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RESEARCH ARTICLE

Chemical proxies of glacier-derived and marine organic matter reveal low mixing in summer-stratified Arctic fjords

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Abstract

The rapid deglaciation of the Arctic increases the flux of terrestrial organic matter into the marine carbon cycle. The proportions, mixing, and turnover rates of organic matter from deglaciated terrestrial and glacial watershed sources are poorly understood in Arctic fjords. We characterized the mixing and flux of dissolved organic matter (DOM) in two Arctic fjords, Kongsfjorden and Scoresby Sund. DOM was sampled and analyzed along the natural mixing gradient from glacial meltwater to the marine waterbody to reveal chemical proxies for glacier-derived organic matter utilizing (ultra)high-resolution mass spectrometry of solid-phase extracted DOM. The molecular composition of DOM in Kongsfjorden was homogenous in elemental ratios of O/C, H/C, and N/C and aromaticity due to high mixing and low glacial run-off. In Scoresby Sund, a strong correlation between DOM composition and salinity was observed. The freshwater proportion of DOM was characterized by a low N/C ratio, unsaturated molecules, and a high terrestrial index. The surface stratification in Scoresby Sund prevented vertical mixing of glacier-derived and marine DOM with denser water masses. Glacial meltwater DOM in Scoresby Sund was similar to terrestrial DOM, suggesting either an unknown source of additional DOM or selective DOM removal processes. In summary, the high proportion of terrestrial DOM proxies suggests a strong imprint of deglaciation on the Arctic carbon cycle.

The Arctic is warming four times as fast as the global average resulting in rapid increase of air and water temperatures, loss of sea ice, melting of the Greenland ice sheet and northward expansion of Atlantic water (Bring et al. 2016; Cantoni et al. 2020; Gjelstrup et al. 2022). The meltwater introduces organic molecules into fjord environments thus influencing biogeochemical processes. These strong shifts may impact the fragile Arctic ecosystem and change turnover and sequestration of atmospheric carbon dioxide (Arrigo and van Dijken 2015; Polyakov et al. 2017). While fjords contribute up to 11% of global marine carbon burial (Smith et al. 2015), it is uncertain how changes to the Arctic climate will affect carbon cycling (Meredith et al. 2019).

The composition and distribution of dissolved organic matter (DOM) in marine systems is controlled by various factors, such as primary production and microbial activity (Jiao et al. 2010; Paulsen et al. 2019), mixing of water masses, physico-chemical degradation, and aggregation (Koch et al. 2014; Verdugo and Santschi 2010). The molecular composition

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Data Availability Statement: Oceanographic metadata from the expedition are archived on PANGAEA: https://doi.org/10.1594/PANGAEA.871015 (Friedrichs et al. 2017). Raw mass spectrometric peaklists and filtered list of molecular formulas have been published at the PANGAEA archive: https://doi.pangaea.de/10.1594/PANGAEA.965354 (Moye et al. 2024). Additionally, data and R-Scripts are accessible at https://gitlab.awi.de/famoye/msm56. Molecular formulas were generated with the Ultra-Mass-Explorer (UME, www.awi.de/en/ume; Leefmann et al. 2019). Data were evaluated using R (R Core Team 2023). The maps were generated using Ocean Data View 5.6.5 (Schlitzer 2023).

and stoichiometric elemental ratios of DOM serve as proxies for biochemical and physiochemical processes of sources and sinks of DOM and are determined by high resolution and accurate mass spectrometry (HR-MS). This analytical method has been used to differentiate between (i) patterns of terrigenous and marine DOM (Koch et al. 2005; Medeiros et al. 2016), (ii) DOM age (Flerus et al. 2012; Jiao et al. 2010), (iii) biodegradation (Koch et al. 2014; Lechtenfeld et al. 2015; Underwood et al. 2019), and (iv) photochemical degradation (Kujawinski et al. 2004).

The composition and turnover of Arctic DOM is poorly understood. Glacial DOM is comparatively old (depleted of ^{14}C), with a high nitrogen content and H/C ratio, indicative of saturated compounds (Bhatia et al. 2010; Lawson et al. 2014; Stubbins et al. 2012). Given its high content of dissolved organic nitrogen, glacial DOM is an important nitrogen source and biostimulates nitrogen-deplete glacier estuaries (Paulsen et al. 2017). Bussmann and Kattner (2000) observed variable concentrations of dissolved organic carbon (DOC) in different Arctic waterbodies (e.g., surface water, halocline, Atlantic water and deep water), suggesting variable carbon flux via production, turnover, and/or mixing processes. Generally, DOC in glacial discharge is low (Hopwood et al. 2020 and references therein). Contrary, DOC of Arctic rivers is two orders of magnitude higher than in fjord water (Dittmar and Kattner 2003). In Kongsfjorden (Svalbard), DOC seasonally increases during phytoplankton spring blooms and summer primary production until the beginning of autumn (October 96.4 ± 9.5 μM) and drops during winter (April 59.4 ± 12.7 μM; Retelletti Brogi et al. 2019). The molecular DOM composition in Kongsfjorden did not vary with environmental parameters and thus correlates with a rapid transformation of organic material (Osterholz et al. 2014).

The DOM composition along natural gradients in estuaries generally follows conservative mixing. Deviations from conservative mixing therefore reveal biological, chemical, or physical sources and sinks of DOM in the mixing zone (Seidel et al. 2015). To track and compare the composition of DOM in Arctic fjords differently affected by glacial meltwater, we chose Scoresby Sund in East Greenland and Kongsfjorden in Svalbard as sampling sites. Both fjords vary in glacial meltwater input and are ideally suited to correlate the impact of freshwater influx and mixing with marine DOM molecular signatures. Scoresby Sund receives a comparatively higher meltwater influx, about 3% (8.3 km^3 a^{-1}) of the total Greenland meltwater (Lewis and Smith 2009), than Kongsfjorden with 1.4 km^3 a^{-1} freshwater influx (Svendsen et al. 2002).

Guided by the hypothesis that ongoing Arctic deglaciation and corresponding influx of terrestrial DOM drastically affects the Arctic carbon cycle, we analyzed compositional changes of DOM along a horizontal mixing gradient to reveal molecular proxies for glacial meltwater-derived DOM and track these along the mixing gradient. These proxies would allow estimations of DOM reactivity and/or additional DOM sources and their impact on biogeochemistry. In a laboratory two endmember mixing experiment between marine DOM and glacier-derived DOM, we tested if DOM proxies of interest revealed a linear response along the glacially influenced natural mixing gradient.

Materials and methods

Study area

Kongsfjorden (West Svalbard) and Scoresby Sund (East Greenland) were sampled in July 2016 during RV *Maria S. Merian* expedition MSM56 (Koch et al. 2019). The cruise track covered 79°N to 70°N and 28°W to 12°E (Fig. 1). Scoresby Sund (local: Kangertittivaq) is the world's largest fjord extending ca. 350 km from its 30 km-wide mouth to the Daugaard-Jensen glacier in Nordvestfjord (local: Kangertertivarmiit Kangertivat). The glacier drains an area of 50,150 km^2 and discharges 10.5 km^3 of meltwater annually (Rignot and Kanagaratnam 2006). Kongsfjorden, in comparison, is just 20 km long, with a mouth opening of 4–10 km and ~ 100 m depth at the inner fjord (Fig. 1). The fjord is influenced by Arctic water in winter, which is replaced by Atlantic water during summer, initiating a spring bloom (Hegseth and Tverberg 2013; Sert et al. 2020). Water samples were taken as close to the marine ice barrier as allowed (minimal salinity: 10.6). Water masses were defined according to oceanographic physical properties (Supporting Information Table S1). Two runoff samples (Supporting Information Tables S2 and S3) were taken from motor boats to retrieve "true" endmember samples.

Sampling and work-up procedures

Water samples were collected from 1.5 to 1397.4 m depth by CTD equipped with Niskin bottles covering the complete depth of the stations. Samples were filtered, acidified to pH 2 for PPL extraction according to Dittmar et al. (2008). The SPE columns were frozen at −20°C until elution with 1 mL of methanol and analyzed as described in Supporting Information S1.1. Methanol extracts were stored at −18°C until measurement to minimize esterification (Flerus et al. 2011). DOC and nutrients were determined as described in Supporting Information S1.2, and S1.3 were adapted from Kattner and Becker (1991) and described elsewhere (Seifert et al. 2019).

Metadata and water mass definitions

The potential temperature (Θ), absolute salinity, potential density (σ_θ) and squared buoyancy frequency N^2 were calculated with R package gsw (Kelley et al. 2017). Further oceanographic data were downloaded from public database PANGAEA (Friedrichs et al. 2017). Water masses (glacial melt water, surface glacial water, Kongsfjorden surface water, Kongsfjorden intermediate water, modified polar water, polar water and Atlantic water) were defined according to oceanographic physical properties (Supporting Information Table S1; Supporting Information Fig. S1; Geuer 2020; Seifert et al. 2019; Tverberg et al. 2019).

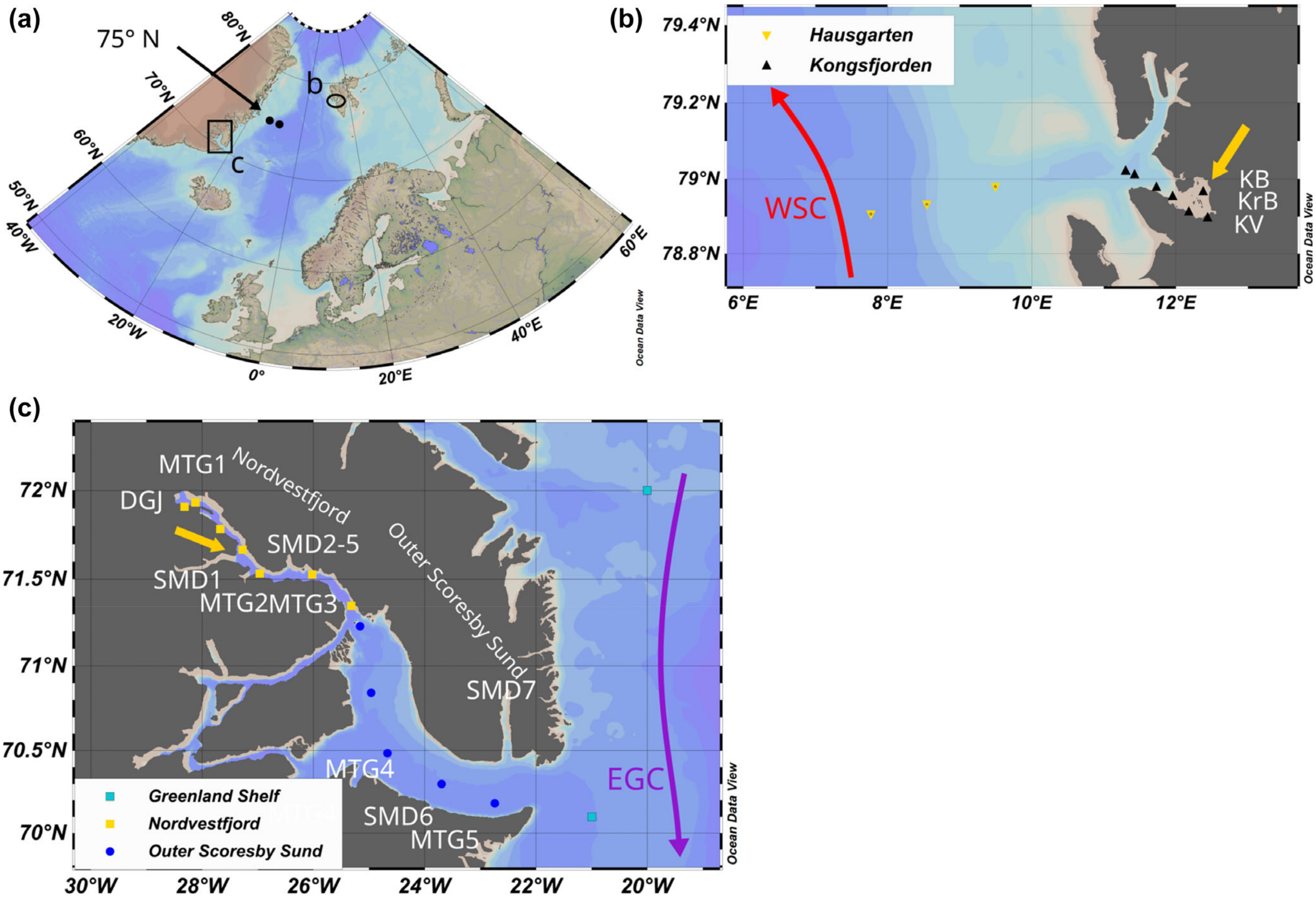

Fig. 1. (**a**) Overview map with two 75°N transect stations; (**b**) Kongsfjorden, Svalbard; (**c**) Scoresby Sund (Kangertittivaq), East-Greenland. Yellow arrows indicate the origin of runoff samples. Major currents: WSC: West Spitsbergen Current (red arrow); EGC: East Greenland Current (purple arrow). Locations of major glaciers in Kongsfjorden: Kongsvegen (KV), Kronebreen (KrB), Kongsbreen (KB). The locations of Daugaard-Jensen glacier (DGJ), several marine terminating glaciers (MTG1-5) and surface meltwater discharges (SMD1-7) are marked in Scoresby Sund (for details *see* Seifert et al. 2019). The maps were generated using Ocean Data View 5.6.5 (Schlitzer 2023).

Mass spectrometry and data evaluation

Although comparative interlaboratory DOM studies using the same sample but different mass spectrometers did not reproduce the molecular sample composition, the compositional trends, as revealed by multivariate statistics, were consistent among different instruments (Simon et al. 2018; Zherebker et al. 2020). In order to verify that sample analyses in our study were robust, we performed all measurements on two different mass spectrometers to safeguard that changes in DOM composition were independent of the chosen mass analyzer. FT-ICR-MS measurements in negative electrospray ionization (ESI) mode were done on a Bruker Solarix 12 T (Bruker Daltonics, Germany) according to Wünsch et al. (2018). FT-Orbitrap-MS analyses were performed on a hybrid high-resolution mass spectrometer (Q-Exactive Plus, Thermo Fisher Scientific, Bremen, Germany). Samples were delivered via binary pump. Detailed measurement conditions are described in Supporting Information S1.5. A small number of samples were insufficient for analysis on both platforms and were only measured by FT-ICR-MS (detailed measurement conditions are described in Supporting Information S1.6). Regular measurement of blanks and a DOM North Sea water lab standard (NSW) ensured analytical reproducibility.

Molecular formulas, data preparation, and indices

Molecular formulas in the range of *m/z* 200–700 were generated by Ultra-Mass-Explorer (UME, www.awi.de/en/ume; Leefmann et al. 2019). The elemental compositions $^{12}C_{\leq\infty}{}^{1}H_{\leq\infty}{}^{16}O_{\leq\infty}{}^{14}N_{\leq 2}{}^{32}S_{\leq 1}$ with a mass accuracy of 0.4 ppm for FT-ICR-MS and 0.9 ppm for the FT-Orbitrap-MS spectra were allowed. The Kendrick mass defect (KMD) and nominal mass (NM) were calculated from *m/z* values (Kendrick 1963). Double bond equivalents (DBE) were calculated, and the DBE-*O* (DBE minus number of oxygen atoms) was set to a maximum of 10 (Herzsprung et al. 2014). Only molecular formulas containing a respective ^{13}C mass signal were considered. Formulas belonging to potential surfactants (Lechtenfeld et al. 2013;

Leefmann et al. 2019) were removed. The FT-ICR-MS data did not contain multiple assignments, whereas 5.97% of Orbitrap peaks matched either [CHO] or [CHO]NS. They were checked for their DBE-*O* value and converted to the respective [CHO] alternatives (Herzsprung et al. 2014). The absolute intensities were converted to relative intensities by sum normalization so that the sum of all intensities per spectra was 1. The Nominal Oxidation State of Carbon (NOSC; LaRowe and Van Cappellen 2011), the Aromaticity Index (AI; Koch and Dittmar 2006; Koch and Dittmar 2016) and the index of degradation (I_{DEG}; Flerus et al. 2012) were calculated for each neutral molecular formula accordingly (*see* Supporting Information S1.7).

The terrestrial index (I_{terr}) was calculated after Medeiros et al. (2016) with 80 molecular formulas (40 positive, 40 negative). Formulas were filtered against all molecular formulas of an in-house database, and only 10 molecular formulas occurring in most of the samples were kept (NEG: $C_{15}H_{16}O_6$, $C_{17}H_{16}O_7$, $C_{17}H_{16}O_8$, $C_{17}H_{18}O_7$, $C_{18}H_{18}O_7$; POS: $C_{17}H_{21}NO_8$, $C_{19}H_{22}O_{10}$, $C_{20}H_{24}O_{10}$, $C_{20}H_{24}O_9$, $C_{20}H_{26}O_9$). The index I_{terr2} was calculated as:

$$I_{terr2} = \frac{\sum_{NEG} I_{abs}}{\sum_{NEG} I_{abs} + \sum_{POS} I_{abs}}$$

Statistical analyses

Statistical analyses were performed with R (R Core Team 2023, for used R-packages, *see* Supporting Information Table S4). Relative intensities were scaled and centered to a standard deviation (sd) of 1, a mean of 0 and a principal component analysis (PCA) was constructed. *P*-values were corrected by Base R function p.adjust and method Holm–Bonferroni (Holm 1979). The freshwater fraction was calculated with the marine endmember salinity (S) of 35.1062 (mean of the three highest salinities): $f_S = (S_{marine} - S)/S_{marine} = (35.1062 - S)/35.1062$ (Medeiros et al. 2015).

Two-endmember mixing experiment compared to theoretical mixing

A laboratory two-endmember mixing experiment was adopted from Seidel et al. (2015) to test the linear response of the FT-Orbitrap MS data to conservative mixing. Briefly, two PPL-extracted DOM samples in methanol, representative of a marine endmember of Atlantic water at Hausgarten (70 m depth, salinity 35.1060, $[DOC] = 40.1\,\mu$ mol L^{-1} and 100 m, salinity 35.0944, $[DOC] = 35.7\,\mu$mol L^{-1}) were mixed with PPL-extracted DOM samples in methanol, representative of endmembers for glacial runoff at Kongsfjorden ($[DOC] = 17.0\,\mu$mol L^{-1}) and Scoresby Sund ($[DOC] = 24.0\,\mu$mol L^{-1}) in ratios of 0:100%, 25:75%, 50:50%, 75:25%, 100:0%, all v/v. Samples were mixed in 1.5 mL glass vials and adjusted to the same level of 1.5 mmol DOC L^{-1} with a 1/1 mixture of methanol and ultrapure water prior to mixing to exclude ionization artifacts due to differences in concentrations. A natural water mass resulting from the mixing of 75% glacial runoff and 25% marine water (i.e., salinity ~ 5) would contain 62% freshwater-derived and 38% marine-derived DOC due to mixing of comparatively low concentrated DOC in glacial water with high DOC concentrated marine water. The equation to convert the ratio of the two-endmember mixing experiment to the natural mixing ratio is given in Supporting Information S1.8.

Results

Characterization of fjord water masses

After removing isotopologues and applying formula filters, an average (sd; Greenacre 2016) of 1160(101) and 1884(92) formulas were assigned by FT-ICR-MS and FT-Orbitrap-MS, respectively. On a presence/absence basis, data obtained by both methods shared 55.4% ($n = 2808$) of formulas, while 9.7% ($n = 491$) and 35.0% ($n = 1773$) were unique to FT-ICR-MS and FT-Orbitrap-MS, respectively. Molecular formulas shared between both instruments represented > 99% of the total intensity for the FT-ICR-MS and > 96% for the FT-Orbitrap-MS.

The average chemical properties of glacier meltwater and surface glacial water were characterized by a weighted average of high unsaturation (aromaticity index, AI, weighted average (weighted sd): 0.025 (0.073), and 0.02 (0.061), respectively) and low N/C ratios (0.006 (0.025) and 0.008 (0.027), respectively). The average terrestrial index (I_{terr2}, 0.15 (0.02), 0.12 (0.01)) was higher, and the average degradation index (I_{DEG}, 0.57 (0.02), 0.62 (0.01)) was lower in glacier meltwater than in surface glacial water (Supporting Information Table S2). The DOC concentrations mostly deviated in glacier meltwater (mean DOC 27.7 μmol L^{-1}; Supporting Information Table S2).

Water masses of similar salinity (33–34.5) were Kongsfjorden surface water, Kongsfjorden intermediate water, polar water, and modified polar water with temperatures as low as −1.5°C (polar water) up to 4.3°C (intermediate water). The concentrations of DOC ranged from 38.7 to 47.1 μmol L^{-1}, except for intermediate water (average of 55.3 μmol L^{-1}). Polar water DOM revealed chemical properties (AI, 0.018 [0.056]), low N/C ratio (0.009 [0.028]), higher I_{terr2} (0.11 (0.01)), and lower I_{DEG} (0.66 (0.02)) more similar to glacier meltwater and surface glacial water with higher unsaturation. Kongsfjorden surface water, Kongsfjorden intermediate water, and modified polar water had similar unsaturation (AI, ~ 0.013), N/C (~ 0.010), I_{terr2} (~ 0.08) and I_{DEG} (~ 0.72) values as Atlantic water. Atlantic water had the highest salinity (34.91) but varied in temperature (0.8–3.8°C) and DOC concentrations from 46.3 to 38.7 μmol L^{-1} (Supporting Information Table S2).

Dissolved organic matter molecular diversity

The surface of Scoresby Sund had the highest molecular diversity (Shannon diversity index, median 6.44, Fig. 2).

Below the surface layer, the molecular diversity dropped to 6.25 at the fjord floor. In Hausgarten, the molecular diversity also decreased with depth, but only from 6.26 to 6.19, while the molecular diversity had no depth trend and was highly variable in Kongsfjorden. The molecular diversity in the Greenland Shelf increased below the surface from 6.28 to 6.42 at 15–40 m and dropped to 6.23 below 40 m. The runoff samples had a diversity of 6.74 in Scoresby Sund and of 6.65 in Kongsfjorden.

Multivariate molecular trends

The first two principal components (PCs) of the PCA (Fig. 3) explained 22% of the variance in FT-ICR-MS data and 25% of the variance in FT-Orbitrap-MS data (*see* also Scree plot in Supporting Information Fig. S3). The range of percentages explained by principal component 1 (PC1; 14.29%) and principal component 2 (PC2; 8.09%) is common to PCA applied to complex data with many variables. The high number of variables in this dataset (i.e., detected masses) is due to the high biogeochemical variance of DOM. In combination with ~ 3300 variables (molecular formulas) and 152 samples, 22% of the variance is explained by the first two of the overall 151 dimensions. The Greenland samples were separated along the first PC axis. The distribution of samples along PC1 correlated with the potential density of the sample origin. The defined water mass (Supporting Information Tables S1–-S3; Fig. 3; Supporting Information Figs. S1 and S2) aligned with the potential density gradient along PC1. Glacial meltwater samples showed the highest PC1 values, followed by surface glacial water and polar water toward Atlantic water near the coordinate origin.

The Svalbard samples aligned almost linearly along PC2 and orthogonal to the Greenland samples (Fig. 3a, PC2). There was no clear correlation between the distribution along PC2 and any of the available environmental data. All trends observed with heuristic methods were consistent among data obtained with both instrument platforms.

Principal component 1 of the FT-ICR-MS dataset significantly correlated with potential density ($\rho=-0.62, p<0.01$), salinity ($\rho=-0.79, p<\ 0.01$), temperature ($\rho=-0.43, p<0.01$) and geolocation (latitude, longitude, $\rho=-0.65$ and $\rho\ =-0.73, p<0.01$, Fig. 3). No significant correlations were found for co-variables, such as sampling depth. Principal component 1 significantly correlated with the total dissolved nitrogen content ($\rho=-0.35, p<0.01$) and the extraction efficiency ($\rho=0.40, p<0.01$). Principal component 2 significantly correlated with the silicate concentration ($\rho=0.32, p<0.01$). The number of molecular formulas detected by FT-ICR-MS

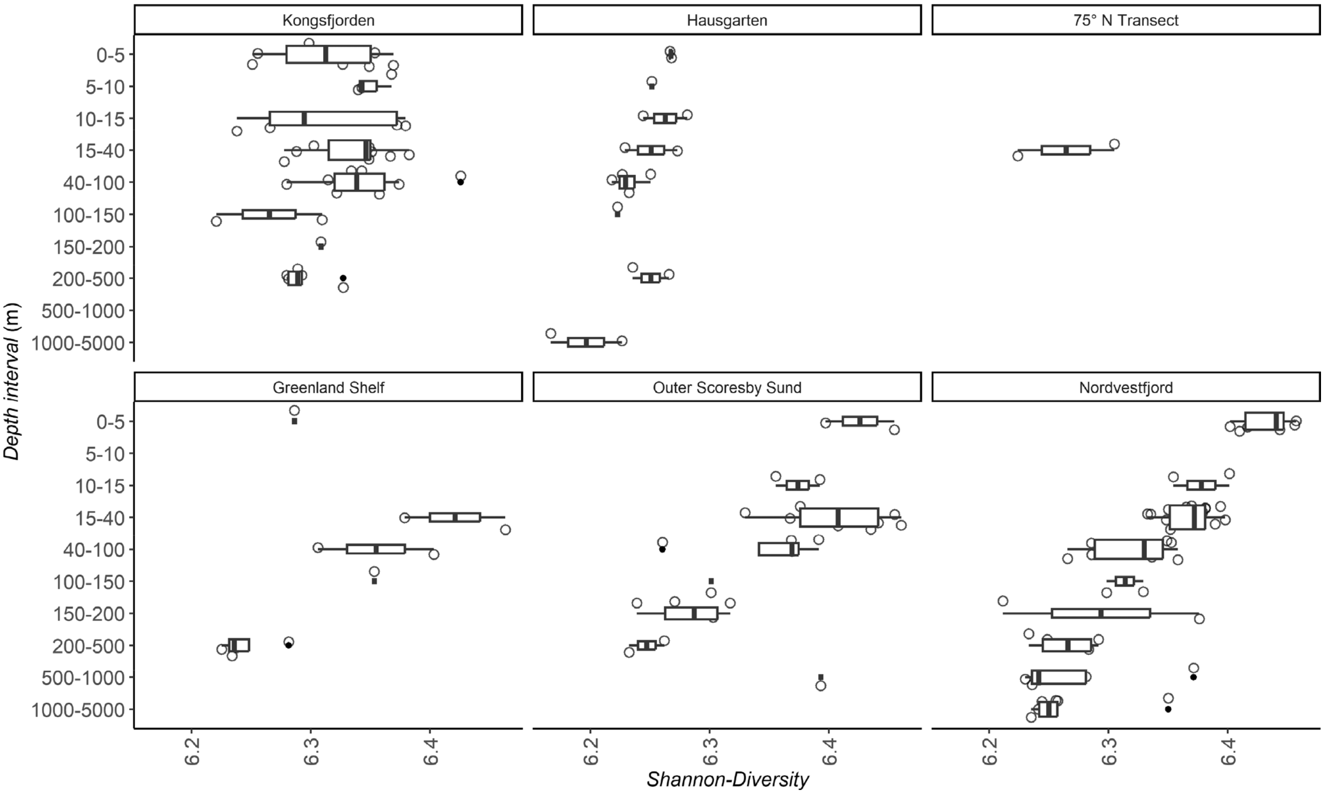

Fig. 2. Molecular diversity measured by the Shannon diversity index of molecular formulas detected by FT-ICR-MS in DOM samples of Kongsfjorden, Greenland Strait, and Scoresby Sund. At depth intervals with insufficient samples to calculate a boxplot, only the median is shown. Samples are marked as open and outliers as filled circles. FT-Orbitrap-MS data revealed a similar distribution (*see* Supporting Information Fig. S2).

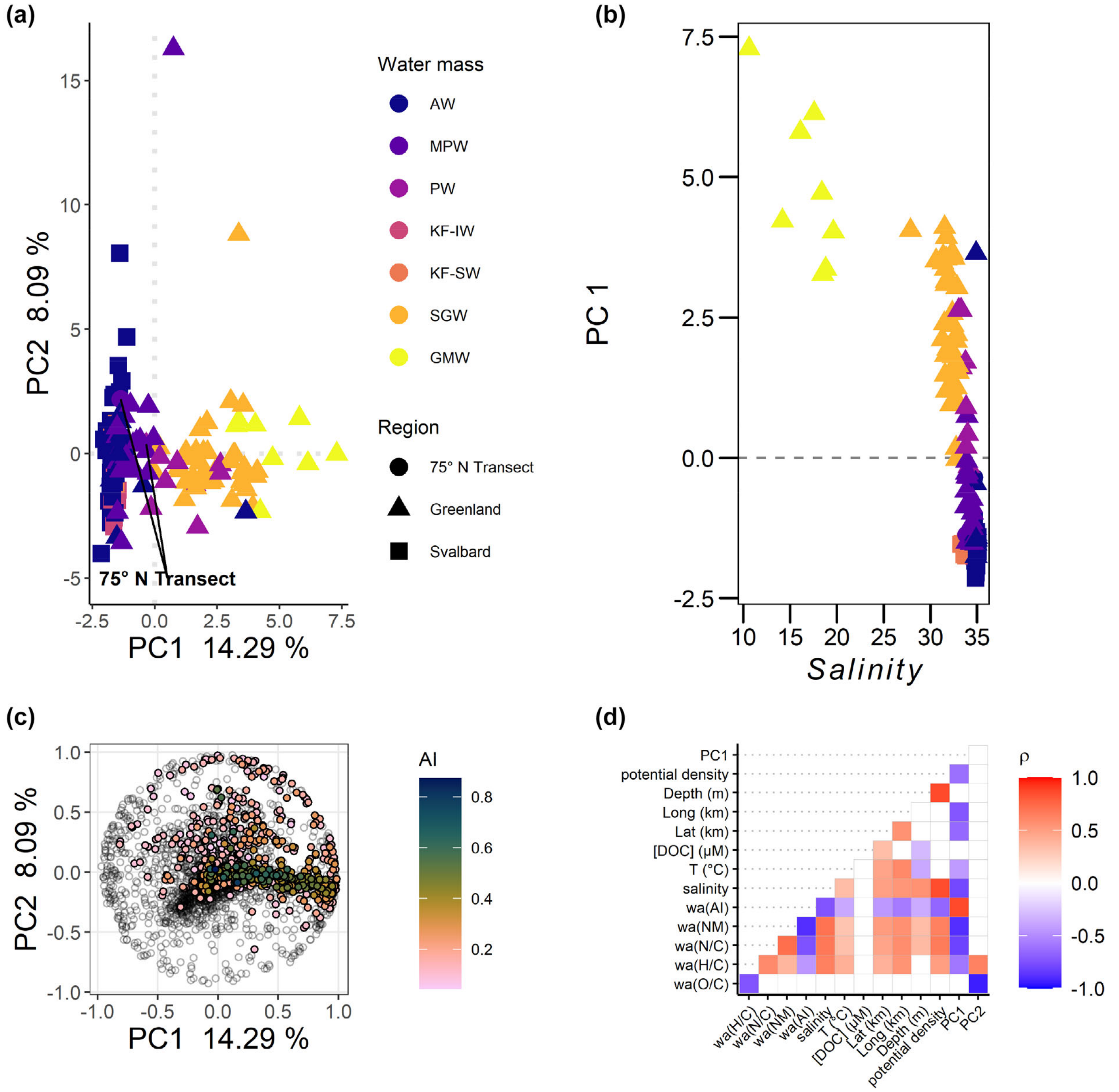

Fig. 3. Principal component analysis of (**a**) FT-ICR-MS molecular formulas based on relative *m/z* intensities (equal to sum of 1 per spectrum). The shape of the marker indicates regions (triangles: Greenland Shelf, Outer Scoresby Sund, Nordvestfjord (combined as Greenland), circles: 75°N transect, squares: AWI Hausgarten, Kongsfjorden (combined as Svalbard)). (a) Water mass, (**b**) PC1 plotted vs. salinity, (**c**) respective loading plot ($\overrightarrow{l} = \overrightarrow{e_\lambda}\sqrt{\lambda}$, $\overrightarrow{e_\lambda} = \text{eigenvector}$, $\lambda = \text{respective eigenvalue}$) to score plot (a). The color scale indicates the respective unsaturation (aromaticity index, AI) for molecular formulas with an $AI > 0$, while molecular formulas with $AI = 0$ are represented in the background. (**d**) Spearman rank correlation between PCs and metavariables. wa: weighted average (weight: absolute intensity). Correlations with $p \geq 0.01$ are blank (p-values corrected by Holm–Bonferroni). GMW: glacial meltwater, SGW: surface glacial water, Kf-SW: Kongsfjorden surface water, Kf-IW: Kongsfjorden intermediate water, PW: polar water, MPW: modified polar water, AW: Atlantic water.

significantly correlated with sampling depth ($\rho = -0.42$, $p < 0.01$ FT-ICR-MS).

The loading plot of the PCA showed the correlation of molecular formulas with PC1 and PC2 (Fig. 3c). The loading value l was calculated as: $l = e_\lambda \cdot \sqrt{\lambda}$, $e_\lambda = \text{eigenvector}$, $\lambda = \text{respective eigenvalue}$. [CHO] formulas strongly correlated with PC1 for both instruments ($|l| > 0.5$). Molecular formulas that correlated positive with PC1 were highly unsaturated (high AI, $\rho = 0.86, p < 0.01$), had a low molecular weight (NM, $\rho = -0.89, p < 0.01$) and were poor in nitrogen (N/C, $\rho = -0.81, p < 0.01$). Principal component 2 correlated with aliphatic (H/C, $\rho = 63, p < 0.01$) and less oxidized (O/C, $\rho = -0.94, p < 0.01$) molecular formulas.

Above 200 m, PC1 and PC2 showed a trend in horizontal (Fig. 4b) and vertical direction from glacier to fjord mouth (Fig. 4d). The vertical trend in Outer Scoresby Sund and

Nordvestfjord closely aligned with water mass distribution (Fig. 4a). The horizontal trend in Kongsfjorden (Fig. 4c) was not visible in the PCA plot (Fig. 3). The variation explained by PC1 resulted from changes of meltwater-influenced surface water (Fig. 4a, glacial meltwater) to deeper waters (modified polar water). Principal component 2 increased from Kongsfjorden to Hausgarten and did not align with the water masses (Fig. 4c,d). These trends were consistent between data obtained with both mass spectrometers.

The contribution of meltwater proxies in Scoresby Sund (i.e., defined as molecular formulas with a positive PC1 expressed as percentage of the total intensity of the integral of all DOM signal from each sample) were responsible for 15.88% of the total intensity in the Atlantic water (average salinity 34.95), 31.95% in the fjords surface sample at lowest salinity (10.61), and 33.25% in the runoff sample (Supporting Information Fig. S5).

Dissolved organic matter characteristics along the salinity gradient

The surface water of Scoresby Sund was highly stratified with a 5 m deep mixed freshwater lens (salinity ~ 18, $\sigma_\theta \approx 15\,\mathrm{kg\,m^{-3}}$) (Fig. 5). The buoyancy frequency squared (N^2) is a measure of the stability of the water column and results from a vertical gradient in density and pressure. The peak at ~ 7 m revealed a strong pycnocline in Nordvestfjord ($N^2 = 0.02\,\mathrm{s^{-2}}$, Fig. 5b). The freshwater lens was thinner in the Outer Scoresby Sund. Only at two stations (576, 598) close to freshwater sources (Supporting Information Figs. S6–S8) a pycnocline was recorded (~ 4 m depth, $N^2 = 0.09\,\mathrm{s^{-2}}$). Below the pycnocline, at about ~ 10 m, the water was gradually well mixed to $\sigma_\theta \approx 27.7\,\mathrm{kg\,m^{-3}}$. The Hausgarten stations close to Fram strait were well mixed throughout the water column. Kongsfjorden was also stratified between a surface layer (salinity ~ 33.7, $\sigma_\theta \approx 26.8\,\mathrm{kg\,m^{-3}}$) in the upper water column, but the peak in N^2 at ~ 10 m was 100 times weaker than in Nordvestfjord ($N^2 \approx 10^{-4}\,\mathrm{s^{-2}}$). The salinity increased below the pycnocline and the water body was well-mixed (salinity ~ 34.9, $\sigma_\theta \approx 28.3\,\mathrm{kg\,m^{-3}}$).

Based on the potential density, N^2 (Fig. 5) and the pycnocline depth, Scoresby Sund samples were classified into ABOVE pycnocline (< 5 m, only in Nordvestfjord), IN pycnocline (only in Outer Scoresby Sund, ~ 2–10 m; in Nordvestfjord no DOM samples were collected in the pycnocline) and BELOW pycnocline (> 10 m) (Fig. 6). Above

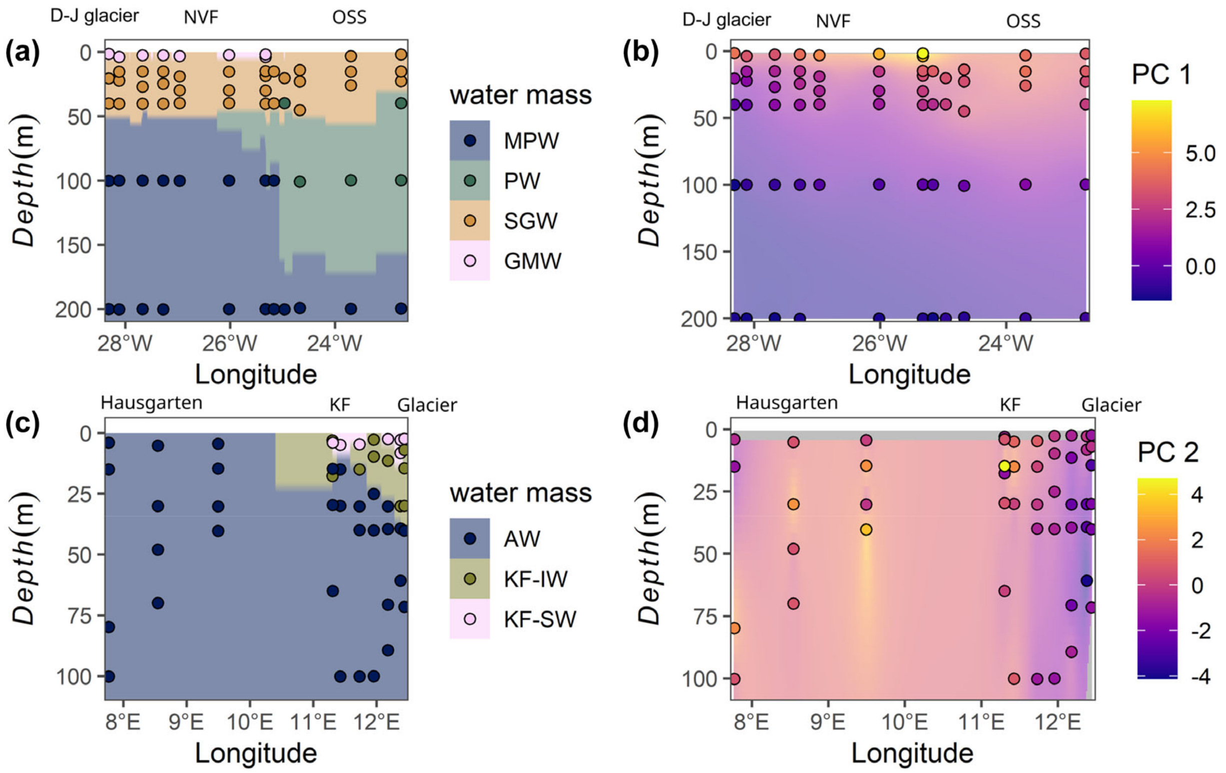

Fig. 4. Water masses in Scoresby Sund aligned with molecular DOM composition. Cross section of the upper water body of (**a**, **b**) Scoresby Sund (D-J: Daugaard-Jensen glacier, NVF: Nordvestfjord, OSS: Outer Scoresby Sund, GS: Greenland shelf) and (**c**, **d**) Kongsfjorden (Kf) and Hausgarten with the water masses (a, c) and PC1 (b) and PC2 (d) (FT-ICR-MS data) mapped onto it. For the accompanying PC1 (Kongsfjorden) and PC2 (Scoresby Sund) and FT-Orbitrap-MS data *see* Supporting Information Fig. S4. Background color of the respective water mass or PC axis were added to guide the eye. GMW: glacial meltwater, SGW: surface glacial water, Kf-SW: Kongsfjorden surface water, Kf-IW: Kongsfjorden intermediate water, PW: polar water, MPW: modified polar water, AW: Atlantic water.

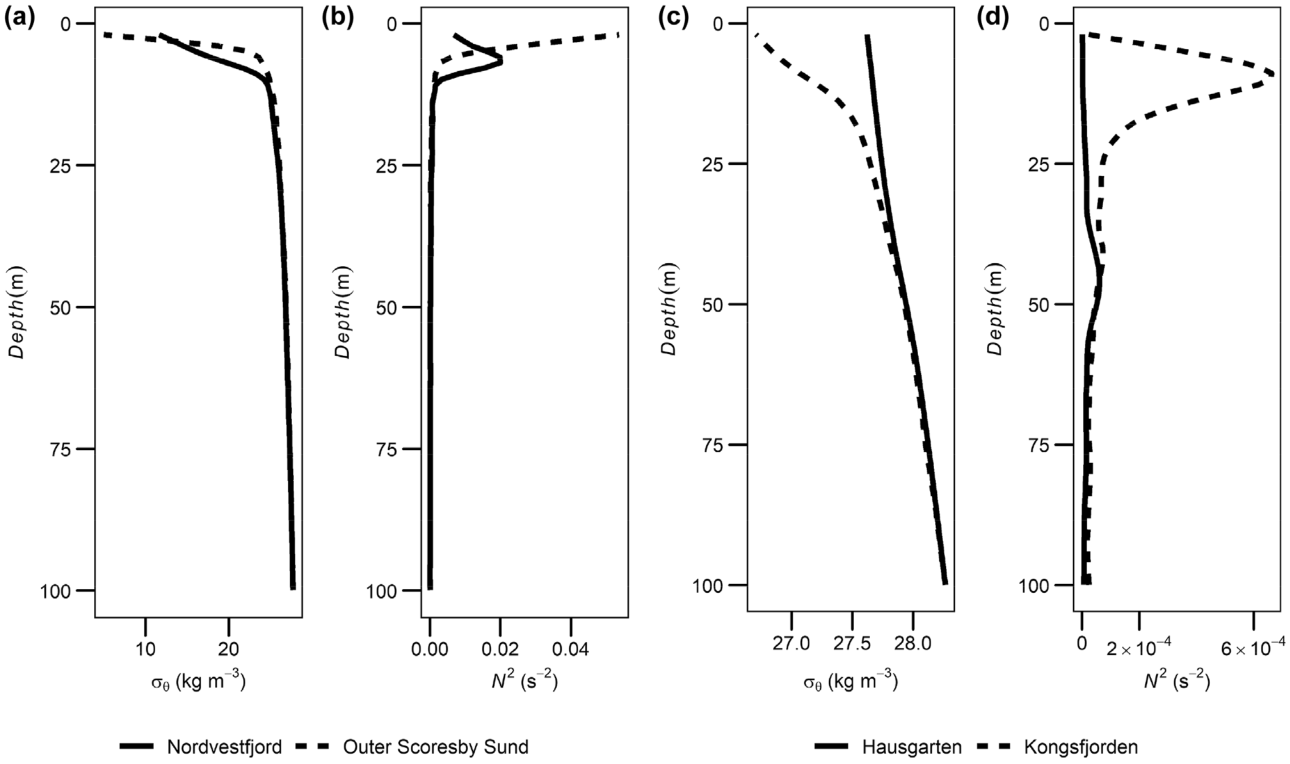

Fig. 5. Interpolated CTD-profiles of potential density (σ_θ) and squared buoyancy frequency (N^2) for the Nordvestfjord, Outer Scoresby Sund (**a**, **b**) and Hausgarten, Kongsfjorden (**c**, **d**). Below 100 m, the water column was well mixed.

the pycnocline, the DOM parameters revealed no distinct changes (Fig. 6, average: I_{DEG}: 0.57, I_{terr2}: 0.15, wa(N/C): 0.0064, wa(nominal mass): 385, wa(AI): 0.0252). Glacial runoff DOM was similar in wa(nominal mass): 385 and wa(I_{DEG}): 0.53, but lower or higher in wa(N/C): 0.0009 and wa(AI): 0.0389. No I_{terr2} value could be calculated. Samples in the pycnocline were comparable to the surface layers. Below the pycnocline, DOM parameters mixed linearly to: I_{DEG}: 0.72, I_{terr2}: 0.08, wa(N/C): 0.0105, wa(nominal mass): 399, wa(AI): 0.0133 at highest salinities.

Conservative mixing of marine and glacier-derived dissolved organic matter

The data of the two-endmember laboratory mixing experiment, using a glacial run-off sample and the marine endmember, mirrored the theoretical mixing model of DOM chemical bulk parameters (N/C ratio, aromaticity index, nominal mass) but varied in precision between parameters and run-off origin. Experimental mixing within the wa(N/C) in Scoresby Sund deviated more from the theoretical mixing line than Kongsfjorden (root mean square error, RMSE: 0.003 and 0.001, respectively; Fig. 7; Supporting Information Fig. S11). This deviation between theoretical and experimental mixing, however, was comparable to the variance within a water mass (Supporting Information Table S5) suggesting no selectivity or significant mass spectrometry effects on ion intensities due to compositional changes which may affect ionization efficiency.

Discussion

Meltwater influx is revealed in glacier-derived dissolved organic matter signatures

In this study, we characterized the DOM composition along Scoresby Sund and Kongsfjorden. Changes in DOM composition along Kongsfjorden were comparatively small (Supporting Information Figs. S9 and S10), supporting earlier findings (Osterholz et al. 2014). Contrary, the DOM composition along Scoresby Sound varied strongly. The glacier-derived DOM signature along the fjord's mixing gradient clearly correlated with salinity, a consequence of high glacial meltwater influx into Scoresby Sund. Changes in DOM composition were characterized by the proportion of heteroatoms of DOM constituents and their degree of unsaturation (aromaticity). Small differences in DOM molecular composition between the inner and outer Kongsfjorden were observed, yet without significant correlations to other environmental variables, suggesting a homogeneous DOM pool due to high mixing rates. As these compositional changes were reproduced by measurement on two mass spectrometers, the observed patterns and correlations are robust.

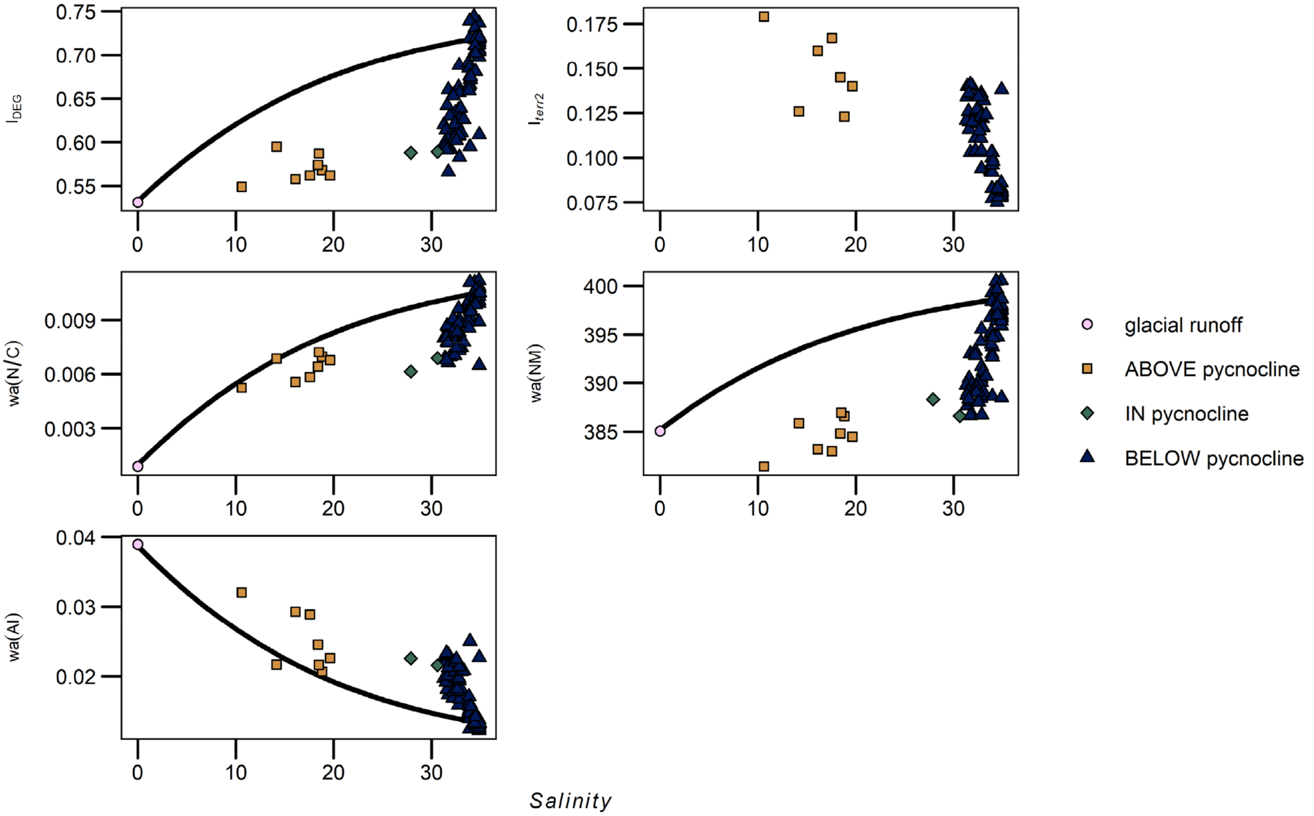

Fig. 6. Characteristics of DOM formulas (FT-ICR-MS) correlated with salinity in Scoresby Sund (degradation index (I_{DEG}), terrestrial index 2 (I_{terr2}), weighted average of molecular N/C ratio, nominal mass, aromaticity index (AI)). Samples were categorized into glacial runoff (pink circle), ABOVE pycnocline (yellow square < 5 m, only in Nordvestfjord), IN pycnocline (green diamond, only in Outer Scoresby Sund, < 10 m) and BELOW pycnocline (blue square, > 10 m). For FT-Orbitrap-MS and FT-ICR-MS data of all provinces *see* Supporting Information Figs. S9 and S10. Samples with insufficient I_{terr2} (FT-ICR-MS: marine samples: 12, glacial runoff 1; FT-Orbitrap-MS: marine samples: 7) formulas were removed. All plots show the theoretical mixing line for a two-endmember model (black continuous line).

Hood et al. (2015) estimated the discharge of organic material from the Greenland ice shelf to be 0.22 ± 0.04 TgC a^{-1} based on DOC concentration measured in Greenland meltwater of 42.5 μmol L^{-1}. In our study, the DOC concentration of Scoresby Sund glacial runoff (~ 24.0 μmol L^{-1}) and meltwater-influenced surface water (27.7 μmol L^{-1}) were comparable to Kellerman et al. (2021) (Russel Glacier outflow ~ 27.5 (5.8) μmol L^{-1}; Svalbard meltwater rivers ~ 15.8 (10.0) μmol L^{-1}) and Paulsen et al. (2017) (Meltwater river, Young Sound, ~ 40 (13) μmol L^{-1}). Together, the data suggest that glacial meltwater flux dilutes DOC along the fjord (e.g., Scoresby Sund mouth surface 54.4 μmol L^{-1}, Young Sound outer fjord 130 μmol L^{-1}; Paulsen et al. 2017). Dissolved organic carbon concentrations below the freshwater layer in Scoresby Sund were higher, likely due to primary production as evidenced by higher chlorophyll *a* fluorescence (Seifert et al. 2019), and depleted below the upper water masses, mainly due to dilution and/or remineralization (Supporting Information Table S2). On the basis of an estimated total meltwater flux of 8.3 km^3 a^{-1} (Lewis and Smith 2009), our results suggest a net flux of more than 2.4 Gg C a^{-1} into Scoresby Sund (24.0 μmol L^{-1} DOC; Supporting Information Table S2).

Scoresby Sund surface water was strongly stratified due to the input of glacial meltwater (salinity 16.73; Supporting Information Table S2; Fig. 5). Its DOM composition was characterized by high molecular richness, high degree of unsaturation (aromaticity), low nitrogen content, low average *m/z*, high terrestrial marker (I_{terr2}) and low I_{DEG} (Supporting Information Table S2; Figs. 3–5, 7), therefore more akin to terrestrial DOM (low N/C, high AI). These results largely agree with Kellerman et al. (2021), reporting high aromaticity, low N/C, lower number of molecular formulas and a higher nominal mass in West Greenland meltwater, in comparison to higher N, lower nominal mass and higher total number of molecular formulas in Svalbard meltwater. Glacial meltwater in Scoresby Sund formed a top layer and caused a pycnocline separating the fjord water below (surface glacial water, salinity ~ 32.00; Supporting Information Table S2; Fig. 5). While the surface water DOM

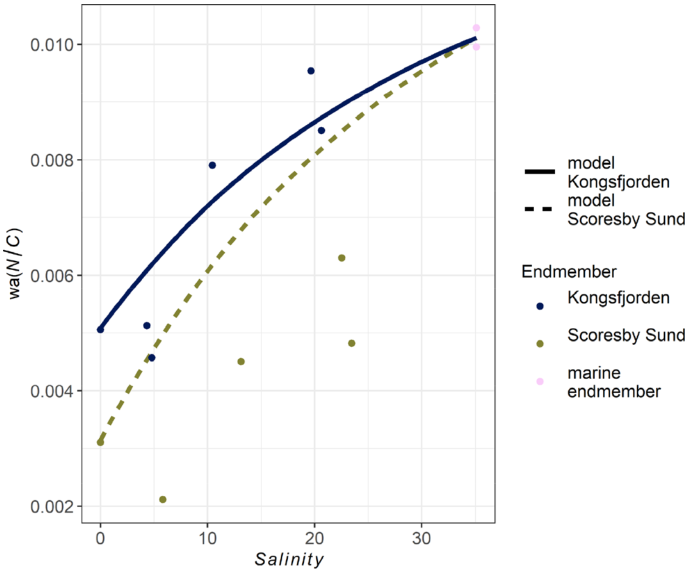

Fig. 7. Experimental mixing of glacial runoff and marine DOM along the salinity gradient in Scoresby Sund and Kongsfjorden by FT-Orbitrap-MS-generated weighted average (weight: absolute intensity) of the molecular N/C ratio. Experimental mixing (dots) of Scoresby Sund (green) and Kongsfjorden runoff (blue) with the marine endmember sample (pink) and theoretical mixing (solid line: Kongsfjorden; dashed line: Scoresby Sund). For salinity calculations *see* Supporting Information S1.8. The endmember mixing experiment verified the validity of the model (also *see* Supporting Information Fig. S11; Supporting Information Table S5).

profile was characterized by glacial imprint, that was relatively decreased in comparison to glacial meltwater (runoff) itself (Supporting Information Table S2; Fig. 3; Supporting Information Fig. S12). The deeper water masses of Scoresby Sund and marine water masses outside the fjord had indistinguishable DOM profiles. They contained more nitrogen, were less aromatic (i.e., lower DBE double bond equivalents per carbon ratio), contained heavier molecules and revealed lower I_{terr2} and higher I_{DEG} (Supporting Information Table S2; Figs. 3–5, 7). Polar water along the Greenland shelf had similar features in comparison to glacial meltwater and surface glacial water, but the inflowing Polar water and recycled Atlantic water in Scoresby Sund (Seifert et al. 2019) could not be distinguished by DOM composition (Fig. 4; Supporting Information Fig. S4). This observation confirmed earlier findings of Geuer (2020), demonstrating a correlation of molecular bulk parameters (especially DBE/C_w, molecular size) and water mass characteristics. All water masses analyzed in this study were subject to mixing and therefore did not match with water masses in a strict oceanographic definition (Geuer 2020; Seifert et al. 2019).

The diversity of molecular features in samples from Scoresby Sund and the Greenland Shelf decreased from surface to deep (Fig. 2), suggesting that glacier-derived DOM is more degraded. Dilution of glacier-derived material or its removal by photodegradation may diminish its diversity in deeper, older seasonal water.

Influx of glacier-derived dissolved organic matter differs between both fjords

Glacial DOM contributes nitrogenous and aliphatic molecular signatures (Bhatia et al. 2010; Lawson et al. 2014; Stubbins et al. 2012). Yet, contrary to prior studies, glacier-derived DOM in Scoresby Sund contained a low proportion of nitrogen and was more similar to terrestrial DOM. This could be either due to glacial meltwater containing terrestrial DOM, or polar marine water entering the fjord mouth with the East Greenland current (Young Sound, NE Greenland; Paulsen et al. 2019; Paulsen et al. 2017). This, however, would be inconsistent with the significant correlation between salinity and terrestrial markers in Scoresby Sund (Figs. 3–7; Supporting Information Figs. S5, S13–S16). Our data rather suggest the terrestrial DOM signature was indeed primarily due to glacial meltwater, with the highest proportion of terrestrial signals found in surface samples of Scoresby Sund (Fig. 6). Notably, fluorescence data of Scoresby Sund DOM, as shown by Wünsch et al. (2018) support this conclusion. Nitrogen-rich aliphatic glacier-derived DOM can support primary production and is thus quickly removed (Kellerman et al. 2021). Therefore, this part of glacier-derived DOM might have been depleted at the time of sampling. The fast turnover of aliphatic, nitrogen-rich material would result in relative enrichment of terrestrial DOM signals. Other processes, such as precipitation or interaction of DOM with glacial sediments, also can selectively remove DOM (Hopwood et al. (2020) and citations therein). In a previous study in West Greenland, high DOM aromaticity correlated with plant and soil sources or possibly paleosols (Kellerman et al. 2021). The latter may explain our observations as well. In contrast, Kongsfjorden DOM was virtually void of terrestrial markers and thus in accordance with Kellerman et al. (2021). The terrestrial index 2 (I_{terr2}) decreased significantly from glacial surface meltwater to deeper Atlantic water in Scoresby Sund (Fig. 6; Supporting Information Tables S2 and S2), matching the aromaticity and N/C ratio. The I_{DEG} increased significantly with the proportion of marine water (Fig. 6) in Scoresby Sund, suggesting that meltwater-derived DOM was less degraded than marine DOM. However, it is unclear if I_{DEG} and I_{terr2} were good predictors for polar glacial samples due to the lack of comparable data. The main source of meltwater in Scoresby Sund is the marine-terminating Daugaard-Jensen glacier, with several marine and land-terminating side glaciers along the fjord (Seifert et al. 2019). Together, our data suggest that the meltwater influx into Scoresby Sund leads to a significant relative enrichment of terrestrial DOM. The surface temperature of both fjord sections was up to 10°C, indicating high solar radiation. Given the comparatively low surface velocity in Nordvestfjord (Seifert et al. 2019), a surface water parcel would have a residence time of 173 d between Daugaard-

Jensen glacier and the Outer Scoresby Sund. In tandem with high radiation, surface DOM was therefore subject to strong photodegradation.

In contrast, the DOM profile of Kongsfjorden did not reveal any terrestrial properties or origins. The DOM composition in Svalbard followed a gradient from the innermost part of Kongsfjorden toward the fjord mouth. This gradient was less pronounced (as were salinity gradients) than in Scoresby Sund. Molecular formulas attributed to the inner fjord had a higher O/C ratio, rarely contained nitrogen, and had significantly higher NOSC and KMD (Supporting Information Fig. S12b, negative group) compared to the fjord mouth and "Hausgarten" (Supporting Information Fig. S12b, positive group). The higher amount of oxygen, low H/C and DBE/O could be attributed to the oxygen in the carbonyl or carboxylic acid functional groups. The DBE/C was high with no change in AI (Supporting Information Fig. S12b, median of the AI was for both groups 0). Therefore, inner Kongsfjorden DOM had a high degree of π-bonds and ring structures compared to the fjord mouth and "Hausgarten." This is in accordance with Atlantic water entering Kongsfjorden and replacing the polar water in spring, and vice versa in autumn (Hegseth and Tverberg 2013; Sert et al. 2020). This mixing and rapid transformation results in rather homogeneous DOM composition (Osterholz et al. 2014; also *see* Geuer 2020). The high similarity of DOM composition in outer Kongsfjorden, "Hausgarten," the 75°N transect and deep Outer Scoresby Sund and Nordvestfjord water may also result from the influx of Atlantic Water into the Fram Strait and the back-transport along the east Greenland shelf into Scoresby Sund beneath polar water from the Arctic Ocean (Seifert et al. 2019). In contrast to our data, Kellerman et al. (2021) reported a significantly higher number of molecular formulas in Svalbard meltwater than in West-Greenland meltwater. The overall influx of meltwater (between 0.21 and 0.25 Gt a^{-1} for Kronebreen and between 0.14 and 0.16 Gt a^{-1} for Kongsbreen; Schellenberger et al. 2015) was lower in Kongsfjorden and caused weaker stratification than in Scoresby Sund (Fig. 5). Kellerman et al. (2021) suggested that Svalbard meltwater DOM was similar to lithogenic organic matter (lower aromaticity, highly [CHO]N rich material), which would explain the more oxidized, less aromatic DOM in our study. However, Kongsfjorden DOM was poor in heteroatoms and the influx of lithogenic DOM would correlate to salinity, something we did not observe. Our data therefore suggest that the high influx of meltwater into the Scoresby Sund increased the molecular diversity across the lateral fjord profile. The overall impact of meltwater on Kongsfjorden, however, was significantly lower and more homogeneous due to lower meltwater influx and higher mixing rates.

Glacier-derived dissolved organic matter dynamics

Arctic fjords are commonly stratified in summer (Mortensen et al. 2013; Svendsen et al. 2002; Hopwood et al. 2020, citations therein). Surface meltwater runoff and melting sea ice form a freshwater layer on top of a mixed transition layer (i.e., surface glacial water in this study), separated by a pycnocline. The mixed transition layer is colder than the surface and builds a thermocline to the underlying warmer and older water masses; however, in Scoresby Sund, this temperature gradient was weak (Supporting Information Fig. S6). The Nordvestfjord is most likely characterized by the mixing of glacier-derived meltwater (DOC $\sim 24.0\ \mu\text{mol L}^{-1}$) with the marine water body, creating a low salinity layer (salinity ~ 10). This pycnocline (Fig. 6) prevents further mixing and diffusion of DOM with the underlying water masses. As a result, DOM in the transition layer below the pycnocline follows conservative mixing (Supporting Information Fig. S5), suggesting the gradient in surface glacial water (Fig. 7) resulted from mixing of glacier-derived and underlying water masses in autumn and winter. Therefore, glacier-derived DOM in surface glacial water would stem from previous melting season(s). The weak thermocline between surface glacial water and deeper Atlantic water in Scoresby Sund does not act as a diffusion barrier, and the gradient remains stable over spring and summer. The freshwater layer was < 5 m in Outer Scoresby Sund (Supporting Information Figs. S7 and S8) and N^2 also revealed a pycnocline in the first few meters of the water column (Fig. 5).

Glacier-derived DOM in the transition layer may have two sources: (1) subglacial discharge from marine terminating glaciers mix with glacier-derived and marine DOM below the pycnocline; (2) glacier-derived DOM from previous years mix with marine DOM during less stratified seasons. Given the weak thermocline, the glacier- and marine-derived DOM supposedly mixed conservatively (Figs. 5, 7; Supporting Information Fig. S5). Deviations of DOM composition from conservative mixing may be explained by biological, chemical, or physical processes leading to a net gain or removal of DOM along the mixing gradient (Seidel et al. 2015). There was a good overlap between experimental and theoretical mixing for Kongsfjorden, but a broader spread was observed for Scoresby Sund (Fig. 7; Supporting Information Figs. S6, S11). Therefore, the results of the mixing experiment should be regarded with caution. Nonetheless, the DOM formula characteristics in Scoresby Sund (Fig. 6; Supporting Information Figs. S9, S10) revealed that the mixing of the glacier-derived DOM did not follow the 2-endmember mixing model, likely because mixing was limited due to a strong pycnocline. The mixing of DOM in the water masses below the pycnocline, on the other hand, was strictly linear and conservative (Fig. 6; Supporting Information Figs. S5, S9, S10, and S17).

Conclusions

The influx of Greenland meltwater with low DOC concentration into fjord systems forms a top layer during summer stratification and results in net dilution of marine DOM in the fjord during seasonal mixing (Paulsen et al. 2019; this study).

The observed influx of low DOC glacial water into Scoresby Sund is unique in comparison to other global estuaries, where instead the organic content of the terrestrial water strongly enriches the composition of the coastal water body. Here we showed that increased stratification also affects the molecular DOM composition. Due to fast DOM turnover (Osterholz et al. 2014), the absolute influence of glacier-derived DOM is expected to be low. Notably, we detected glacier-derived molecular formulas along the entire mixing gradient of surface fjord water samples (Figs. 3c, 5; Supporting Information Fig. S16), suggesting that Greenland coastal water is influenced by a significant influx of DOM bearing terrestrial properties.

Ongoing deglaciation of polar fjords will trigger a high influx of glacier-derived DOM to the Arctic carbon cycle, affecting production, turnover, and vertical flux of DOM, with repercussions on the global marine carbon cycle.

Author Contributions

Jan Tebben, Boris P. Koch, Tilmann Harder, and Philippe Schmitt-Kopplin designed the study. Claudia Burau, Jana K. Geuer, and Boris P. Koch did the fieldwork with the help of the acknowledged crew. Claudia Burau, Jana K. Geuer, Mourad Harir, Jan Tebben, and Fabian Moye acquired the data. Fabian Moye conducted the data analysis. Jan Tebben, Boris P. Koch, and Tilmann Harder contributed to the interpretation. Fabian Moye, Jan Tebben, and Tilmann Harder wrote the manuscript.

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Conflicts of Interest

None declared.

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Supporting Information

Additional Supporting Information may be found in the online version of this article.

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