

SHORT COMMUNICATION

A system for the determination of surface water pCO₂ in a highly variable environment, exemplified in the southern Baltic Sea

Marcin Stokowski*, Przemysław Makuch, Krzysztof Rutkowski, Marcin Wichorowski, Karol Kuliński

Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland

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Abstract Measurement of pCO₂ in highly dynamic coastal zones such as the southern Baltic Sea presents many challenges. In this study, we designed a system to measure pCO₂ and then validated it in a series of laboratory and seagoing tests. The fast response time of the system was shown to provide a better resolution of CO₂ system gradients. In the open waters of the Baltic Sea, the accuracy of the pCO₂ measurements ($\pm 1.3 \mu\text{atm}$) met the requirements of the ICOS ($\pm 2.0 \mu\text{atm}$). In the coastal zone, there was less consistency between pCO₂, DIC and pH measurements, suggesting the need to redefine the quality assurance and control requirements for the measurement of pCO₂ in dynamic regions.

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Rationale

The carbon dioxide (CO₂) system is an integral part of the marine acid-base chemistry that controls seawater pH. Thus, an understanding of the CO₂ system is a prerequisite to investigating present-day phenomena affecting marine biogeochemistry, such as ocean acidification, calcium carbonate (CaCO₃) formation/dissolution and CO₂ exchange at the air-sea interface (Doney et al., 2020; Kuliński et al., 2017). In the Baltic Sea, studies of the CO₂ system have focussed on its open waters (Beldowski et al., 2010; Carstensen et al., 2018; Gustafsson and Gustafsson, 2020; Kuliński et al., 2017; Omstedt et al., 2014; Schneider et al., 2017) whereas much less is known about

* Corresponding author at: Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland.

E-mail address: stokowski@iopan.gda.pl (M. Stokowski).

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the coastal zone, despite the fact that riverine runoff plays an important role in shaping the composition of Baltic Sea water (BACC II Author Team, 2015). Preliminary studies of the Oder River estuary indicated that the CO₂ system in the coastal zone of the southern Baltic Sea is highly dynamic (Stokowski et al., 2020). This was due to the mixing of high-CO₂ (pCO₂ > 2000 μatm) river water with surface seawater largely in equilibrium with the atmosphere. Other important factors controlling the CO₂ system in that region include intensive biological processes, such as organic matter production and remineralisation, driven respectively by the high nutrient loads from land and the high inputs of terrestrial material (Kuliński et al., 2016; Kuliński and Pempkowiak, 2011). Moreover, rivers of the southern Baltic Sea have been recognised as an important source of total alkalinity (TA), as they transport CaCO₃ eroded from limestone-rich catchments (Beldowski et al., 2010; Hjalmarsson et al., 2008). Together, these processes result in a significant spatially and temporally dynamic CO₂-system, reflected by the high variability in its four measurable parameters in the coastal zone: CO₂ partial pressure (pCO₂), TA, dissolved inorganic carbon (DIC) and pH (Stokowski et al., 2020).

Of these, pCO₂, which can be measured with high accuracy from a moving ship, is the sole parameter that can be considered as representative of the highly dynamic CO₂ system that characterises the coastal zone of the Baltic Sea and other coastal systems. For TA and DIC, high-quality measurements are possible only from discrete samples such that they are not spatially representative whereas pH measurements suffer from a lack of both suitable certified reference materials and a suitable sample preservation method (Dickson et al., 2007) and are of lower accuracy (than in the open ocean) under brackish conditions such as those of the Baltic Sea (Dickson et al., 2007). Moreover, the specific composition of Baltic Sea water, especially that of its estuaries, where salinity is low and the organic matter (OM) and particulate inorganic carbon (PIC) concentrations are high, can introduce significant uncertainty in measurements of the CO₂ system and a determination of its properties (Kuliński et al., 2017). A further complication is that high OM concentrations significantly limit interpretations of TA (Hammer et al., 2017; Kuliński et al., 2014) and may directly increase the level of uncertainty in those measurements (Ulfsbo et al., 2015). The presence of suspended CaCO₃ in the waters of the large rivers entering the Baltic Sea (Stokowski et al., 2020) may disrupt measurements and lead to overestimation of both TA and DIC (only dissolved carbonates and bicarbonates contribute to TA and DIC). Measurements of pCO₂ also have their limitations, including the steep gradients in pCO₂ over short distances (Stokowski et al., 2020) such that a measuring system with a short response time is required while the abundance of organic (Pempkowiak and Kupryszewski, 1980) and inorganic (Su et al., 2020) particles leads to clogging of the equipment. In addition, any pCO₂ measurement system requires an air-tight hydraulic installation on the research vessel, a reliable CO₂ detector as well as an appropriate equilibrator, and must be coupled with temperature and salinity measurements. Furthermore, the quality of the pCO₂ data should be confirmed by comparisons with other measurable parameters of the CO₂ system (Dickson et al., 2007). Given

the research challenges in investigating the dynamics of the CO₂ system in marine coastal zones, including conducting measurements in highly dynamic systems influenced by large-volume riverine runoff, we designed and tested a system for obtaining reliable and to a large degree autonomous pCO₂ measurements and then validated its use in a study conducted in the Baltic Sea.

System design

The principles underlying the measurement system and its design reflected a compromise between precise and accurate measurements, a fast response time and resistance to clogging. Generally, there are two types of pCO₂ measuring systems, one consists of flow-through equilibrators and the other of sensors-type systems. Sensors based on cavity ring-down spectroscopy are easy to use and have a response time of 2–5 min (Graziani et al., 2014; Hari et al., 2008; Jiang et al., 2014). However, the precision and accuracy of sensors-type systems still need improvement (Jiang et al., 2014). For the purposes of this study, equilibrator-type systems were preferred due to their much higher precision and accuracy (Körtzinger et al., 1996). There are many types of equilibrators in use, including the shower head (shower-type), marble, passive membrane, liquid-cell (Santos et al., 2012) and bubble (Körtzinger et al., 1996) types and the less popular glass-bed, Weiss and Raschig ring types (Webb et al., 2016). Marble and liquid-cell equilibrators offer the shortest response time but their potential for biofouling is high (Kubo et al., 2017; Santos et al., 2012). Shower- and bubble-type equilibrators have a longer but still relatively short response time and, importantly, are resistant to biofouling and clogging (Körtzinger et al., 1996; Santos et al., 2012). Thus, by coupling shower-type and bubble-type diffusers we were able to design a novel equilibrator with a short response time and the high resistance to clogging necessary for coastal applications.

The equilibrator was designed to be reliable at tilts of ±45° from the vertical position. It was equipped with a temperature sensor and carried a spray-type water diffuser to increase the active surface for air-water gas exchange. The equilibrator has a total volume of 1.0 L, with water accounting for 660 mL and the gas phase for 340 mL. Water flow to the equilibrator is in the range of 0.6–1.0 L min⁻¹ but is optimal at 0.8 L min⁻¹, with the water in the equilibrator thus replaced every 50 s. At a flow of <0.6 L min⁻¹ spray is not formed at the water inlet, while at a flow >1 L min⁻¹ an excess of the aerosol is released, which is not desirable.

A cavity ring-down spectroscope G2101-*i* (Picarro) was used to detect CO₂ in the gas phase. The amount of CO₂ in water vapour was measured in parallel, thus allowing automatic conversion of the result to the molar fraction of CO₂ in dry air (ppm) and further to pCO₂ (μatm). Although the detector offers high-quality laser-based measurements of pCO₂, its construction limits the gas flow to 20 mL min⁻¹ (small air loop in Figure 1). Since this is not fast enough to obtain a short equilibration time and thus a rapid response of the system, an additional ‘big air loop’ (Figure 1) was introduced in which a peristaltic pump was used to obtain a gas flow of 430 mL min⁻¹, determined to be the optimal rate guaranteeing a short equilibration time while avoiding

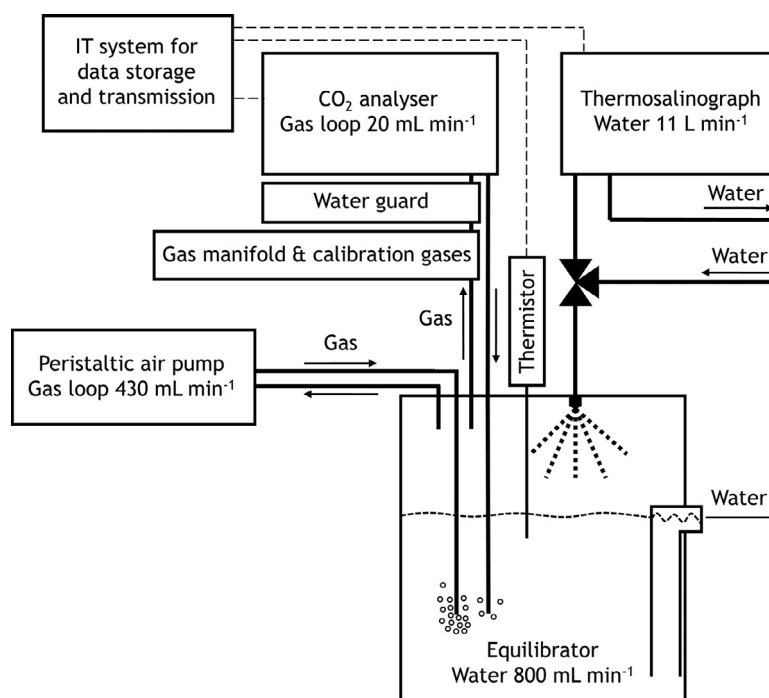


Figure 1 Scheme of the pCO₂ measurement system.

aerosol formation. As the airflow in the equilibrator can be adjusted, the system is independent of the airflow provided (or required) by the gas analyser, which makes it suitable for a variety of detectors. The disadvantage of using the peristaltic pump is the relatively high wear of its tubing, which in our system was overcome by using Tygon tubing, which is poorly permeable to gases and recommended for long deployments. Nonetheless, which the tubing was experimentally determined to be reliable for 168 h, its wear should be regularly monitored. The measuring system was also equipped with a newly developed automated device that shuts off the connection between the equilibrator and the CO₂ detector in case of flooding (Stokowski et al., 2018) (Figure 1). The connection of three calibration gases (artificial air), containing 205, 507 and 598 ppm CO₂, to the CO₂ detector through the automated gas manifold ensured high-quality pCO₂ measurements as well as the detection and correction of potential analyser drift (Figure 1). The entire pCO₂ measuring system, originally intended to be permanently installed on the *r/v Oceania*, can be packed into a box with dimensions of 720 × 600 × 500 mm.

Onboard the *r/v Oceania*, the system was connected to the ship's gas-tight surface water supply system and coupled to a combined thermosalinograph SBE 21 SeaCAT and temperature sensor (SBE 38) installed in the water inlet, located at 2.5 m depth. The obtained *in situ* temperature (T_{is}) and salinity (S) allowed the pCO₂ results to be corrected by applying a temperature coefficient of 0.0423°C⁻¹ (Takahashi et al. 1993) and for computations using CO2SYS (Pierrot et al., 2006). All data from the pCO₂ measuring system and thermosalinograph (including the SBE 38) are streamed to the ship's data storage server. To provide both permanent access to the pCO₂ and CTD data collected during a cruise and performance monitoring from land, a ship-to-shore data distribution system was developed (Figure 1)

allowing data transfer with 15-min resolution. The system provides a ship to shore connection for the local computer network, thus conferring the research equipment of the *r/v Oceania* with a high level of security and low susceptibility to failure through several redundant and independent links. Details of the data collection process and transmission system are provided in the Supplementary material.

Quality tests of the pCO₂ measurements: experimental setup

The quality of the newly designed system was assessed in a series of laboratory and seagoing tests aimed at determining the system's response time and the accuracy of the pCO₂ measurements. The response time was analysed in the laboratory by rapidly switching the water source from Batch 1 to Batch 2, containing seawater of pCO₂ = 778 μatm, and 404 μatm respectively. Batch 1 was obtained by adding <10% tap water to seawater, and Batch 2 by pumping the air (equilibrating with the atmosphere) over 12 h, following the principles described by Webb et al. (2016). The equilibration response time was assessed by calculating the time constant (τ) of the exponential decay (a change of 1-e⁻¹ of the total pCO₂ change, i.e. ~63%) according to Arévalo-Martínez et al., (2013) (Figure 2). The accuracy of the pCO₂ measurements was verified by crosschecking them with the pCO₂ calculated from the pH and DIC, which ensured that they were free of any uncertainty related to the specific matrix of Baltic Sea water (Kuliński et al., 2014). Inconsistencies would not occur in the precise, accurate DIC, pH and pCO₂ data, even for a matrix containing dissolved OM, but would be apparent for TA. Seawater for the laboratory tests was collected in April 2020 from the coastal zone of Gdańsk Bay, at the pier in Sopot (Poland) (sample 1, Figure 3), using

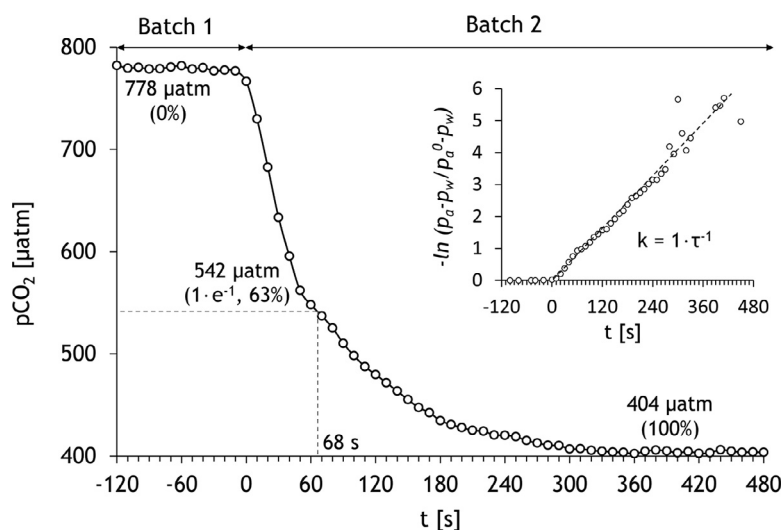


Figure 2 Determination of the $p\text{CO}_2$ response time. The p_a states for $p\text{CO}_2$ at time t , and the p_a^0 and p_w states for $p\text{CO}_2$ in Batch 1 and Batch 2, respectively. The rate constant of the process is k and τ is the time constant. The insert shows a plot of $-\ln(p_a - p_w / p_a^0 - p_w)$ as a function of time. The time constant was calculated from the slope of the regression line.

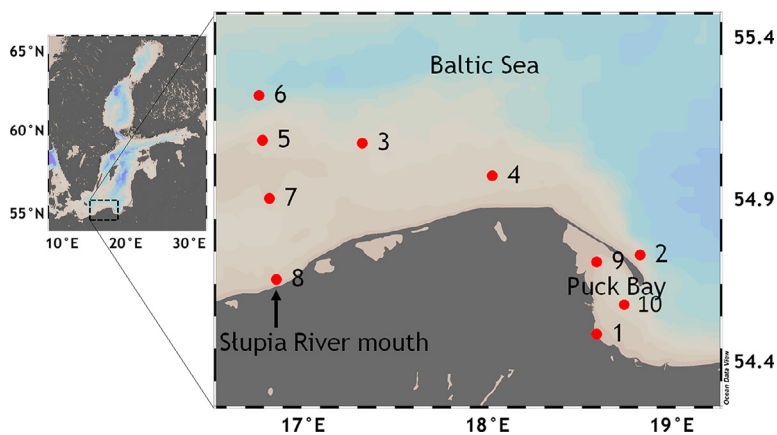


Figure 3 Study area and location of the sampling stations.

horizontal 10-L Niskin bottles and carefully transported to IO PAN. Before and during the experiment, the laboratory was intensively aired to ensure an atmospheric $p\text{CO}_2$ level and ambient temperature in the room and thereby limit CO_2 gas exchange between seawater and the atmosphere (the $p\text{CO}_2$ of the water was $404 \mu\text{atm}$ and thus close to the atmospheric value) (Table 1). After subsamples for DIC (in 40-mL vials) and pH (in 250-mL glass bottles) had been collected, seawater was immediately pumped into the CO_2 system with a peristaltic pump (0.8 L min^{-1}) to measure $p\text{CO}_2$. The pH was measured immediately after sampling while the DIC sample was preserved with $100 \mu\text{l}$ of saturated HgCl_2 and kept in the dark at $\sim 4^\circ\text{C}$ until analysed.

After the laboratory tests, the field operability of the $p\text{CO}_2$ system was verified during a cruise of the *r/v Oceania* in May 2020. The ship's speed during the tests was 9–10 knots. Both $p\text{CO}_2$ and CTD were measured continuously during the cruise. Samples for pH and DIC determinations were collected from the ship's pumping system, which also supplies water for the $p\text{CO}_2$ measurements, at nine stations representing the greatest possible range of environmental

conditions: open Baltic Sea (samples 2–7, Figure 3), the highly productive, shallow and anthropogenically influenced Puck Bay (samples 9 and 10, Figure 3) and the vicinity of the mouth of the Stupia River (sample 8, Figure 3). As in the laboratory tests, pH was measured immediately after sampling, while samples for DIC were preserved (HgCl_2) and stored refrigerated at $\sim 4^\circ\text{C}$. The DIC analyses were conducted no more than 10 days after sampling.

The pH was measured using a flow-through device (HydroFIA pH, Kongsberg GmbH, now 4H Jena Engineering), with the values determined spectrophotometrically (wavelengths: 434 nm and 578 nm). The indicator dye was m-cresol purple and the precision and accuracy of the measurements were ± 0.001 and ± 0.02 respectively (Carter et al., 2013; Clayton and Byrne, 1993; Liu et al., 2015; Mosley et al., 2004).

The DIC samples were analysed with a precision of $5 \mu\text{mol kg}^{-1}$ using a HyPer-TOC analyser (Thermo Electron Corp.) and based on sample acidification as well as NDIR detection of CO_2 . The quality of the measurements was assured by the analysis of certified reference material (provided by

Table 1 Experiments details.

Sample	Region	S (PSU)	T _{is} [°C]	DIC [$\mu\text{mol kg}^{-1}$]	pH (total scale)	pCO ₂ [μatm]	pCO ₂ calculated (DIC + pH) [μatm]	ΔpCO_2 [μatm]
1	Laboratory test	7.45	12.40	1703.8	7.906	414.0	411.8	2.2
2	Open sea	7.74	12.63	1624.8	7.984	322.7	322.8	−0.1
3	Open sea	7.62	11.16	1605.7	8.048	256.4	256.3	0.1
4	Open sea	7.83	11.14	1667.3	7.918	365.1	365.8	−0.7
5	Open sea	7.34	11.49	1649.3	8.093	242.8	241.1	1.7
6	Open sea	7.62	12.59	1590.1	7.998	303.6	305.8	−2.2
7	Open sea	7.92	12.44	1642.7	7.892	403.8	404.9	−1.1
								RSD ± 1.3
8	Coastal (1 km to Stupia River mouth)	7.61	13.84	1711.30	7.953	398.9	388.3	10.6
9	Coastal (Puck Bay)	7.52	11.67	1654.0	7.854	430.6	440.7	−10.1
10	Coastal (Puck Bay)	7.50	11.54	1658.5	7.986	304.8	315.7	−10.9
								RSD ± 12.2

the Marine Physical Laboratory of the Scripps Institution of Oceanography, University of California, San Diego).

The pCO₂ was calculated from the DIC and pH using CO2SYS software (Pierrot et al., 2006) and the dissociation constants for carbonic acid suggested by Millero (2010), the KHSO₄[−] dissociation constant defined by Dickson (1990) and the borate dissociation constant reported by Uppström (1974).

Quality tests of pCO₂ measurements: outcome

The time constant ($\tau=1\cdot\text{k}^{-1}$, Figure 2) determined for the system was 68 s but the realistic response time, measured from the rapid switch between Batch 1 and Batch 2 when a change in the pCO₂ signal of $1\cdot\text{e}^{-1}$ was detected, was 1 min and 44 s. This was because of the additional delay related to gas transport from the equilibrator to the CO₂ detector. Nonetheless, this result is better than the 2 min recommended for pCO₂ measurements by Pierrot et al. (2009). The precision of the analyser was $\pm 1.8 \mu\text{atm}$, based on 200 measurements of the 507-ppm calibration gas at 1-Hz frequency. The laboratory experiment demonstrated the consistency and accuracy of the measured CO₂ system parameters (sample 1, Figure 4, Table 1). The measured pCO₂ was 2.2 μatm higher than the pCO₂ calculated from the pH and DIC (CO2SYS). Results similar to those of the laboratory test were obtained in open Baltic Sea waters, where the pCO₂ differences between the measured and calculated values (ΔpCO_2) oscillated between -2.2 and $+1.7 \mu\text{atm}$, with a relative standard deviation (RSD, $n=6$) of $\pm 1.3 \mu\text{atm}$ (samples 2–7, Figures 3 and 4, Table 1). In the coastal waters (samples 8–10, Figures 3 and 4, Table 1), the ΔpCO_2 was higher, ranging from -10.9 to $10.6 \mu\text{atm}$ and with an RSD of $\pm 12.2 \mu\text{atm}$ ($n=3$). This was likely due to the stronger pCO₂ (but also TA, DIC and pH) gradients in that region, which can be attributed to the mixing of different water masses, spatially diversified biological activity (production and rem-

ineralisation of OM) and the influence of either processes occurring in sediments or upwelling events, among others. These results, however, should not be directly interpreted as the accuracy of the pCO₂ measurements but as the consistency between the pCO₂ and discretely sampled DIC and pH in the highly dynamic regions of the coastal zone. Because pCO₂ was measured continuously whereas the DIC and pH samples were snapshots of water flowing into the equilibrator, the mismatch between measured and calculated pCO₂ values was expected and suggested the presence of very steep, as yet undetected pCO₂ gradients. Nevertheless, our newly designed pCO₂ measuring system, with its fast response time and possible coupling with different CO₂ detectors, was able to depict the variability in the coastal CO₂ system of the Baltic Sea with a relatively high level of detail. Moreover, it offers a substantial improvement over measurements of discretely sampled parameters, in which the sampling resolution is limited and the analyses are time-consuming.

The CO₂ system in the open waters of the Baltic Sea, while less dynamic than that of the sea's coastal zone, is still more variable in space and time than that of the open ocean (Doney et al., 2020; Kuliński et al., 2017; Schneider and Müller, 2018). This accounted for the ability of our newly designed pCO₂ measuring system, when used in open Baltic Sea waters, to fulfil the ICOS requirements ($\pm 2 \mu\text{atm}$), which are state-of-the-art for present-day pCO₂ measurements. The greater uncertainty in our pCO₂ results for the coastal zone indicates that quality requirements for pCO₂ measurements in highly dynamic regions should be set independently, as they will not be identical to those expected for the open ocean. While there is clearly always room for further improvement in the hardware and design of pCO₂ measuring systems, the fast response time of our system (1 min 44 s) but the nonetheless lower quality of the measurements in the coastal zone suggest a limited capacity for the further optimisation of equilibration techniques, especially given the kinetics of CO₂ exchange at the air/sea interface.

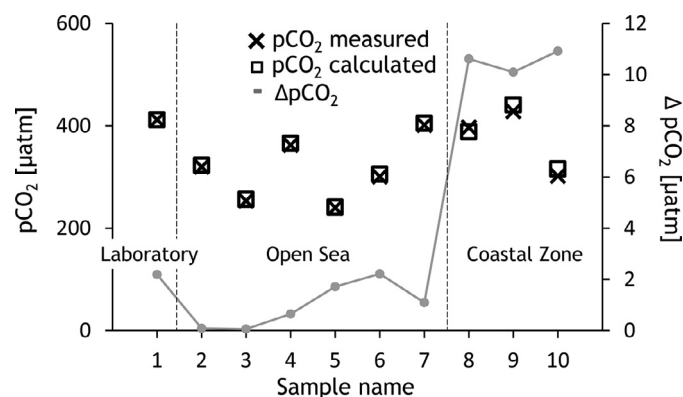


Figure 4 The difference ($\Delta p\text{CO}_2$, grey) between the measured (black cross) and the calculated (CO2SYS, pH+DIC, black square) $p\text{CO}_2$. The absolute values of $\Delta p\text{CO}_2$ are shown (the true $\Delta p\text{CO}_2$ is reported in Table 1).

Our results highlight the need for discussions within the scientific community on the desired quality (and verification) of $p\text{CO}_2$ measurements in coastal regions, which should take into account the natural biogeochemical variability of marine systems and the expected scientific outcome of the measurements.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.oceano.2021.01.001>

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