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.

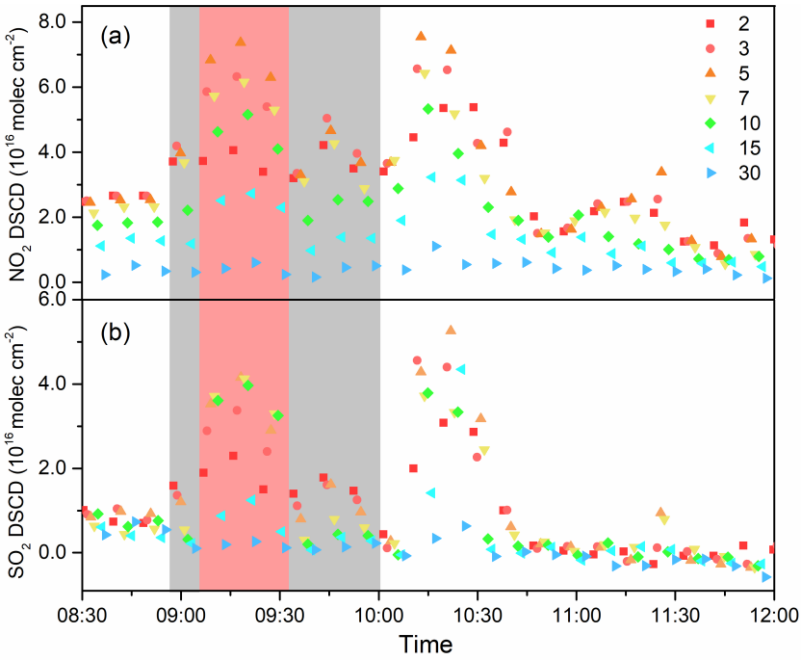

Figure. R1. Diurnal variations of DSCDs of (a) NO_2 and (b) SO_2 on 29 June 2018.

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.

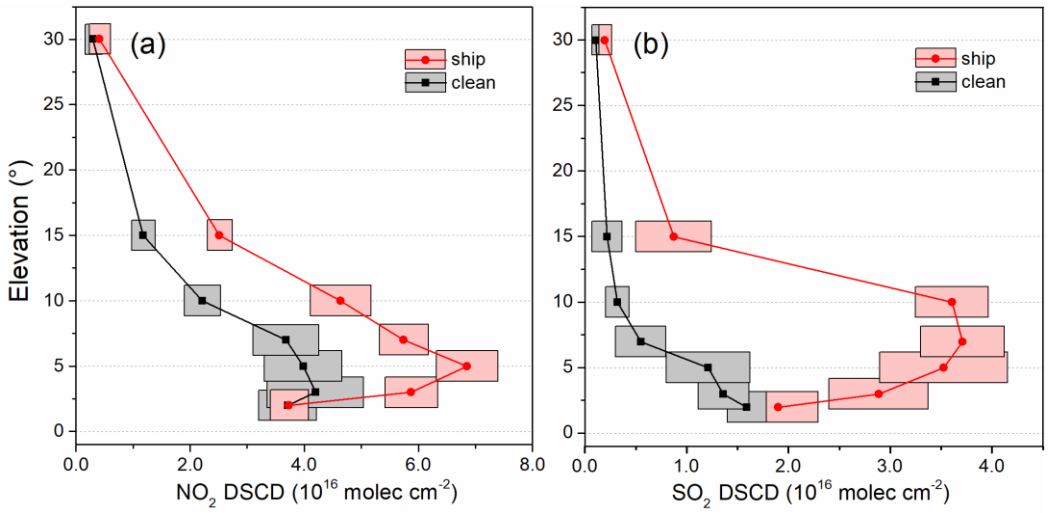

Figure. R2. The distributions of (a) NO_2 and (b) SO_2 DSCDs with elevation angle in ship emission signal and background on June 29, 2018.

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.

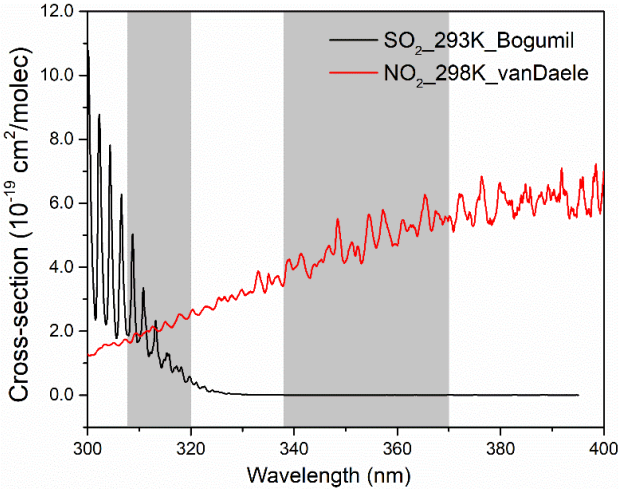

Figure R3. Absorption cross section of NO_2 and SO_2 in the wavelength range of 300~400 nm.

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.

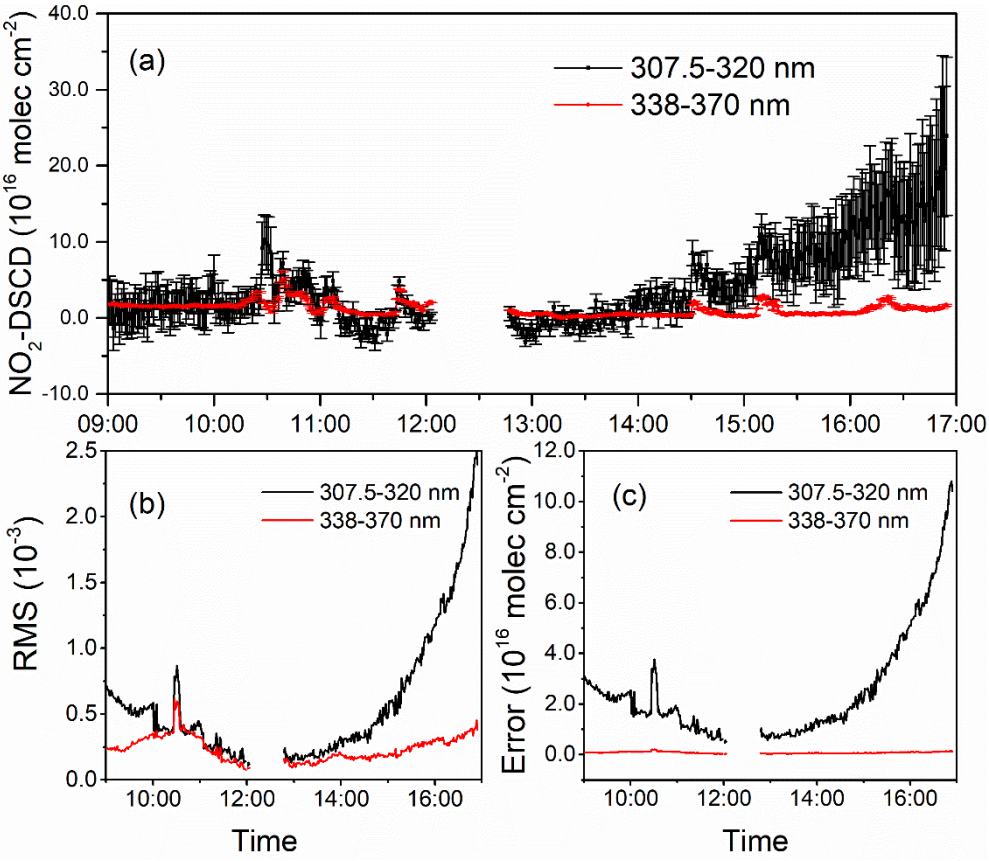

Figure R4. Comparison of NO_2 retrieval with different fitting intervals of 307.5-320 nm and 338-370 nm on 26 June 2018: (a) NO_2 DSCD with error bars, (b) RMS and (c) DSCD error.

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.

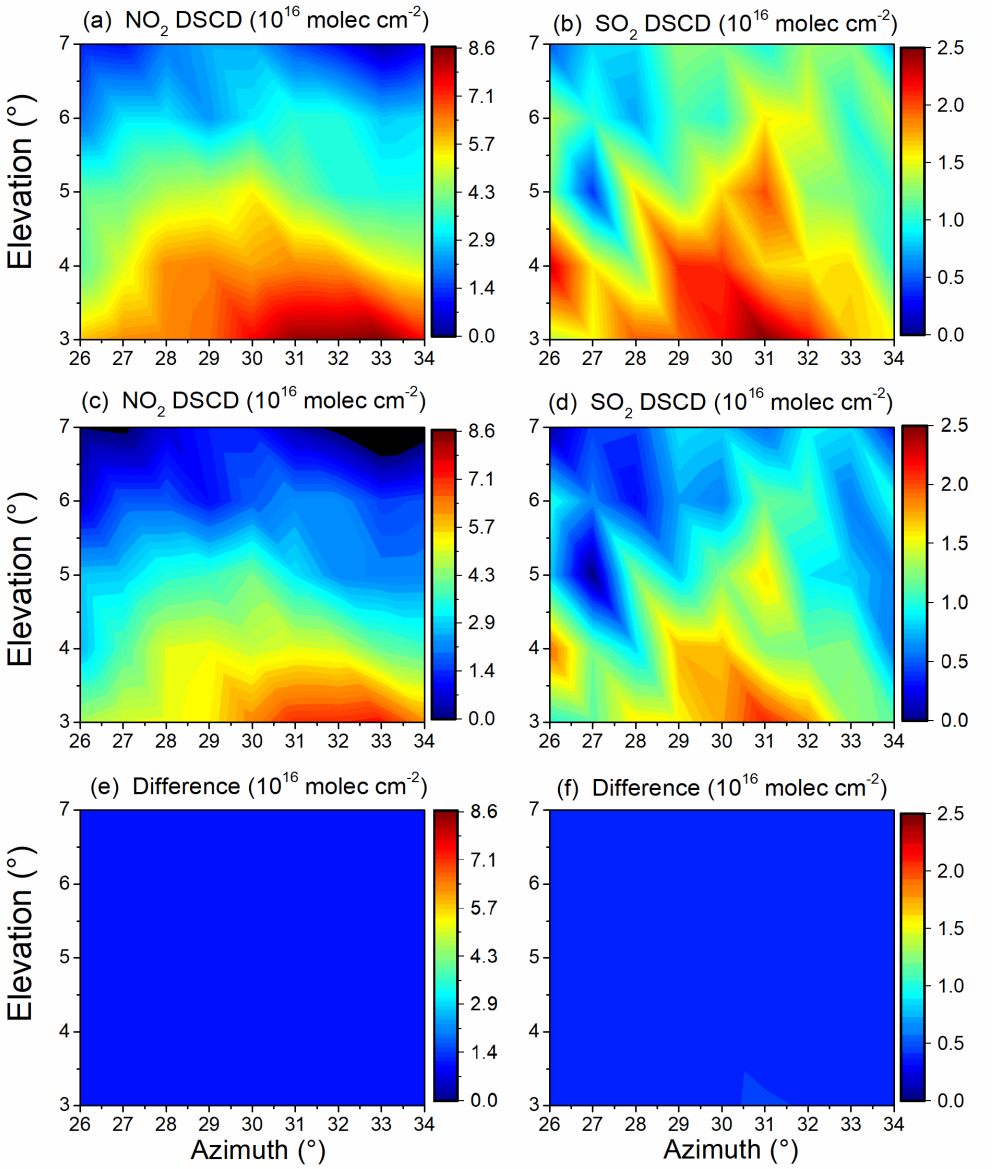

Figure R5. 2-D distributions of measured DSCDs of (a) NO_2 and (b) SO_2 using a reference spectrum collected at elevation 7° and azimuth angle of 10°; and DSCDs of (c) NO_2 and (d) SO_2 using spectrum measured at elevation 7° and 30° azimuth as the reference, (e) and (f) is the difference values between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

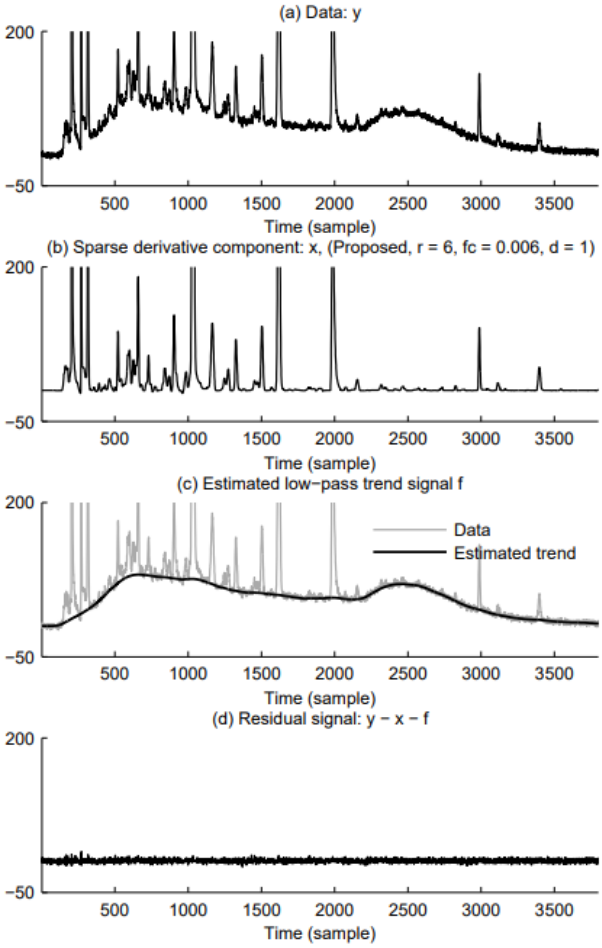

Figure R6. Processing of noisy chromatogram data using BEADS. (a) Chromatogram data with additive noise. (b) Estimated peaks. (c) Estimated baseline. (d) Residual. (Cited from Ning et al., 2014)

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.

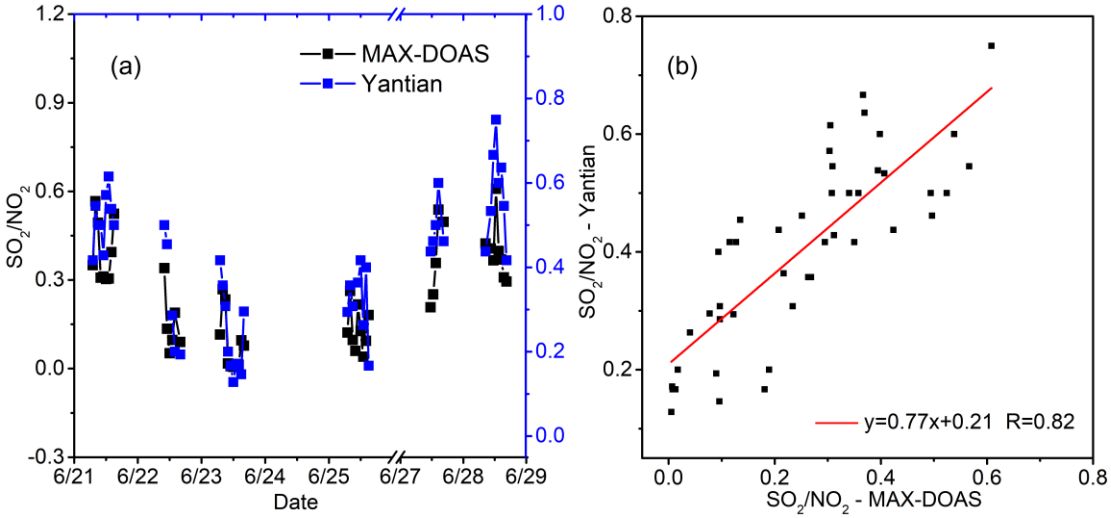

Figure R7. (a) The comparison of hourly mean SO_2/NO_2 of baseline and the ground-surface in-situ measurement at Yantian, and (b) the relationship of SO_2/NO_2 between the MAX-DOAS and Yantian.

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.

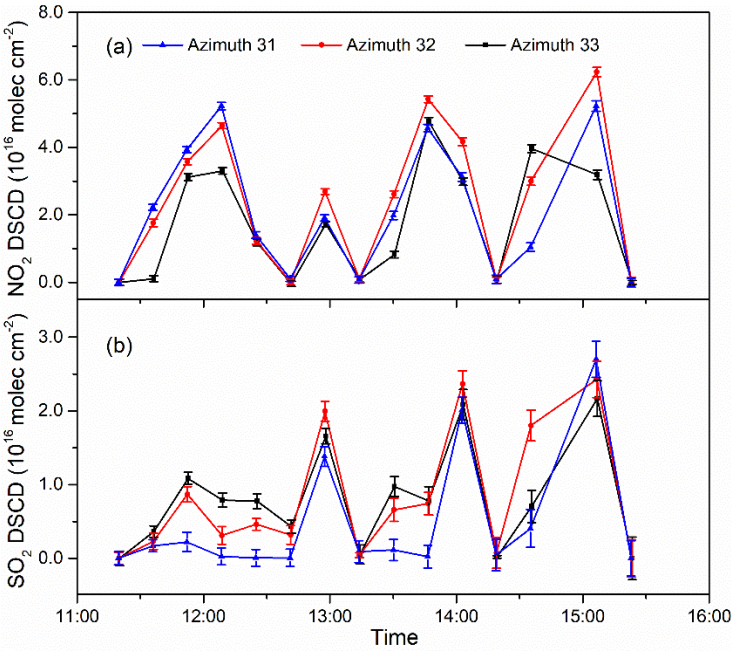

Figure R8. Time series of DSCD of (a) NO_2 and (b) SO_2 measured at 4° elevation angle in three azimuths on August 28, 2017.

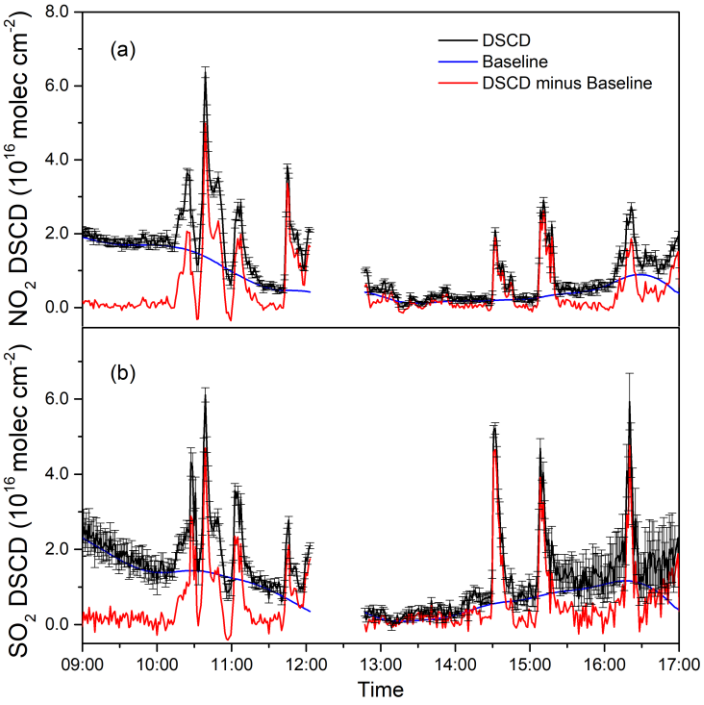

Figure R9. Diurnal variations of DSCDs of (a) NO_2 and (b) SO_2 measured at 7° elevation angle on 26 June 2018.

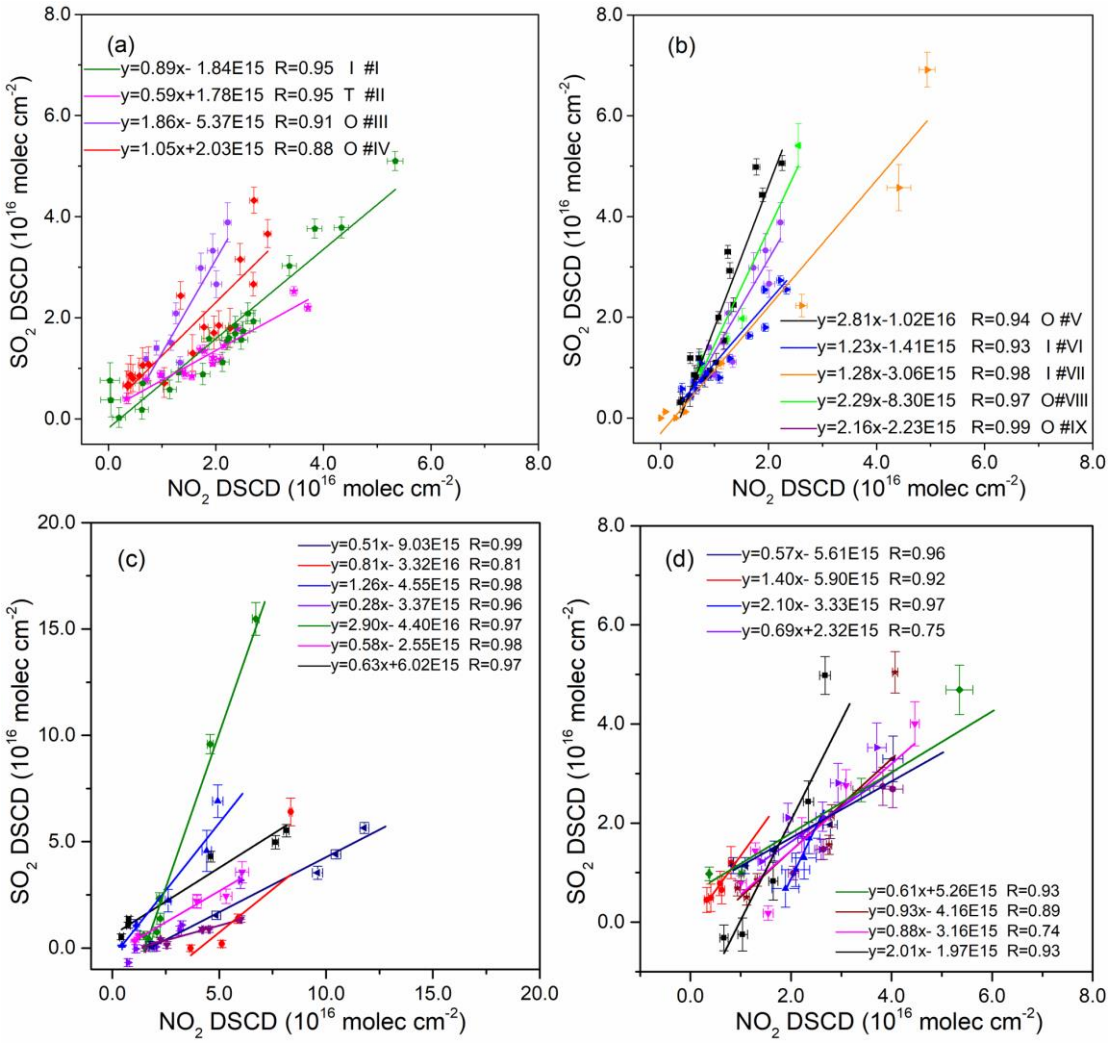

Figure R10. The relationship between SO_2 and NO_2 emitted by several typical vessels, the letter "O" indicates the outbound vessels, "I" indicates the inbound vessels, and "T" indicates the tugboat.

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

Hendrick, F., Müller, J.-F., Clémer, K., Wang, P., De Mazière, M., Fayt, C., Gielen, C., Hermans, C., Ma, J. Z., Pinardi, G., Stavrakou, T., Vlemmix, T., and Van Roozendael, M.: Four years of ground-based MAX-DOAS observations of HONO and NO_2 in the Beijing area, Atmos. Chem. Phys., 14, 765-781, https://doi.org/10.5194/acp-14-765-2014, 2014.

Irie, H., Takashima, H., Kanaya, Y., Boersma, K. F., Gast, L., Wittrock, F., Brunner, D., Zhou, Y., and Van Roozendael, M.: Eight-component retrievals from ground-based MAX-DOAS observations, Atmos. Meas. Tech., 4, 1027–1044, https://doi.org/0.5194/amt-4-1027-2011, 2011

Ning, X., Selesnick, I., and Duval, L.: Chromatogram baseline estimation and denoising using sparsity (BEADS). Chemom. Intell. Lab. Syst., 139, 156-167, https://doi.org/10.1016/j.chemolab.2014.09.014, 2014.

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.