Australia's National
Science Agency

Surface water CO_2 measurements from ships of opportunity

A report for Australia's Integrated Marine Observing System

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Important disclaimer

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Acknowledgments

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Part I System description

1 Introduction

Underway measurements of the fugacity of carbon dioxide (fCO_2) in surface waters and the atmosphere are made using General Oceanics Incorporated Model 8050 or 8060 systems (GO) equipped with LI-COR® gas analysers. The measuring system and data handling are outlined below.

These data are used for constructing global and regional carbon budgets and for the tracking variability in ocean CO_2 uptake and ocean acidification (Tilbrook et al., 2019; Sutton et al., 2021; Friedlingstein et al., 2022). A measurement uncertainty of ±2 μatm for the fCO_2 of surface waters meets the carbon measurement criteria for the Global Ocean Observing System Essential Ocean Variable (EOV) and the Essential Climate Variable requirement (ECV) for the Global Climate Observing System. The EOV/ECV measurement criteria are needed to constrain global ocean CO_2 uptake to within 10%, and to detect decadal trends in surface ocean carbon (Wanninkhof et al., 2019; Sutton et al., 2022). Data release follows FAIR principles for transparent and traceable data (Wilkinson et al., 2016, Tanhua et al., 2019). Data are available through the Australian Ocean Data Network (AODN) as daily near real-time data and a final quality-controlled product released within six months of collection. These data are also made available in annual updates of the Surface Ocean Carbon Atlas, a uniformly quality-controlled data product for the ocean (Bakker et al., 2016) and contribute to the Surface Ocean CO_2 Reference Network (SOCONET) within the Global Ocean Observing System.

2 System components

Major components and ship sensor descriptions used for underway fCO_2 and related biogeochemical measurements are described below. Uncertainties are based on field verification of measurements. Listed accuracies are manufacturer sensor specifications.

Seawater supply

The design of the underway seawater supply and drainage is critical to deliver data to GOOS EOV specifications, with design recommendations in Appendix A. Key considerations are maintaining a reliable seawater supply to the fCO_2 system to ensure the travel time from the intake to the system equilibrator is ideally less than 1-2 minutes and warming is less than 0.6°C in polar waters. The seawater supply to the system should provide a strong bypass flow and pressure (e.g. minimum 30 L/min and 1-2 bar pressure, and higher flow for long pipe runs). The bypass flow is needed to ensure a well flushed supply, help resolve rapid changes across fronts and in coastal regions, and to minimise the potential for biofouling and warming altering the seawater fCO_2. Some of the seawater bypass flow is diverted to the spray equilibration chamber of the fCO_2 system. The seawater flow into the fCO_2 system requires about 4-4.5L/min at 1 bar pressure to supply the main and pre-equilibrator (total of about 2.5

L/min) with the remainder to supply the water jacket of the main equilibrator. Additional flow is required for other sensors.

CO_2 Sensor

Manufacturer: LI-COR either LI-7815, LI-7000 or LI-6262
CO_2 Sensor Resolution: 0.01 ppm
CO_2 Uncertainty Water: ±2 ppm
CO_2 Uncertainty Air: ±0.2 ppm at 420 ppm
Calibration: Four reference standards measured every 3 hours for LI-6252 or LI-7000 sensors, and about every 12 hours for LI-7815 sensors. A set of reference standards takes about 20 minutes before switching to air and seawater measurements. The Li-7815 reports CO_2 mole fraction corrected for water vapour and the LI-6252 and LI-7000 sensors require a correction for residual water vapour measured by the sensors.

CO_2-in-air Reference Gases

Manufacturer: CSIRO Environment, Australia, and NOAA-CMDL, USA. Standards between 0 and 600 ppm are dry and calibrated on WMO X2019 mole fraction scale to cover the range of values expected in the region of measurements.
Uncertainty: ±0.05 ppm.

CO_2 Atmospheric Measurements

Air measurements are made by pumping clean air from an intake outside the ship to the fCO_2 system using 3/8″ o.d. Dekoron® tubing.

Equilibrator

Manufacturer: General Oceanics. Vented shower equilibrator with water jacket. A smaller pre-equilibrator is used to condition air vented into the main equilibrator. The total flow to the equilibrators and water jacket needs to be about 4-4.5 L/min.
Main Equilibrator Water Volume: 0.56 L
Main Equilibrator Headspace Volume: 0.62 L
Main Equilibrator Water Flow Rate: 2.5 L/min
Headspace Gas Flow Rate: 90–120 SCCM

Drying Gas Stream

Manufacturer: General Oceanics and Perma Pure Nafion™
Model: General Oceanics thermoelectric condenser operated at 2-5°C for LI-7815 sensors and an additional in-line Nafion dryer with LI-6252 or LI-7000 sensors.

Sea Surface Temperature

Manufacturer: Sea-Bird Electronics
Model: SBE-38
Accuracy: ±0.001 °C
Resolution: 0.00025 °C
Calibration: Two SBE-38 at the intake can reduce the chance of data loss. Sensors are calibrated annually at CSIRO NATA test facility, Hobart, and field checked against calibrated temperature sensors from CTD casts when possible.

Equilibrator Temperature

Manufacturer: Fluke Hart Scientific®
Model: 1521 or 1523 paired with 5610-9 probe
Accuracy: ±0.01 °C
Resolution: 0.001 °C
Calibration: Calibrated yearly at CSIRO NATA test facility, Hobart.

Laboratory (ambient) Pressure

Manufacturer: GE Druck
Model: DPS81HA-TB-A2-CC-H0-PE, barometric range 400 hPa
Accuracy: ±0.08 hPa
Resolution: 0.01 hPa
Calibration: Factory calibration and periodic checks against Australian Bureau of Meteorology standard barometer.

Equilibrator Headspace Differential Pressure

Manufacturer: Setra® Systems Incorporated
The pressure in the equilibrator is the sum of measurements from a Setra differential pressure sensor connected to the equilibrator headspace and a GE Druck sensor measuring ambient pressure.
Model: 239
Uncertainty: ±0.07 hPa
Resolution: 0.01 hPa
Calibration: Factory calibration. The uncertainty is a combination of the sensor accuracy of ±0.06 hPa and accuracy of reading the sensor by an A/D module of ±0.04 hPa.

Equilibrator seawater flow

Manufacturer: Kobold Messring GmbH
Model: MIM or MIK, 0-10 L/min range
Accuracy: ±0.05 L/min
Resolution: 0.01 L/min
Calibration: Factory calibration.

Equilibrator headspace and vent gas flows

Manufacturer: Honeywell
Model: AWM3100V
Uncertainty: ±5 SCCM
Resolution: 0.1 SCCM
Calibration: Factory calibration, with laboratory check using a flowmeter.

Atmospheric Pressure

Manufacturer: GE Druck
Model: RPT350 or DPS81-HA
Accuracy: ±0.08 hPa
Resolution: 0.01 hPa
Calibration: Factory calibration with periodic checks against Australian Bureau of Meteorology standard barometer.

Sea Surface Salinity

Manufacturer: Sea-Bird Electronics
Model: SBE-45 or SBE-21 thermosalinograph (TSG)
Uncertainty: ±0.03
Resolution: 0.0002
Calibration: Pre-season calibration against IAPSO seawater standards measured at CSIRO, Hobart, using a Guildline Autosal 8400B. Seawater samples are collected from the underway seawater supply, analysed on shore, and used to check salinity measurements. Duplicate TSGs (e.g. ship SBE-21 on main line and SBE-45 near the fCO_2 system) are used to reduce data loss and help to rapidly identify issues including bubble interference and biofouling with either sensor.

Dissolved Oxygen

Manufacturer: Aanderaa
Model: 3835, 4330 or 4835
Uncertainty: ±2 μmol/kg
Resolution: 0.01 μmol /kg
Calibration: Where dissolved oxygen is measured, each sensor is initially calibrated across a range of temperatures and dissolved oxygen, either by the manufacturer or at CSIRO Hobart using a purpose-built calibration system referenced to Winkler titrations (Culberson, 1991), with results fit to a Stern-Volmer equation (Uchida et al., 2008). Subsequent linear calibrations are performed every 6-12 months using another purpose-built system at CSIRO Hobart. The drift over a year for each sensor is typically less than 3 μmol/kg.

Ancillary Ship Data

Meteorological data, ships position and time are taken from the ship's logging system, or a separate GPS and a meteorological station used to provide position, wind speed and direction (e.g. RM Young propeller anemometer or Gill ultrasonic anemometer).

Part II System checks and data quality control

3.1 Pre-deployment checks

The systems are checked in a CSIRO facility in Hobart, Australia, before installation on a ship. New systems should be tested for leaks to ensure components are compliant with ship power requirements.

The seawater measurements are checked against two laboratory-based GO fCO_2 systems by circulating seawater from a temperature-controlled seawater bath of about one cubic metre volume (Figure 1). This test is used to confirm the seawater mole fraction measurements agree to within ±1 ppm prior to installation on a ship. The lab-based GO systems are equipped with stable laser-based CO_2 analysers (LI-COR 7815 or Picarro G2201-i), and all analysers are calibrated using a series of CO_2-in-air standards with known dry CO_2 mole fractions calibrated on the WMO x2019 scale to ±0.05ppm uncertainty.

Figure 1 Test and calibration facility for fCO_2 system pre-deployment checks

3.2 At-sea measurements

The measurement sequence of standard gas, air, and surface water is controlled using National Instruments LabVIEW™ software provided with the fCO_2 system. The procedures are outlined in Pierrot et al. (2009) with some changes resulting from the replacement of earlier analysers (LI-6262 and LI-7000) with LI-7815 CO_2 analysers (Table 1). The LI-6252 and LI-7000 models were used at CSIRO until late 2022 and are still used by many laboratories. The at-sea measurements are checked using daily transmission of data and remote login to the systems from shore.

Table 1 CO_2 analyser operating conditions

Parameter	LI-7815	LI-6262 & LI-7000
[1]Reference gas flow rate, SCCM	120	70
[1]Sample gas flow rate, SCCM	120	90 - 110
[2]Gas flushing time, sec	180	240
Sample gas drying method	condenser only	condenser + Nafion
Sample gas xH2O, mmol/mol	7 - 8	2
Calibration gas interval, hours	12-24	3
Air sample interval, hours	6	3
Analyser zero/span interval	as needed (months)	1 day
Measurement flow mode	continuous	stop-flow
[3]Measurement time	20 second average of 1Hz readings	spot measurement

[1]LI-7815 flow rate is reduced to 120 SCCM by installing a Swagelok® needle valve between the cavity and the vacuum pump.
[2]LI-7815 flushing time depends on the pressure controller used.
[3]Measurement averaging time of 20 seconds is software adjustable for LI-7815 sensors.

Low and high reference gases are used to set the zero and span of the gas analyser response, respectively. The LI-7815 sensor has significantly less drift than earlier model LI-COR CO_2 gas analysers and calibration of the sensor and associated air measurements can be made less frequently. Air measurements are made 6-hourly to resolve temporal and spatial variability. A 12-hourly reference gas measurement interval was chosen to avoid losing large blocks of data (e.g. due to power loss or reference gas flows not set properly). A Valco rotary valve is used to select different gas steams for the CO_2 sensor and with each new gas, time is allowed is allowed to flush the previous sample before recording measurements about every 70 seconds. Data from other sensors (e.g. temperature, salinity, position, meteorology etc.) are polled at the end of each 70 second measurement interval, combined with the CO_2 data, and written as tab separated files. For the LI-7815 sensor, two 20-second average measurements are recorded for each reference gas, followed by four air measurements and the remainder of the measurement cycle is for equilibrator headspace gas.

The GO systems use an Alicat™ Scientific pressure controller to maintain a constant inlet pressure to LI-7815 sensors. The controller is located before the LI-7815 sensor and downstream of the

Valco rotary valve used to change gas streams. The method was developed at CSIRO using a corrosion resistant pressure controller (Alicat, 13-PCS-5PSIG-D), while GO supply a standard controller for non-corrosive gases (Alicat, PC-1PSIG-D-PCV30/5P). The time to flush a new gas stream through the LI-7815 is longer for the standard pressure controller, which is attributed to a small amount of silicone rubber in the flow path adsorbing and releasing CO_2. The flushing time of 180 seconds in Table 1 is based on the corrosion resistant model used by CSIRO, while systems using the standard model should allow up to double this time (Figure 2).

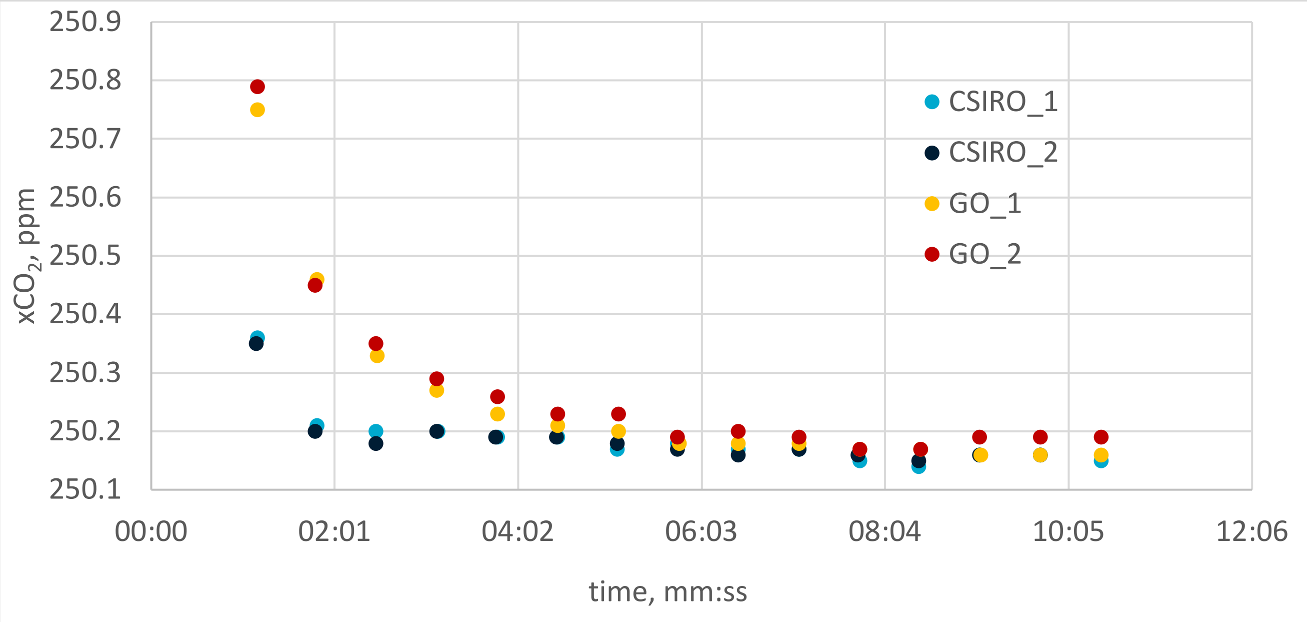

Figure 2 LI-7815 response when switching from 450 ppm to 250 ppm reference gas with different Alicat™ pressure controllers. Each point is a 20 second average of 1 Hz data. CSIRO_1 and CSIRO_2 used a corrosion resistant model, 13-PCS-5PSIG-DPCV30/5P, 5IN, RANGE (-1.5 to 1.5 PSIG, BD, P1: -0.7 to 10 PSIG, P2: -1.5 to 1.5 PSIG, FLOW (100-150 SCCM, air). GO_1 and GO_2 were measured under the same conditions using the controller provided with standard GO systems, PC-1PSIG-D-PCV30/5P 5IN, RANGE (-1.5 to 1.5 PSIG, BD, P1: -0.7 to 10 PSIG, P2: -1.5 to 1.5 PSIG, FLOW (100-150 SCCM, air))

The Valco rotary valve switching bypasses the equilibrator headspace gas for reference gas and air measurements. For surface water measurements, the equilibrator e-fold response time can also influence the time required for stable seawater measurements when there is a step change in either the CO_2 concentration in the equilibrator headspace gas or a rapid change in the seawater fCO_2. The equilibrator has an e-fold response time of about 2 minutes for a water flow of about 1.9 L/min into the main equilibrator and a temperature of 21°C (Pierrot et al., 2008; Webb et al., 2016). The response time is dependent on the water flow rate into the equilibrator and the gas solubility (Butler, 1980) with higher flows and lower temperatures resulting in more rapid response times. At 0°C, the e-fold time will be about 1 minute, while at 30°C the time will increase to about 2.5 minutes, assuming the same water flow and using Ostwald solubility coefficients for seawater calculated from the Bunsen solubility coefficients of Murray and Riley (1971). The time required for 95% re-equilibration of the headspace gas is three times the e-fold time. Provided water flows are adequate to the pre- and main equilibrators and the main vent equilibrator is functioning correctly, changes in seawater CO_2 supplied to the equilibrator is likely to be small over the 70 second measurement interval and extra time allowed for equilibration of the headspace gas is unlikely to be necessary. However, when measurements are switched back to seawater, a large difference in the CO_2 of the headspace gas and seawater may require data to be excluded for longer than the 3- or 4-minute flushing time (Table 1) to maintain a measurement within 2 µatm uncertainty. For example, a 20 µatm step change will equilibrate with the seawater to within 1 µatm within 3 minutes at 0°C and will take 7.5 minutes at 30°C.

3.3 Near real-time data

Near real-time data are transmitted daily when the fCO_2 system is operating. Automatic range checking of variables (Table 2) is used as a preliminary check of the system performance. Out-of-range variables are used to help identify issues related to the different components of the system (e.g. out of range seawater flow, or out of range gas flows to the fCO_2 system). Variable dependencies are used in assessing the data quality (Figure 3). Remote login to the systems are also used for intermittent checks of the system performance.

Table 2 System variables and acceptable measurement ranges. Measurements are either essential (green) for the calculation of fCO_2, are key diagnostic variables (yellow) of sensor performance and the seawater supply, or are additional variables used for data quality control and reporting

Measured variable	Range	fCO_2SW	fCO_2ATM
GPS Date and Time			
Latitude and Longitude			
Atmospheric pressure at sea level	850 – 1100 hPa		
Sea surface temperature	-2 – 35°C		
Sea surface salinity	0 – 37		
[1]SBE21 TSG seawater flow	50 – 65 L/min		
[1]SBE45 TSG seawater flow	1 – 3 L/min		
Vessel speed over ground	0 – 20 knots		
[2]Relative wind speed	0 – 100 knots		
[2]Relative wind direction	0 – 360 degrees		
True wind speed	0 – 100 knots		
True wind direction	0 – 360 degrees		
[3]Seawater supply pressure	1.8 – 2.2 bar		
Water depth	0 – 6000m		
Laboratory air pressure	850 – 1100 hPa		
Equilibrator differential pressure	-1 – 1 hPa		
Equilibrator water temperature	-2 – 33°C		
[4]Equilibrator seawater flow	2.0 – 2.5 L/min		
[5]Equilibrator vent flow	-13 – 15 SCCM		
[6]CO_2 sensor gas flow	70 – 150 SCCM		
[7]Condenser temperature	1.8 – 6.2°C		
LI-6252/7000 mole fraction CO_2	200 – 550 ppm		
LI-6252/7000 mole fraction H_2O	0.1 – 2.5 mmol/mol		

Measured variable	Range	fCO_2SW	fCO_2ATM
[8]LI-6252/7000 pressure	850 – 1100 hPa		
[9]LI-7000 error code	0		
LI-6252/7000 temperature	10 – 41°C		
LI-7815 20-sec average mole fraction CO_2	200 – 550 ppm		
LI-7815 20-sec average mole fraction H_2O	0 – 9000 ppm		
LI-7815 std deviation mole fraction CO_2	0 – 1 ppm		
[9]LI-7815 error code	0		
[10]GO system error codes			

[1]Optimum flow range for TSG salinity values depends on the model. Salinity values are based on seawater conductivity and temperature. Inadequate or zero flow can result in bad values that appear to be within range but are not correct.

[2]Indicator of potential ship stack gas contamination of atmospheric samples.

[3]Optional sensor to identify poor flow to fCO_2 system due to a clogged disk filter before the equilibrator.

[4]Indicates if flow is adequate for a good spray pattern from the equilibrator spray head. The flow rate when the spray becomes inadequate should be identified for each system.

[5]A bi-directional flow from the pre-equilibrator to the main equilibrator maintains laboratory air pressure within the equilibration chamber. Positive values are flow into the equilibrator. Large differences in flow of equilibrator samples compared to reference or atmospheric samples which bypass the equilibration chamber indicate a leak or blockage in the equilibrator circulation loop. A constant reading of about -30 indicates a failed sensor. An Acrodisc™ filter located between the sensor and the equilibrator can extend the life of the flow sensor.

[6]Flow requirements depend on the CO_2 sensor model (Table 1) and sample. The flushing time for each gas for an individual system should be determined by the user.

[7]Required to reduce water vapour in the gas stream to the CO_2 analyser. Condenser temperatures above the range will increase the H_2O mole fraction in the gas stream, and may cause a greater uncertainty in water vapour corrections to CO_2 mole fractions. A poor functioning condenser can cause condensation in the fCO_2 system tubing and system failure, particularly in warmer seas.

[8]Some fCO_2 systems rely on an internal pressure sensor in the CO_2 sensor to measure equilibrator headspace pressure and these must be calibrated frequently. CSIRO only uses systems with Druck pressure sensors.

[9]LI-7000 and LI-7815 sensors transmit error codes. Non-zero codes indicate sensor measurement errors associated with the sensor performance as described in the LI-COR manufacturer manuals.

[10]The GO control software provides multiple diagnostics of the system performance outlined in the GO manual.

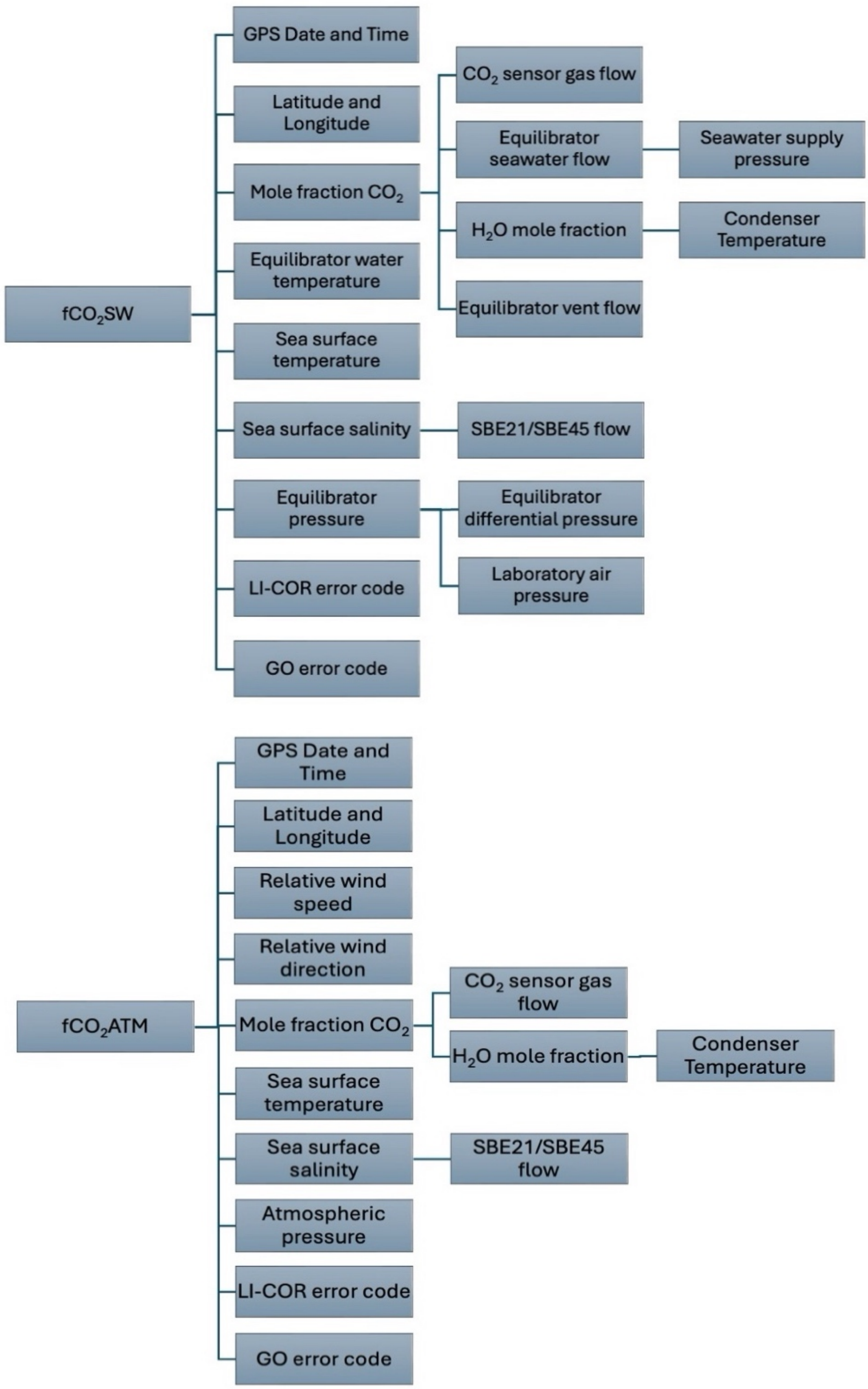

Figure 3 The dependencies of core variables for fCO_2 measurements in seawater (top panel) and air (bottom panel)

A web-based data display (Figure 4) is used to visualise near real-time data and highlight out-of-range values. The display provides additional quality control metrics including the amount of warming between the ship intake and equilibrator and the difference between reference gas measurements and certified values. Provided the ship seawater supply and essential ship variables are working, data returns to EOV/ECV requirements of ±2 μatm uncertainty are typically greater than 97 percent.

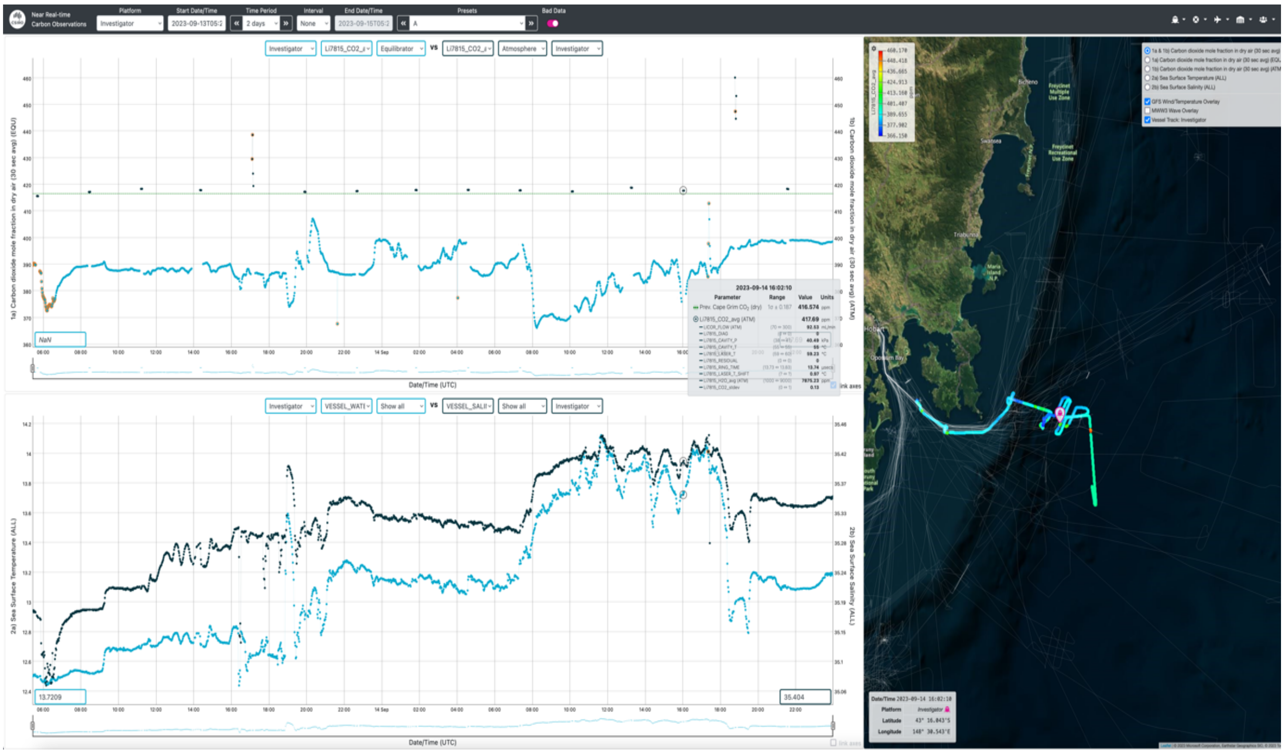

Figure 4 Display of diagnostic variables used to monitor daily system performance. Top left panel, surface water xCO_2 (blue) and air xCO_2 (black). Bottom left panel, sea surface temperature (blue) and salinity (black). Right panel, cruise track with colour-coded surface water fCO_2 values

3.4 Delayed mode data

The data are recalculated with final calibration coefficients applied as described below. The final delayed mode data (Table 4) have WOCE quality flags assigned (good=2, questionable=3, or bad=4) and metadata files written.

- Data with missing variables for the ship or fCO_2 system are marked as missing and removed from calculations. The variable dependencies that can impact LI-COR CO_2 measurements are checked. For example, equilibrator seawater and vent flow rates to the equilibrator can impact the seawater CO_2 mole fraction measurement (Figure 2), and values outside acceptable ranges are flagged as questionable (flag=3), the cause investigated, and the flag value changed to 4 if required. Similar checks are made to ensure the gas flows of air and standards through the LI-COR gas analyser are in acceptable ranges.
- The fCO_2 value of the water is sensitive to warming between the ship intake and equilibrator. The data are next checked to ensure flow and warming of the ship seawater supply from the intake to the equilibrator are within acceptable ranges. The travel time between the ship intake and equilibrator is first checked by comparing the timing of rapid changes in surface water temperature for the intake and the equilibrator temperatures. The target travel time is

1-2 minutes or less and warming of less than 0.4°C, increasing to about 0.6°C in polar waters. When the seawater travel time is greater than 60 seconds, a correction is made to synchronise the intake temperature measurements to other sensor measurements located with the fCO_2 system.

- Surface salinity is checked to ensure flow to the sensor is within range and out-of-range flows are flagged as bad. Intermittent checks of the salinity calibration are made by collecting water samples when the ship is at sea and these samples are analysed using a Guildline 8400B salinometer. All salinometer measurements are referenced to IAPSO seawater standards. A time lag correction calculated from abrupt changes in intake and equilibrator temperatures is used to synchronise the salinity values made next to the fCO_2 system with ship TSGs.
- Air measurements are checked using relative wind speed and direction for signs of contamination of the atmospheric measurements by ship stack gas. Data where relative wind speeds are above $3ms^{-1}$ and with a direction of ±120° from the intake are typically good values. Data with likely contamination are flagged as bad (flag = 4) and not included in the calculation of the air-sea gradient of CO_2.
- After completion of the quality control checks, the measured CO_2 mole fractions are corrected to final values using measurements of the four CO_2-in-air reference gases. The offset between the measured and certified values of each reference gas are linearly interpolated to the times of measurement of the air and equilibrator samples. At each measurement time, a linear regression of offset values for the non-zero reference gases versus certified standard values is used to calculate an adjustment to the measured air and equilibrator values. The LI-7815 sensor has much lower drift with time compared to the LI-6252 or LI-7000 CO_2 analysers. The corrections are typically less than 1 ppm and account for drift of the gas analyser response over time. The corrected mole fractions (dry) for the equilibrator and air samples that are flagged as good or questionable are used to calculate fCO_2.
- For cruises with optode measurements of dissolved oxygen, data with out-of- range water flows are flagged as bad and excluded. Pre- and post-deployment calibrations are compared to determine if the level of sensor drift is within acceptable ranges. and time dependent drift corrections based on pre- and post- deployment calibrations.
- Finalised cruise data files are converted to tab-separated and NetCDF formats. A corresponding metadata file with system component information, ship and voyage details, sensor calibration information, and processing notes detailing data issues and corrections.

Table 3 Data fields and units of final delayed-mode data

Field	Name	Unit	Description
1.	Group/ship		CSIRO/Ship name
2.	CruiseID		Cruise designation
3.	JD_GMT	ddd.hhhh	Decimal day and time of year, GMT time
4.	Date	yyyymmdd	20111231
5.	Time	hh:mm:ss	UTC time
6.	Lat	degrees	Latitude, decimal degrees
7.	Long	degrees	Longitude, decimal degrees
8.	xCO2EQ_PPM	ppm	Mole fraction CO_2 in equilibrator head space gas (dry)
9.	xCO2ATM_PPM	ppm	Mole fraction of CO_2 in the atmosphere (dry)
10.	xCO2ATM_PPM _INTERPOLATED	ppm	Mole fraction of CO_2 in the atmosphere (dry) measured or with values linearly interpolated to sea surface measurement times
11.	Press_Equil	hPa	Equilibrator head space pressure
12.	Press_ATM	hPa	Barometric pressure
13.	TEQ	ºC	Equilibrator water temperature
14.	SST	ºC	Sea surface temperature
15.	SAL	psu	Sea surface salinity
16.	fCO2SW_UATM	µatm	Fugacity of carbon dioxide at surface water salinity and temperature
17.	fCO2ATM_UATM _INTERPOLATED	µatm	Fugacity of CO_2 in the atmosphere, interpolated to seawater measurement times
18.	DfCO2	µatm	fCO_2SW - fCO_2ATM
19.	LICORflow	SCCM	Gas flow through infrared gas analyser
20.	H2Oflow	lpm	Water flow to equilibrator
21.	WindSpd_True	knots	Wind speed
22.	WindDirn_True	degrees	Wind direction, 0 is North and 90 is East
23.	Type		Measurement type (equilibrator, standard or atmosphere)
24.	QC_FLAG		2 = Good 3 = Questionable 4 = Bad (data identified as bad are not reported)
25.	SUBFLAG	-	Secondary flags; 1 = Outside of standard range 2 = Questionable/interpolated SST 3 = Questionable EQU temperature 4 = Anomalous temperature (EQU T-SST > ± 0.6ºC) 5 = Questionable sea-surface salinity 6 = Questionable pressure 7 = Low EQU gas flow **8 =** Questionable air value

3.5 fCO_2SW and fCO_2ATM calculations

The fugacity of carbon dioxide in seawater in the equilibrator is determined using the following equation (Weiss, 1974; Dickson *et al*, 2007; Pierrot *et al*, 2009):

$$fCO_2SWeq = XCO_2(Peq - pH_2Oeq) \bullet \exp[Patm(B + 2\delta)/(R \bullet Teq)] \quad (1)$$

where XCO_2 is the mole fraction (dry) in the equilibrator headspace, Peq is the pressure (atm) in the equilibrator, Patm is atmospheric pressure corrected to sea level, pH_2O is the water vapour pressure (Weiss and Price, 1980) at the temperature (Teq) and salinity (S) of the water in the equilibrator.

$$pH_2Oeq = \exp[24.4543 - 67.4509(100/Teq) - 4.8489\ln(Teq/100) - 0.000544S] \quad (2)$$

R the ideal gas constant (82.0578 $cm^3 \cdot atm/K \cdot mol$), B the virial coefficient of pure CO_2, and δ the cross-virial coefficient of a CO_2-air mixture (Weiss, 1974).

$$B(cm^3/mol) = -1636.75 + 12.0408Teq - 0.032795Teq^2 + 0.0000316528Teq^3 \quad (3)$$

$$\delta(cm^3/mol) = 57.7 - 0.118Teq \quad (4)$$

An empirical equation (Dickson et al., 2007) is used to correct fCO_2 for warming of water between the sea surface (SST) and equilibrator (Teq).

$$fCO_2SW = fCO_2SWeq \bullet \exp[0.0423(SST-Teq)] \quad (5)$$

where fCO_2SW is the fugacity at sea surface temperature (SST) and salinity.

The above equations are applied to the atmospheric measurements of the dry mole fraction of CO_2 in the atmosphere to calculate atmospheric fCO_2 (fCO_2ATM). Peq is replaced with Patm and the calculation of pH_2O uses sea surface temperature and atmospheric pressure corrected to sea level and assumed 100% saturation at the air-sea interface.

The air-sea gradient in fCO_2 is calculated as:

$$DfCO_2 = fCO_2SW - fCO_2ATM \quad (6)$$

Appendix A Installation of underway sensors

Problems related to limited planning for underway sensor requirements are common on ships. These include inadequate space to mount sensors, lack of planning for cable and data runs that require multiple bulkhead penetrations, inadequate seawater supply, drainage not able to handle required flows and requiring major plumbing changes, and inadequate power supplies.

The recommendations listed below are based on setting up underway systems for biogeochemical measurements on multiple ships to deliver high-quality biogeochemical measurements, including to EOV/ECV specifications.

A.1 Intake and seawater supply

1. The seawater intake in the ship hull should, if possible, be located to minimise bubbles and avoid the intake coming out of the water in rough seas and still provide measurements in the surface mixed layer. A shallow intake in the ship bow can compromise data collected by causing bubble interference and air contamination. On smaller vessels, the intake may be best located as deep as possible and forward of propellers.
2. A seawater line separate to water lines used for deck washing or on-deck incubators and large-volume filtration can avoid changes in flow and pressure that can impact underway measurements.
3. The intake pipe from the hull penetration to the seacock should be short and ideally made of copper-nickel to minimise biofouling and corrosion.
4. A reliable sensor for sea surface temperature measurements (e.g. SBE38) should be mounted as close as possible to the intake after the seacock and should be able to be easily removed for maintenance. Dual sensors are a cost-effective way to provide independent check on measurements and avoid data loss if one sensor fails or is being replaced.
5. The intake pump should be downstream of the intake temperature sensor to avoid the pump heating the seawater.
6. Pipework from the hull penetration to instrumentation should be lagged to help reduce the warming between the intake and underway sensor location to less than 0.6°C in polar waters and 0.4°C at lower latitudes.
7. The intake pump should be capable of supplying sufficient flow and pressure to the array of sensors. There should be a constant high flow of seawater through a bypass manifold (e.g. PVC) that runs directly past each instrument and substantially exceeds the total sensor flow and pressure requirements. This is to ensure a short residence time of seawater in the pipework which helps minimise warming of the seawater, and the impact of biofouling by bacterial films that can build up in pipework.
8. The discharge from the bypass manifold is best pumped directly overboard rather than into a ship scupper system, which is often overwhelmed by large volumes of water, particularly when a ship rolls in heavy seas. A separate pressurised drain line in addition to the scupper system can avoid problems later that are difficult to correct.

9. In addition to the discharge of the bypass manifold, many sensors discharge water at atmospheric pressure e.g. into laboratory sink drains, and these drains need to be able to handle the flow in addition to other users. If sink drains are not capable of handling the discharge from the sensors an alternative is to drain into a sump and use a pump with a level sensor to drain the sump.
10. The inlet and seawater supply should have a freshwater connection to allow occasional back flushing of the inlet and underway lines and include another valve for draining the lines to the ship's bilge. Flushing with freshwater and draining the pipework prior to periods of inactivity helps controls biofouling and prolongs the life of pipes. This is ideally done at each port call.
11. Cabling and electronics supplied for remote start-stop of the intake pump and to allow logging of intake sensors.

A.2 Installation of underway sensors

1. Dual salinity and intake temperature sensors are useful for avoiding data loss and provide an independent check of salinity and temperature measurement quality.
2. A dedicated small laboratory for the sensors is useful. If located in a general use laboratory, it is best to isolate the sensors in one part of the laboratory removed from other laboratory users and with easy access for maintenance and cleaning.
3. The location of the sensors should be away from heat sources (e.g. away from engines and large refrigerators) and areas subject to possible salt spray.
4. The air temperature of the space should be controlled as much as possible and hopefully to within 5°C. In tropical regions, high temperatures in the space can amplify problems with water vapour and sensor drift. The air temperature in the instrument space is best if it is at or below about 25°C.
5. A PVC manifold for the seawater supply to the sensors needs to allow rapid flushing of the underway seawater supply and to provide multiple take-off points to instruments. High-purity metering ball valves and fittings (e.g. Georg Fischer **+GF+** 523 PVC-U valves) and pressure control using a back-pressure regulator, such as a Georg Fischer type 586 are useful.
6. Open sink(s) or cup drains allow flow from underway sensors at atmospheric pressure and to provide a tap outlet over a sink for seawater sample collection from the underway supply. Sample collection requires gentle filling of sample bottles and lack of bubble entrainment which means standard laboratory taps with narrow outlets that cause a spray may not be suitable.
7. Freshwater supply to allow for cleaning and backflushing of sensors.
8. Flow requirements for all sensors need to be assessed. Due to the likelihood of seawater spray/corrosion, filtration of water should occur away from the underway instruments and preferably on a separate seawater supply to avoid rapid and intermittent changes in flow rates.
9. Power outlets with appropriate IP rating and clean power are needed for the sensors and preferably on their own subpanel. The power outlets need to be located so they do not take up large amounts of wall space and prevent sensors being mounted on walls.
10. C-channel on walls to allow flexibility with mounting equipment.
11. A clean air-intake from the bow mast to the underway sensor location using 3/8" Dekoron tubing and, where possible, bulkhead penetrations designed to allow a constant run of tubing.
12. Access to nearby sample storage.

13. Capacity to secure CO_2-in-air gas cylinders used for calibration. If not in the laboratory space, then nearby in a location that is accessible and not exposed to seawater spray or rain and with bulkhead penetration(s) for 1/8” gas supply lines. A rack made for easy swapping out of cylinders is ideal.

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