Molecular-Level Chemical Characterization of Dissolved Organic Matter in the Ice Shelf Systems of King George Island, Antarctica

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Antarctic shelf systems play an important role in organic matter circulation on Earth; hence, identifying the characteristics of dissolved organic matter (DOM) can be a good indicator for understanding its origin, as well as climate change. In this study, to identify the characteristics of DOM in the ice shelf systems, surface water was collected from the open sea (OS) and Marian cove (fjord, FJ). Although there were no differences in DOM characteristics between sampling sites in the quantitative analyses, the DOM in the surface water of each region seemed to be more affected by terrestrial than marine biological sources in optical and molecular properties. This finding indicates that the terrestrial DOM related to mosses based on the results of molecular properties: high levels of lipid-like (35–39%) and unsaturated hydrocarbon-like (UH; 27–34%) in both the OS and the FJ regions and significantly higher tannin-like substance and condensed aromatic structures in the FJ than in the OS region. When comparing the FJ transect samples, those nearest to a glacier (FJ1; 0.93 km from the glacier) showed relatively low salinity, high dissolved organic carbon, and high chromophoric DOM, indicating that terrestrial DOM (possibly produced by moss) inflow occurred with the runoff from the freshly melting land ice and glacier. However, no significant differences in molecular composition were detected, suggesting that terrestrial DOM is introduced into the ice shelf systems by melting land ice, and glacier runoff could be a major source of DOM-rich seawater during austral fall when low marine biological activity occurs. This study has a great significance as background data for DOM characteristics in the ice shelf systems due to the enhanced biological activity during the austral summer.

Keywords: dissolved organic matter, terrestrial DOM, glacier runoff, ice shelf systems, King George Island, Orbitrap

INTRODUCTION

The ice shelf systems in Antarctica are one of the important organic carbon reservoirs on Earth. Annually, 2 Pg of carbon is absorbed by the seawaters of the world – approximately half is absorbed by the ice shelf systems, which is significant to the global carbon cycle (Takahashi et al., 2009). Moreover, the ice shelf systems are known to carry algae and microorganisms, which are a major source of organic carbon in seawaters (Nagata and Kirchman, 1992). Additionally, dissolved organic matter (DOM) in seawater is directly emitted from the seawater surface into the atmosphere *via* bubble bursting (i.e., primary marine aerosols or sea spray aerosols), leading to the production of organic-rich particles in the atmosphere over the Antarctica and the Arctic (O'Dowd and De Leeuw, 2007; Rastelli et al., 2017; Park J. et al., 2019). These organic aerosols can constitute large fractions (approximately 80%) of the submicron particle mass during a phytoplankton bloom (Park et al., 2014; Park J. et al., 2019). Therefore, the characterization of DOM in the Antarctic seawater can be a good indicator for understanding its origin as well as contribute to the understanding of marine ecosystem changes and climate change.

Diverse analytical techniques [i.e., UV spectrophotometer, total organic carbon (TOC) analysis, chromatography, and separation of hydrophilic and hydrophobic components using resin] have been generally used for DOM characterization in seawaters (e.g., determination of mass accuracy and unique spectral properties); however, these conventional analysis methods are limited by complicated and time-consuming measurement processes (Hur et al., 2006). The compositional differences and the characteristics of marine DOM are still largely unidentified because the very low concentrations of DOM in seawater, compared to the massive amounts of inorganic sea salts, present a major challenge (Hansell and Carlson, 2002; Park S. et al., 2019). Recently, high-resolution mass spectrometry (HRMS) has been applied to identify the molecular signatures of DOM (Koch et al., 2008; Phungsai et al., 2016; Baek et al., 2019). HRMS has far higher sensitivity and resolving power in identifying mass spectral peaks than the existing mass spectrometry (MS) methods (Koch et al., 2008). In particular, Orbitrap-MS can determine over 1,500 unknown molecular formulae and masses of DOM with high accuracy (even with <0.5 ppm) and resolution (up to 240,000) (D'Andrilli et al., 2015). Orbitrap analysis could improve our understanding of DOM by identifying the possible formulae of DOM assigned with few elements, such as C, H, O, N, and S; other elements are disregarded as they are rare in natural organic matter (Phungsai et al., 2016).

Numerous studies have been conducted in various regions of the hydrosphere on the molecular composition of DOM by HRMS, and different dominant formulae have been identified. For example, unsaturated compounds (70.4 ± 0.6%) were highly dominant in the Mediterranean Sea (Martínez-Pérez et al., 2017), and lipid and lignin were the most abundant in river waters (Sleighter and Hatcher, 2008; Derrien et al., 2017). Particularly, Sleighter and Hatcher (2008) reported a decrease of aromaticity toward offshore from inshore using Fourier-transform ion cyclotron resonance MS. Recently, studies on molecular compositions using HRMS were conducted in arctic areas and reported 38–71% terrestrial components (i.e., lignin) due to the influence of river discharge or melting snow and ice runoff (Hodgkins et al., 2016; Mangal et al., 2017; Brogi et al., 2018). There have also been several studies on DOM in the Antarctic (Dittmar and Koch, 2006; D'Andrilli et al., 2015); however, the samples were collected in austral spring and summer, such that the results were geographically and seasonally limited to cover the whole season of Antarctica. Therefore, the compositions of the Antarctic DOM and its temporal or spatial variations at the molecular level are required to deepen our understanding of Antarctica and its role in global carbon cycle and climate change.

We studied the chemical composition of DOM in the ice shelf systems of King George Island onboard the Korean icebreaker R/V *Araon* from April to May 2018 (austral fall). For this, we collected surface water samples (sampling depth: 0–1 m) from open sea (OS) and fjord (FJ) areas in Antarctica and analyzed the characteristics of the DOM in the samples. The main objectives of this study were (1) to analyze the optical signatures of chromophoric and fluorescent DOM (CDOM and FDOM, respectively, using spectrophotometry, (2) to qualitatively evaluate the chemical properties and the components of DOM on a molecular level using an Orbitrap, and (3) to predict the potential sources of DOM based on the environmental conditions of the Antarctic seawater.

MATERIALS AND METHODS

Sample Collection and Preparation

The Antarctic seawater sampling was conducted onboard the Korean icebreaker R/V *Araon* from April to May 2018 (austral fall). Surface seawater samples were collected from two open sea locations (OS1 and OS2) and four fjord locations (FJ1–FJ4), as shown in **Figure 1**. The open sea areas, OS1 and OS2, were located between the Antarctic peninsula and King George Island (KGI), where the east part of Bransfield Strait meets the Antarctic Slope Front (Thompson et al., 2009). Samples FJ1 to FJ4 (0.94 to 7.05 km from the innermost part of a glacier) were collected from Marian cove, which is a glacier fjord (approximately 4 km in length and 1.5 km in width) located in Maxwell bay on the southwest side of KGI. Tidewater glaciers with a catchment area of approximately 15 km^2 are well developed in the inner cove (especially for sample FJ1). Glacier calving occurs, introducing significant volumes of meltwater and icebergs into the seawater. This glacier retreated approximately 1,700 m from 1956 to 2006 (Lee et al., 2008). In this study, the latitude, the longitude, the temperature, and the salinity of the water samples at each site were measured using a probe for measuring conductivity–temperature–depth connected to a rosette sampler (**Supplementary Table S1**).

Two-liter surface samples were collected at each site and immediately frozen and stored at –20°C in the dark during transport to our laboratory at Ulsan National Institute of Science and Technology in South Korea. Spencer et al. (2007)

FIGURE 1 | Sampling sites in the Antarctic. OS, open sea; FJ, fjord.
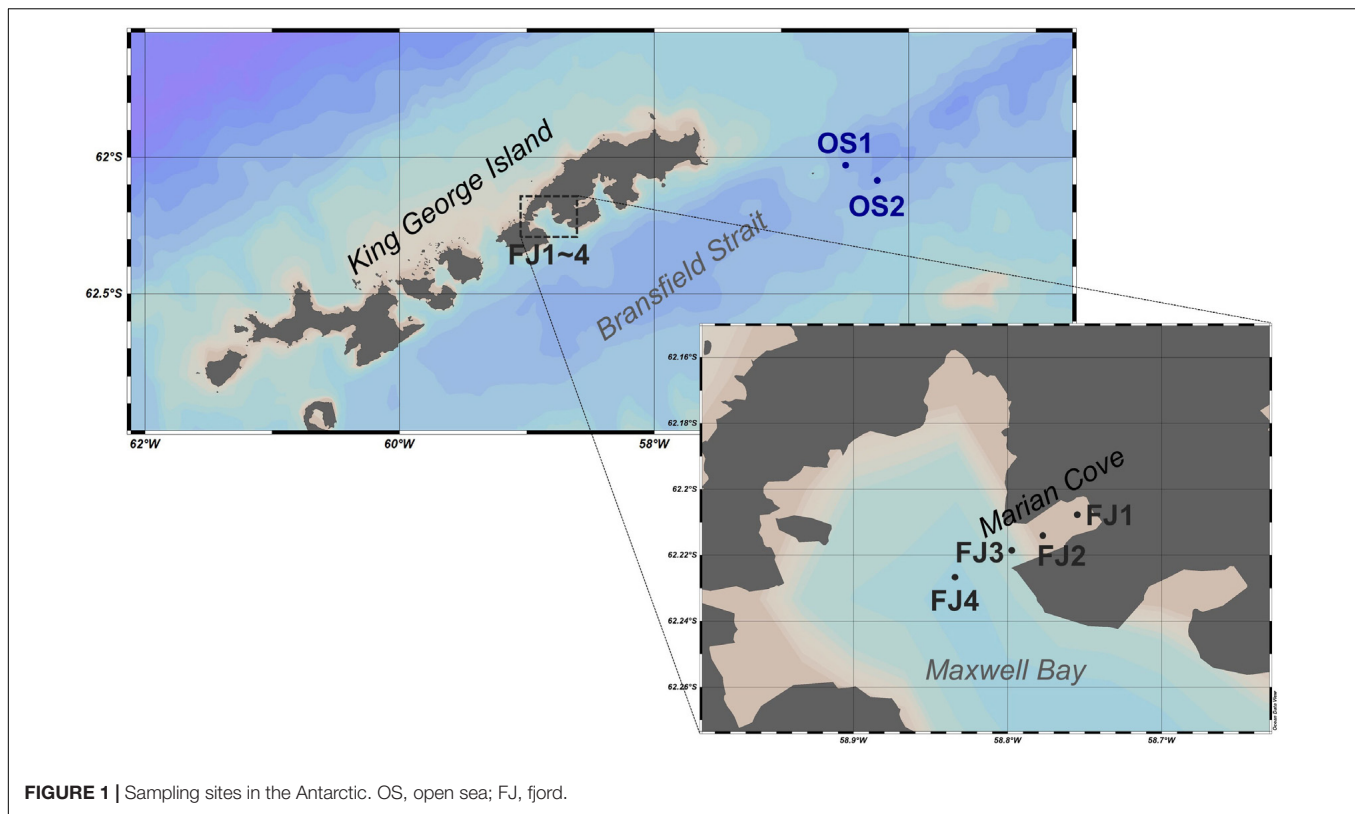
reported that freezing and thawing steps caused decreased DOM concentration and varying DOM composition. However, DOM is a heterogeneous and complex substance because of its various sources and surrounding conditions. The specific characteristics of DOM often generate contrary results in the same analysis. Otero et al. (2007) performed experiments regarding the effects of freezing/thawing on DOM in salt marsh pore water, but they found no variation in DOM fluorescence properties. In addition, Yamashita et al. (2007) and Walker et al. (2009) reported that no problematic differences in DOM characteristics existed between fresh and frozen samples. Consequently, freezing is a commonly used storage method in marine DOM studies (Amon et al., 2003; Stedmon et al., 2011; Chen et al., 2018). The transported samples were then filtered through 0.45-μm cellulose acetate membrane filters (Advantec, Japan) for DOM characterization.

Dissolve Organic Carbon, Dissolved Organic Nitrogen, and Chromophoric DOM Characterization

Filtered samples were loaded into precombusted borosilicate glass vials. The concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) were analyzed using a TOC analyzer (TOC-V_{CPH}; Shimadzu, Japan) equipped with a total nitrogen measuring unit (TNM-1; Shimadzu, Japan) and autosampler (ASI-V; Shimadzu, Japan) by the high-temperature combustion method. All DOC and DON samples (5 ml) were analyzed in duplicate or triplicate, and their standard deviations are presented as error bars in **Figures 2–5**.
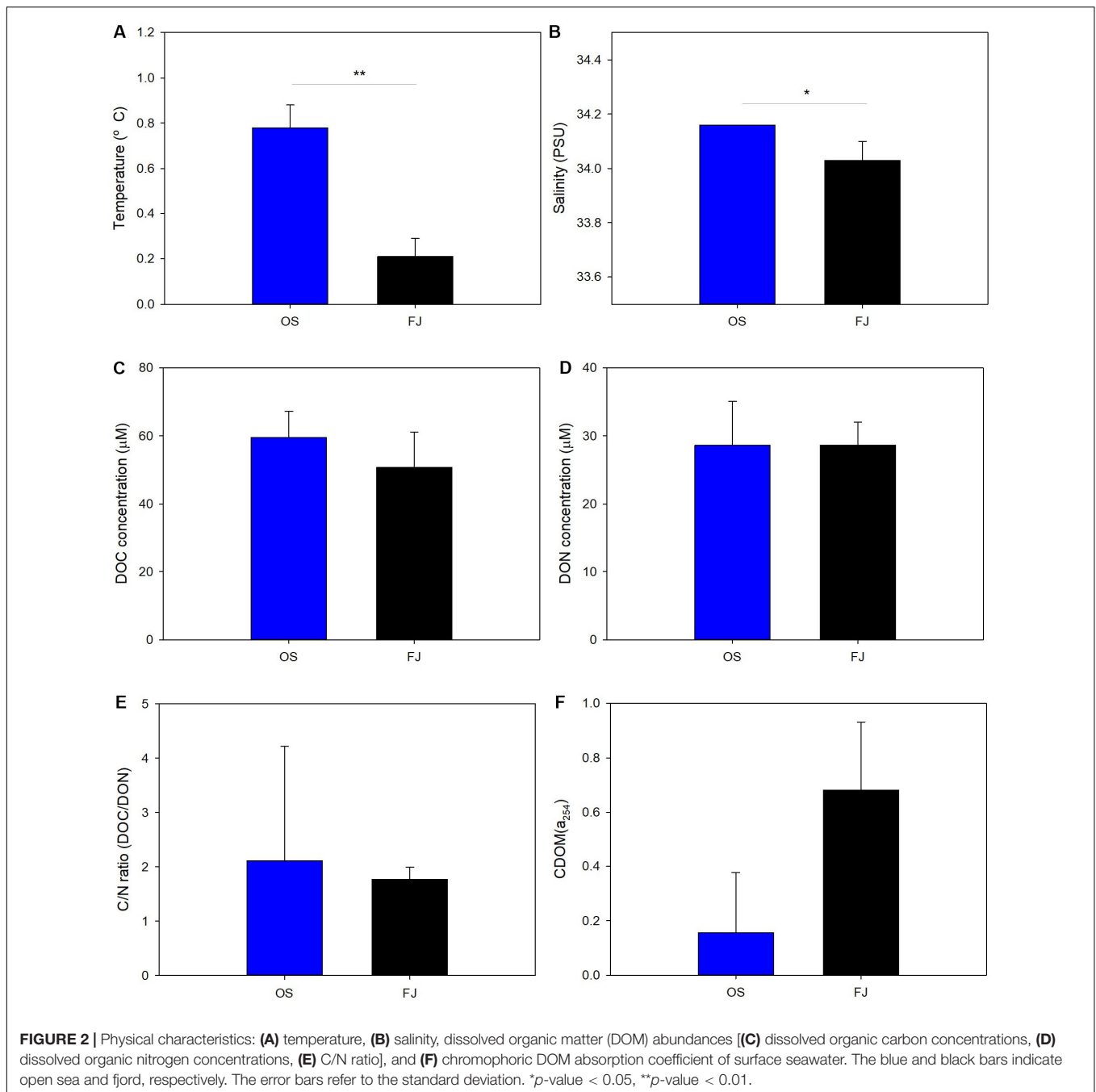
The absorbance of CDOM was measured with a 10-cm quartz cuvette using an ultraviolet–visible spectrometer (Scinco, South Korea). Ultrapure water (18 Mohm) was used as a reference, and the spectra were measured from 190 to 1,100 nm at 1-nm intervals. The optical density at a specific wavelength of the measured absorbance was converted to the CDOM absorption coefficient using the following equation (Bricaud et al., 1981):

$$a(\lambda) = 2.303 \times \frac{A(\lambda)}{l}$$

In the above equation, $a(\lambda)$ is the absorption coefficient (m^{-1}) at λ wavelength, 2.303 is the transform coefficient, $A(\lambda)$ is the optical density at λ wavelength, and l is the optical path length (m). In this study, we derived the CDOM value at 254 nm [i.e., $a(254)$], which is widely used as a proxy for terrestrial DOC in CDOM and DOM studies (Asmala et al., 2012; Zhao et al., 2016).

Fluorescence Characterization

The excitation–emission matrixes (EEMs) of the filtered samples and ultrapure water (18 Mohm) were scanned using a fluorescence spectrometer (Varian, United States). The excitation wavelength range was between 250 and 500 nm, and the emission was between 280 and 600 nm at 10-nm increments. A blank ultrapure water EEM spectrum was extracted from the sample EEMs, and water Raman peak normalization was performed. In this study, the five major fluorescent components were classified based on the criteria of Coble (2007) and quantified based on the

FIGURE 2 | Physical characteristics: **(A)** temperature, **(B)** salinity, dissolved organic matter (DOM) abundances [**(C)** dissolved organic carbon concentrations, **(D)** dissolved organic nitrogen concentrations, **(E)** C/N ratio], and **(F)** chromophoric DOM absorption coefficient of surface seawater. The blue and black bars indicate open sea and fjord, respectively. The error bars refer to the standard deviation. *p-value < 0.05, **p-value < 0.01.

equations in Chen et al. (2003), that is: peaks A (terrestrial humic-like; λ_{Ex} 260 nm/λ_{Em} 400–460 nm), M (marine humic-like; λ_{Ex} 290–310 nm/λ_{Em} 370–410 nm), C (terrestrial humic-like; λ_{Ex} 320–360 nm/λ_{Em} 420–460 nm), B (tyrosine, protein-like; λ_{Ex} 270 nm/λ_{Em} 310 nm), and T (tryptophan, protein-like; λ_{Ex} 270 nm/λ_{Em} 340 nm). Moreover, three indicators as proxies of sources–fluorescence index (FI), humification index (HIX), and biological index (BIX) – were calculated using the excitation and the emission intensities, as described in **Supplementary Table S2**. The FI is known as a proxy for humic substances in aquatic environments and represents the fluorescence intensity ratio at

wavelengths λ_{Ex} 370 nm/λ_{Em} 470 nm and λ_{Ex} 370 nm/λ_{Em} 520 nm (McKnight et al., 2001). When its FI value is larger than 1.9, DOM is considered to originate from microorganisms and contain few aromatic structures. In comparison, FI values smaller than 1.4 are considered as highly correlated with terrestrial DOM, which has highly aromatic characteristics (McKnight et al., 2001). BIX is an index showing the intensity ratio at wavelengths λ_{Ex} 250 nm/λ_{Em} 300–340 nm and λ_{Ex} 250 nm/λ_{Em} 430–480 nm. DOM with BIX values of 0.6 or less are generally of terrestrial origin, while that with values larger than 1 are predominantly of marine biological origin. Furthermore, HIX values are indices of

Liquid Chromatography–Orbitrap Mass Spectrometry

To concentrate the marine DOM, solid phase extraction (SPE) was conducted as a pretreatment step for analysis by Orbitrap-MS. One liter of each pre-filtered water sample was passed through a hydrophilic–lipophilic balanced (HLB) SPE cartridge (6 cc, 500 mg, Oasis-HLB[TM], Waters, United States) under vacuum for DOM extraction. The HLB cartridge was water-wettable and reversed-phase, with the capacity to extract both hydrophobic and hydrophilic compounds, and was therefore used to extract all unknown organic matter in this study. The extraction steps were performed based on the methods described by Hao et al. (2006). Briefly, the SPE cartridges were preconditioned before use by washing with high-performance liquid chromatography-grade methanol and equilibrating with ultrapure water (18 Mohm). For the elution step, the cartridge was first washed with 10 ml of 5% methanol in water; then, the retained DOM was eluted with 10 ml of 100% methanol. The eluates were evaporated under a gentle flow of nitrogen gas at 34°C, reconstituted with 1 ml of methanol, and filtered with syringe filter (0.2 μm, 13 mm, Advantec). The filtered samples were stored at -20°C in the dark before analysis.

The filtered SPE extracts (10 μl) were directly injected into an Orbitrap Q-Exactive spectrometer (Thermo Fisher Scientific, Germany) coupled with liquid chromatography (Ultimate 3000, Dionex Co., United States). The Acclaim[TM] C18 column (2.1 $\times$ 50 mm, 2.2 μm, 120 Å, Thermo Fisher Scientific, United States) was used for chromatographic separation, with methanol as mobile phase at a flow rate of 0.3 ml min^{-1} for 20 min. The negative electrospray ion mode using a heated electrospray ionization source was operated under the following conditions: the flow rate of ultrapure nitrogen sheath gas remained at 7 a.u., the spray needle voltage was maintained at 4.5 kV, and the capillary temperature was 320°C. To obtain mass spectra, a consistent flow rate of 300 μl/min, resolution of 70,000 with full scan mode over the range of m/z 100–1,500, and automatic gain control target of 1×10^6 were set. The LC-Orbitrap-MS was calibrated with Pierce[TM] ESI positive ion calibration solution before analysis to ensure high accuracy. Milli-Q water (18 Mohm) was analyzed following the same procedure as that for the blank test (**Supplementary Figure S3**). Mass spectra and formulae assignment were conducted using a Thermo Xcalibur Qual Browser (ver. 2.5).

The molecular formulae of the m/z 100–900 range with a relative abundance were calculated with MATLAB R2017a. We visualized the molecular formulae using a van Krevelen diagram because it is a powerful graphical approach for explaining the compositions in DOM samples and has recently been applied in DOM characterization studies (Kim et al., 2003; Kim et al., 2004; Herzsprung et al., 2012; Choi et al., 2019). The van Krevelen diagrams were displayed using a FTMS Visualization (i-van Krevelen) package in Python 2.7 for subsequent analysis of ranges

$0 < $ H/C $ < 2.5$ and $0 < $ O/C $ < 1.5$. The molecular formulae in the van Krevelen diagrams were divided into seven categories based on previous studies (Hockaday et al., 2009; Hodgkins et al., 2016): lipid-like (H/C = 1.6–2.0, O/C $\leq$ 0.29), protein-like (H/C = 1.5–2.0, O/C = 0.29–0.6), carbohydrate-like (H/C = 1.5–2.0, O/C = 0.6–1.0), unsaturated hydrocarbon-like (H/C = 1.0–1.6, O/C $\leq$ 0.29), lignin-like (H/C = 0.7–1.5, O/C = 0.29–0.65), tannin-like (H/C = 0.5–1.5, O/C = 0.65–1.0), and condensed aromatic structures (H/C $\leq$ 0.7, O/C $\leq$ 0.4).
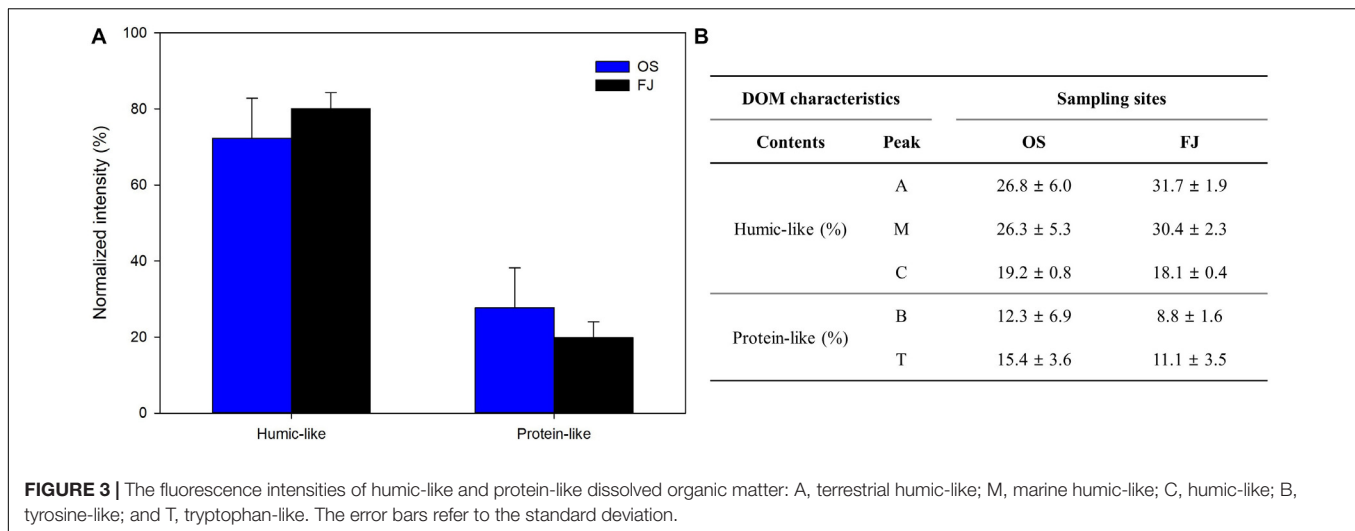
Statistical Analysis

The samples were grouped according to spatial variability and assessed by one-way analysis of variance (ANOVA). In the ANOVA, the p-value indicates the regional difference for each area; the significant differences are considered to be represented by a p-value of <0.05. The one-way ANOVA and a t-test for *post hoc* analysis were calculated using SigmaPlot (Systat, United States).

RESULTS AND DISCUSSION

Water Chemistry and DOM Abundance

The water quality parameters for each sampling station are summarized in **Figure 2** and **Supplementary Table S1**. The surface seawater temperatures, ranging between 0.12 and 0.85°C (at 0–1 m sampling depths), for the OS and FJ samples were measured, with significantly higher temperatures being measured in the OS than in the FJ samples (t-test, $p < 0.01$; **Figure 2A**). The temperatures were close to zero in the FJ samples, with the lowest being FJ1 (**Supplementary Table S1**) – that nearest to the glacier – indicating that surface seawater temperature is susceptible to the influence of ice or glacier. Moreover, the salinity of surface seawater varied between 33.89 and 34.17 PSU, and the average salinity values for the OS and the FJ samples were 34.16 ± 0.00 and 34.03 ± 0.07 PSU, respectively (**Supplementary Table S1**). Slightly lower salinities were observed in the FJ samples, with significant differences between stations (t-test, $p < 0.05$; **Figure 2B**).

Figures 2C,D show the DOC and DON concentrations in the OS and the FJ samples. The average values of DOC and DON for all samples were 53.71 ± 9.79 and 28.62 ± 3.97 μM, respectively, with insignificant differences between OS and FJ. It was similar to the DOC levels in previous studies conducted during austral fall: 43.3 ± 2 μM in April (Carlson et al., 2000) and 45.1 ± 1.6 μM from February to April in Ross Sea (Bercovici et al., 2017). Moreover, from spring to summer, large ranges of DOC values have been recorded in the Antarctic seawater; for example, 41–64 μM DOC was detected in samples collected from November to February (Fang et al., 2020), whereas DOC varied between 40 and 102 μM in the upper mixed layer (Doval et al., 2002). The DOC values measured in this study were 1.1 to 1.9 times lower than those in the austral summer. DOC accumulates in the euphotic zone of the seawater during summer, indicating that the high concentration of DOC was produced *via* biological activities in the previous seasons. Meanwhile, the C/N ratio (DOC/DON) ranged between 1.63 and 2.26, and the

FIGURE 3 | The fluorescence intensities of humic-like and protein-like dissolved organic matter: A, terrestrial humic-like; M, marine humic-like; C, humic-like; B, tyrosine-like; and T, tryptophan-like. The error bars refer to the standard deviation.

DOM characteristics		Sampling sites	
Contents	Peak	OS	FJ
Humic-like (%)	A	26.8 ± 6.0	31.7 ± 1.9
	M	26.3 ± 5.3	30.4 ± 2.3
	C	19.2 ± 0.8	18.1 ± 0.4
Protein-like (%)	B	12.3 ± 6.9	8.8 ± 1.6
	T	15.4 ± 3.6	11.1 ± 3.5

mean value was 1.88 ± 0.26 (**Figure 2E**), which is lower than that in a previous research in which the C/N ratios were between 3 and 95 in Antarctica in the summer season (Thomas et al., 2001). C/N ratios below 5 usually represent a scarcity of algae and other endogenous DOM in the aquatic environment (Ni and Wang, 2015). Thus, it seems that the DOM content in the austral fall of the present study was less influenced by marine biological activity.
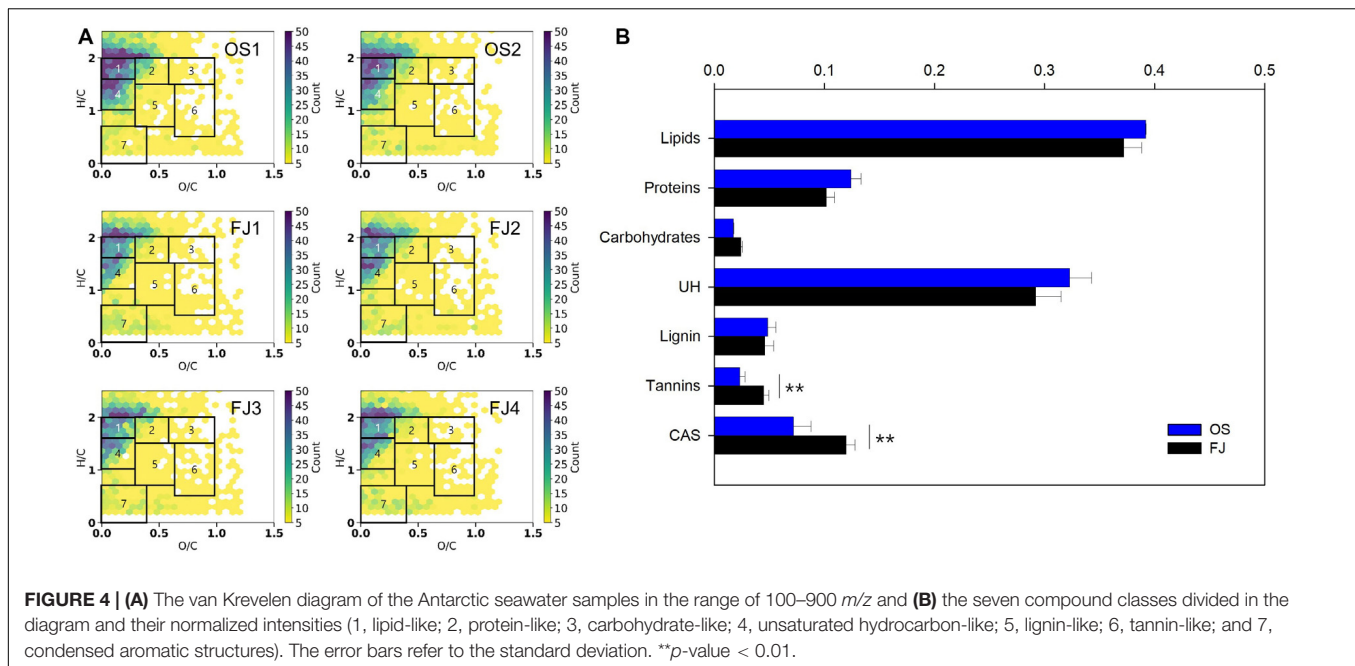
Optical Properties of DOM

The CDOM absorption coefficient values were calculated (**Figure 2F** and **Supplementary Table S2**), and the fluorescence intensities of each peak (A, M, C, B, and T) were calculated as percentages (**Figure 3** and **Supplementary Table S2**) based on previous studies (Chen et al., 2003; Coble, 2007). There were no significant differences between the OS and the FJ areas in both CDOM and FDOM values (t-test, $p > 0.05$), indicating that the surface seawater DOM compositions in open sea and in fjord areas are not different. By the fluorescence peaks, the intensities of humic substances (i.e., peaks A, M, and C) were found to be 1.8 to 5.7 times greater than those of protein-like substances (i.e., peaks B and T, **Figure 3**, and **Supplementary Table S2**). The DOM in fresh water is mainly derived from the degradation of aquatic organic matter from forest and riparian zones where humic substances are high (Baker and Inverarity, 2004). In the case of protein-like substances (i.e., peaks B and T), those are characterized as amino-acid-like DOM derived from marine biological sources. As such, they could be more labile in abundance, depending on the marine biological activity (D'Andrilli et al., 2015). In this study, peaks B and T showed the lowest fluorescent intensity compared to the humic peaks in all sampling site groups (**Figure 3**), which may be related to the low C/N ratios and scarcity of microorganisms. Kang et al. (1997) reported that the biomass of microalgae in the Antarctic is very low during the austral winter due to the lack of radiance. Additionally, protein-like substances – usually characterized by the biochemical degradation of biologically derived metabolites – are generally found in the surface layer during bloom periods (Coble, 2007). Moreover, a comprehensive analysis of the fluorescence intensities of the humic and the protein regions of the EEMs – as well as the FI, BIX, and HIX – indicates that the DOM of the OS and the FJ areas are dominantly derived from terrestrial sources (**Supplementary Figure S1**).

Molecular Properties of DOM and Identification of Source
General Properties of Molecular Compositions by Orbitrap Measurement

To characterize the DOM on a molecular level, it was extracted from the samples using SPE cartridges and then analyzed by Orbitrap. **Figure 4** shows the van Krevelen spectra of the Antarctic seawater samples in the range of 100–900 m/z; a total of more than 3,500 different molecular formulae were identified. The diagrams for all samples exhibited high intensities of lipid-like (35–39%) and unsaturated hydrocarbon-like (UH; 27–34%) substances, as shown in **Figure 4B**. As reported in a previous study, the source of lipid-like and UH-like substances in the Antarctic waters seem to be related to the prevalence of cryptogamic organisms (e.g., moss, lichen, and algae) across Antarctica (Matsumoto et al., 2010). The authors explained that the long chains of hydrocarbons (both saturated and unsaturated) and lipids are likely from the detritus of lichen and/or vascular plants, while the short chains are related to marine biological debris (Matsumoto et al., 2010). However, previously observed results and a satellite map of seasonal variations of chlorophyll-a concentrations in the ice shelf systems showed a rapid decrease after the occurrence of a phytoplankton bloom in March— equivalent to the austral summer (Kang et al., 1997; Vernet et al., 2012; **Supplementary Figure S2**). Additionally, it has been reported that DOM is dependent upon vegetation when marine biological activity is low at temperatures lower than 5°C (Malik and Gleixner, 2013; Roth et al., 2015). Therefore, although further research is needed to determine whether the lipid-like and UH-like substances were affected by the bloom or the plant-derived DOM, the Antarctic surface seawater seems to be more affected

FIGURE 4 | (A) The van Krevelen diagram of the Antarctic seawater samples in the range of 100–900 *m/z* and **(B)** the seven compound classes divided in the diagram and their normalized intensities (1, lipid-like; 2, protein-like; 3, carbohydrate-like; 4, unsaturated hydrocarbon-like; 5, lignin-like; 6, tannin-like; and 7, condensed aromatic structures). The error bars refer to the standard deviation. *******p*-value < 0.01.

TABLE 1 | Studies on dominant compounds in various environments of Antarctica and the Arctic by using high-resolution mass spectrometry (HRMS).
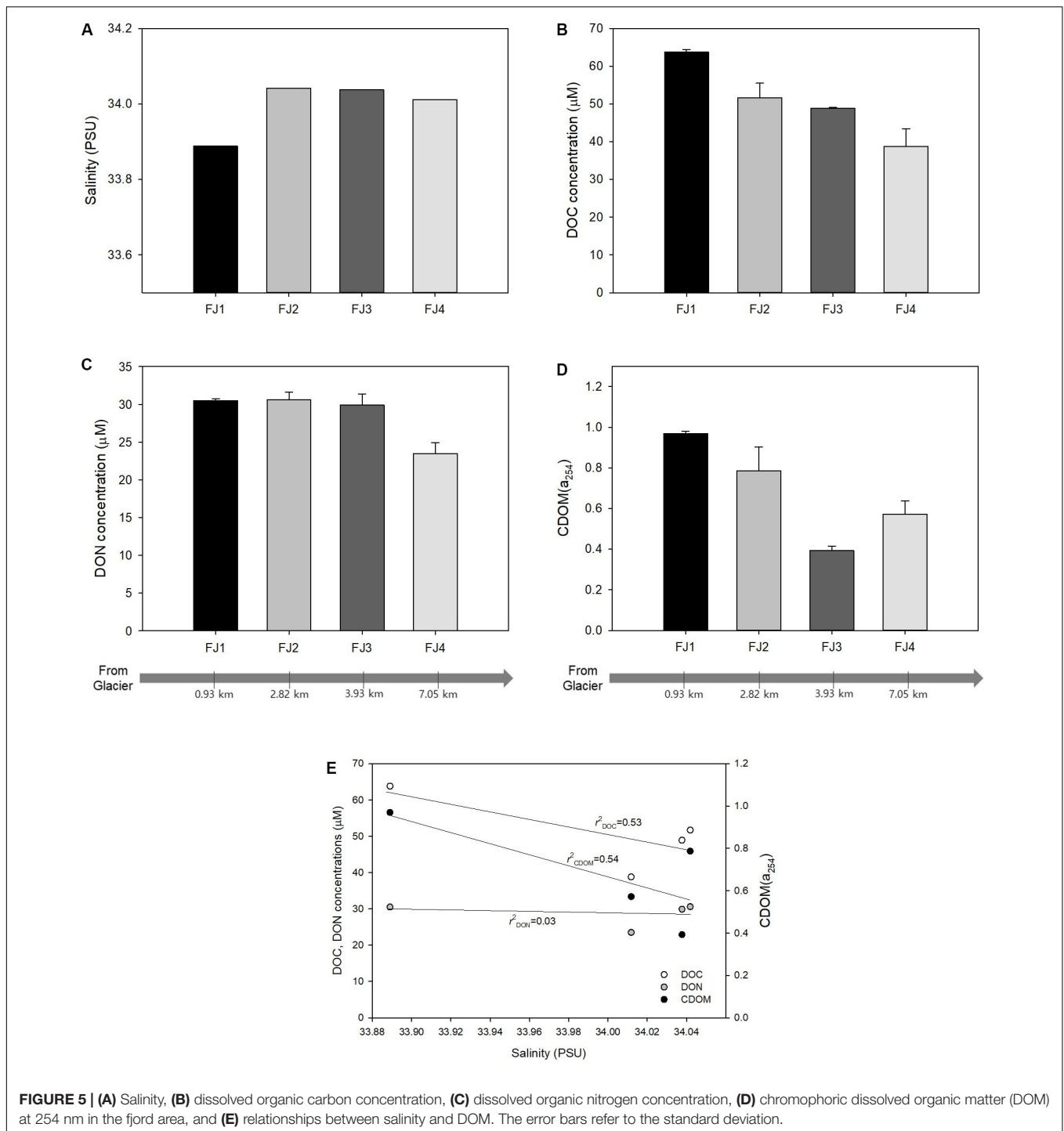
Sampling site	Samples	Sampling date	Dominant compounds	Methods	References
Antarctic	Seawater	November 2004–January 2005	Lignin, Tannins	FT-ICR MS	D'Andrilli et al., 2010
Antarctic	Seawater	Austral summer	Lignin	FT-ICR MS	Koch et al., 2005
Antarctic	Surface and deep seawater	November–January	Lignin	FT-ICR MS	Koch et al., 2008
Antarctic	Seawater	April–May 2018	Lipid-like, Unsaturated hydrocarbon-like	Orbitrap	This study
Arctic	River, wetlands	May 2015	Protein (~61%), Lignin (~64%)	Orbitrap	Mangal et al., 2017
Arctic	Porewater	August–September 2010 June 2011 August 2012	Lignin (48–71%), Tannin (11–42%)	FT-ICR MS	Hodgkins et al., 2016
Arctic	Surface, deep, and bottom of seawater	August 2016	Lignin	FT-ICR MS	Chen et al., 2018
Arctic	Ice core, underlying seawater	April–May 2017	Lignin (38–50%)	FT-ICR MS	Brogi et al., 2018

by the terrestrial DOM of non-algae origin based on the results of the optical properties.

In other studies, DOM in old accumulated snow or long-established glacier ice from the Antarctic region was analyzed, and a large portion of lignin was reported (**Table 1**; Grannas et al., 2006; Antony et al., 2017). Similar to these studies, in the Arctic, lignin was found to be one of the dominant components in various environments during spring flooding, when DOM deposited in snow or ice was mobilized with melting waters (**Table 1**). The differences between this result and those of previous studies may be influenced by the different sampling seasons (**Table 1**). The DOM in this study was collected in the austral fall. It has been reported that the Antarctic ice pack increases up to 21%, and melting rate decreases from the austral fall to winter (Gloersen et al., 1993; St-Laurent et al., 2015). In these circumstances, transference of DOM from ice to seawater is reduced. As such, the difference between this result and that of previous studies in dominant composition is caused by the fact that the DOM that has accumulated

in ice or glacier over long periods of time does not flow into the seawater.
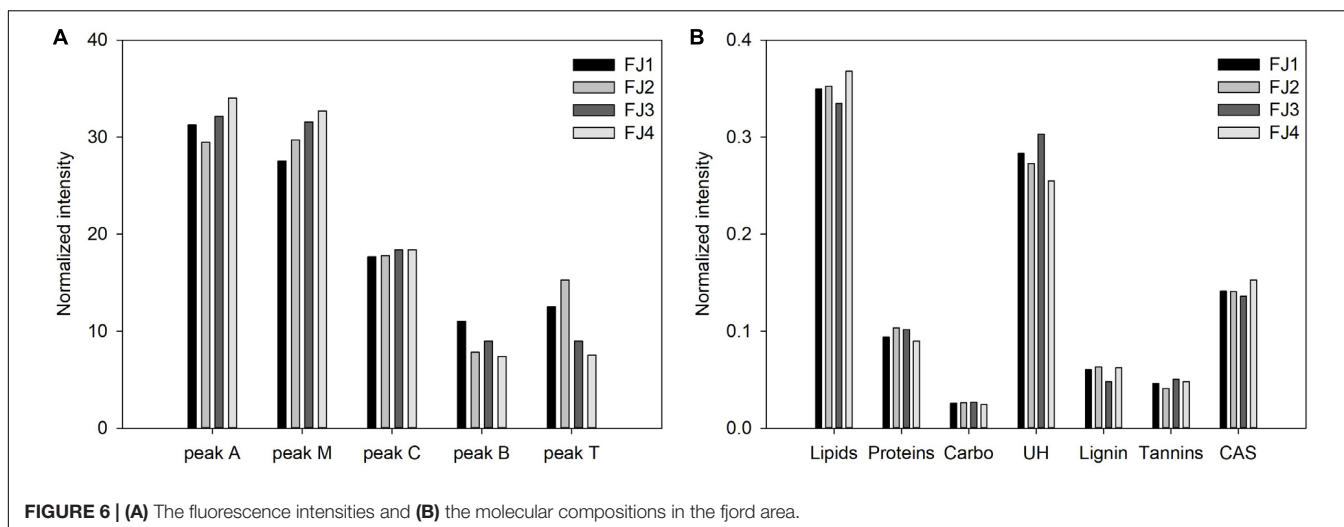
Tannin-like substance and condensed aromatic structures (CAS) were not found in high amounts but were significantly higher in the FJ area than in the OS (**Figure 4B**). This indicates that these substances originated from land rather than from sea. This result is consistent with previous studies in which only compounds originating from plants were found during low marine biological activity and low temperatures in winter (Malik and Gleixner, 2013; Porcal et al., 2015; Roth et al., 2015). Specifically, in glacier areas, DOM has been known to be introduced from the surrounding vegetation and soil, which is captured during the advancement of the glacier or ice sheet in the austral winter (Barker et al., 2009). Among terrestrial sources, tannin-like substance and CAS have been shown to be more related to moss than root plants (Hodgkins et al., 2014). Antarctica is covered with a variety of living organisms adapted to extreme weather conditions—one of the major flora being moss (Fowbert and Smith, 1994; Matsumoto et al., 2010;

FIGURE 5 | (A) Salinity, **(B)** dissolved organic carbon concentration, **(C)** dissolved organic nitrogen concentration, **(D)** chromophoric dissolved organic matter (DOM) at 254 nm in the fjord area, and **(E)** relationships between salinity and DOM. The error bars refer to the standard deviation.

Singh et al., 2018). Despite the very slow growth rate of moss—1 mm per year—moss-covered green areas in Antarctica continue to grow due to climate change. According to a 26-year monitoring study, populations of *Deschampsia antarctica* and *Colobanthus quitensis*, native cryptogamic organisms, increased by 25 and five times, respectively, with increasing temperature (Fowbert and Smith, 1994). Moreover, a recent study, which investigated moss in a 600-km transect in Antarctica, found that moss

growth rates are four to five times faster than those in the 1950s (Amesbury et al., 2017). Therefore, the refractory terrestrial DOM—such as tannin-like substance and CAS—could rapidly increase in the seawaters in Antarctica in the future with the increased growth rate of mosses and melting of land ice and glaciers due to climate change. Furthermore, the findings in this study implicate background results for high marine biological activity in summer.

FIGURE 6 | (A) The fluorescence intensities and **(B)** the molecular compositions in the fjord area.

Influence of the Runoff Water From Freshly Melting Land Ice and Glacier

The concentration and properties of the DOM were investigated according to its distance from a glacier to determine if it was of terrestrial origin. In salinity, it was found that the salinity of FJ1 was lower than that of FJ2–FJ4 (**Figure 5A**). Moreover, there were increasing trends in the concentrations of DOC and CDOM toward the FJ1 site (**Figures 5B,D**). Salinity also negatively correlated with DOC (r^2 = 0.53, **Figure 5E**) and CDOM (r^2 = 0.54, **Figure 5E**) values, although the regressions were not significant (p-values > 0.05). There were no significant trends in DON except for FJ4 (**Figures 5C,E**). These results indicate that DOM created by living organisms on the ground entered the seawater with runoff from the freshly melting land ice and glacier. Previous studies have observed continuous crevassing and erosion of the glacier at the head of Marian cove (Khim et al., 2007; Yoo et al., 2015). The surface waters in this cove are not readily affected by resuspension because the inner basin is deep (120 m), whereas terrestrial and supraglacial meltwaters from the glacier influenced the surface water of the cove, specifically in austral summer (Yoo et al., 2015; Llanillo et al., 2019). Surface water was actively exchanged between Marian cove and Maxwell Bay, and the bay mouth is connected to Bransfield Strait (Yoo et al., 2015). Consequently, terrestrial DOM can be transported to offshore KGI by tides.

Furthermore, there were no trends of FDOM or molecular composition in the FJ area (FJ1–FJ4; **Figure 6**), indicating that there was no change in molecular composition. The biological characteristics were not significant since there were not enough factors that could affect DOM degradation. According to previous studies, the factors that affect DOM degradation include photo-oxidation, marine biological activity, and temperature. These studies support our findings that low light levels and temperatures in winter undermine marine biological decomposition (Porcal et al., 2015; Roth et al., 2015). Particularly, in Marian Cove, the number of microorganisms was lower in austral winter, when water temperatures were relatively low, than in austral spring–summer (Kang et al., 2000, 2002).

To summarize, the DOM concentrations in the ice shelf systems seem to increase by the impact of DOM originating from land and introduced *via* fresh melt runoff from the land ice and glacier. However, there were no significant changes in composition resulting from low marine biological degradation due to low light and temperature. Therefore, we expected that the effect of terrestrial DOM on marine DOM would increase, especially due to increased land ice and glacier runoff caused by climate warming and increased temperature in the austral summer. The increased DOM could increase primary organic-rich aerosol production, which could exacerbate climate warming. Park J. et al. (2019) recently found that the large amount of freshwater from river runoff may substantially impact primary aerosol production, possibly affecting cloud radiative forcing. We further showed that riverine organic matter, especially terrestrial DOC, can be directly emitted from surface seawater to the Arctic atmosphere *via* bubble bursting (Park J. et al., 2019).

CONCLUSION AND ENVIRONMENTAL IMPLICATION

We investigated the characteristics of DOM from the Antarctic surface seawaters using optical spectrometry and Orbitrap-MS and obtained the following results:

- The DOM in the Antarctic seawater was more affected by terrestrial than marine biological sources due to the lower marine biological activities in the austral fall.
- Both lipid-like and UH-like substances were dominant in the ice shelf systems of King George Island, which is believed to be the result of non-algal and terrestrial organisms such as cryptogams spread across Antarctica.
- The DOM in the ice shelf systems was found to be affected by non-algal and terrestrial organisms such as cryptogams without any change in molecular composition, which are introduced *via* land ice and glacier runoff in the austral fall.

Climate warming has caused the rapid growth of cryptogamic organisms and extended their habitat. We could not evaluate the contribution of cryptogamic organisms to increasing DOM in the Antarctic Ocean due to the insufficient sampling numbers (six samples) and sampling location (King George Island). Nonetheless, the effects of terrestrial DOM on marine DOM are expected to increase, especially due to the effects of increased cryptogamic organisms and increased land ice and glacier runoff in the austral summer. Moreover, DOM originating from terrestrial organisms is expected to significantly impact the global atmosphere by increasing the primary organic aerosol production, which could contribute to climate warming. Therefore, more sampling and molecular-level DOM analysis over the Antarctic Ocean should be conducted to provide a much clearer evidence of the contribution of cryptogamic organisms.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**.

AUTHOR CONTRIBUTIONS

JJ carried out the experiments of the Antarctic seawater samples came from the institute involving JiP, SA, K-TP, and S-YH. JiP and KC contributed to the conception of this study and editing the manuscript. K-TP, S-YH, and JoP also contributed to the conception of the study and the interpretation of results. SA collected samples in the Antarctica and helped method section. JJ wrote the manuscript with contributions and comments from all co-authors.

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SUPPLEMENTARY MATERIAL

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