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High vertical resolution measurements of pH, pCO_2, total alkalinity, and dissolved inorganic carbon using a new approach: the carbonate profiler

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Abstract
The equilibrium between the different parameters of the marine carbonate system – dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure of CO_2, and pH – is the core of ocean acidification studies, evaluation of inorganic carbon inventory, and air-sea CO_2 fluxes. To date, it has been challenging to simultaneously measure all those components in the water column due to different sampling methodologies, and especially in stratified waters, where sharp vertical biogeochemical gradients may occur. In this study, we designed a low-cost and easy-to-assemble pumping system, which, combined with a CTD profiler, makes a PUMP-CTD system that can efficiently serve as a precise water column sampler, allowing for simultaneous measurements and sampling of dissolved inorganic carbon, total alkalinity, partial pressure of CO_2, and pH with high vertical resolution. Importantly, this water sampler (denoted as the carbonate profiler) can be easily integrated with equilibrator-based continuous pCO_2 measurement systems, which are routinely used for underway data acquisition, making them suitable for water column sampling as well. We tested the carbonate profiler in the open ocean water column, where we obtained excellent consistency between measured pCO_2 and calculated values based on pH and DIC. Afterwards, we tested the operability of the system by measuring the vertical variability of all the components of the marine carbonate system in the Vistula River estuarine waters (southern Baltic Sea) and within the Arctic fjords affected by continental freshwater runoff. Overall, this system performed outstandingly, with a vertical resolution of half a meter, proving its utility in accurately measuring steep biogeochemical changes in the water column regardless of the analytical method used.

Keywords
Ocean acidification; pH; Total alkalinity; pCO2; Land ocean continuum; Arctic; Baltic Sea

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1. Introduction

The Oceans are key components for mitigating climate change due to their capacity to absorb atmospheric carbon dioxide (CO_2) at the surface and export it to the deeper water layers and sediments (Friedlingstein et al., 2025). Among oceanic regions, coastal areas, which often have very high carbon fixation rates, are key contributors to carbon export driven by intense primary production (Cai, 2011). As such, they are vital components of the global carbon cycling (Bauer et al., 2013; Dai et al., 2022; Regnier et al., 2022). However, the total contribution of these regions to the global carbon budget remains uncertain due to high spatiotemporal biogeochemical variability (Cai, 2011; Resplandy et al., 2018).

Within the coastal areas, estuaries represent complex biogeochemical environments where particulate and dissolved organic and inorganic carbon compounds of both autochthonous and allochthonous origin undergo rapid transformations (Mosley and Liss, 2020). In addition to commonly investigated processes related to organic matter production and remineralization (sink and source of CO_2, respectively), including respiration of terrigenous organic matter (Cross et al., 2018; Kuliński et al., 2016), carbon transformations are also driven here by significant shifts in pH and ionic composition resulting from the mixing of freshwater and seawater. In turn, pH, or concentration of protons ($pH = -\log[H]$), is mainly controlled

by the excess of proton acceptors over proton donors in water, defined as total alkalinity (TA) (Dickson, 1981). In the compounds that make up TA, the largest share comes from two inorganic carbon species, namely bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, which together with dissolved CO_2 (or H_2CO_3) constitute dissolved inorganic carbon (DIC). Therefore, there is an intricate balance between pH, TA, and DIC, which ultimately determines dissolved CO_2 concentrations expressed most often as CO_2 partial pressure (pCO_2) (e.g., Millero, 2007). These four measurable parameters and their chemical interactions are often referred to as the marine carbonate system. Biological, physical and chemical processes continuously alter the delicate equilibrium between these parameters, initiating cascade changes in all of them. Therefore, to estimate the effect of biogeochemical processes and air-sea CO_2 exchange on the carbon inventory and fluxes in the coastal areas, it is necessary to characterize the complex horizontal and vertical distribution of all the marine carbonate system parameters.

While the variables of the marine carbonate system are interrelated, their measurement approaches differ. Generally, pCO_2 is obtained using the well-established underway systems, in which continuously flowing water is equilibrated with a closed air loop where pCO_2 is measured. These systems can provide highly accurate data with uncertainties lower than 2 µatm or 0.5% of the measured values (e.g., Arruda et al., 2020; Stokowski et al., 2021a). However, they are designed and installed on research vessels and ships of opportunity to obtain measurements at a fixed depth corresponding to the water inlet depth of the vessel's pumping system (typically between 2 and 10 m water depth). This setup makes them suitable for studying the horizontal distribution of pCO_2 but inappropriate for resolving vertical gradients in the water column. Although they are being used to estimate air-sea CO_2 fluxes in areas where sharp vertical gradients of CO_2 are expected, it has been demonstrated that differences in the sampling depth can introduce significant errors in the results (e.g., Ahmed et al., 2020; Azevedo et al., 2024). Thus, capturing the vertical distribution of pCO_2 in the water column is essential for precise flux calculations in stratified waters. Recent advances in underwater CO_2 sensors enable in situ measurements of CO_2 in the entire water column (when mounted on CTD profilers) or at a fixed depth for extended monitoring (when deployed in mooring systems). However, they often have lower accuracy and longer response times (between 5 and 20 minutes) than underway systems (Arruda et al., 2020; Clarke et al., 2017; Schar et al., 2010b).

Similarly, high vertical resolution TA, DIC, and pH measurements are challenging due to sampling limitations. Water for these analyses is commonly collected using bathometers, typically mounted in sampling carousels with a vertical resolution not better than 2–3 m, which is often insufficient to study rapid biogeochemical gradients in the water column. Moreover, the number of samples collected in the profile is directly correlated with the number of Niskin bottles mounted in the sampling carousel, which significantly limits the resolution of the sampling. For pH, direct measurements in the water column are also possible using submersible sensors. Several can perform spectrophotometric measurements directly in the water column, providing high-quality data (Bresnahan et al., 2014; Johengen et al., 2015). However, their response time (5–15 minutes) is usually too slow to obtain water column pH profiles with high vertical resolution.

In addition to direct measurements, each of the two marine carbonate variables can be calculated from the other two, which are known from direct measurements or modelling. This requires the use of thermodynamic ion-pairing models describing the carbonate system (Lewis et al., 1998). However, these models are primarily dedicated to open ocean waters where the marine carbonate system is well characterized. Their application in coastal areas remains challenging (Aguado Gonzalo et al., 2025a) due to anomalies in seawater composition and the influence of non-parameterized seawater constituents, leading to significant errors in calculations (Kerr et al., 2023; Kuliński et al., 2017; Ulfsbo et al., 2015). Thus, to characterize the marine carbonate system in coastal regions, it is often necessary to measure the complete set of variables (pCO_2, TA, DIC, and pH). This approach can be considered excessive or redundant in ocean waters. Such comprehensive sampling, especially in stratified waters, requires careful planning, standardization of the vertical resolution, and unification of the sampling technique for all parameters, regardless of the analytical methods used later. This is particularly important for combining state-of-the-art high-quality methods based on collecting discrete samples (TA, DIC, pH) with pCO_2 measurements, which require continuous water flow through the equilibrator (Dickson et al., 2007).

These challenges were the motivation to undertake this study, the aim of which was to design a sampling system that: (i) is capable of simultaneous discrete sampling of TA, DIC and pH and continuous equilibrator-based pCO_2 measurements in a vertical profile, (ii) allows easy switching in water supply between on-station vertical profiling and underway mode, (iii) inexpensive and easy to implement on a variety of vessels, including small ones, and (iv) provides high-quality results describing the marine carbonate system. The latter has been proven by tests made in the open waters of the Greenland Sea, while the operability of the system has been tested in two different coastal environments: the turbid freshwater plumes in the high Arctic fjords and the mid-latitude estuarine system of the Vistula River in the Baltic Sea.

2. Material and methods

2.1 The carbonate profiler

The inspiration for the system setup was a PUMP-CTD concept as reported, for instance, by Strady et al. (2008). However, the PUMP-CTD we designed was coupled with an equilibrator-based pCO_2 measurement system typically used for underway sampling. Thus, this carbonate profiler follows a similar principle as any underway system for pCO_2 measurements: a pump carries water along a pipeline to the ship's laboratory, where it flows continuously through the equilibrator whose headspace is connected by a closed air loop to a CO_2 analyser, while an additional water bypass allows for discrete sampling for TA, DIC, pH or any other parameter. The sole distinction of the carbonate profiler is the water supply, which is a submersible pump attached to the CTD profiler and deployed together with it by a winch. The pump provides water from a desired depth in the water column using a flexible and retractable plumbing system, which is deployed simultaneously with the CTD cable. In this study, we developed a system capable of sampling water from a maximum depth of 60 m, which is generally sufficient to investigate the variability of the carbonate system in both the mixing zone and the photic zone. A simplified scheme of the system installed in r/v *Oceania* is presented in Figure 1.

Our ambition was to develop a system that is inexpensive, transportable, and easy to implement on a variety of vessels, including smaller ones. The latter requires that the system can interoperate with any CTD profiler the vessel is equipped with. In our case, it was a Sea-Bird 19plus (Sea-Bird Electronics, Inc., Bellevue, Washington, USA) to which the submersible pump was attached, ensuring that the water inlets to both units were at the same depth to unify CTD readings with carbonate chemistry measurements. The submersible pump used in this prototype was a Pedrollo 3SR2/28 (www.pedrollo.com, San Bonitacio, Italy), with a deployment depth of approximately 60 m and an adjustable flow rate (through the power controller) between 10–50 L min^{-1} that may further depend on how high the water needs to be pumped above the ocean surface. This high water flow minimized the transport time to the laboratories and greatly exceeded the flow required for continuous pCO_2 measurements (approximately 0.8 L min^{-1}); therefore, excess water was bypassed, allowing for sampling of TA, DIC, and pH, as well as additional in-lab CTD measurements. All the pipes in the system had the same diameter, and narrow pipe connectors were avoided to elude overpressure. The flexible pipe system consisted of a commercially available Gardena Classic ¾" PVC cross-woven fabric hose (Gardena, www.gardena.com, Ulm, Germany), directly connecting the submersible pump to the ship's laboratories. The delay time, which is necessary for sampled water to be transported to laboratories, depends on the length of the hose deployed and the water flow. In our case, it was 19.5 seconds, calculated for a pipe length of 120 m and a water flow rate of 40 L min^{-1}. To minimise temperature changes during sampling, the hose system was not placed under direct sunlight or on warm surfaces. In the laboratories, four T-connectors equipped with flow regulators were installed to split the water flow to: (i) the equilibrator-based continuously measuring pCO_2 sys-

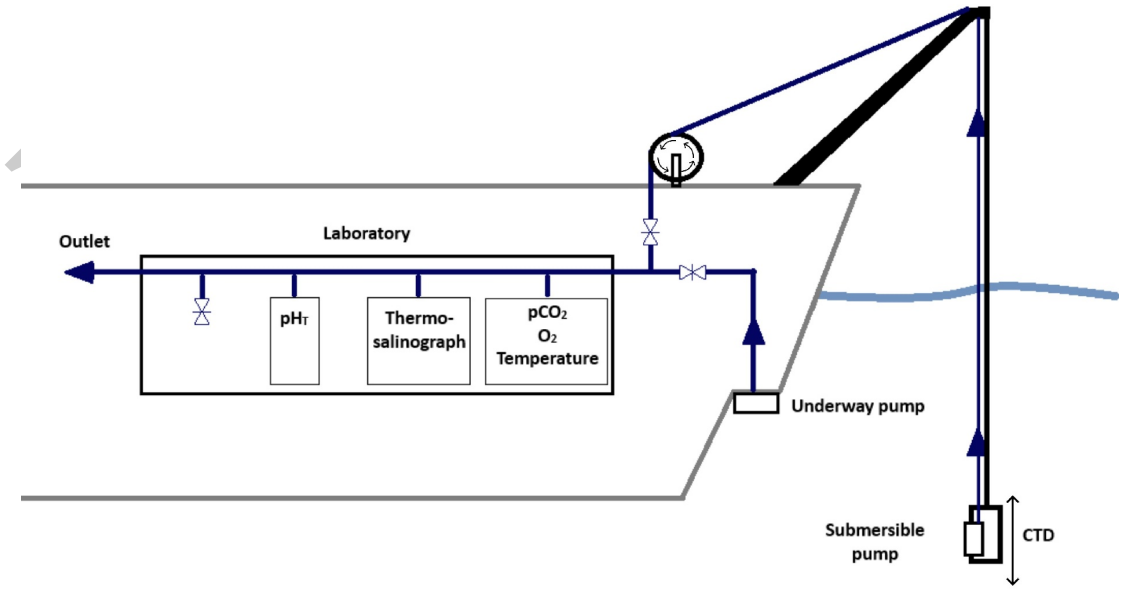

Figure 1. Simplified schematic representation of the carbonate profiler for a semi-continuous, precise sampling of the marine carbonate parameters in the water column.

tem, (ii) the flow-through thermosalinograph, (iii) the pH-spectrophotometer unit, and (iv) free-flowing water for collecting discrete samples for different analyses, in our case, DIC, TA, and in some cases also pH. Furthermore, additional valves enable immediate switching of the water source between the submersible PUMP-CTD and the ship's underway pumping system (having a water inlet at a fixed depth, 2.5 m on r/v *Oceania*), allowing the same laboratory equipment to be used for horizontal and vertical measurements (Figure 1). Importantly, the entire system consists of only quick connectors, making it easy to install, uninstall, and transport.

2.2 The laboratory instrumentation and analytical techniques

Measurements of pCO_2 were carried out using the system described in detail by Stokowski et al. (2021a). The system consists of a bubble-type equilibrator where the seawater flowing in is additionally sprayed using a shower diffuser. The air from the headspace flows along a closed loop through a cavity ring-down spectroscope (CRDS) G2101-I (Picarro). The quality of the measurements was regularly monitored using three gases with different CO_2 concentrations: 0, 205, and 507 ppm, which enabled achieving an accuracy and precision of $\pm$ 1.3 µatm. The effect of temperature changes during water transport from the PUMP-CTD to the laboratory has been corrected using the function proposed by Takahashi et al. (1993) (Eq. 1), so that the pCO_2 measured in the equilibrator, pCO_2(lab), was recalculated to the in situ temperature, pCO_2(in situ).

$$pCO_2(\text{in situ}) = pCO_2(\text{lab}) \times \exp(0.0423 \times (t_{(\text{in situ})} - t_{(\text{lab})})) \quad (1)$$

All pCO_2 measurements were also standardized to 1 atmosphere of pressure to remove the effect of atmospheric pressure changes in the final results, using Equation 2.

$$pCO_2(1\,\text{atm}) = pCO_2(\text{in situ}) \times 1012.25/P \quad (2)$$

The pH measurements were carried out on board using a HydroFIA flow-through spectrophotometric system (CONTROS, 4H-JENA engineering GmbH), directly connected to the carbonate profiler plumbing system. The pH was estimated spectrophotometrically using mCresolPurple as an indicator agent (Carter et al., 2013; Clayton and Byrne, 1993; Liu et al., 2015; Mosley et al., 2004). The accuracy of the pH measurements was ensured by routine measurements of TRIS-buffer (TRIS-CRM-T37) provided by A.G. Dickson (Scripps Institution of Oceanography, USA), which showed an accuracy/precision better than $\pm$ 0.003. All pH measurements were performed at 25°C, and the results were reported on the total scale.

The discrete water samples for analysis of TA and DIC were collected in 270 mL borosilicate glass bottles using the free-flowing bypassed water from the carbonate profiler. Samples were carefully poured from the bottom of the bottle to avoid air bubbles and left overflowing for at least 10 seconds. Next, 1 mL of the sample was removed to allow thermal expansion, and 100 µL of saturated $HgCl_2$ was added to inhibit/prevent biological activity. All the bottles were closed with greased ground-glass stoppers and stored in the dark at +4°C until analysis.

The TA was estimated using the methodology described in Dickson et al. (2003). Open cell titrations were carried out using a Methrom 888 Titrando, equipped with a 1mL burette. Total alkalinity was calculated from the potentiometric titration curves using version V23 of the Python package "Calkulate" (Humphreys and Matthews, 2024). The accuracy of the measurements was estimated by repeated measurements of Certified Reference Material (CRM) batch #CRM-209, provided by A.G. Dickson (Scripps Institution of Oceanography, USA). At least three measurements of CRM were done before and after the batch of samples until a precision better than $\pm$ 2 µmol kg^{-1} was achieved. Any deviation from the CRM values was corrected accordingly, and the accuracy correction was applied to a batch of samples. Each sample was measured in triplicate with a precision always better than $\pm$ 3 µmol kg^{-1}. The same methodology was applied to all samples. However, some were analyzed on board and others in the laboratories of the Institute of Oceanology, Polish Academy of Sciences (IO PAN), within a maximum time of four weeks.

The concentration of DIC was determined using an automated DIC analyzer (Apollo SciTech Inc.), equipped with a Li7815 CO_2 detector and following the methods described by Chen et al. (2015). All the measured samples were cross-calibrated with measurements of the CRMs (same as for TA), assuring an accuracy of $\pm$ 2 µmol kg^{-1} during the sample measurements. Each sample and CRM was measured at least three times until a precision better than $\pm$ 1.5 µmol kg^{-1} was achieved. All the measurements were carried out in the IO PAN laboratories within a maximum of four weeks after collection.

2.3 Calculations of the carbonate system parameters

Calculations of pCO_2 and estimations of the uncertainties related to the calculated values were carried out using the Excel version of the CO_2sys program (Pierrot et al., 2006), as published by Orr et al. (2018). For the calculations, the carbonic acid dissociation constants (K1 and K2) from Lueker et al. (2000) were used together with the $KHSO_4$ from Dickson et al. (1990), the fluoride dissociation constant of Perez and Fraga (1987), and the boron to chlorinity ratio of Lee et al. (2010). All calculations were reported to 1 atmosphere to minimize errors due to recalculations to in situ pressure. The uncertainties related to the dissocia-

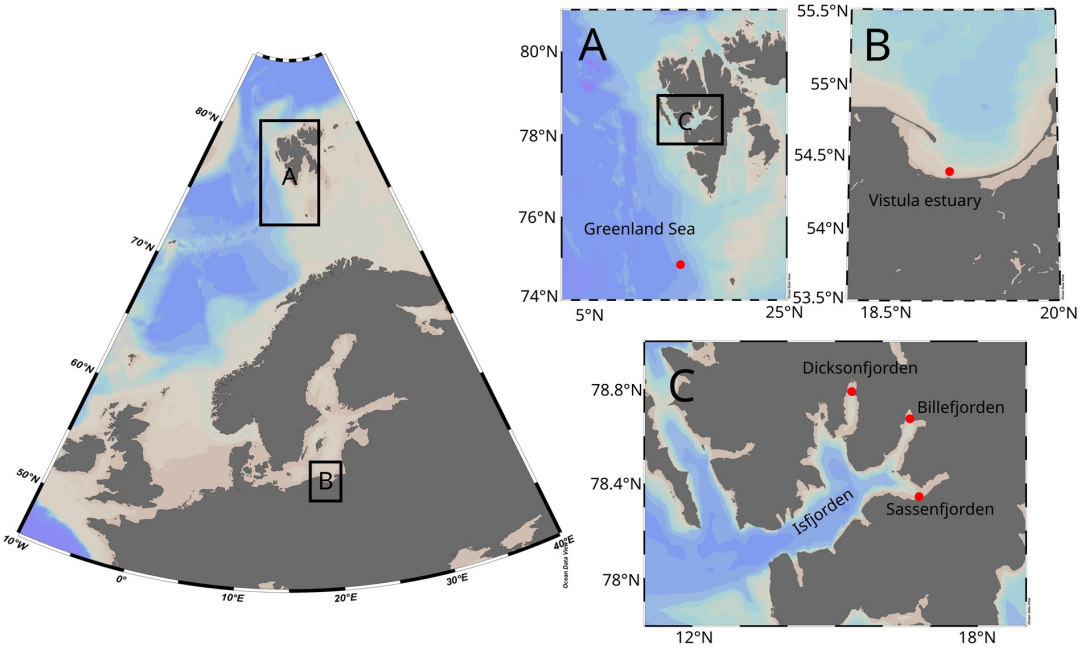

Figure 2. Location of the sampling stations (red dots). A) Greenland Sea. B) Baltic Sea. C) Svalbard fjords.

tion constants used in this study were extracted from Orr et al. (2018).

2.4 Sampling strategy and study area

For this study, sampling was conducted in three different areas, resulting in a total of eight water column profiles collected. Two study areas were located in stratified coastal systems (the Svalbard archipelago and the southern Baltic Sea), and one was located in the open waters of the Greenland Sea (Figure 2). The open ocean profile was sampled in July 2024 (74°59'58.2"N; 13°10'56.9"E), away from continental waters, where the marine CO_2 system is well characterized and where good consistency between measured and calculated values was expected based on previous studies (Aguado Gonzalo et al., 2024). These features enabled us to evaluate the sampling system's ability to simultaneously obtain thermodynamically coherent results for pCO_2, TA, and pH in the water column and verify the quality of the measured pCO_2 by comparing it with the pCO_2 calculated from TA and pH measurements.

In the coastal areas, the tests of the carbonate profiler have been performed in regions known for their highly stratified waters with sharp biogeochemical gradients. These sampling areas enabled us to evaluate the operability and capability of the carbonate profiler in resolving complex vertical variability. Four profiles were collected during spring 2024 within the Vistula River estuary (54°22'40.8"N; 18°55'30.0"E), located in the southern Baltic Sea (Figure 2). This region is characterized by the influence of TA-rich river waters and large gradients in the carbonate system parameters caused by the changing extent of the river plume and thus variable water stratification (Stokowski et al., 2021b). All four profiles were taken in the same location, but at six-hour intervals. The reason for that was to estimate the short-term variability of the carbonate system in the region and assess the reproducibility of the freshwater TA end member from the extrapolated dependency against salinity, which should be relatively conservative in such a short time period.

Additionally, three more profiles were obtained in August 2022 in the high Arctic fjords within the Svalbard archipelago (Figure 2). The sampling locations were selected in areas with a strong influence of freshwater turbid plumes. These plumes are produced by continental runoff, mainly fed by meltwater from land-terminating glaciers, and abrupt biogeochemical gradients are expected within the first 10 meters of the water column (e.g., Meslard et al., 2018; Szeligowska et al., 2020).

3. Results and discussion

3.1 Estimated quality of the carbonate profiler measurements

To demonstrate the system's capability to obtain accurate measurements of carbonate system variables in the water column, we compared measured and calculated (from pH and TA) values of pCO_2 in the oceanic waters of the Greenland Sea. These results, along with their uncertainties, are presented in Figure 3, which also shows the absolute differences between measured and calculated values, ΔpCO_2(meas-calc). Our results indicate that the first five samples collected in the water column (down to a water depth of 40 m) exhibited small variability (SD= $\pm$3.6 µatm) with an average measured pCO_2 of 308.8 µatm. On

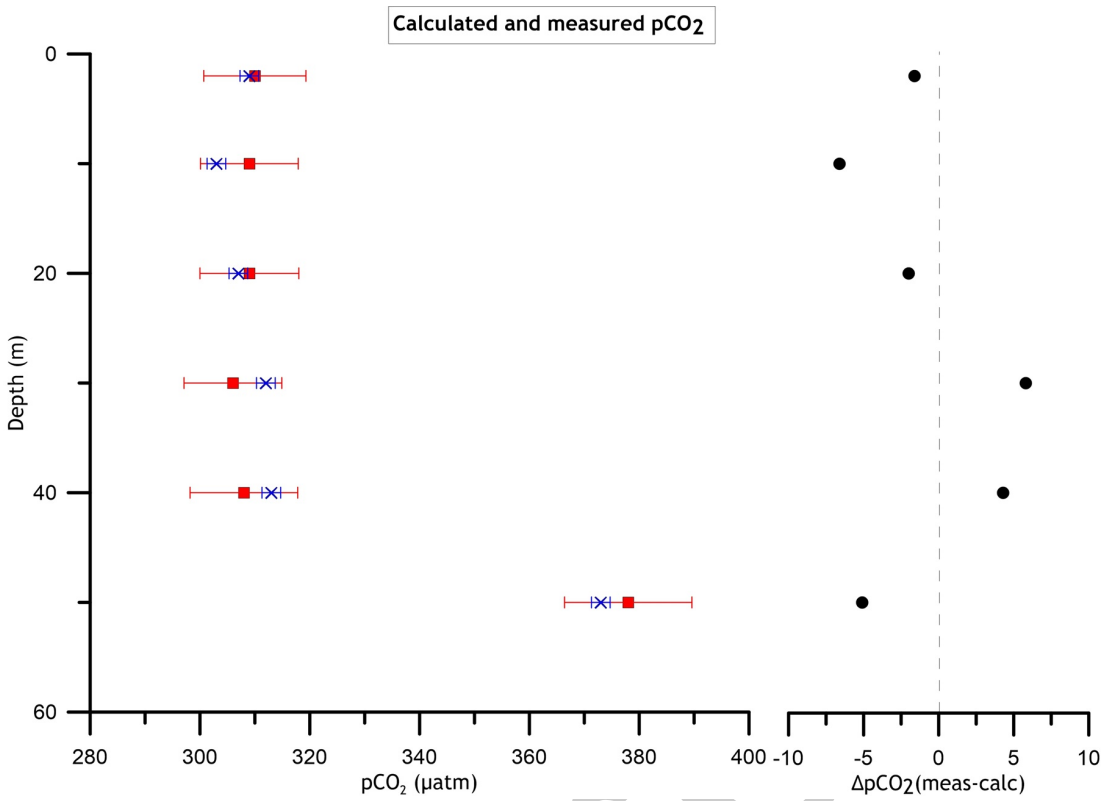

Figure 3. Left: measured (blue cross) and calculated (red square) pCO_2. The error bars indicate the uncertainty in the measured/calculated values. Right: the absolute differences between pCO_2 measured and calculated out of TA and pH.

the other hand, at a water depth of 50 m, the pCO_2 was significantly higher, amounting to 373 µatm, indicating a rapid increase of 64 µatm (Figure 3). The abrupt pCO_2 gradient between 50 and 60 m water depth was also successfully captured by TA and pH sampling, as indicated by the perfect agreement between the measured and calculated pCO_2 values. Hence, the ΔpCO_2(meas-calc) exhibited a low average of $\overline{x}(\mathrm{SD}) = 0.9(\pm 4.5)$ µatm, indicating an excellent performance of the carbonate profiler that enables consistent sampling of different carbonate system parameters despite differences in measurement methodologies requiring either continuous water flow or discrete sampling.

A similar exercise, as presented here, but using only surface data, was presented by Carter et al. (2024). In their study, the authors collected state-of-the-art surface open-ocean pCO_2, pH, and TA data from the Global Ocean Data Analysis Project 2022 update (GLODAPv2.2022) to estimate the (in)consistency between measured and calculated variables of the marine carbonate system. Their results show that the average of the relative difference between measured and calculated (from TA and pH) fCO_2 (fugacity of CO_2) was 1.8% of the measured fCO2 (equivalent to $\pm$ 5.6 µatm for 308.8 µatm). Following the calculation method described by Carter et al. (2024), we transferred our water column results to fCO_2 and presented them as a percentage of the measured value. Our results indicated a relative difference of 1.4 ($\pm$ 4.5 µatm), which is a better agreement than the one previously reported. Similarly to the study by Carter et al. (2024), but restricted to Arctic Oceanic surface waters, Woosley et al. (2017) and Aguado Gonzalo et al. (2024) reported discrepancies between measured and calculated pCO_2 of $\pm$ 5.3 and $\pm$ 5 µatm, respectively, which are slightly worse than the ones reported here ($\pm$ 4.5 µatm). Furthermore, the real observed uncertainty of $\pm$ 4.5 µatm for the difference between measured and calculated pCO_2 was significantly lower than the theoretical one ($\pm$ 9 µatm) derived from the propagation of all the initial uncertainties (see methods). This difference in the uncertainty suggests that any deviations in pCO_2 measured versus pCO2 calculated, ΔpCO_2(meas-calc), are solely due to uncertainties in the thermodynamic model of the marine CO_2 system, while the carbonate profiler guarantees high-quality, continuous pCO_2 measurements that are perfectly consistent with semi-continuous pH measurements and discrete sampling for TA.

This profile took about 25 minutes to complete in total. This time was a result of sampling at each depth and the time required to move the system between sampling levels. The time needed to obtain a complete set of results from a given depth was estimated based on the response time of the pCO_2 equilibrator, which was previously mea-

sured by Stokowski et al. (2021a), where the time to reach 63% of the equlibration (T63) was 68 seconds and an the effective equilibration time (T99) was 1 minute and 44 seconds (approx. 2 min). Thus, we maintained the PUMP-CTD for at least 3 minutes at each depth to ensure that measurements were taken after the equilibrium was reached. The excellent results from the consistency exercise demonstrated that this time was certainly sufficient to reach equilibrium. Based on calculations and earlier estimations by Stokowski et al. (2021a), we believe there is still room to optimize sampling time. Unfortunately, due to operational constraints of the open ocean cruise, no further tests were performed.

Nevertheless, the sampling time was satisfactorily short, especially since samples for additional parameters were taken in parallel. Commercially available submersible CO2 sensors offer a range of response times and effective measurement intervals. However, all of them are slower than the carbonate profiler, which allows easy adaptation of underway surface pCO2 measurement systems for water column sampling. For example, CO2 sensors based on pH indicators (e.g., Sunburst sensors, SAMI-CO_2) have a response time of approximately 5 minutes (Lai et al., 2018). In comparison, sensors based on non-dispersive infrared (NDIR) gas analyzers equipped with hydrophobic equilibration membranes (e.g., Pro-Oceanus Systems Inc. PSI CO_2-ProTM, C-Sense pCO_2, CONTROS HydroC CO_2) have typical measurement intervals and equilibration times of 10 to 15 minutes (Fietzek et al., 2014; Jiang et al., 2014; Schar et al., 2010b; Signori et al., 2021).

In addition to the higher sampling speed, the carbonate profiler system presented here shows excellent pCO2 measurement accuracy (reported above and by Stokowski et al. (2021a)), which is hardly achievable with submersible sensors. For instance, the SAMI-CO2 sensor was able to collect data with an accuracy of $+40 \pm 13$ µatm (x and SD) during a field test (Schar et al., 2010b). In the case of Pro-Oceanus Systems Inc. PSI CO2-ProTM, a similar test reported a $\bar{x}$ and SD of $+9 \pm 14$ µatm (Schar et al., 2010a), while Fietzek et al. (2014) reported an x and SD of -0.6 ± 3.0 µatm using a CONTROS HydroC CO_2.

To sum up, the high-quality water column pCO_2 results obtained in this study, along with the rapid sampling, including the possibility of collecting other carbonate system parameters in parallel, demonstrate the excellent performance of the carbonate profiler we designed, which is currently unachievable for sensor-based measurements on research vessels.

3.2 Performance of the carbonate profiler in highly stratified waters

3.2.1 Test 1: The mid-latitude estuary system of the Vistula River plume

The variability of TA, DIC, pH, and pCO_2, as well as salinity and temperature observed in the first 10 meters of the water column in the estuarine system of the Vistula River plume, is presented in Figure 4. In all the profiles, salinity and pCO_2 increased with depth, while pH, DIC, and TA decreased, indicating that the Vistula River water affecting this area had higher DIC, TA, and pH, and lower pCO_2. These results demonstrate that, thanks to the carbonate profiler, it was possible to resolve steep biogeochemical gradients, with ranges spanning up to 2050 µmol kg^{-1} for TA, approximately 1700 µmol kg^{-1} for DIC, 166 µatm for pCO_2, and 0.58 for pH, respectively. Herewith, DIC, TA and salinity were characterized by rapid changes within the first two meters of the water column and apparently varied among profiles, showing the spectrum of variability in riverine plume dynamics at a single location within the 24-hour sampling period. On the other hand, pCO_2 showed only slight changes within the first two meters, with comparable values between profiles (ranging from 217 to 246 µatm), suggesting strong primary production in the surface water layer, regardless of the scale of the Vistula River impact. Below this level, the pCO_2 increased significantly with depth, reaching values of up to 413 µatm at 10 m. Apart from being the first insight into the carbonate system structure in the water column of the region, these results clearly demonstrate the complexity and the vertical variability in stratified waters. Special attention should be paid to the vertical distribution of pCO_2, which highlights the importance of the sampling depth from which pCO_2 results are obtained for estimating air-sea CO_2 diffusive fluxes, a feature also discussed earlier by Ahmed et al. (2020) and Azevedo et al. (2024). Thus, underway pCO_2 measurements describing horizontal variability should always be combined with vertical profiling in stratified waters. For this, the carbonate profiler designed and described in this study provides an easy-to-use and low-cost solution that can significantly improve the estimation of air-sea CO_2 fluxes.

The relationship between TA and salinity exhibited a conservative behavior during sampling (Figure 5), with an excellent correlation ($R^2 = 0.98$). It demonstrates that the carbonate profiler attached to the CTD (PUMP-CTD) enabled the collection of water from a precise depth where salinity was measured, providing reliable vertical accuracy of sampling for carbonate system parameters. We took water samples at every half-meter interval in the first two meters of the water column and at every meter interval in the deeper water layer. This vertical resolution was sufficient to record the changes in the marine carbonate system parameters in the water column of this stratified area. However, the good correlation between salinity and TA suggests that even higher vertical resolution could be achieved. The freshwater TA end member estimated from the linear regression between salinity and TA collected for all four profiles amounted to 4069 µmol kg^{-1} (SD=12 µmol kg^{-1}). This value exceeds the previously reported range for the Vistula River (from 3136 to 3746 µmol kg^{-1}) by Stokowski

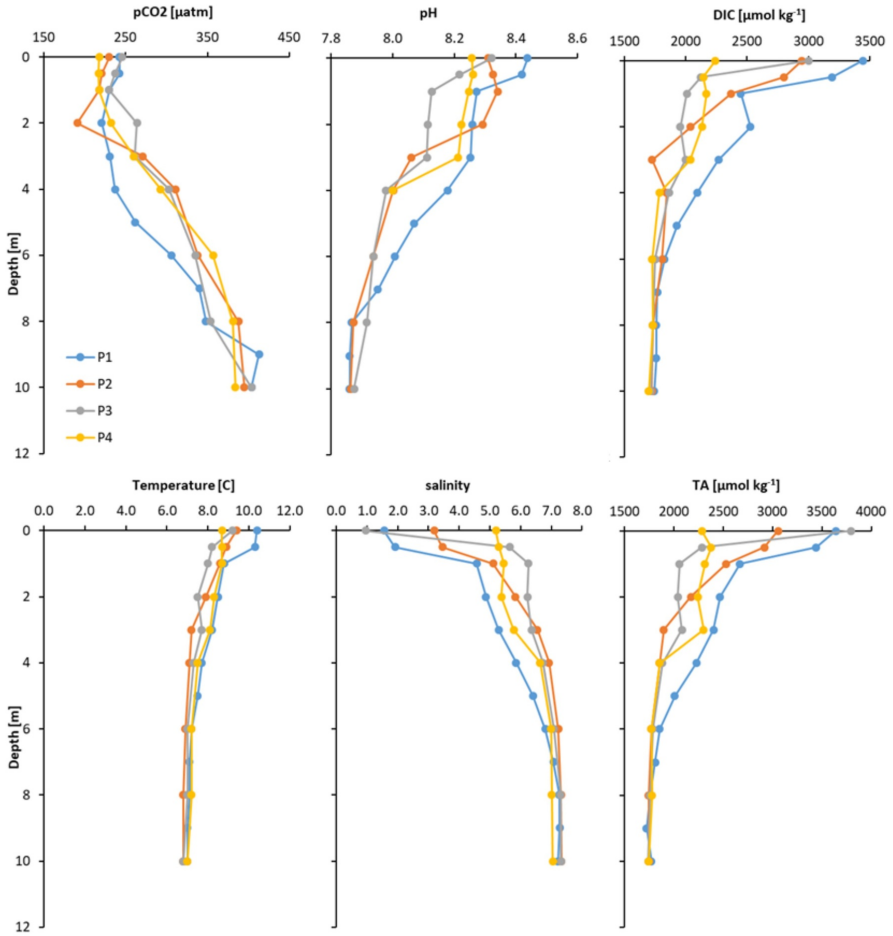

Figure 4. Vertical distribution of pCO2, pH, DIC, TA, temperature, and salinity during four samplings (P1–P4) performed in one spot in the Vistula River plume in 6-hour intervals.

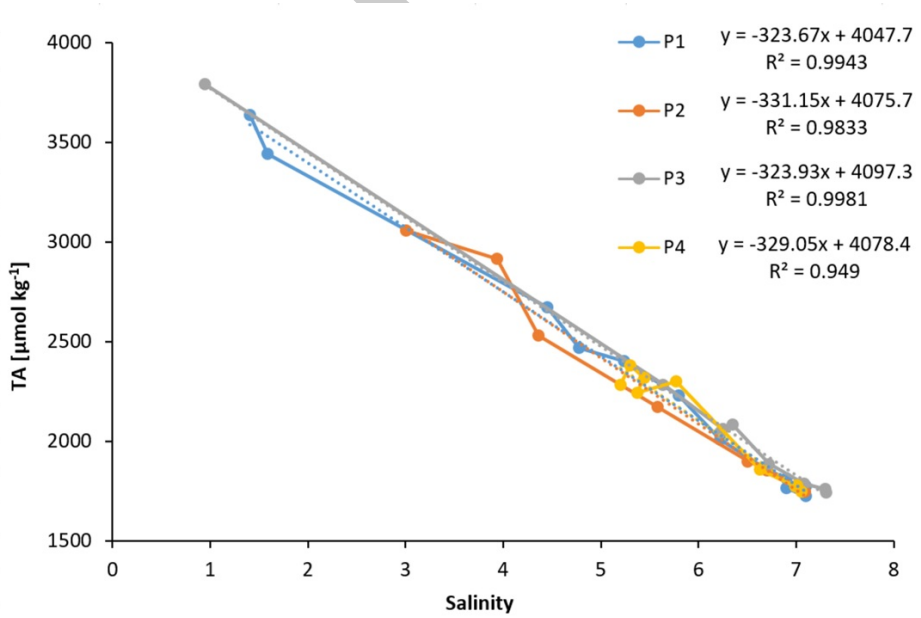

Figure 5. Linear correlation between salinity and TA during the four vertical profiles performed in one spot in the Vistula River plume at 6-hour intervals.

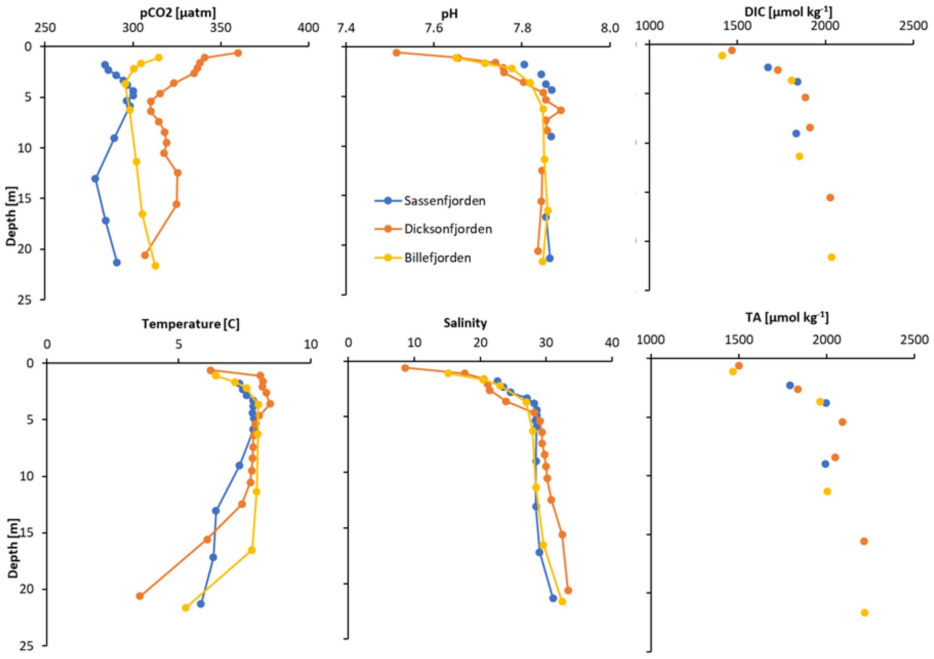

Figure 6. Vertical distribution of the marine carbonate system parameters (pCO2, pH, DIC, TA), temperature, and salinity in the three Spitsbergen fjords.

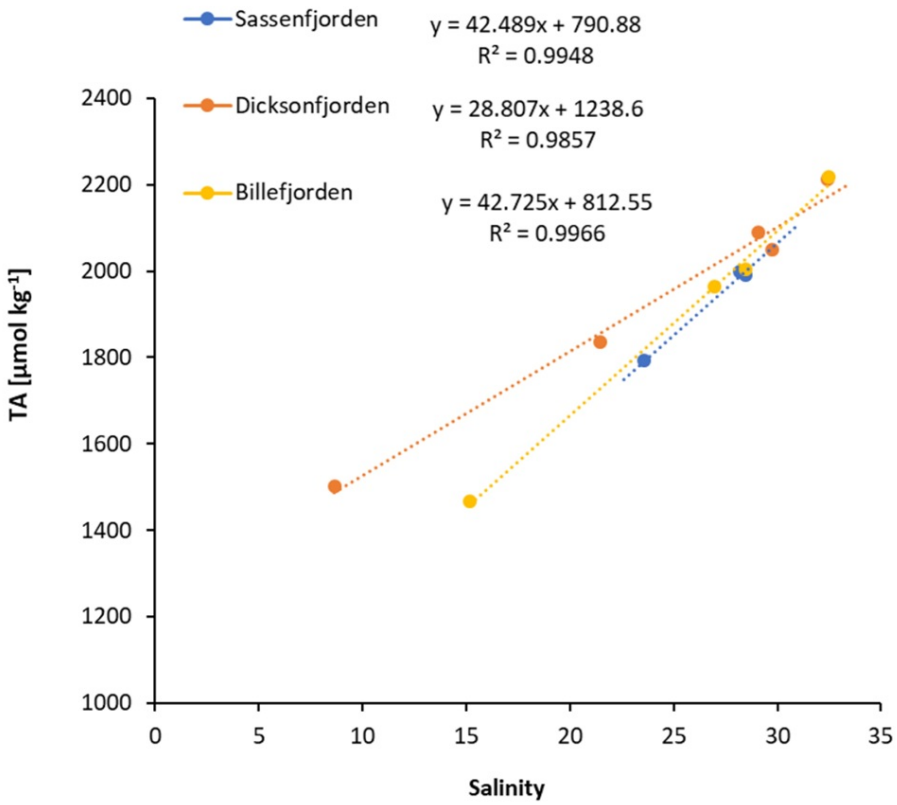

Figure 7. Linear correlation between salinity and TA collected using the carbonate profiler in the high-Arctic fjords of Sassenfjorden, Dicksonfjorden, and Billefjorden.

et al. (2021b), suggesting that the TA freshwater end member varies here in an even broader range than expected. This finding was possible thanks to the application of the carbonate profiler, which allowed for a precise sampling of the surface water layer (where the freshwater spreads) for carbonate system parameters, including TA. Although this result was achieved during operability tests of the carbonate profiler, it is an important contribution towards understanding the role of TA input from continental rivers (the Vistula River is the largest one) in mitigating Ocean Acidification in the Baltic Sea. At the same time, this very high freshwater TA end member (reported in this study for the first time for this region) indicates the need for further research in this area towards better resolving TA loads from the southern Baltic Sea catchment, which is in turn necessary to understand the alkalinity budget in the Baltic (Kuliński et al., 2022). All this demonstrates the utility of the carbonate profiler in resolving complex biogeochemical profiles in stratified waters and in obtaining accurate estimations of freshwater end-member properties by performing only a vertical profile in the vicinity of the estuaries.

3.2.2 Test 2: The turbid plumes of the Arctic fjords

The results from pCO_2, TA, DIC, pH, temperature, and salinity measurements at the three profiles collected within the turbid plumes in the fjord waters are presented in Figure 6. The sampling covered the first 20 meters of the water column in all the locations. The largest biogeochemical gradients, as reflected in all the measured parameters, were recorded in the surface water layer and were clearly related to the water freshening (see Figure 6). The measured salinity varied significantly across all profiles (ranging from 8.66 to 33.31), increasing from the surface to the deeper waters. Out of this range, most of the variability (79% in the Diksonfjorden profile, 74% in Billefjorden, and 71% in Sassenfjorden) occurred in the upper 5 m of the water column. Along with salinity changes, TA, DIC, pCO_2, and pH also exhibited the strongest variation in the uppermost layer. However, in contrast to the Vistula River plume, the freshwater inflow to the fjords diluted the seawater with respect to DIC and TA, which had a pronounced effect on decreasing surface pH, thus enhancing Ocean Acidification in the region.

The abrupt gradients measured in the surface layer of the water column with the vertical variance of TA, DIC, pH, and pCO_2 of up to 588 µmol kg^{-1}, 416 µmol kg^{-1}, 0.34, and 44 µatm, respectively, result from the outflow of turbid water plumes formed in the land-ocean transitional zone (Meslard et al., 2018; Szeligowska et al., 2020). These turbid water plumes usually cover only the first meters of the water column, creating steep biogeochemical gradients that the carbonate profiler has successfully recorded. This seemingly simple task would be unapproachable when using other sampling methods, such as a bathometer. In fact, if we were to collect water from 1 m depth using a 1 m long bathometer, we would collect water from a depth between 0.5 m and 1.5 m. Considering the variability identified in Dicksonfjorden (Figure 6), the water inside the bathometer would have a pH range of 7.51 at the top to 7.74 at the bottom. Thus, measured pH (and any other parameter) would vary significantly depending on the water subsample within the bathometer volume. In contrast, the carbonate profiler offers a straightforward tool for investigating steep biogeochemical gradients by collecting water samples and measuring in situ parameters (e.g., salinity, temperature, turbidity, fluorescence) with a significantly higher vertical resolution. For example, in this exercise, a resolution of 0.5 m was easily achieved.

As shown already for the Vistula River plume (section 5.2.1), it is possible to use the vertical variability of TA and salinity to estimate the TA concentration in freshwater end members with great accuracy. In Spitsbergen fjords, the relationships between TA and salinity revealed different freshwater TA in different fjords, namely 791 µmol kg^{-1} in Sassenfjorden, 813 µmol kg^{-1} in Billefjorden, and 1239 µmol kg^{-1} in Dicksonfjorden (Figure 7). These concentrations fall within the range of previously reported values for Svalbard fjords, which range from 232 to 1412 µmol kg^{-1} (Ericson et al., 2018; Fransson et al., 2015; Koziorowska-Makuch et al., 2023). All this data, including this study, proves that continental runoff in Arctic fjords reduces the TA in surface waters and thus lowers its capacity to absorb atmospheric CO_2 and enhances Ocean Acidification.

Moreover, the measured pCO2 in surface waters (Figure 6) was higher in Dicksonfjorden (360 µatm) and Billefjorden (314 µatm) than in the deeper water layer (approx. 303 µatm), but in Sassenfjorden, the surface pCO_2 was lower (284 µatm). These significant changes may be attributed to the different freshwater sources that influence the fjords. While Dicksonfjorden and Billefjorden are both heavily glaciated catchments, Sassenfjorden is primarily influenced by Sassenelva, a river that drains a permafrost-rich valley (McGovern et al., 2020). Overall, the carbonate profiler allowed us to highlight the complex stratification patterns in the Arctic fjords, which have a direct impact on biogeochemical changes and the structure of the marine carbonate system. Moreover, the data show that continental runoff in the Svalbard archipelago enhances ocean acidification in coastal areas, where its surface waters have a lower capacity to uptake atmospheric CO_2.

4. Conclusion

In this study, we designed a low-cost and easy-to-set-up upper water column sampler that can be easily incorporated into measurement systems on research vessels (and beyond). Combined with the ship's CTD profiler, they form a PUMP-CTD system that can be easily deployed on a variety of vessels regardless of their size and technical sophistication. Just by switching the water source to this PUMP-CTD, it can be used to feed the commonly used systems for

equilibrator-based continuous pCO_2 measurements (typically using the ship's pumping system having the water inlet at a Vfixed depth between 2 and 10 m) and extend their applicability also towards the water column sampling, including the precise sampling of the surface water layer. This is of great importance for accurately measuring seawater pCO_2 at the surface in stratified coastal water bodies (having often strong vertical biogeochemical gradients), which are to be used further for air/sea CO_2 flux calculations. As the water supply from the submersible pump is sufficient to be split, in addition to supplying the equilibrator-based continuous pCO_2 measurements, it also serves other receivers. The system allows for precise sampling of the full set of marine carbonate system parameters, namely TA, DIC, pH, and pCO_2. This feature is extremely useful in coastal waters, which, due to ion anomalies and the significant influence of non-parameterized acid-base constituents of seawater, often require a complete set of data on the structure of the marine carbonate system – a requirement that is considered excessive in open ocean waters.

The test performed in the open waters of the Greenland Sea shows that the system was able to obtain rapid and more accurate pCO_2 measurements in the water column than any other commercial method. Measurements of pCO_2 in the estuarine system of the Baltic Sea and the Spitsbergen fjords show that measurements using the carbonate profiler can be utilized as an easy tool to obtain the vertical distribution of pCO_2, including near-surface results, and thus improve estimations of air-sea CO_2 fluxes in stratified regions. The profiles also demonstrate an excellent capacity to obtain, in parallel with the continuous pCO_2 measurements, automated or discrete pH measurements and discrete samples for TA and DIC, with excellent correlation to in situ measured parameters. We also demonstrated the carbonate profiler's applicability in obtaining accurate estimations of the freshwater end-members' properties by only performing a vertical profile in the vicinity of the estuaries. For this, we used the correlation between precisely sampled TA and in situ salinity. The results from the Baltic Sea showed not only an excellent correlation in the four profiles ($R2 = 0.98$) but also a good reproducibility, i.e., the freshwater TA of 4069 µmol kg^{-1} estimated with the variation of only $\pm$12 µmol kg^{-1} (less than 1% of the estimated value). These TA results confirm the important role of the Vistula River as a net source of TA for the Baltic and reveal very high TA concentrations in the Vistula River that have not been reported before for this region. A similar utility of the carbonate profiler has been observed for the Spitsbergen fjords. However, the estimated TA freshwater end members were much lower and highly variable between the individual fjords (ranging from 790 to 1240 µmol kg^{-1}). Still, all of them demonstrated that the continental runoff in the Svalbard archipelago lowers the buffer capacity of the seawater, reduces its potential to uptake atmospheric CO_2, and enhances Ocean Acidification. To sum up, the carbonate profiler we designed represents an easy-to-implement and low-cost tool allowing the scientific community to obtain state-of-the-art measurements of all the marine carbonate parameters with a vertical resolution better than 0.5 meters, and providing new possibilities for observations and quantifications of ocean acidification, carbon inventory, and air-sea CO_2 fluxes in highly stratified environments.

Data availability

The data presented in this study are publicly available in the online data repositories of GeoNetwork (Aguado Gonzalo et al., 2025b; https://doi.org/10.48457/IOPAN.2025.515).

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Authors contribution

Author contributions: CRediT FG: Conceptualization, Methodology, Writing – review & editing, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. KKo: Data curation, Writing – review & editing. LB: Data curation. AL: Writing – review & editing. KKu: Conceptualization, Methodology, Funding acquisition, Project administration, Supervision, Validation, Writing – review & editing.

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Conflict of interest

None declared.

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