Responses to Editor and Referees of Atmospheric Chemistry and Physics: acp-2017-1132, "Characteristics of marine shipping emissions at berth: profiles for PM and VOCs"

Dear Editor and Referees,

We are pleased to submit our responses to all the comments and revision for manuscript acp-2017-1132. We appreciate all the comments and suggestions that are especially helpful. All the referees' comments have been addressed carefully.

Reviewers' comments are in Blue, Bold.
Authors' responses are in Black.
Revisions in manuscript are in italic.

Best regards with respect,

Huan Liu, representing all authors

Response to Referee's Comments #1

1. **More information is needed about Jingtang port, for example the annual traffic, exposure to other atmospheric emissions such as passing ships and centres of population. A map could be useful here.**

Response:

Thanks for the helpful suggestion. Background information about Jingtang Port is necessary to help explain the significance of exploring the emission characteristics of shipping emissions at berth in this place. The basic information including atmospheric geographic location, annual throughput, traffic, and population are described in the Experimental and Methods part of the manuscript. A map is also provided as you suggested.

Revision in manuscript:

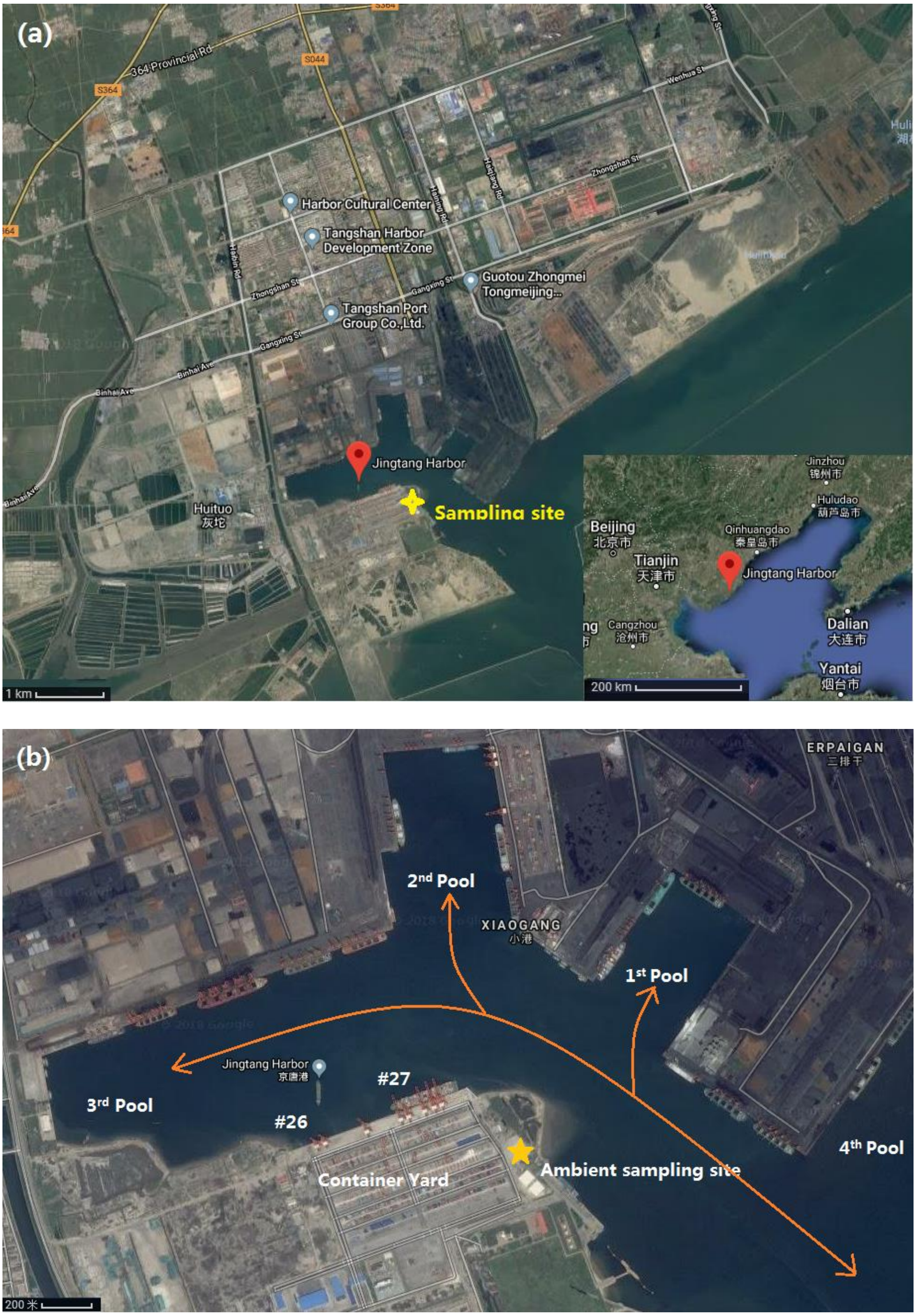
(1) *Page 4, Line 27: The title of Section 2.1.1 is revised as "Information of Jingtang Port, sampling site and ships".*

(2) *Page 4, Line 28- Page 5, Line 20: "Ambient sampling site was located inside Jingtang Port, Tangshan City, Hebei Province, China. Jingtang Port is located in Bohai Bay and belongs to Port of Tangshan, which is among the core ports in domestic emission control area. According to the China Port Yearbook 2015, the annual traffic of ships in Port of Tangshan reached 15084 and the total throughput exceeded 500 million tons, ranking 5th among global port throughputs. Jingtang Port area is surrounded by the Port Economic Development Area, which has a population of 78, 300. Tangshan is a typical industrial city with average $PM_{2.5}$ concentration in winter of 117 $\mu g/m^3$(Zhang et al., 2017). The current $PM_{2.5}$ source apportionment studies in Tangshan did not include shipping emissions due to the lack of basic information and researches. The background information indicates the significance and urgency of studying the impact of shipping emissions and the effect of the fuel switching policy.*

*As is shown in **Fig. 1(a)**, the center of population mainly concentrates in the residential area, located in the north of the port area, about 2km away from the port. About 2.5km in the west of the port area there is a thermal power plant with after-treatment facilities according to the strict emission control standards to power plants in China. Between the port and the other zones are two main roads with trucks driving to carry containers in and out of the port, which is about 1km away from the sampling site. Besides trucks and the power plants, there's no further emission source near the port area.*

*The site for ambient particle collection and instrumental analysis is surrounded by the four pools and the channel, on an open and flat corner close to the #26 and #27 Berth as well as the container yard inside the port, as is shown in **Fig. 1(b)**. No tall buildings exist around the sampling instrument. The distribution of berths, pools and the sampling site guarantees that plumes from ships at berth are prone to reach the sampling instrument."*

(3) ***Figure 1(a)** with the title of "The location and surroundings of Jingtang Port shown in both larger scale and smaller scale" is added to briefly introduce the location of Jingtang Port and its surroundings.*



2. It should be noted that the new Chinese sulphur limit for auxiliary engines corresponds to the global shipping limit that will apply from the year 2020. The findings presented in this manuscript are also relevant to proposals for ships in berth to be able to use electricity from land instead of auxiliary engines – it would be helpful to discuss this

option in the light of the measurements made.

Response:

Yes, we agree that the results presented in this article should be combined with the discussion of the ultimate goal of lowering shipping emissions to the maximum. This issue is discussed in detail from two perspectives in the end of Section 3.5. Both the estimation of emission reduction by other studies and the results of the source apportionment in this study are used to illustrate the importance of land electricity.

Revision in Manuscript:

Page 16, Line 6- Line 22: "The new Chinese sulfur limit for auxiliary engines corresponds to the global shipping limit that will apply from the year 2020. Studies have been done to estimate the effect of the low sulfur fuel limit. On global level, according to Sofiev's (Sofiev et al., 2018) estimation, the global implementation of the 0.5% sulfur content policy can reduce the annual average sulfate concentration by 2-4 $\mu g/m^3$*. However, even after the implementation of 0.5% sulfur limit for ships at berth, the PM and* SO_2 *emissions still remain at a level of 770 and 2500kt respectively. In China ports, under the scenario of all ships changing over to low sulfur fuel (<0.5%) in all China's emission control area, the remaining of at berth PM and* SO_2 *emissions can reach up to 1kt and 8kt respectively in Jing-Jin-Ji port area(Liu et al., 2018). If electricity from land could be applied, these emissions could be further reduced.*

According to the source apportionment of sulfate particles in port area, the number concentration contribution of sulfates from shipping emission at berth are lowered from 35% to 27% after the switching oil policy implementation after January 1st, 2017. The stricter fuel sulfur limit did reduce the contribution of shipping emission, but these emissions would continue to play an important role in atmospheric pollution and electricity from land will be demanded to ameliorate this situation.

In general, PM and SO_2 *emissions can't be eliminated by merely controlling the sulfur content of fuels, though the stricter sulfur limits is an effective way to reduce emissions. Hence the option of using electricity from land will probably help maximizing the emission reduction of* SO_2 *and PM."*

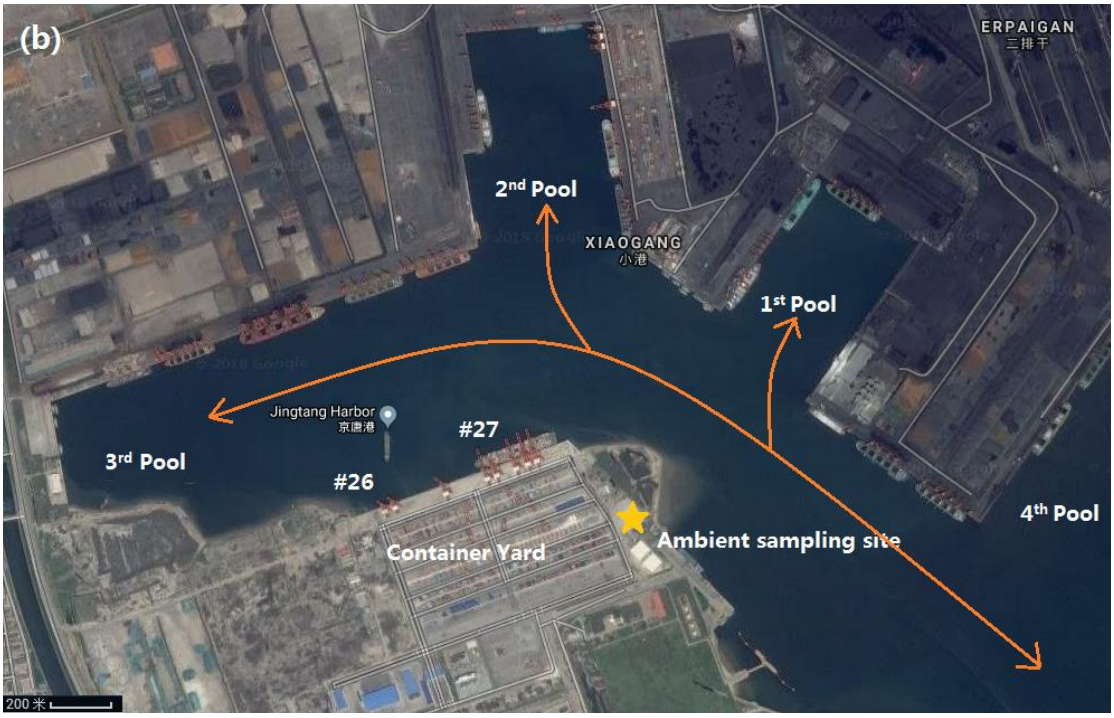
3. **More detail is needed concerning the ambient sampling. Was the sampling site placed so that it was significantly affected by passing ship traffic and/or built up areas and road traffic?**

Response:

Thank you for the important suggestion and information about ambient sampling site should be well introduced. It should be noticed that the collection of particles and VOCs emitted by ships at berth was accomplished via on-board sampling directly from the vessel stacks, not from the plume in the ambient sampling site. All the emission profiles were based on direct sampling from stacks. Ambient particles were sampled by SPAMS in the sampling site and the source apportionment was done using the species profiles combined with all the ambient particle information. The detailed description of the sampling site is added in Section 2.1.1 following the introduction of the port information. An amplified map is used here (**Figure 1 (b)**) in order to clearly illustrate the impact of ships and road traffic on the ambient sampling.

Revision in Manuscript:

(1) A new ***Figure 1(b)*** *is added showing the surroundings of the sampling site in the port area.*



(2) *Page 5, Line 16-20: "The site for ambient particle collection and instrumental analysis is surrounded by the four pools and the channel, located on an open and flat corner close to the #26 and #27 Berth as well as the container yard inside the port, as is shown in **Fig. 1(b)**. No tall buildings exist around the sampling instrument. The distribution of berths, pools and the sampling site guarantees that plumes from ships at berth are prone to reach the sampling instrument."*

4. **In the conclusions, a "slight decrease from 23.82% to 23.61%" is noted. Given the uncertainties involved in the sampling, it may be more reasonable to state that the ratio was unchanged at 24%, unless it can be shown that the ratio can be measured to better that 1% uncertainty.**

Response:

We consider your suggestion very reasonable. Indeed, we didn't take the uncertainty into consideration and the accuracy of sampling and instruments is not high enough to achieve uncertainty better than 1%. Therefore, if the wind direction is not considered, the sulfate number concentration contribution of shipping emissions at berth is considered as unchanged after the switching oil policy implementation during the whole sampling period.

Secondly, we have done some update on the source apportionment of sulfate particles. If taking the variation of wind direction into consideration during sampling, the result is different. After combining the wind direction with the position of sampling site and berths, we selected the ambient data during periods of certain wind direction including northwest, north and conducted source apportionment using the same method. The updated result is 35% before January 1st, 2017 and 27% after January 1st, 2017, indicating a decrease of at berth shipping emission contribution to ambient sulfates.

Revision in manuscript:

(1) *Abstract, Page 1, Line 26-29: "The average percentage of sulfate particles from shipping emissions before and after switching to marine diesel oil kept unchanged at a level of 24%.*

Under certain wind direction with berths on upwind directions, the ratio before and after January 1st is 35% and 27% respectively."

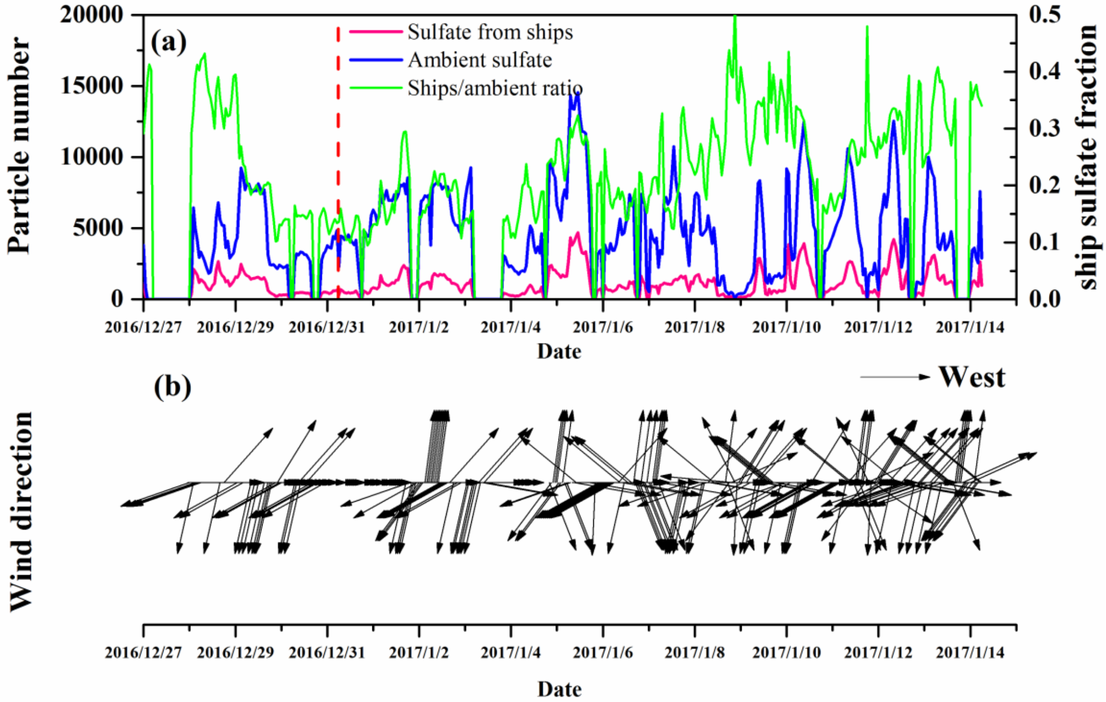
(2) *Text, Page 15, Line 22-Page 16, Line 5: "Generally, the average ratio of ship source sulfate particles to ambient sulfate particles before and after January 1st were 23.82% and 23.61%, respectively. With regard to the uncertainty in sampling, analysis and calculation, the results can be regarded as unchanged at a level of 24%.*

*To better focus on the shipping emissions, we take the wind direction data into consideration. The wind direction of the whole sampling period was shown as **Fig. 9(b)**. According to the geographic positions of berths and wind directions, as the berths mainly distribute in the northwest, north and east direction of the sampling site, wind from these directions will driving the plumes to the sampling site. Moreover, no obvious emission sources other than ships at berth could interfere the ambient sampling.*

Ambient data with wind direction in the range of northwest to southeast (clockwise) were extracted and divided by January 1st, 2017. A total of 10 hours with 37825 particles and a total of 133 hours with 682176 particles were calculated before and after January 1st, respectively. The results considering wind direction for the ratio of sulfates identified as shipping emissions to ambient were 35% and 27% respectively for the two periods, indicating a decrease of at berth shipping emission contribution to ambient sulfates."

(3) *Conclusion, Page 17, Line 13-18: "Comparing post-January 1st data to that of December, the ratio of ship-source sulfate particles to ambient sulfate particles remained unchanged at a level of 24%. When considering the wind direction with berths at upwind, the sulfate contribution of ships at berth could be observed from 35% to 27% before and after the implementation of switching oil policy. The contribution of shipping emissions at berth to the ambient sulfates was lowered by the stricter sulfur limit in fuels."*

(4) *Previous **Figure 10** has now been revised with the change of wind direction upon time as **Figure 9 (a) and (b)**.*



5. **Figure 2: the symbols for ship emissions should be explained. Why are there no error bars for diesel and gasoline?**

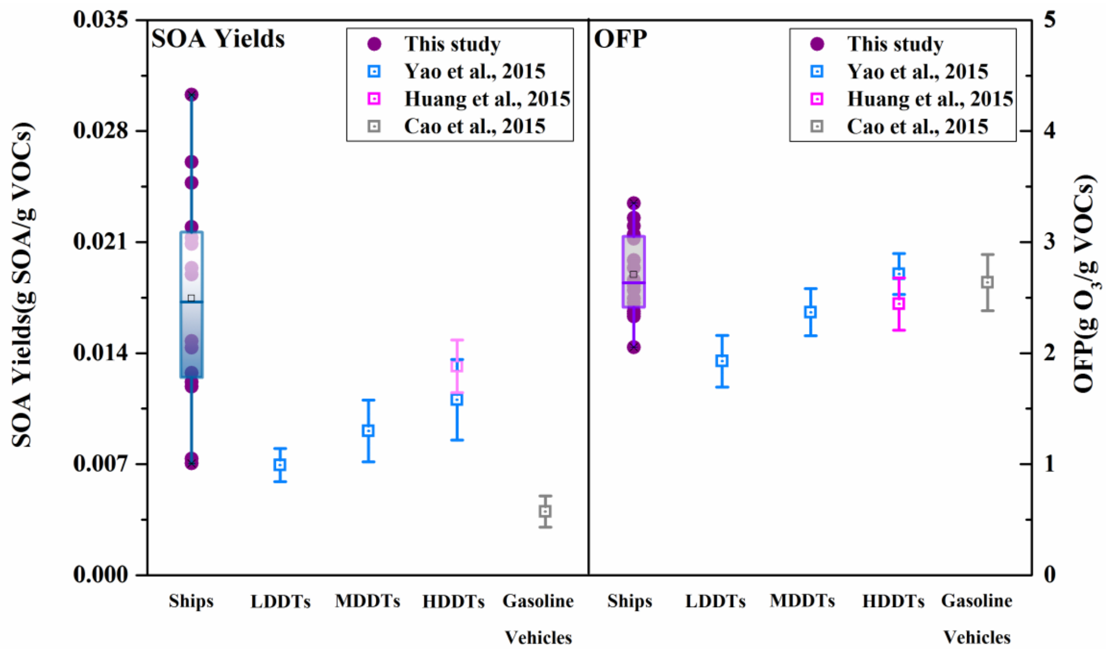
Response:

Accepted. One single purple dot represented a value of SOA yield/OFP of one individual ship. The ranges and error bars are added in **Figure 2** (now renamed as **Figure 3)**. In addition, more data from related researches (Cao et al., 2015; Huang et al., 2015; Yao et al., 2015) are also collected in the revised figure to make a comprehensive comparison between this study and literature results.

Revision in manuscript:

(1) Page 8, Line 15-18: "Also, VOC source profile of 3 types of diesel trucks (light-, middle- and heavy-duty truck respectively) (Yao et al., 2015;Huang et al., 2015) and profiles of heavy-duty diesel trucks in Huang's study(Huang et al., 2015) were referenced to calculate and make comparison."

(2) Previous ***Figure 2*** *has been revised as* ***Figure 3****. Error bars are more data plots from Huang's study are added.*



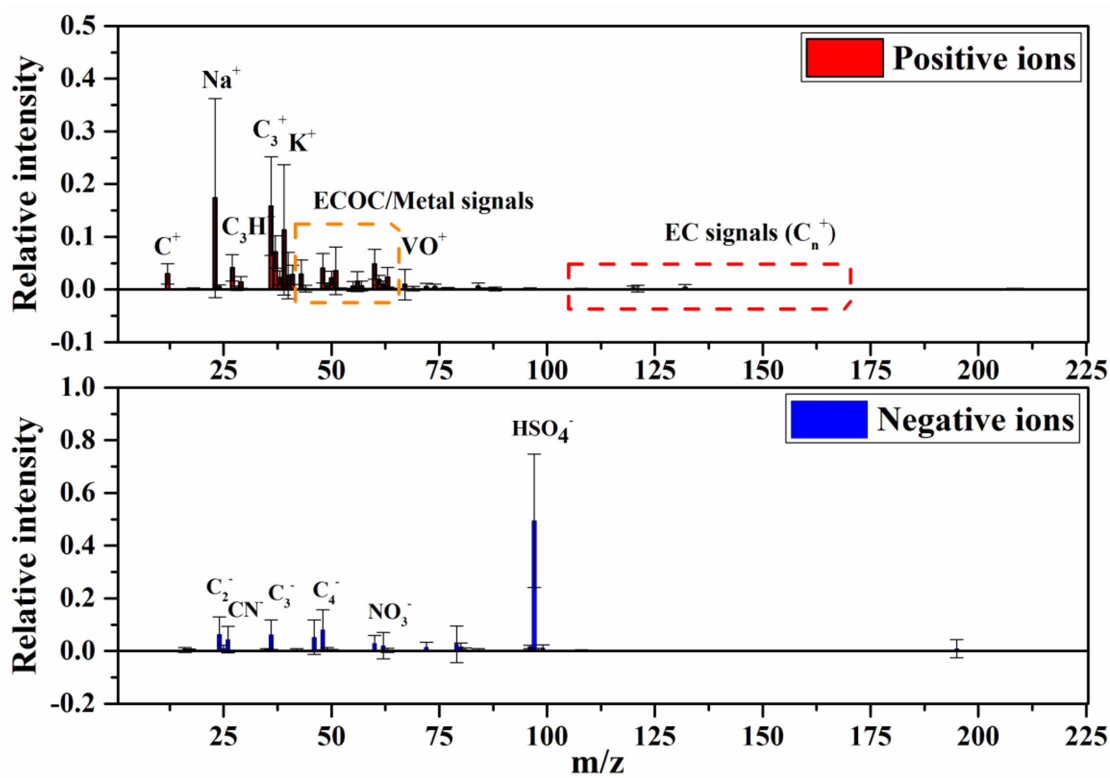
6. **Figure 4 is large and gives unnecessary detail. Delete this figure and show ranges and/or standard deviations in Figure 3.**

Response: Accepted. The original **Figure 3** (now renamed as **Figure 4**) was revised by showing the ranges and standard deviations. The previous **Figure 4** and corresponding contents in the manuscript have been deleted.

Revision in manuscript:

(1) Page 9, Line 12: ***Figure 4*** *and the sentence" Individual ion mass spectra for each ship were shown in Fig. 4." in the text has been deleted.*

(2) Previous ***Figure 3*** *has been revised as* ***Figure 4*** *with standard deviation and typical ion signals have been marked in this figure.*



7. **Figure 7 shows a lack of clear correlation between sulfur and vanadium. 6 ships have high sulfur but low vanadium.**

Response:

Firstly, owing to the fact that vanadium is a typical metallic element existed mostly in heavy fuel oil with higher sulfur content than distillate fuel (Moldanová et al., 2009;Celo et al., 2015), when obvious signal of vanadium occur in the ion mass spectra of particles from a certain ship, this ship is very likely to use heavy fuel oil. Accordingly, the sulfur intensity can be very high. However, for the ships with high sulfur but low vanadium, the actual contents of sulfur and vanadium of fuels used by these ships are unknown and this phenomenon cannot be well explained in this study due to the limit of instrument and the quantity of particles analyzed in each sample. The main instrument applied in this study is SPAMS, which is considered as semi-quantitative and unable to give accurate emission factors of sulfur and vanadium. Moreover, similar studies using the same methods on shipping emissions are very rare. Therefore, this issue demands further exploration.

Revised in manuscript:

Page 12, Line 21-Page 13, Line 2: "Owing to the fact that vanadium is a typical metallic element existed mostly in heavy fuel oil with higher sulfur content than distillate fuels (Moldanová et al., 2009;Celo et al., 2015), when obvious signal of vanadium occurred in the ion mass spectra of particles from ship 13 and ship 17, these ships were very likely to use heavy fuel oils at berth. Accordingly, the sulfur intensity could be very high. However, for the ships with high sulfur but low vanadium, the actual contents of sulfur and vanadium of fuels used by these ships are unknown and this phenomenon cannot be well explained in this study due to the limit of instrument and the quantity of particles analyzed in each sample. The main instrument applied in this study is SPAMS, which is considered as semi-quantitative and unable to give accurate emission factors of sulfur and vanadium. Moreover, similar studies using the same methods on shipping emissions are very rare. Therefore, this issue demands further exploration."

8. Figure 8 does not add important information and can be deleted.

Response:

Your suggestion regarding **Figure 8** is accepted and we has deleted this figure and revised the corresponding contents in the manuscript.

Revision in manuscript:

Page 13, Line 3-8: "The two ships with vanadium signals higher than others included a total particle number of 30009 and among which 2633 were measured with ion mass spectra. In the ion mass spectra of these ships, higher V^+ */* VO^+ *and* HSO_4^- *signals of over 0.8 in relative intensity while the other ships had average* HSO_4^- *relative intensity of 0.59 and no apparent* V^+/VO^+ *signals. Due to the relatively fewer particles of such ships, there might be abnormity in low positive EC signals in their ion mass spectra. Nonetheless, major chemical PM characteristics of different fuel types could be observed through ion mass spectra."*

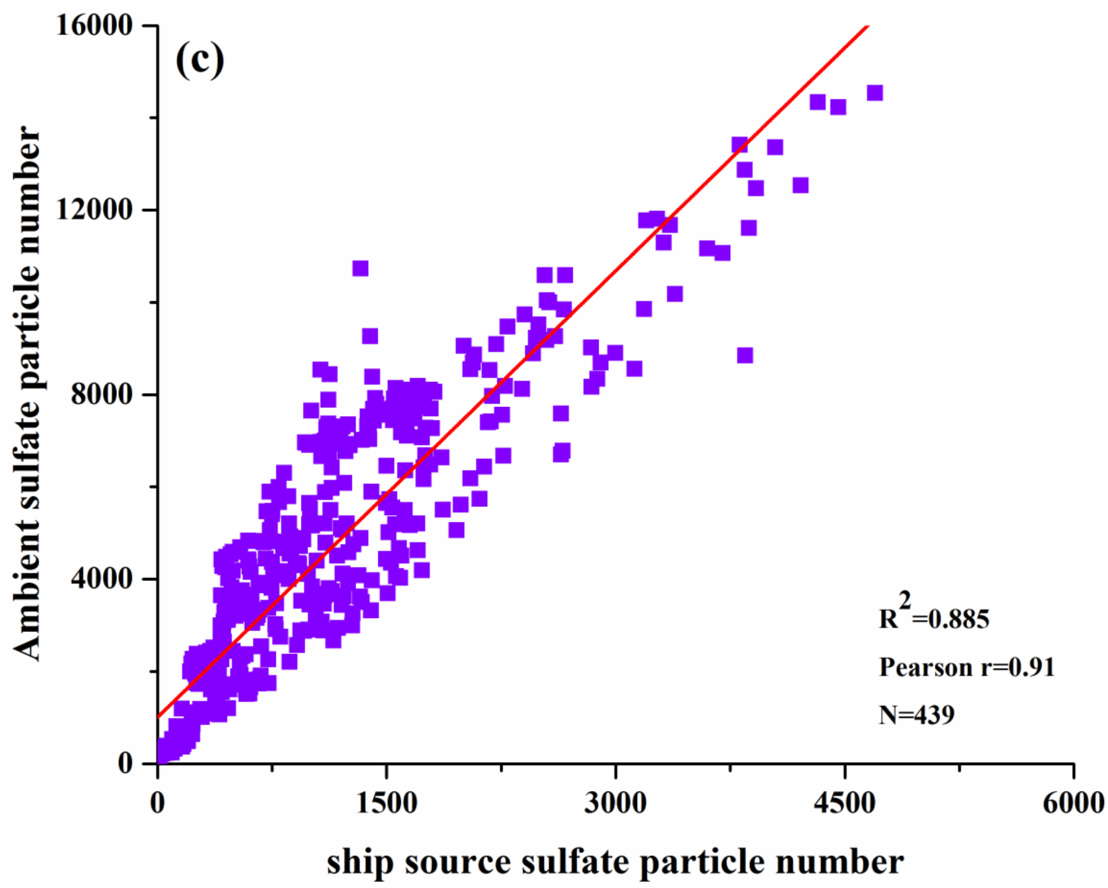
9. Figure 10 – complement with an ambient/vessel correlation.

Response:

Accepted. The previous **Figure 10** has been renamed of **Figure 9**. A scatter plot figure is attached as **Figure 9 (c)** providing the correlation between ambient and ship source sulfate particles. A total of 439 sets of data is presented and Pearson correlation coefficient was 0.91, indicating that those two variables have strong correlation.

Revision in manuscript:

(1) *Page 15, Line 5-7: "A total of 439 sets of data were included in the source apportionment analysis. By linear fitting for ship-source and ambient sulfate particle numbers, the Pearson Correlation Coefficient was 0.91 as shown in* ***Fig. 9(c)****."*



10. Editorial points:

(1) A table of abbreviations is provided as Table 1.

Table 1: Abbreviations

Abbreviations	Full name
BC	black carbon
EC	elemental carbon
ECOC	elemental carbon-organic carbon
GC-MS	gas chromatography-mass spectrometer
HC	Hydrocarbon
HFO	heavy fuel oil
MDO	marine diesel oil
OC	organic carbon
OFP	ozone forming potential
PM	particulate matter
SOA	secondary organic aerosol
SPAMS	single particle aerosol mass spectrometer
VOCs	volatile organic compounds

(2) Descriptions of each figures have been revised to provide more information and explanations.

(3) The language and grammar of the whole article has been reviewed and revised carefully.

Reference

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