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Influence of Biogenic Organics on the Chemical Composition of Arctic Aerosols

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Key Points:
- The molecular compositions of Arctic organic aerosols were identified using an ultrahigh-resolution mass spectrometer (15T FT-ICR MS)
- The molecular characteristics of Arctic organic aerosols showed distinct differences depending on their potential source origin
- The accumulation of biogenic organics in Arctic surface water could significantly influence the chemical properties of Arctic aerosols

Supporting Information:
- Supporting Information S1
- Data Set S1

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Abstract We use an ultrahigh-resolution 15-T Fourier transform ion cyclotron resonance mass spectrometer to elucidate the compositional changes in Arctic organic aerosols collected at Ny-Ålesund, Svalbard, in May 2015. The Fourier transform ion cyclotron resonance mass spectrometer analysis of airborne organic matter provided information on the molecular compositions of aerosol particles collected during the Arctic spring period. The air mass transport history, combined with satellite-derived geographical information and chlorophyll concentration data, revealed that the molecular compositions of organic aerosols drastically differed depending on the origin of the potential source region. The protein and lignin compound populations contributed more than 70% of the total intensity of assigned molecules when the air masses mainly passed over the ocean region. Interestingly, the intensity of microbe-derived organics (protein and carbohydrate compounds) was positively correlated with the air mass exposure to phytoplankton biomass proxied as chlorophyll. Furthermore, the intensities of lignin and unsaturated hydrocarbon compounds, typically derived from terrestrial vegetation, increased with an increase in the advection time of the air mass over the ocean domain. These results suggest that the accumulation of dissolved biogenic organics in the Arctic Ocean possibly derived from both phytoplankton and terrestrial vegetation could significantly influence the chemical properties of Arctic organic aerosols during a productive spring period. The interpretation of molecular changes in organic aerosols using an ultrahigh-resolution mass spectrometer could provide deep insight for understanding organic aerosols in the atmosphere over the Arctic and the relationship of organic aerosols with biogeochemical processes in terms of aerosol formation and environmental changes.

1. Introduction

Aerosols play an important role in Earth's current climate due to their impact on the global radiative balance and cloud microphysics (Brooks & Thornton, 2018; de Leeuw et al., 2011; Gantt & Meskhidze, 2013). Marine aerosols constitute one of the most important natural aerosol systems globally, as oceans cover more than 70% of Earth's surface (Brooks & Thornton, 2018). Marine aerosols comprise primary and secondary aerosol components. Primary marine aerosols consist of sea salt and organic species (de Leeuw et al., 2011). The production of primary marine aerosols occurs at the air-sea interface via the bubble-bursting process, resulting in sea spray particles (O'Dowd & de Leeuw, 2007). Secondary aerosol production occurs through the nucleation of gaseous precursors (e.g., sulfuric acid, ammonia, halocarbons, isoprene, and monoterpenes; Kulmala & Kerminen, 2008; Kirkby et al., 2011; Ehn et al., 2014; Ovadnevaite et al., 2017). Recently, several field and laboratory studies have shown that the physiochemical properties of primary and secondary marine organic aerosols are significantly related to biological activities at the ocean surface (O'Dowd et al., 2004; Facchini, Decesari, et al., 2008; Facchini, Rinaldi, et al., 2008; O'Dowd et al., 2015; Park et al., 2017; Rastelli et al., 2017; Jang, Park, et al., 2019).

The Arctic environment is one region that is the most vulnerable to climate change (IPCC, 2013). Aerosol particles may perturb the radiative balance of the Arctic in numerous ways (Carslaw et al., 2013). The physiochemical properties of Arctic aerosols (e.g., number concentration, size distribution, and major ion composition) exhibit pronounced seasonal variations (Tunved et al., 2004; Udisti et al., 2016). These seasonal variations appear to be controlled by both dominating sources and meteorological conditions. For example, atmospheric constituents in the Arctic are impacted by the transport of particles that originate from continents more intensively during the winter and early spring (known as Arctic haze) than summer. Following the period of Arctic haze, a sharp transition in the properties of aerosol particles has been identified (Hansen et al., 2014; Tunved et al., 2013; Udisti et al., 2016). In particular, dimethyl sulfide-derived SO_4^{2-} plays a key role in the formation and growth of secondary aerosol particles (Giamarelou et al., 2016), and organic-rich particles significantly contribute to the total aerosol mass in the atmosphere over the Arctic during the productive spring-summer period (Park et al., 2017; Willis et al., 2017). Organic aerosols can constitute large fractions (20 to 90%) of the submicron particle mass in the lower troposphere (Kanakidou et al., 2005; O'Dowd et al., 2004). However, the effects of organic aerosols on radiative climate forcing are largely uncertain (Jimenez et al., 2009) because multiple sources, complex aging processes, sea ice loss feedbacks, and source origins of organic aerosols are not fully understood (Gantt & Meskhidze, 2013). To comprehensively investigate the evolution of organic aerosols in the remote Arctic environment, identifying the molecular characteristics of organic particles in the atmosphere is needed, and advanced analytical tools should be applied to directly compare the complicated chemical compositions of organic matter taken from the ocean and atmosphere (Brooks & Thornton, 2018). Therefore, a molecular-level description of organic aerosols is necessary for better understanding the magnitude and direction of ongoing climate changes in this fragile environment.

An ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) has been successfully used to resolve exceptionally complicated organic samples, such as crude oils and various organic matter derived from soil or water, by acquiring ultrahigh-accuracy mass profiles of the samples, resulting in fast and accurate interpretations of the elemental compositions of complicated samples (Antony et al., 2014; Lobodin et al., 2014; Cho et al., 2015; Guigue et al., 2016; Ksionzek et al., 2016; Mazur et al., 2016; Jang, Choi, et al., 2019). Due to the versatile applicability of various ionization methods (i.e., electrospray ionization [ESI], atmospheric pressure chemical ionization, atmospheric pressure photoionization, and laser desorption ionization), an FT-ICR MS can detect a wide range of target molecules, ranging from polar species to nonpolar species (Choi et al., 2017; Rathsack et al., 2015; Vahur et al., 2012). In particular, a high-field FT-ICR MS has been intensively used to elucidate the molecular compositions of atmospheric organic matter (Choi, Kim, et al., 2017; Kourtchev et al., 2014; Nizkorodov et al., 2011; Noziere et al., 2015; Zhao et al., 2013).

Here we use a 15-T FT-ICR MS (15T FT-ICR MS) to generate ultrahigh-resolution mass spectrum profiles of organic substances extracted from Arctic aerosols to obtain sophisticated chemical information on ambient organic aerosols. The resulting data were interpreted to characterize the molecular compositions of the organic substances in ambient fine-sized particles. An air mass back trajectory analysis and the transport history of the air mass arriving at the sampling site were also complementarily used to obtain information on the potential source origins of Arctic organic aerosols.

2. Materials and Methods

2.1. Arctic Aerosol Collection and Ion Analysis

Aerosol particles with equivalent aerodynamic diameters <2.5 μm ($PM_{2.5}$) were collected at Ny-Ålesund, Svalbard Islands (78.9°N, 11.9°E), from 29 April to 20 May 2015 (Figure 1). The use of high-volume samplers is suitable for sampling pristine air containing low particle loading because they can rapidly concentrate large volumes of air and thus improve detection limits. A high-volume air sampler (HV-1000R, Sibata Scientific Technology, Japan) was mounted on the roof of the Gruvebadet observatory, and $PM_{2.5}$ aerosols on a quartz filter were collected every 3 days. The Gruvebadet observatory is located at 50 m above sea level, approximately 1 km southwest of the Ny-Ålesund village. Before sampling, the quartz filters were baked at 450 °C for 8 hr in a furnace to remove organic contaminants. Samplings were carried out at a flow rate of 1,000 L/min every 72 hr. Following collection, the aerosol samples were transferred to prebaked aluminum foil and stored at −20 °C until analysis. Then, one quarter of the filter samples were used for the analysis of the molecular complexes of aerosol particles. An aethalometer (Magee Scientific model AE31), installed at the Zeppelin station (474 m above sea level and 1 km south of the Gruvebadet observatory), was used to

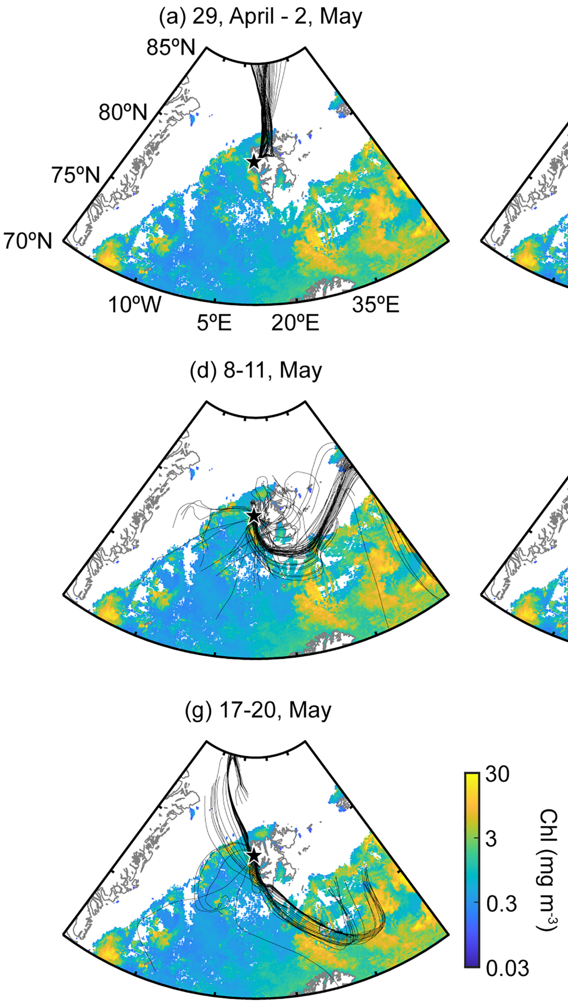

Figure 1. Mean chlorophyll concentration in May 2015 overlaid with the 3-day air mass back trajectories during each sampling period (a–g). The black star symbol indicates the location of the sampling site (78.9°N, 11.9°E).

analyze the concentration of equivalent black carbon by measuring light-absorbing particles at a wavelength of 880 nm (Eleftheriadis et al., 2009). More specifically, the loading correction for this wavelength was considered insignificant, while the instrumental specific absorption coefficient (σ_g = 16.6 m^2/g) was applied to the uncorrected attenuation coefficient values after taking into account a multiscattering 3.5 factor applied in the absorption calculation (Backman et al., 2017). The number concentration and size distribution of aerosol particles were measured at the Gruvebadet observatory using a scanning mobility particle sizer (TSI 3034, for particles within the range of 10–500 nm in a mobility equivalent diameter) and an aerodynamic particle sizer (for particles within the range of 0.5–20 μm in an aerodynamic equivalent diameter). Conversion of aerodynamic to mobility diameter was performed by applying the data-merging approaches reported by Khlystov et al. (2004) to calculate the number concentration of aerosol particles in the ranges of 0.01–2.5 μm in a mobility equivalent diameter. For the measurement of major ions, a 47-mm (diameter) disk filter was punched out from the filter samples. Major ions, including Na^+, on the disk filter were extracted in 50 ml of Milli-Q water and analyzed by a Dionex ion chromatography system (Thermo Fisher Scientific Inc., Waltham, MA, USA), as described in Park et al. (2017).

2.2. FT-ICR MS Analysis

Organic substances from Arctic aerosols were extracted according to the method established by Lin, Rincon, et al. (2012) with some modifications. In brief, the quartz filters (approximately 150 cm^2) were placed in methanol (20 ml) to extract organic matter in a sonication bath for 1 hr. The methanolic extract was filtered using a 0.45-μm polytetrafluoroethylene (Teflon) syringe filter to remove insoluble materials. The filtrates were immediately dried under a gentle nitrogen stream and redissolved with 50% aqueous methanol containing 7% ammonium hydroxide solution for FT-ICR MS analysis in negative ion mode.

Ultrahigh-resolution mass spectra were acquired using a 15T FT-ICR MS (solariX XR™ system, Bruker Daltonics, Billerica, MA, USA) equipped with a standard ESI interface, as demonstrated previously (Choi et al., 2017*;* Choi, Kim*,* et al., 2017) with minor modifications, to obtain the elemental compositions of the aerosol-derived organic substances.

The methanolic extracts were directly infused into the mass spectrometer at a flow rate of 2 μl/min using a syringe pump and analyzed in negative ion mode at a capillary voltage of 4.5 kV. The lower and upper mass limits were set to mass-to-charge (*m/z*) values of 150 and 1,000, respectively. The flow rate of the drying gas was held at 4 L/min, the temperature of the drying gas was maintained at 200 °C, the ion accumulation time was set at 0.05 s, and the transient length was set at 2.79 s for all experiments. Two hundred scans with 8 M words of data were collected per sample, resulting in a mass resolving power greater than 1,000,000 (at *m/z* 400). The instrument was externally calibrated using an arginine solution (10 μg/ml in methanol) before the sample analysis. The data acquisition was controlled by ftmsControl 2.0 software (Bruker Daltonics). The mass spectra obtained from a blank filter extract were used as the control.

2.3. Data Processing and Elemental Composition Assignments

After the acquisition of FTMS spectra with a 15T FT-ICR MS, the FTMS data sets were processed using DataAnalysis (ver. 4.2, Bruker Daltonics) and Composer (Sierra Analytics, Modesto, CA) software to assign the elemental compositions, as previously described (Choi et al., 2018). Briefly, the formula calculator, Composer, was used to calculate the empirical molecular formulas from the masses of singly charged ions extracted from raw spectra in the range of *m/z* 150–1,000. Constraints of up to 100 ^{12}C, 200 ^{1}H, 50 ^{16}O, four ^{14}N, and two ^{32}S atoms were applied for the calculations of the molecular formula. Then, molecular formulas with assignment errors >0.3 ppm and those from the blank filter extract were excluded from further processing. In general, the criterion of the mass accuracy with less than 0.5-ppm errors has been accepted for the data sets derived from ultrahigh-resolution MS analysis (Choi, Ryu*,* et al., 2017*;* Marshall et al., 2013). A van Krevelen plot was used to visualize the assigned chemical compositions based on the atomic hydrogen-to-carbon and oxygen-to-carbon ratios (as shown in Figure 2; Kim et al., 2003). The aromaticity index (AI) proposed by Koch and Dittmar (2006) was utilized to interpret the potential presence of aromatic molecules (AI > 0.5: aromatic species; AI > 0.67: condensed aromatics). The double bond equivalent (DBE) value, representing the sum of rings and double bonds in each molecule, can be calculated from the number of atoms in the chemical formulas by the following equation: $DBE = 1 + C - 0.5\ H + 0.5\ N$.

2.4. Estimation of the Air Mass Transport History

The 3-day air mass back trajectories and hourly positions were determined and combined with satellite-derived geographical information and chlorophyll concentration data to evaluate the transport history of a given air mass arriving at the observation site (Park et al., 2018). Air mass back trajectories and meteorological parameters were estimated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler & Hess, 1998). Meteorological fields from the Global Data Assimilation System at a resolution of 1° × 1° were used for the HYSPLIT model. The 3-day back trajectories were estimated at hourly intervals during each sampling period. We limited our analyses of the air mass back trajectories to 3 days prior to the arrival of the air masses at the sampling site because a 3-day period is generally consistent with the advection time of $PM_{2.5}$ particles (Ghosh et al., 2015). Daily geographical information over the ocean, land, and sea ice domains was acquired from the sea ice index at a 25-km resolution, which was provided by the National Snow and Ice Data Center. Note that the sea ice region was defined as the area with an ice concentration greater than 15% (Stroeve et al., 2016). Then, the origin of the air mass was identified by evaluating the advection time of the 3-day back trajectories over the ocean, land, and sea ice domains (Figures 1 and 3b and Table S1). We ran the HYSPLIT model in a single particle trajectory mode, so the dispersion and loss processes (i.e., dry and wet deposition) of airborne particles were not included (Draxler et al., 2015). However, the trajectory modeling was only undertaken to estimate the transport

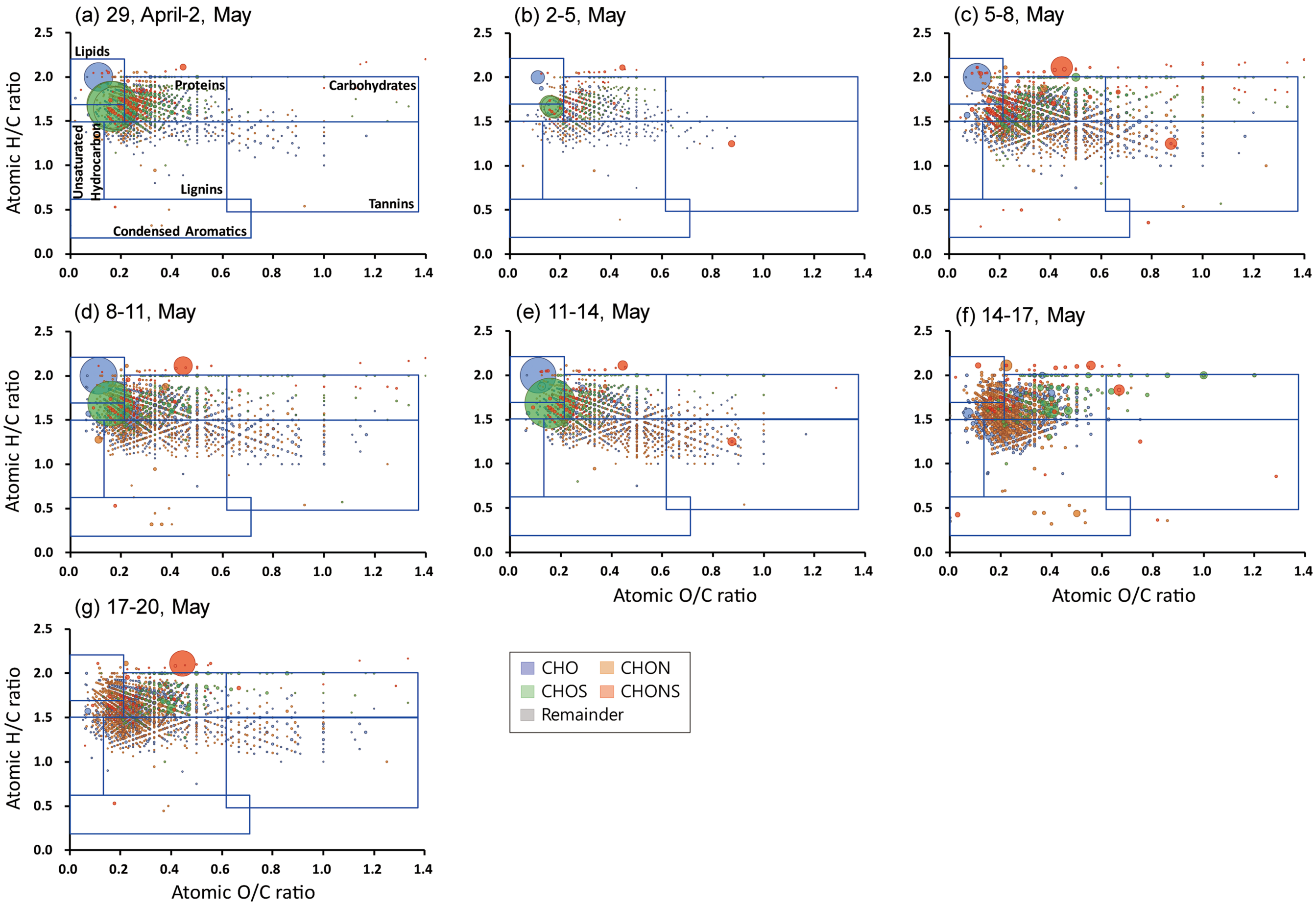

Figure 2. Van Krevelen plots showing the intensity-weighted distributions of chemical classes based on the molar hydrogen-to-carbon and oxygen-to-carbon ratios of the assigned elemental compositions of Arctic organic aerosols analyzed by the electrospray ionization (-) Fourier transform ion cyclotron resonance mass spectrometer (color code: C, H, and O [CHO], blue; C, H, O, and N [CHON], orange; C, H, O, and S [CHOS], green; C, H, O, N, and S [CHONS], red; remainder, gray). The size of each circle is proportional to the intensity of the molecular formula.

history of small particles over a few days. Therefore, these loss processes could be considered negligible (Fleming et al., 2012).

Satellite-derived chlorophyll concentrations are a good proxy for phytoplankton biomass (Siegel et al., 2013). The application of air mass exposure to ocean chlorophyll estimated by combining hourly back trajectory positions with satellite-derived chlorophyll concentration data could provide a good measure for quantitatively investigating the biological exposure history of sampled air over several days before it arrives at the observation site (Arnold et al., 2010; Park et al., 2018). The phytoplankton biomass of the Arctic Ocean surrounding Svalbard was obtained by calculating the 8-day mean chlorophyll concentrations from the level-3 product of the Aqua-Moderate Resolution Imaging Spectroradiometer at a 4-km resolution. Then, the air mass exposure to ocean chlorophyll (E_{chl}) was calculated using equation (1).

$$E_{chl} = \frac{\sum_{t=1}^{72} Chl}{n} \tag{1}$$

Here Chl is the 8-day mean chlorophyll concentration within a radius of 25 km at a given time point ($t = 1$ to 72) along the 3-day air mass back trajectory, and n is the total number of time points for which valid chlorophyll values are available. For a given air mass back trajectory, the time points for which satellite-based chlorophyll concentration data were not available were excluded from the calculation. The time points when the air mass passed over the continent or regions covered by sea ice were assigned a zero chlorophyll value (Park et al., 2018).

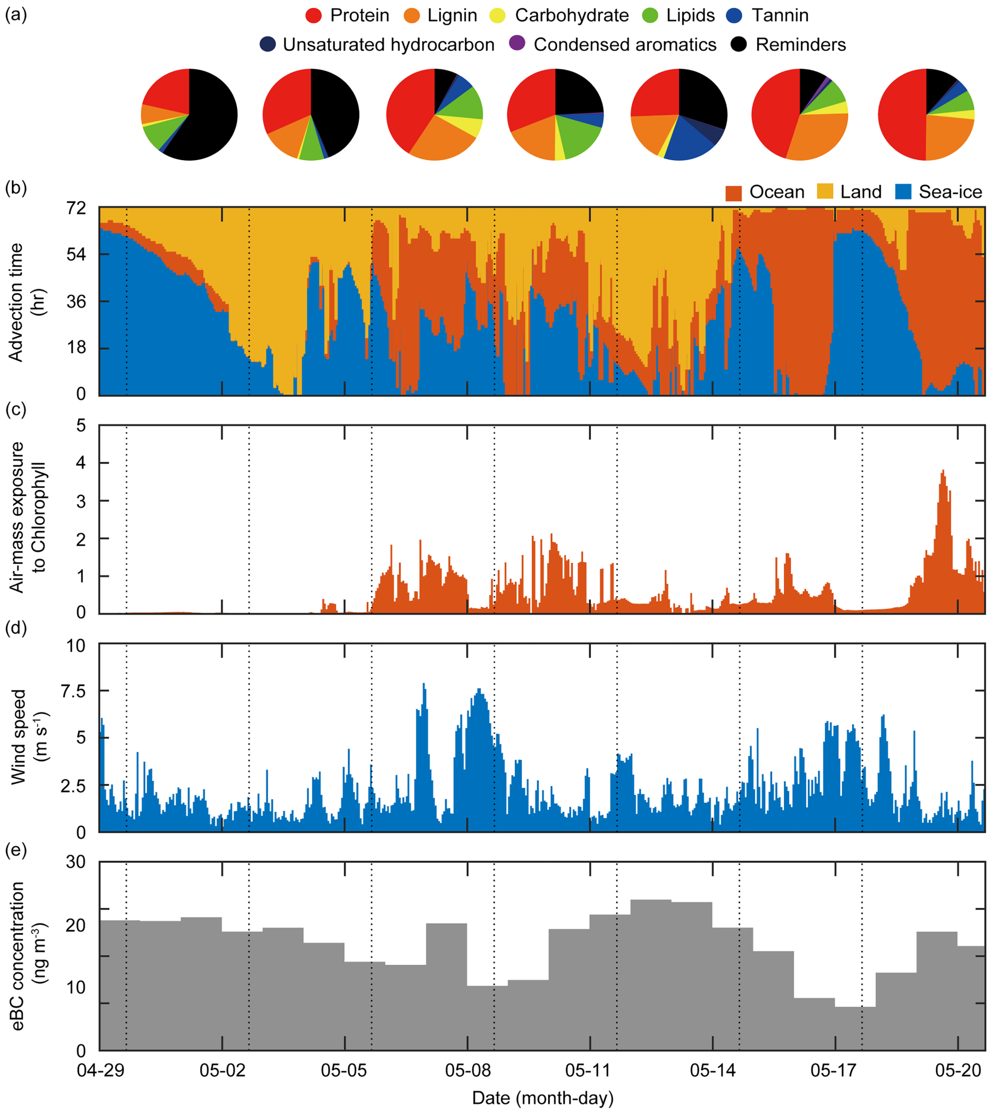

Figure 3. (a) Relative intensities of molecular formulas categorized into proteins, lignins, carbohydrates, lipids, tannins, unsaturated hydrocarbon, condensed aromatics, and remainders during the corresponding sampling period. (b) Advection time of the 3-day air mass back trajectories that passed over three domains, including the ocean, land, and sea ice areas, at an hourly interval. (c) Calculated air mass exposure to oceanic chlorophyll concentration. (d) Hourly wind speed monitored at Ny-Ålesund. (e) Daily mean values for the concentration of black carbon. The dashed lines indicate the period of aerosol particle collection.

3. Results and Discussion

3.1. Ultrahigh-Resolution FT-ICR MS Profiling of Arctic Aerosol-Derived Organic Substances

Methanolic extracts of the organic aerosol samples that were collected in May 2015 were analyzed using an ultrahigh-resolution 15T FT-ICR MS equipped with an ESI source in negative ion mode. After processing the raw data using Composer software, 673 to 1419 chemical formulas of total organic substances were assigned to the ESI (-) FT-ICR MS data. The overall chemical attributions of the organic compounds belonging to the extracts are summarized in supporting information Table S2.

The organic aerosol compounds could be divided into four subgroups based on their elemental composition (i.e., compounds containing only C, H, and O [CHO]; compounds containing C, H, O, and N [CHON]; compounds containing C, H, O, and S [CHOS]; and compounds containing C, H, O, N, and S [CHONS]). The molecular class containing only CHO was the most abundant (36.8%), followed by the CHOS (33.5%), CHON (18.6%), and CHONS (10.9%) classes during the observation period. Following the formula assignments, the molecules were categorized by compound class using various chemical metrics (i.e., proteins, lignins, carbohydrates, lipids, tannins, unsaturated hydrocarbons, and condensed aromatics), as displayed in the van Krevelen plots (Figure 2 and supporting information Figure S1). The ultrahigh resolving power of FT-ICR MS enables the characterization of thousands of organic species in a single mass spectrum. Furthermore, the AI and DBE values and the van Krevelen plots can be used to predict potential sources of the assigned organic substances (Wozniak et al., 2008). The lignin, tannin, protein, and carbohydrate class compounds, which can be classified in van Krevelen plots, are mostly considered to be derived from biogenic sources. More explicitly, lignin, unsaturated hydrocarbon, and tannin class compounds were considered to be likely plant-derived products (also called terrestrial dissolved organic matter [DOM]), while the protein and carbohydrate class molecules were derived from microbes, such as phytoplankton. Clusters of peaks in high-resolution mass spectrum can be structurally related to families of similar compounds. The van Krevelen diagram can be a useful tool for compositional differentiation among samples. Additionally, this diagram allows for an evaluation of the relative significance of structurally related compounds by comparing the relative intensities of assigned molecules (Kim et al., 2003). Given these assumptions, the relative proportion of the intensities of protein and carbohydrate class species were semi-quantitatively separated to those of lignin and unsaturated hydrocarbon class species (Table S2; Nebbioso & Piccolo, 2013; Lu et al., 2015; Mangal et al., 2016). The large values of DBE (>5) and AI (>0.5) of the assigned molecules could indicate the presence of aromatic hydrocarbons and their oxidized derivatives that are typical of anthropogenic sources (Koch & Dittmar, 2006; Noziere et al., 2015). Here the mean DBE and AI values of 4.77 ± 0.21 and 0.12 ± 0.06, respectively, were observed from the Arctic aerosol-derived organic substances during the observation period (see supporting information Table S2). In our previous study, the water-soluble organic matter of urban aerosols collected during winter exhibited larger values of the DBE and AI (10.48 and 0.30, respectively; Choi, Kim, et al., 2017). Furthermore, the aerosol-derived water-soluble organic carbons from rural areas at midlatitudes appeared to have higher mean DBE values (i.e., 5.3–6.2; Lin, Yu, et al., 2012; Mazzoleni et al., 2012) compared to those in the Arctic aerosols presented in this study. Given these observations, the influence of anthropogenic sources on Arctic aerosols seems to be small during the study period. The overall chemical class distributions of the assigned compositions of the Arctic aerosol-carried organic substances are listed in supporting information Table S3.

3.2. Potential Origins of Air Masses: Ocean Versus Non-Ocean

The chemical properties of aerosol particles may dramatically differ depending on their origin and transport histories. The potential origins of the ambient aerosols collected every 3 days in May 2015 were divided into two regimes based on the average advection time of the 3-day back trajectories over the three major domains, including the ocean, land (both the island and mainland), and sea ice, at an hourly interval: ocean origin (>45% advection over the ocean domain) and non-ocean origin (>55% advection over the land and sea ice domains; Figures 1 and 3b and Table S1). For example, the average advection times of the 3-day back trajectories arriving at the sampling site over the ocean, land, and sea ice regions were 40.9 ± 23.8 hr (56.8%), 5.9 ± 6.0 hr (8.2%), and 25.2 ± 22.6 hr (35.0%), respectively, during the period of 17–20 May. Therefore, this period was allocated as having an ocean origin. Note that the average advection time of the 3-day back trajectories above the land domain was 21.7 ± 16.2 hr (30.1%) during the entire sampling period (from 29 April to 20 May), and the average advection time over the Svalbard archipelago (21.4 ± 16.2 hr) was much greater than that over other land domains, including Greenland and the mainland (0.3 ± 0.5 hr), because the back trajectory analysis was limited to 3 days (Figure 1 and Table S4). Exceptionally, the aerosol sample taken from 8 to 11 May was allocated as a transit period because the air mass passed over three major domains at an almost equal rate during this period (i.e., ocean: 34.1 ± 19.2%; land: 34.0 ± 19.9%; sea ice: 31.9 ± 20.4%).

The FT-ICR MS data are generally not quantitative. However, the number of observed assigned molecules and the sum of the intensities show relatively quantitative aspects because all samples were extracted from the same number of filters and analyzed under the same conditions. The total number of assigned molecular formulas was approximately two times greater for ocean-originated Arctic organic aerosols (1,295 ± 199) than that estimated for non-ocean-originated organic aerosols (827 ± 140; supporting information Table S1). In particular, the ocean-originated aerosols were characterized by larger peak numbers and intensities of the assigned molecular formulas involved in proteins and lignins (Figures 3a and 4). When the air mass was over the ocean domain for a longer period (>45% retention), the total intensities of the protein (45.4 ± 4.40%) and lignin (26.4 ± 3.43%) compounds accounted for >70% of the total assigned molecular formulas

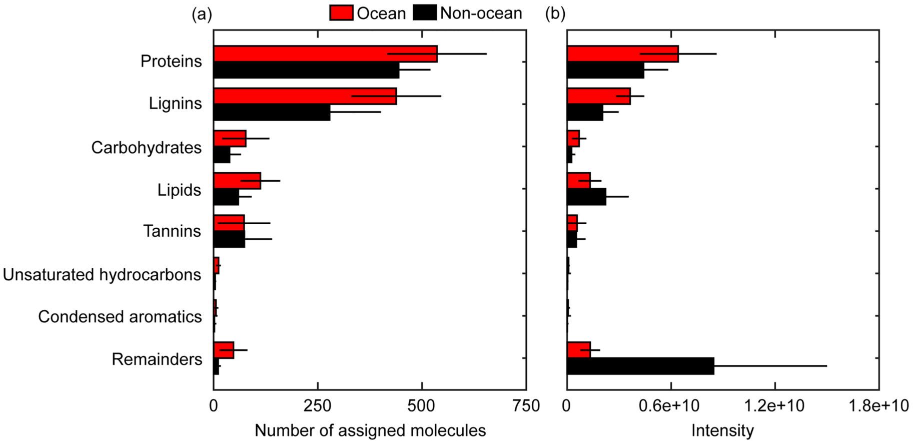

Figure 4. (a) The number of assigned molecules and (b) the total intensity of assigned molecules, including proteins, lignins, carbohydrates, lipids, tannins, unsaturated hydrocarbons, condensed aromatics, and remainders. The red and black bars indicate ocean and non-ocean origins, respectively. Note that ~99% of the intensity of remainders (40.2 ± 7.87% of the total intensity) was accounted for by three CHOS compounds (i.e., $C_{17}H_{28}O_3S$, $C_{18}H_{30}O_3S$, and $C_{19}H_{32}O_3S$) for the non-ocean-originated organic aerosols.

(Figure 3a and supporting information Table S3) and were ~55% greater than those of non-ocean-originated organic aerosols (Figure 4b).

Meanwhile, the non-ocean-originated organic aerosols were described by a higher proportion of the CHOS class species (50.7 ± 11.62%) compared to those (13.0 ± 3.16%) in ocean-originated organic aerosols (see supporting information Table S3). Among the CHOS species in the non-ocean-originated organic aerosols, a dramatic observation of some CHOS compounds that were not categorized into seven classes (shown by the large green circles in Figures 2a, 2b, and 2e) was found, and the chemical compositions of these CHOS compounds (corresponding to m/z of 311.168639, 325.184289, and 339.199939) were estimated to be $C_{17}H_{28}O_3S$, $C_{18}H_{30}O_3S$, and $C_{19}H_{32}O_3S$, whose DBE and AI values were also calculated as 4 and 0, respectively. The intensities of these three molecules account for 40.2 ± 7.87% of the total intensity of the assigned molecular formulas in the non-ocean-originated organic aerosols (Figure 4b). Both the equivalent black carbon concentration and the total number of aerosol particles (in the range of 0.01–2.5 μm in diameter) were approximately 40% and 100% greater, respectively, for the samples of non-ocean origin than those of ocean origin (Table S5). Importantly, the intensity of three CHOS was positively correlated with the corresponding equivalent black carbon concentration, which is a useful indicator of the man-made pollutant ($r^2 = 0.46$; Figure 5a). Meanwhile, the intensity of these CHOS compounds decreased with an increase in wind speed, which was recorded at Ny-Ålesund ($r^2 = 0.37$; Figure 5b). A negative correlation was also found between the intensity of these CHOS compounds and the Na^+ concentration, which is used as the sea spray marker ($r^2 = 0.72$; Figure 5c). Furthermore, the increase in black carbon concentration was noticeable due to the increase in the advection time of the air mass over the Svalbard land area ($r^2 = 0.53$; Figure 5d). Although it is difficult to assure the exact origin of these CHOS compounds with limited data, these results could infer that these CHOS compounds are likely derived from local anthropogenic sources that might originate from the Svalbard region due to the low dispersion of calm weather.

3.3. Influence of Biogenic Organics on the Chemical Properties of Arctic Organic Aerosols

Quantifying the relationship between the marine emissions of organic species and marine biology is a major challenge (Brooks & Thornton, 2018). The influences of the biological activities surrounding the observation site on the chemical composition of organic aerosols were further confirmed by comparing the air mass exposure to oceanic chlorophyll with an FT-ICR MS data set (Figures 6a, 6b, and 6c). The satellite-derived chlorophyll concentrations of the Arctic Ocean surrounding the observation site in 2015 began to increase in April and reach a maximum in May (supporting information Figure S3). The major source of dissolved organic carbon in sea surface water is marine phytoplankton (Thornton, 2013). The major constituent of rapidly growing phytoplankton cells is protein, with a content up to approximately 50% of the phytoplanktonic organic matter, followed by carbohydrates (Myklestad, 2000). In this study, the total number of assigned

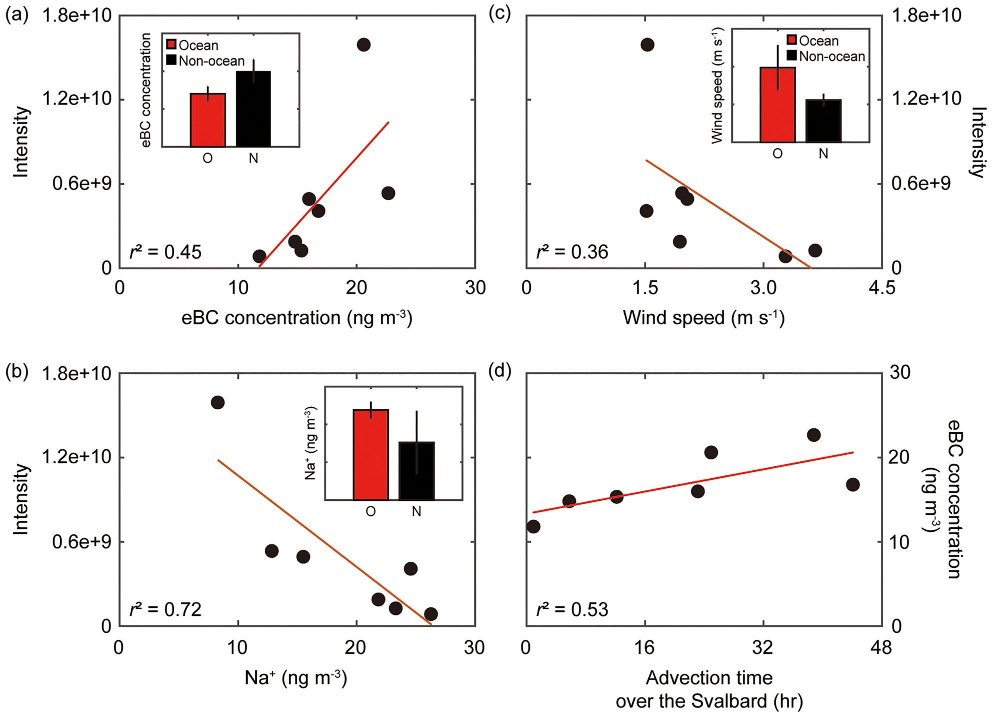

Figure 5. Relationships of the intensities of three assigned molecule formulas, including $C_{17}H_{28}O_3S$, $C_{18}H_{30}O_3S$, and $C_{19}H_{32}O_3S$, with (a) black carbon concentration, (b) the 3-day averaged wind speed, which was recorded in Ny-Ålesund, and (c) Na^+ concentration. (d) The relationship of the black carbon concentration with the advection time over the Svalbard land area. The red line represents the best fit. The inset shows the average black carbon concentration, wind speed, and Na^+ concentration for ocean origins and non-ocean origins. The error bar represents 1 standard deviation from the mean value.

molecular formulas was significantly correlated with the calculated air mass exposure to ocean chlorophyll during the study period ($r^2 = 0.80$, $p < 0.05$, $n = 7$; Figure 6a). In particular, the increases in the intensities of protein and carbohydrate class compounds were noticeable due to the increase in air mass exposure to ocean chlorophyll ($r^2 = 0.64$ and 0.57, respectively; $p < 0.05$; $n = 7$; Figures 6b and 6c).

Recently, a significant proportion of lignin material was found in phytoplankton-released DOM (Mangal et al., 2016). However, lignin and unsaturated hydrocarbon compounds are well established as biomarkers of terrestrial-derived organic matter (Opsahl & Benner, 1997). Arctic rivers discharge a large volume of freshwater (3,300 km^3/year) and terrestrial DOM (25 Tg C/year) into the relatively small Arctic basin (Rachold et al., 2004). Therefore, the concentration of dissolved lignin in Arctic waters was reported to be approximately tenfold greater than those in the Atlantic and Pacific Oceans (Benner et al., 2005). Interestingly, both the intensities of lignin and unsaturated hydrocarbon compounds were positively correlated with the advection time of the air mass over the ocean domain ($r^2 = 0.62$ and 0.77, respectively; $p < 0.05$; $n = 7$; Figures 6e and 6f). Note that two variables, including air mass exposure to chlorophyll and advection time over the ocean are not completely independent. However, these two variables could explain different transport histories of air masses arriving at the observation site since the sea surface chlorophyll concentration in the surrounding ocean varied greatly from region to region (ranging from 0.1 to 80.4 mg/m^3) during the study period (Figures 1 and S2).

Additionally, the relationship between the total intensity of assigned molecules and the air mass exposure to chlorophyll (and advection time over the ocean) was estimated by applying a longer transport period (i.e., 4-, 5-, and 7-day air mass back trajectories) to assess whether or not the correlation analysis was sensitive to the extension of the air mass back trajectory time points. As shown in Figure S4, a positive correlation was also found when applying a longer transport period.

These results support that the accumulation of DOM possibly derived from both marine phytoplankton and terrestrial vegetation at the Arctic sea surface is likely responsible for the enrichment of primary sea spray aerosols during the spring period in Arctic environments. Therefore, air parcels that have traveled longer

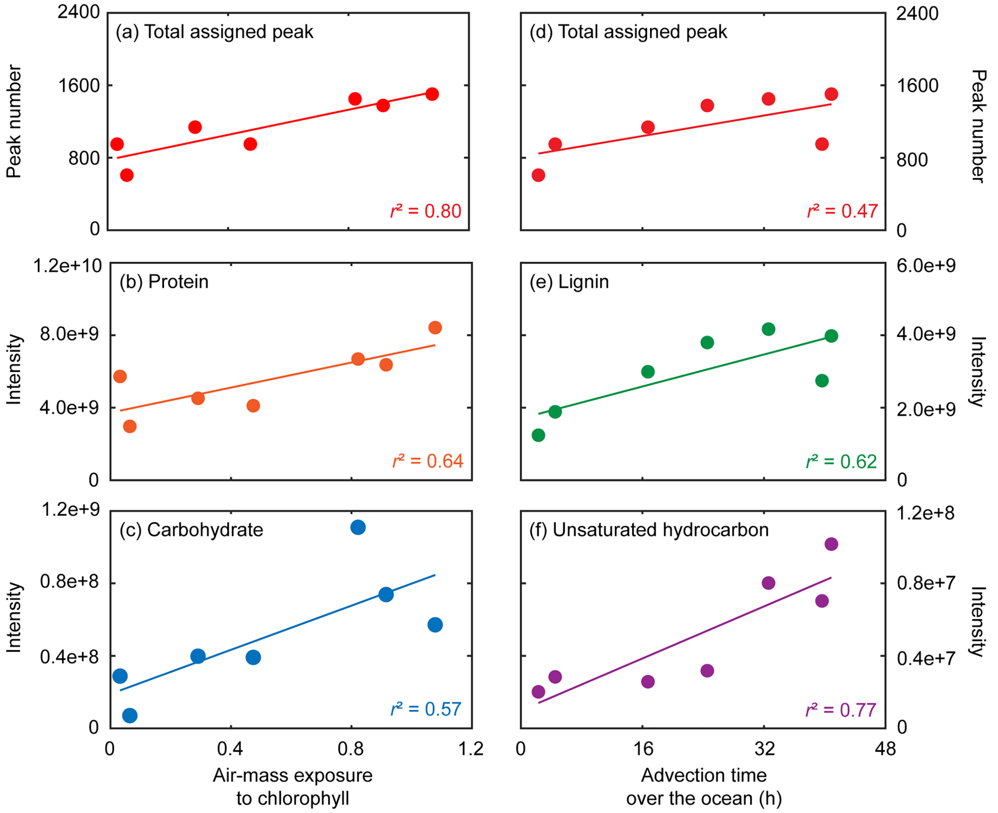

Figure 6. Relationships of the calculated air mass exposure to oceanic chlorophyll concentration with (a) the total number of assigned peaks, (b) the intensity of protein-like molecules, and (c) the intensity of carbohydrate-like molecules. Relationships of the advection time of the air mass over the ocean with (d) the total number of assigned peaks, (e) the intensity of lignin-like molecules, and (f) the intensity of unsaturated hydrocarbon-like molecules. The solid lines indicate the best fit.

distances over the productive Arctic Ocean could have had a greater chance of introducing biologically driven types of organic matter into the Arctic atmosphere. These results could infer that DOM derived from marine phytoplankton and terrestrial vegetation is an important constituent of submicron aerosol particles and could significantly influence the chemical properties of organic aerosols in the remote Arctic atmosphere.

4. Conclusions and Implications

DOM at the sea surface and its linkages with ambient aerosols in remote marine environments remain largely uncertain due to the lack of the comprehensive characterization of the chemical nature of organic substances in marine aerosols (Matsumoto et al., 1997; O'Dowd & de Leeuw, 2007). In this study, we elucidated the first detailed analysis of the molecular composition of Arctic organic aerosols using an ultrahigh-resolution FT-ICR MS, which is a powerful and robust tool for accurately identifying the molecular characteristics of aerosols. In conjunction with the FT-ICR MS data, the air mass transport history combined with satellite-derived geographical information and phytoplankton biomass data was complementarily used to characterize the source origins. We determined that the intensities of major organics (i.e., lignins, proteins, carbohydrates, and unsaturated hydrocarbons) in Arctic aerosols were positively correlated with the air mass exposure to ocean chlorophyll and the advection time of the air mass over the ocean domain during the Arctic spring period. These results could further emphasize the importance of biogenic organics dissolved in the ocean as a source of primary aerosols in remote marine environments. Recent studies have revealed that biological processes occurring near the sea ice region could trigger the formation and growth of organic aerosol particles in the polar region (Dall'Osto et al., 2017; Dall'Osto et al., 2017). Furthermore, Ovadnevaite et al. (2014) reported that North East Atlantic marine aerosol exhibits the highest organic contribution during the summer period than in April and May. Arctic haze originated from industrial and wildfire emissions in the continent also affects the physiochemical properties of aerosol particles, in particular, during winter and early spring time (Abbatt et al., 2019). However, we could not evaluate the effect of sea ice exposure on the chemical properties of Arctic organic aerosols and the chemical properties of the year-round Arctic organic aerosols due to an insufficient sampling period in this study. The long-term observation of the detailed molecular characteristics of aerosol particles could provide more clear evidence for the seasonal variations in aerosol particles and their linkages to multiple processes, such as sea ice melt, localized blooming events, and Arctic haze.

Over the last century, the increase in temperature in the Arctic region has been observed to be 2 times greater than the global average temperature (Corell, 2006). Warming-induced decreases in Arctic sea ice extent could significantly affect the growth of marine biota (Arrigo et al., 2008). Annual net primary production in the Arctic Ocean was reported to increase approximately 30% during the last 30 years due to reduced sea ice extent and a longer growing season (Arrigo & van Dijken, 2015). The Arctic freshwater cycle has also changed drastically, and the annual discharge of freshwater containing terrestrial DOM from the six largest Eurasian rivers into the Arctic Ocean has increased by 7% since the 1940s (Peterson et al., 2002). Such changes in the Arctic environment will also have a substantial impact on the Arctic ecosystems and their biogeochemical cycles. This type of analytical approach to studying the chemical nature of organic aerosols will be useful for deciphering the molecular changes in the natural aerosol properties of remote marine environments. This approach could provide broad insight into the understanding of organic aerosols in the atmosphere over the Arctic and the relationship with the ocean in terms of aerosol formation and environmental changes.

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