Metrological traceability path for marine pCO2 measurement results

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ABSTRACT

Despite the increasing availability of sensors for gathering data on the partial pressure of CO_2 (pCO_2) in the waters of the world's seas and oceans, there is a growing awareness within the scientific community of the pressing need for very high quality measurements of the variable to help monitor the Ocean Acidification threat and, more generally, the effectiveness of overall global CO_2 emission mitigation strategies. This is because discriminating observed variations ascribable to long-term trends from the ones due to natural fluctuations and meeting established criteria to reach the "Climate goal" for marine carbonate system research and monitoring require extremely accurate and traceable pCO_2 measurements to be useable. Here, we present some details on work being done to expand the use of reference-grade CO_2 gas mixtures to help calibrate and/or assess the performances of marine sensors employed for measuring seawater pCO_2.

1. Introduction

The oceans are one of the major components of the global carbon cycle. Seawater has the ability to absorb carbon dioxide (CO_2) from the atmosphere, thus exerting an inhibitory effect on the atmospheric accumulation of CO_2 and partially mitigating the related greenhouse effect [1]. However, when CO_2 dissolves in seawater, the latter becomes more acidic and its pH decreases. Due to the continuous rise of its anthropogenic emissions in the atmosphere, CO_2 is dissolving into the oceans so quickly that natural stabilising buffering mechanisms are not so effective anymore. This results in a rapid and continuous decrease of pH in surface waters which gradually mix into deep layers, and the entire ocean system is affected leading to the phenomenon called "ocean acidification" [2].

While the chemistry of ocean acidification is reasonably predictable, the effects of its biological impacts are not. The phenomenon has already started to show its dramatically negative impacts on ocean ecosystems. Beyond worsening ocean health and lost biodiversity, it will also affect fisheries and aquaculture, threatening food security for millions of people, as well as tourism and other sea-related economies. For these reasons, ocean acidification is often viewed as climate change's "evil twin" [3,4].

Typically, the seawater carbonate system is characterised by directly measuring at least two of four variables: total dissolved inorganic carbon, total alkalinity, the partial pressure of CO_2 (pCO_2) and seawater pH (on the total hydrogen ion scale). In fact, these variables are explicitly mentioned as indicators of ocean acidification in the United Nations (UN) Sustainable Development Goals (SDG), in particular under the SDG 14, target 14.3., description 14.3.1 of the UN 2030 agenda [5].

The importance of measuring pCO_2 lies in its usefulness in the determination of the CO_2 fugacity, $f(CO_2)$, which involves the non-ideal nature of the gas phase of CO_2. In addition to its role in the air-sea gas exchange and the dynamics of the marine carbonate system, pCO_2 is also a helpful indicator of the course and potential ecological impacts of biological processes like photosynthesis and respiration [6].

At present, pCO_2 is one of the few variables of the marine carbonate system that can be measured *in-situ*. Sustained autonomous *in-situ* observations with deployable sensors are allowing measurements of pCO_2 on a wide range of oceanic platforms, improving both the amount of and the accessibility to data on the parameter [7]. However, to monitor ocean acidification as well as the effectiveness of overall global CO_2 emission mitigation strategies, high quality measurements of seawater pCO_2 are required, with sufficient coverage both in time and space to be able to follow the patterns of the marine uptake of CO_2 and help identify regions of the seas and oceans being affected by pronounced changes in the carbonate system. This is particularly true when the goal is to discriminate observed variations ascribable to long-term trends from the ones due to natural fluctuations.

Gaseous standards are attractive choices for making reference measurements due to their stability and direct metrological traceability to the International System of Units (SI). In Italy, gaseous reference standards of CO_2 in air or nitrogen are being produced by the National Institute of Metrological Research - INRiM, the Italian National Metrology Institute (NMI) [8]. Based on the availability of this service, a study was planned in the framework of the ongoing EU-H2020 project MINKE ("Metrology for Integrated marine management and Knowledge-transfer nEtwork") [9] to explore the possibility of extending their use in the control and calibration of sensors for pCO_2 in seawater. The present paper describes the work being performed at INRiM and at the National Institute of Oceanography and Applied Geophysics – OGS, relating to this activity, providing the main details of the approach adopted and some indications as to expected outcomes.

2. Methods and procedures

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Atmospheric Administration (NOAA) realises CO_2-in-air standards and contributes to maintain the World Metrological Organisation Global Atmosphere Watch (WMO-GAW) mole fraction scale for CO_2 in air [10].

Gravimetry is a primary method for preparing static mixtures of stable gaseous analytes in high-pressure cylinders. With this method, CO_2 in air mixtures can be prepared with a relatively low uncertainty (~0.04 %, $k = 2$) by measuring the gas masses with high precision and by using suitable cylinders. As the Italian NMI, INRiM is making the most of its long experience in the preparation of gas standards by the gravimetric method in accordance with the International Standard ISO 6142-1 [11] to produce CRMs of CO_2 in nitrogen (N_2) or in synthetic air, particularly for use at the ambient level measuring range for atmospheric CO_2 [50–1000] μmol·mol^{-1} following the requirements of the International Standards ISO 17034 [12] and ISO 17025 [13]. Furthermore, INRiM has been carrying out extensive work on NDIR photometry applied to the monitoring of CO_2 in air at the ambient levels [14]. The use of common standards and measurement techniques is the only way to ensure better traceability and establish greater comparability between the results of measurements of CO_2 in the marine environment to similar measurements relating to the atmosphere, which are unavoidably strongly associated.

2.1. *Primary reference gas mixtures as pCO_2 reference standards*

At INRiM, two gas mixtures of CO_2 in N_2 were prepared with the gravimetric method, following a consolidated procedure involving its gravimetric facility. This facility is equipped with a mass comparator (PR 10003, Mettler Toledo, Switzerland), having a measurement range of [0.001–10010] g, for the high precision weighing required. The mixtures were prepared in cylinders of aluminum alloy (Luxfer, USA) having an internal volume of 5 L that were filled to a pressure of 100 bar. After the preparation, the CO_2 amount fraction of each mixture was verified by means of a NDIR photometer (URAS 14, ABB, Switzerland), having a measurement range of [0–1000] μmol·mol^{-1} of CO_2. The mixture characteristics are reported in Table 1.

These mixtures were shipped to the OGS, where they are being used to explore the possibility of developing intermediate-level “working” standards for the routine quality control and assessment, and possibly calibration also, of marine sensors employed for measuring pCO_2 in seawater.

2.2. *Linking NMI traceability to field measurements of pCO_2 in seawater*

The main goal of the work being carried out presently at the OGS is the development of a viable experimental framework for exporting the NMI traceability afforded by the INRiM gas standards to measurements of pCO_2 in seawater made with sensors commonly utilized for the routine monitoring of the parameter. The idea is to try and establish an instrumental set-up and methodology to create working standards that can serve as intermediate-level reference material at laboratories or facilities supporting marine monitoring activities or programmes where such sensors are being used, starting from reference-grade gas mixtures like the INRiM ones.

Technically, the scheme envisioned is a modification of a two-stage equilibrator, here in the form of an enclosed temperature calibration bath containing a known volume of stirred clean (filtered) natural seawater and a headspace filled with ambient air. The air in the headspace will be kept recirculating by means of an air pump that draws and returns it to the headspace via connecting tubes. The system shall be maintained at a controlled constant temperature, and pCO_2 concentrations will be constantly monitored independently in both the seawater and air using suitable instrumentation. Subsequently, a CO_2 absorbent column will be inserted in the air circuit to strip away the CO_2 in the airflow continuously. The effect this will have on the pCO_2 concentrations in the air and the seawater will be tracked until the monitoring instruments show stable minimum readings for both. Thereupon, the system will be allowed to settle so that the gas contents of the water and the air are in equilibrium. Once this is assured, the absorbent column in the air circuit will be removed and the airflow restored as before. Then a second simple gas circuit driven by one of the INRiM gas mixtures will be used to produce a series of appropriate step changes in the pCO_2 concentrations of the air and seawater in the bath. At each step change, this latter gas circuit will be disengaged, and the system allowed to settle to a useable (i.e., stable) set-point for the pCO_2 concentration in the seawater.

Table 1
Characteristics of the gravimetric gas mixtures prepared at INRiM.

Mixture identifier	CO_2 amount fraction (gravimetry), X_{CO2} μmol·mol^{-1}	$U(X_{CO2})$ ($k = 2$) μmol·mol^{-1}	Cylinder code
INRiM MINKE 05	393.52	0.40	D247443
INRiM MINKE 06	596.89	0.40	D247446

In a first step, the set-up and the data obtained for the generated set points will be evaluated from the perspectives of the repeatability and reproducibility of the methodology by replicating the experiment a number of times in a planned way over a sufficiently protracted timeframe. Successively, if the results are promising, the capability of the system to work with field sensors of pCO_2 in seawater will be tested.

3. Discussion

The reigning paradigm governing the observing strategy for pCO_2 in seawater in relation to Climate Change distinguishes between two finalities [15]:

- “Weather”, defined as measuring to identify relative spatial patterns and short-term variation;
- “Climate”, defined as measuring to assess long-term trends with a defined level of confidence.

The “Weather” objective requires pCO_2 to be measured with a relative uncertainty of about 2.5 % (10 μatm) whereas, to meet the “Climate” objective, the relative uncertainty of the measurement should be about 0.5 % (2 μatm).

In practice, however, the accuracy requirements for seawater pCO_2 measurements can vary depending on the operational setting (e.g., the coast, the open ocean, etc …), the objectives of the observing activity, and the inherent limitations of the employed measuring technologies. Table 2 reports the recommended accuracy specifications for marine pCO_2 measurement in Europe’s Integrated Carbon Observation System

Table 2
Recommended accuracy specifications for marine pCO_2 measurement in Europe’s Integrated Carbon Observation System (ICOS).

Variable	Frequency of measurement	Desired accuracy
Sea-surface fCO_2 (underway)	Quasi-continuous (at least 1 h^{-1})	±2 μatm
Sea-surface pCO_2 (fixed ocean stations)	At least 3 day^{-1} (coastal) At least 1 day^{-1} (open ocean)	±10 μatm
Atmospheric CO_2 (marine flux towers)	1 h	±1.5 %
CO_2 flux (marine flux towers)	1 h	±5 %
pCO_2 (repeat ocean sections)[a]	At least 1 decade^{-1}	±1 μatm (<±3 μatm, between-cruise)

[a] *Under consideration for adoption.*

(ICOS) [16]. ICOS is a distributed pan-European research infrastructure producing high-quality data on greenhouse gas concentrations in the atmosphere and carbon fluxes between the atmosphere, the land surface and the oceans.

At present, pCO_2 continues to be measured mainly underway employing appropriate instrument setups aboard research vessels and voluntary observing ships. However, nowadays, commercially available sensors for the variable are being deployed more and more on fixed installations like anchored moorings and buoys and have also been tested in a limited way with mobile platforms like floats and gliders.

Currently, the main techniques employed by commercially available sensors used for measuring pCO_2 in seawater are based either on the equilibration of a carrier gas phase with a seawater sample and the subsequent determination of the CO_2 that diffuses through by means of NDIR spectrometry (e.g., the Pro-Oceanus CO_2-Pro and the Contros Hydro-C systems), on reagent-based colorimetry (e.g., the Sunburst SAMI-CO2 sensor) or on species-specific solid-state detectors (principally, optodes), though this last technology is still in a very early stage of development compared with the other two.

Whatever the sensor used, verifying that specifications are being met when it is operating in the field remains a huge challenge. While gas reference standards present undoubtedly superior metrological characterisation and traceability, prudence is required in using them directly for assessments of marine pCO_2 sensor performances where the measurand is really the amount of CO_2 gas dissolved in seawater (i.e., in solution). There are two main reasons why this is so. First, because CO_2 solubility in seawater is a phenomenon governed by complex composition-dependent chemical interactions and equilibria that can condition the pCO_2 measurement. Second, because of the ways that a sensor's specific design and engineering can affect the results. From a purely operational perspective, a further significant factor to consider is the emerging emphasis in marine monitoring programmes on continuous stand-alone or networked real time or near-real time monitoring of the pCO_2 parameter, which means keeping periods of interrupted service of measuring instruments to the absolute minimum necessary. Thus, establishing a relatively easy and cost-efficient way to create reliable NMI-traceable working standards at short notice and use them for regularly checking sensor performances and functionality will represent a significant step forward in the path towards obtaining seawater pCO_2 measurements of the stringent quality required for studying and monitoring climate change, including the worrying ocean acidification phenomenon.

4. Conclusions

Many of the currently available sensors for in-situ measurements of pCO_2 in seawater are gas-based and operate by transferring seawater CO_2 into the gas phase prior to analysis. Gaseous standards are also attractive choices for making reference measurements due to their stability and direct metrological traceability to SI. Thus, developing appropriate pCO_2 working or intermediate-level reference materials based on reference-grade CO_2 gas mixtures for use with seawater pCO_2 sensors may help to progress towards the achievement of the kind of accuracy and metrological traceability required for measurements of the parameter in the critical areas of Climate Change and Ocean Acidification research and monitoring, particularly in the case of autonomous untended deployments.

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