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Ambient measurement of shipping emissions in Shanghai port areas

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Abstract. Growing shipping activities in port areas have generated negative impacts on climate, air quality and human health. To better evaluate the environmental impact of shipping emissions, ambient air quality measurement was carried out at Shanghai port in the summer of 2016. Large throughput capacity and busy shipping traffics of Shanghai port make it an ideal place to characterize shipping emissions. Gaseous (NO, NO_2, SO_2, O_3) and particulate concentrations ($PM_{2.5}$), particle sizes and chemical composition of individual shipping emission particles were continuously monitored for 3 months. High temporal resolution data show that shipping emissions is a major culprit of local air pollution problems. Distinct shipping emission plumes were observed using online measurement in port area. The SO_2 and Vanadium particles numbers were found to correlate best with shipping emissions in Shanghai port. 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, and nitrate peaks in aged particles. Fresh shipping emission particles mainly concentrated in ultra-fine size range where their number contributions are more apparent than their mass. For the coastal port it is found appropriate to separate shipping emissions from land-based emissions by prevalent wind directions. Advanced measurement conducted in the present study show that in port region shipping emissions contributed 36.4 % SO_2, 0.7 % NO, 5.1 % NO_2, -0.9 % O_3, 5.9 % $PM_{2.5}$, 49.5 % Vanadium particles if land-based emissions were included, and 57.2 % SO_2, 71.9 % NO, 30.4 % NO_2, -16.6 % O_3, 27.6 % $PM_{2.5}$, 77.0 % Vanadium particles if land-based emissions were excluded.

Keywords

Shipping emission; Shanghai port; emission source contribution; SPAMS

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1 Introduction

Ship emission constitutes an important source of gaseous and particulate pollution world wide. It was estimated that, in global scale, shipping activities consumed about 2.76×10^8 tons fuels annually, emitting 20.8×10^6 tons NO_x, 9.7×10^6 tons SO_2,1.5×10^6 tons $PM_{2.5}$ and other pollutants (Johansson et al., 2017). These value were expected continue to grow in recent years. The growing shipping activities are attracting research efforts to assess its impact on environment and health issues (Fuglestvedt et al., 2009). For emissions from sea-going vessels in pristine marine environment, ship emissions was often found to affect clouds properties along the cruising routes of ships (Petzold et al., 2008;Coggon et al., 2012), which is relevant to alteration of climate patterns in regional or global scale. In portside or coastal regions, ship emissions could deteriorate the air qualities in these areas or cities at variant degrees (Donateo et al., 2014;Liu et al., 2017), exerting negative effects on the health of local residents (Corbett et al., 2007).

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

In Yangtze River Delta (YRD) region in China the shipping activities increase significantly due to intensified international trades in recent years. The accompanying potential environmental and health problems from shipping in YRD are well recognized (Fu et al., 2017;Zhang et al., 2017;Chen et al., 2018). Global distributions of ship emission indicate that South and Eastern China Sea region have the highest emission densities (Johansson et al., 2017). As shown in an emission inventory in China, shipping traffics emitted about 1.3 Tg SO_2, 1.9 Tg NO_x and 0.16 Tg PM in 2013, with NO_x and PM being equivalent to ~ 34 % and 29 % of total mobile vehicle emissions in China (Fu et al., 2017). To cope with severe air pollution caused by shipping emissions, Shanghai government has initiated Domestic Emission Control Areas (DECA) in YRD to control air pollution from shipping activities. At present stage, by way of DECA regulations in YRD, the sulfur content of 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.

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 constrain the uncertainties inherent to inventories or simulations studies, it is essential that the validation is compared with the actual measurement data (Zhao et al., 2013). In the summer of 2016, an in-site experimental characterization focusing on ship emissions were performed at Shanghai Port, which is the busiest and largest port in China. Gaseous and particulate matters concentrations were online monitored for 3 months to characterize and evaluate ship emissions in port areas. Based on the measurement data, quantitative assessment of the contribution from ship emissions on portside air quality was performed. Shipping emission aerosol particles were characterized by a single particle aerosol mass spectrometer (SPAMS) which was deployed at the same site to sample aerosol in parallel to the gaseous measurement. The SPAMS were utilized to identify ship emission aerosol composition and size with high temporal resolution, which is useful in detecting fast transient ship plumes, as previously demonstrated (Healy et al., 2009;Ault et al., 2010). In addition, the ship emission particle signatures obtained here is valuable in SPAMS source apportionment in future studies. The present study represents 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.

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. 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 in-port air monitoring station locates on the south bank of Yangtze River, 400 m away from the nearest dock. The outlets of main sampling tube, fixed on the roof of the station, are about 3.5m above the ground. To the south and west of site there are intense road traffics of container trucks in surrounding regions and the Shanghai outer ring. Traffic emissions in this direction have important influences to air pollution 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

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 also 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 PMTs. 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. 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 reflect signals from two PMTs are saved for each particle. A $PM_{2.5}$ cyclone was placed at the outlet of sampling tube to obtain the $PM_{2.5}$ cut-point before detection by SPAMS.

2.4 Data analysis

The high temporal resolution of SPAMS makes it very suitable to couple with online gaseous data to identify ship emissions. The quick fluctuations of gaseous concentrations, shifting of wind directions and the interception of particle plumes, were well registered in the high resolution measurement in SPAMS. In addition, present study takes advantage of the unique power of SPAMS to identify individual shipping emission particles based on mass spectral fingerprint. MS pattern of shipping emission particles were first identified and then were utilized to extract them out from all particles. The temporal trends, size distribution, chemical composition, and wind rose of the obtained 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 shipping emission particles from these total analysed 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 individual particle mass spectra to identify MS patterns of shipping emission particles during ship plumes. The concurrent SO_2 concentrations were utilized to locate ship emission plumes when sharp SO_2 peaks occurred, which is typical for RFO combustions (Murphy et al., 2009;Merico et al., 2016). Compared with non-plumes period, the most important diagnostic 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 as

detected previously in other port regions (Ault et al., 2009;Healy et al., 2009;Ault et al., 2010). In this study the Vanadium mass peaks (peak V^+(51) and VO^+(67))) were determined to be a prerequisite to indicate ship particles during plumes. Further explanation on this method of particle identification of shipping emission are provided 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 (Vigilance=0.85; Learning=0.05; Iteration=20) was applied to the searched clusters to generate sub-clusters of particles. 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.

3 Results and discussions

3.1 Identification and statistics of ship emission plumes

In the vicinity of port, the measured ship emission pollutants concentrations often produce sharp peaks in relatively short period (Fig. 2). The sharp peaks are produced by ship emission plumes corresponding to shipping activities such as arrival, hoteling and departure, which typically persist for a few 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 ship plumes. For comparison purpose the averaged SO_2 concentration in Shanghai city and Vanadium particle number concentration during the same period are presented. It is clear that, during plumes tracking period, the SO_2 concentration peaks were well correlated with Vanadium particles number concentration as detected by SPAMS. This result is consistent with previous characterizations studies in portside in other places (Healy et al., 2009;Ault et al., 2010;Merico et al., 2016). During the sampling period the SO_2 concentration in Shanghai city matched very well with port SO_2 concentration except periods during emission plumes. Inspecting the temporal trace lines of SO_2 in port and in urban Shanghai would suggest that the detected SO_2 concentrations in port could be effectively divided into background and regional concentrations which superimpose each other, as similarly noted in subsequent sections.

As typical combustion products, the NO and NO_2 concentrations also exhibit respective elevated concentrations during plumes under favourable wind fields (Fig. 2). However, during the study NO and NO_2 are influenced more strongly by land traffics emissions (mostly from transportation diesel trucks) when the inland wind prevails. Concentrations of NOx during shipping emission plumes suggest they have been slightly aged when reached the site. To understand the this 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 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 concentrations did not show apparent response as that of SO_2 during ship emission plumes, despite the typical

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Atmospheric Chemistry and Physics Discussions

Vanadium particles plumes had reached the site, as shown in Figure 2. The obscure response of $PM_{2.5}$ to ship plumes is explained by the fine particle sizes in relatively fresh shipping emissions, which will be discussed subsequently.

Taking into consideration of all the relevant factors, the present study defines ship plume periods by ways of SO_2 and Vanadium particle number concentrations. For SO_2, a minimum threshold of Δ_{SO2} = SO_2(Port)- SO_2(Shanghai) > 5 ug/m^3 is set to indicate ship plumes. For shipping emission particles, the number concentration of Vanadium particle is considered because in some cases the SO_2 peaks are absent or obscure as typical fresh Vanadium particles are indeed mount up quickly. This is probably caused by anchored ships using oil of low Sulfur 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 Vanadium particle detection speed in ship plumes are set to C_V > 25 particles/hour. That is, ship plumes are defined as either Δ_{SO2} > 5μg/m^3 or C_V>25 particles/hour.

In total about 210 shipping emission plumes were captured during the sampling campaign. Table 1 summarizes the statistics on pollutants concentration 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 atmosphere, 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-based emission sources (principally traffics), non-plume periods during wind from port directions 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 are comparable with that in Shanghai city, regardless of wind direction, which also indicate that a background SO_2 level exist. However, NO_X concentrations in non-plumes from port sector wind are significantly lower than from land directions. This differences suggests that shipping activities are the main emission source of SO_2 plumes in port. For NO_x, due to the specific geographic proximity of Waigaoqiao port, its concentrations were significantly influenced by land-based traffics. In general the O_3 concentrations in port are typically lower than Shanghai urban region by 13-33 %. The lower Ozone level around portside is consistent with higher SO_2 and NO_x concentrations in this area to consume O_3. For $PM_{2.5}$, its concentrations in port area are slightly lower than Shanghai city either in plume or non-plume periods, although Vanadium particles concentrations in plumes are about 4 times higher than in non-plumes (Table 1). Longer period of $PM_{2.5}$ data at the port station also indicate the lower $PM_{2.5}$ concentration compared to Shanghai city, suggesting that it is a general trend at this port site. This effect are supposed to be caused by the clean air advection from the sea and the wiping out effect of adjacent water surface through particle sedimentation. The Vanadium particle 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 %), as recently reported (Liu et al., 2017).

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Atmospheric Chemistry and Physics Discussions

3.2 Characterization of single particle properties from ship emissions

3.2.1 Background and fresh shipping emission particles in port

Particle size and chemical characterization from ship emission was performed by a SPAMS system (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). By using single particle characterization techniques, fresh or 'pure' ship emission particles can be separated from background or aged aerosol based on single particle signatures. It was observed that 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 exists in combustion source characterizations (Spencer et al., 2006;Toner et al., 2006). In another respect, the temporal pattern, wind rose and size of nitrate containing Vanadium particles were disproportionately distributed compared with fresh ones, which distinguished themselves as background ship emission particles (Healy et al., 2009;Ault et al., 2010) (Fig. 3). The 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 Vanadium (51V^+, 67VO^+) peaks, 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 OC is an important composition of ship emission particles (Lack et al., 2009), the organic mass peaks in SPAMS spectra are insignificant compared with metal and EC peaks. It maybe owing to the fact that SPAMS is not so sensitive to organic species due to the low ionization efficiencies in laser ionization (Ulbrich et al., 2009). However, there is indeed an organic cluster of particles were identified in ship plumes, although of minor number fractions, as discussed subsequently.

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

The size distributions of Vanadium particles as shown in Figure 4 indicates fresh Vanadium particles with dominate particle numbers in small size range (<0.5 um), compared with background ones. Although SPAMS detection efficiency declines in smaller size range because of the smaller section to reflect laser light, significant ultra-fine ship emission particles were still detected in this size range. The explanation is that these particles are geometrically non-spherical fractal agglomerates, such as the common shapes for BC particles, which having much larger reflecting cross sections for the sizing laser light and thus be detected in SPAMS. The non-spherical fractal shape of fresh Vanadium particles is typical for fresh combustion process

from other sources. Similar facts were also observed in other single particle mass spectrometer studies focused on ultra-fine size range (Ault et al., 2010).

The size distribution agrees with the sizes of ship emission particles measured in other places (Gonzalez et al., 2011;Merico et al., 2016). For ship exhaust their particle number contributions are more apparent than their mass contributions (Donateo et al., 2014;Jonsson et al., 2011;Merico et al., 2016). Size distribution of fresh particles from ship exhausts 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). Because the particle size and thus the mass of fresh exhaust particles are typically small, it is possible that for source characterization studies the PM loading in exhaust pipes would underestimate their contribution for real atmosphere. Since the secondary processing may occurred on every particle, in this sense that the importance of particle number concentrations in fresh emission plumes will outweigh their initial mass concentrations.

3.2.2 Particle types in fresh ship emission plumes

After the separation of background ship emission particles, fresh Vanadium particles could be identified and retrieved to represent fresh ship emission particles. Further analysis is performed to inspect their composition and emission characters, which will be helpful in particle source identification of SPAMS in future research. In general, the fresh Vanadium particles fall largely into 4 major 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 these four types are common in the dominating SO_4^- peak in addition to other negative EC peaks in spectra, which is consistent with the elevated SO_2 emission in ship emission plumes. The chemical characters of the four particle types are as depicted in Figure 5. In the positive mass spectra the V-OC type are dominated by OC peaks $C_2H_3^+$,$C_2H_5^+$, $C_2H_3O^+$, etc., with non or insignificant EC peaks. 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 Vanadium particles. The V-ECFe type is similar 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).

The chemical composition and size distribution of these four types suggest they have distinct physical properties (Fig. 6). Temporal trends of these 4 types show that their concentrations have diurnal patterns, with higher concentrations in daytime and lower in night-time. The inter-correlations among particle concentrations of the 4 types 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, are found to concentrate in specific cases of plumes. Because the information of individual ships is not yet available, it is therefore not attempt to directly link V-OC particle plumes to specific ship types in the present study. 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 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 um) (Fig. 6). It is noted that the measured aerodynamic size by SPAMS is both dependent 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 are probably the result of internal mixing between V-EC and V-Ash particles. Their size distribution is more similar 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 contributions on regional and local air quality is an important issue in assessing its environment impacts (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 $\mu g/m^3$, 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 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.

Due to its close proximity to urban region, the measurement site is under stronger 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 Vanadium particle numbers (Fig. 7). 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. On the contrary, the SO_2 concentrations and Vanadium particle numbers are dominant only

when winds from port sectors. The hotspots in wind rose of Vanadium particle are probably produced by individual docks along the riverside. The wind dependence of Ozone concentrations is less apparent, except showing depletion in regions of high NO_x and SO_2 levels in wind roses, as previously explained. 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 calculation method of ship contributions are based on the extraction of ship emission plumes from background concentrations of pollutants (Merico et al., 2016):

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

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. Shipping emission contributions of respective pollutants in two reference periods are summarized in Table 2.

As shown in Table 2, shipping emission contribution for SO_2 (36.4 %) are significantly larger than NO (0.7 %), NO_2 (5.1 %), and $PM_{2.5}$ (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 % Vanadium 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 Vanadium concentrations to indicate ship emissions. Considering the methodology differences, it is deemed that the results from the two studies are similar in the scenario that 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

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 Vanadium particles), SO_2 and Vanadium particles show the best responds to ship emission plumes. Using the SO_2 and Vanadium 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 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 Vanadium 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 % Vanadium 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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Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
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Atmospheric Chemistry and Physics Discussions

Figures

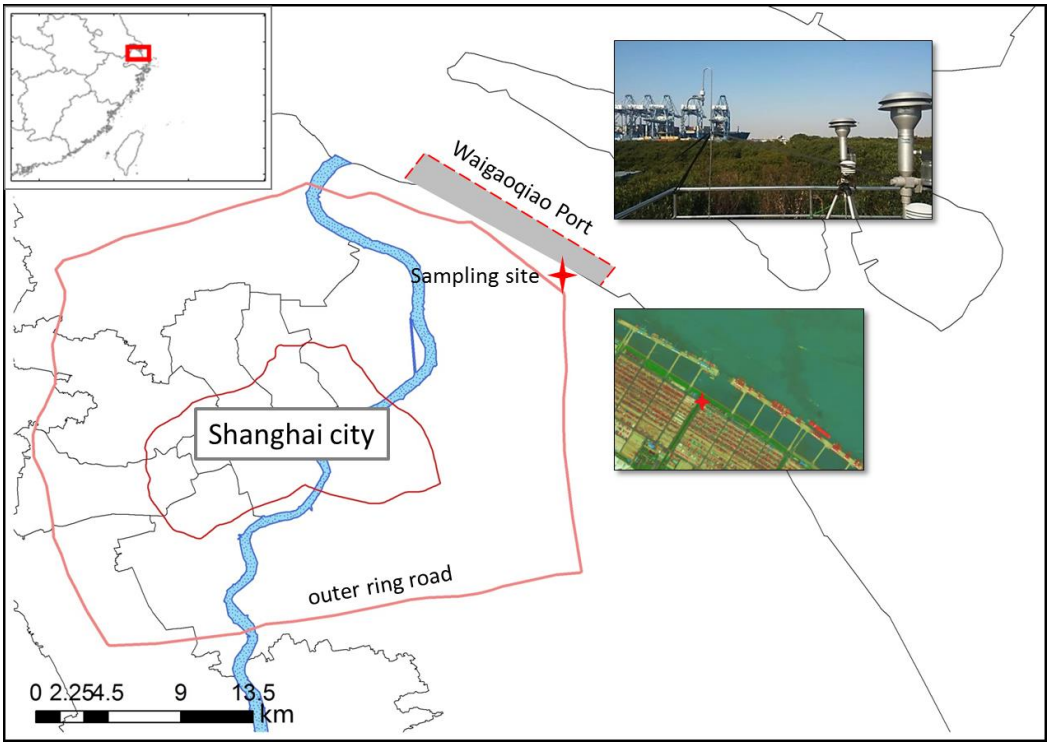

Figure 1: Map of sampling site in Shanghai port and surrounding areas. Port region is indicated by shaded area. The insets are the satellite image of the port site and photo taken on the roof of monitoring station seeing in port direction.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 21 August 2018

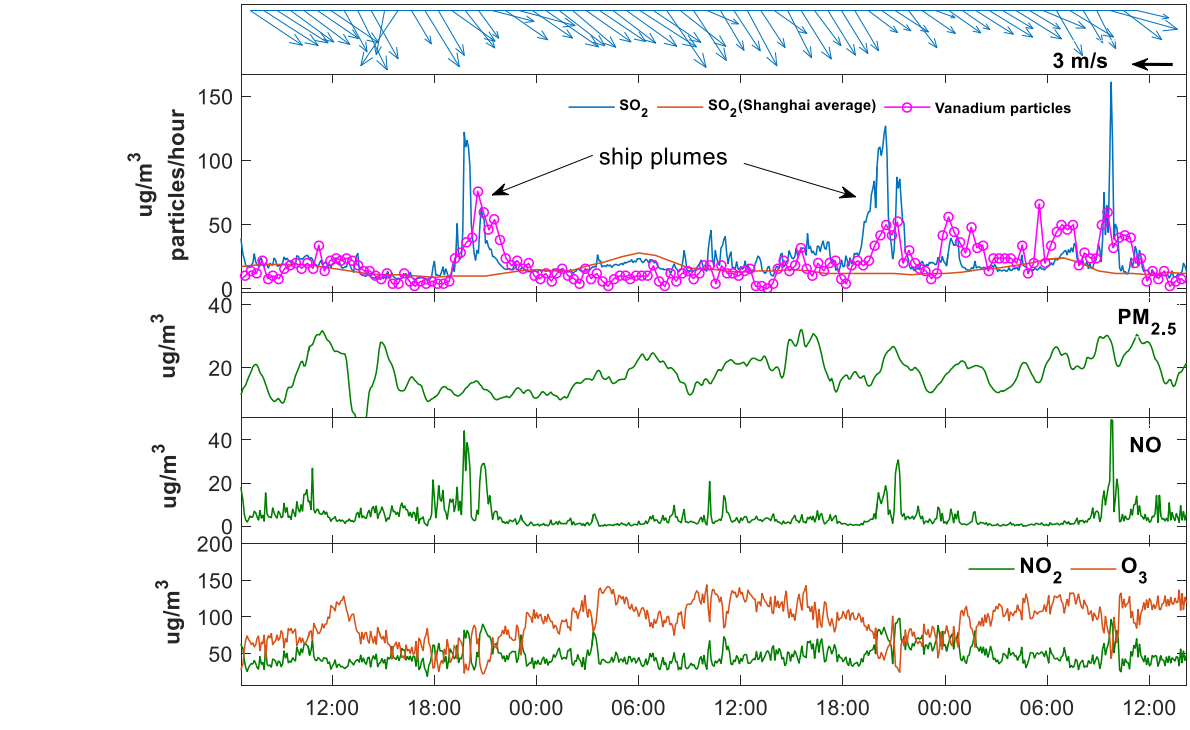

Figure 2: Temporal concentration of pollutants SO_2, NO, NO_2, O_3 and $PM_{2.5}$ during 27-29 August 2016. Contemporary wind direction and speed, SO_2 concentration of Shanghai city and Vanadium particles number concentration as detected by SPAMS are included as a reference.

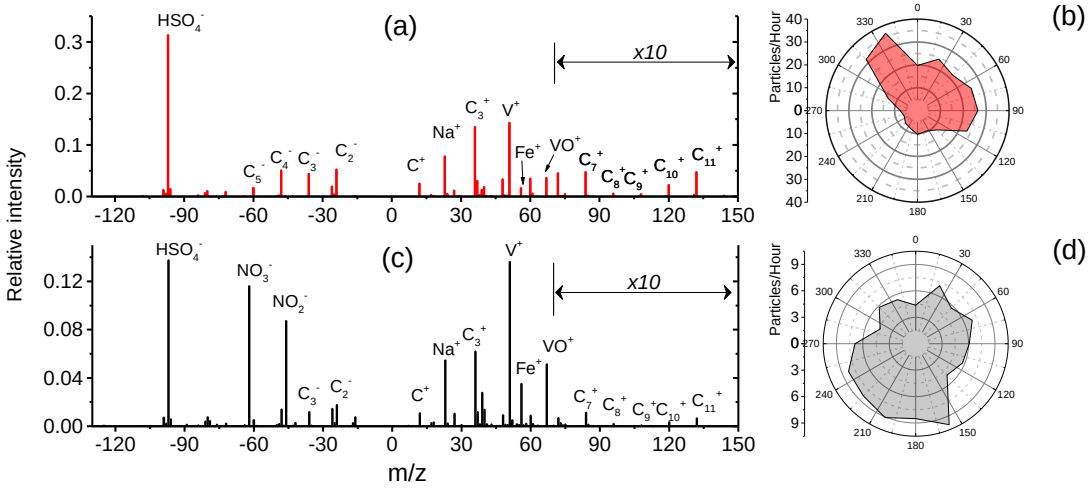

Figure 3: Mean mass spectra of fresh and background ship emission particles in port (a, c) and the wind rose of particle number concentration (in measure of particle number per hour) of these two particle types (b, d). Peaks in mass range of 70-150 in (a) and (c) are magnified by 10 times.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 21 August 2018

Atmospheric Chemistry and Physics Discussions

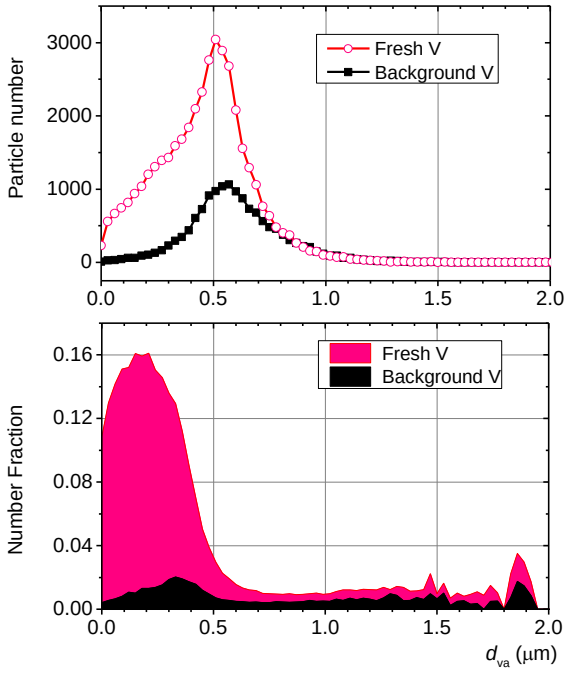

Figure 4: Particle number size distribution of fresh and background ship emission particles by SPAMS (Upper). Size distribution of these fresh and background types of ship emission particles normalized by total particles at each size (Lower).

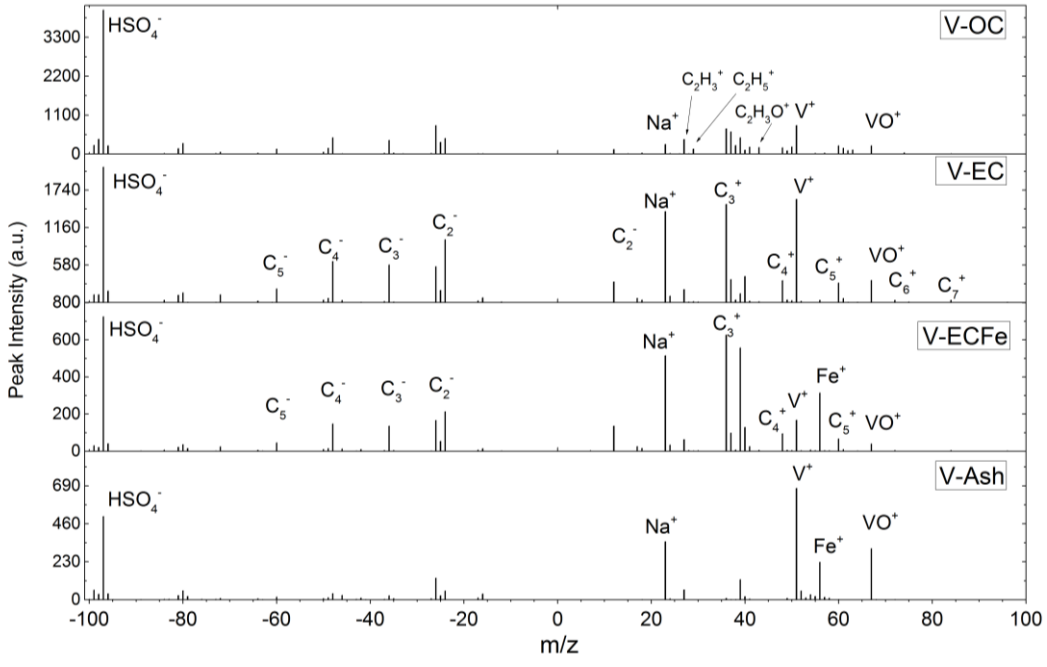

Figure 5: Mean mass spectra of four major particle types from fresh ship emission.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
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Discussion started: 21 August 2018

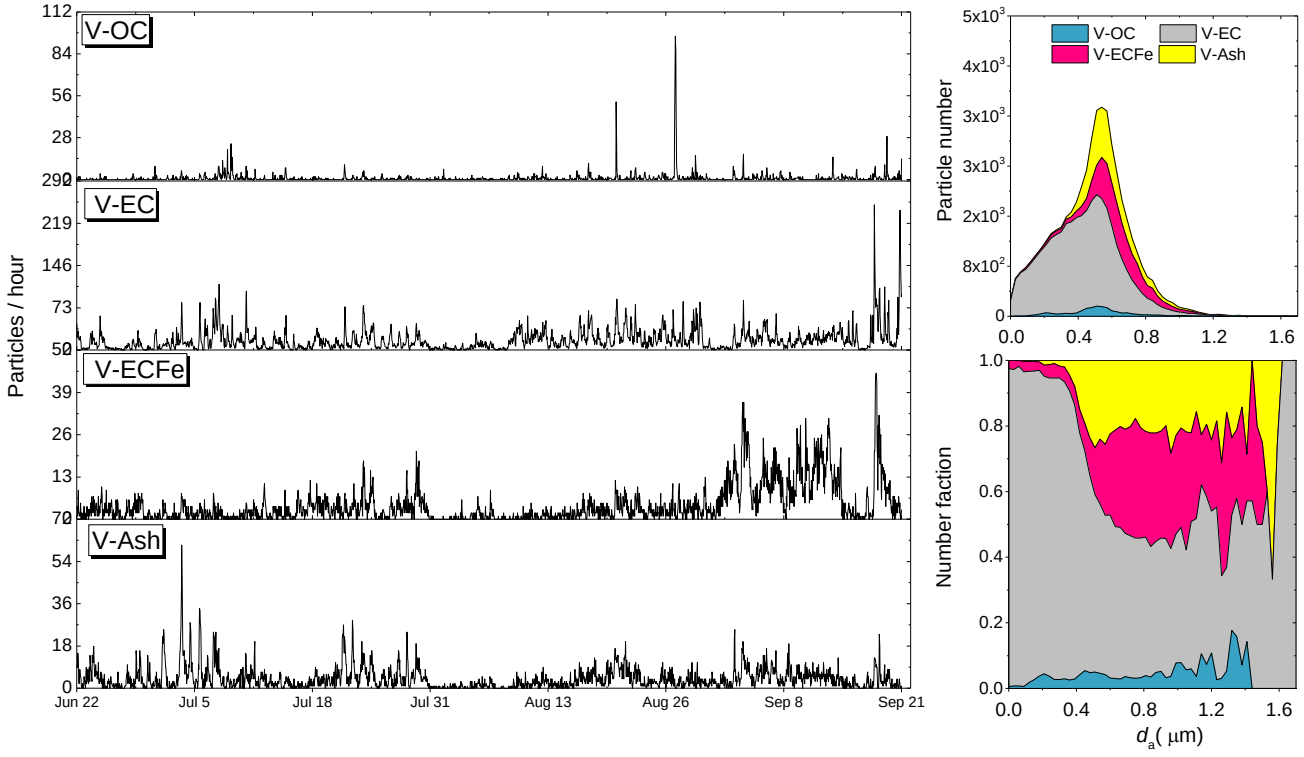

Figure 6: Temporal trend of number concentrations of four fresh Vanadium particle types (Left panel); the number (upper right) and number fraction (lower right) of four Vanadium particle types as a function of particle size.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
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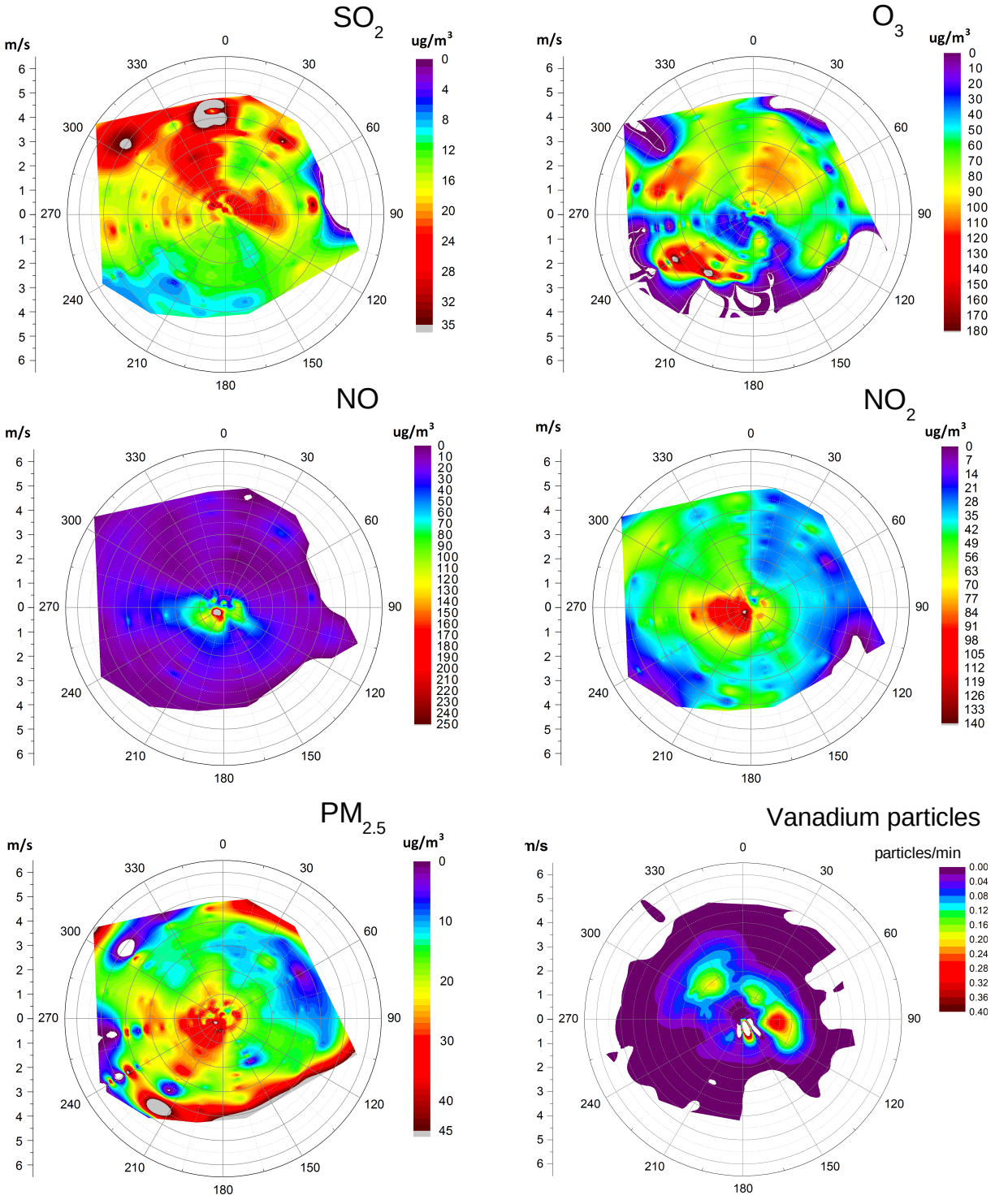

Figure 7: Pollution roses of SO_2, NO, NO_2, O_3, $PM_{2.5}$ and Vanadium particles during the entire study period. Vanadium particles wind rose is calculated based on number concentration measured by SPAMS.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-737
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Atmospheric Chemistry and Physics Discussions

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(ug/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(ug/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(ug/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(ug/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)
$PM_{2.5}$(ug/m^3)	30.2	(14.8~39.6)	25.1	(12.8~32.5)	19.6	(11.6~23.2)	26.7	(13.2~34.1)	31.4	(16~43)
Vanadium particles (#/hour)	47.6	(31~55)	10.9	(5~17)	12.3	(7~19)	22.8	(7~29)		---

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

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

Total 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