Response to comments from reviewer #1

We thank the reviewers for the constructive comments and suggestions, which are very positive on the scientific content of the manuscript. We have revised the manuscript appropriately and addressed all the reviewers' comments point-by-point for consideration as below. The remarks from the reviewers are shown in black, and our responses are shown in blue color. All the page and line numbers mentioned following are refer to the revised manuscript without change tracked.

Reviewer:

Overview: The manuscript present results from half a year of MAX-DOAS ship emission measurements at two different regions in the Chinese emission control area. With some examples the authors show the potential of the DOAS measurement technique to monitor ship emissions in general and of individual ships in transit. This is of high interest for the scientific community, dealing with ship emission measurements. However, the database the authors use for their conclusions is weak. Some analyses have to be improved. So mayor revisions are needed to consider this manuscript for publication in ACP.

General Comments:

1. In the introduction the authors mention SO2 and NO2 to be the "main pollutants of ship emissions" (line 31-32). As the fuel consists of ca. 87% carbon, CO2 is by far the main pollutant in ship plumes. Beside CO2, Nitrogen monoxide (NO) is the second dominant pollutant in ship plumes. NOx is emitted mainly as NO and not as NO2. The NO2 is formed in the plume when the plume ages (NO + O3 –> NO2 + O2). Our measurements within the German ship emission monitoring network usually shows NO/NO2 ratios of above five when the plume age is less than 5 minutes. With increasing time the NO/NO2 ratio decreases to below 1 (age > 15 minutes). The MAX-DOAS instrument cannot measure CO2 and NO. Nevertheless, in the introduction the authors should consider CO2 and NO as the main pollutants of ships. They should also discuss influence of the NO –> NO2 transformation inside the plume to their measurements.

R: We have not considered this point rigorously in previous manuscript. Since the limitation of the wavelength range of the instrument, CO_2 and NO cannot be detected in this study. Therefore, here we mainly focused on the NO_2 and SO_2 emitted by the ship, while the other two main pollutants of CO_2 and NO were not introduced in the Section 1. We have added the introduction about ship emitted NO and CO_2 and the NO/NO_2 ratio in different aged plume in the revised manuscript, as well as related references. Please refer to Line 37-38, 104, 396-402, and 472-473.

2. At the end of the introduction (Line 97-100) and in section 3.3 it is stated that the measurements can be used to estimate a fuel Sulphur content (FSC) from the SO2/NO2 ratio. As already mentioned in the first general comment the amount of NO2 and therefore the SO2/NO2 ratio strongly depends on the age of the plume. Directly at the

stack the SO2/NO2 ratio should be highest and then decreasing with increasing time. The authors should consider this in their description and calculations.

R: Thanks for the comments. We have not considered properly in the previous manuscript. NO can converted to NO_2 by reaction with O_3 in the atmosphere, and the rate of NO conversion to NO_2 is strongly affected by the concentration of O_3 (Han et al., 2011). The average value of O_3 between 08:00 and 17:00 in Yantian was 63.7 ppb during the campaign. Considering the abundance of ozone, the NO emitted by the ship will react with O_3 rapidly to form NO_2 within a few minutes or even faster (Seyler et al., 2017). In addition, NO_2 is photolyzed by UV radiation to release NO and oxygen radicals. In the collision reaction with N_2 or O_2, oxygen radicals react with oxygen molecules to reform O_3. So the conversion between NO and NO_2 is very fast and maintains a dynamic balance with sunlight during the daytime (Singh et al., 1987). It can be considered that the plume measured by MAX-DOAS was stable after the dynamic reaction.

Besides, there is a strong correlation between the DSCDs of SO_2 and NO_2 with the average value of R higher than 0.9 in this study. It proves that there is no significant change in the value of NO/NO_2 in the observed plume. Seyler et al. (2017) and Mellqvist et al. (2017) have used this relationship for ground-based and airborne DOAS measurements of ship plumes to distinguish ships with low (0.1 %) and high (1 %) fuel sulfur content. These experiments have proved that the low and high sulfur oil can be better distinguished based on SO_2/NO_2. (Seyler et al. 2017). The corresponding discussion has been added to the manuscript. Please refer to Line 396-402.

3. Results presented in section 3.1 do represent only one measurement at one day. If the authors have "more than a dozen cycles" (line 220-221), why they don't show an average of all cycles. The presented cycle is a snapshot and might be not representative to draw conclusions. Well, even an average over one afternoon does represent only a snapshot of the situation. The authors should consider this in their discussion or should skip this section.

R: There may be some misunderstandings due to the unclear description. The purpose of Section 3.1 is to investigate the 2-D distribution of retrieved NO_2 and SO_2 DSCDs using 2-D scanning measurement of MAX-DOAS. The hotspots of NO_2 and SO_2 are related to the azimuth of the berth where the ship is docked and the corresponding ship operation status. It is obviously that the 2-D distribution of NO_2 and SO_2 DSCDs changes with time, so that it seems unreasonable to show the average of all scan cycles, which may weaken the spatial distribution of hotspots. However, the results of the rest of the cycles were also shown in Figure 6. It can be seen that the concentration at a given azimuth and elevation is constantly changing throughout the day.

4. Also in Section 3.2 the authors discuss only data from two selected day. To make more general conclusions the authors have to average a longer time period (if possible all Wusong measurements).

R: Thanks for the suggestion. We have further analyzed the data measured at Wusong from January to March 2018. We have combined the hourly mean value of NO_2 and

SO_2 over three months with the wind direction and found that the average DSCDs of NO_2 and SO_2 is higher when the direction of wind is parallel to the observation direction. In addition, the DSCDs of NO_2 and SO_2 also shows a similar trend to ship density. Please refer to the responses to specific comments 17 and 19. This part of the content is also added to the manuscript. Please refer to Line 289-315.

5. Again in section 3.3 the conclusions are based on very little data points (only nine!), which is critical to make general statements. So for sound statements much more data have to be analyzed.

R: Due to the few samples of ship details we obtained on site, only 9 ships were discussed in the conclusion of Section 3.3. We have added more data analysis in Section 3.3. The Figure R1 shows the relationship between SO_2 and NO_2 DSCDs from multiple ships emission during the Yantian observation in June 2018. Figure R1 (c) and (d) are the supplementary analyzed ships but no related fuel information and operative status were available.

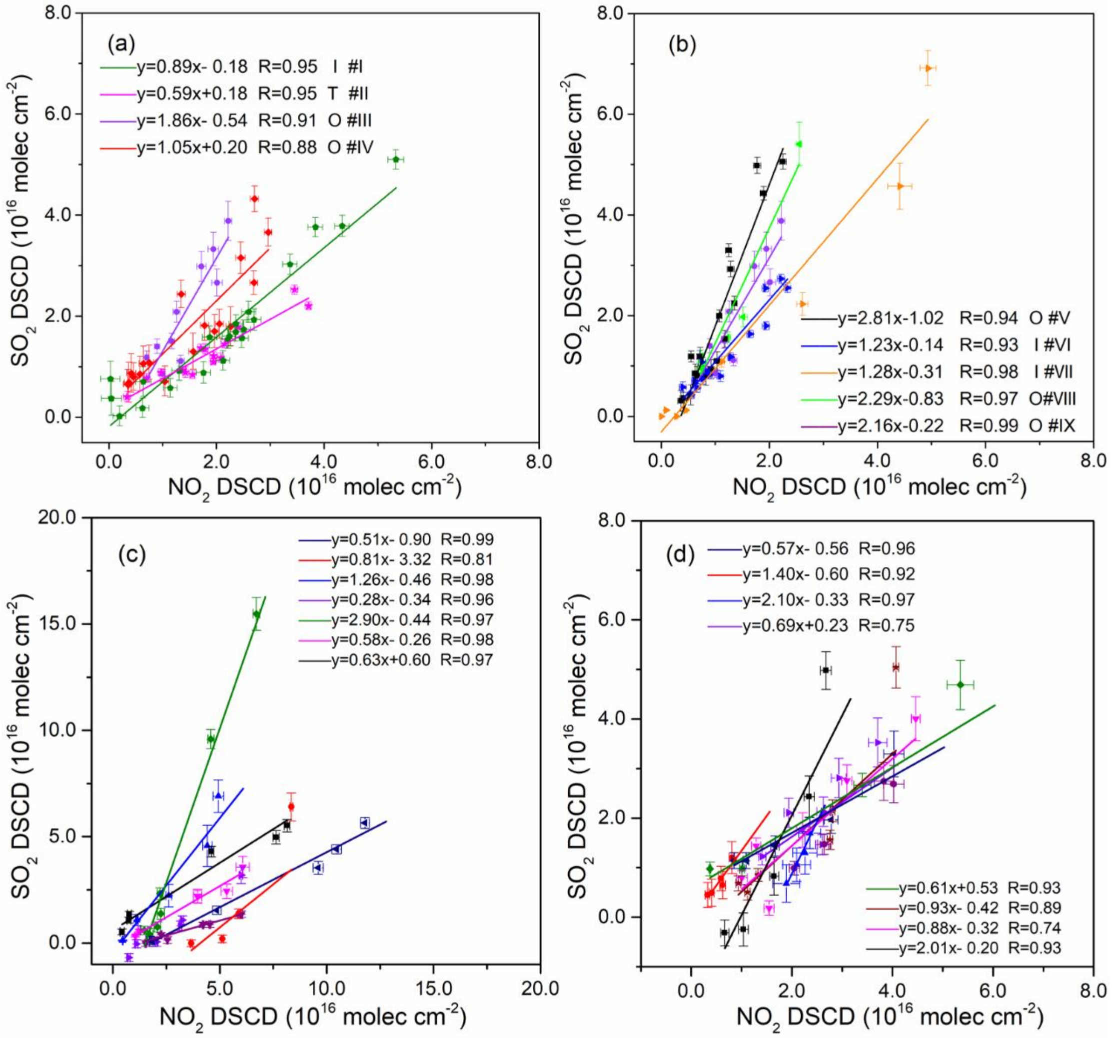

Figure R1. The relationship between SO_2 and NO_2 emitted by several typical vessels, the letter "O" indicates the outbound vessels, "I" indicates the inbound vessels, and "T" indicates the tugboat.

Besides, we have made a statistics for the values of SO_2/NO_2 discharged from 55 ships. The frequency distribution of the slope of SO_2/NO_2 is shown in Figure R2. It shows that the values of SO_2/NO_2 were mostly distributed between 0.0 and 1.5 with the proportion is about 72.7%. Ships with the value of SO_2/NO_2 between 0.6 and 0.9 have the highest proportion, appeared for 15 ships in total. It indicates that most of the fuel used by ships in Yantian Port could be qualified. But there are still some ships may use non-compliant fuel, because the ships with a value of SO_2/NO_2 greater than 1.5 account for 27%. This part of analysis has been added to the manuscript. Please refer to Line 404-415, 442-449, Figure 14 and 15.

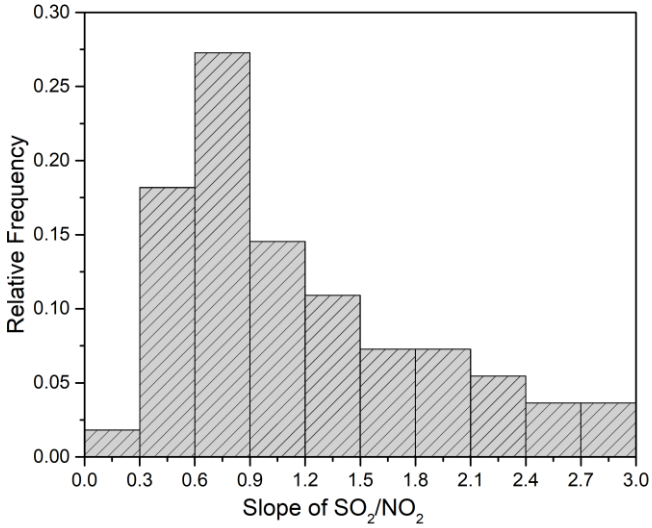

Figure R2. Frequency distribution of the slope of SO_2/NO_2 from 55 ships.

6. At least in the Conclusion the authors should discuss not only the advantages but also the limitations of the MAX-DOAS method, which are: - no NO and CO2 measurements (which are the main components inside the plume) - no measurement during twilight and night.

R: Thanks for this suggestion. We have not discussed the limitations of the MAX-DOAS method so much in previous manuscript. Since MAX-DOAS uses solar scattered light as the source, it cannot be measured at night when there is no sunlight, and there is a large error during twilight and rainy observations. Moreover, the spectrometer used in this experiment covers the range of 296~481 nm, while the strong absorption band of NO is 200~230 nm and CO_2 has a strong absorption in infrared. For the limitations of MAX-DOAS method in ship emissions monitoring, we have discussed in the Conclusion of the manuscript. Please refer to Line 472-474.

Specific comments:

1. Line 15: It is confusing that the authors mention that the measurements took place in Shanghai and Shenzhen and the next sentence starts with "These three typical measurement sites*: : :*" In Section 2.2 it becomes clear that the measurements were performed at three sites in two regions –> please clarify in the abstract.

R: "…… in China's ship emission control area (ECA) of Shanghai and Shenzhen, China. These three typical measurement sites are used to……" has been changed to "……in

China's ship emission control area (ECA) of Shanghai and Shenzhen, China. Three typical measurement sites were selected in these two regions to ……" Please refer to Line 14-15.

2. Line 37: consider also CO2 (see first general comment)
R: We have discussed the impact of CO_2 emissions from ships in manuscript. Please refer to Line 36.

3. Line 42-43: what kind of important role do the ship emitted pollutants play in air quality, human health and climate? Political regulations, monitoring, enforcement, : : :?
R: Pollutants emitted by ships will increase the levels of NO_2, SO_2 and particulate matter in coastal cities, and the emissions will lead to the decline in urban air quality. Pollution from ships will increase mortality in surrounding areas. Nearly 70% of ship emissions occur within 400 km of coastlines, causing air quality problems through the formation of ground-level ozone, sulphur emissions and particulate matter in coastal areas and harbors with heavy traffic. Besides, Ship emissions have a certain degree of impact on the climate. Studies indicate that the cooling due to altered clouds far outweighs the warming effects from greenhouse gases such as carbon dioxide (CO_2) or ozone from shipping, overall causing a negative present-day radiative forcing (RF) (Eyring et al., 2010; Lai et al., 2013; Liu et al., 2016; Yang et al., 2007). Therefore, with the increased awareness of impacts by ship emission, the ship emitted pollutants will be more strictly controlled by Political regulations, monitoring, enforcement and other related departments.

4. Line 53-54: The authors have to distinguish different limits in different ECAs: So the maximum fuel Sulphur Continent (FSC) in ECAs at the US coast and Europe (whole Baltic- and North Sea) is 0.10% S m/m. Inside the Chinese ECA it is 0.50 % S m/m. By 2020 the maximum FSC is 0.50% S m/m all over the world (global Sulphur cap) which is not related to designated ECAs. As the use of exhaust gas treatment systems (Scrubber) is allowed as an alternative, the authors should mention this option, too.
R: China's ECA regulations are different from other regions such as the US and Europe. In China, all ships in the ECAs are required to use fuel with a sulfur content not more than 0.50 % m/m during docking from January 1, 2018. As of January 1, 2019, the ship entering the ECAs should use fuel with a sulfur content of not more than 0.50 % m/m, whether it is sailing or docking. Besides, the maximum FSC in ECAs at the US coast and Europe is 0.10% S m/m. We have distinguished the limits of different ECAs in the manuscript, and also added the content that exhaust gas treatment systems (Scrubber) is allowed as an alternative. Please refer to Line 55-64.

5. Line 57: Are Scrubbers allowed in the Chinese ECA? If yes, this has to men mentioned here, too.
R: Scrubbers is not forbidden in China and we have added this content to the manuscript. Please refer to Line 62.

6. Line 64: ": : : usually fast detecting: : :" –> What is fast (minutes, hours, days,: : :)?
R: Using the portable rapid analyzer of fuel oil sulfur content can complete the detection of sulfur content of fuel in dozens of minutes, the detection accuracy is controlled within the order of 0.1 ppm. Please refer to Line 70.

7. Line 69: the authors should give a reference (e.g. Kattner et al. 2015, or Seyler et al. 2017)
R: Thanks for the suggestion, we have followed and added these two references in the manuscript. Please refer to Line 74.

8. Figure 2: Do the authors have the copyright for the satellite pictures in Fig. b-d? If not, they have to cite the source.
R: We have marked the source of the picture (b) to (d) were cited from Google Earth. Please refer to Figure 1 in revised manuscript.

9. Figure 3: It looks like graph (b) and (d) are mixed up, because the y-scales do not match the y-scales of graph (a) and (c). Can the authors confirm this? If not, the authors should comment in the corresponding discussion (line 170-175) why the scales are different
R: We have not adjusted the y-scales of graph (a) and (c) in order to make the lines of absorption structure look more obvious. Now we have unified the y-scales of NO_2 and SO_2 in both cases. Please refer to Figure 2 in the revised manuscript.

10. Figure 3 (line 180-181): Wouldn't it be better co compare measurements with same elevation angle to minimize differences due to different optical length inside the planetary boundary layer (PBL)?
R: According to the specific comments 9 and 10, two spectra measured at the same elevation angle of 5° on June 22, 2018 were selected to re-plot the Figure 3. Please refer to Figure 2, Line 164-172.

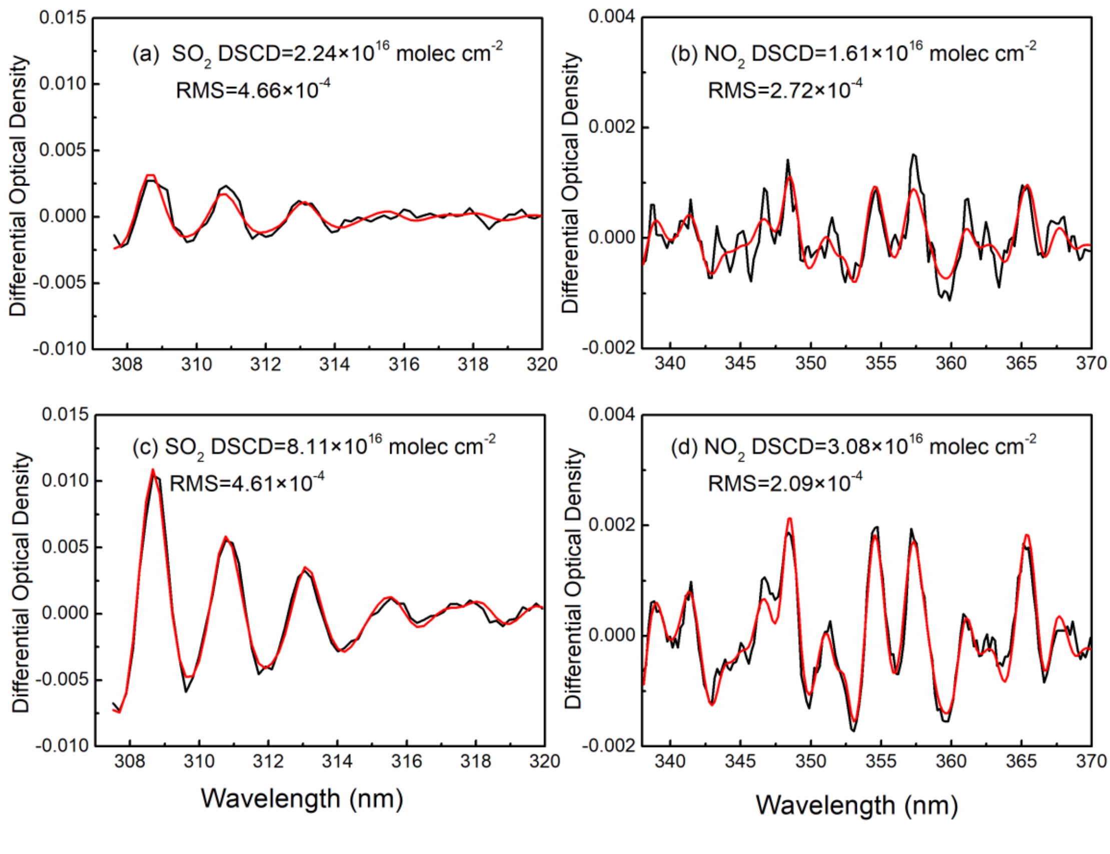

Figure R3. Typical DOAS spectral fitting for SO_2 and NO_2. (a) and (b) show the clean condition of spectrum collected at an elevation angle of 5° at 10:39 LT on 22 June, 2018, while (c) and (d) are the ship plumes polluted case of spectrum measured at an elevation angle of 5° at 09:53 LT on 22 June, 2018. Black lines show the measured atmospheric spectrum and the red line shows the reference absorption cross-section.

11. Line 190: What is located opposite the berth? Any industry which might emit NOx or SO2?

R: Opposite the berth is the South Channel of the Yangtze Estuary. The only sources of NOx and SO_2 could be the ships emissions on the channel, and the main channel is more than two kilometers away from the berth. Behind the building of Pudong MSB, there are green land and residential area. The container yard was located between the building and berths.

12. Line 196: Why only 10◦ angle for the reference spectrum? At 10◦ the way thru the PBL is still long and therefore might be influenced by emissions. Why the authors did not measure at 90◦ or at least at 65◦ like in Wusong?

R: We can collect reference spectrum at 90° angle in Yantian because the instrument was installed outdoors without obstructions. But the instruments in Waigaoqiao and Wusong are installed indoors. Due to the block of the building, higher elevation angle cannot be achieved. Therefore, we choose a relatively clean orientation as reference spectrum. Please also refer to the responses to Reviewer #2, where we showed the comparison of DSCDs results using different reference spectrum. The different choice of reference spectrum can affect the absolute value of DSCDs, but not change the characteristics of 2-D spatial distribution of DSCDs.

13. Figure 4: In my opinion this figure is not necessary to explain the measurements. So if the authors want to save some space, they could skip this figure.
R: Thanks to the reviewer's suggestion. Since the observation method of Waigaoqiao is more complicated than the other two places, the Figure 4 can facilitate the description of the experimental scheme more organized and clear. Besides, this figure can help readers better understand the horizontal and vertical observation methods of MAX-DOAS. So we decide to keep it.

14. Line 208-210: please explain with compass direction (e.g. shift to north-west) to compare it to the given wind direction. What dose “MAINLY came from the south” mean? Here only one measurement (a 15 min scan) is discussed. Dose the wind direction changed during this 15 minute scan?
R: Since there is no weather station in Waigaoqiao, we refer to the wind information provided by the Shanghai urban site. Several stations in Shanghai have shown that the wind was from the SSE at 12:00, and the wind direction was also dominated by the southerly wind in the next two hours. So it could be considered that the wind direction has not changed significantly within 15 minutes.

15. Line 220-221: If the authors have “more than a dozen cycles” why they don’t show an average of all cycles. The presented cycle is a snapshot and might be not representative to draw conclusions.
R: Please refer to the previous responses to the general comments #3.

16. Line 253: ships in navigation or maneuver? Do the authors can exclude emissions from the industry behind the river (visible in Fig 2 (c)) as a source?
R: The ships were in the state of navigation. According to Figure R4, we can see the main green land areas behind the river, including villages and forest parks. In addition, the opposite of the river is a small dock and a station for transporting containers. Due to the lack of relevant research and observations in this region, it is very difficult to estimate the amount of NO_2 and SO_2 emitted from the opposite side, and we have to ignore this part of the source compared with the ship emissions on the channel.

Figure R4. Map of Wusong measurement site and direction of observation, cite from Google Earth.

17. Line 256-268: Why the authors do only check for the influence of wind speed? I would expect a much bigger correlation with wind direction because the optical length inside the polluted air and therefore the response signal is probably increased when the wind transports the polluted air towards the DOAS. On the contrary the optical length inside the polluted air and therefore the response signal is probably less when the wind transports the polluted air perpendicular to the DOAS (out of the field of view). The authors should check the wind direction dependency for all data. Why constant high wind speed (5-6 m/s is not high) unstable atmospheric conditions? As stated above, in my opinion the wind direction is of high importance as well.

R: Thanks for the suggestion, we did not consider carefully before. We have re-analyzed all the data from January to March 2018 and calculated the hourly mean of the NO_2 and SO_2 DSCDs for each elevation angle. The wind rose diagrams of NO_2 and SO_2 at elevation 5° are shown in (a) and (b) of Figure R5. The wind during the observation period mainly comes from NNW. It can be seen that the average of NO_2 DSCDs is small under the wind conditions from North. When the wind direction is parallel to the observation direction (i.e. E and W, the viewing direction of the telescope is pointing to the East), the average DSCDs of NO_2 is significantly higher than the direction of N. Similarly, the average value of SO_2 in the E and W is higher than that in the S and N. It suggests that the optical length inside the polluted air and therefore the response signal is probably increased when the wind transports the polluted air parallel to the DOAS viewing direction.

In order to prove this point more accurately, we have made a statistics in Figure R5 (c) and (d), the perpendicular direction for N and S is the considered wind from 0°±15° and 180°±15°, and the parallel direction for E and W is considered wind from 90°±15° and 270°±15°. It can be seen from (c) and (d) that the NO_2 and SO_2 DSCDs are quite different in these two types of wind directions. When the wind is parallel to the observation direction (E and W), 34 percent of NO_2 is greater than 3.00×10^{16} molec cm^{-2}, 31 percent of SO_2 is greater than 1.5×10^{16} molec cm^{-2}. However, in the perpendicular

direction (N and S), the occurrence of high DSCDs of NO_2 and SO_2 is significantly less than that of parallel direction. We have added this part to the manuscript. Please refer to Line 289-304.
Besides, because of the average wind speed is less than 3.7 m/s during the observation period, so we set the wind speed higher than 5m/s as the condition of unstable atmospheric.

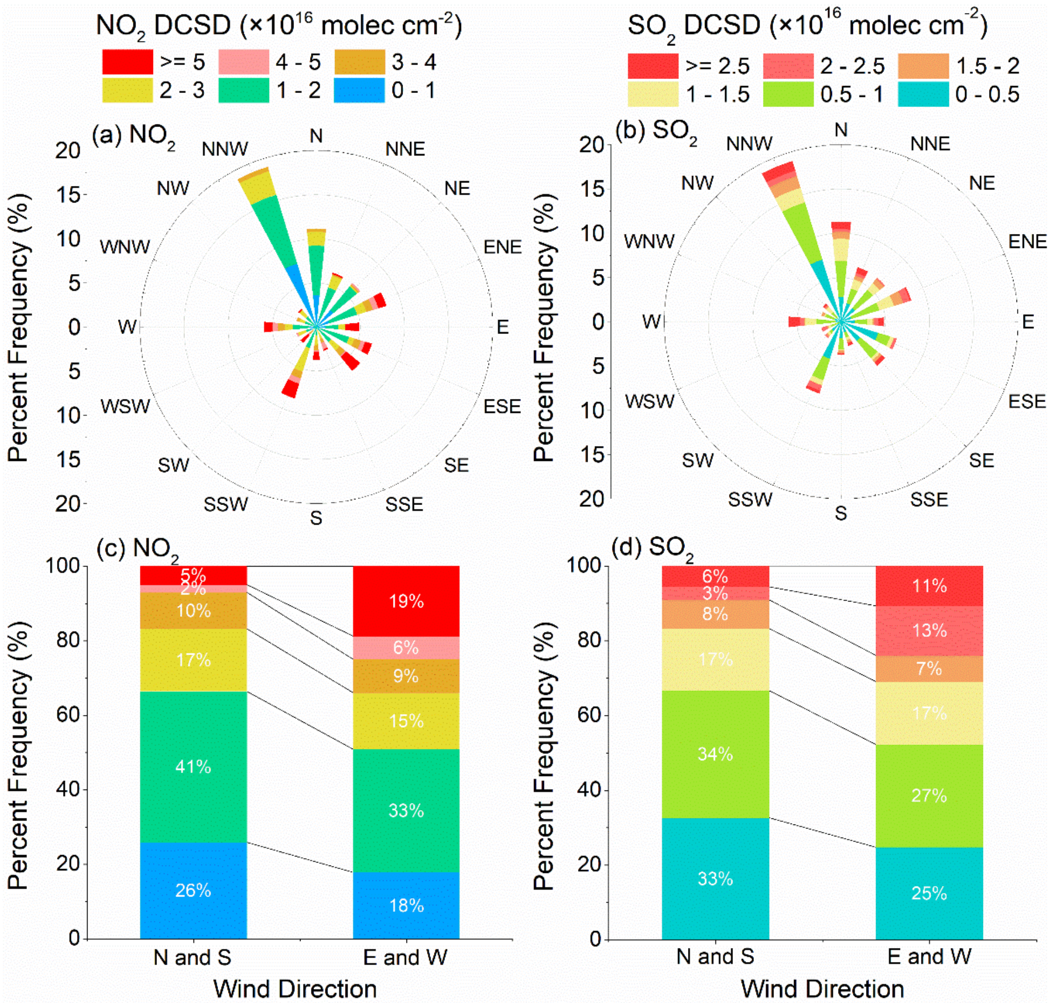

Figure R5. The dependence of (a) and (c) of NO_2 and (b) and (d) of SO_2 DSCDs on wind directions from January to March 2018 at elevation 5°.

18. Line 263-264: The close relation of SO2 and NO2 signal to the flow of ships (better use "ship density) is not clear on March 09 12:00-14:00. At this time the ship density is constant but SO2 and NO2 decrease.
R: As mentioned in manuscript and Figure R5 and R6 in response, the DSCDs of NO_2 and SO_2 was affected by many factors, including wind speed and direction, as well as ship density. So the DSCDs changes are not exactly the same as the ship density trend. Please also refer to the responses to specific comments 19.

19. Figure 7 and corresponding discussion: If the authors want to correlate SO2 and NO_2 with traffic density and meteorological conditions, they should use all data and not

only data from two days. They should create scatter plots (e.g. ship density on x and SO2 on y-axis) to find correlation coefficients. As the authors give a scan time of 7 minutes for the Wusong measurements (Table 1), each box-whisker-plot is based on only 4 measurements. This is not valid for this kind of plots. If the authors use all azimuth angles in one box, this is also not valid, because of different optical length and therefore not comparable measurement conditions.

R: It is true that the amount of data in two days is too little to prove the conclusion of this part. We have added more data during the observation period to show the relationship between ship density and the DSCDs of NO_2 and SO_2 at elevation 5°.

Due to lack of the data of ship density from MSB office, we have to count manually the ship density during each hour based on the real-time photos taken by the instrument. In this way, over fifty photos need to be manually checked and counted for each measured hour, which costs lots of time and also contains uncertainties to some extent. Therefore, we have looked through all the photos from January 30 to February 13, 2018 and another two days in Fig. 7 (January 1 and March 9, 2018). In total, 17 days were used to discuss the relationship between ship density and DSCDs of NO_2 and SO_2, as shown in Figure R6.

In Figure R6, the hollow squares in the middle of the box represent the mean value, and the solid lines in the middle represent the median. The upper and lower edges of the box are 25% and 75% quantiles, respectively. It is found from Figure R6 that as the ship density increases, the hourly mean values of NO_2 and SO_2 show an upward trend. Since the fuel used by the ship is inconsistent, and the speed and direction of win are also affect the DSCDs, it is difficult to find the linear relationship between ship density and DSCDs every hour in this complex environment. However, we have made the linear analysis of the ship density and the corresponding average of the DSCDs (the hollow squares in the middle of the box). The DSCDs of SO_2 has a high correlation coefficient with ship density (R=0.97), while the correlation of NO_2 is relatively weak (R=0.86) due to the more complicated emission sources nearby. We have added this part to the manuscript. Please refer to Line 306-315.

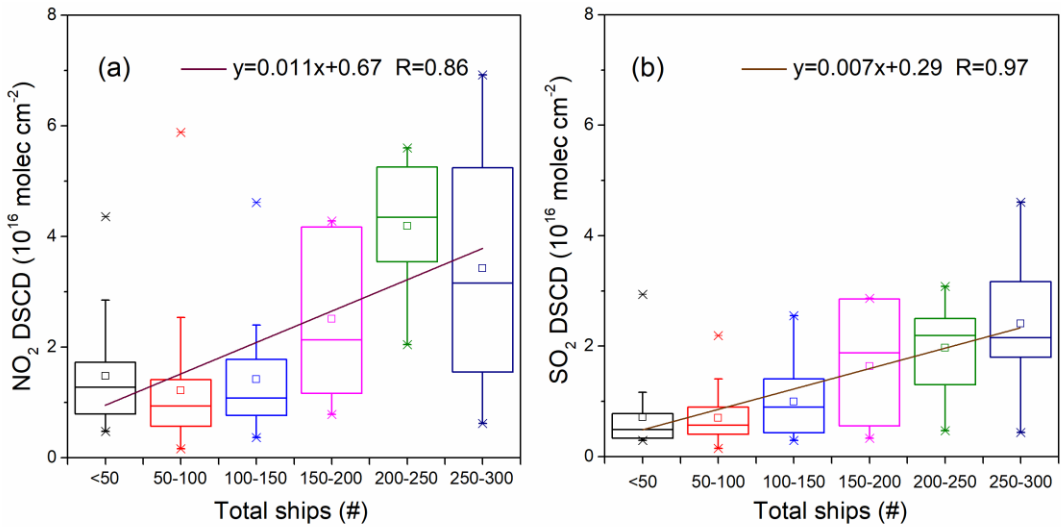

Figure R6. Relationship between DSCDs of (a) NO_2 and (b) SO_2 and ship density.

20. Line 276-279: This conclusion might be true, but has to be proved not only by a snapshot but by an average as indicated in the comment above.
R: Please refer to the responses to specific comments 17, 18 and 19.

21. Line 282-283: To support the conclusion that the ships are the main source for NO2, the authors should roughly estimate the influence of the surrounding emission sources (especially the main roads and highway, because this could be a significant NO2 source).
R: Due to the lack of relevant research in the areas of Wusong site, we are unable to obtain the influence of the surrounding emission sources accurately. We have installed two active LP-DOAS (Long-Path DOAS) in the Wusong MSB and Fudan University Jiangwan Campus in March of 2018, respectively. The locations of Wusong and Fudan have been shown in Figure R7 (a), and the red arrow indicates the light path of the two LP-DOAS. The campus is 4 kilometers away from Wusong and is considered to be free of pollution because the campus is almost covered by green spaces and have no major emission sources.
Considering the synchronization of data, concentration of NO_2 from March 15 to March 30, 2018 have been analyzed. During the observation, the average value of NO_2 in Fudan campus and Wusong site is 12.42 ppb and 30.50 ppb, respectively. In order to make a clearer explanation, we have shown the time series of NO_2 in a short segments of three days as an example in Figure R7 (b). We have calculated the difference of NO_2 between Wusong and Fudan campus, which is considered to represent the sum of NO_2 emissions from ships and surrounding sources at Wusong area. For the red line in Figure R7 (b), the rapidly changing part is discharged by the ships, while the smooth part may come from surrounding emission sources such as roads and highway. After a rough estimation, the proportion of NO_2 emitted by ships is more than 47%. However, this estimation are quite rough and more accurate conclusion need be furthered with multiple measurements and technical method.

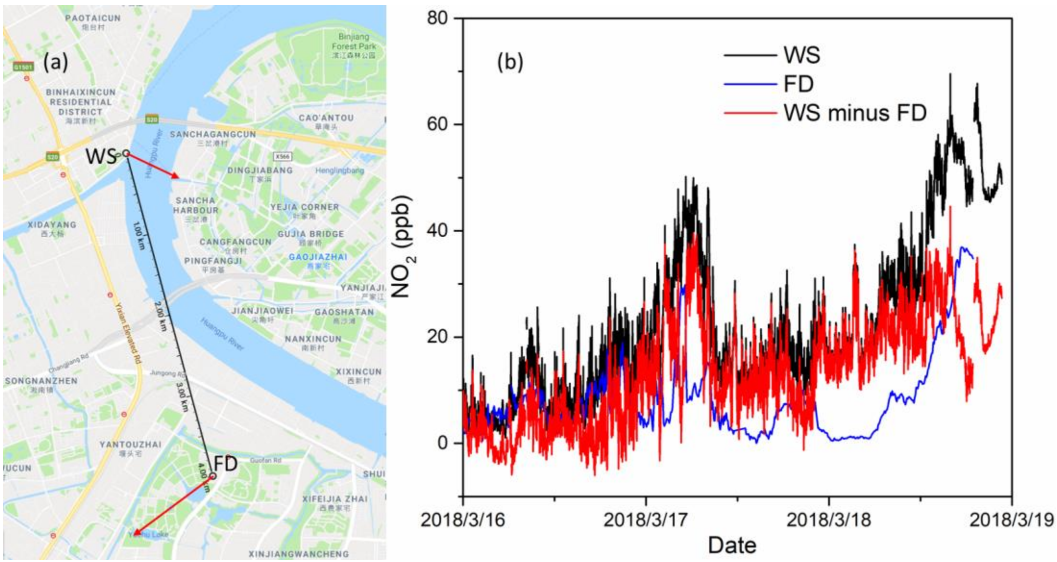

Figure R7. The locations of the LP-DOAS measurements at Wusong site and Fudan campus (a), the viewing direction and distance of instrument is indicated by a red arrow, cite from Google Maps, and (b) time series NO_2 concentration from March 16 to March 19, 2018.

22. Line 285-287: The meaning of this sentence in not clear. Do the authors mean that they want to use the complicated MAX-DOAS inland waterway measurements to check ships for compliance with fuel Sulphur regulations? It is not clear how the authors want to compare a theoretical SO2 emission (which unit?) with the MAX-DOAS measurement result (column density). This has to be explained in more detail. In my opinion comparing only SO2 from theoretical emissions to DOAS measurements does not work, because from the DOAS measurements you don't know whether you measure in line or perpendicular to the plume.

R: Thanks for the suggestion. We have not expressed it clearly in this sentence, and we have reorganized the sentence. Please refer to Line 324-329. It is difficult for regulatory authorities to achieve fuel detection for each ship due to the large ship density in complicated inland waterways. So the application of remote sensing technology could provide support to regulatory authorities. The theoretical NO_2 an SO_2 concentration of plume exhausted from the chimney can be calculated based on the legally sulfur content and ship activity data. Besides, combined with the diffusion model of plume, the theoretical concentration of SO_2 on the observation path of MAX-DOAS can be obtained. Therefore, MAX-DOAS can be used to mark the suspicious ships on the complicated inland waterways according to whether the observed SO_2 concentration exceeds the theoretical value.

23. Line 292: largest container ports related to what? China, Asia, World?

R: Yantian Port in Shenzhen is the largest single port area with the largest container throughput in China. According to the survey, Shenzhen Port is the third port of the world container port in 2017, and Yantian Port is the main port of Shenzhen Port. So the Yantian Port is one of the largest container port in China and even in the world.

24. Line 305-308: Why the big container vessel does not show any NO2 signal but the tug do so? The container vessel should emit even more NOx than the two tugs. Please discuss.

R: We have not noted this phenomenon in detail before. Due to the unreasonable setting of the color bars, the signal of the big ship looks very weak. We have re-adjusted the color bars in Figure R8 to make the emission signals of several ships look more intuitive. According to Figure R8 (b), we can observe that the signal of NO_2 emissions from large ships are obvious. Please also refer to Figure 10 in manuscript.

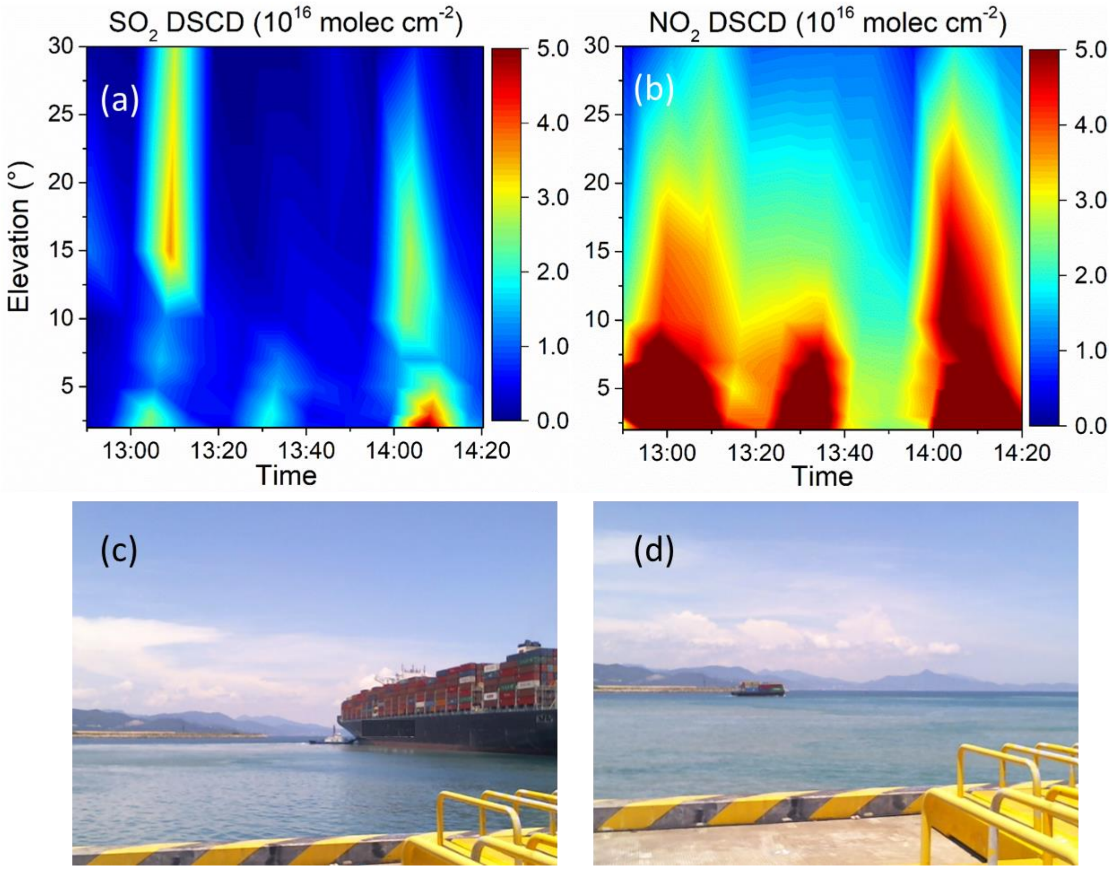

Figure R8. Measured DSCDs of (a) SO_2 and (b) NO_2 during 12:55~14:20 and live photos taken by the camera at (c) 12:56 and (d) 13:22 on May 26, 2018.

25. Line 314-316: This sentence put a question mark onto the measured plumes at 13:00 and 13:30. So the authors have to state that for the two earlier measurements no other ship could have caused the high signals (e.g. based on AIS analysis).

R: We have determined through AIS information and on-site records that there are no other ship emissions disturbances for the two earlier measurements, and we have made corresponding corrections to this sentence. Please refer to Line 358-359.

26. Line 323: How the emissions are related to the operational status (was not discussed before)?

R: In general, under given conditions, emissions from vessels for propulsion engines and auxiliary engines can be estimated by equations (1) - (3) (Zhang et al., 2017).

$$E = Load \times Activity \times EF \times FCF \times CF \qquad (1)$$

$$Load = MCR \times LF \qquad (2)$$

$$LF = (V_{actual} / V_{maximum})^3 \qquad (3)$$

Where

E = emissions, g;

Load = engine power, kW;

MCR = maximum continuous rating, kW;

LF = load factor, dimensionless;

V_{actual} = actual speed, knots;
$V_{maximum}$ = maximum speed, knots;
Activity = ship activity time, h;
EF = emission factor, g/kWh;
FCF = fuel correction factor, dimensionless;
CF = control factors for emission reduction measures, dimensionless.
According to formula (1), when the EF, FCF, and CF are constant, the ship's emissions are closely related to the power, activity time and the speed of ship. Unfortunately, we cannot get all the parameters in the formula in this study. However, it can be found by estimation that the emissions will increase when the power increases. We have added this part of the discussion to the manuscript. Please refer to Line 407-408.

27. Line 326-327: “we try to further detailed SO2 emissions from the measurement” –>the meaning is not clear. Do the authors want to say that they try to analyze detected plumes in more detail?
R: Thanks for the suggestion, we did not express this sentence clearly. We try to analyze the detected plumes in more detail. This sentence has been re-phrased, please refer to Line 369-370.

28. Line 339: Which mathematical method? How the baseline is calculated (e.g. running mean or median; which averaging interval?)?
R: The mathematical algorithm used here is BESDS (baseline estimation and denoising using sparsity). Specifically, the baseline is modeled as a low-pass signal and the series of peaks is modeled as sparse with sparse derivatives. Moreover, to account for the positivity of peaks, both asymmetric and symmetric penalty functions are utilized (Ning et al., 2014). The specific methods and principles we have supplemented in the manuscript. Please refer to Line 238-240, and also refer to the responses to Reviewer #2.

29. Line 351-355: The use of fuels with different Sulphur content is one possible explanation for the observation of different SO2/NO2 ratios. The age of the plume and the direct NO2 emissions is another plausible explanation. As already mentioned in the first general comment, ships mainly emit NO but not NO2. Therefore, directly at the stack the SO2-NO2 ratio is highest. When the plume ages NO2 is formed and the SO2-NO2 ratio decreases. NO2 emissions are dependent on the kind of engine and the burning temperature of the engine as well. The authors have to consider this in their discussion.
R: Thanks for the suggestion, we have considered the impact of NO and added this part of the discussion to the manuscript. Please refer to the previous responses to the general comments #1 and #2.

30. Line 359-361: Is the main engine really operated with fuel with higher Sulphur content than the auxiliary engine? Do the authors have a source for this statement? I

thought inside the Chinese ECA the maximum allowed fuel Sulphur content is equal to that allowed at berth.

R: The detailed questionnaire of vessel information was obtained by boarding inspection. The inspector took fuel samples of several ships and brought them back to the laboratory for testing. The results shows that the sulfur content data in the questionnaire can be considered to be accurate after verification. The Figure R9 provides examples of two ships. Besides, there is no 0.5% requirement for ships in navigation during our observation period in 2018. Please also refer to the responses to the specific comments #4 and #31.

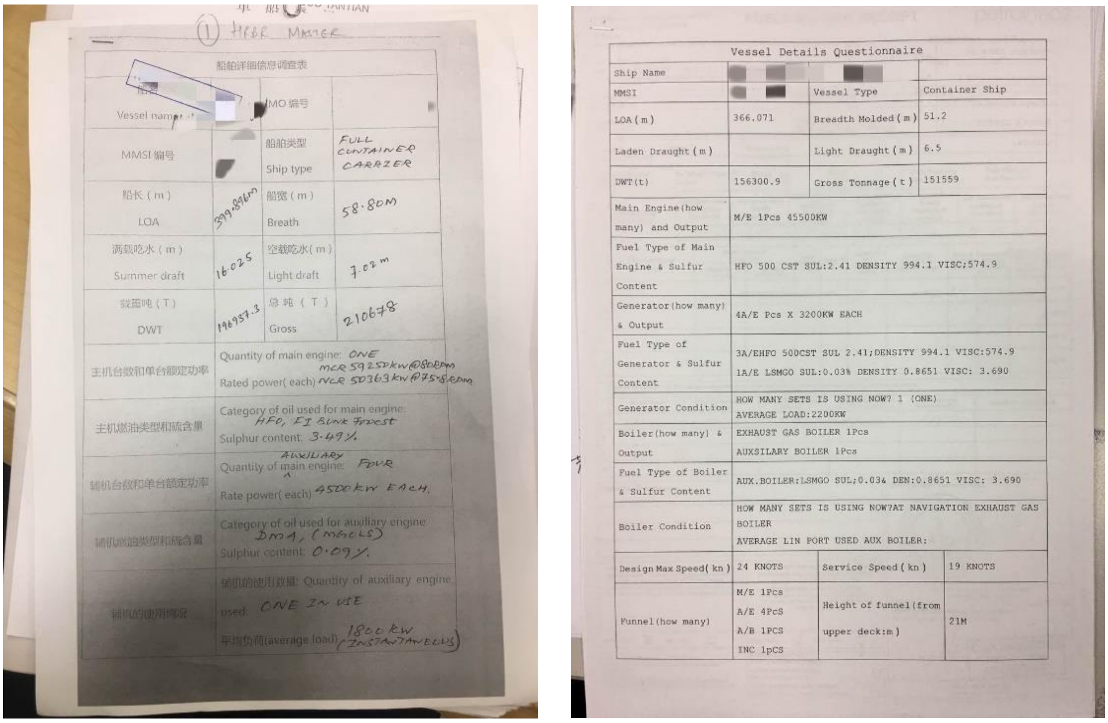

Figure R9. The detailed questionnaire of vessel information: two example ships.

31. Line 381: Do the authors mean vessel #IX instead of cargo #IV? What about vessel #V and #VIII? Are they allowed to use fuels with Sulphur content above 3% inside the Chinese ECA? I thought the limit is 0.5%.

R: The "#IV" has been changed to "#IX". Please refer to Line 431.

In China, all ships in the ECAs are required to use fuel with a sulfur content not more than 0.50 % m/m during docking from January 1, 2018. As of January 1, 2019, the ship entering the ECAs should use fuel with a sulfur content of not more than 0.50 % m/m, whether it is sailing or docking. So, there is no 0.5% requirement for ships in navigation during the observation period in 2018.

32. Line 391-394: from the SO2-NO2 ratio displayed in Fig. 12 it is not obvious which is the "irregular observed ratio". I do agree that if the SO2-NO2 ratio is above 1.5 this is an indication for the use of fuel with high Sulphur content. But from this point of view vessel III, V, VIII, and IX should be indicated as non-compliant. Is it possible to estimate a kind of detection limit for the observation of non-compliant vessels? Is it

possible to distinguish between 0.4 (compliant) and 0.8 (non-compliant)? This would address also the conclusion (Line 410-412).

R: Thanks to the reviewers, vessel III, V, VIII, and IX were considered as ships that use unqualified fuel due to the high ratio of SO_2/NO_2. According to the nine samples in Figure 12, the detection limit for the observation of non-compliant vessels we set is 1.5. More legally fuel sulfur content and ship activity data are needed to help us find a reasonable way to distinguish the compliant and non-compliant vessels. It is difficult to distinguish between 0.4 (compliant) and 0.8 (non-compliant) until now, which can be more accurately estimated along with the data of load factor and emission factor during the actual operation in the future. Some explanations have been added to the manuscript. Please refer to Line 440-447.

Technical corrections

Line 15: ships instead of ship

R: The "ship" has been changed to "ships". Please refer to Line 16.

Line 22: ad "the" in front of SO2/NO2: : :

R: The "the" have been added. Please refer to Line 23.

Line 26: Combining instead of Combined

R: The "Combined" has been corrected to "Combining". Please refer to Line 27.

Line 27: What is meant with "logical Sulphur content"

R: By combining the measured data with the actual operating parameters of the ship, the ship's emission model and the diffusion model of the plume, the sulfur content of the fuel used by ship will be calculated. Here we used "logical sulphur content" to represent the assumed S% in emission model estimation, which should be legal.

Line 28: "more accurate way" –> than what?

R: Here we describe the prospective of MAX-DOAS application for the surveillance of ship emissions. In this study, the empirical ratio of SO_2/NO_2 was only concluded based on the DOAS measurements and several samples of ships. By combining with ship emission estimated by actual operation parameters and logical sulfur content, more accurate ratio of SO_2/NO_2 for compliance could be obtained, which can improve the accuracy of the surveillance of ship emissions by MAX-DOAS measurements.

Line 44: ad "of" in front of "kilometers"; remove "the" in front of "most.

R: We have corrected them. Please refer to Line 45-46.

Line 53: areas instead of zones

R: The "zones" has been changed to "areas". Please refer to Line 55.

Line 57: should or must?

R: The meaning expressed here is "should".

Line 85: close instead of closed
R: The "closed" has been changed to "close". Please refer to Line 90.

Line 95: ad "the" in front of instrument
R: We have added "the". Please refer to Line 101.

Line 105-106: ": : :and stored in form of spectrum" –> It is not clear what is meant. The MAX DOAS instrument records spectra which represents the intensity of scattered sunlight at different wave length (please give the scan interval). For each viewing direction and measurement interval a separate spectrum is recorded.
R: The spectrometer records the intensity of solar scattered light in the wavelength range from 296 nm to 481 nm, there are 1024 data points with an average scan interval of 0.18 nm. The spectrum is stored as a file, it not only contains the light intensity at 1024 bands, but also contains the corresponding time, date, solar zenith angle, solar azimuth angle, and elevation angle, etc. Please refer to Line 143.

Table 1: The measurement sites name and locations should start in the same line the operations AZ starts. At the moment it is little bit confusing that the line where the AZ is given starts above the site names.
R: We have followed the suggestion and made the correction. Please refer to Table 1.

Table 1: The authors should give the number of scan cycles, as well. As the measurements in Waigaoqiao last less than one day and one can takes 15 minutes I think there are not many scans available for analysis.
R: Please refer to the previous responses to the general comments #3.

Line 186: ad "of" in front of "more than"
R: The "of" have been added in front of "more than". Please refer to Line 199.

Line 189: ad "of" in front of "ships at"
R: The "of" have been added in front of "ships at". Please refer to Line 202.

Line 194: remove "can" in front of "covers about"
R: The "can" has been removed. Please refer to Line 207.

Line 204: increase instead of increases
R: The "increases" has been changed to "increase". Please refer to Line 217.

Line 242: write "Beside of ocean-going ships, inland waterway vessels also contribute significantly to the amount of ship emissions: : : " instead of "Besides oceangoing ship emissions, inland waterway vessels also contributed significantly to the ship emissions: : :" –> not the emissions, but the ships are ocean-going :-)
R: This sentence has been modified in the manuscript. Please refer to Line 255.

Line 245: close instead of closed
R: The “closed” has been changed to “close”. Please refer to Line 258.

Line 246-247: This sentence is not clear. I suggest to split it.
R: We have split this sentence. “It is only channel to the upstream of Huangpu River. There are some non-container terminals near the measurement site, which mainly handles goods in domestic trading”. Please refer to Line 259-260.

Line 251: ad a space (direction of)
R: The space has been added. Please refer to Line 264.

Line 252: lane instead of lanes
R: The “lanes” has been changed to “lane”. Please refer to Line 265.

Line 256: use singular instead of plural: impact of ship traffic; measurement data
R: We have corrected them. Please refer to Line 270.

Line 273: what do the bars and the stars do represent?
R: The bars is called whisker line, whiskers extend from each end of the box to the internal and external limits. The star is composed of “-” and “×”, “-” represents the maximum and minimum, and “×” are 1% and 99% quantiles. Please refer to Line 285-287.

Line 291: see instead of See
R: We have corrected it. Please refer to Line 333.

Line 299: remove “orderly” in front of “inbound”
R: The “orderly” has been omitted. Please refer to Line 340.

Line 300: 2018 instead of 2019; two dots at the end
R: We have corrected them. Please refer to Line 342.

Line 302: remove “were” in front of “occurred”
R: The “were” has been removed. Please refer to Line 344.

Line 310: was instead of were
R: The “were” has been changed to “was”. Please refer to Line 352.

Line 323: “more or less” –>please be more precise!
R: The “more or less” has been removed. Please refer to Line 366.

Line 325: “for” instead of “with the”
R: The “with the” has been changed to “for”. Please refer to Line 368.

Line 330: “was” instead of “can be”
R: The “can be” has been changed to “was”. Please refer to Line 373.

Line 331: “stand for the peak concentration” –>do the authors mean “represent the peak concentration”?
R: The “stand for” has been changed to “represent”. Please refer to Line 373.

Line 337-338: It is difficult to get the meaning of this sentence. Do the authors want to say that with temporal high resolved measurements (60 sec) it was possible to resolve individually the plume signals of passing ships? Please rephrase.
R: Here we want to express that only a single elevation angle is observed instead of scanning all elevation angles can help us get more data at elevation 7°. Please refer to Line 378-379.

Line 340: Comma after DSCDs
R: The “comma” has been added after “DSCDs”. Please refer to Line 383.

Line 342: “are present” behind cm-2
R: The “are present” has been added. Please refer to Line 385.

Line 345: remove “In addition” in front of “the increases of pollutants”
R: The “In addition” has been removed. Please refer to Line 388.

Line 368: “on” instead of “about”
R: The “about” has been changed to “on”. Please refer to Line 419.

Line 374: “is” instead of “are”
R: The “are” has been changed to “is”. Please refer to Line 425.

Line 379: ad “the” in front of “plume”
R: The “the” has been added in front of “plume”. Please refer to Line 429.

Line 380: “increase” instead of “growth”
R: The “growth” has been changed to “increase”. Please refer to Line 429.

Line 381: “to note” instead of “noted”; “circle instead of “dot”
R: We have corrected them. Please refer to Line 430.

Line 390: ad “high” in front of “sulfur content”
R: The “high” has been added in front of “sulfur content”. Please refer to Line 438.

Line 393: “compliance monitoring” instead of “compliance”
R: The “compliance” has been changed to “compliance monitoring” Please refer to Line

441.

Line 397: write “In this study we performed MAX-DOAS measurements to observe ship emissions of SO_2 and NO_2 in Shanghai: : :” instead of “In this study, we have performed the MAX-DOAS measurements observe the ship emissions of SO_2 and NO_2 in Shanghai: : :”

R: We have improved it. Please refer to Line 452.

Line 400: delete comma

R: The comma has been deleted. Please refer to Line 455.

Line 402: better “: : : are correlated to ship traffic density at stable and unstable atmospheric: : :”

R: We have improve it. Please refer to Line 457-458.

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Zhang, Y., Gu, J., Wang, W., Peng, Y., Wu, X., and Feng, X.: Inland port vessel emissions inventory based on Ship Traffic Emission Assessment Model–Automatic Identification System, Adv. Mech. Eng., 9(7), 1–9, https://doi.org/10.1177/1687814017712878, 2017.

Response to comments from reviewer #2

We thank the reviewers for the constructive comments and suggestions, which are very positive to improve scientific content of the manuscript. We have revised the manuscript appropriately and addressed all the reviewers' comments point-by-point for consideration as below. The remarks from the reviewers are shown in black, and our responses are shown in blue color. All the page and line numbers mentioned following are refer to the revised manuscript without change tracked.

Reviewer
The paper presented by Cheng et al. has reported the shore-based MAX-DOAS measurements of ship emitted SO2 and NO2 under three different conditions in China's ship emission control area (ECA), i.e. ship docked at berth, navigation in the inland waterway and inbound/outbound in the deep water port. Although the detection of SO2 and NO2 by MAX-DOAS has been developed for many years, the employments for ship emission surveillance are an interesting application of the MAX-DOAS technique. I think the manuscript fits to the scope of ACP, especially for this special issue. I recommend publication after the authors addressed the following comments.

Major concerns:
1. The authors use the SO2 and NO2 DSCDs measured at different elevations for the evaluation of ship emissions. However, the vertical distribution of background SO2 and NO2 are quite different. It is not clear that how do the authors separate the ship emissions of SO2 and NO2 signal from the background? This information has to be supplemented in section 2.
R: The explanation about the difference of SO_2 and NO_2 signal of ship emissions and background has not been discussed in detail before. Now we have added it in Section 2.3. Please refer to Line 185-195. In order to better demonstrate the NO_2 and SO_2 concentration in background and emission signal, several typical cycles in June 29th were selected as examples, the selected cycles was boxed out in Figure R1. The data marked with the red and gray shadow is the DSCDs of signal and background, and these two cases have been further shown in Figure R2.

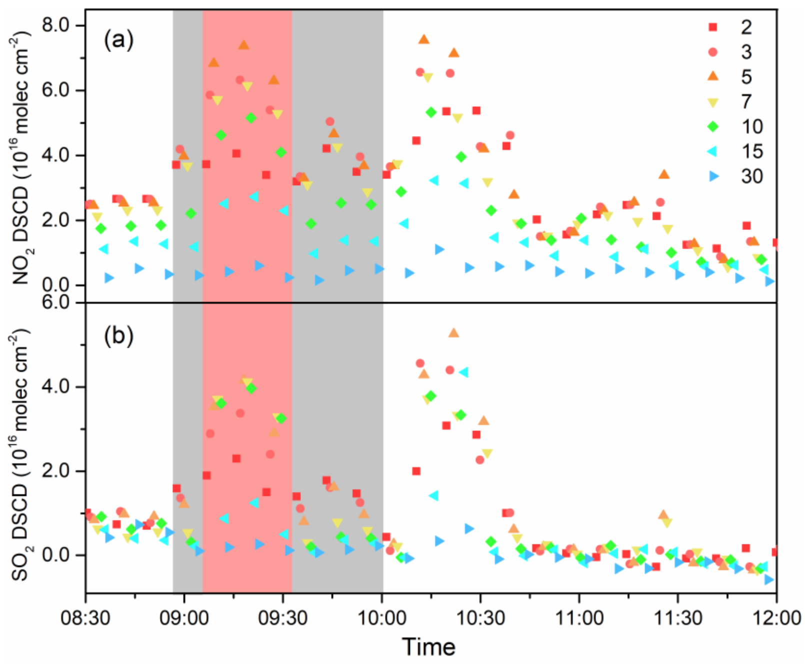

Figure. R1. Diurnal variations of DSCDs of (a) NO_2 and (b) SO_2 on 29 June 2018.

Figure. R2 shows the vertical distributions of NO_2 and SO_2 DSCDs with the elevation angle when there is a ship passing through and not. It can be observed that the DSCDs of NO_2 and SO_2 decrease slowly with increasing angle under clean conditions, during which the maximum values of NO_2 and SO_2 DSCDs are 5.03×10^{16} molec cm^{-2} at elevation 3° and 1.78×10^{16} molec cm^{-2} at elevation 2°, respectively.

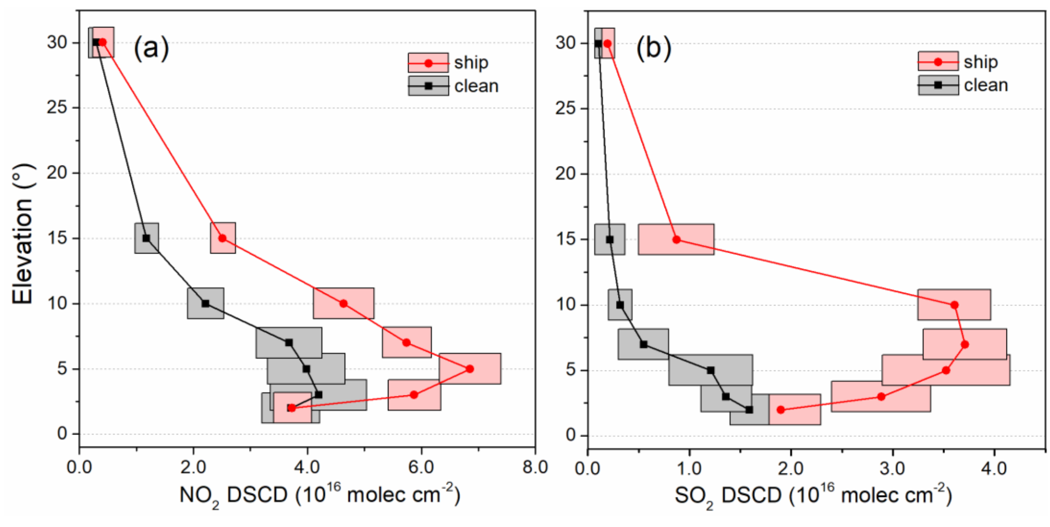

Figure. R2. The distributions of (a) NO_2 and (b) SO_2 DSCDs with elevation angle in ship emission signal and background on June 29, 2018.

In contrast, the NO_2 and SO_2 DSCDs increased significantly when ships passed, showing the maximum values of NO_2 and SO_2 DSCDs of 7.36×10^{16} molec cm^{-2} at elevation 5° and 4.15×10^{16} molec cm^{-2} at elevation 5°, respectively. And the highest value of SO_2 generally appears between elevation angle 5° and 10°. Therefore, it can be concluded that the signal of ship emissions of SO_2 and NO_2 can be easily identified and separated from the background clean conditions when there is a ship passing nearby, which can be further confirmed by the AIS information, on-site photos and records, etc.

2. The sectioning of section 2 is not very logical. I suggest the authors follow the order of "instrument", "spectral retrieval" and "ship emissions identification".
R: Thanks for the constructive suggestion. We have followed the order of "instrument", "spectral retrieval" and "ship emissions identification", and reorganized the Section 2. Please refer to Section 2 from Line 109-195.

3. In section 2.3, the SO2 and NO2 DSCDs are retrieved at different spectral ranges. How do the authors compensate the effect of wavelength dependency? If it is not considered in the retrieval, an error analysis is required.
R: The configuration of SO_2 and NO_2 spectral analysis was based on many previous studies, e.g. Hendrick et al., 2014; Irie et al., 2011; Seyler et al., 2017; Wang et al., 2014. So the common fitting window of 307.5-320 nm and 338-370 were used for SO_2 and NO_2, respectively. As it can be seen in Fig. R3, the strong absorption band of SO_2 is below 325 nm, where the NO_2 absorption are relatively weak. It means that the wavelength band of SO_2 analysis window should be shorter than that of NO_2.

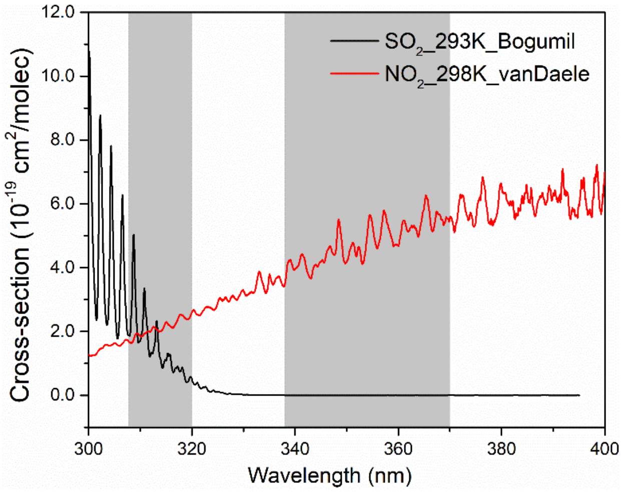

Figure R3. Absorption cross section of NO_2 and SO_2 in the wavelength range of 300~400 nm.

Since it is obvious that the SO_2 analysis cannot be performed well in longer wavelength over 325 nm, we have tried the analysis of NO_2 with the same fitting interval of SO_2 in 307.5~320 nm. As shown in the Fig. R4 (a), we found that the NO_2 DSCD values from fitting window of 307.5~320 nm are larger than that in 338-370 nm and simultaneously shows considerable uncertainties. In addition, Fig. R4 (b) and (c) show that fitting interval of 307.5~320 nm for NO_2 generates even larger RMS and DSCDs error compared to the results from fitting within 338~370 nm. It suggests that the DSCDs from same fitting window will bring large uncertainty and error in the results. Finally, we decided to use the different fitting intervals for SO_2 and NO_2.

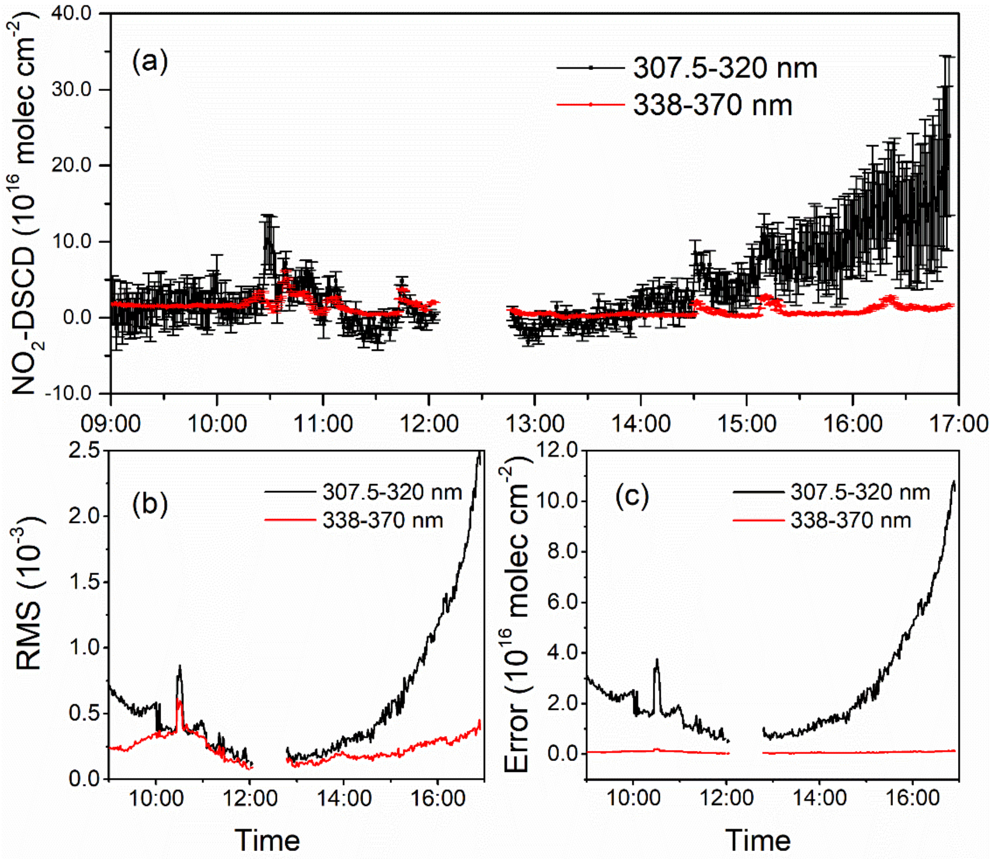

Figure R4. Comparison of NO_2 retrieval with different fitting intervals of 307.5-320 nm and 338-370 nm on 26 June 2018: (a) NO_2 DSCD with error bars, (b) RMS and (c) DSCD error.

Regarding to the compensation of wavelength dependency effect, we think the way to use the ratio of SO_2 to NO_2 DSCDs to identify the ship emission will not be impacted by the effect of wavelength dependency. Because the fixed analysis fitting window was applied for all campaigns and the ratio will not contain the wavelength dependency effect (or in presence as the systematic deviations).

4. Sect. 3.1, In the 2D scanning, the authors used the reference spectrum measured at azimuth angle of 10, however, it can be seen from Fig. 2(b) that this direction are still pointing to the berth. How to confirm the impacts of ship emission in the reference spectrum has been excluded? Alternatively, how to evaluate the uncertainties on the absolute value of DSCDs due to this?

R: We agreed with this point. In Section 3.1, it aims to prove that MAX-DOAS can recognize the spatial distribution of emission plume. Due to the limitation of the instrumental installation, the zenith-sky spectrum cannot be collected and used for the reference spectrum. So we have to select the measured spectrum at a relatively clean horizontal angle as the reference spectrum, i.e. elevation 7° at azimuth 10°. The 2-D distribution of retrieved NO_2 and SO_2 DSCDs were displayed in Fig. R5 (a) and (b). Under the same fitting configuration, the measured spectrum collected at elevation 7° at azimuth 30° in the 2-dimensional scanning cycle was also selected as reference spectrum for analysis, and the distribution of NO_2 and SO_2 DSCDs were shown in Fig.

R5 (c) and (d).

Fig. R5 (e) shows the difference between DSCD of NO_2 obtained by two analysis configurations. The difference between Fig. R5 (a) and Fig. R5 (c) were averaged at is 1.23×10^{16} molec cm^{-2}, and no obvious difference in spatial distribution. This result indicates that the selection of reference spectrum may affect the absolute value, however, do not change the 2-D distribution of retrieved NO_2 DSCDs. Similarly, Fig. R5 (f) shows the difference in SO_2 between Fig. R5 (b) and Fig. R5 (d), and the average value of Fig. R5 (f) is 4.14×10^{15} molec cm^{-2}. Therefore, we choose the spectrum with less trace gas absorption as the reference according to Fig. R5.

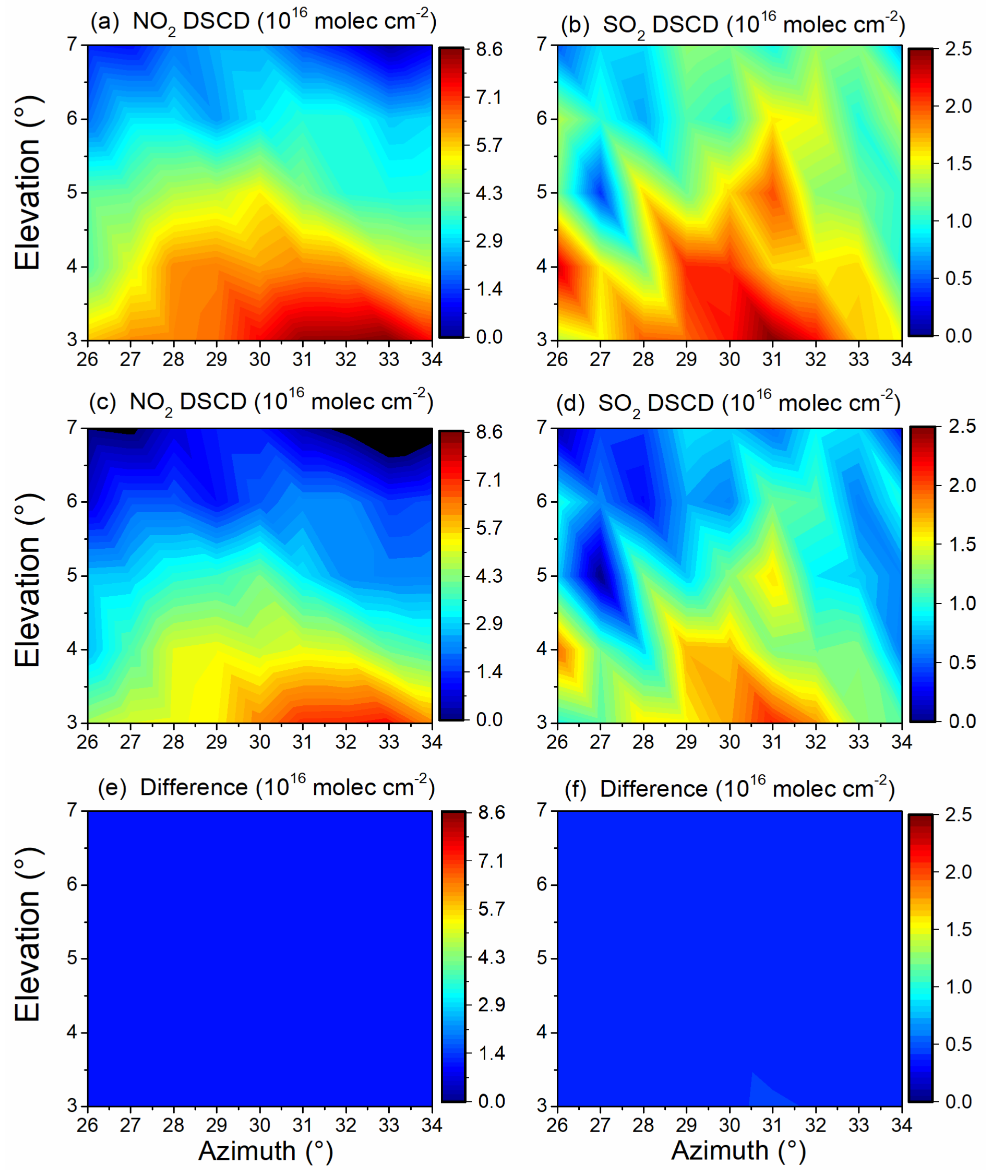

Figure R5. 2-D distributions of measured DSCDs of (a) NO_2 and (b) SO_2 using a reference spectrum collected at elevation 7° and azimuth angle of 10°; and DSCDs of (c) NO_2 and (d) SO_2 using spectrum measured at elevation 7° and 30° azimuth as the reference, (e) and (f) is the difference values between (a) and (c), (b) and (d).

5. Both in Sect. 3.1 and 3.3, the authors used the mathematic method to the slowly

change of DSCDs in temporal pattern. I think the author should introduce something more about why this method can be used here? And the basic principle? In line 340, how to prove that the baseline represents the diurnal variations of DSCDs mostly due to the change of light path caused by solar zenith angle and the background emissions?
R: The mathematical algorithm used here is BESDS (baseline estimation and denoising using sparsity). Specifically, the baseline is modeled as a low-pass signal and the series of peaks is modeled as sparse with sparse derivatives. Moreover, to account for the positivity of peaks, both asymmetric and symmetric penalty functions are utilized. Figure. R6 (a) shows the original data before processing, (b) shows the peak after removal of the baseline, while the black line in (c) represents the baseline and (d) is the residual. More details can be referred to Ning et al., 2014. The specific methods and principles we have supplemented in the manuscript. Please refer to Line 238-240.

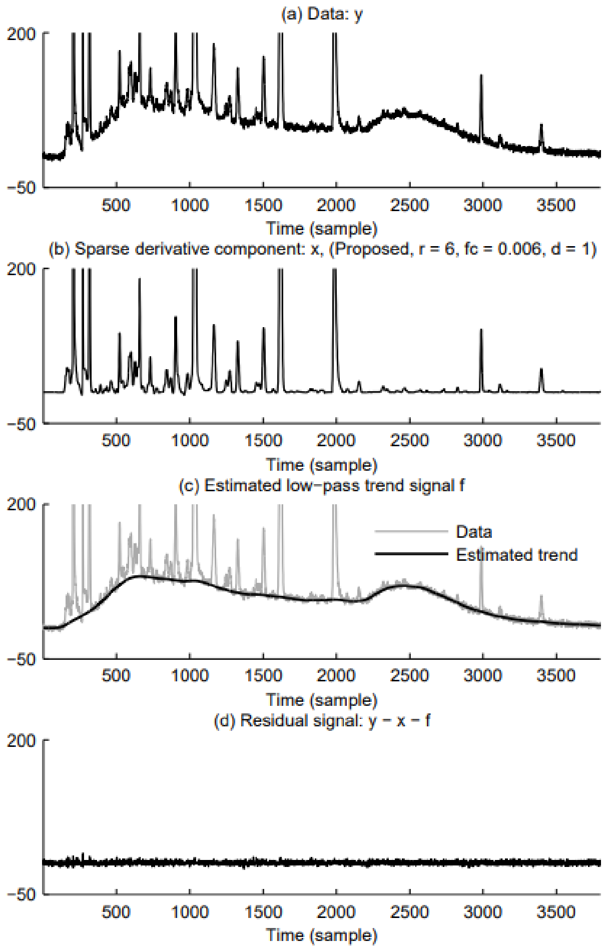

Figure R6. Processing of noisy chromatogram data using BEADS. (a) Chromatogram data with additive noise. (b) Estimated peaks. (c) Estimated baseline. (d) Residual. (Cited from Ning et al., 2014)

Affected by the solar zenith angle, the light path decreased initially, followed by an increase during the day, which is consistent with the trend presented by the baseline of DSCDs in Figure 12. Besides, Figure R7 shows the comparison between baseline and data of Yantian monitoring station for six days during the June 2018. The comparison of hourly mean SO_2/NO_2 of baseline and the ground-surface in-situ measurement at Yantian shows that these two datasets agreed well with each other with a correlation coefficient R of 0.82, suggesting that the information of SO_2/NO_2 in the baseline are quite consistent with the that of the ambient.

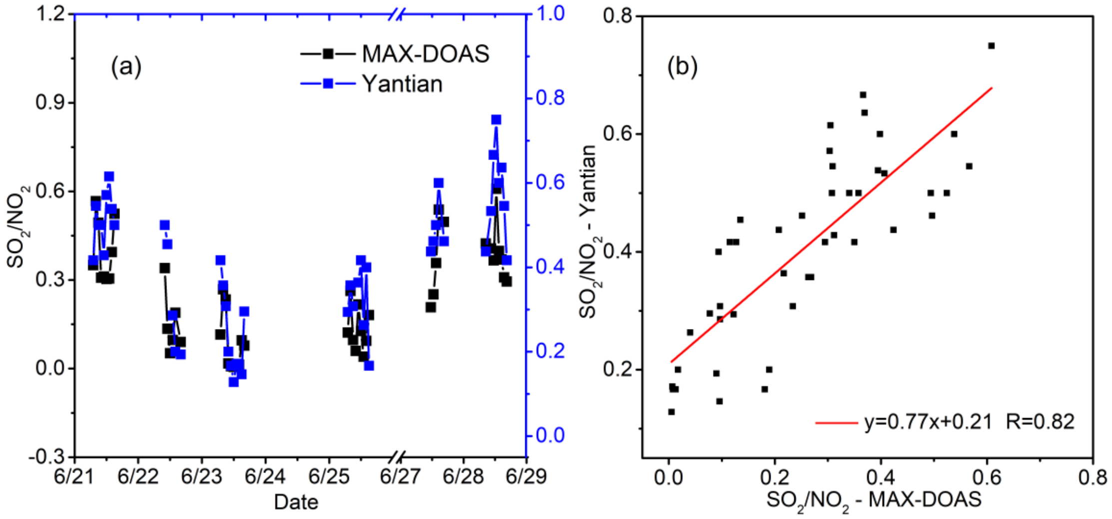

Figure R7. (a) The comparison of hourly mean SO_2/NO_2 of baseline and the ground-surface in-situ measurement at Yantian, and (b) the relationship of SO_2/NO_2 between the MAX-DOAS and Yantian.

6. The authors have mentioned that it is difficult to distinguish the single ship plume. How do the authors derive the emissions from different vessels (Figure 11)? How the data are filtered? What is the error?

R: Thanks for the suggestion. Due to the large density of ships and the wide variety of ships at the measurement site of Wusong, we have mentioned in Section 3.2 that it is difficult to distinguish the single ship plume in the busy inland waterway. However, for the observation site in Yantian, Shenzhen, the atmospheric background is cleaner, and the density of the vessels is much less than that of Wusong site. We are able to distinguish the single ship plume based on changes in DSCD of SO_2 and NO_2 in Section 3.3. The increment of DSCDs can be considered as the consequence of ship emission. Besides, we also verify the operation of the ship based on information such as on-site records and AIS. Please also refer to the previous responses to the comment 1 of the major concerns.

Minor comments

1. What is the typical error of the measurements? Please put the error bars on figure 6, 10 and 11.

R: Please refer to Figure 6, Figure 12 and 13 in manuscript. We have also showed them here as Fig. R8, R9 and R10.

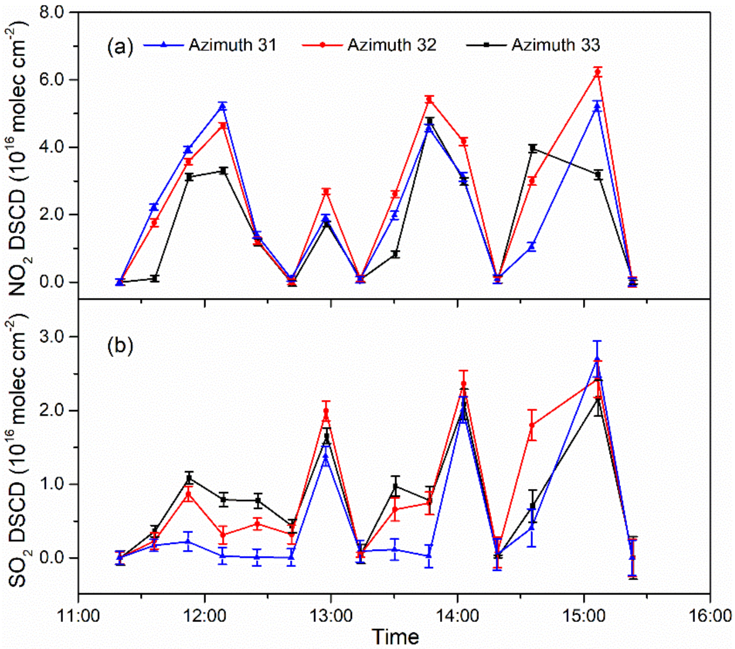

Figure R8. Time series of DSCD of (a) NO_2 and (b) SO_2 measured at 4° elevation angle in three azimuths on August 28, 2017.

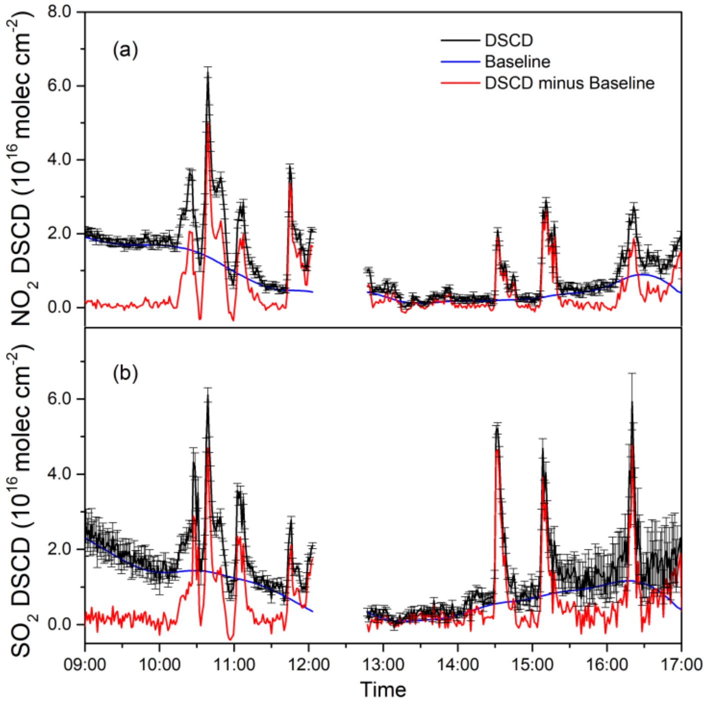

Figure R9. Diurnal variations of DSCDs of (a) NO_2 and (b) SO_2 measured at 7° elevation angle on 26 June 2018.

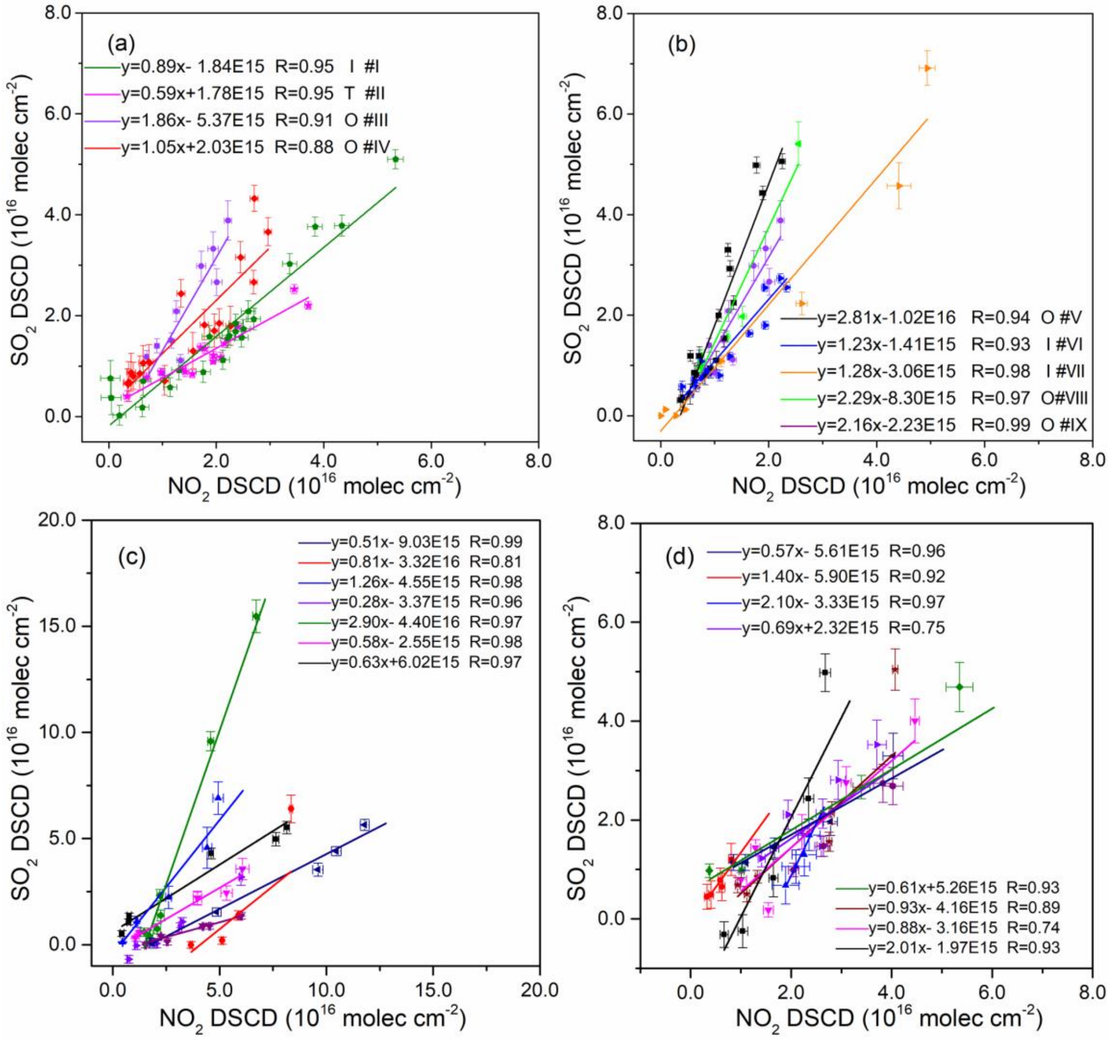

Figure R10. The relationship between SO_2 and NO_2 emitted by several typical vessels, the letter "O" indicates the outbound vessels, "I" indicates the inbound vessels, and "T" indicates the tugboat.

2. Figure 11 is very busy. It is difficult to see the differences between each species. Maybe the authors can separate it into 2 to 3 subplots. More detailed caption is required.

R: Thanks for the suggestion. The previous Figure 11 was divided into two subplots and added error bars. Please refer to (a) and (b) of Figure 13 in manuscript and Figure R10 above. In addition, the (c) and (d) of Figure 13 show the relationship between SO_2 and NO_2 emitted by other 15 typical vessels during the observation period, as suggested by Reviewer #1.

Technical corrections

Line 17, "berth" to "berths"

R: The "berth" has been corrected to "berths". Please refer to Line 18.

Line 105, "instruments" to "instrument", "observe" to "observes"

R: The "instruments" has been changed to "instrument", the "observe" has also corrected to “observes”. Please refer to Line 142.

Line 111, “less trace gas absorptions”
R: The “small” has been changed to “less”. Please refer to Line 146.

Line 112, what is the slope column concentration? It should be the slant column density.
R: We have corrected it to “slant”. Please refer to Line 147.

Line 122, “impacted by”
R: The “impacted” has been changed to “impacted by”. Please refer to Line 183.

Line 174, “unqualified NO2 and SO2 DSCDs” to “unsatisfied spectral fitting”, and “fitting results” to “DSCDs results”.
R: The “unqualified NO_2 and SO_2 DSCDs” has been changed to “unsatisfied spectral fitting”, the “fitting results” has been changed to “DSCDs results”. Please refer to Line 170.

Table 1 title, “operative” to “operation”; in the line of “Yantian”, “Smaller” with unnecessary capital letter.
R: The “operative” has been changed to “operation”, the unnecessary captical letter of “Smaller” has been corrected. Please refer to Table 1, Line 131.

Table 2, whether the O4 absorption was included in the SO2 fitting range? What’s meaning of symbol “–” standing for here?
R: The O_4 absorption was not included in the SO_2 fitting range, and the “--” was changed to “/”. Please refer to Table 2.

Line 191, “multiple berth” to “multiple berths”
R: The “multiple berth” has been changed to “multiple berths”. Please refer to Line 204.

Line 226, “the residual after background subtraction”
R: The “the residual of background subtraction” has been changed to “the residual after background subtraction”. Please refer to Line 238.

Line 247, “boxes serving”?
R: The “boxes serving” has been changed to “goods”. Please refer to Line 260.

Line 268, “around 5 mâA˘ cs-1 on March 9” ´
R: We have added “on” before the date of “March 9”. Please refer to Line 281.

Line 277, “impacting” to “influencing”
R: The “impacting” has been changed to “influencing”. Please refer to Line 318.

Line 292 and 293, “meters” can be shorten as “m”

R: We have corrected it. Please refer to Line 334 and 335.

Line 300, there are two dots in the end of the sentence. Please delete one.
R: The excess dot has been deleted. Please refer to Line 342.

Fig. 11, I suggest to also indicate the inbound and outbound status of the vessels to easily exam the relationship with slope.
R: Figure 11 in the manuscript has been modified. We have added the letter “O” to indicate the outbound vessels, “I” for the inbound vessels, and “T” for the tugboat. Please refer to the Figure 13, Line 415.

Line 371, SO2-to-NO2 > SO2/NO2, also in the rest of the manuscript.
R: The “SO_2-to-NO_2” in the manuscript has been changed to “SO_2/NO_2”. Please refer to Line 424 and other places.

Line 381, IV or IX?
R: It should be IX. Please refer to Line 431.

Line 405, where is the 2-D DSCDs map at Yantian in manuscript?
R: It was a mistake. Since the experiment at Yantian only observes a single azimuth, there is no 2-D DSCDs map. We have corrected it. Please refer to Line 459.

Line 390 and 410, what the ratios of SO2/NO2 of inbound vessels and tugboat? Lower than 1.3 or 1.5? Please keep the consistency of description.
R: We have kept them consistent and the value is determined to be 1.5. Please refer to Line 437 and 465.

References

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Seyler, A., Wittrock, F., Kattner, L., Mathieu-Üffing, B., Peters, E., Richter, A., Schmolke, S., and Burrows, J. P.: Monitoring shipping emissions in the German Bight using MAX-DOAS measurements. Atmos. Chem. Phys., 17, 10997–11023, https://doi.org/10.5194/acp-17-10997-2017, 2017.

Wang, T., Hendrick, F., Wang, P., Tang, G., Clémer, K., Yu, H., Fayt, C., Hermans, C., Gielen, C., Müller, J.-F., Pinardi, G., Theys, N., Brenot, H., and M. Van Roozendael.: Evaluation of tropospheric SO_2 retrieved from MAX-DOAS measurements in Xianghe, China., Atmos. Chem. Phys., 14, 11149–11164, https://doi.org/10.5194/acp-14-11149-2014 , 2014.

Surveillance of SO_2 and NO_2 from ship emissions by MAX-DOAS measurements and implication to compliance of fuel sulfur content

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Abstract.

With the increased concerns on the shipping emitted air pollutants, the feasible technology for the surveillance is in high demand. Here we presented the shore-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements of emitted SO_2 and NO_2 from ships under different traffic conditions in China's ship emission control area (ECA) of Shanghai and Shenzhen, China. Three typical measurement sites were selected in these two regions~~These three typical measurement sites are used~~ to represent emission scenarios of ships docked at berth, navigation in the inland waterway and inbound/outbound in the deep water port. With 2-dimensional scanning, the observation shows that the hotspots of SO_2 and NO_2 can be quickly and easily located from multiple berths. Although the MAX-DOAS measurements can not distinguish the single ship plume in the busy shipping lanes of inland waterway area, it certificates that the variations of SO_2 and NO_2 levels are mainly impacted by the ship traffic density and atmospheric dispersion conditions. In the open water area with low density of vessels, the MAX-DOAS measurements can capture the pulse signal of ship emitted SO_2 and NO_2 very well, and characterize the peaks altitude and insistent duration of the individual ship plumes. Combined with the ship information of activity data, rated power of engine and fuel sulfur content, it was found that the SO_2/NO_2 ratio in single plume is usually low (<1.5) for inbound vessel due to the usage of auxiliary engine with less power and clean fuel of low sulfur content. Meanwhile, the unexpected high SO_2/NO_2 ratio implies the fuel usage with sulfur content exceeding limit of regulations. Therefore, the observed SO_2/NO_2 ratio in the plume of single ship can be used as the index for the compliance of fuel sulfur content, and then tag the suspicious ship for further enforcement. ~~Combined~~ Combining the ship emission estimated by actual operation parameters and logical sulfur content, the shore-based MAX-DOAS measurement will provide the fast and more accurate way for the surveillance of ship emissions.

1 Introduction

Sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) are the important air pollutants, and also recognized as the non-negligible main pollutants of ship emissions (Corbett et al., 1999; Endresen et al., 2003; Eyring et al., 2010; Matthias et al., 2010). Both of them can engage in the atmospheric chemical reactions to produce aerosols and acid rain, and further have negative effects on the air quality, climate system, and human health, as well as acidification of terrestrial and marine ecosystem (Berglen et al., 2004; Seinfeld and Pandis, 2006; Singh, 1987). Moreover, NO_2 is also the key substance to form photochemical smog (Dimitriades, 1972). With the rapid growth of the transportation volume, air pollution has become the most challenging environmental issue in the shipping industry, such as the emissions of CO_2, SO_2, NOx, particles and greenhouse gases. CO_2 and NO are the main pollutants emitted by ships, and NO is rapidly converted to NO_2 by reaction with O_3. (Eyring et al., 2005; Becagli et al., 2012; Coggon et al., 2012; Diesch et al., 2013; Lauer et al., 2007; Seyler et al., 2017). Eyring et al. (2010) reported that ships contribute 15% of global NOx emissions and 4-9% of SO_2, respectively. In the view of spatial distribution, global hotspots with high SO_2 and NO_2 emissions were identified to be the regions in Eastern and Southern China Seas, the sea areas in the south-eastern and southern Asia, the Red Sea, the Mediterranean, North Atlantic near the European coast, and along the western coast of North America, etc. (Johansson et al., 2017). In China, ship emitted pollutants play important roles in the air quality, human health and climate (Lai et al., 2013; Liu et al., 2016; Yang et al., 2007). It not only affects the air quality in coastal areas, but even influences the inland areas hundreds of kilometers away from the emission sources (Lv et al., 2018). The port city is the most affected by ship pollution, followed by cities along the river. As an example, ship emitted SO_2 and NOx occupied for 12.4% and 11.6% of total emissions of the whole city of Shanghai in 2012, respectively, while there could be 64% of primary $PM_{2.5}$ contributed by ships in Shanghai Port transported to inland region (Fan et al., 2016; Zhao et al., 2013).

In order to reduce the negative impacts of ship emissions, the European Union and the United States have implemented regulations in an effort to decrease ship emissions (Kattner et al., 2015), among which the fuel quality regulation has been proven to be the most effective measures for addressing the issue of sulphur oxides (SOx) and particulate matter (PM) emissions in many countries. Besides, the International Maritime Organization (IMO, 2009) also has set up multiple emission control zone areas (ECA) worldwide. It stipulates that all ships shall use fuel oil with a sulfur content not more than 0.5% (mass fraction) during the berthing of all ports within the ECA by 2020. By 2020, the maximum FSC is 0.50% S m/m all over the world, and it is worth noting that the maximum fuel sulfur content in ECAs at the US coast and Europe is 0.10 % S m/m, while in China's ECA it is 0.50 % S m/m. The regulations also set limits for pollutant emissions such as NOx and CO_2 in the exhaust gas. Alternatively, the exhaust gas treatment system could be another option. Since January 1st, 2017, ships berth at the core ports of three designated Domestic Emission Control Area (DECA) in Pearl River Delta (PRD), the Yangtze River Delta (YRD) and the Bohai Rim (Beijing-Tianjin-Hebei area) of China should use fuel with sulphur content less than or equal to 0.50% (MOT, 2015). As of January 1, 2019, the ship entering the ECAs should use fuel with a sulfur content of not more than 0.50 % m/m, whether it is sailing or docking. Currently, the scrubber is also the alternative way to reduce the ship emission in China. As a consequence, it is obviously that the reliable and practical monitoring system are highly demanded for the implementation of ECA regulations.

The common options to monitor ship emissions can be classified into two categories: estimates based on activity data or written documentation; and measurements of on-board fuel sample and exhaust gas made on board the ship. Basically, the continuous online monitoring of fuel and exhaust gas on-board is the highly effective and accurate supervision means, but less operability in practice. For the regulatory party, fuel sampling and document inspection are currently the common measures and the sulfur content in the fuel is usually fast detecting after the ship is docked in dozen of minutes. Besides, other technical methods has been developed to determine both SO_2 and NOx emissions, such as a new type of ship exhaust gas detection technology that mounts a portable sniffer/instrument on board a ship or on a helicopter (Beecken et al., 2015; Berg et al., 2012; Murphy et al., 2009; Villa et al., 2016). Alternatively, shore-based remote sensing is another effective way to measure the ship plume and further estimate the sulfur content, when ships pass the lanes or dock at berth (Kattner et al. 2015; Seyler et al. 2017).

Remote sensing technique shows the advantages of fast detection, easy operation and high automation. Besides the passive "sniffing" method with in-situ instrumentation, optical remote sensing technique can detect the variation of the light properties after interaction with the exhaust plume and corresponding SO_2 and NO_2 emission in the plume, such as differential optical absorption spectroscopy (DOAS), light detection and ranging (LIDAR), and the ultraviolet camera (UV-CAM) technique (Balzani et al., 2014; Seyler et al., 2017). LIDAR system can be used to retrieve a 2-dimentional concentration distribution by scanning through the ship plume, and to obtain the ship emissions combing the wind and concentration profiles. McLaren et al. (2012) employed active long-path DOAS technique to measure NO_2-to-SO_2 ratios in ship plumes and speculate on its relationship with the sulfur content of fuels. UV camera has been successfully applied to measure the SO_2 concentrations and emission rates of moving and stationary ship plumes (Prata, 2014).

DOAS technique allows to identify and quantify the absorption of variety of species showing characteristic absorption features in the wavelength range (Platt and Stutz, 2008). It has been widely used for trace gases measurements in several decades, especially very mature for NO_2 and SO_2 (Edner et al., 1993; Mellqvist and Rosén, 1996; Platt et al., 1979). As an expanded apparatus, the multi-axis differential optical absorption spectroscopy (MAX-DOAS) measurements are high sensitivity to aerosols and trace gases in the lower troposphere by observing scattered sunlight under different viewing angles closed to the horizontal and the zenith directions (Hönninger et al., 2004; Ma et al., 2013; Sinreich et al., 2005; Wang et al., 2014). Due to its portability, MAX-DOAS instrument can be carried on the ship to observe the vertical column densities (VCDs) of NO_2 and SO_2 along the cruise, during which high levels of pollutants were found close to the busy port and dense lanes (Hong et al., 2018; Schreier et al., 2015; Takashima et al., 2012; Tan et al., 2018). In addition, MAX-DOAS has been successfully employed for monitoring shipping emissions directly. Premuda et al. (2011) used the ground-based MAX-DOAS measurements to evaluate the NO_2 and SO_2 levels in ship plume discharged from the single ship in the Giudecca Strait of the Venetian Lagoon. Seyler et al. (2017) have utilized MAX-DOAS to perform long-term measurements of NO_2 and SO_2 from shipping emissions in the German Bight, and evaluated the reduction in SO_2 levels after implement stricter sulfur limits in shipping fuel.

In this study, the shore-based MAX-DOAS measurements were employed to measure the NO_2 and SO_2 in ship plumes for different ship traffic environments of Shanghai and Shenzhen, China. Combined with the photos taken by the camera of the instrument and AIS (Automatic Identification System) information, it is verified that emissions of ships at berth, passing through the inland waterway and open sea areas can be successfully detected. The measurements can also provide the fuel sulfur content information of individual ship by comparing the emitted NO_2 and SO_2 in the plume considering the effects of plume age. With the fuel sample analysis and ship activity data, it suggests that the shore-based MAX-DOAS method shows the feasibility and reliability of surveillance for ship emitted SO_2 and NO_2 and further allows to know compliance of fuel sulfur content.

2 Measurements and method

2.1 MAX-DOAS measurements for ship emissions

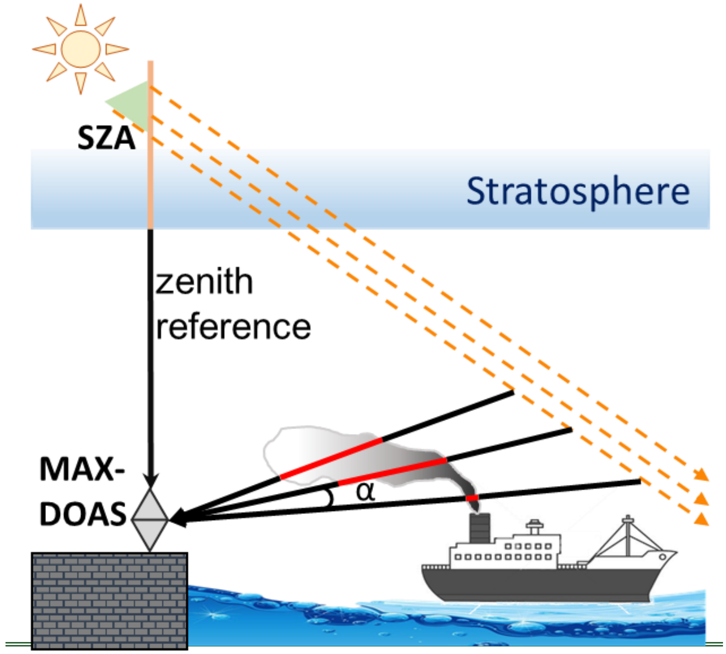
The algorithm of DOAS is basically based on Lambert-Beer law, which describes the extinction of radiation through the atmosphere (Platt and Stutz, 2008). MAX-DOAS instrument observes scattered sunlight from various viewing directions and stored in the form of spectrum (e.g. Hönninger et al., 2004; Sinreich et al., 2005). The spectral analysis generates the measured SCD (slant column densities), defined as the integral of the trace gas concentration along the entire optical path including the SCDs in the troposphere and the stratosphere. (e.g. Platt and Stutz, 2008, Wagner, et al., 2010).

The stratospheric absorption has been assumed as the same level in all spectra taken within one scan cycle, so we generally choose the spectrum with less trace gas absorption as the reference, such as the spectrum measured in zenith direction. The slant column concentration of the trace gas measured at each lower elevation angle (α) is represented by DSCD (differential SCD), which is the gas information of the measured slant column densities minus background densities in the reference spectrum.

$$\begin{aligned} DSCD(\alpha) &= SCD(\alpha) - SCD(ref) \\ &= SCD(\alpha)_{trop} + SCD_{strat} - SCD(ref)_{trop} - SCD_{strat} \\ &= SCD(\alpha)_{trop} - SCD(ref)_{trop} \qquad (1) \end{aligned}$$

For ship emissions measurements, the DSCDs of pollutants at low elevation angles should express the change of integrated concentrations along the light path after contamination by the exhaust plume, which collects scattered sunlight passing through ship plumes. Figure 1 depicts the schematic diagram of ground-based MAX-DOAS measurements of ship emissions. The

~~telescope is pointed towards the ship lanes or the direction of ship passed through. Consequently, the measured spectra at low elevation angle will be impacted by the plumes of ship emissions~~



2.~~2~~ 1 Instrument setup and sites

In this study, the MAX-DOAS instrument has been designed and assemble by the authors (Zhang et al., 2018a). It mainly consists of a receiving telescope, a spectrometer (Ocean Optics, QE65 Pro), and a computer to control the measurements. Driven by the two-dimensional stepper motor system, the telescope can collect the scattered sunlight from different elevation angles in vertical and azimuth angles in horizontal. The scattered light is converged by the lens to the fiber bundle connected to the spectrometer. The receiving sunlight is dispersed by a grating, detected by a CCD detector and recorded by the spectrometer covering the wavelength range from 300 to 480 nm with a resolution about 0.5 nm Full Width at Half Maximum (FWHM). As a new designed feature, a camera has been configured on the MAX-DOAS apparatus, which moves coaxially with the receiving telescope and can record the scene and sky conditions same as the views of telescope. The scanning of telescope can be set in the sequence of several elevation angles from close to horizontal and 90° and then move to next azimuth angle for another vertical scanning sequence. Due to the different ship traffic conditions, the types of ship passing in inland waterway and seaside ports are different in size and tonnage. Therefore, the configuration of observing geometric angels were adjusted dependent on the conditions of ships, as referred in Table 1.

The MAX-DOAS measurements of ship emissions were performed in two typical port cities of Shanghai and Shenzhen in China. As shown in Fig. ~~2~~1(a), sea areas in surrounding Shanghai and Shenzhen city are located in the ECA of Yangtze River Delta and Pearl River Delta. In Shanghai, two different ship traffic scenarios were considered, i.e. ships at berth in Waigaoqiao container port area (31.36° N, 121.58° E, Fig. ~~2~~1(b)), and ships passing through inland waterway of the downstream of Huangpu River at Wusong area (31.37° N, 121.50° E, Fig. ~~2~~1(c)). In Shenzhen, the measurements were carried out in the deep water port of Yantian (114.29° E, 22.56° N, Fig. ~~2~~1(d)). More details about the environments and operation configurations of measurement were listed in Table 1.

Table 1. Measurements details and ~~operative~~ operation configurations of MAX-DOAS.

Sites	Locations and periods	Operations*	Environment types
Waigaoqiao, Shanghai	31.36° N, 121.58° E 28/08/2017	AZ: 26° to 34°; ELE: 3°, 4°, 5°, 6°, 7°; Spectrum temporal resolution: 15-30 s; Completed scanning cycle: 15 min.	Viewing to: berths; Ships: container ship.
Wusong, Shanghai	31.37° N, 121.50° E 30/12/2017-18/05/2018	AZ: 85°; ELE: 0°, 1°, 2°, 3°, 4°, 5°, 6°, 8°, 65°; Spectrum temporal resolution: 40 s; Completed scanning cycle: 7 min.	Viewing to: inland waterway with high traffic volume; Ships: a wide variety of ships and small in size
Yantian, Shenzhen	114.29° E, 22.56° N 23/05/2018-30/06/2018	AZ: 75°; ELE: 2°, 3°, 5°, 7°, 10°, 15°, 30°, 90°; Spectrum temporal resolution: 60 s; Completed scanning cycle: 9 min.	Viewing to: open sea areas with ~~S~~smaller traffic volume; Ships: container ship as the main part

*AZ: azimuth angle in horizontal direction; ELE: elevation angle in vertical direction.

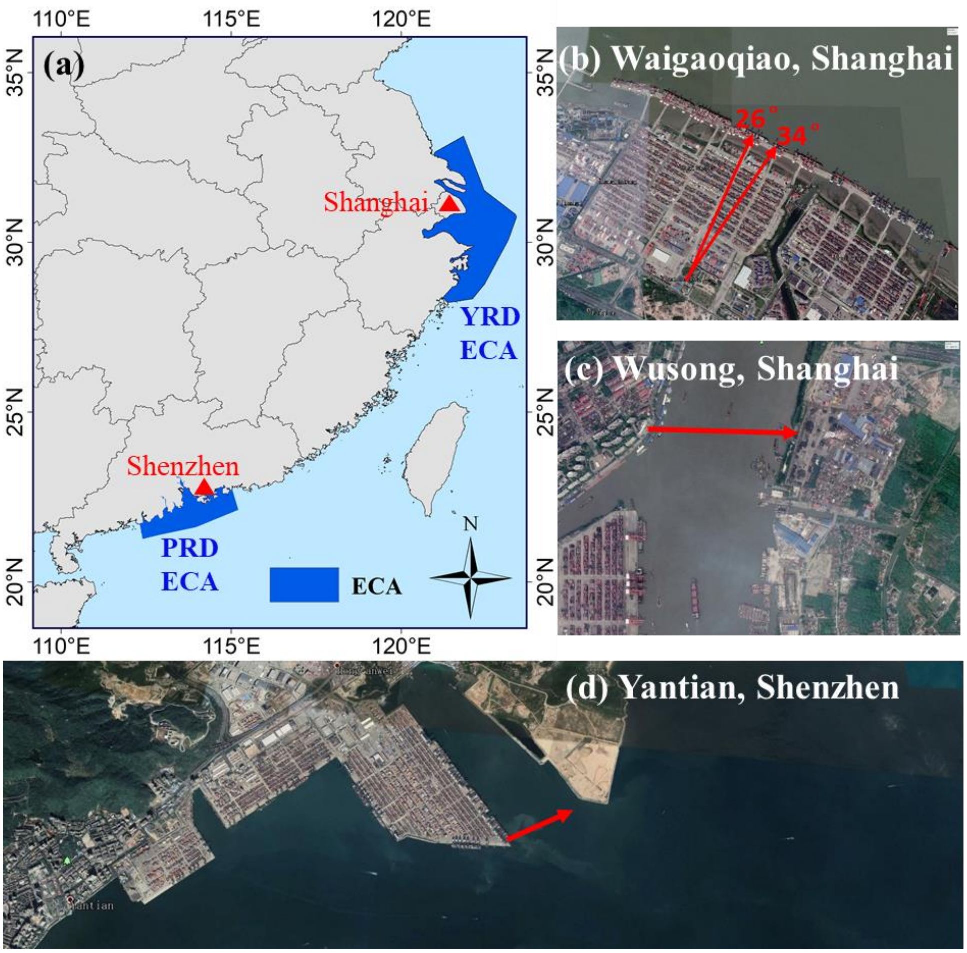


Figure 12. The YRD and PRD Domestic Emission Control Area (DECA) in China and locations of the MAX-DOAS measurements in coastal cities of Shanghai and Shenzhen: Waigaoqiao Port and Wusong Wharf in Shanghai, and Yantian Port in Shenzhen. The viewing direction of instrument azimuth angle is indicated by a red arrow. (b) to (d) cited from Google Earth.

2.3 2 DOAS spectral analysis

The algorithm of DOAS is basically based on Lambert-Beer law, which describes the extinction of radiation through the atmosphere (Platt and Stutz, 2008). MAX-DOAS instrument observes scattered sunlight from various viewing directions and records the ~~stored in the form of~~ spectrum (e.g. Hönninger et al., 2004; Sinreich et al., 2005).

The spectral analysis generates the measured SCD (slant column densities), defined as the integral of the trace gas concentration along the entire optical path including the SCDs in the troposphere and the stratosphere. (e.g. Platt and Stutz, 2008, Wagner, et al., 2010). The stratospheric absorption has been assumed as the same level in all spectra taken within one scan cycle, so we generally choose the spectrum with less trace gas absorption as the reference, such as the spectrum measured in zenith direction. The slant column concentration of the trace gas measured at each lower elevation angle (α) is represented by DSCD (differential SCD), which is the gas information of the measured slant column densities minus background densities in the reference spectrum.

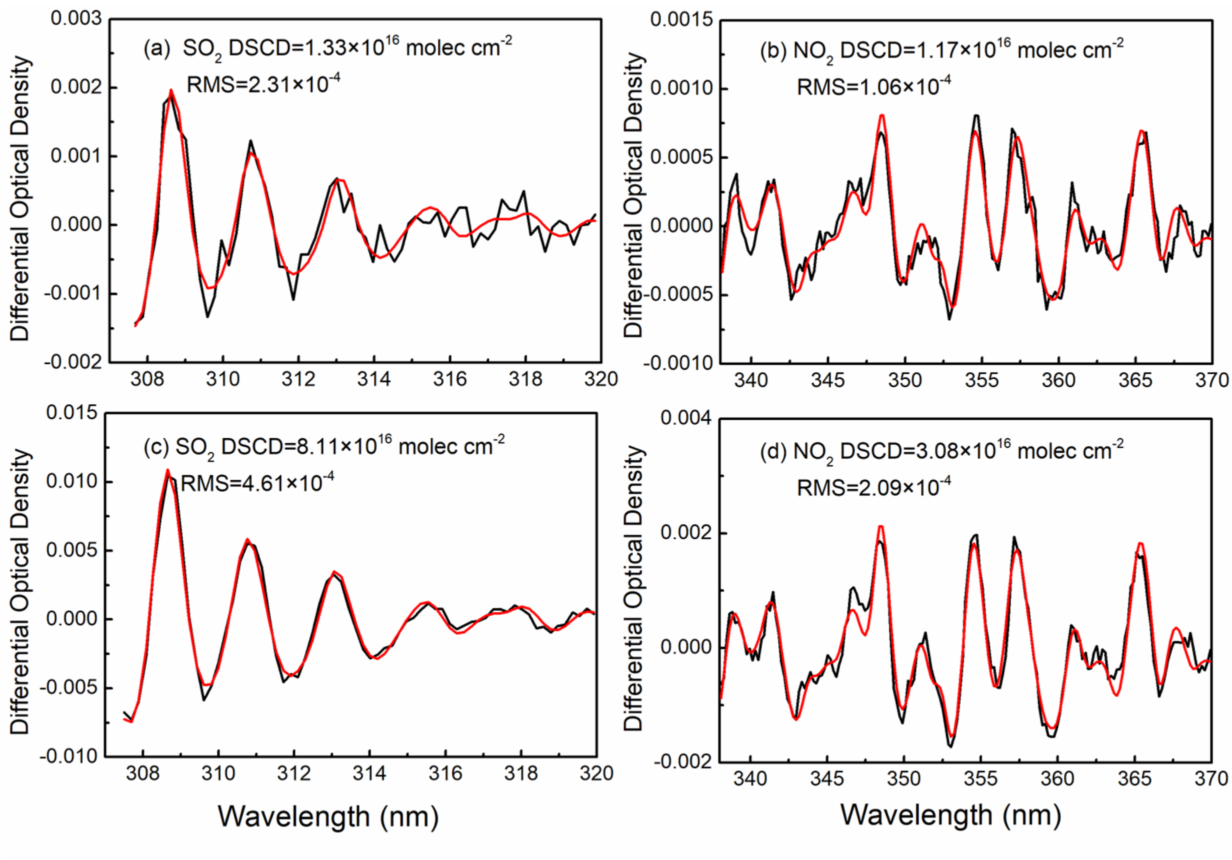
$$\begin{aligned} DSCD(\alpha) &= SCD(\alpha) - SCD(ref) \\ &= SCD(\alpha)_{trop} + SCD_{strat} - SCD(ref)_{trop} - SCD_{strat} \\ &= SCD(\alpha)_{trop} - SCD(ref)_{trop} \qquad (1) \end{aligned}$$

Based on the DOAS principle, the measured scattered sun-light spectra are analyzed using the QDOAS spectral fitting software, which is developed by BIRA-IASB (http://uv-vis.aeronomie.be/software/QDOAS/). The fitting wavelength intervals of SO_2 and NO_2 are 307.5-320 nm and 405-430 nm, respectively. Trace gases with absorptions in relevant fitting windows and Ring spectrum were included. The details of spectral fitting configuration are listed in Table 2. Wavelength calibration was performed by using high-resolution solar reference spectrum (Chance and Kurucz, 2010). The offset and the signal of the dark current were measured every night and extracted automatically from the measured spectra before spectral analysis. Consequently, the DSCDs of SO_2 and NO_2 were yielded by taken the measured spectrum at 90° as the Fraunhofer reference spectrum.

Table 2. Configuration of spectral fitting for SO_2 and NO_2

Parameters	SO_2	NO_2
Fitting window	307.5–320 nm	338–370 nm
NO_2	298 K (Vandaele et al., 1998)	
SO_2	293 K (Bogumil et al., 2003)	/
O_4	~~–~~/	293 K (Thalman and Volkamer, 2013)
O_3	223 K & 243 K (Serdyuchenko et al., 2014)	223 K(Serdyuchenko et al., 2014)
BrO	/	293 K (Fleischmann et al., 2004)
CH_2O	298K (Meller and Moortgat, 2000)	
Ring	Calculated by QDOAS	
Polynomial Degree	3	5
Intensity Offset	Constant	

Figure ~~3~~ 2 shows the typical spectral fitting of measured spectra with and without ship plume contamination. The obvious absorbing structures of SO_2, NO_2 and fairly low residuals can be observed in both conditions of polluted spectrum (collected at elevation angle of ~~7~~5° at ~~11:04~~10:39 LT on ~~26~~ 22 June, 2018) and clean spectrum (collected at elevation angle of 5° at 09:53 LT on 22 June, 2018). By contrast, the retrieved SO_2 and NO_2 DSCDs of 8.11×10^{16} and 3.08×10^{16} molec cm^{-2} in polluted case are significantly higher than those in clean condition of ~~2.31~~2.24×10^{16} and ~~1.06~~1.61×10^{16} molec cm^{-2}. It demonstrates the high sensitivity of measurements to ship plumes and the good performance of the spectral fitting. In this study, a threshold of residual < 1×10^{-3} is used for screen out the ~~unqualified NO_2 and SO_2 DSCDs~~ unsatisfied spectral fitting, and 94.57% of NO_2 ~~fitting~~ DSCDs results and 76.26% of SO_2 fitting results remains in further discussion. The uncertainties for the spectral analysis of SO_2 were higher because of the weak scatter sunlight intensity and lower signal-to-noise at the short wavelengths.



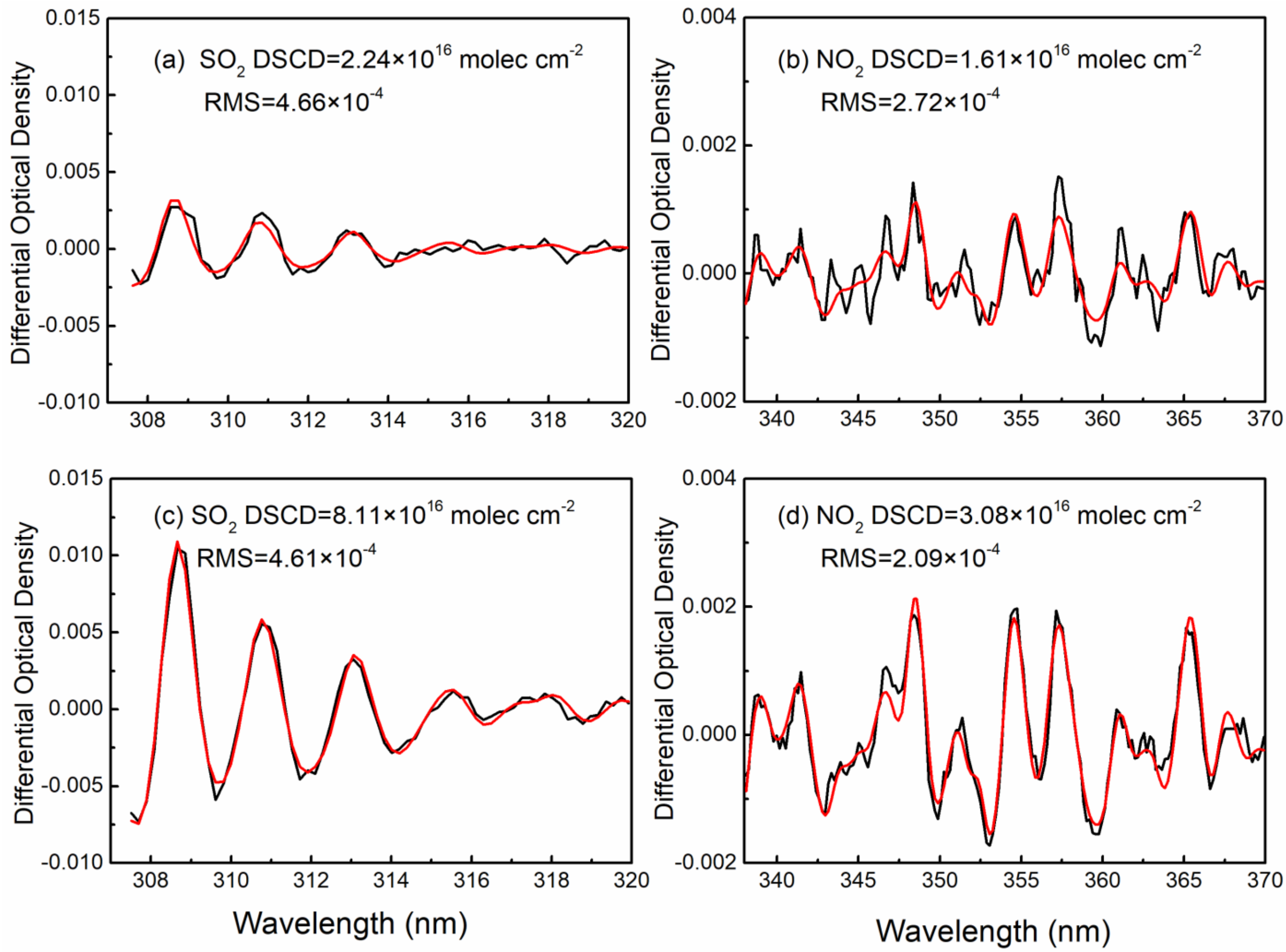
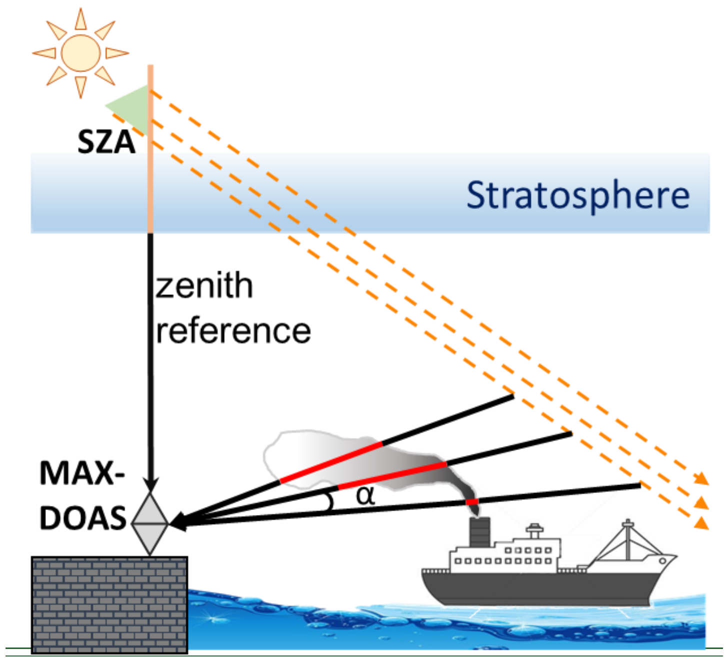


Figure ~~3~~2. Typical DOAS spectral fitting for SO_2 and NO_2. (a) and (b) show the clean condition of spectrum collected at an elevation angle of ~~7~~5° at ~~11~~10:~~04~~ 39 LT on ~~26~~ 22 June, 2018, while (c) and (d) are the ship plumes polluted case of spectrum measured at an elevation angle of 5° at 09:53 LT on 22 June, 2018. Black lines show the measured atmospheric spectrum and the red line shows the reference absorption cross-section.

2. ~~1~~3 MAX-DOAS measurements for ship emissions

For ship emissions measurements, the DSCDs of pollutants at low elevation angles should express the change of integrated concentrations along the light path after contamination by the exhaust plume, which collects scattered sunlight passing through ship plumes. Figure ~~1~~3 (a) depicts the schematic diagram of ground-based MAX-DOAS measurements of ship emissions. The telescope is pointed towards the ship lanes or the direction of ship passed through. Consequently, the measured spectra at low elevation angle will be impacted by the plumes of ship emissions.

In order to better demonstrate the background concentration of NO_2 and SO_2, several typical cycles on June 29 were selected as examples. Figure 3 (b) and (c) show the vertical distributions of NO_2 and SO_2 DSCDs with the elevation angle when there is a ship passing through and not. It can be observed that the DSCDs of NO_2 and SO_2 decrease slowly with increasing angle under clean conditions, during which the maximum values of NO_2 and SO_2 DSCDs are 5.03×10^{16} molec cm^{-2} at elevation 3° and 1.78×10^{16} molec cm^{-2} at elevation 2°, respectively. In contrast, the NO_2 and SO_2 DSCDs increased significantly when ships passed, showing the maximum values of NO_2 and SO_2 DSCDs of 7.36×10^{16} molec cm^{-2} at elevation 5° and 4.15×10^{16} molec cm^{-2} at elevation 5°, respectively. And the highest value of SO_2 generally appears between elevation angle 5° and 10°.



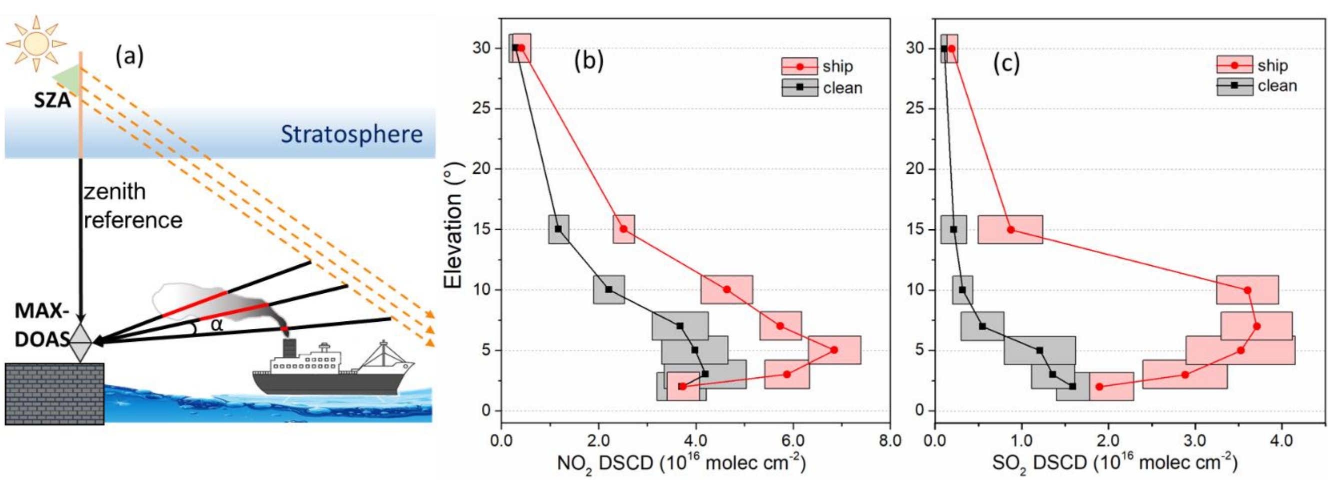


Figure 13. (a) Schematic diagram of MAX-DOAS measurement geometry for monitoring ship emissions, and the distributions of (b) NO_2 and (c) SO_2 DSCDs with elevation angle on June 29, 2018..

3 Results and discussion

3.1 Identifying the emissions of ship at berth

The measurement site at Waigaoqiao Container Terminal is located on the south bank of the Yangtze River, and close to the confluence of Yangtze River and Huangpu River. The Terminal has a total quay length of more than one kilometer, and its three container berths are able to accommodate the fifth and sixth generation container ships. The special location determines that it is the important traffic route for ships to enter or leave the Yangtze River, Shanghai Port, and Waigaoqiao wharf. In order to detect the emissions of ship at berths, the MAX-DOAS instrument is placed on a fifth floor at the building of Pudong MSB (Maritime Safety Bureau). The distance between the instrument and berth is about 1.4 km. Since no other constructions obscured, multiple berths can be seen directly in the viewing of the MAX-DOAS instrument. Considering the size and chimney height of berthed ships, the MAX-DOAS telescope was set to scan vertically in sequence of 3°, 4°, 5°, 6°, and 7° (indicated with angle α in Fig. 4). In horizontal, telescope ranged from 26° to 34° (the viewing angle from north in clockwise) and yielded a range of angle β, which can covers about 195 m quay length. After completing one full scanning in both vertical and horizontal, a 2-D distributions of DSCDs in front view of the instrument can be generated. To avoid the interference of pollutants absorptions in the reference spectrum, the spectrum measured at azimuth angle of 10° was considered as the reference spectrum in the background area without the direct ship emissions pollution.

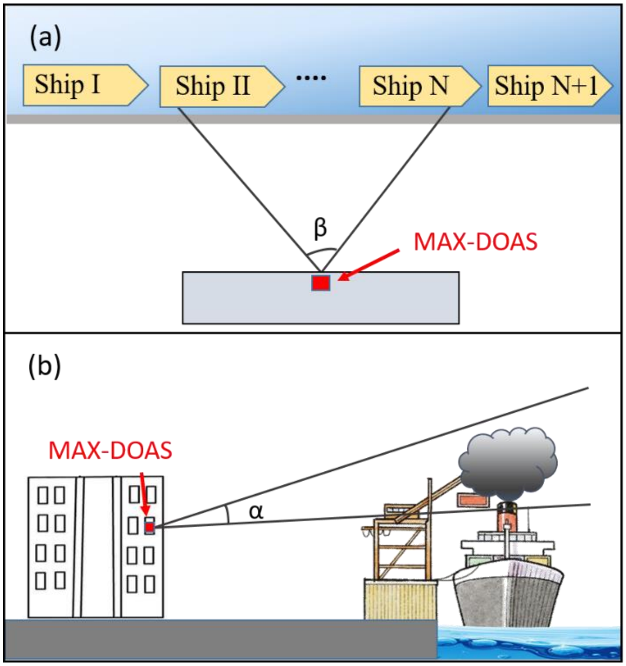


Figure 4. The observational geometry of MAX-DOAS for identifying the emissions of ship at berth in Waigaoqiao port, Shanghai: (a) top view and (b) side view.

Figure~~.~~ 5(a) and (b) shows the spatial distributions of SO_2 and NO_2 DSCDs in horizontal and vertical during a complete scanning sequence, respectively. Large spatial gradients can be observed for both SO_2 and NO_2 levels, while the pollutants concentrations are in general higher at lower elevation angels and declined with the increase~~s~~ of height. The highest SO_2, i.e. DSCDs up to 2.5×10^{16} molec cm^{-2}, appeared in horizontal azimuth of 31° and elevation of 3° and attenuated in the direction toward left-upward. Similarly, hot-spots of NO_2 with DSCDs of $7.0\sim8.0\times10^{16}$ molec cm^{-2} are centered between 31° and 33° in horizontal at elevation of 3°, and decreases in periphery. It should be noted that the hot-spots of SO_2 and NO_2 distribution are shifted to the left accordingly while the height is raised. It is implied that the plumes containing SO_2 and NO_2 emitted at the bottom in the observational field of view, dispersed and diluted in left-up ward, and the weather recorded that the wind at this test site mainly came from the south. Combined with the real scene shown in Fig. 5(c), the rectangle encircled by dash line indicates the range of MAX-DOAS telescope scanning. It can be seen that there are smoke clusters discharged by ship at the right part of the picture, which is correspond to the azimuth angle between 31° and 33°. And under the action of the wind, the plume spreads to the left of the observational view.

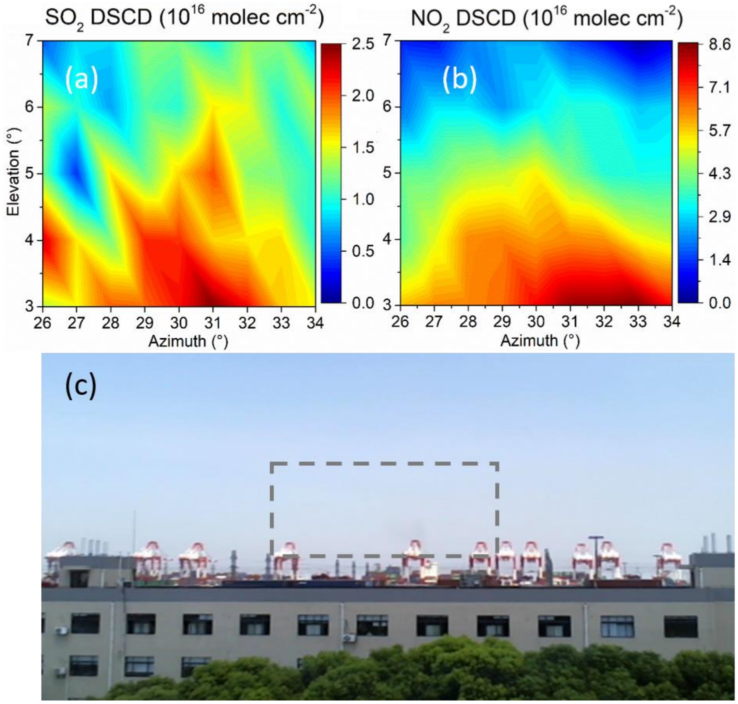
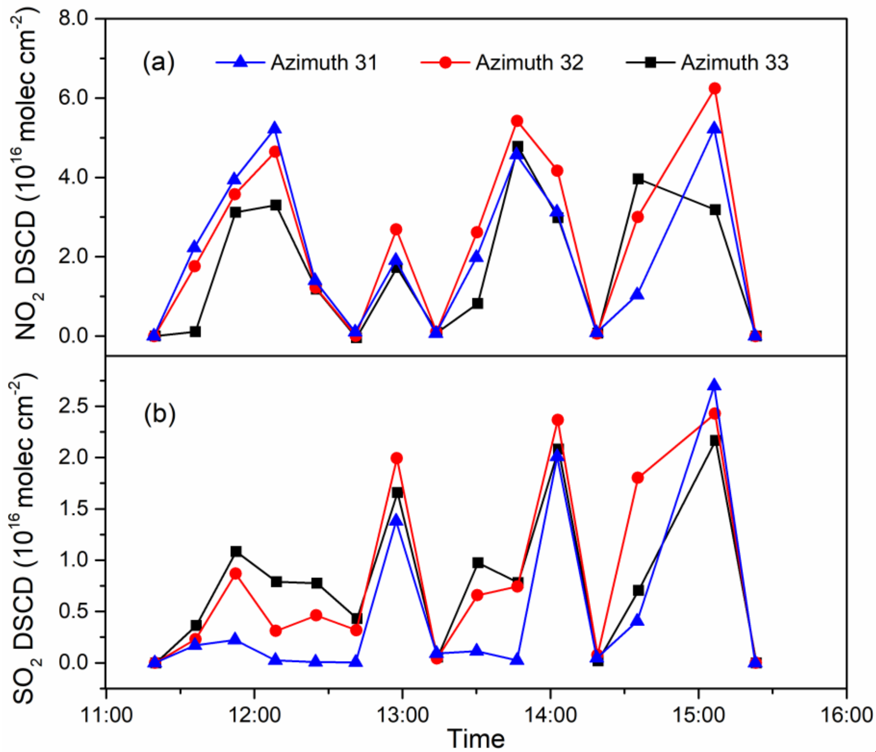


Figure 5. Distributions of measured DSCDs of (a) SO_2 and (b) NO_2 from emissions of ship at berth during 12:04~12:20 in 28 August, 2017 and (c) live photo captured by camera of MAX-DOAS instrument. The dash line rectangle indicates the observational view of MAX-DOAS.

Since a full 2-D scanning sequence in horizontal and vertical directions took about 15 minutes, more than a dozen cycles in total can be performed during the afternoon. In view of the identified emission source position above, the DSCDs of NO_2 and SO_2 observed at elevation 4° and azimuth angle between 31°-33° were selected to display the temporal pattern of emissions at berth. In general, the level of NO_2 DSCDs is much higher than SO_2, because there are considerable NOx emission of in port trucks between the berth and the instrument, whereas there no other obvious emission source of SO_2. In order to show the variations of DSCDs with less interference due to light path change, we used the mathematic method to remove the slowly change from the trend line of NO_2 and SO_2 DSCDs, and kept the residual ~~of~~ after background subtraction in the Fig. 6. The baseline is modeled as a low-pass signal, while the series of peaks is modeled as sparse with sparse derivatives. Moreover, to account for the positivity of peaks, both asymmetric and symmetric penalty functions are utilized (Ning et al., 2014). Afterwards, four significant increases of SO_2 levels can be observed during this afternoon, accompanied with NO_2 enhancements at approximately same moment, which can be verified by the real scene photos showing evidently the emitted plumes from the expected exhausting position.



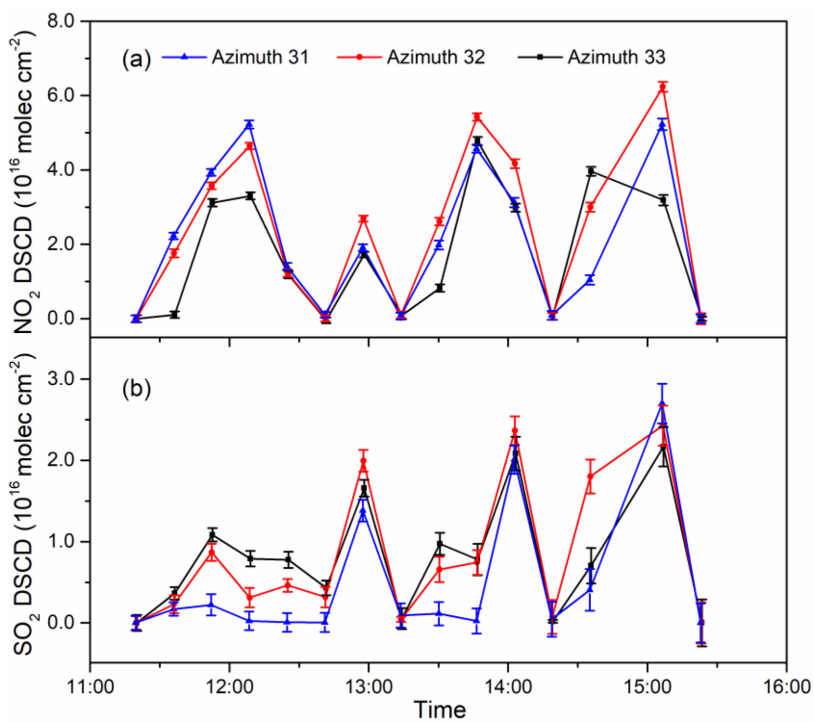


Figure 6. Time series of DSCD of (a) NO_2 and (b) SO_2 measured at 4° elevation angle in three azimuths on August 28, 2017.

Therefore, it can be concluded that the concentration of NO_2 and SO_2 gases contained in the plume emitted by the container ships and the corresponding discharge position at berth were identified and monitored remotely by the 2-D MAX-DOAS observation. This application of 2-D MAX-DOAS is similar to the Imagine DOAS (IDOAS) technique, which is also used to map the 2-dimensional spatial distribution of polluted gases, such as the distribution of SO_2 in plumes of the industrial point sources (General et al., 2014; Pikelnaya et al., 2013). It suggests that the 2-D DOAS technique has the potential to measure the polluted gases mapping from the ships.

3.2 Ship emissions at inland waterway

Besides of ocean-going ships~~emissions~~, inland waterway vessels also contribute~~d~~ significantly to the amount ship emissions (Kurtenbach et al., 2016; Pillot et al., 2016; Zhang et al., 2017). To consider this situation, the MAX-DOAS instrument was installed at the outside windowsill on the third floor of Wusong MSB Building (121°29′ E, 31°22′ N) from December 30, 2017 to May 18, 2018. The measurement site is located in the downstream of Huangpu River and close~~d~~ to the confluence into the Yangtze River. It is only channel to the upstream of Huangpu River.~~,~~ There are some non-container terminals near the measurement site, ~~and also some other non-container terminals are located nearby,~~ which mainly handles ~~boxes serving~~goods in domestic trading. As a consequence, a large number of ships entering and leaving the wharf area every day, and the lanes in the downstream of Huangpu River suffers from dense ship traffic. By checking the synchronized photos taken by the camera attached to the instrument, it is found that the types of vessels passing through are in a wide variety, such as medium and small sized container ships, passenger vessels, bulker and cargo ships. In addition, the traffic volume in the area is quite high, even up to hundreds of ships per hour. As shown in Fig. ~~2~~1(c), the view direction of MAX-DOAS measurements in Wusong area is pointed perpendicularly to the river lane~~s~~. The observed signal of pollutants mainly come from the emissions of ships in navigation. The elevations angles were set in scanning sequence of 0°, 1°, 2°, 3°, 4°, 5°, 6°, and 8°. The spectrum measured at 65° was utilized as the reference since the zenith direction is blocked to some extent by the MSB building.

In order to illustrate the impact~~s~~ of ship traffic volume and meteorological conditions, measurement~~s~~ data of 30-min averaged wind speed, observed NO_2 and SO_2 DSCD on two representative days of January 1, and March 9, 2018 were shown in Fig. 7, as well as the corresponding number of passing ships. It can be seen from Fig. 7(a) that January 1 and March 9 were selected to represent days under stabile and unstable atmospheric conditions. The average SO_2 DSCDs changed from 1.8×10^{16} to 3.0×10^{16} molec cm^{-2}, while average NO_2 DSCDs varied between 4.0×10^{16} and 1.1×10^{17} molec cm^{-2} on January 1. On March 9, the SO_2 and NO_2 average DSCDs ranged 1.0×10^{16} to 2.7×10^{16} molec cm^{-2} and 2.5×10^{16} to 1.0×10^{17} molec cm^{-2}, respectively. According to the ship traffic density shown in Fig. 7(b), the diurnal variations of SO_2 and NO_2 DSCDs are obviously closely related to the flow of the ships (quantitative information). Although the averaged SO_2 and NO_2 DSCDs levels are comparable during these two days, the ship traffic flow on March 9 was overall 50% higher than January 1, which may imply the important role of meteorological conditions. Considering the dense ship lanes, the ship emitted pollutants are easily to be accumulated under the unfavorable condition with lower wind speed less than 2 m·s^{-1} on January 1. In the contrary, the ship emissions along the lanes can be spread for better diffusion when the averaged wind speed is around ~~on~~ 5 m·s^{-1} on March 9.

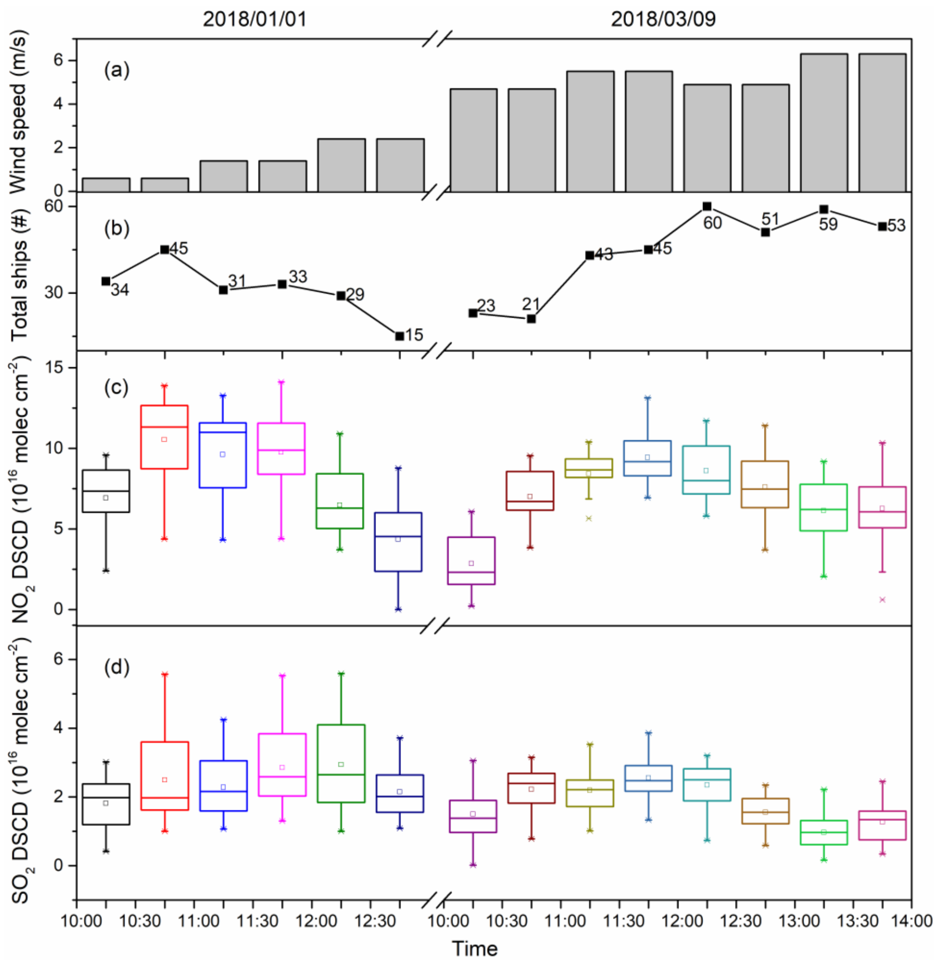


Figure 7. 30-min averaged wind speed, ship traffic volume, observed NO_2 and SO_2 DSCDs from 10:00 to 13:00 on January 1 and 10:00 to 14:00 on March 9 at Wusong Wharf measurement site. The hollow squares in the middle of the box represent the mean value, and the solid lines in the middle represent the median. Whiskers extend from each end of the box to the internal and external limits. "-" represents the maximum and minimum, and "×" are 1% and 99% quantiles. The upper and lower edges of the box are 25% and 75% quantiles, respectively.

In order to investigate the impacts of wind on the observed DSCDs, the wind rose diagrams of NO_2 and SO_2 DSCDs at elevation 5° from January to March 2018 are shown in of Fig. 8(a) and (b). It can be found that the wind mainly comes from NNW during the observation period. The average of NO_2 DSCDs is small under the wind conditions from North. When the wind direction is parallel to the observation direction (i.e. E and W, the viewing direction of the telescope is pointing to the East), the average DSCDs of NO_2 is significantly higher. Similarly, the averaged SO_2 DSCDs under the east and west wind is higher than that in the S and N. It suggests that the optical length inside the polluted air and therefore the response signal is probably increased when the wind transports the polluted air parallel to the DOAS viewing direction. In Figure 8 (c) and (d), the perpendicular direction for N and S is considered wind from 0°±15° and 180°±15°, and the parallel direction for E and W is considered wind from 90°±15° and 270°±15°. It can be seen that the NO_2 and SO_2 DSCDs are quite different in these two types of wind directions. When the wind is parallel to the observation direction (E and W), 34% of NO_2 DSCDs and 31% of SO_2 DSCDs are greater than 3.00×10^{16} molec cm^{-2} and 1.5×10^{16} molec cm^{-2}, respectively. However, under the perpendicular direction (N and S), the occurrence of high DSCDs of NO_2 and SO_2 significantly decreased compared to parallel direction.

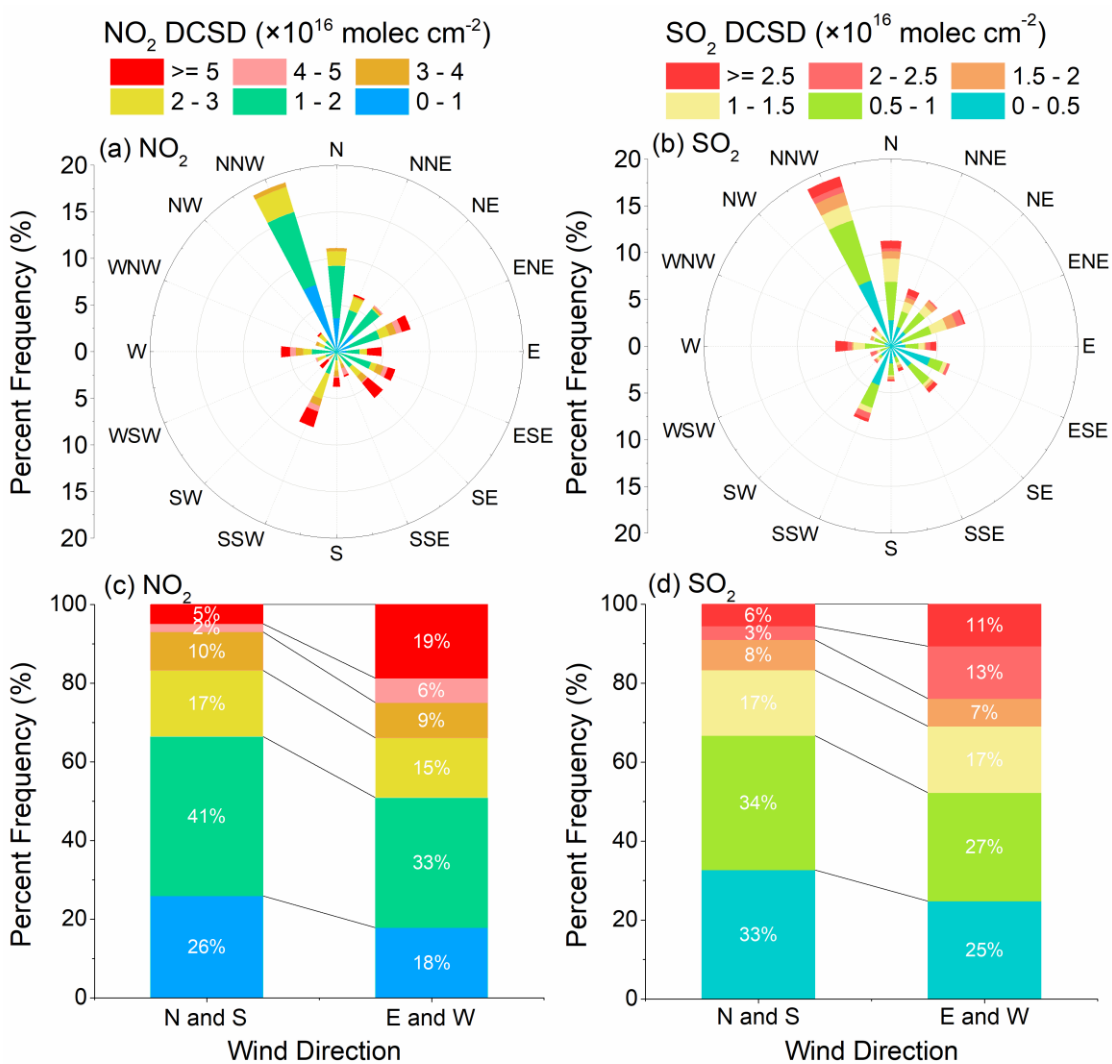


Figure 8. The dependence of (a) and (c) of NO_2 and (b) and (d) of SO_2 DSCDs at elevation 5° on wind directions from January to

March 2018.

Based on the real-time photos taken by the instrument, we have counted the ship density manually to discuss its relationship with observed DSCDs of NO_2 and SO_2 at elevation 5°, as shown in Figure 9. It is obvious that the hourly means of NO_2 and SO_2 DSCDs show an upward trend as the ship density increases. Since the fuel used by the ship is inconsistent, and the wind speed and direction also affect the DSCDs, it is difficult to find the clear linear relationship between hourly data of ship density and DSCDs in this busy inland waterway environment. From the prospective of statics, the averaged NO_2 and SO_2 DSCDs of binned ship density group (the hollow squares in the middle of the box) shows a strong positive correlation with the ship density, showing the correlation coefficient R of 0.86 and 0.97, respectively. The relatively higher R of SO_2 also suggests that the main impacts of SO_2 from ship emission source over there, however, more complex sources of NO_2 nearby.

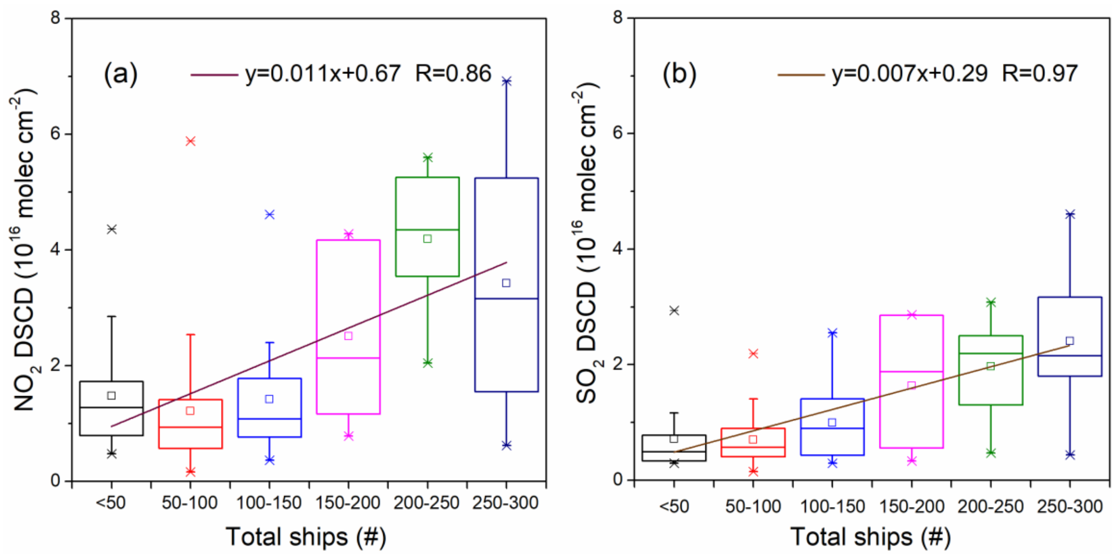


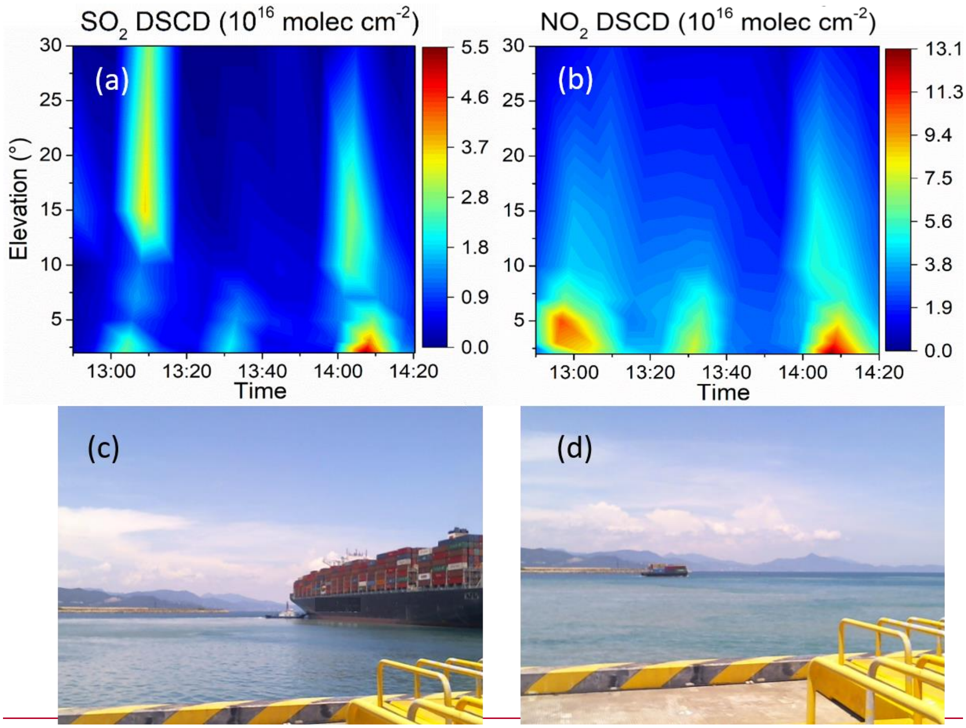
Figure 9. Relationship between DSCDs of (a) NO_2 and (b) SO_2 at elevation 5° and ship density.

In general, it can be concluded from the continuous ~~five~~ several months measurements at Wusong MSB site that the ship ~~traffic volume~~density and meteorological conditions are the two major factors ~~impacting~~ influencing the observed NO_2 and SO_2 levels in this typical inland waterways. For similar diffusion situations, the MAX-DOAS instrument can accurately detect the elevated pollutants concentrations with the increased number of ships. However, due to the busy ship lanes in front of the instrument, the MAX-DOAS instrument usually observes signal of pollutants in the plumes from multiple ships together, and the navigation speed of ships are relatively faster compared to the period of a completed scan measurement. So it is very hard to distinguish the single plume from the mixture. It is another shortcoming of this measurement that the MAX-DOAS measured NO_2 are considerably impacted by surrounding other emission sources, such as main roads and highways nearby. Since it is less practical for regulatory authorities to achieve fuel detection for each ship in this busy inland waterways, the remote sensing of MAX-DOAS measurement still offer the prospect of surveillance of ship emissions. Based on the legally sulfur content and ship activity data, the theoretical NO_2 an SO_2 concentration of plume exhausted from the chimney can be calculated. By combining with the diffusion model of plume, the theoretical concentration of SO_2 on the light path of MAX-DOAS observation can be obtained. Afterwards, ~~Aiming to inspect the compliance of fuel sulfur content, the prospects of the MAX-DOAS application for the complicated inland waterways is used to mark~~ the suspicious ship using fuel with excess sulfur content can be identified. ~~, by comparing with the theoretical SO_2 emission estimated from the legally fuel sulfur content and ship activity data.~~

3.3 Ocean-going ship emissions

Another shipping traffic scenario was also considered for the MAX-DOAS measurements at Yantian Port (114°29′ E, 22°56′ N), located on the east side of Shenzhen in the Pearl River Delta emission control zone (~~See~~ see Fig. ~~2~~1). Yantian Port is one of the largest container port, which has 20 large deep-water berths with a quay length of 8,212 m~~eters~~ and water depth alongside of 17.4 m~~eters~~, which is benefit to the ocean-going vessels with a length of more than 300 m docked. Unlike the measurement sites above, the distinct feature of shipping traffic in Yantian Port is the huge size of inbound and outbound vessels and the much less traffic density. The MAX-DOAS instrument was installed at the shore of the central operation zone of the Yantian Port from May 23, 2018. As can be seen in Fig. ~~2~~1(d), the view direction of MAX-DOAS was pointed to the lanes in the eastward sea area. Due to lack of other emission sources in the front, the MAX-DOAS observation can easily capture the pollutants in single plume from the individual ~~orderly~~ inbound and outbound ship, as manifested in Fig. ~~8~~10.

Figure ~~8~~10(a) and (b) presents the altitude dependence of observed SO_2 and NO_2 DSCDs around noontime on May 26, ~~2019~~2018~~.~~. During the observational period, there were three apparent peaks of SO_2 and NO_2 DSCDs, i.e. 13:00, 13:30 and 14:10. The increases of both pollutants levels ~~were~~ occurred simultaneously. For the first pulse around 13:00, the higher levels of SO_2 DSCDs are distributed above 10° elevation, whereas the strong signals of NO_2 are concentrated below elevation angle of 5°. This can be explained by the fact that the container ocean-going vessel and tugboat behave differently in emission and operation. Fig. ~~8~~10(c) proved that there a large container ship is outbound at 12:55 with assistance of two tugs. It is obvious that height of outlet is very high for large container ships, but quite low for the tugboat. Since the tugboat are usually operated in the port area, its fuel usage always obey the regulations of ECA and shows high quality. Thus, stronger SO_2 signal appeared at high altitude due to the container ship emission, while NO_2 hotspots closed to the sea surface contributed by the tugboat emission. During the period around 13:30, both DSCDs of SO_2 and NO_2 were slightly increased and allocated below elevation 7°. According to the live photo in Fig. ~~8~~10(d), there only a small container ship ~~were~~ was passing through about 1 km away in front view of the instrument. Considering the distance between the ship and instrument, the height of exhaust outlet should be related to a lower elevation angle, where the corresponding strong signal of emitted pollutants are expected to be observed. Additionally, obvious SO_2 and NO_2 signals were found around 14:10, during which high SO_2 were distributed among elevation angle 10° to 15°, but strong signals of SO_2 and NO_2 were both found near the sea surface. However, no ship was captured by the live photos. It can be inferred from the AIS information that the observed signal of plume was dispersed from the ship in another lane instead of this in the front view of the instrument. Besides, the AIS information also confirmed that there are no other ship emissions disturbances for the two earlier measurements.



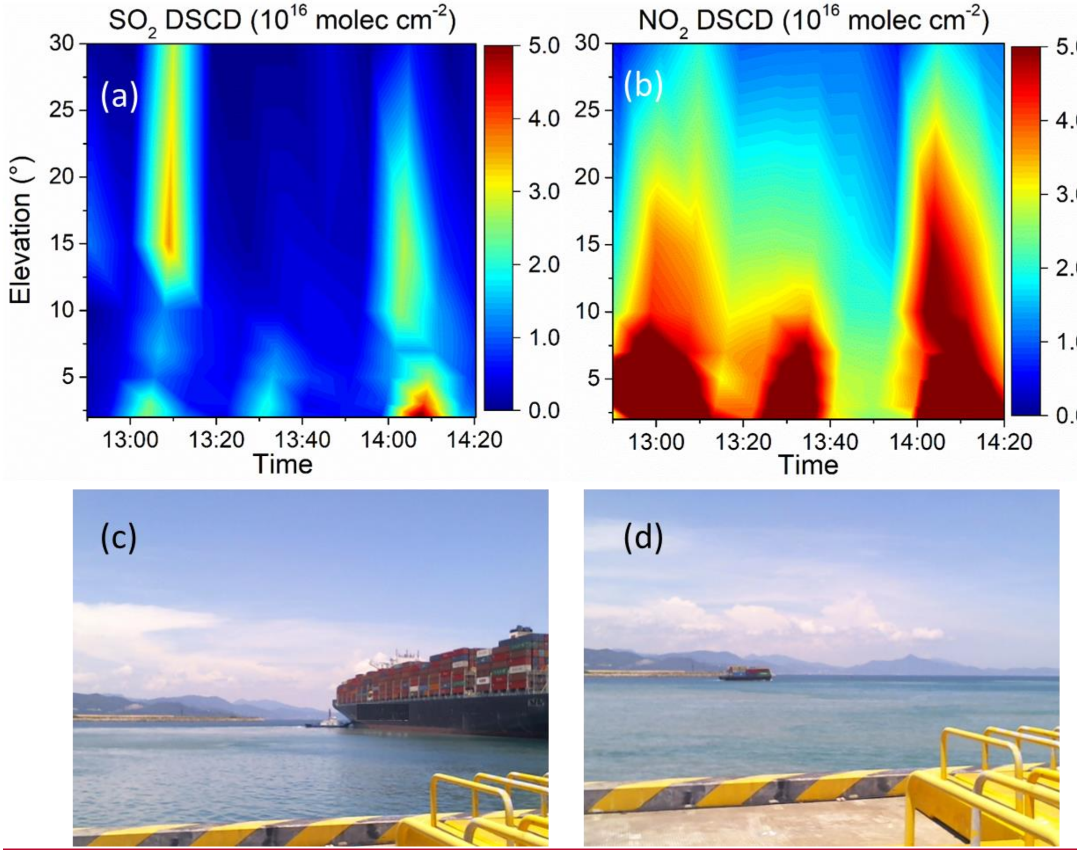


Figure ~~8~~10. Measured DSCDs of (a) SO_2 and (b) NO_2 during 12:55~14:20 and live photos taken by the camera at (c) 12:56 and (d) 13:22 on May 26, 2018.

In general, the characteristics of observed SO_2 and NO_2 DSCDs distributions on height are to some extent related to the ship size, its distance from the instrument and operational status, as well as the atmospheric stability~~ more or less~~. Based on the example discussion above, the MAX-DOAS measurement in Yantian port can detect the pollutants in single plume from individual ship and provide the information about vertical distribution of pollutants ~~with the~~for conditions of low ship traffic volume. Considering the large discrepancies of SO_2 signals in altitudes, we try to analyze the detected plumes in more detail ~~further detailed SO_2 emissions from the measurement~~ and obtain the representative observation elevation. According to the live photos, a large container ship entered the field of view at 09:51 on June 22, 2018, which moved very slowly and emitted a distinct black smoke. Figure ~~9~~ 11 shows the distribution of SO_2 DSCDs in plumes at different elevation angels. The SO_2 DSCDs peaked at 8.17×10^{16} molec cm^{-2} between elevation angles of 5° and 7°, and decreased with height. It ~~can be~~was found that the DSCDs observed at elevation angle 7° are suitable to ~~stand for~~represent the peak concentrations in the plumes considering the chimney height of ship and its horizontal distance from MAX-DOAS instrument.

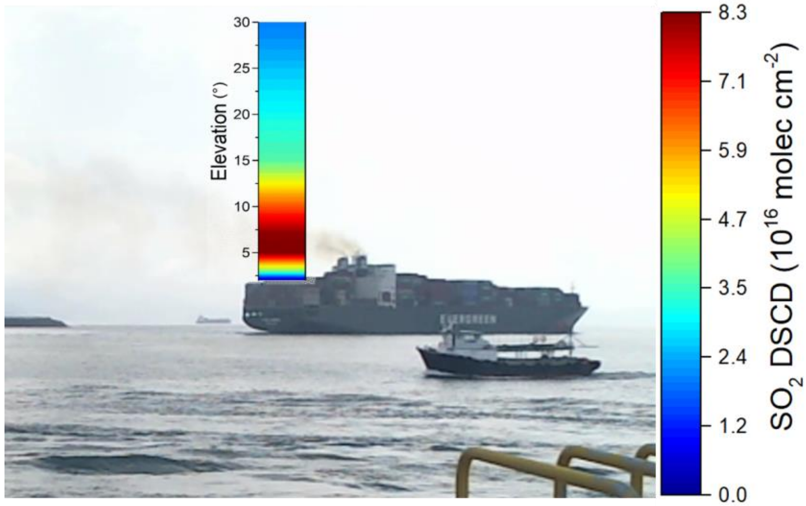
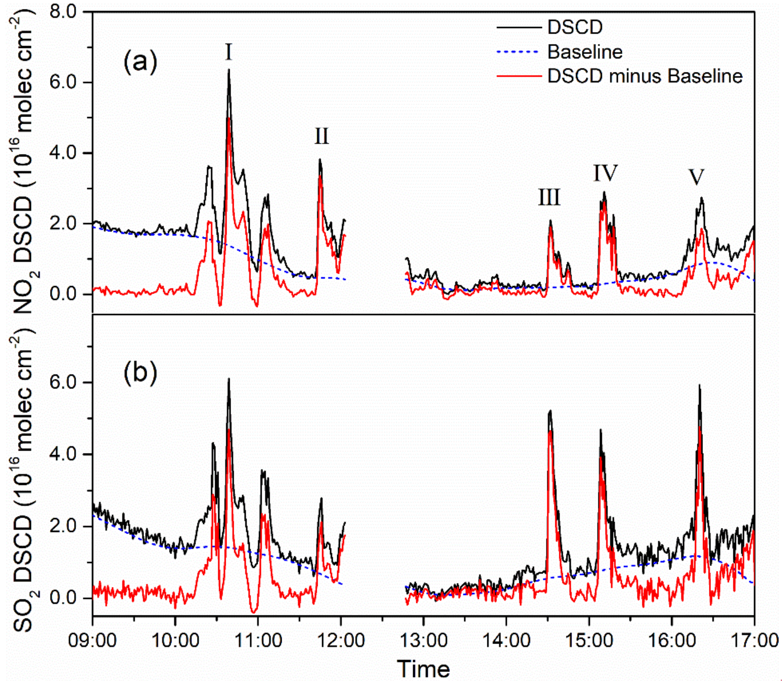


Figure ~~9~~11. A typical distribution of SO_2 DSCDs in the smoke plume of ship on June 22, 2018

Instead of the full elevations scanning, with the temporal high resolved measurements (60 s) at single 7° elevation, it is possible to resolve individually the plume signal of passing ships. Thus, the diurnal profiles of SO_2 and NO_2 DSCDs at 7° elevation~~s~~ on June 26, 2018 were further investigated as presented in Fig. ~~10~~12. ~~With the high temporal resolution measurements of 60 s,~~ ~~T~~There multiple peaks of SO_2 and NO_2, with the highest DSCDs of SO_2 and NO_2 exceeding 6.00×10^{16} molec cm^{-2}, occurred due to the emissions of the occasional passing ships. By applying the mathematical method, a baseline (the blue dotted line in Fig. ~~10~~12) can be extracted from the DSCDs trend lines (the black solid line in Fig. ~~10~~12). The baseline represents the diurnal variations of DSCDs, mostly due to the change of light path caused by solar zenith angle and the background emissions. Finally, it can be found that seven synchronous peaks of SO_2 and NO_2 levels higher than 2.00×10^{16} molec cm^{-2} are present in the trend line (the red solid line in Fig. ~~10~~12). Validated by the live photos of the instrument and the AIS information, these kind of sharp increased concentration of pollutants are originated from the ship plumes passed by. It suggests the high sensitivity of MAX-DOAS measurements to the change of SO_2 and NO_2 contents in the atmosphere. ~~In addition, t~~The increases of pollutants levels lasted from 10 min to half an hour, which is related to the durations of the ship movement in the field of view.



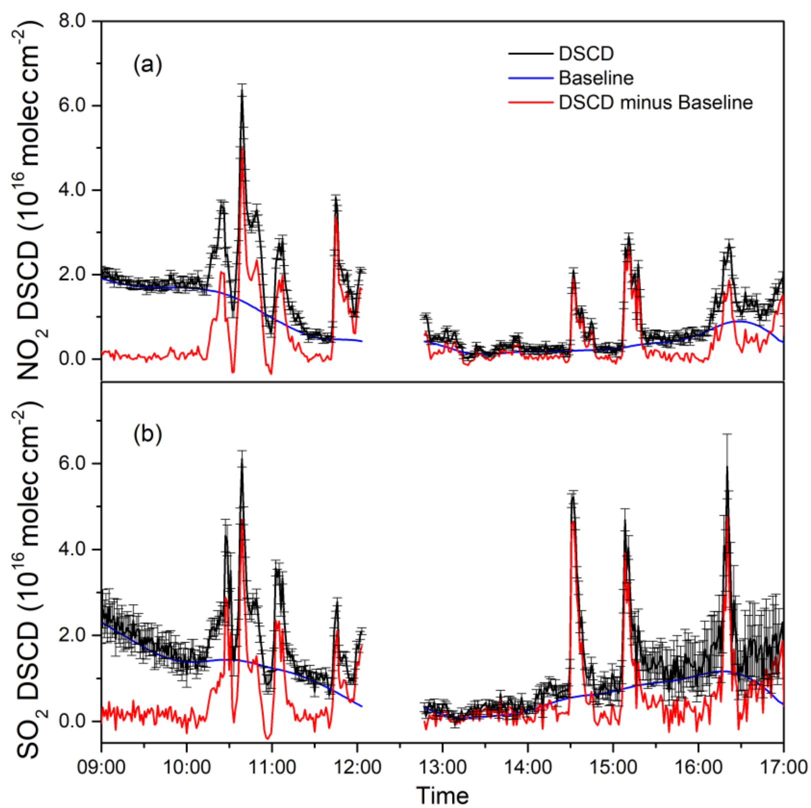
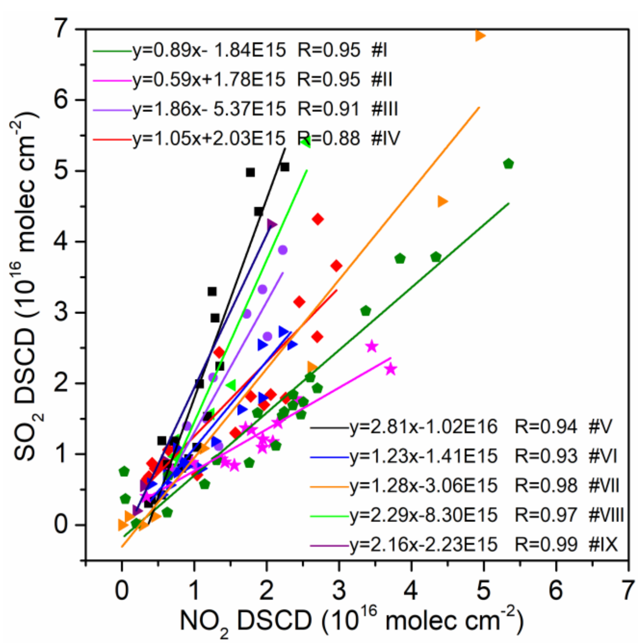


Figure ~~10~~12. Diurnal variations of DSCDs of (a) NO_2 and (b) SO_2 measured at 7° elevation angle on 26 June 2018.

Moreover, it should be noticed that the amplitude of each peak varied differently, which implies that the DSCDs ratio of SO_2 to NO_2 for each peak may reveal the emission information of fuel sulfur content of individual vessels (Seyler et al., 2017; Mellqvist et al., 2017). However, it is important to note that the NO_2 is formed by the reaction of NO and O_3 in the plume, so the SO_2/NO_2 ratio depends on the age of the plume to a certain extend. The ambient O_3 between 08:00 and 17:00 was averaged at 63.7 ppb in Yantian during the campaign. Considering the abundance of ozone, the NO emitted by the ship will react with O_3 rapidly to form NO_2 within a few minutes or even faster (Seyler et al., 2017). In addition, the conversion between NO and NO_2 is very fast and maintains a dynamic balance with sunlight during the daytime considering the photolysis of NO_2 (Singh et al., 1987). Therefore, the SO_2/NO_2 ratio in the observed plume could be in a stable conditions and less impacted by the fresh emitted NO. Thus, the linear regression analysis between SO_2 and NO_2 DSCDs were performed to infer the fuel sulfur content. Figure ~~11~~ 13 presents the analysis results of ~~nine~~ 24 different vessels. The strong correlation relationship between SO_2 and NO_2 DSCDs are the obvious evidence of the significant homologies of emission sources between SO_2 and NO_2. Nevertheless, the slope of different vessels highly changed from 0.~~59~~ 28 to 2.~~81~~90, indicating the diversity of the SO_2 emission intensity in the ship plumes. In general, the SO_2 emission are directly related to the fuel sulfur content and engine operation status of the ships according to the emission model estimation, e.g. the power, activity time and the speed of ship (Fan et al., 2016; Zhang et al., 2018b). The outbound vessels usually leave from the shore slowly with the help of tugboat, and then speed up sailing into the sea. It calls the main engine to power the navigation during this process, and the fuel used by the main engine has a higher sulfur content than the auxiliary machine. In contrast, the main engine of vessel is usually shut down during the inbound process. Therefore, the ratio of SO_2/NO_2 DSCDs in the plume emitted by the outbound vessel could be higher than the inbound one.



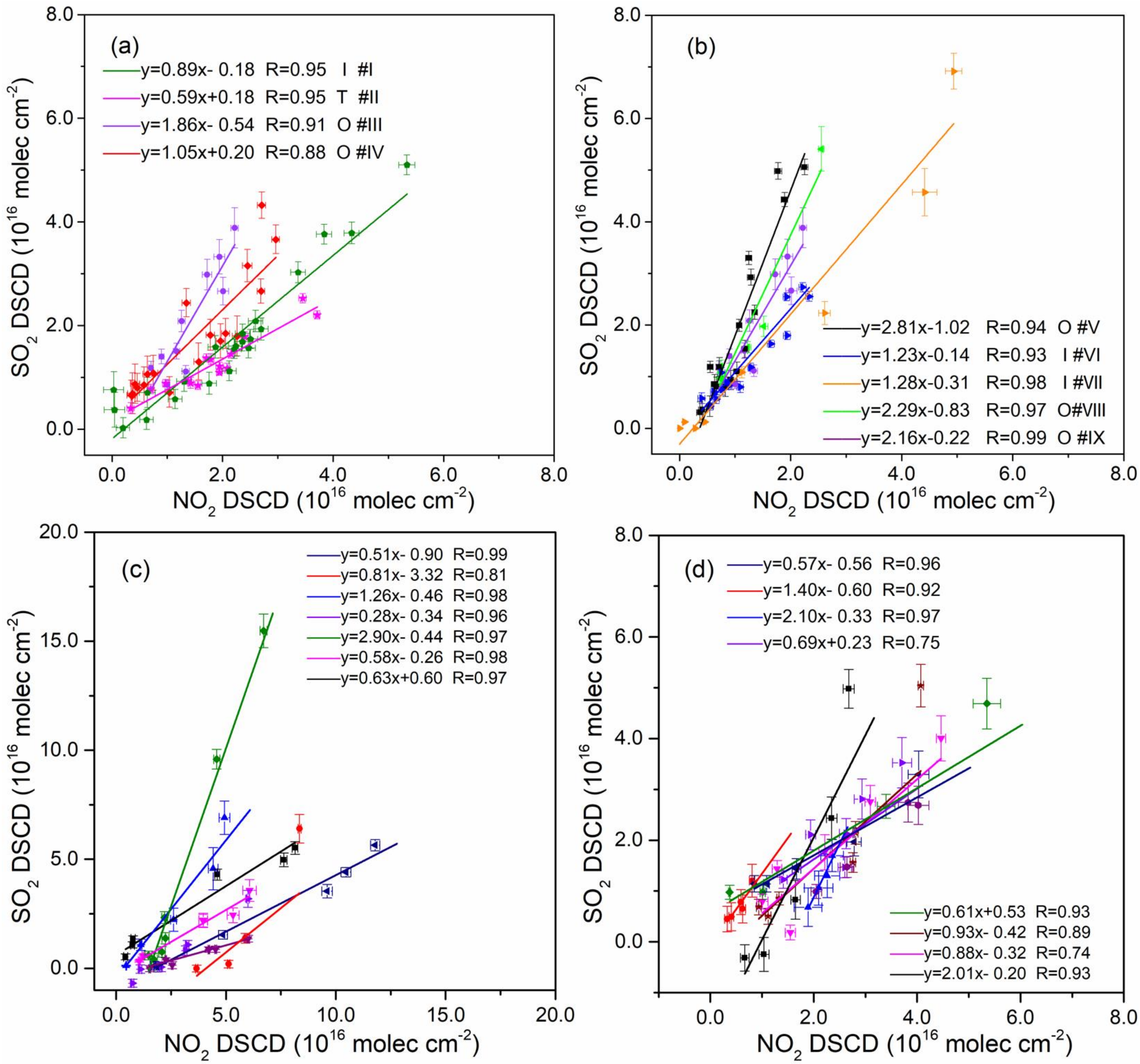


Figure 1113. The relationship between SO_2 and NO_2 emitted by several typical vessels.

During the MAX-DOAS observation, we have also carried out some fuel sample analysis, investigation on the activity data and engine parameters of these vessels, among which five of them are the vessels in Fig. 120. Therefore, we indicated the different status of these nine vessels in Fig. 124, along with the information about on the rated power of engine and fuel sulfur content individually, in which the inbound and outbound shows the rated power of main and auxiliary engine, respectively.

The vessel #II is a tugboat operated in the port area, which uses the fuel with lowest sulfur content of 0.001% and shows minimum ratio of SO_2~~-to-~~/NO_2 in DSCDs. Furthermore, the inbound vessel #I, #VI and #VII (indicated by diamond in Fig. 14~~2~~) ~~has~~ have switched off the main engine when it arrived in the front of the MAX-DOAS instrument, moved under the towing of tugboat and docked by inertia finally. Additionally, the sulfur content of fuel are much lower in auxiliary engine than main engine. So SO_2~~-to-~~/NO_2 ratios of inbound vessels ~~are~~ is much lower than that of outbound vessels. The other vessels, indicated by circle in Fig. 14~~2~~, are all in outbound. Under the launch of main engine and high sulfur content in fuel, these vessels exhibited relatively higher ratios of SO_2~~-to-~~/NO_2 over 2.0, except for vessel #IV. Due to the usage of much more cleaner fuel with sulfur content of 1.28%, the vessel #IV presented the lowest ratio of SO_2~~-to-~~/NO_2 among all the outbound vessels. Compared to vessel #III with similar rated power of engine, it can be observed that the ratio of SO_2~~-to-~~/NO_2 in the plume increased with the ~~growth~~ increase of fuel sulfur content for vessels. This phenomenon is also applicable to cases of vessel #V and #VIII. It is worth ~~noted~~ to note that the ~~dot~~ circle of outbound cargo #~~IV~~ IX is deviated from others, which has very low rated power but very high ratio of SO_2~~-to-~~/NO_2 > 2.0. So it can be recognized as a suspicious ship using fuel with sulfur content exceeding the regular limit.

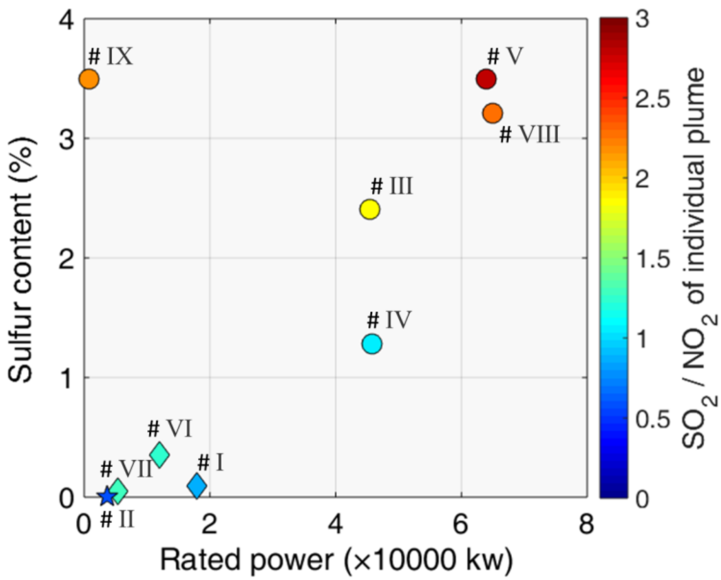


Figure 14~~2~~. The relationship between the ratio of SO_2/NO_2 obtained by linear regression, the fuel sulfur content and engine rated power of all nine vessels. Tugboat, inbound and outbound vessels are represented by pentagram, diamond and circles, respectively.

Basically, the ratios of SO_2~~-to-~~/NO_2 in the plume discharged from the inbound vessel and the tugboat are usually lower than 1.5 for normal condition, which is much smaller than that of outbound vessels using high rated power engine and high sulfur content fuel. For outbound vessels, the ratios of SO_2~~-to-~~/NO_2 are more related to the fuel sulfur content. The irregular observed ratio of SO_2 to /NO_2 can tag the vessel not obeyed to the sulfur content limitation. Therefore, the MAX-DOAS measurement provides a promising technology for compliance monitoring of fuel sulfur content by investigating the ratio of SO_2 to /NO_2 in the plume and the more accurate estimation with load factor and emission factor for the actual operation. Besides, the statistics of SO_2/NO_2 ratios in discharges were performed for 55 ships during the observation. The frequency distribution of the slope of SO_2/NO_2 is shown in Figure 15. It shows that the values of SO_2/NO_2 were mostly distributed less 1.5, which occupied about 72.7%. Ships with the ratio of SO_2/NO_2 between 0.6 and 0.9 shared the highest proportion. It indicates that most of the fuel used by ships in Yantian Port could be qualified. However, there are still some ships may use non-compliant fuel, because the ships with a value of SO_2/NO_2 greater than 1.5 account for 27%.

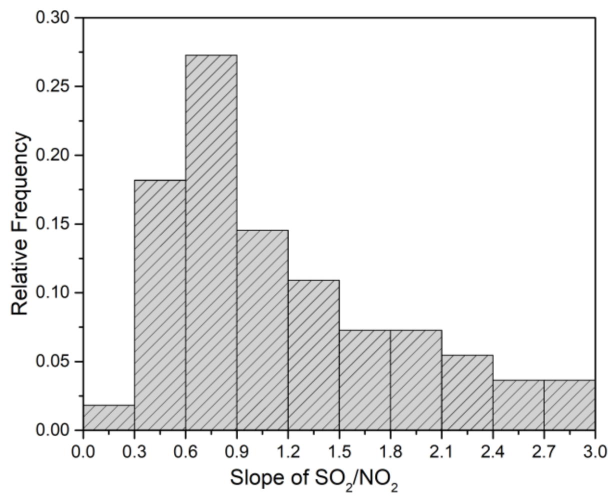


Figure 15. Frequency distribution of the slope of SO_2/NO_2 from samples of 55 vessels.

Conclusion

In this study, we have performed the MAX-DOAS measurements observe the ship emissions of SO_2 and NO_2 in Shanghai and Shenzhen, China for three different typical ship traffic conditions. At Waigaoqiao container terminal in Shanghai, the SO_2 and NO_2 exhausted by ship at berth can be easily identified for the locations and intensity of emission from the 2-dimensional MAX-DOAS observation. At the inland waterway area of Wusong Wharf, it is difficult to determine the single ship emissions due to the dense traffic volume and complex background environment. The long-term MAX-DOAS measurements shows that the changes of SO_2 and NO_2 are proportional correlated to ship traffic density atflow whether in stable and unstable atmospheric conditions. However, better dispersion under unstable atmospheric condition are favorable for the decrease of pollutants levels. For open sea waters in Yantian deep water port, the 2-dimensional DSCDs of SO_2 and NO_2 measuredmapped by MAX-DOAS are highly sensitive to the emitted plumes of vessels passing through in front of the shore-based instrument, which shows the significant increase of pollutants concentrations and 10-30 min duration of the emission signals. Considering the distance and size of the vessels, the DSCDs observed at elevation angle 7° are the hotspots of the concentration in altitude, and further selected to investigate the fuel sulfur content. According to the linear regression of SO_2 and NO_2 DSCDs, the ratio of SO_2 ~~to~~ /NO_2 are found to be very helpful to infer the levels of sulfur emission. Combined the fuel sample analysis and inquiry of the vessel data, the SO_2/NO_2 ratio in the plume are usually lower than 1.~~3~~ 5 for the inbound vessel and the tugboat, whereas is much smaller than that of other vessels. The abnormal high ratio of SO_2 ~~to~~ /NO_2 in the plume usually implies the vessel could not be in compliance with the sulfur content limitation.

In summary, the advantages of optical remote sensing and mature for SO_2 and NO_2 detection are beneficial to MAX-DOAS measurement for the ship emission. These applications at different ship traffic scenarios demonstrated the feasibility of shore-based MAX-DOAS to observe the emitted SO_2 and NO_2 from vessels docked at berth, navigation in the lanes, inbound and outbound operations. Nevertheless, the main ship emitted pollutants of NO and CO_2 cannot be monitored due to the limitation of the observed wavelength range. Since MAX-DOAS uses solar scattered light as the source, it cannot be measured at night when there is no sunlight, and there is a large error during twilight and rainy observations. For the prospects, the combination of MAX-DOAS remote sensing of ship plumes and the estimation on emissions with theoretical fuel sulfur contents and actual operation data will provide the promising approach for surveillance in the future.

Data availability. Data are available for scientific purposes upon request to the corresponding authors.

Author contributions. YC, SW and BZ designed and implemented the research, as well as prepared the manuscript; JZ, YG and RZ contributed to the MAX-DOAS measurements at different sites; YC and SW carried out the MAX-DOAS retrieval and analysis combined with other auxiliary data; YL, YZ, YQ and WM provided constructive comments and support for the ship emissions research of this study.

Competing interests. The authors declare that they have no conflict of interest.

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