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Review

Essential Ocean Variables for Marine Environment Monitoring: Metrological Case Studies

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Abstract: Monitoring the state of oceans and their evolution in space and time is of fundamental importance as they are severely impacted by climate change, showing an increase in temperature, acidity and stratification. The role of metrology in the marine sector is relevant for helping oceanographers consolidate measurement approaches already in place by introducing concepts like metrological traceability and measurement uncertainty. The aim of this paper is to present some examples of successful and potential applications of metrology in oceanographic research, with a focus on past and ongoing activities in the framework of joint research cooperation, which could be applied by oceanographers to consolidate the comparability of data acquired in different experimental conditions, and places and time for some essential ocean variables. Scientific cooperation in the framework of joint research projects is particularly useful for supporting measurement capabilities in marine research worldwide, and the technologies and methods developed so far represent a starting point for improvements in international monitoring networks. These techniques may be applied by laboratories and centres working in the marine sector. Applications and possible future developments will also be discussed in this paper.

Keywords: essential ocean variables; metrological traceability; uncertainty evaluation; climate change; metrological case studies



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1. Introduction

Monitoring the state of oceans and their evolution in space and time is of fundamental importance, due to the relevance and impact they have on Earth's global cycle [1]. The oceans are severely impacted by climate change, with key indicators being an increase in temperature, acidity and stratification. These changes are responsible for the alteration of marine ecosystems and an increased vulnerability of many marine species [2].

The Global Ocean Observing System (GOOS), a programme run through UNESCO Intergovernmental Oceanographic Commission (IOC), has established a framework for ocean observation centred on essential ocean variables (EOVs). GOOS expert panels identified 31 EOVs that include physical (e.g., temperature, salinity, currents, ice), biogeochemical (e.g., dissolved gases and nutrients, acidification, particulate matter and tracers) and biological (e.g., phytoplankton) parameters. The importance of these variables for monitoring the oceans' state is underlined by the presence of 19 GOOS EOVs among the 54 essential climate variables (ECVs) defined by the Global Climate Observing System (GCOS).

EOVs monitoring is fundamental for capturing trends and assessing comparability among different networks, different principles and methods. However, in many cases, a multidisciplinary and coordinated approach to establish fundamental metrological robustness in EOVs observation is lacking. In this context, documented traceability to the International System of Units (SI) for EOVs, including proper quality assurance tools

(e.g., reference materials, interlaboratory comparisons, uncertainty evaluation) is currently needed. The paramount role of EOVs as key indicators for ocean life is acknowledged by the entire scientific community and is required to inform policy makers and international management in the framework of climate change studies, use of marine resources and coastal development [3–5]. Another important aspect is the temporal scale at which shifts in biological systems can be detected, which vary for each EOV and therefore influence the properties being monitored and the length of the time-series. Collaboration between the scientific and policy sectors is required to improve human and infrastructure capacity worldwide. This also necessitates developing new and more automated observing technologies and application of international standards and best practices.

As an example, the authors in [6] developed a particular model called “driver-pressure-state-impact-response—DPSIR”, to identify biological and ecological EOVs for implementation within the global ocean observing system. This model was developed following several steps: (1) study of relevant international agreements to identify societal drivers and pressures on marine resources and ecosystems; (2) evaluation of the temporal and spatial scales of variables (measured by more than 100 observing programmes); (3) analysis of the impact of these variables and their contribution to address societal and scientific questions. This kind of approach could also be implemented for other types of EOVs to evaluate their impact and to study new strategies for the correct exploitation of data collected from their monitoring.

In the present paper, the authors focus on three variables related to their main fields of expertise, i.e., temperature (surface and subsurface temperature), partial pressure of CO₂ and stable carbon isotopes. Metrological case studies found in the literature (Science Direct and other international databases) will be considered, and metrological research examples from the outcomes of different European joint research projects in metrology will be presented. The principal aim of this work is to contribute to spreading concepts of metrological research, which were consolidated into the traditional sectors of physical sciences and to oceanographic research and marine monitoring sectors too. The final goal, which is foreseen by the entire metrological community, is to create a bridge and to support cooperation between the scientists working in these two sectors.

In the EURAMET framework [7], several projects concerning metrology for environmental and climate change-related issues were funded by the EU and carried out by consortia of national metrology institutes (NMIs), designated institutes (DIs) and other institutions involved in this field.

Within EURAMET, the establishment of the European Metrology Network (EMN) for climate and ocean observation represents another initiative [8]. The EMN is intended as a network of European NMIs, DIs and affiliated partners that supports the application of metrology and the science of measurement to climate and ocean observation. In particular, the EMN is working to assure metrological support for the following initiatives: observations from in situ sensors, networks and satellite sensors, and their transformation into bio and geophysical quantities such as EOVs for the ocean sector.

These represent the basis for environmental information services that are used for numerous applications and which benefit commerce and society as a whole. As already mentioned, metrology can help to assure that measurements and observation records are comparable across users, methods and time, and that they are robust and stable enough to support end-users when establishing the fit-for-purpose nature of such records.

Within the European funding programme HORIZON 2020, several opportunities for cooperative research were present. An example is the project MINKE—Metrology for Integrated Marine Management and Knowledge-Transfer Network [9], which started in 2021 and is ongoing. MINKE gathers several institutions and laboratories working in the oceanographic sector and NMIs to create a network for cooperation in the marine science. They also involve countries outside Europe, promoting transnational access to research infrastructures of consortium partners involved and the growing sector of citizen science.

2. The Role of Metrology for Ocean Studies

The oceanographic community is concerned by a wide variety of quantities and uses of very different techniques to measure EOVs. Oceanographic research institutions are well organised at the European and international levels, usually covering most EOVs, and requirements addressing quality assurance and quality control (QA/QC) are in place to improve data measurement. However, the fundamental metrological principles, e.g., metrological traceability and evaluation of measurement uncertainty, are in several cases missing, even though these steps are essential to obtain robust data to support reliable long-term observation, even multi-decadal, of trends [10]. Such principles play a fundamental role in covering GOOS/GCOS quality requirements for EOVs. In this framework, a close collaboration between oceanographic and metrological communities could be very useful for sharing respective efforts and competences in order to address the metrological requirements for EOVs.

NMIs and DIs are devoted to the establishment of metrological traceability of measurement results, by defining shared references agreed at the international level, realising proper measurement standards and developing fit-for-purpose calibration procedures.

National governments and organisations, non-governmental organisations and research institutions must cooperate to define strategies for monitoring and observation in a system that integrates the GOOS, the Marine Biodiversity Observation Network (MBON) and the Ocean Biogeographic Information System (OBIS). In Figure 1, a graphic representation of this cooperation at the international level is presented. The outer (blue) circle indicates the direct links between users and top-level organisations. In this complex observation system, NMIs and DIs are progressively becoming part of the marine observation network.

An additional point is represented by the need for agreed terminology and a set of common standards for metadata, a common data format to facilitate the international data exchange and ensure harmonisation of understanding.

The evaluation of measurement uncertainty is also a key point. In many cases, uncertainty calculation cannot simply be applied to in situ ocean measurements for several reasons: stable and repeatable laboratory conditions cannot be realised in natural environments, field sensors may drift and often they cannot be recovered for re-calibration. The role of metrology in this context is to develop easy-to-use methods for uncertainty evaluation in oceanography and establish quantified measurement uncertainty as a key quality indicator of EOVs, by considering oceanographic practice and issues.

The commitment of metrology to support oceanographic research, in the broadest framework of studies on climate change, is a central point both at the European and at international level, with several ongoing projects dealing with these open issues. In September 2022, an international workshop was organised by the World Metrological Organisation (WMO) in conjunction with the Bureau International des Poids et Mesures (BIPM) titled “Metrology for Climate Action” [11], which aimed at discussing the most recent open issues to support action for reduction of climate change operating in all environmental compartments. The objective of this workshop was to open a discussion on these themes and collect recommendations from those involved in the measurement field.

The workshop was organised along two major themes; the first one was entitled ‘Metrology in support of the physical science basis of climate change and climate observations’, and covered the role of metrology in supporting scientific understanding of the physical basis of Earth’s climate and its evolution with time. It included metrology for climate monitoring associated with in situ and remote measurements together with techniques for uncertainty propagation. The second theme of the workshop was titled ‘Metrology as an integral component of operational systems to estimate greenhouse gas emissions based on accurate measurements and analyses’. It highlighted the role of metrology in supporting the mitigation of the emission of greenhouse gases and the monitoring of natural sinks. Outcomes have been collected and published in a comprehensive report [11].



Figure 1. Scheme of the connections between the GOOS, the MBON and the OBIS proposed for biodiversity assessments [4]. (Reproduced from [4]. Copyright © 2018 Muller-Karger, Miloslavich, Bax, Simmons, Costello, Sousa Pinto, Canonico, Turner, Gill, Montes, Best, Pearlman, Halpin, Dunn, Benson, Martin, Weatherdon, Appeltans, Provoost, Klein, Kelble, Miller, Chavez, Iken, Chiba, Obura, Navarro, Pereira, Allain, Batten, Benedetti-Checchi, Duffy, Kudela, Rebelo, Shin and Geller. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY)).

3. Metrological Case Studies for Ocean Temperature (Subsurface and Surface Temperature)

The EMRP joint research project *MeteoMet* (2011–2014) [12] focused on the traceability of some ECVs to the SI and the evaluation of calibration uncertainties. Its follow-up *MeteoMet2* (2014–2017) [12] extended the investigation to additional variables and contributions to the measurement uncertainty [13,14]. The goal of these projects was to make improvements towards a comprehensive evaluation of uncertainty contributions and the metrological traceability of the measurement of the main ECVs defined by GCOS and involved in meteorological observations and climate change. The improvement of recorded ECV data should lead to active steps towards uncertainty reduction. This project was divided into three areas of observation: air, sea and land. For the sea section, the ECVs surface and subsurface (deep-sea) temperature were considered.

The activities carried out within these projects started from the needs indicated by GCOS “Long-term, high-quality and uninterrupted observations of the atmosphere, land and ocean [...] vital for all countries, as their economies and societies become increasingly affected by climate variability and change” [15]. Observations can be deemed of high quality only if they are based on a continuous and sustained traceability to the SI and have associated uncertainties with the measured ECVs.

In the *MeteoMet2* project, one of the key oceanic ECVs, i.e., temperature, was considered to monitor and understand decadal changes in heat content and flow. An extensive study of the effect of the main influence quantities on thermometers was carried out to reduce the measurement uncertainty and validate their characterisation. Some of the activities aimed to improve the accuracy and traceability of temperature measurements in oceans, in particular:

- the development of instruments and facilities to study the dependence on the pressure of deep-sea thermometers and to validate pressure-correction models [16,17];
- performing thermodynamic calibrations of deep-sea thermometers to evaluate the uncertainties of such models or to propose improved ones [18];
- the development of temperature sensors distributed along optical fibres for the improvement of the metrological traceability of sea-surface and sea-profile temperature measurement results [19].

The application of the concepts of calibration and evaluation of measurement uncertainty is not easy, especially in sectors involving measurements in the field and in adverse environmental conditions. The following examples show possible ways to bypass these issues and to use successfully metrology in the application of particular oceanographic instrumentation and methodologies.

3.1. Subsurface Temperature

Subsurface temperature is described by GCOS as:

“A fundamental variable that is required to monitor variability and change in the physical environment of the ocean, energy flows, climate patterns and sea level. Many other physical variables are derived from subsurface temperature along with subsurface salinity, including subsurface density, geostrophic circulation, heat transport and steric sea level. Heat uptake by the global ocean accounts for more than 90% of the excess heat trapped in the Earth system in the past few decades. This ocean heat uptake helps to mitigate surface warming but, in turn, increases the global ocean volume through thermal expansion, and thus results in global-mean sea-level rise, accounting for about one third of the increase observed over the past few decades”.

Deep-sea sensors, like the Sea-Bird Electronic (SBE) devices, are used around the world as the de facto standard for oceanographic measurements. For laboratory applications, SBE 35 thermistors are laboratory-standard thermometers, providing 1 mK uncertainty in temperature measurements according to the manufacturer’s specifications. Calibration is performed at water and gallium fixed points, and linearisation coefficients are determined from calibrations at eleven equally spaced temperatures from $-1.5\text{ }^{\circ}\text{C}$ and $32.5\text{ }^{\circ}\text{C}$, realised by means of a 50-L stirring bath. An independent characterisation, especially if made in thermodynamic temperature, is needed to assess the manufacturer’s linearisation model and to provide a way of further reducing calibration uncertainties.

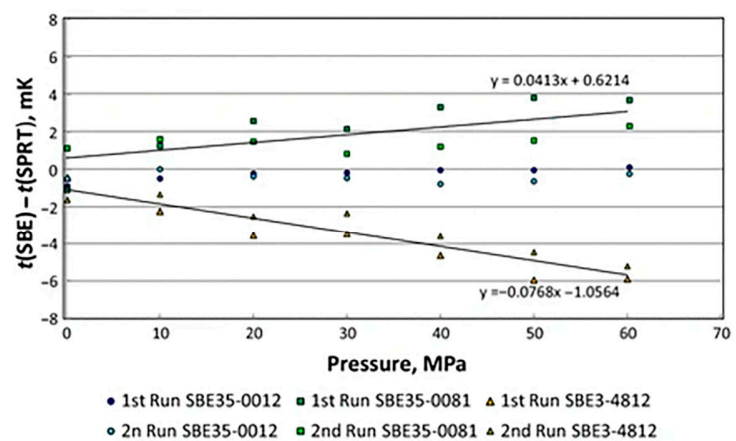
SBE CTD profiling systems are also used as standard units for the combined measurement of conductivity, temperature and depth, for in situ deep-sea measurements. With such systems, temperature is measured by using SBE 3 thermistors having moderate accuracy but showing faster response time than SBE 35, which is a necessary feature because immersion speeds can be as high as $1\text{ m}\cdot\text{s}^{-1}$. This is essential because, given the extremely high cost of ship time, the measurement is always a trade-off between the required accuracy and the available ship time. In this sense, the accuracy is limited by the dynamic effects related to the combination of immersion speed and sensor response time. The study of the behaviour of different oceanographic devices and probes in the field, for measuring temperature profiles, needs to be supported by accurate statistical analysis and uncertainty evaluation of the data obtained from these sensors. This approach could be used to compare their performances with other types of sensors and with data from reference climatology. This particular “delayed-mode” quality control is used in some cases for instruments that are not recollected after sampling campaigns, thus they are not recalibrated. This means that the collected data could suffer some measurement drift or offset. In [20], a comparison between Argo floats and shipboard CTDs was performed for temperature and salinity profiles in the Mediterranean Sea, under space-time conditions as close as possible. The authors collected and elaborated on a big set of data (acquired in a time span of 12 years) and highlighted the biases between different sensors (XBT, Argo floats and ship-based

CTDs) for temperature profiles, which should be taken into account to homogenise data processing and to support studies involving ocean modelling.

The determination of the effect of some quantities of influence on measurements carried out by deep-sea sensors is fundamental when defining the related corrections to be applied to measurements and the uncertainty contributions to be included in the overall calibration uncertainty budget. A comparison between SBE 35 and SBE 3 deep-sea thermometers was carried out to determine pressure effects on temperature measurements in a range from 0 °C to 10 °C and pressures in a range from 0.1 MPa to 60 MPa (corresponding to a depth of about 6000 m). In Figure 2, the facility used in [16] for this comparison is shown, together with a graphical summary of the temperature difference between three tested SBE devices. The aim was to consolidate the results for in situ measurements and to improve the uncertainty budgets by supplying direct traceability to the lowest-uncertainty temperature standards. The characterisation of deep-sea thermometers was carried out by several metrology institutes to provide a comprehensive analysis of the metrological characteristics of SBE 35 thermometers, based on results obtained from the study of influence quantities and a thermodynamic characterisation.



(a)



(b)

Figure 2. (a) Immersion of a comparator block in the pressure chamber; (b) Temperature difference between three SBE devices and the reference standard platinum resistance thermometers (SPRTs) at each investigated pressure [16]. (Reproduced from [16], with permission of Springer Nature, 2023).

Another aspect considered the thermodynamic characterisation of oceanographic reference thermometers between 5 °C and 35 °C, in order to address two needs related to temperature measurements in the oceanographic scientific community.

The first need was the assessment of uncertainty due to the linearisation of the measurement model (or the calibration function). The independent thermodynamic characterisation, performed at the highest level of accuracy, aimed to verify that linearisation uncertainty contributions were well below 0.5 mK. The reason for choosing thermodynamic measurements is to overcome the limits of the (non-thermodynamic) ITS-90: between −5 °C and 35 °C, ITS-90 uncertainties may quickly increase above 0.5 mK, making validation impossible. On the contrary, if reference temperatures are measured thermodynamically, global uncertainties may be kept below 0.5 mK and the SBE 35’s linearisation equation verification becomes possible.

The second need was implicitly expressed in Thermodynamic Equation Of Seawater-2010 (TEOS-10) [21]. Although seawater thermodynamic properties depend on salinity,

pressure and thermodynamic temperature, use of the ITS-90 temperature is recommended, which is not a thermodynamic quantity (even though it provides traceability to the kelvin). Conversions from ITS-90 to thermodynamic temperature are possible but with large additional uncertainties (up to 0.5 mK), making direct thermodynamic temperature calibrations preferable.

Another important pathway in the field of the monitoring of subsurface temperature profiles is linked to the use of modelling and computational techniques (e.g., machine learning tools, such as artificial neural networks), together with the use of remote sensing techniques [22,23]. Deeper ocean remote sensing is gaining significance because recent data indicate an influence of climate variability on the deeper ocean. Many subsurface phenomena also show surface manifestations that can be studied by using models to derive key parameters for the deeper ocean [24,25].

An example of investigations on the effects of ocean fronts on the reconstruction of vertical temperature profiles in the Northwest Pacific Ocean is presented in [26]. The authors show a metrological approach for the validation of their proposed method, based on four mapping models working on linear and second-order polynomial regressions. These models were trained with SST and sea level anomaly (SLA) input data, while the model validation was carried out by calculating the mean bias and standard deviation on an independent dataset, which was not included in the training process.

The possibility to combine in situ measurements with metrologically characterised and calibrated sensors, and prediction models based on remote sensing data, opens a wide range of possibilities in the study of subsurface ocean phenomena, in particular related to temperature variations.

3.2. Sea-Surface Temperature

GCOS describes Sea Surface Temperature (SST) as:

“A vital component of the climate system as it exerts a major influence on the exchanges of energy, momentum and gases between the ocean and atmosphere. SST largely controls the atmospheric response to the ocean at both weather and climate time scales. Daily variations in SST can exceed 3 °C and could alter the surface energy budget by more than 10 Wm⁻² over the tropics and subtropics. Therefore, the SST and horizontal gradients in SST are also important for coupling with the atmosphere for sub-seasonal to seasonal prediction timescales. The spatial patterns of SST reveal the structure of the underlying ocean dynamics, such as, ocean fronts, eddies, coastal upwelling and exchanges between the coastal shelf and open ocean”.

In Figure 3, the global ocean sea surface temperature trend map obtained from the observations reprocessing of Copernicus Marine Service [27] is shown. This map gives an immediate visual idea of the increase in SST worldwide, in the timeframe spanning from 1993 to 2021. It is clear that there is an urgent need for corrective actions to counteract the trend of global warming, which is also affecting the marine environment.

About 1600 buoys are currently installed around the world for monitoring EOVs. They are equipped with different devices according to the EOVs, but in some cases, they do not provide reliable values due to a lack of traceability of the measurement instruments and/or to wrong uncertainty evaluations, where some parameters of influence are missing. New sensors based on Bragg grating optical fibres were developed within MeteoMet2 project, to be independent of sea water pressure, in order to measure the drift of thermometers currently in use in underwater observatories and buoy-observatories on the near-surface, such as the OBSEA (Vilanova i la Geltrú, Barcelona, Spain). The developed techniques can be applied to the design of temperature sensors for measuring the sea-surface temperature and sea-temperature profile in situ and in continuous. Considering that the complexity of sensor extractions from underwater to surface induces laboratories to broaden recalibration periods, with consequent degradation of measurement accuracy, monitoring the thermometer drift by optical fibre sensors has the advantage of reducing the uncertainty of sea temperature measurements performed by underwater temperature sensors. In addition,

a distributed temperature sensor, based on optical fibre Bragg grating and mounted in a “model” buoy-observatory system, was intended to perform traceable measurements of the sea-temperature profile along 20 m of depth and to test the possibility of measuring the near-SST in situ.

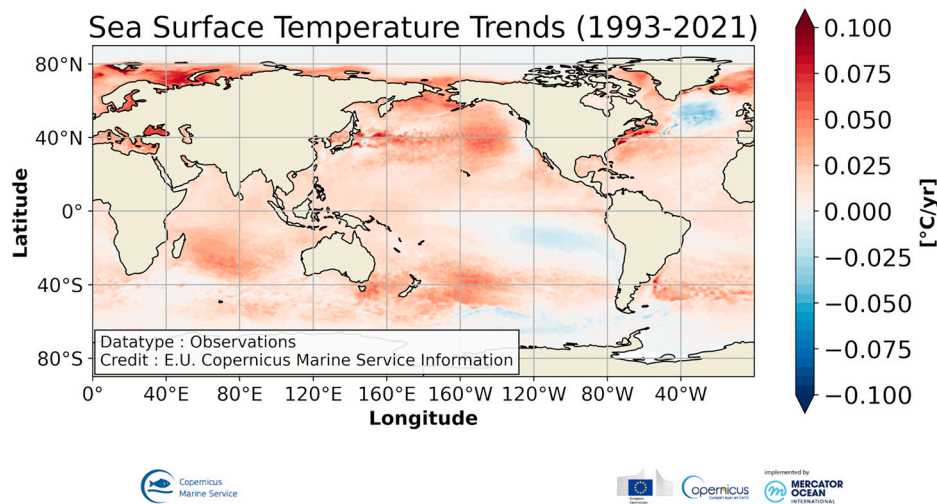


Figure 3. Global map of linear trends from monthly, filtered time series of SST between 1993 and 2021 [27]. (Ref. [27] to be updated as follows: Copernicus Marine Service in product SST-GLO-SST-L4-REP-OBSERVATIONS-010-024). E.U. Copernicus Marine Service Information (CMEMS). Marine Data Store (MDS). DOI: 10.48670/moi-00243 (Accessed on 5 August 2023)).

Two prototypes of distributed temperature sensors based on optical fibre Bragg grating were developed. The first one was used to obtain traceable measurements of the seawater profile and near-sea surface temperature (profile fibre). The second one was used to control the drift of the fibre described before and to measure the drift of the thermometers sited in the underwater observatory-buoy system (control fibre).

For this activity, the underwater observatory OBSEA and the buoy attached to the observatory (provided by the Spanish National Metrology Institute, CEM), were used. In addition, INRiM climatic chamber *Earth Dynamics Direct Investigation Experiment* (EDDIE), developed during the MeteoMet project, was exploited. This promising technique is subject to further study, to improve the set-up and the assigned measurement uncertainties. The experimental in situ set-up is shown for clarity in Figure 4. Figure 4 demonstrates that the optical fibres, after their optical and thermal characterisation, were deployed and connected to the buoy and the OBSEA underwater observatory, which was deployed on the seabed at a depth of 20 m. The optical fibres were used to carry out traceable measurements of the sea temperature profile and the sea surface temperature.

SST has traditionally been measured in situ, and since the 1970s its monitoring has been recorded by satellite-borne radiometers. Satellites radiometers measure the radiance emitted by the sea surface; the radiance measurements are sensitive to ocean skin temperature, to the atmospheric physical state and constituents and to the sea state [28]. Several methods were developed to determine these sources of inaccuracy to evaluate radiance measurement uncertainties [29,30]. To ensure the validity of retrieved SST from satellite monitoring, it is necessary to carry out comparisons with independent in situ measurements. The resulting SST retrievals from satellite observations can be used to generate global datasets with spatial-temporal consistency only after validation. Several examples of methodologies for the validation of satellite SST measurements can be found in the literature. The recent application of machine learning techniques in this field supports the retrieval of the satellite SST measurements and is particularly helpful in cases where there is an insufficient number of in situ skin temperature measurements for deriving the algorithm coefficients [31–35].

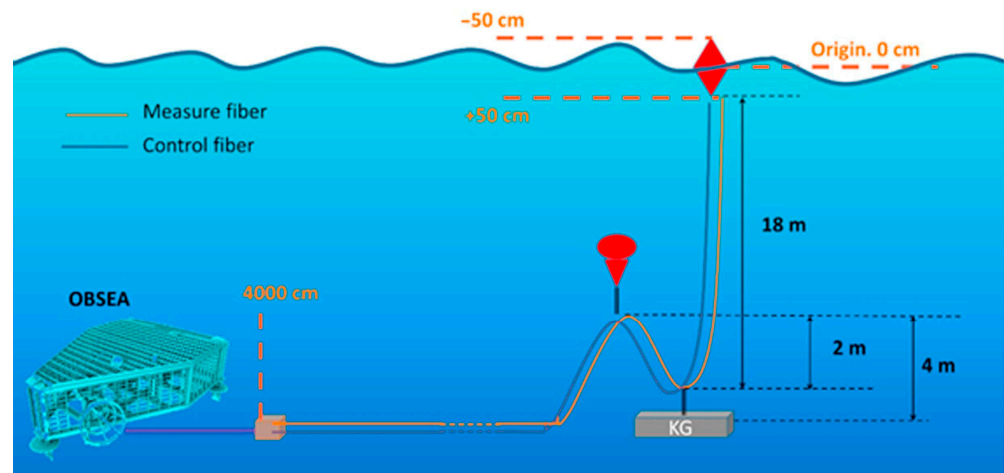


Figure 4. Schematic representation of the experimental set-up [19]. (Reproduced from [19], with permission from Elsevier, 2023).

4. Metrological Case Studies for Ocean Carbon Cycle

4.1. Partial Pressure of CO₂ ($p\text{CO}_2$) in Seawater

The observed rising levels of CO₂ in the atmosphere, caused largely by anthropogenic emissions, are responsible for fundamental changes in marine carbonate chemistry as the oceans act as a sink for atmospheric CO₂. The importance of measuring the partial pressure of CO₂ in water ($p\text{CO}_2$) lies in its usefulness in the determination of the fugacity of CO₂, $f(\text{CO}_2)$, which involves the non-ideal nature of the gas phase of CO₂. The fugacity coefficient is defined as the ratio between fugacity and partial pressure, and its magnitude is a function of temperature and gas phase composition. In addition to its role in the air-sea gas exchange context and Earth's CO₂ system, $p\text{CO}_2$ is also a helpful indicator of the course and potential ecological impacts of biological processes like photosynthesis and respiration.

This EOv is linked to the inorganic carbon EOv, together with total alkalinity (TA) and the dissolved inorganic carbon (DIC). This connection is introduced well by GCOS:

“The ocean is a major component of the global carbon cycle, absorbing enormous quantities of carbon in natural cycles driven by ocean circulation, biogeochemistry and biology. Since seawater has a very high capacity for absorbing carbon, the ocean has an inhibitory effect on the atmospheric accumulation of carbon dioxide and related greenhouse effect. [...] The chemical pathways of the inorganic carbon in the ocean mean that this uptake causes a decline in ocean pH, also known as ocean acidification”.

At present, $p\text{CO}_2$ is one of the few variables of the water carbon cycle that can be directly measured in situ. There is a wide availability of in situ sensors and analytical methodologies used to monitor $p\text{CO}_2$ in marine environments, but there are still many open issues, such as the differences in adopted calibration methodologies, the application of non-validated procedures and the lack of suitable metrological traceability paths and of operational harmonisation for field measurements. Another problem is related to the scarcity and expensiveness of proper reference materials to calibrate the instruments used for $p\text{CO}_2$ monitoring.

Compact measurement systems for $p\text{CO}_2$ in seawater with membrane tubes and non-dispersive infrared gas analyser (NDIR) have been developed in the recent past [36]. Typically, the measurement principle is based on the diffusion of gaseous CO₂ (dissolved in seawater) through the membrane into flowing air inside a tube. The CO₂ amount fraction determination in the air is carried out by NDIR. When the equilibrium between the water and the air is achieved, the $p\text{CO}_2$ levels in seawater are monitored automatically and continuously. According to the requirements of the Integrated Carbon Observation System (ICOS), such measurements have a target uncertainty of $\pm 2 \mu\text{atm}$. This system has reduced size and it requires only a small power supply in order to deploy the membrane equilibrator

directly in seawater, and it has wide application. Considering that the measuring principle is the same used to monitor CO₂ levels in the atmosphere, and that the atmospheric CO₂ amount fraction is closely linked to *p*CO₂ in water, a strong connection between the measurement standards used in the two different environmental compartments is highly desirable [37].

The primary reference for Earth system's research-related CO₂ measurements is the World Meteorological Organisation Global Atmosphere Watch (WMO/GAW) CO₂ mole fraction scale (identified as WMO-CO₂-X2019) [38]. It is based on 19 primary standards which cover a nominal CO₂ amount fraction ranging from 250 μmol·mol⁻¹ to 800 μmol·mol⁻¹. The standards are made by natural air contained in high-pressure aluminium cylinders, where CO₂ levels are modified with a spike of a 10% CO₂ parent mixture in natural air. A promising approach could be the provision, on a larger scale, of appropriate reference gas mixtures to be used as measurement standards in the calibration of *p*CO₂ sensors, due to the stability of the CO₂ in the gas mixtures. Intermediate-level standards and working standards could represent a more affordable and widespread traceability source, while NDIR photometry application could be potentiated.

In recent years, the Global Ocean Acidification Observing Network (GOA-ON) has addressed the issue of the uncertainties of carbonate system variables. GOA-ON was established as a collaborative international network to address three main goals: improving understanding of the conditions of global ocean acidification (OA); improving the understanding of ecosystem response to OA; acquiring and exchanging data and knowledge needed to optimise the OA modelling and its impacts. To ensure that the quality of the measurements is appropriate and fit-for-purpose to address the relevant problems, GOA-ON proposed two levels of uncertainty: the "weather goal" and the "climate goal". The GOA-ON weather goal focuses on individual measurements and is aimed to assess spatial and short-term variations (e.g., diurnal variability). The climate goal is stricter and emphasises the need to identify and deciphering decadal trends. To frame its goals, GOA-ON proposed different target uncertainties. The relative uncertainty in calculated carbonate ion concentration must be less than 10% for the weather goal. For the climate goal, the uncertainty of a difference in carbonate ion concentration over time must be less than 1%. Starting from these thresholds, back calculations were made to define the corresponding maximum permissible uncertainties in measured input variables. For the weather goal, measurement uncertainties should be no larger than 0.02 for pH and 10 μmol·kg⁻¹ for TA and DIC, while the relative uncertainty for *p*CO₂ must be lower than 2.5%. For the climate goal, the corresponding estimates of uncertainties are 0.003 for pH, 2 μmol·kg⁻¹ for TA and DIC and 0.5% for *p*CO₂. An interlaboratory comparison suggested that most research groups currently measuring ocean pH, TA and DIC were able to achieve the weather goal, whereas rather few were able to meet the criteria of the climate goal [39]. The same study highlighted that in some cases the measurement uncertainty could be underestimated, particularly when uncertainty values are based only on repeatability (short-term precision) and thus neglecting other possible uncertainty sources [40]. Another measurement inter-comparison was carried out to compare multiple groups of sensors in a well-controlled environment. A 5000 L tank was modified to vary several parameters i.e., TA, pH, *p*CO₂, temperature and salinity, while keeping constant various properties for each individual test. This set-up was used to test the response of every instrument with the capability of calculating CO₂ parameters together over a wide range of values. In this intercomparison, the tested instruments showed adequate precision and accuracy in the detection of the modified conditions in the test facility, which represented the natural variability in coastal, open ocean and deep ocean environments. It was also highlighted that pH or *p*CO₂ can be combined with TA to completely characterise the CO₂ system [41].

Examples of this are represented by measurements carried out in regions such as the coastal areas, where *p*CO₂ variability is highly uncertain because of the complexity of physical and biogeochemical processes (e.g., tidal mixing or riverine inputs) [42]. Measurement of *p*CO₂ carried out in regions such as the coastal areas can present additional

challenges, given that these areas highly dynamic. Ad hoc systems to measure $p\text{CO}_2$ in these environments can be found in the literature, which were validated in laboratory and with sea tests. As an example, the system in [43] showed a fast response time and provided a better resolution for CO_2 system gradients. In the open waters of the Baltic Sea, $p\text{CO}_2$ measurements achieved an accuracy of $\pm 1.3 \mu\text{atm}$, thus meeting the ICOS requirements of $\pm 2.0 \mu\text{atm}$. In the coastal zone, less consistency between $p\text{CO}_2$, DIC and pH measurements was shown, suggesting the need to redefine the QA/QC requirements for $p\text{CO}_2$ measurement in dynamic regions.

Another key issue in the determination of $f(\text{CO}_2)$ in surface water is that some key physio-chemical characteristics related to this EOv are not fully solved, like its dependence on temperature. The $f(\text{CO}_2)$ is usually measured in situ by means of autonomous underway systems near SST. On the other hand, subsurface measurements are typically carried out on individual discrete samples at a fixed temperature (20°C). The data acquired in [44] refer to cruises spanning the major ocean basins from 1992 to 2020 and showed a temperature dependence of $4.13 \pm 0.01\% \text{ }^\circ\text{C}^{-1}$, which is in close agreement with a widely used previous empirical estimate of $4.23 \pm 0.02\% \text{ }^\circ\text{C}^{-1}$ (for the North Atlantic Ocean). The authors in [44] addressed several aspects of this metrological issue:

- Determination of temperature dependence by comparing underway measurements at SST and discrete measurements at 20°C ;
- Factors that influence temperature dependence;
- Comparison of $f(\text{CO}_2)$ calculated from DIC and TA, based on discrete and underway $f(\text{CO}_2)$ data;
- Possible sources of analytical bias for underway CO_2 systems and discrete CO_2 systems used.

One limitation encountered in this research activity was represented by the non-exact co-location of the samples; this means that the same water was not sampled for the discrete measurements and the underway measurements, thus leading to some error in the data collected. However, the difference in time and location between underway and discrete samples depended on cruise and dataset (with maximum differences of 1 h and 50 km, respectively). The average and standard deviation of the co-location were 1.6 min and 8 min for time and 1.4 km and 7 km for distance, respectively.

Another issue could be represented by the fact that the underway $f\text{CO}_{2w}$ measurements were made with an air-water equilibrator located in the research laboratory on-board at a temperature generally slightly above SST due to warming of water inside the ship. The underway $f\text{CO}_2$ data were adjusted for the temperature difference of ($\approx 0.1\text{--}0.2^\circ\text{C}$) between equilibrator and SST using a $4.23\% \text{ }^\circ\text{C}^{-1}$ temperature adjustment.

Finally, the empirical relationships described in this paper were based on 30 years of data and covered a range of temperatures and different seawater chemistry, with TA/DIC in the range 1.06–1.24 and with a mean of 1.15 ± 0.03 (for $n = 1798$). Over this timeframe, DIC levels grew for the increase in anthropic CO_2 emissions, causing the TA/DIC to decrease by $\approx 1\%$. This analysis highlighted that increases in the DIC of seawater lead to a slightly weaker temperature dependence.

The temperature dependence for each cruise was determined by assuming either a constant dependency of the natural logarithm of $f\text{CO}_{2w}$, $\ln(f\text{CO}_{2w})$ with temperature (T), or a linear dependence of $\ln(f\text{CO}_{2w})$ with temperature.

This work represents a valuable example of the systematic approach for monitoring and data collection in the various ocean basins, in order to constitute a large and comprehensive dataset of underway and discrete $f(\text{CO}_2)$ samples that supports studies on this EOv, its temperature dependence and its relation with other variables such as TA and DIC. The large dataset of co-located underway and discrete $f\text{CO}_{2w}$ samples covered all ocean basins but with most data on the Atlantic Ocean. The temperature dependencies have uncertainties and differences that cannot be attributed to the time of measurement, temperature or chemical composition but are assumed to be primarily caused by small analytical biases. For accurate temperature corrections, knowledge of the TA/DIC is neces-

sary and the authors suggested the determination of the dependency using the carbonate dissociation constants.

Another example of study on the seasonal and spatial variability of the CO₂ system parameters in the Northeast Atlantic Ocean, close to the Canary basin, is reported in [45]. Data collected during a one-year sampling campaign (February 2019–February 2020), showed a seasonal and spatial variability of $f\text{CO}_{2w}$ strongly driven by the seasonal temperature variation. The surface waters of the studied region acted as a CO₂ sink during the autumn–winter period and as a CO₂ source during the spring–summer season.

Historically, the South Atlantic Ocean was less sampled than the North Atlantic Ocean, but some examples can be found in the literature [46]. The use of satellite monitoring is now helping the study of this extended ocean area, improving the understanding of the carbonate system variable distribution, mainly $f\text{CO}_{2w}$ and also extending study in the Southern hemisphere. In [46], the authors developed seasonal algorithms to study $f\text{CO}_{2w}$ trends and its dynamics along the Southwestern Atlantic Ocean. Monthly satellite images, acquired in the period August 2011–June 2015, were considered for several parameters (SST, salinity and chlorophyll-a) and used to evaluate the seasonal fields of $f\text{CO}_{2w}$. The SST was found to be mainly responsible for seasonal variations in the values of $f\text{CO}_{2w}$, but the changes of DIC and TA were also important drivers.

4.2. Stable Carbon Isotopes

As previously stated, the DIC in seawater has a fundamental role in understanding the properties of the oceanic carbon reservoir within the global carbon cycle. The stable carbon isotopes ¹²C and ¹³C of atmospheric CO₂ and its dissolved forms within the ocean can also be used to estimate the fluxes between the atmospheric and marine compartments. However, the use of stable isotope analysis to investigate the carbon uptake by marine phytoplankton or the reconstruction of past oceans requires a sound understanding of seawater chemistry and associated carbon isotope fractionation [47].

The global distribution of $\delta^{13}\text{C}$ values for CO₂ and methane (CH₄) dissolved in inorganic and organic carbon (DIC, DOC), particulate organic matter (POM) and carbonates, is summarised schematically in Figure 5 [48]. The different arrows in Figure 5 represent the exchanges within and between environmental compartments of the different carbon forms. The values of $\delta^{13}\text{C}$ -CO₂ of atmospheric CO₂ are closely linked to global climate evolution and change. On the other hand, the marine $\delta^{13}\text{C}$ in DIC can be used as a water-mass tracer to support the quantification of the anthropogenic CO₂ uptake of the oceans.

The use and monitoring of the ratio ¹³C/¹²C (generally expressed in the delta notation, $\delta^{13}\text{C}$) as a marker to discriminate between CO₂ of anthropogenic origin and derived from natural sources, is well known in the atmospheric measurement community. Within the EURAMET framework, the EMPIR joint research projects SIRS [49] and STELLAR [50] were carried out in order to develop a new infrastructure including measurement standards, methods and instrumentation to underpin measurements of stable isotopes of CO₂, which enable CO₂ origin to be identified.

The usefulness of ¹³C isotope as a tracer of the ocean's carbon cycle is, however, "observation limited" [51]. The ocean uptake of CO₂ produced by burning ¹³C-depleted fossil fuels causes a progressive lightening of the oceanic inorganic carbon pool, a phenomenon also known as "oceanic ¹³C Suess effect". The observation of this phenomenon can be also used to estimate the anthropogenic carbon fraction of the DIC. The improvements in $p\text{CO}_2$ measurements with field portable spectrometers open the possibility of underway $\delta^{13}\text{C}$ observations across large portions of the surface ocean. The information provided by such datasets would lead to a substantial improvement in $\delta^{13}\text{C}$ -based estimates of organic matter export rate and of the air-sea ¹³CO₂ flux. Comparing this latter term to depth-integrated ¹³CO₂ inventory changes in the water column will allow a discrimination between anthropogenic CO₂ change due to air-sea CO₂ flux from changes occurring by physical transport through ocean circulation.

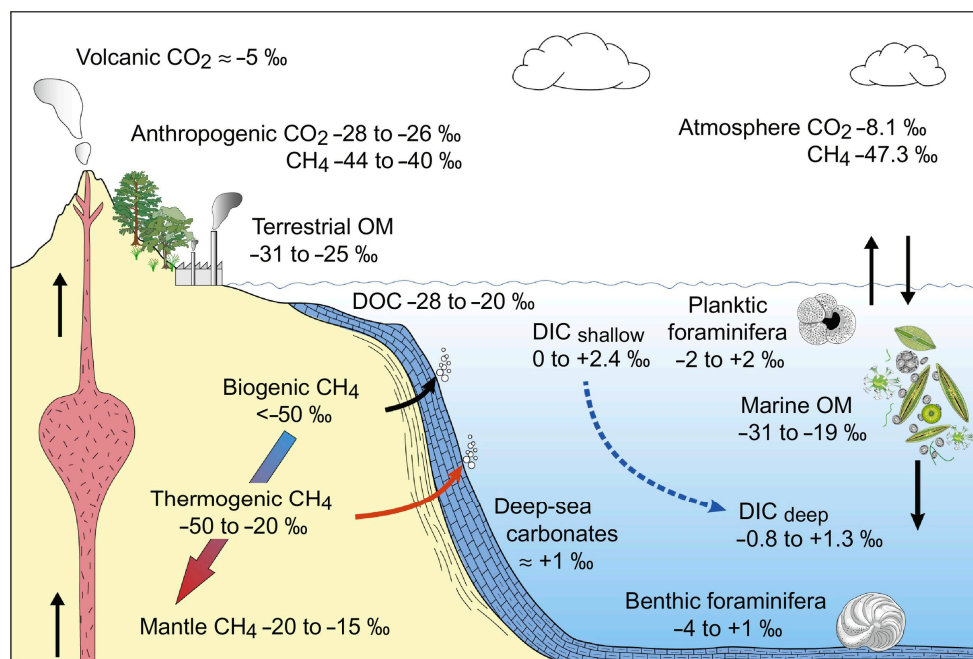


Figure 5. Global distribution of $\delta^{13}\text{C}$ value ranges in CO_2 , CH_4 , DIC, DOC, POM and carbonates [48]. (Reproduced from [48], with permission from Elsevier, 2023).

The role of the global surface ocean as a source and sink for atmospheric CO_2 and the air-sea CO_2 flux strengths can be also quantified by measuring $f(\text{CO}_2)$ as well as DIC concentration and its isotopic composition in surface seawater. Research is ongoing in this field; as an example, the technique called “continuous wave” cavity ring-down spectroscopy (cw-CRDS) was applied to autonomous underway measurements of $f(\text{CO}_2)$ and of $\delta^{13}\text{C}$ in DIC ($\delta^{13}\text{C}(\text{DIC})$) [52]. In this work, both quantities were continuously and simultaneously measured during a field deployment on two research cruises in the Atlantic Ocean by using a conventional air-sea equilibrator set-up. The obtained data were then compared against reference measurements by an established underway CO_2 monitoring system and isotope ratio mass spectrometry (IRMS) of individual water samples. The authors reported an agreement within $\Delta f(\text{CO}_2) = 0.35 \mu\text{atm}$ for atmospheric values and $\Delta f(\text{CO}_2) = 2.5 \mu\text{atm}$ and $\Delta \delta^{13}\text{C}(\text{DIC}) = 0.33\text{‰}$ for seawater measurements. As for $f\text{CO}_2$, “calibration-free” monitoring is feasible, while the measurement of accurate $\delta^{13}\text{C}$ requires the use of reference standards on a daily basis. With the measurement system presented in [52], the online monitoring of $f(\text{CO}_2)$, $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{13}\text{C}(\text{DIC})$ aboard moving research vessels was demonstrated, opening the possibility of measurement campaigns with high spatial and temporal resolution.

5. Conclusions

In the present paper, the importance of monitoring the state of the oceans and its evolution in space and time is highlighted, in particular for the relevance and impact on Earth’s global cycle of those key points. The changes occurring in the oceans are responsible for the alteration of marine ecosystems and for an increased vulnerability of many marine species. The application of metrology in the marine sector is therefore needed, in particular for the usefulness of metrological concepts such as metrological traceability and measurement uncertainty, to consolidate the measurements in this framework and to assure the comparability of the acquired data in different experimental conditions, places and time. Some examples of successful and potential applications of metrology in oceanographic research at the European and international level were presented, with a focus on past and ongoing activities in the framework of research cooperation. The presented results, especially those obtained in the framework of joint research projects, are

available to the oceanographic community. Their follow-up could foster the cooperation between the metrological and the marine research communities.

In particular, examples of cooperation such as the ones ongoing within the project MINKE [9] represent a promising direction for oceanographic research. Potentiating transnational access to research infrastructures around the globe, the commitment of people through citizen science and communication to the public on scientific issues and outcomes are also key pillars to these initiatives.

Many areas for improvement are still open, in particular the agreement on a common terminology for the two communities, the assurance of metrological traceability to the International System of Units, as well as the definition of common best practices in the monitoring of different EOVs. An important point is represented by training on specific metrological issues for those operating in the oceanographic sector like the evaluation of measurement uncertainty, for example.

In this sense, INRiM is continuously working to assure metrological traceability for temperature measurements in situ in the various environmental compartments, by maintaining temperature standards, developing appropriate calibration procedures and improving measurement uncertainties. INRiM is also carrying out activities to produce appropriate primary reference standards of CO₂ in gas phase at known amount fraction by gravimetry to calibrate *p*CO₂ sensors. In addition, intermediate-level standards and working standards, which could represent a more economic and widespread traceability source, are under development within the H2020 MINKE project, in cooperation with the National Institute of Oceanography and Applied Geophysics (OGS, Italy).

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