IMOS underway CO_2 dataset report

Dataset: AA_2013_288-340_V1 fCO2 IMOS.txt

Voyage Information:

MV *Aurora Australis* voyage AA1314V1

Departed:	Hobart, Tasmania,	October 15, 2013
Arrived:	Hobart, Tasmania,	December 07, 2013

Principal Investigator:

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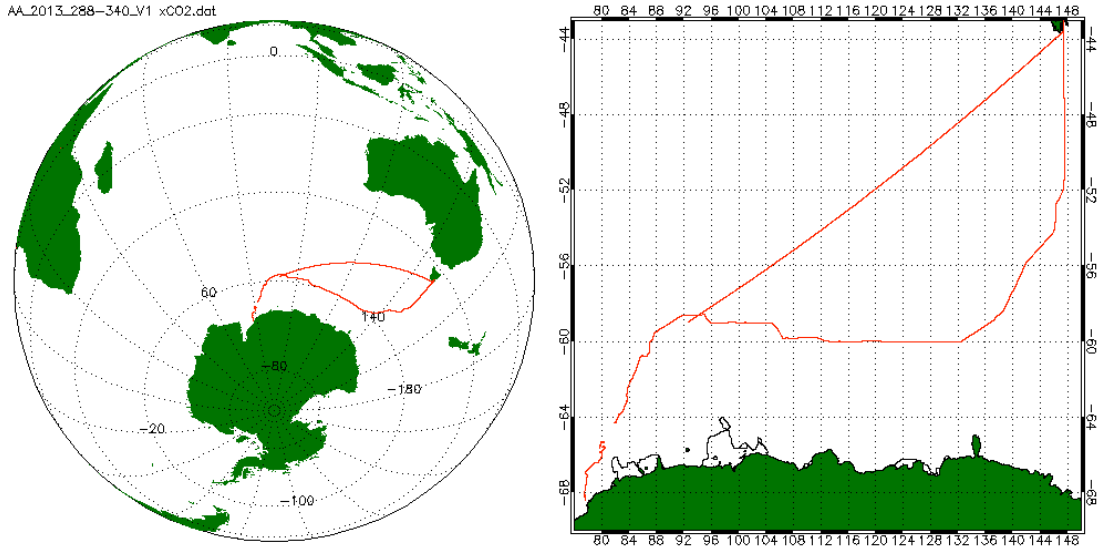
Track:



Ship Details:
Name: Aurora Australis
Call Sign: VNAA
Home Port: Hobart, Australia
Ship owner: P&O Polar

Citation

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

Tilbrook, B., J. Akl and C. Neill (2013) Integrated Marine Observing System underway CO_2 data for *Aurora Australis* voyage AA1314V1, http://www.imos.org.au.

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	CA06898	0.0
2	CA01610	299.41
3	CA01669	353.01
4	CA01673	402.15

Seawater intake and ancillary data

The seawater intake is at about 6 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 SBE21) mounted in the oceanographic lab next to the pCO_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.

System Description:

Equilibrator:	Showerhead, water volume of ~0.5 L, headspace ~ 0.8 L.
Water flow rate:	2 to 3.0 l/min
Headspace gas flow rate:	60-120 ml/min
Measurement method:	Infrared absorption of dried gas.
CO_2 Sensor:	Licor 7000, Serial # IRG4-0910
Resolution/Uncertainty:	±0.3 μatm for equilibrator and atmospheric fCO_2
Equilibrator temperature:	Hart 1521 thermometer (S/N A8B266), 5610-9 probe (S/N B0727114), accuracy ± 0.01°C.
Equilibrator pressure:	Setra Model 239 (S/N 2223344), accuracy ± 0.15 hPa.
Atmospheric pressure:	Druck RPT350 (S/N 2729757), accuracy ± 0.15 hPa. calibrated annually against Druck DPI141 barometric sensor and Bureau of Meteorology barometric pressure standard.
Sea Surface Temperature:	Seabird SBE38, accuracy ± 0.01°C.
Salinity:	Seabird SBE 21 thermosalinograph mounted in the oceanographic lab next to the pCO_2 system, accuracy ±0.01.

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. Data with missing parameters or obvious outliers for the ship or fCO_2 system parameters are marked as missing and removed from the calculations. Parameter values are flagged as good (flag=2), questionable (flag=3), or bad (flag=4), depending on the range of values expected. 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 2 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 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):

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

where XCO_2 is the mole fraction (dry) in the equilibrator headspace, P is the pressure in the equilibrator; 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:

The ship's underway thermosalinograph (salinity), sea surface temperature and meteorological data were collected and calibrated by the Australian Antarctic Division Data Centre.

A second micro thermosalinograph SBE-45 was run next to the pCO_2 system. Data data from this instrument was used when the primary AAD sensor data was missing, specifically between 15/10/2013 12:19 and 18/10/2013 02:22. The average difference between the AAD and the CSIRO thermosalinograph salinities is -0.007.

In the period between 12/11/2013 06:44 and 15/11/2013 02:26, while the ship was in heavy sea ice, the pCO2 system and SBE-45 were being flushed with fresh water and logging was not stopped. The vessel thermosalinograph shows correct salinity values, but the second TSG shows freshwater flowing through the pCO_2 system. All data during this period was flagged as bad and excluded.

The time lag between the intake temperature and the equilibrator temperature on this cruise is of less than 60 seconds. This time lag was not applied to the SST data.

Acknowledgements:

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References

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