Contents

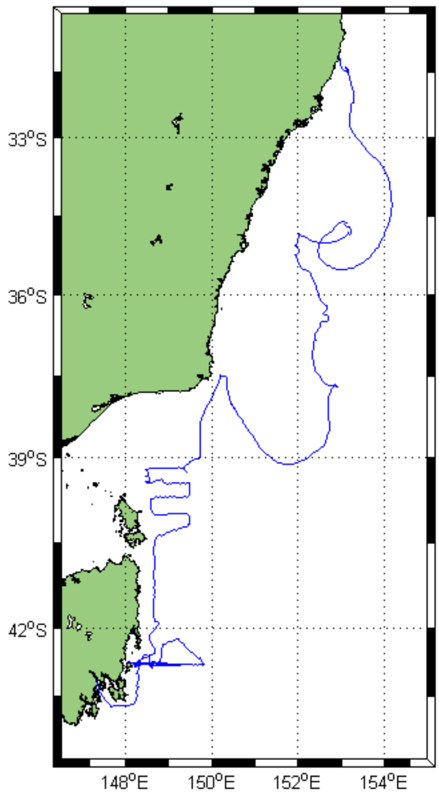
Saildrone SD1007

Dataset:

```
SAILDRONE_20180327T233000Z_SD1007_FV01_SD1007-CO2-1803-delayed_END_20180531T210000Z_C-20181012T112459Z.nc
```

Deployment information

Saildrone Track:



Platform:

```
SD1007
```

Platform code:

```
SD1007
```

Deployment code:

```
SD1007_1
```

Start date

```
20180327T233000Z
```

End date

```
20180531T210000Z
```

Mooring Bounds: North West South East

```
-43.329    -31.403    147.34    154.18
```

Data history

Data report submission:

```
not submitted
```

Most recent report update:

```
07-08-2019
```

Investigators:

Bronte Tilbrook, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia Email: Bronte.Tilbrook@csiro.au

Abe Passmore, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia Email: Abraham.Passmore@csiro.au

Erik van Ooijen, CSIRO Oceans and Atmosphere, Castray Esplanade, Hobart, TAS 7000, Australia Email: Erik.Vanooijen@csiro.au

Mooring deployment

Deployed

```
27-03-2018 23:00
```

Recovered

```
01-06-2018 00:00
```

Vessel

```
Saildrone SD1007
```

Moored sensors:

NOAA PMEL ASVCO2 s/n

```
0009
```

Seabird SBE Prawler s/n

```
0038
```

Aanderaa Optode s/n

```
700
```

pH sensor s/n

```
9506
```

Field personel

```
Erik van Ooijen,Abe Passmore
```

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*

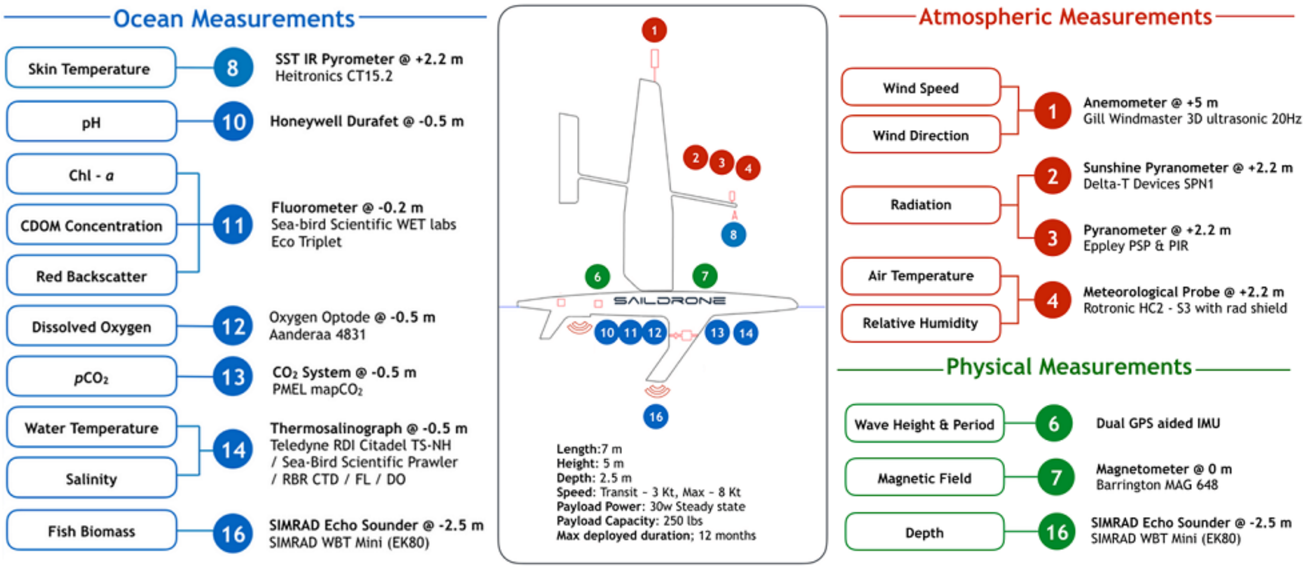
General system description and procedures

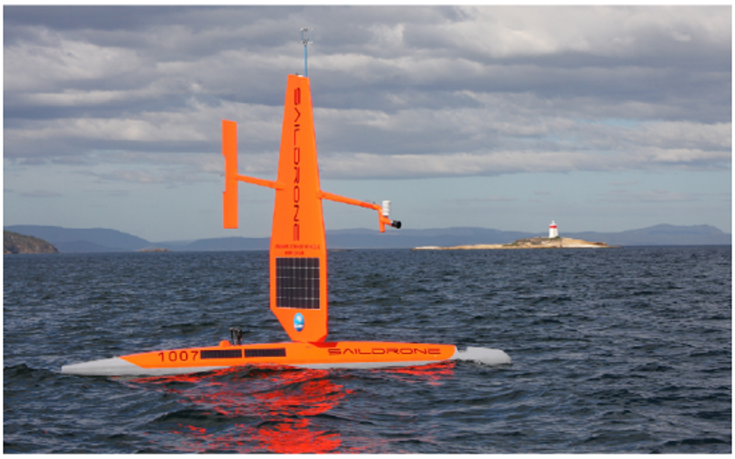
Instrumentation and methods

Measurements are made with a NOAA PMEL pCO2 monitoring system (ASVCO2), a Seabird Prawler CTD, mounted on the keel of the saildrone, 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 ASVpCO2, SBE16Plus V2 and the optode are mounted on the keel 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 0.5 or 2 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 400-550 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 Prawler.

A DuraFET-based sensor (Martz et al., 2010, pumped system) is fitted for measuring Total pH and is mounted on the keel at about 1m water depth

Design





The Saildrone has an extensive and flexible payload system which is capable of using a wide variety of sensor systems. The configuration below is being used by the CSIRO to conduct environmental assessments at offshore CCS sites and incorporates, sensors that measure the physical, chemical and acoustic properties of water column and atmosphere above. As part of regular maintenance and to minimise the effects of biofouling, the saildrone is recovered typicaly every six months and newly calibrated sensors are 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 SBE Prawler CTD is polled for the temperature, salinity, and dissolved oxygen data for each ASVCO2 measurement sequence, with additional measurements made each hour. The Prawler CTD 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 (SScripps 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 and the DO sensor 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).

For DO and pH high frequency data is available, which is quality controlled seperately and is incorporated in the NetCDF file.

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):

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

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

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

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 exteral 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,pco2,fco2
2018/03/29,06:00:00
2018/03/29,18:00:00
2018/05/31,01:00:00
> MAX SD_PRESS_LICOR_EQUIL_PUMP_OFF
2018/04/15,22:00:00
2018/05/04,12:00:00
2018/05/04,13:00:01
2018/05/31,01:00:00
2018/05/31,05:00:01
2018/05/31,11:00:00
2018/05/31,12:00:00
2018/05/31,14:00:01
2018/05/31,17:00:00
> MAX SD_RH_EQUIL_PUMP_OFF
2018/03/27,23:30:00
2018/03/28,00:30:00
> MAX SD_RH_TEMP_SPAN_PUMP_OFF
2018/03/27,23:30:00
Invalid High Frequency DO data
2018/03/25,18:00:00-2018/03/27,04:00:00
2018/03/27,05:00:00-2018/03/27,06:13:00
2018/03/27,22:01:00-2018/03/27,23:24:00
2018/03/28,01:35:00
Invalid High Frequency pH data
2018/03/27,02:15:30-2018/03/27,02:21:00
2018/03/27,04:30:00-2018/03/27,05:57:00
2018/03/27,22:03:00-2018/03/27,22:51:00
2018/06/06,22:06:58-2018/06/07,04:51:00
```

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 recorded before deployment-> Action: Manually set to bad:
2018/03/27,23:30:00
Reason: Low values for DO-> Action: High Frequency DO data Manually set to questionable:
2018/03/27,23:38:00-2018/03/28,03:27:00
Reason: Outliers in DO-> Action: Manually set to bad:
2018/03/28,00:30:00
2018/03/28,01:30:00
2018/03/28,02:30:00-2018/03/28,03:00:01
Reason: Outliers in Salinity-> Action: Manually set to bad:
2018/04/12,01:00:01
2018/04/14,20:00:00
2018/04/14,21:00:01
2018/05/04,12:00:00
2018/05/31,01:00:00
2018/05/31,05:00:01
2018/05/31,09:00:00
2018/05/31,12:00:00
2018/05/31,13:00:00
2018/05/31,15:00:01
2018/05/31,17:00:00
Reason: Outliers in fCO2-> Action: Manually set to bad:
2018/03/28,04:30:00
2018/05/05,20:00:01
2018/05/05,21:00:00
2018/05/05,22:00:01
2018/05/05,23:00:00-2018/03/28,04:30:00
Reason: Outliers in pH-> Action: High Frequency pH Manually set to bad:
2018/03/27,02:24:00-2018/03/27,04:27:00
2018/03/27,06:00:00-2018/03/27,22:00:00
2018/03/27,23:46:51-2018/03/28,01:46:51
2018/04/06,19:48:00-2018/04/06,20:18:00
Manual set to bad data
Reason:Outliers in pH
27-Mar-2018 23:30:00-28-Mar-2018 03:00:01
Manual set to bad data
Reason:Outliers in pH
06-Apr-2018 20:00:01
Manual set to bad data
Reason:Outliers in pH
05-May-2018 21:00:00-05-May-2018 22:00:01
```

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
ASVCO2 time stamp:		
fCO2 sea water	98.833252	2033
XCO2 atmosphere	99.805542	2053
Sea Surface Temperature	99.951386	2056
Sea Surface Salinity	99.416626	2045
Dissolved Oxygen	99.173554	2040
Total pH	99.611084	2049
High Frequency sample data:		
pH time stamp:		
Total pH	98.129458	33155
DO time stamp:		
Dissolved Oxygen	97.522036	94375

Data summary:

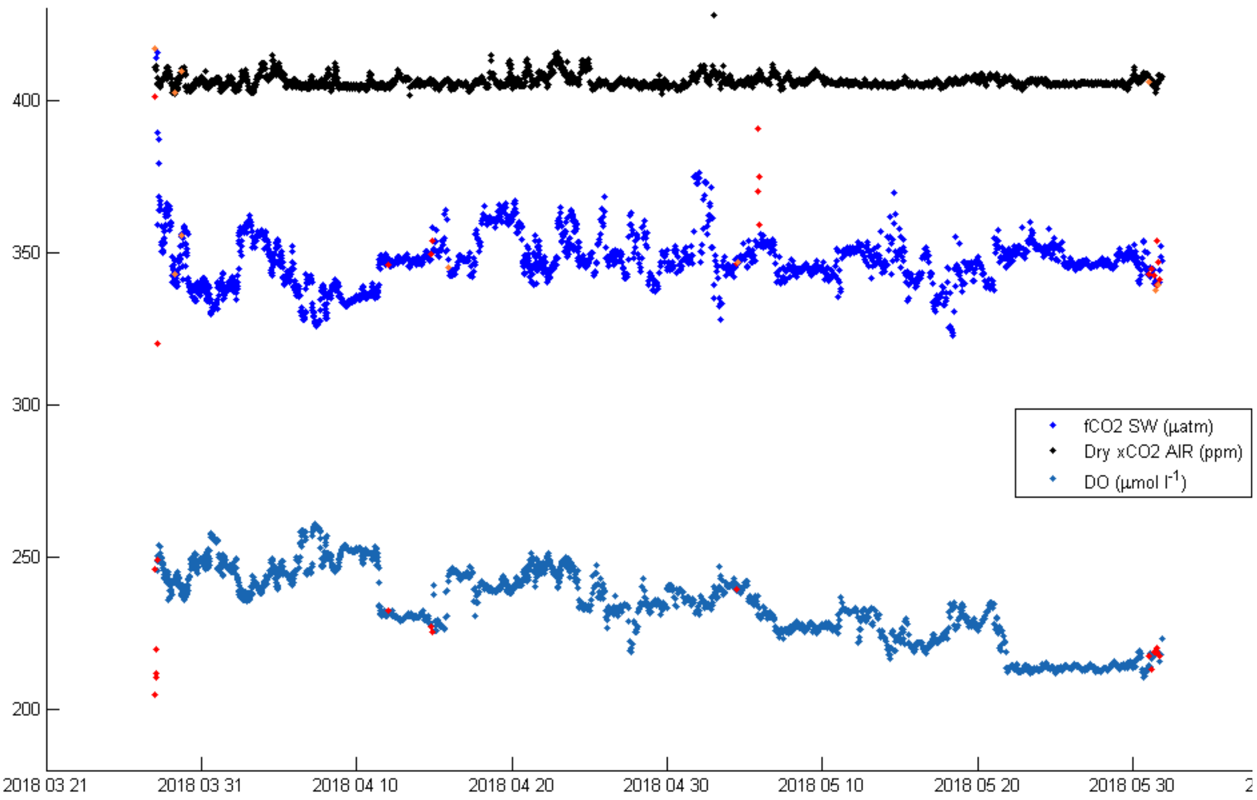


Figure 1: xCO2 (ppm) for air, fCO2 (µatm) and Dissolved Oxygen (DO; µmol/l) for sea water. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

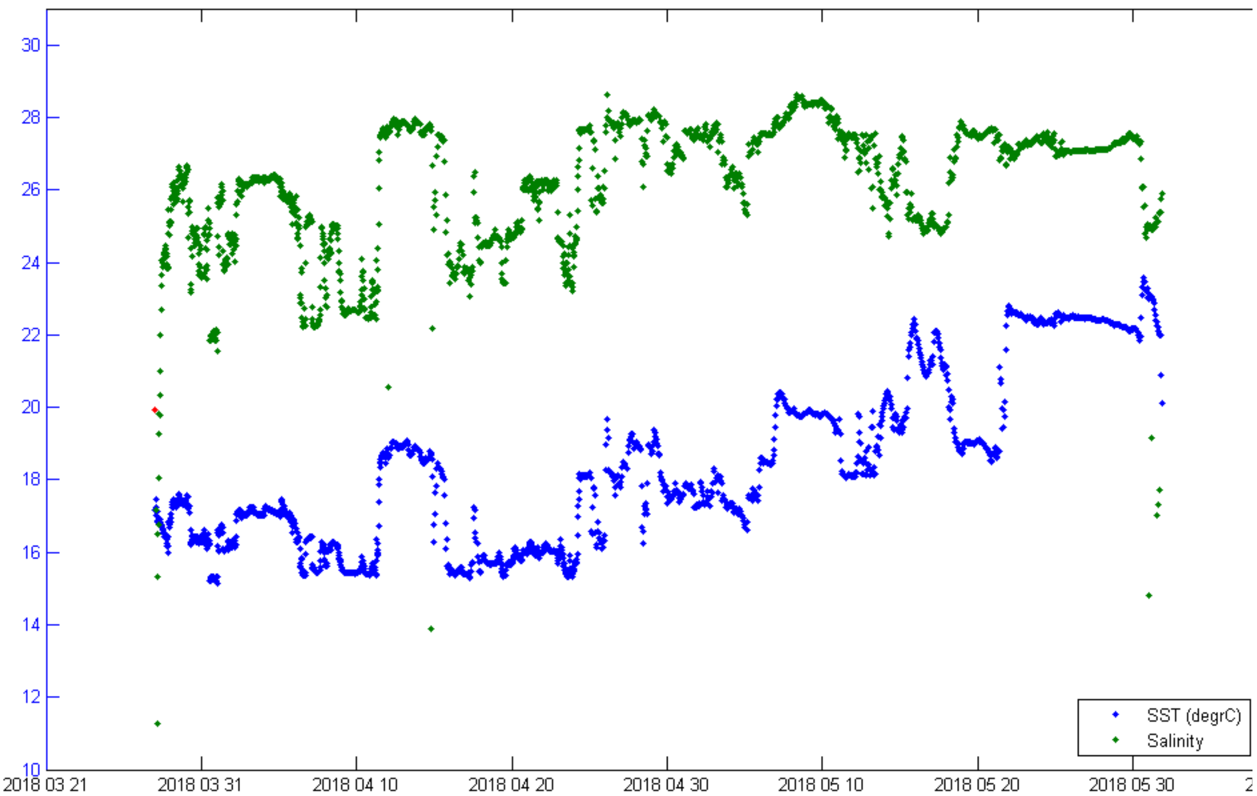


Figure 2: Temperature and salinity.

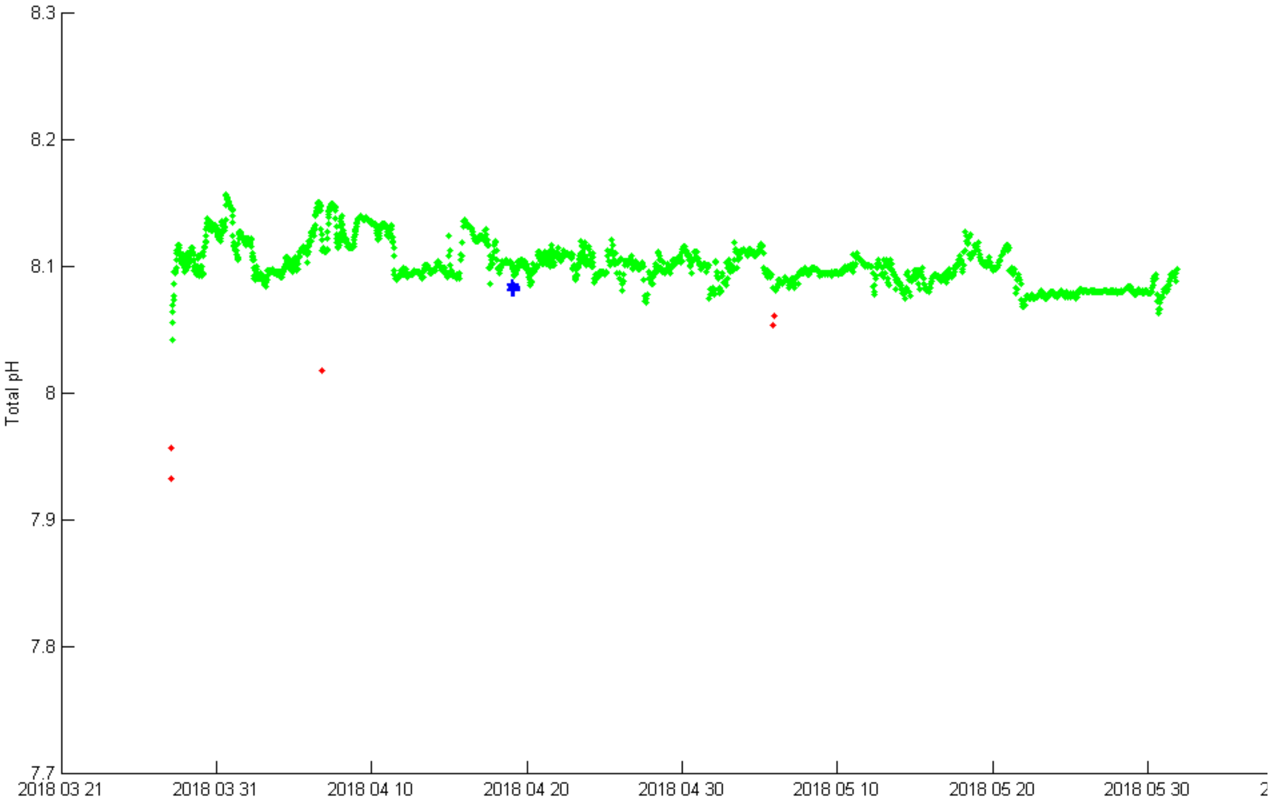


Figure 3: Total pH SeapHox. Bottle samples are indicated in blue.

Appendix 1: Instrumentation specifications

Seaology pCO2

```
MANUFACTURER:NOAA PMEL, Seattle, USA
WEBSITE: https://www.pmel.noaa.gov/
MODEL: ASVCO2
SERIAL NO: 0009
FIRMWARE VERSION: 02.19
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: 14-Nov-2017
```

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: EN3132
GAS CYLINDER PRESSURE, PRE-DEPLOYMENT: 3000 psi
GAS CYLINDER PRESSURE, POST-DEPLOYMENT: 2000 psi
```

```
CO2-IN-AIR CONCENTRATION (WMO X2007): 402.74 PPM
CALIBRATION DATE: 2017-04-19
```

O2 Sensor:

```
MANUFACTURER:Aanderaa, Norway
WEBSITE: http://www.aanderaa.com/
MODEL: 4831
SERIAL NO: 700
FOIL BATCH NO: 1517M
RESOLUTION: <1 μM
UNCERTAINTY: < 1 μmol/l, based on Winkler oxygen titrations at CSIRO, Hobart
CALIBRATION DATE:PRE-DEPLOYMENT: 28-Feb-2018 POST-DEPLOYMENT: 28-Feb-2018
```

CTD Sensor (Equilibrator and Sea Surface):

```
MANUFACTURER:Sea-Bird Electronics, Bellevue, Washington, USA
WEBSITE: http://www.seabird.com/
MODEL: SBE Prawler
SERIAL NO: 0038
RESOLUTION: 0.0001 °C; 0.00005 S/m
UNCERTAINTY: 0.005 °C; 0.0005 S/m
CTD DEPTH: 1 m
CALIBRATION DATE: 28-Sep-2017
```

pH sensor:

```
MANUFACTURER:Scripps Institution of Oceanography, USA
MODEL: Scripps DuraFET
SERIAL NO: 9506
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     14
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 Temparature    -2     40
SBE Salinity    0     42
Optode DO    50     400
```

Appendix 3: Instrument calibration coefficients

```
Oxygen optode calibrations coefficients for optode 4831 serial number 700 foil number 1517M:


Coefficient    Pre-deployment    Post-deployment
C1    0.0025978    0.0025978
C2    0.00011169    0.00011169
C3    1.834e-06    1.834e-06
C4    211.72    211.72
C5    -0.41417    -0.41417
C6    -53.431    -53.431
C7    4.172    4.172
```

Salinity Drift correction:

```
Data corrected based on post deployment calibration by CSIRO calibration facility. Original calibration was found incorrect
```

References

Alliance for Coastal Technologies (2010) Performance Demonstration Statement, PMEL MAPCO2/Battelle Seaology pCO2 Monitoring System, UMCES Technical report Series: Ref. No. [UCMES]CBL 10-092, URL: http://www.act-us.info/Download/Evaluations/pCO2/PMEL_MAPCO2_Battelle_Seaology/

LI-COR Application Note 129. The Importance of Water Vapor Measurements and Corrections, URL: http://www.licor.com/env/applications/gas_analysis.html

Thompson, R. (1985) A Note on Restricted Maximum Likelihood Estimation with an Alternative Outlier Model. Journal of the Royal Statistical Society. Series B (Methodological),47(1), 53-55.

Uchida, H., T. Kawano, I. Kaneko and M. Fukusawa (2008) In situ Calibration of Optode-based Oxygen Sensors. Journal of Atmospheric and Oceanic Technology, 25, 2271-2281.

Culberson, C. H., (1991). Dissolved oxygen. WHP Operations and Methods, WHPO 91-1, WHP Office, Woods Hole Oceanographic Institution, Woods Hole, Mass. U.S.A.

Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of non-ideal gas. Marine Chemistry, 2, 203-215.

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A. J. Sutton, C. L. Sabine, S. Maenner-Jones, N. Lawrence-Slavas, C. Meinig, R. A. Feely, J. T. Mathis, S. Musielewicz, R. Bott, P. D. McLain, H. J. Fought, and A. Kozyr (2014) A high-frequency atmospheric and seawater pCO2 data set from 14 open-ocean sites using a moored autonomous system. Earth System Science Data, 6, 353-366. doi:10.5194/essd-6-353-2014.

Cooperative Global Atmospheric Data Integration Project. 2013, updated annually. Multi-laboratory compilation of synchronized and gap-filled atmospheric carbon dioxide records for the period 1979-2012 (obspack_co2_1_GLOBALVIEW-CO2_2013_v1.0.4_2013-12-23). Compiled by NOAA Global Monitoring Division: Boulder, Colorado, U.S.A. Data product accessed at http://dx.doi.org/10.3334/OBSPACK/1002

Todd R. Martz,James G. Connery, and Kenneth S. Johnson (2010) Testing the Honeywell Durafet for seawater pH applications, Limnol. Oceanogr.: Methods 8, 2010, 172–184. doi 10.4319/lom.2010.8.172.

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.

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

```
No attachments
```
