New particle formation events observed at the King Sejong Station, Antarctic Peninsula – Part 2: Link with the oceanic biological activities

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Abstract. Marine biota is an important source of atmospheric aerosols in the remote marine atmosphere. Long-term observations (from 2009 to 2016) of the physical properties of atmospheric aerosol particles measured at the Antarctic Peninsula (King Sejong Station; 62.2°S, 58.8°W) and satellite-derived estimates of the biological characteristics were analyzed to identify the link between new particle formation and marine biota. New particle formation events in the Antarctic atmosphere showed distinct seasonal variations, with the highest values occurring during austral summer (December, January and February). Interestingly, new particle formation events were more frequent in the air masses that originated from the Bellingshausen Sea than in those that originated from the Weddell Sea. The monthly mean number concentration of nanoparticles (2.5−10 nm in diameter) was >2-fold when the air masses passed over the Bellingshausen Sea than the Weddell Sea, whereas the biomass of phytoplankton in the Weddell Sea was more than ~70% higher than that of the Bellingshausen Sea during the austral summer period. Dimethyl sulfide (DMS) is of marine origin and its oxidative products are known to be one of the major components in the formation of new particles. Both satellite-derived estimates of the biological characteristics (dimethylsulfoniopropionate (DMSP; precursor of DMS) and phytoplankton taxonomic composition) and in situ methanesulfonic acid (MSA; oxidation product of DMS) analysis revealed that DMS(P)-rich phytoplankton were more dominant in the Bellingshausen Sea than in the Weddell Sea. Furthermore, the number concentration of nanoparticles was positively correlated with the biomass of phytoplankton during the period when DMS(P)-rich phytoplankton predominate. These results indicate that oceanic DMS emissions could play a key role in the formation of new particles; moreover, the taxonomic composition of phytoplankton could affect the formation of secondary organic aerosols in the Antarctic Ocean.

1 Introduction

Aerosols in the atmosphere significantly influence radiative forcing directly (by scattering incoming radiation) and indirectly (by modifying cloud micro-physical properties) (IPCC, 2013). Considering that the ocean surface accounts for approximately 70% of the total surface of the Earth, the marine aerosols are globally one of the most
5   important natural aerosol systems (O'Dowd et al., 2004; Leck and Bigg, 2005; O'Dowd and De Leeuw, 2007). Marine aerosols consist of primary and secondary aerosols. The primary aerosols are produced via the bubble bursting process and include mostly sea-salts and organic matter (O'Dowd and De Leeuw, 2007). Secondary aerosols (resulting from gas-to-particle conversion) are produced in the marine atmosphere through several different processes (e.g., binary, ternary and ion-induced) (Kulmala et al., 1990; Korhonen et al., 1999; Lee et al.,
10   2003; Lovejoy et al., 2004). Biogenic volatile organic compounds emitted into the marine atmosphere through air-sea gas exchange, and their oxidative products can be involved in new particle formation events via the nucleation of stable clusters of the order of 0.5–1 nm in size (O'Dowd and De Leeuw, 2007).

In the Antarctic, most submicron aerosol particles are derived from natural sources rather than from long-range transport of anthropogenic sources (Ito, 1989; Kyrö et al., 2013). The Southern Ocean has been considered as the
15   most significant source of secondary organic aerosols in the Antarctic atmosphere, especially during the phytoplankton bloom period (Asmi et al., 2010; Yu and Luo, 2010). In addition, high biological activities in melt ponds and at sea-ice edges also have an important influence on the total burden of organic aerosols (Kyrö et al., 2013; Dall'Osto et al., 2017). The Antarctic Peninsula is one of the three areas of the globe facing drastic regional warming, and it undergoes rapid environmental changes (i.e., increased temperature, acidification, shallowing
20   mixed layer depth, sea-ice decline, increased light, increased nutrient supply, reduced salinity and glacial retreat) (Clarke et al., 2007; Deppeler and Davidson, 2017). Such environmental changes in this region could significantly affect the marine ecosystem. Marine phytoplankton influence aerosol properties by releasing various organic compounds back into the atmosphere. The Antarctic Ocean is known to be a significant source of numerous biogenic volatile organic compounds including dimethyl sulfide (DMS), organic nitrogen and halogenated organic
25   compounds (Laturnus et al., 1996; Beyersdorf et al., 2010; Dall'Osto et al., 2017; Giordano et al., 2017). In particular, the Antarctic Ocean is the region with the highest sea-surface DMS concentration (Lana et al., 2011). Observations of both DMS and its oxidative products (i.e., methanesulfonic acid (MSA) and non-sea-salt SO_4^{2-}) in Antarctica show a clear seasonal cycle with a minimum in austral winter and a maximum in austral summer (Prospero et al., 1991; Minikin et al., 1998; Preunkert et al., 2007; Read et al., 2008). DMS is produced by a
30   complex marine biota food-web mechanism (Stefels et al., 2007; Park et al., 2014a). Phytoplankton produce dimethylsulfoniopropionate (DMSP) and then some of the DMSP is converted into gaseous DMS through enzymatic cleavage (Simó, 2001). The biogenic emission of DMS from the ocean is the largest natural sulfur source to the atmosphere (Andreae, 1990) and, the oxidation of DMS in the marine atmosphere is a key process contributing to the formation of new particles (Park et al., 2017). Once the DMS in the sea-surface is emitted into
35   the atmosphere, it is rapidly converted into SO_2 and MSA through the photochemical oxidation process. The SO_2 and MSA formed from DMS tend to contribute to the formation of new particles via nucleation processes and eventually serve as nuclei for cloud formation (Charlson et al., 1987). Secondary organic aerosols contribute to a large fraction of the submicron aerosol mass in the atmosphere, affecting clouds and climate (Jimenez et al., 2009). However, secondary organic aerosols are a source of considerable uncertainty in understanding current climate

change (Shiraiwa et al., 2017). In particular, the formation of new particles in the remote marine atmosphere and their association with marine biota remains poorly quantified.

In this study, we aimed to identify the link between new particle formation and marine biota at a remote Antarctic site, where biological productivity is the highest in the global ocean. To this end, we analyzed the physical and chemical properties of aerosol particles at King Sejong Station (62.2ºS, 58.8ºW) on the Antarctic Peninsula from 2009 to 2016. To study the oceanic biological characteristics surrounding the observation site, we analyzed satellite-derived estimates including the chlorophyll concentration, total DMSP concentration and taxonomic composition of marine phytoplankton.

2 Experimental Methods

2.1. Aerosol measurements

King Sejong Station (62.2ºS, 58.8ºW) is located on the Antarctic Peninsula where severe climate change is occurring (Fig. 1a). The aerosol observatory is approximately 400 m southwest of the main facilities of King Sejong Station and approximately 10 m above sea level (m.a.s.l). Continuous observations of the physical properties of aerosol particles in the Antarctic atmosphere were conducted between March 2009 and December 2016 at the observatory. The number concentration of aerosol particles (CN) was measured using two condensation particle counters (CPCs) that have different measurement range limits for particle diameter: particles larger than 2.5 nm ($CN_{2.5}$; TSI model 3776) and particles larger than 10 nm (CN_{10}; TSI model 3772). The difference in the particle number concentration between the two CPCs (i.e., particles between 2.5 and 10 nm in diameter) was interpreted as an indication of the existence of newly formed nanoparticles ($CN_{2.5-10}$). An Aethalometer (Magee Scientific model AE16) was used to analyze the concentration of black carbon by measuring light-absorbing particles at the 880 nm wavelength. To avoid local influence on the aerosol properties, data with a black carbon concentration of >100 ng were excluded. Data were also excluded when the wind direction was between 355° and 55°. This is because the north-eastern direction is designated the local air pollution sector due to emissions from the power generators and crematory. More detailed information regarding the aerosol particle analysis at King Sejong Station is provided by Kim et al. (2017 and 2018).

For analysis of chemical properties of aerosol particle, an air sampler equipped with a PM_{10} impactor (collecting particles <10 µm in aerodynamic equivalent diameter) was used to collect aerosol particles. The sampler was mounted on the roof of the aerosol observatory and sampled particles every 24 hours during the summer period in 2013 and 2014 (explicitly, from 14 January to 28 February in 2013, and from 1 December 2013 to 13 January 2014). Half of a 47-mm Teflon filter was used to measure major ions including MSA. The MSA (and the other ions) collected on the filter was extracted into about 10 mL (18 MΩ Milli-Q) in ultrasonic bath for 20 min. MSA was determined by an ion chromatography system (Dionex, Thermo Fisher Scientific Inc.) following the procedure described by Becagli et al. (2012). For MSA, reproducibility on real samples was better than 5%. Filter blank concentrations for methanesulphonate were always below the detection.

2.2. Air-mass back trajectories

The air mass back trajectories and meteorological parameters were obtained using the Hybrid Single-Particle Lagrangian Integrated Trajectories model (Draxler and Hess, 1998). The 2-day air mass back trajectories and hourly positions were determined and combined with satellite-derived geographical information to identify the travel history of the air mass arriving at the observation site. Daily geographical information on sea-ice, and the land and ocean area was obtained from the Sea Ice Index at a 25-km resolution provided by the National Snow and Ice Data Center (NSIDC). The oceanic region adjacent to the observation site was surrounded by two different ocean basins, namely, the Bellingshausen and Weddell seas. To evaluate the influence of the oceanic biological characteristics on the occurrence of new particle formation, we limited our analysis to the air masses that had exposure predominantly to the ocean area. Specifically, the origin of the hourly air mass arriving at the observation site was divided into two ocean domains (i.e., the Bellingshausen and Weddell seas). Then, all air mass back trajectories were grouped into one of the two ocean domains by only selecting the 2-day air mass back trajectories that had >90% retention in a given ocean domain.

2.3. Phytoplankton biomass, DMSP and taxonomic composition analysis

Satellite-derived ocean color provide a good measure of analyzing the phytoplankton characteristics of the Southern Ocean (Siegel et al., 2013; Haentjens et al., 2017). The phytoplankton biomass of the two ocean domains was estimated by calculating the chlorophyll concentration from the Moderate Resolution Imaging Spectroradiometer on the Aqua (MODIS-Aqua) satellites at 4 km resolution during the study period (2009–2016). The trajectory concentration of the air masses originating from the two ocean domains was calculated from the ratio of the number of hourly trajectory points passing over each grid cell ($1° \times 1°$) to the total number of hourly trajectory points (Kim et al., 2011), as shown in Fig. 1a. We limited our analysis of satellite-derived chlorophyll concentration to the ocean area for which the trajectory concentration was approximately over 0.1% (55–65°S, 40–60°W for the Weddell Sea and 55–65°S, 60–80°W for the Bellingshausen Sea). The total DMSP concentration in the sea-surface was estimated using the algorithm developed by Galí et al. (2015). The algorithm for the total DMSP concentration was based on the satellite-derived chlorophyll concentration and the light exposure regime (see Supplement for more information). We estimated the taxonomic phytoplankton composition of the two ocean domains using the PHYSAT method. This method is a bio-optic model that was specifically developed to identify the dominant phytoplankton groups from ocean color measurements. Phytoplankton groups are generally characterized by specific pigment, shape and size that have different light scattering and absorption properties (Alvain et al., 2005). Therefore, the PHYSAT method can be used to classify sea-surface phytoplankton into five groups including diatoms, Prochloroccocus, nanoeucaryotes, Synechococcus and phaeocystis simultaneously with the chlorophyll concentration (Alvain et al., 2008; Mustapha et al., 2014). The monthly data set of phytoplankton groups at a resolution of 9 km was obtained from the PHYSAT database (http://log.univ-littoral.fr/Physat), and was estimated between 1997 and 2010. The period of the PHYSAT analysis did not coincide with the period of aerosol analysis. This is because the PHYSAT method was developed and calibrated based on daily global data derived from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) that had been operated from September 1997 to December 2010.

3 Results and Discussion

3.1. Seasonal variabilities of nanoparticles at King Sejong Station

The number concentration of aerosol particles increased gradually from early spring, peaked in the austral summer period (December, January and February) and then began to decrease (Fig. S1). The number concentration of nanoparticles (2.5–10 nm in diameter, $CN_{2.5-10}$), which is an indication of newly formed particles, also shows distinct seasonal variation. The physical aspects of new particle formation event observed at the same site are explained in detail in Kim et al. (2018) that submitted in this issue. The 2-day air mass back trajectory combined with geographical information showed that approximately 78.5% of the hourly trajectory points were assigned to the ocean, followed by sea-ice (16.3%) and land (5.2%) during the austral summer period (Fig. S2). The hourly mean concentration of nanoparticles matched with the hourly air mass back trajectory in this study. A total of 22,469 hourly mean number concentrations of nanoparticles were measured above the Antarctic atmosphere over the 8 years. Approximately 38.2% of the hourly mean number concentration of nanoparticles, which satisfy the >90% retention of hourly trajectory points over the two ocean domains, were used to estimate the link between new particle formation and the oceanic biological characteristics around the observation site. The monthly mean number concentration of nanoparticles that originated from the Bellingshausen Sea was highest in January (835.9 ± 2673.2 cm^{-3}) and ~2.5-times greater than that which originated from the Weddell Sea (332.0 ± 920.7 cm^{-3}; Fig. 1b and Table S1). The differences in the number concentration of nanoparticles that originated from the two ocean domains were particularly noticeable during the months of January and February (699.2 ± 2454.8 cm^{-3} for the Bellingshausen Sea and 302.5 ± 744.6 cm^{-3} for the Weddell Sea, $p < 0.001$; Fig. 1b and Table S1). However, the differences were not evident between April and October (85.9 ± 231.6 cm^{-3} for the Bellingshausen Sea and 75.0 ± 90.0 cm^{-3} for the Weddell Sea, $p = 0.145$; Fig. 1b and Table S1).

3.2. Biological characteristics surrounding the observation site

In general, the abundance and composition of phytoplankton show distinct spatial and seasonal variation in the Antarctic Ocean (Sullivan et al., 1993). Primary production in the Antarctic Ocean is strongly controlled by various factors such as iron limitation, light availability and mixed layer depth (Arrigo et al., 1999; Sedwick et al., 2007; Park et al., 2013). The composition of the phytoplankton community is poorly studied in the Antarctic Ocean except for the marginal zone at the Antarctic Peninsula. Nevertheless, both phaeocystis and diatoms (mainly *Phaeocystis antarctica* and *Fragilariopsis cylindrus*) are well known as dominant phytoplankton groups in the Antarctic Ocean during the phytoplankton bloom period (Kropuenske et al., 2009; Arrigo et al., 2010). The monthly mean chlorophyll concentration around the observation site (55ºS–65ºS, 40ºW–80ºW) began to increase in October and reached its maximum in November and December during the study period (Fig. S3a). The biological characteristics of the two ocean domains showed notable differences. The monthly mean chlorophyll concentration in the Weddell Sea (0.49 ± 0.07 mg m^{-3}) was ~70% higher than that of the Bellingshausen Sea (0.29 ± 0.05 mg m^{-3}) during the phytoplankton growth period (October–February; Fig. 2a and Fig. S3b). The PHYSAT analysis, which was applied from 1997 to 2010, revealed that the distribution of the dominant phytoplankton groups showed distinct patterns (Fig. 2b). Diatoms were the most abundant and ~35% of the satellite pixels were dominated by diatoms during the austral summer period in the Weddell Sea (Fig. 2b and Fig. S4b). Conversely,

the dominance of phaeocystis increased significantly and accounted for more than 50% in the Bellingshausen Sea during the months of January and February, while the contribution of the diatom decreased below 10% (Fig. 2b and Fig. S4a).

The production of DMS and DMSP is species-specific. For example, diatoms, picoplankton (i.e., Synechococcus and Prochloroccoccus) and most nanoeucaryotes are known to be DMS(P)-poor species. Conversely, phaeocystis and dinoflagellates have a high cellular DMSP content and many of them possess a DMSP cleavage enzyme that can convert DMSP into gaseous DMS (Keller, 1989; Stefels et al., 2007; Park et al., 2014b). In particular, *Phaeocystis antarctica* was reported to be a dominant species in terms of DMS production in the Antarctic Ocean during the bloom period (Gibson et al., 1990; Schoemann et al., 2005), exhibiting a cellular DMSP concentration in phaeocystis 10–100 times that of diatoms (Hatton and Wilson, 2007; Stefels et al., 2007). Therefore, the DMSP to chlorophyll ratio can reflect the differences in the taxonomic composition of the two ocean domains (Park et al., 2018). The DMSP to chlorophyll ratio in the Bellingshausen Sea (110.2 ± 27.8 mmol g^{-1}) was ~2-fold higher than that of the Weddell Sea (72.2 ± 8.3 mmol g^{-1}) between December and February in 2009–2016 (Fig. 2c and Fig. S5).

3.3. Influence of phytoplankton on aerosol formation

MSA in the marine atmosphere forms exclusively from the photooxidation of DMS, and shows strong seasonal variation (Ayers and Gras, 1991; Savoie et al., 1993; Preunkert et al., 2008). A previous study has reported that the highest values for both MSA and the scattering Ångström exponent (SAE; qualitative examination of the aerosol optical mean size) were observed at the Marambio Station (64.3°S, 56.6°W) on the Antarctic Peninsula during austral summer in 2013–2015 (Asmi et al., 2018). The MSA concentration of the fine aerosol particles measured at the King Sejong Station during the summer period in 2013 and 2014 was broadly consistent with the number concentration of nanoparticles. The MSA concentration also showed distinct differences depending on the air mass origin. The inflow of the air masses from the Bellingshausen Sea increased the concentration of MSA in the aerosol particles. Notably, the MSA concentration that originated from the Bellingshausen Sea was ~7-times higher than that which originated from the Weddell Sea during the austral summer period in 2013–2014 (Fig. 3). Although the period of satellite observations and in situ chemistry analysis is not exactly the same, both multi-year satellite-derived biological characteristics and aerosol chemistry data support the interpretation that there was higher abundance of DMS(P)-rich phytoplankton in the Bellingshausen Sea than in the Weddell Sea during the austral summer period (Fig. 2, Fig. 3, Figs. S3, S4 and S5).

In the 8-year record, the monthly mean chlorophyll concentration was positively correlated with the monthly mean number concentration of nanoparticles for the air masses that originated from the Bellingshausen Sea in January and February ($r^2 = 0.69$, $n = 12$, $P < 0.05$; Fig. 4a). During this period, the contribution of the DMS(P)-rich phaeocystis to the chlorophyll concentration was highest in the Bellingshausen Sea (i.e., DMSP to chlorophyll ratio >100 mmol g^{-1}; dominance of phaeocystis >50%; dominance of diatoms <10%; Fig. 2, Fig. S4a and Fig. S5). Conversely, the increase in the chlorophyll concentration was not correlated with the increase in the number concentration of nanoparticles in the Weddell Sea (Fig. 4b). As a consequence, the higher occurrence of nanoparticles from the Bellingshausen Sea inferred from our analysis was likely to be associated with a higher

abundance of DMS(P)-rich phytoplankton, whereas the lower occurrence of nanoparticles from the Weddell Sea appeared to be associated with a higher abundance of DMS(P)-poor phytoplankton.

4 Conclusions

5   The physical properties of aerosol particles measured above the remote Antarctic Peninsula over 8 years were analyzed in conjunction with the satellite-derived biological characteristics around the observation site. These results show that the formation of nanoparticles was strongly associated not only with the biomass of phytoplankton but, more importantly, also its taxonomic composition in the Antarctic Ocean. Previous studies have reported that diatoms have a competitive advantage under conditions in which the mixed layers are shallow

10   and the light levels are relatively high. Conversely, phaeocystis is well adapted to conditions in which mixed layers are deep and light levels are variable (e.g., Weber and El-Sayed, 1987; Arrigo et al., 1999; Goffart et al., 2000; Alvain et al., 2008; Arrigo et al., 2010). These results are consistent with the distribution of phytoplankton groups in the Bellingshausen and Weddell seas. Given that the mixed layer depth in the Bellingshausen Sea (45.6 ± 4.1 m) was relatively deeper than that of the Weddell Sea (36.2 ± 3.8 m; Fig. S6) during the austral summer

15   period, the growth of DMS(P)-rich phaeocystis may therefore be more favorable in the Bellingshausen Sea.
Sea-surface warming and freshening is commonly associated with a shallowing of the mixed layer depth (Capotondi et al., 2012). The warming trend has shown the spatial complexity across the Antarctic Ocean in recent decades (Turner et al., 2005). Therefore, all regions of the Antarctic Ocean will experience different changes in phytoplankton productivity and taxonomic composition in response to the climate change (Deppeler and Davidson,

20   2017). Changes in the marine ecosystem could significantly influence the formation of aerosols and clouds in the remote marine atmosphere (Wang et al., 2018). Continuous measurements of the physiochemical properties of aerosols and key nucleation compounds are needed to improve our knowledge regarding the association between marine biota and the formation of aerosol particles and to understand their climate feedback roles in the remote marine environment.

25   **Author contributions**

KTP, JEH, TWK, JSK and YYJ designed the study. YYJ and YTG analyzed the physical properties of the aerosol particles. HSB, SB and RT operated the air sampler and analyzed the MSA. KTP and JEH wrote the manuscript.

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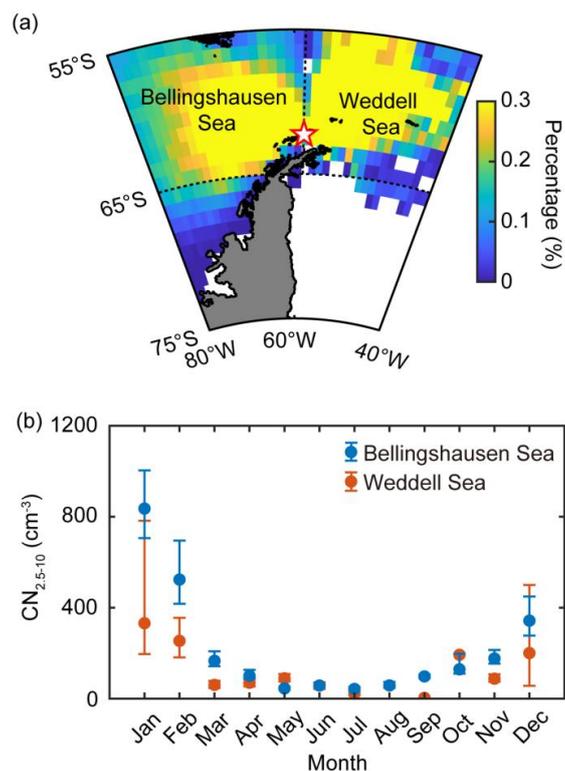
Figure 1: (a) Back-trajectories of the air masses arriving at King Sejong Station (62.2ºS, 58.8ºW; star symbol),
Antarctic Peninsula. The colors indicate the percentage (%) of the air mass located at that spot during the 2 days
prior to arriving at the observation site. Note that the air mass back-trajectories that did not have >90% retention
in the two selected ocean domains (i.e., Bellingshausen and Weddell Seas) were excluded. (b) Seasonal variation
of nanoparticles (2.5–10 nm in diameter, $CN_{2.5-10}$) observed at King Sejong Station between March 2009 and
December 2016. Blue and red symbols indicate the number concentration of nanoparticles that originated from
the Bellingshausen and Weddell seas, respectively. The error bars indicate the 95% confidence interval estimated
by bootstrap method from the monthly $CN_{2.5-10}$ data (see Table S1 for more detailed statistical analysis).
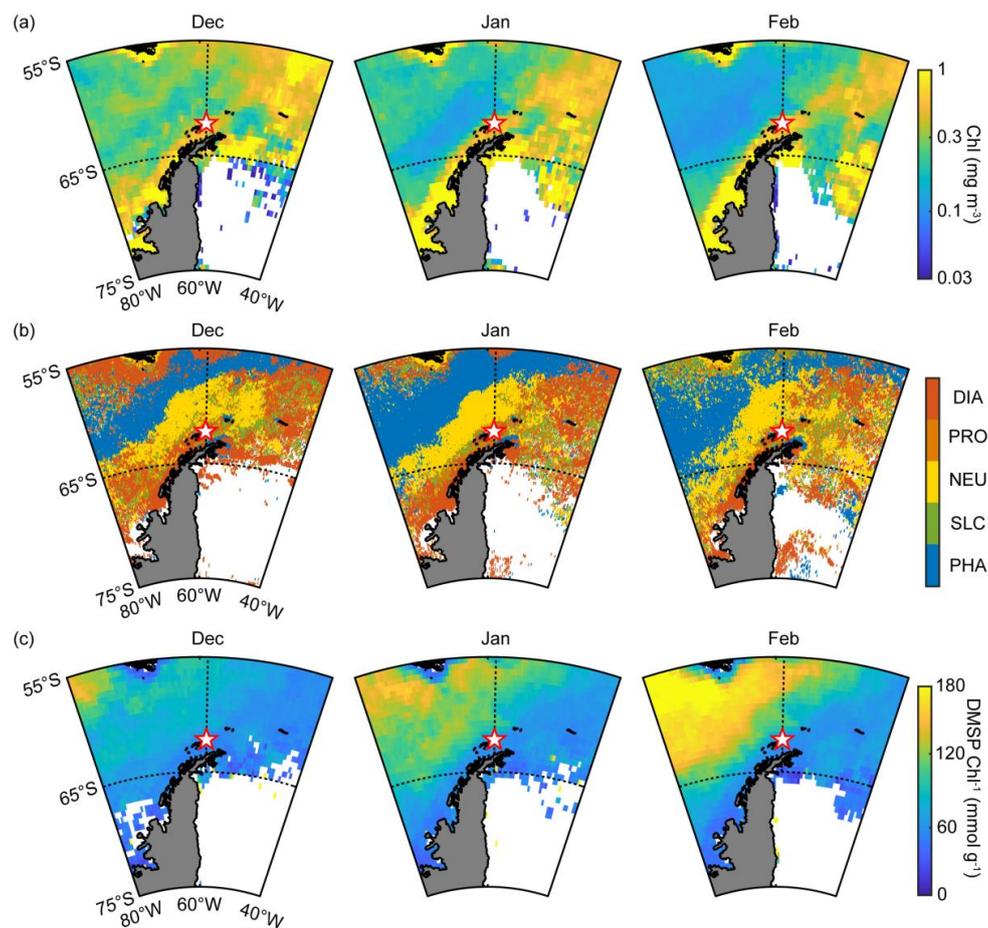
Figure 2: (a) Monthly mean chlorophyll concentration during the months of December, January and February in 2009–2016, (b) phytoplankton taxonomic composition including diatoms (DIA), Prochloroccoccus (PRO), nanoeucaryotes (NEU), Synechococcus (SLC) and phaeocystis (PHA) during the months of December, January and February in 1997–2010, (c) monthly mean DMSP to chlorophyll ratio during the months of December, January and February in 2009–2016. Note that the phytoplankton taxonomic composition was estimated using the SeaWiFS (Sea-viewing Wide Field-of-View Sensor) ocean color sensor which is available from September 1997 to December 2010.
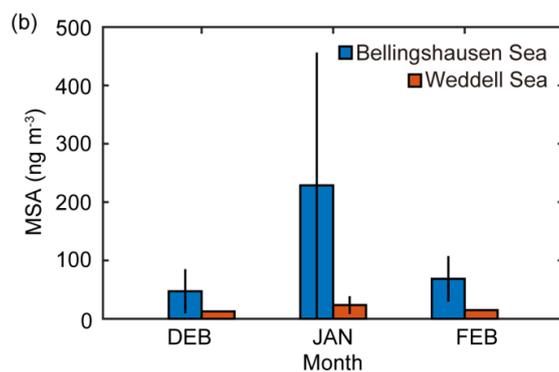
Figure 3: Monthly mean MSA concentration that originated from the Bellingshausen Sea (blue bars) and the Weddell Sea (red bars) during the months of December, January and February in 2013 and 2014. The error bars indicate 1 standard deviation (1σ) from the monthly mean values.
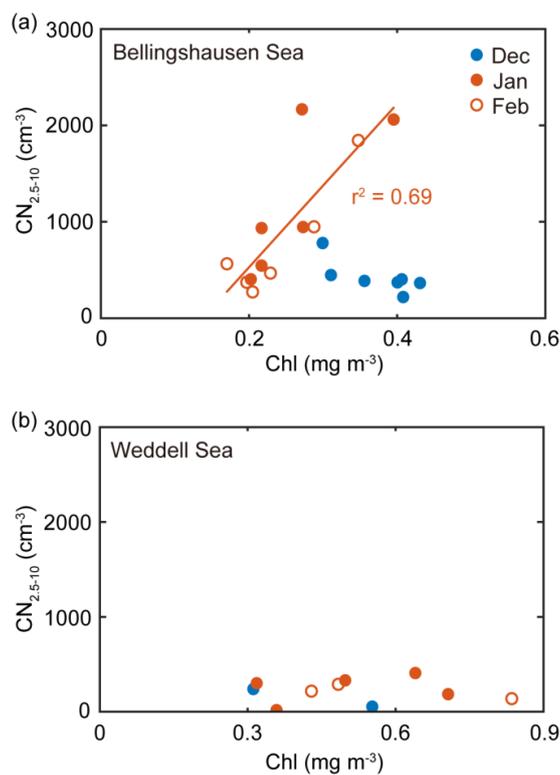
Figure 4: (a) Relationship between the monthly mean chlorophyll concentration for the Bellingshausen Sea (55°S–65°S, 60°W–80°W) and the monthly mean number concentration of nanoparticles that originated from the Bellingshausen Sea in 2009–2016. (b) Relationship between the monthly mean chlorophyll concentration for the Weddell Sea (55°S–65°S, 40°W–60°W) and the monthly mean number concentration of nanoparticles that originated from the Weddell Sea in 2009–2016. The filled blue, filled red and open red symbols indicate the data obtained in December, January and February, respectively. The solid lines represent the best fit.