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Key Points:

- In Kongsfjorden, an Arctic glacier fjord, freshwater from glacier runoff and ice meltwater decreases phosphate, alkalinity, and DOM concentrations
- Estuarine mixing is the major driver of summer CO₂ undersaturation in glacially modified waters, and near-corrosive conditions were observed
- Future changes will amplify ocean acidification in the inner-fjord surface waters

Supporting Information:

- Supporting Information S1

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Glacial Drivers of Marine Biogeochemistry Indicate a Future Shift to More Corrosive Conditions in an Arctic Fjord

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Abstract A detailed survey of a high Arctic glacier fjord (Kongsfjorden, Svalbard) was carried out in summer 2016, close to the peak of the meltwater season, in order to identify the effects of glacier runoff on nutrient distributions and the carbonate system. Short-term weather patterns were found to exert a strong influence on freshwater content within the fjord. Freshwater inputs from glacier runoff and ice meltwater averaged ($\pm$ SD) low nitrate ($1.85 \pm 0.47 \mu\text{M}$; $0.41 \pm 0.99 \mu\text{M}$), orthophosphate ($0.07 \pm 0.27 \mu\text{M}$; $0.02 \pm 0.03 \mu\text{M}$), dissolved organic carbon ($27 \pm 14 \mu\text{M}$ in glacier runoff), total alkalinity ($708 \pm 251 \mu\text{mol kg}^{-1}$; $173 \pm 121 \mu\text{mol kg}^{-1}$), and dissolved inorganic carbon ($622 \pm 108 \mu\text{mol kg}^{-1}$; $41 \pm 88 \mu\text{mol kg}^{-1}$), as well as a modest silicate concentration ($3.71 \pm 0.02 \mu\text{M}$; $3.16 \pm 5.41 \mu\text{M}$). $p\text{CO}_2$ showed a nonconservative behavior across the estuarine salinity gradient with a pronounced undersaturation in the inner-fjord, leading to strong CO₂ uptake from the atmosphere. The combined effect of freshwater dilution and atmospheric CO₂ absorption was the lowering of aragonite saturation state to values that are known to negatively affect marine calcifiers (Ω_{Ar} , 1.07). Glacier discharge was therefore a strong local amplifier of ocean acidification. Future increases in discharge volume and the loss of marine productivity following the retreat of marine-terminating glaciers inland are both anticipated to further lower Ω_{Ar} within inner-fjord surface waters. This shift may be partially buffered by an increase in the mean freshwater total alkalinity as the fractional importance of iceberg melt to freshwater fjord inputs declines and runoff increases.

Plain Language Summary During summer 2016, we surveyed a glacier fjord in the Svalbard archipelago to study the effect of glaciers on the marine ecosystem over the melting season. We measured the quantities of the dissolved nutrients that can potentially fertilize downstream waters in watercourses fed by glacier discharge and in small icebergs calved from marine-terminating glaciers in the fjord. All these sources of freshwater had negative (diluting) or modest fertilizing effects, as the quantities of most nutrients were lower than that in marine waters. Glacier-derived freshwater also had limited concentrations of carbonates derived from limestone erosion, hence mixing between fresh and saline waters created favorable conditions for the absorption of carbon dioxide from the atmosphere. This process further increased the corrosivity of surface fjord waters creating conditions that are not suitable for some organisms that produce carbonate shells. Future glacier retreat will change both the fjord circulation and the freshwater properties. These modifications are expected to further increase the corrosivity of surface waters, locally amplifying the ocean acidification process caused by increasing concentrations of atmospheric carbon dioxide.

1. Introduction

The Arctic is a hotspot for the effects of climate change. Atmospheric temperatures are rising 2–3 times faster than other areas around the globe, resulting in loss of sea-ice coverage of 26% in July and 35% in August between 1979 and 2016 (Onarheim et al., 2018), a retreat of most marine-terminating glaciers and a loss of glacier and ice sheet volume (Meredith et al., 2019). Anthropogenic climate change has driven recent increases in the annual discharge volume of freshwater from the Greenland Ice Sheet and smaller Arctic glaciers, with the total annual freshwater runoff into the North Atlantic and Arctic Oceans rising by 400 km³ from 1995 to 2016 (Bamber et al., 2018). In glaciated fjords, the seasonal release of meltwater from glaciers and melting icebergs has numerous consequences on the coastal marine environment, including the

alteration of fjord-scale circulation (Straneo et al., 2011; Torsvik et al., 2019), water column structure (Meire et al., 2017; Sejr et al., 2017), the carbonate system (Fransson et al., 2015; Meire et al., 2015), nutrient concentrations (Kanna et al., 2018; Meire et al., 2016), and light availability to support primary production (Halbach et al., 2019; Murray et al., 2015). These perturbations potentially affect the metabolism of microbes and the structure of coastal plankton communities (Cauvy-Fraunié & Dangles, 2019; Matsuno et al., 2020) by changing the availability of resources that sustain primary production or instigating changes in the foraging behavior of higher organisms (Arendt et al., 2011; Arimitsu et al., 2012; Lydersen et al., 2014). Furthermore, many of these forcings are interlinked and thus changes to either the magnitude of freshwater fluxes or freshwater characteristics; for example, the fraction of ice melt, surface runoff, and subsurface runoff can result in a series of interacting effects on coastal biogeochemistry and productivity (Hopwood et al., 2018; Meire et al., 2017). Recent studies have highlighted the importance of the entrainment within subglacial discharge plumes from marine-terminating glaciers for driving fjord-scale circulation, nutrient supply, and productivity (Cape et al., 2019; Kanna et al., 2018) and suggest that significant changes are likely to occur when marine-terminating glaciers retreat and transition into land-terminating systems (Torsvik et al., 2019). The loss of entrainment from glacier retreat is generally expected to decrease fjord-scale productivity, which will likely have knock-on effects for the carbonate system. With the shallow retreating marine-terminating glaciers within Kongsfjorden (Kronebreen and Kongsvegen) predicted to transition into land-terminating glaciers in coming decades (Torsvik et al., 2019), Kongsfjorden presents an interesting case study from which to study the linkages between glaciers and marine biogeochemistry (Halbach et al., 2019).

Oceans have adsorbed 20%–30% of annual anthropogenic CO₂ emissions in the past two decades (Bindoff et al., 2019), resulting in a decrease of pH and carbonate ion concentration, a process known as ocean acidification (OA). A combination of several factors makes the Arctic Ocean one of the most vulnerable areas to OA: low temperatures, higher freshwater inputs relative to other ocean basins, and high productivity in summer under ice-free conditions all increase CO₂ drawdown from the atmosphere (Bates & Mathis, 2009; Yamamoto-Kawai et al., 2009). At intermediate depths, the intrusion of CO₂ rich waters from the Atlantic Ocean (Luo et al., 2016) and the formation of brine (Anderson et al., 2010) further act to increase the CO₂ content of the Arctic Ocean (Terhaar et al., 2020).

While the OA process in the Arctic Ocean has been the focus of much research, the precise mechanisms by which meltwater from glaciated regions affects carbonate chemistry and modulates OA in coastal seawater are not yet well elucidated (Evans et al., 2014; Fransson et al., 2015; Meire et al., 2015). In general, freshwater derived from glacier runoff or melting icebergs has a low alkalinity concentration. The release of meltwater into the marine environment therefore lowers the alkalinity of fjordic waters and thus reduces the buffering capacity of these marine systems. In productive fjords, especially where subglacial discharge drives entrainment of macronutrients into surface layers and sustains prolonged summertime phytoplankton blooms, the negative effects of alkalinity dilution may be offset by pCO₂ uptake through biological activity (Meire et al., 2015). However, in the absence of significant biological activity, lower alkalinity leads to reduced calcite saturation states and corrosive conditions in seawater which negatively affects calcifying organisms (Evans et al., 2014). In order to characterize the effects of glacier discharge on fjord-scale biogeochemistry and carbonate availability throughout the meltwater season, a comprehensive survey of inner-Kongsfjorden (Spitsbergen, Svalbard) was undertaken during summer 2016. The evolution of sea-water mass distribution and properties was analyzed with respect to the seasonal effects of the summertime peak in runoff. An extensive sampling of glacier runoff from pro-glacial streams and ice melt from floating icebergs allowed the definition of marine and freshwater endmembers that mix within the fjord. Applying an estuarine mixing approach, the sources and processes controlling the distribution of key nutrients (nitrate, phosphate, silicic acid), dissolved organic matter, and carbonate system parameters (based on direct measurements of three variables: pH, total alkalinity [TA], and dissolved inorganic carbon [DIC]) were constrained.

2. Materials and Methods

2.1. Study Area

This study was conducted in the inner part of Kongsfjorden, an Arctic fjord in northwest Spitsbergen, the main island of the Svalbard archipelago. The fjord does not have a pronounced sill at the mouth, but its topography shows a main pit (300 m depth) separated from a number of inner small pits (<100 m depth) by

Figure 1. Map of Kongsfjorden and the surrounding area (western Spitsbergen, Svalbard, Norway). Bathymetry reconstruction (Kartverket@CC BY 4.0) shows deep zones in blue and shallow zones in red. Black dashed lines indicate the position of glacial fronts in August 2016. White dashed lines indicate the different areas of CTD profiles in Figure 3: outer zone (OZ), northern zone (NZ), southern zone (SZ), and southern Kongsbreen zone (SKZ). Individual marine stations, including the section displayed in Figures 4 and 6 (box) and the station numbers, are shown in white. Land stations for the sampling of glacial drainages are shown with the same colors used for Figures 5 and S4: red Bayelva river, blue drainages from Lovenbreen, green northern shore. Triangles indicate “low sediment” streams, crosses supraglacial runoff and the asterisk drainage from the Kronebreen glacier.

shallow moraines (<30 m depth), whose emerging parts constitute the main island of Lovenøyane (Figure 1). The total volume of Kongsfjorden has been estimated as 29.4 km³ (Aliani et al., 2016; Ito & Kudoh, 1997).

Five tidewater glaciers surround the inner fjord, providing the main source of freshwater: Blømstrandbreen, Conwaybreen, Kongsbreen, and Kronebreen—which forms a continuous front with Kongsvegen. The Ossiian Sarsfjellet peak separates Kongsbreen into two fronts: the northern part calving into the fjord and the southern part which was land-terminating in July–August 2016. In addition to marine-terminating glaciers discharging meltwater and ice into the fjord, land-terminating glaciers also feed several small braided streams (1–3 km long) around the fjord. By far, the largest discharge of freshwater from land-terminating glaciers comes from the Bayelva River (≈4.5 km in length) on the fjord’s southern shore, which delivers meltwater from the glaciers Vestre Brøggerbreen and Austre Brøggerbreen.

The oceanographic conditions in western Spitsbergen fjords are modulated by the presence of the currents flowing around the Svalbard Archipelago. On the shelf, cold and relatively fresh Arctic Water (ArW) flows northward in a coastal current, whereas off the shelf the West Spitsbergen Current flows in the same direction constituting the northernmost extension of the Norwegian Atlantic Current that transports warm and saline Atlantic Water (AW) ($T \geq 3^\circ\text{C}$ and $S \geq 34.9$) (Cottier et al., 2005) northward. Much of the AW entering Kongsfjorden mixes with ArW as it crosses the shelf and is termed Transformed Atlantic Water (TAW) ($1^\circ\text{C} < T < 3^\circ\text{C}$ and $S > 34.6$). Cold but more saline Atlantic waters ($1^\circ\text{C} < T < 3^\circ\text{C}$, $S > 34.9$), with minimal ArW influence, are termed Cooled Atlantic Waters (CAW) following Sundfjord et al. (2017). Surface water (SW) forms locally from glacial melt and river runoff and occupies the surface layer of the fjord during spring and summer, with salinities <34.0. Intermediate Water (IW) forms with mixing of waters of

Atlantic origin (AW or TAW) with overlying fresher SW and occupies the intermediate layer in the fjord. During autumn and winter, two other water masses are formed: Local Water (LW) and Winter Cooled Water. These waters can be detected throughout the year in confined depressions within the inner fjord (Cottier et al., 2005; Hop et al., 2006).

2.2. Data Collection

From 24 July to 10 August 2016, six oceanographic surveys (pHinS1–pHinS6) were carried out with R/V Teisten in Kongsfjorden within the framework of pHinS project (RIS-ID 10527). Profiles of hydrographic data were acquired at 70 stations and seawater samples were collected at a subset of 60 stations. Forty additional hydrographic profiles were provided by the “Snow” (RIS-ID 10050) and “Common Sense” (RIS-ID 10548) research projects (NYA1: 29 May 2016; NYA5: 30 June 2016) conducted in spring 2016.

Conductivity-temperature-depth (CTD) data were acquired with a Seabird 19plus SeaCAT profiler equipped with a TURNER Cyclops turbidimeter. Seawater samples for chemical analyses were collected using 10 L Niskin bottles at 1–7 depths per station, depending on the depth of the station (9–304 m), with more intensive sampling of SW layers.

Seawater samples for the determination of dissolved oxygen (DO, $\mu\text{mol L}^{-1}$) were collected in 60 ml borosilicate glass bottles and spiked with Winkler reagents. Samples for macronutrients (nitrate, NO_3^- ; nitrite, NO_2^- ; reactive silicic acid, $\text{Si}(\text{OH})_4$; orthophosphate, PO_4^{3-} ; $\mu\text{mol L}^{-1}$), dissolved organic carbon (DOC, $\mu\text{mol L}^{-1}$), and dissolved organic nitrogen (DON, $\mu\text{mol L}^{-1}$) were syringe filtered using precombusted (450°C, 4 h) GF/F filters, placed in acid-washed high-density polyethylene (HDPE) vials and stored at -20°C until analysis.

Seawater samples for the determination of pH, DIC (in $\mu\text{mol kg}^{-1}$), and TA (in $\mu\text{mol kg}^{-1}$) were collected in 300 and 1,000 ml borosilicate glass bottles, respectively (Dickson et al., 2007). Sample lids were immediately greased (Apiezon L), sealed with positive pressure on the lid and stored refrigerated (4°C) in the dark until analysis at “Dirigibile Italia” Arctic Station (Ny Ålesund, Svalbard). If the samples could not be analyzed within 24 h of collection, they were poisoned by the addition of 100 μl of saturated HgCl_2 solution.

Ice samples (1–2 kg) from small icebergs (maximum visible length above waterline < 20 m) floating in the fjord were collected from R/V Teisten and returned to the laboratory in insulated plastic boxes (Hopwood et al., 2017). Ice was rinsed with deionized water and melted in low-density polyethylene (LDPE) bags submerged in a water bath such that minimal air was introduced into the meltwater and to maintain a low temperature in the meltwater. Approximately, the first 20% of ice to melt was discarded by draining the LDPE bags as a precaution against contamination. After melting overnight, samples for the determination of DIC and TA were then extracted with a silicone tube, minimizing the contact with the atmosphere and stored as per marine samples. Samples for nutrient analysis were collected and frozen in HDPE vials.

From 27 July to 16 August 2016, glacial drainages surrounding the fjord were sampled with physical parameters recorded and samples for chemical analysis retained for 55 sampling points (Figure 1). This included supraglacial streams and proglacial watercourses from the moraines to the coast (0–5 km in length). Freshwater temperature and conductivity were measured with a portable Conductivity-Meter (LF325, WTW). For chemical parameters, a 10 L carboy was submerged in streams until bubbles were removed. Subsamples were then collected using a silicone tube for the determination of nutrients, DOC, DON, DIC, pH, and TA.

Meteorological data series at Ny Ålesund (station n. 99910; Lat. $^\circ\text{N}$ 78.9230, Long. $^\circ\text{E}$ 11.9333; 8 m above mean sea level) were downloaded from the eKlima portal of the Norwegian Meteorological Institute (URL: <http://www.met.no/>), for the period 2000–2016. Data refer to daily averaged air temperature (T_{AIR} ; $^\circ\text{C}$), air pressure (P_A ; hPa), wind speed (W_S ; m s^{-1}), and precipitation (P ; mm). Since 2009, daily visual observations of snow cover (S_C ; %) and measurements of snow depth (S_D ; cm) were carried out around the meteorological station.

2.3. Analytical Methods and Data Elaboration

CTD and turbidity profiles were processed using a window filter (running median; $n = 5$), and data were averaged every 0.5 m of depth. Potential temperature (Θ , ITS-90; $^\circ\text{C}$), salinity (Practical Salinity Scale, PSS-78), and potential density anomaly (σ_Θ , sigma-theta) were calculated from CTD data.

DO samples were analyzed by the Winkler method (Grasshoff, Ehrhardt, Kremling, & Anderson, 1999) with an automated Metrohm 798 MPT Titrino potentiometric titration system ($CV = 0.17\%$ at $210 \mu\text{mol L}^{-1}$) and used to calculate Apparent Oxygen Utilization (AOU) (Benson & Krause, 1984). The determination of nutrients was carried out following standard colorimetric methods (Grasshoff, Ehrhardt, Kremling, & Anderson, 1999) using an OI-Analytical (Flow Solution III) autoanalyzer.

Samples for the determination of DOC and TDN were analyzed by high-temperature catalytic oxidation, using a Shimadzu TOC-V analyzer equipped with a total nitrogen module (TNM-1) and an ASI-V autosampler (Grasshoff, Ehrhardt, Kremling, & Anderson, 1999). DOC was determined with triplicate measurements ($CV < 2\%$) against a four-point potassium hydrogen phthalate calibration ($r^2 > 0.999$) using a nondispersive IR detector. TDN was determined in triplicate ($CV < 2\%$) by chemiluminescence against a three-point calibration of potassium nitrate solution ($r^2 > 0.999$). The total blank of the system ($1.5 \pm 0.9 \mu\text{M C}$ for DOC, undetectable for DON) and the efficiency of the oxidation step was checked daily by the analysis of ultra-pure Millipore Q water (conductivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) and standard solutions. The concentration of DON was calculated as $\text{TDN} - \text{NO}_3^- - \text{NO}_2^-$; thus, DON values reported in this study are inclusive of dissolved ammonium.

Due to high turbidity in the fjord waters, all TA samples and sediment rich pH samples were prefiltered with $0.45 \mu\text{m}$ Durapore © (Millipore) membrane using an online filtration system suitable for DIC and pH measurements (Bockmon & Dickson, 2014). The filtration system was tested using CRM and low sediment fjord waters, and no meaningful error was introduced (effect of filtration on $\text{pH} < 0.001$).

DIC was measured using an infrared DIC analyzer (Apollo SciTech AS-C3) on an acidification and purging unit combined with a LI-COR 7000 CO_2 gas analyzer. The instrument was calibrated every 24 h using DIC/TA certified references materials (CRM batches 151 and 146 provided by Prof A. G. Dickson, Scripps, California).

TA was determined according to Dickson et al. (2007), using an automated open cell potentiometric titration system (Apollo AS-ALK2) equipped with a Thermo Scientific combination electrode with the Orion 3* pH meter calibrated using pH 7 and 10 buffers (Merck, Centipur buffers). A 0.1 M HCl , 0.7 M KCl solution was used as titrator for the fjord water samples and 0.05 M HCl (in deionized water) as titrator for freshwater samples. The titrator solution was characterized by titration against CRM (batch 151 or 146) before the analysis of each batch of samples. CRMs were further analyzed every 10 samples to correct for electrode drift. Analytical precision (one-sigma; 1σ) was calculated as the absolute difference between sample duplicates divided by $2/\sqrt{\pi}$ (Thompson & Howarth, 1973), producing values of ± 3.8 and $\pm 1.7 \mu\text{mol kg}^{-1}$ for DIC and TA, respectively.

pH in marine samples was determined spectrophotometrically using m-cresole purple as indicator (Clayton & Byrne, 1993; Dickson et al., 2007) using 10 cm glass cells held in a thermostat bath at $20 \pm 0.05^\circ\text{C}$. pH values are reported on the total hydrogen ion scale at 20°C (pH_{20}). For this parameter, the precision (1σ) determined on duplicate measurements ($n = 21$) (Thompson & Howarth, 1973) was $\pm 0.003 \text{ pH units}$. CRMs (batch 151 or 146) were measured regularly, and pH values were corrected for the offset. For river and ice samples ($S < 0.5$), a Thermo Scientific glass electrode was used to determine the pH. It was calibrated, prior to use, at 20°C with pH 7 and 10 buffers (Merck, Centipur buffers), and the values were reported on NBS scale ($\text{pH}_{\text{NBS } 20}$).

The choice of carbonic acid dissociation constants to calculate the other variables of the carbonate system in this dynamic environment is critical due to the strong salinity gradient and low temperatures. Calculations were performed with the CO2SYS program (Excel version 2.1, Lewis & Wallace, 1998; Pierrot et al., 2006), using the sulfate constants from Dickson (1990) and parameterization of borate from Lee et al. (2010). After testing several pairs of constants for inorganic carbon, the constants from Roy et al. (1993) were chosen, as they are suitable for a wide range of temperatures and salinities and yielded minimum differences between the calculated and measured variables. Mean residuals (i.e., difference between measured and calculated parameters) were -0.001 for pH_{20} , $+6.9 \mu\text{mol kg}^{-1}$ for DIC, and $+0.3 \mu\text{mol kg}^{-1}$ for TA, with no salinity or concentration dependence ($r^2 < 0.05$ for linear regressions of all parameters). To minimize the errors on calculated parameters (Orr et al., 2018), pH_{20} and TA data were used to calculate $p\text{CO}_2$, pH at in situ temperature and depth, and aragonite

Figure 2. Comparison between meteorological conditions at Ny Ålesund in January–August 2016 and monthly statistics (median, 1°–3° quartiles) in 2000–2015: daily average air temperature (T_{AIR} ; °C, left panel) and snow depth (S_D ; cm, right panel). Snow depth data are available only since 2009. The dates of oceanographic surveys in Kongsfjorden are also shown.

saturation state (Ω_{Ar}). Inorganic nutrient concentrations ($Si(OH)_4$ and PO_4) were also included in the carbonate system calculations.

Freshwater content (FWC) at each CTD station (FWC; cm) was calculated by a depth integration of freshwater ratio profiles using the trapezoidal rule. Freshwater ratios were obtained dividing the salinity measured at each depth by the salinity of a seawater endmember (34.947 ± 0.025), calculated as the median ($\pm SD$) of the values in the deeper layer (100–300 m depth) in the fjord mouth (Station. 1) over the whole study period. Subsequently, the total quantity of freshwater within the area of Kongsfjorden (FWC_T ; km^3) was estimated for each survey as a product between the median value of FWC for stations on each survey date and the sea surface area of the fjord ($128.5 km^2$).

The effects of estuarine mixing processes on chemical parameters were investigated in water masses with intermediate salinity by considering linear dilution plots that account for the mixing of the three main water endmembers in the fjord: glacier runoff, ice melt from glaciers/icebergs, and coastal seawater.

A conservative mixing between two water endmembers with concentrations $[C_1]$ and $[C_2]$ implies that the concentration in any sample ($[C_s]$) is linearly related to the fractions of the endmembers contained in the sample (M_1 and M_2) (Equation (1)).

$$[C_s] = [C_1] M_1 + [C_2] M_2, \text{ where } M_1 + M_2 = 1. \quad (1)$$

With respect to the carbonate system parameters, TA and DIC mix conservatively across a salinity gradient (Zeebe & Wolf-Gladrow, 2001); whereas pCO_2 , pH, and carbonate mineral saturation states are always subjected to a nonlinear effect of salinity on the carbonate system equilibria. To account for this difference, the theoretical linear dilution models of TA and DIC were calculated for the range of salinities observed in the fjord. The dilution curves of pH, pCO_2 , and Ω_{Ar} , both at in situ and at a fixed temperature, were obtained as polynomial interpolation (second degree, $r^2 > 0.92$) of the theoretical TA, DIC, temperature, and nutrient concentrations across the salinity gradient (see section 3.5). Contour plots along the section, θ -S plots and data analysis of Figure 9 were performed using Ocean Data View software (Schlitzer, 2020).

3. Results

3.1. Characterizing the 2016—Melting Season in Kongsfjorden

Air temperature (T_{AIR}) increased significantly through spring reaching the annual maximum on 11 July 2016 ($+9.8^\circ C$). Throughout the study period, values of surface air temperature were often higher than those observed over the time period 2000–2015, and snow depth seldom exceeded 20 cm the prior winter, a value significantly lower than observed in this area for 2009–2015 (Figure 2). The earliest hydrological survey (NYA1) was conducted during the phase of snow melting while the six oceanographic surveys of the pHinS project were carried out shortly after the annual peak in T_{AIR} and when snow had completely disappeared from the fjord. Weather conditions during pHinS surveys were rather homogeneous, the only major

Figure 3. (a) θ -S plot of water types in Kongsfjorden in summer 2016 (LW = Local Water, IW = Intermediate Water, CAW = Cooled Atlantic Water, AW = Atlantic Water, SW = Surface Water). Colors refer to the different areas within the fjord showed in Figure 1: outer zone (OZ), northern zone (NZ), southern zone (SZ), and southern Kongsbreen zone (SKZ). (b) Potential temperature and (c) salinity, reported in PSU in the section of Figure 1, based on CTD profiles acquired during cruises pHinS5–pHinS6.

exception being a storm (mean wind speed of 8.3 m s^{-1}) observed during the survey pHinS4 (31 July 2016) (Text S1).

3.2. Evolution of Hydrological Conditions and Runoff

As per previous surveys within Kongsfjorden (Cottier et al., 2005; Sundfjord et al., 2017; Svendsen et al., 2002), the main “pit” within the fjord, to the south of Blomstrandhalvøya Island (305 m depth), was occupied by saline and cold water of oceanic origin (CAW; Cooled Atlantic Water); the characteristics of which did not significantly change during the surveys (Figure 3 and Figure S3 in the supporting information, Table 1). The overlaying layer (50–250 m depth) was occupied by Atlantic water ($T > 3^\circ\text{C}$), except close to the marine-terminating glacier fronts where inflow of Atlantic water was impeded by the Lovenøyane sill. The layer between 20 and 50 m, and the inner part of the fjord was occupied by IW, formed from the mixing between surface fjord waters, warm surface shelf waters, and the underling seawater (Figures 3, S2, and S3). The coldest water (LW) was observed in the innermost pit adjacent to the southern front of Kongsbreen glacier (southern Kongsbreen zone [SKZ] in Figure 1) with little variability over the study period indicating limited mixing with overlying waters (Figures 9 and S2, Table 1). The presence of low-salinity SW strongly increased from spring to summer, leading to salinities as low as 16.24 in the inner area of the fjord (SKZ in Figure 1; cruise pHinS4).

Within the inner-fjord, defined by the Lovenøyane sill, a northward decrease of seawater temperature and salinity indicated a significant freshening and cooling effect of the glaciers as evidenced by a relative

Table 1
Physical and Chemical Properties of the Water Masses in the Kongsfjorden: Number of Samples (*n*) Average Values, Standard Deviation and Range of Variability Observed During the Whole Studied Period (24 July to 10 August 2016)

Water mass	AW (<i>n</i> = 17)				CAW (<i>n</i> = 2)				LW (<i>n</i> = 10)				IW (<i>n</i> = 21)				SW (<i>n</i> = 130)			
	Avg (std)	Min	Max		Avg (std)	Min	Max		Avg (std)	Min	Max		Avg (std)	Min	Max		Avg (std)	Min	Max	
Temp. (°C)	4.37 (0.86)	3.25	6.90		2.40 (0.20)	2.20	2.60		0.57 (0.03)	0.54	0.62		4.95 (0.82)	3.26	6.86		4.51 (0.69)	2.17	6.05	
Sal.	34.81 (0.10)	34.68	35.02		34.94 (0.01)	34.93	34.95		34.65 (0.01)	34.64	34.66		34.30 (0.18)	34.03	34.63		29.93 (4.02)	16.24	33.93	
DO (μM)	332 (11.54)	312	352		317 (0.14)	317	317		312 (2.30)	306	314		335 (4.19)	321	342		349 (11.69)	327	371	
AOU (μM)	−10 (16.26)	−38	13		19 (1.84)	17	21		42 (2.30)	39	47		−17 (7.93)	−34	−1		−18 (8.02)	−42	−3	
NO ₂ + NO ₃ (μM)	2.80 (1.70)	0.68	6.43		8.25 (1.75)	6.50	9.99		7.73 (1.06)	5.56	9.06		1.79 (0.84)	0.43	4.35		1.38 (0.49)	0.43	2.39	
Si(OH) ₄ (μM)	1.61 (0.78)	0.49	3.10		4.22 (0.62)	3.60	4.83		1.01 (0.17)	0.64	1.26		1.25 (0.35)	0.35	1.82		1.84 (1.13)	0.78	5.44	
PO ₄ (μM)	0.34 (0.14)	0.12	0.56		0.60 (0.07)	0.53	0.67		0.46 (0.06)	0.39	0.57		0.23 (0.05)	0.09	0.34		0.13 (0.06)	0.01	0.23	
NO ₂ (μM)	0.15 (0.14)	0.00	0.46		0.42 (0.15)	0.27	0.56		0.26 (0.05)	0.15	0.34		0.14 (0.11)	0.00	0.49		0.09 (0.20)	0.00	0.87	
DOC (μM)	173.7 (86)	74.3	340.2		231.6 (32)	199.2	263.9		307.7 (128)	130.5	503.5		225.8 (130)	54.5	484.0		213.2 (49)	39.9	233.2	
DON (μM)	8.7 (5.54)	0.2	20.3		11.9 (5.04)	6.9	17.0		14.7 (8.00)	2.7	29.9		11.1 (6.48)	3.4	23.2		11.2 (1.99)	3.0	9.6	
DIC (μmol kg ^{−1})	2,095 (53)	1,935	2,160		2,163 (17)	2,145	2,180		2,158 (27)	2,118	2,210		2,060 (30)	2,001	2,118		1,847 (203)	1,243	2,082	
TA (μmol kg ^{−1})	2,317 (12)	2,288	2,344		2,329 (0)	2,329	2,329		2,308 (18)	2,259	2,323		2,276 (26)	2,183	2,316		2,050 (213)	1,385	2,243	
pH _T 20°C	7.919 (0.046)	7.838	7.994		7.810 (0.010)	7.800	7.820		7.789 (0.010)	7.766	7.805		7.952 (0.024)	7.882	8.002		7.993 (0.021)	7.930	8.023	
pH _T	8.170 (0.039)	8.092	8.222		8.083 (0.007)	8.075	8.090		8.100 (0.011)	8.075	8.118		8.198 (0.023)	8.112	8.217		8.246 (0.022)	8.104	8.281	
pCO ₂	284 (27.83)	244	342		344 (5.64)	339	350		332 (9.00)	317	352		260 (17.12)	247	325		215 (22.07)	149	252	
Ω Ar	2.15 (0.20)	1.81	2.48		1.65 (0.04)	1.61	1.69		1.62 (0.04)	1.53	1.68		2.29 (0.11)	1.98	2.55		2.11 (0.20)	1.07	2.33	

Note. AW = Atlantic Water; CAW = Cooled Atlantic Water; LW = Local Water; IW = Intermediate Water; SW = Surface Water.

Figure 4. Depth-integrated freshwater content (FWC; cm) at Kongsfjorden hydrological stations, from 29 May to 10 August 2016. Total freshwater content (FWC_T) is also reported. Dashed line indicates the limit of the area where the freshwater budget was estimated (128.5 km²).

minimum in θ -S plots ($T = 3.15$; $S = 33.05$; Figure 3a). However, it is important to note that the hydrological characteristics of upper water column (<50 m depth) were highly variable, both spatially and temporally (Figure 4), due to the effects exerted by meteorological conditions and the multiple locally distinct freshwater outflows around the fjord.

The turbidity of the water column in the inner fjord was generally high, especially within the plumes of freshwater generated by riverine and glacial discharges. During cruises pHinS1–pHinS3, turbidities often >30 NTU down to 30 m (Figure S2) were measured in front of the Kongsvegen–Kronebreen glaciers, likely exerting a strong negative influence on light availability and primary production (Halbach et al., 2019). The high turbidity arising from sediment release during the summer peak of meltwater has also been observed by continuous measurements of total suspended matter at the mooring “Dirigibile Italia”, located at Station 4 (Figure 1) (D’Angelo et al., 2018). While the relationship between sediment load and discharge is complex, a general increase in the spatial extent of sediment plumes is expected with the increase of freshwater discharge in the fjord (D’Angelo et al., 2018).

The accumulation of freshwater in the fjord is regulated by the balance between the rate of runoff and the circulation rate of coastal waters. Inflow of Atlantic seawater mainly occurs through the channel to the south of Blomstrandhalvøya Island, and outflow of fresher coastal waters mainly occurs through the northern channel (Svendsen et al., 2002). Within each survey in 2016, the FWC was similar for all hydrological stations, but mean FWC significantly increased with time until the end of July indicating that the field activity encompassed the annual peak of freshwater accumulation within the fjord (Figure 4). The total FWC in the fjord rose from 29 May to 25 July (0.05 to 0.35 km³). It remained high until 31 July and then decreased sharply during the last two surveys in August (0.19–0.21 km³) following the passage of a short storm 31 July 2016.

Figure 5. Temperature, orthophosphate (PO_4), nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$), silicate (Si(OH)_4), pH measured at 20°C on NBS pH scale, dissolved inorganic carbon (DIC), and total alkalinity (TA) in proglacial streams and supraglacial runoff as a function of the distance from the mouths of the watercourses (i.e., 0 km at the fjord). The colors indicate different catchments (Bayelva, Lovénbreen) or areas as shown in Figure 1.

3.3. Glacier Runoff and Ice Melt Properties

Supraglacial runoff, originating from the melting of surface ice in the ablation zone of the glaciers, showed significantly lower Si(OH)_4 , PO_4^{3-} , TA, DIC, and pH than freshwater samples collected elsewhere, whereas the difference in NO_3^- content, comparing supraglacial runoff with other water courses, was less pronounced (Figure 5, Table S1).

Three proglacial streams draining from the Brøggerbreen glacier, which combine to form the Bayelva river, also showed distinct chemical characteristics. The eastern stream originates from Austre Brøggerbreen, a cold based glacier, and had low temperature, TA, DIC, and Si(OH)_4 concentrations. The central stream,

Figure 6. Biogeochemical properties of fjord waters along the section of Figure 1 based on data acquired during cruises pHinS5–pHinS6: nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$), silicate (Si(OH)_4), phosphate (PO_4), apparent oxygen utilization (AOU), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), CO_2 partial pressure ($p\text{CO}_2$), pH on the total pH scale, Aragonite saturation state (Ω_{Ar}) at in situ conditions, total alkalinity (TA), and dissolved inorganic carbon (DIC).

generated by a lateral tongue of the same glacier, was characterized by several water ponds with sluggish circulation and had higher temperatures, higher Si(OH)_4 , TA, and DIC concentrations. In the Bayelva catchment, pH values were, on average, higher than in the water streams draining from the Lovénbreen glacier (>8.0 in its lower course). The freshwater concentration of PO_4^{3-} was consistently low ($<0.5 \mu\text{M}$), with little variability between water courses. The concentrations of DOC and DON in glacier runoff were similarly universally low (means $\pm$ SD of $36.5 \pm 35.0 \mu\text{M C}$ and $4.6 \pm 5.7 \mu\text{M N}$), with a low DOC/DON ratio (5.9 ± 3.7) (Figure S4). Three water courses, located in SW and NE areas of the fjord (shown as triangles in Figures 1, 5, and S4), were characterized by higher temperatures, lower turbidities, and a different chemical composition. TA and DIC values measured at their mouth were more than two times higher than the other drainages, the concentrations of dissolved silicic acid and nitrate up to 10 times higher.

Nutrient concentrations in ice were extremely low for all macronutrients, (Table S1). DIC and TA concentrations were also low, relative to glacier runoff, and quite variable.

3.4. Biogeochemical Characteristic of Fjord Waters

AOU was mostly negative or around zero in surface fjord waters ($-30 \mu\text{M} < \text{AOU} < 0 \mu\text{M}$) indicating that these waters were oversaturated in oxygen or in equilibrium with the atmosphere. The only exception was at Station 8, where slightly positive values ($6 \mu\text{M} < \text{AOU} < 18 \mu\text{M}$) were observed at the surface within the turbid glacial plume (Figure 6). Below the surface (between 5 and 40 m), AOU decreased (down to $-30 \mu\text{M}$) both in the outer and inner part of the fjord. In the deeper layer (below 40 m), AOU gradually increased with depth within the CAW and reached the maximum values in the most isolated LW (up to $47 \mu\text{M}$ at SKZ) (Figure 9, Table 1). In contrast, AOU values remained negative down to the bottom in both frontal areas of Kronebreen and Kongsbreen N. in the presence of high turbid plumes in the overlying water column (Figures 6, S2, and S5).

The patterns of nitrate and phosphate distribution were similar, with low concentrations from the surface down to a depth of 25 m (the lowest measured concentrations were $0.43 \mu\text{M N}$ and $0.01 \mu\text{M P}$). Nitrate and phosphate concentrations increased within AW and CAW in the outer part of the fjord and also in LW (Table 1, Figures 6 and 9), but remained low down to the bottom in the frontal area of both Kronebreen and Kongsbreen N. (Figures 6 and S5). The concentration of $\text{Si}(\text{OH})_4$ was high both in SW (up to $5.44 \mu\text{M}$) and within AW and CAW (up to $4.83 \mu\text{M}$, Station 1), but low in the isolated LW. $\text{Si}(\text{OH})_4$ concentrations reached the lowest concentrations in the subsurface layer (between 15 and 40 m) affected by the inflow of open seawaters ($0.35 \mu\text{M}$, Station 1, 25 m) (Table 1, Figures 6 and 9).

In the inner part of the fjord, the average concentrations ($\pm\text{SD}$) of DOC ($214 \pm 116 \mu\text{M C}$) and DON ($11.0 \pm 6.9 \mu\text{M N}$) in seawater were very variable and mostly high. This was especially the case for DOC in the subsurface layers adjacent to the freshwater plumes, as well as at the bottom of the pits. Lower values were found only in the intermediate layer of Station 1, mainly occupied by AW (Table 1, Figure 6) and occasionally in some SWs.

TA and DIC concentrations showed an increasing trend, from the surface toward the bottom (Figure 6). The lowest values of both parameters were measured at the surface, in the SKZ (TA = $1,385 \mu\text{mol kg}^{-1}$, DIC = $1,243 \mu\text{mol kg}^{-1}$, S = 19.17). The highest TA concentrations were recorded at the bottom of Station 1 and in the outer part of the fjord, whereas DIC peaked at the bottom in both CAW and LW (Figures 6 and 9, Table 1).

During the study period, the fjord was always strongly undersaturated in $p\text{CO}_2$, with respect to atmospheric levels ($X\text{CO}_2$ 395 ± 1 ppm; average value July–Aug 2016, Kongsfjorden, Zeppelin station) (<http://ebas.nilu.no>), with surface values ranging from 149 to $253 \mu\text{atm}$ and values never exceeding $352 \mu\text{atm}$ even in the deeper layers (Figures 6 and S5, Table 1). pH ranged from 8.281, at the surface in the northern area (Figure S5), to 8.075, near the bottom within CAW and LW mirroring the trend for $p\text{CO}_2$.

Aragonite saturation state (Ω_{Ar}) was generally low at the surface, down to 1.07 at low salinities (SKZ), indicating close to corrosive conditions. Ω_{Ar} increased in the subsurface layer, between 15 and 40 m, and was up to 2.55 in the outer part of the fjord in concomitance with AOU lower than $-34.2 \mu\text{M}$ (Station 1). Ω_{Ar} values decreased again at depth, down to 1.68 measured at the bottom within CAW and LW water masses, whereas it remained above 2.1 at bottom in the frontal area of Kongsbreen N. (Table 1, Figures 6 and S5).

3.5. Freshwater Dilution and Estuarine Processes

The direct effects of glacier melting and estuarine mixing processes were investigated in upper waters, which were defined, for this analysis, as those with salinity <34.2 . Linear dilution plots of the three main endmembers were used: glacier runoff, ice melt from glaciers/icebergs, and subsurface coastal waters (Table 2).

Freshwater endmembers were defined as median concentrations of the samples collected at the river mouths and from drifting icebergs. The two river sampling points located in the SW area and characterized by high concentrations of inorganic component (Figure 1, red triangles) were excluded from dilution models because they were located outside the study area. The hydrological and biogeochemical analysis of fjord waters presented in the previous sections lead to the definition of the seawater endmember as coastal waters (20–50 m

Table 2
Water Endmembers Used in the Dilution Models in This Study, Compared With Literature Data of Arctic Rivers and Greenland Catchments

Source	Dissolved macronutrients (μM)			DOC (μM)	DON (μM)	DIC ($\mu\text{mol kg}^{-1}$)	TA ($\mu\text{mol kg}^{-1}$)
	$\text{NO}_3 + \text{NO}_2$	PO_4	Si				
Arctic River water	5.7 ^{a,d}	0.56 ^{a,b,d}	95 ^{a,d}	670 ^{a,d,e}	14 ^{a,d}	1,110 $\pm$ 44 ^{a,f}	1,048 ^{a,e}
Ice melt (lit)	1.4 $\pm$ 0.9 ^g	0.2 $\pm$ 0.2 ^g	13 $\pm$ 15 ^g	No data	No data	80 $\pm$ 17 ^h	50 $\pm$ 20 ^h
Median ice melt (this study)	0.4 $\pm$ 0.99	0.02 $\pm$ 0.03	0.02 $\pm$ 0.04	No data	No data	41 $\pm$ 88	173 $\pm$ 121
Glacier runoff (lit)	2.0 $\pm$ 0.2 ^{g,i,j}	0.2 $\pm$ 0.1 ^{g,i,j}	36 $\pm$ 10 ^{a,g}	80 $\pm$ 67 ^{j,k}	No data	209 $\pm$ 50 ^l	No data
Median glacier runoff (this study)	1.8 $\pm$ 0.47	0.07 $\pm$ 0.27	3.71 $\pm$ 2.34	27 $\pm$ 14	3.1 $\pm$ 1.98	622 $\pm$ 108	708 $\pm$ 251
Inflowing seawater (this study) ^c	1.2 $\pm$ 0.53	0.19 $\pm$ 0.06	1.06 $\pm$ 0.33	240 $\pm$ 108	14.7 $\pm$ 6.9	2,055 $\pm$ 27	2,269 $\pm$ 44

^aThese estimates are discharge volume weighted for respective source catchments. ^bTotal dissolved phosphorous (inclusive of PO_4 and dissolved organic phosphate). ^cDefinition ($S = 34.2\text{--}24.7$, depth 20–50 m, turbidity < 7 NTU). ^dHolmes et al. (2012). ^eCooper et al. (2008). ^fTank et al. (2012). ^gMeire et al. (2016). ^hMeire et al. (2015). ⁱHawkings et al. (2015). ^jHopwood et al. (2016). ^kBhatia et al. (2013). ^lRyu and Jacobson (2012).

of depth) entering in the fjord and not yet affected by local terrestrial discharges ($S = 34.2\text{--}34.7$; turbidity < 7 NTU).

Nonconservative behavior of the major nutrients in the upper waters of Kongsfjorden was evident (Figure 7), with a notable contrast between nitrate, phosphate, and silicate. Several $\text{NO}_3^- + \text{NO}_2^-$ datapoints at low salinity were consistent with a simple dilution of seawater with ice meltwater (which decreases the concentration) and/or with river water (which slightly increases the concentration). However, data were broadly distributed both above and below the range of concentrations that could be explained by dilution alone. Si (OH)₄ and PO_4^{3-} showed pronounced positive and negative deviations over the salinity gradient, respectively.

DOC and DON concentrations were lower in freshwater than in seawater, and their concentrations increased along the dilution gradient with a broad distribution, reaching levels ($>450 \mu\text{M}$) that are unusual in marine coastal systems (Figure 7).

TA was significantly correlated with salinity, ($r^2 = 0.836$, $n = 138$), with a zero-intercept ($679 \mu\text{mol kg}^{-1}$) similar to that determined for riverine and glacial endmembers (Figure 8). Freshwater inputs were also the main driver of DIC variability in these waters, as shown by the significant DIC/ S correlation and the value of the intercept ($r^2 = 0.856$, $n = 138$; $y_0 = 513 \mu\text{mol kg}^{-1}$) during the entire period studied. These observations further verified the selection of TA and DIC endmembers in freshwater. Data for pH, $p\text{CO}_2$, and Ω_{Ar} showed significant deviation from the theoretical models of dilution, particularly at the lowest range of salinities (Figure 8). Freshwater dilution alone would lead to low $p\text{CO}_2$ values, strongly undersaturated with respect to the atmosphere ($X\text{CO}_2 \text{ air} = 395 \text{ ppm}$), with calculated $p\text{CO}_2$ values as low as $89 \mu\text{atm}$ for runoff and even lower ($47 \mu\text{atm}$) for ice melt at the lowest recorded salinity ($S = 16.23$). Carbonate saturation state decreased at lower salinities (down to $\Omega_{\text{Ar}} = 1.07$ at $S = 16.23$), more than expected from the mixing models which would have led only to theoretical Ω_{Ar} values as low as 1.56–1.66. Aragonite saturation state, calculated at in situ temperature, displayed a significant linear correlation with salinity ($r^2 = 0.805$; Text S2), and the subsurface waters displayed higher values in comparison to the mixing model, up to 2.46.

3.6. Biogeochemical Properties of Isolated Deep Waters

LW, trapped at the bottom in the frontal area of southern Kongsbreen (SKZ area, Figure 1), was characterized by lower inorganic nutrient concentrations as a function of oxygen utilization when compared to the other deep water masses ($S > 34.2$, depth > 40 m) within the fjord, (Table 1, Figure 9). Despite the high AOU values, PO_4 concentrations remained lower than $0.6 \mu\text{M}$, $\text{NO}_3 + \text{NO}_2$ never exceeded $10 \mu\text{M}$ and Si (OH)₄ concentrations were three times lower than within the other fjord waters dominated by respiration.

$p\text{H}_{20}$ values within LW were the lowest measured during this study and changed consistently with oxygen consumption compared to the other water masses of the fjord (Figure 9), with a significant correlation between $p\text{H}_{20}$ and AOU ($r^2 = 0.977$; $n = 35$).

Figure 7. Inorganic and organic nutrient concentrations (μM) in the upper waters (S < 34.2) versus salinity and conservative mixing models generated by ice melt from drifting icebergs (blue line) and glacier runoff (orange line) with SW entering the fjord (34.2 < S < 34.7; depth 20–50 m, turbidity < 7 NTU). Dashed lines indicate the upper and lower quartiles for conservative mixing.

Despite lower pH_{20} in LW compared to CAW and a negligible difference between TA in these waters (Table 1, Figures 9 and S6), the in situ pH of LW was higher than that of CAW. Ω_{Ar} showed no average difference between the bottom of these two pits (Figures 9 and S6).

4. Discussion

Conditions encountered during this study can be considered to represent a polar fjord system subjected to the most intense annual phase of melting and calving of glaciers, during a year characterized by an unusually intense warming.

Winter 2016 was a record breaking warm season in the Arctic (note the warm anomalies in the study area, see Figure 2a) as a consequence of a significant El Nino event (Cullather et al., 2016). The lowest winter

Figure 8. Inorganic carbon parameters in the upper waters ($S < 34.2$) versus salinity, compared with mixing models of ice melt from drifting icebergs (blue line) and glacier runoff (orange line) with the seawater entering the fjord ($S = 34.2$ – 34.7 ; depth 20–50 m, turbidity < 7 NTU). Dashed lines indicate the upper and lower quartiles for conservative mixing; for $2\Omega_{Ar}$ the differences were too small and are omitted for clarity.

maximum sea ice extent in the satellite record to date led to prolonged exposure of the ocean surface to solar radiation (Richter-Menge & Mathis, 2017). In the following summer 2016, the Svalbard archipelago experienced higher than usual SST, although the anomaly was not as extreme as in other areas (e.g., Barents Sea, Richter-Menge & Mathis, 2017). Considering the recent large scale warming of the Arctic (Cohen et al., 2014), including Svalbard (Gjelten et al., 2016; Isaksen et al., 2016), with several very recent years of record breaking warm temperatures (Richter-Menge et al., 2019) the climate conditions in 2016 may be anticipated to become more common in future decades (e.g., Hanssen-Bauer et al., 2019).

In addition to the direct effect of increased temperatures on ice melt, a scarcity of snow limits the growth and extension of landfast ice in the fjord (Wang et al., 2015) and enhances the loss of ice from the glaciers in summer, facilitating larger runoff (Svendsen et al., 2002). Higher annual freshwater discharge from across the Svalbard archipelago is predicted until midcentury under a Representative Concentration Pathway (RCP)

Figure 9. Biogeochemical properties of Local Water (LW) in comparison with all the other bottom waters (depth > 40 m, $S > 34.2$) within the fjord: Intermediate Waters (IW), Atlantic water (AW), and Cooled Atlantic Water (CAW). Data are shown as a function of oxygen consumption, expressed as apparent oxygen utilization (AOU). (a) Nitrate + nitrite; (b) Silicic acid; (c) Phosphate; (d) Dissolved inorganic carbon; (e) pH measured at 20°C ; (f) Aragonite saturation state. Temperature is shown with the color scale, water masses are shown in the plot (a).

4.5 climate scenario, followed by a subsequent decrease due to sustained annual mass loss from the Svalbard Ice Cap (Bliss et al., 2014).

In the drainage basin of Kongsfjorden, the differing thermal characteristics of glaciers, the variable composition of the bedrock (Dallmann, 2015), and the varying degrees of interaction between ice/meltwater and sediment cause a high spatial and temporal variability in the chemical properties of freshwater at the point of discharge into the fjord. The lower temperature, TA, DIC, and $\text{Si}(\text{OH})_4$ concentrations of Eastern Bayelva stream suggest a fast flow with limited chemical weathering. On the contrary, the higher values of the central, slower, stream are likely a consequence of a longer residence time of freshwater and of enhanced meltwater-sediment interaction (Figure 5, Table S1).

In proglacial streams, pH varied between streams and along the water courses. Qualitatively, this variability may have been controlled by the stream velocity and size, with the wider rivers having slower velocities with lower $p\text{CO}_2$ and more basic pH (e.g., the Bayelva is a well-defined, sediment rich, wide stream with relatively basic pH) (Nowak & Hodson, 2014). Fast flowing, smaller streams such as most of the other freshwater outflows along the fjord's southern coastline had more acidic pH, due to weak buffering capacity (low TA) and strong $p\text{CO}_2$ gas exchange.

The higher temperatures and lower turbidities observed in three water courses (shown as triangles in Figures 1, 5, and S4) suggest a prolonged residence time of freshwater in freshwater bodies. Yet relatively high $\text{Si}(\text{OH})_4$ and TA likely also indicate a change in bedrock or weathering process compared to other streams (Ryu & Jacobson, 2012; Wadham et al., 2010).

Overall, from a biogeochemical and physical perspective, the inner-Kongsfjorden can be considered as a two layer system, with an upper layer strongly influenced by glacier runoff and ice melt and an intermediate layer (20–50 m of depth) with higher temperatures, low nutrient concentrations, and negative AOU values (Figures 3 and 6). Seawater entering the inner-fjord at 20–50 m depth has the characteristics of the mixed

layer surface seawater of the outer part of the fjord, far from the direct influence of meltwater. Inflowing water has increased oxygen concentrations (negative AOU values), high pH, and low nutrient concentrations as a result of primary production outside the fjord (Fransson et al., 2016; Piquet et al., 2014). This water crosses the Lovenøyane ridge and enters inner Kongsfjorden forming the main water type and mixes with meltwater in this innermost area. The shallow sills of the Lovenøyane ridge limit the entrance of nutrient rich deeper waters to the frontal area of both the Kongsvegen-Kronebreen and North Kongsbreen glaciers (Figures 6 and S5). Hence, the subglacial plumes bring to SWs relatively impoverished in macronutrients compared to deeper glacier fjord systems (e.g., Cape et al., 2019; Kanna et al., 2018). However, Halbach et al. (2019) demonstrate that these plumes are still significant sources of bioavailable N to SW, in the form of ammonium, sourced from the benthic boundary layer. The AOU minimum observed in the subsurface layer of Lovenøyane sill area (down to $-29.6 \mu\text{M}$, Figure 6) and higher PO_4 concentrations close to the sill (up to $0.20 \mu\text{M}$, Station. 4, Figure 6) are consistent with the occurrence of mixing that brings macronutrients closer to the surface and stimulates primary production.

4.1. Glaciers as Nutrient Sources and Sinks

Proglacial runoff, ice melt, and freshwater influenced fjord a were characterized by lower concentrations of NO_3 and PO_4 , relative to other freshwater sources of nutrients to the Arctic marine environment (Table 2), but they were similar to nutrient levels observed elsewhere in glaciated catchments around the North Atlantic (Meire et al., 2016). The concentrations of these nutrients were also imbalanced (*sensu* Redfield's model) (Redfield, 1958), with a deficiency of PO_4 with respect to NO_3^- .

PO_4 inputs into the fjord from ice melt and runoff were negligible, yet a significant deficit compared to calculated concentrations from estuarine mixing was evident at low and intermediate salinity (Figures 7a and 7c). Over the same salinity range, the dissolved nitrogen pool did not show a similar negative balance as the concentrations of NO_3^- and DON were generally within the expected conservative mixing lines (Figures 7a and 7e). A strong removal of PO_4 with respect to the dilution line would be expected to be primarily caused by biological uptake, yet this would concurrently remove bioavailable nitrogen. The absence of a drawdown of NO_3 might however indicate a pelagic productivity mainly fueled by NH_4^+ , which is expected when phytoplankton growth takes place in coastal zones at low levels of irradiance (Cozzi et al., 2008) and is consistent with the enhanced benthic NH_4 supply from mixing close to the glacier fronts (Halbach et al., 2019).

However, DON showed positive balances in seawater similar to NO_3^- , indicating that DON uptake, if present, might be masked by other nonconservative processes like (i) a fast dissolution and remineralization of particulate organic nitrogen to NH_4 or (ii) the presence of other inputs of DON/ NH_4 in the fjord waters than the runoff (such as a sedimentary source, Halbach et al., 2019, which is consistent with the observed DON distribution, Figure 6). Another plausible explanation for the anomalous deficit of PO_4 is high concentrations of Fe-oxyhydroxides, which constitute a small, but nonnegligible PO_4 sink in temperate estuaries (Windom et al., 1991). Labile particulate Fe concentrations in Kongsfjorden are extremely high compared to temperate estuaries (up to $50 \mu\text{M}$; Hopwood et al., 2017), and thus the Fe- PO_4 sink may be stronger than observed for temperate river-estuary systems. While this Fe- PO_4 sink has not been quantified in glacier estuaries, our observations are consistent with the negative PO_4 anomalies associated with high turbidity in Sermilik Fjord (West Greenland, Cape et al., 2019) suggesting turbid glacier plumes are PO_4 sinks.

Si(OH)_4 was the only macronutrient to show extensive nonconservative enrichment over the estuarine salinity gradient (Figure 7). This phenomenon is, in the absence of strong biological uptake within estuarine waters, observed widely in river estuaries due to dissolution of labile particulate Si phases under saline, alkaline conditions (Windom et al., 1991). Si(OH)_4 in glacier runoff is initially enriched above the Redfield ratio compared to NO_3 and PO_4 , and hence, as shown in other Arctic glacier estuaries (Brown et al., 2010; Hawkings et al., 2017; Meire et al., 2016), glacier runoff is an imbalanced nutrient supply providing silicic acid but minimal NO_3/PO_4 to the marine environment (Meire et al., 2016).

The low Si(OH)_4 concentrations measured within the LW trapped in the inner pit are particularly intriguing, given the enrichment in this nutrient observed in upper waters and the high sediment loads for that area (>30 NTU for most of the study period). Were estuarine particulate Si dissolution the dominant Si source and entirely controlled by the salinity, or pH gradient making particulate Si dissolution more favorable in

the marine environment than in freshwater (Hawkings et al., 2017), a high Si(OH)_4 signal would be expected in LW. The consistently low Si(OH)_4 concentrations in LW possibly suggests either a role for light in silicate dissolution or indicates an unexpectedly strong dissolved Si sink within the inner pit.

The fraction of DOC generated within this coastal marine environment far exceeds that usually observed in offshore seawaters and that delivered from terrestrial sources—consistent with prior C isotope work within the fjord (Holding et al., 2017). Accordingly, DOC increased with salinity (Figure 7) and an increase in freshwater discharge, either from runoff or ice melt, would be expected to further dilute DOC concentrations within the fjord.

4.2. Impact on the Carbonate System of Surface Runoff and Calving Glaciers

Freshwater input from direct ice melting and glacier runoff has the potential to affect water column chemistry, air-sea CO_2 fluxes, and the OA state in several ways. TA in Arctic glacial discharge ranges between 20 and $550 \mu\text{mol kg}^{-1}$ (Hopwood et al., 2020) and is less than half the average concentration in Arctic rivers (Table 2). A bedrock containing calcite and dolomite surrounds Kongsfjorden, (Dallmann, 2015) so TA values for Kongsfjorden runoff lie within the upper part of this range (Fransson et al., 2016). This result is further confirmed by the average chemical composition of freshwater measured during this study (Table S2). Some outflows had TA exceeding $2000 \mu\text{mol kg}^{-1}$. Similarly, TA in freshly collected ice melt was three times higher than for ice melt from icebergs collected in a Greenlandic fjord (Table. 2) (Meire et al., 2015), yet comparable to samples from Tempelfjorden (median $140 \mu\text{mol kg}^{-1}$; $n = 6$) (Fransson et al., 2015) which is surrounded by the same type of bedrock.

Arctic rivers are generally DIC-rich, due to the remineralization of a large pool of organic matter, and have a low TA:DIC ratio. This chemical characteristic leads to wintertime concentrations of CO_3^{2-} approaching zero levels, which is one of the main drivers of the low Ω_{Ar} values observed in the Arctic coastal region (Tank et al., 2012). Conversely, in the Kongsfjorden catchment, relatively low concentrations of DIC were measured, leading to generally higher TA:DIC ratios (1.29 in glacier runoff; up to 4.0 in ice melt). This implies a shift of carbonate equilibria toward higher CO_3^{2-} concentrations and a lower “corrosivity” of freshwater, as will be further discussed in this section.

Low surface $p\text{CO}_2$ values are common in fjord systems affected by glacier runoff, and can be driven by either biological CO_2 uptake or physical processes, with the importance of these two main drivers thereby varying spatially and seasonally (Ericson et al., 2018; Meire et al., 2015; Rysgaard et al., 2012; Sejr et al., 2011). The estuarine model of our study highlights the importance of mixing during summer in Kongsfjorden. The theoretical dilution curve alone leads to surface $p\text{CO}_2$ values ($92 \mu\text{atm}$ glacier runoff; $47 \mu\text{atm}$ ice melt) even lower than those measured ($163 \mu\text{atm}$), with a $p\text{CO}_2$ drop of $-170 \mu\text{atm}$ for surface runoff and $-210 \mu\text{atm}$ for ice melt, compared to the marine endmember. The low values of the simple mixing model arise both as a result of the chemical composition of freshwater and also from the nonconservative behavior of $p\text{CO}_2$ during mixing along a temperature and salinity gradient (Meire et al., 2015; Whitfield & Turner, 1986).

If the same dilution curve were calculated but with temperature constant (Figure S7b) during the mixing of inflowing warmer seawaters (5.3°C) with colder freshwaters (3.97°C at $S = 16.23$), the $p\text{CO}_2$ decrease would be reduced ($-155 \mu\text{atm}$ surface runoff, $-205 \mu\text{atm}$ ice meltwater). The temperature decrease of 1.32°C therefore accounts for 8% and 3% of the theoretical $p\text{CO}_2$ decrease calculated for glacier runoff and ice melt, respectively.

A larger effect arises from the salinity change. This mixing effect can lead to strong $p\text{CO}_2$ undersaturation in glaciatic fjords, even if freshwater was initially in equilibrium with atmospheric $p\text{CO}_2$. Results from Greenland (Meire et al., 2015) indicate a theoretical $p\text{CO}_2$ drop as high as $\sim 170 \mu\text{atm}$ at 0°C , along the salinity gradient from 33.5 to 16, due to this thermodynamic effect of salinity. If we apply the same approach herein, the effect of variation in salinity alone can lead to a $p\text{CO}_2$ drop of the same order of magnitude; $-125 \mu\text{atm}$ for surface runoff and $-180 \mu\text{atm}$ for glacial melt (at $S = 16$ and 0°C).

$p\text{CO}_2$ values calculated from experimental data from Kongsfjorden never reached the extremely low values calculated from mixing alone. The most likely explanation was an ongoing increase of surface $p\text{CO}_2$ due to absorption of atmospheric CO_2 , driven by the strong marine undersaturation. At higher salinities, and especially in the subsurface layer (blue dots in Figure 8), less influenced by air-sea CO_2 exchange, $p\text{CO}_2$ was

mostly lower than calculated from the dilution model. These deviations, while smaller than that observed at surface, suggest a nonnegligible role of photosynthesis in removing CO_2 .

The theoretical effect of freshwater inputs is an increase in pH, which is particularly sharp for the less buffered (i.e., lower TA) ice meltwaters. At the lowest recorded salinity ($S = 16.23$), the theoretical pH values were 8.635 for dilution with melted ice and 8.476 for dilution with riverine freshwater. This represents increases of +0.437 and of +0.278 pH units respectively, compared to the marine endmember. As already noted for $p\text{CO}_2$, this variation is partially due to the temperature change, with lower temperatures shifting carbonate chemistry equilibria toward higher pH values. Keeping temperature constant (Figure S7a), the theoretical increases of pH with salinity would have been slightly smaller (+0.414 and +0.255, respectively). Hence, only 5%–8% of the total pH increase can be attributed to temperature change; most of the increase is due to the salinity effect. Compared to the calculated dilution curves, observational pH data showed little variability, with values below the theoretical range in shallow low-salinity waters and slightly above the theoretical range at the highest salinity. This was particularly the case in SWs (Figure S3), with a trend that suggests rapid CO_2 absorption from the atmosphere. The impact of glacial melting on the potential “corrosivity” of marine waters is better described by Ω_{Ar} dynamics than pH. Freshwater dilution leads to a decrease in Ω_{Ar} , with temperature having little or negligible influence on this saturation state (Figure S7c). The calculated values of Ω_{Ar} at $S = 16.23$ (1.63 when freshwater consists of ice melt and 1.53 for freshwater consisting entirely of glacier runoff) remained higher than what is estimated for the dilution by Arctic rivers (Tank et al., 2012). Undersaturation ($\Omega_{\text{Ar}} < 1$) around the coastal Arctic Ocean has been estimated to occur at salinities below 18–24, while in Kongsfjorden, taking into account only dilution, Ω_{Ar} undersaturation could presently occur only at salinities close to that of freshwater (<5). The lower corrosivity potential in Kongsfjorden is explained by the higher TA:DIC ratios of freshwater sources. This creates a shift of carbonate equilibria toward higher CO_3^{2-} concentrations and consequently toward higher Ω_{Ar} values within the fjord.

Experimental results showed a sharper than calculated Ω_{Ar} decrease at low salinities, with a significant Ω_{Ar}/S correlation ($r^2 = 0.80$), confirming the trend evidenced in similar fjords elsewhere in Svalbard (Ericson et al., 2019; Fransson et al., 2015). To allow a better comparison, we calculated the freshwater fraction (ffw%; ref. salinity 34.8) according to Ericson et al. (2019). The $\Omega_{\text{Ar}}/\text{ffw}\%$ regression of our study (slope -0.027 ; $r^2 = 0.80$) agrees well with a study in Tempelfjorden (Ericson et al., 2019) which was based on a smaller data set spanning two melting seasons (-0.032 for 2016 and -0.028 for 2017). Our results clearly show that this trend does not derive only from freshwater dilution, but it is also partially due to absorption of atmospheric CO_2 , driven by the strong $p\text{CO}_2$ undersaturation. Overall, 65% of the Ω_{Ar} drop at $S = 16.23$ can be explained by freshwater dilution and 35% from atmospheric CO_2 absorption. Only the combination of these two processes can presently lead to potentially corrosive conditions which would have occurred only at salinities <13 during the meltwater peak of July–August 2016. Under the same conditions, at salinities <19, Ω_{Ar} reaches values <1.4 which is detrimental for more sensitive Arctic organisms (Fransson et al., 2016).

The same processes that explain $p\text{CO}_2$ variability can explain pH variability too. Yet it is important to note that, unlike for oceanic upwelling zones or CO_2 rich riverine estuaries, neither pH nor $p\text{CO}_2$ alone would track near-corrosive conditions in coastal areas impacted by glacial melt (Evans et al., 2014). In Kongsfjorden, the situation generally reverses and the more corrosive waters in the upper layer have the highest pH and the lowest $p\text{CO}_2$ values.

The situation changes in the bottom waters (depth > 40 m, $S > 34.2$) where the lowest Ω_{Ar} values were associated with the highest $p\text{CO}_2$ and the lowest pH (Figure S6). The good correlation between pH_{20} and AOU (Figure 9) indicates that respiration was the main driver of pH variability within all these water masses. This was also the case for LW trapped at the bottom of the SKZ despite its isolation and wintry origin. Despite the strongly positive AOU values of LW, Ω_{Ar} values were similar to those observed within the CAW, at the bottom of the outer pit. The lower temperatures of LW and the shallower depth of SKZ dampened the increase of acidity within LW. The environmental conditions at the bottom of these two pits therefore remained above the harmful threshold of 1.4 for Ω_{Ar} for sensitive species.

4.3. Future Changes in the Kongsfjorden Carbonate System

An increase of atmospheric CO_2 to 486 ppm (+91 ppm increase), will be reached by 2050 according to an RCP 4.5 scenario or by 2040 according to a RCP 8.5 scenario. Assuming that all other variables remain constant,

and keeping the same air-sea disequilibrium in CO_2 observed in summer 2016, indicates at what salinity threshold corrosive Ω_{Ar} conditions may be observed in the future. This simplified approach, indicates that a 486 ppm atmospheric XCO_2 would allow Ω_{Ar} undersaturation to be reached at salinities <21 , values that were observed in 6%–17% of the stations during the freshwater peak in 2016 (pHinS1–pHinS3). $\Omega_{\text{Ar}} < 1.4$ will be reached at salinities <27 that were reached in most of the stations (60%–100%) during the 2016 meltwater peak. In reality, discharge is expected to increase until approximately midcentury under the same RCP 4.5 scenario which will facilitate further freshening of the fjord in summer and so Kongsfjorden may approach summertime conditions which are mostly $\Omega_{\text{Ar}} < 1.4$, and often corrosive this century.

There are, however, other confounding factors which may moderate or enhance these changes. As submarine discharge from marine-terminating glaciers promotes estuarine circulation during summer (Halbach et al., 2019; Torsvik et al., 2019), changing the position of the calving fronts of presently marine-terminating glaciers will have profound downstream implications. In coming decades, the Kongsbreen and Kronebreen terminus will retreat onto land. Fjord-scale modeling then suggests stratification will increase in the upper layer of the fjord (Torsvik et al., 2019) and decrease the extent to which freshwater release entrains deep marine-waters within the discharge plume (Carroll et al., 2016). The model developed by Torsvik et al. (2019) that does not include an increase in freshwater discharge, estimates an average summer decrease of 2 for surface salinities in the inner Kongsfjorden contrasting the present-day terminus with a land-terminating one. If we apply this decrease, which is likely conservative given the anticipated increase in discharge, in addition to the 2050 RCP 4.5 XCO_2 increase, surface Ω_{Ar} undersaturation would occur in 13%–25% of the fjord stations during the annual freshwater peak (pHinS1–pHinS3) and values of $\Omega_{\text{Ar}} < 1.4$ would occur across the whole fjord area.

There are two other effects which may also strongly influence the extent of future corrosivity. Glacier runoff in Kongsfjorden has higher alkalinities compared to ice melt (Table 2), and thus as glaciers around the fjord retreat, TA in the mean freshwater endmember will probably increase due to a declining contribution of direct melt input into the fjord and increased meltwater-sediment interaction. This increase in the mean TA freshwater endmember may slightly buffer the anticipated increase in corrosivity.

In addition, the long-term response of primary production within the fjord to glacier retreat will also exert an influence on biological $p\text{CO}_2$ drawdown. A decline in productivity is expected from the reduced entrainment of nutrients associated with marine-terminating glaciers as they retreat inland. Complete loss of the entrainment effect would reduce N supply by approximately 19%–32% compared to the present day (Halbach et al., 2019). To what extent this, and other changing dynamics between light, stratification and nutrient-limitation, will affect future fjord-scale productivity in the inner-fjord, and thus $p\text{CO}_2$ drawdown, remains to be determined quantitatively. Yet in general, a modest decline in productivity would be expected in the inner-fjord, which would decrease $p\text{CO}_2$ drawdown in sub-surface waters and thereby lower pH and lower Ω_{Ar} . In summary, corrosive conditions are not presently plausible within Kongsfjorden, and $\Omega_{\text{Ar}} < 1.4$ conditions only occur close to the peak of the meltwater season in the inner fjord. However, the area of the fjord subject to $\Omega_{\text{Ar}} < 1.4$ conditions throughout summer is likely to expand in coming decades. Furthermore, as peak discharge is approached this century it is possible that summertime conditions within the fjord may become largely corrosive.

5. Conclusions

Our study captured the seasonal progression of fjord FWC during one of the warmest summers recorded in Svalbard following a record warm winter in the whole Arctic. Moreover, the effect of a storm in rapidly changing FWC in this coastal system was also fortuitously captured.

The characterization of freshwater loads from proglacial runoff and ice melting sources indicates that future changes to the nature of freshwater input will affect the biogeochemistry of the fjord system. In particular, retreat of marine-terminating glaciers will increase the mean TA and $\text{Si}(\text{OH})_4$ of freshwater entering the fjord. Mixing models indicate that meltwater is a small or negligible source of DOM and NO_3^- , a sink for PO_4^{3-} , and a modest source of $\text{Si}(\text{OH})_4$ and TA.

Freshwater inputs in the stratified shallow low salinity waters cause a strong $p\text{CO}_2$ undersaturation, which enhances atmospheric CO_2 absorption in the inner area of the fjord. This process decreases the carbonate

mineral saturation state of surface waters, leading to corrosive conditions at low salinities. Perturbations of the carbonate system under future climate scenarios are mainly expected to further amplify the shift toward corrosive conditions in inner-fjord surface waters. Such changes (increasing atmospheric $p\text{CO}_2$, increasing discharge rates, loss of primary production and longer fjord freshwater residence times associated with the retreat of tidewater glaciers) could be partially buffered by the increase of TA in proglacial streams as glaciers retreat inland. Nevertheless, shallow fjord systems like Kongsfjorden may still experience a relatively sharp change toward closer-to-corrosive conditions in SWs in coming decades, with corrosive conditions plausibly present across much of the fjord surface at the peak of the meltwater season by midcentury.

Data Availability Statement

The complete data set gathered during the pHinS project and used for this paper is available in Pangaea data repository: <https://doi.pangaea.de/10.1594/PANGAEA.904171>; <https://doi.pangaea.de/10.1594/PANGAEA.904170>; <https://doi.pangaea.de/10.1594/PANGAEA.904168>; and <https://doi.pangaea.de/10.1594/PANGAEA.904145>.

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