

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. NO_x 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, CO₂ and NO cannot be detected in this study. Therefore, here we mainly focused on the NO₂ and SO₂ emitted by the ship, while the other two main pollutants of CO₂ and NO were not introduced in the Section 1. We have added the introduction about ship emitted NO and CO₂ and the NO/NO₂ 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 be converted to NO₂ by reaction with O₃ in the atmosphere, and the rate of NO conversion to NO₂ is strongly affected by the concentration of O₃ (Han et al., 2011). The average value of O₃ 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 O₃ rapidly to form NO₂ within a few minutes or even faster (Seyler et al., 2017). In addition, NO₂ is photolyzed by UV radiation to release NO and oxygen radicals. In the collision reaction with N₂ or O₂, oxygen radicals react with oxygen molecules to reform O₃. So the conversion between NO and NO₂ 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 SO₂ and NO₂ 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/NO₂ 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 SO₂/NO₂. (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 NO₂ and SO₂ DSCDs using 2-D scanning measurement of MAX-DOAS. The hotspots of NO₂ and SO₂ 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 NO₂ and SO₂ 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 days. 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 NO₂ and

SO₂ over three months with the wind direction and found that the average DSCDs of NO₂ and SO₂ is higher when the direction of wind is parallel to the observation direction. In addition, the DSCDs of NO₂ and SO₂ 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 SO₂ and NO₂ 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.

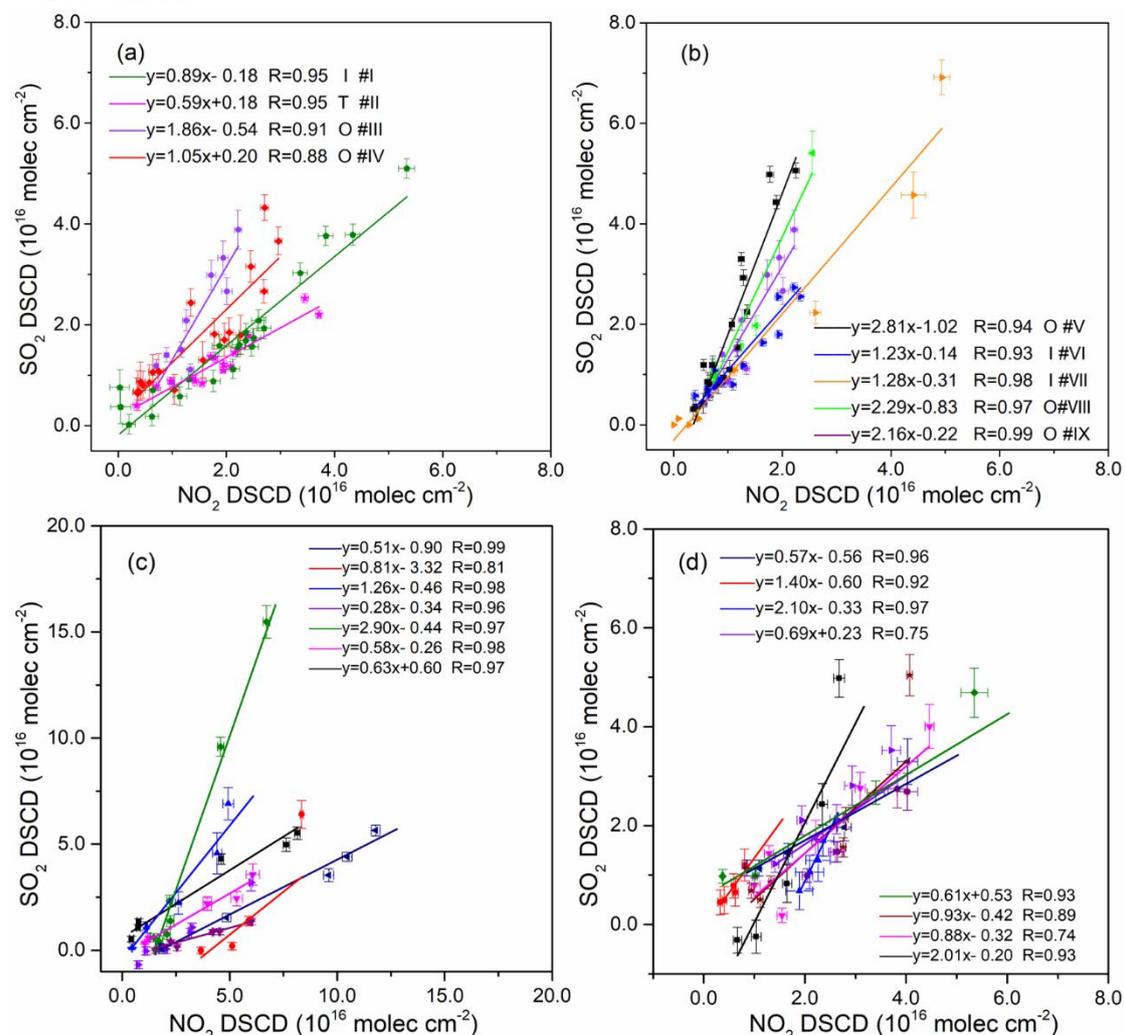


Figure R1. The relationship between SO₂ and NO₂ emitted by several typical vessels, the letter “O” indicates the outbound vessels, “I” indicates the inbound vessels, and “T” indicates the tugboat.

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.

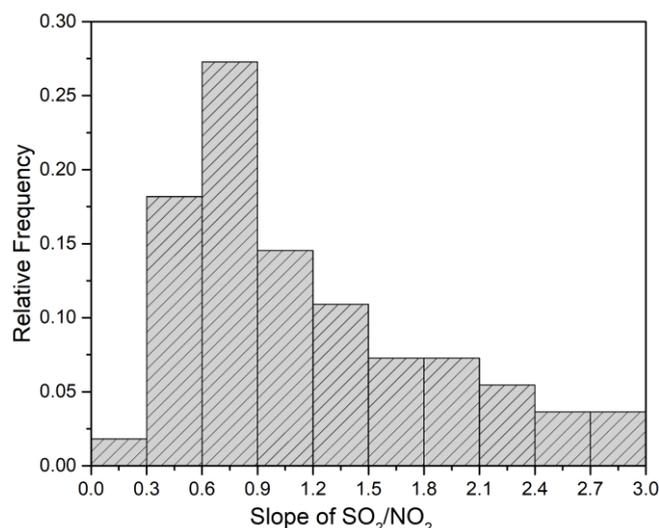


Figure R2. Frequency distribution of the slope of SO_2/NO_2 from 55 ships.

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 CO₂ 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 CO₂ 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 NO₂, SO₂ 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 (CO₂) 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 Content (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 be 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 NO₂ and SO₂ in both cases. Please refer to Figure 2 in the revised manuscript.

10. Figure 3 (line 180-181): Wouldn't it be better to 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.

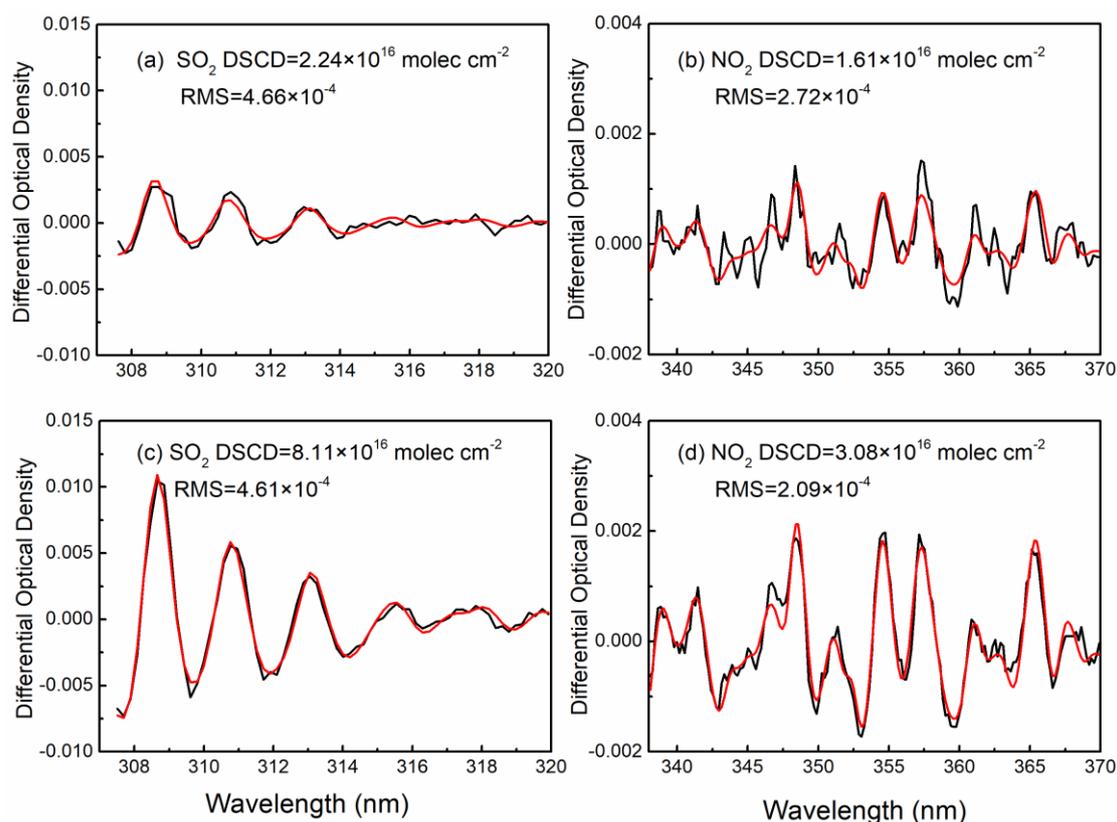


Figure R3. Typical DOAS spectral fitting for SO_2 and NO_2 . (a) and (b) show the clean condition of spectrum collected at an elevation angle of 5° at 10:39 LT on 22 June, 2018, while (c) and (d) are the ship plumes polluted case of spectrum measured at an elevation angle of 5° at 09:53 LT on 22 June, 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 NO_x or SO_2 ?

R: Opposite the berth is the South Channel of the Yangtze Estuary. The only sources of NO_x 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 NO₂ and SO₂ 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 NO₂ and SO₂ DSCDs for each elevation angle. The wind rose diagrams of NO₂ and SO₂ 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 NO₂ 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 NO₂ is significantly higher than the direction of N. Similarly, the average value of SO₂ 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 NO₂ and SO₂ 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 NO₂ is greater than 3.00×10¹⁶ molec cm⁻², 31 percent of SO₂ is greater than 1.5 ×10¹⁶ molec cm⁻². However, in the perpendicular

direction (N and S), the occurrence of high DSCDs of NO₂ and SO₂ 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.

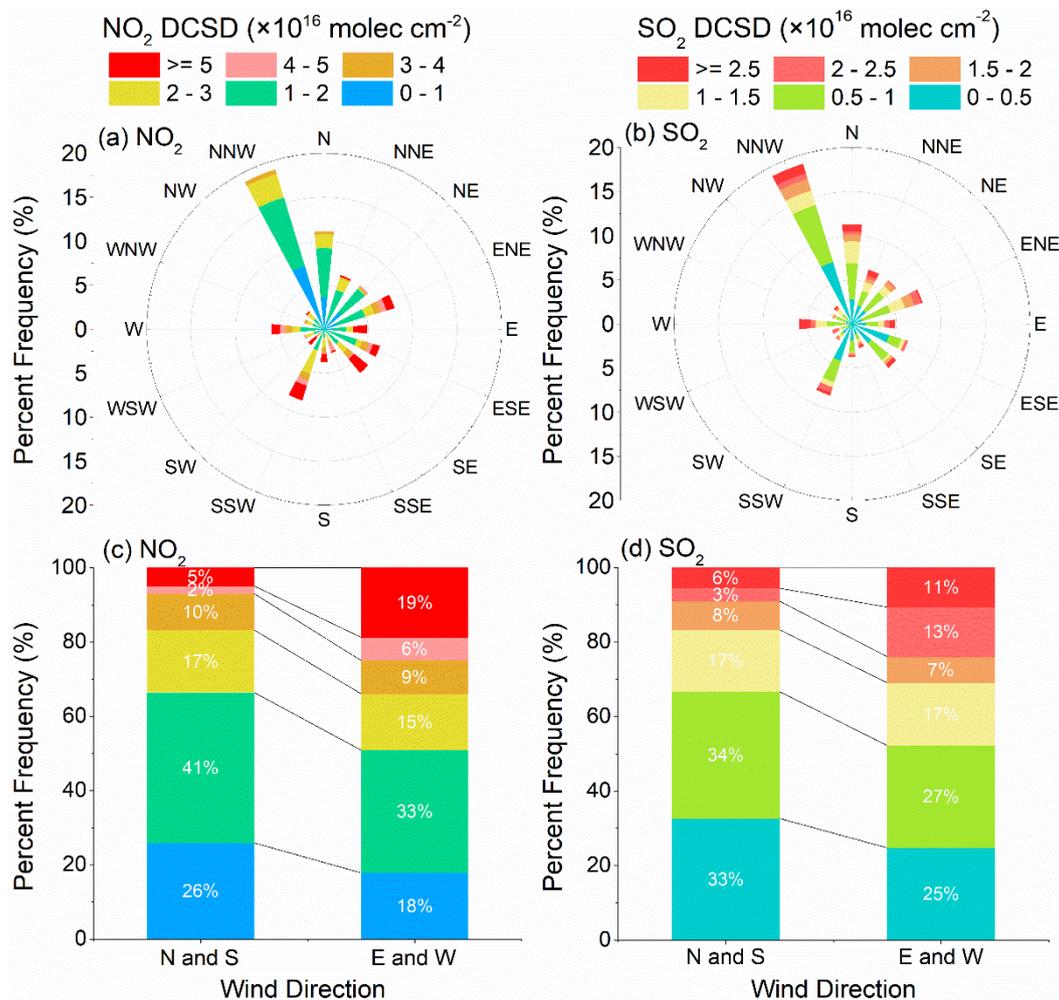


Figure R5. The dependence of (a) and (c) of NO₂ and (b) and (d) of SO₂ DSCDs on wind directions from January to March 2018 at elevation 5°.

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 NO₂ and SO₂ 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 NO₂ 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 NO₂ and SO₂ 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 NO₂ and SO₂, 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 NO₂ and SO₂ 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 SO₂ has a high correlation coefficient with ship density (R=0.97), while the correlation of NO₂ 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.

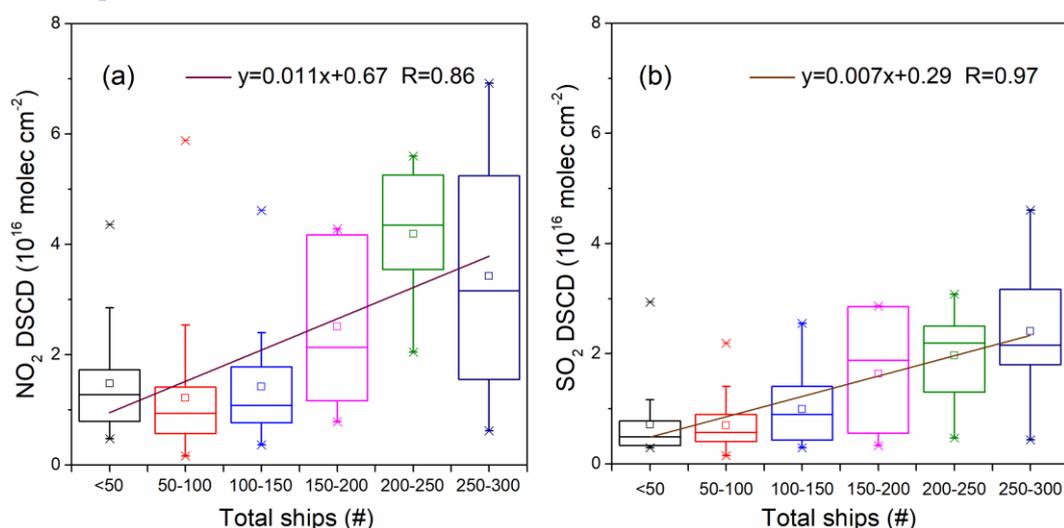


Figure R6. Relationship between DSCDs of (a) NO₂ and (b) SO₂ and ship density.

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 NO₂ from March 15 to March 30, 2018 have been analyzed. During the observation, the average value of NO₂ 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 NO₂ in a short segments of three days as an example in Figure R7 (b). We have calculated the difference of NO₂ between Wusong and Fudan campus, which is considered to represent the sum of NO₂ 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 NO₂ 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.

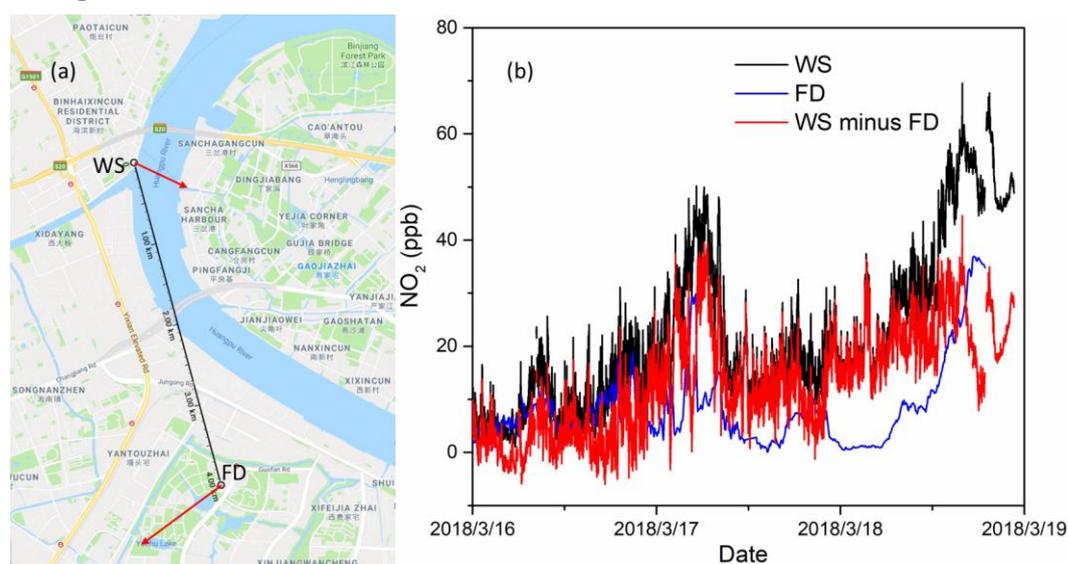


Figure R7. The locations of the LP-DOAS measurements at Wusong site and Fudan campus (a), the viewing direction and distance of instrument is indicated by a red arrow, cite from Google Maps, and (b) time series NO₂ concentration from March 16 to March 19, 2018.

22. Line 285-287: The meaning of this sentence is 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 NO₂ and SO₂ 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 SO₂ 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 SO₂ 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 NO_x 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 NO₂ emissions from large ships are obvious. Please also refer to Figure 10 in manuscript.

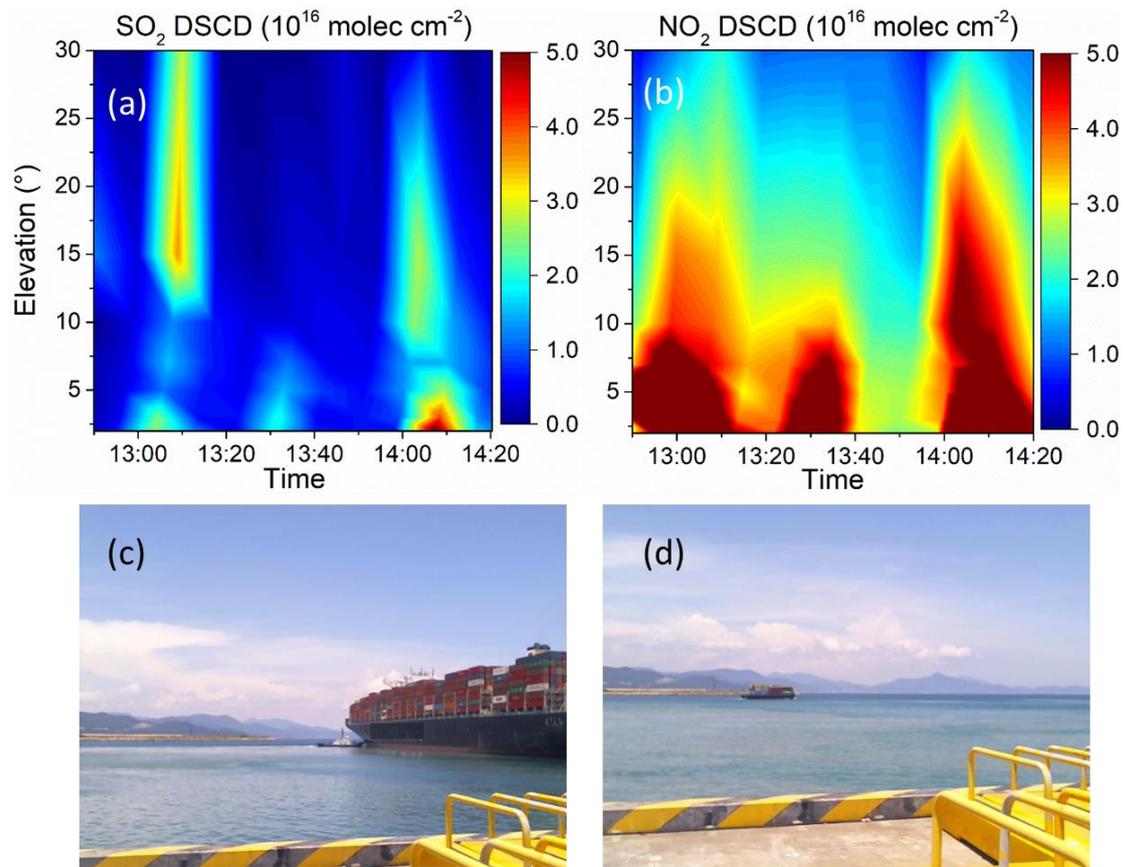


Figure R8. Measured DSCDs of (a) SO_2 and (b) NO_2 during 12:55~14:20 and live photos taken by the camera at (c) 12:56 and (d) 13:22 on May 26, 2018.

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).

$$E = \text{Load} \times \text{Activity} \times \text{EF} \times \text{FCF} \times \text{CF} \quad (1)$$

$$\text{Load} = \text{MCR} \times \text{LF} \quad (2)$$

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

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.

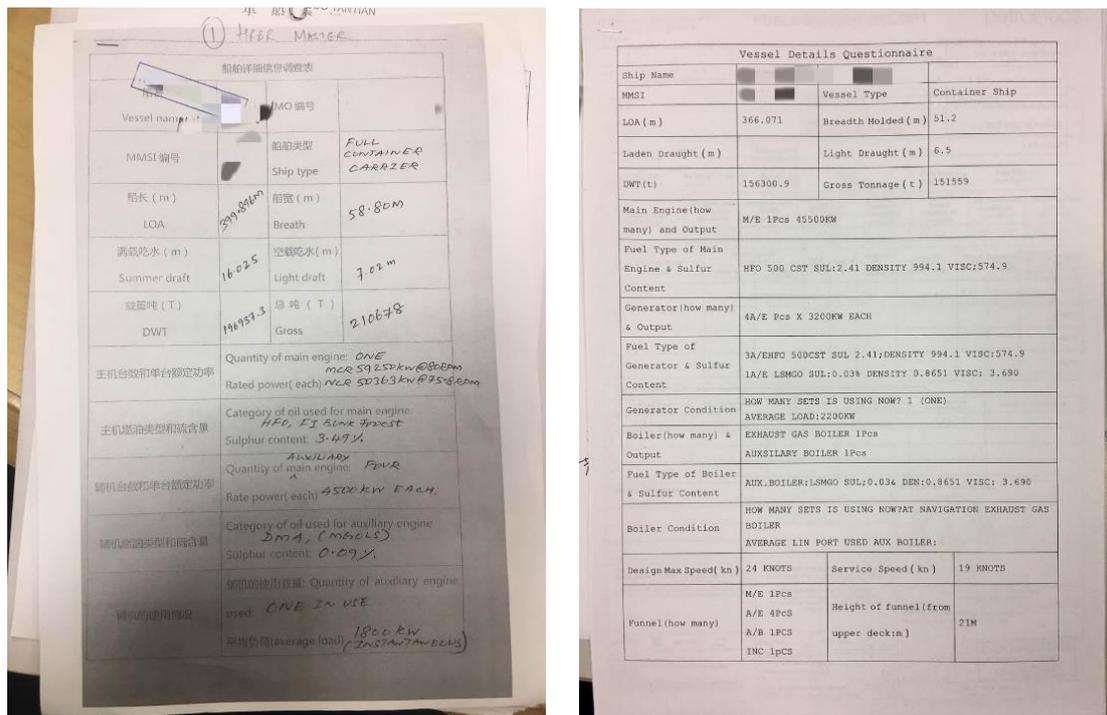


Figure R9. The detailed questionnaire of vessel information: two example ships.

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 SO₂/NO₂. 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 SO₂/NO₂ 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 SO₂/NO₂ 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 SO₂ and NO₂ in Shanghai: : :” instead of “In this study, we have performed the MAX-DOAS measurements observe the ship emissions of SO₂ and NO₂ 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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