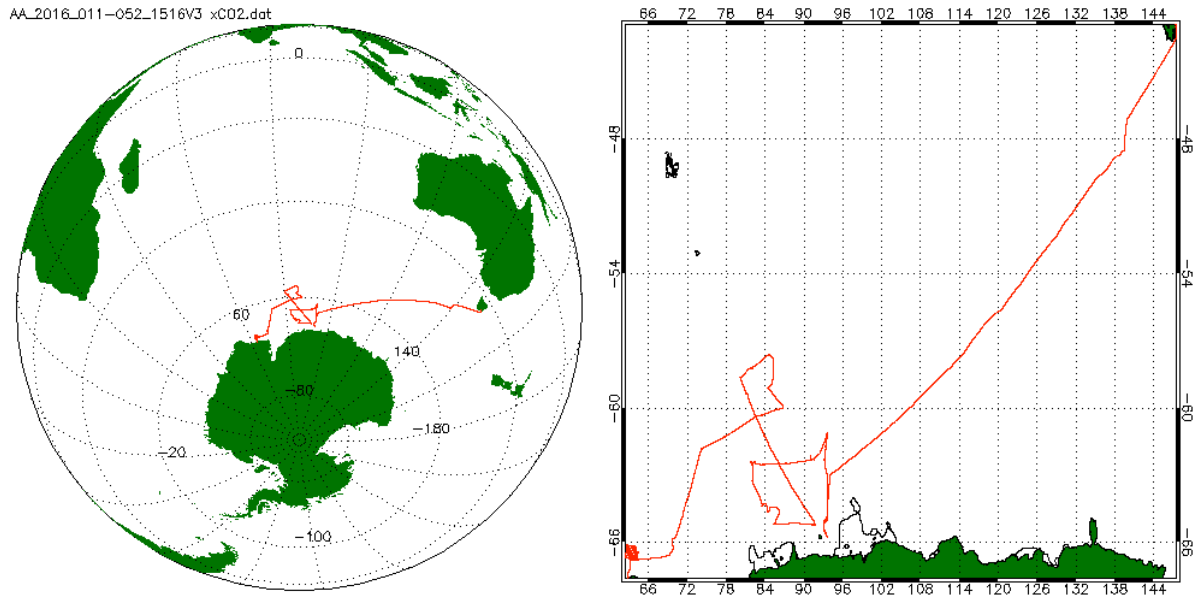
IMOS underway CO_2 dataset report

Dataset: IMOS_09AR20160111_UW.csv

Cruise Information:

Experiment Name: Integrated Marine Observing System (IMOS)
Experiment Type: Ship Of Opportunity Program (SOOP)
Cruise_ID (Expocode): 09AR20160111
Cruise_Info: ***AA1516V03***
Geographical Region: Southern Ocean.
Westernmost Longitude: 62.40940
Easternmost Longitude: 147.46719
Northernmost Latitude: -42.88236
Southernmost Latitude: -67.60137
Cruise Dates (YYYYMMDD)
Start_Date: 20160111
End_Date: 20160315
Ports of Call:
Hobart, Australia and Mawson Station, Antarctica.
Vessel Name: RV Aurora Australis, ICES Platform Code: 09AR, Call Sign: VNAA, Platform Class: 31 Research Vessel, MMSI: 503043000, IMO: 8717283
Vessel ID: 09AR
Vessel Owner: P&O Maritime Services

Track:



Citation

Publications that use these data should reference the data source as:

> Tilbrook, B., J. Akl and C. Neill (2016) Underway CO_2 data for *Aurora Australis* voyage AA1516V3, [SOOP-CO2 data page URL], accessed [date-of-access].

CO_2 System Overview:

The fugacity of carbon dioxide (fCO_2) in surface seawater was measured using a General Oceanics Inc. automated system (Model 8050; Pierrot *et al* 2009). Seawater is sprayed into an equilibration chamber and CO_2 in the headspace gas equilibrates with the seawater. The headspace gas is pumped through a thermoelectric condenser followed by a nafion drying tube, before flowing through a Licor 7000 non-dispersive infrared gas analyser used to measure the CO_2 mole fraction (xCO_2) of the dried air. The gas flow is stopped temporarily for the CO_2 measurements, which are made at atmospheric pressure. A set of four CO_2 standards (Table 1) that cover the range of CO_2 values expected in the ocean are analysed about every three hours to calibrate the gas analyser. Atmospheric xCO_2 (dry) is measured after the standards by pumping clean outside air from an intake on the forward mast of the ship.

Table 1. CO_2-in-air standard values measured on the WMO-X2007 mole fraction scale

Cylinder no.	Cylinder number	CO_2 (ppm)
1, installed 21/09/2015	CA06857	0.0
2, installed 21/09/2015	CB09937	255.93
3, installed 21/09/2015	CA07699	380.52
4, installed 21/09/2015	CA05426	451.12

Seawater intake and ancillary data

The seawater intake is at about 4 m depth. A remote temperature sensor (Seabird Electronics SBE38) located at the intake is used to measure sea surface temperature (SST). Sea surface salinity is measured using a thermosalinograph (Seabird Electronics SBE45) mounted in the oceanographic lab next to the fCO_2 system. The travel time between the intake and CO_2 system is typically about 70 seconds with warming usually less than 0.7ºC in cold waters near freezing. The thermosalinograph water is from the same intake and supply line. Meteorological data, salinity, SST, and ships position and time are taken from the ship's logging system.

Equilibrator Design:

Depth of Seawater Intake: 4 m.
Location of Seawater Intake: The intake is located in the propeller shaft tunnel approximately 4m below the waterline and 10m forward of the stern gland on the port side of the vessel.
Equilibrator Type: Weiss style shower equilibrator with water jacket, General Oceanics.
Equilibrator Volume: 1.2 L
Water Flow Rate: 2.3 L/min
Headspace Gas Flow Rate: 70 - 150 ml/min
Vented: Yes
Drying Method for CO2 in Water:
Thermoelectric condenser (2-5 °C), and Perma Pure (Nafion dryers). Dried to <2 H2O mmol/mol.
Additional Information: Equilibrator with water jacket and vented through a smaller equilibrator.

CO2 in Marine Air:
Measurement: A set of 5 records every 3-4 hours
Location and Height: Mounted ~16m above sea level on the bridge deck outside the Met lab on the port side.
Drying Method:
Thermoelectric condenser (2-5 °C), and Perma Pure (Nafion dryers). Dried to <2 H2O mmol/mol.

CO2 Sensor:

Measurement Method: CO2 mole fraction in dry air (non-dispersive infrared gas analyzer), stopped flow.
Manufacturer: LI-COR
Model: LI-7000 sn: IRG4-0910

Frequency: Every 80 sec, except during calibration routines.
Resolution Water: 0.01 ppm
Uncertainty Water: 2 ppm
Resolution Air: 0.01 ppm
Uncertainty Air: ± 0.2 ppm at 350 ppm
Manufacturer of Calibration Gas:
Std 1 CA06857: 0 ppm 22 Apr 2015, Std 2 CB09937: 255.93 ppm 02 Dec 2013, Std 3 CA07699: 380.52 ppm 20 Jun 2008, Std 4 CA05426: 451.12 ppm 10 Jun 2015. Reference standards were calibrated on WMO-X2007 mole fraction scale for CO2-in-air at CSIRO Marine and Atmospheric Research, Melbourne. Uncertainty = ± 0.05 ppm.
CO2 Sensor Calibration:
The LI-COR analyser is calibrated using four reference standards measured every 3-4 hours. The instrument zero and span are set daily using the low and high reference standards.
Environmental Control:
Method References:
Pierrot D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessen, A. Olsen, R. A. Feely, C. E. Cosca (2009). Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. Deep-Sea Research II, 56, 512-522.

Sea Surface Temperature:

Location: Approximately 150mm inboard from the intake.
Manufacturer: Sea-Bird Electronics
Model: SBE-38 sn: 0395.
Accuracy: ± 0.001 °C (1 mK)
Resolution: 0.00025 °C (0.25 mK)
Calibration: June 2015.
Comments: Sensor maintain by the Australian Antarctic Division.

Equilibrator Temperature:

Location: Probe 60 mm below water line inside the equilibrator.
Manufacturer: Fluke Hart Scientific.
Model: 1521 sn: A66752 pared with probe 5610-9 sn: B072714.
Accuracy: ± 0.025 °C
Resolution: 0.001 °C
Calibration: The meter and pared probe were calibrated as a system on the 28 May 2015 in a NATA facility at CSIRO, Hobart.
Warming: 0.4 - 0.6 °C
Comments:

Equilibrator Pressure:

Location: Attached to equilibrator headspace.
Manufacturer: Setra
Model: 239 sn: 2223344.
Accuracy: ± 0.052 hPa
Resolution: 0.01 hPa
Calibration: Factory calibration.
Comments:
The equilibrator pressure is the differential pressure reading from the Setra-239 attached to the equilibrator headspace added to a pressure reading made using a GE Druck RPT350 sensor located at the outlet of the LI-COR analyser when the analyser is vented to laboratory air for a measurement.

Atmospheric Pressure:

Location: Mounted ~16m above sea level on the bridge deck outside the Meteorological lab on the port side with a velocity head.
Manufacturer: Vaisala
Model: PTB220 sn: A3920002.

Accuracy: ± 0.15
Resolution: 0.01 hPa
Calibration: June 2015. Sensor maintain by the Australian Antarctic Division.
Comments:

Sea Surface Salinity:

Location: Next and inline with water supply to the fCO2 system.
Manufacturer: Sea-Bird Electronics
Model: SBE-45 sn: 0368
Accuracy: ± 0.005 PSU
Resolution: 0.0002 PSU
Calibration: Pre-season calibration made on the 31 Jul 2015, at CSIRO Hobart.
Comments:

Other Sensors:

Location: The instrument is located in the Oceanographic lab, next to the fCO2 system and approximately 20-30 m downstream from the intake.
Manufacturer: Sea-Bird Electronics
Model: SBE-21 sn: 2797
Accuracy: 0.002 PSU (± 0.001 S/m and ± 0.01 °C).
Resolution: 0.0002 PSU.
Calibration: June 2015. Sensor maintain by the Australian Antarctic Division.
Comments:
SBE-21 data was not included, this sensor was used to corroborate the readings of the SBE-45.

Data Fields and Units:

Field	*Name*	*Unit*	*Description*
1.	Group/ship	-	CSIRO/Astrolabe
2.	CruiseID	AAYyYyV#	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 of CO_2 in the equilibrator head space (dry).
9.	xCO2ATM_PPM	ppm	Mole fraction of CO_2 in the atmosphere (dry) measured every 4 hours after standard runs
10.	xCO2ATM_PPM _INTERPOLATED	ppm	Mole fraction of CO_2 in the atmosphere (dry) measured every 4 hours after standard runs and values linearly interpolated to the times shown
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
18.	DfCO2	μatm	fCO_2SW - fCO_2ATM
19.	LICORflow	ml/min	Gas flow through infrared gas analyser
20.	H2Oflow	lpm	Water flow to equilibrator
21.	WindSpd_True	m/s	Wind speed.
22.	WindDirn_True	degrees	Wind direction, 0 is North and 90 is East.
23.	Type	-	Measurement type (equilibrator, standard or atmosphere)
24.	WOCE_QC_FLAG	-	2 = Good 3 = Questionable 4 = Bad (data identified as bad are not reported).
25.	SUBFLAG	-	Secondary flags, only for questionable measurements, WOCE flag 3 (Pierrot *et al* 2009): 1 = Outside of standard range 2 = Questionable/interpolated SST 3 = Questionable EQU temperature 4 = Anomalous (EQU T-SST)(±0.6ºC) 5 = Questionable sea-surface salinity 6 = Questionable pressure 7 = Low EQU gas flow 8 = Questionable air value 10 = Other, water flow

Quality control and data reduction:

Parameters logged by the fCO_2 system and ship sensors are quality controlled after each voyage.

1. Parameter values are flagged as good (flag=2), questionable (flag=3), or bad (flag=4), depending on the range of values expected. Data with missing parameters or obvious outliers for the ship or fCO_2 system parameters are flagged as bad and removed from the calculations. Many of the ship and CO_2 system parameters are not reported in the final dataset, but are used to establish that the system is functioning correctly. For example, water flow rates to the equilibrator below 1.8 LPM are flagged as questionable and the cause investigated with the flag value changed to 4 if the flow has been interrupted or is insufficient. Similar checks are made to ensure the gas flow through the infrared gas analyser is in a suitable range (50 to 120ml/min). The list of parameters checked are:

   CO_2 system data quality controlled:

   GPS date and Time

Latitude and Longitude
Water flow rate
Gas flow rates through licor analyser
Atmospheric pressure
Equilibrator pressure
Equilibrator water temperature
Mole fraction CO_2
Water vapour in gas stream
Licor NDIR temperature

Ship's data quality controlled:

GPS date and time
Latitude and Longitude
Sea surface temperature
Sea surface salinity
Relative wind speed and direction
True wind speed and direction

2. The data sets are next evaluated for excessive warming of the seawater flowing to the equilibrator, and for contamination of the atmospheric measurements by ship stack gas.

   The fCO_2 value in the water is sensitive to warming between the ship intake and equilibrator. 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 (SST) and the equilibrator temperatures. The travel time or lag time is normally about 70 seconds. The warming in the system used on MV *Aurora Australis* is typically about 0.4 °C, increasing to about 0.6°C in cooler regions.

   Atmospheric CO_2 values can be influenced by contamination from ship stack gas. The atmospheric air intake is located on the Port side above the wheelhouse to collect air in the front part of the ship within about 20m of the ship stacks. The relative wind speed and direction recorded by the ship meteorological sensors are used to assess if anomalous atmospheric measurements could be due to stack gas contamination. Data where wind speeds are above $3ms^{-1}$ and with a direction of ±60° of the bow are typically good values. Data with likely stack gas contamination are flagged as bad (flag = 4) and not included in the calculations outlined below.

3. After completion of the quality control checks, the measured mole fractions are corrected to final values using measurements of the four CO_2-in-air standards (Table 1). The standards are run about every four hours to bracket the air and equilibrator measurements. The offsets between the measured and certified values of each standard are linearly interpolated to the times of measurement of the air and equilibrator samples. At each measurement time, a linear regression of offset values versus certified standard values is used to calculate the offset to apply to the measured air and equilibrator values. The corrections are typically small (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 flagged as good are then used to calculate the fugacity of CO_2. Only data flagged as good or suspect are reported in the final data set.

fCO_2SW and fCO_2ATM:

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

$$fCO_2eq = XCO_2(P_{eq} - pH_2O)\exp(P_{atm}(B + 2\delta)/(R \bullet T_{eq}))$$

where XCO_2 is the mole fraction (dry) in the equilibrator headspace, P is the pressure (atm) in the equilibrator or atmosphere; pH_2O is the water vapour pressure (Weiss and Price, 1980) at the temperature of water in the equilibrator (T_{eq}) and its salinity:

$$pH_2O(atm) = \exp(24.4543 - 67.4509(100/T_{eq}) - 4.8489\ln(T_{eq}/100) - 0.000544S)$$

R the ideal gas constant (82.0578 $cm^3 \cdot atm/K \cdot mol$), B the virial coefficient of pure CO_2, and the cross virial coefficient of a CO2-air mixture (Weiss, 1974).

$$B(cm^3/mol) = -1636.75 + 12.0408T_{eq} - 0.032795T_{eq}^2 + 0.0000316528T_{eq}^3$$

$$\delta(cm^3/mol) = 57.7 - 0.118T_{eq}$$

An empirical correction (Copin-Montegut, 1988) is applied to account for warming of water between the sea surface and equilibrator. The same equations are applied to the measurements of the mole fraction of CO_2 in atmospheric gas, using the sea surface temperature and atmospheric pressure.

The air-sea gradient in fCO_2 is calculated as: $DfCO_2 = fCO_2SW - fCO_2ATM$
where fCO_2SW is the bulk surface seawater value and fCO_2ATM the atmospheric value.

Processing Comments:

All values prior to 20160111 10:07:37 were excluded. This is the starting point of the cruise outside the Derwent Estuary.

There was insufficient seawater flowing to the fCO2 system during the times listed below. These data records were flagged as 'bad' and excluded for calculations. 20160121 07:28:52 to 20160121 07:40:50;
20160121 17:58:14 to 20160121 21:17:38;
20160122 07:50:35 to 20160122 07:57:46;
20160122 11:39:54 to 20160122 11:47:05;
20160128 23:48:49 to 20160129 01:19:44;
20160131 01:45:40 to 20160131 04:06:50;
20160131 07:16:43 to 20160131 07:51:42;
20160131 11:07:17 to 20160131 11:35:58;
20160131 12:39:02 to 20160131 13:38:51;
20160131 21:34:13 to 20160201 03:03:13;
20160204 07:55:05 to 20160204 16:45:28;
20160210 23:29:58 to 20160211 00:23:47;
20160214 01:49:46 to 20160214 04:17:47.

There is no SST data between 20160122 10:16:31 to 10:51:11. These records were flagged as 'bad' and excluded for calculations.

The ship's underway sea surface temperature, salinity, and meteorological data were collected and calibrated by the Australian Antarctic Division Data Centre. The salinity values used on this cruise, correspond to a second thermosalinograph installed next in-line with the water supply of the fCO2 system and calibrated and maintained by CSIRO.

EQU Observations: 41920, QCed: 91% good 9% bad (data in the Derwent River was flagged as bad).

ATM Observations: 1311, QCed: 72% good 28% bad.

Acknowledgements:

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References

Copin-Montegut, C. (1988) A new formula for the effect of temperature on the partial pressure of CO_2 in sea water, *Marine Chemistry*, 25, p29-37 (incl. Corrigedum, Marine Chemistry (1989) 27, pp143-144).

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