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Recommendations for autonomous underway $p\text{CO}_2$ measuring systems and data-reduction routines

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ABSTRACT

In order to facilitate the collection of high quality and uniform surface water $p\text{CO}_2$ data, an underway $p\text{CO}_2$ instrument has been designed based on community input and is now commercially available. Along with instrumentation, agreements were reached on data reduction and quality control that can be easily applied to data from these systems by using custom-made freeware. This new automated underway $p\text{CO}_2$ measuring system is designed to be accurate to within $0.1 \mu\text{atm}$ for atmospheric $p\text{CO}_2$ measurements and to within $2 \mu\text{atm}$ for seawater $p\text{CO}_2$, targeted by the scientific community to constrain the regional air–sea CO_2 fluxes to $0.2 \text{ Pg C year}^{-1}$. The procedure to properly reduce the underway $p\text{CO}_2$ data and perform the steps necessary for calculation of the fugacity of CO_2 from the measurements is described. This system is now widely used by the scientific community on many different types of ships. Combined with the recommended data-reduction procedures, it will facilitate producing data sets that will significantly decrease the uncertainty currently present in estimates of air–sea CO_2 fluxes.

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1. Introduction

The world's oceans are the largest sustained sink of carbon dioxide released to the atmosphere. It is now estimated that about $1.8 \text{ Pg C year}^{-1}$ go into the ocean, but the uncertainty is still quite large ($\sim 0.7 \text{ Pg C year}^{-1}$) (Takahashi et al., 2009). Different regions of the oceans are not equivalent with respect to CO_2 absorption. Some regions, such as the Equatorial Pacific, release CO_2 to the atmosphere (Feely et al., 2006), whereas others like the North Atlantic absorb it (Lüger et al., 2006). In addition to this regional variability, a large temporal variability can occur. Our ability to estimate the sources and sinks of CO_2 in the oceans depends on the accuracy of the field data used to calculate regional and global fluxes. These flux estimates, in turn, can be used to validate computer models that predict future $p\text{CO}_2$ levels. Improving the constraints on these models is essential to bettering our understanding of the oceanic carbon system; hence, the

importance of increasing the number of our observations, both in space and time.

The flux of CO_2 across the sea surface is directly proportional to the difference in the fugacity of CO_2 ($f\text{CO}_2$) between the atmosphere and the seawater. The fugacity is obtained by correcting the partial pressure of CO_2 ($p\text{CO}_2$) for non-ideality of the gas with respect to molecular interactions between CO_2 and other gases in air, thus making $p\text{CO}_2$ an important parameter to measure. The measurement systems for $p\text{CO}_2$ installed on stationary platforms such as buoys supply good temporal, but limited spatial information. Installations on vessels of opportunity provide limited information on temporal variations of less than a month, but the spatial coverage is better. Over 3 million data points are currently available (Takahashi et al., 2009), but to reach the goal of a fully operational surface ocean CO_2 observing system, agreement on the recommended design of an underway $p\text{CO}_2$ measuring system is desirable. A wide variety of designs is still in use throughout the scientific community. An international intercomparison exercise (Körtzinger et al., 2000) has shown that some designs, although sound in principle, lead to significant errors in $f\text{CO}_2$ results. In addition, although the past decade saw a

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substantial increase in the number of measurements, some regions are still greatly under-sampled, particularly between 30°S and 50°S and the increase in data has been mostly in regions with prior observations (Takahashi et al., 2009). This article describes the characteristics of an underway $p\text{CO}_2$ system designed to meet the community's goal of being able to constrain the regional fluxes to $0.2 \text{ Pg C year}^{-1}$ as recommended in Bender et al. (2002), which translates into measuring the atmospheric $f\text{CO}_2$ to within $0.1 \mu\text{atm}$ and the seawater $f\text{CO}_2$ to within $2 \mu\text{atm}$ (Bender et al., 2002). After deployment of the first units, it was recognized that differences in data treatments produced larger than expected differences in the calculated results and that standard procedures to reduce and report the $f\text{CO}_2$ data obtained from underway systems were needed. These procedures are detailed here. This work was done in coordination with the International Ocean Carbon Coordination Project (IOCCP) with the goal to meet the key climate monitoring principles of robust and uniform instrumentation which produces measurements that are traceable to standards (Trenberth et al., 2002).

2. Characteristics of the design

The design and mode of operation of the system were decided upon by a large group of $p\text{CO}_2$ experts during a workshop held at the NOAA Atlantic Oceanographic and Meteorological Laboratory (AOML) in Miami, Florida in 2002. The workshop was motivated by the need of the community to agree on requirements for autonomous systems in order to produce high quality and comparable data sets. The system is designed to operate fully unattended with only routine maintenance in port. It was decided that the new system would be patterned after systems combining air–water equilibrators with an infrared analyzer for detection, which have been in use for over 40 years (Takahashi, 1961). Recent examples of systems in operation are described in Wanninkhof and Thoning (1993) and Feely et al. (1998).

The system is compact and operates by directing seawater flow through a chamber (the equilibrator) where the CO_2 contained in the water equilibrates with the gas present in the chamber (the headspace gas). To determine the CO_2 in this headspace gas, it is pumped through a non-dispersive infrared analyzer, which measures its CO_2 mole fraction ($x\text{CO}_2$) instantaneously, and then returned to the equilibrator thus forming a closed loop. Periodically, atmospheric air is also pumped through the analyzer and its CO_2 mole fraction is measured. The analyzer is calibrated with four CO_2 standard gases at regular intervals (up to six standards can be used). The unattended use on ships is facilitated by its ability to shut down before its integrity becomes compromised, such as by a leak of seawater and by an automatic back-flushing routine that reduces the growth of organisms and fouling. It can run unattended for months at a time with only periodic minimal maintenance and can transmit its data daily via satellite communication, thus allowing near real-time data analysis and remote troubleshooting.

2.1. General description

The schematic of the system is shown in Fig. 1. The system is composed of three enclosures that compartmentalize the different functions of the system. The “wet” box contains the elements where water circulates. It includes the equilibrators, the condenser, water flow meter, and the valves controlling the water circulation. A shelf separates the pumps, electronic modules, and Nafion[®] drying tubes from the “wet” elements. The “dry” box contains the analyzer, the gas selecting valve, the computer, and the power supplies. The “deck” box (not shown) includes the

Iridium satellite modem, the GPS receiver, and an external pressure transducer. This relatively compact packaging allows the system to be installed in hostile environments such as engine rooms.

2.2. Water circulation

The seawater enters the system at a rate of $1.5\text{--}2 \text{ l min}^{-1}$ via a three-way valve, which can act as an emergency shut-off valve, and then passes through a $200 \mu\text{m}$ filter before entering the equilibrator through a spiral nozzle. The nozzle creates a spray of water that maximizes the CO_2 equilibration process between the seawater and the headspace gas contained in the equilibrator. The seawater exits the equilibrator over a standpipe covered by an “inverted cup”, which effectively isolates the headspace gas from the ambient air. The top of the standpipe is vented to the outside so that pressure or suction in the drain line will not affect the equilibrator.

The headspace inside the equilibrator is maintained at ambient pressure by a vent. During the international indoor seawater pool $p\text{CO}_2$ intercomparison exercise organized by the National Institute for Environmental Studies (NIES) held at the National Research Institute of Fishery Engineering, Hazaki, Japan in March 2003 (<http://ioc3.unesco.org/ioccp/Docs/TsukubaWSdocs/WG1SummaryRpt.pdf>), it was observed that the system showed a small bias ($1\text{--}2 \text{ ppm}$) towards ambient air concentration due to exchange of surrounding air through that vent. This bias disappeared when the vent was connected to a secondary equilibrator, which is a smaller version of the main equilibrator. Any gas lost from the main equilibrator is replaced with the pre-equilibrated headspace gas in this vent equilibrator. This secondary equilibrator increased the total seawater flow requirement to $3\text{--}4 \text{ l min}^{-1}$.

When connected to a source of fresh water, the seawater filter can be back-flushed by switching the three-way valve mentioned previously. Fresh water is then circulated through the filter in the opposite direction to the seawater flow, thus removing the bigger particles and preventing the filter from clogging. During back-flushing, fresh water flows through both equilibrators, which will reduce the accumulation of organisms and organic material that produce or consume CO_2 . The back-flushing schedule is user-controlled via the software and is important for unattended use.

2.3. Gas circulation

Three types of gases are analyzed by the system. These are the standards, the atmospheric air, and the headspace gas from the equilibrator. An 8-port, 16-position electronic valve (VALCO) selects which gas is sent to the analyzer. Therefore, the system can accommodate up to six standard gases besides the atmospheric and headspace gases.

The standards are directly connected to the VALCO valve and are vented through a three-way valve after exiting the analyzer. Typical flow rates for standards are in the range of $50\text{--}60 \text{ ml min}^{-1}$ for 4 min to allow adequate flushing of the lines while conserving the gases as much as possible.

The atmospheric air, which is sampled at the bow of the ship to minimize contamination by stack gases, is pulled to the system at a high flow rate ($0.5\text{--}2 \text{ l min}^{-1}$). Most of this flow is vented right after the pump in order to minimize the residence time of the atmospheric air in the usually very long gas line. The air that is not vented is dried in a condenser that is cooled to $4\text{--}5 \text{ }^\circ\text{C}$ by a Peltier thermoelectric device. This partially dried air flushes a chamber that is vented and remains at ambient pressure. The dried air inside the chamber is used as the counter flow in the Nafion[®]

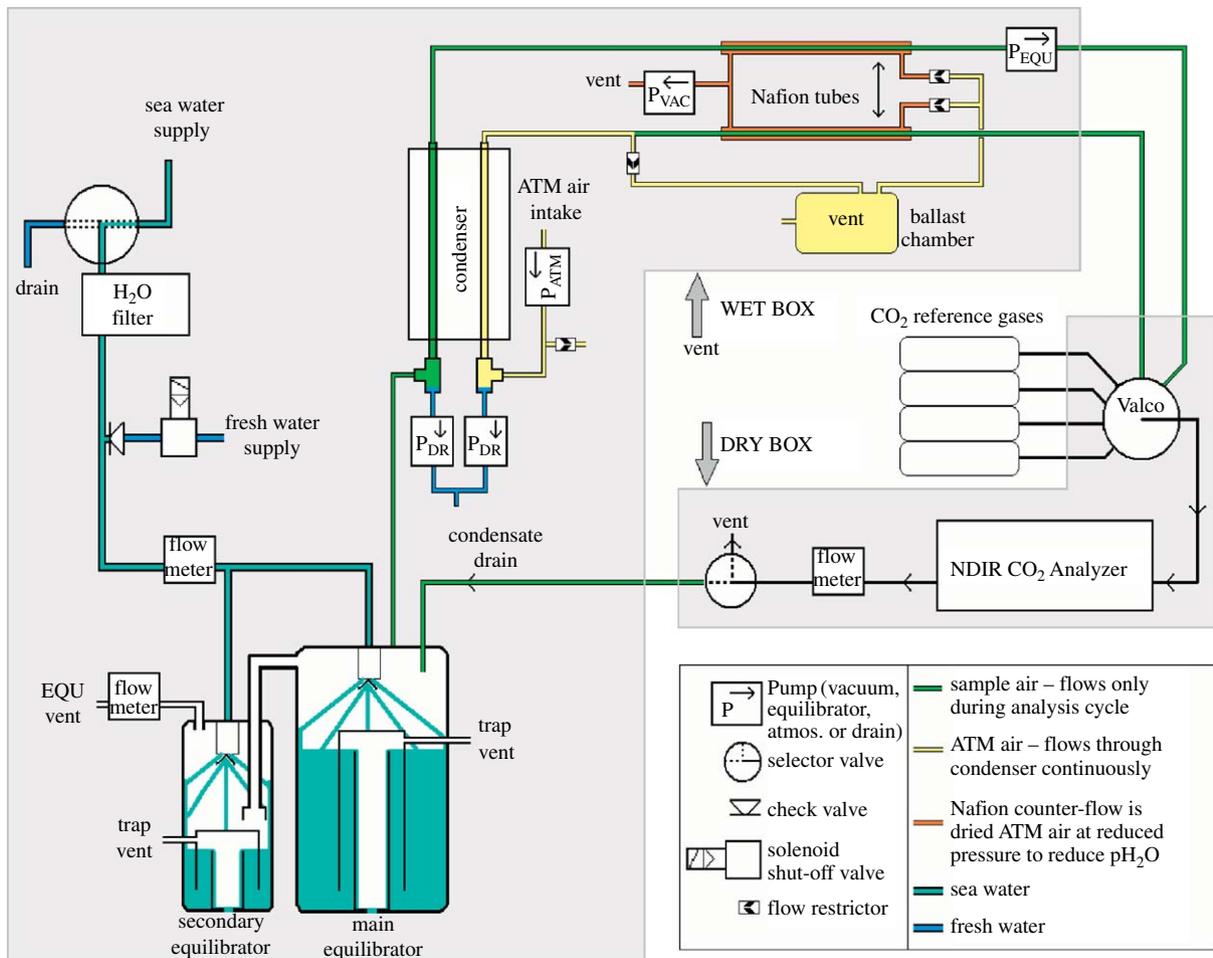


Fig. 1. Schematic of the underway $p\text{CO}_2$ system.

tubing. A vacuum pump pulls the dried air from the chamber first through a fixed restrictor and then through the Nafion[®] tubes, thus creating an absolute pressure difference and corresponding partial pressure gradient for water vapor across the membrane. When atmospheric air is measured, some of the partially dried air ($80\text{--}100\text{ ml min}^{-1}$) is pushed through a Nafion[®] tube, the analyzer and out a vent instead of flushing the chamber.

The headspace gas, when being measured, is circulated in a closed loop through the analyzer at a rate similar to that of the atmospheric air ($80\text{--}100\text{ ml min}^{-1}$). It is dried first in the condenser, then in a Nafion[®] tube prior to entering the analyzer and being returned to the equilibrator. Typically, the water mole fraction ($x_{\text{H}_2\text{O}}$) in the dried gas is about two parts per thousand (ppt), which corresponds to a dew point temperature of about -20°C . At intervals determined by the user, the liquid water condensed out of the sample air streams is removed by peristaltic pumps.

2.4. Analyzer

The analyzer used to measure the CO_2 in the sample gas stream is a non-dispersive infrared analyzer built by LICOR[®]. The system can accommodate three models, according to the user's need: the LI-6262, LI-7000, and LI-840. The LI-840, having a lower accuracy and higher signal-to-noise ratio, will likely not meet the specified accuracy of 0.2 ppm for atmospheric air samples, but some users find it adequate for their needs. The CO_2 measurements are

corrected for the dilution by water vapor and band-broadening pressure effect by the firmware internal to the analyzer such that they report a dry mole fraction. The sample gas is dried to a water mole fraction of about 2 ppt, making this correction small and minimizing the errors associated with it. The analyzer (LICOR) is typically flushed for 4 min before the first analysis of a given sample type and 1–2 min between subsequent analyses of the same type. The 4-min flush is necessary to completely purge the NDIR cell of the previous sample (such as when changing from one standard to another or from standards to equilibrator air) while the shorter flush represents the user's desired sample interval between successive equilibrator measurements. The gas flow is stopped for 10 s during which time the normally closed gas stream is opened to the ambient pressure via a three-way solenoid located after the analyzer. At the end of the 10 s, a 1-s averaged reading is taken.

In the factory configuration of the LICOR, the internal pressure transducer is connected directly to the optical cell contained in the analyzer. The gas present in the tubing connecting the pressure transducer to the cell is never properly flushed and will most likely have a different CO_2 mole fraction than the sample stream. When the sample gas flow is stopped for more than 10 s, this gas of different concentration diffuses back into the cell and contaminates the sample. To prevent such an effect, the connection of the pressure transducer has been moved further downstream from the cell. The LICOR is calibrated regularly by measuring a set of four standards every 2.5–3 h. Before starting a series of seawater measurements, it is flushed with the standard

gas whose concentration is the closest to the last seawater value in order to minimize the perturbation from pushing the gas content of the analyzer into the equilibrator.

2.5. Sensors

Different types of sensors are used throughout the system for analytical, troubleshooting, and quality control purposes. Accurate measurement of temperature of the seawater in the equilibrator is critical as the isochemical dependence of $f\text{CO}_2$ on temperature is about $15 \mu\text{atm } ^\circ\text{C}^{-1}$. As shown by Körtzinger et al. (2000), large discrepancies in equilibrator temperature measurements exist between systems from different groups, which result in significant errors in $f\text{CO}_2$ values. The temperature in our system is measured inside the equilibrator by a very accurate ($\pm 0.01^\circ\text{C}$) and stable Hart® digital thermometer with a thermistor probe. Temperature also is recorded inside the LICOR analyzer, the condensers, the deck box, and the dry box. It has been found that the response of the analyzer is sensitive to surrounding temperature changes. To minimize this effect, an electronics board adjusts the speed of the fan ventilating the dry box automatically while it monitors the temperature inside the box containing the analyzer.

Pressure is also monitored inside the equilibrator, inside the analyzer and at the deck box. The pressure transducer for the equilibrator is differential, meaning that it measures the pressure difference between the equilibrator and the ambient air, which is given by the LICOR pressure transducer when the measurement is made in stop flow mode and vented to the air. The deck box transducer measures the atmospheric pressure, which can differ by several millibars from the pressure inside the ship due to forced ventilation.

A water flow meter measures the combined seawater flow through both equilibrators. A gas flow meter, located at the exit of the LICOR, measures the sample gas flow. Another gas flow meter on the vent of the secondary equilibrator indicates how much ambient air is coming in or out. High flows indicated by this sensor suggest leaks in the gas circulation loop, which is a common cause of biases in underway $p\text{CO}_2$ systems. Water sensors positioned at the exit of the condenser and at the bottom of the wet box will alert the software when water is detected and will prompt the shut down of the system to prevent damage or flooding of the instrument. In addition to these regular sensors, the system is capable of interfacing with and logging data from optional external instruments with RS-232 outputs (e.g., fluorimeters, thermosalinographs, or optode oxygen sensors).

2.6. Telemetry

The deck box contains an Iridium satellite modem, which can transmit the data to a shore-side computer once a day. This allows near real-time display of the data as well as a means to troubleshoot the system while at sea and service it appropriately when the ship is dockside. Additionally, two-way satellite communications on some ships allow the system to be re-configured remotely, making it flexible to changing external conditions.

2.7. Software

The software running the system is written in the National Instruments Labview® environment. It has been written to maximize the autonomy of the system and its adaptability to different installation configurations. The software monitors the gas flow rate of the equilibrator headspace gas through the analyzer and adjusts the pump speed to keep the flow within a

user-specified range. The software checks for the presence of liquid water at critical places and can close a valve to shut down the intake water and stop the operation of the system. It also monitors the GPS signal and can put the system into a sleep mode in user-selected areas, thereby avoiding contamination of the system by silt and polluted water such as that often found in ports. The user can define limits on any sensor readings, such as temperatures or flows, as a trigger to either put the system to sleep or shut it off. The analyses are done according to a sequential list of the types of samples (e.g., standards, atmospheric air, and headspace gas) to run and the number of measurements of each type to make (see Table 1). That, combined with the user programmable flushing times of the analyzer mentioned previously, determines how often each sample is measured.

2.8. Equilibrator performance

The system is able to respond quickly to changes in the CO_2 concentration of seawater, thus capturing the fine features in the CO_2 variability of the ocean. The exchange time for the water in the main equilibrator is between 30 and 45 s, depending on flow rate. Fig. 2 shows the equilibrator response when the seawater flowing through the system is suddenly changed to seawater with lower $p\text{CO}_2$ at $t \sim 4$ min and then changed back to the original seawater at $t \sim 14$ min. The seawater temperature was around 11°C and had an approximate flow rate of 2 l min^{-1} . The headspace gas was circulated through the analyzer at about 50 ml min^{-1} . The

Table 1
Typical timing sequence.

Step	Type	No. of repetition
1	ZERO	1
2	SPAN	1
3	STD 1	1
4	STD 2	1
5	STD 3	1
6	STD 4	1
7	ATM	10
8	EQU	100
9	Loop back to step 3	5
10	BACK FLUSH	1
11	STD 1	1
12	STD 2	1
13	STD 3	1
14	STD 4	1
15	Loop back to step 1	

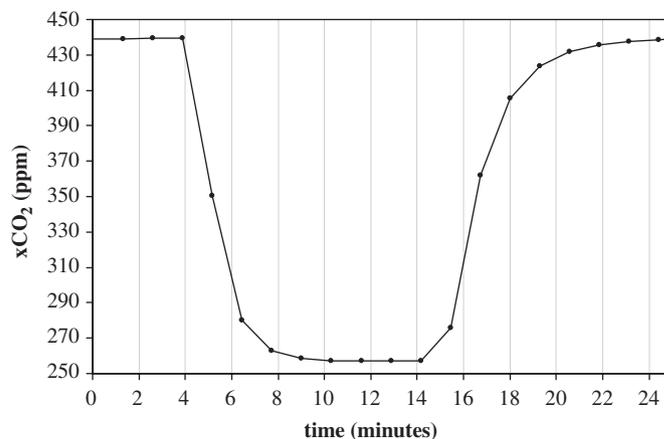


Fig. 2. Equilibrator response to changing CO_2 concentration in seawater. The response time is about 2 min.

response time, or e-folding time (the time it takes for the equilibrator to reduce the perturbation in $x\text{CO}_2$ by a factor of 1/e) is shown to be about two minutes. The test performed here is more realistic as it mimics the system measuring two water masses of different $f\text{CO}_2$.

3. Data reduction

In October 2005, select participants of the NOAA Underway $p\text{CO}_2$ program and CARBOOCEAN programs met in Miami, Florida, to develop uniform data-reduction procedures for underway $p\text{CO}_2$ measuring systems. A comparative data-reduction exercise showed significant differences in the calculated values of up to 1.7 ppm in $x\text{CO}_2$ and $2 \mu\text{atm}$ in $f\text{CO}_2$. After identifying the sources of the differences, the participants agreed upon data collection, quality control and calculation procedures that are presented below. These recommendations have been incorporated in the updated version of the DOE handbook of methods for analysis of carbon dioxide in seawater (Dickson et al., 2007).

3.1. Data collection

In order to calculate the $f\text{CO}_2$ properly, a number of parameters are necessary, which are not always recorded on custom built $p\text{CO}_2$ systems. These are the temperature and pressure inside the equilibrator at the time of equilibration, as well as the atmospheric pressure (for atmospheric $f\text{CO}_2$ determinations) and sea-surface temperature. The pressure inside the infrared analyzer also should be measured as it is used by the analyzer to correct the analog signal for any pressure effects. These parameters are important and need to be measured accurately. In order to achieve the desired accuracy of the system of $0.2 \mu\text{atm}$ for atmospheric measurements and $2 \mu\text{atm}$ for surface seawater measurements, the pressures need to be known to within ± 0.2 mbars and the temperature to within ± 0.01 °C. The analyzer should be calibrated every 2.5–3 h using a minimum of three standards, although four are recommended, with concentrations covering the range encountered in the working area and traceable to the World Meteorological Organization (WMO) scale. Two of these standards should closely bracket the atmospheric value. The sampling sequence will depend on the region covered, and highly variable areas such as the Equatorial Pacific will require a higher measuring frequency than other regions where the $f\text{CO}_2$ is more stable over time. As a guideline, the following sequence is recommended: a full set of standards should be measured every 2.5–3 h, followed by a set of 5–10 air samples at 1-min intervals. Seawater should be measured in sets of 50–100 samples at 1- or 2-min intervals, depending on the spatial variability of the region being sampled, before the next full set of standards. Although not critical, it is preferable for the analyzer to be zeroed and spanned once a day. Each zero/span procedure should be bracketed by full sets of standards in order to properly interpolate the standard values and correct for instrument drift as described below.

Data loss will sometimes occur due to periodic hardware malfunction and, depending on the type of data, $f\text{CO}_2$ values can still be calculated with minimal error provided that the synthetic data either is estimated with a reasonable accuracy or has a minor effect on the calculations. In many cases, sea-surface temperatures and equilibrator temperatures co-vary with a fairly constant offset between the two, which makes it possible to estimate one measurement from the other with a reasonable degree of uncertainty. During the 2005 workshop, it was agreed that equilibrator temperatures could be interpolated from existing data if the loss was for less than $\frac{1}{2}$ h and estimated from sea-surface temperatures if the loss was for a greater period of time.

However, in highly variable regions such as frontal zones where the temperature can change by several degrees over $\frac{1}{2}$ h, interpolation might not be appropriate and estimation from sea-surface temperatures is recommended. Likewise, sea-surface temperatures could be estimated from equilibrator temperatures if the data have not been recorded for periods of time longer than $\frac{1}{2}$ h (see Table 2). The time it takes for the seawater to travel from the intake, where the sea-surface temperature is measured, to the equilibrator can amount to a few minutes and should be taken into account before estimates can be made.

3.2. Quality control

Data are quality-controlled, and flagged according to the World Ocean Circulation Experiment (WOCE) guidelines which, for underway data purposes, consist of three values: a flag value of 2 indicates a good measurement; a value of 3 signifies a questionable measurement and 4, a bad measurement. A measurement can be questionable for a wide variety of reasons, some of which might not be crucial for some applications. In order to give the end user the possibility to judge the questionability of the measurement, a two-stage flagging routine is proposed for the final data files. One column will contain the main QC flags according to the WOCE convention. Another column will contain a second set of QC flags (sub-flags) that will give additional information on questionable measurements (WOCE flag 3) for users who might wish to use the data if the issue does not degrade the measurement substantially. A set of 10 secondary flags (or sub-flags) has been advocated and is given in Table 3.

3.3. Calculations

The post-cruise calculation of the $f\text{CO}_2$ from the raw data involves several steps which to date have been treated differently by different groups (e.g., which analyzer output, which interpolation method, or which temperature correction should be used). The different methods or equations and resulting disparity can generate significant differences in the end result, even when

Table 2
Actions recommended for missing data.

Missing data	Action for short drop-out periods (< 1/2 h)	Action for long drop-out periods (> 1/2 h)
Equ. Temperature	Interpolated or estimated from SST	Estimated from SST
Sea-surface temperature	Interpolated or estimated from EQU T	Estimated from EQU T
Salinity	$f\text{CO}_2$ not reported	Interpolated or default value
Position	Interpolated	$f\text{CO}_2$ not reported
Air measurements	Flask data	Flask data

Table 3
Values of the flags and sub-flags proposed for underway $p\text{CO}_2$ data.

<i>WOCE flags</i>	
2—Acceptable measurement	
3—Questionable measurement	
4—Bad measurement. Data will not be reported in the final data file	
<i>Sub-flags (only for WOCE flag 3)</i>	
1—Outside of standard range	6—Questionable pressure
2—Questionable/interpolated SST	7—Low EQU gas flow
3—Questionable EQU temperature	8—Questionable air value
4—Anomalous (EQU T–SST) (± 1 °C)	9—Interpolated standard
5—Questionable sea-surface salinity	10—Other, see metadata

starting from the same raw data. The section below describes the method that was agreed upon.

The LICOR analyzer output is either the raw voltage in millivolts or the internally calculated xCO_2 in ppm. The use of xCO_2 is recommended due to the fact that this output not only is linearized by an internal calibration using a fifth degree polynomial but also can be averaged by the analyzer as well as corrected for the dilution and band-broadening effects due to water vapor.

Differences in handling the standards' data also can bring about non-negligible differences in the calculated results. It is recommended to measure a full set of standards every 2.5–3 h, during which the drift in the analyzer's response is assumed to be linear. This assumption will decrease in validity as the time between sets of standards increases. The following method is recommended to correct the xCO_2 values recorded by the analyzer. First, each standard is linearly interpolated to the times of the measurements of atmospheric air (ATM) and of the equilibrated headspace (EQU). If the samples are not bracketed by standards, the last standard values measured are used instead of extrapolated values. For each ATM or EQU measurement, a full set of interpolated standard values is therefore obtained which is then linearly regressed using least-square analysis to produce an individual calibration curve for that measurement. Finally, this calibration curve is used on the analyzer ppm output to give an xCO_2 value corrected for any instrument drift, as observed by measuring the standards (see Fig. 3).

A linear regression is used instead of a second-order polynomial, used by others, to generate the calibration curve for each measurement for several reasons: the output xCO_2 of the detector

is linearized by the factory; tests have been conducted using up to seven standards and have shown that a second-order polynomial did not fit the data appreciably better than a linear regression; finally, these tests also have shown that a linear regression would estimate an out-of-range value better than a second-order fit would. The results of the tests are shown in Table 4. The measured concentrations shown in column 3 of Table 4 were plotted against the certified values and fitted to either a linear equation or a second-order polynomial. The resulting coefficients were used to calculate the "fitted" values, using the measured concentrations as input. The differences between these "fitted" values and the certified ones are shown in columns 4 and 5 in the table. The standard errors are statistically the same for both methods. The same calculations were done, fitting only standards 2–5. The differences between fitted and certified values are shown in columns 6 and 7 only for standards 1 and 6, which were not used in the fits. In this case, standards 1 and 6 are treated as out-of-range unknowns. Standard 1 is out-of-range by 120 ppm and both extrapolations (linear and polynomial) give reasonable estimates, although the polynomial fit gives a more accurate value. On the other hand, the error in the estimate of standard 6, which is about 300 ppm out-of-range, is a lot larger when using the polynomial fit.

The atmospheric air measurements should be made as a set of 5–10 analyses immediately after the standards since the accuracy requirements for the air values are higher than those of the equilibrated headspace samples. After flagging bad or questionable points, the good measurements in each set should be averaged. Bracketing averaged atmospheric analyses are linearly interpolated to obtain an atmospheric air value at each seawater measurement.

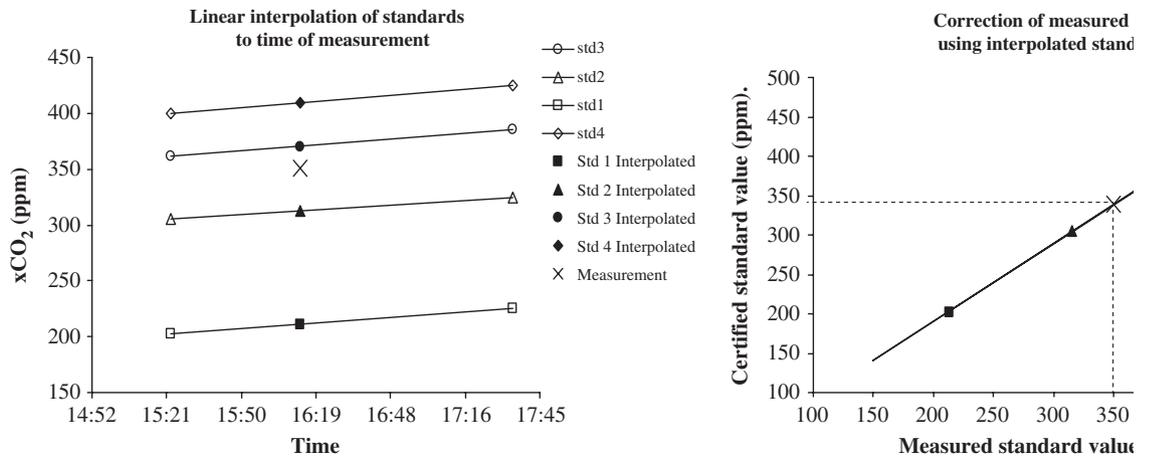


Fig. 3. Illustration of the xCO_2 correction using the measured standard. The top figure shows a measurement (cross symbol) between two sets of standards (open symbols). The closed symbols represent the values of the standards linearly interpolated at the time of the measurement. The bottom figure shows how the linear fit of the interpolated standard values from the top figure is used to correct the measured value.

Table 4
Results of test for fitting standards using different methods.

	Certified concentration	Measured concentration	Fitted-Cert. fitting all values		Fitted-Cert. extrapolation fitting STD 2–5	
			Linear	Polynomial	Linear	Polynomial
STD 1	203.92	205.48	0.08	0.22	0.83	–0.10
STD 2	328.12	328.96	–0.43	–0.44		
STD 3	350.44	351.73	0.06	0.03		
STD 4	448.29	449.28	–0.07	–0.16		
STD 5	508.38	509.87	0.53	0.43		
STD 6	794.94	795.24	–0.17	–0.07	–1.65	–4.9
			$\sigma = 0.36$	$\sigma = 0.34$		

When equilibrium is reached inside the equilibrator, the fugacity of CO₂ in the headspace gas is proportional to the concentration of CO₂ in the circulating seawater, according to Henry's law. That fugacity is given by

$$f(\text{CO}_2)_{\text{equT}}^{\text{wet}} = (p\text{CO}_2)_{\text{equT}}^{\text{wet}} \exp \left\{ \frac{B(\text{CO}_2, \text{equT}) + 2(1 - (x_{\text{CO}_2})_{\text{equT}}^{\text{wet}})^2 \delta(\text{CO}_2, \text{equT})}{R \times \text{equT}} \right\} P_{\text{atm}} \quad (1)$$

where equT is the temperature (K) of the equilibrator and P_{atm} is the atmospheric pressure (atm), $R = 82.0578 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$, and $B(\text{CO}_2, T)$ and $\delta(\text{CO}_2, T)$ are the virial coefficients for CO₂ (Weiss, 1974).

$B(\text{CO}_2, T)$ in $\text{cm}^3 \text{ mol}^{-1}$ is given by

$$B(\text{CO}_2, T) = -1636.75 + 12.0408T - 3.27957 \times 10^{-2}T^2 + 3.16528 \times 10^{-5}T^3 \quad (2)$$

and $\delta(\text{CO}_2, T)$ in $\text{cm}^3 \text{ mol}^{-1}$ by

$$\delta(\text{CO}_2, T) = 57.7 - 0.118T \quad (3)$$

The air inside the equilibrator is assumed to be at 100% humidity whereas it is dry when measured inside the analyzer. For that reason, a correction using the water vapor pressure is applied to the dry mole fraction measured and is given by

$$(p\text{CO}_2)_{\text{equT}}^{\text{wet}} = (x_{\text{CO}_2})_{\text{equT}}^{\text{dry}} [P_{\text{equ}} - p\text{H}_2\text{O}(\text{SSS}, \text{equT})] \quad (4)$$

where $(x_{\text{CO}_2})_{\text{equT}}^{\text{dry}}$ is the CO₂ mole fraction measured by the analyzer and $p\text{H}_2\text{O}$ is the water vapor pressure at the sea-surface salinity and temperature of the equilibrator (equT). P_{equ} is the pressure inside the equilibrator.

Internal algorithms in the analyzer are used to determine the $(x_{\text{CO}_2})_{\text{equT}}^{\text{dry}}$ by correcting the signal for dilution and band-broadening effects by water vapor. For a headspace gas having a H₂O mole fraction of 2 ppt, this correction amounts to 0.5–0.7 ppm in $x\text{CO}_2$ and 1.5 ppm for a $x\text{H}_2\text{O}$ of 4 ppt. Since the ATM and EQU gases are dried, water vapor level in the gas reaching the analyzer is low, thus reducing the uncertainty involved in applying this correction.

The equation recommended to calculate the water vapor pressure is that of Weiss and Price (1980) given by (atm):

$$p\text{H}_2\text{O}(S, T) = \exp(24.4543 - 67.4509(100/T) - 4.8489 \ln(T/100) - 0.000544S) \quad (5)$$

where S and T are the salinity and temperature (K), respectively. Alternatively, it also can be calculated using the method described in Dickson et al. (2007) using a Chebyshev polynomial representation of the pure water part and the osmotic coefficient of seawater. However, this algorithm is more complex and results compare to within 0.15% for salinities between 32 and 37 and SST from 0 to 30 °C.

A correction is then applied to compensate for the difference in temperature between the equilibrator and the sea surface. Several methods are available (Copin-Montegut, 1988; Goyet et al., 1993; Takahashi et al., 1993; Weiss et al., 1982). Unlike the relationship of Weiss et al. (1982), the empirical correction factor of Takahashi et al. (1993) was determined for isochemical conditions, which makes it more appropriate for this application. The empirical temperature dependence varies with alkalinity and TCO₂ but the variations are relatively small over the alkalinity and TCO₂ range of the open ocean and will introduce a small uncertainty for temperature differences of less than 1 K, as it is generally the case. However, a full experimental characterization of the temperature effect of $f\text{CO}_2$ is warranted.

Using the empirical temperature dependence of Takahashi et al. (1993) yields

$$(f\text{CO}_2)_{\text{SST}}^{\text{wet}} = (f\text{CO}_2)_{\text{equT}}^{\text{wet}} \exp\{0.0423(\text{SST} - \text{equT})\} \quad (6)$$

where SST is the sea-surface temperature in the same units as equT .

The equations used to calculate the atmospheric fugacity are the same as those described above with the difference that the atmospheric pressure (as measured by the “deck box”) and the SST should be used instead of the equilibrator pressure and temperature. Also, no temperature correction (Eq. (6)) is applied.

3.4. Reported data

There have been several recommendations provided by different international groups on how to present data in a uniform fashion (see http://cdiac.ornl.gov/oceans/underway_data_format.htm for reporting data to the Carbon Dioxide Information Analysis Centre (CDIAC) or the CarboOcean group). They are broadly similar with the same underlying philosophy of providing “raw” data of analyses, standards, temperatures, and pressures such that the $f\text{CO}_2$ and $p\text{CO}_2$ can be recalculated. Calculated parameters differ slightly between different recommendations. Below (Table 5) is a list of the data and variable names that are considered “final data” and which are reported to data centers such as CDIAC (<http://cdiac.ornl.gov/>). In addition, the ancillary data (e.g., fluorescence, wind speed, air temperature) also would be reported. The default value for bad data will be –9.

Two programs have been written in order to facilitate the application of these guidelines to reduce underway $p\text{CO}_2$ data. One is in Visual Basic for Excel[®] and the other is in Matlab[®]. These programs are available from the authors and will be posted on the CDIAC website for open access.

4. Performance and deployment

In 2003, a unit was tested against the Japanese National Institute for Environmental Studies system during an International Indoor

Table 5
Reported final data and variable names.

Variable name	Data
Group/ship	Group/ship
Cruise ID	Cruise ID (example RB0501)
JD_GMT	Julian Day (or Year Day) on the GMT time scale
Date	Date
Time	Time
Lat	Latitude
Long	Longitude
$x\text{CO}_2\text{EQ_PPM}$	Headspace CO ₂ mole fraction
$x\text{CO}_2\text{ATM_PPM}$	Atmospheric CO ₂ mole fraction (measured values, at the time taken)
$x\text{CO}_2\text{ATM_PPM_INTERPOLATED}$	Atmospheric CO ₂ mole fraction (interpolated values; corresponding to the time of $x\text{CO}_2\text{EQ}$ measurement using the good air values bracketing)
Press_Equil	Pressure inside the equilibrator
Press_ATM	Atmospheric pressure (e.g. from deck unit)
TEQ	Equilibrator temperature
SST	Sea-surface temperature
SAL	Salinity
$f\text{CO}_2\text{SW_UATM}$	$f\text{CO}_2$ for seawater measurements
$f\text{CO}_2\text{ATM_UATM}$ (interpolated)	$f\text{CO}_2$ for atmospheric measurements, calculated using the interpolated ATM mole fractions
DFCO ₂ _UATM	Difference between air–sea $f\text{CO}_2$
WOCE_QC_FLAG	Primary flags
SUBFLAG	Secondary flags

Seawater Pool $p\text{CO}_2$ Intercomparison exercise held at the National Research Institute of Fishery Engineering, Hazaki, Japan in March 2003 (<http://ioc3.unesco.org/ioccp/Docs/TsukubaWSdocs/WG1SummaryRpt.pdf>). Although there is no way to know that the NIES system was perfectly accurate, it was generally accepted as the reference system at the intercomparison exercise. Fig. 4 shows that the system performed very well and tracked the NIES system with less than $0.5 \mu\text{atm}$ difference.

Since 2003, a total of 18 systems have been built and used all over the world. Fig. 5 is a map showing where the systems have been deployed. Another 20 units have been delivered by General Oceanics, Inc. in Miami, Florida, who produces them commercially to customers around the globe. Each system is fully tested and compared against two other systems prior to delivery. All three systems have to agree to within $\pm 1 \text{ ppm}$ when measuring water with $x\text{CO}_2$ varying over a 400 ppm range before the production unit is sent to the customer (see Fig. 6).

As an example of a system in operation, the M/V *Skogafoss*, an Icelandic cargo ship, was outfitted with a system in 2003. The ship transits between Reykjavik, Iceland and Boston, MA on a monthly basis (see Fig. 7). During the transit, seawater measurements are made roughly every minute and atmospheric data are collected every 2 h. The system is calibrated with four standard gases ranging from 200 to 450 ppm, two of them having values bracketing the atmospheric value closely. The ship is also outfitted with a thermosalinograph from SeaBird Electronics (SBE-21) recording the salinity every 10 s.

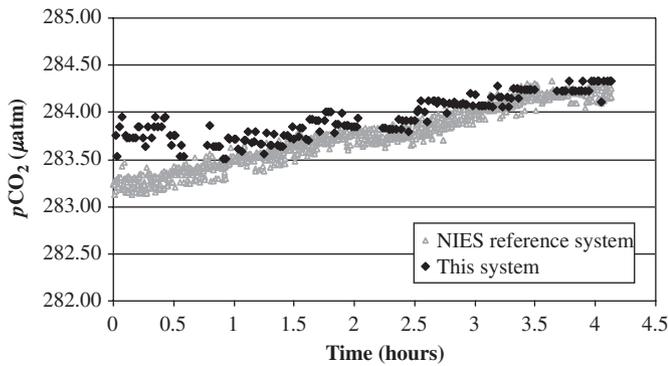


Fig. 4. Results from the $p\text{CO}_2$ intercomparison exercise held in Japan in March 2003. The system agreed with the NIES reference system to within $\pm 0.5 \mu\text{atm}$.

Fig. 8 is a plot of calculated differences in $f\text{CO}_2$ between the air and the underlying seawater for three transits in the months of December 2003, August 2004, and February 2005. These transits

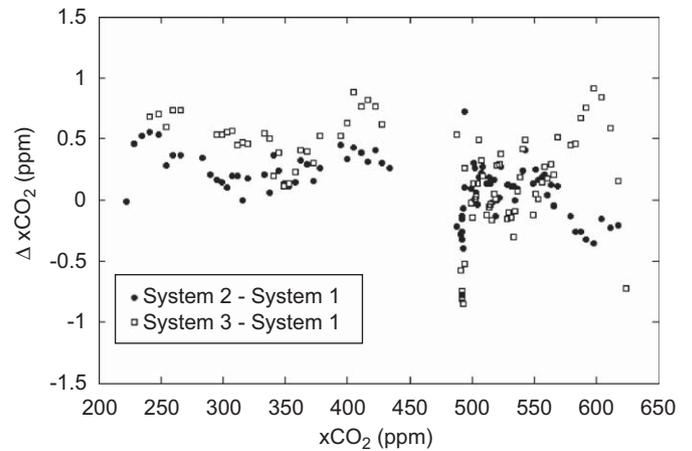


Fig. 6. Results of in-lab intercomparison test of three systems before they are shipped to customers. Systems have to agree to within $\pm 1 \text{ ppm}$ while $x\text{CO}_2$ varies between 200 and 600 ppm before they can be shipped.

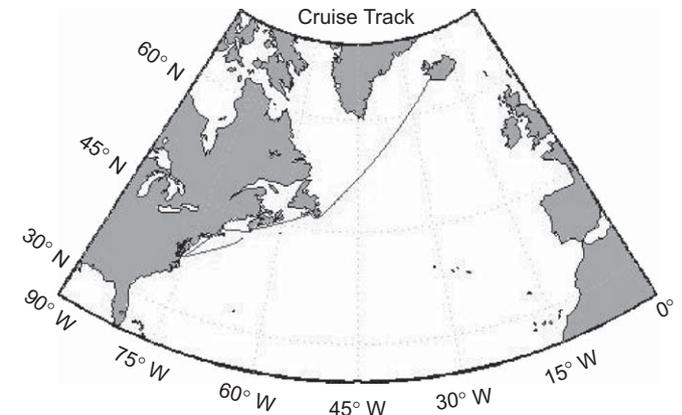


Fig. 7. Cruise Track of the M/V *Skogafoss* which transits monthly between Boston, MA, and Iceland.

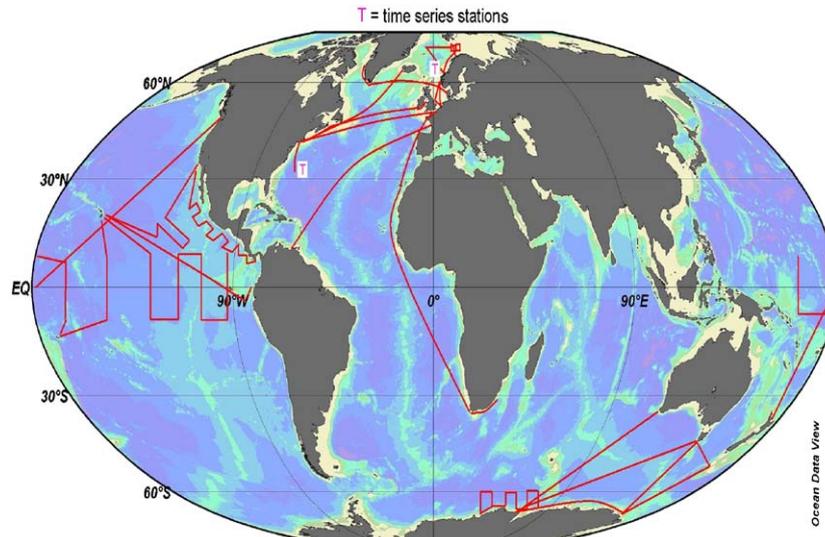


Fig. 5. Cruise tracks showing the location of $p\text{CO}_2$ systems described here in operation around the globe.

were selected to show the regional and seasonal variability one can expect in this region of the North Atlantic.

In the sub-polar gyre, east of longitude 50°W, the $f\text{CO}_2$ observed in August is markedly lower than that observed in the winter due to the effect of a spring bloom that happens around April–May in that region (Corbière et al., 2007; Takahashi et al., 1993). The decrease in $f\text{CO}_2$ due to the decrease in temperatures in the winter is overcome by the upwelling of CO_2 -rich waters so that the sub-polar gyre changes from a moderate sink in the summer to a weak source of CO_2 in the winter. West of that region along the track, the increase in $f\text{CO}_2$ in the summer months is due to the increase in temperature of the water (see Fig. 9). In the winter, the upwelling of CO_2 -rich waters does not fully compensate for the decrease of $f\text{CO}_2$ due to the decrease of temperatures so that this region goes from being a weak sink in the winter to a moderate source in the summer.

The atmospheric values measured near Reykjavik, Iceland are compared with the record of flask data collected at the Icelandic station of the NOAA/ESRL's Global Monitoring Division (Storhofdi, Vestmannaeyjar, Iceland) in Fig. 10. To compare it with our system, the flask data have been linearly interpolated to our sampling time. Although we expect the error in the estimates from such a procedure to be high due to the fairly high variability of the atmospheric CO_2 (within a week, the $x\text{CO}_2$ commonly vary

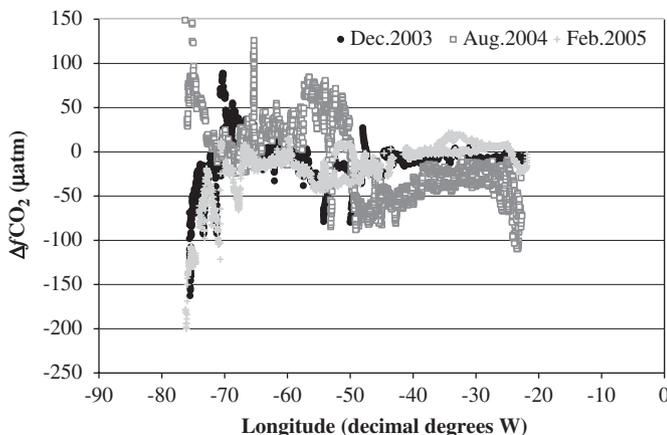


Fig. 8. Plot of $\Delta f\text{CO}_2$ (sw-atm) between Iceland and North America in December 2003, August 2004, and February 2005 measured onboard the M/V *Skogafoss*.

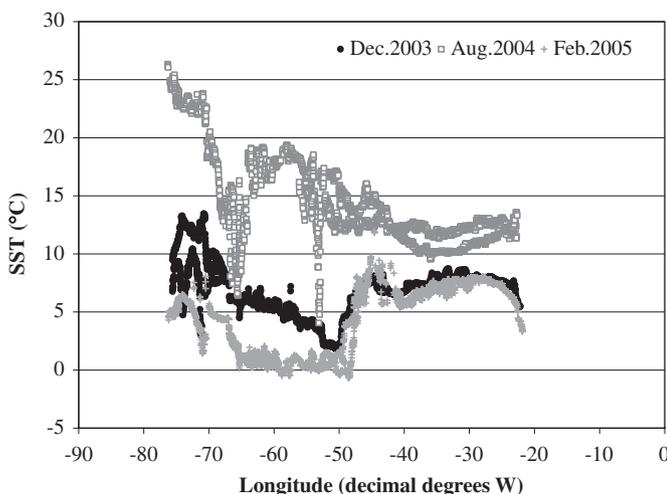


Fig. 9. Sea-surface temperature between Iceland and North America in December 2003, August 2004, and February 2005 measured onboard the M/V *Skogafoss*.

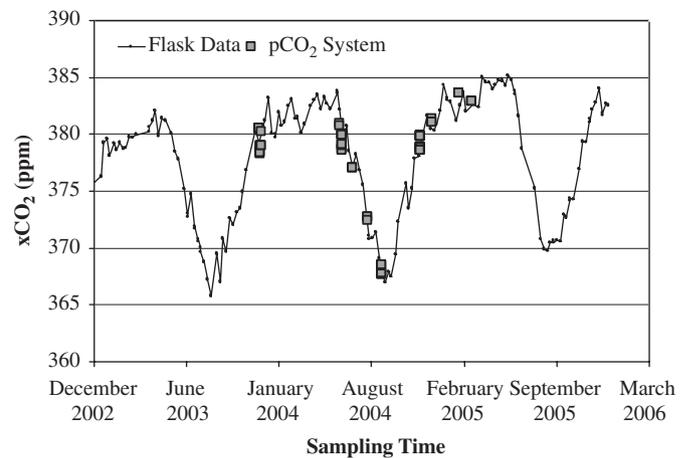


Fig. 10. Flask data collected at the Icelandic station of the NOAA/ESRL Global Monitoring Division compared with the atmospheric measurements of the $p\text{CO}_2$ system.

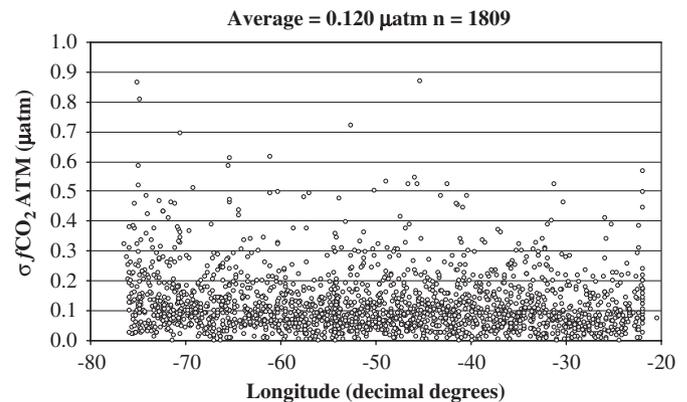


Fig. 11. Standard deviations of atmospheric fugacity measurements made on board the M/V *Skogafoss*.

by as much as 2 ppm) and despite the close proximity to land, the values measured by the system agree with the flask data to ± 0.8 ppm.

The precision of the system for atmospheric measurements is shown in Fig. 11, which is a plot of the standard deviations of the fugacity measurements made within 10 min of each other versus longitude for the 3 years that the system was onboard the M/V *Skogafoss*. The average standard deviation is $0.120 \mu\text{atm}$, which is below the $0.2 \mu\text{atm}$ accuracy limit.

The M.V. *Nuka Arctica* transits monthly between Norway and Greenland with a $p\text{CO}_2$ system onboard (Olsen et al., 2008). Its track crossed the M.V. *Skogafoss* path between Iceland and Greenland, allowing us to compare the systems installed on these two different vessels. The data collected in early February 2005 are compared in Fig. 12, which shows that the two systems agree with each other within the specified accuracy of $2 \mu\text{atm}$.

5. Conclusion

With more than 25 units manufactured, the system described here is quickly becoming the standard for underway $p\text{CO}_2$ measurements. It is compact and versatile enough to be used on any platform, ranging from a laboratory bench to the engine room of a commercial ship, and requires minimal maintenance. Its wide use will allow the collection of $p\text{CO}_2$ data sets of comparably good

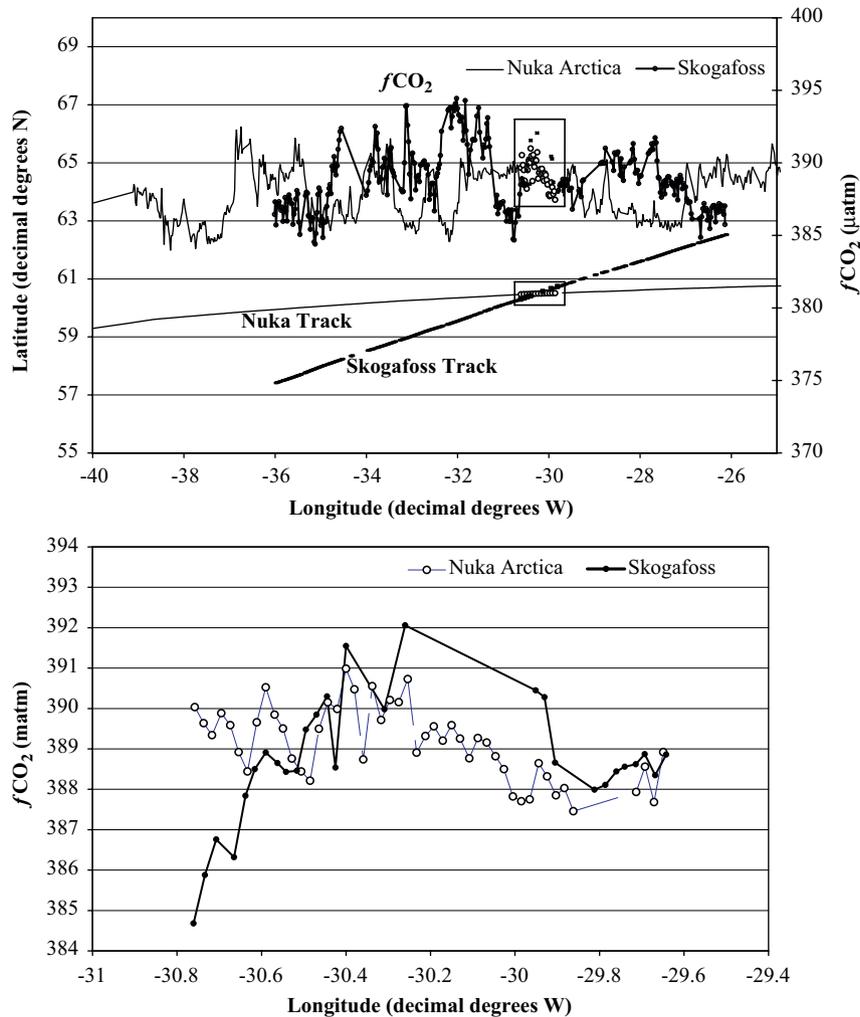


Fig. 12. Comparison of Nuka Arctica and Skogafoss measurements at a cross-over region. The bottom graph is a close-up view of the cross-over data enclosed in the box in the top graph.

quality. The accuracy of $2 \mu\text{atm}$ for seawater and $0.2 \mu\text{atm}$ for atmospheric air that the system can achieve will enable the community to reach the goal of constraining the air–sea CO_2 flux to 0.2PgCyear^{-1} (Bender et al., 2002). The recommended data-reduction procedures will further ensure that the calculated $f\text{CO}_2$ values are consistent between the different data sets. The flagging system proposed, as well as the data to be reported, will increase the usefulness of data sets and allow potential users to better judge the quality of the data. Two programs, one in Visual Basic for Excel[®] and another in Matlab[®], have been written to aid in the application of the proposed procedures and can be obtained from the authors. They will be posted on the CDIAC website as well.

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References

- Bender, M., Doney, S., Feely, R.A., Fung, I.Y., Gruber, N., Harrison, D.E., Keeling, R., Moore, J., Sarmiento, J., Sarachik, E., Stephens, B., Takahashi, T., Tans, P.P., Wanninkhof, R., 2002. A Large Scale Carbon Observing Plan: In Situ Oceans and Atmosphere (LSCOP). Nat. Tech. Info. Service, Springfield, p. 201.
- Copin-Montegut, C., 1988. A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. *Marine Chemistry* 25 (1), 29–37.
- Corbière, A., Metz, N., Reverdin, G., Brunet, C., Takahashi, T., 2007. Interannual and decadal variability of the oceanic carbon sink in the North Atlantic subpolar gyre. *Tellus B* 59 (2), 168–178.
- Dickson, A.G., Sabine, C.L., Christian, J.R. (Eds.), 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3.
- Feely, R.A., Wanninkhof, R., Milburn, H.B., Cosca, C.E., Stapp, M., Murphy, P., 1998. A new automated underway system for making high precision $p\text{CO}_2$ measurements onboard research ships. *Analytica Chimica Acta* 377 (2–3), 185–191.
- Feely, R.A., Takahashi, T., Wanninkhof, R., McPhaden, M.J., Cosca, C.E., Sutherland, S.C., Carr, M.E., 2006. Decadal variability of the air–sea CO_2 fluxes in the Equatorial Pacific Ocean. *Journal of Geophysical Research-Oceans* 111 (C8), S90.
- Goyet, C., Millero, F.J., Poisson, A., Shafer, D.K., 1993. Temperature dependence of CO_2 fugacity in seawater. *Marine Chemistry* 44 (2–4), 205–219.
- Körtzinger, A., Mintrop, L., Wallace, D.W.R., Johnson, K.M., Neill, C., Tilbrook, B., Towler, P., Inoue, H.Y., Ishii, M., Shaffer, G., Torres Saavedra, R.F., Ohtaki, E., Yamashita, E., Poisson, A., Brunet, C., Schauer, B., Goyet, C., Eiseid, G., 2000. The international at-sea intercomparison of $f\text{CO}_2$ systems during the R/V Meteor Cruise 36/1 in the North Atlantic Ocean. *Marine Chemistry* 72 (2–4), 171–192.
- Lüger, H., Wanninkhof, R., Wallace, D.W.R., Körtzinger, A., 2006. CO_2 fluxes in the subtropical and subarctic North Atlantic based on measurements from a volunteer observing ship. *Journal of Geophysical Research-Oceans* 111 (C6), 6020–6024.
- Olsen, A., Brown, K.R., Chierici, M., Johannessen, T., Neill, C., 2008. Sea-surface CO_2 fugacity in the subpolar North Atlantic. *Biogeosciences* 5 (2), 535–547.
- Takahashi, T., 1961. Carbon dioxide in the atmosphere and in Atlantic Ocean water. *Journal of Geophysical Research* 66, 477–494.

- Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W., Sutherland, S.C., 1993. Seasonal-variation of CO₂ and nutrients in the high-latitude surface oceans—a comparative study. *Global Biogeochemical Cycles* 7 (4), 843–878.
- Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F., Watson, A., Bakker, D.C.E., Schuster, U., Metz, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Sabine, C., Hoppema, M., Olafsson, J., Arnarson, T.S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., de Baar, H.J.W., Nojiri, Y., Wong, C.S., Delille, B., Bates, N.R., 2009. Climatological mean and decadal change in surface ocean pCO₂, and Net Sea–air CO₂ flux over the global oceans, *Deep-Sea Research II*, this issue [[doi:10.1016/j.dsr2.2008.12.009](https://doi.org/10.1016/j.dsr2.2008.12.009)].
- Trenberth, K.E., Karl, T.R., Spence, T.V., 2002. The need for a systems approach to climate observations. *Bulletin of the American Meteorological Society* 83 (11), 1593–1602.
- Wanninkhof, R., Thoning, K., 1993. Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods. *Marine Chemistry* 44 (2–4), 189–204.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* 2, 203–215.
- Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry* 8, 347–359.
- Weiss, R.F., Jahnke, R.A., Keeling, C.D., 1982. Seasonal effects of temperature and salinity on the partial pressure of CO₂ in seawater (Pacific Ocean). *Nature* 300 (5892), 511–513.