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Effect of sea ice retreat on marine aerosol emissions in the Southern Ocean, Antarctica



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Marine aerosols were determined with high-time-resolution firstly in the polynya regions, Antarctic.
- Sea salt aerosols were the dominant sources accounting for more than 60% in the SO.
- Sea salt aerosols increased by more than 30% as sea ice concentrations decreased from 85% to 30%.
- Sea ice melt increased the biogenic gases emissions and resulted in the increase of biogenic aerosols.



ARTICLE INFO

Article history: Received 13 April 2020 Received in revised form 16 June 2020 Accepted 4 July 2020 Available online 20 July 2020

Editor: Pingqing Fu

Keywords: Sea ice Sea salt aerosols Methane sulfonic acid (MSA) Nss-SO₄⁻⁻ Climate

ABSTRACT

Sea ice retreat in the polar region is expected to increase the emissions of sea salt aerosols and biogenic gases, which may significantly impact the climate by increasing cloud condensation nuclei (CCN) population and changing solar radiation. In this study, aerosol compositions were measured at high-time-resolution (1 h) with an in-situ gas and aerosol composition monitoring system in polynya regions of the Southern Ocean (SO) to access the effects of sea ice concentrations on the sea salt aerosol (SSA) and secondary biogenic aerosol (SBA) in the SO. SSA emissions increased by more than 30% as sea ice concentration decreased from 85% to 29%. However, SSA emissions did not increase monotonically as the sea ice concentrations by enhancing the air-sea exchanges of SBA precursor gases and the release of algae from sea ice. Positive correlations between SSA and wind speed were present in different sea ice regions, while SBA didn't reveal an obvious correlation with wind speed in the SO. The impact of wind speed on the SSA emissions were very different, Higher slope value of 41.83 and 35.81 were present in the DSI and SIF region, while the value was only about 16.74 in the SIC region. The results extended the knowledge of the effect of future sea ice retreat on marine aerosol emissions and potential climate changes in the polar region.

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1. Introduction

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Marine aerosols are one of the most important sources of atmospheric natural aerosol particles at the global level (Spracklen et al., 2008; Vignati et al., 2010). They directly and indirectly alter the energy budget by absorbing and scattering solar radiation and acting as cloud condensation nuclei (CCN) (Quinn et al., 2017; O'Dowd and Leeuw, 2007). Marine aerosols commonly comprise of primary aerosols, associating with the production of sea spray aerosols, and secondary aerosols. Sea spray aerosols, such as sea salt aerosol (SSA) and organic matter, are customarily generated from the bubble-bursting processes (O'Dowd and Leeuw, 2007). Marine secondary aerosols are often associated with marine biogenic sulfur cycles and marine organic compounds emission (Gantt et al., 2009). Dimethyl sulphide (DMS) is derived from marine phytoplankton and then emitted into the atmosphere via air-sea exchanges (Dall'Osto et al., 2017; O'Dowd and Leeuw, 2007; Chang et al., 2011). DMS is easy to be oxidized by radicals to form sulfate (SO₄²⁻) and methane sulfonic acid (MSA) in the atmosphere (Barnes et al., 2006; Ghahremaninezhad et al., 2016).

Sea salt aerosols are one of the largest sources of primary aerosols in the marine atmosphere. The mass flux of SSAs is about $1-3 \times 10^4$ Tg yr⁻¹ at a global scale (Quinn et al., 2017; Warneck, 1988), SSAs are considered to be the dominant contributor to aerosol light scattering in the marine boundary layer (MBL) (Jacobson, 2001; Takemura et al., 2002). The investigation of SSAs has been carried out in previous studies (Spiel, 1998; Stokes et al., 2013; Collins et al., 2014; Wang et al., 2015; Lee et al., 2015; Prather et al., 2013). Generally, SSAs concentration and biogenic gases are associated with wind speed (Lewis and Schwartz, 2004; Nightingale et al., 2000). Marine secondary aerosols, however, depend on their precursor gases, such as DMS and isoprene. Global oceanic DMS emissions have been estimated to be 18–34 Tg yr⁻¹ (Lana et al., 2011; Simó, 2001). Air-sea DMS fluxes are mainly determined by sea water DMS concentration and wind speed in the open ocean (Nightingale et al., 2000). The generation of SSA and air-sea exchanges of biogenic gases in the open oceans has been reported in previous studies (Spiel, 1998; Stokes et al., 2013; Marandino et al., 2013). However, the emissions of DMS and SSAs are still uncertain and short in knowledge, when sea surfaces are covered with sea ice.

Sea ice concentration is defined as the percentage of an area which is covered with sea ice. High sea ice concentrations in marine regions decrease the heat, momentum, and gases exchanges between the air and sea (Vaughan et al., 2013; Gilgen et al., 2018). Studies have shown that more sea salt particles and DMS are released to the atmosphere in the Arctic Ocean, when the sea ice melts (Browse et al., 2014). Modeling results also illustrates that sea ice retreat will increase the SSA population by a factor of 2 to 3 by 2100 in the Arctic regions during summer time (Struthers et al., 2013). Consequently, SSAs would become the main source of atmospheric aerosol particles in the Arctic (Deshpande and Kambra, 2014). Besides, studies have found that Arctic sea ice melting can also result in new particle formation (NPF) in the atmosphere (Dall'Osto et al., 2017). It has been confirmed that sea ice melting will alter the emissions of SSAs and biogenic gases in Arctic regions (Gilgen et al., 2018; Browse et al., 2014). However, it remains unclear how changes in sea ice concentration impact the emissions of primary and secondary aerosols. The lack of direct observations makes it challenging to address. Due to the threat of global warming poses on sea ice, it is particularly important to consider this question. As global warming melts sea ice in the SO during austral spring and summer times, the decrease of sea ice concentrations may alter the emissions of marine aerosols and affect regional climate in the Antarctica. The sea ice melting in the SO during austral summer time will change the air-sea fluxes of DMS and the formation of aerosols in the SO.

In this study, we aim to determine how changes in sea ice concentrations impact the emissions of primary and secondary marine aerosols in the SO. We analyzed the variations of aerosol chemical compositions using high-time-resolution instruments in different sea ice concentration regions of the Ross Sea (RS), Antarctica. Furthermore, the impact factors on marine aerosol emissions were also characterized to study the effect of sea ice melting on the marine aerosol emissions in the SO.

2. Experimental methods and observation regions

The observations were carried out by R/V "Xuelong" with two legs in the RS, Antarctica (60°S to 78°S, 160°E to 185°E, Fig. 1) with different sea ice concentrations. The leg I was carried out from December 2 to 20, 2017, when high sea ice concentration was present in the RS during this period (Fig. 2c). The leg II was conducted in the same region from January 13 to February 14, 2018, when the RS was almost free of sea ice (Fig. 2d).

2.1. Aerosol observation instrument and sampling method

The aerosol compositions were monitoring at high-time resolution using an in-situ gas and aerosol composition monitoring system (IGAC, Model S-611), which was employed on the R/V "Xuelong" (Fig. S1). The sampling inlet with a total suspended particulate (TSP) sampler was located at the bow of the vessel. The sampling inlet was about 20 m above the sea surface in this study.

The measurement of gases and aerosols using an IGAC system on board has been described in detail by Yan et al. (2019). The gases and aerosols are separated and converted into liquid effluent for on-line chemical analysis at an hourly temporal resolution (Liu et al., 2017). An on-line ion chromatography (IC) system (Dionex ICS-3000) was used to analyze the anions and cations of gases and aerosols samples. The calibration curves with six to eight concentrations of standard solutions are illustrated in Fig. S2, with R² above 0.997. The detection limits for MSA⁻, SO²₄⁻, Na⁺, and Cl⁻ were 0.09, 0.12, 0.03, and 0.03 μ g·L⁻¹ (aqueous solution), respectively. Nss-SO²₄⁻ concentrations were calculated from the following equation:

$$\left[nss - SO_4^{2-}\right] = \left[SO_4^{2-}\right]_{total} - K\left[Na^+\right] \tag{1}$$

where, *K* equals 0.252, the weight ratio of sulfate and sodium in seawater (Millero and Sohn, 1992). The temporal distribution of $nss-SO_4^{2-}$ is shown in Fig. S3.



Fig. 1. The cruise tracks of the observation in the Ross Sea (RS). Leg I was carried out during the early December (December 2 to 20, 2017). Leg II was carried out from January 13 to February 14, 2018 in the RS, covering a large scale of 50°S to 78°S, 160°E to 185°E.



Fig. 2. Spatial distributions of total aerosol water soluble ions concentration and sea ice concentration in the Ross Sea, Antarctica during the cruise; (a) aerosol mass concentration during leg I (ng·m⁻³), (b) aerosol mass concentration during leg II (ng·m⁻³), (c) average sea ice concentration during leg I from the satellite, (d) average sea ice concentration during leg II from the satellite.

2.2. Metrological parameters and satellite data of sea ice

Meteorological parameters such as temperature, humidity, wind speed and direction were monitored continuously using an automated meteorological station deployed in the R/V "Xuelong". In this study, remote sensing data was used to show the spatial and temporal distributions sea ice concentration in the RS, Antarctica. Sea ice concentration data from the daily 3.125-km AMSR2 dataset (available at https://seaice.uni-bremen.de) (Spreen et al., 2008).

3. Results and discussion

3.1. Spatial distributions of aerosol concentration and sea ice in the RS

In this study, a bulk average sea ice data from the satellite remote sensing was used to classify the sea ice level in the SO. Due to the spatial resolution limiting of satellite data, three different sea ice level regions were characterized. Sea ice coverage region (SIC) is defined as those regions with ice concentration larger than 80%. Most of the sea surfaces are covered with sea ice in SIC, however, polynyas are existed in those regions. Drifting sea ice region (DSI) is an area with sea ice concentration between 15% and 80%. A considerable number of floating ice is present in the sea surfaces in this region. Sea ice free region (SIF) is defined as those areas with sea ice concentration lower than 15%.

Aerosol mass concentrations ranged from 44.7 to 1950.1 ng·m⁻³, with an average of 500.9 \pm 307.1 ng·m⁻³ (n = 277) in the SIC region (Fig. 2a). The mean concentration increased to 1144.1 \pm 625.9 ng·m⁻³ (n = 132), ranging from 343.9 to 5431.9 ng·m⁻³ in the DSI region (Fig. 2a). High aerosol concentrations were also observed in the SIF region, and ranged from 491.5 to 6033.8 ng·m⁻³ with an average of 791.1 \pm 704.8 ng·m⁻³ (n = 779, Fig. 2b). The mean aerosol concentration in SIF and DSI region was higher than in the SIC region, indicating

that sea ice melting increased the emissions of marine aerosols in the SO. However, the aerosol concentration in the SIF region was lower than that in the DSI region. This was caused by the enhance of SSA emission in the DSI region, which will be further discussed in Section 3.4.

3.2. Variations of aerosol water-soluble ions during the cruise

The relationship between sea ice concentrations is illustrated in Fig. 2. It is readily apparent that the concentration of marine aerosols increased as sea ice concentration decreased. The temporal distributions of aerosol water soluble ions (WSI) are shown in Fig. 3, to clarify the influence of sea ice concentration on different marine aerosols. Na⁺ derived from SSA (Teinila et al., 2014), is an important component of marine atmospheric aerosols (Yan et al., 2018). High concentrations of Na⁺ were observed in DSI and SIF regions, with an average of $609.9 \pm 497.3 \text{ ng} \cdot \text{m}^{-3}$ (*n* = 132) and $395.8 \pm 561.4 \text{ ng} \cdot \text{m}^{-3}$ (*n* = 779), respectively (Fig. 3a). While the mean concentration of Na⁺ was only 143.1 \pm 202.6 ng·m⁻³ (n = 227) in the SIC region. High concentrations of Na⁺ were also present in low sea ice concentration region (SIF), when high wind speeds were present (Fig. 3a). The temporal distributions of Mg^{2+} , Cl^- , F^- , and K^+ were comparable to those of Na^+ (Fig. 3a and b). Strong positive correlation between Na⁺ and Mg²⁺ (slope = 0.122, $R^2 = 0.98$) were observed in this study (Fig. S4a). Note that the ratio of Mg^{2+} to Na^+ is 0.122, consisting with the mass ratio of Mg^{2+} to Na^+ (0.121) in the sea water, indicating that Mg^{2+} was also derived from SSAs in this study. Similar with Mg²⁺, positive correlations between Na⁺ and Cl⁻ ($R^2 = 0.96$, Fig. S4b) indicated that Na⁺ and Cl⁻ had the same source.

MSA⁻ is regarded as a useful marker for marine biogenic sources (Legrand and Pasteur, 1998), because MSA⁻ forms exclusively from the oxidation of DMS in the marine atmosphere (Sorooshian et al., 2007). The mean concentrations of MSA⁻ were 43.8 \pm 22.4 ng·m⁻³, 55.5 \pm



Fig. 3. Temporal distributions of aerosol WSI and wind speed and direction. (a) Time series of Na^+ concentration, (b) time series of Mg^{2+} , Ca^{2+} , K^+ , F^- and Cl^- concentrations, (c) time series of SO_4^{2-} concentration, (d) time series of MSA⁻ concentration, (e) time series of NH_4^+ , NO_2^- and NO_3^- concentrations, (f) time series of wind speeds and wind directions.

26.8 $\text{ng}\cdot\text{m}^{-3}$ and 38.3 \pm 27.6 $\text{ng}\cdot\text{m}^{-3}$ in SIC, DSI and SIF regions, respectively (Fig. 3d). These observations were consistent with MSA levels reported during the cruise conducted in the Antarctica from October 1992 to January 1993 (De Baar et al., 1995), ranging from 2 ng·m⁻³ to $360 \text{ ng} \cdot \text{m}^{-3}$ in the cruise. The observed MSA levels in this study consisted with the observation results reported in the SO and Antarctica (Minikin et al., 1998; Preunkert et al., 2007; Chen et al., 2012; Preunkert et al., 2008). The measured MSA⁻ concentrations in the SIC region were higher than the MSA⁻ value in the SIF region. Although high concentrations of sea ice were present in the SIC regions, polynyas were formed in these regions, as sea ice began to melt in the early December in the SO. The release of iron (Wang et al., 2014) and algae (Boetius et al., 2013) from melting sea ice caused an increase in phytoplankton species (Taylor et al., 2013) and a consequent increase in DMS generation and emission (Hayashida et al., 2017), which in turn caused an increase in atmospheric MSA level due to the oxidation of DMS.

Different from MSA⁻, SO₄⁻² is derived from different sources, such as SSAs, anthropogenic emission, marine biogenic and volcanic sources (Legrand and Pasteur, 1998; Hayashida et al., 2017). In high latitude regions of the SO, SO₄⁻² is mainly associated with SSAs and biogenic sources (Berresheim et al., 1998). The mean SO₄²⁻² concentrations were 222.8 \pm 58.7 ng·m⁻³ and 252.4 \pm 45.8 ng·m⁻³ in the SIF and DSI region, respectively, while the mean level of SO₄²⁻² was 192.7 \pm 111.5 ng·m⁻³ in the SIC region. The observed mean SO₄²⁻² concentrations were consistent with the results reported by Minikin et al. (1998), with a mean value of 115.0 ng·m⁻³ in Halley, 312.0 ng·m⁻³ in Neumayer and 372.0 ng·m⁻³ in Dumont d'Urville in the summer time. The temporal distribution of SO₄²⁻² was not consistent with the distribution so Na⁺ or MSA⁻ in this study (Fig. 3), as SO₄²⁻² was impacted by

both SSAs and biogenic sources. Generally, when sea salt SO_4^{2-} was the dominant sources of the SO_4^{2-} , the temporal distribution of SO_4^{2-} had the constant trend with Na⁺. Similarly, while SO_4^{2-} from oxidation of DMS was the dominant sources of the SO_4^{2-} , SO_4^{2-} would have the similar variation trend with MSA. However, SO_4^{2-} was often impacted by sea salt SO_4^{2-} and biogenic SO_4^{2-} in the SO (Berresheim et al., 1998), in this case the temporal of SO_4^{2-} was different from the distributions of Na⁺ and MSA⁻, suggesting that SO_4^{2-} may be impacted by various sources depending on regions.

The levels of NH_4^+ were very low throughout the observation period, with an average of 23.8 \pm 12.6 ng·m⁻³, 22.2 \pm 7.5 ng·m⁻³ and 15.1 \pm 8.6 ng·m⁻³ in the SIC, DSI and SIF region, respectively (Fig. 3e). NH₄⁺ is generated from its precursor gas NH₃, which primarily originates from the ocean, such as a few sources of NH₃ include zooplankton excretion and bacterial remineralization of phytoplankton-derived organic matter (Carpenter et al., 2012). Previous studies have suggested that sea ice melt is a significant source of ammonium in the Arctic (Tovar-Sanchez et al., 2010) and Antarctic (Thomas and Dieckmann, 2002), as ammonia has been found enriched in Antarctica sea ice produced from the biological activity within the sea ice. That is the reason why higher concentration of NH₄⁺ was present in the high sea ice concentration region than in the low sea ice concentration region. NO_x^- (NO_2^- and NO_3^-) is also regarded as a secondary aerosol compound in the atmosphere, which can be derived from natural sources in the SO (Wolff, 1995) as well as by human activities in the coastal Antarctic regions (Mazzera et al., 2001). High concentrations of NO_x^- are often observed in urban or coastal atmospheric aerosols (Yan et al., 2015). However, the concentrations of NO₂⁻ and NO₃⁻ were extremely low in this study, with an average of 18.0 \pm 43.3 ng·m⁻³ and 5.4 \pm 13.1 ng·m⁻³ throughout the cruise respectively (Fig. 3e). The contributions of NH_4^+ , NO_2^- , and NO_3^- components to the total WSI were low in the SO, comparing with the SSAs and biogenic sulfur components.

3.3. Effect of wind speeds on aerosol emissions in different sea ice concentrations

Marine aerosol emissions are also impacted by wind speed. As discussed above, SSA and SBA were the dominant components, accounting for more than 90% of the total WSI (Fig. S5). Na⁺ and MSA⁻ were considered to be the markers of SSA and SBA in the marine atmosphere (Yan et al., 2018; Legrand and Pasteur, 1998), respectively. Therefore, Na⁺ and MSA⁻ components were discussed here to represent the SSA and SBA.

High concentrations of Na⁺ were present in the SIF and DSI regions (Fig. 4a), indicating that SSA emissions increased when sea ice concentrations decreased. Note that the average concentration of Na⁺ in DSI was much higher than the average value of Na⁺ in the SIF region, suggesting that sea ice concentration was not the only factor influencing SSA emissions. The relationships between Na⁺ concentrations and wind speeds in different sea ice concentration regions are also illustrated in Fig. 4c. Positive correlations between Na⁺ concentrations and wind speeds were present in SIC ($R^2 = 0.69$), DSI ($R^2 = 0.75$) and SIF $(R^2 = 0.22)$ regions. However, the impact of wind speed on the SSA emissions were very different, as the slope reached up to 41.83 and 35.81 in the DSI and SIF region, while the value is only about 16.74 in the SIC region. Therefore, high sea ice concentrations depressed the wind-born SSAs. It is worth noting that SSA emissions did not decrease monotonically with the increasing sea ice concentrations in this study. The highest Na⁺ concentrations occurred in the DSI region, which was in accordance with the largest slope occurred in the DSI region. These results reveal that sea ice may potentially enhance the SSA emissions in some conditions (such as in some sea ice concentration ranges), comparing with sea ice free regions.

Similar with SSA, the highest MSA⁻ concentrations were also observed in the DSI region. However, the average MAS⁻ level in the SIC region was higher than in the SIF region (Fig. 4b). The MSA⁻ concentrations were not associated with the wind speed in the three different sea ice concentration regions (Fig. 4d). MSA⁻ concentrations are mainly determined by its precursor gas (DMS), radicals and environmental conditions (solar radiation, temperature and relative humidity etc.) (Barnes et al., 2006). The air-sea fluxes of DMS increase with wind speed (Nightingale et al., 2000) and decrease with sea ice concentration increases (Browse et al., 2014). However, the atmospheric DMS levels were also influenced by the water DMS level, deriving from the marine phytoplankton. That is the reason why MSA⁻ levels did not reveal a direct correlation with wind speed and sea ice concentrations.

3.4. Effect of sea ice changes on marine atmospheric aerosols

To determine how changes in sea ice concentrations affect different types of marine aerosol emissions, aerosol particles were classified as three types based on their sources, such as SSA, SBA and N-aerosols. SSA is derived directly from the sea surface via bubble-bursting. High concentrations of sea ice reduce the interactions between air and sea. Furthermore, wind-generated waves may decline in high sea ice concentration regions. Both factors decreased the generation of SSA in high sea ice concentration regions. In this study, Na⁺, Mg²⁺, K⁺, Cl⁻, F⁻, and Br⁻ were classified as SSA, as these species were commonly found in the sea water. Moreover, good correlations between these species were present in the aerosols in this study (Table S1). SSA accounted



Fig. 4. Impact factors on marine aerosol emissions. (a) Relationship between Na⁺ and sea ice concentration, (b) relationship between MSA⁻ and sea ice concentration, (c) correlation between Na⁺ and wind speed in different sea ice concentration regions, (d) effect of wind speed on MSA⁻ concentration in different sea ice concentration regions.



Fig. 5. Relative fraction of different types of aerosol in the SO.

for 81.55% of the total aerosols in the DSI region, 76.06% in the SIF region and 51.11% in the SIC region (Fig. 5). These factions were consistent with the average contribution of sea salt (85%) in the open water of Antarctica (Dall'Osto et al., 2017). The results were associated with the variations of Na⁺ concentrations illustrated in Fig. 4a, which confirmed that high sea ice concentration depressed SSA emissions. But SSA emissions in the DSI region were even higher than in the SIF region, indicating that the increased of SSA emissions with the decreased of sea ice was non-linear. Generally, the air-sea exchanges were enhanced as the sea ice concentration decreased, resulting in the increase of SSA emission. However, when the sea ice decreased to a special level, the collision between sea water and sea ice would enhance the sea water spray, which may significantly increase the formation of SSA. That is the main reason why SSA did not increase linearly with the sea ice concentration decreased. But more observations are required to clarify the relationship between SSA and sea ice in the near future.

Secondary biogenic aerosols, comprising of MSA⁻ and nss-SO₄²⁻ (Fig. S3), are secondary aerosols. High percentages of SBA were present in the SIC region, accounting for 39.98%, following by 20.40% in the SIF region and 13.42% in the DSI region. N-aerosols (NH₄⁺, NO₂⁻ and NO₃⁻) are another secondary aerosols (Xu et al., 2013), which are commonly found in the atmosphere. High percentages of N-aerosols were found

in the SIC region, accounting for 8.9% of the total WSI in this study, following by 5.13% in the DSI region and 3.54% in the SIF region. Sea ice becomes a barrier of the exchange of biogenic gases between air and sea (Gilgen et al., 2018), which may decrease the air concentrations of these gases because of the decrease of air-sea exchanges. However, the effect of changing sea ice concentrations on marine secondary aerosol emissions is indirect and complicated. Sea ice melting will not only enhance the air-sea DMS fluxes, but will also alter the production and release of DMS (Dall'Osto et al., 2017; Karl et al., 2013). Moreover, the formation of secondary aerosols was also impacted by the atmospheric conditions, such as radicals, solar radiation and temperature.

4. Implication of sea ice retreat on marine aerosol emissions in the polar regions

Sea ice plays a fundamental role in regulating key earth system processes, including nutrient cycling, air-sea gas exchanges, and climate changes in the Arctic and Antarctic regions (Gilgen et al., 2018; Patterson et al., 2019). Modeling simulations predict that the Arctic sea ice areas will decrease from 6.1×10^6 to 3.4×10^6 km² in late summer by 2050 due to the rising temperatures (Gilgen et al., 2018). Unlike the Arctic Ocean, the sea ice changes in the Antarctica seas are slight



Fig. 6. Schematic image of the impact of sea ice concentration on different aerosol emissions and climate effects.

with the Southern Ocean warming (IPCC5, 2013). A rapid decrease of sea ice in the Antarctica occurred in the spring 2016 has been reported by Stammerjohn et al. (2016). The reduction in sea ice has implications for the emission of aerosols into the atmosphere. Our results suggested that the decrease of sea ice concentration in the spring and summer times in the SO significantly increased SSAs burden in the atmosphere. Additionally, the DMS production and emission were also changed in the SO due to the sea ice retreat in the polar regions (Fig. 6). The enhancement of air DMS concentrations resulted in the increase of SBA concentration in the atmosphere.

Sea ice retreat in the Arctic and Antarctica in the spring and summer times is expected in the future as the continuous global warming, which will affect marine aerosol emissions. The increase in SSA and SBA emissions will increase cloud condensation nuclei (CCN) population. The increases in the number of CCN modulate cloud properties, which enhance the reflection of solar radiation. Hence, the sea surface temperature declines, as the solar radiation reaching the sea surface decrease, which affects the marine phytoplankton activity and further impacts the production and release of DMS (Fig. 6). The observation results in this study extended the knowledge regarding the effects of sea ice changes on marine aerosol emissions in polar regions and their potential climate changes. The burdens of SSA and SBA in the polar atmosphere are determined by a combination of factors. Such factors include the interaction of polar marine microorganisms, seasonality, sea ice coverage, presence or absence of sea spray, and atmospheric heterogeneous processes (Gilgen et al., 2018).

5. Conclusions

An underway aerosol monitoring system was used to determine the aerosol compositions in different sea ice concentration periods in the Southern Ocean (SO), to access the potential effects of sea ice melting on marine aerosol emissions in the SO. SSA was the dominant component of atmospheric aerosols, accounting for 51.11% of aerosols in the SIC region and 76.06% in the SIF region. SBA was another major aerosols in the SO, accounting for 39.98% in the SIC region and 20.40% in the SIF region.

SSA emission increased by more than 30% as sea ice concentration decreased from 85% to 29%. Furthermore, SSA emission did not increase monotonically as sea ice concentration decreased. For example, the highest SSA concentrations were present in the DSI region. Positive correlation between Na⁺ concentrations and wind speed were present in the SIC ($R^2 = 0.69$), DSI ($R^2 = 0.75$), and SIF ($R^2 = 0.22$) regions. The highest slope values between Na⁺ and wind speed occurred in the DSI region, indicating that the existence of sea ice may increase SSA emission in some special conditions. Further studies are required to clarify the variation of SSA emission with sea ice concentration.

The effect of sea ice changes on marine secondary aerosol emissions was indirect and complicated. Therefore, future work should be carried out on the effect of sea ice retreat on the biogenic gases emissions and their conversion processes in the atmosphere, as well as their potential climate effects in the polar regions.

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2020.140773.

Code and data availability

The data used in the figures, as well as the time series of the cruise tracks, aerosol chemical compositions obtained from the IGAC, as well as wind speeds and directions, temperature and RH, are available at https://DOI 10.17605/OSF.IO/B72FS. Codes for the analysis are available from JP upon request.

CRediT authorship contribution statement

Jinpei Yan: Conceptualization, Writing - original draft, Data curation, Visualization, Supervision, Project administration, Funding acquisition.

Jinyoung Jung: Writing - review & editing, Funding acquisition. **Qi Lin:** Formal analysis, Data curation. **Miming Zhang:** Investigation, Resources. **Suqing Xu:** Data curation. **Shuhui Zhao:** Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study is financially supported by Qingdao National Laboratory for Marine Science and Technology (No. QNLM2016ORP0109), the Natural Science Foundation of Fujian Province, China (No. 2019 J01120), the Response and Feedback of the Southern Ocean to Climate Change (RFSOCC2020-2025), the Chinese Projects for Investigations and Assessments of the Arctic and Antarctic (CHINARE2017-2020), the National Natural Science Foundation of China (No. 41941014), the international cooperation program managed by the National Research Foundation of Korea (NRF-2019K2A9A2A06025329) and NSFC (41911540471). Jinyoung Jung was supported by grants from Korea Polar Research Institute (KOPRI) (PE20140). The authors gratefully acknowledge Guangzhou Hexin Analytical Instrument Company Limited for the on-board observation technical assistance, and Zhangjia Instrument Company Limited for the IGAC technical assistance and data analysis.

References

- Barnes, I., Hjorth, J., Mihalopoulos, N., 2006. Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere. Chem. Rev. 106, 940–975.
- Berresheim, H., Huey, J.M., Thorn, R.P., Eisele, F.L., Tanner, D.J., Jefferson, A., 1998. Measurements of dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, and aerosol ions at Palmer Station, Antarctica. J. Geophys. Res. 103, 1629–1637.
- Boetius, A., Albrecht, S., Bakker, K., Bienhold, C., Felden, J., Fernandez-Mendez, M., 2013. Export of algal biomass from the melting arctic sea ice. Sci 339, 1430–1432.
- Browse, J., Carslaw, K.S., Mann, G.W., Birch, C.E., Arnold, S.R., Leck, C., 2014. The complex response of Arctic aerosol to sea-ice retreat. Atmos. Chem. Phys. 14, 7543–7557.
- Carpenter, LJ., Archer, S.D., Beale, R., 2012. Ocean-atmosphere trace gas exchange. Chem. Soc. Rev. 41, 6473–6506.
- Chang, R.Y.-W., Sjostedt, S.J., Pierce, J.R., Papakyriakou, T.N., Scarratt, M.G., Michaud, S., Levasseur, M., Richard Leaitch, W., Abbatt, J.P.D., 2011. Relating atmospheric and oceanic DMS levels to particle nucleation events in the Canadian Arctic. J. Geophys. Res. Atmos. 116, D1716. https://doi.org/10.1029/2011JD015926.
- Chen, L., Wang, J., Gao, Y., Xu, G., Yang, X., Lin, Q., Zhang, Y., 2012. Latitudinal distributions of atmospheric MSA and MSA/nss-SO²₄ – ratios in summer over the high latitude regions of the Southern and Northern Hemispheres. J. Geophys. Res. Atmos. 117, D10306. https://doi.org/10.1029/2011jd016559.
- Collins, D.B., Zhao, D.F., Ruppel, M.J., Laskina, O., Grandquist, J.R., Modini, R.L., Stokes, M.D., Russell, L.M., Bertram, T.H., Grassian, V.H., Deane, G.B., Prather, K.A., 2014. Direct aerosol chemical composition measurements to evaluate the physicochemical differences between controlled sea spray aerosol generation schemes. Atmos. Meas. Tech 7, 3667–3683.
- Dall'Osto, M., Deddows, D.C.S., Tunved, P., Krejci, R., Strom, J., Hansson, H.C., Yoon, Y.J., Park, K.T., Becagli, S., Udisti, R., Onasch, T., O'Dowd, C.D., Simo, R., Harrison, R.M., 2017. Arctic sea ice melt leads to atmospheric new particle formation. Sci. Rep. 7 (3318). https://doi.org/10.1038/s41598-017-03328-1.
- De Baar, H.J., De Jong, J.T., Bakker, D.C., Löscher, B.M., Veth, C., Bathmann, U., Smetacek, V., 1995. Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean. Nature 373, 412–415.
- Deshpande, C., Kambra, A., 2014. Physical properties of the arctic summer aerosol particles in relation to sources at Ny-Alesund, Svalbard. J. Earth Syst. Sci. 123, 201–212.
- Gantt, B., Meskhidze, N., Kamykowski, D., 2009. A new physically-based quantification of marine isoprene and primary organic aerosol emissions. Atmos. Chem. Phys. 9, 4915–4927. https://doi.org/10.5194/acp-9- 4915-2009.
- Ghahremaninezhad, R., Norman, A.-L., Abbatt, J.P.D., Levasseur, M., Thomas, J.L., 2016. Biogenic, anthropogenic and sea salt sulfate size-segregated aerosols in the Arctic summer. Atmos. Chem. Phy. 16, 5191–5202.
- Gilgen, A., Huang, W.T.K., Ickes, L., Neubauer, D., Lohmann, U., 2018. How important are future marine and shipping aerosol emissions in a warming Arctic summer and autumn? Atmos. Chem. Phys. 18, 10521–10555.
- Hayashida, H., Steiner, N., Monahan, A., Galindo, V., Lizotte, M., Levasseur, M., 2017. Implications of sea-ice biogeochemistry for oceanic production and emissions of dimethyl sulfide in the Arctic. Biogeosciences 14, 3129–3155.
- IPCC5, 2013. The Physical Science Basis. Working Group I contribution to the fifth assessment report of the intergovernmental panel on climate change.

Jacobson, M.Z., 2001. Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols. J. Geophys. Res. 106, 1551–1568.

Karl, M., Leck, C., Coz, E., Heintzenberg, J., 2013. Marine nanogels as a source of atmospheric nanoparticles in the high Arctic. Geophys. Res. Lett. 40, 3738–3743. https:// doi.org/10.1002/grl.50661.

Lana, A., Bell, T.G., Simó, R., Vallina, S.M., Ballabrera-Poy, J., Kettle, A.J., Dachs, J., Bopp, L., Saltzman, E.S., Stefels, J., Johnson, J.E., Liss, P.S., 2011. An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean. Glob. Biogeochem. Cycles 25, GB1004. https://doi.org/10.1029/2010GB003850.

Lee, C., Sultana, C.M., Collins, D.B., Santander, M.V., Axson, J.L., Malfatti, F., Cornwell, G.C., Grandquist, J.R., Deane, G.B., Stokes, M.D., Azam, F., Grassian, V.H., Prather, K.A., 2015. Advancing model systems for fundamental laboratory studies of sea spray aerosol using the microbial loop. J. Phys. Chem. A 119, 8860–8870.

Legrand, M., Pasteur, E.C., 1998. Methane sulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow. J. Geophys. Res. 103, 10991–11006.

Lewis, E.R., Schwartz, S.E., 2004. Sea Salt Aerosol Production. Mechanisms, Methods, Measurements, and Models. American Geophysical Union, Washington, DC.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., Zhu, T., 2017. Fine particle pH during severe haze episodes in northern China. Geophys. Res. Lett. 44, 5213–5221.

Marandino, C., Tegtmeier, S., Krüger, K., Zindler, C., Atlas, E., Moore, F., Bange, H.W., 2013. Dimethylsulphide (DMS) emissions from the western Pacific Ocean: a potential marine source for stratospheric sulphur? Atmos. Chem. Phys. 13, 8427–8437.

Mazzera, D.M., Lowenthal, D.H., Chow, J.C., Watson, J.G., 2001. Sources of PM₁₀ and sulfate aerosol at McMurdo Station, Antarctica. Chemosphere 45, 347–356.

Millero, F.J., Sohn, M.L., 1992. Chemical Oceanography. CRC Press, Boca Raton, Fla, p. 531. Minikin, A., Legrand, M., Hall, J., Wagenbach, D., Kleefeld, C., Wolff, E., Pasteur, E.C., Ducroz, F., 1998. Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation. J. Geophys. Res. 103, 10975–10990.

Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-Goddard, R.C., 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. Glob. Biogeochem. Cycles 14, 373–387.

O'Dowd, C.D., Leeuw, G.D., 2007. Marine aerosol production: a review of the current knowledge. Phil. Trans. R. Soc. A 365, 1753–1774.

Patterson, M., Rhodes, R., Allen, C., 2019. Understanding past changes in Southern Ocean sea ice. Eos 100. https://doi.org/10.1029/2019E0119803.

- Prather, K.A., Bertram, T.H., Grassian, V.H., Deane, G.B., Stokes, M.D., Demott, P.J., Aluwihare, L.I., Palenik, B.P., Azam, F., Seinfeld, J.H., Moffet, R.C., Molina, M.J., Cappa, C.D., Geiger, F.M., Roberts, G.C., Russell, L.M., Ault, A.P., Baltrusaitis, J., Collins, D.B., Corrigan, C.E., Cuadra-Rodriguez, L.A., Ebben, C.J., Forestieri, S.D., Guasco, T.L., Hersey, S.P., Kim, M.J., Lambert, W.F., Modini, R.L., Mui, W., Pedler, B.E., Ruppel, M.J., Ryder, O.S., Schoepp, N.G., Sullivan, R.C., Zhao, D., 2013. Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol. Proc. Natl. Acad. Sci. U. S. A. 110, 7550–7555.
- Preunkert, S., Legrand, M., Jourdain, B., Moulin, C., Belviso, S., Kasamatsu, N., Fukuchi, M., Hirawake, T., 2007. Interannual variability of dimethylsulfide in air and seawater and its atmospheric oxidation by-products (methanesulfonate and sulphate) at Dumont d'Urville, coastal Antarctica (1999–2003). J. Geophys. Res. 112, D627. https://doi. org/10.1029/2006jd007585.

Preunkert, S., Jourdain, B., Legrand, M., Udisti, R., Becagli, S., Cerri, O., 2008. Seasonality of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: inland versus coastal regions. J. Geophys. Res. 113, D1516. https://doi.org/10.1029/ 2008[D009937.

Quinn, P.K., Coffman, D.J., Johnson, J.E., Upchurch, L.M., Bates, T.S., 2017. Small fraction of marine cloud condensation nuclei made up of sea spray aerosol. Nat. Geosci. 10, 674–679.

Simó, R., 2001. Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links. Trends in Ecology & Evolution 16, 287–294.

Sorooshian, A., Lu, M.L., Brechtel, F.J., Jonsson, H., Feingold, G., Flagan, R.C., Seinfeld, J.H., 2007. On the source of organic acid aerosol layers above clouds. Environ. Sci. Technol. 41, 4647–4654. Spiel, D.E., 1998. On the births of film drops from bubbles bursting on seawater surfaces. J. Geophys. Res. 103, 24907–24918.

Spracklen, D.V., Arnold, S.R., Sciare, J., Carslaw, K.S., Pio, C., 2008. Globally significant oceanic source of organic carbon aerosol. Geophys. Res. Let. 35, L12811. https://doi.org/ 10.1029/2008GL033359.

Spreen, G., Kaleschke, L., Heygster, G., 2008. Sea ice remote sensing using AMSR-E 89 GHz channels. J. Geophys. Res. 113, C02S03.Stammerjohn, S., Scambos, T., Blunden, J., Arndt, D.S., 2016. State of the climate in 2016:

Stammerjohn, S., Scambos, T., Blunden, J., Arndt, D.S., 2016. State of the climate in 2016: Antarctica. Bulletin of the American Meteorological Association. 98, S1–S280.Stokes, M.D., Deane, G.B., Prather, K., Bertram, T.H., Ruppel, M.J., Ryder, O.S., Brady, J.M.,

Stokes, M.D., Deane, G.B., Prather, K., Bertram, T.H., Ruppel, M.J., Ryder, O.S., Brady, J.M., Zhao, D.A., 2013. Marine aerosol reference tank system as a breaking wave analogue for the production of foam and sea-spray aerosols. Atmos. Meas. Tech 6, 1085–1094.

Struthers, H., Kirkevag, A., Seland, O., Martensson, E.M., Noone, K., Nilsson, E.D., 2013. Climate-induced changes in sea salt aerosol number emissions: 1870 to 2100. J. Geophys. Res. Atmos. 118, 670–682.

Takemura, T., Nakajlma, T., Dubovik, O., Holben, B.N., Kinne, S., 2002. Single-scattering albedo and radiative forcing of various aerosol species with a global three-dimensional model. J. Clim. 15, 333–352.

Taylor, M.H., Losch, M., Bracher, A., 2013. On the drivers of phytoplankton blooms in the Antarctic marginal ice zone: a modeling approach. J. Geophys. Res. 118, 63–75.

Teinila, K., Frey, A., Hillamo, R., Tulp, H.C., Weller, R., 2014. A study of the sea-salt chemistry using size-segregated aerosol measurements at coastal Antarctic station Neumayer. Atmos. Environ. 96, 11–19.

Thomas, D.N., Dieckmann, G.S., 2002. Antarctic sea ice-a habitat for extremophiles. Sci. 295, 641–644.

Tovar-Sanchez, A., Duarte, C.M., Alonso, J.C., Lacorte, S., Tauler, R., Galban-M alagon, C., 2010. Impacts of metals and nutrients released from melting multiyear Arctic sea ice. J. Geophys. Res. 115, C07003. https://doi.org/10.1029/2009JC005685.

Vaughan, D., Comiso, J., Allison, I., Carrasco, I., Kaser, G., Kwok, R., Mote, P., Murray, T., Paul, F., Ren, J., Rignot, E., Solomina, O., Steffen, K., Zhang, T., 2013. Observations: cryosphere. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Vignati, E., Facchini, M.C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., O'Dowd, C.D., 2010. Global scale emission and distribution of sea-spray aerosol: sea-salt and organic enrichment. Atmos. Environ. 44, 670–677.

Wang, S., Bailey, D., Lindsay, K., Moore, J.K., Holland, M., 2014. Impact of sea ice on the marine iron cycle and phytoplankton productivity. Biogeosciences 11, 4713–4731.

Wang, X., Sultana, C.M., Trueblood, J., Hill, T.C.J., Malfatti, F., Lee, C., Laskina, O., Moore, K.A., Beall, C.M., McCluskey, C.S., Cornwell, G.C., Zhou, Y., Cox, J.L., Pendergraft, M.A., Santander, M.V., Bertram, T.H., Cappa, C.D., Azam, F., DeMott, P.J., Grassian, V.H., Prather, K.A., 2015. Microbial control of sea spray aerosol composition: a tale of two blooms. ACS Cent. Sci. 1, 124–131.

Warneck, P., 1988. Chemistry of the Natural Atmosphere. San Diego Academic.

Wolff, E., 1995. Nitrate in polar ice. Ice Core Studies of Global Biogeochemical Cycles. Springer-Verlag, New York, pp. 195–224.

Xu, G., Gao, Y., Lin, Q., Li, W., Chen, L., 2013. Characteristics of water-soluble inorganic and organic ions in aerosols over the Southern Ocean and coastal East Antarctica during austral summer. J. Geophy. Res. Atmos. 118, 13303–13318.

Yan, J., Chen, L., Lin, Q., Li, Z., Chen, H., Zhao, S., 2015. Chemical characteristics of submicron aerosol particles during a long-lasting haze episode in Xiamen, China. Atmos. Environ. 113, 118–126.

Yan, J., Lin, Q., Zhao, S., Chen, L., Li, L., 2018. Impact of marine and continental sources on aerosol characteristics using an on-board SPAMS over Southeast Sea, China. Environ. Sci. Pollution Res. 25, 30659–30670.

Yan, J., Jung, J., Zhang, M., Xu, S., Lin, Q., Zhao, S., Chen, L., 2019. Significant underestimation of gaseous methanesulfonic acid (MSA) over Southern Ocean. Environ. Sci. Technol. 53, 13064–13070.