphere. Statistics of pollutants during plumes show that the concentrations of SO_2 in plumes are about 3 times higher than the background concentrations. In non-plumes SO_2 concentrations in port share the trend of regional background level. Results show that the NO_x concentrations in port site are under much stronger influences from land emissions. The O_3 is depleted by primary NO_x and SO_2 emissions around the port, resulting 11-33 % ozone Ozone consumption compared with urban region of Shanghai. For particulate matters, shipping emitted PM is more embodied by the number concentrations rather than the mass concentrations ($PM_{2.5}$) during plumes.~~

~~Individual particle size and chemical composition from shipping emission are online characterized in parallel with other measurement. It is found that, similar as SO_2, the ship emission particles in port could also be divided into fresh and background types. The mass spectra of fresh ship emission particles produce dominant peaks of EC, sulfate and trace metals (V, Ni, Fe and Ca). Due to the low ionization efficiencies of organics, OC is only identified only in a small group of particles. Size distributions show that ship emission particles are more concentrated in fine size range (< 0.5 μm), which is mainly fractal EC agglomerates. Further classifying of ship emission particles indicates that trace metals are present in ash spheres of larger aerodynamic diameters, either externally or internally mixed with EC particles.~~

~~Based on the measured gaseous and particulate concentration, shipping emission contributions to the air quality in Shanghai port area is quantitatively evaluated. The contributions of ship emissions are evaluated in two scenarios where the land emission sources are either included or excluded. With the inclusion of land-based emission sources, contributions of ship emission are mainly embodied in SO_2 (36.4 %) and vVanadium particle number concentrations (49.5 %). The ship emissions to $PM_{2.5}$ is 5.9 % if include the land emission sources. NO_x contribution from shipping emissions is insignificant if include land traffic sources. However, if land sources are excluded, shipping contributions of NO_x became prominent comparable with that of SO_2. 16.6 % of Ozone concentration is found to be depleted by ship emitted NO_x and SO_2 during wind from port direction. With the exclusion of land sources, ship emissions are found to contribute 27.6 % of $PM_{2.5}$ and 77 % vVanadium particle numbers in port area.~~

Disclaimer

The content of this paper does not necessarily reflect the views and policies of the HKSAR Government, nor does mention of trade names or commercial products constitute an endorsement or recommendation of their use.

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Figures

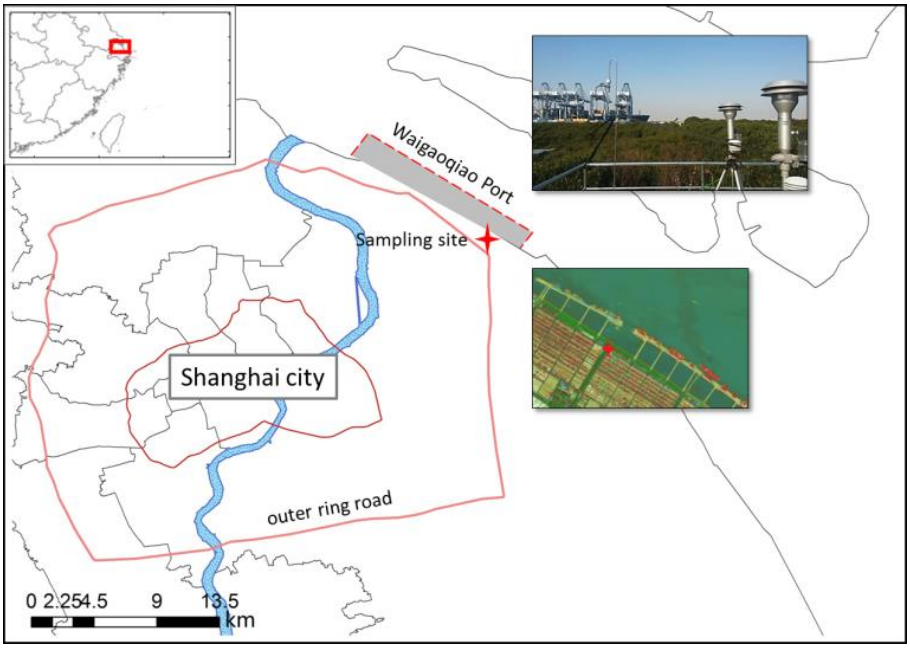

Figure 1: Map of sampling site in Shanghai port and surrounding areas. Port region is indicated by shaded area. The insets are the satellite image of the port site and a photo taken on the roof of monitoring station seeing in port direction.

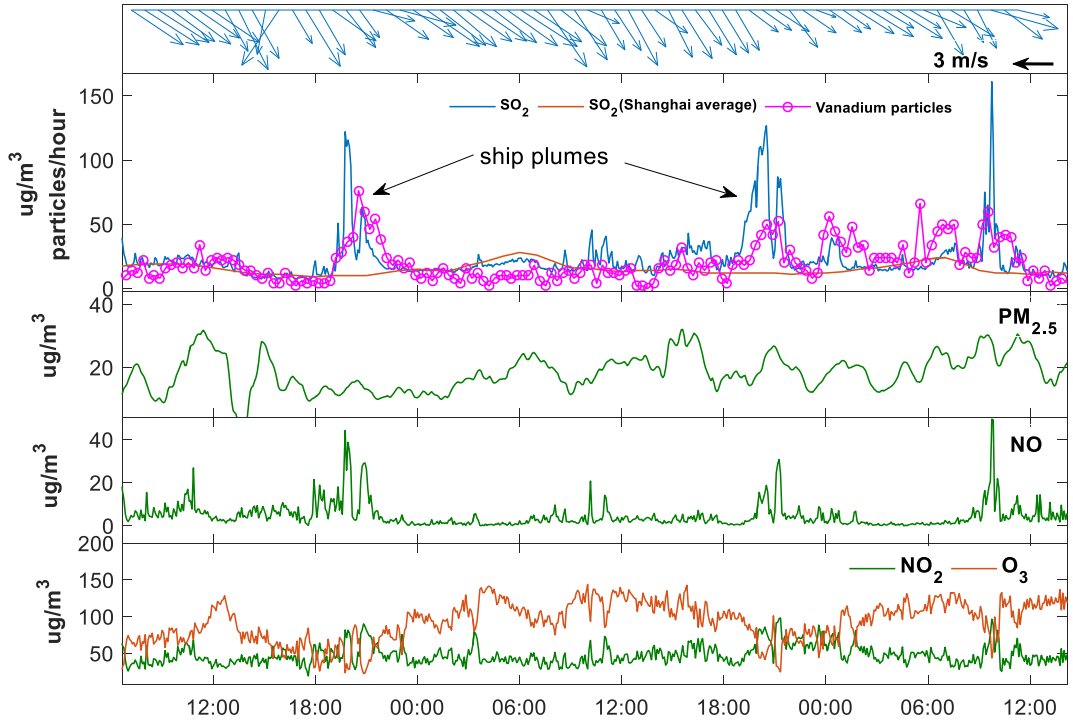

Figure 2: Temporal concentration of pollutants SO_2, NO, NO_2, O_3 and PM2.5 during 27-29 August 2016. Contemporary wind direction and speed, SO2 concentration of Shanghai city and vVanadium particles number concentration as detected by SPAMS are included as a reference.

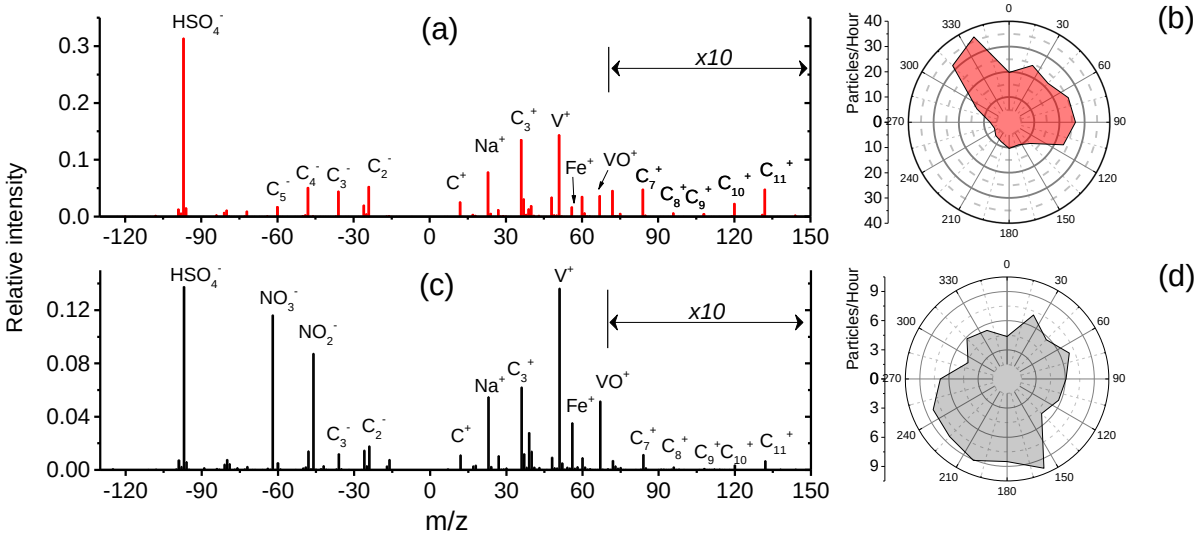

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Figure 3: Mean mass spectra of fresh and background ship emission particles in port (a, c) and the wind rose of particle number concentration (in measure of particle number per hour) of these two particle types (b, d). Peaks in mass range of 70-150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

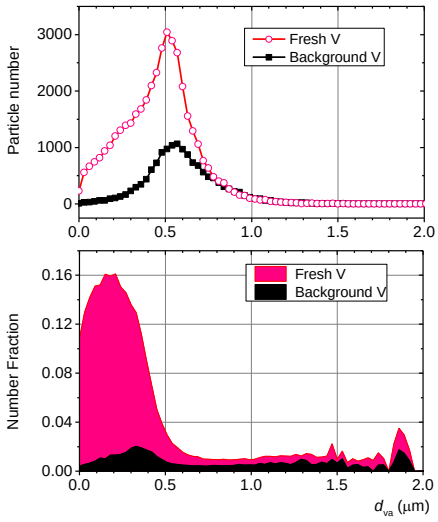

Figure 4: Particle number size distribution of fresh and background ship emission particles by SPAMS (Upper). Size distribution of these fresh and background types of ship emission particles normalized by total particles at each size (Lower).

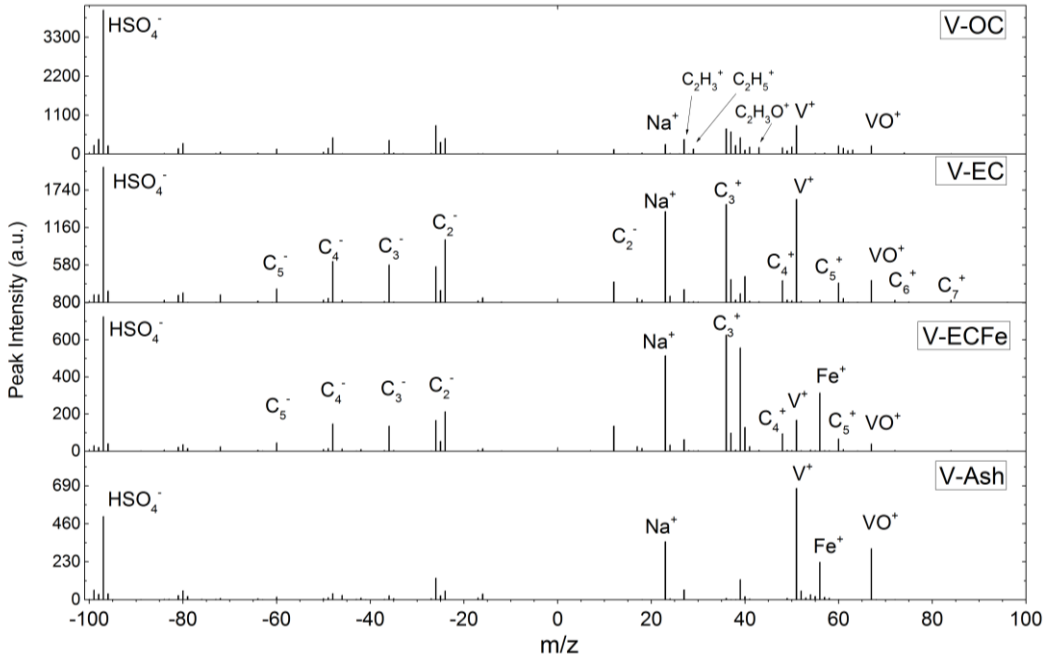

Figure 5: Mean mass spectra of four major particle types from fresh ship emission.

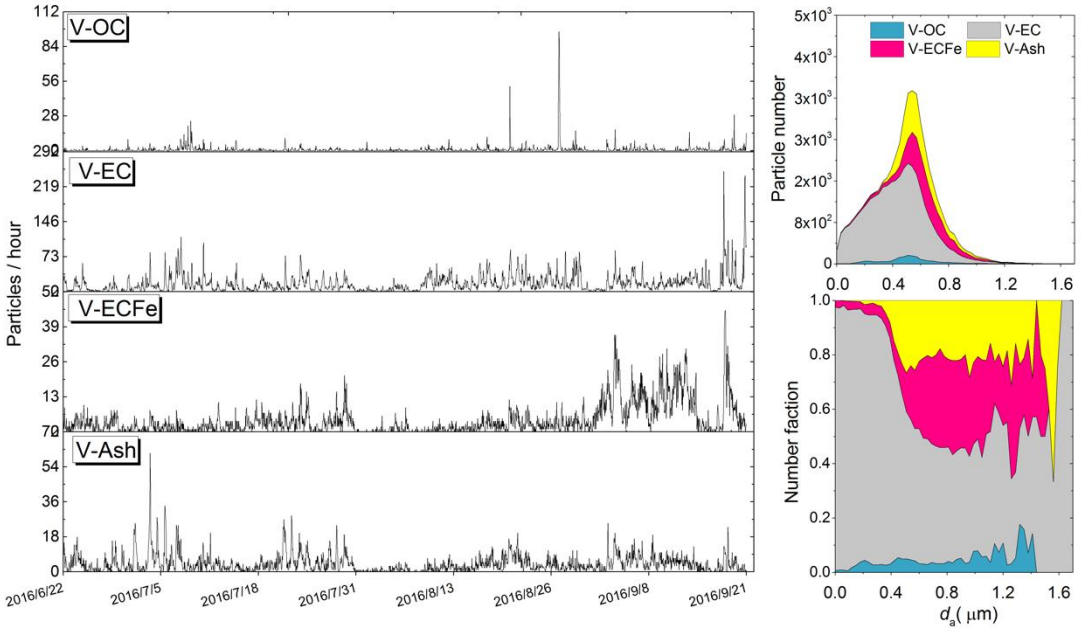

Figure 6: Temporal trend of number concentrations of four fresh v~~V~~anadium particle types (Left panel); the number (upper right) and number fraction (lower right) of four v~~V~~anadium particle types as a function of particle size.

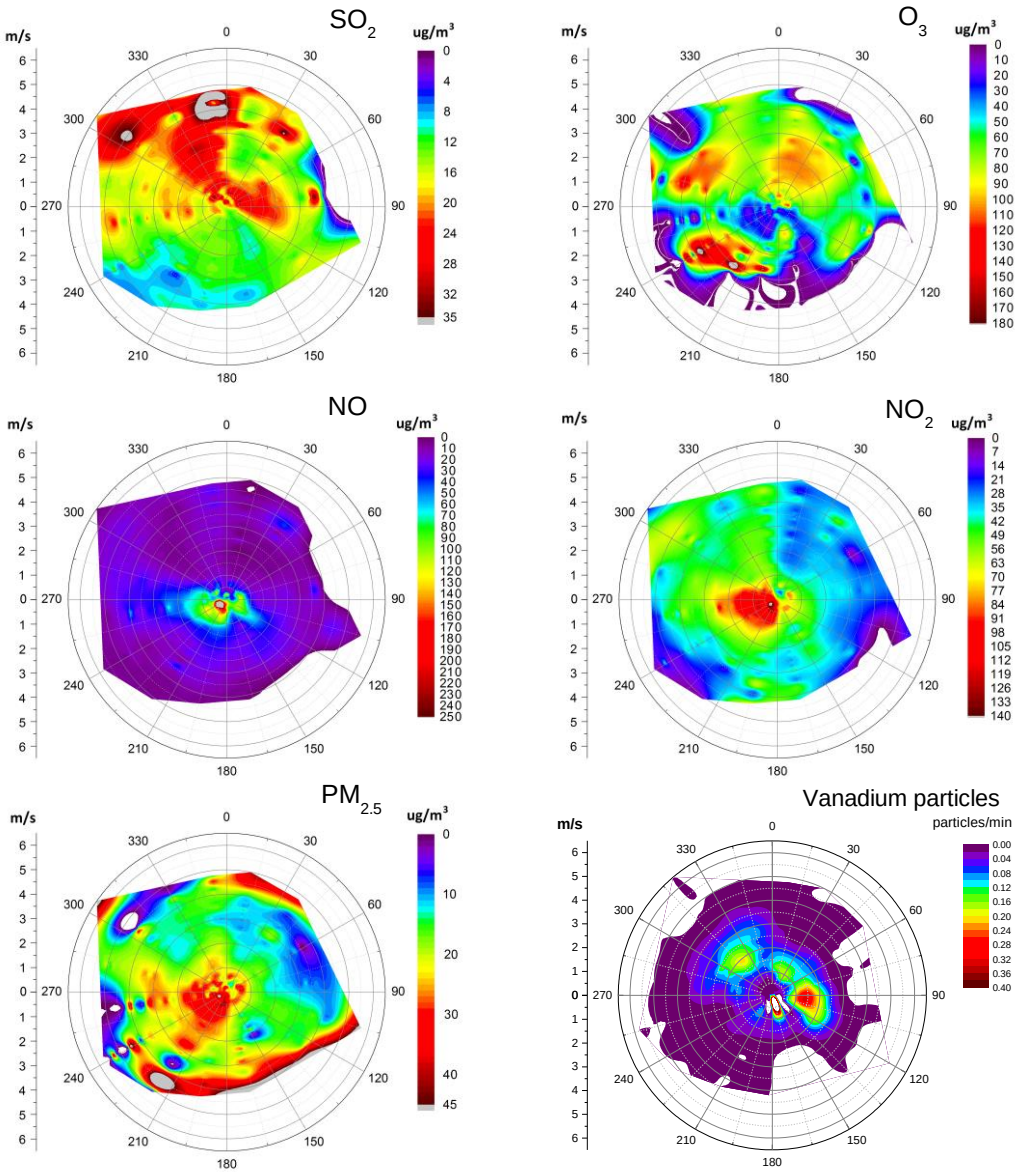

Figure 7: Pollution roses of SO_2, NO, NO_2, O_3, $PM_{2.5}$ and v~~V~~anadium particles during the whole study period. Vanadium particles wind rose is based on number concentration as measured by SPAMS.

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 vVanadium 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.

	~~SO_2~~	~~NO~~	~~NO_2~~	~~O_3~~	~~$PM_{2.5}$~~	~~Vanadium particles*~~
~~Entire period (include land emissions):~~	~~36.4%~~	~~0.7%~~	~~5.1%~~	~~-0.9%~~	~~5.9%~~	~~49.5%~~
~~In port sector (exclude land emissions):~~	~~57.2%~~	~~71.9%~~	~~30.4%~~	~~-16.6%~~	~~27.6%~~	~~77.0%~~

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

(%)		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*	(0-0.4μm)	79.2	(73.9, 85.0)	57.1	(50.6, 64.0)
	(0.4-0.8μm)	75.3	(68.1, 82.0)	44.7	(38.1, 52.3)
	(0.8-2.5μm)	76.6	(70.4, 82.9)	47.0	(41.3, 52.9)
	(0-2.5μm)	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"

1. *Wind rose of the port site during the study*

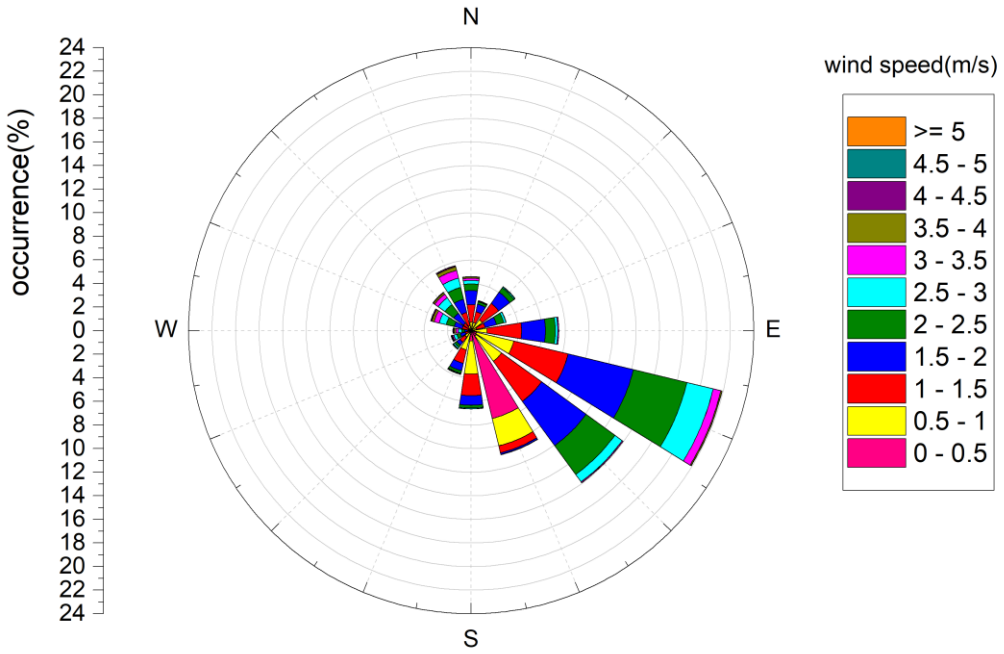

Figure S1. Portside wind rose during the study period.

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 ~~inclusion~~ interferences of particles from land sources. Therefore, ~~in present study the online single particle measurement was utilized to indicate the occurrence of shipping emission plumes,~~ 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.

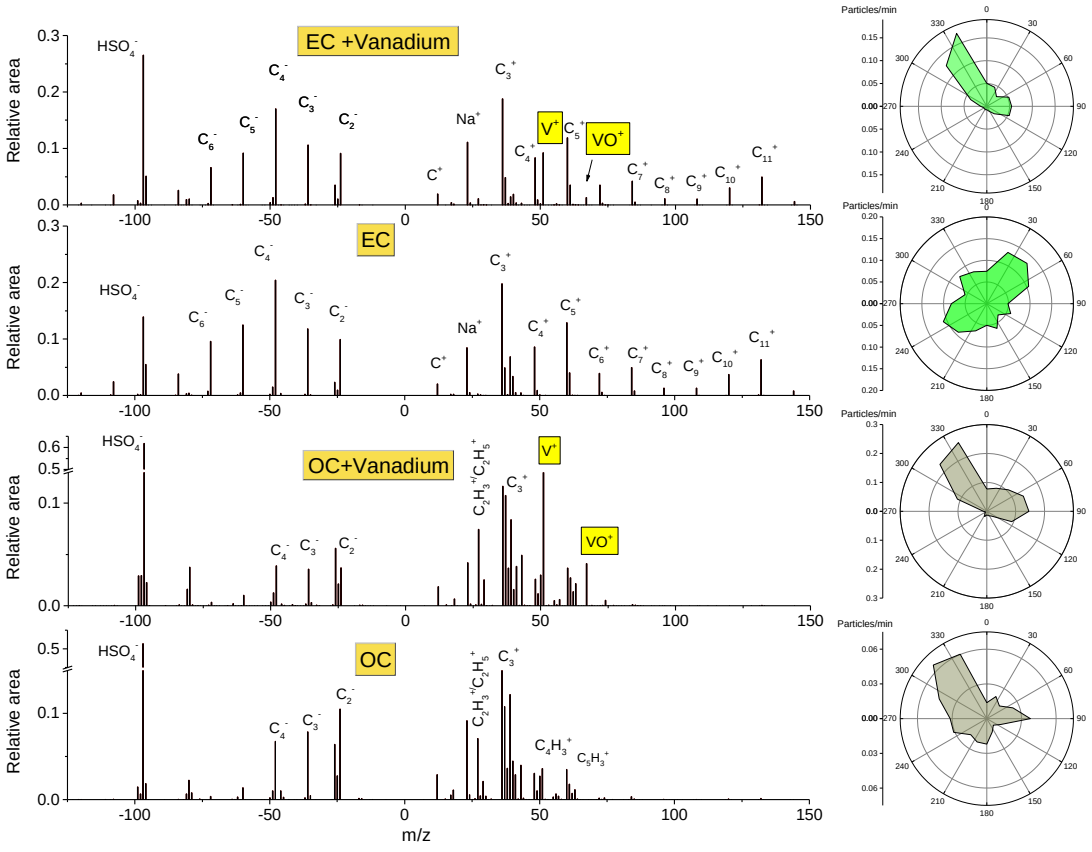

Figure S2. Mass spectra and wind roses of representative particle clusters with and without Vanadium peaks.

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