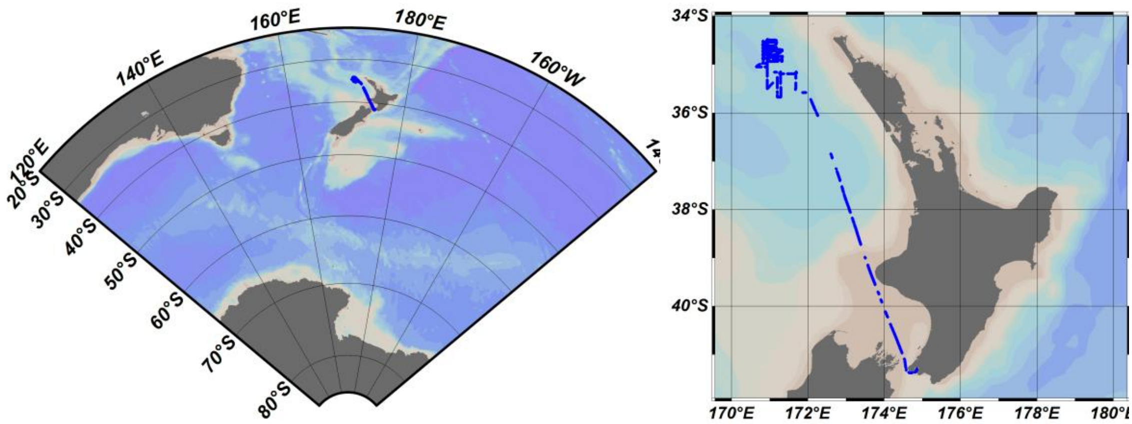
NIWA underway CO_2 System Report

Voyage Information: RV *Tangaroa* voyage TAN1407

Departed:	Wellington	02 June 2014 (UTC)
Arrived:	Wellington	15 June 2014 (UTC)
Data start:	11-June-2014	01:43:08 (UTC)
Data end:	15-June-2014	07:22:23 (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:



Principal Investigator
Dr Kim Currie
NIWA
PO Box 56
Dunedin, New Zealand

Instrumentation
Andrew Marriner (NIWA), John McGregor (NIWA)

Data Quality Control
Andrew Marriner (NIWA), Murray Smith (NIWA)

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

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

Currie , K., A Marriner and M. Smith, (2014) Underway CO_2 data for RV *Tangaroa* voyage TAN1407, [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 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

Cylinder no.	Cylinder number	CO_2 (ppm)
1	3485	0.00
2	3488	334.15
3	3492	394.59
4	3496	416.31

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	TIME	days since 1950-01-01 00:00:00	Analysis time
2	LATITUDE	degrees_north	Latitude in decimal degrees north
3	LONGITUDE	degrees_east	Longitude in decimal degrees east
4	TEMP	Degrees Celsius	Sea surface temperature from SBE38
5	TEMP_2	Degrees Celsius	Equilibrator water temperature
6	PSAL	psu	Sea-surface-salinity from SBE21
7	Press_ATM	hPa	barometric pressure from ship's weather station
8	Press_Equil	hPa	equilibrator head space pressure
9	xCO2ATM_PPM	ppm	mole fraction of CO2 in the atmosphere (dry)
10	xCO2ATM_PPM_	ppm	mole fraction of CO2 in the atmosphere (dry)

	INTERPOLATED		with values linearly interpolated to the times shown
11	xCO2EQ_PPM	ppm	mole fraction of CO2 in the equilibrator head space (dry)
12	fCO2SW_UATM	μatm	fugacity of carbon dioxide at surface water salinity and temperature
13	fCO2ATM_UATM_INTERPOLATED	μatm	fugacity of CO2 in the atmosphere) with values linearly interpolated to the times shown
14	DfCO2	μatm	Difference between fCO2SW and fCO2ATM
15-28	VARIABLE_quality_control		WOCE quality control flag: 2 = Good 3 = Questionable 4 = Bad (data identified as bad are not reported).

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.

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 are report 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: $DfCO_2 = fCO_2SW - fCO_2ATM$

Processing Comments:

Ship's underway thermosalinograph, sea surface temperature and meteorological data were collected and calibrated annually.
Cylinder 1 was not used during this cruise (0 ppm).

Acknowledgements:

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References

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Questions and comments:

Dr. Kim Currie,
NIWA
PO Box 56
Dunedin
New Zealand
ph: +64- 3-479 5249
email:kim.currie@niwa.co.nz