

## Contents

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- [ACCSP Heron Island - Wistari CO2 mooring](#)
- [General system description and procedures](#)
- [Data reduction and quality control](#)
- [Data report](#)
- [Appendix 1: Instrumentation specifications](#)
- [Appendix 2: Range limits](#)
- [Appendix 3: Instrument calibration coefficients](#)
- [Additional information:](#)
- [Citation:](#)
- [References](#)
- [Attachments](#)

## ACCSP Heron Island - Wistari CO2 mooring

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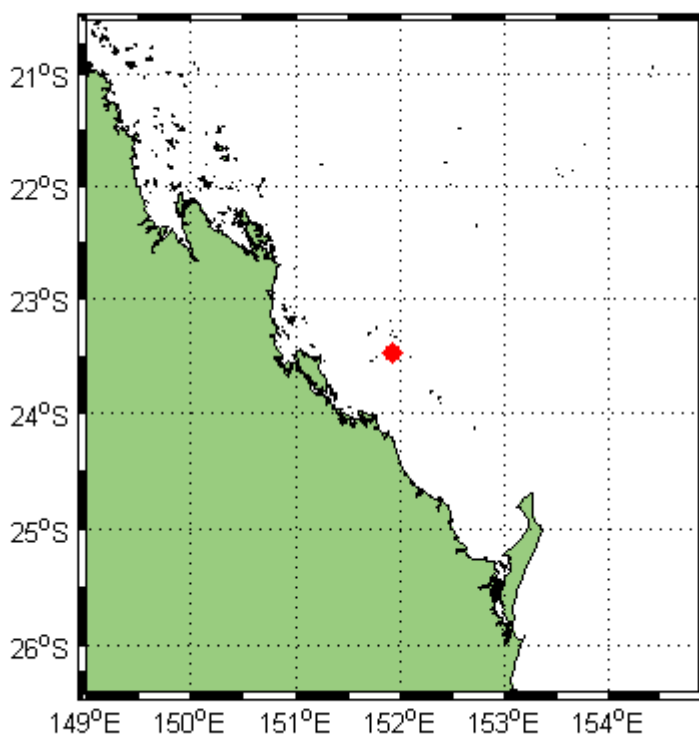
### Dataset:

IMOS\_ANMN-AM\_GST\_20210327T100000Z\_GBRWIS\_FV01\_GBRWIS-CO2-2103-delayed\_END\_20210920T040000Z\_C-

### Deployment information

#### Location:

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



Water Depth:

16m

Platform:

IMOS\_ANMN-AM\_C02\_GST

Platform code:

GBRWIS

Deployment code:

GBRWIS\_22

Expocode:

09FS20210327

Start date

20210327T100000Z

End date

20210920T040000Z

Mooring Bounds: North West South East

-23.45887      -23.45806      151.9264      151.9272

### Data history

Data report submission:

10-03-2022

Most recent report update:

01-03-2022

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## Mooring deployment

Deployed

27/03/2021 03:15

Recovered

20/09/2021 02:50

Vessel

Heron Island Mooring

*Moored sensors:*

Battelle MApCO2 s/n

0122

Seabird SBE 16pus\_V2 s/n

6508

Aanderaa Optode s/n

1245

Field personel

Erik van Ooijen, Gary Curtis

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** [degr] *Latitude*

**LONGITUDE** [degr] *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*

**ΔfCO2** [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** [μmol/l] *Concentration O2 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*

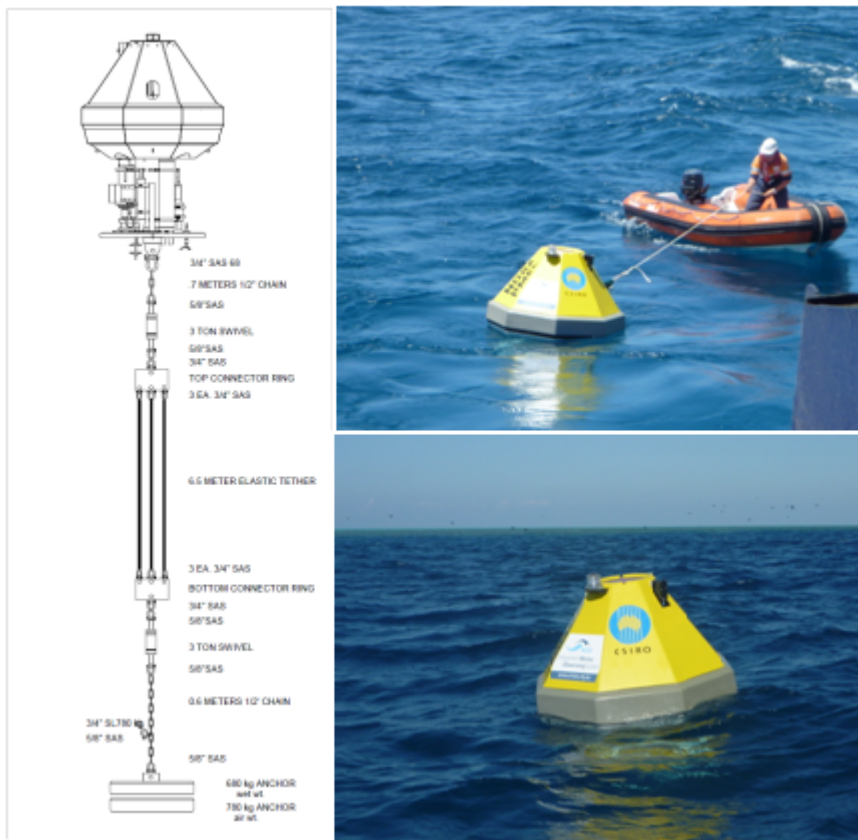
## General system description and procedures

### Instrumentation and methods

Measurements are made with a Battelle Seaology pCO<sub>2</sub> monitoring system (MApCO<sub>2</sub>), 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 MapCO<sub>2</sub>, SBE16Plus V2 and the optode are located at about 1m water depth. The CO<sub>2</sub> 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 CO<sub>2</sub>. 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 CO<sub>2</sub> gas and a high CO<sub>2</sub> standard span gas (typically 450-550 micromol/mol), which bracket the range of CO<sub>2</sub> mole fractions in seawater and air. The zero CO<sub>2</sub> gas is generated by cycling air through a soda lime chamber and silica gel to remove CO<sub>2</sub> and water vapour, respectively. The CO<sub>2</sub> 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/cccl/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 MapCO<sub>2</sub> 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 CO<sub>2</sub>-in-air reference gases (0, 260, 370, 450 micromol/mol) at CSIRO, Hobart. The sensor measurement using factory calibrations for the LI-CO<sub>2</sub> 820 is typically within 1 micromol/mol of the reference gas value. If the LI-COR 820 measurements and the CO<sub>2</sub>-in-air reference gas values are different by more than 2 micromol/mol, a correction is applied to Li-CO<sub>2</sub> 820 output based the reference gas values. A seawater bath operated over a range of temperatures and CO<sub>2</sub> expected in the field is then used to check the MapCO<sub>2</sub> system (equilibrator and LI-COR 820 measurement) against a General Oceanics 8050 CO<sub>2</sub> 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 CO<sub>2</sub> values are compared to Globalview CO<sub>2</sub> products, although these can result in some variability due to limited data in Globalview to constrain atmospheric boundary layer CO<sub>2</sub> measurements in coastal regions of the Southern Hemisphere.

A SBE16plus V2 CTD is polled for the temperature, salinity, and dissolved oxygen data for each MApCO<sub>2</sub> 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,  $R = 82.0578 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ,

$B(CO_2, T) = -1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3$  and,

$\delta(CO_2, T) = 57.7 - 0.118T$

### 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 ( $DOraw$ ) are calculated using the Stern-Volmer equation (Uchida et al., 2008), and the corresponding pre- and post- calibration coefficients (Appendix 3);

$$DO_{raw} = \frac{(c4 + c5T_{opt})/(c6 + c7Bp) - 1}{c1 + c2T_{opt} + c3T_{opt}^2}$$

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 = -6.24097e-3, B1 = -6.93498e-3, B2 = -6.90358e-3, B3 = -4.29155e-3, C0 = -3.11680e-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 (HSO4-) 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:

```
> MAX SD_XCO2_EQUIL_PUMP_ON
2021/06/19,04:00:00
Optode data out of range or interpolation failed
2021/09/19,00:00:00-2021/09/19,06:00:00
2021/09/19,14:00:00-2021/09/19,18:00:00
2021/09/20,00:00:00-2021/09/20,04:00:00
XC02 Span pump off or post cal out of range
2021/06/26,20:00:00-2021/06/26,22:00:00
2021/07/06,16:00:00-2021/07/06,18:00:00
```

#### 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: D0 outlier likely due to fouling-> Action: Manually set to bad:

2021/09/10,18:00:00-2021/09/10,22:00:00

2021/09/11,18:00:00-2021/09/11,22:00:00

2021/09/12,16:00:00-2021/09/13,02:00:00

2021/09/13,10:00:00-2021/09/14,06:00:00

2021/09/14,14:00:00-2021/09/15,08:00:00

2021/09/15,12:00:00-2021/09/20,04:00:00

Reason: Data recorded after recovery-> Action: Manually set to bad:

2021/09/20,04:00:00

Reason: fCO2 outliers-> Action: Manually set to questionable:

2021/06/14,16:00:00-2021/05/02,20:00:00

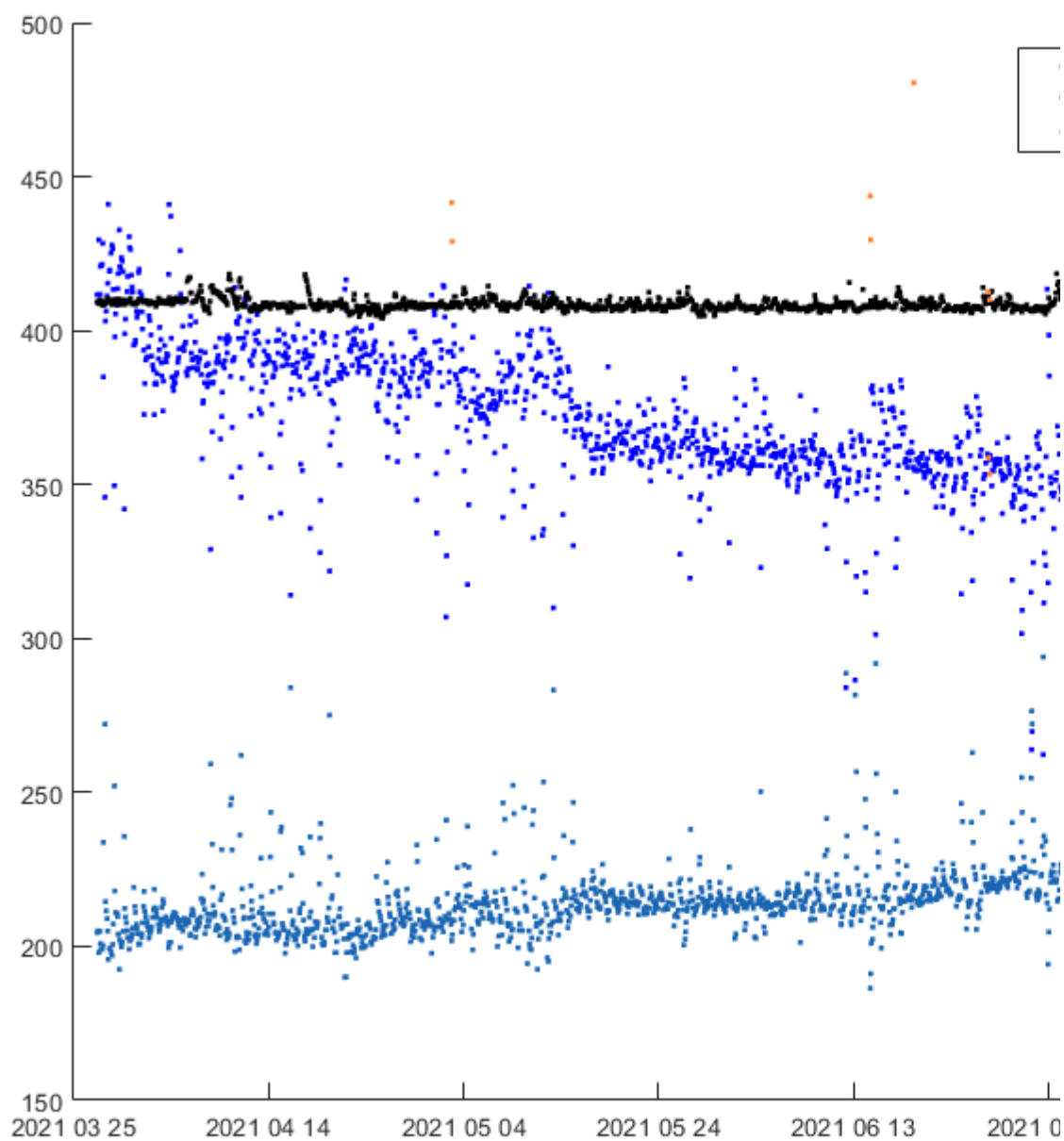
Low salinity values are verified using NRS data at MAI site (<http://www.csiro.au/tasman/nrsweb/>) and BOM flood history data ([http://www.bom.gov.au/tas/flood/flood\\_history/flood\\_history.shtml](http://www.bom.gov.au/tas/flood/flood_history/flood_history.shtml)).

#### Final data quality summary:

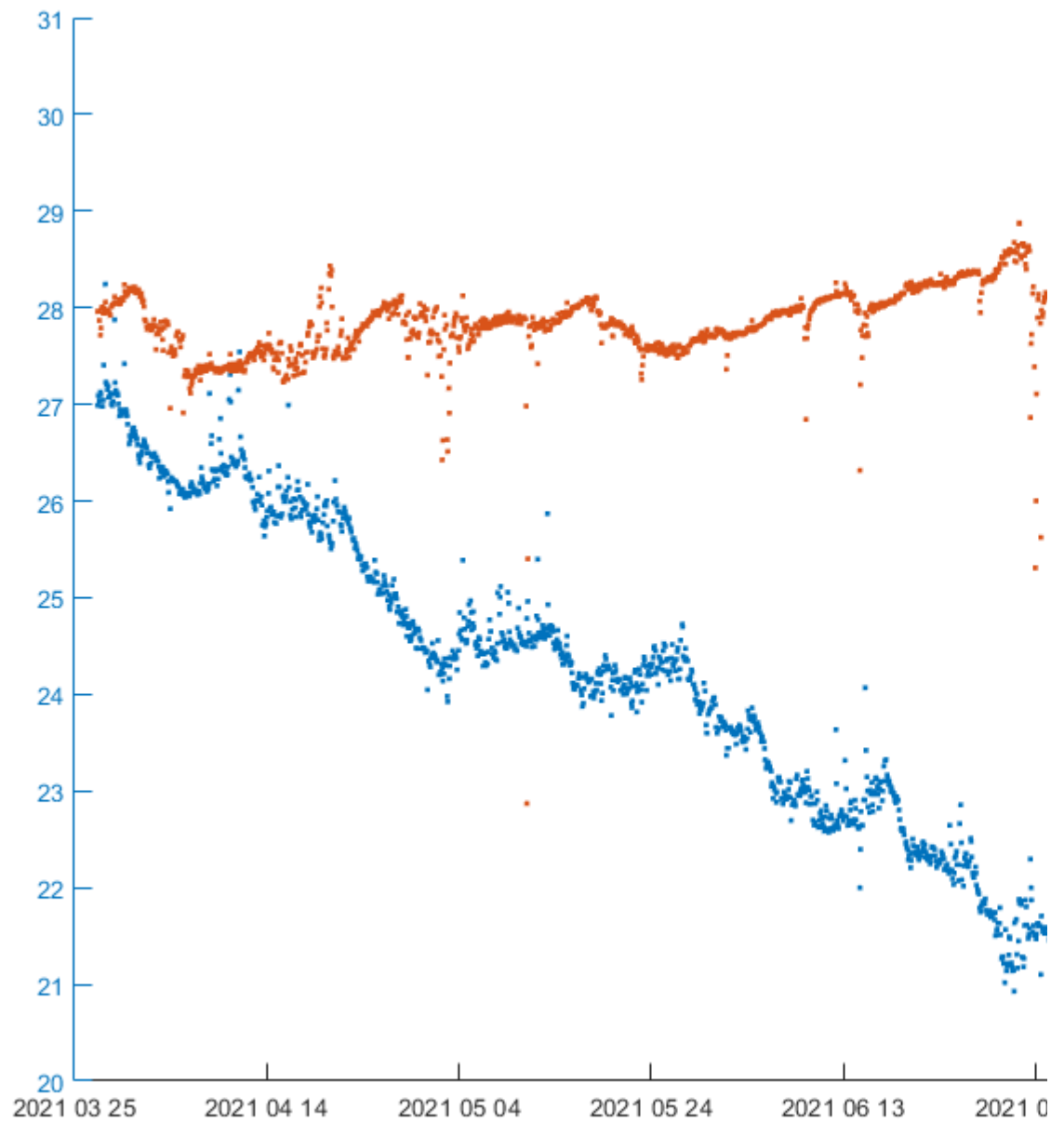
Parameter	% flag = 2 good	Number Points
fCO2 sea water	99.528746	2112
XC02 atmosphere	99.811499	2118
Sea Surface Temperature	100.000000	2122
Sea Surface Salinity	99.952875	2121
Dissolved Oxygen	99.528746	2112
Total pH	100.000000	2122

#### Data summary:

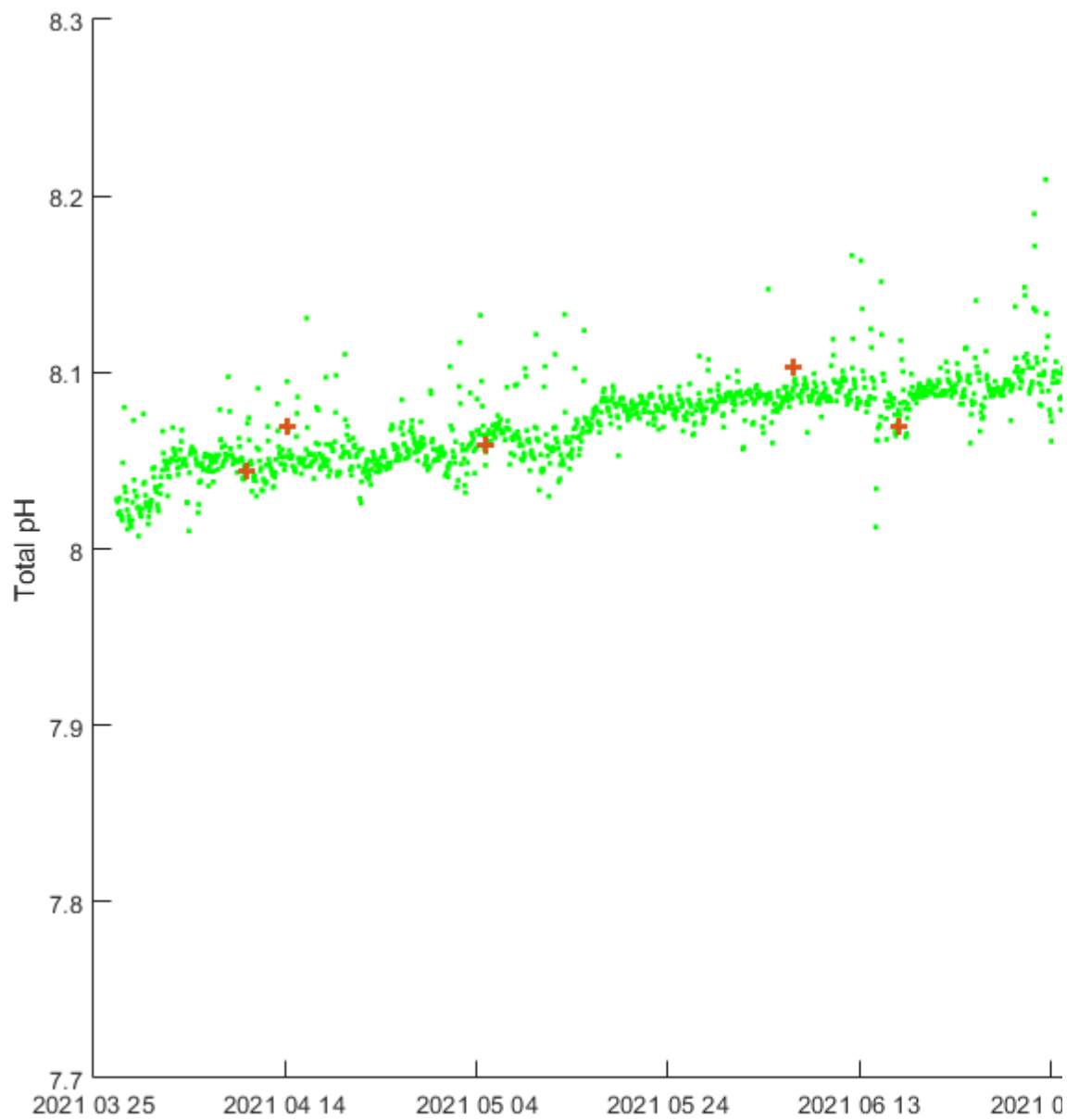




**Figure 1:** xCO<sub>2</sub> (ppm) for air, fCO<sub>2</sub> (µatm) and Dissolved Oxygen (DO; µmol/l) for sea water. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.



**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

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### Seaology pCO<sub>2</sub>

MANUFACTURER: Battelle Memorial Institute, Columbus, Ohio, USA  
WEBSITE: <http://battelle.org/our-work/national-security/maritime-systems>  
MODEL: Seaology  
SERIAL NO: 0122  
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)  
PRESSURE RESOLUTION: 0.01 KPa  
PRESSURE UNCERTAINTY: < 0.5 KPa, Based on laboratory comparison against Druck DPI 142 pressure transducer  
CALIBRATION DATE: 01/04/2021

#### Relative Humidity Sensor:

MANUFACTURER: Sensirion Humidity Sensor, USA  
WEBSITE: <http://www.sensirion.com>  
MODEL: SHT71  
MEASUREMENT RANGE: 0–100%  
ACCURACY:  $\pm 3\%$  (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: 1400 psi  
GAS CYLINDER PRESSURE, POST-DEPLOYMENT: 1000 psi  
CO2-IN-AIR CONCENTRATION (WMO X2007): 554.72 PPM  
CALIBRATION DATE: 2015-06-16

#### O2 Sensor:

MANUFACTURER: Aanderaa, Norway  
WEBSITE: <http://www.aanderaa.com/>  
MODEL: 3830  
SERIAL NO: 1245  
FOIL BATCH NO: 2408  
RESOLUTION: <1  $\mu\text{M}$   
UNCERTAINTY: < 1  $\mu\text{mol/L}$ , based on Winkler oxygen titrations at CSIRO, Hobart

CALIBRATION DATE: PRE-DEPLOYMENT: 02-Jun-2020 POST-DEPLOYMENT: 02-Jun-2020  
 OPTODE USED: SBE optode  
 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: 6508  
 RESOLUTION: 0.0001 °C; 0.00005 S/m  
 UNCERTAINTY: 0.005 °C; 0.0005 S/m  
 CTD DEPTH: 1 m  
 CALIBRATION DATE: 11-06-2020

#### pH sensor:

MANUFACTURER: Scripps Institution of Oceanography, USA  
 MODEL: Scripps SeapH0x  
 SERIAL NO: 8  
 RESOLUTION: 0.001  
 UNCERTAINTY: 0.02  
 CALIBRATION: Calibrated using IMOS DIC and TALK bottle sample

### Appendix 2: Range limits

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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 D0	50	400

### Appendix 3: Instrument calibration coefficients

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Oxygen optode calibrations coefficients for optode 3830 serial number 1245 foil number 2408:

Coefficient	Pre-deployment	Post-deployment
C1	0.0025623	0.0025623
C2	0.00011061	0.00011061
C3	1.7756e-06	1.7756e-06
C4	231.4	231.4
C5	-0.2393	-0.2393
C6	-39.648	-39.648
C7	4.0711	4.0711

Seabird SBE16plus V2, serial number 6508 calibration coefficients:

Temperature	Coefficient
TA0	0.0012784
TA1	0.00026008
TA2	-3.5007e-07
TA3	1.5179e-07
T0FFSET	0

Salinity	Coefficient
G	-1.0438
H	0.14088
I	-0.00024748
J	3.7791e-05
CPCOR	-9.57e-08
CTCOR	3.25e-06
CSLOPE	1

### Additional information:

The CO<sub>2</sub>/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 CO<sub>2</sub> system timeseries measurements from Wistari Channel, Heron Island, Australia. <http://imos.aodn.org.au/imos123/>

### References

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## Attachments

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No attachments