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ACCSP Heron Island - Wistari CO2 mooring

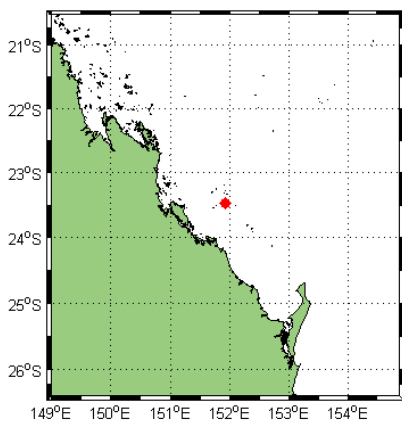
Dataset:

IM05_ANMN-AM_GST_20220516T120000Z_GBRWIS_FV01_GBRWIS-CO2-2205-delayed_END_20221101T000000Z_C-20230227T090519Z.nc

Deployment information

Location:

Heron Island - Wistari Channel, Queensland; -23.4585, 151.9268



Water Depth:

16m

Platform:

IM05_ANMN-AM_CO2_GST

Platform code:

GBRWIS

Deployment code:

GBRWIS_24

Expocode:

09F520220516

Start date

20220516T120000Z

End date

20221101T000000Z

Mooring Bounds: North West South East

-23.459 -23.45791 151.9263 151.9273

Data history

Data report submission:

27-02-2023

Most recent report update:

27-02-2023

Investigators:

Bronte Tilbrook, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia. Email: Bronte.Tilbrook@csiro.auCraig Neill, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia. Email: Craig.Neill@csiro.auErik van Ooijen, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia. Email: Erik.Vanooijen@csiro.auAbe Passmore, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia. Email: Abe.Passmore@csiro.auJames Black, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia. Email: J.Black@csiro.au

Mooring deployment

Deployed

2022-05-16 03:00

Recovered

2022-10-31 21:30

Vessel

Heron Island Mooring

Moored sensors:

Battelle MApCO2 s/n

118

Seabird SBE 16pus_V2 s/n

01606843

Aanderaa Optode s/n

1622

Field personel

Abe Passmore, Garry Curtis, Shannon Palmer

Instrumentation

Erik van Ooijen

Quality control

Erik van Ooijen

Data file description:

Variable [Unit] Description =====

TIME [YYYY-MM-DDThh:mm:ssZ] Time and Date, ISO8601

LATITUDE [deg] Latitude

LONGITUDE [deg] Longitude

XCO2_DRY_SW [μmol/mol] Mole fraction of CO2 in the equilibrator head space

XCO2_DRY_AIR [μmol/mol] Mole fraction of CO2 in the atmosphere

fCO2_WET_SW [μatm] Fugacity of carbon dioxide at surface water, corrected for water vapour at surface water salinity and temperature

dFCO2 [μatm] Delta fCO2 = (fCO2_WET_SW - fCO2_WET_AIR)

ATMOSPHERIC PRESSURE [kPa] Atmospheric pressure

EQUILIBRATOR PRESSURE [kPa] Equilibrator pressure

SEA SURFACE TEMPERATURE [degC] Sea surface temperature

EQUILIBRATOR TEMPERATURE [degC] Equilibrator temperature

SALINITY [PSS] *Sea surface salinity*

DISSOLVED_OXYGEN [$\mu\text{mol/l}$] *Concentration O_2 in surface sea water*

WOCE QC flag 2=good, 3=questionable, 4=bad

SUB_FLAG 24-bit number, internal QC

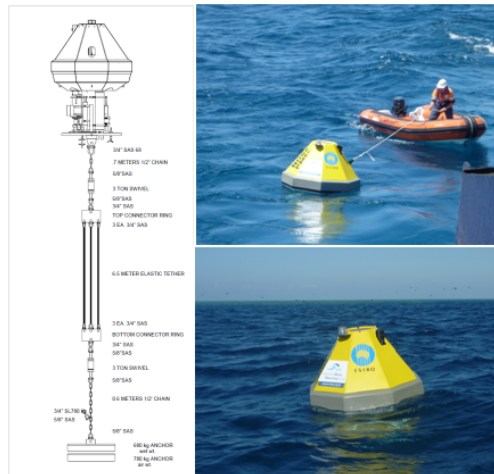
PH Total pH surface water

General system description and procedures

Instrumentation and methods

Measurements are made with a Battelle Seaology pCO₂ monitoring system (MApCO₂), a Seabird SBE16plusV2 CTD, mounted on a surface buoy similar to the system described in Sutton et al. (2014), with an Aanderaa optode used to measure dissolved oxygen concentrations. The seawater sensor intakes for the MApCO₂, SBE16plus V2 and the optode are located at about 1m water depth. The CO₂ measurement uses a bubble equilibrator (Sutton et al., 2014), where the air from the equilibrator headspace is circulated through a LI-COR 820 non-dispersive infrared detector (NDIR) for measurement of CO₂. The system carries out an automated measurement sequence every 2 or 3 hours, depending on the instrumentation setup. At the beginning of each measurement sequence, the NDIR undergoes a two point calibration with a zero CO₂ gas and a high CO₂ standard span gas (typically 450-550 micromol/mol), which bracket the range of CO₂ mole fractions in seawater and air. The zero CO₂ gas is generated by cycling air through a soda lime chamber and silica gel to remove CO₂ and water vapour, respectively. The CO₂ span gas is prepared by the NOAA Earth Systems Research Laboratory in the USA and calibrated on the WMO X2007 scale with a standard deviation of 0.06 micromol/mol (<http://www.esrl.noaa.gov/gmd/cc/airstandard.html>). Each measurement cycle of zero and span gas, equilibrator headspace, and air takes 20 minutes with the equilibrator headspace measurement occurring at about 17 minutes followed by the air measurement. The pressure measurements are considered the same for the equilibrator headspace gas and air measurements due to the design of the MApCO₂ system (Sutton et al., 2014) as are the temperature and salinity of the surface seawater and the equilibrator measured by the Seabird SBE16plusV2.

Location and mooring design



The Heron Island Wistari mooring is located on the east side of Heron Island in the Wistari Channel in about 16m water depth. A 700kg anchor holds the mooring buoy in position, which is connected to the surface buoy via a 16.5m bungee used to dampen wave action. As part of regular maintenance and to minimise the effects of biofouling, the mooring is recovered every six months, the mooring line checked and replaced if necessary, and a replacement surface buoy and newly calibrated sensors swapped in.

Testing and calibration procedures

The LI-COR 820 sensor response is checked before and after each deployment using a range of CO₂-in-air reference gases (0, 260, 370, 450 micromol/mol) at CSIRO, Hobart. The sensor measurement using factory calibrations for the LI-CO₂ 820 is typically within 1 micromol/mol of the reference gas value. If the LI-COR 820 measurements and the CO₂-in-air reference gas values are different by more than 2 micromol/mol, a correction is applied to LI-CO₂ 820 output based the reference gas values. A seawater bath operated over a range of temperatures and CO₂ expected in the field is then used to check the MApCO₂ system (equilibrator and LI-COR 820 measurement) against a General Oceanics 8050 CO₂ sensor to ensure the systems agree within 2 micromol/mol. Pressure measurements are made using the LI-COR 820 pressure sensor, checked against a Druck DPI142 pressure indicator and verified to agree within 0.5 kPa before and after each deployment. The air CO₂ values are compared to Globalview CO₂ products, although these can result in some variability due to limited data in Globalview to constrain atmospheric boundary layer CO₂ measurements in coastal regions of the Southern Hemisphere.

A SBE16plus V2 CTD is polled for the temperature, salinity, and dissolved oxygen data for each MApCO₂ measurement sequence, with additional measurements made each hour. The SBE16plusV2 temperature and salinity measurements use either factory calibrations for initial deployments, or annual calibrations performed at a certified National Australian Testing Authority facility at CSIRO, Hobart. The optodes are calibrated before and after deployments at CSIRO, Hobart, using a purpose built calibration system, referenced to dissolved oxygen measurements made using modified Winkler titrations (Culbertson, 1991). The calibrations cover a range of temperatures and oxygen concentrations that occur in the field and new calibration coefficients are generated to fit a Stern-Volmer equation (Uchida et al., 2008).

The DuraFET-based SeapHet sensor (Satlantic or Scripps design, Martz et al., 2010) obtains a sample hourly. The sensor uses a single pair of bottle samples for DIC and Alkalinity taken on site for calibration, where CO₂SYs is used for the calculation of pH (see next section).

Data reduction and quality control

Fugacity

After recovery of the instrument the data from the MApCO₂ and the SBE16plus is downloaded. The data are recorded at each 2 or 3 hourly measurement interval as blocks of measurements of equilibrator headspace gas, air, zero and span gas values. The data blocks are checked for size and the MApCO₂ data is checked for outliers and corrected using the Thomson Tau method (Thompson, 1985).

The NDIR detection is based on the absorption of infrared light by CO₂. For each measurement cycle, the zero and span gas are analysed immediately before equilibrator air or atmospheric gas measurements to calibrate the LI-COR 820 NDIR response and provide a measurement of the CO₂ mole fraction in the gas stream. The gas stream analysed by the NDIR is only partially dried by flowing the gas through silica gel and the same light absorbed by CO₂ is also absorbed by water vapour present in the gas. A dilution correction is applied to account for the presence of water vapour that is measured in the gas using a humidity sensor (LI-COR Application note 129):

$$xCO_2 = \frac{xCO_2^{raw}}{(1 - w/1000)}$$

where w is calculated water vapour mole fraction and xCO_2^{raw} is the raw data value for the CO₂ mole fraction measured in the gas stream by the LI-COR 820 NDIR.

The partial pressure of CO₂ in the water is calculated by applying a water vapour pressure correction:

$$pCO_2 = xCO_2(P - p[H_2O])$$

with,

$$p[H_2O] = \exp 24.4543 - 67.4509 \frac{100}{T} - 4.8489 \ln \frac{T}{100} - 0.000544S$$

the calculated water vapour pressure of the equilibrator sample at the sea surface temperature, T (K), and Salinity, S (Weiss and Price, 1980) and P is the total pressure in atmospheres.

The partial pressure of CO₂ is converted to fugacity using (Weiss, 1974):

$$fCO_2 = pCO_2 \exp \frac{P(B(CO_2, T) + 2\delta(CO_2, T))}{RT}$$

where, $R = 82.0578 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, $B(\text{CO}_2, T) = -1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3$ and, $\delta(\text{CO}_2, T) = 57.7 - 0.118T$

Dissolved oxygen

Two voltage signal ($V0$ and $V1$) related to the bphase (Bp) and the temperature ($Topt$, in degrees Celsius) by:

$$Bp = 12V0 + 10; Topt = 9V1 - 5$$

from the Aanderaa optode are measured and stored by the SBE16plus. From these values a pre- and post-calibrated dissolved oxygen values (DO_{raw}) are calculated using the Stern-Volmer equation (Uchida et al., 2008), and the corresponding pre- and post- calibration coefficients (Appendix 3);

$$DO_{raw} = \frac{(c4 + c5Topt)/(c6 + c7Bp) - 1}{c1 + c2Topt + c3Topt^2}$$

This value for dissolved oxygen applies to use in fresh water and therefore needs to be compensated for seawater salinity using:

$$DO_{sc} = DO_{raw} \exp S(B0 + B1T_S + B2T_S^2 + B3T_S^3) + C0S^2$$

With S the salinity obtained by the SBE16plus and

$$T_S = \ln \frac{298.15 - T}{273.15 + T}$$

With T the temperature obtained in Celsius by the SBE16plus, and $B0 = -6.24097\text{e-}3$, $B1 = -6.93498\text{e-}3$, $B2 = -6.90358\text{e-}3$, $B3 = -4.29155\text{e-}3$, $C0 = -3.11680\text{e-}7$.

Subsequently, a drift correction is calculated and applied from the calibration data for each of the pre- and post-calibrated and salinity compensated values. From these values an average value for the dissolved oxygen (DO) and a standard deviation (SD_DO) is obtained, which is interpolated at the time when the MAPCO2 equilibrator pump off cycle ends.

pH

The raw pH voltage data obtained by the instrument for both the internal as external reference pH values are calibrated using a single DIC and Total Alkalinity sample pair obtained at the site when the sensor is taking a sample. The pH on the total scale (pHt) at in-situ temperature and salinity is calculated using DIC and total alkalinity with CO2SYS (Van Heuven et. al. 2011), using the Lueker et al (2000) K1/K2 dissociation constants, bisulfate (HSO_4^-) dissociation constant of Dickson (1990), the hydrofluoric acid dissociation constant of Perez and Fraga (1987) and the boron-salinity ratio of Uppstrom (1979). The maximum total phosphate and silicate concentrations measured at the Maria Island site of 0.5 and 1.8 micromol/kg, respectively, cause less than a 0.001 reduction in pHt and are assumed zero for the calculation. The calculated pH value is then used to calibrate the linear response of pH vs the raw voltages and calculated for both internal and external references, where the internal reference pH values are published. The external pH values are used as a QC test for the internal pH data. More details can be found in P.J. Bresnahan et. al. (2014) and T. Martz et. al (2010)

Data report

Automated data quality control report:

For first order quality control, automated checking of value ranges for a number of diagnostic parameters are checked, and subflags assigned to values outside the accepted ranges listed in Appendix 2. The summary results of the automated data checking procedure were:

Flagged data points:

```
XC02 Span pump off or post cal out of range
2022/05/28, 06:00:00
2022/08/27, 06:00:00
2022/10/23, 02:00:00
```

Delayed mode quality control report:

After automated checking, data are plotted and manually checked in a final delayed mode quality control with WOCE (<http://cchdo.ucsd.edu/formats>) quality flags used, where 2=good, 3=questionable, 4=bad, with the following result:

```
Reason: Data obtained after recovery-> Action: Manually set to bad:
2022/11/01,00:00:00
Reason: Data possibly obtained after recover-> Action: Manually set to questionable:
2022/10/31,22:00:00
Manual set to bad data
Reason:Data obtained after recovery
31-Oct-2022 22:00:00-01-Nov-2022
```

Low salinity values are verified using NRS data at MAI site (<http://www.csiro.au/tasman/nrsweb/>) and BOM flood history data (http://www.bom.gov.au/tas/flood/flood_history/flood_history.shtml).

Final data quality summary:

Parameter	% flag = 2 good	Number Points
fCO2 sea water	99.752842	2018
XC02 atmosphere	99.752842	2018
Sea Surface Temperature	99.901137	2021
Sea Surface Salinity	99.901137	2021
Dissolved Oxygen	99.950568	2022
Total pH	99.901137	2021

Data summary:

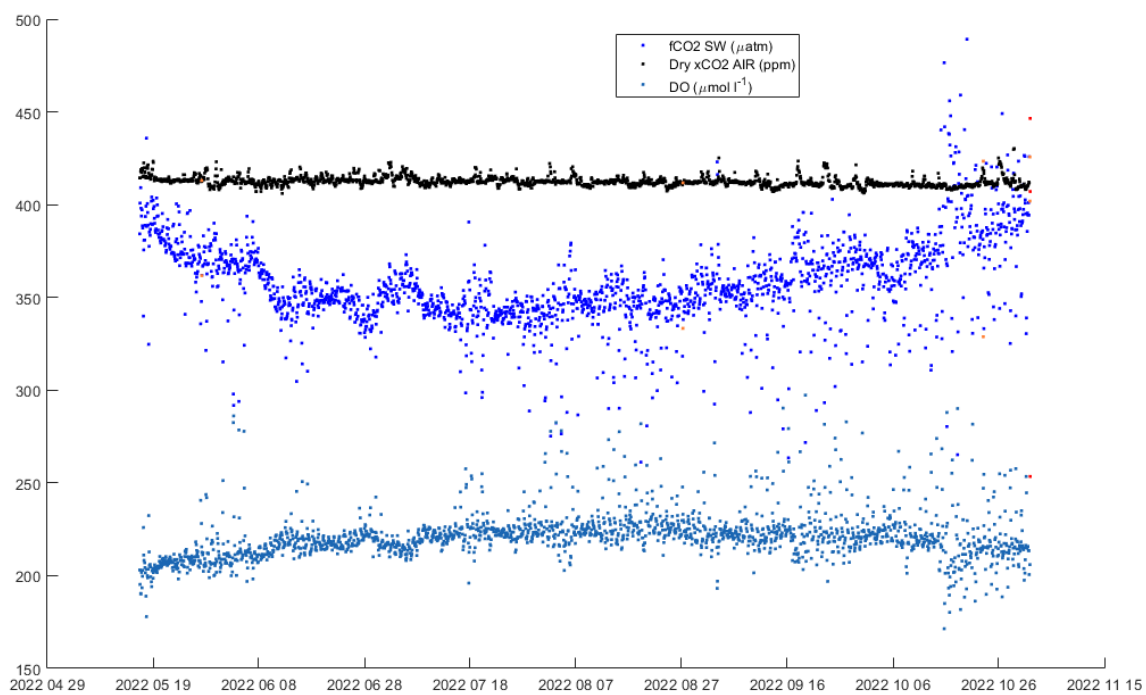


Figure 1: xCO₂ (ppm) for air, fCO₂ (μatm) and Dissolved Oxygen (DO; μmol/l) for sea water. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

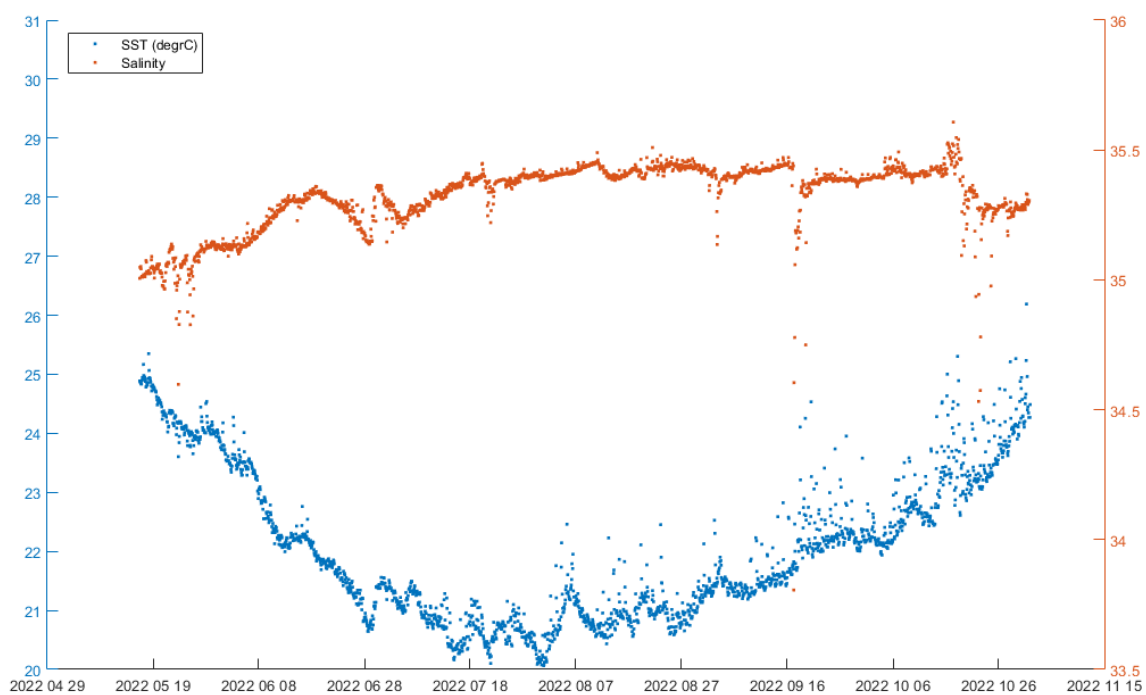


Figure 2: Sea Surface Temperature and Salinity. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

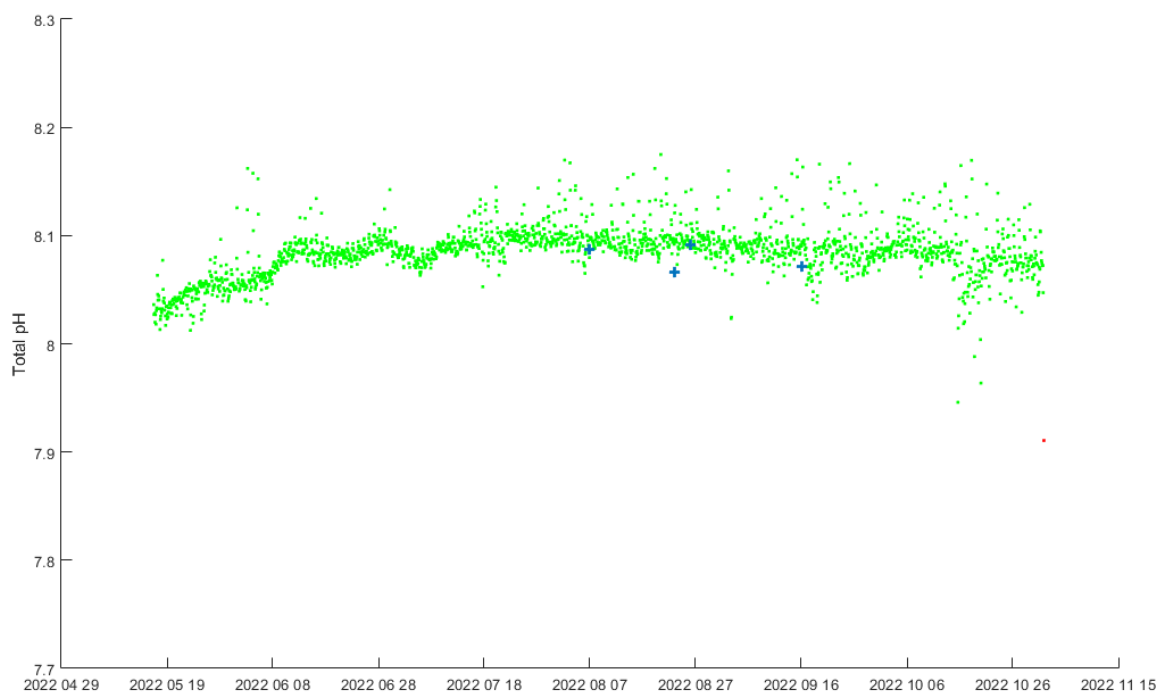


Figure 3: Total pH SeapHox. Bottle samples are indicated in blue.

Appendix 1: Instrumentation specifications

Seaology pCO2

MANUFACTURER: Battelle Memorial Institute, Columbus, Ohio, USA
 WEBSITE: <http://battelle.org/our-work/national-security/maritime-systems>
 MODEL: Seaology
 SERIAL NO: 118
 FIRMWARE VERSION: 3.18
 EQUILIBRATOR DESIGN: Bubble Equilibrator
 EQUILIBRATOR VOLUME: Less than 100 ml of air equilibrating with an unlimited volume of seawater
 HEADSPACE GAS FLOW RATE: ~600 cc/min
 VENTED: yes
 INTAKE DEPTH: 1m
 MEASUREMENT METHOD: Absolute, non-dispersive infrared (NDIR) gas analyser

CO2 and Equilibrator and Air Pressure Sensor:

MANUFACTURER: LI-COR, Lincoln, Nebraska, USA
 WEBSITE: <http://www.licor.com/env/>
 MODEL: LI-820
 CO2 RESOLUTION: 0.1 $\mu\text{mol/mol}$
 CO2 UNCERTAINTY: < 2 $\mu\text{mol/mol}$ based on comparisons in the laboratory before and after deployment with four WMO X2007 referenced gas standards (0, 260, 370, 450 $\mu\text{mol/mol}$) and < 2 $\mu\text{mol/mol}$ based on pre-deployment comparison in the laboratory with equilibrator headspace measurements of seawater made using a General Oceanics model 8050 pCO2 measurement system (General Oceanics, Miami, Florida, USA).
 PRESSURE RESOLUTION: 0.01 KPa
 PRESSURE UNCERTAINTY: < 0.5 KPa, Based on laboratory comparison against Druck DPI 142 pressure indicator
 CALIBRATION DATE: 2021-07-11

Relative Humidity Sensor:

MANUFACTURER: Sensirion Humidity Sensor, USA
 WEBSITE: <http://www.sensirion.com>
 MODEL: SHT71
 MEASUREMENT RANGE: 0-100%
 ACCURACY: +/- 3% (20-80% RH)
 CALIBRATION: Factory calibration before purchase
 RH CORRECTION: yes

CO2 Span Gas:

MANUFACTURER: NOAA Earth Systems Laboratory, USA
 CYLINDER NUMBER: JB03780
 GAS CYLINDER PRESSURE, PRE-DEPLOYMENT: 1000 psi
 GAS CYLINDER PRESSURE, POST-DEPLOYMENT: 750 psi
 CO2-IN-AIR CONCENTRATION (WMO X2007): 554.72 PPM
 CALIBRATION DATE: 2015-06-22

O2 Sensor:

MANUFACTURER: Aanderaa, Norway
 WEBSITE: <http://www.aanderaa.com/>
 MODEL: 4175
 SERIAL NO: 1622

FOIL BATCH NO: 1023
 RESOLUTION: <1 μ M
 UNCERTAINTY: < 1 μ mol/l, based on Winkler oxygen titrations at CSIRO, Hobart
 CALIBRATION DATE: PRE-DEPLOYMENT: 02-Jun-2020 POST-DEPLOYMENT: 02-Jun-2020
 OPTODE USED: Seaphox optode (pumped)
 PERCENT DRIFT CORRECTION APPLIED: 0%

CTD Sensor (Equilibrator and Sea Surface):

MANUFACTURER: Sea-Bird Electronics, Bellevue, Washington, USA
 WEBSITE: <http://www.seabird.com/>
 MODEL: SBE 16plusV2_seacat
 SERIAL NO: 01606843
 RESOLUTION: 0.0001 °C; 0.00005 S/m
 UNCERTAINTY: 0.005 °C; 0.0005 S/m
 CTD DEPTH: 1 m
 CALIBRATION DATE: 22-07-2021

pH sensor:

MANUFACTURER: Scripps Institution of Oceanography, USA
 MODEL: Scripps SeapHox
 SERIAL NO: 8
 RESOLUTION: 0.001
 UNCERTAINTY: 0.02
 CALIBRATION: Calibrated using IMOS DIC and TALK bottle sample

Appendix 2: Range limits

Range limits for assigning flags to instrument diagnostic parameters. Values outside the ranges are automatically flagged as bad. Max SD is the maximum standard deviation of all readings at each measurement time.

Variable Min Max

Span Value Deviation	-5	5
Zero Value Deviation	-5	5
Delta pressure Atmosphere	5	9
Delta pressure Equilibrator	5	9
Max SD_XCO2_EQUIL_PUMP_ON		10
Max SD_xCO2/ pCO2/ fCO2		2
Max SD_PRESS_LICOR_EQUIL_PUMP_OFF		0.05
MAX SD_PRESS_LICOR_AIR_PUMP_OFF		0.1
MAX SD_TEMP_LICOR air/equil/span		0.1
MAX SD_RH_AIR_PUMP_OFF	1	
MAX SD_RH_EQUIL_PUMP_OFF	1	
MAX SD_RH_TEMP_AIR_PUMP_OFF		0.05
MAX SD_RH_TEMP_EQUIL_PUMP_OFF		0.05
MAX SD_RH_SPAN_PUMP_OFF	3	
MAX SD_RH_TEMP_SPAN_PUMP_OFF		0.05
SBE Temperature	-2	40
SBE Salinity	0	42
Optode DO	50	400

Appendix 3: Instrument calibration coefficients

Oxygen optode calibrations coefficients for optode 4175 serial number 1622 foil number 1023:

Coefficient	Pre-deployment	Post-deployment
C1	0.0024333	0.0024333
C2	0.00010627	0.00010627
C3	1.8836e-06	1.8836e-06
C4	233.2	233.2
C5	-0.22753	-0.22753
C6	-36.921	-36.921
C7	4.0737	4.0737

Seabird SBE16plus V2, serial number 01606843 calibration coefficients:

Temperature	Coefficient
TA0	0.0012933
TA1	0.00025771
TA2	-1.5521e-09
TA3	1.3852e-07
TOFFSET	0

Salinity	Coefficient
G	-0.99513
H	0.15866
I	-0.00028957
J	4.7348e-05
CPCOR	-9.57e-08
CTCOR	3.25e-06
CSLOPE	1

Additional information:

The CO2/acidification mooring at the Heron Island was initially funded through and Ocean Carbon and Acidification project of the Australian Climate Change Science Program awarded to BT. The mooring is now funded through the Integrated Marine Observing System - supported by the Australian Government through the National Collaborative Research Infrastructure Strategy. Users of these data are requested to cite the data source as below and to send copies of manuscripts to the PI prior to submission to ensure data are accurately represented.

Citation:

We rely on users of these data to recognise the effort required to obtain data by citing these data as:

B. Tilbrook, E. van Ooijen, C. Neill, A. Passmore and J. Black (2018) Ocean and atmosphere CO2 system timeseries measurements from Wistari Channel, Heron Island, Australia. <http://imos.aodn.org.au/imos123/>

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Attachments

No attachments

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