NIWA underway CO_2 System Report

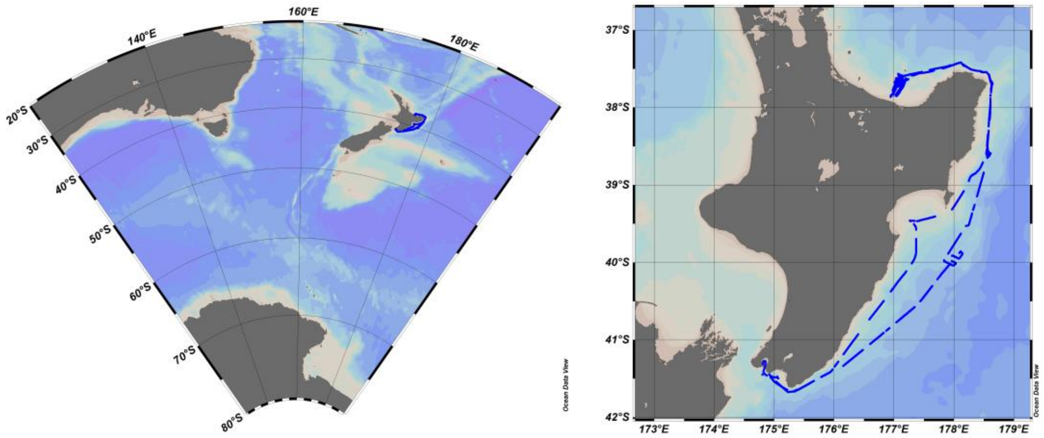
Voyage Information: RV *Tangaroa* voyage TAN1806

Expocode 61TG20180702

Departed:	Wellington	02 July 2018	(UTC)
Arrived:	Wellington	22 July 2018	(UTC)
Data start:	03 July 2018	01:23:19 (UTC)	
Data end:	22 July 2018	00:00:55 (UTC)	

This dataset was collected on the National Institute of Atmospheric Research (NIWA) ship *RV Tangaroa* (http://www.niwa.co.nz/vessels/rv-tangaroa).

Track:



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Data Quality Control

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Institutional Reference

https://www.niwa.co.nz/atmosphere/programme-overview/oceanic-control-of-atmospheric-composition

Acknowledgment

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Distribution statement

Citation:

Any publication that uses these data should reference the data source as:

Currie, K., and A Marriner, (2018) Underway CO_2 data for RV *Tangaroa* voyage TAN1806

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 four hours to calibrate the gas analyser. The standard gas concentrations are on the WMO-X2007 mole fraction scale for CO_2-in-air. Atmospheric XCO_2 (dry) is measured after the standards by pumping clean outside air from an intake on a mast above the bridge of the ship.

Table 1. CO_2-in-air standard values

Standard Number	Cylinder Number	CO_2 (ppm)
1	BOC	0.00
2	3742	336.62
3	3496	398.78
4	3765	451.34

Seawater intake and ancillary data

The seawater intake is located at about 5.5m depth beneath the ship. Sea surface salinity is measured using a thermosalinograph (Seabird Electronics SBE21) located next to the CO_2 system. A remote temperature sensor (Seabird Electronics SBE 38) located at the bow intake is used to measure sea surface temperature (SST). The travel time between the intake and CO_2 system is typically about 3 minutes with warming usually less than 0.5ºC. The thermosalinograph water is teed off one meter before the CO_2 system, meteorological data, salinity, SST, and ships position and time are taken from the ships logging system. These parameters and the data quality are maintained and calibrated by NIWA.

Data Fields and Units:

Field	Variable Name	Unit	Description
1	Expocode	61TGyyyymmdd	
2	GROUP	Text string	Group carrying out the measurements NIWA New Zealand
3	YD_UTC	Decimal day	Julian day (day of year)
4	DATE_UTC	ddmmyyyy	Date in Coordinated Universal Time
5	TIME_UTC	hh:mm:ss	Time in Coordinated Universal Time
6	LATITUDE	degrees_north	Latitude in decimal degrees north
7	LONGITUDE	degrees_east	Longitude in decimal degrees east
8	xCO2EQ	ppm	mole fraction of CO2 in the equilibrator head space (dry)
9	xCO2ATM	ppm	mole fraction of CO2 in the atmosphere (dry)
10	xCO2ATM_ INTERPOLATED	ppm	mole fraction of CO2 in the atmosphere (dry) with values linearly interpolated to the times shown
11	PRES_EQU	hPa	equilibrator head space pressure
12	Press_ATM@SSP	hPa	barometric pressure from ship's weather station

13	TEMP_EQU	Degrees Celsius	Equilibrator water temperature
14	SST	Degrees Celsius	Sea surface temperature from SBE38
15	SAL	permil	Sea-surface-salinity from SBE21
16	fCO2_SW@SST	μatm	fugacity of carbon dioxide at surface water salinity and temperature
17	fCO2_ATM_interpolated	μatm	fugacity of CO2 in the atmosphere, with values linearly interpolated to the times shown
18	dfCO2	μatm	Difference between fCO2SW and fCO2ATM
19	WOCE-QC_FLAG		WOCE quality control flag: 2 = Good 3 = Questionable 4 = Bad (data identified as bad are not reported).
20	QC_SUBFLAG	Text string	Description of why data was flagged 3

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 less than 1.5 L/min 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 (40 to 120 ml/min). The underway instrument system is flushed daily with fresh water, the data from this time is removed. 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

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 usually about 3 minutes, although this can vary due to ship engineers altering the flow rates through the water line and other users removing water. The lag is accounted for in the warming calculation. High lags cause some smearing of the equilibrator temperature signal, relative to the SST, are also expected to cause some smoothing of the fCO_2 signal. The warming in the system used on RV *Tangaroa* is typically less than 0.5 °C, with higher values expected in cooler regions, or when water flow problems occur. Data with excessive warming (>0.6°C) is examined to evaluate the cause. The higher lags can result in greater warming when the ship is in cooler waters. Low water flow rates are typically associated with anomalously high warming and these data are flagged as bad.

Atmospheric CO_2 values can be influenced by contamination from industrial and population centres and from contamination with ship stack gas. The intake above the bridge of the ship is within about 20m of the ship's auxiliary stacks. The data with likely stack gas contamination are flagged as bad (flag = 4) and not included in the calculations outlined below. The mean and standard deviation of the remaining data are determined, and values outside mean ± 2 σ are flagged as bad (flag = 4)

3. After completion of the quality control checks, the measure 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 (about 1 to 2 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 (flags 2 and 3) 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_{eq} is the headspace 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 δ is 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: $DfCO_2 = fCO_2SW - fCO_2ATM$

Processing Comments:

Ship's underway thermosalinograph, sea surface temperature and meteorological data were collected, and calibrated annually.

Data processing was done using pCO2Sys V1.27 (D. Pierrot, 2018)

Acknowledgements:

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References

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