

## Responses to Reviewers' comments

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Title: Characteristics of biogenically-derived aerosols over the Amundsen Sea, Antarctica

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Note: Reviewers' comments are highlighted in **blue**, while our responses to reviewers are in **black**.  
The revisions in the manuscript were highlighted to make easily readable for the editors and reviewers.

Prof. Lynn M. Russell

Co-Editor

Atmospheric Chemistry and Physics

USCD, Scripps Institution of Oceanography

United States

Dear Professor Russell,

We have attached an electronic copy of manuscript file ready to go to press entitled "Characteristics of biogenically-derived aerosols over the Amundsen Sea, Antarctica" by Jinyoung Jung, Sang-Bum Hong, Meilian Chen, Jin Hur, Liping Jiao, Youngju Lee, Keyhong Park, Doshik Hahm, Jung-Ok Choi, Eun Jin Yang, Jisoo Park, Tae-Wan Kim, and SangHoon Lee for publication in Atmospheric Chemistry and Physics (acp-2019-133). We have modified our text based on the referee's comments. We appreciated that the comments from referees improved our manuscript a lot. We believe that the comments from referees were clearly responded in our modified manuscript.

We are looking forward to hearing about your decision. Thank you for your consideration.

Sincerely yours,

Jinyoung Jung

## **Anonymous Referee #1:**

### **Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)**

In the first review I asked the authors to provide additional evidence on the contribution of anthropogenic nssSO<sub>4</sub>, mainly due to the fact that the authors claimed the anthropogenic contribution accounted for more than half the nssSO<sub>4</sub> at times (Biological nssSO<sub>4</sub> accounted for as little as 39% therefore anthropogenic nssSO<sub>4</sub> accounted for the remaining 61%). The method used by the authors to estimate the contribution of anthropogenic nssSO<sub>4</sub> relies on the use of the MSA to nssSO<sub>4</sub> ratio. I disagree with the accuracy of this method based on publications showing the lack of correlation due to long range transport of particles and previously mentioned limitations of the method due to the conversion of MSA to nssSO<sub>4</sub> (the latter has been incorporated in the text by the authors). While the authors have indicated that the method can be useful as a qualitative indicator, they have provided quantitative results. The significant contribution of anthropogenic nssSO<sub>4</sub> indicated in this manuscript is a major claim if accurate. The accuracy of this method is further questionable because of the applied MSA/nssSO<sub>4</sub> ratio, which is derived from Palmer station measurements. While this location is geographically closest these ratios have been shown to range .065 to .508 (Savoie and prospero 1989, Arimoto et al 1996, ) and the contrast in the biological activity in the Asmundsen Sea and Palmer Station with the Southern Ocean would suggest a single value is not a good representation especially if providing quantitative results. The complications of calculating the non-biogenic contribution of nssSO<sub>4</sub> is also discussed in Legrand et al 2017, Legrand and Pasteur 1998 and Piel et al. 2006. Finally, the negative values of anthropogenic nssSO<sub>4</sub> mentioned are also indicative of the limitations in the accuracy of the method. Therefore, I find it necessary to provide more evidence due to the limitations in using the MSA/nssSO<sub>4</sub> as an indicator, or the removal of quantitative results on the contribution of anthropogenic nssSO<sub>4</sub>.

(Response) We really appreciate for Referee #1's comments. We have realized that the method using the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio for the quantitative estimation of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> have limitations, as Referee #1 pointed out. Now we have found out that the high contribution of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> in our study region, especially in the Southern Ocean, was because we used the single value of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio observed at Palmer Station. Referee #1 also pointed out that more evidence should be provided to explain the high contribution of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> in our study region. Unfortunately, we do not have any data on another anthropogenic tracer, such as <sup>210</sup>Pb. Consequently, we have decided to remove the description of the anthropogenic nss-SO<sub>4</sub><sup>2-</sup> contribution, according to Referee #1's comments. In addition, we have used the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios published by previous studies (i.e., Berresheim et al., 1990; Ayers et al., 1991; Bates et al., 1992; Savoie et al., 1993; Legrand and Pasteur, 1998; Chen et al., 2012; Jung et al., 2014) that were carried out in the Southern Ocean and coastal Antarctic stations during the austral summer to estimate the contribution of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup>.

According to Referee #1's comments, we have revised section 3.4 as follows: "During the cruise, the

MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in bulk aerosols varied from 0.12 to 0.70 (mean: 0.35 ± 0.17), with lower ratios in marine aerosols collected over the Southern Ocean (range: 0.12–0.51, mean: 0.26 ± 0.14) and higher values over the Amundsen Sea (range: 0.20–0.70, mean: 0.44 ± 0.16), showing a similar variation trend ( $r = 0.92$ ,  $p < 0.01$ ) to that of MSA (Fig. 5b). This result suggests that atmospheric MSA plays a key role in the variation in MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the Southern Ocean and the Amundsen Sea during the austral summer since atmospheric nss-SO<sub>4</sub><sup>2-</sup> concentrations in the Southern Ocean were quite comparable to the values in the Amundsen Sea. It is worth noting that this study was carried out over the Southern Ocean and the Amundsen Sea during the austral summer. Consequently, to estimate the contribution of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> to total nss-SO<sub>4</sub><sup>2-</sup>, it is required to use the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios observed through long-term monitoring in the Southern Ocean and the Amundsen Sea during the austral summer. There have been several field studies investigating the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in the Southern Ocean during the austral summer (range: 0.32–0.53, the South Pacific (40°S–45°S), Berresheim et al., 1990; range: 0.12–0.24, Cape Grim (40°41'S , 144°41'E), Ayers et al., 1991; range: 0.17–0.32, the South Pacific (30°S–60°S), Bates et al., 1992; range: 0.096–0.49, the South Pacific (40°S–56°S), Jung et al., 2014). In this study, we applied an average value (0.29 ± 0.16) of the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios reported by previous studies mentioned above, to estimate biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> in the Southern Ocean. For the Amundsen Sea, due to the lack of long-term monitoring data for MSA/ nss-SO<sub>4</sub><sup>2-</sup> in the Amundsen Sea, we also applied an average value (0.40 ± 0.29) of the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios measured in the coastal Antarctic region (range: 0.15–0.93, 50°S–70°S, Chen et al., 2012) and the coastal Antarctic stations (mean: 0.508, Palmer Station, Savoie et al., 1993; mean: 0.31 ± 0.05, Halley Station, Legrand and Pasteur, 1998; mean: 0.33 ± 0.06, Neumayer Station, Legrand and Pasteur, 1998; mean: 0.17 ± 0.02, Dumont D'Urville Station, Legrand and Pasteur, 1998) during the austral summer. Based on the average values of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios measured by previous studies in the Southern Ocean and Antarctic coastal regions, mean contributions of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> to the total nss-SO<sub>4</sub><sup>2-</sup> in the Southern Ocean and the Amundsen Sea were estimated to be 91 ± 48% and 109 ± 40%, respectively, suggesting that biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> dominates the atmospheric budget of nss-SO<sub>4</sub><sup>2-</sup> in the Southern Ocean and the Amundsen Sea. However, the contributions of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> for several aerosol samples, where the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios were higher than the average values, were somewhat overestimated. The most likely cause of the overestimation, especially in the Amundsen Sea, is the differences of biological productivity and DMS source strength in the ocean adjacent to the coastal Antarctic stations since we used the average value of the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios measured in various geographical locations around Antarctica due to the lack of data for sulfur-containing aerosols over the coastal Antarctic region. Further observational field studies, therefore, are required to fill the data gap over the Southern Ocean and coastal Antarctic region.” (Page 11, line number 20–page 12, line number 15).

Besides, we have removed from section 3.4 the following sentence: “, and that atmospheric nss-SO<sub>4</sub><sup>2-</sup> observed in the Southern Ocean was affected by anthropogenic sources” (page 11, line number 23–25).

We also have modified Figure 5 by removing concentrations of biogenic and anthropogenic nss-SO<sub>4</sub><sup>2-</sup> from Figure 5 (page 35) and have added the references (i.e., Berresheim et al., 1990; Ayers et al., 1991) to the manuscript (page 21, line number 9–11; page 20, line number 28–29).

The text below is each response to the reviewer responses to Reviewer #1.

1. No there were not anthropogenic nssSO<sub>4</sub> concentrations in Hudson et al 1998, however, anthropogenic nssSO<sub>4</sub> concentrations is not the only way of determining if the marine boundary layer is influenced by anthropogenic pollutants. Hudson et al. 1998 looked at particle concentration and back trajectories to identify cases that were influenced by continental/anthropogenic particles and found only the closest measurements (north of -44 S) were influenced by continental/anthropogenic particles. The cases with back trajectories over the continent consistently contained higher particle concentrations.

It is impossible to follow the back trajectories from their starting point. There are too many for a single plot. There are only a few trajectories that have intercepted with continental sources. Do these correspond to cases with higher anthropogenic nssSO<sub>4</sub>? I suspect the main anthropogenic source would be from over continents. If the authors have other references to suggest there are other major sources of anthropogenic nssSO<sub>4</sub> in the Southern Ocean, then they should be included in the text.

(Response) We thank Referee #1 for Referee #1's comments. As Referee #1 suspected, we observed high nss-SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> concentrations during the collection of aerosol samples A1 and A13 when air masses originated from the Southern Ocean and thereafter swept over large regions of New Zealand (Fig. S4) (page 10, line number 24–26). In addition, we could not find any reference to suggest that there are other major anthropogenic sources of nss-SO<sub>4</sub><sup>2-</sup> in the Southern Ocean. As we already have responded above, the main cause of the high contribution of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> in the Southern Ocean was the use of the single value of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio measured at Palmer Station.

2. I do not understand your reasoning on why nssSO<sub>4</sub> in the Amundsen Sea was formed by the condensation of DMS oxidation products onto existing particles. Sanchez et al. 2018 identified two sulfate particle types from single particle measurements and showed one, which contained mostly sulfate mass, corresponded to new particle formation in the free troposphere that was then entrained into the boundary layer. The second particle type was less than 50% sulfate and did not correspond to entrainment of particles from the free troposphere indicating it was likely from the condensation of DMS oxidation products onto pre-existing particles. I understand that new particle formation in the free troposphere is out of the scope of this paper, but with the measurements in this manuscript identifying whether nssSO<sub>4</sub> is from DMS oxidation products condensed onto existing particles or new particle formation does not seem possible. My original reference to Sanchez et al. 2018 was intended to show that MSA and DMS do not necessarily correlate strongly with nssSO<sub>4</sub> because of the possibility of long range transport of nssSO<sub>4</sub> to regions

where MSA and DMS are low in concentration (Korhonen et al. 2008; Woodhouse et al. 2010) and physical processes, such as the mixing of DMS and particles across the boundary layer inversion, are necessary for the formation of nssSO<sub>4</sub> particles. Therefore, the lack of a correlation of MSA and nssSO<sub>4</sub> should not be considered an indicator of anthropogenic influence. At least not without another anthropogenic tracer.

(Response) We are grateful to Referee #1 for Referee #1's comments. We have realized that the description that nss-SO<sub>4</sub><sup>2-</sup> in the Amundsen Sea was formed by the condensation of DMS products onto existing particles was our speculation. Besides, we also have realized that the statistically insignificant relationship between nss-SO<sub>4</sub><sup>2-</sup> and MSA in the Southern Ocean does not always result from the influence of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> because of the possibility of long-range transport of nss-SO<sub>4</sub><sup>2-</sup> to the regions where MSA and DMS concentrations are low, as Referee #1 pointed out. Consequently, according to Referee #1's comments, we have revised our manuscript as follows: "Unlike MSA, the mean nss-SO<sub>4</sub><sup>2-</sup> concentration in the Amundsen Sea was comparable to that in the Southern Ocean, although the variation trend of nss-SO<sub>4</sub><sup>2-</sup> in the Amundsen Sea was similar to that of MSA, suggesting that nss-SO<sub>4</sub><sup>2-</sup> was affected by marine source and large-scale transport (Korhonen et al., 2008). Indeed, nss-SO<sub>4</sub><sup>2-</sup> showed a strong correlation ( $r = 0.98$ ,  $p < 0.01$ ) with MSA in the Amundsen Sea, whereas no relationship was found between them in the Southern Ocean ( $r = 0.51$ ,  $p > 0.05$ ) (Fig. S3), suggesting that the local emission of DMS is a significant source of nss-SO<sub>4</sub><sup>2-</sup> in the Amundsen Sea. It is worth mentioning that nss-SO<sub>4</sub><sup>2-</sup> can be formed from the homogeneous nucleation of new particles involving H<sub>2</sub>SO<sub>4</sub> or from the condensation of gas-phase DMS oxidation products onto existing particles (e.g., Covert et al., 1992; Quinn and Bates, 2011). Recently, Sanchez et al. (2018) identified two types of SO<sub>4</sub><sup>2-</sup> particles using an Event-Trigger Aerosol-Mass-Spectrometer (ET-AMS), and reported that 63% of SO<sub>4</sub><sup>2-</sup> was derived from newly formed particles in the free troposphere and 38% of SO<sub>4</sub><sup>2-</sup> was formed from the condensation of DMS products onto existing particles in the clean marine conditions, revealing the importance of phytoplankton-produced DMS emission for CCN in the Atlantic. In this study, it is hard to distinguish nss-SO<sub>4</sub><sup>2-</sup> derived from new particle formation from nss-SO<sub>4</sub><sup>2-</sup> formed by the condensation of DMS products onto existing particles because of the limitations related to the method to collect data. However, the significant correlation of nss-SO<sub>4</sub><sup>2-</sup> with MSA in the Amundsen Sea suggest that DMS emission from the Amundsen Sea plays a crucial role in the formation of nss-SO<sub>4</sub><sup>2-</sup> aerosol particles that can act as CCN. On the other hand, the statistically insignificant relationship between nss-SO<sub>4</sub><sup>2-</sup> and MSA in the Southern Ocean could result from the influence of anthropogenic sources in the Southern Ocean. During the cruise, as shown in Fig. 5a, high (> 0.1 μg m<sup>-3</sup>) nitrate (NO<sub>3</sub><sup>-</sup>) concentrations were observed during the collection of aerosol samples A1 and A13 when air masses originated from the Southern Ocean and thereafter swept over large regions of New Zealand (Fig. S4); however, NO<sub>3</sub><sup>-</sup> concentrations in the other samples were quite low (< 0.03 μg m<sup>-3</sup>). Although NO<sub>3</sub><sup>-</sup> was observed in the other aerosol samples, we cannot assert that all aerosol samples were influenced by anthropogenic sources without another anthropogenic tracer data set (e.g., <sup>210</sup>Pb) because, in addition to anthropogenic sources, NO<sub>3</sub><sup>-</sup> can be produced in clouds (Hegg and Hobbs, 1988) or derived

from a weak oceanic source (Luo et al., 2018). Nevertheless, our results suggest that nss-SO<sub>4</sub><sup>2-</sup> in the two samples collected over the Southern Ocean were most likely affected by anthropogenic sources, resulting in the lack of correlation. Another possible explanation for the insignificant relationship between nss-SO<sub>4</sub><sup>2-</sup> and MSA is entrainment of nucleated nss-SO<sub>4</sub><sup>2-</sup> particles into the marine boundary layer of the Southern Ocean from the free troposphere by turbulent diffusion and large-scale transport (Korhonen et al., 2008; Woodhouse et al., 2010). Sanchez et al. (2018) reported that the lack of correlation between SO<sub>4</sub><sup>2-</sup> particle and atmospheric DMS (or its oxidation products) could result from the competition for DMS and its oxidation products with the competing sinks of condensation onto existing particles and vertical transport to the free troposphere. The lack of correlation between nss-SO<sub>4</sub><sup>2-</sup> and MSA in the Southern Ocean, therefore, could have resulted from the influence of anthropogenic sources and the input of nss-SO<sub>4</sub><sup>2-</sup> from the free troposphere. Although our data set is not sufficiently complete to allow a meaningful analysis of this likely explanation, the result for nss-SO<sub>4</sub><sup>2-</sup> concentrations from this study would be valuable for filling the data gap, especially for the Amundsen Sea during the austral summer, and be helpful for validation of modeling of sulfur-containing aerosols. (Page 10, line number 8–page 11, line number 7).

Besides, to clarify the context of section 3.3, we have moved the following sentences to the first paragraph of section 3.3: “Surprisingly, our mean nss-SO<sub>4</sub><sup>2-</sup> concentration in the Amundsen Sea was about 1.5 and 2.5 times higher than those observed at American Samoa (14.25°S, 170.58°W,  $0.41 \pm 0.17 \mu\text{g m}^{-3}$ , seasonal average (December–February) from 1990–1992, Savoie et al., 1994) and over the South Pacific (8°S–55°S, mean:  $0.25 \pm 0.17 \mu\text{g m}^{-3}$ , range: 0.094–0.62  $\mu\text{g m}^{-3}$ , January–March 2009, Jung et al., 2014), respectively. In addition, the mean nss-SO<sub>4</sub><sup>2-</sup> concentration in the Amundsen Sea was also a factor of 1.6–4.4 higher than those observed at Palmer Station ( $0.24 \pm 0.16 \mu\text{g m}^{-3}$ , December 1990–March 1991, Savoie et al., 1993), Halley Station ( $0.14 \pm 0.017 \mu\text{g m}^{-3}$ , monthly mean in January from 1991–1993, Legrand and Pasteur, 1998), Neumayer Station ( $0.38 \pm 0.13 \mu\text{g m}^{-3}$ , monthly mean in January from 1983–1995, Minikin et al., 1998), and Dumont D’Urville Station ( $0.34 \pm 0.039 \mu\text{g m}^{-3}$ , monthly mean in January from 1991–1995, Minikin et al., 1998) during the austral summer.” (page 9, line number 32–page 10, line number 7).

We also have removed from section 3.3 the following sentence: “Considering the high MSA concentration and DMS flux in the Amundsen Sea as mentioned above in section 3.2, the high nss-SO<sub>4</sub><sup>2-</sup> concentration in the Amundsen Sea from this study is likely affected much more by biogenic than anthropogenic sources.”

We have added the references (i.e., Hegg and Hobbs, 1988; Covert et al., 1992; Korhonen et al., 2008; Woodhouse et al., 2010; Luo et al., 2018) to the manuscript (page 23, line number 23–24; page 22, line number 14–15; page 24, line number 18–20; page 29, line number 14–16; page 25, line number 3–5).

3. I am not sure what part of my response the authors thought was an opinion. NO<sub>3</sub> is produced in clouds

(Hegg and Hobbs 1988) and can have small marine sources (Luo et al 2018). Here are a few publications that show nitrate formation in clouds. Sulfate can also be produced in clouds (Hegg and Hobbs 1988). Therefore, your correlation of  $\text{NO}_3$  with  $\text{nssSO}_4$  in the remote southern ocean is much more likely due to cloud processing and not anthropogenic sources. It is not reasonable to use nitrate “solely as an indicator of anthropogenic contribution in this study” if the values are so low that they do not appear to be affected by anthropogenic sources. There are two spikes, A1 and A13, that could possibly be associated with anthropogenic sources. Maybe those cases have back trajectories over continents?

(Response) We apologize to Referee #1 for saying Referee #1’s comment as an opinion. We have realized that  $\text{NO}_3^-$  is not a good tracer for anthropogenic source because of the fact that  $\text{NO}_3^-$  can be produced in clouds and derived from marine source, as Referee #1 pointed out. As Referee #1 mentioned, we observed the high  $\text{NO}_3^-$  concentrations during the collection of aerosol samples, A1 and A13 when air masses originated from the Southern Ocean and thereafter swept over large regions of New Zealand; however,  $\text{NO}_3^-$  concentrations in the other samples were quite low. Consequently, based on Referee #1’s comments, we have revised our manuscript as follows: “On the other hand, the statistically insignificant relationship between  $\text{nss-SO}_4^{2-}$  and MSA in the Southern Ocean could result from the influence of anthropogenic sources in the Southern Ocean. During the cruise, as shown in Fig. 5a, high ( $> 0.1 \mu\text{g m}^{-3}$ ) nitrate ( $\text{NO}_3^-$ ) concentrations were observed during the collection of aerosol samples A1 and A13 when air masses originated from the Southern Ocean and thereafter swept over large regions of New Zealand (Fig. S4); however,  $\text{NO}_3^-$  concentrations in the other samples were quite low ( $< 0.03 \mu\text{g m}^{-3}$ ). Although  $\text{NO}_3^-$  was observed in the other aerosol samples, we cannot assert that all aerosol samples were influenced by anthropogenic sources without another anthropogenic tracer data set (e.g.,  $^{210}\text{Pb}$ ) because, in addition to anthropogenic sources,  $\text{NO}_3^-$  can be produced in clouds (Hegg and Hobbs, 1988) or derived from a weak oceanic source (Luo et al., 2018). Nevertheless, our results suggest that  $\text{nss-SO}_4^{2-}$  in the two samples collected over the Southern Ocean were most likely affected by anthropogenic sources, resulting in the lack of correlation.” (page 10, line number 23–31).

4. I did not misunderstand your manuscript. I understood 39%- 139% is biologically derived contribution of  $\text{nss-sulfate}$ , but this number also indicates the anthropogenic contribution was up to 61% (when the biological contribution is only 39%) and therefore, at times, more than half of the  $\text{nssSO}_4$  is anthropogenic in the Amundsen Sea. And even higher in the southern ocean (76%). Again stronger evidence is needed to make such a claim. This may simply not be possible with the measurements made in this experiment. An anthropogenic tracer that is also formed naturally in the remote southern ocean is necessary for such an analysis.

(Response) We apologize to Referee #1 for our misunderstanding of Referee #1’s comments. As we already responded above, the main cause of the high contributions of anthropogenic  $\text{nss-SO}_4^{2-}$  in the Southern Ocean and the Amundsen Sea was the use of the single value of  $\text{MSA/nss-SO}_4^{2-}$  ratio measured

at Palmer Station. Furthermore, because of the limitations of method using MSA/nss-SO<sub>4</sub><sup>2-</sup> and the absence of another anthropogenic tracer, such as <sup>210</sup>Pb, in this study, we have removed the contribution of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> from section 3.4 and revised our manuscript according to Referee #1 comments (page 11, line number 20–page 12, line number 15).

## Anonymous Referee #5:

### Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

Reviewers 3 and 4 point out the discrepancies of WIOC and WSOC and wind speed. Figure S6 (should be in manuscript instead of supplement) clearly shows that the measured atmospheric WIOC and WSOC are not associated with the air sea flux of primary sea spray particles. This is not surprising for WSOC since it is produced in the atmosphere by secondary processes (good correlation with MSA in figure 8C) but why not WIOC? Similarly, in Figure 7, the WIOC and WSOC to Na ratios have similar relationships to wind speed and DOC. Why would that be true if WSOC is a secondary aerosol?

(Response) We are grateful to Referee #5 for Referee #5's comments. According to Referee #5's comment, we have added Figure S6 as Figure 8 to the manuscript (page 38). Thus, we also have changed the numbers of Figures 8–10 to Figures 9–11 (pages 39–41; page 17, line number 6; page 17, line number 7; page 17, line number 29; page 18, line number 3; page 18, line number 7; page 18, line number 12; page 18, line number 17).

Referee #5 asked why the measured atmospheric WIOC was not associated with the air-sea flux of primary sea spray particles. In this study, we investigated relationships of WIOC and WSOC concentrations with mean wind speed and Na<sup>+</sup> concentration in the fine modes since both WIOC and WSOC were primarily associated with the fine mode particles (Figs. 6a and 6b). As shown in Fig. 8a, no relationship was found between the submicron WIOC and mean wind speed. In addition, the submicron WIOC showed no statistically significant relationships with submicron Na<sup>+</sup> over the Southern Ocean and the Amundsen Sea (Fig. 9a), although WIOC was highly enriched in the fine mode sea spray particles (Fig. 7b) (page 16, line number 19–24). As mentioned in section 3.6, under higher wind speed conditions, the enrichment of organic matter in sea spray aerosols can be diluted by larger sea-salt particles. Furthermore, the increase in sea-salt particle flux under higher wind speed conditions shifts the sea spray aerosol size distribution towards larger sizes and accelerates their dry deposition and gravitational settling from the atmosphere (de Leeuw et al., 2011). Thus, these insignificant relationships between WIOC and Na<sup>+</sup> in the fine modes could result from the differences in local wind speeds and local biological activities, such as sea surface DOC concentration, because wind speed, a key factor determining sea spray aerosols, controls the local flux rather than local concentration of marine particles (Monahan and O'Muircheartaigh, 1986) (page 16, line number 25–31).

In section 3.6, we have discussed the inverse relationships of WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios with mean wind speed and the positive relationships of those ratios with sea surface DOC concentration in the Amundsen Sea. During the sampling period, both WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios showed inverse relationships with mean wind speed ( $r = -0.82$ ,  $p < 0.01$  and  $r = -0.76$ ,  $p < 0.01$ , respectively) (Figs. 7c and 7d). The highest WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios were observed in the aerosol sample (i.e., A5)

collected in biologically active region (i.e., in situ Chl-a concentration was highest ( $6.9 \text{ mg m}^{-3}$ )) under calm conditions (i.e., mean wind speed was lowest ( $4.4 \text{ m s}^{-1}$ )). Previous studies (Quinn et al., 2015 and references therein) reported that the production of particles highly enriched in organic material derives fragmentation of the film cap from which much of the seawater has drained prior to bursting, leaving behind a film that is highly enriched surfactant material, resulting in an enrichment in OC relative to seawater in the freshly emitted sea spray aerosol. In addition, BVOCs can be produced photochemically from the biologically productive sea surface water and emitted to the atmosphere following the excitation of dissolved organic matter found in the presence of surfactant films, leading to the production of secondary organic aerosol (Liss and Duce, 1997; Ciuraru et al., 2015; Mungall et al., 2017). Our results, therefore, suggest that accumulation of organic matter at the sea surface in biologically productive seawater under low wind speed conditions makes a favorable condition for transferring the organic matter to the atmosphere through the bubble bursting process and the condensation of BVOCs on pre-existing sea spray aerosols, resulting in formation of sea spray aerosols that are considerably enriched in the organic matter (O'Dowd et al., 2004; van Pinxteren et al., 2017). However, the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios drastically decreased with increasing mean wind speed, suggesting that the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios were diluted by wind speed-dependent sea-salt emissions. Under higher wind speed conditions, larger sea-salt particles could be transported upward and change the size distribution of sea spray aerosols, resulting in the higher enrichment of sea-salt in sea spray aerosol, with very little contribution from organics (Gantt et al., 2011; de Leeuw et al., 2011). Furthermore, the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios observed in the biologically active region (i.e., higher in situ Chl-a concentrations) did not always show higher values. Therefore, these results from this study suggest that the wind speed is a significant factor influencing the organic mass fractions of sea spray aerosols in our study region, and that Chl-a is not wholly adequate as a proxy for the biological activity responsible for the organic material comprising the aerosol. We found more pieces of evidence which reflect that both marine biological activities and the wind speed can affect the organic mass fraction of sea spray aerosol. Sea surface DOC and POC concentrations have been used as a proxy for the organic mass fraction of sea spray aerosol (e.g., Facchini et al., 2008; Russell et al., 2010; Gantt et al., 2011; Quinn and Bates, 2011; Quinn et al., 2014) since DOC and POC are derived from biological activities in the ocean (Hansell and Carlson, 2001; Henson et al., 2012). As shown Figs. 7e and 7f, both the WSOC/Na<sup>+</sup> and the WIOC/Na<sup>+</sup> ratios showed strong positive relationships with sea surface DOC concentrations measured in the Amundsen Sea when the mean wind speed exceeded  $7 \text{ m s}^{-1}$ ; however, when the mean wind speed was lowest (i.e., aerosol sample A5), both the WSOC/Na<sup>+</sup> and the WIOC/Na<sup>+</sup> ratios sharply increased, although sea surface DOC concentration was low. It appears that the sea surface DOC concentration in the Amundsen Sea was less influenced by wind speed during our cruise, suggesting that DOC in the upper water column was already well mixed in the austral summer (average surface mixed layer depths:  $25 \pm 19 \text{ m}$ , Yager et al., 2016), and that DOC produced by biological activity affected the enrichment of primary (i.e., bubble bursting) and secondary (i.e., gas-to-particle conversion of BVOC derived from the excitation of dissolved organic matter, Ciuraru

et al., 2015) OC in sea spray aerosols. These results indicate that both biological activity and the wind speed are crucial factors influencing the organic mass fraction of sea spray aerosol as mentioned above. (page 14, line number 18–page 15, line number 19).

We also have added the references (i.e., Quinn et al., 2015; Liss and Duce, 1997; Ciuraru et al., 2015; Mungall et al., 2017; van Pinxteren et al., 2017; de Leeuw et al., 2011) to the manuscript (page 26, line number 32–33; page 24, line number 34; page 22, line number 6–7; page 26, line number 3–6; page 29, line number 4–6; page 22, line number 19–20).

The authors try to explain the OC/Na vs wind speed dependence on ocean mixing. How deep was the ocean mixed layer? If it was more than 1 m, wind/wave mixing should have little effect on surface OC content.

(Response) We thank Referee #5 for Referee #5's comment. We have realized that ocean mixing was not a main cause of the inverse relationships of WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios with mean wind speed. As we already have responded above, the upper water column was already well mixed in the austral summer (average surface mixed layer depths: 25 ± 19 m, Yager et al., 2016) (page 15, line number 13–15). Previous studies (Quinn et al., 2015 and references therein) reported that the production of particles highly enriched in organic material derives fragmentation of the film cap from which much of the seawater has drained prior to bursting, leaving behind a film that is highly enriched surfactant material, resulting in an enrichment in OC relative to seawater in the freshly emitted sea spray aerosol. In addition, BVOCs can be produced photochemically from the biologically productive sea surface water and emitted to the atmosphere following the excitation of dissolved organic matter found in the presence of surfactant films, leading to the production of secondary organic aerosol (Liss and Duce, 1997; Ciuraru et al., 2015; Mungall et al., 2017). Our results, therefore, suggest that accumulation of organic matter at the sea surface in biologically productive seawater under low wind speed conditions makes a favorable condition for transferring the organic matter to the atmosphere through the bubble bursting process and the condensation of BVOCs on pre-existing sea spray aerosols, resulting in formation of sea spray aerosols that are considerably enriched in the organic matter (O'Dowd et al., 2004; van Pinxteren et al., 2017). However, the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios drastically decreased with increasing mean wind speed, suggesting that the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios were diluted by wind speed-dependent sea-salt emissions. Under higher wind speed conditions, larger sea-salt particles could be transported upward and change the size distribution of sea spray aerosols, resulting in the higher enrichment of sea-salt in sea spray aerosol, with very little contribution from organics (Gantt et al., 2011; de Leeuw et al., 2011) (page 14, line number 21–page 15, line number 1).

We also have removed the following sentence from section 4: “when the wave breaking thoroughly mixes the organic-enriched sea surface layer with the underlying relatively organic-poor water.” (page 19, line number 16–18).

## Anonymous Referee #6:

### Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

Even though I was not one of the original reviewers, I do not feel that the authors have addressed the discrepancies pointed out by the reviews in the revised manuscript. Also, the explanations for the OC/Na vs wind speed dependence are not convincing, nor is the discrepancy between why secondary components would be wind speed dependent.

(Response) We thank Referee #6 for Referee #6's comment. As Referee #6 pointed out, our previous responses were not enough to explain the discrepancies pointed out by the Referees. We have revised our manuscript according to Referees' comments. Please see our responses to Referee #1 and Referee #5.

Referee #6 pointed out that the explanation for the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios vs. wind speed dependence are not convincing and asked why secondary components would be wind speed dependent. During the sampling period, both WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios showed inverse relationships with mean wind speed ( $r = -0.82$ ,  $p < 0.01$  and  $r = -0.76$ ,  $p < 0.01$ , respectively) (Figs. 7c and 7d). The highest WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios were observed in the aerosol sample (i.e., A5) collected in biologically active region (i.e., in situ Chl-a concentration was highest (6.9 mg m<sup>-3</sup>)) under calm conditions (i.e., mean wind speed was lowest (4.4 m s<sup>-1</sup>)). Previous studies (Quinn et al., 2015 and references therein) reported that the production of particles highly enriched in organic material derives fragmentation of the film cap from which much of the seawater has drained prior to bursting, leaving behind a film that is highly enriched surfactant material, resulting in an enrichment in OC relative to seawater in the freshly emitted sea spray aerosol. In addition, BVOCs can be produced photochemically from the biologically productive sea surface water and emitted to the atmosphere following the excitation of dissolved organic matter found in the presence of surfactant films, leading to the production of secondary organic aerosol (Liss and Duce, 1997; Ciuraru et al., 2015; Mungall et al., 2017). Our results, therefore, suggest that accumulation of organic matter at the sea surface in biologically productive seawater under low wind speed conditions makes a favorable condition for transferring the organic matter to the atmosphere through the bubble bursting process and the condensation of BVOCs on pre-existing sea spray aerosols, resulting in formation of sea spray aerosols that are considerably enriched in the organic matter (O'Dowd et al., 2004; van Pinxteren et al., 2017). However, the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios drastically decreased with increasing mean wind speed, suggesting that the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios were diluted by wind speed-dependent sea-salt emissions. Under higher wind speed conditions, larger sea-salt particles could be transported upward and change the size distribution of sea spray aerosols, resulting in the higher enrichment of sea-salt in sea spray aerosol, with very little contribution from organics (Gantt et al., 2011; de Leeuw et al., 2011). Furthermore, the WSOC/Na<sup>+</sup> and WIOC/Na<sup>+</sup> ratios observed in the biologically active region (i.e., higher in situ Chl-a concentrations) did not always show higher values. Therefore, these results from this study suggest that the wind speed is a significant factor influencing the organic mass fractions of sea spray aerosols in our study region and that Chl-a is not wholly adequate as a proxy for the biological activity

responsible for the organic material comprising the aerosol (page 14, line number 18-page 15, line number 5).