

**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,

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 2

1. As stated in the manuscript, a total of 93 VOC species were detected and all of them have carbon numbers larger than four. Is it due to the limitation of the equipment and analyzing method used that lower carbon compounds were not detected? Or, that is a real atmospheric phenomenon?

### Response:

Thank you for coming up with this issue. First it should be noticed that not all of the 93 detected species have carbon number smaller than 4. Only alkanes, olefins and aromatics have more than 4 carbons and some haloalkanes and oxygenated compounds detected in this study have carbon number of 1-3. This issue is mainly relevant to the analysis method and instruments. VOCs were analyzed and calibrated by GC-MS 5975/7890 according to the USEPA methods of TO-15 and PAMS. Due to the limit of chromatographic column used during the analysis period, some typical organic compounds such as aldehydes and short chain carbonyls with carbon number lower than 4 were not detected in this study. The relatively high concentration of acetone shown in the VOCs column figure is in correlation with other study (Reda et al., 2015) in which emission factors of VOCs are detected. And according to previous studies (Gentner et al., 2012), compounds with higher carbon numbers (usually higher than 6) are more relevant to secondary organic aerosol yields.

### Revision in manuscript:

Page 6, Line 5-8: "Owing to the limit of chromatographic column property equipped on the GC-MS, alkanes and olefins with carbon number smaller than 4 were not detected. VOCs with carbon number larger than 6 are more relevant to the yield of secondary organic aerosols (Gentner et al., 2012)."

2. A large amount of Na-rich particles are found in the sampled exhaust from the ships, which has been attributed to full of sea salt in the intake of ships. If so, could sea salt also have perturbations on other elements such as K, Mg, and Fe as well as OC? Would such a perturbation depend on environmental and meteorological conditions during the sampling time?

### Response:

First we admit that the opinion of attributing the peak of  $\text{Na}^+$  and the existence of Na-rich particles to the sea salt is not precise. In view of the composition of fuel combusted by marine engine, Na does exist with a mass concentration of around 13-22mg/kg in several samples of heavy fuel oil (HFO) and lower content in marine diesel oil (Moldanová et al., 2013; Lack et al., 2009). Moldanova (Moldanová et al., 2009) analyzed particle from ship exhausts by using two-step laser mass spectrometry and  $\text{Na}^+$  was observed with obvious peak in the mass spectra. According to Sippula's (Sippula et al., 2014) research on marine diesel engine, Na can also exist in lubrication oil and be exhausted along with the lubrication and grinding process.

It is widely recognized that the metal content existed in exhausted particles has strong correlation with that in fuel (Celo et al., 2015; Moldanová et al., 2013). Although the content of Na is obviously lower than that of vanadium in fuel (55-133.8mg/kg), the peaks of  $\text{Na}^+$  in ion mass spectra are mostly higher than peaks of  $\text{V}^+/\text{VO}^+$  signal from exhausts. This phenomenon indicate that there are external sources of Na and one of the most possible sources is sea salt, whose typical elements are Na. In conclusion, the Na-rich particles come from a multiple source of both fuel

composition and sea salt perturbation.

According to literature study (O'Dowd et al., 1997; Fitzgerald, 1991), sea salt aerosol is rich mainly in inorganic elements such as Mg, K, Cl and Na. Therefore, there might exist perturbation regarding K, Mg and Na. The content of K in exhausted particles is also higher than the other elements with their contents comparable to K in fuels. The mechanism of K from is similar to that of Na. The content of Mg in marine fuels is obviously lower than other metallic elements (Moldanova et al., 2009; Sippula et al., 2014; Winnes and Fridell, 2012) (e.g. <1mg/kg in Moldanova's research) and almost no  $Mg^+$  signals are observed in the ion mass spectra because of the probable interference of  $C_2^+$  signal sharing the same m/z of 24. As for Fe, it is rarely mentioned to exist widely in sea salt. Due to the fact that OC is predominant content in engine exhausts, the perturbation from sea salt OC can be ignored even if there exists such perturbation.

Considering the fact that the particles were directly collected from inside the exhaust pipes, which is unlike the plume capture in the open air, the possibility of external impacts is greatly lowered. And no discussions with regard to this issue are founded in other relevant measurements.

**Revision in manuscript:**

*Page 10, Line 14-Page 15, Line 1: "In view of the composition of fuel combusted by marine engine, Na does exist with a mass concentration of around 13-22mg/kg in several samples of heavy fuel oil (HFO) and lower content in marine diesel oil (Moldanova et al., 2013; Lack et al., 2009). Moldanova (Moldanova et al., 2009) analyzed particle from ship exhausts by using two-step laser mass spectrometry and  $Na^+$  was observed with obvious peak in the mass spectra. According to Sippula's (Sippula et al., 2014) research on marine diesel engine, Na can also exist in lubrication oil and be exhausted along with the lubrication and grinding process. It is widely recognized that the metal content existed in exhausted particles has strong correlation with that in fuel (Celo et al., 2015; Moldanova et al., 2013). Although the content of Na is obviously lower than that of vanadium in fuel (55-133.8mg/kg), the peaks of  $Na^+$  in ion mass spectra are mostly higher than peaks of  $V^+/VO^+$  signal in exhaust. This phenomenon indicate that there are external sources of Na and one of the most possible sources is sea salt, whose typical elements are Na. In conclusion, the Na-rich particles come from a multiple source of both fuel composition and sea salt perturbation. Only particles with relative area of  $Na^+$  obviously higher than other positive ions were counted as Na-rich particles. The same rule also adapted to K-rich particles. Owing to the fact that the content of K in most marine fuels is lower than that of Na, V and other typical metallic elements, one of the possible sources of K-rich particles is sea salt (O'Dowd et al., 1997), which is similar to the source of Na-rich particles."*

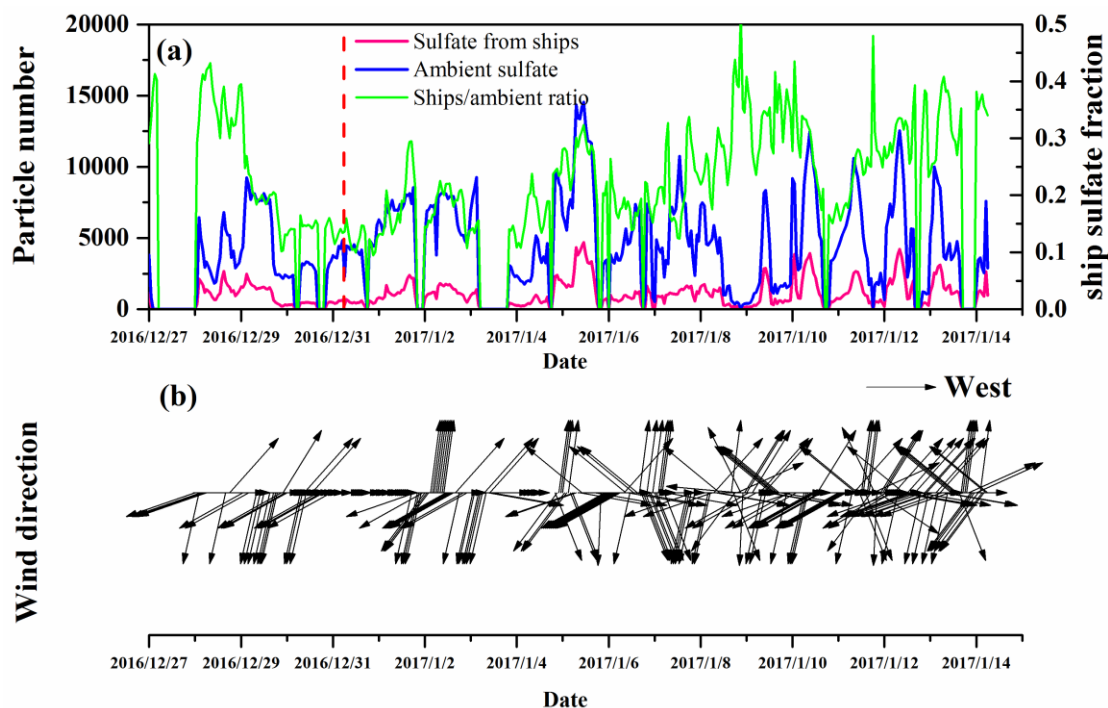
**3. As described in the manuscript, ambient particle sampling was conducted from 27 December 2016 to 15 January 2017. However, the positions of the ships and measurement site during the experiment are not well introduced. Since the ambient particle sampling was conducted in an open atmosphere, the local meteorological conditions should have a large influence on the experimental results. The ship plume effect needs to be investigated in detail.**

**Response:** Your comments regarding the influence of meteorological conditions are quite helpful and illuminating. Wind direction is recognized as the most significant meteorological conditions. Owing to the variation of wind direction and the position distribution of berths, yards and sampling sites, the contribution of each sources identified by the ambient sampling instrument may change. For example, winds from the north and north east will expose plumes from ships to

the sampling site, while west wind may bring the emissions from power plant and diesel truck exhausts from the container yard next to the sampling site. Therefore, the ships plume effect needs to be discussed considering wind directions.

**Revision in manuscript:**

- (1) 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 **Figure 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.”*
- (2) 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 1<sup>st</sup> is 35% and 27% respectively.”*
- (3) 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 1<sup>st</sup> 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 1<sup>st</sup>, 2017. A total of 10 hours with 37825 particles and a total of 133 hours with 682176 particles were calculated before and after January 1<sup>st</sup>, 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.”*
- (4) Conclusion, Page 17, Line 13-18: *“Comparing post-January 1<sup>st</sup> 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.”*
- (5) Previous **Figure 10** has now been revised with the change of wind direction upon time and renamed as **Figure 9 (a) and (b)**.



**4. It is unclear and misleading to use a percentage to describe the ratio of sulfate particles from shipping emissions (a flux) over ambient sulfate particles (a concentration).**

**Response:** First we should admit that the description of methodology may be not precise enough and caused some misunderstanding. Actually the sulfate particles from shipping emissions in the Section 3.5 are not those collected via on-board sampling. The basic principle of the source apportionment in this study is to identify the ambient sulfate particles with ion mass characteristics similar to those sampled directly from the exhaust pipes. This process is achieved by neural network and iterations via MATLAB. The description of methodology is revised accordingly.

**Revision in manuscript:**

Page 14, Line 21-27: “The first step was to identify and extract ship-source particles out of all that were sampled and analyzed by SPAMS. The identification was based on information obtained from the analyzed ion mass spectra after on-board sampling. Then by algorithm calculation via MATLAB, certain particles were identified as from ship exhaust according to the similarity to the defined characteristics. The next was to extract sulfate particles from the identified particles from ships and ambient, respectively. This step was accomplished by finding particles as sulfates with  $m/z = -97$  or  $-80$ , which represented  $\text{HSO}_4^-$  and  $\text{SO}_3^-$ , two typical markers of sulfates. Finally the temporal (1h resolution) number change of identified sulfate particles from ships and ambient particles as well as the ratio was obtained.”

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