Summary

Introduction and Rationale

Seawater carbonate chemistry is described by the concentration and the reactions in seawater of the different carbonate species: CO_2 (carbon dioxide), HCO_3^- (bicarbonate ion), and CO_3^{2-} (carbonate ion). Part of the CO_2 gas ($CO_{2(g)}$) entering the water column remains in the form of dissolved gas ($CO_{2(aq)}$), while part reacts with H_2O to form carbonic acid (H_2CO_3), which rapidly dissociates into H^+ (hydrogen ion) and HCO_3^- that can further dissociate to CO_3^{2-}, releasing another H^+ (Eqs. 1, 2, and 3) (Dickson et al., 2007). Both these dissociation stages are described by the temperature-, pressure- and salinity-dependent dissociation constants k_1 and k_2 (Eqs. 4 and 5) (Millero, 2010).

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \quad (1)$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (3)$$

$$k_1 = \frac{[CO_2^*]\,[H^+]}{[HCO_3^-]} \quad (4)$$

$$k_2 = \frac{[HCO_3^-]\,[H^+]}{[CO_3^{2-}]} \quad (5)$$

where CO_2^* is a total concentration of $CO_{2(aq)}$ and an undissociated form of carbonic acid, H_2CO_3. Therefore, the dissociation of $CO_{2(aq)}$ increases H^+ concentration in seawater and thus reduces its pH ($pH = -\log_{10}[H^+]$).

The total sum of the concentrations of the different inorganic carbon species in seawater is denoted as the dissolved inorganic carbon (DIC) (Eq. 6).

$$DIC = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (6)$$

In the surface ocean, at a temperature of 17°C and a salinity of 35, approximately 92% of the DIC is in the form of bicarbonate ions, around 7% exists as carbonate ions, the other two species ($CO_{2(aq)}$ and H_2CO_3) constitute together only 1%, from which, 0.1 % is in the short living form of H_2CO_3. Thus, H_2CO_3 is not considered directly relevant for chemical or biological processes (e.g., Riebesell et al., 2010).

Although $CO_{2(aq)}$ represents only about 1% of the DIC pool, its concentration relative to the atmospheric level is crucial for the direction of the air-sea CO_2 gas exchange. When the concentration of CO_2 in the ocean surface is lower than in the atmosphere, there is a net flux of CO_2 to the seawater, while it is released from the seawater when its concentration is higher than in the atmosphere.

Since 1850, about 25% of total anthropogenic CO_2 emissions have been taken up by the oceans (Friedlingstein et al., 2025). As a consequence, the global ocean DIC inventory has increased, and the seawater pH has decreased, a phenomenon known as ocean acidification (OA). The pH decrease, which is currently about 0.017 per decade (IPCC, 2019), would be even larger if it were not for the presence of strong bases in the seawater (Ma et al., 2023), which capture some of the H^+ ions in the buffer reaction. Typically, this reaction is illustrated with carbonate ions (Eq. 7).

$$CO_{2(aq)} + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^- \quad (7)$$

Although carbonate chemistry is most crucial for regulating ocean pH, other ions in seawater can also act as proton acceptors, controlling the pool of free protons in water. The excess of proton acceptors

over proton donors in seawater (or bases over acids), approximating the oceanic buffering capacity, is defined as the total alkalinity (TA) (Wolf-Gladrow et al., 2007). The TA in seawater is quantified as:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - [HNO_2] + [\text{minor bases - minor acids}] \quad (8)$$

Since TA is to a large extent salinity-dependent, it is relatively constant in open waters, whereas in coastal waters it shows significant temporal and spatial variability. Regardless of the total concentration and location, the dominant share of TA is mostly bicarbonates and carbonates, usually about 90%. In open waters, borates contribute a few percent to the TA, while other substances play a rather minor role and are often considered irrelevant. In coastal, estuarine, and fjord systems, however, these commonly negligible substances become more important either because of their unusual contribution and/or elevated concentrations (ion anomalies), and can largely contribute to TA. For instance, the contribution of organic compounds with acid-base properties in waters rich in dissolved organic matter can have a large contribution to the TA (Hunt et al., 2011; Kerr et al., 2021; Kuliński et al., 2017; Yang et al., 2015).

Commonly, four measurable parameters are used to describe the structure of the carbonate system in seawater (also denoted as marine CO_2 system) . The mass conservation is defined by (1) the DIC. The charge balance is parametrized by (2) the TA. The speciation of inorganic carbon species is controlled by (3) the pH. And the potential to transfer inorganic carbon between the atmosphere and the ocean surface is determined by (4) the partial pressure of seawater CO_2 (pCO_2) (Dickson et al., 2007).

In the well-characterized carbonate system of the open ocean, these four measurable variables (TA, DIC, pH and pCO_2) can be calculated using ion-pairing models through the set of thermodynamic and mass-balance equations (e.g. Lewis et al., 1998). For these calculations, two of the four variables are needed as input parameters, along with temperature and salinity. Besides TA, DIC, pH, and pCO_2, these models can also estimate the contributions and concentrations of different inorganic carbon species, including CO_3^{2-}. The concentration of CO_3^{2-} is ultimately used to determine the saturation states of aragonite (Ωar) and calcite (Ωcal), two crystal forms of calcium carbonate ($CaCO_3$) used by calcifying organisms to build their exoskeletons, therefore they are key parameters for understanding ecosystem health and sensitivity against OA. However, in coastal waters, the presence of unparametrized components in the ion-pairing models (such as organic compounds with acid-base properties) can induce errors (sometimes above the limits to resolve regional and short-term variability in the marine CO_2 system), expressed as over- or underestimations of the calculated parameters, including Ωar and Ωcal.

The Arctic Ocean is particularly efficient at absorbing anthropogenic CO_2 due to the higher solubility of the gas in its cold waters, which, on the other hand, makes the region especially sensitive to OA (von Schuckmann et al., 2024). Moreover, rising temperatures are increasing the extent and duration of sea ice-free areas, thereby enhancing air-sea CO_2 fluxes. The effect of OA is further amplified by seawater freshening caused by meltwater inflow from sea ice and glaciers, which is responsible for reducing TA and the buffer capacity in surface water layers (Zhang et al., 2020). Furthermore, river runoff remains a significant source of freshwater to the Arctic Ocean. Although the Arctic Ocean accounts for only 1% of the total oceanic volume, it receives approximately 11% of the global continental runoff, and this effect has been exacerbated in recent decades by the increase in precipitation in drainage basins (e.g. Capelle et al., 2020 and reference therein). On the other hand, the expansion of ice-free, open waters and the increase in nutrient supply have increased net primary production (NPP). This mechanism reduces CO_2 concentration and increases pH in the photic layer, counteracting OA.

Therefore, there is a direct feedback mechanism between anthropogenically driven changes in the Arctic cryosphere, air-sea CO_2 fluxes, and NPP, all of which transform the carbonate equilibrium of surface

waters and thus influence OA in different directions. **To quantify present and project future changes in OA, carbon cycling, and carbon inventory in the Arctic, it is necessary to accurately measure changes in the marine carbonate system and attribute the main drivers of these changes. Despite the significant exposure of Arctic waters to OA, the contributions of individual drivers to changes in its surface pH remain poorly quantified**.

Moreover, due to the harsh environmental conditions and logistical constraints, measurements of the carbonate system in Arctic waters are scarce. In most cases, only two (out of four) variables of the carbonate equilibrium are measured, and the others are calculated using ion-pairing balance models. This is despite the Arctic region being heavily influenced by meltwater, continental runoff, and enhanced primary production, all of which have the potential to cause atypical seawater composition and thus affect the quality of results estimated by the models. **Even though it is suspected that the accuracy of the calculated variables is likely reduced, to date, there have been no dedicated assessments demonstrating the uncertainty of the calculated values in Arctic coastal areas. There is also no study reporting clear guidelines about how to obtain high-quality calculated values of the carbonate system, which are ultimately the backbone for OA studies, ecosystem health and carbon inventory in the Arctic region.**

The scarcity of measurements and potential limitations in the quality of mathematically determined carbonate system variables are not the only problems. The high spatial (including vertical) and temporal variability of the marine carbonate system in Arctic coastal waters makes its characterization, and thus OA studies, a difficult task. Sampling of different carbonate system (and other biogeochemical) parameters is most often performed by collecting water with traditional Niskin-bottle-based devices, offering only sparse vertical resolution. **The lack of a system allowing for continuous, high-resolution water-column sampling of different variables of the marine carbonate system limits our ability to explore the rapid biogeochemical transformations in the photic zone, where melted sea ice, continental runoff, CO_2 air-sea gas exchange, and primary production interact simultaneously and have the most significant impact.**

Research hypotheses

Taking into account the actual state of knowledge on the marine carbonate system in Arctic waters, as well as research needs related to gaps in understanding, the following **research hypotheses** have been proposed:

1) Despite the direct influence of sea ice meltwater on TA and DIC, NPP is the main driver of pH changes in the surface layer of the Arctic open waters during the summer season.
2) The accuracy of the calculated carbonate system parameters using ion-pairing models is reduced in Arctic coastal areas compared to open ocean waters, limiting the quality of OA studies.
3) High-resolution vertical sampling of the marine carbonate system parameters reveals fine-scale biogeochemical variability in the surface layer induced by continental runoff and sea ice/glacier meltwater in Arctic coastal areas.

Goals

The main overarching aim of this PhD dissertation was to provide new insights into the structure and variability of the marine carbonate system in understudied Arctic waters, including the biogeochemically complex coastal areas. This was done considering the limitations of the possible sampling area and the challenges of providing high-quality, high-resolution data to link the variability of the marine carbonate system to the influence of continental runoff, sea ice meltwater, primary production, and temperature, with special focus on the Atlantic sector of the Arctic region. The specific **research goals** included:

I. To characterize the interannual spatial variability of the marine carbonate system in surface waters of the Fram Strait and to identify and quantify the main physical and biological drivers behind these transformations.
II. To identify quality limitations in the use of thermodynamic ion-pairing models to calculate TA, DIC, pH, and pCO_2 in open and coastal Arctic waters and to provide concise guidelines for obtaining high-quality data on the carbonate system.
III. To provide a solution for simultaneous sampling of all four carbonate system parameters (and other biogeochemical variables) with high vertical resolution in stratified, biogeochemically complex Arctic coastal waters.

Study area

The study has been mostly conducted in the North Atlantic region, and particularly in the Greenland Sea and the Fram Strait, as well as on the west shelf of Svalbard, including its adjacent fjords. This region has been recognized as one of the most effective areas in absorbing atmospheric CO_2 (e.g. Land et al., 2013) and, at the same time, one of the most productive areas in the Arctic (Cherkasheva et al., 2025; Slagstad et al., 2015). It is also known for its intensive water and heat exchange, where the East Greenland Current transports cold, low-salinity waters, together with sea ice, southwards along the Greenland shelf slope. On the other hand, the West Spitsbergen Current carries warm, more saline waters northward along the continental slope of the Archipelago of Svalbard (Beszczynska-Möller et al., 2012). Moreover, the Greenland Sea is the main gateway for Arctic sea ice (Spreen et al., 2020), and the resulting sea ice meltwater reduces surface water salinity. All this means that the surface waters in this region, which are so actively absorbing CO_2 and thus heavily exposed to OA, are characterized by dynamic interactions among different water masses with a wide range of physical, biological, and chemical properties (e.g., temperature, salinity, nutrient concentrations, and NPP). This provides an ideal setup for decoupling and quantifying the influence of different factors shaping spatial and temporal variability of the marine carbonate system in open waters – a feature that has been explored in Publication 1.

Moreover, the significant inflow of freshwater into the coastal zone of Svalbard (sea ice/glacier meltwater and continental runoff), and into the open waters of the Greenland Sea (sea ice meltwater), entails a decrease in TA, and therefore in the buffering capacity of seawater, increasing the vulnerability of these areas to OA. Simultaneously with the enhanced OA effect, freshwater inflow can complicate OA research itself by causing ion anomalies and introducing inorganic and organic non-parameterized substances, which can introduce errors when thermodynamic ion-pairing models are used to calculate carbonate system parameters. This phenomenon has been addressed in Publication 2.

Furthermore, the spread of freshwater is often accompanied by sharp salinity and biogeochemical gradients and by water column stratification, making precise water sampling of the carbonate system parameters challenging. The latter aspect has been investigated in Publication 3, which, in addition to the research in the waters of the North Atlantic, was enriched with additional measurements carried out in the Baltic Sea - a basin characterized by high riverine runoff and steep biogeochemical gradients in the water column.

Methods

The three publications included in this dissertation are largely based on my own measurements of temperature, salinity, pH, pCO_2, TA, and DIC taken in the East Greenland Sea and the Fram Strait (during summer 2021 and 2024), the continental shelf and fjords of the west coast of Svalbard (summer 2021 and 2022), and the Baltic Sea (spring 2024). In the case of Publication 1, the open waters data I collected during 2021 were merged with an existing database covering the same set of variables measured in 2019 and 2020 in the same region.

The analytical methodology I used in my experimental doctoral research included:

- The pCO_2 measurements were obtained from the headspace of a bubble-type equilibrator equipped with an additional spray-type water diffuser using a cavity ring-down spectroscope (CRDS) G210-I (Picarro) – the system described in detail by Stokowski et al. (2021). The equilibrator was receiving a constant flow of seawater from a pump located in Kingstone (surface water) and/or from a submersible pump ("carbonate profiler") in the case of Publication 3. To estimate temperature changes during the transport through the pipeline, temperature was always recorded at the inlet of the system and in the equilibrator.
- The pH was measured on a total pH scale (Clayton and Byrne, 1993) using a spectrophotometric method based on m-cresol purple (m-CP) dye using a HydroFIA pH (CONTROS, 4H JENA Engineering GmbH).
- The concentration of DIC (µmol kg^{-1}) was determined by acidifying the samples and measuring the resulting CO_2 (Chen et al., 2015). This was done using an automated DIC analyzer (Apollo SciTech Inc.) equipped with a Li7815 CO_2 detector.
- The TA concentration in the samples (µmol kg^{-1}) was estimated by closed-cell potentiometric titration as described by Dickson et al. (2007). Importantly, all TA and DIC measurements have been performed against certified reference materials provided by the Marine Physical Laboratory of the Scripps Institution of Oceanography, University of California, San Diego (Dickson et al., 2003).
- Underway salinity and temperature were measured with an SBE 21 SeaCAT thermosalinograph and an additional temperature probe SBE 38 located at the water inlet and measuring in situ temperature (Sea-Bird Scientific), while water column temperature and salinity data were measured using the CTD-rosette (SBE9/11, Sea-Bird Scientific).
- Calculations of the marine carbonate system components (DIC, TA, pH, and pCO_2) were done using the EXCEL version 2.3 of the ion-pairing model CO2SYS (Publication 1) and the updated version of the EXCEL CO2SYS provided by Orr et al. (2018) (Publication 2 and 3).

A detailed description of the sampling procedure, sample preservation, and analytical techniques was provided in the individual publications. This also refers to ancillary variables (e.g., concentration of phosphate, silicate, and oxygen saturation). Furthermore, some data from 2019 and 2020 were measured using different analyzers (but the same methodology). Related analytical details are described in Publication 1.

Overview of the results

This summary contains only brief descriptions of the results. More detailed information may be found in the individual publications that make up this PhD dissertation.

To achieve the first research goal, the spatial and interannual variabilities of the carbonate system data (TA, DIC, pH, and pCO_2), temperature, and salinity collected during 2019, 2020, and 2021 in the surface waters of the Fram Strait and the Eastern Greenland Sea were analyzed and presented in Publication 1. The results show that the study area was characterized by significant spatial hydrodynamic variability, which is reflected in changes in salinity (from 30.0 to 35.2) and temperature (from -0.5 °C to 8.5 °C). The TA concentrations clearly followed the distribution pattern of salinity, which suggests conservative mixing of TA. Extrapolation of the strong linear correlation between these two parameters indicates that the TA concentration for the zero-salinity end-member amounted to 420 µmol kg^{-1}. This agrees with previously reported values for sea ice (441 µmol kg^{-1}) (Rysgaard et al., 2007), indicating sea ice meltwater as the main driver of TA changes in the area.

To describe the influence of sea ice meltwater on DIC, previously reported data for sea ice DIC as the zero-salinity end-member (Rysgaard et al., 2007) and winter surface DIC as the high salinity end-member were used to determine the linear relationship between DIC and salinity (see Publication 1 and references therein). Then, the DIC determined by this function from measured salinity has been compared with measured DIC (Publication 1, Figure 5), and the difference between the two has been

attributed to (NPP). The results showed that NPP plays an important but secondary role in the spatial and interannual variability of DIC in surface waters and has a rather minor effect on TA changes.

Moreover, the interannual spatial distribution of salinity and temperature was correlated with the percentage of the study area covered by sea ice. The results showed that the year with the lowest sea ice cover (2021, with 16.7% of the study area covered by sea ice) was also the year with the lowest surface temperatures and the lowest surface water salinity. In the same way, the year with the largest area covered with sea ice (2019 with 49.9%) was also the year with the highest surface salinity and temperature. This revealed that the volume of summer-melted sea ice plays the main role in interannual changes in the distribution of sea surface temperature, salinity, and, by extension, TA and DIC in the study area.

Since the clear and strong influence of meltwater from sea ice on TA and DIC variability was confirmed, a thermodynamic ion pairing model (CO2SYS) was used to verify hypothesis 1) and to check whether this variability still has a lower potential than NPP to influence seawater pH. The calculations performed revealed that NPP was indeed the primary process driving pH variability in the region (Publication 1, Figure 9). Due to high interannual variability, NPP was responsible for pH changes in surface waters ranging from 0.10 in some years to 0.22 in others. Temperature and salinity variability in the study area were responsible for pH changes of up to 0.14 and 0.1, respectively. The calculations also showed that some minor part of pH variability in the region (up to 0.02) can be due to unparametrized processes and/or atypical seawater constituents not included in the commonly used thermodynamic models (denoted as inconsistencies in publication 1).

In Publication 1, the first research goal was achieved, and the reported results confirmed the first hypothesis: the high spatial and interannual variabilities of surface TA and DIC during summer in the North Atlantic, being driven by salinity (or volume of sea ice meltwater) changes, are not the primary drivers of the pH (and pCO_2) variability that is principally regulated by NPP.

In addition to the results used to test the first hypothesis, Publication 1 also provided high spatial resolution pCO_2 data collected during 2019, 2020, and 2021, which showed that other medium- and small-scale physical processes (e.g., mesoscale/submesoscale eddies) may contribute to rapid changes in pCO_2 and thus in the marine carbonate system. However, the mechanisms responsible for them cannot be understood solely from surface measurements. To describe and quantify these processes, it would be necessary to sample pCO_2, as well as other carbonate system variables, with high vertical resolution in the upper water column. Therefore, these results confirm the validity of the third hypothesis and the third research objective, pointing to the need for fine-scale water-column measurements (in this case, pCO_2) to understand the mechanism behind the variability of the carbonate system in the surface water layer.

The results from Publication 1 also clearly showed that the thermodynamic ion-pairing model can produce errors in pH calculations due to unparametrized processes and seawater constituents – a feature addressed in the second hypothesis and the second research goal. In Publication 1, pH was calculated from DIC and TA, as planned in the study. However, in such calculations, which are often the basis of OA studies, various combinations of all four carbonate system variables can be used, and the final errors may differ depending on the initial pair of carbonate variables used. To summarize and understand the limitations of the commonly used thermodynamic ion-pairing model, as proposed in the second research objective, the oceanic and coastal data collected in 2021 were used to compare the calculated values of TA, DIC, pH, and pCO_2 to the in situ measurements of the same values (Publication 2). The dispersion of the difference between measured and calculated values is commonly reported in similar studies as the average of the differences between measured and calculated values, together with their standard deviation. However, this statistical approach does not accurately reflect the data's dispersion around the "real values". In Publication 2, as part of the guideline for OA studies, it was proposed to use the 68th percentile, along with the rationale for this choice.

Together with the error reporting method, Publication 2 proposed a reference for distinguishing between "good quality" and "bad quality" data based on the weather-quality threshold for OA studies established by Newton et al. (2014). In our dataset, the threshold between good quality and low quality corresponds to a relative standard uncertainty of 10 μmol kg^{-1} for DIC and TA, 0.020 for pH, and 7 μatm for pCO_2.

The detailed analysis of estimated errors from Arctic coastal and ocean samples is presented in Publication 2, while the summary of the quality assessment is provided in Table 4 of this publication. The results indicate that high-quality calculated values can generally be obtained from oceanic samples. Only pH and pCO_2 as an input pair should be strictly avoided in calculations. On the other hand, values calculated from coastal samples generally produce low-quality datasets. Only pH and pCO_2 can be calculated with satisfying accuracy: for pH, using as input pairs TA and pCO_2 or DIC and pCO_2, and for pCO_2, using as input pairs DIC and pH.

In addition to the input carbonate system parameters, it is also recommended to include the concentrations of phosphates and silicates, as they can directly influence the carbonate equilibrium and thus the quality of the calculations. The evaluation of the contribution of these two input parameters demonstrates that not including them in the calculations generate an error between 1.9% and 7.2%.

The development of sensors capable of collecting in-situ pH and pCO_2 data with high temporal resolution has opened new possibilities to study OA in Arctic waters. Unfortunately, our study shows that pH and pCO_2 cannot be used together as input data for calculating other parameters. Therefore, in publication 2, we evaluate the feasibility of using TA calculated from salinity (TA_s) using a linear relationship developed from the collected dataset. Results demonstrate that applying TA_s together with either pH or pCO_2 produces slightly larger errors (than when using measured TA) but generally good-quality data. This opens new perspectives for long-term studies of OA, carbon inventory, and ecosystem health in Arctic coastal areas.

The results obtained in Publication 2 show that the absolute uncertainty in the calculations of the marine carbonate system is significantly larger in coastal regions than in oceanic waters, thereby positively verifying hypothesis 2. In addition to highlighting limitations in the use of thermodynamic ion-pairing models in Arctic coastal and oceanic waters, Publication 2 also provides concise guidelines for the research community to conduct high-quality OA-related research in this OA-sensitive region.

To achieve the third research objective and obtain high-resolution vertical measurements of the carbonate system parameters (including pCO_2) in highly stratified environments (e.g., near continental and glacier runoff), a new sampling approach was proposed (Publication 3). The system consists of a commonly used CTD profiler (Sea-Bird 19plus, Sea-Bird Electronics, Inc., Bellevue, Washington, USA), coupled with a submersible pump and hose to form a PUMP-CTD, which was then combined with a traditional underway equilibrator-based pCO_2 measuring unit. The system, denoted as the "carbonate profiler", can measure temperature and salinity in situ and transport seawater from selected depths to laboratories on a research vessel, enabling continuous measurements of temperature, salinity, pH, and pCO_2 and simultaneous discrete sampling for TA and DIC (and other biogeochemical variables) with high vertical resolution throughout the water column.

To demonstrate the capabilities of the carbonate profiler, a consistency test similar to the one presented in Publication 2 was performed in the ocean waters of the North Atlantic (Publication 3, Figure 3). Excellent agreement was demonstrated between measured pCO_2 in the water column and the pCO_2 calculated from water-column TA and pH, with a mean difference of $\bar{x}$ (SD) = 0.9 (±4.5) μatm, confirming the high quality of the coupling of both continuous measurements and discrete sampling.

A second sampling quality test was performed in the estuarine waters of the Vistula River (Baltic Sea). Four profiles (one every 6 hours) of TA, DIC, pH, pCO_2, salinity, and temperature were collected (Publication 3, Figure 5). The high performance of the carbonate profiler was assessed by reproducibly

precise estimation of the TA freshwater end-member (4069 µmol kg^{-1}, SD ±12 µmol kg^{-1}) based on the four vertical profiles.

Furthermore, sampling of turbidity plumes in high Arctic fjords demonstrated that the carbonate profiler can reveal rapid biogeochemical changes driven by freshwater inflow in the upper 5 meters of the water column (Hypothesis 3). The results demonstrate not only excellent performance of this sampling method but also provide evidence that a vertical resolution of 0.5 m is achievable for all carbonate system parameters (Publication 1, Figure 6). Moreover, the relationship between TA and salinity estimated from data collected with the carbonate profiler provides new insights into the freshwater TA end-members, ranging from 790 to 1240 µmol kg^{-1}, showing that continental runoff and glacier meltwaters in the Svalbard archipelago lower the buffer capacity of the seawater, reducing its potential to uptake atmospheric CO_2, and enhancing OA.

The studies presented in Publication 3 confirm that implementing simple modifications to sampling techniques enables the acquisition of high vertical resolution data on the carbonate system in stratified, biogeochemically complex coastal areas, and for resolving its rapid variability with high accuracy, thus confirming hypothesis 3.

Conclusions

The results and conclusions provided in the three publications compiled in this doctoral thesis successfully achieve all the objectives and positively verify the three research hypotheses. Furthermore, this work makes a groundbreaking contribution to Arctic research, with the following key findings:

- The mixing of sea ice meltwater and Atlantic water is the main driver for TA and DIC changes in the surface layer of the Fram Strait and the Greenland Sea.
- Although NPP exhibits strong interannual variability, it is the primary factor influencing pH in the Greenland Sea and Fram Strait surface waters. Temperature and salinity play a secondary (but also important) role.
- Determining marine carbonate system variables using the ion-pairing model generates significantly larger errors for Arctic coastal waters than for oceanic waters.
- Only three combinations of input parameters generate good quality data using the ion-pairing model in Arctic coastal waters: TA and pCO_2, DIC and pCO_2, and DIC and pH; other combinations should be avoided, and especially the pair of pCO_2 and pH.
- TA derived from salinity together with pCO_2 measurements can be used to calculate pH with high accuracy, which opens new possibilities for long-term OA studies in Arctic coastal waters.
- The influence of continental runoff and glacier/sea ice meltwater generates complex, sharp biogeochemical gradients in the surface layers of Arctic coastal waters and lowers the buffer capacity of seawater, reducing its potential to absorb atmospheric CO_2 and increasing ocean acidification.
- Easy-to-implement and inexpensive sampling system modifications combining a CTD profiler, a submersible pump and an underway pCO_2 measurement system fill a technology gap in studying changes in carbonate chemistry in stratified Arctic coastal waters.