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IMOS Maria Island CO2 mooring

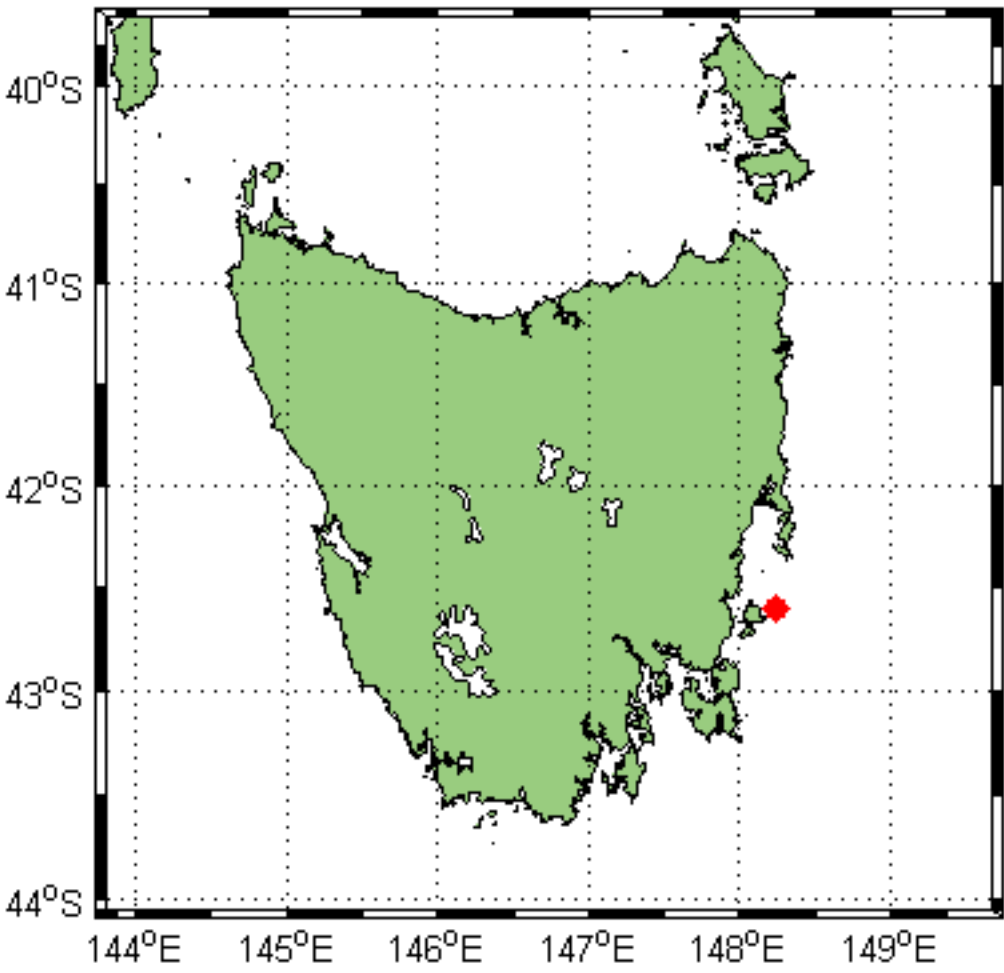
Dataset:

09FS20170207\_maria\_12

Deployment information

Location:

Maria Island, Tasman Sea;-42.6023,148.2335



Water Depth:

95m

Platform:

IMOS\_ANMN-AM\_CO2\_GST

Platform code:

NRSMAI

Deployment code:

NRSMAI\_12

Start date

20170207T100000Z

End date

20170912T220000Z

Mooring Bounds: North West South East

-42.63236      -42.57222      148.1517      148.3153

Data history

Data report submission:

08/11/2017

Most recent report update:

01-11-2017

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Mooring deployment

Deployed

07/02/2017 08:00

Recovered

11/09/2017 23:00

Vessel

Maria Island Mooring

Moored sensors:

Battelle MApCO2 s/n

0116

Seabird SBE 16pus\_V2 s/n

01606574

Aanderaa Optode s/n

1449

pH sensor s/n

316

Field personel

Phil deBoer,Gary Curtis

Instrumentation

Erik van Ooijen

Quality control

Erik van Ooijen

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

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 [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 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/ccl/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.

A DuraFET-based sensor (Martz et al., 2010) is mounted for measuring Total pH and is located at about 1m water depth

### Location and mooring design



The Maria Island Reference station mooring is located on the shelf off eastern Tasmania in about 95m water depth. A 700kg anchor holds the mooring buoy in position. Two acoustic releases are located above the anchors and are connected to the surface buoy via a 15m 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 (Culberson, 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 , pH sensor (when present) 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 xCO2raw 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):

$$fCO_2 = pCO_2 \exp \frac{P(B(CO_2, T) + 2(1 - xCO_2)^2 \delta(CO_2, T))}{RT}$$

where,  $R = 82.0578 cm^3 mol^{-1} K^{-1}$ ,  $B(CO_2, T) = -1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3$  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 ( $DO_{raw}$ ) 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  $B0 = -6.24097e-3$ ,  $B1 = -6.93498e-3$ ,  $B2 = -6.90358e-3$ ,  $B3 = -4.29155e-3$ ,  $C0 = -3.11680e-7$ .

Subsequently, a drift correction of 1.61% per year is 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. From these samples the total pH is calculated using CO2SYS (Van Heuven et. al. 2011), using the Hansson and Mehrbach K1K2 dissociation constants and the Dickson & TB of Uppstrom 1979 KSO4 dissociation constants. 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:*

```
Flash data corrected; too many points deleted or standard deviation is too high.
2017/07/07,10:00:00-2017/07/07,12:00:00
XCO2 Span pump off or post cal out of range
2017/03/07,08:00:00-2017/03/07,10:00:00
2017/05/19,22:00:00-2017/05/20,00:00:00
2017/05/21,22:00:00-2017/05/22,00:00:00
2017/07/07,10:00:00-2017/07/07,12:00:00
2017/07/11,10:00:00-2017/07/11,12:00:00
2017/07/12,10:00:00
2017/07/15,12:00:00-2017/07/15,14:00:00
2017/07/28,12:00:00
2017/07/31,14:00:00-2017/07/31,16:00:00
2017/08/02,10:00:00-2017/08/02,12:00:00
2017/08/31,12:00:00
2017/09/09,14:00:00
XCO2 Zero pump off or post cal out of range
2017/03/07,08:00:00-2017/03/07,10:00:00
```

*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:

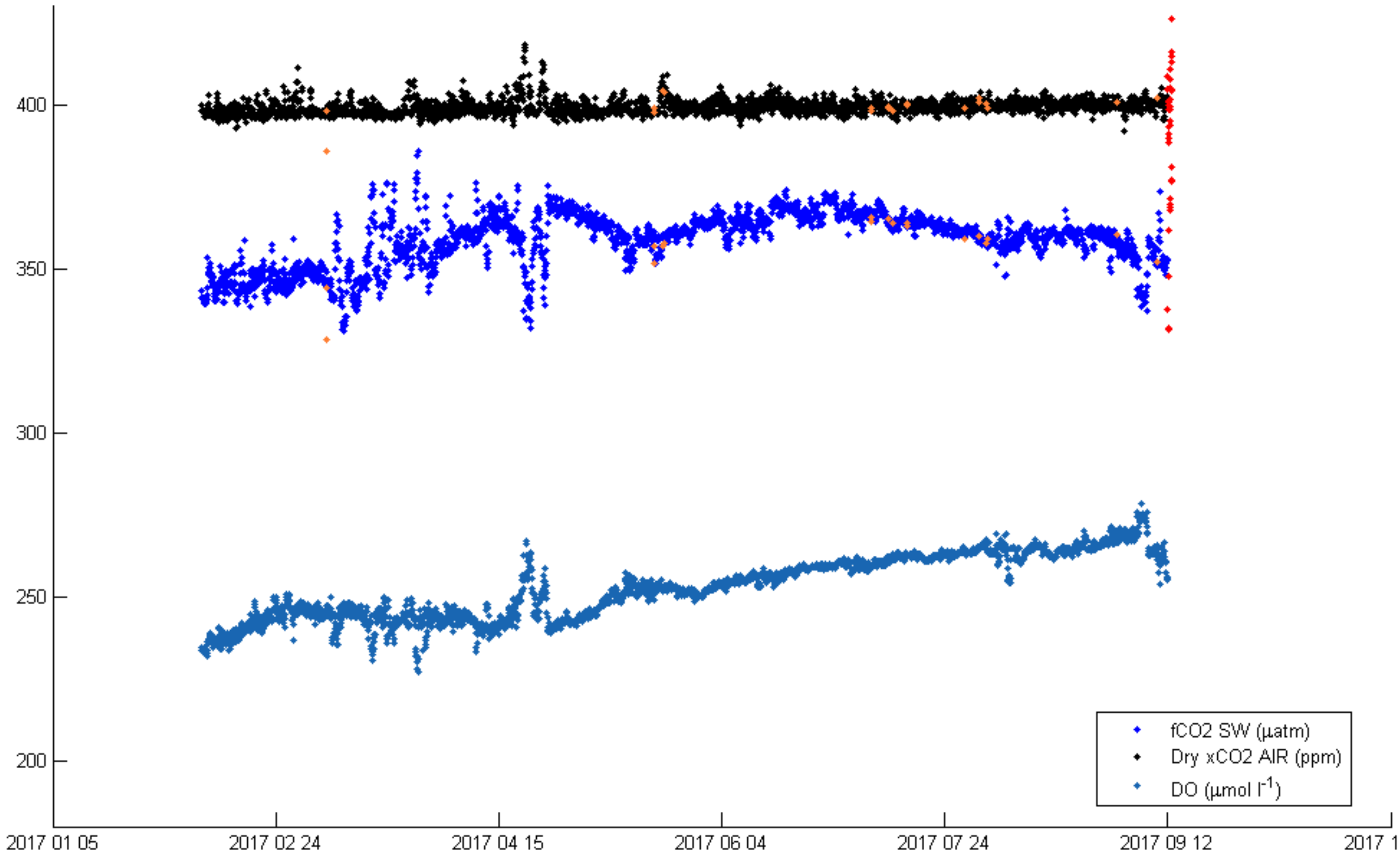
Reason: Data obtained after recovery-> Action: Manually set to bad:  
2017/09/12,00:00:00-2017/09/12,22:00:00  
Reason: Single outlier in Salinity-> Action: Manually set to questionable:  
2017/05/08,14:00:00  
Manual set to bad data  
Reason:pH data obtained after recovery  
11-Sep-2017 16:00:00-12-Sep-2017 22:00:00

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)).

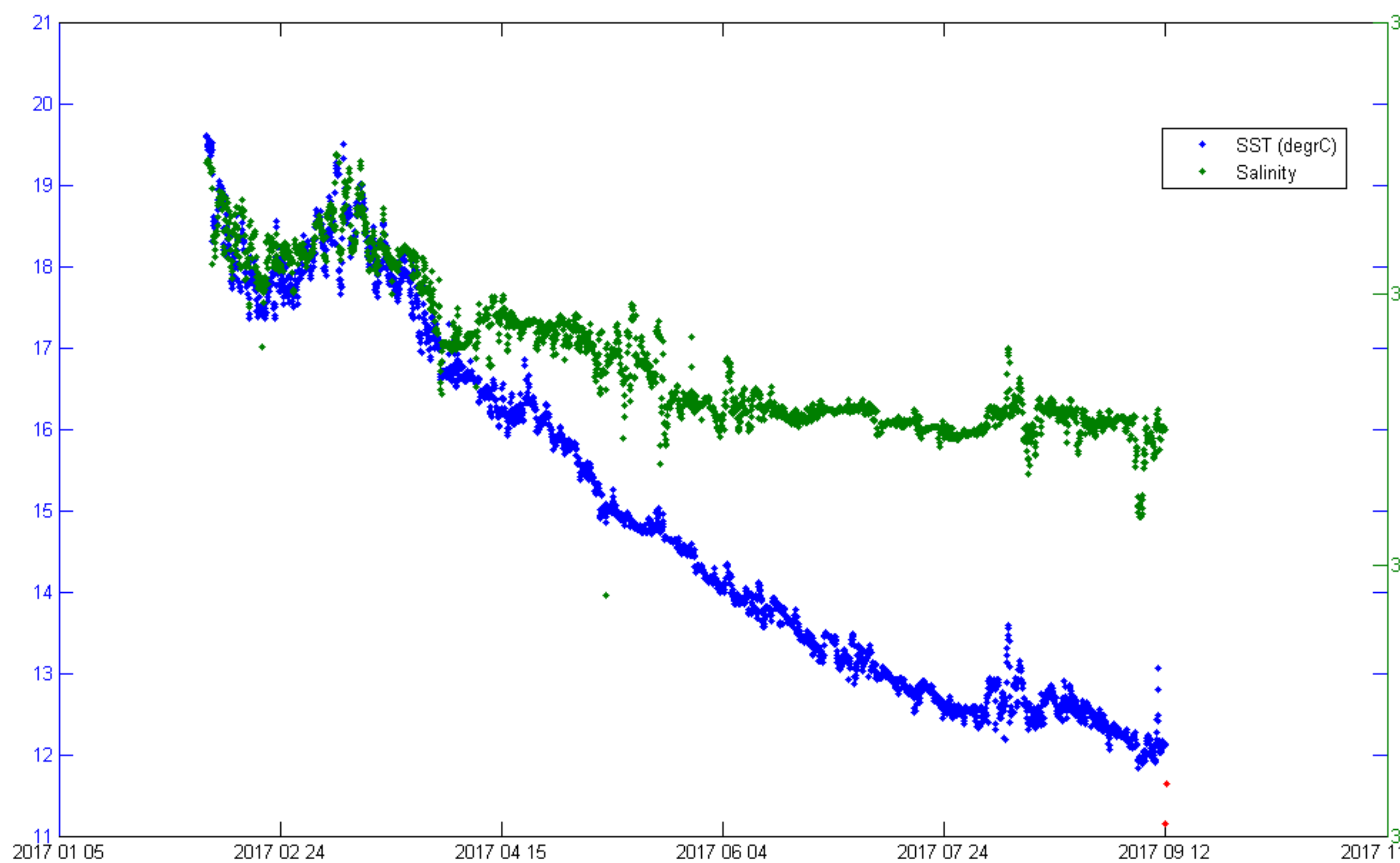
Final data quality summary:

Parameter	% flag = 2 good	Number Points
fCO2 sea water	98.774416	2579
XCO2 atmosphere	98.774416	2579
Sea Surface Temperature	99.540406	2599
Sea Surface Salinity	99.502106	2598
Dissolved Oxygen	99.540406	2599
Total pH	99.387208	2595

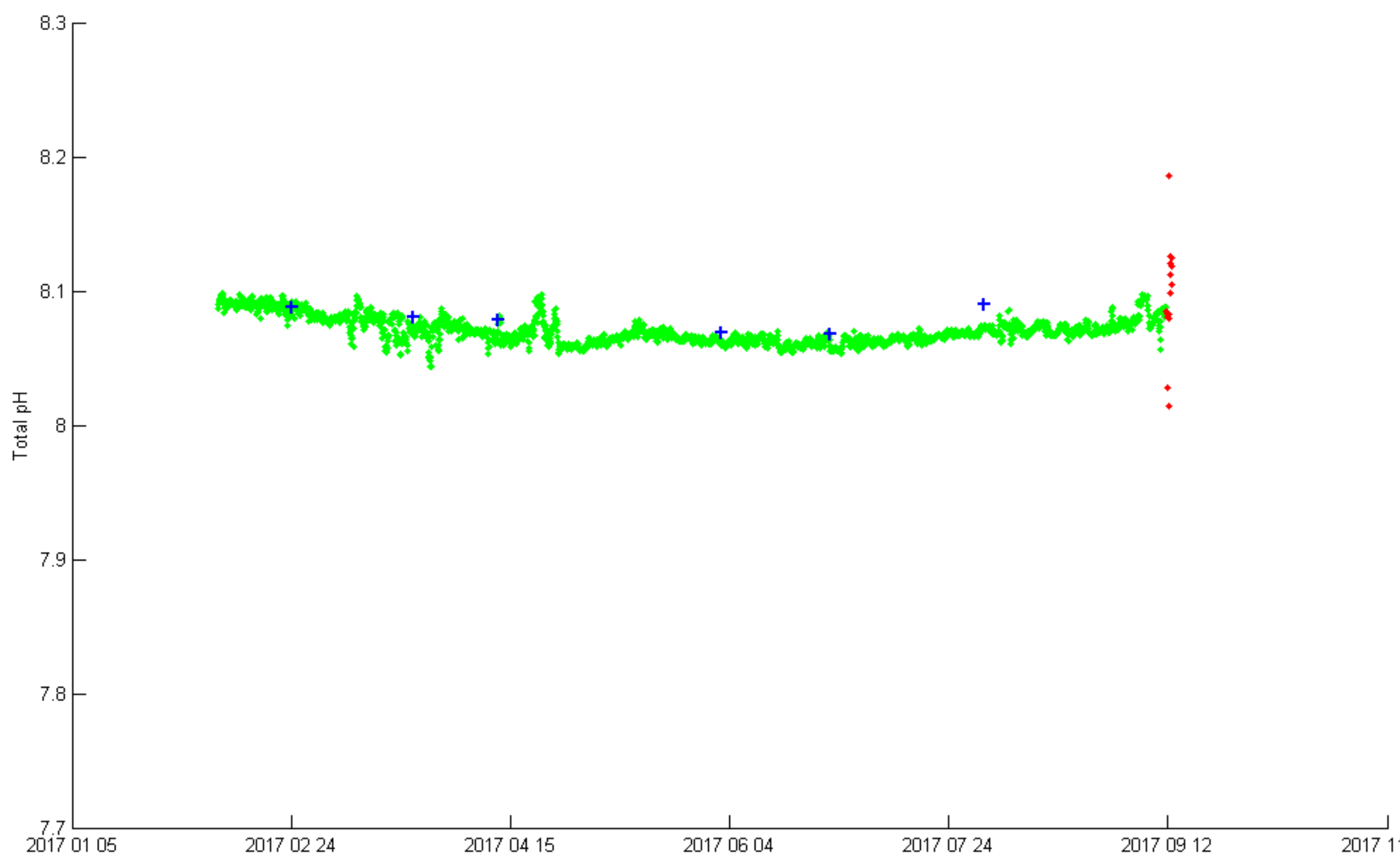
Data summary:



**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:** Temperature and salinity.



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

## Appendix 1: Instrumentation specifications

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: 0116  
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 μmol/mol  
CO2 UNCERTAINTY: < 2 μmol/mol based on comparisons in the laboratory  
before and after deployment with four WMO X2007 referenced gas standards (0, 260, 370, 450 μmol/mol)  
and < 2 μmol/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: 04/11/2016

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

CO2 Span Gas:

MANUFACTURER:NOAA Earth Systems Laboratory, USA  
CYLINDER NUMBER: JB03339  
GAS CYLINDER PRESSURE, PRE-DEPLOYMENT: 1350 psi  
GAS CYLINDER PRESSURE, POST-DEPLOYMENT: 520 psi  
CO2-IN-AIR CONCENTRATION (WMO X2007): 519.48 PPM  
CALIBRATION DATE: 2012-07-30

O2 Sensor:

MANUFACTURER:Aanderaa, Norway  
WEBSITE: http://www.aanderaa.com/  
MODEL: 4175C  
SERIAL NO: 1449  
FOIL BATCH NO: 5009  
RESOLUTION: <1 μM  
UNCERTAINTY: < 1 μmol/l, based on Winkler oxygen titrations at CSIRO, Hobart  
CALIBRATION DATE:PRE-DEPLOYMENT: 06-Oct-2016 POST-DEPLOYMENT: 06-Oct-2017

CTD Sensor (Equilibrator and Sea Surface):

MANUFACTURER:Sea-Bird Electronics, Bellevue, Washington, USA  
WEBSITE: http://www.seabird.com/  
MODEL: SBE 16plusV2\_seacat  
SERIAL NO: 01606574  
RESOLUTION: 0.0001 °C; 0.00005 S/m  
UNCERTAINTY: 0.005 °C; 0.0005 S/m  
CTD DEPTH: 1 m  
CALIBRATION DATE: 12-04-2016

pH sensor:

MANUFACTURER:Scripps Institution of Oceanography, USA  
MODEL: Satlantic SeaFET  
SERIAL NO: 316  
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	2	
MAX SD_RH_EQUIL_PUMP_OFF	2	
MAX SD_RH_TEMP_AIR_PUMP_OFF		0.05
MAX SD_RH_TEMP_EQUIL_PUMP_OFF		0.05
MAX SD_RH_SPAN_PUMP_OFF	2	
MAX SD_RH_TEMP_SPAN_PUMP_OFF		0.05
SBE Temperature	-2	40
SBE Salinity	0	42
Optode O2	100	400

Appendix 3: Instrument calibration coefficients

Oxygen optode calibrations coefficients for optode 4175C serial number 1449 foil number 5009:

Coefficient	Pre-deployment	Post-deployment
C1	0.0025978	0.0026798
C2	0.00010941	0.00011308
C3	1.8046e-06	1.7876e-06
C4	232.94	232.26
C5	-0.29632	-0.3302
C6	-39.463	-40.726
C7	4.0542	4.048

Seabird SBE16plus V2, serial number 01606574 calibration coefficients:

Temperature	Coefficient
TA0	0.0012877
TA1	0.00026331
TA2	-6.9155e-07
TA3	1.6858e-07
TOFFSET	0

Salinity	Coefficient
G	-1.0438
H	0.14398
I	-0.00012969
J	2.9202e-05
CPCOR	-9.57e-08
CTCOR	3.25e-06
CSLOPE	1

Salinity Drift correction:

no

Additional information:

The CO2/acidification mooring data was sourced as part of the Integrated Marine Observing System (IMOS) – supported by the Australian Government through the National Collaborative Research Infrastructure Strategy and the Super Science Initiative.

Citation:

Users of these data are requested to cite the data source and to send copies of manuscripts to the PI prior to submission to ensure data are accurately represented.

B. Tilbrook, E. van Ooijen, C. Neill (year), Integrated Marine Obsering System fCO2 timeseries measurements for the ocean and atmosphere from Maria Island, Tasmania, Australia (42.596S,148.238E). <http://imos.aodn.org.au/imos123/>.

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LI-COR Application Note 129. The Importance of Water Vapor Measurements and Corrections, URL: [http://www.licor.com/env/applications/gas\\_analysis.html](http://www.licor.com/env/applications/gas_analysis.html)

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Van Heuven, S., Pierrot, D., Rae, J.W.B., Lewis, E., Wallace, D.W.R., (2011). MATLAB Program Developed for CO2 System Calculations. [http://dx.doi.org/10.3334/CDIAC/otg.CO2SYS\\_MATLAB\\_v1.1](http://dx.doi.org/10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1).

Philip J. Bresnahan Jr., Todd R. Martza, Yuichiro Takeshita, Kenneth S. Johnson, and Makaila LaShomba, (2014). Best practices for autonomous measurement of seawater pH with the Honeywell Durafet, Methods in Oceanography 9 (2014) 44–60, <http://dx.doi.org/10.1016/j.mio.2014.08.003>

Attachments

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No attachments