Responses to Referees' comments

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Title: Characteristics of methanesulfonic acid, non-sea-salt sulfate and organic carbon aerosols over the Amundsen Sea, Antarctica
Authors: 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
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Note: Referee's comments are high lightened in **blue**, while our responses to reviewers are in **black**. The revisions in the manuscript was highlighted to make easily readable for the Co-Editor and the Referees.

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 methanesulfonic acid, non-sea-salt sulfate and organic carbon 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 Referees' 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:

The authors have improved the quality of the manuscript by focusing more on their results that are supported by evidence. Below are a couple very minor comments. I suggest the manuscript be published after minor revisions.

Page 10 line 10 - “without another anthropogenic tracer data set (e.g., 210Pb)” A citation showing this as an anthropogenic tracer is necessary here.

Page 10 line 12 “Nevertheless, our results suggest that 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.” I suggest changing “were most likely” to “may be” due to the lack of evidence. Also since you mention shortly after this sentences that atmospheric processes could play a role.

(Response) We thank Referee #1 for Referee #1’s comments. The comments from Referee #1 were related to that from Referee #7, who strongly recommended to remove the discussion on aerosol NO_3^- and the influence of anthropogenic sources from the manuscript. According to Referee #7’s comment, we have removed from section 3.3 the following sentences: “the statistically insignificant relationship between 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 µg m^{-3}) nitrate (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, NO_3^- concentrations in the other samples were quite low (< 0.03 µg m^{-3}). Although 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}Pb) because, in addition to anthropogenic sources, 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 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.” (these sentences were written on page 10, line number 5−13 in the previous manuscript).

Anonymous Referee #7:

All over the manuscript, the key scientific terms are not well defined. MSA is present in both the gas and the condensed forms in the atmosphere. As it is appeared that the author only present the condensed form, a clear notation such as MSA (s) would prevent a such confusion. In addition, the authors should make it clear that the presented DMS flux is not directly observed rather calculated assessments from wind and dissolved DMS observations. Furthermore, a quantitive assessment on uncertainty associated with the flux calculation should be discussed.

(Response) We thank Referee #7 for Referee #7’s comments. We have differentiated between gaseous MSA ($MSA_{(g)}$) and particulate MSA ($MSA_{(p)}$) according to Referee #7’s comment. To differentiate between $MSA_{(g)}$ and $MSA_{(p)}$, we have revised the sentences in Introduction as follows: “After emission to the atmosphere, DMS is oxidized by the hydroxyl (OH), nitrate (NO_3), and bromine oxide (BrO) radicals to form either gaseous methanesulfonic acid ($MSA_{(g)}$) or sulfur dioxide (SO_2). While $MSA_{(g)}$ rapidly condenses onto existing particles (forming particulate MSA, $MSA_{(p)}$), SO_2 is further oxidized to nss-SO_4^{2-}” (page 2, line number 12−14). Besides, we have revised “MSA” to “$MSA_{(p)}$” in the manuscript, including Abstract, Introduction, Results and discussion, Conclusions and Figures.

Referee #7’s pointed out that we should make it clear that the presented DMS fluxes in this study were not directly observed, but calculated assessments. We agree to the Referee #7’s comment. Referee #7 also pointed out that a quantitative assessment on uncertainty associated with the flux calculation should be discussed. However, we have used the DMS flux data reported by Kim et al. (2017), who calculated sea–air DMS fluxes using sea surface DMS concentrations and shipboard wind speed data monitored during our cruise. Besides, each DMS flux in Figs. 4(a) and 4(b) represents its mean value and standard deviation for each aerosol sampling time. Nevertheless, we have estimated the uncertainty in DMS flux in the Amundsen Sea region to be about 25% using four different gas transfer velocity (k) values, which have been discussed in section 3.2 (page 8, line number 30−page 9, line number 4). Consequently, we have revised our manuscript as follows: "To investigate the relationship between atmospheric $MSA_{(p)}$ and DMS flux, we used the DMS flux data reported by Kim et al. (2017), who calculated sea–air DMS fluxes using sea surface DMS concentrations and shipboard wind speed data monitored during our cruise. Details of the measurement of sea surface DMS concentration and the sea–air DMS flux calculation are given by Kim et al. (2017)." (page 8, line number 25−28). In addition, we have revised the caption of Figure 4 as follows: "Figure 4. Dimethylsulfide (DMS) flux (reported by Kim et al., 2017) (a) against aerosol sample I.D. and the correlation between $MSA_{(p)}$ concentration and DMS flux (b). The DMS fluxes were calculated using sea surface DMS concentrations and shipboard wind speed data monitored during the cruise. Details of the measurement of sea surface DMS concentration and DMS flux calculation are given by Kim et al. (2017). Each DMS flux in both panels (a) and (b) represents its mean value and standard deviation for each aerosol sampling time. The gray hatched areas in panel (a) denote that no DMS measurement was conducted. Pink solid circle line in panel (a) indicates the mean and standard deviation of wind speeds for each aerosol sampling time. Double arrows in panel (a) show the sampling locations of aerosol samples. In panel (b), the red line indicates the correlation between $MSA_{(p)}$ concentration and DMS flux." (page 28).

Discussion on the controlling factor of MSA (s) is mainly dependent upon the DMS flux. It seems that the discussion assumes the calculated DMS flux is directly related with DMS concentration in the atmosphere and subsequently MSA (s) should be linearly correlates with the DMS flux. However, I am not entirely convinced by the underlying assumption. The material flux is a determinant for the atmospheric presence of the given substance but not necessarily for the only determinant. As the authors described, DMS over the Southern Ocean has a fairly lengthy lifetime (a few days), so transport may also play an important role to determine the presence of DMS. The subsequent gas phase oxidation process of DMS is also quite complicated, which likely results in a non-linear relationship between DMS and MSA (g). Therefore, the relationship between DMS and MSA (s) cannot be contained in a linear relationship. Furthermore, it comes to me as an insufficient argument that MSA (s) was observed in the higher level over the Amundsen Sea. According to Figure 4a), the statistics is mostly driven by one data point (A9), otherwise, the MSA (s) over the Amundsen Sea appears around the same level to the other part of the Southern Ocean.

(Response) We thank Referee #7 for Referee #7's comments. We have realized that the underlying assumption was not reasonable as Referee #7 pointed out. According to Referee #7's comments, we have revised our manuscript as follows: "The DMS flux (reported by Kim et al., 2017) averaged for the duration of each aerosol sampling showed a somewhat similar variation trend to that of atmospheric $MSA_{(p)}$ concentration (Fig. 4a), but no correlation was found between atmospheric $MSA_{(p)}$ and DMS flux ($r = 0.18$, $p > 0.05$, Fig. 4b). DMS fluxes typically rely on gas transfer velocity (k), which is frequently parameterized as a function of wind speed (Wanninkhof, 2014). Measurement and parameterization of the gas transfer velocity are more challenging and subject to greater uncertainty, particularly at high wind speeds (Smith et al., 2018). Wanninkhof et al. (2014) reported that there is a considerable uncertainty in k, especially, under the strong wind condition. About 20% uncertainty was estimated at a global mean wind speed ($7.3\ m\ s^{-1}$). When we applied four different k values (W92, W99, N00, W14), the uncertainty in DMS flux in the Amundsen Sea region was about 25%. As the gas transfer velocity increases with increasing wind speed, DMS flux can be overestimated especially, in higher latitudes where DMS is commonly found at high concentrations in surface water, and where both low temperatures and high winds are typical (McGillis et al., 2000). In addition to the uncertainty in DMS flux, the insignificant relationship between atmospheric $MSA_{(p)}$ and DMS flux could result from various complexities in the rate of oxidation of DMS to form atmospheric MSA$_{(p)}$ and long-range transport of atmospheric MSA$_{(p)}$ from biogenically active region, given the lifetime of DMS is approximately 1–2 days (Kloster et al., 2006; Read et al., 2008). Although we found no significant relationship between atmospheric MSA$_{(p)}$ concentration, in situ sea surface Chl-a concentration, the relative biomass of *P. antarctica* and the local sea–air DMS flux, the higher atmospheric MSA$_{(p)}$ concentrations observed over the Amundsen Sea compared to those over the Southern Ocean and in coastal Antarctic regions most likely resulted from complex linkage between these factors." (page 8, line number 28−page 9, line number 10). Besides, we have removed from section 3.6 the following sentence: "As described in section 3.2, Kim et al. (2017) observed extremely high DMS concentrations (> 150 nM) in surface water during our cruise, and MSA$_{(p)}$ concentration showed a strong correlation with DMS flux in the Amundsen Sea." (this sentence was written on page 13, line number 20−22 in the previous manuscript). We also have modified Figure 4b (page 28).

In addition, Referee #7 pointed out that the MSA$_{(p)}$ concentrations observed over the Amundsen Sea appear to be the same level to those over the Southern Ocean if one data point (A9) is excluded. Although the higher atmospheric MSA$_{(p)}$ was mostly driven by one data point, we believe that we cannot rule out it. Besides, atmospheric MSA$_{(p)}$ observed over the Amundsen Sea showed a significant relationship with WSOC as shown in Fig. 8c. Consequently, it is reasonable to describe that the higher atmospheric MSA$_{(p)}$ level was observed over the Amundsen Sea, compared to those over the Southern Ocean.

As the authors acknowledged, higher nitrate concentrations in the aerosol phase cannot be attributed to the anthropogenic influences without further evidences. I would strongly recommend to remove the discussion from the manuscript.

(Response) We thank Referee #7 for Referee #7's comment. As Referee #7 pointed out, we have realized that higher aerosol NO_3^- concentrations cannot be attributed to the anthropogenic influences without further evidences. Therefore, we have removed from section 3.3 the following sentences: "the statistically insignificant relationship between 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 µg m^{-3}) nitrate (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, NO_3^- concentrations in the other samples were quite low (< 0.03 µg m^{-3}). Although 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}Pb) because, in addition to anthropogenic sources, 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 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." (these sentences were written on page 10, line number 5−13 in the previous manuscript). We also have removed Figure 5(a) (page 29) and the related references (i.e., Hegg and Hobbs, 1988 and Luo et al., 2018) from the manuscript. Besides, to clarify the context, we have revised our manuscript as follows: "On the other hand, a possible explanation for the insignificant relationship between nss-SO_4^{2-} and MSA$_{(p)}$ in the Southern Ocean is entrainment of nucleated nss-SO_4^{2-} particles into the marine boundary layer of the Southern Ocean from the free troposphere by turbulent diffusion and large-scale transport." (page 10, line number 6−8). We also have revised "The lack of correlation between nss-SO_4^{2-} and MSA$_{(p)}$ in the Southern Ocean, therefore, could have resulted from the influence of anthropogenic sources and the input of nss-SO_4^{2-} from the free troposphere." to "The lack of correlation between nss-SO_4^{2-} and MSA$_{(p)}$ in the Southern Ocean, therefore, could have resulted from the input of nss-SO_4^{2-} from the free troposphere." (page 10, line number 11−12).

Finally, the discussion on attributing the protein-like substances in the aerosol phase to the BVOCs are highly misleading. BVOCs are by-products of photosynthetic processes but not biomaterial containing protein. Therefore, the discussion, appearing in Section 3.7 requires a substantial overhaul.

(Response) We are grateful to Referee #7 for Referee #7's comments. We have realized that the discussion on attributing the protein-like components in aerosols to the BVOCs is highly misleading, as Referee #7 pointed out. According to Referee #7's comment, we have revised the discussion on the relationship between the protein-like component and the relative biomass of diatoms as follows: "Ice algae, commonly found in polar sea ice and surrounding waters, are largely dominated by diatoms (Roberts et al., 2007), which are an important contributor to aerosols by emission of aerosol-forming volatile (e.g., alkyl-amines) and non-volatile (e.g., mycosporine-like amino acids) organic nitrogen in the Antarctic sea ice region (Dall'Osto et al., 2017). Previous studies (e.g., Facchini et al., 2008b; Miyazaki et al., 2011) provided the evidence that volatile emissions of alkyl-amine from marine algae can represent an important source of marine secondary organic aerosol. Moreover, Dall'Osto et al. (2017) observed that the fluorescence signal for protein-like component was positively correlated to organic nitrogen originated from the melted Antarctic sea ice floes, indicating that protein-like component was associated with organic nitrogen derived from the microbiota of sea ice and sea ice-influenced ocean. Although we have no aerosol water-soluble organic nitrogen dataset, our results provide additional evidence that marine algae can influence fluorescent property of marine aerosols. Interestingly, we found that fluorescence intensity of C1 showed a significant positive relationship with the relative biomass of diatoms ($r = 0.89$, $p < 0.01$); however, it was negatively correlated with the relative biomass of *P. antarctica* ($r = –0.79$, $p < 0.05$) (Figs. 10c and 10d). Given the dominance of diatoms in the marginal sea ice zone during the cruise and the significant positive relationship between fluorescence intensity of protein-like C1 and the relative biomass of diatoms, it is plausible, therefore, that biological processes of diatoms are an important factor in controlling the abundance of protein-like component in water-soluble organic aerosols over the Southern Ocean and the Amundsen Sea, although further studies are necessary to clarify this point." (page 14, line number 18−33).

Because we have found out that fluorescence properties in aerosol samples do not represent fluorescence properties of WSOC, but those of water-soluble organic aerosols, we have revised the title of section 3.7 from "Fluorescence properties of WSOC over the Southern Ocean and the Amundsen Sea" to "Fluorescence properties of water-soluble organic aerosols over the Southern Ocean and the Amundsen Sea" (page 13, line number 22). Consequently, we also have revised the sentences related to the revised title as follows:

1. "To further elucidate the sources of water-soluble organic aerosols, we investigated the fluorescence properties of submicron aerosols using EEM-PARAFAC. Fluorophores in water-soluble organic aerosols were divided into three primary types on the basis of their peak position." (page 13, line number 30−32).

2. "Moreover, the fluorescence properties of water-soluble organic aerosols revealed that protein-like components are most likely produced as a result of biological processes of diatoms." (page 15, line number 20−21).

3. "The fluorescence properties of water-soluble organic aerosols investigated using fluorescence excitation-emission matrix coupled with parallel factor analysis (EEM-PARAFAC) revealed that protein-like components were dominant in our marine aerosol samples, representing 69–91% of the total intensity." (page 1, line number 25−27).

4. "(4) estimate the source of atmospheric water-soluble organic aerosols using a fluorescence technique (page 3, line number 28−29).

We also have added the references (i.e., Dall'Osto et al., 2017; Facchini et al., 2008b; Roberts et al., 2007) to the manuscript.

References

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