

Development of a Chemical Sensor for the Measurement of Dissolved Inorganic Carbon in Seawater

Dissertation

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Epigraph

“For a successful technology, reality must take precedence over public relations, for Nature cannot be fooled.”

- Richard P. Feynman

Summary

The increasing anthropogenic CO₂ emissions have exacerbated global climate change with a strong impact on both the atmosphere and the oceans. As a major sink for atmospheric CO₂, the ocean plays a critical role in the regulation of global carbon levels. However, the continuous uptake of CO₂ results in significant physico-chemical alterations such as ocean acidification. These changes have affected marine ecosystems and biogeochemical cycles. To mitigate global climate change, various ocean-based CO₂ removal (CDR) strategies, both natural and technological, are under investigation. The successful implementation of these strategies requires robust monitoring, reporting, and verification frameworks, which depend on the availability of reliable and high-resolution observational tools with known quality.

Key uncertainties remain regarding the long-term efficiency and impacts of CDR methods. The availability of sensors is, therefore, essential to close these knowledge gaps. While autonomous sensors for pH and *p*CO₂ are relatively mature, *in-situ* dissolved inorganic carbon (DIC) sensors and analyzers are still in an early stage of development. Given the central role of DIC in the quantification of carbon fluxes and assessment of ocean carbon sequestration, the advancement of autonomous DIC sensors is important.

This thesis presents the development of a novel, autonomous DIC sensor for seawater measurements. The work details a stepwise sensor development process from a bench-top prototype to a fully submersible system. Both versions operate on a conductometric detection principle in combination with a gas diffusion sequential injection analysis (GD-SIA). During each measurement, a small volume (~ 2 mL) of seawater is acidified to convert all inorganic carbonate and bicarbonate species into gaseous CO₂, which then diffuses through a gas-permeable membrane into an alkaline solution. The resulting change in conductivity is directly proportional to the DIC concentration.

Optimization of the analyzer involved a series of physical and chemical modifications. Physical optimizations included the refinement of two key components, - (i) a custom-made four hollow brass electrode detection cell, and (ii) a custom-made gas exchange unit (GEU) with a “Tube In A Tube” configuration. Chemical optimizations focused on reagent

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concentrations and reaction kinetics to maximize CO₂ diffusion, signal stability, and analytical precision.

The bench-top analyzer was validated through controlled laboratory experiments and tested in multiple field trials. Each measurement required 15 minutes and less than 2 mL of each reagent. It achieved an analytical precision of measurement of ± 4.9 and $9.7 \mu\text{mol kg}^{-1}$ in laboratory and field deployments, respectively, meeting ‘Weather Quality’ standards for ocean carbonate measurements. Based on the success of the bench-top analyzer, an *in-situ* version was developed. The new system retained the core architecture but featured a compact, robust, and pressure-resistant housing suitable for shallow water deployments (maximum 10 m water depth). The *in-situ* sensor was deployed in multiple field trials and demonstrated an analytical precision of measurement of $< 20 \mu\text{mol kg}^{-1}$, with each measurement completed in 20 minutes. The accuracy of both systems was assessed using certified reference material (CRM) and sub-standard reference material (RM).

The high-frequency DIC data collected during field deployments in the North Sea and the Kiel Fjord provided new insights into the short-term variability and environmental drivers of carbonate system dynamics in coastal and estuarine systems. These data resolved high spatial and temporal resolution which overcomes the limitations of traditional discrete sampling method and demonstrated the potential of the analyzer to enhance carbonate system monitoring.

Overall, the work in this thesis showed the development of a novel, cost-effective, and autonomous DIC analyzer with an aim to address a critical technological gap in marine biogeochemical research. The analyzer supports a range of scientific applications, from real-time ocean acidification monitoring to verifications of ocean-based CDR interventions.

Zusammenfassung

Die zunehmenden anthropogenen CO₂-Emissionen haben den globalen Klimawandel verschärft, was sich sowohl auf die Atmosphäre als auch auf die Ozeane stark auswirkt. Als wichtige Senke für atmosphärisches CO₂ spielt der Ozean eine entscheidende Rolle bei der Regulierung des globalen Kohlenstoffgehalts. Die kontinuierliche Aufnahme von CO₂ führt jedoch zu erheblichen physikalisch-chemischen Veränderungen wie der Versauerung der Ozeane. Auswirkungen auf die marinen Ökosysteme und biogeochemischen Kreisläufe haben. Um den globalen Klimawandel abzuschwächen, werden verschiedene natürliche und technologische Strategien zur CO₂-Entfernung (CDR) aus dem Meer untersucht. Die erfolgreiche Umsetzung dieser Strategien erfordert robuste Überwachungs-, Berichterstattungs- und Überprüfungsrahmen, die von der Verfügbarkeit zuverlässiger und hochauflösender Beobachtungsinstrumente mit bekannter Qualität abhängen.

Nach wie vor bestehen große Unsicherheiten in Bezug auf die langfristige Effizienz und die Auswirkungen der CDR-Methoden. Die Verfügbarkeit von Sensoren ist daher entscheidend, um diese Wissenslücken zu schließen. Während autonome Sensoren für pH und *p*CO₂ relativ ausgereift sind, befinden sich *in-situ* Sensoren und Analysatoren für gelösten anorganischen Kohlenstoff (DIC) noch in einem frühen Entwicklungsstadium. Angesichts der zentralen Rolle von DIC bei der Quantifizierung von Kohlenstoffflüssen und der Bewertung der Kohlenstoffspeicherung im Ozean ist die Weiterentwicklung autonomer DIC-Sensoren wichtig.

In dieser Arbeit wird die Entwicklung eines neuartigen, autonomen DIC-Sensors für Messungen im Meerwasser vorgestellt. Die Arbeit beschreibt einen schrittweisen Sensorentwicklungsprozess von einem Tischprototyp bis zu einem vollständig tauchfähigen System. Beide Versionen arbeiten mit einem konduktometrischen Detektionsprinzip in Kombination mit einer sequentiellen Gasdiffusionsinjektionsanalyse (GD-SIA). Bei jeder Messung wird ein kleines Volumen (~ 2 mL) Meerwasser angesäuert, um alle anorganischen Karbonat- und Bikarbonatarten in gasförmiges CO₂ umzuwandeln, das dann durch eine gasdurchlässige Membran in eine alkalische Lösung diffundiert. Die

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daraus resultierende Änderung der Leitfähigkeit ist direkt proportional zur DIC-Konzentration.

Die Optimierung des Analysators umfasste eine Reihe von physikalischen und chemischen Modifikationen. Zu den physikalischen Optimierungen gehörte die Verfeinerung von zwei Schlüsselkomponenten: (i) eine speziell angefertigte Detektionszelle mit vier hohlen Messingelektroden und (ii) eine speziell angefertigte Gasaustauscheinheit (GEU) mit einer „Tube in a Tube“-Konfiguration. Die chemischen Optimierungen konzentrierten sich auf die Reagenzkonzentrationen und die Reaktionskinetik, um die CO₂-Diffusion, die Signalstabilität und die analytische Präzision zu maximieren.

Das Tisch-Analysegerät wurde in kontrollierten Laborexperimenten validiert und in mehreren Feldversuchen getestet. Für jede Messung wurden 15 Minuten und weniger als 2 mL jedes Reagenz benötigt. Das Gerät erreichte eine analytische Messgenauigkeit von $\pm 4,9$ bzw. $9,7 \mu\text{mol kg}^{-1}$ bei Labor- und Feldversuchen und erfüllte damit die „Weather Quality“-Standards für Ozeankarbonatmessungen entspricht. Auf der Grundlage des Erfolgs des Tisch-Analysegeräts wurde eine *in-situ*-Version entwickelt. Das neue System behielt die Kernarchitektur bei, verfügte aber über ein kompaktes, robustes und druckfestes Gehäuse, das für den Einsatz in flachem Wasser (maximal 10 m Wassertiefe) geeignet ist. Der *in-situ*-Sensor wurde in mehreren Feldversuchen eingesetzt und zeigte eine analytische Messgenauigkeit von $< 20 \mu\text{mol kg}^{-1}$, wobei jede Messung in 20 Minuten abgeschlossen war. Die Genauigkeit beider Systeme wurde mit zertifiziertem Referenzmaterial (CRM) und Substandard-Referenzmaterial (RM) bewertet.

Die hochfrequenten DIC-Daten, die während der Feldeinsätze in der Nordsee und der Kieler Förde gesammelt wurden, lieferten neue Einblicke in die kurzfristige Variabilität und die umweltbedingten Triebkräfte der Dynamik des Karbonatsystems in Küsten- und Flussmündungssystemen. Diese Daten boten eine hohe räumliche und zeitliche Auflösung, die die Grenzen der herkömmlichen diskreten Probenahme überwindet und das Potenzial des Analysators zur Verbesserung der Überwachung des Karbonatsystems demonstriert.

Insgesamt zeigte die Arbeit in dieser Dissertation die Entwicklung eines neuartigen, kosteneffektiven und autonomen DIC-Analysators mit dem Ziel, eine kritische

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technologische Lücke in der marinen biogeochemischen Forschung zu schließen. Der Analysator unterstützt eine Reihe wissenschaftlicher Anwendungen, von der Echtzeit-Überwachung der Ozeanversauerung bis zur Überprüfung von CDR-Maßnahmen im Meer.

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1. Introduction

1.1 Background

1.1.1 Anthropocene

The Earth system consists of five naturally evolving and interconnected components: the atmosphere, hydrosphere, lithosphere, biosphere, and, since the onset of human activity, the anthroposphere (Raupach & Canadell, 2010). The dynamics of the systems are primarily governed by external forces, including astronomical and geophysical factors (de Claudino-Sales, 2020). However, with the intensification of human activities, the natural evolutionary trajectory of the living organisms on Earth is undergoing rapid and unprecedented change (Monroe et al., 2018). Nobel laureate Paul Crutzen distinguished the significance of this change and conceptualized the term ‘Anthropocene’ to distinguish it from the preceding Holocene, an epoch or geological period when humans became the dominant force of the Earth System (Paul, 2002).

1.1.2 Global Warming and Green House Gas

Since the industrial revolution (approximately 1750 to the early 19th century), human-induced perturbations, such as fossil fuel combustion, deforestation, industrialization, have significantly intensified climate change by accelerating the anthropogenic emissions of greenhouse gases (GHGs), aerosols, and their precursor. Among the well-mixed GHGs, CO₂ has the largest share and exhibits the most substantial growth in global emissions. The GHGs absorb infra-red radiation and trap heat within the Earth’s atmosphere preventing it from escaping into space.

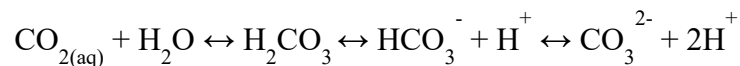
The increase in anthropogenic GHGs emissions is recognized as the dominant driver of global surface warming, with CO₂ contributing approximately 0.8 °C of warming between 2010 and 2019 relative to pre-industrial levels (IPCC, 2023). Historically cumulated CO₂ emissions over the past 2000 years reveal two distinct trends: prior to the industrial revolution (~1750), atmospheric CO₂ concentration remained relatively stable at ~ 280

ppm, whereas post-1750, concentrations have monotonically increased, surpassing 420 ppm in 2024 (data courtesy: National Oceanic and Atmospheric Administration, USA). This represents an approximate 58 % increase in CO₂ levels between 1850 and 2019, compared to the increase observed between 1850 and 1989 (Devries, 2022; IPCC, 2023).

1.1.3 Ocean Carbonate Chemistry

Covering 71% of Earth's surface, the ocean is the largest carbon reservoir (Friedlingstein et al., 2022), primarily storing carbon in the form of dissolved inorganic carbon (DIC). It contains approximately 60 times more DIC than the pre-industrial atmosphere, making it a key regulator of atmospheric CO₂ and a crucial component of the global carbon cycle (Zeebe & Wolf-Gladrow, 2009). Since 1750, the ocean has absorbed approximately one-third of anthropogenic CO₂ emissions through air-sea gas exchange driven primarily by abiotic processes such as gas solubility, temperature-dependent kinetics, and the carbonate buffering system (Friedlingstein et al., 2023, Devries, 2022).

The exchange of CO₂ between the ocean and the atmosphere is mediated by a series of chemical reactions (Doney et al., 2009). Gaseous CO₂ dissolves in seawater to form aqueous CO₂, which then reacts with seawater to form carbonic acid (H₂CO₃). This weak acid dissociates into bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) ions, maintaining oceanic pH balance, following the reaction:



These chemical reactions governing the oceanic carbonate system are reversible and operate near equilibrium, maintaining the ocean's buffering capacity. At a typical surface seawater pH of 8.2, inorganic carbon distribution is approximately 90% HCO₃⁻, 9% CO₃²⁻, and 1% dissolved CO₂ (F. J. Millero et al., 2002).

1.1.4 Quantification of ocean carbonate chemistry

The oceanic inorganic carbonate system is defined by four primary variables - dissolved inorganic carbon (DIC), total alkalinity (TA), pH, and the fugacity of CO₂ (fCO₂).

(1) Dissolved Inorganic Carbon (DIC) is the sum of the dissolved carbonate species in seawater, carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}),

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

(2) Total Alkalinity (TA) is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors, that is simply the buffering capacity of seawater, representing the ability to neutralize strong acids. It includes contributions not only from carbonate species but also from borate, silicate, phosphate, and organic ions,

$$\text{TA} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] + \text{minor compounds}$$

(3) pH is the negative logarithm of the total hydrogen ion concentration in seawater, and it is a direct assessment of ocean acidity,

$$\text{pH} = -\log_{10}[\text{H}^+]$$

(4) fugacity of CO_2 ($f\text{CO}_2$) is a measure the of the tendency of CO_2 to escape from or dissolve into seawater, representing the exchange potential between the ocean and atmosphere. It is directly proportional to the aqueous CO_2 in seawater.

Additionally, a fifth variable, carbonate ion concentration $[\text{CO}_3^{2-}]$, is in increasing consideration due to its ecological significance for calcifying organisms such as bivalve larvae and pteropods (Sharp & Byrne, 2019; Zeebe & Wolf-Gladrow, 2001). The carbonate system can be derived mathematically from measurements of at least two of these variables, supplemented with measurements of temperature, salinity, and macronutrient concentrations. The CO2SYS software is commonly used to calculate the required carbonate system parameters (Lewis et al., 1998; Martz et al., 2015a; F. J. Millero, 2007) with DIC and $p\text{CO}_2$ or DIC and pH pairs yielding the lowest errors in the estimation of the remaining parameters (F. J. Millero, 2007).

1.1.5 Oceanic Carbon Pumps

Natural oceanic CO_2 uptake and carbon sequestration occur through three interlinked processes (Volk & Hoffert, 1985).

Solubility Pump

The solubility pump is the physical mixing of CO₂ via thermohaline circulation. Cold, high-latitude waters enhance CO₂ solubility and transport carbon to deep waters, keeping it isolated from the atmosphere. On the other hand, upwelling allows for waters to resurface with the reemission of some of the stored carbon into atmosphere.

Carbonate Pump

The carbonate pump is regulated by marine calcifiers. Mainly, coccolithophores and foraminifera precipitate calcium carbonate (CaCO₃) to form shells and skeletons. Upon their death, shells dissolve at depth and contribute to DIC pools or accumulating in sediments.

Biological carbon pump or soft tissue pump

Phytoplankton fix atmospheric CO₂ through photosynthesis, producing organic carbon. A fraction sinks as particulate organic carbon (POC), where microbial remineralization regenerates CO₂, which is either sequestered in deep waters or returned to the surface via upwelling.

1.1.6 Ocean Acidification

Ocean acidification (OA) results from increased atmospheric CO₂, which dissolves into seawater and leads to increased concentration of H⁺, reduced pH, and decreased carbonate ion availability (Zeebe, 2012). The carbonate equilibrium is disrupted with a reduction of the saturation state (Ω) necessary for biomineralization in marine calcifiers such as corals, mollusks, and foraminifera. Due to its strong link to rising atmospheric CO₂ levels and climate change, OA has been described as “the other CO₂ problem” (Doney et al., 2009) and “the evil twin of global warming” (Pelejero et al., 2010).

Long-term time-series observations (1983 - 2023) in the Sargasso Sea (North Atlantic Ocean), near the island of Bermuda, have recorded a pH decline of 0.0752 units (approximate 30% increase in H⁺) at a rate of -0.018 ± 0.001 per decade (Bates & Johnson, 2023). Projections indicate a pH decrease of 0.3 to 0.4 pH units by 2100, a rate of

acidification unprecedented in the past two million years (Caldeira & Wickett, 2005; Hönlisch et al., 2012). One of the most immediate and significant consequences of OA is its impact on marine ecosystems, particularly calcifying organisms such as corals, mollusks, and foraminifera. The associated decline in Ω ($\Omega < 1$) threatens marine biodiversity, known as a “calcification crisis” (Fabry et al., 2008).

Ocean Acidification Tracers

The effect of OA is assessed through direct measurement of long-term changes in pH and carbonate chemistry. Several key metrics and tracers are employed to quantify and predict the extent of OA and its implications for marine systems:

(1) The Revelle factor (R) quantifies the ocean’s buffering capacity/sensitivity towards changing carbonate chemistry in seawater in terms of pH changes (L. Q. Jiang et al., 2019). It is defined as the ratio of the relative change of seawater $p\text{CO}_2$ (or $\text{CO}_{2(\text{aq})}$) to the relative change in DIC under constant temperature, salinity, and TA (Revelle & Suess, 1957) :

$$R = (\Delta p\text{CO}_2/p\text{CO}_2)/(\Delta \text{DIC}/\text{DIC})$$

A lower R-value indicates a higher efficiency in absorbing anthropogenic CO_2 . Furthermore, its derivative parameters, e.g., the sensitivity of DIC and TA to changes in carbonate equilibrium, provide additional insights into the ocean’s carbonate buffering capacity (Eggleston et al., 2010).

(2) The difference ($[\text{TA} - \text{DIC}]$) between TA and DIC serves as a tracer for deciphering temperature-normalized pH and future OA developments (Xue & Cai, 2020). Since both TA and DIC exhibit conservative and linear mixing properties, they remain relatively constant despite variations in temperature and pressure. Hence, it is considered a convenient way. However, its applicability in low-salinity regions, such as oxygen minimum zones (OMZs), is limited as it may produce highly uncertain results due to minimal $[\text{TA} - \text{DIC}]$ values.

In addition, indirect tracers derived from observational and analytical data are also utilized (Patra & Puneekar, 2025). The observational tests focus primarily on micropaleontological analysis (e.g., foraminifera test morphology) and geochemical markers. The analytical

data-based tracers generally include (1) measuring the content of calcium carbonate (CaCO_3) of marine sediments, (2) measuring stable isotopes of Boron ($\delta^{11}\text{B}$) to directly quantify seawater pH, (3) linking Calcium ($\delta^{44/40}\text{Ca}$) to TA variation, (4) measuring elemental ratio of B:Ca, Uranium:Calcium (U:Ca) to reconstruct marine carbonate chemistry and quantifying seawater CO_3^{2-} ion concentration, and etc.

1.1.7 Carbon dioxide removal

To effectively mitigate global climate change and accelerate the reduction of excess atmospheric CO_2 on human timescales, robust international climate agreements are essential. The Paris Climate Agreement (COP21) set the ambitious goal ‘*to limit global temperature rise to well below 2 °C above pre-industrial levels and pursue efforts to limit the increase to 1.5 °C*’. To minimize global warming, a rapid yet sustainable reduction in anthropogenic CO_2 emissions is required, alongside scalable pathways toward net-zero CO_2 emissions in the coming decades (Figure 1.1).

Natural processes alone would require decades to centuries to remove the excess atmospheric CO_2 and reach the temperature goal. The IPCC Special Report on Global Warming of 1.5°C (Masson-Delmotte et al., 2019) emphasizes that all viable mitigation pathways will require the deployment of carbon dioxide removal (CDR) strategies to drastically reduce greenhouse gas emissions and offset residual emissions. The CDR is considered an essential tool to achieve net-zero CO_2 emissions, particularly in hard-to-abate sectors. Estimates suggest that between 100 to 1,000 Gt of CO_2 must be removed globally over the 21st century to sustain net-zero emissions and meet the Paris Agreement targets (Lamb et al., 2024).

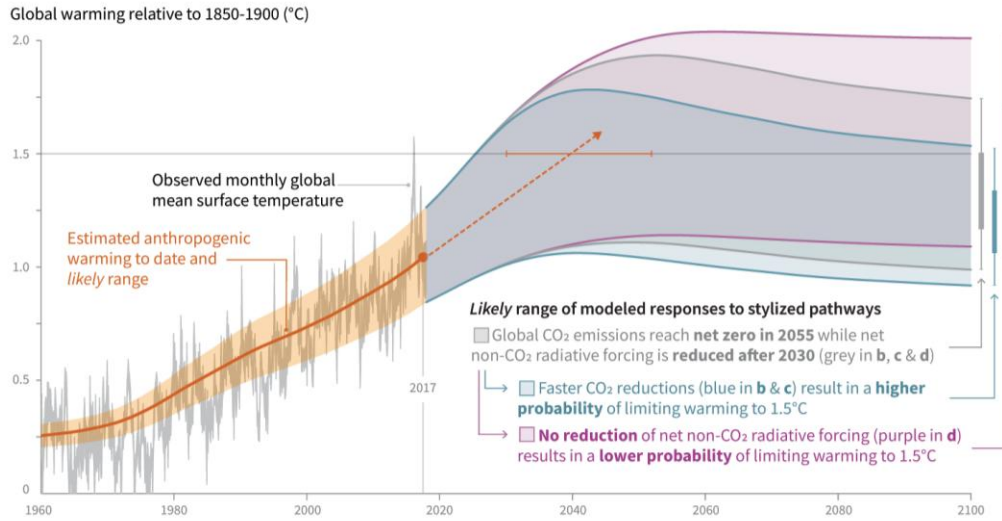


Figure 1.1. Observed global warming relative to the pre-industrial year (°C) and modeled responses to stylized pathways for net-zero carbon emission by the year 2100 (IPCC, 2022).

According to the IPCC 6th Assessment Report (AR6), CDR refers to technologies, practices, and approaches that remove CO₂ from the atmosphere and durably store it in geological, terrestrial, or ocean reservoirs, or in products, as a mitigation strategy (Pathak et al., 2022). These methods are broadly categorized into terrestrial- and ocean-based approaches, incorporating both nature-based solutions and engineered technologies.

Terrestrial CDR strategies focus on restoring and enhancing natural carbon sinks, such as afforestation/reforestation, soil carbon sequestration, and enhanced weathering, as well as industrial solutions like direct air capture or bioenergy coupled with geological carbon sequestration (Fuhrman et al., 2019). However, terrestrial CDR faces limitations, including land availability, high costs, energy demands, and resource constraints. These challenges may create conflicts with broader societal objectives, including the United Nations Sustainable Development Goals (SDGs) (Fuhrman et al., 2019). Additionally, land-based carbon sequestration is constrained by competing land-use demands, as only 29% of the Earth's surface is terrestrial, much of which is occupied by human settlements and used for agriculture and natural ecosystems, reducing the feasibility of large-scale CDR deployment.

In contrast, ocean-based CDR (marine CDR) offers a promising option for carbon sequestration, leveraging the vast capacity of marine environments (Friedlingstein et al., 2023). Unlike terrestrial CDR, which directly removes CO₂ from the atmosphere, marine CDR strategies generally operate indirectly by enhancing natural carbon storage and sequestration processes within marine systems (Doney et al., 2025). However, concerns regarding potential ecological impacts and legal frameworks governing marine interventions remain significant. In 2024, the International Tribunal for the Law of the Sea ruled in its Advisory Opinion on Climate Change that “*anthropogenic GHG emissions into the atmosphere constitute pollution of the marine environment*” (International Tribunal for the Law of the Sea, 2024). Therefore, comprehensive risk assessments are necessary to evaluate the effects of marine CDR strategies on ocean chemistry, ecosystems, and global carbon cycles (Oschlies et al., 2025).

1.1.8 Marine carbon dioxide removal

To enhance the ocean’s capacity for CO₂ uptake, storage, and long-term sequestration, various marine carbon dioxide removal (mCDR) methods have been proposed that integrate both nature-based and technological interventions and target biotic or abiotic carbon cycles (Figure 1.2).

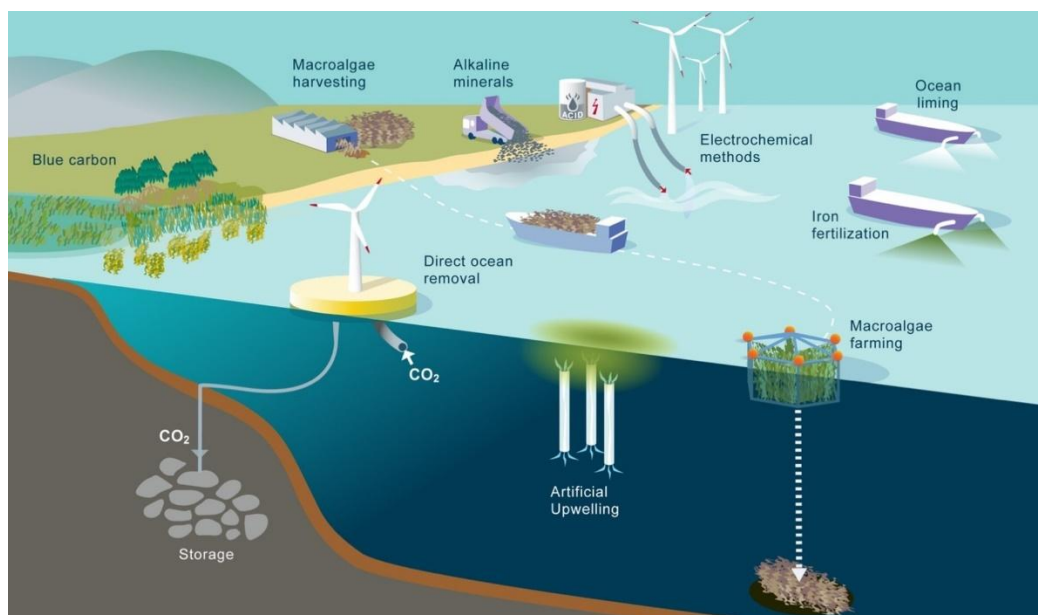


Figure 1.2. Schematic of various methods suggested for marine CDR. Schematic from Oschlies et al., 2025.

Biotic mCDR methods focus primarily on the restoration and protection of natural habitats and ecosystems (e.g., blue carbon management) and on the augmentation of the biological carbon pump (e.g., artificial upwelling, macroalgae cultivation, and ocean fertilization). Abiotic mCDR approaches use geochemical, electrochemical, and technological interventions (e.g., ocean alkalinity enhancement (OAE), artificial downwelling, deep storage, direct CO₂ capture) to sequester and store the excess CO₂ from the atmosphere (Cooley et al., 2023; Doney et al., 2025; NASEM (National Academies of Sciences, 2022)) (Figure 1.3).

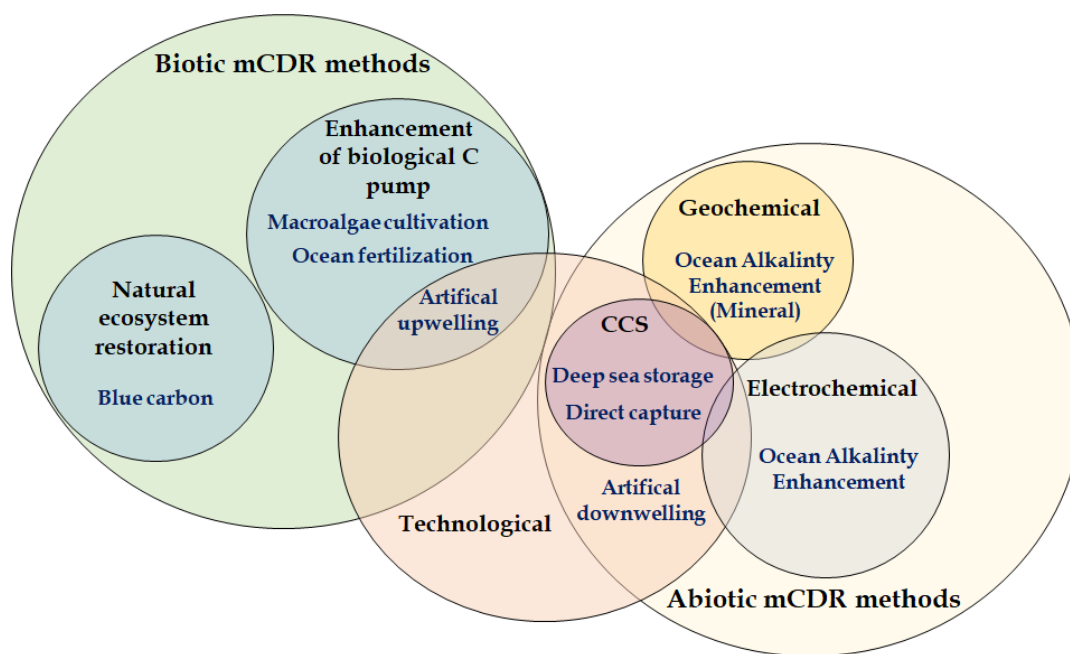


Figure 1.3. Venn diagram of different categories of biotic and abiotic mCDR methods. Diagram inspired by (Ho & Bopp, 2024).

1.1.8.1 Biotic mCDR methods

Biotic mCDR enhances carbon sequestration by (1) increasing photosynthetic carbon fixation and (2) reducing respiration-driven CO₂ release. This approach optimizes the balance between carbon uptake and outgassing in surface waters and reinforces long-term sequestration through the biological carbon pump (Oschlies et al., 2025). The biological carbon pump plays a crucial role in atmospheric CO₂ regulation, with modeling studies indicating that its complete shutdown would result in a 200 ppm increase in atmospheric CO₂ over several hundred years (NASEM (National Academies of Sciences, 2022)).

Blue Carbon

Vegetated coastal ecosystems or Blue Carbon Ecosystems (BCEs) like tidal salt marshes, mangrove forests, and seagrass meadows, sequester carbon through photosynthesis and store organic carbon in sediments under low-oxygen, high salinity conditions that inhibit decomposition (Duarte et al., 2013; McLeod et al., 2011 Oschlies et al., 2025). Despite

covering only $\sim 0.5\%$ of the global seafloor, BCEs contribute more than 50% of marine sediment carbon burial (Macreadie et al., 2021). However, the loss of BCE leads to the rapid release of stored carbon from biomass and sediment, reducing their future sequestration potential.

Conservation and restoration of BCEs offer co-benefits such as biodiversity enhancement and climate adaptation (Bertram & Merk, 2020), yet uncertainties remain regarding (1) variable carbon burial rates, (2) potential methane (CH_4) and nitrous oxide (N_2O) emissions, (3) resilience to climate and anthropogenic stressors like sea-level rise, storms as well as coastal development and pollution, and (4) cost-effectiveness (Rosentreter et al., 2021; Williamson & Gattuso, 2022).

While BCE restoration has a high technological readiness level and local governability, its scalability for global CDR remains limited (Gattuso et al., 2021).

Artificial Upwelling

Artificial upwelling (AU) is a geo-engineered process designed to transport nutrient-rich deep ocean water to the ocean surface in order to stimulate primary production and enhance biological carbon sequestration (Lovelock & Rapley, 2007). While AU strengthens the biological pump, the interplay with the solubility pump remains complex, as CO_2 outgassing may offset sequestration benefits (Jürchott et al., 2023). Site-specific quantitative analysis of carbon to nutrient stoichiometry, across different oceanic regions, depths, and seasons is required to assess the effectiveness of AU (Karl & Letelier, 2008). Large-scale AU implementation faces challenges such as potential disruption of ocean stratification, alteration of oceanic circulation patterns, and negative effects on Earth's radiative balance (Oschlies, Pahlow, et al., 2010). Various types of AU mechanisms, including wave-powered and electrical pumps, perpetual salt fountains, brackish water uplift pumps, air-bubble pumps, and air-lift pumps have been tested (Pan et al., 2016), yet long-term operational feasibility remains uncertain (Koweek, 2022). Theoretical models suggest potential efficacy, but ocean biogeochemistry complexity introduces uncertainty (NASEM (National Academies of Sciences, 2022)). Recent studies proposed the integration of artificial upwelling with macroalgae and seagrasses cultivation, particularly

in nutrient-polluted regions, to optimize macro-nutrient balance and enhance ecosystem benefits (Hurd et al., 2022; Pan et al., 2016).

Macroalgae Cultivation

Cultivation of macroalgae, often referred to as ‘Ocean afforestation’, is an emerging mCDR approach that leverages photosynthetic CO₂ uptake by large marine algae such as kelp and seaweed (N’Yeurt et al., 2012). Macroalgae sequester CO₂ via photosynthesis, with sequestration occurring through (1) deep-sea export of sinking organic matter and (2) commercial applications (e.g., biofuels, food, pharmaceuticals, and bioplastics) reducing net carbon footprints (NASEM (National Academies of Sciences)), 2022; Oschlies et al., 2025). Natural macroalgal ecosystems contribute to carbon storage via POC and recalcitrant dissolved organic carbon (DOC) (Krause-Jensen & Duarte, 2016). While macroalgal cultivation is well-established in Asia-Pacific regions (Chung et al., 2011), large-scale expansion raises concerns including (1) impacts on ocean chemistry and biodiversity (Boyd et al., 2022), (2) halocarbons emissions that may affect atmospheric chemistry (Leedham et al., 2013), (3) nutrient depletion in surface waters termed as ‘nutrient robbing’ and (4) potential increase of deep-sea anoxia (Oschlies et al., 2025). Studies have shown that, to reach the CDR potential, macroalgal cultivation can be combined with artificial upwelling to resolve the issue macronutrients availability (Berger et al., 2023; Wu et al., 2023). Despite practical obstacles, pilot studies in South Korea demonstrated feasibility (Chung et al., 2013). Future research is needed to assess long-term carbon sequestration efficacy and ocean-atmosphere CO₂ equilibration (Hurd et al., 2022, 2024; Krause-Jensen & Duarte, 2016). On a local-scales, macroalgae cultivation supports aquaculture by mitigating nutrient pollution, improving water quality, and reducing the effects of ocean acidification, deoxygenation, and eutrophication (Chung et al., 2011; GESAMP, 2019; Neori et al., 2004).

Ocean Fertilization

Ocean fertilization refers to the addition of micronutrients (e.g., iron) or macronutrients (e.g., nitrogen, phosphorus, silica) to the surface ocean to stimulate photosynthetic CO₂ fixation and carbon export (NASEM (National Academies of Sciences, 2022)).

Iron is a crucial element for phytoplankton metabolism (Morel & Price, 2003) and iron fertilization has been proposed as a means to enhance the biological carbon pump (Martin, 1990). The pioneering work of John Martin showed a correlation between CO₂ captured in ice cores and dust deposition (a primary source of iron to the ocean).

Studies showed that, in the Southern Ocean, subarctic North Pacific and Eastern Equatorial Pacific Ocean, a perennial surplus of nutrients (High Nutrient Low Chlorophyll, HNLC) is found and in these regions, iron is found to be a limiting nutrient for primary producers (Boyd et al., 2007; Morel & Price, 2003). In these regions iron fertilization was used to boosts phytoplankton blooms and enhance carbon sequestration (Bakker et al., 2001).

Between 1993 and 2003, 13 large-scale open ocean iron fertilization experiments were conducted, but only one (Southern Ocean Iron Experiment (SOFeX)-South) demonstrated significant carbon export (Buesseler & Boyd, 2003, Boyd et al., 2007; GESAMP, 2019; Yoon et al., 2016).

Modeling suggests that continuous iron addition on the entire Southern Ocean or at ocean-basin scales over decades might be required to sequester 2 - 4 Gt CO₂ per year (Oschlies, Koeve, et al., 2010). However, challenges include (1) remineralization of fixed carbon and CO₂ re-exposure, (2) uncertainties in long-term CO₂ storage (NASEM (National Academies of Sciences, 2022)), (3) potential ecosystem shifts ('nutrient robbing' and deep-sea oxygen depletion) (Gnanadesikan et al., 2003), (4) increased nitrification and production of nitrous oxide (N₂O), offsetting sequestration benefits (Jin & Gruber, 2003).

Iron fertilization may induce production of dimethyl sulfide (DMS), potentially reducing global temperatures but could also stimulate emission of halocarbons, methane (CH₄), and isoprene. These gases are accountable for both positive and negative feedbacks on climate change (Law, 2008). Despite uncertainties, further research is required to evaluate biological pump dynamics and carbon export efficiency in ocean iron fertilization.

1.1.8.2 Abiotic mCDR methods

Abiotic mCDR approaches primarily target the ocean's solubility and carbonate pumps to enhance air-sea CO₂ exchange by modification of surface seawater chemistry. This can be achieved by a decrease in DIC concentrations, thereby reducing surface pCO₂, or by an

increase in total alkalinity to shift the DIC equilibrium towards bicarbonate and carbonate ions.

Ocean Alkalinity Enhancement

Alkalinity represents the buffering capacity of a solution to neutralize acid. In the marine system it is naturally produced through the weathering of alkaline minerals such as limestone or basalt. Enhancing ocean alkalinity shifts seawater carbonate chemistry equilibrium towards bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. Additions of alkaline minerals such as limestone, basalt, or silicate materials promotes atmospheric CO_2 absorption by shifting carbonate chemistry to a lower oceanic $p\text{CO}_2$ (Kheshgi, 1995). Additionally, Ocean Alkalinity Enhancement (OAE) mitigates ocean acidification by raising seawater pH (Albright et al., 2016; Doney et al., 2009, 2020).

Minerals such as olivine, basalt, limestone and alkaline industrial byproducts are potential alkalinity sources (Rau & Caldeira, 1999; Renforth, 2019). Reactive compounds like quick lime (CaO) or portlandite (Ca(OH)_2) accelerate alkalinity enhancement but pose risks local supersaturation with possible reduction of CO_2 removal efficiency with spontaneous precipitation of calcium carbonates (Hartmann et al., 2023; Renforth & Henderson, 2017). Silicate minerals have low solubility rates per unit surface area and require fine particle sizes ($\leq 1 \mu\text{m}$) (GESAMP, 2019) and significant energy input to induce dissolution on suitable timescales (Hangx & Spiers, 2009). Additionally, trace metals in silicate minerals may impact marine ecosystems with potential risks up to higher trophic levels (Guo et al., 2024).

Electrochemical OAE employs seawater electrolysis to produce strong acids and base. Seawater alkalinity is thus enhanced with the neutralization of acid components in seawater while increasing pH (House et al., 2007; Rau et al., 2013). However, energy demand and safe disposal of by-products (e.g., chlorine gas) remain challenging (Eisaman et al., n.d.; La Plante et al., 2023).

The application of OAE in open oceans and on large-scales still faces uncertainties, particularly on the feedbacks of marine ecosystems and characterization of alkaline materials. However, coastal ecosystems (e.g., coral reefs) and upwelling zones may serve

as initial tests sites with potential use of wastewater effluent as an alkalinity delivery vector (Cai & Jiao, 2022; Feng et al., 2016).

Artificial Downwelling

Artificial downwelling (AD) enhances the export of DOC and POC by transport of CO₂-saturated cold surface waters (region of North Atlantic Deep Water) into the ocean interior, reinforcing the solubility pump (Zhou & Flynn, 2005). This technique can be integrated with artificial upwelling to mitigate the outgassing of CO₂-rich subsurface waters (Doney et al., 2025). While regional tests have explored hypoxia mitigation (Stigebrandt et al., 2015; Stigebrandt & Liljebladh, 2010), no empirical studies have assessed carbon fluxes through AD. Its efficiency as a potential mCDR pathway is still only based on model simulations. Large-scale implementation requires direct sequestration assessments, potentially through measurements of carbon export in sediment traps, gliders, and profiling floats (NASEM (National Academies of Sciences, 2022)).

Carbon Capture and storage

The fundamental concept of Carbon Capture and storage (CCS) is to capture CO₂ from industrial installations before atmospheric release and transport it in specific geological formations or in the deep-sea environment (Metz, 2005). Capture processes include post-combustion, pre-combustion, and oxyfuel combustion, followed by separation via absorption, adsorption or membrane filtration (Leung et al., 2014).

Proposed CCS approaches include (1) direct ocean injection, (2) seafloor liquid CO₂ storage, and (3) geological storage. Direct injection of CO₂ at depth leads to dissolution into carbonate and bicarbonate ions with the aim of deliberately accelerating the natural oceanic uptake of CO₂ (Marchetti, 1977). While deep-sea injection minimizes local biotic impacts at depths greater than 3 km, CO₂ dissolution may amplify ocean acidification due to the lower buffering capacity of deep waters compared to surface waters (NASEM (National Academies of Sciences, 2022)).

High abundance of natural liquid CO₂ was observed on the seabed of Taiwan and assumed to have originated from a hydrothermal field (Inagaki et al., 2006). The liquid CO₂ lake

was stabilized by a liquid CO₂/CO₂-hydrate interface. Controlled deep-sea (4 km depth) injection trials suggest limited immediate ecosystem impact (Brewer et al., 2005), but long-term acidification risks require further studies (Feely et al., 2004, GESAMP, 2019).

Geological formations such as offshore sandstone (saline aquifers and depleted oil/gas reservoirs), unconsolidated deep-sea sediments, and basalt rock formations at the seafloor can be used to store CO₂ due to the high pressures and low temperatures observed in such locations. However, appropriate porosity, thickness, and permeability of the reservoirs are needed for stable and long-term storage (Solomon et al., 2008). Offshore sandstone reservoirs, such as those utilized in the Sleipner (Norwegian sector of the North Sea) and Snøhvit (Barents Sea) projects (Vielstädte et al., 2019), offered existing infrastructures and useful geological information. In deep-sea sediments, CO₂ hydrates can form barriers at the liquid CO₂ pore water interface, which can prevent leakage (Koide et al., 1997). Sequestration of CO₂ in basaltic crust facilitates the formation of carbonate minerals in the form of stable and nontoxic divalent metal cations (Ca²⁺, Mg²⁺, Fe²⁺) with a high affinity for carbonation reactions (Goldberg et al., 2008). The feasibility of CO₂ mineral sequestration in basaltic rocks was demonstrated by a pilot project, CarbFix (Aradóttir et al., 2011).

CCS deployment necessitates robust monitoring programs for potential CO₂ leakage. A controlled release of CO₂ was conducted at the Goldeneye complex in the North Sea as a part of a European Union funded project, ‘Strategies for Environmental Monitoring of Marine Carbon Capture and Storage’ (STEMM-CCS), to simulate a leakage and test novel detection and quantification approaches (Connelly et al., 2022; Esposito et al., 2021; Flohr et al., 2021; Martínez-Cabanas et al., 2021). Following in the footsteps of basalt-CO₂-seawater interactions from the CarbFix project and technological development aspects from the STEMM-CCS project, the ‘Alternate scenarios, Innovative technologies, and Monitoring approaches for Sub-Seabed Storage of carbon dioxide’ (AIMS³) project took place as part of mCDR research cluster CDRMARE, funded by the German Government (German Ministry for Research and Education (BMBF) together with the North German states) (<https://aims3.cdrmare.de/>). The AIMS³ project explores CO₂ storage in mid-Atlantic Ridge basalt formations (MORF) at the Reykjanes Ridge, south of Iceland. Initial

field work was conducted to study the geo-physicochemical signature in the area and to set the stage for an injection pilot experiment (Kopf et al., 2024).

1.1.9 Challenges of CDR

The effectiveness of mCDR approaches in achieving long-term climate mitigation depends on multiple interdependent factors, including scientific understanding, technological readiness, large-scale deployment potential, cost effectiveness, environmental risks, carbon storage permanence and robust monitoring, reporting, and verification (MRV) frameworks. Additionally, social acceptance and governance frameworks play crucial roles in shaping implementation (Brunner et al., 2024). Practical implementation of mCDR still faces challenges associated with engineering feasibility, environmental risks, and long-term carbon stability with a current need to improve carbon cycle understanding and enhance MRV systems for sustained climate benefits (Doney et al., 2025).

1.1.10 Monitoring and development of novel sensors

Effective mCDR deployment requires accurate quantification of carbon removal efficiency, sequestration durability, and environmental impact assessment across open-ocean and coastal experiments (NASEM (National Academies of Sciences, 2022)). For CCS projects, pre-deployment baseline monitoring is also essential (Connelly et al., 2022). Boyd et al., 2023 proposed the concept of ‘Essential Ocean Variables’ (EOVs) from the Global Ocean Observing System (GOOS) to include air-sea CO₂ flux, wind speed, and other key parameters in the context of the Framework for Ocean Observation (Tanhua et al., 2019). Recently, the National Aeronautics and Space Administration (NASA) has launched its newest Earth-observing satellite, PACE (Plankton, Aerosol, Cloud, ocean Ecosystem) (<https://pace.gsfc.nasa.gov/>), and it can be used for assessing possible ecological side effects of mCDR deployments. Additionally, autonomous ocean monitoring platforms, including biogeochemical (BGC) Argo floats, gliders, uncrewed surface vehicles (USV), and autonomous underwater vehicles (AUVs) facilitate long-term high-frequency observations of ocean chemistry. These platforms could measure parameters like pH, dissolved gases such as methane and CO₂. Development of robust

sensors requires extensive innovation and long validation periods (~ 20 years) (Sastri et al., 2019). To ensure data reliability and usability, measurement interpretation must align with the FAIR (findability, accessibility, interoperability, and reuse) principles and Ocean Best Practices (OBP), with a goal "to have methods that are accepted and widely adopted across ocean exploration, operations, and practices" (Boyd et al., 2023; Hörstmann et al., 2021; Pearlman et al., 2019; Wilkinson et al., 2016).

1.1.11 Autonomous measurement of ocean carbonate system

To achieve high-resolution, near real-time monitoring of the ocean carbonate system, advancements in sensor technology are required. Autonomous pH sensors, based on a potentiometry technique with ion-sensitive field effect transistors (ISFETs) (Martz et al., 2010) and a spectrophotometry technique with pH-sensitive indicator dyes (Martz et al., 2003; Seidel et al., 2008), optical detection principle (REDFLASH technology, PyroScience GmbH Sensor Technology) are commercially available. Similarly, $p\text{CO}_2$ sensors rely on spectrophotometric or absorbance/fluorescence-based chemical techniques, as well as membrane-separated IR absorption spectrometry, to enable autonomous operation (Körtzinger et al., 1996; Martz et al., 2015b; Nakano et al., 2006). Prior to commercialization, these sensors underwent rigorous testing in the laboratory and field settings, often integrated into profiling floats stationary and mobile (Fiedler et al., 2013a; Fietzek et al., 2011; Z. P. Jiang et al., 2014; D. Pierrot et al., 2009).

Recent advancements have led to the development of automated *in-situ* TA analyzers based on (1) microfluidic with closed-cell titration (Dartmouth Ocean Technologies, DOT) (Sonnichsen et al., 2023), (2) lab-on-a-chip technology with single-point open-cell titration using optical measurement (Schaap et al., 2025), and (3) spectrophotometric technique for shallow water (Qiu, Li, et al., 2023). The Woods Hole Oceanographic Institution (WHOI) has developed an automated dissolved inorganic carbon (DIC) analyzer based on electrochemical detection (Sayles & Eck, 2009), whereas the Multiparameter Inorganic Carbon Analyzer (MICA) allowed for simultaneous measurements of pH, DIC, and $p\text{CO}_2$ using spectrophotometry (Wang et al., 2007). A refined portable version, MICA III, is more compact and cost-effective, extending its capabilities to pH, DIC, and TA measurements

(Adornato et al., 2016). Further efforts combined MICA with the Spectrophotometric Elemental Analysis System (SEAS) into a new instrument (SEAS-DIC) for autonomous *in-situ* DIC measurements in both laboratory and field applications (Liu et al., 2013).

1.1.12 Data quality standards

To ensure the reliability of carbonate system measurements, the Global Ocean Acidification Observing Network (GOA-ON) has established two data quality standards ‘climate’ and ‘weather’ quality (Newton et al., 2015a). Climate quality data support long-term assessment of anthropogenically-driven changes in hydrographic and carbon chemistry, with a required relative standard uncertainty of 1% ($\pm 2 \mu\text{mol kg}^{-1}$ for DIC measurements). Weather quality data capture short-term spatial variations to assess localized ocean acidification impacts, with a required relative standard uncertainty of 10% ($\pm 10 \mu\text{mol kg}^{-1}$ for measurements of DIC). Measurement accuracy is typically validated against Certified seawater Reference Material (CRM) prepared in the Dickson Laboratory at Scripps Institution of Oceanography (A. G. Dickson, 2010). However, inter-laboratory comparisons indicate that while most laboratories were able to achieve ‘weather’ quality data, only 25% met ‘climate’ quality standards (Bockmon & Dickson, 2015).

1.1.13 Development of autonomous DIC analyzers

Autonomous sensors play a crucial role in monitoring mCDR approaches and improve our understanding of the inorganic carbon cycle, net community metabolism, air-sea gas exchange, and carbon export processes (Seidel et al., 2008). Given the need for high spatial and temporal resolution in ocean biogeochemical studies, continuous innovation in autonomous and *in-situ* sensor technologies is imperative. While significant progress has been made in autonomous TA and DIC instruments, further refinements and integration of novel techniques remain ongoing. The concentration of DIC in seawater samples is typically determined by (i) acidification of the sample to convert all inorganic carbonate species into gaseous CO_2 , (ii) extraction of CO_2 through a gas-permeable membrane, and (iii) detection of extracted gas through various analytical methods, with the exception of Dual Isotope Dilution and Cavity Ring-Down Spectroscopy. Established techniques

include coulometric analysis, Nondispersive infrared (NDIR) technique, Spectrophotometry, Gas Chromatography, Ultraviolet (UV) absorbance spectroscopy, Isotope ratio Cavity-Ring down spectroscopy, Membrane Introduced Mass Spectrometry, and electrochemistry.

Coulometric technique

The coulometric technique is considered the “Standard Operating Procedure” to measure DIC (Andrew G. Dickson et al., 2007). Following liquid-to-gas extraction, stripped CO₂ is transported to a carrier gas stream to a titration cell, where it is titrated by the reduction of H₂O at a platinum cathode. The use of thymolphthalein as an indicator allows for the determination of the equivalence point, detected photometrically. The amount of CO₂ is proportional to the amount of current by Faraday's constant (Johnson et al., 1987; Lei & Xian-Kun, 1997; Robinson & Williams, 1991). A Multi-sample Automated Natural sample Analyzer (MANA) was developed based on this method (Natchanon et al., 2014), and it was capable of measuring seawater DIC with analytical precision and accuracy of $\pm 1.0 \mu\text{mol kg}^{-1}$ and $+ 1.2 \mu\text{mol kg}^{-1}$, respectively at a rate of 4 measurements per hour in the laboratory. The performance of MANA was compared with a commercially available Single Operator Multi-parameter Metabolic Analyzer (SOMMA). Coulometry method is the most preferred in oceanographic research as it achieves high precision ($< 1 \mu\text{mol kg}^{-1}$), although it requires large sample volumes ($\sim 0.3\text{-}1 \text{ L}$), hazardous reagents such as ethanolamine and hydroxyethyl carbamic acid, and complex protocols (A. G. Dickson & Goyet, 1994; Kaltin et al., 2005; King et al., 1985).

Non-Dispersive Infra-Red technique

In the Non-Dispersive Infra-Red (NDIR) technique, the extracted CO₂ diffuses across a microporous hydrophobic membrane via a liquid-to-gas exchange after which it passes through a dehumidifier and dryer to remove residual moisture from the carrier gas (Hales et al., 2004). The CO₂ content is determined by measuring its mole fraction in the gas phase using NDIR absorbance spectroscopy. This technique has been successfully implemented in an automated, continuous flow-through analyzer for ship-based on-site measurements with reported accuracy and precision of 0.1% ($1 \mu\text{mol kg}^{-1}$) and a measurement rate of ~ 36

s per analysis (Bandstra et al., 2006; Goyet & Snover, 1993a; Hales et al., 2004; Kaltin et al., 2005; Kanamori, 1982; Kimoto et al., 2002). Moreover, the NDIR approach has been successfully integrated into monitoring platforms. The Moored Autonomous DIC (MADIC) system achieves precisions of $\sim \pm 5 \mu\text{mol kg}^{-1}$ (Fassbender et al., 2015). Commercially available NDIR-based DIC analyzers, such as the AS-C3 (Apollo SciTech) and LI-7000 (LICOR), offer benchtop measurement capabilities with precision and accuracy better than $\pm 2.0 \mu\text{mol kg}^{-1}$ (Wang et al., 2013).

Spectrophotometry technique

The spectrophotometry technique combined with gas diffusion separation and flow injection analysis (GD-FIA) analysis relies on the complete equilibration of $p\text{CO}_2$ between an acidified seawater sample and an acceptor solution containing pH sensitive indicator dye (with known TA) across a gas-permeable membrane (Teflon AF 2400 tubing). Post equilibrium, DIC is inferred directly from changes in the indicator pH (bromocresol purple) and measured via spectrophotometric absorbance at different wavelengths (432, 589, and 700 nm) (Byrne et al., 2002; Liu et al., 2013; Wang et al., 2007, 2013, 2015). The Spectrophotometric Elemental Analysis System (SEAS)-DIC, the first automated *in-situ* DIC analyzer based on this technique, was tested in a field trial where it achieved an accuracy and precision of $\sim 2 \mu\text{mol kg}^{-1}$ with a measurement rate of approximately once per minute (Liu et al., 2013). A bench-top system, based on this method, was tested in field with a continuous flow of seawater, achieved rapid response (~ 60 s) and a precision and accuracy of $\pm 3.6 \mu\text{mol kg}^{-1}$, and $\pm 6.0 - 6.7 \mu\text{mol kg}^{-1}$, respectively (Wang et al., 2013). An improved version, incorporated a continuous flow-analysis technique to achieve precision of $2.5 \mu\text{mol kg}^{-1}$ with a sampling frequency of 45 measurements per hour using only ~ 0.5 mL of sample (Stoll et al., 2001). Additionally, direct measurement of CO_3^{2-} speciation can be performed using ultraviolet (UV) spectroscopic observations of lead Pb (II) spectra. Pb is introduced into the seawater sample to form the PbCO_3^0 complex, whose concentration varies in response to dissolved CO_3^{2-} . UV absorbances of specific wavelengths (234 and 250 nm) were used to determine CO_3^{2-} levels. This technique has demonstrated high analytical precision ($\pm 1.71 \mu\text{mol kg}^{-1}$) and accuracy ($\pm 2.03 \mu\text{mol kg}^{-1}$) in shipboard applications (Byrne & Yao, 2008; Easley et al., 2013).

Gas Chromatography (GC) technique

In this technique, extracted CO₂ is separated using a GC column after reaching equilibrium and then transferred to a stable isotope ratio mass spectrometer via an interface. A simple and inexpensive valve system was developed in combination with a commercial Varian 3400 gas chromatograph coupled to a Finnigan MAT 252 mass spectrometer via a Ni-Pt-Cu combustion reactor (gas chromatograph-combustion-isotope ratio mass spectrometer GC-C-IRMS, USA) and was used to calculate the ratio of ¹³C/¹²C ($\delta^{13}\text{C}$) and therefore DIC concentrations (precision $\sim < 10 \mu\text{mol kg}^{-1}$) (Salata et al., 2000). Originally based on methods developed by Weiss & Craig, 1973, the technique has since been refined. The modified approach used a thermal conductivity detector (TCD) and achieved a precision of $\sim \pm 3.1 \mu\text{mol kg}^{-1}$ using 12 mL of sample with an analysis time of 14.5 min per measurement (Hansen et al., 2013a).

Mass spectrometry technique

In the Underwater mass spectrometry (UMS) technique, CO₂ is diffused from the acidified sample through a gas-permeable polydimethylsiloxane (PDMS) membrane and hence analyzed by a membrane inlet mass spectrometer (MIMS) (Bell et al., 2007). The instrument is capable of measurements of DIC in the ocean's upper 2 km with a vertical resolution of ~ 1 m (Bell et al., 2011). This system has relatively high-power consumption, but it can provide simultaneous, detailed profiles of a variety of dissolved gases and volatile organic compounds (VOCs). No reports on measurement precision have been published to date.

Isotope ratio - Cavity ring-down spectroscopy (CRDS) technique

Both DIC and the isotopic ratio of ¹³C/¹²C ($\delta^{13}\text{C}$) are measured from surface seawater using this technique (K. Huang et al., 2015; Su et al., 2019). K. Huang et al., (2015) introduced the dual-isotope dilution and cavity ring-down spectroscopy (DID-CRDS) technique, where a ¹³C-labeled DIC sample is spiked into the seawater before measurement. This approach achieved a precision of $\sim \pm 0.4 \mu\text{mol kg}^{-1}$ with a sampling frequency of 4 minutes, demonstrating data quality comparable to well-established coulometric and nondispersive infrared methods. Su et al., (2019) developed an alternative approach using a CO₂

extraction device coupled with CRDS, achieving $\pm 1.5 \mu\text{mol kg}^{-1}$ precision in the laboratory and $\pm 0.7 \mu\text{mol kg}^{-1}$ precision in shipboard measurements, with a sampling time of 11 minutes. Their results were comparable in quality to high-precision isotope ratio mass spectrometry (IRMS). While both studies showed the high potential of CRDS for DIC and isotope ratio measurements, challenges remain in the development of a fully autonomous underwater sensor based on this technique.

Electrochemical technique - Conductometry technique

Electrical conductivity of a liquid solution is measured by passing an electric current through it, and it is represented as the reciprocal of electrical resistivity. Between two parallel planar electrodes, the electrical conductivity (σ in Siemens per meter, S m^{-1}) of an electrolytic solution is inversely related to the resistance of ions in a solution (R in ohms, Ω):

$$R = \left(\frac{l}{A}\right) \frac{1}{\sigma} = \frac{K}{\sigma}$$

where A is the effective cross-sectional area, l is the distance between the electrodes, and K is the cell constant, which depends on the electrode geometry and is defined as the ratio of the distance between the electrodes (l in m) and the effective area (A in m^2) of the electrodes. Depending on the selection of electrolyte solutions, different conductivity ranges can be achieved by changing electrode geometries, e.g., to achieve a low conductivity range, electrodes with low cell constant values ($\sim 0.1 \text{ cm}^{-1}$) can be used, whereas higher cell constant values ($> 1 \text{ cm}^{-1}$) are recommended for a higher conductivity range (Fouletier & Fabry, 2013).

In recent studies for developing a DIC sensor/analyzer, contactless and contacting electrode configurations have been used to develop a detection cell. In contactless electrode cells, Capacitively Coupled Contactless Conductivity Detection (C^4D) technique is utilized, where the electrodes are kept isolated. It reduces the potential of biofouling on the electrodes over time (Kubán & Hauser, 2008). It has also been commercialized by eDAQ Pty Ltd, Australia. On the other hand, the contacting electrodes offer two-, three- and four-electrode configurations with hollow tubes. The basic design contains a working (W),

working sense (WS), counter (C), and reference (R) port (Gamry Instruments, USA). The operational principle is based on providing alternating/direct current to one electrode (connecting W/C port) and measuring the change in voltage change from the C/R port. In two-electrode configuration, W and WS ports are connected to one electrode, whereas R and C ports are connected to a second electrode. In this setup, S port measures the complete voltage dropped by the current across the whole electrochemical cell: W/WS, electrolyte solution, and C/R. In three-electrode setup, R is separated and placed between W/WS and C ports. The R port ensures a stable reference potential, allowing for better control over the potential at W port and hence minimizes polarization effects on W port (Harris et al., 2023). In a four-electrode system, WS is also decoupled from W port, and hence the outer two electrodes receive current, whereas the inner two electrodes measure output voltage. This configuration offers higher measurement ranges and stable measurement over time, as the inner electrode prevents ion accumulation at the electrodes due to its high impedance.

Conductometric technique has been widely used due to its low detection limits, high selectivity, and ability to quantify small charged species. In this technique, CO₂ diffuses through an acidified seawater sample via liquid-to-liquid gas extraction across a gas-permeable membrane. The membrane separates the sample from an acceptor solution either ultrapure deionized water or an alkaline solution like NaOH, where CO₂ dissociates into H⁺, HCO₃⁻, and CO₃²⁻ ions. The resulting changes in conductivity of the acceptor solution are detected in conductivity cells, and the response is directly proportional to the concentration of DIC in the sample (Hall & Aller, 1992). To achieve this, electrochemical detection cell is hence combined with gas diffusion flow injection analysis (GD-SIA). Over time, significant advancements have been made to enhance sensor stability and measurement accuracy (Aoki et al., 1993a; Bresnahan & Martz, 2018; Carlson, 1978; Hoherčáková & Opekar, 2005; Martinotti et al., 2012; Monk, 2020a; Monser et al., 2004a; Pencharee et al., 2012; Sayles & Eck, 2009; Tweedie, MacQuart, et al., 2020). To address the issue of electrode fouling, contactless electrode systems have also been developed (Hoherčáková & Opekar, 2005), and different contacting electrode configurations, including two-, three-, and four-electrode systems, have been tested to improve accuracy and reliability of conductivity-based DIC measurements (Bhattacharya et al., 2024; Martinotti et al., 2012; Monk, 2020a; Sayles & Eck, 2009).

The advantage of using this technique is that the design of the electrodes is inherently simple and can be easily modified to enhance performance. It requires low power, inexpensive materials, and no toxic reagents are used (Hall & Aller, 1992). However, a key limitation of this technique is that the conductivity cell is highly sensitive to temperature fluctuations and susceptible to measurement drift over time. These challenges require careful sensor design to ensure appropriate temperature compensation procedures and long-term stability.

1.1.14 Thesis motivation

Recent research highlights the ongoing development of DIC sensors and indicates the necessity of autonomously achieving high-precision and high-accuracy data for comprehensive characterization of the oceanic carbonate system. At present, no commercially available *in-situ* DIC sensor exists. Development of such a sensor with autonomous technologies capable of providing reliable, high-resolution DIC measurements will facilitate the understanding of oceanic carbonate chemistry. This motivates to develop an autonomous *in-situ* DIC sensor capable of producing precise and accurate datasets.

The objective of this thesis is to design and develop a novel, cost-effective, autonomous, *in-situ* DIC sensor based on electrochemical detection, specifically, conductometric technique, to obtain high-quality DIC data. The research is within the framework of the AIMS³ project, which includes the development of cost-effective sensors (pH, optical $p\text{CO}_2$, and electrochemical DIC) and innovative autonomous platforms. A key goal of the work package is to enhance our ability to identify, detect, and quantify carbonate speciation within the water column, particularly in response to potential CO_2 leakages in the deep ocean at CCS sites. While the aim is to design sensors for deep-sea applications, these new sensors can also be used to study the spatial and temporal variability of carbonate dynamics in shallower waters in order to contribute to a better understanding of ocean acidification and biogeochemical processes.

1.1.15 Thesis overview

The focus of the thesis is to develop an autonomous, cost-effective DIC sensor capable of measuring DIC in deep seawater (potential CO₂ leakages at CCS sites) with high precision and accuracy. The proposed conductivity-based DIC analyzer/sensor is based on a similar principle as described previously, i.e., sample is first acidified to convert all inorganic carbonate and bicarbonate species into gaseous CO₂, and the CO₂ is then diffused through a gas-permeable membrane into an alkaline solution, where the change in conductivity is measured. This change is directly proportional to the DIC concentration. The development stages of this sensor went through a few basic steps, e.g., (1) laboratory test to develop a benchtop system - (a) optimization of components and hence design of a working prototype which fulfills basic functionality, (b) development of a working protocol, (c) establishing dependence of DIC and basic environmental parameters, e.g., temperature, salinity on measurements, and (d) develop an underwater version (shallow and deep water) with a more compact design based on the benchtop system and test its functionality, (2) field test - (a) testing the benchtop and underwater system for certain period to develop robust data processing method, (b) compare measured DIC data with other commercial inorganic carbonate sensors' data to establish credibility of the analyzer's measurement.

Chapter 1 is the introduction of the thesis.

Chapter 2 describes the development and laboratory optimization of a bench-top prototype automated DIC analyzer. The study primarily investigates the effect of temperature and salinity on NaOH conductivity and CO₂ gas diffusion. Optimization experiments were conducted with respect to (1) chemical parameters, e.g., gas exchange time and reagents consumption, acid types and their concentrations, and (2) physical parameters, e.g., pump flow rate, length of GEU, and membrane types. These experiments helped to establish a measurement protocol and data processing technique. Additionally, the analyzer's operational robustness and performance were evaluated in the Baltic Sea during a field campaign. This chapter has been published *Analytica Chimica Acta*:

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Chapter 3 presents results from two field tests conducted in the Kiel Fjord and the North Sea of the benchtop prototype DIC analyzer alongside commercial sensors. The chapter provides a detailed statistical analysis of the measured DIC variations in relation to other environmental parameters. This work is in preparation for submission.

Chapter 4 discusses the development and laboratory optimization of an automated *in-situ* DIC sensor, adapted from the benchtop version but with fluidic pathways and components redesigned for compactness. The sensor was successfully deployed in the Baltic Sea and the Kiel Fjord with the data used to refine temperature compensation algorithms for improved data processing. The results were further compared with discrete samples and commercial sensors to validate its performance. The work is in preparation for submission.

Chapter 5 presents a comprehensive summary of the key findings from this study and offers recommendations for future research with a focus on potential improvements and applications of the developed DIC sensor.

2. Development of an Autonomous On-Site Dissolved Inorganic Carbon Analyzer using Conductometric Detection

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Abstract

Background: The increase in anthropogenic CO₂ concentrations in the Earth's atmosphere since the industrial revolution has resulted in an increased uptake of CO₂ by the oceans, leading to ocean acidification. Dissolved Inorganic Carbon (DIC) is one of the key variables to characterize the seawater carbonate system. High quality DIC observations at a high spatial-temporal resolution is required to improve our understanding of the marine carbonate system. To meet the requirements, autonomous DIC analyzers are needed which offer a high sampling frequency, are cost-effective and have a low reagent and power consumption.

Results: We present the development and validation of a novel analyzer for autonomous measurements of DIC in seawater using conductometric detection. The analyzer employs a gas diffusion sequential injection approach in a “Tube In A Tube” configuration that facilitates diffusion of gaseous CO₂ from an acidified sample through a gas permeable membrane into a stream of an alkaline solution. The change in conductivity in the alkaline medium is proportional to the DIC concentration of the sample and is measured using a detection cell constructed of 4 hollow brass electrodes. Physical and chemical optimizations of the analyzer yielded a sampling frequency of 4 samples h⁻¹ using sub mL reagent volumes for each measurement. Temperature and salinity effects on DIC measurements were mathematically corrected to increase accuracy. Analytical precision of $\pm 4.9 \mu\text{mol kg}^{-1}$ and $\pm 9.7 \mu\text{mol kg}^{-1}$ were achieved from measurements of a DIC reference material in the laboratory and during a field deployment in the southwest Baltic Sea, respectively.

Significance: This study describes a simple, cost-effective, autonomous, on-site benchtop DIC analyzer capable of measuring DIC in seawater at a high temporal resolution as a step towards an underwater DIC sensor. The analyzer is able to measure a wide range of DIC concentrations in both fresh and marine waters. The achieved accuracy and precision offer an excellent opportunity to employ the analyzer for ocean acidification studies and CO₂ leakage detection in the context of Carbon Capture and Storage operations.

2.1 Introduction

Anthropogenic activities including fossil fuel combustion, deforestation and cement production have resulted in an increase of carbon dioxide (CO_2) concentrations in the Earth's atmosphere. The oceans have taken up about 39 % of the excess carbon from the atmosphere over the past two centuries (Ridge & McKinley, 2021; Sabine & Tanhua, 2009; Zeebe et al., 2008) leading to a change in the chemical balance in seawater that is referred to as 'ocean acidification'. Ocean uptake of CO_2 decreases seawater pH while increasing bicarbonate (HCO_3^-) and decreasing carbonate (CO_3^{2-}) concentrations. This change in the carbonate system reduces the ocean's capacity to absorb future emissions of anthropogenic CO_2 (Doney, 2010). To characterize the seawater carbonate system, measurements of at least two of the four primary variables (i.e., pH, partial pressure of CO_2 ($p\text{CO}_2$), Total Alkalinity (TA) and dissolved inorganic carbon (DIC)) along with temperature, salinity and macronutrients are required to allow the calculation of the others. Dissolved inorganic carbon is defined as the sum of all of the inorganic carbon species in a solution, which include HCO_3^- , CO_3^{2-} and undissociated carbonic acid (H_2CO_3) (A. G. Dickson et al., 2007; Easley et al., 2013). Furthermore, DIC is one of the most preferred variables as it is more sensitive towards the changes in carbonate chemistry caused by photosynthesis and respiration (Fassbender et al., 2015) and does not explicitly depend on pressure and temperature (when expressed as $\mu\text{mol kg}^{-1}$) (Bresnahan & Martz, 2018). In order to improve our understanding of the marine carbonate system, high quality and high spatial-temporal resolution observations of DIC are required. This is providing a demand for the development and application of low-cost autonomous analyzers with a low reagent and power consumption.

Laboratory analysis of DIC in seawater is commonly performed in three steps: (i) acidification of the sample to convert all carbonate species into gaseous CO_2 ; (ii) extraction of CO_2 from the seawater matrix; (iii) detection of the extracted CO_2 by e.g., coulometry, nondispersive infrared (NDIR) spectrophotometry, gas chromatography, ultraviolet absorbance spectroscopy, dual isotope dilution and cavity-ring down spectroscopy, membrane introduced mass spectrometry and electrochemical detection (Goyet & Snover, 1993b; Miró et al., 2003).

An autonomous instrument has been reported (Natchanon et al., 2014) for the coulometric analysis of DIC in seawater with an analytical precision of $\pm 1.0 \mu\text{mol kg}^{-1}$ and a reported bias for Certified Reference Material (CRM) of $1.2 \mu\text{mol kg}^{-1}$. The system operated semi-automatically, but required relatively large sample volume ($\sim 0.3\text{-}1 \text{ L}$) and used hazardous chemicals (ethanolamine and thymolphthalein) (Natchanon et al., 2014). The NDIR approach was employed for *in-situ* DIC monitoring on a mooring (Moored Autonomous DIC (MADIC)), achieving a precision of $\sim \pm 5.0 \mu\text{mol kg}^{-1}$ (Fassbender et al., 2015). A Multiparameter Inorganic Carbon Analyzer (MICA) capable of simultaneous spectrophotometric measurements of pH, DIC, and atmospheric and dissolved $p\text{CO}_2$ was reported with a precision and accuracy for DIC of $\pm 2.4 \mu\text{mol kg}^{-1}$ and $2.2 \pm 6 \mu\text{mol kg}^{-1}$, respectively (Wang et al., 2007). Whilst these techniques offer valuable capabilities for *in-situ* DIC monitoring, they have some potential limitations. For example, the NDIR (MADIC) system is sensitive to calibration conditions (e.g., temperature and pressure), and interferences from other gases (e.g., methane) can lead to inaccuracies. The MICA has a relatively long response time (7 samples h^{-1}) and the multiparameter measurement can introduce complexity in resolving interferences between different components. In general, these instruments are expensive to acquire and maintain, and they may face challenges during deployment and recovery from e.g. moorings under harsh weather environments.

In the recent years, measurements of DIC using electrochemistry have gained popularity due to the low maintenance, inexpensive components, use of non-toxic reagents, low power and reagent consumption and potential for miniaturization (Table 2.1). In particular, the combination of conductometric techniques with gas diffusion sequential injection analysis (GD-SIA) has been explored. Workers have investigated various aspects of GD-SIA, including design, gas diffusion membrane properties and geometric configurations (Bresnahan & Martz, 2018) (Tweedie et al., 2019; Tweedie, MacQuart, et al., 2020; Tweedie, Sun, et al., 2020). The two most widely used gas exchange units (GEU) geometries are planar and cylindrical (Bresnahan & Martz, 2018) (Aoki et al., 1993b; Byrne et al., 2002; Martinotti et al., 2012; Monk, 2020b; Pencharee et al., 2012; Sayles & Eck, 2009). Cylindrical GEUs, characterized by high aspect ratios and larger contact surface areas for reagents, are known to be robust and resilient and offer a simpler design compared to planar GEUs.

In conductometric detection, the most commonly used techniques involve (i) contactless capacitively coupled conductivity detectors (C⁴D) (Bresnahan & Martz, 2018; Hoherčáková & Opekar, 2005; Monk, 2020b; Pencharee et al., 2012; Yan et al., 2020) and (ii) contacting electrode cells (Aoki et al., 1993b; Carlson, 1978; Henríquez et al., 2014; Martinotti et al., 2012; Monser et al., 2004b; Sayles & Eck, 2009). The contacting electrode systems with two or four-electrode configurations can be used to measure the conductivity of a liquid sample. A two-electrode system offers a simple design as the applied Alternating Current (AC) and the measurement of the potential difference take place using the same electrodes. The measured resistance also includes the electrode interface impedance that has to be considered for accurate determination of the conductivity. As the same pair of electrodes is used for voltage drive and measurements, the actual area of the electrode is unknown and its tendency for coating can potentially affect the sensitivity of the measurements over time. In a four-electrode system, AC is applied to the outer pair of electrodes, and the resulting voltage is measured across the inner pair of electrodes. The separation of current-inducing and voltage-measuring electrodes allows for a constant and potentially increased electrode area and almost completely eliminates the influence of cable resistance. As a consequence, the impedance is reduced and the dependence on the electrical double layer is substantially minimized, and hence the impact on the actual conductivity measurement of a solution is lower compared to the two-electrode systems (Ishai et al., 2013; Kaidaorva et al., 2019). The stability and sensitivity of conductivity measurements is greatly improved in four-electrode configurations compared to the conventional two-electrode design. Moreover, as measurements indicate actual conductivity independent of electrode conditions, the physical design of the four-electrode configurations allows for measurements with higher accuracy over a greater range of conductivity (Brown, 1974; Ginzkey, 1977; Gong et al., 2008; Justin et al., 2011; Thirstrup & Deleebeeck, 2021). Studies have shown that the four-electrode system is mostly useful in the low-frequency range (100 Hz - 20 kHz), whereas the two-electrode cell performs better in the higher frequency range (12-100 MHz) (Chang et al., 2008). However, in practical applications, the fabrication of high-frequency components requires complicated integrated circuit designs, frequent tuning, and the system is prone to electrical interference noise (Kaidaorva et al., 2019). The four-electrode cell is susceptible to proximity effects,

i.e. the external current fluctuations are induced by any nearby conducting objects, but this effect can be eliminated through the use of a special electrode configuration (X. Huang et al., 2011). Additionally, in the context of dielectric spectroscopy applications, the four-electrode system is susceptible to electrode polarization and requires additional approaches to eliminate the interfering impedance associated with potential-sensing electrodes (Ishai et al., 2013; Mazzeo & Flewitt, 2007). In our study, we have not observed disadvantages with the four-electrode system that can compromise the precision and accuracy of DIC measurements, but assessment of long-term electrode performance will be required.

Different electrode materials have been evaluated for conductivity cells (Aoki et al., 1993b; Carlson, 1978; Martinotti et al., 2012; Monser et al., 2004b; Sayles & Eck, 2009) (Table 2.1), with gold (Au) and platinum (Pt) and stainless-steel electrodes considered to be the most stable electrodes over a long time of use. As these electrodes are expensive, evaluation of the performance of more cost-effective electrodes, including brass is desirable.

Among conductometric DIC analyzers, the Robotic Analyzer for the TCO₂ System (RATS) achieved a precision of ± 2.7 in the laboratory and $\pm 3.6 \mu\text{mol kg}^{-1}$ during *in-situ* measurements, with a relatively low sampling frequency and high reagent and sample consumption (Table 2.1) (Sayles & Eck, 2009). The use of solenoid micro-pumps and a C-cell (Tubino's electrode) design, reduced sample and reagent consumption for a system that allowed measurements of 15 DIC samples hr^{-1} with a precision of 0.7 % (RSD) (Henríquez et al., 2014). Further progress in gas-diffusion flow analysis in conjunction with electrical conductivity was undertaken in the development of an underway system for DIC determination in estuarine waters where a precision of 0.56 % (RSD) and a sampling frequency of 12 samples hr^{-1} were achieved with only 100 μL of sample for each measurement (Yan et al., 2020).

Table 2.1. Overview of DIC analyzers based on conductometric technique

Technique	Electrode design	Membrane type	Range ($\mu\text{mol kg}^{-1}$)	Precision (0.5 % RSD ~ 10 $\mu\text{mol kg}^{-1}$)	Accuracy ($\mu\text{mol kg}^{-1}$)	Samples hr^{-1}	Reagent Consumption	Stage	Ref.
2-electrode	Gold	PTFE ^(a)	1750-5000	10 % RSD	3.3 %	8	500 μL HCl ^(b) , 7.5mL Ultrapure water, 500 μL sample	Shipboard measurement	(Martino et al., 2012)
	Stainless steel	PTFE	50-5000	>1 % RSD	-	*2 min Gas exchange	H ₂ SO ₄ ^(c) and NaOH ^(d)	Lab test	(Aoki et al., 1993b)
3-electrode	Platinum	Teflon AF2400		$\sim \pm 2.7\text{-}3.6 \mu\text{mol kg}^{-1}$ or $\sim 0.1 \%$ RSD	$\pm 1 \mu\text{mol kg}^{-1}$	~ 1	4.7mL H ₃ PO ₄ ^(e) , 3.8mL NaOH, 2.5mL sample	On mooring	(Sayles & Eck, 2009)
	Tungsten Oxide	PTFE	$\sim 50\text{-}1000$	RSD 1.42 %	-	30	HCl, Sodium Acetate, 200 μL sample	Lab test	(Monser et al., 2004b)
	C-cell (Tubino's electrode)	Flon LACHAT membrane	80-9000	RSD 0.7 %	-	15	H ₂ SO ₄ and NaOH, 0.99 mL sample	Lab test	(Henríquez et al., 2014)
	Commercial	Teflon AF2400	200-10000	RSD 0.56 %	$\sim 2\text{-}8 \mu\text{mol kg}^{-1}$	12	H ₂ SO ₄ and NaOH, 100 μL sample	Under way	(Yan et al., 2020)
C ⁴ D	Ti/Au deposition on PMMA ^(f) Microfluidic design	50 μm PDMS ^(g)	1000-3000	$\sim \pm 5 \mu\text{mol kg}^{-1}$ or 0.25 % RSD	-	*15 min Gas exchange	Total 500 μL	Lab test	(Tweedie, Sun, et al., 2020)
	eDAQ ET127 detector	Teflon/PTFE	-	$\sim \pm 2 \mu\text{mol kg}^{-1}$ or 0.1 % RSD	-	* 8.3min Gas exchange	100 μL sample, <100 μL acid, $\sim 750 \mu\text{L}$ NaOH	Lab test	(Bresnahan & Martz, 2018)
	Brass electrode	Accurel microporous membrane	200-2000	$< \pm 10 \mu\text{mol kg}^{-1}$ or 0.32 % RSD	-	90	H ₂ SO ₄ and NaOH (also Ultrapure water)	Under way	(Penchar et al., 2012)
	Copper electrode	Silicone	10-1000	RSD 4-7 %	-	15	H ₂ SO ₄ and Tris (pH 9.5)	Lab test	(Hoherčáková & Opekar, 2005)

4-electrode	Brass electrode	Teflon AF2400	500-3000	$\pm 4.9 \mu\text{mol kg}^{-1}$ and $\pm 9.7 \mu\text{mol kg}^{-1}$ (lab and field respectively)	$\pm 1 \mu\text{mol kg}^{-1}$	4	H ₃ PO ₄ and NaOH	On-site	Current study
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^(a) Polytetrafluoroethylene, ^(b) Hydrochloric acid, ^(c) Sulphuric acid, ^(d) Sodium Hydroxide, ^(e) Phosphoric acid, ^(f) Titanium/ Gold deposition on Polymethyl methacrylate material, ^(g) Polydimethylsiloxane, *exact information about Samples hr⁻¹ was not available

In this study, we developed an autonomous on-site analyzer for DIC determination in seawater. For the detection cell, we used a 4-contacting electrode configuration that, to our knowledge, has not been reported before for conductometric DIC measurements in seawater. Additionally, we explored the use of electrodes made of a cost-effective material (brass) with a performance comparable to reported electrode systems using more expensive electrode materials e.g., Pt and Au. The use of brass considerably reduces the cost of the DIC analyzer (Martinotti et al., 2012; Sayles & Eck, 2009). Moreover, the configuration of the fluidics was designed to facilitate a reduced gas exchange time and increased sampling frequency. As an advantage, our new setup has a lower reagent consumption (0.2 mL of H₃PO₄ and 0.75 mL of NaOH for each measurement) compared to reported conductometric DIC analyzers (Martinotti et al., 2012; Sayles & Eck, 2009).

The performance of the novel electrode design in combination with the new GD-SIA setup was evaluated. The effects of temperature and salinity on the conductivity measurements were assessed and mathematical corrections were derived from laboratory-based analyses. Optimization experiments were conducted under controlled laboratory settings, while operational robustness and analyzer performance were evaluated in the Baltic Sea during a field campaign.

2.2 Materials and methods

2.2.1 Reagents and solutions

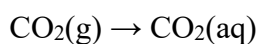
All chemical solutions were prepared with analytical grade reagents. High purity water (Milli-Q, 18.2 M Ω .cm, Millipore) was used in all experiments. A stock solution of DIC (0.1 M) was prepared by dissolving 0.53 g of sodium carbonate (Na₂CO₃, Honeywell

FlukaTM, Germany) and 0.42 g of sodium bicarbonate (NaHCO₃, Carl Roth) salts in 100 mL of high purity water. A working DIC standard solution (2000 µmol kg⁻¹) was prepared by dilution of the stock solution in high purity water. A stock saline solution of 0.7 M ionic strength was prepared by addition of 35 g sodium chloride (NaCl, Merck) to 1 L of high purity water. Subsequent diluted saline samples (salinity 5, 10, 15, 20, 25, 30) were prepared by serial dilution of the stock solution and its salinity was measured by Conductivity Meter (WTW LF 340, with probe TetraCon 523, Germany) in terms of g L⁻¹. A 10 % phosphoric acid (H₃PO₄) solution was prepared by dilution of 85 % ortho-H₃PO₄ (Carl Roth) in high purity water. A stock solution of 0.25 M sodium hydroxide (NaOH) was prepared by dissolution of 2.49 g NaOH (Merck) in 250 mL of high purity water. The working NaOH solution (7mmol L⁻¹) and a range of additional NaOH solutions (3, 4, 7, 10, 15, 18, 20 mmol L⁻¹) were obtained by dilutions in high purity water.

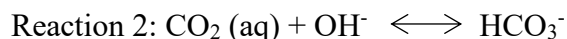
Measurements accuracy was determined by analysis of a batch of GEOMAR in-house DIC reference material (RM) with a concentration of $1985 \pm 1.1 \text{ } \mu\text{mol kg}^{-1}$ (<https://www.icos-otc.org/node/183>).

2.2.2 Analytical principle

The analyzer utilizes a liquid-to-liquid extraction technique where CO₂ from an acidified sample diffuses through a gas permeable membrane into an aqueous alkaline NaOH solution. The activity of CO₂ within seawater samples, whether in a natural state or after acidification, is higher than that of the acceptor alkaline solution (Denbigh, 1981). This difference in activity facilitates a quantitative exchange of CO₂ across the membrane (Sayles & Eck, 2009). The partial pressure gradient is directly proportional to the concentration of CO₂ present in the seawater sample (Martinotti et al., 2012). The subsequent chemisorption of CO₂ in NaOH, follows a two-step reaction process in the high pH range (Darmana et al., 2007; Sayles & Eck, 2009). At first, CO₂ gas is physically absorbed in water as aqueous CO₂:



Subsequently, aqueous CO₂ reacts with hydroxide ions (OH⁻) of the alkaline solution and produces HCO₃⁻ and CO₃²⁻:



Reaction 1 dominates at the initial stage in the high pH range, increasing the CO₃²⁻ concentration compared to that of HCO₃⁻ (Miró et al., 2003). On the other hand, OH⁻ decreases rapidly via reactions (1) and (2) with a concomitant decrease in pH. In the next step, OH⁻ is further consumed to produce HCO₃⁻ in the low pH range.

The molar equivalent conductivity of OH⁻ at 25 °C is 198.3 S cm² equiv⁻¹, and of CO₃²⁻ is 69.3 S cm² equiv⁻¹ and HCO₃⁻ 44.5 S cm² equiv⁻¹ (R. A. Robinson & Stokes, 2012). Hence, in the subsequent chemical reactions, the conductivity decreases. Reaction 1 dominates when the DIC concentration is ≤ 2800 μmol kg⁻¹, resulting in the most substantial reduction in conductivity (~300 S cm² equiv⁻¹). Moreover, reaction 1 exhibits the fastest reaction rate, facilitating the maximum absorption of CO₂ (M. Yoo et al., 2013). At DIC concentrations exceeding 3000 μmol kg⁻¹, reaction 2 becomes gradually more dominant, leading to a subsequent decrease in the sensitivity of the CO₂ addition to the alkaline solution and ultimately resulting in a non-linear relationship between the sample DIC concentration and conductivity of the alkaline solution (Sayles & Eck, 2009).

The measurement of electrical conductivity of the NaOH solution was conducted by employing a linear set-up with 4 hollow cylindrical brass electrodes. The lengths of the electrodes are equal and they are placed equidistant. The operational principle is based on the utilization of the two outer electrodes as an AC source and the inner pair to measure the voltage. Before and after the reaction with CO₂, the NaOH solution is pumped through the electrodes producing a change in voltage across the electrodes proportional to the amount of CO₂. In this study, the change in voltage was reported as conductivity. The electrical conductivity (σ in Siemens per meter, S m⁻¹) of an electrolytic solution is inversely related to the resistance of ions in a solution (R in ohms, Ω) between two parallel planar electrodes:

Chapter 2

$$R = \left(\frac{l}{A}\right) \frac{1}{\sigma} = \frac{K}{\sigma}$$

where A is the effective cross-sectional area, l is the distance between the electrodes and K is the cell constant which depends on the electrode geometry and is defined as the ratio of the distance between the electrodes (l in m) and the effective area (A in m²) of the electrodes. The conductivity range depends on K, hence different electrode geometries would allow to achieve a different conductivity resolution. For measuring a low range of conductivity, electrodes with low cell constant values ($\sim 0.1 \text{ cm}^{-1}$) can be used, whereas higher cell constant values ($> 1 \text{ cm}^{-1}$) are recommended for a higher conductivity range (Fouletier & Fabry, 2013). For conductivity cells with more than two electrodes, an integral formula is used (Ashokan et al., 2023)

$$R = \int_0^l \frac{l}{A(l)} \frac{1}{\sigma} dl$$

The cell constant cannot be accurately calculated only from the cell geometry, as the electric field between electrodes is non-uniform. Therefore, the cell constant can be deduced from the cell calibration procedure with cell resistance and electrical conductivity values.

In this study, the conductivity value is obtained from a polynomial relationship:

$$\text{Conductivity (in mS cm}^{-1}\text{)} = \sum_{i=0}^5 a_i \times X$$

where $a(i)$ are the calibration coefficients and X is the device digital output.

Calibration coefficients:

$$a(0) = -1.8258$$

$$a(1) = 2.5042 \times 10^{-5}$$

$$a(2) = -2.5087 \times 10^{-11}$$

$$a(3) = 3.7187 \times 10^{-17}.$$

2.2.3 Apparatus and experimental set-up

2.2.3.1 System overview

The DIC analyzer consisted of primarily three components, i.e., (i) a SIA system, (ii) a GEU, and (iii) a conductivity detector. A schematic block diagram showing the fluidic arrangement of the analyzer is shown in Figure 2.1.

2.2.3.2 GD-SIA system

A programmable bidirectional syringe pump (Cavro pump XCalibur, Tecan system, Switzerland) was used to propel variable amounts of sample and reagents through the components of the SIA system. The pump consisted of a gastight 2.5 mL syringe (Hamilton, USA) coupled with a stepper motor with volumetric precision of 0.05 %. The pump was connected to a 3-port (V1) and a 9-port (V2) distribution valves to selectively withdraw samples (RM or calibration standards) and reagents (NaOH and H₃PO₄) with predefined quantities. All the solutions were drawn and not pushed through the system by the syringe pump, avoiding the need for separate pumps dedicated to individual reagents (Sayles & Eck, 2009) . As the syringe served as a waste container, it minimized the risk of cross-contamination from previous sample or reagent. Designated ports in V2 were selected to draw sample and acid into a mixing loop (200 μ L, PEEK tubing: OD $\times$ ID 0.06'' $\times$ 0.03''). The mixed acidified sample was carried into the GEU to allow diffusion of CO₂ into the NaOH solution. The system was fully automated and controlled by a script written in Python (version 3.9). The power to the pumps and the valves was supplied by a power supply (TTI-Thurlby Thandar Instruments, EL302Tv, Triple output linear bench power supply) (24V DC, 1.5 amp) and connected to the computer via a DA-15 connector and an RS-232 serial interface. Python package pyserial v.3.5 was used to access the serial ports.

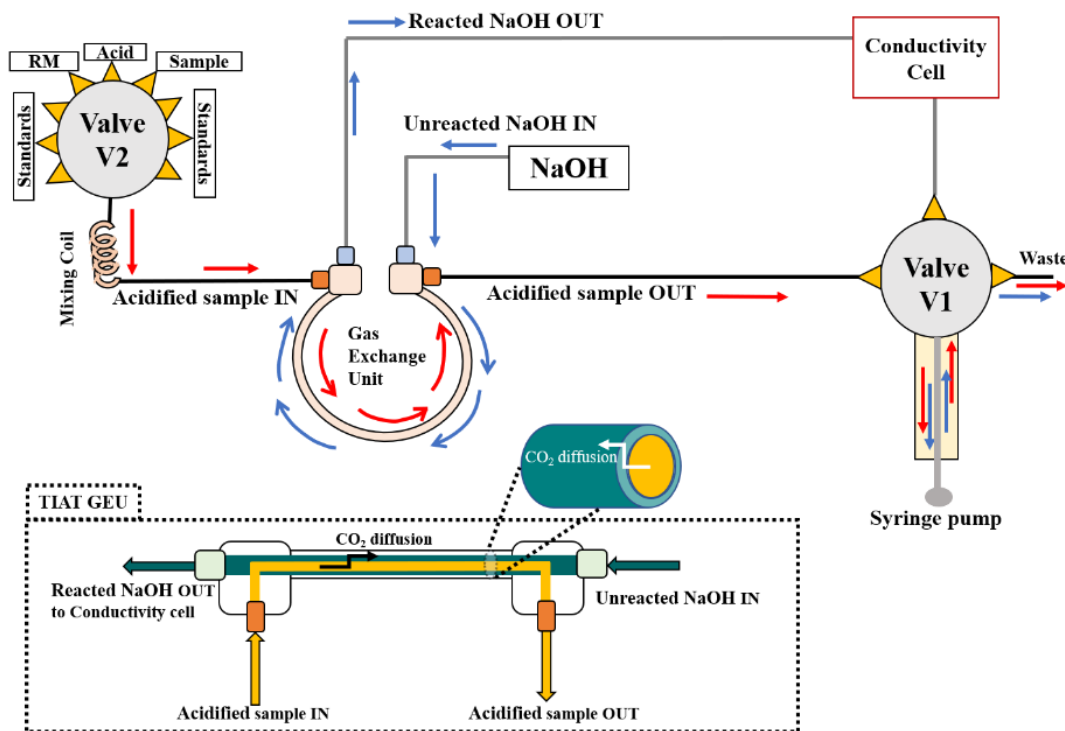


Figure 2.1. Schematic of the DIC analyzer, including Tube in a Tube gas exchange unit (TIAT GEU), Reference Material (RM), Sodium Hydroxide (NaOH), 9-port valve (V2) and 3-port valve (V1).

2.2.3.3 Gas Exchange Unit (GEU)

Two different cylindrical units for gas exchange were tested, (i) a custom-made TIAT GEU and (ii) commercial GEU (polydimethylsiloxane (PDMS) XA-10: PermSelect® 10 cm. sq. Tinymodule, USA). The custom-made TIAT GEU consisted of an outer polyetheretherketone tube (PEEK tube: O.D. $\times$ I.D. 1/16'' $\times$ 0.04'') and an inner gas-permeable amorphous fluoropolymer tube (Teflon AF-2400 tubing, Biogeneral, USA; O.D. $\times$ I.D. 0.029'' $\times$ 0.024'') with a wall thickness of 63.5 μm . Teflon AF2400 is widely used as a gas-permeable membrane due to its high CO_2 gas permeability (280,000 centi-Barrer), which is two orders of magnitude higher than that of polytetrafluoroethylene (PTFE), allowing faster gas exchange time and a higher sampling frequency (Nakano et al., 2006; Smart et al., 1995). The PTFE membrane is porous in structure with a higher possibility (10-10000 fold higher) of ion leakage compared to PDMS. This phenomenon masks the conductivity measurement regarding CO_2 transfer, making PTFE unsuitable as a gas permeable membrane for seawater measurements (Tweedie et al., 2019). Moreover,

PTFE membranes are susceptible to membrane rupture under high pressure, potentially leading to measurement failure. Whilst PDMS is a widely used gas-separation membrane, its water permeability is 1-2 orders of magnitude higher than CO₂ which can lead to deviations in conductimetric measurements (De Jong et al., 2006). Teflon AF2400 consists of a superhydrophobic material, and has 6-fold higher gas permeance capability than PDMS and has a high tendency to form uniform thin films (M. J. Yoo et al., 2018). Teflon AF2400 is a non-conductive material and is specifically designed for low ion permeability. Therefore, Teflon AF 2400 has been widely chosen as a gas permeable membrane for DIC analyzers, as it minimizes interferences caused by the ionic composition of the sample. Teflon AF2400 exhibits a weak negative dependence on temperature and a high chemical resistance (Pinnau & Toy, 1996), making it suitable for long-term use. Three different lengths of TIAT GEUs were evaluated: 10 cm, 30 cm, and 90 cm.

The Teflon AF2400 tube was fixed inside the PEEK outer tube with PEEK Nuts (Super Flangeless™ Nut, Standard Knurl, Natural PEEK, 1/16" OD Tubing, 5/16-24 Flat Bottom) and blue ferrules (Flangeless Ferrule, Blue ETFE, 1/16 " OD Tubing, 1/4-28 Flat-Bottom; 1/EA) through PEEK Tees (Cole Parmer, IDEX Low-Pressure, 0.050 " Bore, 1/8 " OD Tubing, 1/4-28 Flat Bottom) from two opposite ends. The inlet and outlet connection Tees were connected to the valves. The schematic of the GEU is shown in Figure 2.2. In general, the fabrication of cylindrical GEUs is simpler than that of planar GEUs and the use of HPLC fittings provides a complete enclosure of the membrane (Bresnahan & Martz, 2018; Monk, 2020b). The outer PEEK tube was used for the NaOH solution, whereas the inner Teflon AF2400 tube was used for the acid-sample mixture.

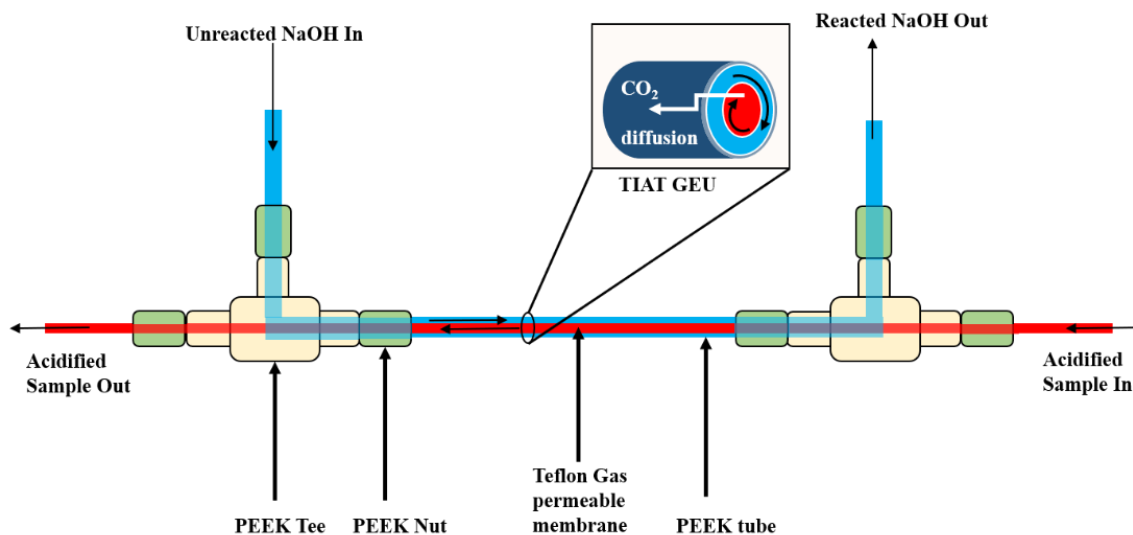


Figure 2.2. Schematic diagram of Gas Exchange Unit (GEU), with Polyether Ether Ketone (PEEK) parts.

In the commercial GEU module, 32 hollow gas permeable silicone membranes were configured in a hollow fiber yielding a surface area of 10 cm². The reported CO₂ permeability coefficient of silicone is 3250 Barrer, which is ~ 13.8 % higher than Teflon AF2400. The geometric details of all the GEUs and the volumes of each TIAT used in this study are mentioned in Table S2.1.

2.2.3.4 Conductivity cell: Contacting 4-electrode configuration

A custom-designed 4-electrode cell (Sea & Sun Technology GmbH, Germany) was used (Figure 2.3). The cell consisted of four hollow cylindrical brass electrodes of equal lengths (Albion Alloys Precision metals, UK, 20 mm long, O.D. × I.D. 0.5 mm × 0.3 mm) connected in-series and equi-spaced by Tygon tubing (AltecTM; orange/green; I.D. 0.38 mm, space between two electrodes: ~ 1 mm). The four terminals were located in symmetrical positions across the center of the cell with the two outer terminals used as an AC source and the two inner terminals as voltage measurement electrodes to ensure a uniform electric field between terminals (Ramos et al., 2008). The conductivity cell configuration was fixed in epoxy resin for structural support. A Negative Temperature Coefficient (NTC) Temperature was integrated through a PEEK tee at the inlet of the

conductivity cell and used to record the temperature of the NaOH solution prior to conductivity measurements. The internal volume of the electrode system was 6 μL .

The peak-to-peak voltage on the cell was 2.5 V, and the frequency 1 KHz. Applying a voltage of 2.5 V produced a current of 0.24 mA. The cell constant is a physical quantity of the cell and was between 1 and 2 mm^{-1} . To develop the detection cell, the cell constant was empirically tuned to the electronics. The cell was calibrated in a customized flow-through calibration setup using a low conductivity reference solution (Sea & Sun Technology GmbH, Germany). Moreover, the cell was calibrated with respect to a temperature probe (NTC Temperature Probe, Sea & Sun Technology GmbH, Germany) to develop a polynomial equation between the temperature and conductivity. The equations were used to obtain the final value of the conductivity and therefore the range is given as 0-10 mS cm^{-1} .

The design of the detection set-up allowed for the preservation of the brass electrodes as they were not directly in contact with saline water samples, thereby preventing potential corrosion or biofouling of the electrode surfaces.

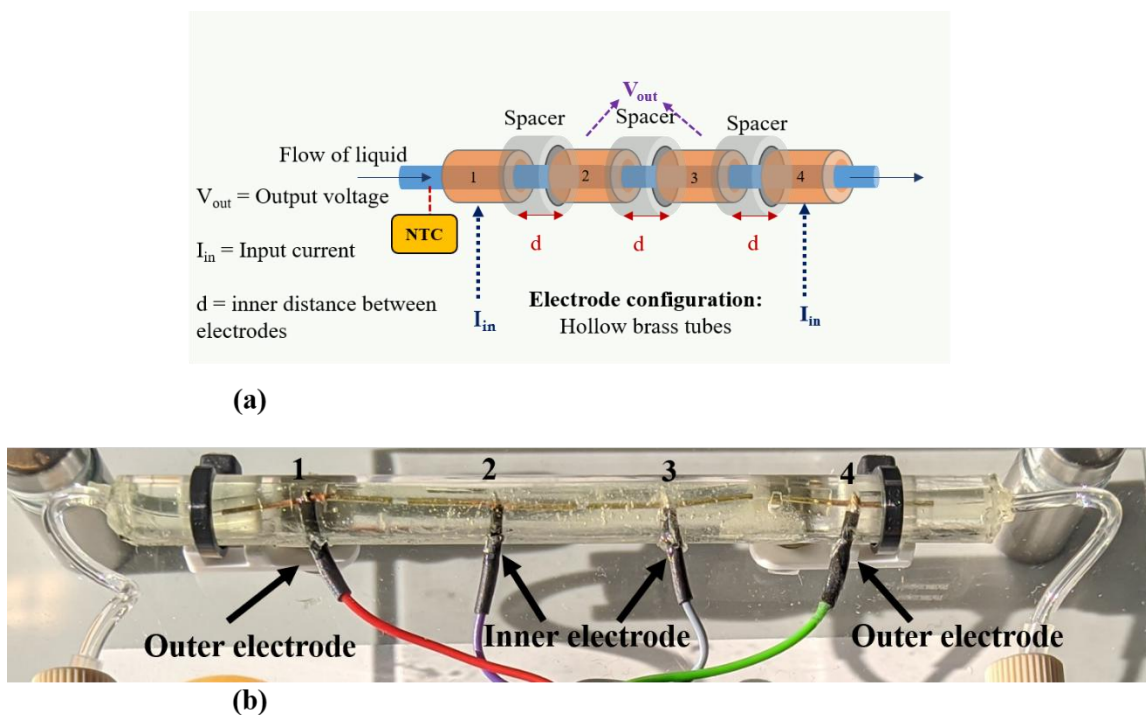


Figure 2.3. (a) Schematic diagram of 4-electrode configuration, (b) Photograph of the conductometer detection cell with 4-electrode configuration.

2.2.3.5 Conductivity data processing

Quantification of the signal was performed through the measurement of the change in conductivity (Δ_{cond}):

$$\Delta_{\text{Cond}} = \text{Peak height (H)} = \text{Post baseline value} - \text{Minimum value of peak (unit in mS cm}^{-1}\text{)}$$

As conductivity is strongly affected by temperature, a linear relationship between the raw conductivity values of the NaOH solution and temperature was experimentally derived. The regression coefficients were used to normalize the H and obtain the 'temperature normalized Peak height (H_T).

$$H_T = \frac{\text{Peak height}}{m \times T + c} \text{ (unit in mS cm}^{-1}\text{)} \quad (1)$$

where m and c are the experimentally derived slope and intercept coefficients of the regression line between conductivity of the NaOH solution and temperature, respectively,

and T is temperature in $^{\circ}\text{C}$. H_T is directly proportional to the DIC concentration (unit in $\mu\text{mol kg}^{-1}$).

Temperature corrections in conductivity measurements are usually carried out by normalizing the measurements to 20°C . However, in our case, a simplified and direct normalization approach was adopted to calculate H_T . This approach provides better results and is discussed in the supporting information (Discussion 1 in SI).

2.2.4 Measurement protocol

A graphical unit interface (GUI) written in Python (version v3.9) was used to control the pump and valve motions, regulate solution volumes, and set flow rates. The GUI allowed for autonomous and continuous analysis (Figure S2.2 in SI). Each analysis consisted of 6 steps as follows: system flush, withdraw of NaOH, withdraw of sample, acidification of sample, gas exchange, conductivity measurement. Detailed descriptions of each step can be found in the supporting information (Discussion 2 and Figure S2.1 in SI).

2.2.5 Laboratory Tests

Laboratory experiments were carried out under controlled conditions. Reagents, standards and the GEUs were fully immersed in a temperature-controlled water bath (Discussion 3 in SI). For temperature experiments, the temperature of the water was regulated between 1 and 30°C by sequentially increasing and then decreasing the temperatures in 5°C step changes. A solution of 7 mmol L^{-1} NaOH was continuously pumped through the conductivity cell to test the effect of temperature variations on the baseline conductivity.

Potential variations in the conductivity signal due to sample salinity changes were investigated by measurements of eight DIC standard solutions ($2000\text{ }\mu\text{mol kg}^{-1}$) with salinities ranging from 0 to 35. The effect of temperature and salinity on gas exchange and the conductivity signal was studied within a temperature range spanning from 4.3°C to 33.6°C for two salinity solutions (0 and 35).

The gas exchange abilities of 3 cylindrical GEUs of 3 different lengths (10, 30, and 90 cm) and one commercial GEU were investigated by analysis of a DIC standard solution (2000

$\mu\text{mol kg}^{-1}$) for gas exchange periods ranging from 0 to 60 min. Furthermore, the conductivity signal of a solution of 7 mmol L^{-1} NaOH at flow rates of 50 to $1200 \mu\text{L min}^{-1}$ was investigated using a DIC standard solution of $2000 \mu\text{mol kg}^{-1}$. Similar experiments were performed using a range of different NaOH concentrations (3 to 20 mmol L^{-1}), and calibration experiments of the system were designed using 7 mmol L^{-1} NaOH (flow rate $300 \mu\text{L min}^{-1}$) for a DIC concentration range of $500\text{-}3000 \mu\text{mol kg}^{-1}$.

2.2.6 Field measurements

The DIC analyzer was deployed onboard *RV Littorina* in the southwest Baltic Sea on 12-16 September 2022 (Figure S2.3 in SI). Continuous autonomous measurements of DIC in surface waters were performed for 3 days, along with the daily analysis of a control DIC standard solution ($2000 \mu\text{mol kg}^{-1}$). A total of 14 discrete surface water samples were collected from the ship's underway seawater supply and stored in Pyrex glass bottles for subsequent analysis in the laboratory using the same DIC system. Detailed information on the onboard installation of the system and discrete sample collection are provided in the supporting information (Discussion 4 in SI).

2.2.7 Statistical analysis

Statistical analyses on the experimental data were performed in Origin Pro 2023 (Learning Edition, Origin Lab Corp., U.S.A). All data are presented as mean $\pm$ 1 standard deviation (S.D.).

2.3 Results and discussion

2.3.1 Temperature effect on baseline conductivity

Conductivity is a proxy for the concentration and mobility of ions in terms of average velocity, and hence is a function of temperature (Gray, 2005). A low viscosity solution allows for a better movement of ions, and therefore a more efficient transfer of charge occurs compared to a higher viscosity solution. As the temperature increases, the collision frequency of ions within a solution increases and the viscosity decreases and conductivity

increases. The conductivity of seawater generally behaves non-linearly at enhanced temperatures ($> 25\text{ }^{\circ}\text{C}$) (F. Millero et al., 2001). However, in the temperature range typically observed for seawaters ($0\text{--}30\text{ }^{\circ}\text{C}$), a linear equation is commonly used. Studies have reported a conductivity-temperature correction factor for bases of 0.02 (a 2 % increase in conductivity per $1\text{ }^{\circ}\text{C}$ increase in temperature) (Barron & Ashton, 2005; Hayashi, 2004; Hem, 1985). The electrical conductivity of a baseline signal of 7 mmol L^{-1} NaOH was recorded and the average conductivity data ± 1 S.D. (~ 500 data points for each corresponding temperature) were plotted against temperature (Figure 2.4). The conductivity signal exhibited a positive linear correlation with temperature with a coefficient of determination (r^2) of 0.9898. The slope of the regression was 0.028 which is close to the reported correction factor of 0.02 (Hayashi, 2004).

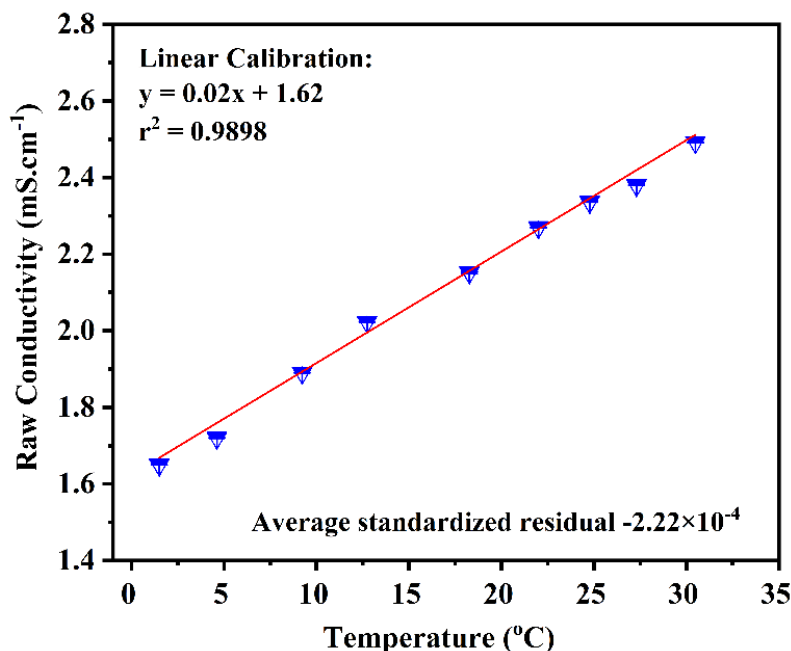


Figure 2.4. Linear regression fit (red solid line) between average raw electrical conductivity ± 1 S.D. of a solution of 7 mmol L^{-1} NaOH and temperature (1.8 and $30\text{ }^{\circ}\text{C}$): $y = 0.028x + 1.62$, $r^2 = 0.9898$.

The derived regression coefficients were used to correct the conductivity measurements for the effect of temperature. The Temperature Normalized Peak Height (H_T) was calculated by considering the corresponding measured temperature (equation 1).

2.3.2 Salinity and temperature effect on CO₂ diffusion

Salinity differences of the sample matrix can affect the electrical conductivity during measurements of DIC in natural water samples. The effect of salinity on the conductivity signal produced following gas exchange of a DIC standard solutions (2000 $\mu\text{mol kg}^{-1}$) at eight different salinities (0-35) is shown in Figure 2.5A. The change in H_T with salinity showed a linear behavior ($r^2 = 0.9718$). The analytical signal decreased from $0.39 \pm 2 \times 10^{-3}$ to $0.33 \pm 5 \times 10^{-3} \text{ mS cm}^{-1}$ with increasing salinity from 0 to 35. The change in conductivity was primarily due to the change in the ionic strength of the standard solutions. The dissociation of carbonic acid increases with an increase in the ionic strength which decreases $p\text{CO}_2$ and, consequently the conductivity of the CO₂ receiving NaOH solution. Moreover, ions from the salt reduce the dissociation rate of the acid ions during the acid sample reaction (F. J. Millero et al., 2010). This results in a lower CO₂ production during the gas exchange period.

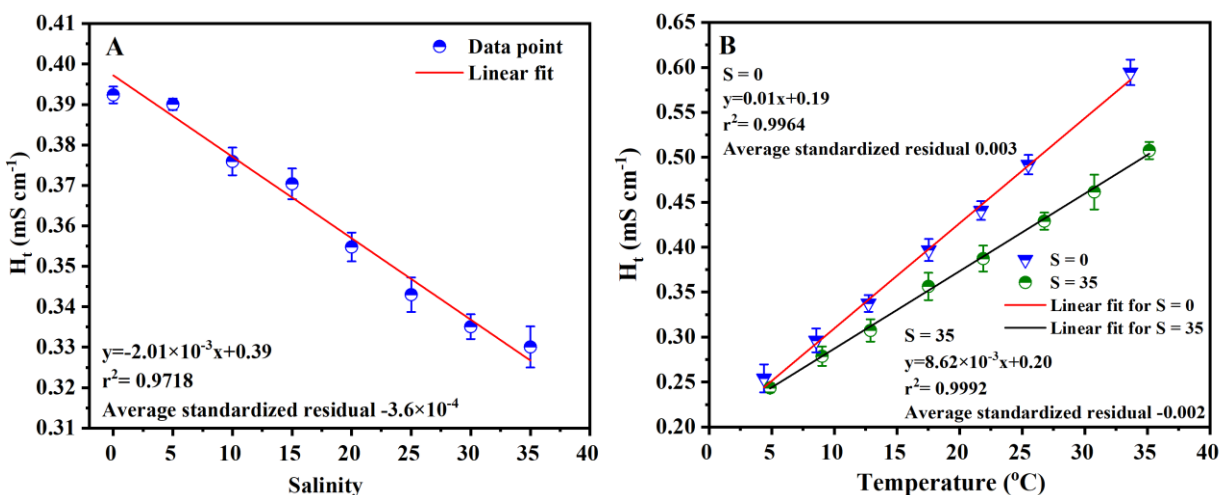


Figure 2.5. (A) Linear regression fit (red solid line) between mean $H_T \pm 1$ S.D. values (number of repetitions, $n = 6$) following gas exchange of a 2000 $\mu\text{mol kg}^{-1}$ DIC standard solution vs. salinity of the DIC solutions ($y = -2.01 \times 10^{-3}x + 0.39$, $r^2 = 0.9718$), and (B) Plot of mean $H_T \pm 1$ S.D. values ($n=6$) of 2000 $\mu\text{mol kg}^{-1}$ DIC standard solution vs. temperature for DIC standard solutions with salinity 0 and 35. Data are shown in half blue triangle ($S = 0$) and half green circle ($S = 35$). The solid red lines refer to the linear regression with $y = 0.01x + 0.19$ ($r^2 = 0.9964$) for $S = 0$ and $y = 8.62 \times 10^{-3}x + 0.20$ ($r^2 = 0.9992$) for $S = 35$.

The effect of temperature on the gas exchange was investigated for salinities 0 and 35. Dissolved inorganic carbon solutions of 2000 $\mu\text{mol kg}^{-1}$ with salinities 0 and 35 were measured within a temperature range spanning from 4.3 °C to 33.6 °C. The change in conductivity in terms of H_T was plotted against temperature (Figure 2.5B). The analytical signal of the two solutions showed positive linear relationships with temperature. However, the slope of the linear regression of the solution at salinity 0 decreased by 22.7 % when salinity was increased to 35. Overall, a two-dimensional effect on conductivity measurements was observed with increasing temperature: (i) an increased ion movement in the electrodes altering the baseline conductivity of NaOH, and (ii) an increased diffusion of CO_2 through the membrane post gas exchange. Since the first effect was corrected using equation 1, the observed variation in conductivity (2nd temperature normalized conductivity (H_T^*)) (Figure 2.5B) was exclusively attributed to the changes in the CO_2 diffusion.

$$H_T^* = \frac{\text{Temperature normalized Peak height}}{0.01 \times T + 0.19} \quad (\text{unit in mS cm}^{-1}) \quad (2)$$

At higher temperatures, there is a shift towards increased formation of gaseous CO_2 from the DIC due to a change in the thermodynamic equilibrium constants ($K(\text{CO}_2)$, K_1 and K_2) (Becker et al., 2011).

These experiments allowed us to evaluate the effect of salinity and temperature on the conductivity measurements of a DIC solution. The change in the sample matrix due to different salinities affected the analytical conductivity signal but it could be quantified and compensated by using correction factors (Figure 2.5A). Similarly, the effect of temperature on the gas exchange was determined and mathematically quantified (Figure 2.5B) and equation 2 was used in later experiments. Therefore, in order to obtain valid conductivity data for DIC analysis, both salinity and temperature measurements are required. The following equation is used to correct both temperature and salinity effect ($H_{S,T}^*$) in seawater samples:

$$H_{S,T}^* = \frac{\text{2nd temperature normalized conductivity } (H_T^*)}{-0.002 \times S + 0.39}$$

2.3.3 Gas exchange time and reagents consumption

The performance of different types and lengths of GEUs was investigated to determine the optimal GEU design and gas exchange time after sample acidification. Figure 2.6 shows H_T^* plotted against gas exchange time (0.01 to 60 min) for each GEU. The GEU were tested independently with varying amounts of sample and acid to fill the entire volume of each GEU and adjusted to obtain optimal mixing ratios between acid and sample (Discussion 5 of SI).

For all the GEUs tested, a sharp increase in the analytical signal was observed with gas exchange times increasing from 0.01 to 2 min. The H_T^* increased approximately 1.6 times and 1.2 times when the exchange time increased from 0.1 to 5 min for the custom-made Teflon AF2400 TIAT units and commercial silicone GEU, respectively. The 30 cm and 10 cm GEUs showed maximum gas exchange at 20 and 50 min in terms of maximum analytical signal, respectively, whereas the 90 cm GEU required only 5 min to reach the maximum signal. This indicates that a greater surface area allowed for a faster gas exchange time. A 5 min waiting time allowed for a greater than 97 % CO_2 diffusion through the membrane. The conductivity signal increased by only ~1.5 % when the gas exchange time was longer than 5 min, and therefore this option of 5 min was chosen for further optimization and the demonstration experiments as it allows for an increased measurement frequency.

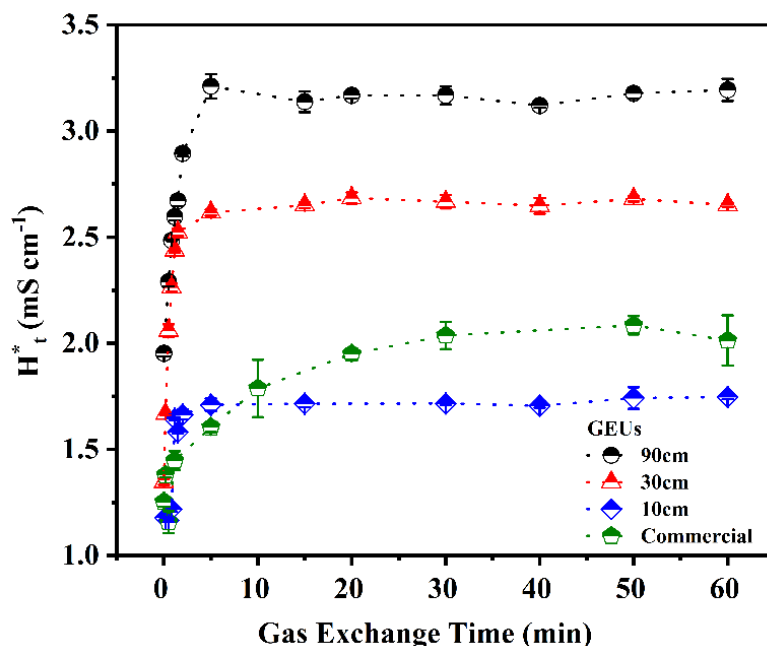


Figure 2.6. Analytical signal of mean $H_T^* \pm 1$ S.D. of post gas exchange of 2000 $\mu\text{mol kg}^{-1}$ DIC solution ($S=0$) ($n = 6$) vs. gas exchange time for 4 different GEUs (90 cm, 30 cm, 10 cm custom-made Teflon AF2400 TIAT GEUs and a commercial silicone GEU). Concentration of NaOH solution was 7 mmol L^{-1} .

The commercial GEU showed the highest analytical signal after a gas exchange time of 50 min suggesting a lower permeability efficiency than the custom-made TIAT units. Although the surface area of the commercial GEU was nearly 10 and 1.7 times larger than that of the 10 and 30 cm GEUs, respectively, the analytical signal obtained from the commercial GEU was in between the ones obtained from the 10 and 30 cm GEUs. After a 5 min gas exchange time, only about 77 % of the total CO_2 permeated through the commercial GEU. This suggested that the surface area was not the only control on the transfer of CO_2 through the membrane. The internal structure of the commercial GEU consisted of a mesh of twisted hollow tubes that allowed for possible formation of bubbles during pumping that could have decreased both the stability and intensity of the conductivity signal.

Reagent consumption plays a crucial role in the utilization of the DIC analyzer for long-term field deployments. The amount of NaOH required for the analysis of one sample is directly proportional to the internal volume of the GEU. The 10, 30, and 90 cm GEUs required 300, 700, and 1500 μL of NaOH respectively, whereas the commercial GEU

required 1000 μL for each measurement. The relatively high amount of reagent required by the commercial GEU in combination with a considerably low conductivity signal-gas exchange time ratio and the frequent formation of bubbles in the flow lines, determined the exclusion of this unit from further tests. Among the three custom-made cylindrical TIAT GEUs, the 30 cm long GEU was considered as the most suitable due to the moderately low reagent consumption and best analytical signal-gas exchange time ratio. Therefore, the unit was used in further optimization experiments.

2.3.4 NaOH solution flow rate

Figure 2.7 shows the analytical signal H^*_T against flow rate of a NaOH solution (7 mmol L^{-1}) obtained from measurements of a 2000 $\mu\text{mol kg}^{-1}$ DIC solution ($S=0$). The NaOH solution was pumped following 5 min gas exchange using the 30 cm GEU to the conductivity cell at flow rates ranging from 50 to 1200 $\mu\text{L min}^{-1}$. At the slowest flow rate (50 $\mu\text{L min}^{-1}$), an analytical signal of 2.59 mS cm^{-1} was recorded. The conductivity signal decreased by 27.5 % at a flow rate of 1200 $\mu\text{L min}^{-1}$. The signal decreased linearly at a rate of $5.72 \times 10^{-4} \text{ mS cm}^{-1}$ per 1 $\mu\text{L min}^{-1}$ increase in NaOH flow rate. The decrease in signal with increasing flow rates suggested that longer contact times between the solution and the electrodes resulted in higher signals. Moreover, at higher flow rates ($>1000 \mu\text{L min}^{-1}$) the stability of the analytical signal decreased (S.D. = 0.36 for 1000 $\mu\text{L min}^{-1}$ and 0.056 for 1200 $\mu\text{L min}^{-1}$) compared to flow rates below 400 $\mu\text{L min}^{-1}$ (average S.D. = 0.022 for 50-400 $\mu\text{L min}^{-1}$). It is possible that the formation of bubbles at higher flow rates contributed to the observed decrease in analytical signal. As the drop in the analytical signal for a flow rate of 300 $\mu\text{L min}^{-1}$ was only 7 % compared to a flow rate of 50 $\mu\text{L min}^{-1}$, this flow rate was chosen as appropriate and allowing a measurement frequency of 4 samples h^{-1} .

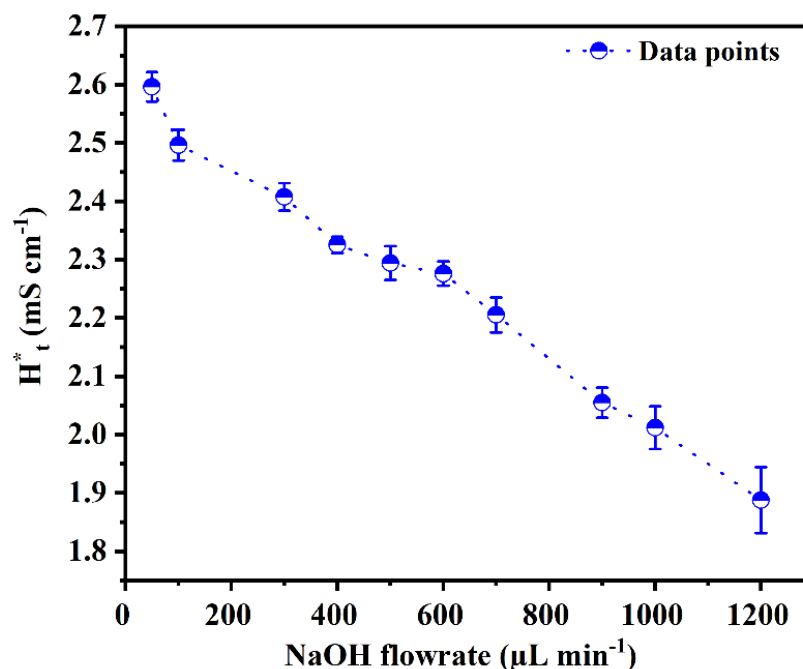


Figure 2.7. Analytical signal of mean $H_T^* \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. flow rate (50 to $1200 \mu\text{L min}^{-1}$) of a 7 mmol L^{-1} NaOH solution. A gas exchange time of 5 min was utilized with a gas exchange unit of 30 cm in length.

2.3.5 NaOH solution concentration and system calibration

The effect of different concentrations of NaOH on the CO_2 absorption capacity in terms of change in electrical conductivity H_T^* was tested by utilizing a range of NaOH concentrations from 3 to 20 mmol L^{-1} . The use of ultrapure water as an acceptor solution for CO_2 has been reported (Martinotti et al., 2012), but the diffusion of CO_2 into an alkaline acceptor stream ($\text{pH} > 8$) is expected to be faster and more efficient (Pencharee et al., 2012). The capacity to absorb CO_2 generated from the acidification of a DIC solution of $2000 \mu\text{mol kg}^{-1}$ into a stream of NaOH is shown in Figure 2.8 as H_T^* plotted against NaOH concentration ($n=6$). The S.D. of the baseline conductivity of the 3 mmol L^{-1} NaOH solution was $\pm 0.01 \text{ mS cm}^{-1}$ and that of 20 mmol L^{-1} NaOH was $\pm 0.06 \text{ mS cm}^{-1}$ which produced more uncertainty during measurements. An increase of 16% in the analytical signal was observed with an increase of NaOH concentrations from 3 to 4 mmol L^{-1} , whereas the signal increased by 8.9% for an increase from 7 to 10 mmol L^{-1} . At higher NaOH concentrations (14 to 20 mmol L^{-1}), the analytical signal increased further by 20.4

%. During measurements with the higher NaOH concentrations, i.e., 14-20 mmol L⁻¹, an additional volume of 50 % of fresh NaOH solution was required to flush the reacted NaOH out of the electrode cell compared to the amount needed for lower concentrations of NaOH. This could have been caused by potential polarization of the electrodes due to enhanced accumulation of a large number of ions (OH⁻, CO₃²⁻ and HCO₃⁻). Therefore, more NaOH solution was required to remove the effect of polarization resulting in longer analysis times and a higher reagent consumption.

Figure 2.9A shows the analytical signals H_T^* of 3 and 20 mmol L⁻¹ NaOH solutions used as acceptor streams for the measurements of 6 DIC calibration standards between 500 and 3000 µmol kg⁻¹. The conductivity signal of the 3 mmol L⁻¹ NaOH solution increased linearly for DIC measurements between 500 and 1500 µmol kg⁻¹ whereas signal saturation was observed at higher DIC concentrations. The H_T^* signal ranged from 0.27 to 2 mS cm⁻¹. Previous studies have shown that the use of low NaOH concentrations (0.2-2 mmol L⁻¹) of NaOH does not provide a complete reaction at high DIC concentrations (> 1500 µmol kg⁻¹ in this study) due to a low pH (< 8) of the solutions and incomplete absorption of NaOH (Pencharee et al., 2012). However, low NaOH concentrations (3 mmol L⁻¹) appeared to be suitable for DIC measurements in the lower range (500-1500 µmol kg⁻¹) with a good linear response ($r^2 = 0.9750$, $p < 0.1$).

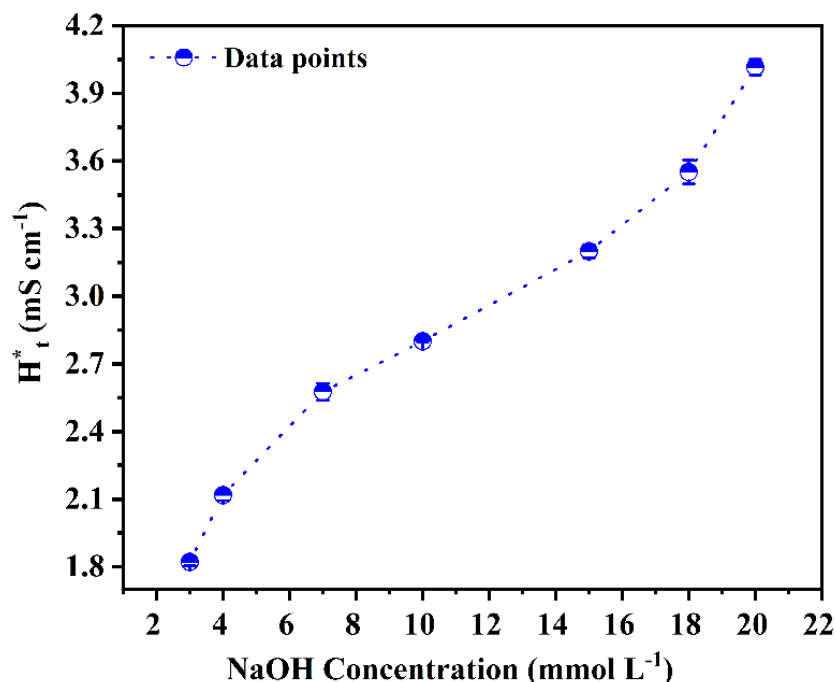


Figure 2.8. Analytical signal of mean $H_T^* \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. NaOH concentration ($3\text{--}20 \text{ mmol L}^{-1}$). A gas exchange time of 5 min was utilized with a gas exchange unit of 30 cm in length.

The range of H_T^* for the 20 mmol L^{-1} NaOH solution showed a wider distribution ($1.74\text{--}6.2 \text{ mS cm}^{-1}$) compared to H_T^* from 3 mmol L^{-1} NaOH. The analytical signal showed a non-linear behavior at low DIC concentrations ($500\text{--}1000 \mu\text{mol kg}^{-1}$). It is possible that the signal was suppressed as the number of carbonate ions were substantially lower compared to the NaOH ions. However, within the DIC range of $1000\text{--}3000 \mu\text{mol kg}^{-1}$ a linear behavior was observed for 20 mmol L^{-1} NaOH, but the polarization effect could distort the stability of the signal over long-term use.

Figure 2.9B shows H_T^* versus DIC for calibration standards with concentrations between 500 and $3000 \mu\text{mol kg}^{-1}$, and using a solution of 7 mmol L^{-1} NaOH as acceptor stream. The analytical sensitivity was $0.0014 \text{ mS cm}^{-1}$ per $\mu\text{mol kg}^{-1}$, indicating a significant linear relationship ($r^2 = 0.999$, $p < 0.001$) within the tested DIC range (Table S2.2 in SI). The values of H_T^* ranged between 0.8 and 4.5 mS cm^{-1} with an RSD value of 0.9% . In line with published work (Sayles & Eck, 2009), the use of a 7 mmol L^{-1} NaOH solution as acceptor stream for CO_2 absorption hence was deemed optimal for most oceanographic

measurements (1600-2800 $\mu\text{mol kg}^{-1}$ DIC range). This is due to fact that the number of NaOH ions is optimal to absorb the CO_2 produced by the acidification of this range of DIC solution (Ager & Howard, 1987; Hikita et al., 1976; Mansourizadeh et al., 2010; McCleskey, 2011; Monk, 2020b; M. Yoo et al., 2013).

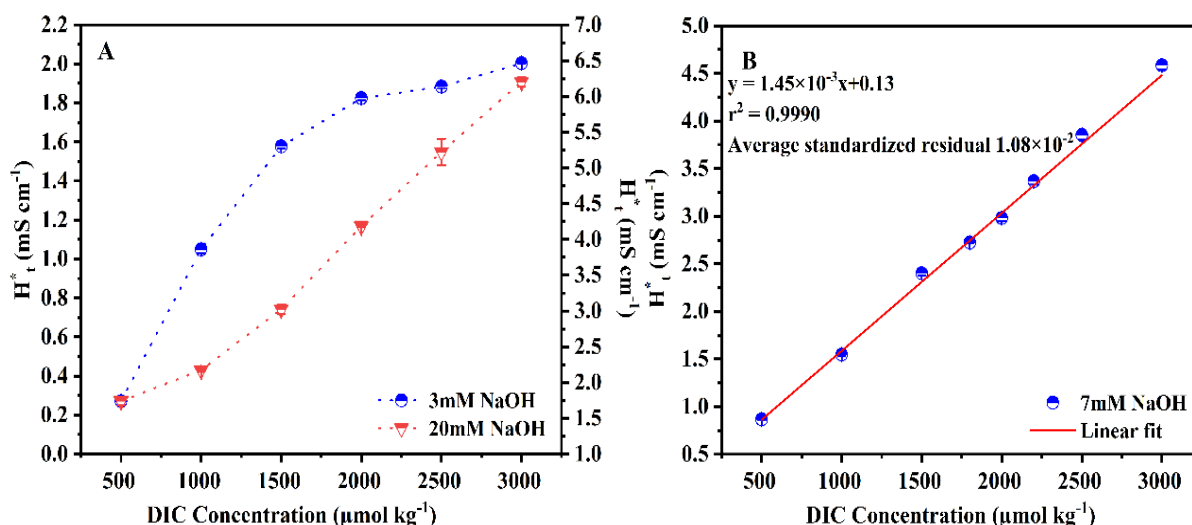


Figure 2.9. (A) Analytical signal of mean $H_T^* \pm 1$ S.D. of DIC calibration solutions using 3 mmol L^{-1} and 20 mmol L^{-1} NaOH solution ($n = 6$) as acceptor solutions, and (B) Linear regression fit (red solid line) of mean $H_T^* \pm 1$ S.D. vs. DIC calibration standards using 7 mmol L^{-1} NaOH as acceptor solution ($n=6$). A gas exchange time of 5 min was utilized with a gas exchange unit of 30 cm in length.

2.3.6 Field demonstration

The performance of the DIC analyzer was tested in the southwest Baltic Sea during a 3-day field campaign. The stability of the system was determined by regular measurements of a standard DIC solution (2000 $\mu\text{mol kg}^{-1}$) yielding an average standard deviation (± 1 S.D.) of $\pm 9.7 \mu\text{mol kg}^{-1}$ over the 3 days (total 6 data points with 6 replicates). Accuracy was assessed by using RMs ($n=6$) and a one-point calibration factor was used to correct DIC concentrations. Temperature and salinity corrections were applied to all the raw conductivity measurements prior to calculation of the DIC concentrations. A total number of 28 measurements of surface water DIC was recorded during the campaign. Figure 2.10 shows the time series of DIC concentrations (half blue circles), with the highest measured DIC concentration of 1793 $\mu\text{mol kg}^{-1}$, and the lowest 1620 $\mu\text{mol kg}^{-1}$.

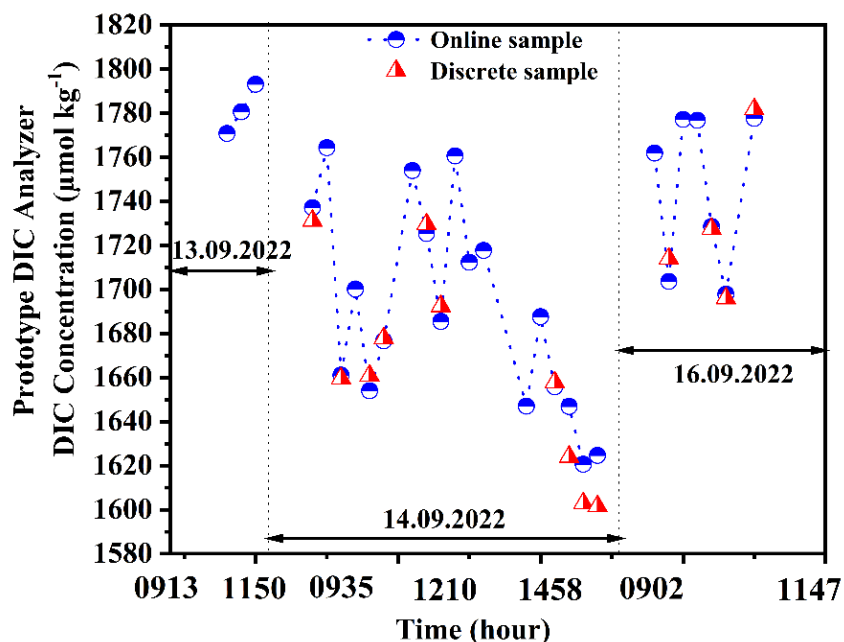


Figure 2.10. Time series of DIC concentrations on 13.09.2022, 14.09.2022 and 16.09.2022 in surface waters of the south-west Baltic Sea. Half blue circles refer to onboard measurements and half red triangles are the DIC concentrations of discrete sample analyzed in the laboratory. A gas exchange time of 5 min was utilized with a gas exchange unit of 30 cm in length. A 7 mmol L⁻¹ NaOH solution was used with a flow rate of 300 μL min⁻¹.

Following the campaign, 14 discretely collected water samples were measured in the laboratory by the DIC analyzer, and shown as half red triangles in Figure 2.10. Good agreement was observed between the laboratory and on-board sample measurements at the corresponding time of collection ($2.8 \pm 10.8 \mu\text{mol kg}^{-1}$) with a significant positive correlation of $r^2 = 0.9488$ ($p < 0.05$) between the DIC concentrations (Figure 2.11A).

As an additional evaluation of instrument performance, measurements of RM (1985 $\mu\text{mol kg}^{-1}$, treated as unknown sample) were performed over four consecutive days. The DIC concentration of the RM was 1986 $\mu\text{mol kg}^{-1}$ ($n=24$) resulting in a slight overestimation (1 $\mu\text{mol kg}^{-1}$) in calculated DIC concentration, whereas the achieved precision was $\pm 4.9 \mu\text{mol kg}^{-1}$ (Figure 2.11B).

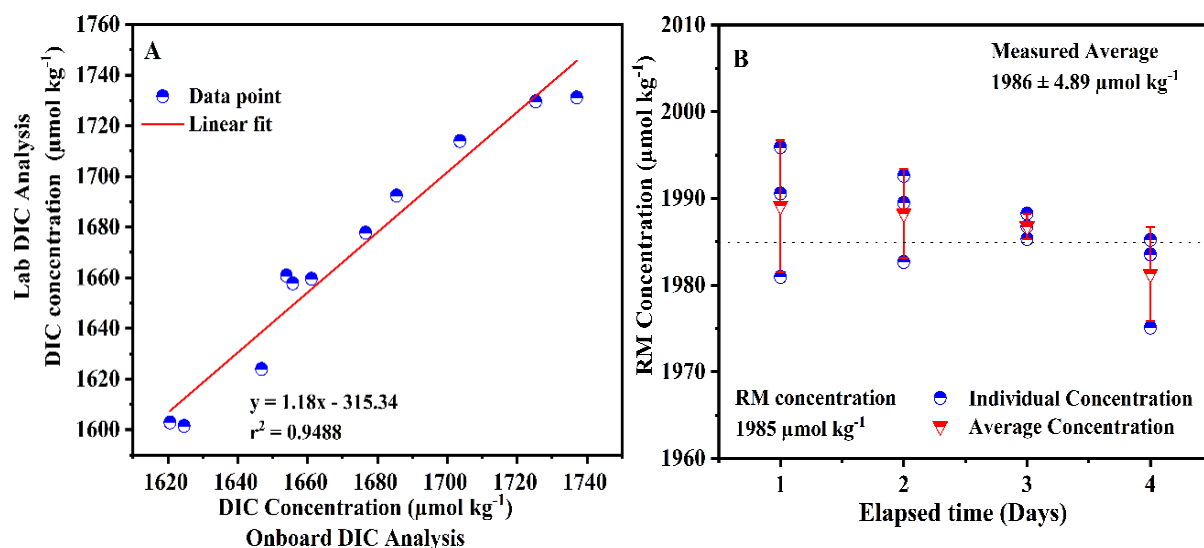


Figure 2.11. (A) Linear regression fit (red solid line) between laboratory and onboard DIC measurements by the DIC system ($y = 1.18x - 315.34$, $r^2 = 0.9488$), (B) DIC concentrations of reference material (RM) measured by the DIC analyzer over 4 consecutive days in the laboratory. Blue half circles refer to individual data while red half triangles refer to average ± 1 S.D. The dashed line is the average measured concentration.

2.4 Conclusions and future perspectives

The development of a novel autonomous gas diffusion sequential injection analyzer for the determination of DIC in seawater is reported. The DIC analyzer utilizes sample acidification with subsequent CO_2 diffusion through a gas permeable membrane into an acceptor solution of 7 mmol L^{-1} NaOH. A flow cell with 4 hollow contacting brass electrodes is used to measure the change in conductivity following CO_2 absorption. A 30 cm long custom-made tube in a tube configuration was employed for the CO_2 transfer, with Teflon AF2400 as membrane material. The system exhibited a linear relationship for DIC concentrations between 500 and $3000 \mu\text{mol kg}^{-1}$, making it suitable for a variety of marine applications. Evaluation of temperature and salinity influences on the conductivity measurements provided correction factors that greatly improved data quality. The system can be employed to assess DIC dynamics in surface seawaters in near real-time at a frequency of $4 \text{ samples hr}^{-1}$ with low reagent consumption (0.2 mL of H_3PO_4 , 0.75 mL of NaOH for each measurement), as was successfully demonstrated in the southwest Baltic

Sea. The system configuration, measurement protocol and raw data correction procedure have allowed us to achieve an analytical precision of $\pm 4.9 \mu\text{mol kg}^{-1}$ and $\pm 9.7 \mu\text{mol kg}^{-1}$ by measuring a DIC reference material in the laboratory and a field deployment in the southwest Baltic Sea, respectively.

The next step in the DIC analyzer development is bidirectional: (1) perform long duration (months) on-site measurements with the current analyzer to assess and correct potential drift and interferences (this work is currently ongoing) and (2) build an *in-situ* instrument based on the principles of the current device for deployment in coastal and oceanic waters of depths up to 3000 m. The basic configuration, e.g., SIA and gas exchange unit, detection cell of the submersible system will be based on the current prototype system but will be miniaturized using e.g. solenoid pumps. The electronics, flow channels and the reagents will be packed in three interconnected compartments of an acrylic (or titanium for deep water deployment) housing. The first two compartments will be filled with oil and the reagents will be stored in gas-impermeable bags. Initially, a long-term test in shallow water (<10 m) is planned, followed by a demonstration deployment in the deep ocean at 2500 m near the mid-Atlantic ridge. This will allow fast and reliable *in-situ* measurements of DIC in coastal and deep ocean waters for observations of the carbonate system, including monitoring of potential leakages of CO₂ from carbon capture and storage operations.

Supporting Information

A list of the contents of Supporting Information. **Table S2.1:** Overview of geometric details of the four tested Gas Exchange Units (GEUs). **Discussion 1:** Normalization protocol of salinity and temperature correction on raw conductivity value **Discussion 2:** Measurement protocol and sampling procedure. **Figure S2.1:** Screenshot of raw conductivity and temperature during sample measurements. **Figure. S2.2:** Screenshot of the graphical user interface (Python v 3.9). **Discussion 3:** Description of Temperature control system. **Discussion 4:** Field measurements. **Figure S2.3:** Photograph of (A) 200L water tank used for continuous surface water supply to commercial instruments as well as to the DIC system and (B) DIC system installation on the RV *Littorina*. **Discussion 5:** Comparison of GEUs, Acid type and concentrations. **Figure S2.4:** Analytical signal of

mean $H^*_T \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. sample volumes added with acid for 4 different GEUs (A) 30 cm, (B) 90 cm and (C) 10 cm TIAT GEU, and (D) commercial GEU. **Figure S2.5:** Analytical signal of mean $H^*_T \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. different acid concentrations. Two different acids, H_3PO_4 and HCl were used. **Table. S2.2:** Slope and intercept including their standard deviations, t-values, and the probabilities for the calibration curve of the 7 mmol L^{-1} NaOH solution shown in Figure 9B.

CRediT

EA and ME conceptualized the study. ME, EA and SB designed and developed the system. SB performed laboratory experiments, methodology development, field samples measurements, data processing, writing of original draft of manuscript. ME guided the laboratory and field work, developed autonomous measurement script. ME, EA, TT provided constant guidance throughout the process. EA provided funding acquisition. All authors contributed to the interpretation of the results and agreed to published version of the manuscript.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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2.5 Supporting Information:

Table S2.1. Overview of geometric details of the four tested Gas Exchange Units (GEUs)

Diffusion path length (cm)	Acceptor volume (μL)	Volume inside membrane (μL)	Acceptor SA mm^2	Sample SA mm^2	Membrane type
10	38	29	319	191	Teflon
30	115	87	958	575	Teflon
90	346	262	2875	1725	Teflon
Commercial GEU	Not specified	Not specified	Not specified	1000	Silicone

Discussion 1:

Normalization protocol of salinity and temperature correction on raw conductivity value:

The temperature correction of the conductivity measurement is generally expressed by the following equation:

Compensated Conductivity = $\frac{\text{Measured Conductivity}}{1 + \alpha \times (T - T(\text{reference}))}$, where α is the temperature correction factor and T (reference) is generally chosen as 20 °C.

In this study, a simplified and direct calculation was applied:

Compensated Conductivity = $\frac{\text{Measured Conductivity}}{m \times T + c}$, where m and c are the slope and intercept of the linear regression relationship between conductivity and temperature. The temperature dependence of conductivity was linear and strong ($r^2 = 0.9898$) and the calculated α value was close to 0.02 as reported in the literature (for bases 0.02%) (Figure 2.4) (Barron & Ashton, 2005).

Case 1 and 2 represent the temperature and salinity normalization steps on the raw conductivity value at 20 °C and at the temperature when sample was measured, respectively.

Case 1: Temperature and salinity correction where conductivity is normalized to 20 °C:

$$H(20) = \frac{H}{1+0.02 \times (T-T(20))}, H^*(20) = \frac{H(20)}{0.19+0.01 \times T}, H^*(S, 20) = \frac{H^*(20)}{0.39-0.002 \times S}$$

Case 2: Temperature and salinity correction on conductivity at T, i.e, the temperature of each sample during measurement:

$$H(T) = \frac{H}{1.62+0.02 \times T}, H^*(T) = \frac{H(T)}{0.19+0.01 \times T}, H^*(S, T) = \frac{H^*(T)}{0.39-0.002 \times S}$$

H(20) and H(T) are the normalized conductivity values obtained by correcting the baseline conductivity value of fresh NaOH solution with respect to a temperature range (Figure 2.4). A further normalization was then applied on H(20) and H(T), obtained from the CO₂ gas exchange behavior of a DIC standard solution (salinity 0) with respect to a range of temperatures (Figure 2.5B). In both cases, T is the temperature recorded during the conductivity measurement and it was close to 18 °C (laboratory environment). Finally, the salinity correction was applied by measuring a DIC standard solution in a range of saline solutions (maintaining temperature at ~20 °C, Figure 2.5A).

Here is an example to show the difference in the results obtained in each of these cases: The peak height and corresponding temperature values of a Reference Material (RM) (salinity 35 g L⁻¹) and a standard DIC solution (2000 µmol kg⁻¹ at salinity 0) were chosen as an example. The recorded temperature (T) was 18 °C. In case of RM, the mean value (n = 4) of H^{*}(S,20) was twice that of as H^{*}(S,T), while the Relative Standard Deviation (RSD) in Case 1 and Case 2 were 0.19 % and 0.2 %, respectively. This showed that the achieved precisions of respective RM values were close. Furthermore, the accuracy was checked by making the standard DIC solution as an unknown sample. The value obtained from Case 1 always showed that the actual DIC value was overestimated by a value of 80-100 µmol kg⁻¹ compared to Case 2. In order to improve the accuracy, the correction protocol of Case 2 was further adapted for the calculation of field sample data.

Discussion 2:

Measurement protocol and sampling procedure

Each analysis of a DIC sample consisted of 6 steps:

- (1) Sample valve is opened and the pump draws an aliquot of sample (or standards during calibration) to flush the mixing coil and the inner tube of the GEU for 2 times to remove any residual CO_2 from the previous samples. The sample valve is closed and the syringe is emptied,
- (2) NaOH valve is opened and an aliquot of fresh NaOH is drawn through the gas exchange tube to flush out residual reacted NaOH ($\text{NaOH} + \text{CO}_2$). This step includes flushing, priming, and filling up the GEU and the conductivity cell with fresh NaOH solution to establish a baseline value. The NaOH valve is closed and the syringe is emptied,
- (3) sample valve is opened. The mixing coil and the sample tube of GEU are flushed with an aliquot of a fresh sample (or standards) for 3 times. This step ensures the priming of the tubes and removes any possible bubbles prior to acid introduction. The sample valve is closed and the syringe is emptied,
- (4) the sample (or standards) and acid valves are sequentially opened to draw the sample (or standards), which is then mixed with the acid in a 200 μL mixing coil. The spiral design of the mixing coil ensures the effective mixing of the two solutions. The sample and acid valves are closed and the syringe is emptied,
- (5) the acidified sample is left in the gas exchange unit (GEU) for a specified time (gas exchange time). During this time CO_2 diffuses through the gas-permeable membrane into the acceptor NaOH solution,
- (6) following the gas exchange time, NaOH valve is opened and NaOH is slowly drawn from the GEU to the conductivity cell. The NaOH valve is closed and the syringe is emptied. Conductivity and temperature of NaOH are recorded by the conductivity cell and an NTC probe, respectively as shown in [Figure S2.1](#).

Raw conductivity data of two measurement cycles is shown in Figure S2.1. Figure S2.2 shows the graphical user interface written in Python (v3.9) used for control and autonomous measurements.

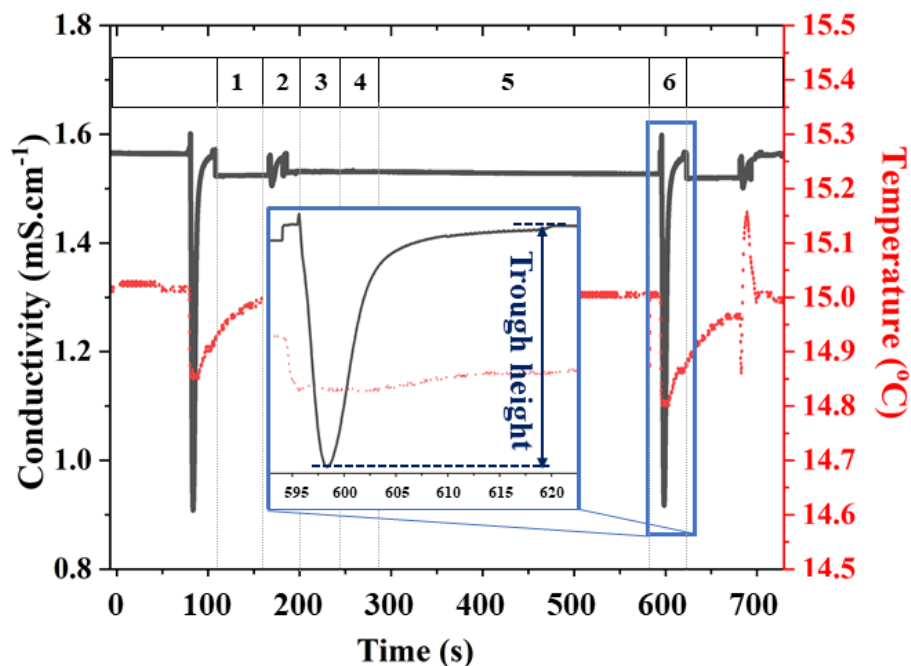


Figure S2.1. Screenshot of raw conductivity and temperature during sample measurements.

Discussion 3:

Description of Temperature control system

A temperature control system was assembled in the laboratory to simulate different temperature environments. A commercial water bath (Fischer Brand FBC 720) was used to regulate the temperature. The water was circulated through a plastic container (~ 10 L) with inlet and outlet ports connected to the water bath via silicon tubing. The temperature of NaOH flowing through the conductivity cell was recorded by the internal NTC probe.

Chemical reagents and the GEUs were immersed in the plastic container. The water temperatures were set on the water bath while the water temperature in the plastic container was monitored and recorded with an external temperature sensor (Testo 176T4, Four-channel temperature data logger). The plastic container was insulated to minimize the influence of external temperature changes.

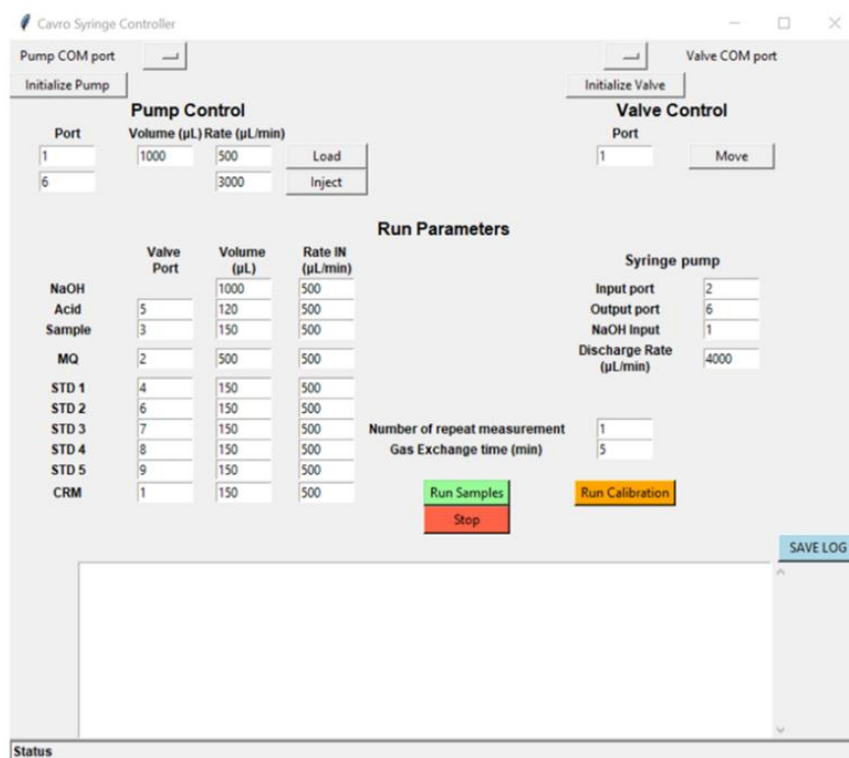


Figure S2.2. Screenshot of the graphical user interface (Python v 3.9).

Discussion 4

Field measurements

A 200 L water tank was continuously supplied by surface seawater at a flow rate of 600 L hr^{-1} (Figure S2.3A). To enable continuous water flow to the DIC analyzer, a water line connection was established from the tank into the laboratory. Figure S2.3B shows the installation of the DIC system inside the ship's lab.

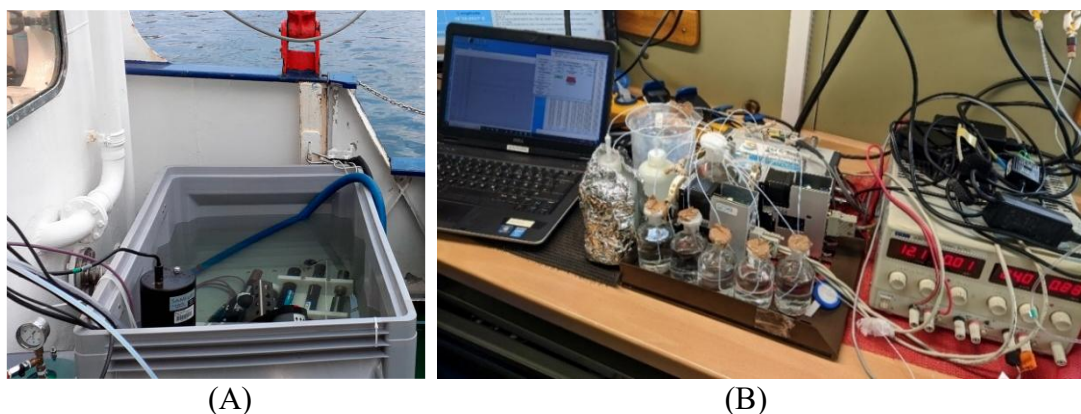


Figure S2.3. Photograph of (A) 200L water tank used for continuous surface water supply to commercial instruments as well as to the DIC system and (B) DIC system installation on the RV *Littorina*.

A total of 14 surface seawater discrete samples were collected from the sampling line outlet. Discrete samples were collected into 100 mL clean narrow mouth borosilicate glass bottles with air-tight glass stoppers. A spike of 100 μL 100% saturated Mercuric Chloride (HgCl_2) was added (Sample : HgCl_2 = 1000 : 1) to each sample to prevent biological activity. The bottle lids were greased and immediately placed to avoid the exchange of CO_2 with the atmosphere before analysis at the land-based laboratory.

Discussion 5:

Comparison of GEUs

Sample-acid mixing ratio and membrane type were tested by using two structurally different GEUs (Table S2.1). Each GEU was independently tested with different total sample volumes by varying the amount of acid. Figure S2.4 depicts the variation of normalized peak height with respect to the added sample volume where the amount of acid was a variable parameter. The volume of acid was increased from 50 μL to 400 μL for the 30 and 90 cm GEUs whereas for the 10 cm GEU and the commercial GEU, a maximum of 200 μL of acid was used. In the 30 cm TIAT GEU, the total volume of acidified sample varied from 400 μL to 1000 μL , whereas for the 90 cm, the total volume of acidified sample was from 500 μL to 1000 μL . The X-axis represents the total volume of the sample mixed

with acid. For example, 50 μL acid was followed by 400 μL to 800 μL sample making the total acidified sample volume 450 μL to 850 μL .

The total volume of an acidified sample was chosen so that fully mixed acid/sample reaches the GEU without leaving any remaining acidified sample aliquot at the edge of the GEU. For each GEU, the volume of acid was also increased by keeping the same volume of the total added sample volume. This allowed us to fill most of the portion of GEU with acidified solution and determine the acid-sample mixing ratio. A section of the mixing coil was first filled with 1M H_3PO_4 followed by the sample. Each of the acidified sample was allowed for 5 minutes of gas exchange time. The flow of eluted NaOH (7 mmol L^{-1}) and acidified sample was in a counter direction to maximize the diffusion of CO_2 through the membrane. The change in conductivity data was normalized using [equation 2](#) (manuscript) to compensate for the temperature effect.

The experiment had two main objectives: (i) finding the highest signal according to the positioning of acidified sample into the membrane to avoid acidified samples remaining beyond the extreme ends of the GEU membrane, and (ii) finding the optimal acid mixing ratio.

For each GEU, with increasing total acid volume, an increase in analytical signal was obtained with increasing sample volume. The 30 cm and 90 cm GEUs were able to transfer CO_2 from acidified samples with maximum conductivity signals of 2.36 and 3.26 mS cm^{-1} , respectively, whereas for the 10 cm and commercial GEU the maximum analytical signal was obtained 1.71 and 1.9 mS cm^{-1} , respectively. The observed higher analytical signals indicated that the whole portion of the acidified sample was within the membrane of the GEU. For 30 cm, 90cm and commercial GEUs, the highest analytical signal was obtained with $\sim 800\text{-}900 \mu\text{L}$ of total volume of acidified sample, whereas for the 10 cm GEU, the total volume of the acidified solution was $\sim 700 \mu\text{L}$. Figure S2.4 shows the highest values of normalized heights obtained from each set of acid additions for the 4 different GEUs. About $200 \mu\text{L}$ of acid was mixed suggesting $\sim 30 \%$ of acid was needed to produce maximum CO_2 while mixed with $600\mu\text{L}$ (total $800 \mu\text{L}$ acidified sample) sample for 30 cm GEU. While testing with a higher amount of acid, i.e., above $300 \mu\text{L}$, the analytical signal showed lower signal with respect to that of $200 \mu\text{L}$ acid. Furthermore, the measurement

was stopped when total acidified sample exceeds 600 μL , due to the fact that the total volume already crosses the edge of 30 cm GEU. It was observed that with the 90 cm GEU, 200 μL of acid was required to reach the maximum analytical signal. But with the increase of total acidified sample amount, the signal slowly dropped in contrast to that of 30 cm GEU. This was due to fact that the sample surface area was 3 times higher in the 90 cm GEU compared to that of the 30 cm GEU allowing for higher diffusion area for CO_2 within the 5 minutes of gas exchange time. Therefore, by increasing the surface area, it was possible to reduce sample amount as well as gas exchange time for each measurement. The 10 cm GEU offered the minimum surface area with respect to any other GEU presented here (191 mm^2) and it requires a total acidified sample of $\sim 700 \mu\text{L}$ with 550 μL of sample to produce a high analytical signal with $\sim 27\%$ acid requirement. On the other hand, the commercial GEU was able to diffuse more CO_2 when only 25 % of acid was used. Theoretically, the gas permeability coefficient for silicone membranes is higher compared to Teflon, with less amount of acid required to allow diffusion of the produced CO_2 . However, the analytical signal obtained from the commercial GEU was lower than that obtained from the 30 cm GEU although the surface of the commercial GEU was ~ 1.7 times greater than that of the 30 cm GEU. To explore further the behavior of each GEU and CO_2 diffusion we performed additional tests by considering different gas exchange times.

Acid type and concentrations

Two different acids, i.e., HCl and H_3PO_4 were used to test the efficiency of the gas exchange process from the 30 cm cylindrical TIAT GEU using a freshly prepared $2000 \mu\text{mol kg}^{-1}$ DIC solution. The acidified solution was kept inside the GEU for 5 minutes and following the reaction with the acceptor solution ($7 \text{ mmol L}^{-1} \text{ NaOH}$), the analytical signal of conductivity was recorded.

Although both acids are strong and have been used in previous studies, the use of H_3PO_4 is commonly used in commercial sensors to lower the pH of the solution to < 4 , so that CO_2 can start to diffuse. Three different concentrations of acid were tested, i.e., 0.02, 0.1 and 1 mol L^{-1} to evaluate the release of CO_2 from the DIC solution. During each analysis, 400 μL of sample was mixed with 200 μL of acid. Figure S2.5 shows the variation of

conductivity for each case in terms of normalized peak heights with respect to three different acid concentrations.

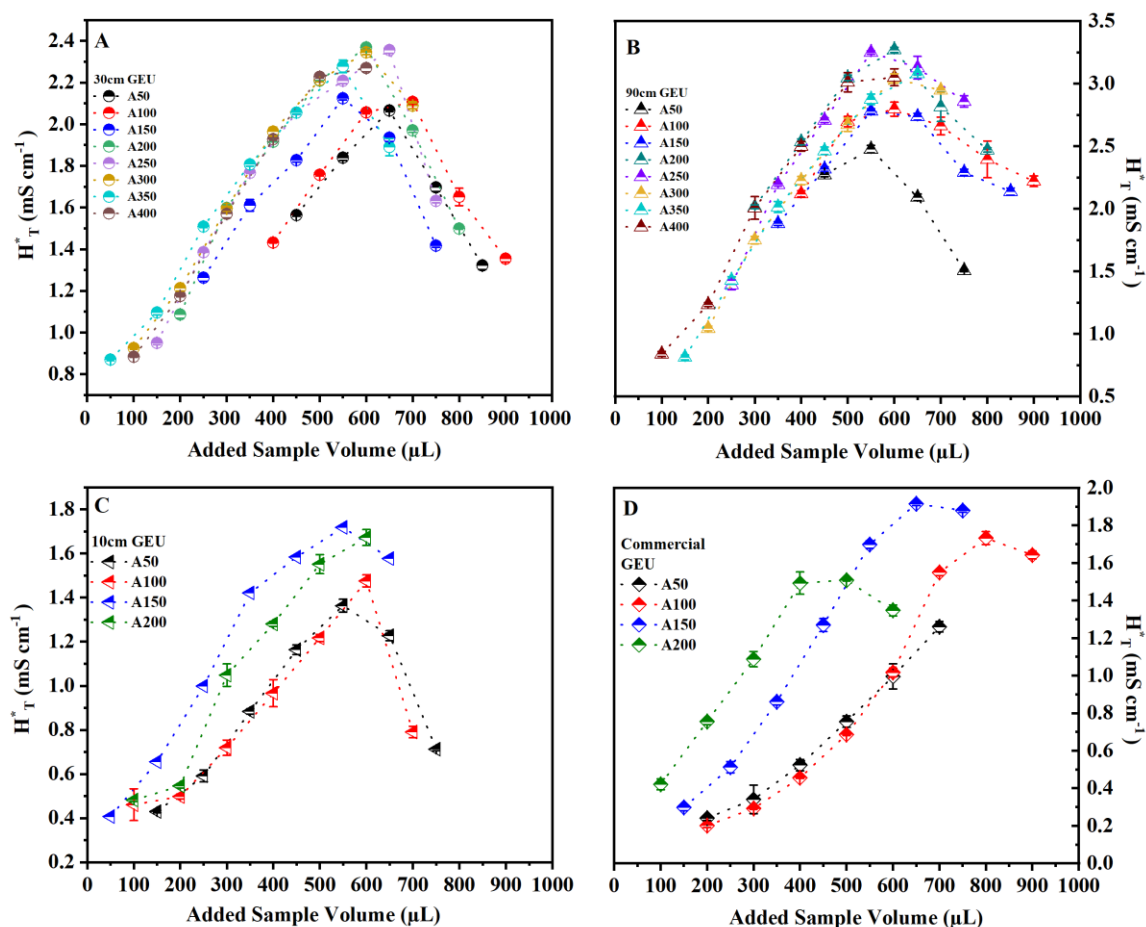


Figure S2.4. Analytical signal of mean $H_T^* \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. sample volumes added with acid for 4 different GEUs (A) 30 cm, (B) 90 cm and (C) 10 cm TIAT GEU, and (D) commercial GEU.

An increase in analytical signal of $\sim 0.7 \text{ mS cm}^{-1}$ was observed when 0.02 mol L^{-1} and $0.1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ was used compared to same concentrations of HCl . The stronger analytical signal when using H_3PO_4 implies more CO_2 production from the same batch of $2000 \mu\text{mol kg}^{-1}$ DIC solution. Also, with the highest concentration of acid i.e., 1 mol L^{-1} , the analytical signal of H_3PO_4 is still 0.17 mS cm^{-1} greater compared to that of HCl .

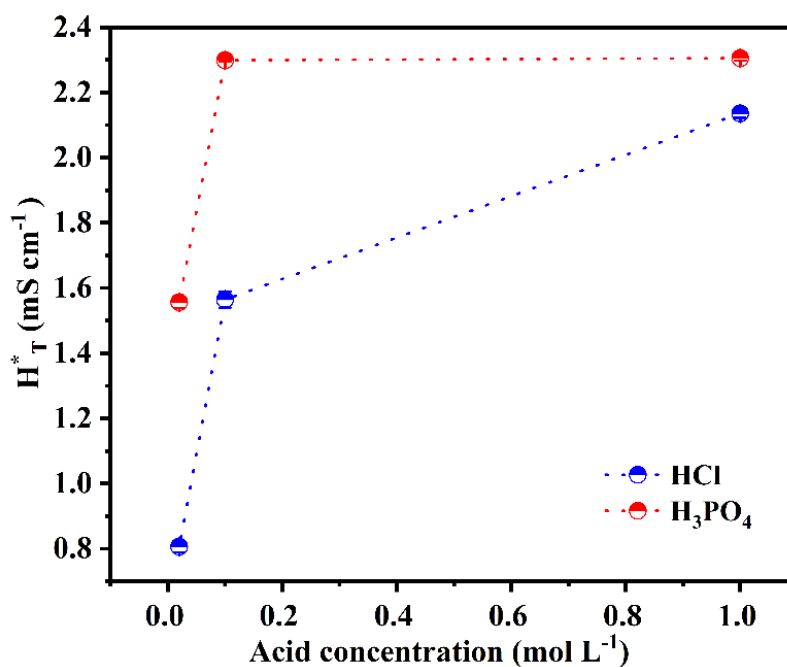


Figure S2.5. Analytical signal of mean $H_T^* \pm 1$ S.D. of post gas exchange of $2000 \mu\text{mol kg}^{-1}$ DIC solution ($n = 6$) vs. different acid concentrations. Two different acids, H_3PO_4 and HCl were used.

Following acid addition to the DIC solution, the pH of the solution was determined. Acidified solutions with both acids with concentrations of 0.1 and 1 mol L^{-1} had a $\text{pH} < 4$, whereas with the lowest concentration, i.e., 0.02 mol L^{-1} of acid, the $\text{pH} > 4$. Although the pK_a value, which is the dissociation constant (K_a) further represented as $-\log_{10} K_a$ (pK_a), of H_3PO_4 (2.16) is greater than that of HCl (-9.3), suggests higher strength to dissociate and ion exchange, the triprotic structure of H_3PO_4 allows it to donate 3 protons in contrast of monoprotic HCl . Therefore, after the first deprotonation, there is possibility to encourage two more deprotonation reactions in equilibrium state with the remaining protons, suggesting more CO_2 extraction from the sample. The result obtained from this experiment, suggested the use of either 0.1 mol L^{-1} or 1 mol L^{-1} H_3PO_4 was preferred over HCl . For the further experiments, 1 mol L^{-1} H_3PO_4 was used to assure maximum CO_2 diffusion from higher concentration of DIC ($> 2000 \mu\text{mol kg}^{-1}$).

Table S2.2. Slope and intercept including their standard deviations, t-values, and the probabilities for the calibration curve of the 7 mmol L⁻¹ NaOH solution shown in Figure 2.9B.

	Value	Standard Error	t-value	Prob> t
Intercept	0.139	0.018	7.717	2.482×10^{-4}
Slope	1.45×10^{-3}	17×10^{-6}	85.57	1.715×10^{-10}

3. Field applications of an autonomous Dissolved Inorganic Carbon analyzer: high resolution spatio-temporal observations in dynamic fjord and coastal waters

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Abstract

Fjord and coastal waters are characterized by a high temporal and spatial variability in carbonate chemistry, influenced by (1) physical forces such as wind, tide, precipitation, and river inputs, (2) biological processes including photosynthesis and respiration, and (3) anthropogenic activities. In these dynamic systems, dissolved inorganic carbon (DIC) exhibits rapid fluctuations that occur on a sub-hourly basis. Understanding the drivers of DIC variability and their role in regulating the carbonate system requires high-resolution spatial and temporal DIC measurements, for which currently no on-site commercial instrumentation is available. To address this gap, a newly developed miniaturized benchtop DIC analyzer using conductometric detection and a sampling frequency of 15 minutes was deployed in coastal settings. The performance of the analyzer was evaluated during (a) a 25-day deployment at a pier in Kiel Fjord, and (b) a 4-day campaign in the German Bight.

Ancillary data, including temperature, salinity, dissolved oxygen, nitrate, $p\text{CO}_2$, pH, and chlorophyll-a were collected using commercial sensors to interpret DIC variability and characterize the carbonate system. In Kiel fjord, the DIC concentration ranged from 1825 to 2229 $\mu\text{mol kg}^{-1}$ with a mean concentration of 2021 $\mu\text{mol kg}^{-1}$, whereas the DIC concentration in the German Bight ranged from 1915 to 2273 $\mu\text{mol kg}^{-1}$ with a mean concentration of 2095 $\mu\text{mol kg}^{-1}$. DIC concentrations were primarily influenced by photosynthesis, respiration, and air-sea gas exchange. The DIC analyzer achieved measurement precisions of $7.24 \pm 3.69 \mu\text{mol kg}^{-1}$ ($n = 96$) in Kiel fjord and $5.48 \pm 4.19 \mu\text{mol kg}^{-1}$ ($n = 20$) in the German Bight, meeting ‘weather quality’ standards (precision of $\pm 10 \mu\text{mol kg}^{-1}$). Discrete DIC samples were collected and analyzed using a commercial DIC analyzer to validate the field measurements, and indicated an accuracy of $-15 \mu\text{mol kg}^{-1}$ ($n = 32$) and $+10 \mu\text{mol kg}^{-1}$ ($n = 29$) for the Kiel fjord and North Sea deployments, respectively. These results demonstrate the DIC analyzer’s capacity for stable and high-resolution DIC measurements in complex coastal and estuarine environments.

3.1 Introduction

The oceans are critical to the global carbon cycle and have absorbed approximately one-third of the total anthropogenic CO₂ emissions since the onset of the industrial revolution (Friedlingstein et al., 2023). The uptake of CO₂ has led to ocean acidification, a process marked by a gradual decrease in ocean pH (Gruber et al., 2019), increase in the partial pressure of CO₂ ($p\text{CO}_2$) and total dissolved inorganic carbon (DIC), while reducing the carbonate ion levels (Doney et al., 2009). The dynamics of the seawater carbonate chemistry are complex, governed by both physiochemical processes, e.g., circulation and mixing, and heat exchange with the atmosphere, and biological processes, including photosynthesis, bacterial oxidation of organic matter and calcification (García-Ibáñez et al., 2024).

The carbonate chemistry of coastal waters and estuaries is further influenced by geomorphology and geochemistry of the drainage basin, freshwater inflow, nutrient loading, tidal dynamics, and episodic weather events (Miller & Ketchum, 1983). Coastal systems are typically impacted by growing population pressures, food demands and industrial development. Despite their ecological and societal significance, coastal regions often lack the extensive temporal and spatial monitoring (Syvitski et al., 2012).

Four carbonate variables in seawater (pH, Total Alkalinity, $p\text{CO}_2$, and DIC) can be directly measured (A. G. Dickson et al., 2007). The dissolved form of CO₂ occurs in three inorganic species: bicarbonate ions (HCO₃⁻), carbonate ions (CO₃²⁻), and undissociated carbonic acid (H₂CO₃), and the sum of all these species is defined as DIC (Zeebe, 2012). The concentration of DIC is a critical variable, as it provides insights into key biogeochemical processes. Specifically, DIC concentrations are indicative of the dynamics between biological activities, such as photosynthesis and respiration by microbial organisms, and abiotic processes, including the dissolution and precipitation of carbonate minerals. Additionally, DIC is determined by air-sea CO₂ exchange, which is modulated by temperature-dependent solubility and gas exchange dynamics (Bass et al., 2013).

To effectively disentangle these processes in coastal and oceanic waters, long-term, high-resolution time-series datasets are required. This would help to delineate potential seasonal

patterns, effects of episodic weather events, and the influence of natural or anthropogenic variability. Short-term episodic or extreme events may have greater impact on the chemical balance of the carbonate system compared to gradual change driven by rising atmospheric CO₂ (Waldbusser & Salisbury, 2014; Wright-Fairbanks et al., 2020). Observations during such events would provide detailed insights into how the carbonate system responds to the dynamic environmental conditions and support the development of an integrated observation and modeling system that describes the environmental drivers of coastal waters (Baschek et al., 2017; Doney et al., 2009).

A detailed observation of dynamic carbonate systems requires continuous observations, which can be effectively achieved using autonomous instruments that require minimum human intervention. For long-term, high-frequency observations of DIC, excellent advances have been made in the development of automated analyzers capable of directly measuring DIC concentration in the field (Bass et al., 2012; Fassbender et al., 2015; Natchanon et al., 2014; Wang et al., 2007). An electrochemical DIC analyzer with conductometric detection achieved a sampling frequency of 1 sample hour⁻¹ with a precision of ± 2.7 in laboratory settings and $\pm 3.6 \mu\text{mol kg}^{-1}$ in the field (Sayles & Eck, 2009). The development of DIC analyzers is still a challenge, particularly in terms of sampling frequency, stability, ruggedness, measurement precision, and reagent consumption. Developments are increasingly focused on establishing more simplified and cost-effective analytical techniques. In this study, a novel miniaturized benchtop DIC analyzer has been employed to automatically measure DIC in coastal and fjord waters. Technical details of the analyzer have been described in Bhattacharya et al., 2024.

This study quantitatively assessed the contributions of various processes controlling DIC at two study sites: (1) a 25-day temporal observation in the Kiel fjord and (2) a 4-day investigation of spatial variability in coastal waters of the North Sea. The analyzer produced high-resolution DIC measurements at an interval of 15 min (i.e., four samples per hour). Additional laboratory measurements from discretely collected samples were used to validate the accuracy of the analyzer's measurements. The aim of this paper is threefold: (1) demonstrate the capability of the prototype DIC analyzer to determine temporal and spatial variability in DIC in highly dynamic systems, (2) develop a universal

data processing protocol, and (3) determine the biogeochemical processes that influence carbonate chemistry, especially, DIC dynamics in Kiel fjord and the North Sea.

3.2 Material and methods

3.2.1 Hydrographic setting

3.2.1.1 Measurements from a pier in Kiel Fjord

The performance of the DIC analyzer was evaluated during a field deployment on the pier of GEOMAR in the inner Kiel fjord (54°19'48.78" N, 10°08'59.44" E) for a period of four weeks from 27th July to 25th August 2023 (Figure 3.1A). Kiel fjord is a 15 km long inner coastal water body and located in the southwestern part of the Kiel Bight (54°19'–54°30' N, 10°06'–10°22' E) (Nikulina et al., 2008; Schröder et al., 2021) (Figure 3.1B). The fjord has an average depth of ~ 13 m, and the depth ranges between 10 to 12 m in the inner section (250 m wide, southern part) and up to 20 m in the outer section (~7.5 km wide) (Nikulina et al., 2008). The temporal variations in salinity are influenced by the inflow of saline waters from the North Sea, fresh waters from the Schwentine River, and brackish waters from the eastern Baltic Sea (Schröder et al., 2021). The Schwentine River has a catchment area of 722.55 km² and an average annual discharge of 202 million m³. Additional freshwater inputs come from rainwater runoff from the city of Kiel (Geißler et al., 2021; Schröder et al., 2021). The water in the inner Kiel fjord is generally well-mixed, except during the summer months when salinity and temperature gradients cause strong stratification of the water column, accompanied by high surface water temperatures (Nikulina et al., 2008). Changes in water level fluctuations (referred to as tide gauge) of up to ± 1 m are driven by wind and pressure gradients in the Baltic Sea (Geißler et al., 2021). The Kiel Fjord also experiences significant anthropogenic pressures due to its proximity to urban infrastructure, shipyards, military and sports harbors, and wastewater discharges from a population of approximately 250,000 in the surrounding area.

3.2.1.2 Measurements from research vessel in the North Sea

The DIC analyzer was deployed in the German Bight of the southeastern North Sea as part of the Sternfahrt-10 expedition onboard RV *Littorina* from 4th to 7th September 2023 (Figure 3.1C and D) (Bussmann et al., 2023). The transect covered the outflow of the Elbe estuary and the region between Cuxhaven (53.85 N, 8.68 E), Helgoland (54.18 N, 7.88 E), and Büsum (54.13 N, 8.85 E). The German Bight is influenced by riverine discharges from the Elbe and Weser rivers, the inflow of saline waters from the North Sea, microbial processes, and strong tidal dynamics (EY, 2017; Hebbeln et al., 2003). The carbonate chemistry of the North Sea is influenced by river inputs, biological productivity and respiration processes, tides that govern water circulation, wind speed and direction, stratification, and coastal upwelling (Brasse et al., 1999a). This region is one of the most intensively investigated areas, with research focusing on the carbon cycle, primary production, metabolism, sediment dynamics, and extreme episodic events (Brasse et al., 1999a, 2002a; Kamjunke et al., 2023; Reimer et al., 1999; Salt et al., 2016; Voynova et al., 2017a). However, despite this extensive research, high-resolution data on DIC concentrations obtained during field expeditions remain limited. During the second study, the DIC analyzer was installed in the laboratory of RV *Littorina* (Figure 3.1C). A 200 L water tank was installed on the deck of the vessel and continuously supplied with surface water from 1.5 m depth (Figure 3.1D). The DIC analyzer was connected to a water line to continuously supply water from the tank using a submerged water pump with an output of 600 L/h (Eheim, Deizisau, Germany).

3.2.2 Function of the DIC analyzer

The DIC analyzer operates with sequential injection analysis involving CO₂ gas diffusion across a Teflon tube into an alkaline solution, followed by conductometric detection in a configuration with four hollow brass electrodes. The analyzer utilizes a 30 cm long “Tube In A Tube” (TIAT) to enable the diffusion of gaseous CO₂ from the sample after acidification (phosphoric acid, 10 % or 1.91 mol L⁻¹) through a gas permeable membrane (Teflon AF2400) into a stream of sodium hydroxide (7 mmol L⁻¹). The change in

conductivity in the alkaline solution is detected by the electrodes and is directly proportional to the DIC concentration of the sample.

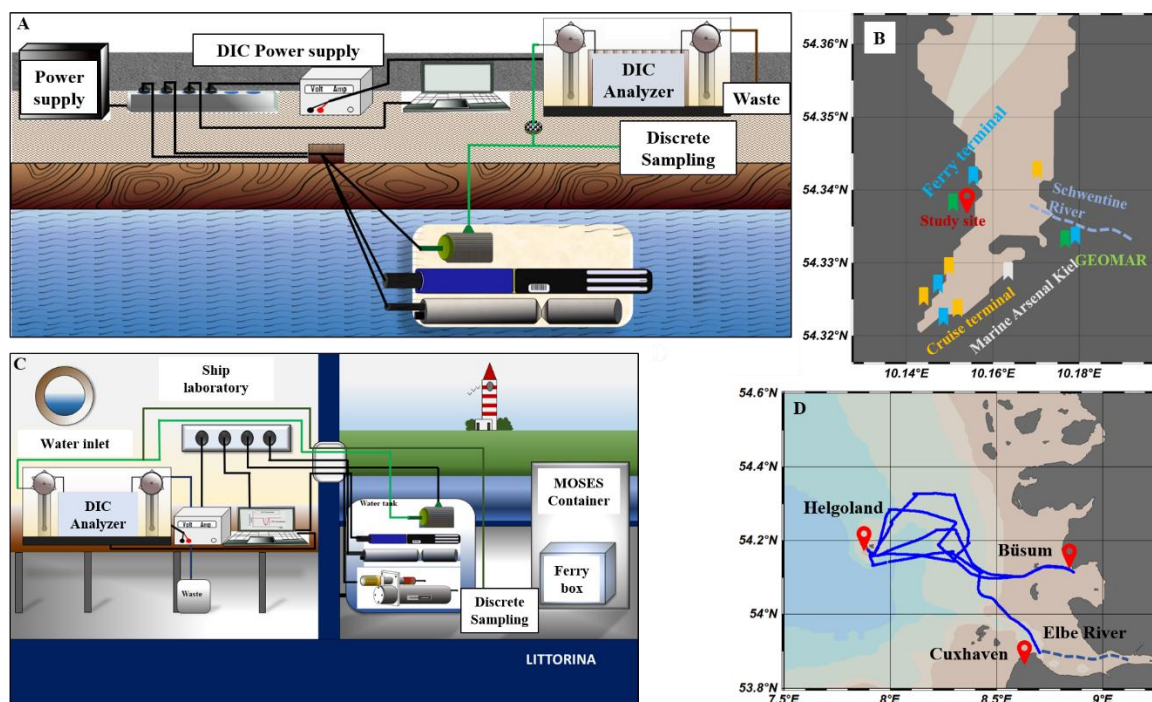


Figure 3.1. (A) Schematic diagram of the field deployment of the DIC analyzer on the pier in the Kiel Fjord along with temperature, salinity, and oxygen probe, nitrate sensor, and a submersible pump, (B) geographic location of the study site in the Kiel Fjord and nearby establishments (color indicated). The Schwentine River is indicated by a blue dashed line (source: Ocean Data View), (C) schematic diagram of the ship-board deployment of the DIC analyzer along with temperature, salinity, and oxygen probe, nitrate sensor, $p\text{CO}_2$ sensor and submersible pump inside a water tank onboard RV *Littorina* during the Sternfahrt-10 MOSES expedition, and (D) transect of the expedition in the German Bight. The Elbe River is indicated by a blue dashed line (source: Ocean Data View).

The analyzer was employed for autonomous measurements of DIC in surface waters. In the first study, the analyzer was installed on a pier and housed in a waterproof container (Figure 3.1A). It continuously measured from 27th July to 10th August 2023 and again from 16th to 25th August 2023 for a total of 25 days. Data between 10th and 15th August could not be retrieved due to a mechanical issue with the syringe pump at the sample inlet port. Surface water was continuously supplied to the analyzer by a submerged water pump with an output of 600 L/h (Eheim, Deizisau, Germany). The water flow was bifurcated into two streams: one directed to the analyzer's sample inlet and the other as an outflow to collect

discrete water samples. The sample inlet of the analyzer was equipped with a 0.8 μm polyethersulfone syringe filter (Pall Life Sciences, USA) to prevent the entry of particles into the internal fluidics. A DIC standard (2000 $\mu\text{mol kg}^{-1}$) (ratio of sodium carbonate (Na_2CO_3) to sodium bicarbonate (NaHCO_3) = 1.26 : 1 in deionized water) was prepared in the laboratory prior to deployment and used as a control during both deployments (Bhattacharya et al., 2024). The analyzer was programmed to automatically measure the DIC standard once per day in order to assess measurement stability and precision throughout the deployment period. The daily value of the DIC standard was obtained from the average of six consecutive measurements. All the reagents and the DIC standard were stored in air-tight borosilicate glass bottles. Each measurement requires 0.2 mL of H_3PO_4 , 0.75 mL of NaOH, and ~ 2 mL of sample, with a sampling frequency of 4 samples per hour. Detailed description and analytical methods of the analyzer have been described by Bhattacharya et al., 2024.

3.2.3 Additional sensor deployment

For the time-series deployment in the first study, an EXO1 probe (YSI, Xylem, USA) was used to measure temperature, salinity, and dissolved oxygen (DO) with a sampling interval of one minute. Additionally, a nitrate sensor (OPUS, TriOS GmbH, Germany) measured surface water nitrate concentrations with a sampling interval of one minute. Both sensors along with the submersible pump, were mounted on an acrylic frame positioned on the pier at a depth of ~ 1 m. Prior to the deployment, the DO probe was calibrated in the laboratory using one-point air-saturated water, whereas the other probes of the EXO1 system were factory-calibrated. To calibrate the DO probe, air-saturated water was prepared by continuous bubbling of deionized water with an aquarium pump and an air stone for over one hour. The nitrate sensor was calibrated by taking a reference absorbance spectrum in nitrate-free (deionized) water before and after deployment. A detailed procedure for nitrate sensor calibration is reported elsewhere (Nehir et al., 2021).

Additionally, the GEOMAR pontoon facility provides continuous time-series *in-situ* data of several biogeochemical and physical variables of the Kiel Fjord as a part of the Kiel Marine Organism Culture Center (KIMOCC) environmental data monitoring program.

Measurements of the partial pressure of CO₂ ($p\text{CO}_2$) were recorded at an interval of one minute using a CONTROS HydroC CO₂ sensor (4H-Jena Engineering GmbH, Germany) (duration: 4th-25th August). The sensor was deployed at 1 m depth.

Weather data (wind speed, temperature, relative humidity, precipitation, solar irradiation) were obtained from the GEOMAR weather station located near the study site, with measurements available at 8-minute intervals. Tide (in meters) for the Kiel Fjord was acquired from the Intergovernmental Oceanographic Commission Sea Level Monitoring Facility (<http://www.ioc-sealevelmonitoring.org/station.php?code=kiel>).

During the study aboard RV *Littorina*, the EXO1 probe and the nitrate sensor were used to measure surface water temperature, salinity, DO, and nitrate concentration, with a sampling frequency of one minute. A submersible $p\text{CO}_2$ infra-red sensor (HydroC, 4H-Jena Engineering GmbH, Germany) was employed to measure CO₂ partial pressure ($p\text{CO}_2$) (Fiedler et al., 2013b) (Figure 3.1C). Prior to the deployment, the sensors were calibrated according to manufacturers' specifications. Additional hydrographic variables (chlorophyll-a and pH) along with GPS data were recorded with a Ferrybox system (4H-Jena Engineering GmbH, Germany) installed on the research vessels (Petersen, 2014).

3.2.4 Discrete water sampling

During the deployment on the pier, a total number of 43 discrete water samples were collected for laboratory DIC analysis in order to validate the measurements from the DIC analyzer. The samples were collected twice a day, once in the morning and/or in the evening, following the best practice procedures outlined by Dickson et al., 2007. The DIC samples were stored in 250 mL narrow-mouth borosilicate glass bottles with air-tight glass stoppers. To inhibit biological activity, 250 μL saturated mercuric chloride solution was added to each sample. The bottle lids were greased and immediately sealed to avoid atmospheric CO₂ exchange until laboratory analysis following the best practices for ocean CO₂ measurements (Andrew G. Dickson et al., 2007). These discrete samples were also used to measure pH using a SAMI pH sensor (Sunburst, USA).

Samples for nutrient analysis were collected in 14 mL low-density polypropylene plastic tubes (Greiner Bio-One GmbH) after filtration through 0.45 μm polyethersulfone filter (Fisher Scientific) and frozen at - 20 °C until analysis.

A total number of 31 discrete surface water samples for DIC and nutrients were collected at hourly intervals during the four-day transects aboard RV *Littorina*. Both DIC and nutrient samples were collected following the same procedures as described above.

3.2.5 Analytical methods

The DIC analyzer was calibrated in the laboratory using three prepared DIC standards (1720, 1908, and 2098 $\mu\text{mol kg}^{-1}$) before and after the deployment in Kiel Fjord. The values of the DIC standards were validated using an Apollo SciTech DIC auto-analyzer (Model AS-C3), based on Non-Dispersive Infra-Red detection, along with measurements of ICOS sub-standard DIC reference materials (RM) with a concentration of $1985 \pm 1.1 \mu\text{mol kg}^{-1}$ (ICOS Ocean Thematic Centre, Norway) (<https://www.icos-otc.org/node/183>).

All discrete DIC samples were analyzed using the Apollo DIC analyzer (AS-C3, Apollo SciTech, LI-7000, LICOR, USA). Samples were first acidified with 1.91 mol L⁻¹ H₃PO₄, allowing the released CO₂ to diffuse and then purged using high purity nitrogen gas. The total CO₂ gas was then detected using a LICOR-7000 infrared analyzer (LI-COR Environmental, USA). Laboratory DIC measurements of discrete water samples were calibrated against RM used daily throughout the measurement period in the laboratory. Each sample was analyzed at least five times. Based on all the RM measurements, average precision and accuracy of ± 2.71 and $\pm 9.83 \mu\text{mol kg}^{-1}$, respectively (n = 52) were achieved. The precision is comparable to the replicate measurements and inter-laboratory comparisons of Certified Reference Material (CRM) from Dr. A.G. Dickson at the Scripps Institution of Oceanography (Bockmon & Dickson, 2015). The ICOS RM was used as the availability of the Dickson CRM was limited during and following the COVID period.

Nutrient samples were analyzed at GEOMAR using an air-segmented nutrient autoanalyzer (QuAAtro, Seal Analytical Ltd.) based on standard wet-chemical colorimetric techniques. Results from discrete nutrient sample analyses (NO₃⁻) were used to correct data recorded

by the nitrate sensor (Nehir et al., 2021). The raw pH values obtained from the discrete samples were processed using the software SAMI QC pH (v 4.0).

3.2.6 Data processing and analysis

The DIC analyzer measured the conductivity of a NaOH solution. A change in the background conductivity signal of the alkaline solution was observed upon diffusion of CO₂ from the acidified seawater sample. This change was quantified as (Δ Cond):

$$\Delta \text{ Cond} = \text{Peak height (H)} = \text{Post baseline value} - \text{Minimum value of peak (unit in mS cm}^{-1}\text{)}$$

The term H is directly proportional to the concentration of DIC. However, as conductivity is strongly affected by temperature, H was normalized with respect to temperature to calculate peak height following the method described by Bhattacharya et al., 2024. In both deployments, water temperature measurements, extracted from the EXO1 sensor and matched to the DIC analyzer's measurement time, were used for the normalization. The influence of salinity on the raw conductivity values of the DIC analyzer was found to be minor in the study by Bhattacharya et al., 2024 and therefore, no salinity correction was required during data processing. Based on this, the calibration factor was determined by measuring DIC standards which were prepared in deionized water (salinity = 0). This study aimed to develop a universal calibration process that would accurately determine DIC concentrations without requiring site-specific salinity adjustments.

For the time-series measurements of DIC in the Kiel Fjord, the analyzer was calibrated twice in the laboratory, i.e., before and after the deployment. The DIC concentrations were calculated by applying a linear drift correction on these two calibration factors (details in Discussion and Supporting Information). These calibration standards were validated by analyses of RMs. The DIC concentrations of discrete samples were checked to compare the field DIC concentrations.

All data from sensors presented in this study were processed using Python software (version 3.9). A Savitzky–Golay filter with a window size of 101 data points and a polynomial order of two was applied on the raw sensor data to reduce noise. Statistical

analyses on the experimental data were performed using open-source libraries using Python software and Origin Pro 2023 (Learning Edition, Origin Lab Corp., U.S.A). All data are presented as mean $\pm$ 1 S.D. Maps were generated using Ocean Data View software (Schlitzer, 2002).

3.3 Results

3.3.1 Observations in Kiel Fjord

The diel variations in salinity, temperature, DO, $p\text{CO}_2$, DIC (analyzer), NO_3^- in surface waters of the Kiel Fjord during the deployment are presented in Figure 3.2, together with ancillary variables (wind speed, solar irradiation, precipitation, and change in water level).

The deployment period was divided into three phases with respect to change in temperature and salinity: (i) 26th July - 4th August: decrease in average temperature from 16.9 °C to 15.2 °C and a sharp increase in salinity from 20.07 to 17.86, (ii) 5th - 14th August: increase in average temperature from 15.1 °C to 16.2 °C and steady decrease in salinity from 18.1 to 19.5, and (iii) 15th - 25th August: steady temperature with a mean value of $\sim 16.7 \pm 1$ °C and salinity with a mean value of 19.6 ± 0.4 (Figure 3.2).

A statistical distribution of all measured variables, including temperature, salinity, DO, NO_3^- , $p\text{CO}_2$, and DIC, are presented in Table 3.1. During the deployment, salinity varied between 17.6 and 21.4, with a mean value of 19.9 ± 0.8 . In contrast, the temperature ranged from 14.7 to 19.5 °C, with a mean of 16.7 ± 1 °C, which is lower than normal for that time of the year (Nehir et al., 2022; Qiu, Esposito, et al., 2023). Salinity fluctuations were particularly pronounced during precipitation events. During the first phase, the mean salinity was 19.8 ± 1.1 , whereas, during the second and third phases, the mean salinity values were 20.4 ± 0.3 and 19.6 ± 0.4 , respectively. In contrast, a steady increase in the mean temperature was observed over the deployment period, with values of 15.9 ± 0.8 °C, 16.4 ± 0.4 °C, and 17.8 ± 0.5 °C observed for each phase, respectively.

A total number of 1644 of data points were recorded by the DIC analyzer. The analyzer measured approximately 74 data points per day, with a sampling frequency of 15 min, excluding the standard measurements. The mean diel variation of DIC throughout the

deployment was $150 \pm 56 \mu\text{mol kg}^{-1}$. During the three phases, the mean DIC value gradually decreased: $2048 \pm 89 \mu\text{mol kg}^{-1}$ during the first phase, $2010 \pm 62 \mu\text{mol kg}^{-1}$ in the second phase, and $1999 \pm 72 \mu\text{mol kg}^{-1}$ in the third phase. The maximum DIC value of $2229 \mu\text{mol kg}^{-1}$ was recorded during the first heavy precipitation phase, whereas the minimum value of $1825 \mu\text{mol kg}^{-1}$ occurred during the third phase along with a rise in temperature. The largest diurnal variation in DIC, $\sim 300 \mu\text{mol kg}^{-1}$, was observed on 30th July, followed by a minimum change of $\sim 80 \mu\text{mol kg}^{-1}$ the next day. Additionally, a total number of 43 discrete samples were collected during the whole deployment, with a mean DIC concentration of $1990 \pm 34 \mu\text{mol kg}^{-1}$.

Surface DO value showed a gradual decrease during the first phase, with the lowest value of $\sim 46\%$ observed on the day of the highest precipitation. The mean surface DO was mostly undersaturated during the whole deployment period ($77 \pm 12 \%$). Low DO values were observed to be consistent with elevated $p\text{CO}_2$ levels. The $p\text{CO}_2$ values ranged from 484 - 1470 μatm , with a mean value of $831 \pm 193 \mu\text{atm}$. The measured pH values from the discrete samples were in the range of 7.5 - 8, with a mean value of 7.8 ± 0.1 ($n = 42$).

Nutrient levels in the water were generally low throughout the deployment. Following the first phase, NO_3^- gradually increased to approximately $5 \mu\text{mol L}^{-1}$ from $\sim 1 \mu\text{mol L}^{-1}$. During the second phase, NO_3^- levels remained stable at around $2 \mu\text{mol L}^{-1}$. However, during the third phase, higher NO_3^- concentrations were observed, corresponding with lower salinity values. Towards the end of the deployment, sensor readings showed significant variability, likely caused by biological growth on the instrument's optical window.

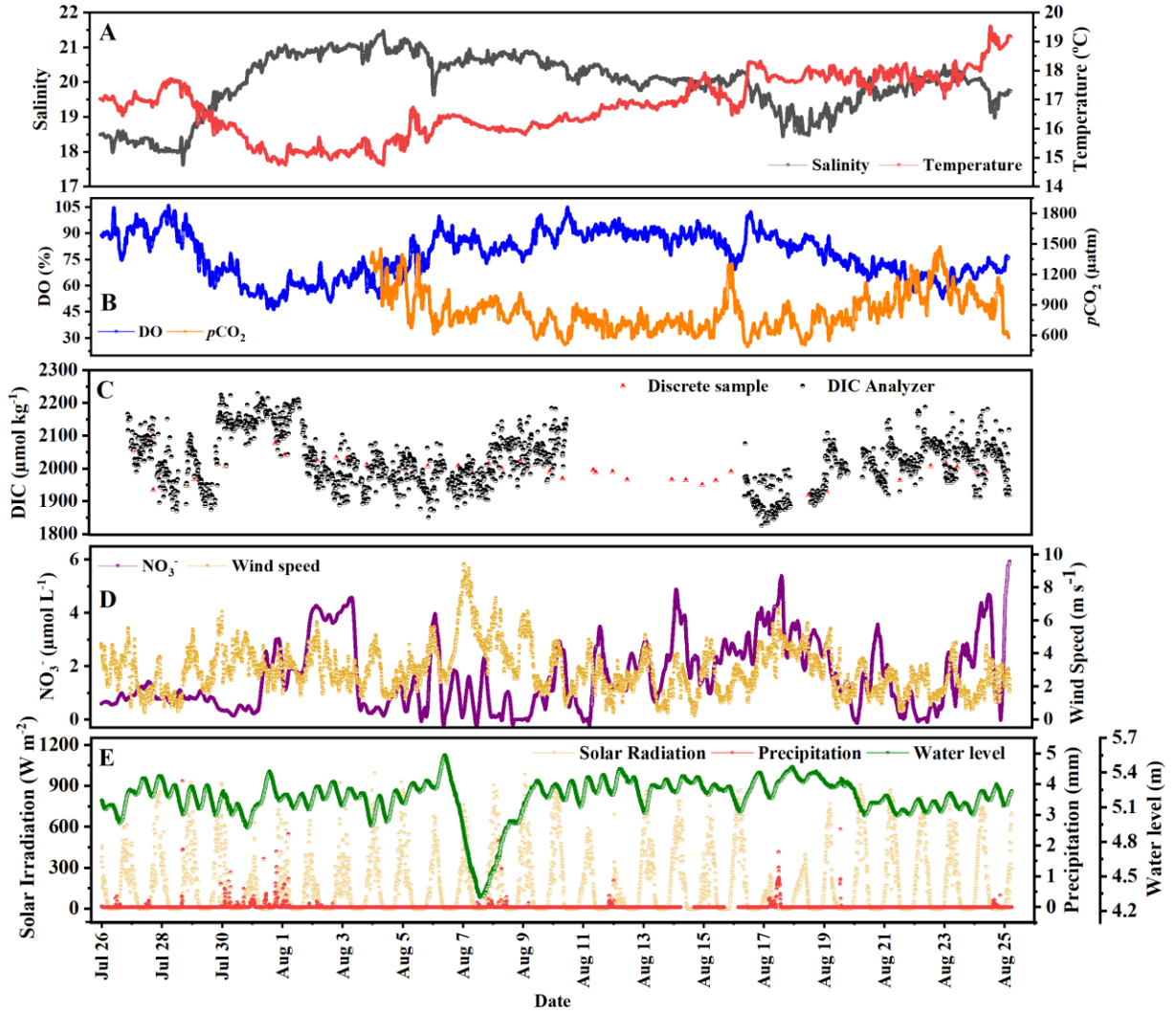


Figure 3.2. Time-series of measurements of (A) salinity (black) and temperature (red), (B) DO (blue) and $p\text{CO}_2$ (orange), (C) data from the DIC analyzer (black dots) and discrete sample data (red triangles measured by the NDIR method), (D) NO_3^- (violet) and wind speed (dark yellow), (E) solar radiation (light yellow), precipitation (red dots) and (change in) water level (green) obtained from multiple sensors deployed at the GEOMAR pier in Kiel Fjord in summer July 27th to August 25th, 2023.

3.3.2 Observations in the German Bight

The second part of the study focused on assessing the performance of the DIC analyzer during the Sternfahrt-10 MOSES research expedition in the North Sea (Figure 3.1D). Figure 3.3 and S3.1 illustrate the spatial variability of key variables, including salinity, DO and $p\text{CO}_2$, pH, chl-a, nutrients, and DIC along the cruise track. A statistical analysis of all

measured values (temperature, salinity, DO, nutrients, $p\text{CO}_2$, DIC, pH, chl-a) is provided in Table 3.1.

Figure 3.3 shows a sharp increase in salinity from a minimum value of ~ 19 near Cuxhaven and ~ 27 near Büsum to a maximum value of ~ 32 near Helgoland. In the German Bight, salinity was relatively constant, with a mean value of 29.6 ± 1.7 . The mean seawater temperature was 19.7 ± 0.3 °C, with a minimum value of ~ 18 °C near Cuxhaven, gradually increasing towards the North Sea. The highest seawater temperature was observed near the coastal waters of Büsum, with an average value of 20.1 ± 0.1 °C. The DO concentrations were consistently below saturation levels in the coastal waters of Cuxhaven and Büsum, with an average value of 98 ± 3 %. In the open water of the North Sea, the average DO concentration was 104 ± 6 %, with some areas showing supersaturation of DO due to primary productivity, reaching a maximum value of 126 %. These elevated DO values were consistent with low $p\text{CO}_2$ (~ 400 μatm).

The highest $p\text{CO}_2$, approximately 600 μatm , was observed in the waters near Büsum, gradually decreasing towards the waters of the German Bight, with $p\text{CO}_2$ ranging between 376 and 549 μatm . The pH distribution exhibited an inverse relationship with $p\text{CO}_2$, with values ranging from 7.9 to 8.2 near the coast (Figure S3.2). As $p\text{CO}_2$ decreased, pH values gradually increased, stabilizing at an average of 8.2 ± 0.06 in the German Bight.

The concentration of chl-a in the region showed a strong correlation with DO, indicating enhanced photosynthetic activity and phytoplankton biomass (Figure S3.2). The lowest chl-a concentration, 0.5 $\mu\text{g L}^{-1}$, was recorded near Helgoland, with generally lower values observed in the open North Sea compared to areas close to land. However, prominent autotrophic zones showed higher chl-a concentration, aligning with elevated DO levels, further confirming intense biological productivity in these areas.

Dissolved nutrient concentrations were highest in the coastal water near Cuxhaven, ranging from 17.5 to 54.4 $\mu\text{mol kg}^{-1}$, and were inversely related to salinity (Figure S3.2). Nutrient levels gradually decreased from 16.7 ± 1.4 $\mu\text{mol kg}^{-1}$ near Büsum towards the German Bight waters with a mean concentration of 9.1 ± 2.9 $\mu\text{mol kg}^{-1}$.

Chapter 3

Table 3.1. Statistical summary for the DIC analyzer and ancillary data during the two deployments

Variables		Kiel Fjord	German Bight
Temperature T (°C) (EXO1)	Min - Max	14.7 - 19.5	20.4 - 18.8
	Average $\pm$ 1 S.D.	16.7 $\pm$ 1.0	19.7 $\pm$ 0.3
	n	42,945	1,676
Salinity (EXO1)	Min - Max	17.6 - 21.4	18.7 - 31.7
	Average $\pm$ 1 S.D.	19.9 $\pm$ 0.8	28.5 $\pm$ 2.2
	n	42,945	1,833
DO (%) (EXO1)	Min - Max	46 - 105	89 - 130
	Average $\pm$ 1 S.D.	77 $\pm$ 12	105 $\pm$ 6
	n	42,945	1,835
NO₃⁻ (μmol kg⁻¹) (Opus)	Min - Max	0 - 5.9	2.8 - 54.1
	Average $\pm$ 1 S.D.	1.6 $\pm$ 1.2	12.1 $\pm$ 7.9
	n	41,976	1,834
pCO₂ (μatm)	Min - Max	484 - 1470	-
	Average $\pm$ 1 S.D.	831 $\pm$ 193	-
	n	29,056	-
DIC (μmol kg⁻¹)	Min - Max	1825- 2229	1915 - 2273
	Average $\pm$ 1 S.D.	2021 $\pm$ 81	2095 $\pm$ 62
	n	1,644	60
pCO₂ (μatm) (HydroC)	Min - Max	-	371 - 600
	Average $\pm$ 1 S.D.	-	448 $\pm$ 47
	n	-	9,248
pH (Ferry box)	Min - Max	-	7.8 - 8.3
	Average $\pm$ 1 S.D.	-	8.1 $\pm$ 0.07
	n	-	2,374
Chlorophyll-a (μg L⁻¹) (Ferry box)	Min - Max	-	0.5 - 3
	Average $\pm$ 1 S.D.	-	1.1 $\pm$ 0.3
	n	-	2,615

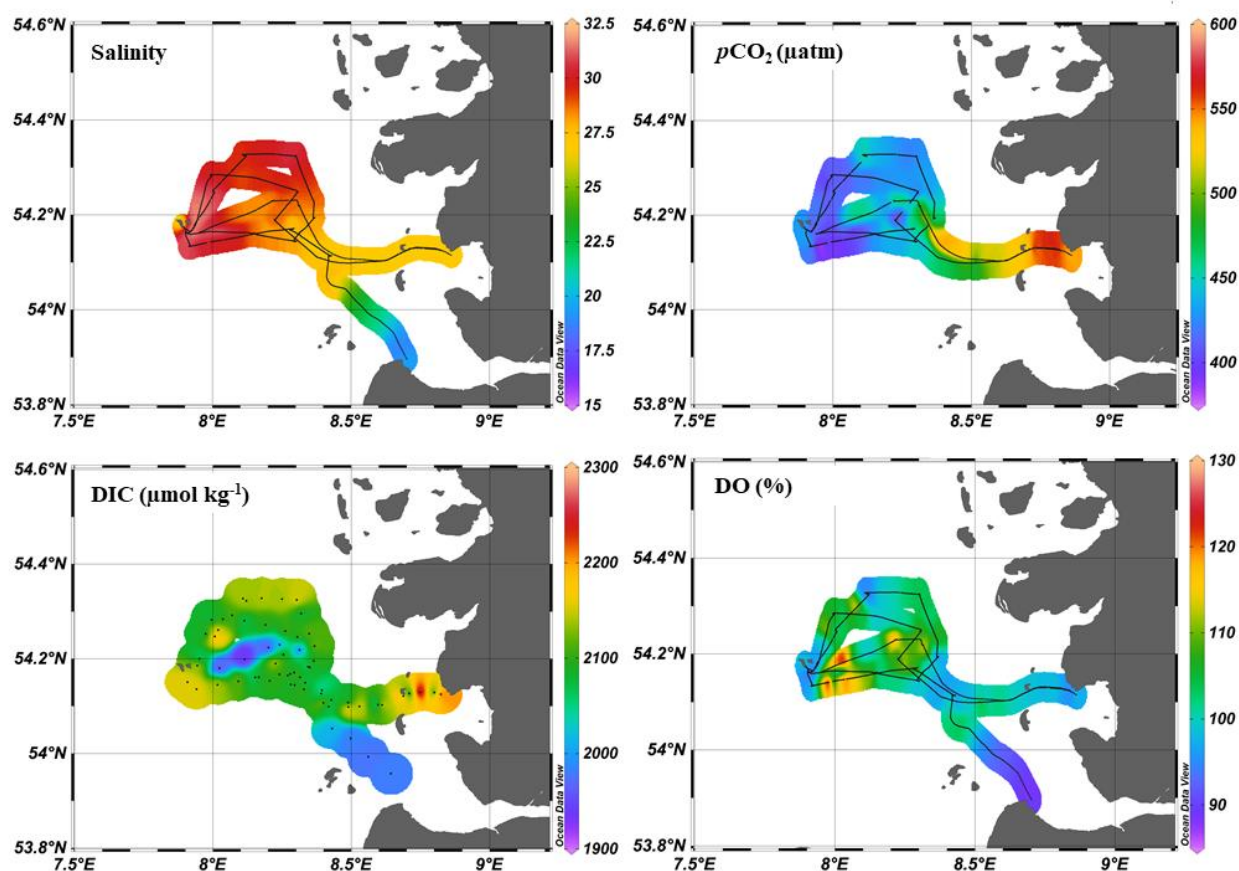


Figure 3.3. Distributions of surface salinity (top left), $p\text{CO}_2$ (top right), DIC (bottom left), and DO (bottom right) obtained from EXO1 probe, DIC analyzer, and HydroC sensors recorded during the Sternfahrt-10 MOSES research expedition. Color bars represent the value ranges of all the variables on the right side of each graph.

The surface distribution of DIC showed high spatial variability along the transect. The DIC analyzer recorded 60 data points, with a mean value of $2095 \pm 62 \mu\text{mol kg}^{-1}$. Concentrations of DIC ranged from 1977 to $2157 \mu\text{mol kg}^{-1}$ on the first day (between Cuxhaven and Helgoland), 2051 to $2188 \mu\text{mol kg}^{-1}$ on the second day (northeast of Helgoland), 2055 to $2273 \mu\text{mol kg}^{-1}$ on the third day (between Helgoland and Büsum), and 1915 to $2097 \mu\text{mol kg}^{-1}$ on the last day (between Büsum and Helgoland). Lower DIC concentrations were observed in waters close to the Elbe outflow (Cuxhaven $\sim 1977 \mu\text{mol kg}^{-1}$) and in the waters with enhanced productivity near Helgoland ($\sim 1935 \mu\text{mol kg}^{-1}$). In contrast, higher concentrations were found near the waters close to Büsum, ranging from 2070 to 2273

$\mu\text{mol kg}^{-1}$. Additionally, a total of 31 discrete samples were collected during the transect, with a mean DIC concentration of $2066 \pm 27 \mu\text{mol kg}^{-1}$.

3.4 Discussion

3.4.1 Kiel Fjord

To evaluate the stability of the analyzer and to check potential instrumental drift, two calibrations were conducted, one before and one after the deployment. The calibrations showed a drift of approximately 30 % in the slopes of the two calibration sets, which most likely occurred due to instrumental drift (Figure 3.4A). A linear drift correction was applied on a sub-hourly interval (matching the DIC measurement frequency) on the slopes and intercepts of the two calibration sets. This new set of calibration factors was implemented to calculate the DIC concentrations (Discussion 1 and Figure S3.3 in the supporting information). The performance of the DIC analyzer was evaluated by comparing discrete DIC samples measured in the laboratory using the Apollo DIC analyzer with onboard measurements from the DIC analyzer. The comparison yielded a linear regression of:

$$y = 1.76 (\pm 0.31) x - 1463 (\pm 608)$$

and a Pearson's correlation coefficient (r) of 0.8 ($p < 0.001$, $n = 21$), excluding outliers (Figure 3.4B). This correlation demonstrates that the slope and offset between the measurements of discrete samples and real-time samples were 1.76 and 1463 $\mu\text{mol kg}^{-1}$, respectively, which can be attributed to one primary factor, i.e., the temperature inside the analyzer was higher than the seawater temperature, especially during the daytime. As the measurement of DIC using the conductometric technique is sensitive to temperature variation, the temperature of the NaOH solution should be considered in addition to the seawater temperature. However, due to temperature fluctuation inside the analyzer, no temperature relation with raw conductivity value was found. The raw conductivity value was only normalized with respect to the ambient seawater temperature (EXO1 probe). Therefore, a stable temperature environment inside the analyzer is required to produce more accurate data.

The measurement precision during the whole deployment was determined to be $7.24 \pm 3.69 \mu\text{mol kg}^{-1}$ ($n = 96$) from the daily standard measurements, which is close to the ‘Weather Quality’ measurement ($\pm 10 \mu\text{mol kg}^{-1}$) (Newton et al., 2015b). The accuracy was calculated as the difference between the DIC values measured by the DIC analyzer and the measurement of discrete samples, and it showed deviations of $-15 \mu\text{mol kg}^{-1}$ ($n = 32$).

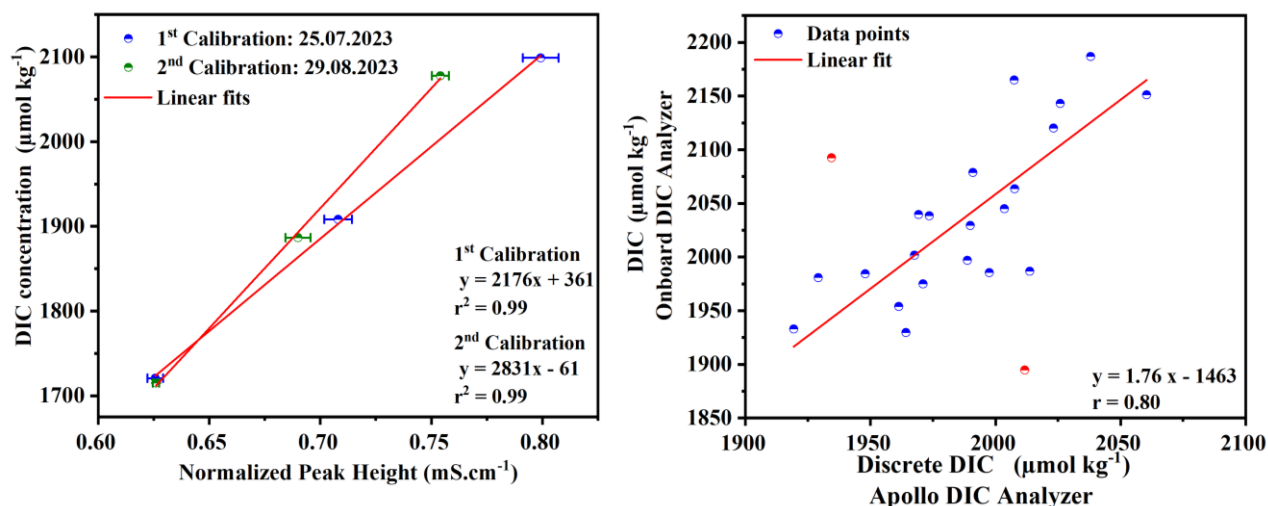


Figure 3.4. Linear regression fit (solid red lines) of (A) temperature normalized peak height ± 1 S.D. of DIC calibration standards before (blue circles) and after (green) the study in the Kiel Fjord (The second calibration factors were used to analyze the also data obtained from the DIC analyzer during the Sternfahrt-10 MOSES research expedition in the North Sea), and (B) DIC concentrations from the DIC analyzer against laboratory analysis of discrete water samples collected during the study in the Kiel Fjord ($y = 1.76x - 1463$, $r = 0.8$, $n = 21$) and the red circles were excluded as the time of collection did not match with measurement timestamps from the analyzer.

A comparison was performed to check the DIC concentrations obtained from the DIC analyzer and theoretically calculated DIC (Discussion 2 and Figure S3.4 in the supporting information). At first, theoretical TA values were calculated using a model described by Lee et al., 2006, and also using the *in-situ* salinity and temperature data from EXO1. This TA dataset, along with *in-situ* $p\text{CO}_2$ data, was further used in the CO2Sys program to compute theoretical DIC values (Lewis et al., 1998; D. E. Pierrot et al., 2011). The range of the theoretical DIC values was from 1990 to 2105 $\mu\text{mol kg}^{-1}$ with a mean value of $2054 \pm 22 \mu\text{mol kg}^{-1}$, whereas the theoretically calculated pH values ranged from 7.5 to 7.9 with a mean value of 7.7 ± 0.08 , closely aligning with the trend and range of pH values obtained from the discrete samples. The result showed that approximately 40 % of the data points

were considered out of the (real-time) measured DIC range (i.e., 1825- 2229 $\mu\text{mol kg}^{-1}$). This discrepancy is likely due to the higher small-scale heterogeneity in near-coastal or estuarine water carbonate chemistry, where localized factors such as weather events and freshwater inflows play a more significant role than in the open ocean (Staudinger et al., 2018). In dynamic environments like the Kiel Fjord, DIC values are strongly influenced by biogeochemical processes and the mixing of different waters. Therefore, while the analyzer showed robust performance with high-frequency measurements, the challenges posed by the highly variable coastal environment should be considered when interpreting the results. This comparison hence, proves that a routine measurement of high quality and high-frequency DIC is primarily needed to specifically understand the carbonate chemistry system of fjords or estuarine waters.

To understand the key drivers of variance of different environmental variables and analyze their interaction during the three phases, a principle component analysis (PCA) with four components was performed. The PCA analysis effectively reduces the complex multivariate data into a lower-dimensional representation and it helps to identify key influences on carbon dynamics in different environmental settings. Figure 3.5 shows the 3D PCA plot (PC1, PC2, and PC3) with the contribution of ten variables, i.e., DO, salinity, temperature, $p\text{CO}_2$, wind speed, solar radiation, precipitation, tide gauge, nutrients, and DIC. The three different phases are depicted as ellipses representing 95% confidence regions. The PCA analysis captured a cumulative variance of 66.9% from the total dataset, with PC1 explaining the highest variance, followed by PC2, PC3, and PC4. The first component, PC1, explained 21.88 % of the total variations and exhibited a strong positive loading on salinity and $p\text{CO}_2$, whereas a strong negative loading on DO and temperature, as shown in table 3.2. PC1 can be considered as to represent the “salinity/physical factor,” and the 1st phase (blue ellipse) appeared to be influenced by these physical factors. It indicates that high DIC levels might be associated with higher salinity and lower oxygen concentrations. The second component, PC2, showed 20.61 % of the total variations, which is strongly influenced by precipitation and tide gauge. The third component, PC3, explained 13 % of the total variance and emphasized the influence of wind speed and solar radiation. Both PC2 and PC3 can be considered to represent the “external environmental factors”. The 2nd phase (green ellipse) shows separation along PC2 and PC3, indicating an

influence of tidal changes and wind speed in comparison to other phases. This suggests that in the 2nd phase, DIC variations might be driven by mixing processes and tidal effects. The 3rd phase (orange ellipse) showed a widespread along PC3, highlighting the role of solar radiation and nutrient dynamics. In this condition, DIC might be influenced by biological processes (e.g., nutrient uptake and photosynthesis). This suggests a dynamic environment with significant water movement, which can affect CO₂ exchange and mixing processes. Finally, the fourth component, PC4, explained 11.36 % of the total variations

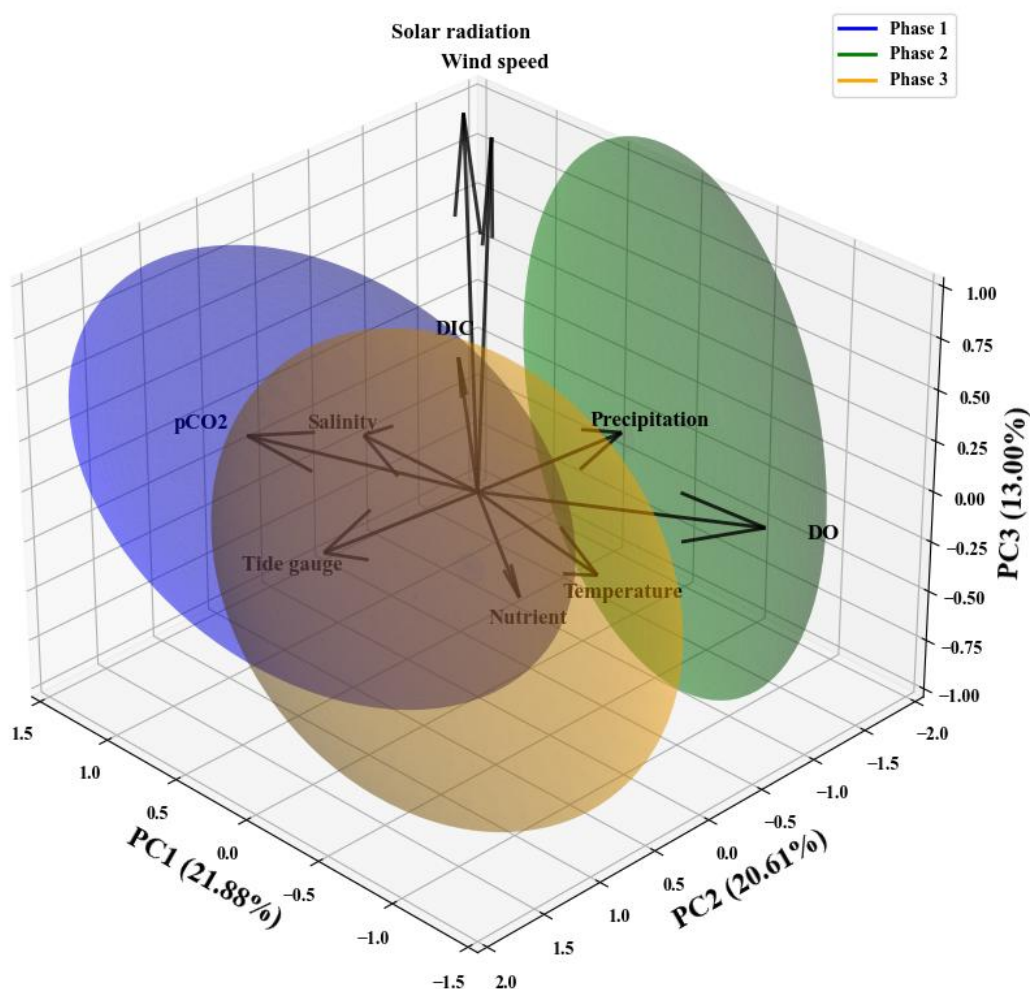


Figure 3.5. A 3D plot of Principal Component Analysis showing the first three principal components of DO, salinity, temperature, $p\text{CO}_2$, wind speed, solar radiation, precipitation, water level, nutrients, and DIC in three phases. PC1, PC2, and PC3 for all the parameters account for 55.49 % of the data. The ellipses correspond to the 95 % confidence regions of three phases.

where nutrients highlighted a strong positive impact, and this variability was not captured by the first three PCs. PC4 can be represented as the “combination of biological and chemical factors”. In the 3rd phase, the strong influence of nutrients on PC4 suggests that biological processes are critical drivers of DIC dynamics.

The inverse relationship between DIC and nutrients suggests that in nutrient-rich waters, biological activity (e.g., uptake by phytoplankton) might lower DIC concentrations. The 2nd phase showed higher variability in this group, and this could be due to a wider range of DIC levels, possibly influenced by fluctuating temperature and salinity conditions. The moderate positive loading of DIC on PC3 (0.208) indicated that the variations of DIC contribute to the spread along the PC3 axis, enhancing the variability seen in the 2nd phase (Table 3.2). The smaller spread suggests that the DIC levels in the 1st and 3rd phases are influenced by similar environmental factors, such as stable temperature and salinity ranges.

Table 3.2. Correlation matrix showing correlation coefficients of all variables with each principle component (PC1, PC2, PC3, and PC4)

Variables	PC1 (21.88 %)	PC2 (20.61 %)	PC3 (13 %)	PC4 (11.36 %)
DO	-0.518	-0.343	0.024	-0.143
Salinity	0.534	-0.274	-0.151	0.209
Temperature	-0.492	0.236	0.084	-0.138
$p\text{CO}_2$	0.405	0.308	0.049	-0.337
Wind speed	0.055	-0.123	0.634	0.226
Solar radiation	0.054	-0.023	0.702	0.101
Precipitation	-0.019	-0.512	-0.011	-0.111
Tide gauge	-0.048	0.608	0.066	0.134
Nutrient	-0.134	0.028	-0.152	0.825
DIC	0.107	-0.073	0.208	-0.169

Correlation plots between salinity, $p\text{CO}_2$, and DO for three separate phases are presented in Figure S3.5A and B. A negative correlation between DO and salinity was observed, with Pearson’s correlation coefficients (r) of - 0.88, - 0.61, and - 0.51 for the respective phases. This suggests that as salinity increases, DO levels decrease significantly across all phases.

Similarly, a negative correlation was found between DO and $p\text{CO}_2$ with r values of - 0.31 (weak correlation due to limited data during sensor maintenance), - 0.69, and - 0.76 for three phases, respectively, indicating that higher $p\text{CO}_2$ levels are typically associated with lower oxygen concentrations related to respiration of organic material. These relationships between DO and $p\text{CO}_2$ provide valuable insights into the underlying biological and physical processes. On the biological side, photosynthesis and respiration play a key role, with photosynthesis driving CO_2 consumption and oxygen production, while respiration has the opposite effect. On the physical side, gas exchange dynamics and temperature variation are influential factors (DeGrandpre et al., 1997; Kuss et al., 2006). During summer, elevated temperatures reduce the solubility of atmospheric CO_2 , which leads to higher $p\text{CO}_2$ levels in the water. At the same time, warm surface waters enhance primary production, increasing oxygen levels as CO_2 is consumed through photosynthesis (Kuss et al., 2006). Increased $p\text{CO}_2$ levels during summer is also indicative of wind-driven transfer of deeper waters to the surface, often associated with higher salinity. In shallow coastal areas of the Baltic Sea, the interaction between the water column and sediment surface further contributes to elevated CO_2 levels due to mineralization processes occurring at the sediment-water interface (Hammer et al., 2014). These dynamics highlight the complex interplay between physical forces and biological activity in shaping the observed relationships between salinity, $p\text{CO}_2$, and DO in the Kiel Fjord, and these correlations are also supported by the PCA.

The DIC values obtained from the analyzer exhibited a weak correlation with salinity during the first two phases, while a Pearson's r value of 0.51 was observed during the third phase (Figure S3.5C). The weak correlations in the first two phases can likely be attributed to heavier precipitations and storm activity, which also disrupted typical temperature and salinity patterns, leading to significant variability in the water mass characteristics. Terrestrial run-off and river inputs during heavy precipitation events, each with varying DIC concentrations, may have further complicated the typical conservative DIC-salinity relationship. For example, during the heaviest precipitation event (~ 4 mm), there was a sharp decrease in DIC concentration ($\sim 125 \mu\text{mol kg}^{-1}$), reflecting the strong influence of freshwater inputs on the system. The inverse relationship between DIC and DO, supported by the PCA, which was typically observed over a diel cycle (Discussion 3 and figure S3.6),

further supports the role of biological processes as the dominant driver of gas fluxes, with photosynthesis increasing DO levels during the day and lowering inorganic carbon concentrations, while respiration at night consumes oxygen and produces CO₂. A stronger correlation between DIC and other variables was observed during the 3rd phase, with DIC showing a negative correlation with DO ($r = -0.73$) and a moderate positive correlation with $p\text{CO}_2$ ($r = 0.53$) (Figure S3.5D and E). These correlations were more pronounced as temperature increased, suggesting that both biological and physical processes played a significant role in driving DIC dynamics. The weakest correlation with DO ($r = -0.29$) occurred during the first phase, likely due to the turbulent conditions caused by the storm, which affected the mixing and exchange processes, reducing the consistency of the relationship. Similarly, during the second phase, a moderate correlation between DIC and $p\text{CO}_2$ ($r = 0.46$) was recorded, reinforcing the influence of both biological and physical processes, including water mass mixing and precipitation-driven runoff, on DIC dynamics.

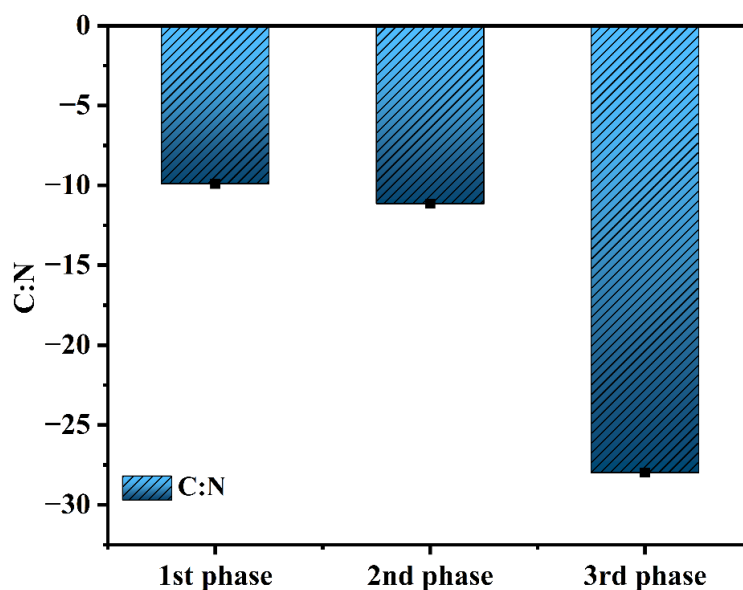


Figure 3.6. Distribution of C : N derived from NO₃⁻ and DIC concentrations during the three phases.

Rivers supply enhanced loads of nitrogen, which are transformed into organic matter and undergo continuous remineralization. This process enriches the system with CO₂, often

leading to oversaturation of CO₂ and undersaturation of DO (Emerson & Hedges, 2008; Stokowski et al., 2020), patterns that were also observed during this study period. To understand how the distribution of nitrogen species is linked to that of inorganic carbon, the proportional changes in DIC and nutrient concentrations were assessed and compared with the Redfield ratio, i.e., the stoichiometric ratios of the (Gruber, 2008; Redfield, 1934). The observed C : N during the three phases were - 9.9, - 11.15, and - 27.98, respectively, and these values were lower than the classic Redfield ratio C : N = 6.6 (Figure 3.6). This deviation is primarily due to the different waters (estuarine water instead of Baltic Sea water) and the movement and mixing of water masses due to wind, river input, and land run-off. The reaction of photosynthesis and respiration processes are also contributing factors (Gruber, 2008). During the 1st two phases, the NO₃⁻ uptake was more than that of the 3rd phase, whereas more regeneration of NO₃⁻ was found in surface water than DIC during the 3rd phase. Higher C : N suggests N loss due to denitrification and the occurrence of deep remineralization (Esposito et al., 2021; Gruber, 2008). The strong inverse relationship between *p*CO₂ and DO is driven by the net effect of biological production and remineralization of organic matters (Figures S3.5B), with the relationship also being influenced by the differing equilibration times of O₂ and CO₂ with the atmosphere (Schneider & Müller, 2018). Wind-driven mixing and tidal events further complicate the picture, as they bring nutrient-rich subsurface waters to the surface, which enhance CO₂ production and O₂ consumption as respiration increases. This mixing process, along with the observed trends in temperature and salinity, drives the system towards higher CO₂ levels, particularly in regions with greater biological activity and physical disturbances. On the other hand, DIC exhibited a strong inverse correlation with temperature ($r = - 0.68$, picture not shown), suggesting a moderate influence of air-sea gas exchange. This pattern indicates that during the summer, carbon dynamics in this region are regulated by the combination of physical and biological processes.

3.4.2 German Bight

The performance of the DIC analyzer was evaluated by comparing onboard DIC measurements using the DIC analyzer with laboratory measurements using the Apollo DIC

analyzer. The comparison yielded reliable data, showing a strong correlation with a linear regression of:

$y = 0.71 (\pm 0.09) x + 610 (\pm 182)$, $r = 0.85$ ($p < 0.001$, $n = 27$), excluding the data points when measurement time did not match sampling time (Figure 3.7A). The measurement precision was $5.48 \pm 4.19 \mu\text{mol kg}^{-1}$ ($n = 20$), whereas the accuracy was $+10 \mu\text{mol kg}^{-1}$ ($n = 29$) during the 4-day cruise in the North Sea. Coastal environments are subject to several significant DIC sources, including respiration, benthic calcium carbonate (CaCO_3) dissolution, denitrification, and sulfate reduction. Meanwhile, key sinks include photosynthesis and CaCO_3 precipitation within the water column, nitrification and sulfide oxidation in sediments. Additionally, land-derived inputs of organic matter and nutrients play a crucial role in balancing production and respiration in these ecosystems (Borges & Gypens, 2010; Carstensen et al., 2018).

Surface salinity distribution data (ranging between 19 and 25) indicated enhanced river discharge from the Elbe River along the outer estuary of the west coast of Schleswig-Holstein. In this region, salinity ranged from ~ 26 to 32, with the coastal waters near Büsum exhibiting the highest surface water temperature ($\sim 20^\circ\text{C}$). A significant deviation from the linear relationship between DIC and salinity was observed near the coast, likely due to the mixing of riverine water and land runoff (Figure 3.7B). The variation in DIC values along the transect reflected the characteristics of different waters, with the highest DIC concentration ($2273 \mu\text{mol kg}^{-1}$) recorded near Büsum, where both water temperature ($\sim 20^\circ\text{C}$) and salinity (> 26) were elevated. This high DIC concentration could be attributed to sediment-water interactions, including processes such as sediment respiration and anaerobic degradation (e.g., denitrification and sulfate reduction) (Brasse et al., 1999b; Cai et al., 2017), which are common in coastal and estuarine regions.

Samples from the German Bight (Figure 3.7B) collected across high salinity gradients showed a decrease in DIC concentrations, suggesting that primary production, especially during spring bloom, plays a dominant role in regulating carbon distribution rather than simple mixing with river water. In areas with low salinity, a non-linear relationship between salinity and DIC was observed (Figure 3.7B). This can be explained by the "titration" effect (an enhancement of the carbonate buffer), where freshwater mixes with

seawater enriched in carbonate ions (CO_3^{2-}), increasing bicarbonate ions (HCO_3^-) (Brasse et al., 2002b). Additionally, precipitation and evaporation influence salinity, which in turn affects the solubility and dissociation of CO_2 . Variations in both salinity and temperature alter DIC speciation and CO_2 solubility, amplifying the observed trends in $p\text{CO}_2$ (Carstensen et al., 2018). These processes demonstrate the complex interplay between physical and biological factors in regulating carbon dynamics in the coastal and estuarine environments of the German Bight.

The carbonate system in the North Sea and surrounding coastal regions exhibits a nonlinear behavior, with $p\text{CO}_2$ levels increasing more sharply than DIC concentrations, particularly with increasing temperature and salinity (Melzner et al., 2013). In highly saline waters, $p\text{CO}_2$ levels were notably low ($\sim 376 \mu\text{atm}$), suggesting these waters were below atmospheric equilibrium, acting as carbon sink (Figure 3. S2). On average, marine areas were near equilibrium with atmospheric CO_2 , with a mean $p\text{CO}_2$ of $423 \pm 20 \mu\text{atm}$.

During summer, surface waters often become undersaturated in CO_2 due to intensive primary production. Stratification of the water column during this period prevents the upward mixing of CO_2 from below the thermocline, reinforcing undersaturation at the surface. This enhanced primary production leads to net autotrophic conditions in the North Sea (Brasse et al., 2002b). Studies indicate that air-sea CO_2 flux contributes to less than 10% of the total variation in $p\text{CO}_2$, with biological processes playing the dominant role (Cai et al., 2004). Therefore, during summer, $p\text{CO}_2$ distribution in surface waters is largely driven by biological activity, outweighing the influence of temperature increases. In contrast, the coastal waters showed greater variability in $p\text{CO}_2$ compared to the open ocean. Inputs from rivers deliver organic particulate and dissolved materials to coastal areas, where they undergo remineralization in the water column. This leads to $p\text{CO}_2$ supersaturation ($\sim 593 \mu\text{atm}$) and CO_2 outgassing (Brasse et al., 2002b). These high $p\text{CO}_2$ values align closely with elevated DIC concentrations (Figure 3.7C), suggesting that remineralization processes in coastal waters significantly influence carbon dynamics and CO_2 fluxes in these regions. The DO distribution along the salinity gradient of the transect showed moderate oxygen utilization ($\sim 88 \%$) in the low-salinity waters and oxygen supersaturation ($\sim 125 \%$) at higher salinities (Figure S3.2). The sediments in the estuary,

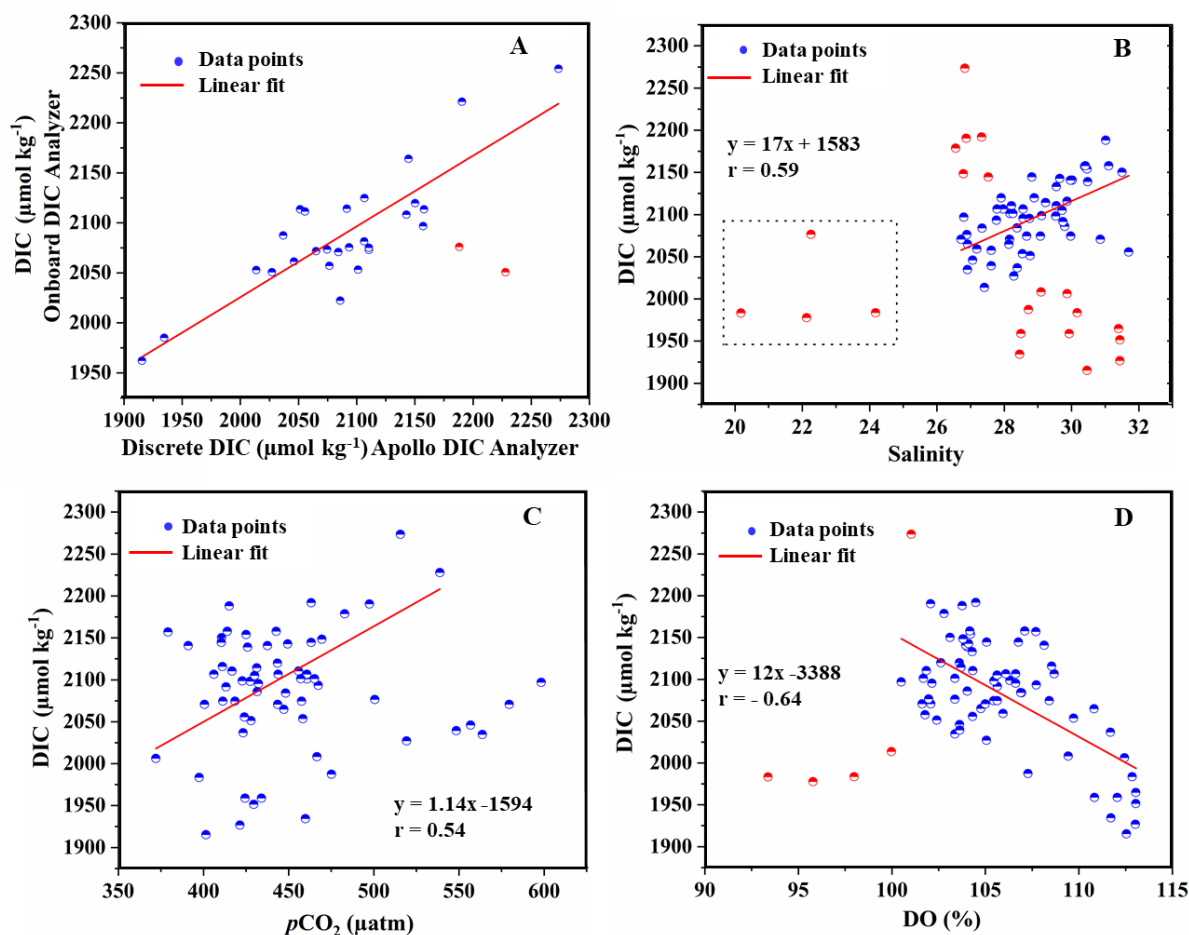


Figure 3.7. Linear regression fit (solid red line) between DIC concentrations from the DIC analyzer against laboratory analysis of (A) discrete water samples collected during the Sternfahrt-10 MOSES research expedition in the North Sea ($y = 0.71x + 610$, $r = 0.85$, $n = 27$). The red circles were excluded as the time of collection did not match the measurement timestamps from the analyzer. Linear regression fit (solid red line) between mean DIC concentrations from the DIC analyzer with respect to (B) salinity, (C) $p\text{CO}_2$, and (D) DO during the Sternfahrt-10 MOSES research expedition. The data points shown in red circles are considered outliers as freshwater inputs as low saline water and anomalous data points from conservative relations. The red circles are considered outliers as freshwater input, low saline water and anomalous data points from conservative relation.

composed mainly of organically rich muds, result from the flocculation of colloidal materials carried by rivers and the concentrations of particulate organic carbon. These sediments are a site of intense anaerobic processes, which lead to reduced DO levels in the surrounding estuarine waters (Gattuso et al., 1998). A negative correlation between DIC and DO was observed, indicating that primary production and decomposition processes largely influenced the distribution of carbon species (Figure 3.7D). This trend aligns with the presence of elevated phytoplankton biomass, which is associated with higher oxygen

saturation (Kamjunke et al., 2023). Elevated DO levels at higher salinities further suggest active photosynthesis driving oxygen supersaturation, while lower DO levels near the estuary reflect the impact of anaerobic decomposition in sediment-rich environments. During the summer, pH levels are typically elevated, driven by increased biological production during the spring bloom (Blackford & Gilbert, 2007), with a strong anticorrelation with $p\text{CO}_2$ (Figure S3.2). The particularly high pH observed in August was likely a result of a coastal bloom triggered by the influx of nutrients and possible water column stratification. Elevated nutrient concentrations were detected in the low-salinity waters near the Elbe estuary, likely caused by organic matter degradation, redox conditions, basin drainage chemistry, and anthropogenic influences (Cai et al., 2004). In contrast, marine waters typically exhibited nitrogen depletion in summer, suggesting efficient nutrient uptake by marine organisms. This nutrient pattern highlights a highly productive zone near the estuary's mouth, where tidal dynamics transport nutrients into the estuary during flood tides and out toward the bay during ebb tides. The low-salinity waters that reached the German Bight were initially characterized by elevated chl-a concentration, likely due to the seaward transport of a coastal bloom previously observed near Cuxhaven (Figure 3.3 & S3.1) (Voynova et al., 2017b). These high chl-a levels could be likely attributed to excess nutrient inputs from the river, supporting the dominance of coastal phytoplankton species that find optimal growth conditions with sufficient nutrients when moving away from the estuary. High nutrient loads from rivers can lead to eutrophication, significantly boosting net ecosystem production and promoting a system dominated by primary production. Nutrient loading, especially of nitrogen and phosphorus, often fuels phytoplankton blooms that can drive substantial biogeochemical changes in coastal ecosystems (Gattuso et al., 1998; Lohrenz et al., 1997).

3.5 Conclusion and Future Perspectives

The autonomous DIC analyzer was successfully tested under diverse field conditions, including Fjord, estuarine, and coastal waters, demonstrating its robustness, stability, and wide applicability in capturing high-resolution data. While the analyzer has achieved 'Weather Quality' measurement precision, there is room for improvement to reach the 'Climate Quality' measurement ($< \pm 2 \mu\text{mol kg}^{-1}$). In the current study, the post-processing

of raw data includes temperature normalization, linear drift correction as foundational steps for a universal data processing framework to calculate final DIC concentrations. It can be refined through developing a more robust universal post-processing procedure by (1) testing across different water masses to apply site-specific salinity correction and (2) applying conditions for seasonal differences within the annual DIC cycles. It could eliminate the need for pre-calibration and streamline future applications. Moreover, to generate more accurate results, all the calibration procedures for the whole deployment can be done using only one RM/CRM instead of lab-made standards. Additionally, the temporal dataset from the Kiel Fjord and the spatial dataset from the North Sea provided by the DIC analyzer allowed us to unravel the hydrodynamic and biogeochemical processes occurring in these highly dynamic coastal and estuarine waters. Unlike the relatively stable carbonate chemistry of the open ocean, these regions experience rapid changes, often on an hourly to sub-hourly scale, that cannot be effectively captured by traditional manual sampling and lab-based analysis. Real-time measurements from the DIC analyzer filled this gap, providing the high-frequency datasets needed to better understand these fast-changing systems. The integration of additional sensor data (e.g., temperature, salinity, dissolved oxygen, nutrients, pH, and $p\text{CO}_2$) during these studies enhanced the comprehensive understanding of the environmental conditions and improved the functionality of the analyzer in terms of data processing. A comparison of sensor data with previous studies indicated that the physiochemical properties of the Kiel Fjord are changing over time, likely due to anthropogenic inputs, commercial utilization of the area, and abrupt weather changes. Statistical analysis of DIC variability along with other environmental factors, offers valuable insights into the drivers of temporal and spatial fluctuations in the carbonate dynamics in these complex systems. Our findings suggest that during summer, biological activity has a more significant impact on DIC trends and carbon cycling than physical or chemical processes alone. In the future, the development and deployment *in-situ* of the DIC analyzer is planned. This will support long-term investigations on the carbon dynamics, allowing for detailed spatial and temporal analysis of DIC alongside other environmental variables. These efforts will help to identify carbon sinks and sources in these regions and enable the generation of multi-year, high-frequency datasets across different seasons. Such studies will also contribute to develop new algorithms linking

carbonate chemistry with other oceanographic properties, improving the parametrization of biogeochemical models. Ultimately, this knowledge will be critical for developing scientific models and sustainable management strategies in response to ongoing global environmental changes.

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CRedit authorship contribution statement

Sayoni Bhattacharya: Writing - original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Mario Esposito:** Writing - review & editing, Supervision, Investigation, Conceptualization, installation of the analyzer and sensors on the deployment platform. **Toste Tanhua:** Writing - review & editing, Supervision. **Eric P. Achterberg:** Writing - review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. **Data availability** Data will be made available on request.

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3.6 Supporting information

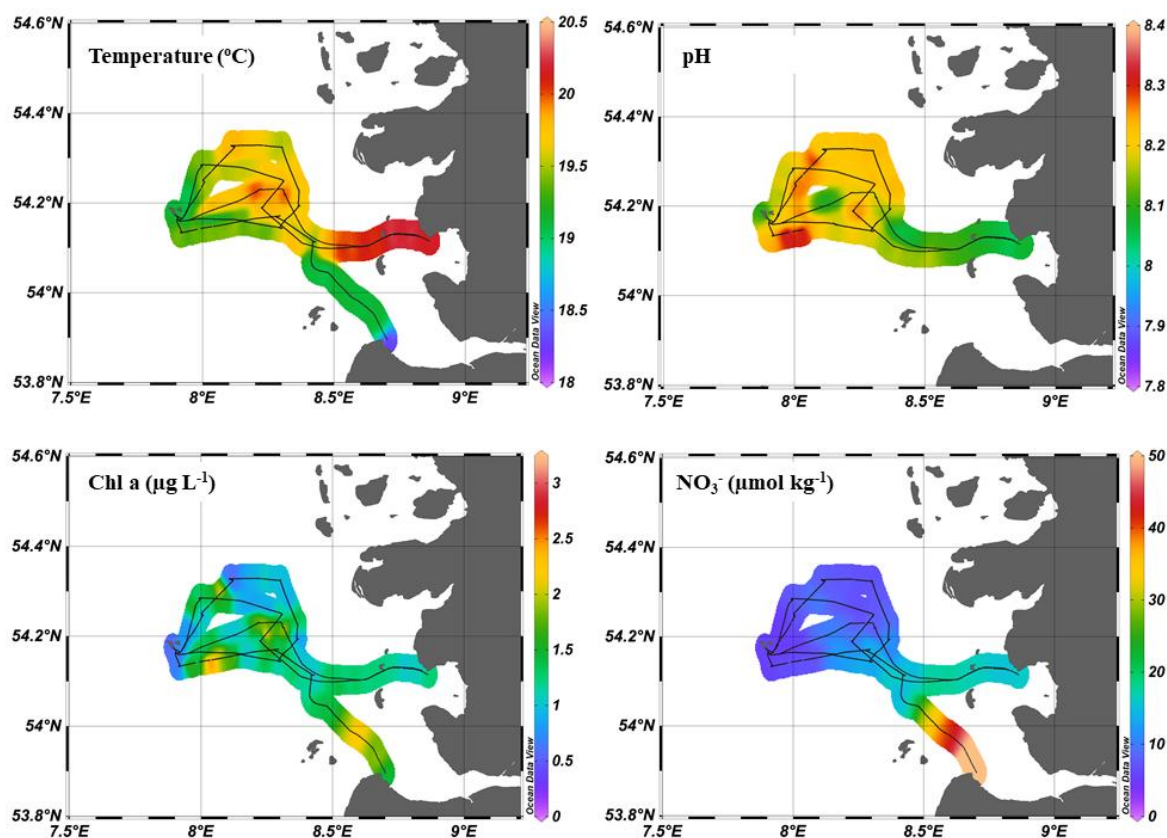


Figure S3.1. Distributions of surface temperature (top left), pH (top right), chl-a (bottom left), and NO_3^- (bottom right) obtained from EXO1 probe, the ferry box, and Opus sensors, respectively, recorded during the Sternfahrt-10 MOSES research expedition. Color bars represent the value ranges of all the parameters on the right side of each graph.

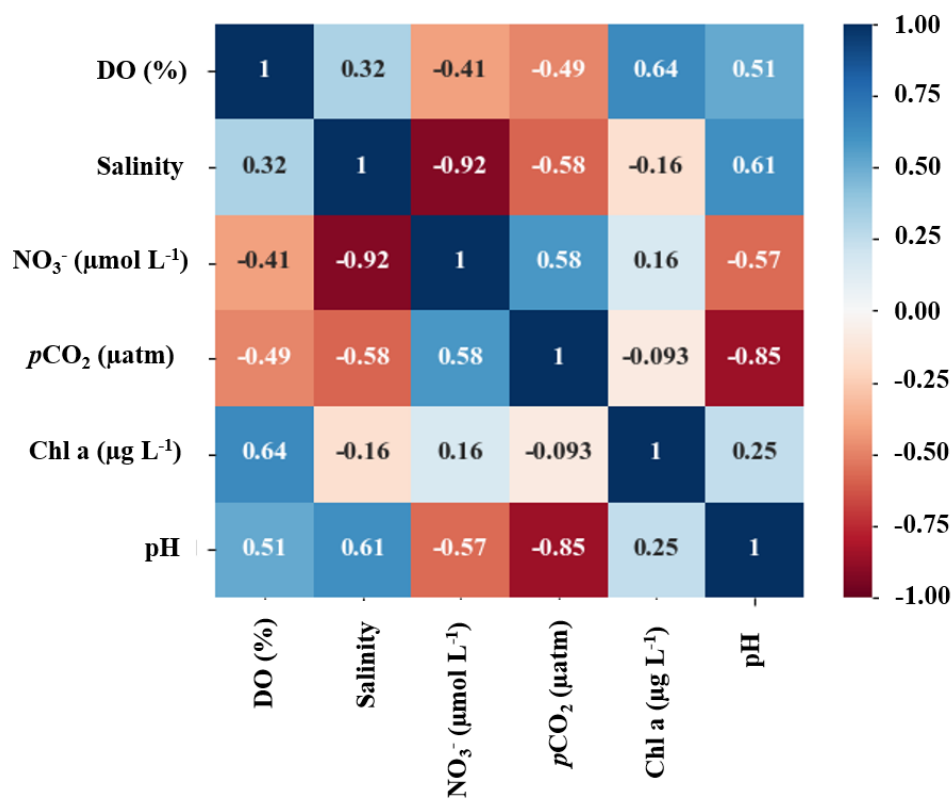


Figure S3.2. Spearman correlation matrix of sensor data points during Sternfahrt-10 MOSES research expedition on 4th - 7th September 2023; Positive correlation coefficients are illustrated in blue boxes, negative ones in red.

Discussion 1:

DIC calculation from raw data

The calculation of DIC concentrations from the raw dataset was tested using three approaches: (A) Linear drift correction: it was applied due to a slight drift (~30%) observed in the slopes during pre- and post-calibration tests. Following temperature correction and (A) linear drift correction on calibration factors, the DIC values ranged from 1825 - 2229 μmol kg⁻¹ with a mean value of 2021 ± 81 μmol kg⁻¹, (B) 2nd calibration factor applied to the whole dataset: it showed the DIC range as 1825 - 2592 μmol kg⁻¹ with a mean value of 2201 ± 169 μmol kg⁻¹, and (C) 1st calibration factor applied to the whole dataset: the DIC concentration ranged from 1556 to 2312 μmol kg⁻¹ with a mean value of 1925 ± 167 μmol kg⁻¹ (Figure S3.3). The direct application of only the calibration factors (first or second)

across the entire dataset resulted in a wider range of DIC values, which did not align with the measurements of discrete DIC samples. This inconsistency highlights the importance

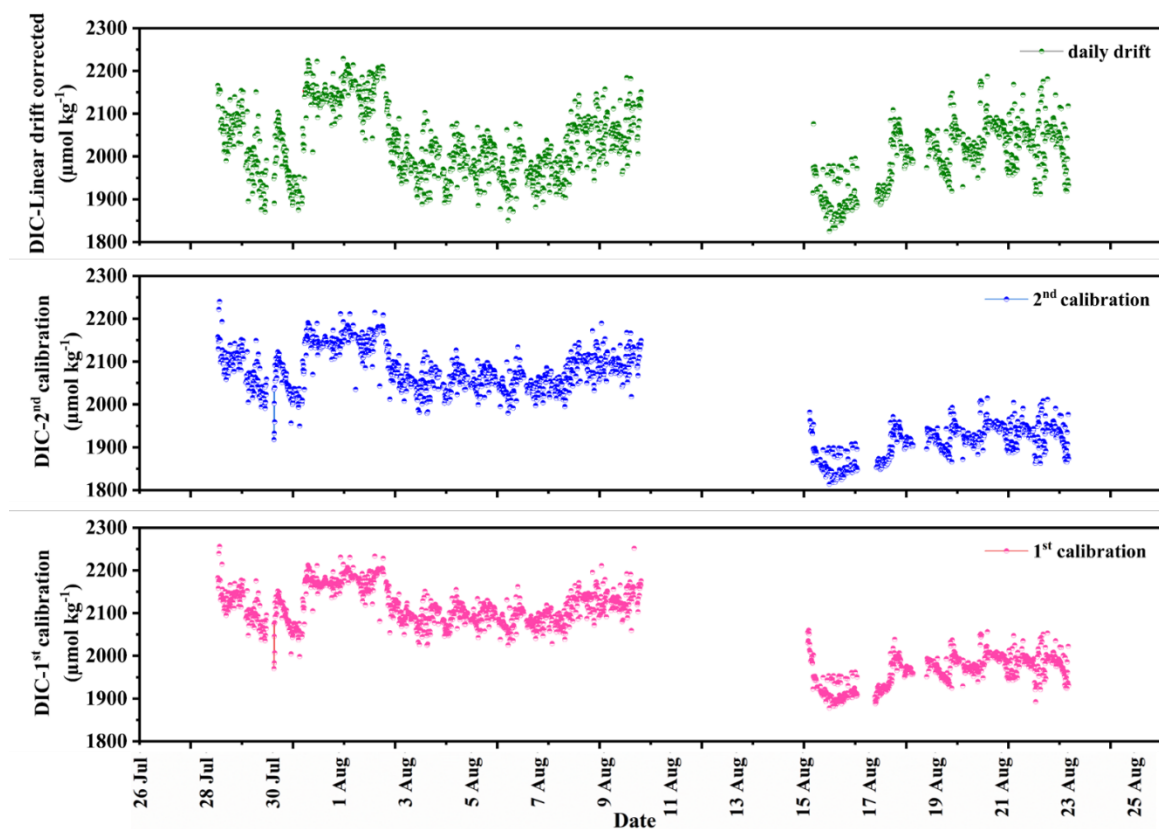


Figure S3.3. Time series variation in DIC was calculated using (A) linear drift correction, (B) 2nd, and (C) 1st calibration factor on the whole dataset.

of addressing potential instrumental drift. In this case, implementing a simple linear drift correction effectively resolved the issue and allowed for more accurate DIC calculations. This approach ensures the reliability of the DIC dataset, aligning it more closely with independently validated discrete sample measurements.

Discussion 2:

Comparing DIC concentration obtained from the DIC analyzer and theoretically from CO₂SYs

To compare the DIC values obtained from the DIC analyzer with theoretically derived data, concentrations of total alkalinity (TA) were used. In the Baltic Sea, TA values deviate from direct calculations due to strong influences from salinity and the mixing of different water

masses (Hammer et al., 2014; Müller et al., 2016). Consequently, theoretical TA values were estimated using one of the models for the North Atlantic Ocean region of (30°N - 80°N) as described by Lee et al., 2006, based on *in-situ* salinity and temperature data from EXO1. These theoretical TA values, along with *in-situ* $p\text{CO}_2$ data, were then used as input parameters in the CO2Sys program to compute theoretical DIC values (Lewis et al., 1998; D. E. Pierrot et al., 2011). The theoretical DIC values ranged between 1990 and 2105 $\mu\text{mol kg}^{-1}$ with a mean value of $2054 \pm 22 \mu\text{mol kg}^{-1}$. Correspondingly, theoretical TA values ranged from 2081 and 2164 $\mu\text{mol kg}^{-1}$ with a mean value of $2113 \pm 16 \mu\text{mol kg}^{-1}$. This theoretical TA range was higher than previously reported values ($1967 \pm 18 \mu\text{mol kg}^{-1}$), likely due to the lower salinity range ($\sim 13 - 17$) in earlier studies compared to the higher salinity ($\sim 17 - 21$) observed during this summer period varied (Qiu, Esposito, et al., 2023). The calculated pH values ranged from 7.5 to 7.9 with a mean value of 7.7 ± 0.08 , closely aligning with the trend and range of pH values obtained from the discrete samples.

The DIC values obtained from the analyzer showed a significant relationship with theoretically calculated DIC values, with the regression equation of:

$$y = 0.36x + 1339, r = 0.78 \text{ (Figure S3.4)}$$

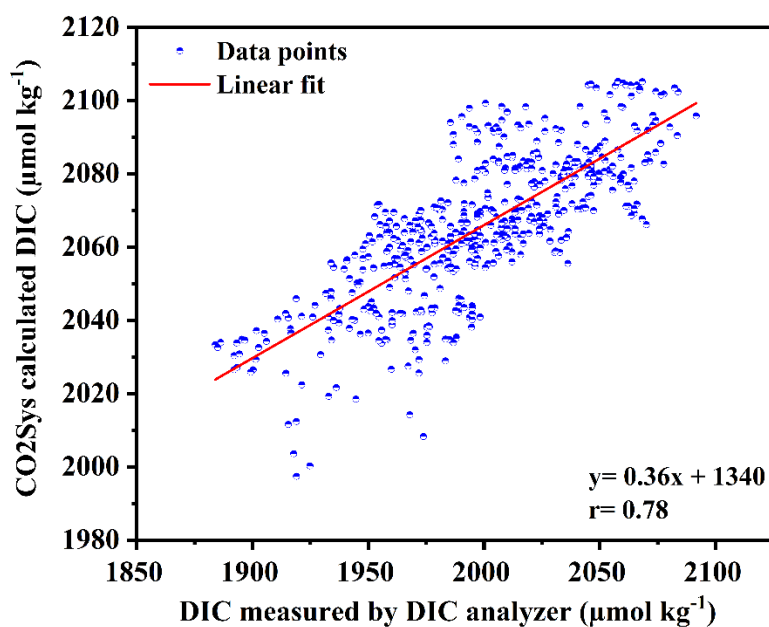


Figure S3.4. Linear regression fit (solid red line) between all DIC values obtained from the DIC analyzer against calculated DIC concentrations from CO2Sys (n=512) using theoretical TA and *in-situ* $p\text{CO}_2$ measurements as a pair.

This close alignment between the measured and calculated values further supports the accuracy and reliability of the DIC analyzer. However, approximately 40 % of the data points were considered outliers, likely due to the salinity range used for TA calculation being outside the range suitable for this study. In dynamic environments like the Kiel Fjord, DIC values are strongly influenced by biogeochemical processes and the mixing of different water masses. The outliers could be attributed to the incomplete mixing of water layers, which can lead to inconsistency between directly measured DIC and theoretically derived values, particularly when using parameters more applicable to open-ocean conditions. Coastal regions tend to exhibit greater variability in DIC measurements due to these factors, leading to more pronounced deviations from theoretical predictions based on more stable oceanic conditions.

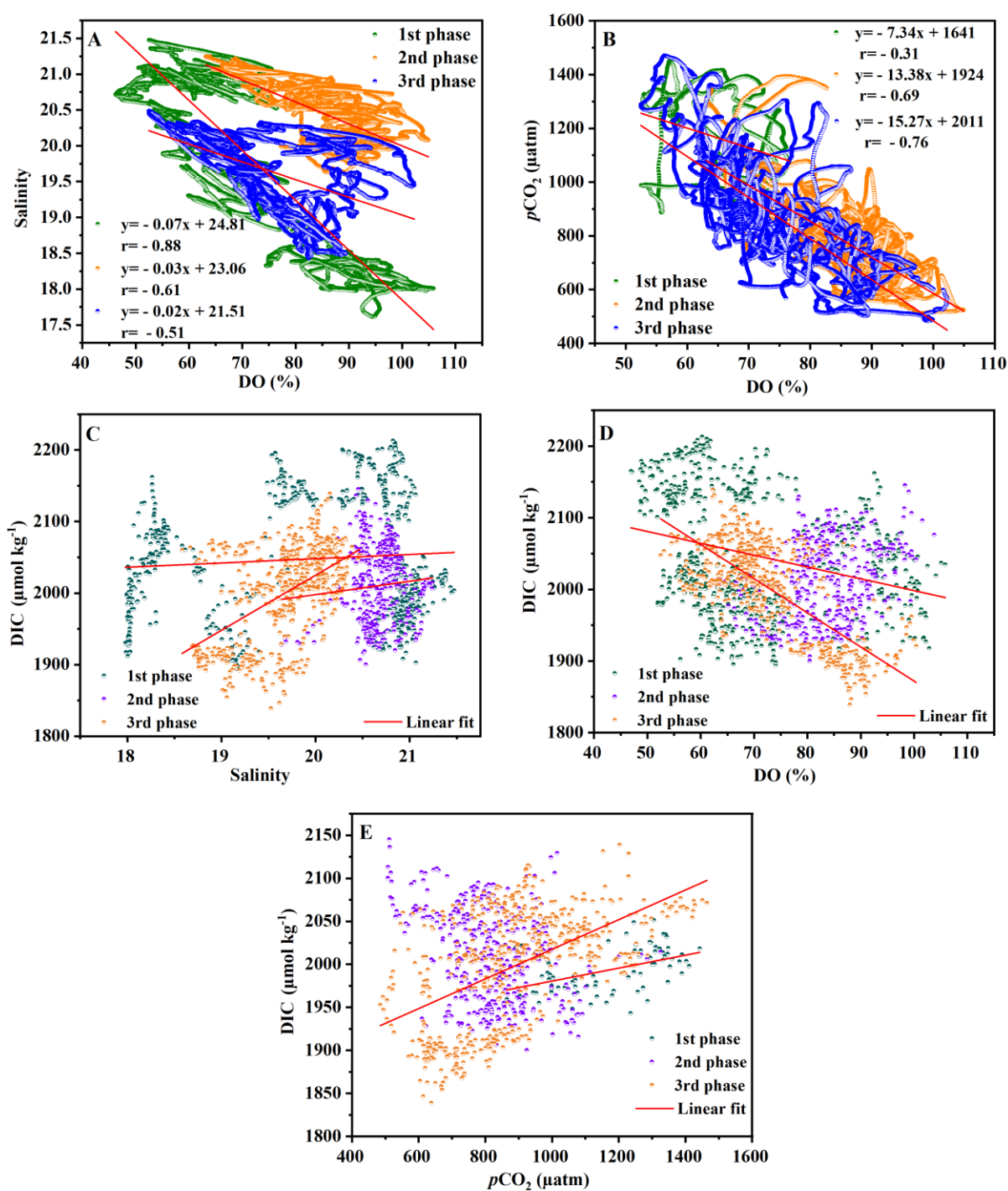


Figure S3.5. Linear regression fits (solid red lines) plots between (A) salinity and DO and (B) $p\text{CO}_2$ and DO (green circles represent the first, orange circles represent the second, and blue circles represent the third phases respectively). Linear regression fits (solid red lines) between DIC concentrations from the DIC analyzer with respect to laboratory analysis of (C) salinity, (D) DO, and (E) $p\text{CO}_2$ (dark green circles represent first, violet circles represent second and orange circles represent third phases respectively) during the study in the Kiel fjord.

Discussion 3:

Diel variation of DO and DIC

The maximum diurnal variations in DO and DIC were recorded during the first heavy precipitation event. Levels of DIC closely mirrored DO changes, with nighttime DIC (~ 2 hours) starting from around $2165 \mu\text{mol kg}^{-1}$ and decreasing to a minimum of $\sim 1951 \mu\text{mol kg}^{-1}$ during the daytime (~ 14 hours). Meanwhile, DO increased from $\sim 80\%$ at night to $\sim 105\%$ during the day on 30th July. On 1st August, following the sustained heavy rainfall, DIC further decreased from $\sim 2266 \mu\text{mol kg}^{-1}$ at night to $\sim 2111 \mu\text{mol kg}^{-1}$ during the day, while DO increased from $\sim 45\%$ at night to $\sim 68\%$ during daytime.

This pattern of inverse variation between DIC and DO aligns with previous studies showing that temperature alone accounts for only about 1 % of the observed variability in dissolved gas concentrations (de Montety et al., 2011). The most significant diurnal variations in DIC ($\sim 13\%$) and DO ($\sim 37\%$) were observed during heavy precipitation events, likely driven by enhanced photosynthetic activity during periods of high biological productivity. Similar observations of large variations in DIC concentrations ($\sim 100\%$) have been reported in tropical floodplains (Bass et al., 2013). Low DO value at night can be linked to nutrient-rich inflows from anthropogenic sources (Nimick et al., 2011), which may fuel respiration

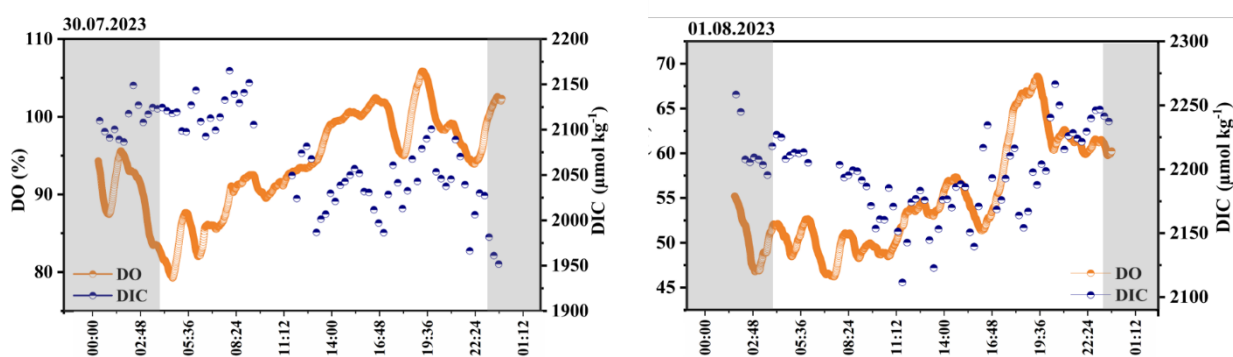


Figure S3.6. The diel variations in DO (orange) and DIC (blue) on 30th July and 1st August 2023 during the study in the Kiel fjord.

processes and further deplete oxygen. Moreover, smaller fluctuations in DIC and DO could also be influenced by the movement of water masses driven by wind and other physical

forces. While the primary drivers of DIC dynamics are biological processes such as carbon fixation and air-sea CO_2 exchange, other processes such as precipitation of carbonates and riverine inputs of DIC also contribute. The loss of HCO_3^- and CO_3^{2-} ions, promoting carbonate mineral precipitation, plays a role in altering DIC levels in some parts of the Baltic Sea (Stokowski et al., 2020).

4. Development of an autonomous *in-situ* Dissolved Inorganic Carbon sensor and field application in dynamic estuarine and coastal waters

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Abstract

An autonomous *in-situ* DIC sensor was developed for real-time dissolved inorganic carbon (DIC) measurements in seawater using a conductometric detection technique. The measurement approach uses a 20 cm gas exchange unit with a “Tube In A Tube” configuration to facilitate gaseous CO₂ diffusion from an acidified sample into a stream of alkaline solution (NaOH), followed by detection with four hollow brass electrodes.

The *in-situ* DIC sensor was tested under laboratory conditions to assess its performance, optimize the measurement protocol, and determine long-term physical and chemical analysis stability. The performance of the sensor was evaluated during (a) a 3-day trial in the Baltic Sea and (b) a 21-day deployment in the Kiel Fjord. To account for temperature-dependent conductivity variations, the sensor was equipped with two temperature probes, measuring external (ambient seawater) and internal (NaOH solution inside the housing) temperatures. Investigation revealed that both temperature datasets are required to construct a correction model for raw conductivity values. Additionally, a daily drift correction was also incorporated into the data processing method by performing *in-situ* calibration, ensuring accurate DIC data. Using the optimized data processing method, the observed DIC concentration range in Kiel Fjord was between 1661 and 2296 $\mu\text{mol kg}^{-1}$, with a mean value of $1978 \pm 150 \mu\text{mol kg}^{-1}$. The sensor operated with a measurement cycle of 20 min, achieving a measurement precision of $16.8 \pm 8.46 \mu\text{mol kg}^{-1}$ ($n = 32$). The measurement accuracy was $-12 \mu\text{mol kg}^{-1}$, as calculated by comparing DIC data from the sensor with laboratory-obtained data from discretely collected samples.

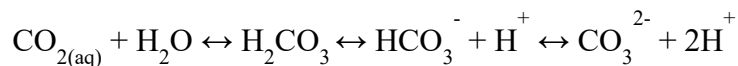
Data from the DIC sensor showed good correlations with other environmental parameters, including pH and oxygen, obtained from commercial sensors deployed during the Kiel Fjord study. It demonstrated the capability of the newly developed *in-situ* DIC sensor to provide real-time, high-quality DIC measurements in complex and dynamic coastal environments. The sensor represents a significant advancement in autonomous carbonate system monitoring and has potential applications in both ocean acidification studies and CO₂ leakage detection in Carbon Capture and Storage (CCS) operations.

4.1 Introduction

The combustion of fossil fuels, land-use changes, and the increase in the production of cement have led to an unprecedented emission of carbon dioxide (CO₂). Over the past 63 years, the CO₂ concentration in the atmosphere has increased from 317 ppm (in 1958) to 425 ppm (in 2024) (<https://gml.noaa.gov/ccgg/trends/>). To effectively mitigate global climate change and limit the temperature increase to 1.5 °C (Masson-Delmotte et al., 2019), decarbonization of the economy is required (Boyd et al., 2023), and also an active removal and safe sequestration of excess CO₂ away from the atmosphere, using terrestrial and marine CO₂ removal (mCDR) strategies (Pathak et al., 2022).

Among various mCDR approaches, carbon capture and storage (CCS) is considered to significantly achieve a stable solution over next several decades (Metz, 2005). It involves chemical capture of CO₂ from an active source followed by long-term storage in geological formations, e.g., offshore sandstone (saline aquifers and depleted oil/gas reservoirs), unconsolidated deep-sea sediments or basalt rock formations at the seafloor (Solomon et al., 2008). The storage of CO₂ in such geological locations requires appropriate porosity and permeability of the reservoir, with good sealing capability and a stable environment. Such long-term geological storage of CO₂ can potentially leak CO₂, and a comprehensive monitoring program (Measurement, Monitoring, and Verification (MMV)) is required to attribute and quantify the potential leakage. This motivates to develop autonomous sensors dedicated to monitor the inorganic carbonate parameters, i.e., DIC, pH and partial pressure of CO₂ ($p\text{CO}_2$) (equivalent to $f\text{CO}_2$) at CCS sites. The sensors will be used to identify, detect, and quantify any possible CO₂ leakage from CCS site under high pressure and low-temperature environment.

When CO₂ mixes with seawater, it will dissolve and will go through a series of chemical reactions. It first forms aqueous CO₂, which then reacts with water molecules to produce carbonic acid (H₂CO₃), which dissociates into hydrogen (H⁺), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) ions, following the reaction (Zeebe, 2012):



To understand the oceanic inorganic carbonate chemistry, four fundamental carbonate parameters, i.e., Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), pH, and fugacity of CO₂ ($f\text{CO}_2$), along with the physical property of seawater (i.e., equilibrium constants, temperature, salinity, and pressure) are considered.

Numerous analytical techniques have been developed to quantify DIC concentrations in seawater, and Table 4.1 provides a list of these techniques which have been published in peer-reviewed journals. Except Dual Isotope Dilution and Cavity Ring-Down Spectroscopy, the analysis of DIC generally follows three steps: (i) acidification of the sample to convert carbonate species into gaseous CO₂, (ii) diffusion of CO₂ into gas phase, and (iii) detection of the diffused CO₂ concentration. All these sensors are in various stages of development, i.e., lab-based, underway, underwater.

Currently, there is no commercially available *in-situ* DIC sensor, and some developments towards robust *in-situ* sensors capable of producing high-quality data are in progress. Several *in-situ* autonomous DIC sensors have been developed and are undergoing field demonstrations: (1) Robotic Analyzer for the TCO₂ System (RATS), based on a three-electrode conductometric detection technique (Sayles & Eck, 2009), (2) Moored Autonomous DIC (MADIC) system, based on NDIR method (Fassbender et al., 2015), (3) Channelized Optical System (CHANOS) for measuring DIC and pH, based on spectrophotometry (Wang et al., 2013), (4) lab-on-chip (LOC) DIC sensor, based on capacitively coupled contactless conductivity detection (C⁴D) (Monk, 2020a), (5) Spectrophotometric Elemental Analysis System for measuring DIC (SEAS-DIC), also based on spectrophotometry method are few mentionable ones.

A benchtop DIC analyzer was recently developed and tested in various field deployments (Bhattacharya et al., 2024; Kopf et al., 2024). The measurement principle of the analyzer was based on the conductometric detection technique. The analyzer included a detection cell designed with a novel four-contacting hollow brass electrode configuration in combination with a gas diffusion sequential injection flow analysis (GD-SIA) method. The design of the fluidics and the measurement protocol were optimized to facilitate high throughput measurements with lower reagent consumption compared to reported conductometric DIC analyzers (Martinotti et al., 2012; Sayles & Eck, 2009). Laboratory-

based tests showed a measurement precision of $\pm 4.9 \mu\text{mol kg}^{-1}$, with a sampling frequency of four samples per hour. Time-series DIC data collected during field deployments demonstrated that the analyzer has achieved an analytical precision of $\pm 7.24 \mu\text{mol kg}^{-1}$ during a month-long deployment in Kiel Fjord.

Table 4. 1. A comparative review of DIC sensors with different measurement techniques

Techniques	Precision ($\mu\text{mol kg}^{-1}$)	Sampling frequency (per hour)	Reference
Coulometry	$\pm 0.5 - 1.0$	4	(Natchanon et al., 2014)
Non-Dispersive Infrared (NDIR) Detection	± 5	3	(Fassbender et al., 2015)
Spectrophotometry	± 3.6	> 60	(Wang et al., 2013)
Gas Chromatography	± 3.1	4	(Hansen et al., 2013b)
Dual Isotope Dilution and Cavity Ring-Down Spectroscopy	± 0.4	15	(K. Huang et al., 2015)
	± 0.7	~5	(Su et al., 2019)
Membrane-Introduced Mass Spectrometry	not specified	not specified	(Bell et al., 2011)
Electrochemical detection - Conductometry	± 3.6	1	(Sayles & Eck, 2009)

The present study describes the development and evaluation of a novel autonomous *in-situ* DIC sensor, which can be deployed at depths of up to 10 m. This development process is a part of the Alternate scenarios, Innovative technologies, and Monitoring approaches for Sub-Seabed Storage of carbon dioxide (AIMS³) project (<https://aims3.cdrmare.de/>), which ultimately aims to develop a deep water (~ 2 km) *in-situ* DIC sensor capable of autonomously measuring data with high-precision and high accuracy to monitor changes in DIC concentration following any potential CO₂ leak at CCS injection sites. The working principle and the core design of the current sensor build upon the framework of the

previously developed benchtop DIC analyzer (Bhattacharya et al., 2024). The fluidic system was specifically optimized to enable time-series measurements at a fixed location. The integrated software included (1) *in-situ* calibration to adapt with real-time environmental variations instead of laboratory-based calibrations and (2) automated periodic cleaning cycles of the fluidics, which reduces biofouling and the need for frequent maintenance, thereby enhancing autonomous operation during long-term deployments. A robust data processing method was developed, which included (1) temperature compensation on raw conductivity data using two temperature probes equipped within the sensor and (2) drift correction factor, obtained from *in-situ* calibration, implemented to primarily eliminate potential drifts in the detection cell and gradual changes in the reagent composition.

In this study, the performance of the newly developed autonomous *in-situ* DIC sensor, was demonstrated in the Kiel Fjord (southwestern Baltic Sea) in summer 2024. The DIC dataset was compared with other environmental parameters, e.g., sea surface temperature, sea surface salinity, dissolved oxygen (DO), pH, etc., obtained from a suite of commercial sensors deployed on a pier at GEOMAR. The applicability of the robust data processing method was evaluated, and it aimed to generate high-quality data from such dynamic coastal waters.

4.2 Material and methods

4.2.1 Reagents and solutions

The phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) solutions were prepared using analytical-grade reagents, following the protocol described in Bhattacharya et al., 2024. A 0.95 mol L^{-1} H_3PO_4 solution was prepared by dilution of 85 % ortho- H_3PO_4 (Carl Roth) in deionized water (Milli-Q, $18.2 \text{ M}\Omega \text{ cm}$, Millipore). A stock solution of 0.25 mol L^{-1} NaOH was prepared by dissolution of 2.49 g NaOH (Merck) in 250 mL of deionized water, and a working NaOH solution (10 mmol L^{-1}) was prepared by further dilution in deionized water. To assess accuracy of the measurements, a fresh batch of certified reference material (CRM, batch#210, A.G. Dickson, Scripps Institution of Oceanography, USA) with a DIC

concentration of $2046.37 \pm 0.32 \mu\text{mol kg}^{-1}$ was used during the field deployment. All the reagents and CRM were stored in gas-impermeable, UV-protected EVA infusion bags (MIB 1000, Hegewald Medizinprodukte GmbH, Germany) to prevent gas exchange and ensure stability over time.

A stock solution of DIC (0.1 M) was prepared by dissolving 0.53 g of sodium carbonate (Na_2CO_3 , Honeywell Fluka™, Germany) and 0.42 g of sodium bicarbonate (NaHCO_3 , Carl Roth) in 100 mL of deionized water. Five calibration standards, i.e., 1700, 1850, 2046, 2150, and 2300 $\mu\text{mol kg}^{-1}$ were used for laboratory calibration. A fresh CRM batch was spiked with the DIC stock solution, resulting in concentrations of 2150 and 2300 $\mu\text{mol kg}^{-1}$, while an aliquot of the same CRM batch was diluted with deionized water, yielding concentrations of 1700 and 1850 $\mu\text{mol kg}^{-1}$. The DIC concentrations of the calibration standards were measured in the Apollo SciTech DIC auto-analyzer (AS-C3, Apollo SciTech, LI-7000, LICOR, USA) with respect to the CRM (2046 $\mu\text{mol kg}^{-1}$). All the calibration standards were stored in infusion bags.

4.2.2 Apparatus and experimental set-up

4.2.2.1 System overview

The sensor has a compact structure and is divided into three primary compartments: (i) a lower section, which consists of a gas exchange unit (GEU) and reagent bags, (ii) a middle section, which contains pumps, valves and fluidics, and (iii) an upper section, which includes (a) detection unit, i.e., conductivity cell and (b) electronics. The middle and upper compartments were enclosed within a pressure (allows a maximum depth of 10 m) and water-resistant chamber (Figure 4.1). The sensor is 60 cm in height and 20 cm in diameter and has a total weight of ~7 kg.

Lower compartment

The lower compartment is exposed to the ambient water during deployment and includes the GEU and the reagent bags, securely connected to the sensor body using polyetheretherketone (PEEK) Nuts (Super Flangeless™ Nut, Standard Knurl, Natural PEEK, 1/16" OD Tubing, 5/16-24 Flat Bottom) and blue ferrules (Flangeless Ferrule, Blue

ETFE, 1/16 " OD Tubing, 1/4-28 Flat-Bottom; 1/EA). The PEEK tubings (OD $\times$ ID 0.06'' $\times$ 0.03'') were used for all fluidic connections. A cylindrical "Tube In A Tube" (TIAT) GEU configuration of 20 cm length was prepared. The GEU consisted of an outer PEEK tube of O.D. $\times$ I.D. 1/16'' $\times$ 0.04'' and an inner gas-permeable amorphous fluoropolymer tube (Teflon AF-2400 tubing, Biogeneral, USA; O.D. $\times$ I.D. 0.029'' $\times$ 0.024'') with a wall thickness of 63.5 μ m. The outer PEEK tube was used for the NaOH solution, whereas the inner Teflon AF2400 tube was used for the acid-sample mixture. A countercurrent flow of NaOH and the acid-sample mixture was employed to enhance the gas exchange efficiency (Monk, 2020b; Wang et al., 2013). The inlet and outlet connections of the GEU were assembled using PEEK Tees (Cole Parmer, IDEX Low-Pressure, 0.050 " Bore, 1/8 " OD Tubing, 1/4-28 Flat Bottom) and connected to the valves located in the middle compartment. The design of the GEU is described in detail in Bhattacharya et al., 2024. The sample inlet was connected to a 0.8 μ m polyethersulfone syringe filter (Pall Life Sciences, USA) to prevent clogging of the internal fluidics. An external temperature probe (Pt100, Sea & Sun Technology GmbH, Germany) was also part of this section to record ambient seawater temperature during a deployment.

Middle compartment

Two diaphragm pumps (MCP Series - 50 Metering Pumps, Takasago Fluidic Systems, USA) and two three-way isolation valves (NRResearch, USA) were integrated into the fluidics compartment to propel reagents and sample through the different sections of the sensor. The first valve (V1) was configured to selectively draw and move samples and CRM. The second valve (V2) controlled the flow of acid. One pump (P1) was used to draw the acid-sample mixture into the inner tube of the GEU, allowing the acidified sample to pass through and subsequently be discharged to waste. Tubing dimensions were investigated to optimize acid-sample mixing, with the aim of eliminating the need for separate mixing units. The second pump (P2) was connected to the NaOH bag to direct the flow through the four-electrode conductivity cell and then to waste. The flows of the pumps and operation of the valves were optimized to precisely draw and transport fixed volumes of reagents and samples in a fully automated setup.

Top compartment

The conductivity cell consisted of a custom-designed four-electrode configuration (Sea & Sun Technology GmbH, Germany). Four hollow cylindrical brass electrodes of equal lengths (Albion Alloys Precision metals, UK, 20 mm long, O.D. $\times$ I.D. 0.5 mm $\times$ 0.3 mm) were connected in series using Tygon tubing (Altec™; orange/green; I.D. 0.38 mm) with an intra-electrode spacing of $\sim$ 1 mm. Each electrode featured a central symmetrical terminal, where the outer terminals provided an alternating current (AC), and the inner terminals measured the voltage drop across the inner electrodes. The measured voltage is then converted into conductivity using custom electronics developed by Sea & Sun Technology GmbH. A Negative Temperature Coefficient (NTC, Sea & Sun Technology GmbH) probe was integrated into the system through a PEEK tee at the inlet of the conductivity cell to record the temperature of the NaOH solution flowing toward the cell prior to analysis. This allows accurate temperature compensation for conductivity measurements. Additional details of the cell are provided in Bhattacharya et al., 2024.

To ensure the autonomous operation of the sensor, a Raspberry Pi (RASP PI 4 B 1GB) and a HAT Brick (Tinkerforge GmbH, Germany) were implemented as the central processing unit. The Raspberry Pi was chosen due to its cost-effectiveness, compact size, and versatile applications. Communication was established via ethernet connection through a client-server protocol. In addition, a Python (version 3.9) script was developed to control pumps and valves (part of measurement protocol), acquire raw data from the conductivity board, process data, and display the final output (peak height in terms of conductivity; see Data processing and analysis section) with a timestamp. The graphical user interface (GUI) of this script is connected with the protocol (see Results and Discussion section). A 4-channel solid-state relay (Tinkerforge, GmbH, Germany) was used to activate the valves and pumps. Python package pyserial v.3.5 was used to access the serial port of the conductivity meter. The sensor was powered by a TTI-Thurlby Thandar Instruments EL302R power supply (24V DC, 1.5 amp).

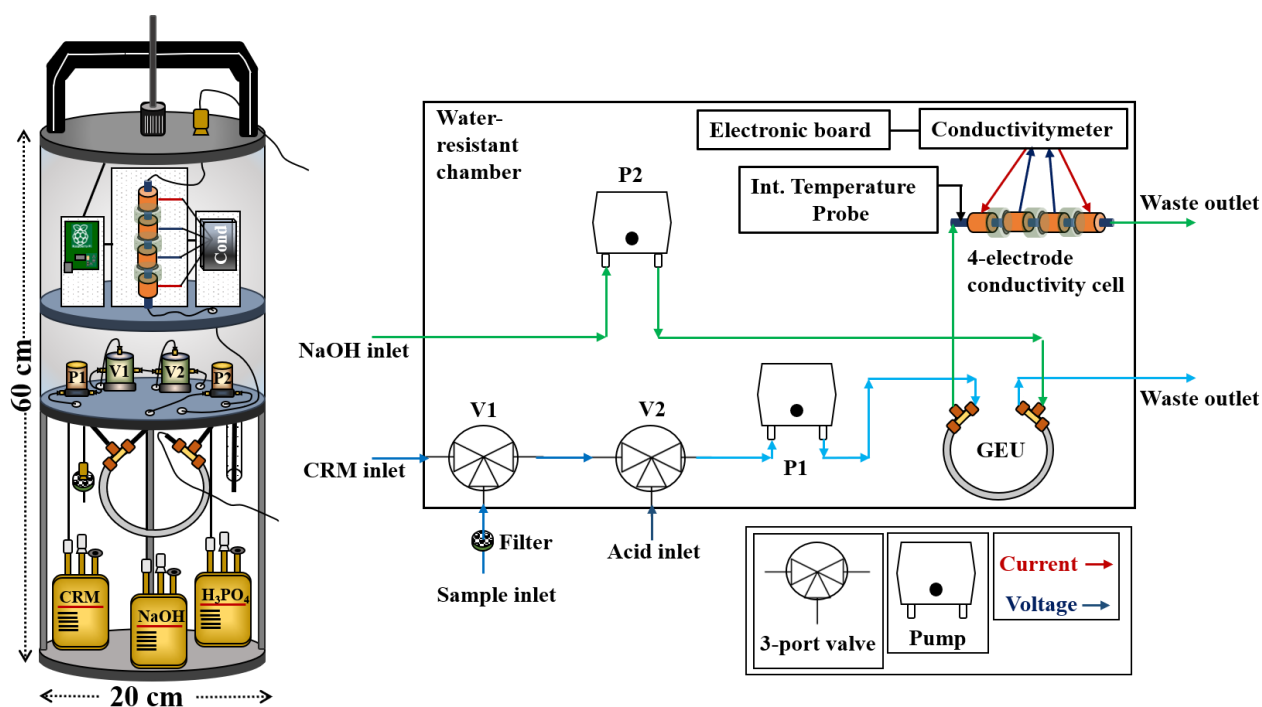


Figure 4.1. Schematic diagram of the *in-situ* DIC sensor (left), fluidic connections inside the sensor (right).

4.2.3 Analytical principle of the sensor

The sensor employs a liquid-to-liquid extraction technique using a gas diffusion sequential injection analysis (GD-SIA), where (1) CO_2 gas diffuses from acidified sample/CRM across the gas-permeable Teflon tube of the GEU, and (2) the diffused CO_2 mixes into the NaOH solution as it flows through the outer tube of the GEU. The change in electrical conductivity of the NaOH solution, before and after CO_2 absorption, is quantified using the conductivity cell comprising four hollow cylindrical brass electrodes arranged linearly. The electrical conductivity (σ in Siemens per meter, S m^{-1}) of the electrolytic solution is directly related to the change in voltage. The NaOH solution is sequentially pumped through the electrodes, first as a baseline measurement and then following CO_2 absorption, thereby producing a change in voltage across the electrodes. The voltage change is proportional to the concentration of dissolved CO_2 in the sample (DIC). The analytical principle underlying this technique is discussed in detail in Bhattacharya et al., 2024.

The sensor is equipped with two temperature probes, one external and one internal. The external probe monitors the ambient seawater temperature, providing insight into the environmental conditions at the deployment site. Since this probe is positioned near the GEU, the recorded temperature also represents the temperature at which CO₂ diffusion occurs. The internal probe, on the other hand, measures the temperature of the NaOH solution inside the conductivity cell as well as the temperature inside the housing during measurements. Recording both external and internal temperatures allows for additional temperature corrections, ensuring accurate compensation for temperature-dependent conductivity variations in the measurement process.

4.2.4 Laboratory test

4.2.4.1 Optimization tests

Laboratory experiments were conducted under controlled conditions to optimize the measurement protocol of the DIC sensor. The analytical signal was evaluated using a 20 cm GEU coupled to a sample-acid mixing loop and a 1.5 cm long straight tube, both containing a volume of 200 μL . Signal responses were compared with the GEU without a mixing loop to assess the impact of mixing efficiency. To investigate the potential effects of sample carry-over and variability in gas exchange, three different concentrations of H₃PO₄, i.e., 0.19, 0.95, and 1.91 mol L⁻¹, were tested. The optimal concentration of NaOH was determined through comparative calibration using three different concentrations. Additionally, different gas exchange times were investigated to identify an optimized measurement protocol that enables high-throughput operation while eliminating carry-over effects.

To evaluate the performance of the sensor within a DIC range of 1700 - 2300 $\mu\text{mol kg}^{-1}$, laboratory calibration tests were conducted. Additionally, reagent stability over time and the potential drift of the conductivity cell were assessed. Fresh batches of NaOH and H₃PO₄ were prepared, and a fresh batch of CRM was measured in the laboratory. All the reagents and the CRM were stored in gas-impermeable mixing bags. The CRM was measured five times per day with a measurement frequency of one hour over a period of seven days.

4.2.5 Data processing and analysis

The conductivity signal of NaOH was recorded prior to and post diffusion of CO₂ into the NaOH solution. The difference between the drop-in conductivity (corresponding to the measurement of NaOH + CO₂) and the NaOH conductivity baseline value was used to quantify the DIC concentration. The difference is represented as the Peak Height (H), defined as:

$$H = \text{Post baseline value} - \text{Minimum value of the signal (unit in mS cm}^{-1}\text{)}$$

The H values were automatically calculated using Python software (version 3.9) during each measurement. The post-data processing method was designed to correct H using a two-step correction approach:

(1) Temperature normalization to calculate H_{norm} :

The H values are sensitive to temperature variation, and it was found that H is directly dependent on temperature variation (Bhattacharya et al., 2024). In this study, two temperature probes were installed, the external probe to measure *in-situ* seawater temperature and the internal probe to measure NaOH solution during conductivity measurements. Both these probes produced linear regression with respect to H, e.g.,

$$H = m \times T + c, \text{ where } m \text{ is the slope, } c \text{ is the intercept and } T \text{ is temperature.}$$

The H values were, therefore, normalized with respect to the corresponding temperature:

$$H_{\text{norm}} = \frac{H}{m \times T + c}$$

(2) A further correction was applied on H_{norm} from the daily correction factor obtained from measuring CRM to obtain $H_{\text{norm, final}}$. A linear drift correction was applied on H_{norm} for each day dataset:

Corrected Value = Measured Value - (Drift Rate $\times$ Time), where Drift Rate is the change in the measured value per unit of time.

These mathematical corrections on H values were used to compute the final DIC concentration.

Statistical analysis of the dataset was performed using open-source Python libraries and Origin Pro 2023 (Learning Edition, Origin Lab Corp., U.S.A). All data are presented as mean $\pm$ 1 standard deviation (S.D). A Savitzky-Golay filter with a window size of 101 data points and a polynomial order of two was applied to the raw sensor data to reduce noise.

4.2.6 Field deployments

4.2.6.1 Hydrographic setting

The Baltic Sea

The performance of the *in-situ* DIC sensor was evaluated during a field trial in the southwest Baltic Sea (including the area of Kolberger Heide). The trial was conducted onboard RV *Littorina* from 24th to 26th June 2024 (Figure 4.2).

During this deployment, the *in-situ* DIC sensor was installed in a 200 L water tank placed on the deck of the RV *Littorina*. The tank was continuously supplied with surface seawater to ensure real-time measurement conditions (Figure 4.2). The sensor was fixed within a metal frame and kept in a submersed condition inside the tank to simulate deployment conditions. The sensor was programmed for continuous measurements at 20-minute intervals. Additionally, CRM was measured twice per day ($n = 4$ for each time), once before starting and once after completing the transect, to assess measurement accuracy and potential drift. The sample inlet of the sensor was equipped with a 0.8 μm polyethersulfone syringe filter (Pall Life Sciences, USA) to prevent the entrance of particles into the internal fluidics.

The Kiel Fjord

The *in-situ* DIC sensor was further evaluated during a 21-day field deployment in the inner Kiel Fjord (54°19'48.78" N, 10°08'59.44" E) at the GEOMAR pier from 4th to 24th July 2024 (Figure 4.3).

During the deployment, the *in-situ* DIC sensor was deployed along with three commercial sensors, i.e., an EXO1 probe (YSI, Xylem, USA), a nitrate UV sensor (OPUS, TriOS GmbH, Germany), and a stand-alone pH optode sensor (AquapHOx-L-PH, PyroScience

GmbH, Germany). The EXO1 system was used to measure real-time temperature, salinity, dissolved oxygen (DO), and depth (water pressure). The nitrate sensor measured the seawater nitrate concentration and the pH sensor was used to automatically measure seawater pH. All sensors were configured to measure samples with a sampling frequency of one minute. The DIC sensor, sensors, and a submerged water pump (Eheim, Germany) were securely fixed within a metal frame and deployed at a depth of approximately 2 m,

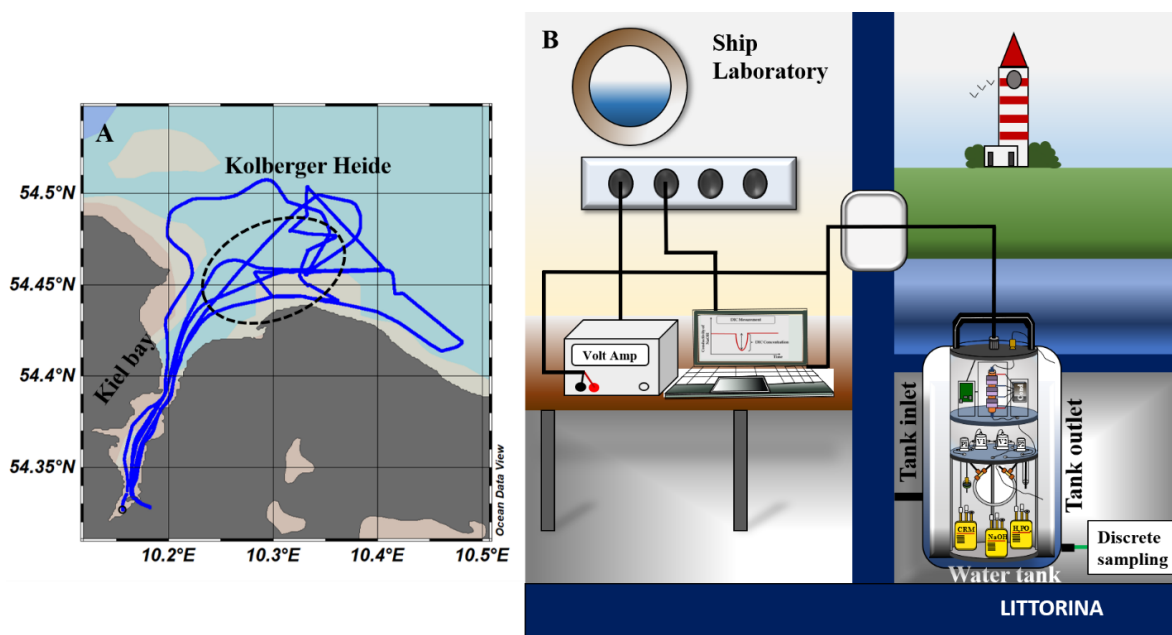


Figure 4.2. (A) Transect of the expedition in the Baltic Sea. The region of Kolberger Heide is indicated by a dashed line circle (source: Ocean Data View), (B) a schematic diagram of the ship-board deployment of the *in-situ* DIC sensor inside a water tank onboard *RV Littorina*.

anchored to the pier. The outlet of the submerged water pump, with an output of 600 L/h, was used to collect discrete water samples for DIC and nutrient analysis in the laboratory. The DIC sensor was programmed to perform hourly measurements ($n = 20$ per day) and included daily CRM measurements ($n = 2$ per day). Before each CRM measurement, the fluidic system was flushed with acid to prevent possible accumulation of biological substances.

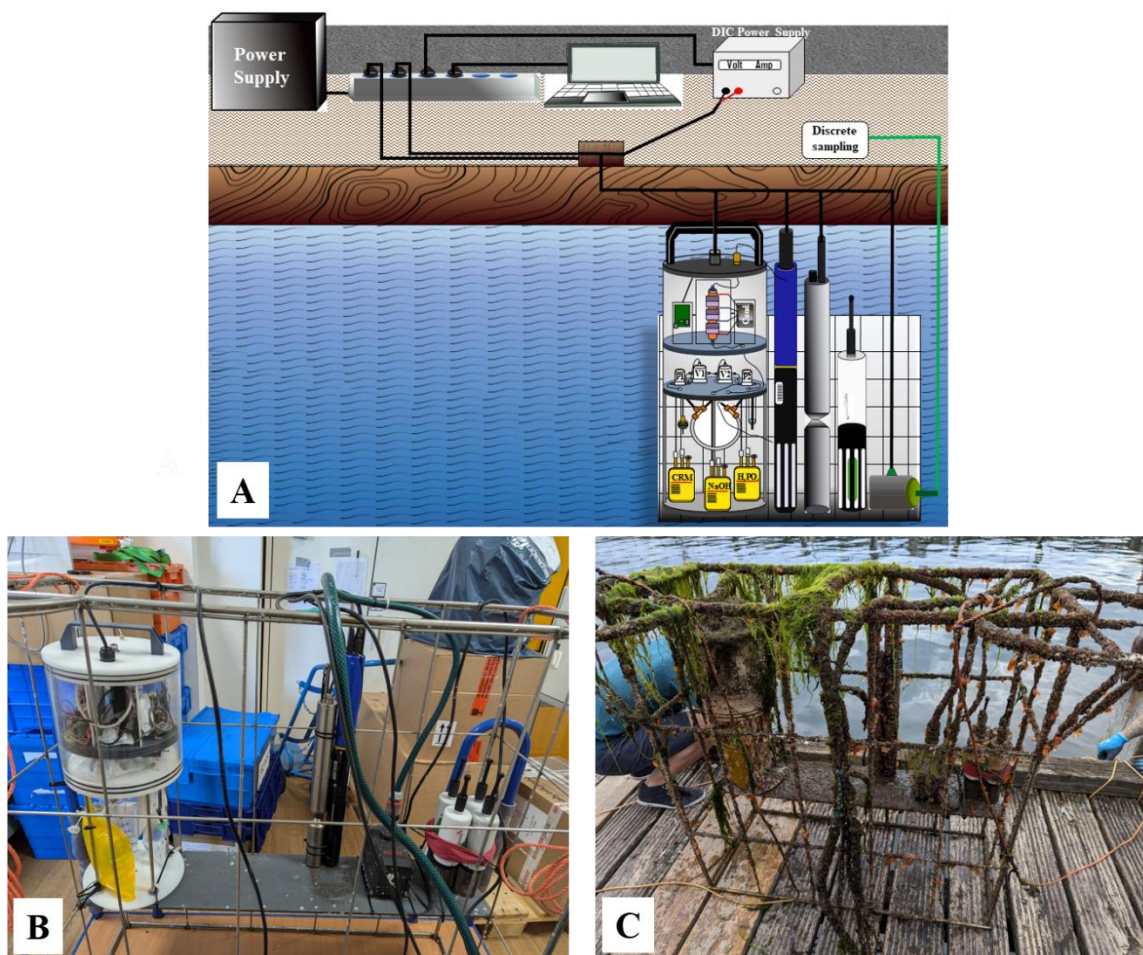


Figure 4.3. (A) Schematic diagram of the field deployment of the *in-situ* DIC sensor on the pier in the Kiel Fjord along with temperature, salinity, oxygen probe, nitrate sensor, pH sensor, and a submersible pump on a frame, (B) picture of the frame before, and (C) after deployment.

4.2.7 Sensor data

Prior to every deployment, all sensors were calibrated to ensure measurement accuracy. The oxygen probe of the EXO1 system was calibrated in the laboratory using one-point air-saturated (100%) water calibration. The nitrate sensor was calibrated by recording a reference absorbance spectrum in deionized water both before and after deployment. The detailed calibration procedure of the nitrate sensor is reported in Nehir et al., 2021. The pH sensor was calibrated using a standard calibration kit provided by the manufacturer, which included pH 2 and pH 10 calibration solutions. Additionally, during the study in Kiel Fjord, partial pressure of CO₂ ($p\text{CO}_2$) data was recorded using a CONTROS HydroC CO₂ sensor

(4H-Jena Engineering GmbH, Germany). The $p\text{CO}_2$ sensor recorded measurements at a one-minute interval.

4.2.8 Discrete water sampling

A total number of 42 discrete water samples (30 from the Baltic Sea and 12 from the Kiel Fjord) were collected for laboratory DIC analysis, following the best practice procedures outlined by Dickson et al., 2007. The DIC samples were stored in 250 mL clean, narrow-mouth borosilicate glass bottles with air-tight glass stoppers. Saturated mercuric chloride solution (250 μL) was added to each sample to stop further biological activity. During the Kiel Fjord deployment, additional discrete water samples were collected to measure inorganic nutrients (NO_3^-). Nutrient samples were stored in 14 mL low-density polypropylene plastic tubes (Greiner Bio-One GmbH) after filtration through a 0.45 μm polyethersulfone filter (Fisher Scientific) and frozen at - 20 °C until analysis.

4.2.9 Analytical methods

All discrete DIC samples were analyzed using an Apollo SciTech DIC auto-analyzer. The nutrient samples were analyzed at GEOMAR using an air-segmented multi-macronutrient autoanalyzer (QuAAtro, Seal Analytical Ltd.), following standard wet-chemical colorimetric techniques. The results from discrete nutrient samples were used to adjust the measurement offsets recorded by the nitrate sensor (Nehir et al., 2021).

4.3 Results and discussion

4.3.1 Optimization tests

The efficiency of liquid-liquid mixing is strongly influenced by the geometry of the mixing interface. In this study, the mixing performance between the DIC solution and acid was evaluated using two different configurations of mixing tubes, a spiral mixing loop and a straight tube, with a larger diameter than the GEU, designed to induce velocity gradients. The curvature of a spiral loop induces mixing efficiency under laminar flow conditions (Mansour et al., 2020). In contrast, sudden contractions or expansions in tube diameter

potentially amplify turbulence generation and increase mixing efficiency (Lü et al., 2016). The analytical responses were compared across the three configurations by measuring DIC standards. The highest conductivity signal was observed with the straight tube, followed by the spiral loop, which yielded approximately 35 % lower signal intensity. The lowest response was obtained when no mixing apparatus was used. The use of diaphragm pumps in the current design of the DIC sensor, which generates pulsed flow, may facilitate the turbulent flow and hence promote efficient mixing when paired with different cross-section tubes. As a result, the straight tube was selected for further experiments.

The analytical signal obtained from using three different acid concentrations was evaluated while keeping a constant volume of NaOH solution. The objective of this experiment was to determine the optimal acid concentration while minimizing the NaOH volume requirement. Figure 4.4A illustrates three representative conductivity profiles (1, 2, and 3) obtained using 0.19, 0.95, and 1.91 mol L⁻¹ of H₃PO₄ for the analysis of one DIC solution with a concentration of ~ 1900 µmol kg⁻¹. The highest analytical signal of ~ 1.34 mS cm⁻¹ was observed when 1.91 mol L⁻¹ H₃PO₄ was used, whereas the signals were 1.04 and 0.97 mS cm⁻¹ for that of 1.91 and 0.95 mol L⁻¹ of H₃PO₄, respectively. A higher concentration of acid facilitates more CO₂ production from the DIC solution, resulting in a higher conductivity signal (Bhattacharya et al., 2024). However, it will require a proportionally higher volume of NaOH for a complete reaction with all the diffused CO₂. When the NaOH volume is insufficient, the conductivity signal does not return to baseline post-reaction, indicating residual CO₂ in the acceptor stream. At the lowest test acid concentration, i.e., 0.19 mol L⁻¹, the acid strength was inadequate to completely convert DIC into CO₂, leading to an underestimation of DIC - particularly in solutions with high DIC concentrations. In contrast, the raw analytical signal obtained using the 0.95 mol L⁻¹ H₃PO₄ showed complete acidification of the solution, while the baseline conductivity was achieved after each measurement, confirming the sufficient neutralization capacity of the selected NaOH volume.

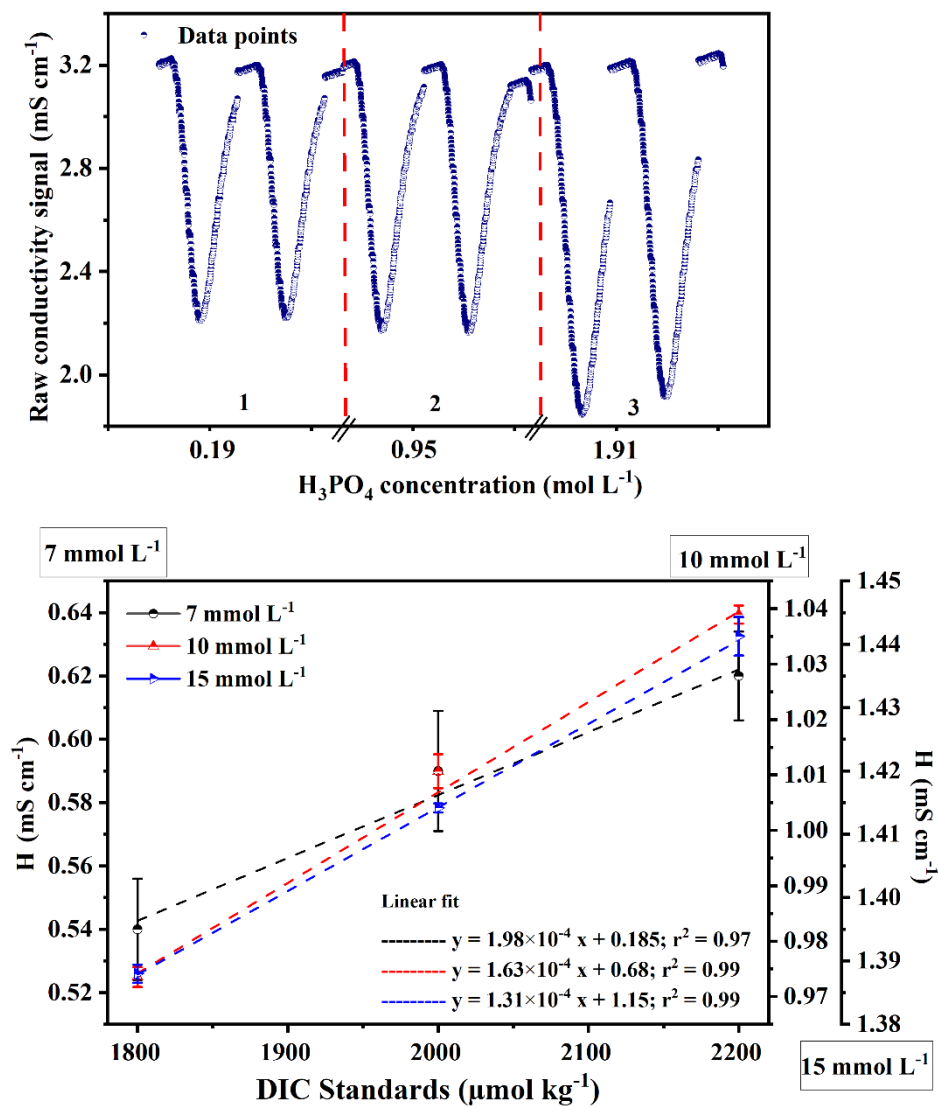


Figure 4.4. (A) Two consecutive raw conductivity signals recorded during measurements of a DIC standard solution ($\sim 1900 \mu\text{mol kg}^{-1}$) using (1) 0.19, (2) 0.95, and (3) 1.91 mol L⁻¹ H₃PO₄, (B) Linear regression fit of mean $H \pm 1$ S.D. values ($n = 4$) with respect to three DIC standard solutions compared for three different NaOH concentrations, 7, 10 and 15 mmol L⁻¹. Data are shown in half-black circles (7 mmol L⁻¹ NaOH), half-red triangles (10 mmol L⁻¹ NaOH), and half-blue triangles (15 mmol L⁻¹ NaOH). The dashed lines refer to the linear regression with corresponding color representations.

The selected acid concentration (0.95 mol L⁻¹) was further evaluated to assess its mixing efficiency with solutions of different DIC concentrations (Figure 4.4B). This test was paired with three different concentrations of NaOH, 7, 10, and 15 mmol L⁻¹, to find the optimal NaOH concentration for this configuration. The NaOH concentration range was chosen from the previous study, which demonstrated that the H value linearly increased

within this range of NaOH concentrations (7 - 15 mmol L⁻¹) (Bhattacharya et al., 2024). A simple calibration experiment was conducted by measuring three DIC standards (1800, 2000, and 2200 µmol kg⁻¹; n = 4 for each) mixed with 0.95 mol L⁻¹ H₃PO₄. Each calibration dataset exhibited a strong linear correlation, showing the efficacy of each NaOH solution (Fig. 4B). The absolute range of H values was highest with 7 mmol L⁻¹ NaOH. However, the corresponding regression coefficient (r²) values were lower than those of the 10 and 15 mmol L⁻¹ NaOH tests. This indicates that 7 mmol L⁻¹ NaOH was insufficient to completely react with CO₂ produced from the standards with higher DIC concentrations. Between 10 and 15 mmol L⁻¹ NaOH, the obtained sensitivity (slope) using 10 mmol L⁻¹ NaOH was higher, and as a result, this NaOH concentration was chosen along with 0.95 mol L⁻¹ H₃PO₄.

Experiments were performed to assess potential carry-over effects from a previous solution. When blank (deionized water) solutions were introduced after DIC solutions, a residual signal equivalent to ~ 7 % of the previous solution was noticed. To reduce this effect, different gas exchange times were tested with incorporating additional flushing steps. A previous study reported that a GE time of 5 min was sufficient to diffuse more than 97 % CO₂ through a 30 cm GEU (Bhattacharya et al., 2024). In the current study, with a 20 cm GEU, a gas exchange time of 2 min with a 3-min pre-flush was found to be optimal, reducing carry-over to 5 % or less. Based on these findings, an optimized measurement protocol for field deployment was established, balancing analytical sensitivity, reagent consumption, and measurement frequency.

4.3.2 Measurement protocol

Based on the results from the optimization tests, a sequential sample processing of the *in-situ* DIC sensor was structured that included 7 steps and it was integrated with a GUI (Figure 4.5). The steps are outlined as follows:

(1) the sample valve (V1) is opened, and pump (P1) draws an aliquot of sample/CRM (4.8 mL), flushing the inner tube of the GEU and all the connecting tubes. After flushing, V1 is closed,

(2) the sensor waits for 3 minutes, allowing any residual acidified sample in the GEU to complete CO₂ diffusion before introducing fresh reagents,

(3) the pump for NaOH (P2) is started, and an aliquot of fresh NaOH (0.5 mL) is drawn through the gas exchange tube. This step allows for the flushing out of residual reacted NaOH (NaOH + CO₂), and fills up the GEU and the conductivity cell with fresh NaOH solution,

(4) V1 is opened, and 0.4 mL of sample is drawn into the GEU, new sample is loaded. V1 is closed,

(4) acid valve (V2) is opened, and 35 µL of H₃PO₄ is moved into the GEU. This step initiates the mixing of acid and sample. V2 is closed,

(5) V1 is reopened, and an additional 70 µL of sample is drawn into the GEU, allowing effective mixing inside the GEU. V1 is then closed,

(6) the acidified sample is left in the gas exchange unit (GEU) for 2 minutes, allowing CO₂ diffusion across the gas-permeable membrane into the acceptor NaOH solution, and

(7) P2 is started, and NaOH is directed into the conductivity cell. The conductivity cell and NTC probe record conductivity and internal NaOH temperature, respectively.

Each analysis requires a total time of 20 minutes, using 5.9 mL of sample/CRM, 35 µL (an additional 300 µL each day for flush) of 0.95 mol L⁻¹ H₃PO₄, and 1.7 mL of 10 mmol L⁻¹ NaOH.

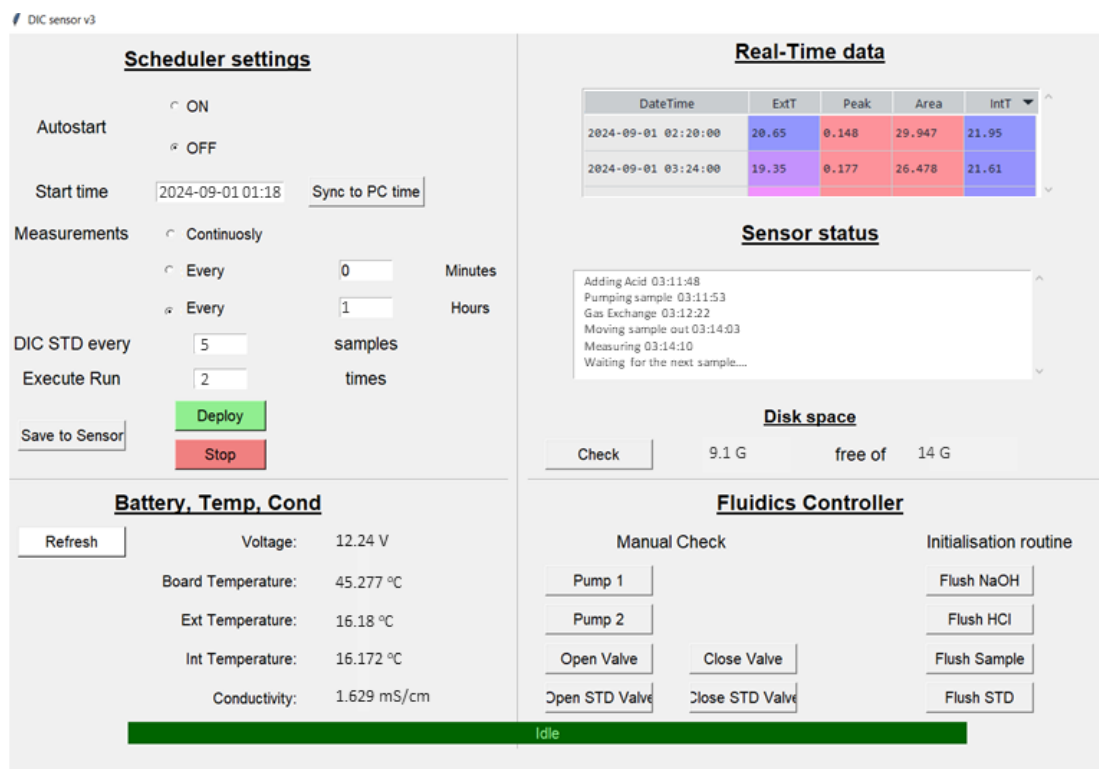


Figure 4.5. Screenshot of the graphical user interface (Python v 3.9) used to control the measurement protocol.

4.3.3 Performance evaluation and stability assessment of the *in-situ* DIC sensor under laboratory conditions

The performance of the *in-situ* DIC sensor was evaluated under controlled laboratory conditions using five standard solutions with DIC concentrations of 1700, 1850, 2000, 2150, and 2300 $\mu\text{mol kg}^{-1}$ at a constant laboratory temperature of $17.39 \pm 0.5^\circ\text{C}$, applying the measurement protocol. The sensor exhibited a linear response within this concentration range, yielding a linear regression of:

$$y = 4.82x - 0.03, r^2 = 0.98 \text{ (} p < 0.001 \text{)} \text{ (Figure 4.6).}$$

To assess the stability of the sensor, a 7-day experiment was conducted in the laboratory. The recorded laboratory temperature ranged between 15.54 and 20.65 °C with both internal and external temperature probes. Three key variations in conductivity data were observed from this experiment. Over 7 days, the baseline conductivity exhibited a gradual increase

of 0.2 mS cm^{-1} , corresponding to a DIC variation of $67 \mu\text{mol kg}^{-1}$, which suggests potential conductivity cell drift or gradual chemical change of NaOH despite storage in gas-impermeable bags. Temperature fluctuations of $< 5 \text{ }^{\circ}\text{C}$ resulted in a baseline conductivity

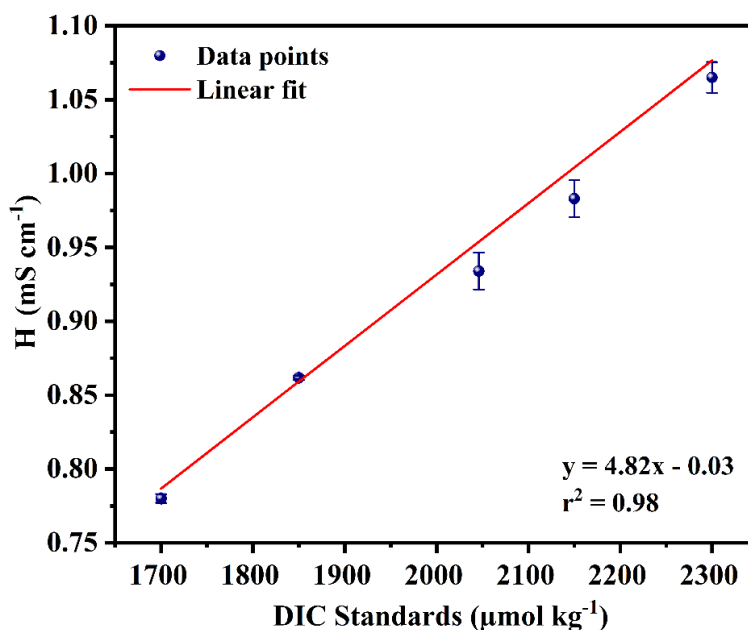


Figure 4.6. Linear regression fit (solid red line) of $H \pm 1 \text{ S.D.}$ with respect to five DIC calibration standards ($y = 4.82x - 0.03$, $r^2 = 0.98$).

change of 0.05 mS cm^{-1} , equivalent to a DIC variation of $17 \mu\text{mol kg}^{-1}$, suggesting only a minor temperature effect on conductivity. Furthermore, H increased by 0.29 mS cm^{-1} over the 7-day period, suggesting a DIC variation of $96 \mu\text{mol kg}^{-1}$. These findings demonstrate that (1) the conductivity cell tends to drift over time (2) reagent stability deteriorates over extended periods, and (3) temperature fluctuations within a controlled range ($< 5 \text{ }^{\circ}\text{C}$) have a comparatively minor effect on conductivity values. As a result, the conductivity cell drift and reagent instability contribute significantly to measurement uncertainty. Therefore, the application of a daily correction factor based on CRM measurements is recommended in conjunction with temperature normalization to ensure accurate and robust DIC quantification during long-term field deployments.

4.3.4 Field deployment and performance evaluation of the *in-situ* DIC sensor in the Baltic Sea and Kiel Fjord

The Baltic Sea

During this field test, the DIC sensor was kept inside the water tank with continuous water supply to simulate a field deployment. This three-day study primarily aimed for testing the structural rigidity of the housing and understanding the stability of the components during field measurements over time. A total number of 83 data points, including CRM measurements, were successfully recorded; however, the raw conductivity values exhibited no significant correlation with temperature variation. This is due to the fact a mean temperature difference of 6.5 ± 3.32 °C between the external and the internal temperature probe was recorded due to partial submersion of the sensor inside the tank. The external temperature recorded the *in-situ* seawater temperature, which also translated into the temperature measurements during the gas exchange process immediately after sample acidification, whereas the internal temperature corresponded to the measurement of the conductivity of NaOH + CO₂ inside the cell. This significant temperature difference introduced discrepancies in the measurement of DIC concentrations, as both CO₂ diffusion efficiency and conductivity are highly sensitive to temperature variation (Bhattacharya et al., 2024).

Hence, the data from this deployment was primarily used to validate the measurement protocol and assess the analytical precision over the whole deployment period. The precision obtained from daily CRM measurement was 14.5 ± 9.61 µmol kg⁻¹ (n = 10) over these three days, after excluding the data where the temperature difference between two probes was higher than 5 °C.

This study suggests that to effectively compensate for the temperature dependence of H values, both temperature datasets should be incorporated into the data-processing method, ensuring measurement accuracy and dataset reliability.

The Kiel Fjord

During the Kiel Fjord deployment, the two temperature probes recorded water temperature, capturing both the *in-situ* seawater temperature recording, the gas diffusion temperature, and the temperature of the NaOH inside the housing during measurements. Since the sensor was fully submerged in seawater, both probes recorded comparable temperatures. Linear correlations were obtained between the temperature datasets and H as follows:

$$H = 0.08 \times (\text{ext. } T) + 1.28 \text{ (Pearson's } r = 0.64) \quad (1), \text{ and}$$

$$H = 0.07 \times (\text{int. } T) + 1.33 \text{ (} r = 0.63 \text{)} \quad (2).$$

Both probes indicated similar linear variability with respect to H, and therefore, only one temperature relation was integrated in the normalization process. The external temperature probe showed a stronger correlation with H compared to the internal temperature probe. Therefore, H values were normalized using the first equation:

$$H_{\text{norm}} = \frac{H}{0.08 \times T + 1.28} \quad (3)$$

During the deployment, the CRM was analyzed daily, allowing the application of a daily correction factor to H_{norm} values to calculate the final DIC concentration. The factor was utilized as a linear correction factor to check daily drift and a calibration factor to calculate the DIC concentration. This demonstrated the sensor's capability to perform *in-situ* calibration without necessitating any pre- and post-calibration in the laboratory, adapting to real-time environmental variation. Each measurement of the CRM was calculated from the mean of two consecutive replicate analyses. The post-data processing method, therefore, included (1) temperature normalization to calculate H_{norm} and (2) daily linear correction factors derived from CRM measurements. The combination of temperature normalization and daily correction substantially improved the accuracy and reliability of DIC measurements.

A total number of 360 DIC data points were recorded by the sensor during the 21 days of deployment in the Kiel Fjord. The sensor functioned smoothly throughout the deployment period of 21 days. The temperature recorded by the external probe of the sensor and EXO1 system showed a linear relation ($T_{\text{DIC}} = 0.97 \times T_{\text{Exo}} + 0.30$, $r^2 = 0.99$), and hence, the

temperature data from the DIC sensor was used for data processing. The mean temperature difference between the internal and external temperature probe of the sensor was 1.5 ± 1.08 °C during the deployment, potentially resulting from the heat generation of the pumps and/or electronic board. Using the post-data processing method, the measurement precision of the sensor was $16.8 \pm 8.46 \mu\text{mol kg}^{-1}$ ($n = 32$), based on 16 days of CRM measurements. The remaining CRM data could not be retrieved due to air-bubble accumulation inside the CRM bag.

The DIC concentrations ranged from 1661 to 2296 $\mu\text{mol kg}^{-1}$, with a mean value of $1978 \pm 150 \mu\text{mol kg}^{-1}$. To assess the measurement accuracy of the sensor, a total number of 12 discrete samples were collected, matching the measurement time of the sensor. These samples were subsequently analyzed in the laboratory using the Apollo DIC analyzer. The mean DIC concentration of the discrete samples was $1972 \pm 161 \mu\text{mol kg}^{-1}$, with a range of 1778 - 2277 $\mu\text{mol kg}^{-1}$. A strong linear correlation was observed between the *in-situ* sensor data and laboratory-based measurements is shown in figure 4.7. The comparison yielded a linear regression of:

$$y = 0.94 (\pm 0.10) x + 86 (\pm 199), r^2 = 0.89 (p < 0.001, n = 11).$$

The accuracy of measurements by the sensor was determined from the quantitative differences between the data obtained from these two techniques, and it showed a mean underestimation of 12 $\mu\text{mol kg}^{-1}$. This result suggests that the current data processing method incorporates drift correction followed by temperature normalization. Although a deployment period of 21 days is insufficient for a comprehensive analysis of the data collected by the *in-situ* DIC sensor, the implementation of the data-processing method and the measurement protocol offered a preliminary foundation to generate reliable DIC measurements.

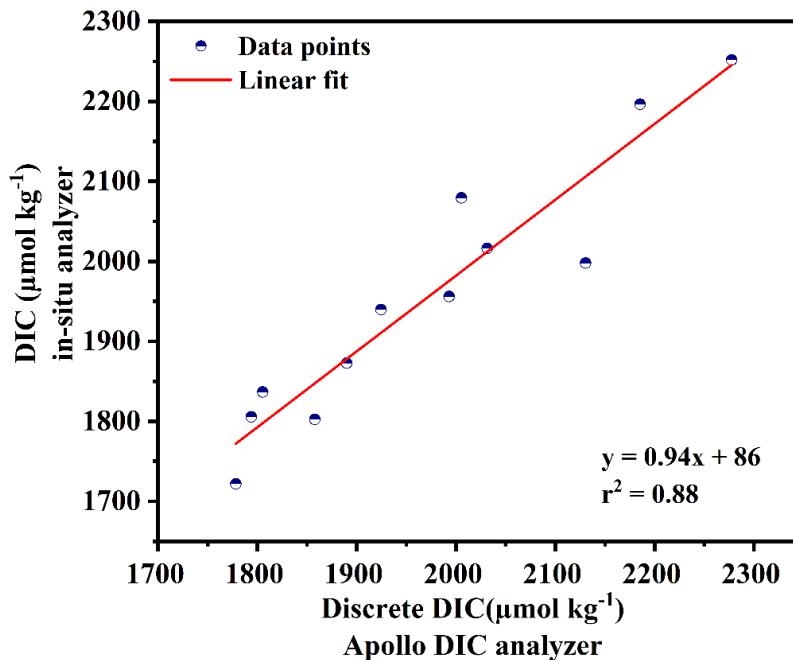


Figure 4.7. Linear regression fit (solid red line) between DIC concentrations from the DIC sensor against laboratory analysis of discrete water samples collected during the study in the Kiel Fjord.

4.3.5 Environmental variability of *in-situ* DIC measurements in the Kiel Fjord

During the 21-day long deployment period in the Kiel Fjord, the DIC values obtained from the sensor were compared with other environmental parameters, i.e., salinity, temperature, DO, NO_3^- , $p\text{CO}_2$, and pH, obtained from commercial sensors deployed alongside the DIC instrument. Figure 4.8 illustrates the temporal variability of key parameters measured in the sub-surface water (~ 2 m) of the Kiel Fjord during the deployment. A detailed statistical distribution of these parameters, including DIC, is described in Table 4.2.

During the deployment, salinity varied between 13.72 and 20.25, with a mean value of 17.2 ± 1.53 , whereas the observed temperature ranged from 11.90 to 20.37 °C, with a mean value of 16.6 ± 2.16 °C. These two hydrographic parameters exhibited a strong negative linear correlation ($r = -0.79$) (Figure 4.8). The DO values showed a strong temporal variability, fluctuating between 42 % (undersaturated) and 110 % (oversaturated), with a mean value of 84 ± 13 %. The pH values ranged from 7.46 to 8.32, with a mean value of

7.9 ± 1.48 . The NO_3^- concentrations measured by the nitrate sensor exhibited inconsistency due to electrical connection issues at the beginning of the deployment and later due to biofouling (mussel growth) on the sensor's measurement window, leading to increased variability. The NO_3^- values showed a wide range ($0.01 - 4.66 \mu\text{mol kg}^{-1}$), with a mean value of $0.9 \pm 1.01 \mu\text{mol kg}^{-1}$. The $p\text{CO}_2$ values exhibited significant variability, ranging from 448 to 1804 μatm , with a mean value of $937 \pm 279.8 \mu\text{atm}$. The mean diel variations of DO, pH, and $p\text{CO}_2$ were recorded as 6.24 %, 0.07, and 135 μatm , respectively. The DO values exhibited a strong positive correlation with pH ($r = 0.8$), both influenced by temperature (Figure 4.8). The DO remained above 80% for most of the deployment, except on July 7 and July 15, when it dropped below 60%. This pattern was also reflected in salinity and $p\text{CO}_2$ trends, however, with weaker negative correlations ($r = -0.54$ and -0.48 , respectively) (Figure 4.8).

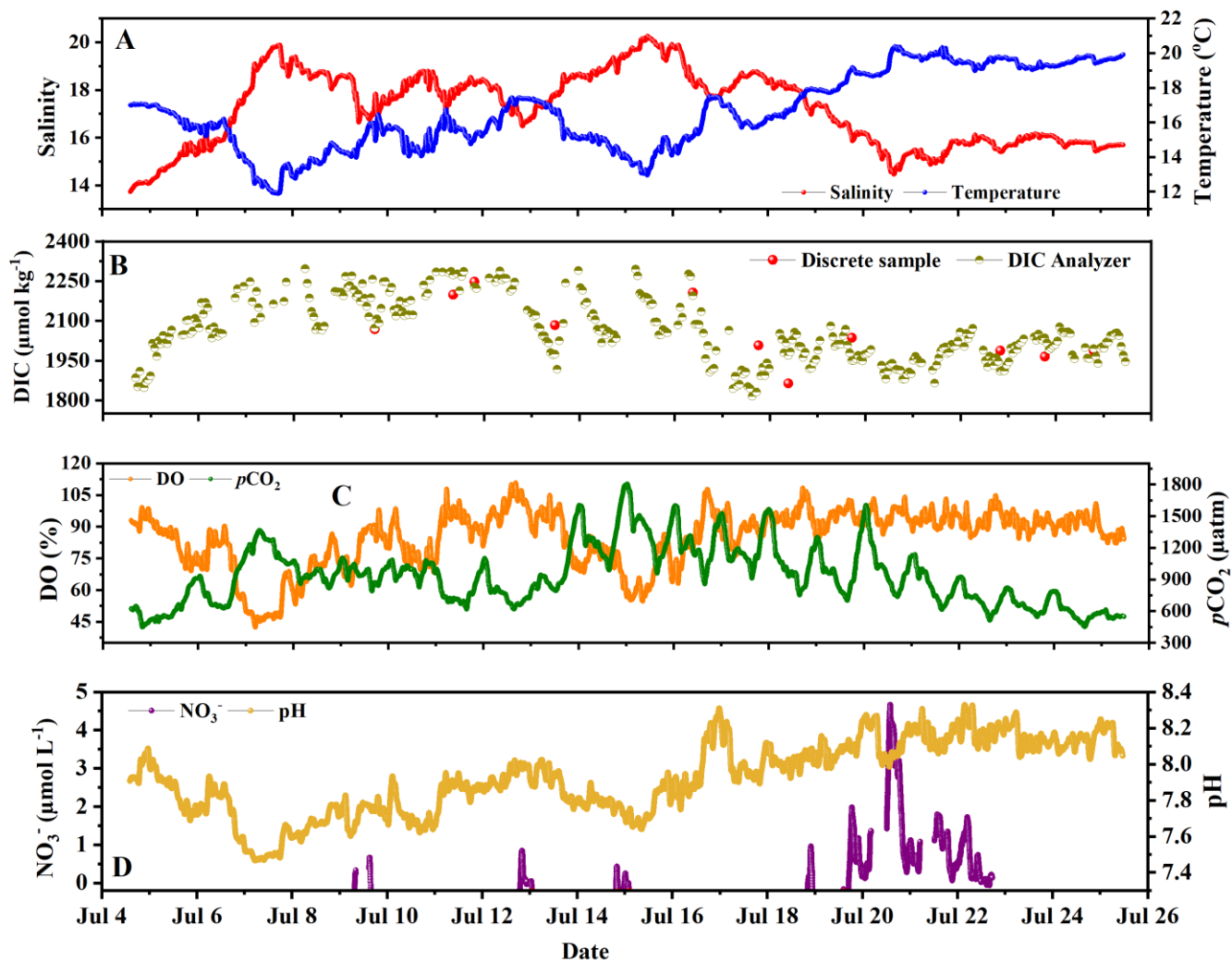


Figure 4.8. Temporal variation of (A) salinity (red) and temperature (blue), (B) DIC data measured by the DIC sensor (dark yellow) and discrete sample data measured by the Apollo DIC analyzer (red), (C) DO (orange) and $p\text{CO}_2$ (green), and (D) NO_3^- (purple) and pH (yellow) obtained from commercial sensors deployed at a depth of 1.5 m at the GEOMAR pontoon from 4th to 24th July 2024.

Table 4. 2. Statistical summary of sensors' data and DIC measurements from the sensor during the pontoon deployment in the Kiel Fjord

Parameter		Kiel Fjord
Temperature (°C)	Min - Max	11.90 - 20.37
	Average $\pm$ 1 S.D.	16.6 $\pm$ 2.16
	n	29982
Salinity	Min - Max	13.72 - 20.25
	Average $\pm$ 1 S.D.	17.2 $\pm$ 1.53
	n	29982
DO (%)	Min - Max	42 - 110
	Average $\pm$ 1 S.D.	84 $\pm$ 13
	n	29982
NO ₃ ⁻ (μmol kg ⁻¹)	Min - Max	0.01 - 4.66
	Average $\pm$ 1 S.D.	0.9 $\pm$ 1.01
	n	3698
pCO ₂ (μatm)	Min - Max	448 - 1804
	Average $\pm$ 1 S.D.	937 $\pm$ 279.8
	n	25655
DIC (μmol kg ⁻¹)	Min - Max	1661 - 2296
	Average $\pm$ 1 S.D.	1978 $\pm$ 150
	n	360
pH	Min - Max	7.46 - 8.32
	Average $\pm$ 1 S.D.	7.9 $\pm$ 1.48
	n	29982

The DIC concentrations exhibited strong negative correlations with DO ($r = -0.72$) and pH ($r = -0.75$) (Figure 4.9). The mean diel variation of DIC was $2063 \pm 108 \mu\text{mol kg}^{-1}$, whereas it varied by $53 \pm 22 \mu\text{mol kg}^{-1}$ within a diel cycle. The diel trends of DIC values were consistent with salinity, whereas DO and pH exhibited an inverse relationship with DIC (Figure 4.8). The maximum diurnal variation in DIC was observed on 16th July, coinciding with significant fluctuations in DO, salinity, temperature, and pH.

The weak correlations between $p\text{CO}_2$ and other carbonate parameters, i.e., pH and DIC (Figure 4.9) can be attributed to two primary factors, i.e., (1) the $p\text{CO}_2$ sensor was located ~ 50 m away from the deployment site, possibly measuring a different water mass, and (2) the $p\text{CO}_2$ sensor required yearly maintenance prior to deployment that unfortunately was

not performed. On the other hand, DIC showed a strong correlation with pH and DO, suggesting the reliability of DIC data measured by the sensor. Moreover, data from sensors deployed in the same frame showed good correlations with each other over the deployment period except $p\text{CO}_2$. These findings further validate the performance of the *in-situ* DIC sensor in capturing carbonate system dynamics in these highly dynamic waters.

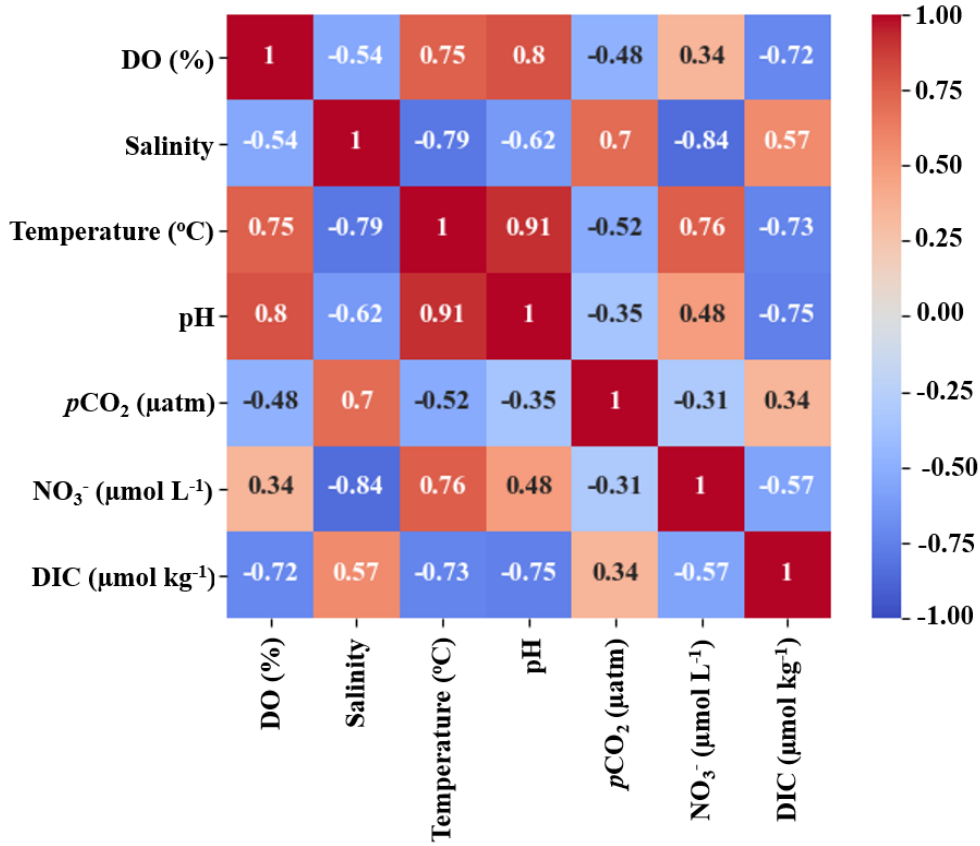


Figure 4.9. Spearman correlation matrix of sensors' data, including DIC data from the sensor during the field deployment in the Kiel Fjord during the period 4th - 24th July 2024. Positive correlation coefficients are illustrated in red boxes, and negative ones in blue.

The inner section of the Fjord is approximately 250 m wide and has an average depth of 13 m (Nikulina et al., 2008; Schröder et al., 2021). The water of the inner Kiel Fjord is influenced by the mixing of multiple water sources, i.e., the influence of high-saline water input from the North Sea, low-saline freshwater inflow from the Schwentine River, and brackish water from the eastern Baltic Sea (Geißler et al., 2021; Schröder et al., 2021).

During summer, the carbonate chemistry of the Fjord is governed by a complex interplay between enhanced primary production and elevated gas release driven by increased temperature, which directly affects CO₂ and O₂ gas exchange dynamics in the water mass (DeGrandpre et al., 1997; Kuss et al., 2006). Moreover, due to its proximity to urban infrastructure, the Fjord experiences significant anthropogenic influence, including inputs from shipyards, military harbors, and wastewater discharges from a population of approximately 250,000 in the surrounding area. A detailed discussion of the hydrographic and biogeochemical characteristics of the Kiel Fjord has been provided in Chapter 3. A comprehensive analysis of this data collected by the *in-situ* DIC sensor demonstrated the successful performance of the sensor in dynamic coastal water and offered preliminary insights into the key environmental parameters that influence the carbonate system in the Kiel Fjord.

4.4 Conclusion and Future Perspectives

In this study, an autonomous *in-situ* DIC sensor was successfully tested under laboratory conditions and during two field deployments. The sensor demonstrated robustness, stability, and long-term operational reliability. The housing design was engineered to withstand water depths up to 10 m, ensuring its applicability in shallow coastal and estuarine environments. During the field deployments, the sensor exhibited consistent performance, validating its rigid structural design and measurement stability over time. A comprehensive data processing method was developed to enable accurate DIC concentration. As DIC measurements using the conductometric technique are sensitive to temperature fluctuations, two temperature probes were integrated into the system. The measurement protocol was successfully implemented, exhibiting the capability of *in-situ* calibration without requiring pre- and post-calibration with multiple DIC standards in the laboratory. Instead, a single daily correction factor derived from one CRM/standard measurement was sufficient to ensure data reliability, streamlining the calibration process and improving operational efficiency.

The DIC concentrations recorded by the sensor showed diurnal variations and also exhibited typical correlations with hydrographical and biogeochemical parameters during the deployment in the Kiel Fjord, further affirming the reliability of the measurement system and the efficacy of the data processing approach. The sensor currently operates with a measurement cycle of 20 min and achieves a measurement precision of $16.8 \pm 8.46 \mu\text{mol kg}^{-1}$. However, further optimization of pumping rates and chemical reaction times will ensure the potential to enhance precision and increase measurement frequency, thereby achieving higher-resolution data.

In the future, the sensor will be tested in different water temperatures ($T > 30 \text{ }^{\circ}\text{C}$ and $< 0 \text{ }^{\circ}\text{C}$) to evaluate the functionality of the measurement protocol. Variation in temperatures significantly impacts gas exchange dynamics, particularly the diffusion of CO_2 into NaOH during the gas exchange process, requiring additional investigation to enhance the sensitivity of each measurement. This study will further contribute to the development of a more robust and universally applicable data processing method, ensuring accurate DIC quantification across a broader range of environmental conditions.

Moreover, the design of a next-generation *in-situ* DIC sensor is currently under development, based on the same conductometric detection principle, but designed for deep-sea deployments (1 - 2 km depth). This deep-sea adaptation will facilitate ocean-based CO_2 storage monitoring as a part of a project of ‘Alternate scenarios, Innovative technologies, and Monitoring approaches for Sub-Seabed Storage of carbon dioxide’ (AIMS³), particularly for detecting CO_2 leakages at Carbon Capture and Storage (CCS) sites.

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CRedit authorship contribution statement

Sayoni Bhattacharya: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Mario Esposito:** Writing – review & editing, Supervision, Investigation, Conceptualization, installation of the sensor and sensors on the deployment platform. **Toste Tanhua:** Writing – review & editing, Supervision. **Eric P. Achterberg:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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5. Conclusion and Future Direction

5.1 The DIC analyzer

This thesis presents the development of an autonomous analyzer designed for high-precision seawater measurements of DIC. The analyzer uses a conductometric detection technique in combination with a gas diffusion sequential injection analysis (GD-SIA) fluidic system. The measurement principle follows the traditional DIC quantification method. The seawater sample is first acidified to convert all DIC species into gaseous CO₂. A gas-permeable membrane allows the diffusion of CO₂ into a stream of alkaline acceptor solution. The resulting change in conductivity of the alkaline solution, proportional to the DIC concentration, is measured.

The detection unit includes a novel, custom-designed contacting electrode configuration consisting of four hollow brass tubes arranged at equal distances. An alternating current (AC) is continuously applied to the electrodes, and the resulting voltage difference is measured as a proxy for conductivity. To obtain efficient gas exchange, the analyzer employs a custom-made gas exchange unit (GEU) with a “Tube In A Tube” (TIAT) configuration. The setup consists of an inner gas-permeable tube through which the acidified sample flows and an outer gas-impermeable tube containing the alkaline solution, which flows in the opposite direction to maximize CO₂ diffusion efficiency.

The development process followed a stepwise approach starting with the design and optimization of a benchtop prototype, followed by field testing to assess performance and reliability. Based on the insights gained from these trials, an *in-situ* version of the analyzer was developed and also validated in additional field trials. The development process, experimental findings, and performance evaluations are discussed in Chapters 2, 3, and 4 of this thesis.

5.2 Main Outcomes

Chapter 2 describes the development of a prototype bench-top DIC analyzer, with a focus on the optimization of both the measurement protocol and data processing method. The optimization process involved a systematic evaluation of chemical and physical parameters with the aim of providing optimal balance between reagent consumption and measurement frequency while minimizing errors. Key chemical optimization tests included the use of different NaOH and H₃PO₄ concentrations, gas exchange time variations, and the use of variable NaOH flow rates to enhance measurement precision. Physical optimizations consisted mainly of the comparison between different types of gas exchange units. Gas diffusion efficiency was evaluated through a custom-designed TIAT GEUs consisting of a Teflon AF2400 gas permeable membrane fixed inside a PEEK tube, with three variations in lengths 10, 30, and 90 cm long and a second commercial GEU made of polydimethylsiloxane (PDMS). Despite its higher gas permeability coefficient, the commercial GEU exhibited a weaker conductivity signal compared to the Teflon-based GEU for the same gas exchange time and acidified sample volume. The final measurement protocol required 0.2 mL of 10% H₃PO₄ and 0.75 mL of 7 mmol L⁻¹ NaOH for each measurement using the 30 cm TIAT GEU.

Since both conductivity and gas exchange efficiency are temperature dependent, a comprehensive correction model was developed to account for temperature variations, ensuring accurate conversion of raw conductivity data into DIC concentrations. Salinity tests showed minimal impact on conductivity under stable temperature conditions. With the optimized measurement protocol, the analyzer was able to measure samples within a wide range (500 - 3000 $\mu\text{mol kg}^{-1}$) of DIC concentration with a sampling frequency of 4 samples per hour. and analytical precisions of $\pm 4.9 \mu\text{mol kg}^{-1}$ and $\pm 9.7 \mu\text{mol kg}^{-1}$ in the laboratory and in field deployment, respectively, meeting ‘weather quality’ standards (precision of $\pm 10 \mu\text{mol kg}^{-1}$).

In Chapter 3, two field deployments are presented to assess the performance of the prototype bench-top DIC analyzer in highly dynamic estuarine and coastal waters. The analyzer was fixed on the GEOMAR pier in 2023, from 27th July to 25th August, and

installed onboard RV *Littorina* from 4th to 7th September to measure surface waters of the German Bight, south-eastern North Sea. During the 1st deployment, the syringe pump had some mechanical issues, so measurements were paused for 5 days. Besides that, the analyzer was able to autonomously measure 1644 data points in the Kiel Fjord and 60 data points in the German Bight. To validate the measurements, 43 and 31 discrete samples were collected during the respective deployments. The analyzer showed potential instrumental drift over time, which was mathematically corrected using the linear drift correction method. The data processing method provided measurement precisions of ± 7.24 and $\pm 5.48 \mu\text{mol kg}^{-1}$ in the Kiel Fjord and the German Bight, respectively, meeting ‘Weather Quality’ standards. The DIC values obtained from the analyzer showed good agreement with discrete samples, with calculated accuracy as -15 and $+10 \mu\text{mol kg}^{-1}$ for the Kiel fjord and North Sea deployments, respectively. In this chapter, diurnal variations of DIC in addition to hydrographic and other carbonate parameters, are also presented. The data were used to explain carbonate system dynamics within the region. Statistical analysis of the relationships between DIC and other parameters, e.g., DO, $p\text{CO}_2$, and salinity, gave insights into the drivers of temporal and spatial fluctuations in carbonate dynamics in these complex systems. The carbonate chemistry of these regions changes on an hourly to sub-hourly scale, and traditional manual sampling and lab-based analysis alone cannot capture the detailed physicochemical processes in these systems. Real-time measurements from the DIC analyzer filled this gap, providing datasets at high frequency.

In Chapter 4, an autonomous *in-situ* DIC sensor was developed based on the success of the bench-top analyzer. The hardware and the fluidics were modified to make the sensor compact and pressure-resistant (capable of operating at depths up to 10 m). A new measurement protocol was created based on a long-term physical and chemical stability test performed in the laboratory. The performance of the sensor was subsequently evaluated in (1) a 3-day (24th - 26th June 2024) field trial in the Baltic Sea onboard RV *Littorina* and (2) during a 21-day (4th - 24th July 2024) deployment in the Kiel Fjord at a depth of 2 m. The sensor was equipped with two temperature probes, and the findings showed a significant impact of temperature on conductivity measurement. The sensor achieved measurement precision and accuracy of $\pm 16.8 \mu\text{mol kg}^{-1}$ and $-12 \mu\text{mol kg}^{-1}$, respectively, with a measurement frequency of 20 minutes. The DIC measurements obtained from the

sensor were further combined with ancillary environmental parameters, including salinity, temperature, DO, nutrients, and pH obtained from commercial sensors deployed in the Kiel Fjord. The results showed good correlations between DIC and the other parameters. These preliminary results confirmed the capability of the sensor to successfully function in a complex carbonate system. A major improvement in the post-processing was the development of a simplified correction approach. Based on the temperature variation recorded from the two T probes, a revised data processing method was developed. Additionally, a daily correction factor was applied from the *in-situ* calibration performed using only one CRM measurement. It eliminated the necessity of performing pre- and post-calibration with multiple DIC standards. This significantly reduced operational complexity and made the sensor more practical for long-term autonomous deployments.

Overall, this thesis presents the development process of an autonomous *in-situ* DIC sensor, which is based on its bench-top prototype version, that offers real-time data acquisition with the capability of *in-situ* calibration. A robust post-data processing method facilitates reliable and high-quality data analysis, making the sensor suitable for diverse applications, e.g., monitoring leakage in the CCS injection site or studying the rapid change in the marine carbonate system. The creation of an optimized measurement protocol additionally ensures long-term deployment feasibility while keeping the balance between reagent consumption and measurement frequency. Finally, it utilizes cost-effective components to reduce sensor production costs and enable broader sensor deployment scope across the scientific community with a lower budget.

5.3 Future work

The developed *in-situ* DIC sensor has demonstrated promising performance, but further improvements are needed to enhance measurement precision, accuracy, and operational efficiency. One of the main limitations observed was the carryover effect from previous samples, which required flushing of all the fluidics in between measurements. Future modifications, possibly of the pump flow rates or the fluidics design, are under consideration to improve sample throughput and reduce carryover.

Another key aspect of improvement lies in refining the data processing method. Future work will focus on the conduction of a comprehensive calibration across different salinity and temperature ranges to incorporate the salinity effect under different temperature conditions. The sensor is equipped with two temperature probes, and the definition of a precise correlation between the two onboard probes, one affecting conductivity and the other linked to gas exchange, will enhance the robustness of the system. Additionally, the cell constant of the detection unit should be fine-tuned to increase conductivity resolution and improve measurement sensitivity and data quality.

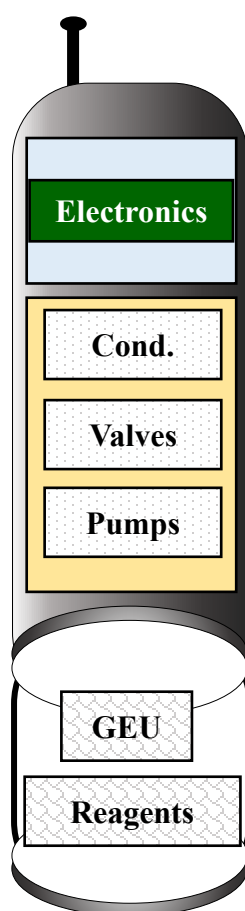


Figure 5.1. Schematic of a proposed design of the deep water DIC sensor.

The short-term field trials in Chapters 3 and 4 demonstrated the analyzer/sensor's capability to measure DIC in a dynamic coastal environment. However, further research is

required to investigate the long-term environmental influences on DIC variability across different water masses. Extended field deployments in diverse marine settings, ranging from estuaries and fjords to open oceans, will be essential to assess the performance stability of the sensor over time.

A significant part of this research involves the development of a deep-water version of the sensor as part of the AIMS³ project. The findings of this thesis confirmed that the existing components are suitable for shallow-water deployment; however, their application to deep-water conditions might require modifications. The deep-water version will retain the fundamental design of the shallow-water sensor but will feature a more compact and pressure-resistant structure for greater depths. The proposed design of the deep-water sensor will have primarily three compartments (Figure 5.1). The first compartment will be dedicated to the electronics with a single electronic board to integrate both hardware and software controls. Inside the second compartment, the detection unit will be housed in an oil-filled chamber to compensate for pressure changes. Pressure tests on valves and pumps have started, and the valves have successfully passed initial tests. The GEU and the reagent bags will be kept in the third compartment using materials suitable for deep-sea conditions. A rechargeable battery for standalone deployment is preferred but cable and external battery are also considered options.

The deep-water sensor is planned to be mounted on a platform along with other carbonate sensors, including a new $p\text{CO}_2$ and pH sensor, to enable autonomous CO_2 leakage monitoring at CCS injection sites. The use of cost-effective materials is one of the primary goals for the development of the three sensors as part of the AIMS³ project.

Beyond CCS applications, the sensors have potential for oceanic carbonate system monitoring, where concentrations are highly dynamic and influenced by seasonal variations, carbonate weathering, precipitation, and CO_2 outgassing. The integration of this technology into global ocean monitoring networks, such as the Global Ocean Acidification Observing Network (GOA-ON) for tracking ocean acidification trends and the Global Ocean Observing System (GOOS) for large-scale ocean-climate studies, would significantly enhance observational capabilities. Understanding the natural variability in the oceanic carbonate system requires a comprehensive global dataset. This goal could be

efficiently achieved through the deployment of autonomous sensors on diverse ocean platforms, thereby reducing dependence on conventional ship-based monitoring. However, the current lack of high-quality autonomous sensors highlights the need for continued innovation and development within the scientific community.

In addition to applications for marine carbonate system monitoring, the DIC sensor has the potential to be adapted for riverine carbonate system studies, where hydrochemistry is highly dynamic and influenced by both natural and anthropogenic processes. Natural sources of DIC in river water are primarily dependent on seasons, and precipitation, carbonate weathering, soil CO₂ dissolution, photosynthesis/respiration cycle, degradation of organic matter, and CO₂ outgassing process (Atekwana & Krishnamurthy, 1998; Battin et al., 2023). Rapid urbanization and anthropogenic inputs, particularly from wastewater treatment plants, introduce additional uncertainties in estimating riverine carbon fluxes and natural carbon sinks (Long et al., 2024). The global concentration of DIC in rivers generally varies from 900 to 5000 $\mu\text{mol kg}^{-1}$ (Lu et al., 2017), and external perturbation needs to be constrained to estimate the carbon budgets. The current DIC analyzer has been demonstrated to be capable of measurements of a wide range (500 - 3000 $\mu\text{mol kg}^{-1}$) of DIC. Modifications in reagent concentrations and detection cell range would allow the use of the sensor for high-resolution riverine carbon flux studies.

Understanding and predicting marine and riverine systems along with their impacts on global climate, require high-resolution *in-situ* observations. While traditional discrete sampling methods are valuable, they are limited in capturing the fine-scale temporal and spatial variability of these dynamic environments. While autonomous sensors for measuring DO, $p\text{CO}_2$, pH, and nutrients are already commercially available, DIC and TA sensors are still emerging. Ongoing studies focus on simultaneous measurement of DIC and TA by developing a multi-parameter analyzer (Wang et al., 2007). The coupling of these next-generation sensors with data networks and machine learning-based data assimilation will be crucial for the management and observation of physical and biogeochemical processes in the ocean, assessment of ocean acidification impacts and monitoring of marine mCDR methods.

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7. Statement of Declaration

I, Sayoni Bhattacharya, hereby declare that I have written this Ph.D. thesis independently, under compliance of the rules for good scientific practice of the German Research Foundation. I declare that I used only the sources, the data and the support that I have clearly mentioned. Moreover, I assure that this Ph.D. thesis has not been submitted for the conferral of a degree elsewhere, neither in part or as a whole, and that none of my academic degrees has ever been withdrawn. Published or submitted for publication manuscripts are identified at the relevant places.

Sayoni Bhattacharya

Kiel, May 2025

