

Responses to Reviewer #1

We truly grateful for the reviewers' positive assessments of our manuscript and the helpful suggestions. We have revised the manuscript carefully according to the reviewers' comments. Point-to-point responses are given below, the original comments are black in color, while our responses are in blue. The line number are referred to the revised manuscript.

General comments

(1) Can the results be used to improve satellite retrievals over similar marine areas?

R: In general, the ship-based measurements are very helpful for the improvements of satellite retrievals over sea areas. For example, the ground-based data are rarely reported for the open oceanic areas, so there are lack of the validations for satellite products. Moreover, the ship-based MAX-DOAS results can provide the relatively actual vertical distributions of atmospheric aerosol and trace gases, which can be introduced into the retrieval scheme as the input parameters of forward radiative transfer model to improve the accuracy of satellite products over sea areas.

However, the spatial coverages of ship-based measurements are limited to the cruise track, which is insufficient compared to the satellites spatial resolution in this study. So it is difficult to directly assimilate the measured profiles by ship-based measurements to recalculate the AMF using for satellite SCD conversion to VCD in large scale. Nevertheless, we used the simulated profiles from WRF-chem model with a spatial resolution of $20\text{ km} \times 20\text{ km}$ to recalculate the AMF for satellite retrieval over the whole measurement areas. Consequently, the USTC's satellite products were confirmed more accurate than NASA's products in previous studies (Hong et al., 2018; Liu et al., 2016; Xing et al., 2017).

(2) Does this study prove that ship emissions in this area are stronger than previously assumed?

R: Generally, there could be two approaches to quantify the ship emissions using the

ship-based MAX-DOAS measurements. The first idea is the measuring of pollutants emission of individual ship and obtaining the data of ship numbers and activities for summation of the total emissions. In this study, the MAX-DOAS instrument has not been used to track the ship plume. So it's impossible to quantify the ship emission of single ship, suggesting that this approach is not suitable herein. Alternatively, the ship-based MAX-DOAS measurement can be used to encircle a sea area to quantify the emissions of this encircled area like the ground-based mobile vehicle-borne application. Then, the ship emission can be further determined by the difference between the fluxes entering and leaving the areas (Wang et al., 2012).

So we tried to quantify the ship emissions using the emission flux calculation method described in previous mobile DOAS studies (Shaiganfar et al., 2017; Shaiganfar et al., 2011; Wu et al., 2013). According the cruise track in Fig. 1(b), it is hard to find an encircled area during the campaign. So we selected the measurements on 27 June as a case study. As shown in Figure R1, we first assumed an encircled area, indicated with the black rectangle, along the ship track for emission estimation. The downwind boundary line of the area (marked by the letter c) were observed by ship-based measurements.

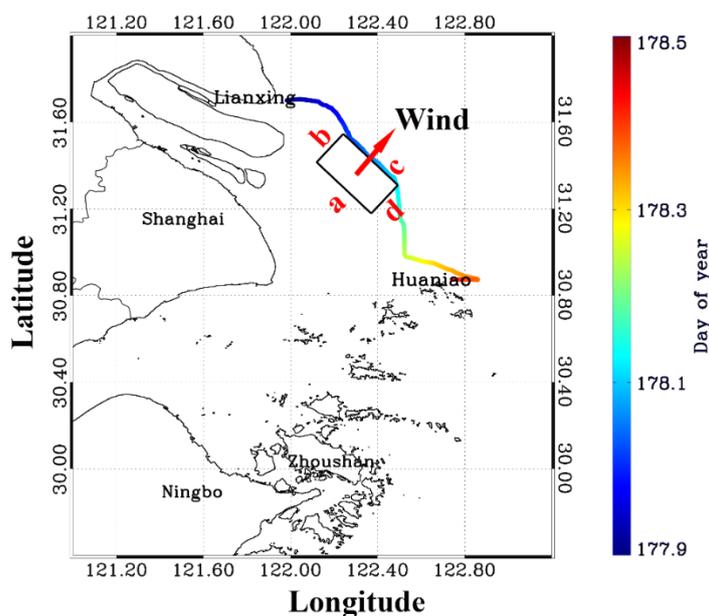


Figure R1. A sketch map of emission estimation, the colored line is the cruise track of ship-based measurements on 27 June 2017, while the black rectangle indicates an assumed encircled area with one boundary line (marked by the letter c) were observed by ship-based measurements.

The flux transported through this boundary can be achieved through the formula:

$Flux \approx \sum VCD_i \cdot \omega_i \cdot v_i \cdot \Delta t_i$, where ω is wind speed, v is ship speed. If the fluxes passed into the area from other boundary lines were not considered, the $Flux$ can be used to represent the emissions of this area but with significant overestimation.

Under this simplification and assumption, we have chosen a period of 1-hour ship-based measurements, corresponded to the travel distance of 14.4 km along the boundary (c). With an averaged wind speed of 2 m/s on 27 June, the emission results of NO₂ and SO₂ were estimated to be 9.19×10^{24} molec/s and 2.03×10^{24} molec/s for this assumed area (103.68 km²), respectively.

Compared to other studies, it can be found that the estimated emission of NO₂ (214.31 tonnes/yr/km²) and SO₂ (65.86 tonnes/yr/km²) are much higher than previous reported data for this sea area (Fan et al., 2016; Fu et al., 2017). Fu et al. (2017) have reported that the annual emission intensity of NO_x and SO₂ in the Yangtze River Delta (YRD) area (where the MAX-DOAS measurements were performed) were 3.76 and 2.78 Ton/km². The statistical average intensities of NO_x and SO₂ were 17 and 7.1 tonnes/yr/km² at the intersection hub of the coastal shipping lanes and the Yangtze River Channel, however, the highest regional emission intensities of NO_x and SO₂ can increase to 1.0×10^4 and 1.3×10^4 tonnes/yr/km², respectively (Fan et al., 2016).

Therefore, the observed ship emission by MAX-DOAS are relatively reasonable and comparable. The overestimations can be mainly explained by:

- (1) In this simplified pattern, the fluxes transported into the area have not been taken into account, which lead to the overestimations to some extent.
- (2) The ship emissions are concentrated in the ship lane and port areas, showing the obviously different emission intensities in spatial pattern. Due to the different areas of these researches, the comparison may result larger discrepancies.
- (3) Another possible reason could be that the different methodology of emission estimation also yields the systematic deviation.

According to the discussion above, it can prove that the MAX-DOAS method is applicable for the ship emission estimation in practical. However, the operations of

measurements and cruise need to be designed more delicate, if the ship-based MAX-DOAS is aiming to quantify the ship emission over oceanic area. For example, the cruise of ship-based measurements can be planned to encircle a sea area, and the telescope has been pointed to the ship smokestack for the scanning of emission plume.

(3) The scientific methods are described in detail, but I'm still a little confused about the MAX-DOAS retrieval. You describe two types of retrievals, a VCD retrieval based on a geometric AMF from one elevation angle (plus zenith for reference) and a more precise one based on optimal estimation using the full scan of 7 angles. If you have the time to perform full scans, why do you include the first VCD retrieval? Did you compare the two results, the VCDs from single elevation angles and VCDs derived from the profiles?

R: The geometric AMF approach is a simple and quick method to obtain the VCDs, which is also verified by optimal estimation method. Previous study shows that the results by these two methods were highly consistent, especially in marine environment, where the atmospheric boundary layer are usually very low (Schreier et al., 2015). As shown in Figure R2, we have compared the VCDs obtained by these two different ways. VCDs of NO_2 , SO_2 , and HCHO showed a good agreement between these two methods with a correlation coefficient R of 0.94, 0.76, and 0.93, respectively.

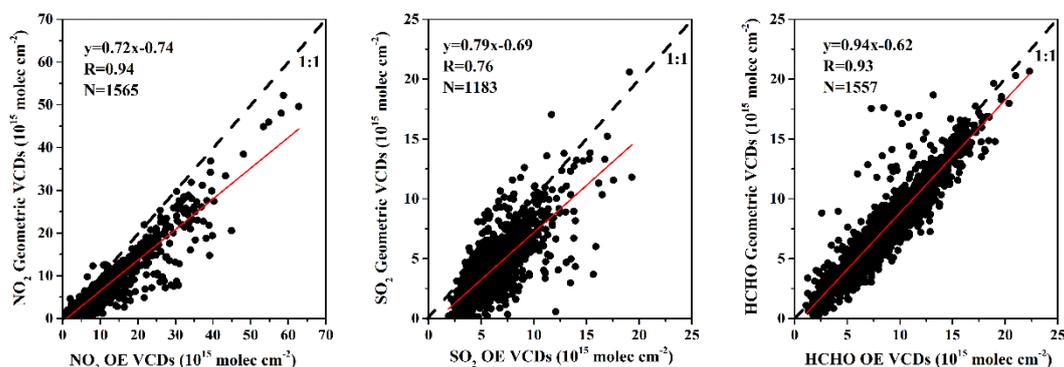


Figure R2. Comparison of (a) NO_2 , (b) SO_2 and (c) HCHO VCDs obtained by geometric AMF approach and derived from the profiles.

(4) The MAX-DOAS retrieval provides aerosol profiles as a first step to derive trace gas profiles. Did you look at the aerosol profiles as well? Do they justify using the trace

gas VCD retrieval based on the geometric AMF which doesn't account for aerosols? For the retrieval you calculate dAMFs anyway, why do you use a geometric approximation then?

R: As described in Section 2.2.3 of the manuscript, we used the HEIPRO algorithm for MAX-DOAS profile retrieval during this campaign, which is based on the Optimal Estimation Method (OEM, (Rodgers, 2000)). The retrieval algorithm takes into account the aerosol profile retrieval firstly and then adopts the retrieved aerosol scenario to profile the trace gases.

Since we focused on the trace gases in this paper, no aerosol retrieval results were presented. However, aerosol profile retrieval is the precondition of trace gases profile. We always take into account the aerosol profiles first. For example, Figure R3 shows the aerosol profiles corresponding to the three cycles in Figure 12 of the manuscript. The reason of using geometric AMF to obtain trace gases VCDs and the verification were also discussed above. Please refer to the responses to Q(3).

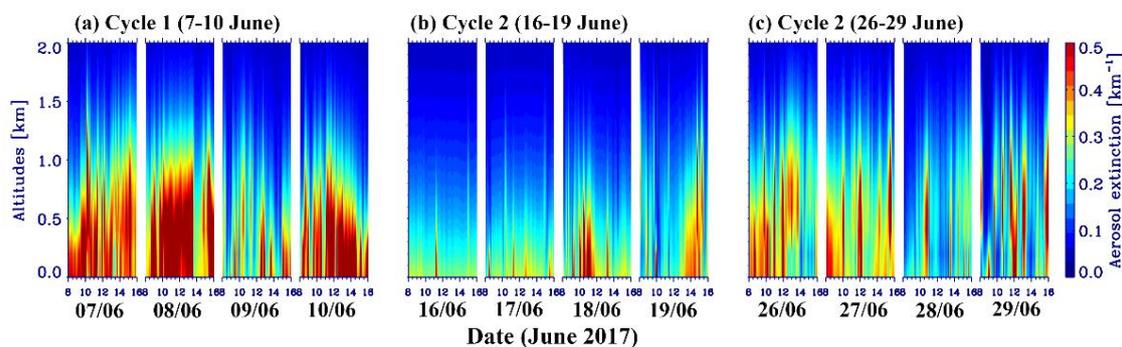


Figure R3. Vertical profiles of aerosol extinction during the three typical observation periods same as Fig. 12 in manuscript.

(5) Using only 2 elevations is typically used in a mobile setup when the concentrations change quickly, e.g. in traffic, and a full scan typically in a fixed setup where you have enough time under stable conditions to scan several elevations angles. Maybe you switch between the two scanning modes depending on what scenario is more appropriate?

R: The typical cruising speed of the measurements is about 5 m/s, and one full scanning sequence of 7 elevation angles takes about 4 min. So the travel distance during one

sequence is about 1.2 km. Considering the relatively short time period and distance, it can be treated as a stable condition. So we just used this multi-elevation angles scanning mode in the campaign.

(6) Your spectrometer covers the range 300-460 nm, why don't you use the 400-460 nm wavelength range for the NO₂ retrieval, where NO₂ has pronounced absorption structures and is less influenced by O₃ absorption?

R: As we all know, the pronounced NO₂ absorption structures cover large wavelength range, so the NO₂ DSCD can easily be retrieved in the wavelength interval of 338-370 nm too. In addition, the O₄ has strong absorption peaks at 360.8 nm, which can be covered by the fitting window of 338-370 nm. NO₂ and O₄ fitting in same wavelength range is convenient for the further NO₂ profile retrieval, which is based on the aerosol information retrieved by O₄ DSCD. Besides, the range 338-370 nm is also widely employed for O₄ and NO₂ retrieval together in previous DOAS studies (Hong et al., 2018; Johansson et al., 2008; Roscoe et al., 2010; Wu et al., 2018).

Here, we also analyzed the NO₂ DSCDs in the fitting window of 400-460 nm. Figure R4 presents the comparison of the NO₂ DSCDs retrieved in 338-370 nm and 400-460 nm wavelength range. The results of two different fitting windows agreed very well with each other, showing a high correlation coefficient R of 0.986 and the slope is 0.98.

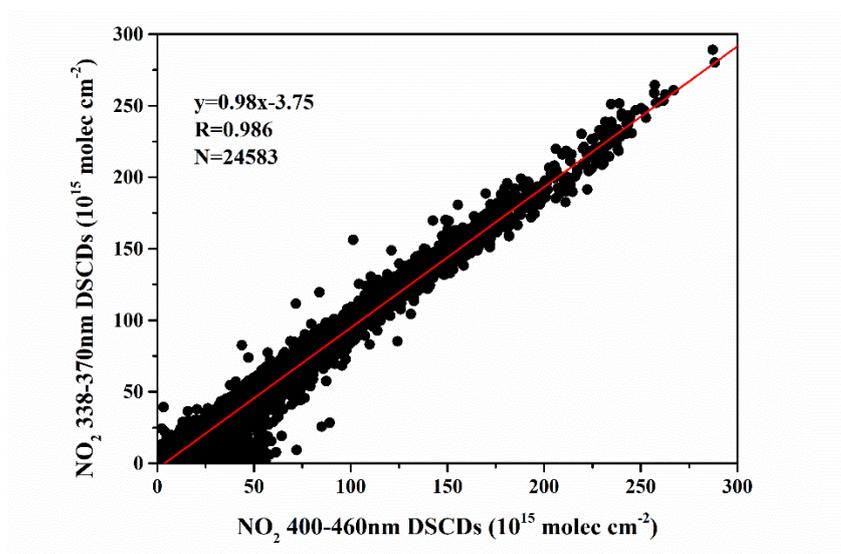


Figure R4. Comparison of NO₂ DSCDs retrieved using 338-370 nm and 400-460 nm wavelength ranges.

Technique corrections

- ① page 2, line 56 “quantify kinds of the atmospheric trace gases” -> “quantify different kinds of atmospheric trace gases” (that sounds more fluent to me, but it’s just a suggestion)
- ② page 2 line57 “Based on the DOAS principle, the quantitative of the trace gases was acquired from the narrow band absorption structures of the different trace gases, which were separated from the broad and parts caused primarily by the atmospheric scattering and their broad band absorption (Platt and Stutz, 2008)” -> “The DOAS principle makes use of the fact that narrow trace gas absorption structures can be separated from broad band absorption and atmospheric scattering (Platt and Stutz, 2008)” (or something like that)
- ③ page 2 line 59 “The named Multi-AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument is designed ...”-> “The Multi-AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument is designed ...”
- ④ page 3 line 69 “...trace gases concentrations...” -> “...trace gas concentrations...”
- ⑤ page 4 198 “The cruise of ship-based observation” -> maybe just “The measurement cruise”
- ⑥ page 4 line99 “The ship-based measurements campaign” -> “The ship-based measurement campaign”
- ⑦ page 12 line254 “...impacted by the airflows transport...” -> “...impacted by airflow patterns...”
- ⑧ page 12 line258 “...showed the air masses were came from inland area...” -> “...showed the air masses coming from inland areas...”
- ⑨ line 272 “These two data sets time agreed well...” -> “These two data sets time agree well...”

R: We have followed these suggestions and corrected the mistakes accordingly.

Reference:

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Responses to Reviewer #2

We really appreciate the reviewers for the valuable and constructive comments, which are very useful for the improvement of the manuscript. We have replied the reviewers' comments point-to-point in below. The reviewers' comments are cited in black, while the responses are in blue. All the line number are referred to the revised manuscript.

(1) What's the purpose of comparison between ground measurements and satellite retrieval here? In line 396 of section 4, the authors said "In order to validate the ship-based MAX-DOAS measurements...", however, satellite retrieval of trace gases have considerable uncertainties.

R: The unsuitable expression may lead to the confusion. The comparison between ship-based measurements and satellite retrieval can validate with each other. The ground-based data were commonly compared with satellite products in previous studies, however, the satellite products over marine areas were rarely validated by ground-based methods. In this study, the comparison between ship-based measurements and satellite data are aiming to provide validation of spaced observation over marine areas. We have re-phrased the sentence. Please refer to Line 418 to 420.

(2) Line 267, 10 km radius of location of ship-based measurements is selected to match with satellite pixel, but the satellite pixel especially the OMPS is much larger than this scope, how realize it?

R: The size of OMPS pixel is about $50 \times 50 \text{ km}^2$, which is indeed too large for the comparison. In this study, the OMPS satellite products were firstly gridded in a high spatial resolution of $0.05^\circ \times 0.05^\circ$, as described in Line 299 of the manuscript. For the typical cruising speed of 5 m/s, the travel distance is about 18 km within one hour (13:00-14:00 LT cover the satellites overpass time). To keep the consistency of temporal and spatial coverages, the area with the center of central longitude and latitude of ship-based measurements between 13:00 and 14:00 LT and radius of 10 km was chosen to average the satellite results.

(3) The current data analysis did not well support the authors' conclusion robustly. Daily satellite observation can provide regional view of the distribution of gaseous pollutants, why the authors only show monthly data? How did the daily satellite data compare with of daily values of in the track of ship-based measurements? To reveal the transport and air pollution over sea, typical daily case is suggested.

R: Considering the ship-based measurements were carried out for almost a whole month from 2 to 29 June 2017 and satellite data are occasionally absent for some days, we presented the monthly averaged satellite results to reveal the general spatial distributions during the ship-based measurements. For the daily comparison, we presented the time series and correlation analysis of the satellite data and ship-based measurements in Figure 6 to 8 of the manuscript. High correlation coefficient R of 0.83, 0.76 and 0.69 were reported for NO₂, SO₂, and HCHO, respectively.

To follow the suggestion, some typical daily cases of NO₂ VCDs observed by these two instruments were shown in Figure R1. These two measurements and wind filed (black arrow) were overlapping plotted together, where the trajectories of ship-based measurements were indicated with the white lines and the central position of ship-based measurement during 13:00 to 14:00 LT were marked by black points.

It can be observed that these two data sets were highly consistent in the spatial distributions. Combining with the wind direction information, the air masses came from clean sea areas on 2 and 16 June, whereas originated from polluted inland areas on 7 and 27 June. Therefore, the observed NO₂ VCDs are substantially lower on 2 and 16 June compared to measurements on 7 and 27 June. Under the cleaner air masses from sea area, the hot spots of NO₂ pollution on 2 and 16 June are mainly located in the inland areas and some oceanic areas with strong ship emissions, which is blamed to local emissions. When the wind came from the polluted continental area, the NO₂ pollution spread from inland to the sea areas close to the coastal line on 7 and 27 June. It suggests that the air quality over sea areas were significantly influenced by pollutants transported from inland areas and even for the sea areas far from the coastal line.

The discussion about the daily case of air pollution transports was also added in the

manuscript. Please refer to Line 312 to 330.

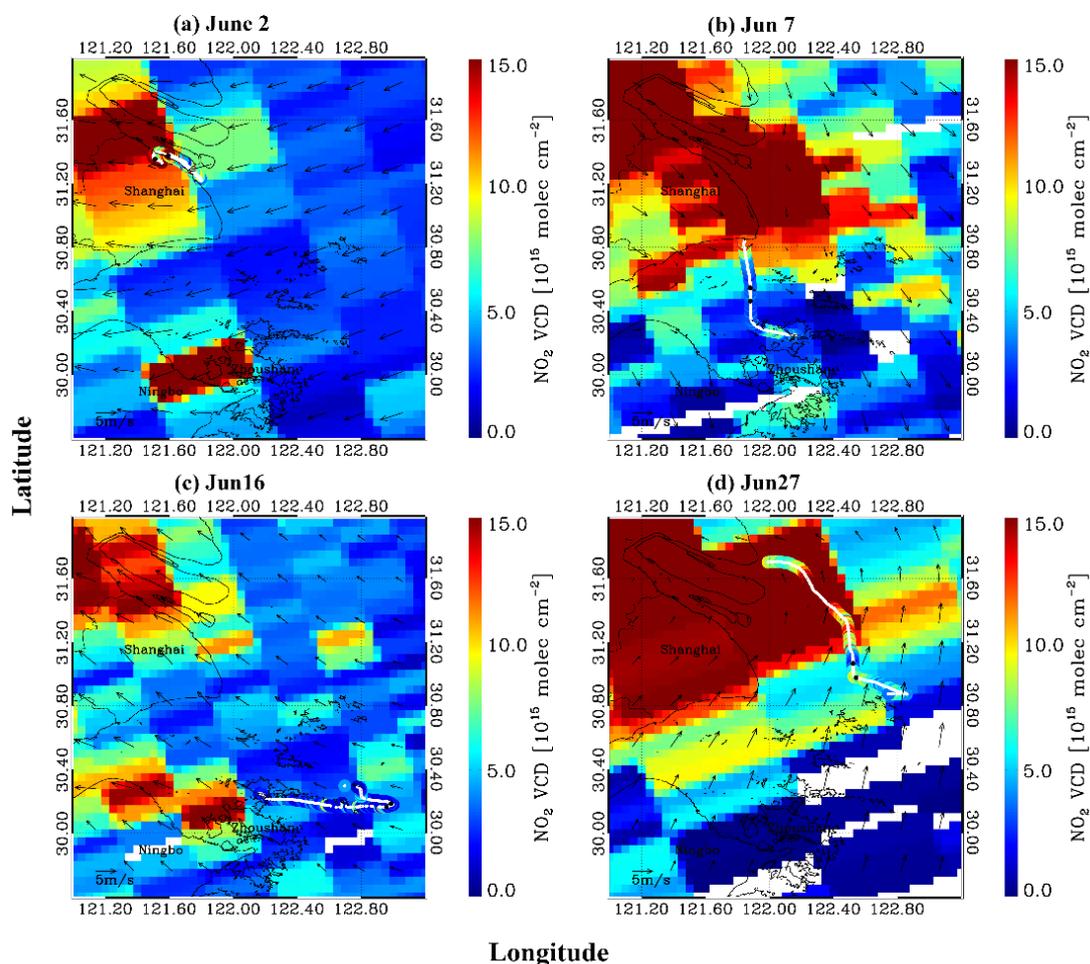


Figure R1. Comparison of OMI and ship-based measured NO₂ VCDs on (a) 2, (b) 7, (c) 16, and (d) 27 June. The ship-based measurements were plotted overlap in the base map of OMI products, and the wind field were indicated with black arrows.

(4) It is important for the authors to clarify and emphasize what's new in their work and what's their new finding?

R: The novelty of this study were highlighted in the introduction and conclusion parts of the manuscript. It can be briefly summarized as: the ship-based MAX-DOAS measurements were first performed in the Eastern China Sea (ECS) area, and the typical trace gases spatial distribution were characterized. Meanwhile, the ship-based measurements are compared with satellite productions which is useful to validate the satellite retrieval in marine areas. The spatial distribution of these pollutant gaseous

suggests that the air quality of the marine boundary layer in the ECS are mainly impacted by the air masses originated from the polluted inland areas and the local ship emissions. We also reported the vertical structure of NO₂, SO₂, and HCHO in the ECS area. High concentration pollutants were identified in the sea areas of important ports and channels, which is related to the shipping emissions. Combining with the on board O₃ lidar instrument, we have discussed the O₃ formation process over marine areas. This study provided further understanding of the main air pollutants in the marine boundary layer of the ECS area.

Tropospheric NO₂, SO₂, and HCHO over the East China Sea, using ship-based MAX-DOAS observations and comparison with OMI and OMPS satellites data

Wei Tan¹, Cheng Liu^{1,2,3,6,*}, Shanshan Wang^{4,5,*}, Chengzhi Xing², Wenjing Su², Chengxin Zhang², Congzi Xia², Haoran Liu², Zhaonan Cai⁷, Jianguo Liu¹

¹Key Lab of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, China

²School of Earth and Space Sciences, University of Science and Technology of China, Hefei, 230026, China

³Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

⁴Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP³), Department of Environmental Science and Engineering, Fudan University, Shanghai, 200433, China

⁵Shanghai Institute of Eco-Chongming (SIEC), No.3663 Northern Zhongshan Road, Shanghai, 200062, China

⁶Anhui Province Key Laboratory of Polar Environment and Global Change, USTC, Hefei, 230026, China

⁷Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, Beijing 100029, China

*Correspondence to: Shanshan Wang (shanshanwang@fudan.edu.cn), Cheng Liu (chliu81@ustc.edu.cn)

Abstract. In this study, ship-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements were performed in the Eastern China Sea (ECS) area in June 2017. The tropospheric Slant Column Densities (SCDs) of nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and formaldehyde (HCHO) were retrieved from the measured spectra by the Differential Optical Absorption Spectroscopy (DOAS) technique. Using the simple geometric approach, the SCDs of different trace gases observed at 15° elevation angle were adopted to convert into tropospheric Vertical Columns Densities (VCDs). During this campaign, the averaged VCDs of NO₂, SO₂, and HCHO in the marine environment over ECS area are 6.50×10^{15} molec cm⁻², 4.28×10^{15} molec cm⁻² and 7.39×10^{15} molec cm⁻², respectively. In addition, the ship-based MAX-DOAS trace gases VCDs were compared with satellite observations of Ozone Monitoring Instrument (OMI) and Ozone Mapping and Profiler Suite (OMPS). The daily OMI NO₂ VCDs agreed well with ship-based MAX-DOAS measurements showing the correlation coefficient R of 0.83. Besides, the good agreements of SO₂ and HCHO VCDs between the OMPS satellite and ship-based MAX-DOAS observations were also found with correlation coefficient R of 0.76 and 0.69. The vertical profiles of these trace gases are achieved from the measured Differential Slant Column Densities (DSCDs) at different elevation angles using optimal estimation method. The retrieved profiles displayed the typical vertical distribution characteristics, which exhibits the low concentrations of < 3, < 3, and < 2 ppbv for NO₂, SO₂, and HCHO in clean area of the marine boundary layer

35 far from coast of the Yangtze River Delta (YRD) continental region. Interestingly, elevated SO₂ concentrations can be observed
intermittently along the ship routes, which is mainly attributed to the vicinal ship emissions in the view of the MAX-DOAS
measurements. Combined with the on-board ozone lidar measurements, the ozone (O₃) formation was discussed with the
vertical profile of HCHO/NO₂ ratio, which is sensitive to the increases of NO₂ concentration. This study provided further
understanding of the main air pollutants in the marine boundary layer of the ECS area and also benefited to formulate the
40 policies regulating the shipping emissions in such costal area like YRD region.

1 Introduction

Nitrogen dioxide (NO₂), sulfur dioxide (SO₂) and formaldehyde (HCHO) are the important atmospheric trace gases which play
a major role in the atmospheric chemical processes. NO₂ participates in the formation of ozone (O₃) and reacts with hydroxyl
radicals (OH), the strongest oxidizing agent in the atmosphere, to produce aerosols and acid rain, which are harmful to both
45 buildings and human health (Seinfeld and Pandis, 2006; Lelieveld and Dentener, 2000; Lelieveld et al., 2002). NO₂ may also
has important impacts on the greenhouse effect (Solomon et al., 1999). Besides natural sources, high-temperature combustion
processes, e.g. fossil fuel burning, accidental and intentional biomass burning, are estimated to contribute the major emissions
of nitrogen oxides (NO_x=NO₂+NO) (Lee et al., 1997). SO₂ contributes to the formation of sulfate aerosols and acid rain, both
of which have negative effects on the climate and human health, as well as lead to building acid corrosion (Hutchinson and
50 Whitby, 1977; Pope and Dockery, 2006; Longo et al., 2010). The dominant anthropogenic emissions of SO₂ are the burning of
fossil fuels, smelters, and oil refineries, whereas the discharge of active volcanoes is the major natural source. HCHO is the
predominant product of the oxidation of many Volatile Organic Compounds (VOCs) by OH radical and is abundant throughout
the atmosphere. Therefore, elevated HCHO levels can be related to the emission of reactive Non-Methane Volatile Organic
Compounds (NMVOCs) originating from biogenic, pyrogenic or anthropogenic sources (Fu et al., 2007; Millet et al., 2008;
55 Stavrakou et al., 2009a; 2009b).

The Differential Optical Absorption Spectroscopy (DOAS) technique is widely used to identify and quantify different kinds
of the atmospheric trace gases. The DOAS principle makes use of the fact that narrow trace gas absorption structures can be
separated from broad band absorption and atmospheric scattering~~Based on the DOAS principle, the quantitative of the trace
gases was acquired from the narrow band absorption structures of the different trace gases, which were separated from the
60 broad band parts caused primarily by the atmospheric scattering and their broad band absorption~~ (Platt and Stutz, 2008). The
~~named~~ Multi-AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument is designed to observe scattered
sunlight under different viewing angles closed to the horizontal and the zenith direction, which can provide high sensitivity to
tropospheric aerosols and trace gases (Hönninger et al., 2004). In the past decades, the MAX-DOAS method has been
successfully used for many atmospheric trace gases observation on different platforms, such as NO₂, SO₂, HCHO, HONO and

65 others. The most common application is ground based measurement (e.g. Irie et al., 2011; Pinardi et al., 2013; Wang et al., 2014; Chan et al., 2015; Xing et al., 2017). Meanwhile, the mobile platform observations has been developed rapidly, e.g. car-based observations (Johansson et al., 2008; Shaiganfar et al., 2011; Wang et al., 2012; Shaiganfar et al., 2017), aircraft-borne observations (Baidar et al., 2013; Dix et al., 2016), and ship-based observations (Sinreich et al., 2010; Takashima et al., 2012; Peters et al., 2012; Schreier et al., 2015; Hong et al., 2018).

70 Usually, the trace gasesgas concentrations are very low in remote marine environments considering there are no emission sources except the ship traffic and some other natural sources. Previous ship-based MAX-DOAS studies reported that NO₂ Vertical Column Densities (VCDs) were basically low ($< 0.50 \times 10^{15}$ molec cm⁻²) due to the absence of obvious NO_x emission sources nearby, and the NO₂ concentrations in marine boundary layer extracted from profile retrieval are < 30 pptv in the open and clean tropical sea area of the South China and Sulu Sea (Schreier et al., 2015). Times series of SO₂ magnitudes were found
75 to be consistent with tropospheric NO₂ over there and occasionally increased if the measurements taken in a busy shipping lane. Over western Pacific and Indian Ocean area, the background value of NO₂ concentration was less than ~ 0.2 ppbv over the remote ocean (Takashima et al., 2012). Peters et al. (2012) found that HCHO VCDs over the remote ocean exhibit a diurnal pattern with maximum values of 4×10^{15} molec cm⁻² at noontime over the western Pacific Ocean, and corresponding retrieved peak concentrations were up to 1.1 ppbv at higher altitudes around 400 m. However, these pollutants concentrations increased
80 to a high value when the measurements were taken close to the shore, busy ports, or vessels (Takashima et al., 2011; Peters et al., 2012; Schreier et al., 2015). So far, the air quality of marine boundary layer in the China coastal area are rarely reported.

In this study, we used the ship-based MAX-DOAS measurements to report the column densities and temporal-spatial distributions of NO₂, SO₂, and HCHO in the marine environments over the East China Sea (ECS) area in June 2017. During this campaign, the cruise ship mainly navigated at the sea area surround Yangtze River Delta (YRD) region, which is the
85 confluence of the coastal shipping routes and inland water transportation on the Yangtze River. It is the busiest waterways of the ECS area and also the one of the three key Ship Emission Control Zones (ECZs) of China. The YRD coastal port cluster is composed of >15 ports, of which Shanghai and Ningbo-Zhoushan have served as the largest two container ports in the world since 2013. With the flourish shipping industry, the throughputs of YRD ports strikes the new highs continuously and caused the considerable ship emissions of SO₂, NO_x and PM_{2.5}, which has significant impacts ~~to~~on the local and regional air pollution
90 in both offshore and inland area of YRD region (Fan et al., 2016; Zhang et al., 2017). Due to the rapid development of urbanization and industrialization, as well as expanding population, the continental YRD region also suffered from the ecological degradation and environmental problems at the same time, e.g. atmospheric fine particle and O₃ pollution (Chen et al., 2017; Song et al., 2017).

In this paper, both the VCDs and vertical distributions of NO₂, SO₂ and HCHO from ship-based MAX-DOAS measurements,
95 as well as the ozone profiles from on-board lidar, have been firstly reported for the ECS area covering the Yangtze River

Estuary and surrounding YRD region waters. The spatial distributions of these gaseous pollutants by ship-based measurements were compared to satellite observations, and further used to discuss the air pollutant transports between continental and sea areas. Moreover, ozone formation over sea area was investigated. These observed data sets are vital for the better understanding of the air quality in marine boundary layer along the coastline of China and helpful for regulating the air pollution in coastal area.

2 Methodology

2.1 The measurement ~~cruise of ship-based observation~~

The ship-based measurements campaign was implemented over the offshore marine area of the ECS covering the Yangtze River Estuary and YRD region coast in summer from 2 to 29 June, 2017 (Fig. 1(a)). Before the departure, measurement instruments were installed and debugged at Gongqing port (point A in Fig. 1(b), 31.33° N, 121.55° E) of Shanghai on 1 June 2017. As indicated in Fig. 1(b), the ship set sail on 2 June 2017 from Gongqing port by way of Yangshan port (B, 30.62° N, 122.09° E), and Daishan islands (C, 30.25° N, 122.16° E) and Hagnzhou Bay area. After encircled Zhoushan islands (29.99° N, 122.20°), the ship moved forward to Shengsi islands (D, 30.71° N, 122.45° E) and Huaniao islands (E, 30.85° N, 122.68° E). Then, the ship was heading to Lianxing port in Jiangsu Province (F, 31.72° N, 121.87° E) and passing through Huaniao islands finally back to Gongqing port on 29 June, 2017. As shown in Fig. 1 the ship cruise routes not only covered the busy waters in YRD region but also passed ed though some clean marine area 100 km away from the continental coast.

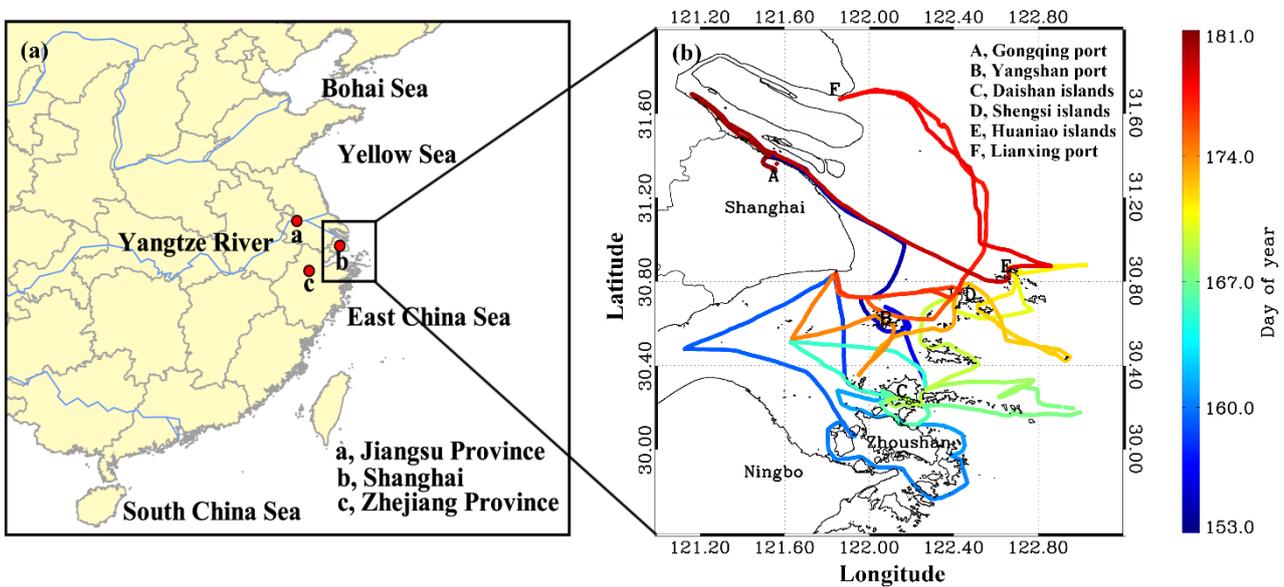


Figure 1. Location (a) and cruise routes (b) of the ship-based d campaign from 2 to 29 June, 2017 (DOY 153 to 181).

2.2 Ship-based MAX-DOAS measurements

2.2.1 Instrument setup

An integrated and fully automated MAX-DOAS instrument was fixed on a 1.5 m height tripod top at the stern deck of the ship. This compact instrument consists of an ultraviolet spectrometer (AvaSpec-ULS2048L-USB2) covering the spectral range of 300-460 nm with a spectral resolution of 0.6 nm, a one-dimensional CCD detector (Sony ILX511, 2048 individual pixels) and a stepper motor driven the telescope to collect scattered sunlight from different elevation angles (angle between the horizontal and the viewing direction, α). Besides, the controlling electronic devices, connecting fiber, and other necessary devices are mounted inside too. To avoid the impact of emission plums from the ship itself, the azimuthal angle of the telescope unit kept at 130° relative to the heading direction of the observation ship. The telescope was scanning in the sequence of elevation angles of 3°, 5°, 7°, 10°, 15°, 30°, and 90°. The duration of an individual spectrum measurement was about 30 s and the each scanning sequence took about 4 min. The daily measurements were automatically controlled by a built-in computer combined with a spectral collection software when the Solar Zenith Angle (SZA) less than 75°. Moreover, a high-precision Global Position System (GPS) data receiver was configured to record the real-time coordinate positions and the track the ship cruise.

2.2.2 Spectral analysis

Based on the DOAS principle, the measured scattered sun-light spectra are analyzed using the QDOAS spectral fitting software suite developed by BIRA-IASB (<http://uv-vis.aeronomie.be/software/QDOAS/>). The detailed configuration of spectral fitting are listed in Table 1. The fitting wavelength interval of NO₂, O₄, SO₂ and HCHO are 338-370 nm, 338-370 nm, 305-317.5 nm and 336.5-359 nm, respectively. Trace gases absorption cross sections of NO₂ at 220 K, and 298 K (Vandaele et al., 1998), SO₂ at 298 K (Vandaele et al., 2009), HCHO at 297 K (Meller and Moortgat, 2000), O₃ at 223 K and 243 K (Serdyuchenko et al., 2014), O₄ at 293 K (Thalman and Volkamer, 2013), BrO at 223 K (Fleischmann and Hartmann, 2004), the Ring spectrum, a Fraunhofer reference spectrum and a low order polynomial are included in the DOAS fitting. The wavelength calibration was performed using a high resolution solar spectrum (Chance and Kurucz, 2010). Dark current spectrum and electronic offset spectrum were used to correct measurement spectra before the spectra analysis.

Table1. DOAS spectral fitting of NO₂, O₄, SO₂, and HCHO

Parameter	Data source	Trace gases		
		NO ₂ & O ₄	SO ₂	HCHO
Wavelength range		338-370 nm	305-317.5 nm	336.5-359 nm
O ₄	Thalman and Volkamer (2013), 293K	√	×	√
NO ₂	Vandaele et al. (1998), 220K, 298K, I ₀ - correction (10 ¹⁷ molec cm ⁻²)	√	√(only 298K)	√(only 298K)
SO ₂	Vandaele et al. (2009), 298K	×	√	×
HCHO	Meller and Moortgat (2000), 297K	√	√	√

O ₃	Serdyuchenko et al. (2014), 223K, 243K, I ₀ - correction (10 ²⁰ molec cm ⁻²)	√	√	√
BrO	Fleischmann et al. (2004), 223K	√	√	√
Ring	Ring spectra calculated with QDOAS according to Chance and Spurr (1997)	√	√	√
Polynomial degree		5	5	5
Wavelength calibration	Based on a high resolution solar reference spectrum (SAO 2010 solar spectra)			

The spectral analysis yields the measured Slant Column Densities (SCDs), the integrated trace gas concentration along the light path through the atmosphere. For MAX-DOAS spectral analysis, the measured spectrum at 90° was selected as the Fraunhofer reference spectrum for the DOAS fitting of the measured spectra at other elevation angles in each scan sequence. So the generated results are the difference of the SCDs between the measured spectrum and that of the Fraunhofer reference spectrum, usually referred as Differential Slant Column Densities (DSCDs). Figure 2 shows a typical DOAS spectral fitting of the measured spectrum collected at elevation of 15° at 10:13 Local Time (LT) on 7 June 2017. The retrieved DSCDs of NO₂ (Fig. 2a), O₄ (Fig. 2b), SO₂ (Fig. 2c), and HCHO (Fig. 2d) are 2.28×10^{16} , 1.90×10^{43} , 1.84×10^{16} , and 4.46×10^{16} molec cm⁻², respectively. All these fittings displayed the evident absorption structures of the trace gases and fairly low residuals, which demonstrates the good performance of the spectral fitting. In this study, a threshold of residual $< 2.5 \times 10^{-3}$ are used to filter the unsatisfied fitting results of NO₂, O₄, and HCHO. Afterwards, the qualified DSCDs results remains 99.37%, 99.37%, and 99.79%, respectively. Considering the weak scattered sunlight signals and low signal-to-noise ratio around 300 nm, where the SO₂ has strongly structured absorption, the threshold of residual for SO₂ is set to 5.0×10^{-3} and 70.05% of the fitting results are meet matching this criterion.

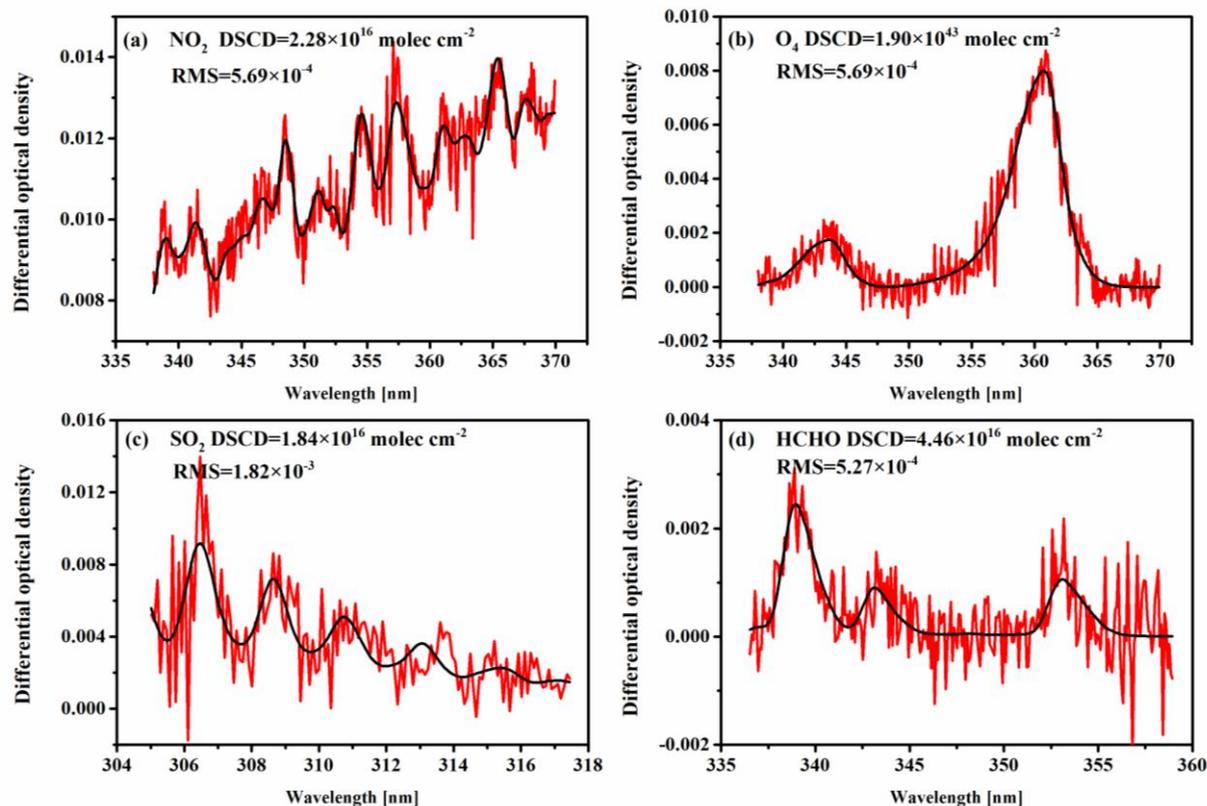


Figure 2. Typical DOAS spectral fittings for (a) NO₂, (b) O₄, (c) SO₂, and (d) HCHO. The spectrum was collected at elevation of 15° at 10:13 LT on 7 June 2017. The black curves show the reference absorption cross section scaled to measured atmospheric spectrum (red curves) by DOAS fitting.

2.2.3 Retrieval of the trace gases VCDs and profiles

To obtain the tropospheric Vertical Column Density (VCD) of trace gas, the DSCDs has to convert using tropospheric Differential Air Mass Factors (DAMFs) by Eq. (1) (Wagner et al., 2010):

$$VCD_{trop} = \frac{DSCDs}{DAMFs} = \frac{DSCDs(\alpha)}{AMF(\alpha) - AMF(90^\circ)} \quad (1)$$

The Air Mass Factors (AMFs) calculation is approached by the so called geometric approximation method (Hönninger et al., 2004; Wagner et al., 2010), which is simple and convenient, simultaneously, is also validated by radiative transfer simulations (Solomon et al., 1987; Shaiganfar et al., 2011).

$$AMF(\alpha) = 1/\sin(\alpha) \quad (2)$$

Using Eq. (1) and Eq. (2), the tropospheric DAMF was estimated to be 2.86 and 1 for elevation angles of 15° and 30°, respectively. Previous ground-based MAX-DOAS studies shown that the most appropriate choice for the elevation angle could probably be 30° for the geometric approximation approach (Halla et al., 2011; Brinksma et al., 2008). Nevertheless, elevation 15° also works well for the conversion of DSCDs into VCDs in ship-based MAX-DOAS campaign since the last scattering point is generally above the trace gases layer for elevation angle 15° in the lower boundary layer over the sea (Schreier et al., 2015). In addition, due to the longer light path through the boundary layer, the observations at 15° elevation angle are more sensitive compared to 30°. Consequently, the VCDs of NO₂, SO₂, and HCHO were approached from DSCDs of 15° elevation angle by the geometric approximation method in this study.

To obtain the vertical distribution of trace gases, we used the HEIPRO algorithm (HEIdelberg PROfile, developed by IUP Heidelberg) for MAX-DOAS profile retrieval (Frieß et al., 2006; Frieß et al., 2011; Frieß et al., 2016). The HEIPRO retrieval algorithm is based on the Optimal Estimation Method (OEM, Rodgers, 2000) and coupled with the radiative transfer model SCIATRAN (Rozanov et al., 2005) as the forward model. Because the existence of aerosol has strong impacts on the scattered light path in the atmosphere, the retrieval algorithm takes into account the aerosol profile retrieval first and then adopts the retrieved aerosol scenario to profile the trace gases. In this study, an exponential decay a priori profile with a scale height of 1.0 km is used as the initial profile for both the aerosol and trace gases retrieval. The total aerosol optical depth and trace gases VCDs of such a priori profile is 0.2 and 7.27×10^{15} molec cm⁻², respectively. The uncertainty of the aerosol and trace gases a priori profile is set to 100% and correlation length is set to 0.5 km. In the radiative transfer model, the parameters of single scattering albedo, asymmetry parameter and ground albedo are assumed to be 0.92, 0.68 and 0.06 for the marine environment. The retrieved profile of aerosol extinction and trace gases concentration has the resolution of a fixed grid of 200 m from sea

surface to 3 km altitude. The criteria that the relative error of profile retrieval larger than 50% or degree of freedom of signal smaller than 1.0 are used to filter the profile results. Afterwards, about 1.1%, 23.4%, and 7.2% of all measurements were discard for NO₂ SO₂, and HCHO profile retrievals, respectively.

2.3 OMI and OMPS satellite data

The Ozone Monitoring Instrument (OMI) was launched on July 2004 on-board the NASA Aura satellite (Levelt et al., 2006). It is an imaging spectrometer covering the wavelength range from 270 to 500 nm, which receives the light signal of scattered in the Earth's atmosphere and reflected by the Earth's surface. OMI aims to monitor ozone, NO₂, and other minor trace gases distribution with high spatial resolution (about 13 × 24 km²) and daily global coverage. OMI is operated on a sun-synchronous orbit, and the overpass time is about 13:45 LT. However, OMI has suffered from a so-called "row anomaly" and lost several cross-track positions data (Boersma et al., 2011). In this study, we use USTC-OMI tropospheric NO₂ products (Liu et al., 2016; Su et al., 2017). To generate the USTC-OMI products, the NO₂ SCDs are retrieved from the OMI Level 1B VIS Global Radiances Data (OML1BRVG) based on the DOAS method. To convert into NO₂ VCDs more accurately, AMFs are calculated with the input of the localized NO₂ and atmospheric temperature and pressure profiles derived from WRF-Chem chemistry transport model simulations. The WRF-Chem chemistry transport model have using the National Centers for Environmental Prediction (NCEP) Final operational global analysis (FNL) meteorological data.

The Ozone Mapping and Profiler Suite (OMPS) instruments was launched on 28 October 2011 on board the Suomi National Polar-orbiting Partnership (Suomi-NPP) satellite. The OMPS Nadir Mapper (OMPS-NM) is one of three sensors of the OMPS suite instruments. It contains a UV spectrometer cover the wavelength range between 300 and 380 nm with a full width half maximum (FWHM) of 1 nm. It has a high spatial resolution of 50 × 50 km² and high time resolution of daily global coverage (Dittman et al., 2002; Seftor et al., 2014; González Abad et al., 2016). Its equator crossing time in the ascending node is 13:30 LT. In this study, the OMPS satellite observation data were used to retrieve the USTC-OMPS tropospheric SO₂ and HCHO products. Similar to the USTC-OMI tropospheric NO₂ VCDs, the SO₂ and HCHO VCDs are produced in two-steps approach too, i.e. first the SCDs of SO₂ and HCHO retrieval from the measured scattered sunlight spectra, and conversion to the SO₂ and HCHO VCDs by applying the calculated AMFs based the WRF-Chem chemistry transport model simulations results.

2.4 Ozone Lidar

During this campaign, an O₃ lidar was also on board co-located with the MAX-DOAS instrument, which was developed by Anhui Institute of Optics and Fine Mechanics (AIOFM) using Differential Absorption Lidar (DIAL) technology. The laser pulse of the lidar is at 316 nm, usually with the energy of about 90 mJ and a repetition frequency of 10 Hz. The laser beam is emitted with a divergence of 0.3 milliradian (mrad) and the receiving telescope with a field of view (FOV) of 0.5 mrad, resulting in an overlap height of approximately 300 m. The O₃ profiles in the lower troposphere were obtained using DIAL

retrieval algorithms. The lidar observation has the high vertical resolution of 7.5 m and the temporal resolution about 12 min. In order to improve the signal to noise ratio, the retrieved vertical distribution O₃ concentrations were averaged in 100 m gridded. Additionally, the O₃ concentration profiles with relative errors above 20% were removed from the further discussion.

3 Results and discussion

3.1 Trace gases tropospheric VCDs

Based on the spectral analysis and the geometric AMF approach, we obtained the VCDs of different trace gases along the ship cruise combined with the GPS received geo-position data. Figure 3 shows the spatial distributions of NO₂, SO₂ and HCHO VCDs along the route over the ECS area. The missing data are due to the power failure and instrumental malfunction during the campaign, as well as the measurements taken under bad weather conditions (e.g., heavy rain day). During the campaign, the NO₂ VCDs varied from 1.00×10^{15} molec cm⁻² to 5.52×10^{16} molec cm⁻² with a mean value of 6.50×10^{15} molec cm⁻². As shown in Fig. 3(a), high level of the NO₂ VCDs, almost as three time as the average of the whole cruise, were observed at the ship lanes of the south channel of the Yangtze River Estuary and the way to Lianxing port (located in Qingdong of Jiangsu Province), as well as the busy port of Ningbo-Zhoushan area. The SO₂ VCDs are ranged from 1.00×10^{15} molec cm⁻² to 1.77×10^{16} molec cm⁻² with an average of 4.28×10^{15} molec cm⁻². Fig. 3(b) shows the elevated SO₂ value (i.e. $> 8.63 \times 10^{15}$ molec cm⁻², about the 95th percentile value, ~ 2.02 times of mean value) are appeared in the same places as NO₂, such as the ship lanes closed to the Gongqing port, Ningbo-Zhousan port. For the HCHO, the averaged VCDs is 7.39×10^{15} molec cm⁻² in range of 1.02×10^{15} molec cm⁻² to 3.16×10^{16} molec cm⁻². As in Fig. 3(c), the enhanced HCHO columns were found in the section of the cruise in Hangzhou Bay area, which is different with NO₂ and SO₂ spatial distribution. Moreover, high value of HCHO VCDs $> 1.0 \times 10^{16}$ molec cm⁻² also dispersed over some hot spots as NO₂ and SO₂.

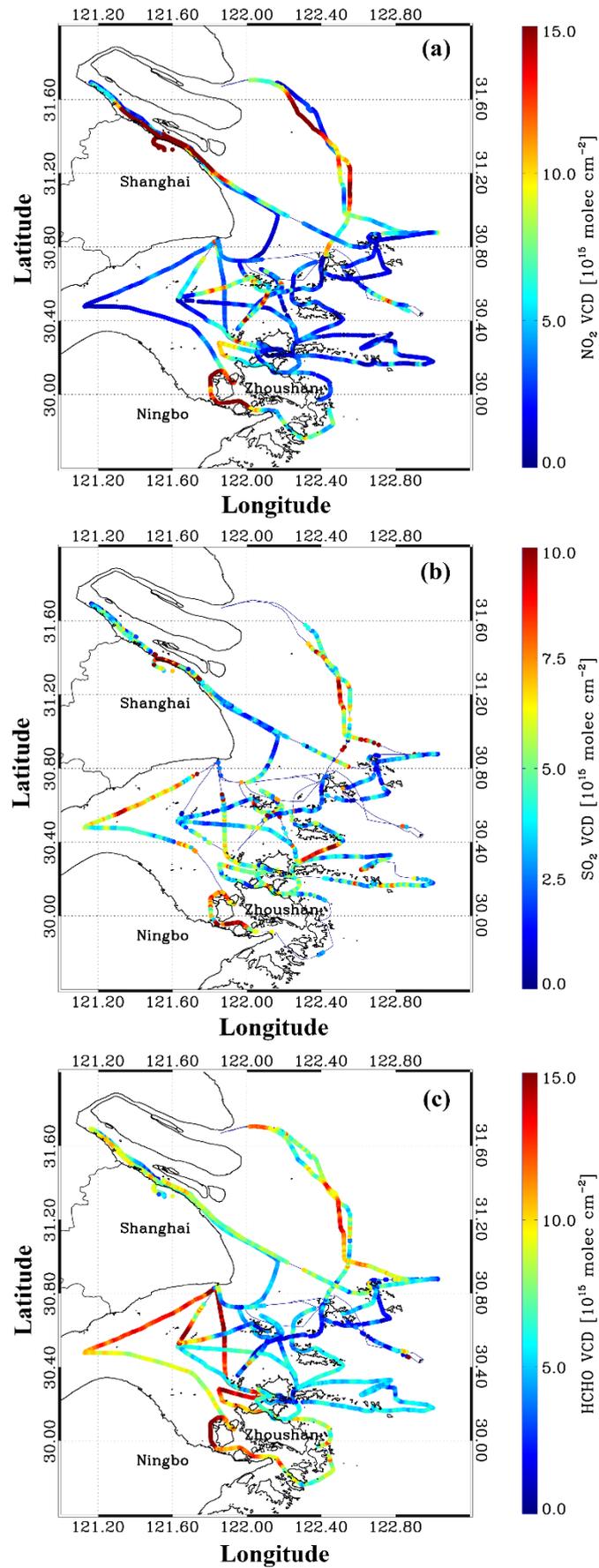


Figure 3. The spatial distributions of the trace gases VCDs of (a) NO₂, (b) SO₂ and (c) HCHO along the cruise route of the ship-based campaign in June 2017.

235 The coastal waters of YRD region, including Jiangsu, Shanghai, and Zhejiang, is the busiest sea area of ECS, and the continental YRD region is also one of the most developed industrial city cluster of china or even the world. Therefore, previous studies found that the air qualities in coastal sea and inland area were affected by the ship-emitted pollutants under cruising and maneuvering conditions together with the continental anthropogenic pollutants (e.g. Zhao et al., 2013; Fu et al., 2014). In order to investigate impacts of ship emissions, we obtained the dependence of NO₂, SO₂ and HCHO VCDs on longitude in

240 Fig. 4. It can be found that most of the peaks of trace gases are occurred at the geolocations of busy ports and ship lanes, whereas lower values are observed at remote oceanic area (Fan et al., 2016). The spatial distribution of NO₂, SO₂ and HCHO over sea areas are mainly dominant by the local emission source of ships, ports, and even the coastal factories.

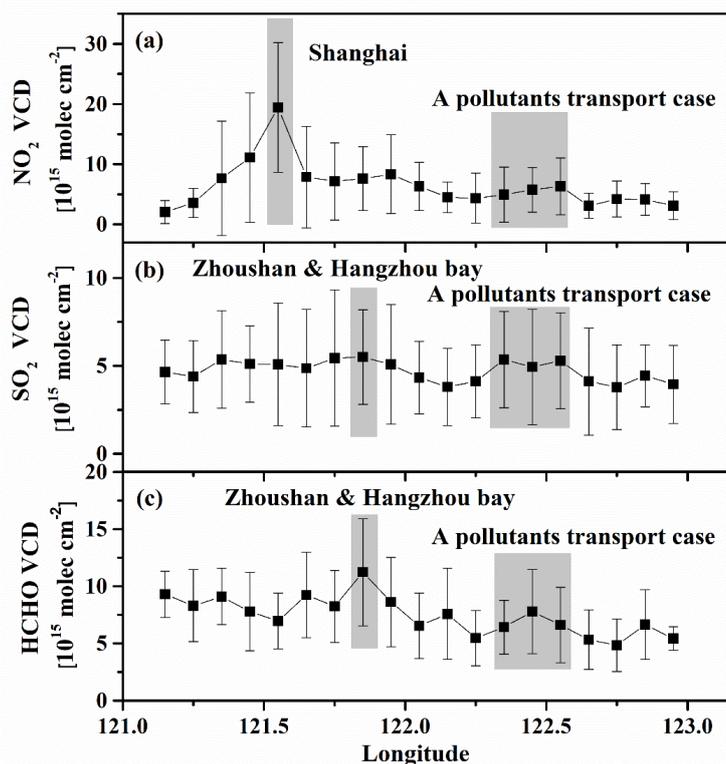
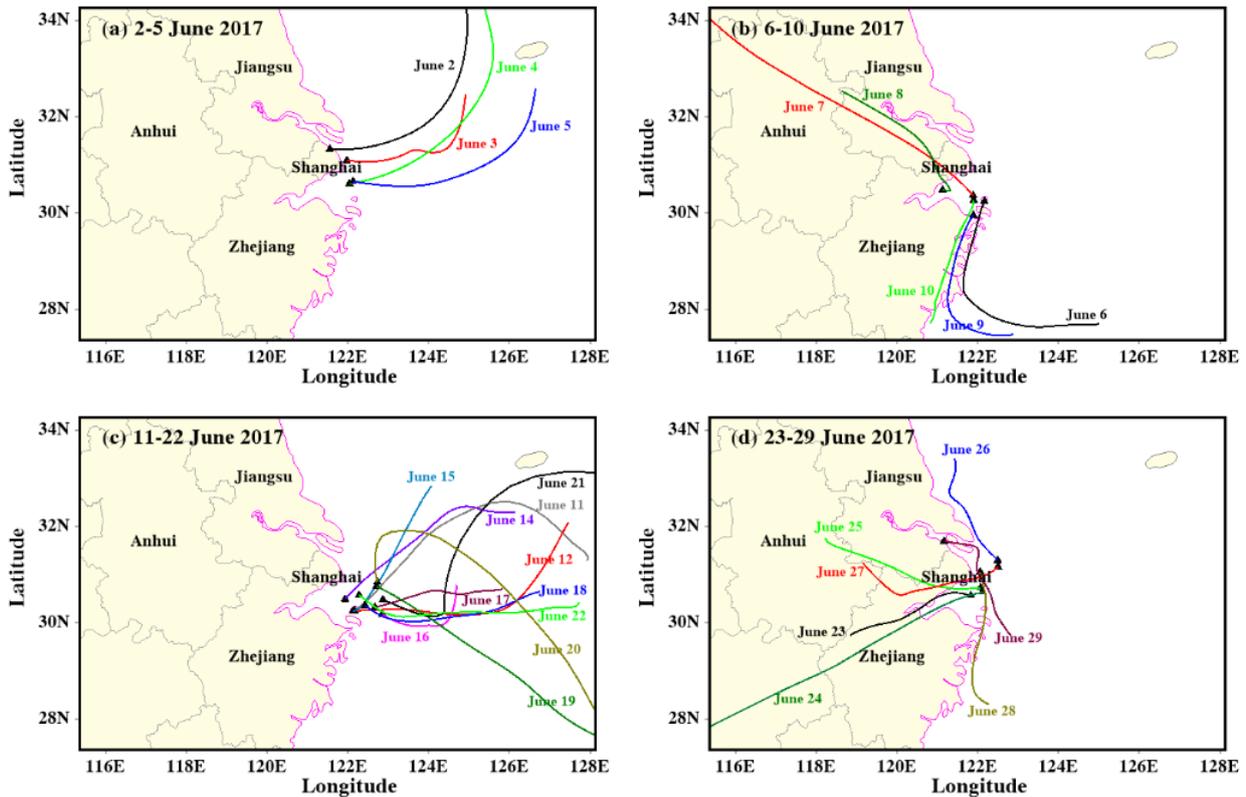


Figure 4. The variations of trace gases tropospheric VCDs with longitude: (a) NO₂, (b) SO₂ and (c) HCHO.

245 Besides, the spatial distribution of trace gases is also influenced significantly by the meteorological conditions especially wind speed and wind direction. Here, we calculated 24-h backward trajectories of 300 m altitude air masses by applying the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model, which is developed by the National Oceanic and Atmospheric Administration-Air Resource Laboratory (NOAA-ARL) (<http://ready.arl.noaa.gov/HYSPLIT.php>) (Stein et al., 2016). The Global Data Assimilation System (GDAS) meteorological data with a spatial resolution of 1°×1° and 24 vertical

250 levels was used in the trajectory simulations process. Figure 5 displays the daily 24-h backward trajectories results for in four periods, which illustrated the origin of the air masses arrived at the endpoint (indicated by black triangle) at 04:00 UTC (12:00 LT).



255 **Figure 5. Daily 24-h backward trajectories of air masses at the 300 m altitude for (a) 2 to 5 June, (b) 6 to 10 June, (c) 11 to 22 June and (d) 23 to 29 June, 2017.**

In Fig. 5(a) and (c), the air masses were originated from clean sea area of the duration from 2 to 5 and 11 to 22 June, 2017. It suggested that the observed air pollutants were less impacted by ~~the~~ airflows transport patterns, however, were mainly from the local emission sources. For example, the high concentration of pollutants was reported on 2 and 3 June, during which the measurements were implemented on busy ship lanes in the south channel of Yangtze River Estuary. In contrast, the trace gases VCDs were much lower during the most days of 11 to 22 June, when the measurements were taken place over the clean sea area. Figure 5(b) and (d) showed the air masses ~~were~~ came coming from inland areas during 6 to 10 and 23 to 29 June, respectively. As shown in Fig. 3, high values of NO₂, SO₂ and HCHO VCDs, the corresponding 95th percentile are 1.81×10^{16} , 1.05×10^{16} , and 1.31×10^{16} molec cm⁻² for these two days, have been found during the ship cruise from Shengsi islands to Lian Xiang port and back to Huaniao islands on 26 and 27 June, 2017. The air mass was original from the coastal industrial zone on 26 June and the city center of Shanghai on 27 June. This pollution episodes can be speculated mainly blame to pollutants transported from inland cities and coastal areas combined with ship emissions in nearby waters.

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3.2 Comparison with OMI and OMPS satellite products

In order to compare the ship-based MAX-DOAS and satellite data, we have to make them for comparable temporal and spatial coverage. The ship-based MAX-DOAS measured VCDs are averaged for 13:00 to 14:00 according to the OMI and OMPS instruments overpass time of about 13:45 LT and 13:30 LT. The satellite products are averaged within 10 km radius of the

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center position of ship cruise between 13:00 and 14:00 LT considering the cruising speed around 8-15 km h⁻¹. Moreover, satellite data with larger error (relative error >100%) and cloud impacts (cloud fraction > 0.5) were excluded from the inter-comparison. Hence, there remains 14 days of observation for NO₂, SO₂ and HCHO VCDs comparison.

275 Figure 6(a) shows the time series of the NO₂ VCDs inter-comparison between ship-based MAX-DOAS measurements and OMI satellite observations. These two data sets agree well with each other and have a high correlation coefficient (R) of 0.83 in Fig.6 (b). However, OMI satellite observations were higher than the ship-based MAX-DOAS results in some days, which is different from the comparisons over continental areas where the satellite observation are usually much smaller than ground-based data (Liu et al., 2016). The larger discrepancies on 8, 15 and 20 June were observed in the remote ocean area, 280 implying the possible larger uncertainties of the VCDs retrieval in such clear marine environment.

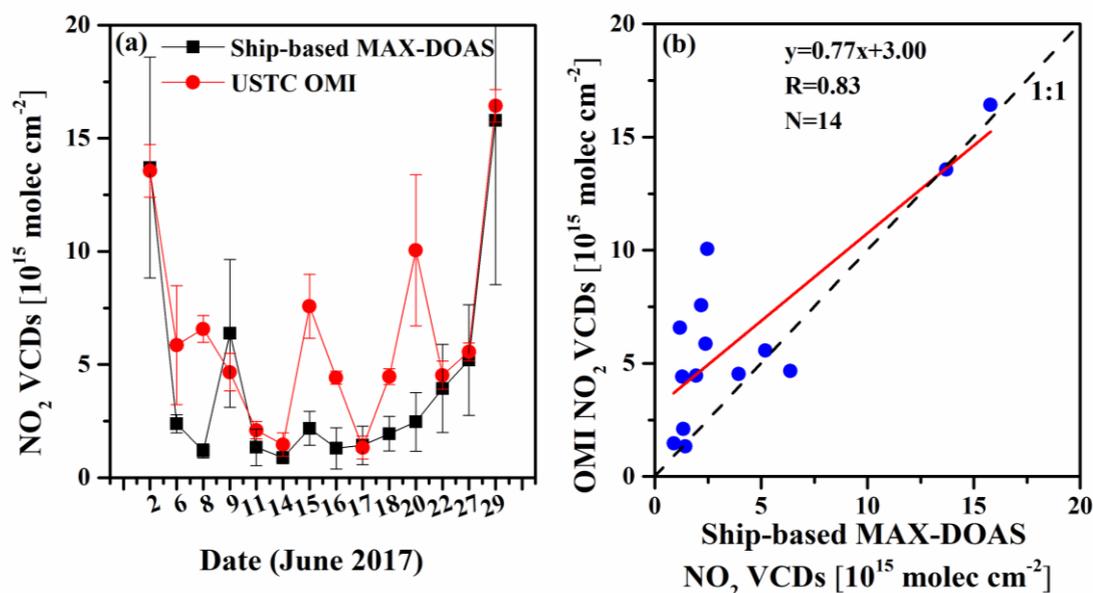


Figure 6. Time series (a) and correlation analysis (b) of the tropospheric NO₂ VCDs measured by ship-based MAX-DOAS and OMI satellite during this campaign.

For the inter-comparison with ship-based MAX-DOAS, the spaced products of SO₂ and HCHO VCDs were retrieved from OMPS satellite. The time series of the SO₂ VCDs measured by ship-based MAX-DOAS and retrieved from OMPS satellite observations were displayed in Fig. 7(a). These spaced and ship borne data exhibited similar temporal trends during the campaign, showing a correlation coefficient (R) of 0.76 in Fig. 7(b). Figure 8(a) presents the time series of the HCHO VCDs measured by ship-based MAX-DOAS together with the satellite data retrieved from OMPS observations, which also show a good agreement with a correlation coefficient (R) of 0.69 in Fig. 8(b). Besides, we also found that the trace gases VCDs of NO₂, SO₂ and HCHO from spaced observation by OMI and OMPS satellites are higher than ship-based MAX-DOAS measurements in marine environment.

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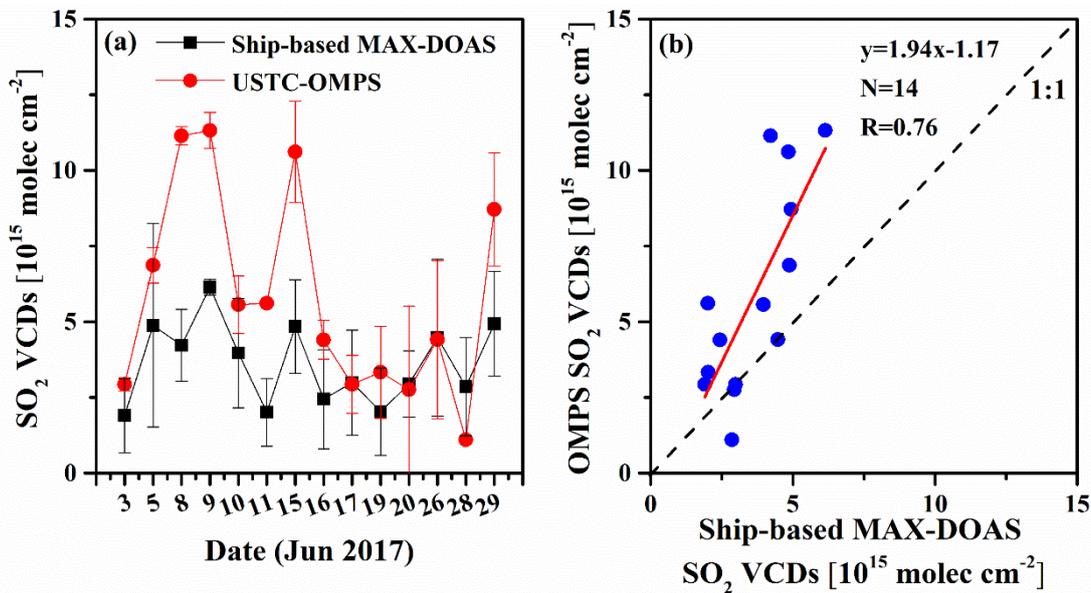


Figure 7. Time series (a) and correlation analysis (b) of the tropospheric SO₂ VCDs measured by ship-based MAX-DOAS and OMPS satellite during this campaign.

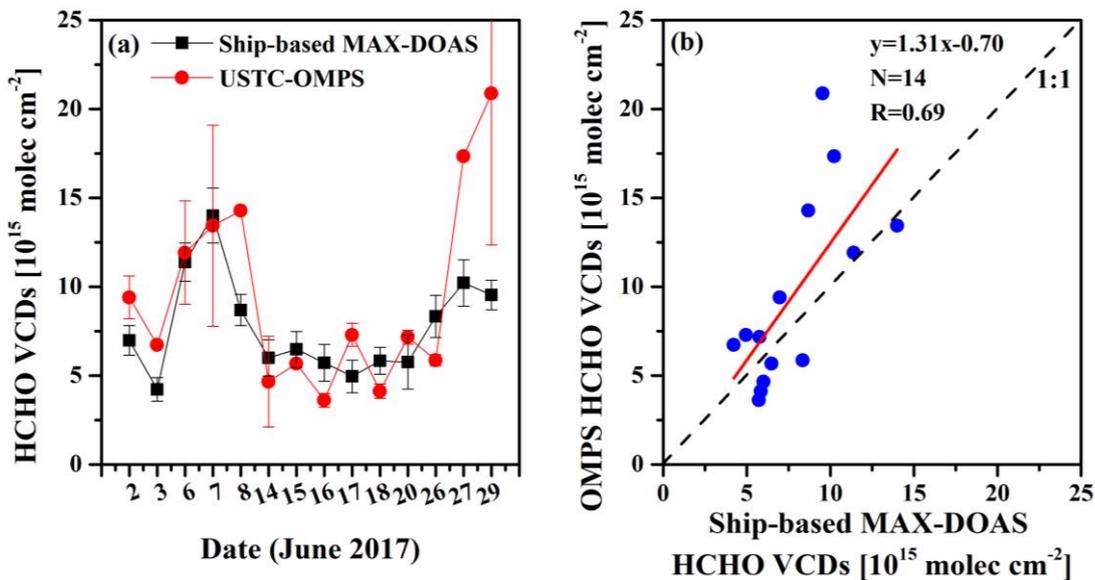


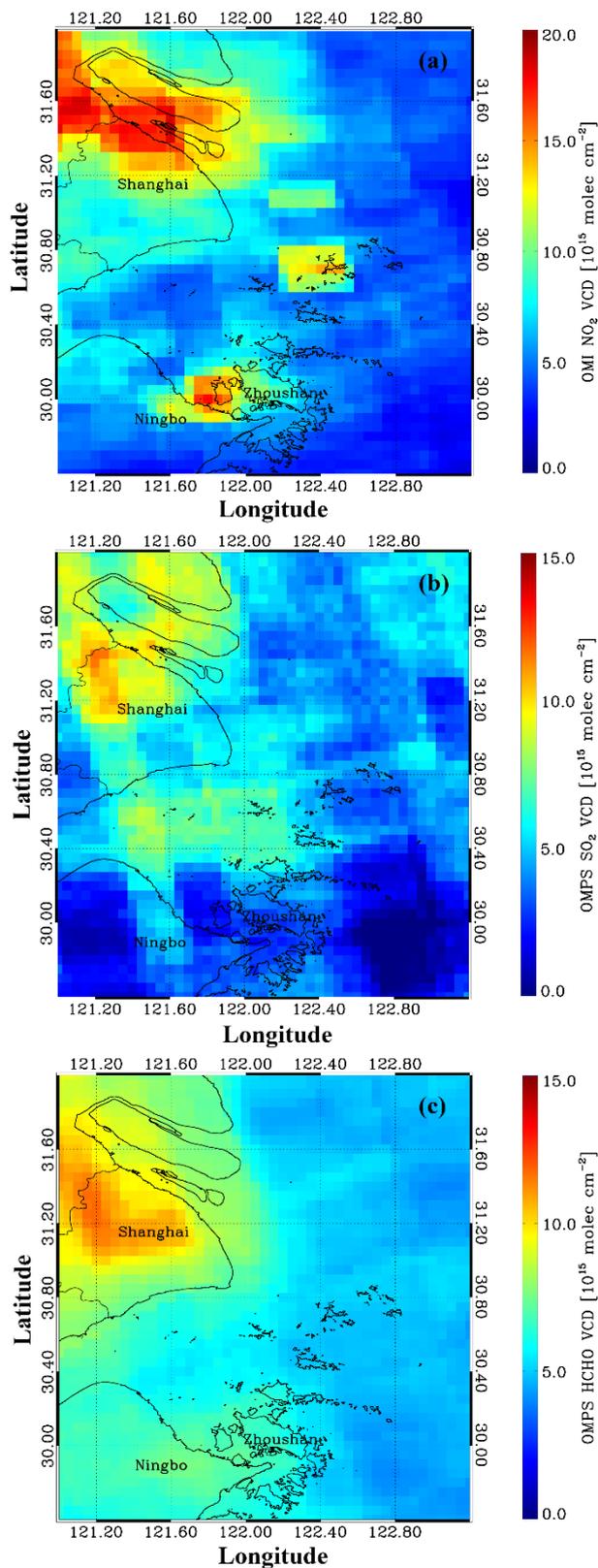
Figure 8. Time series (a) and correlation analysis (b) of the tropospheric HCHO VCDs measured by ship-based MAX-DOAS and OMPS satellite during this campaign.

To characterize the spatial distribution of tropospheric NO₂, SO₂ and HCHO VCDs, the monthly averaged tropospheric products of OMI satellite NO₂ and OPMPs SO₂, HCHO in June 2017 were demonstrated in Fig. 9. The satellite data was error (relative error >100%) and cloud (cloud fraction > 0.50) filtered and gridded in a high spatial resolution of 0.05°×0.05°. Due to the different emission sources and formation mechanisms, these three trace gases show the distinct features of spatial distributions. In Fig. 9(a), the hot spots of NO₂ distributions were distributed at the coastal of the Yangtze River at Shanghai city and Jiangsu Province, Ningbo-Zhoushan port and Shengsi islands. For the spatial distributions of SO₂ in Fig. 9(b), both

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305 Qidong in Jiangsu province, northwest part of Shanghai city and the Hangzhou bay express relatively high values, and even over some sea areas where are dense waterways and ship lanes. In addition, the main hot spots is located at urban area of Shanghai city for HCHO spatial distributions in Fig. 9(c). In summary, all of the three trace gases have high values in some polluted continental areas, e.g. Shanghai city center and northwest area, while hot spots over sea areas are mainly consistent with the heavily vessels and ports emission areas.



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Figure 9. The monthly averaged spatial distributions of the trace gases VCDs of (a) NO₂, (b) SO₂ and (c) HCHO of the OMI and OMPS satellite observations in June, 2017.

Since the daily satellite observation can provide the detailed regional view of the spatial distribution of the gaseous pollutants, the daily distribution of NO₂ VCD were further compared between OMI data and ship-based results. Fig. 10 presents the comparison for days of 2, 7, 16 and 27 June, where the trajectories of ship-based measurements were shown in color coded indicating with the white lines of cruise route and the position of ship-based measurements during 13:00 to 14:00 LT were marked by black point. It can be observed that the color coded ship-based measurements can generally achieved a good agreement with the spatial distribution of satellite data, except for somewhere on 27 June.

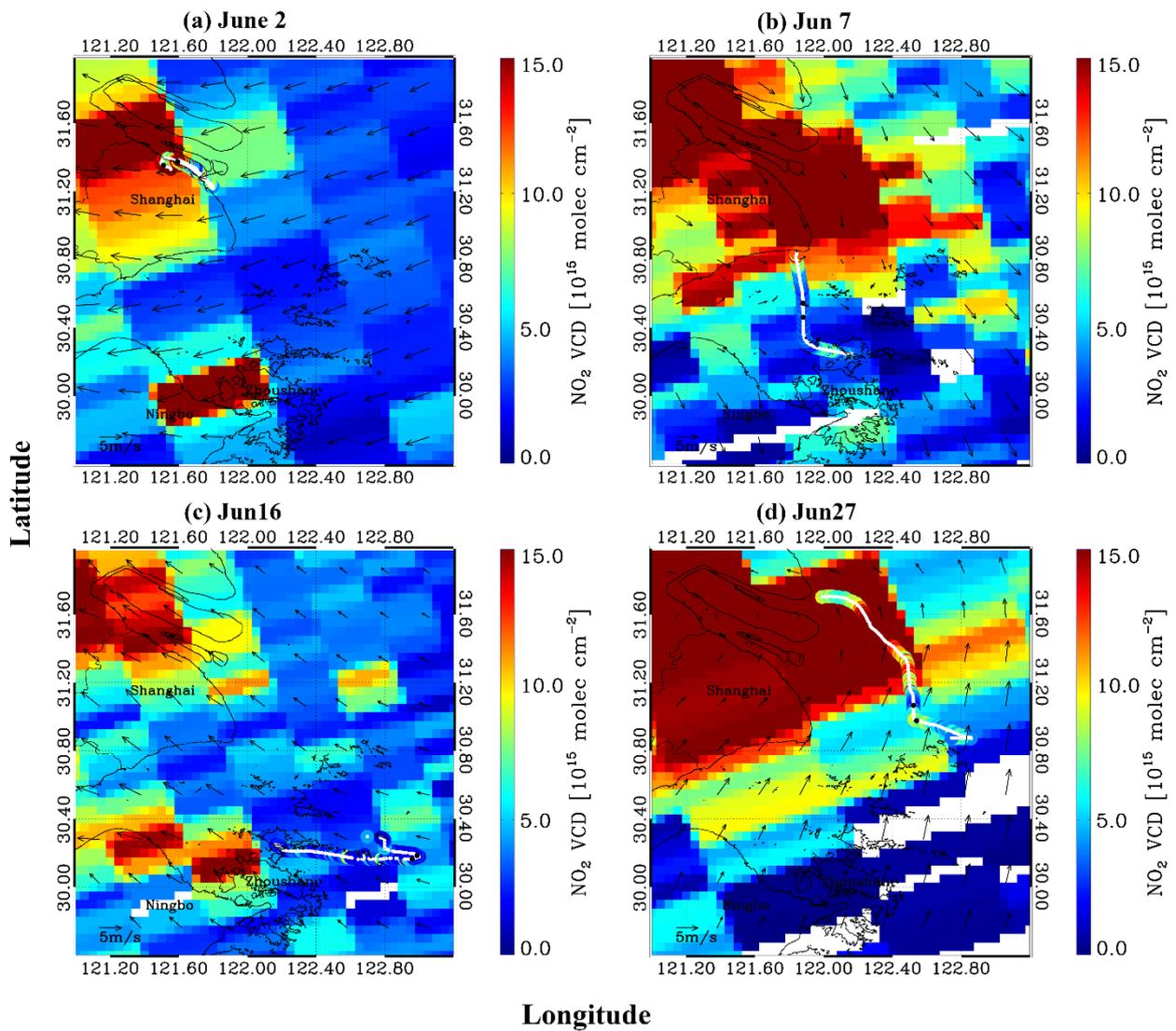


Figure 10. Comparison of OMI and ship-based measured NO₂ VCDs on (a) 2, (b) 7, (c) 16, and (d) 27 June. The ship-based measurements were plotted overlap in the base map of OMI products, and the wind field were indicated with black arrows.

To reveal some typical pollution transport process, the wind filed (black arrow) were overlap plotted together. Combining with the wind information, the air masses came from clean sea areas on 2 and 16 June, but originated from polluted inland areas on 7 and 27 June. Therefore, the observed NO₂ VCDs over inland and sea areas were substantially lower on 2 and 16 June compared to measurements on 7 and 27 June. Under the oceanic wind conditions, hot spots of NO₂ VCDs are mainly located in the inland areas and sea areas with high shipping emission intensities, which can be blamed to the impacts of local emissions. When the wind blow from continent on 7 and 27 June, it can be found that the NO₂ pollution has been spread from inland to the downwind water areas close to the coast and even for the sea areas far from the coastal line. It suggest the significant influences of the pollutants transported from inland on the air quality over sea waters.

3.3 Tropospheric NO₂, SO₂ and HCHO profiles

In order to obtain vertical distribution of trace gases, we followed the method described in Sect. 2.4 to retrieve the vertical profiles of NO₂, SO₂ and HCHO. Daily profiles results are available and three typical observation periods were presented for different characteristic areas, as indicated in Fig. 4011. The measurements during cycle 1 from 7 to 10 June were located at Hangzhou Bay and Zhoushan islands areas. In cycle 2 from 16 to 19 June, the ship cruise were in the clean waters way far from the coastlines. In cycle 3 of 26 to 29 June, the measurement carried on through a long path way, which passed through clean to polluted areas over the waters of Shanghai, Qidong, and the areas of the Yangtze River Estuary.

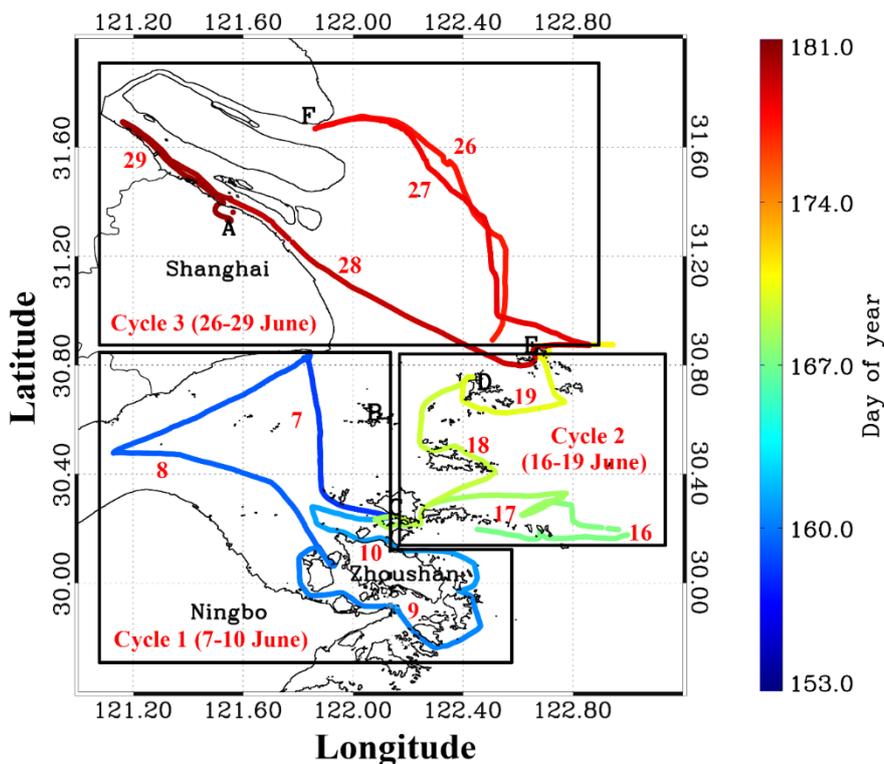


Figure 4011. Three typical observation periods in characteristic observation areas.

Figure 4112(a)-(c) showed the diurnal variations of the vertical profiles of NO₂, SO₂ and HCHO concentrations during these three cycles. It is obvious that the trace gases concentrations of NO₂, SO₂ and HCHO in cycle 2 were lower than that of the

others, which also can be confirmed in spatial distribution of trace gases VCDs in Fig. 3. By extracting the lowest 500 m grids
345 of the retrieved profiles, the observed concentrations of NO₂, SO₂, and HCHO were < 3 ppbv, < 3 ppbv and < 2 ppbv in such
clean marine boundary layer. It can be explained by the fact that the measurements of cycle 2 were performed in the relative
remote sea area, which is far away from the YRD continental region and less impacted by the inland emission sources, especial
under the favor meteorological condition of clean air masses from the remote ocean (in Fig. 5(c)). However, the higher levels
of the trace gases were found during cycle 1 and 3. For example, the concentrations of NO₂, SO₂ and HCHO in the marine
350 boundary layer all increased to high values on 9 and 29 June.

To track the cruise on 9 June, the ship was passing through the channel between Ningbo and Zhoushan islands, where is the
Ningbo-Zhoushan Port, the world top 1st port ranking by container throughput. The Ningbo-Zhoushan Port has been reported
to account for about one-third of the national port-level emissions inventories in China (Fu et al., 2017). The hourly variation
of pollutants emissions behaved to reach peaks during 09:00~14:00 and varied with vessel types (Yin et al., 2017). The
355 backward trajectory on 9 June shows that air mass was originated from the coastal area. It is inferred that this pollution episode
was mainly attributed to the ship emission from coastal and ocean going vessels, as well as the cargo handling equipment in
the ports areas. On 29 June, the observation was performed along the Yangtze River toward upstream until 121.15°E and then
back to Gongqing port of shanghai. This waterway is the only channel to the upstream of the Yangtze River and consequently
dense with the inland ships. Moreover, Taicang Port and some industrial zones were distributed along the coastline areas.
360 Therefore, industrial factories and ship emissions, as well as the transports from inland city, lead together to this elevated
pollutants levels.

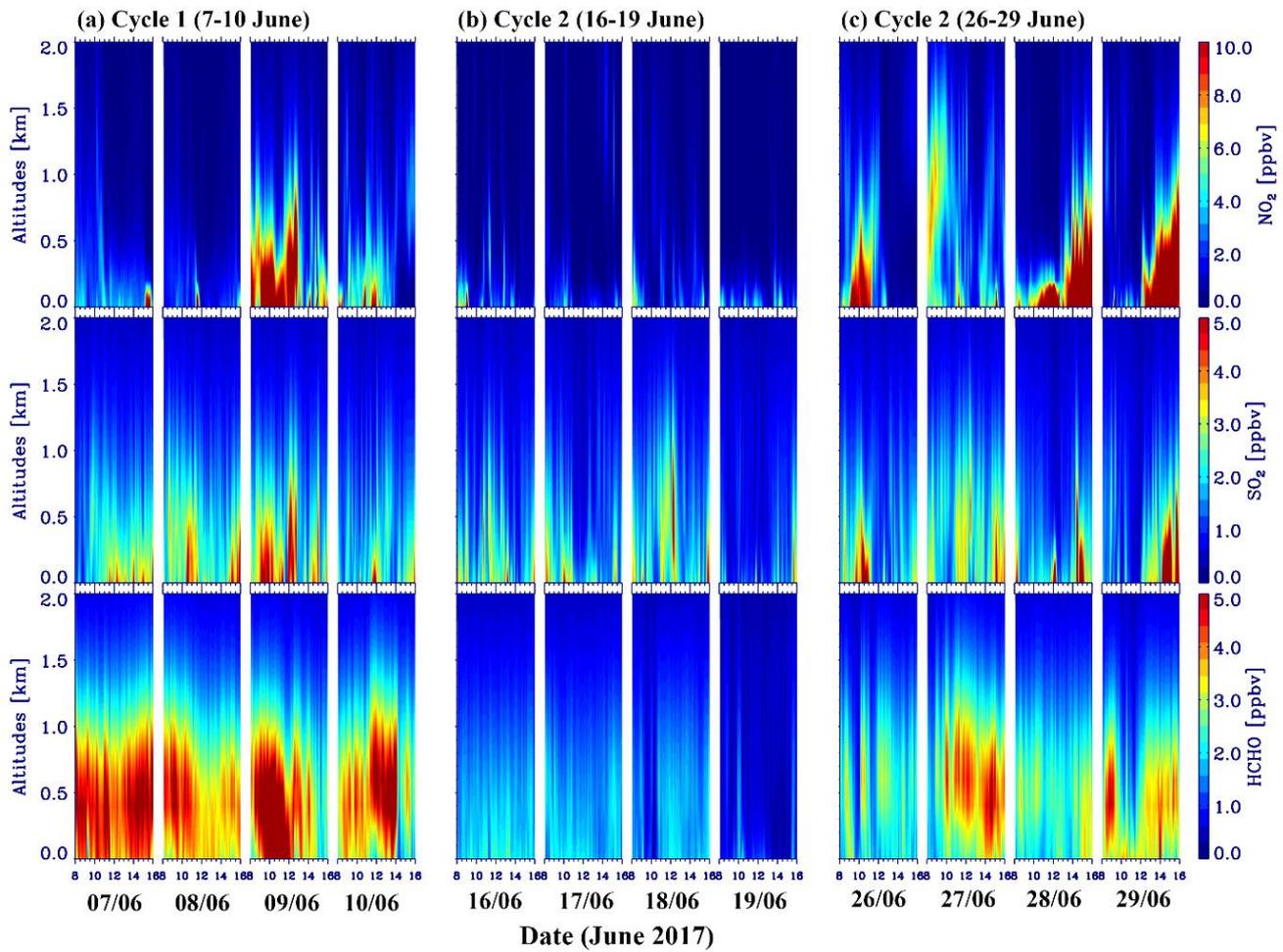


Figure 412. Vertical profiles of NO₂, SO₂ and HCHO concentrations during the three typical observation periods: (a) measurements taken at Hangzhou bay and Zhoushan islands on 7 to 10 June, (b) measurements carried on a relative clean area on 16 to 19 June, and (c) measurements implemented on the areas of the Yangtze River Estuary on 26 to 29 June.

In addition, the vertical distributions of NO₂, SO₂ and HCHO in marine boundary layer have unique features. The high NO₂ concentrations were observed closed to the sea surface and decreased with height in vertical. For the layer below 500 m, lowest and highest NO₂ concentrations were found < 3 ppbv in cycle 2 and > 10 ppbv during cycle 1 and 3, respectively. Almost all the measured NO₂ concentrations in the marine boundary layer during this campaign are larger than the background value over the western Pacific and Indian Ocean (< 0.2 ppbv) (Takashima et al., 2012) and over the South China and Sulu Sea (< 30 pptv) (Peters et al., 2012). Due to the sulfur-containing marine fuels, ship emissions are the primary source of SO₂ over the seas. Therefore, the intermittent enhanced SO₂ signals were detected during the whole cruise as shown in Fig. 412, even for the relative clean area in cycle 2 where the SO₂ concentrations exceeded 3 ppbv sometimes. It implies that the frequently observed SO₂ pulses are the emissions from the kinds of vessels in the vicinity or even from the cruise ship itself.

As distinguished from patterns of NO₂ and SO₂ vertical profiles, the highest HCHO concentrations are located at the elevated altitudes (about 500 m) during the days of cycle 1 and 3, since there is no HCHO sources from the sea surface. The similar phenomenon was also reported in the study over remote western Pacific Ocean, where the highest concentrations of HCHO occurred at the altitudes of 400 m (Peters et al., 2012). Furthermore, extremely high HCHO concentrations of > 5 ppbv appeared during the ship cruised along coastal and busy ports areas in cycle 1 and 3, while the low concentration about 1.2 ppbv were measured in cycle 2. However, the observed lowest levels HCHO in marine boundary layer of ECS area were almost equal to the highest value (~ 1.1 ppbv) measured at remote western Pacific Ocean (Peters et al., 2012). The behavior of NO₂, SO₂ and HCHO concentrations highlighted the obvious shipping emissions along the ship lanes and close the busy ports, and further significant impacts on the regional air quality over the ECS areas.

3.4 Ozone formation

Figure 42-13 presents the on-board DIAL observed vertical distributions of ozone concentrations from 300 m up to 2 km Above Sea Level (ASL) during the campaign. Except the absence on 13 and 28 June due to the power failure, there were 26 days measurement results. It is found that the ozone concentrations in the marine environment showed a characteristic vertical structure that the O₃ concentrations increased with the altitude from 300 m to 1.0 km ASL, and high values > 100 ppbv were mostly distributed at altitudes higher than 1 km ASL. However, the high ozone concentrations were detected from 300 m and spread to 1.4 km on 7 and 8 June. For the diurnal patterns, the O₃ concentrations usually began to increase at morning with the enhancing solar radiation, and accumulated to arrive the daily peak in the afternoon, then declined with the decreases of sun illumination. The similar diurnal variations were also reported in previous studies over continental area, e.g. the measurements in vicinal Hangzhou, Zhejiang Province (Su et al., 2017). It indicated the daytime intense photochemical processes in the marine boundary layer.

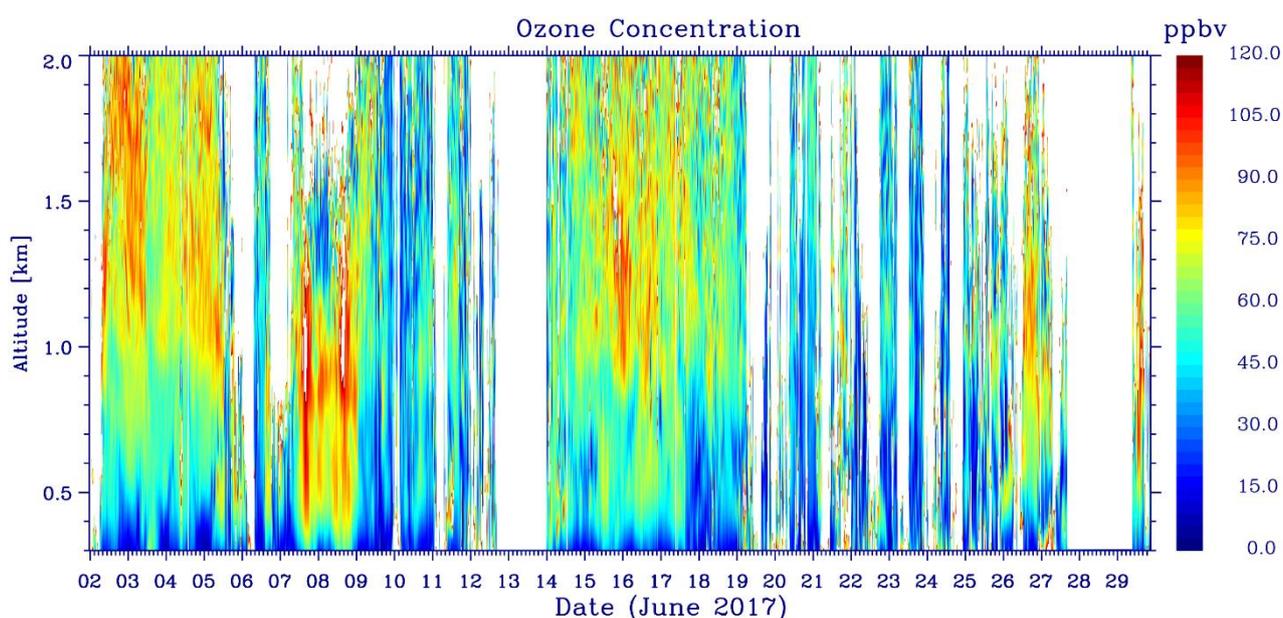


Figure 12.13. Time series of the vertical profiles of the O₃ concentrations measured by the ozone lidar in June 2017.

400 In order to investigate the formation and consumption processes of ozone, we integrated the vertical profiles of O₃ by lidar and NO₂, HCHO profiles from MAX-DOAS together. We averaged the daily profiles of O₃ and ratio of HCHO/NO₂ during the intense photochemical periods between 09:00 and 15:00 LT. Figure 13-14 shows the vertical-resolved comparisons between O₃ and HCHO/NO₂ ratio profiles on 7 to 10 June. Referred to Fig. 11.12, the NO₂ concentrations were higher ~~in-on~~ 9 and 10 but lower ~~in-on~~ 7 and 8, while the HCHO concentrations kept in high levels during the whole cycle 1 of 7 to 10, June. Accordingly, the ratios of HCHO to NO₂ on 7 and 8 were higher than that of 9 and 10, June. Meanwhile, the O₃ concentrations ranged at different altitudes from 70 to 100 ppbv in the marine boundary layer on 7 and 8, however, were below 60 ppbv on 9 and 10, June. It can be inferred that the high O₃ episodes on 7 and 8 June were controlled by the NO_x-regime of ozone formation, because the O₃ concentration dropped significantly with the increases of NO_x concentration and simultaneous decreases of HCHO/NO₂ ratio. As shown in Fig. 5(b), air masses on 7 and 8 June originated from northwest inland area, however, from southwest coastal area on 9 and 10 June. The air masses transportation from different regions may also contribute to this ozone pollution episode. Furthermore, it can be concluded that the high O₃ concentrations exceeding 60 ppbv can be expected while the ratios of HCHO to NO₂ larger than 1.5 and vice versa during this case.

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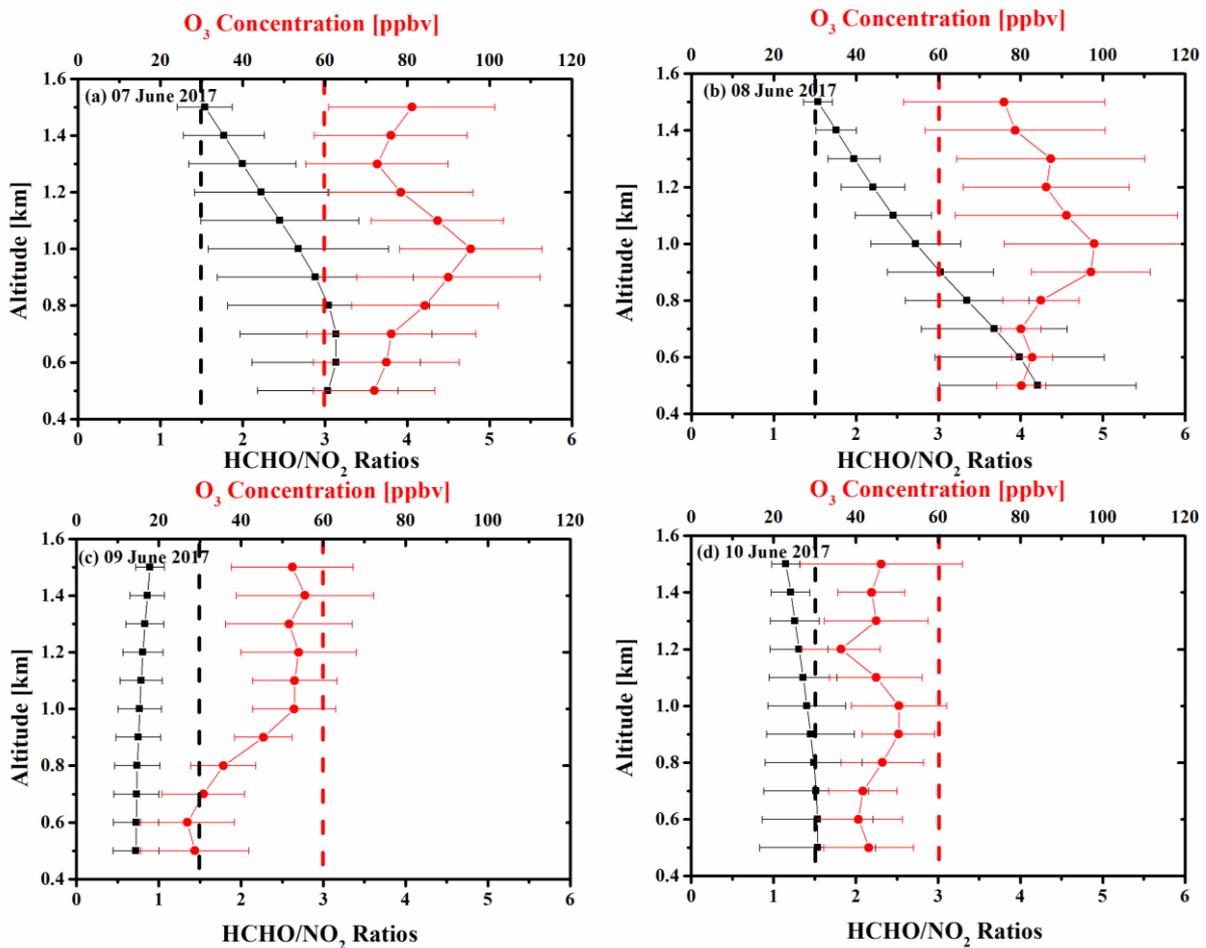


Figure 1314. The daily averaged vertical profiles of O₃ concentrations and HCHO/NO₂ ratios at different altitudes between 09:00 and 15:00 on 7 to 10 June, 2017.

4 Summary and conclusions

In this paper, ship-based MAX-DOAS and ozone lidar measurements were performed in the YRD region over the ECS area from 2 to 29 June 2017. During this campaign, the measured VCDs of NO₂, SO₂ and HCHO were firstly reported to be 6.50×10^{15} , 4.28×10^{15} and 7.39×10^{15} molec cm⁻², respectively for ECS area. In order to [provide validation of spaced observation over marine areas](#)~~validate the ship-based MAX DOAS measurements~~, the ship-based measured tropospheric NO₂, SO₂ and HCHO VCDs were compared with the satellite ~~observations~~[products](#). Both NO₂, SO₂ and HCHO showed good agreements between MAX-DOAS results and satellite products with a correlation coefficient R of 0.83, 0.76 and 0.69, respectively. Furthermore, the spatial distribution of trace gases along the ship cruise demonstrated that the enhanced pollutions of trace gases are usually related to the emissions from vessels in vicinal waterways and busy ports area. In general, the levels of trace gases decreased with the distance from the coastlines, whereas the exceptional case that high values observed on 26 and 27 June at relative remote sea areas was mainly owing to the transport process from continental area with the favor of meteorological conditions.

The daily vertical profiles NO₂, SO₂, and HCHO were obtained by the retrieval from MAX-DOAS measurements by HEIPRO algorithm. The trace gases concentrations in the bottom of marine boundary layer are < 3, < 3, and < 2 ppbv of NO₂, SO₂, and HCHO respectively over the relative clean areas far from offshore of the YRD region. However, we also found elevated SO₂ concentration frequently during the cruise, which is blamed to the ships emissions nearby. Combined the ratio of HCHO/NO₂ profiles from ship-based MAX-DOAS with O₃ vertical profiles from the ozone lidar, the typical O₃ formation were identified related to the increases of the NO₂ concentration and relative lower HCHO/NO₂ ratios. This study highlighted the strong impacts of shipping emissions on the air quality in marine boundary layer of ECS areas, which need to be regulated urgently in the coming future, especially for the YRD region where the world top 2 ports are located.

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