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Joint European Research Infrastructure for Coastal Observatories

Science, Services, Sustainability

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1.EXECUTIVE SUMMARY

Carbon is an important element in marine biogeochemistry, used for tracking the health of the ecosystem, and thus its monitoring is of great importance. The inorganic carbonate system consists of four variables (C_T - total inorganic carbon; A_T - total alkalinity; pCO_2 - partial pressure of CO_2, pH), which each can be readily measured. For the open ocean conditions, the whole inorganic carbonate system can be determined by measuring just two of these variables. The guidelines given by Dickson et al. (2007) form the basis for all carbonate system measurements. The large salinity variability, high biological activity and river inflows in the coastal regions of the seas generate challenges for both the measurement and modelling of the carbonate system. The large spatio-temporal variability in carbonate system variables calls for high-frequency measurements.

The carbonate system of the European coastal seas is measured using different protocol, mostly following guidelines established by the Integrated Carbon Observation System (ICOS). The harmonised marine network of ICOS consists of several types of stations, with differing requirements and guidelines. Use of quality-controlled databases such as the Surface Ocean CO_2 Atlas (SOCAT) provides benefits of quality assurance, harmonisation, and findability. Due to the novelty of the many sensor-based carbonate measurement systems, inter-calibration workshops have proved to bring new insights into the accuracy, operability, and shortcomings of these sensors.

2.INTRODUCTION

2.1. Importance of carbon system parameters

The inorganic carbon system is of pivotal importance for the understanding of ecosystem functioning in coastal seas. Carbon is the major component of organic matter, and biogeochemical changes through primary production or mineralisation can be closely followed by monitoring the inorganic carbon system. The mineralisation of organic carbon is the main driver of the oxygen demand in organic-rich (eutrophied) waters. Carbon system parameters thus link the nutrient-based (total N and P, inorganic N and P), the primary-production-based (Chl a, Secci depth), and the respiration-based (oxygen debt, area of suboxia) indicators for coastal management, as defined in the European Marine Strategy Framework Directive (MSFD), as well as in regional conventions, such as the HELCOM Convention (Baltic), Barcelona Convention (Mediterranean), Bucharest Convention (Black Sea), and OSPAR Convention (North-East Atlantic and North Sea). The inorganic carbonate system also largely determines the acid-base system of brackish and saline waters, and thus, governs acidification. Thus, all strategies to monitor ocean acidification require monitoring of carbonate system parameters in precise, accurate and long-term traceable manner.

2.2. Measurement maturity and best practises for the open ocean

The carbonate system can be determined by the measurement of four biogeochemical variables: the total alkalinity (A_T), total inorganic carbon (DIC or C_T), the acidity of seawater (on a negative logarithmic scale, i.e. the pH) and the partial pressure of CO_2 (pCO_2). For the open ocean, with its limited range of these variables, the measurement of all four variables is straightforward, with rigid Standard Operation Protocols (SOPs), outlined in e.g. Dickson et al. (2007) or Pfeill et al. (2013). For the open ocean, the entire carbonate system can be described by exact determination of two of these four parameters, from which the other two can be readily calculated using publicly available code for the majority of scientific data handling programs. However, these calculations, depending on the set of parameters used as input parameters, are not without uncertainties, which should be considered and quantified (Orr et al., 2018). Additional care must be taken due to the fact that enrichment of compounds in coastal waters that contribute to the acid-base balance, such as organic matter or hydrogen sulphide, have to be taken into account or may even require determination of an additional variable of the CO_2 system (Kuliński et al., 2014, Ulfsbo et al., 2015).

In the open ocean, pCO_2 (or the fugacity, fCO_2) is measured almost exclusively in surface waters using air—sea equilibration systems coupled to infrared spectroscopy (see Pfeill et al., 2012). The data are curated and quality-controlled through the SOCAT project, a community-driven effort to produce and update products like the Surface Ocean CO_2 Atlas (latest release 2023, https://socat.info/index.php/2023/06/20/v2023-release/). In Europe, since recently, a large part of the operational surface fCO_2 measurements are performed under the umbrella of the European Integrated Carbon Observation System Research Infrastructure (ICOS RI).

For the ocean interior, most data are collected for C_T and A_T, the two conservative parameters of the oceanic CO_2 system, while in principle, calculation of the CO_2 system is also possible from the couple C_T/pH or A_T/pH. However, despite the high accuracy and precision of pH measurements for open waters (~0.003 pH units), calculation from C_T and A_T is more robust and accurate. Calculation from pCO_2 and pH is not recommended (Steinhoff, 2020). A compilation of ocean carbon system data and relevant auxiliary data, including some additional quality control efforts, are frequently updated via the Global Ocean Data Analysis Project (GLODAP; Lauvset et al., 2024).

To achieve higher spatiotemporal resolution, sensor-based solutions are commercially available. Out of the four measurable parameters, only pCO_2-sensors have reached a maturity which appears promising for long-term deployment, however not reaching accuracy and long-term stability even near to the state-of-the-art options stated above. The status of knowledge will be briefly addressed here.

2.3. Challenges for determination of the inorganic carbon system in coastal seas

In coastal seas, high biological activity, river discharges, and variations in salinity create technical challenges for measuring the carbonate system components as well as modelling of the carbonate system. The behaviour of the carbonate system differs in coastal areas, even within regional seas, and some of the analytical instrumentation cannot be readily applied due to e.g. lack of reference material covering the entire range of values encountered in coastal seas, lack of parameterisation in high/low salinity regions, or ranges of values out of the specified working range of the instruments.

Additionally, at lower salinities with a high fraction of freshwater, the assumption that the acid-base system of the water is completely determined by the carbonate system and components that can be directly scaled to salinity (e.g. borate) might not be strictly valid anymore. Examples for this are anomalous borate concentrations (Kuliński et al., 2018), or a non-negligible contribution of alkalinity by organic acids (Kuliński et al., 2014, Ulfsbo et al., 2015). In euxinic waters, the contribution of hydrogen sulfide to alkalinity needs to be considered (Almgren et al., 1976). In these cases, determination of more than two of the parameters listed above might be required to fully describe the carbonate system.

In contrast to these enhanced challenges to readily determine the carbonate system in coastal seas, the nature of coastal systems actually requires a higher spatiotemporal resolution to address carbon system variability caused by higher productivity, higher imprint of tidal and diurnal cyclicity, a stronger impact of benthopelagic coupling, and various other drivers (e.g. Carstensen and Duarte, 2018; Carstensen et al., 2019; Honkanen et al., 2021). While the large amplitude of shifts in inorganic carbon parameters might allow reduced requirements on accuracy and precision of measurements, it is of utmost importance to be readily able to assess these levels of uncertainty.

This report therefore seeks to provide some information and recommendations on measurements of the carbonate system in coastal waters.

3.MAIN REPORT

3.1. Overview of Carbon System instrumentation within JERICO-S3

Within the JERICO RI community, carbonate observations are done in largely differing coastal ecosystems across the pan-European coastal seas and for versatile purposes, using different instruments and protocols.

Areas	**T (C°)**	**S (psu)**	**pCO_2 (uatm)**	**pH**	**Spring**	**Summer**	**Autumn**	**Winter**	**Comments**
Norwegian Sea (region)	0...18	6…34	100… 490	8.2… 8.0	Sink	Source	-	Source	Variation on open ocean relatively small compared to coastal areas
North Sea (region)	4…20	9…34	175… 500	8.5… 7.8	Sink	Sink	-	Source	Deep areas sink year round

Baltic Sea (region)	0... 25	0…20	100… 700	8.4… 7.9	Sink	Sink	Source	Source	Low salinity challenge in pH measurements
Mediterranean Sea (point)	7…29	31…38	280… 470	8.2… 8.1	Sink	Source		Sink	River impact significant

Table 1: Overview of the range of some physical and biogeochemical parameters covered in the JERICO network, compiled as part of Deliverable 4.5 of JERICO-NEXT.

Typical coastal conditions observed during the intensive measurement period (April 2017 - March 2018) of JERICO-NEXT project on selected European Sea areas. The lowest pCO_2-concentrations were found to be linked with biological activity in all regions. The ranges given above describe the observations during the intensive period only, at certain sites much higher and lower values have been recorded.

During the JERICO Days held in Lisbon in June 2022, a workshop was organised to identify the carbonate system measurement protocols used in the JERICO RI. Before the meeting, a questionnaire (Fig. 1) was sent to all leads of the Pilot Super Sites (PSSs) and the Integrated Regional Sites (IRSs) to provide information on the systems used for the inorganic carbon measurement at their measurement sites. The inquired information included the set of measured carbonate and supporting variables, measurement methods, accuracy of the measurement, standard operating procedures, quality control schemes, measurement range of each variable in addition to a few free text form questions regarding the measurement and data policies.

Based on the response to the inquiry, the carbonate system was measured to some extent in the Baltic Sea, the Danish Straits, North Sea and in the Northern Adriatic Sea, using fixed stations and ships of opportunity (FerryBoxes, in the framework of ICOS and the carbon community usually referred to as Ship of Opportunity, SOOP). A large range of systems was identified. For example, pCO_2 was observed using equilibrator systems, membrane systems, or calculated from other carbonate variables. The large range of values of carbonate system variables in coastal systems reflect the strong seasonality. Standard Operating Procedures (SOPs) protocols showed some variation, but the guidelines of Dickson et al. (2007) were adopted widely. For the Quality Control (QC), ICOS OTC QC protocols were used in some platforms but in many cases, not published QC methods were used. The data were published in many different databases, but in the case of pCO_2, most often in SOCAT, using strict and traceable quality control steps, resulting in a quality assessment of the data reflected by an established flagging scheme (Lauvset et al. 2018).

The workshop clearly showed that the selection of the fit-for-purpose instrumentation, best practices, quality control protocols, as well as the selection of appropriate databases are needed for a harmonised and quality-controlled coastal ocean carbon system data product.

However, these requirements are often not readily in place for a successful coastal carbonate system data management.

The questionnaire and the account of the feedback on the questionnaire as well as some of general conclusions drawn are provided in Annex I.

3.2. Major sources of best practices and quality control

The measurement of carbon system parameters in the open ocean is straightforward and SOPs are readily in place. This has been an essential requirement to reach the demanding goals for accuracy and precision to meet some of the key applications of these measurements, such as

- integrated flux estimates for the global ocean based on surface pCO_2 measurements and smart interpolation tools (see e.g. respective part of the Global Carbon Budget, Friedlingstein et al., 2023)
- quantification of the propagation of anthropogenic carbon into the ocean's interior (e.g. Lauvset et al., 2024).

For the measurement of pCO_2 and accompanying parameters in surface waters, straightforward SOPs, documentation requirements and quality control has been developed within the European Integrated Carbon Observation System Research Infrastructure (ICOS RI). The ICOS RI aims to quantify the greenhouse gas balance in Europe. ICOS consists of a harmonised network of monitoring stations, observing the greenhouse gasses in the atmosphere, terrestrial ecosystems and marine ecosystems.

The ICOS Ocean Thematic Centre (OTC) coordinates the marine stations within ICOS. The labelling process of ICOS OTC guarantees the high quality of data from these stations after the labelling has been passed (Skjelvan et al. 2019). The ICOS OTC observation network includes ships of opportunity (SOOPs, Ferryboxes), fixed stations, and marine flux towers. ICOS OTC acknowledges the large spatiotemporal variability in the carbonate system within the coastal areas, and thus they evaluate each station individually, related to what is achievable (Skjelvan et al., 2019).

Ships of opportunity usually feature continuously operating seawater sampling techniques using flow-through systems. To meet the highest criteria of the ICOS OTC standards for ship of opportunity pCO_2 observations, one should follow the best practices given by Dickson et al. (2007) and use an infrared gas analyzer connected to a headspace equilibrator, equipped with at least two standard reference gases, in order to achieve the climatological goal of 2 µatm (Pierrot et al., 2009; Lorenzoni and Benway, 2012). Over the last few years, the implementation of cavity enhanced absorption spectroscopy sensors (CEAS) has also been pushed forward (Steinhoff and Neill, 2020), for example on the SOOP Finnmaid, operating in the Baltic Sea (https://meta.icos-cp.eu/labeling/). The procedures required for labelling a SOOP station for pCO_2 are strongly related to the criteria developed by SOCAT (Pfeil et al., 2009). One of the requirements critical for coastal applications is the "bracketing" of the dynamic range of the measurement values (CO_2 mole fraction) by calibration gases. In particular in eutrophic coastal and marginal seas, this is difficult as the range of highest quality calibration gasses is limited to approximately 200—800 µatm (A. Jordan, ICOS CAL, personal communication). Coastal systems can easily have pCO_2 values outside this range on both ends.

The fixed stations typically consist of surface buoys or moorings with carbonate system instruments measuring in one or several depths. In contrast to the carbonate measurements on the ship of opportunity, these sites may comprise multiple measurement techniques for the measurement of pCO_2 (Coppola et al. 2016). Even though providing scientifically important high temporal resolution series of data, e.g. targeting the seasonality of the coastal carbonate system, these alternative sensors (compared to the headspace equilibrator based systems) at the moment do not fulfill the required climatological goal of 2 µatm, and are classified with lower quality flags in databases such as SOCAT (Wanninkhof et al., 2013). Following the ICOS OTC guidelines, these stations are required to use at least one reference gas or monthly collection of either pH-A_T or pH-C_T samples, allowing for an independent calculation of the variable measured by the respective sensor. Many of these alternative sensors are using membranes which can be easily affected by biofouling (Wanninkhof et al., 2013), and are prone to drift. Some of the most commonly used sensors do not allow the measurement of a calibration gas and require post-calibration by the company, making independent quality-control during deployment impossible. Due to the need to cover coastal variability with high spatial and temporal resolution, often paired with a limited requirement for accuracy and precision for coastal process studies, if has been attempted by the coastal research community to work with sensors with low energy demand and moderate costs, but often with fragmented or no clear SOPs in place. However, several procedures and reports from sensor assessments exist, and the Ocean best practise repository (https://www.oceanbestpractices.org/) is a great source of information on experience and recommendations for sensor-based pCO_2 applications (e.g. Obolensky and Körtzinger, 2019; Macovei et al., 2021).

The carbonate observations typically require use of a number of certified reference materials or calibration gasses for the verification of the instrumentation. In general, the variation in the carbonate system observed in coastal regions outweighs the one of the open oceans, which needs to be taken into account when choosing the set of the reference material or calibration gases. As the salinity in coastal conditions may deviate from the oceanic conditions, care must be taken when using reference materials, most often suitable for the oceanic conditions. Still, it is established to parameterise in particular instrumentation for the measurement of C_T/A_T with an oceanic certified reference material (CRM), at current stage exclusively delivered to the ocean community by an effort of the Dickson laboratory at SCRIPPS (Dickson, 2010). Establishment of a European facility for the production of carbon system reference materials is currently on the work plan of the ICOS OTC. In the last couple of years, regularly executed round robin experiments (Quasimeme) have been extended to include some samples with lower salinity/total alkalinity.

The purpose of the carbonate system observations determine the measurement requirements. To study the long-term changes in the carbonate system (climate goal), such as the ocean acidification, higher accuracy is required than for the measurements to identify spatial patterns or short-term variation, so-called weather goal (Newton et al., 2015). In coastal regions with larger carbonate system variability than in the open oceans, larger amounts of data and longer time series are required to detect small trends within the carbonate system (Pimenta and Grear, 2018). ICOS OTC has set higher temporal frequency requirements for these measurements in the coast than in the open sea.

3.3. Intercalibration attempts

The performance of intercalibration exercises has a long history in the research of the marine carbonate system, and has played a pivotal role to achieve harmonised instrumentation capable of reaching the 2 µatm accuracy goal (e.g. Körtzinger et al., 2000). Intercalibration workshops can reveal important insights into how different carbonate instruments operate in the environmental conditions of the coastal seas which can show large spatio-temporal variability.

JERICO-NEXT organised an intercalibration workshop, called INTERCARBO, for different carbonate system instruments in Oslo in 2018. At the station of Norsk institutt for vannforskning, seawater collected from the Oslofjord was analysed in differing pCO_2, temperature, salinity and alkalinity conditions. This experiment, consisting of 15 different carbonate system instruments, woke the JERICO community to acknowledge the challenges of measuring the carbonate system with varying instruments. It also highlighted the technical challenges faced when organising carbonate system intercomparison workshops, for instance the difficulties of the bubbling the sample water to reach the aimed carbonate system conditions, as well as different levels of preparation and handling.

Based on the earlier experiences and shortcomings of intercalibration exercises, ICOS OTC arranged a pCO_2 intercalibration workshop in Flanders Marine Institute in Belgium in 2021. A large set of pCO_2 instruments were deployed in a water tank, where the pCO_2 and temperature were manipulated. Compared to the earlier experiments, a limited number of highly trained experts performed the experiment as well as instrument handling. Also, the post-processing was harmonised. Instruments were grouped into four categories: a) underway instruments with air-water equilibration, b) underway instruments with membrane equilibration, c) autonomous instruments for sea surface applications, d) autonomous instruments which are submersible. The particular idea of the workshop was to assess the range of uncertainty under optimal conditions between the individual systems, as well as to identify main sources of other errors and uncertainties. The test runs comprised 6 setups with 3 pCO_2 levels (low, medium, high) as well as two temperature regimes (low/high). The results of this workshop would be a highly relevant resource for this deliverable due to its high importance for the scope of D6.8. but the publication of the results has unfortunately not yet been published yet. Still, some preliminary results can be summarised here:

- All equilibration-type instruments were within a 5 µatm range, and all but one stayed within the 2 µatm range for most of the time, demonstrating that the 2 µatm criterion was met under these optimal conditions.
- The underwater membrane-based systems mostly stayed within 15 µatm, some clearly showing different behavior under different temperature regimes. In many cases, this performance deviates from manufacturer specifications.
- The autonomous surface instruments performed mostly well, usually within 5 µatm, with some indication for an effect of temperature on the performance.
- The submersible instruments performed very well at the beginning, but drifted in different directions towards the end of the one-week deployment period, showing deviations up to 40 µatm on the last run with high pCO2 and high temperatures.

It has to be emphasised that this intercalibration tried to define the maximum reachable performance of the instruments, using the same standard materials, and a harmonised data handling protocol. One of the clear outcomes of the study is that in the planning of the deployment of sensors on permanent platforms, the opportunities for quality check by discrete sampling (usually AT, CT) to derive reliable points in time for intercomparison should have high priority.

3.4. Intercomparison opportunities

Due to the aforementioned special needs for carbon system instrumentation in coastal seas (spatio-temporal resolution, dynamic range, limited power supply, spatial restrictions on small boats), sensor development and testing is often driven by the coastal community, and has a long legacy within JERICO. In that respect, it has been proven useful to seek for opportunities to check performance against an established measurement system. One good example is the study by Macovei et al. (2021), who performed a long-term intercomparison of a membrane-based equilibration system versus an equilibrator-based system on a SOOP in the North Sea. The study is based on the frequent crossover of two independent lines in the Skagerrak area.

An asset for this approach for the European Research Infrastructures and communities addressing marine carbon system parameters is currently developed in the framework of the Horizon Europe project GEORGE (Grant No. 101094716; Next generation multiplatform ocean observing technologies for Research Infrastructures). Apart from a variety of sensor development and improvement efforts, the work comprises the construction of a test stand for sensors on the SOOP Finnmaid, one of the labelled ICOS lines. The system provides continuous high quality data for pCO_2, pH (which is recorded spectrophotometrically), and the amendment of a continuous-flow system for A_T is considered within the project. The line has a round trip time between Lübeck (Germany) and Helsinki (Finland) of only three days, covers a large brackish salinity range, and a high dynamic range for pCO_2, pH, and the carbon system in general (e.g. Schneider and Müller, 2018). The rationale for the development within GEORGE, a joined effort of several European RIs, is to provide an easy to access testbed for sensors, with effortless provision of all potentially relevant auxiliary parameters, as well as state-of the art, validated values for pCO_2, pH (and the concentrations of CH_4 and N_2O). Once in operation, the platform will allow easy-to-go experiments for the performance tests of carbon system sensors, including short-term (days to months) drift.

3.5. Recommendations

The measurement purpose and the site specificities determine the techniques to apply. The measurement guidelines given by Dickson et al. (2007) are widely adopted as a main reference for the high quality carbonate system observations. These guidelines dictate the preferred measurement techniques and calculations. In addition, the principal investigator should follow the requirements and recommendations given by the ICOS OTC for different kinds of measurement platforms.

Coastal ship-based or coastal station-based measurements should try to use state-of-the-art equilibration-based instrumentation for pCO_2, in order to reach the climate goal and to contribute to the important goal of assessing long-term trends in the marine carbon source-sink balance, and follow progress and recommendations by ICOS OTC closely.

The coastal carbonate system is often characterised by large spatial and temporal variability. The frequency of the observations should be high enough to capture this variability. The range of the variability needs to be taken into account when selecting the methods and reference materials.

Some of the methods for carbonate system measurements have reached very high standards for accuracy and precision for open ocean waters. However, these narrow ranges of uncertainty often cannot be reached for coastal waters. Reasons might be the unavailability of high-precision reference materials over the entire dynamic range (e.g. the calibration gasses for CO_2), lack of parameterisation or instrument certification out of the typical open ocean range (e.g dye characterisation for spectrophotometric pH measurements or alkalinity measurements far off the concentration of Certified Reference Material), or corruption of the measurement principle by variable water properties (i.e. influence of salinity on potentiometric measurements).

The need for high spatiotemporal resolution, low power consumption and other constraints leads to a large demand - and high innovation potential - for sensors for coastal waters, with sensors for carbon system parameters amongst them. However, the resulting setups are often not well characterised and lack fully mature SOPs. Care should be taken to validate/characterise these novel approaches with fully mature state-of-the-art reference methods, or high precision wet chemical point measurements (i.e. C_T/A_T). For the latter approach, it has to be considered that coastal-specific enrichment of compounds might complicate/hamper these calculations. This has to be emphasised, as it challenges the applicability of some of the SOPs and quality control approaches established for the open ocean, which is often overlooked. Also, it is recommended to scrutinise the Ocean Best Practices System resources for applicable recommendations and SOPs.

Within the European Research Infrastructure “landscape”, the ICOS RI (Oceans) and the Euro-Argo RI are particularly relevant for carbon system parameter measurements in coastal waters, having reached a high level of standardisation and rigid quality control processes. In that regard, it is recommended to follow the outcome and use the facilities and developments of the project GEORGE currently funded within Horizon 2020.

Respecting the FAIR (Findability, Accessibility, Interoperability, and Reusability) principles, the data should be published using harmonised and quality-controlled databases, such as SOCAT. For new methods and sensors for measuring coastal carbonate system parameters, all efforts should be taken to do a proper and well-documented uncertainty assessment. With a proper and traceable error estimate, data can be selected by any potential user based on the demands of the planned application.

4.OUTREACH, DISSEMINATION AND COMMUNICATION ACTIVITIES

This deliverable report will be publicly available and open to the science community. It will be shared with respective consortia such as the ICOS MSA or the members of the GEORGE project. The status assessment of carbon system parameter measurements within JERICO has been discussed during the JERICO-S3 workshop in 2022. The posting of this report on the Ocean Best Practises repository will be considered.

5.CONCLUSIONS

The measurement and modelling of the carbonate system in the coastal seas is a challenge and still requires special attention. Due to large spatiotemporal variability and high dynamic range, some of the readily developed standard operating procedures for open ocean measurements, as well as specific instrumentation or the performance specifications of this instrumentation, might not be readily applicable to measurements in coastal seas. Resulting recommendations are given in Chapter 3.5.

6.ANNEXES

ANNEX I: File: JERICO_S3_Del_6-8_Appendix_I_Worshop_documentation.pdf
Presentation of the questionnaire and the results of the feedback to the questionnaire on carbon system parameter measurements in the JERICO network, and some general conclusions, Jericho Week 2022, March 15-18, presented by L. Laakso (FMI).

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