# NIWA underway CO₂ System Report

**Voyage Information**:   RV *Tangaroa* voyage TAN2409
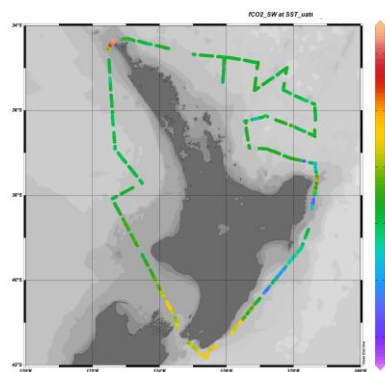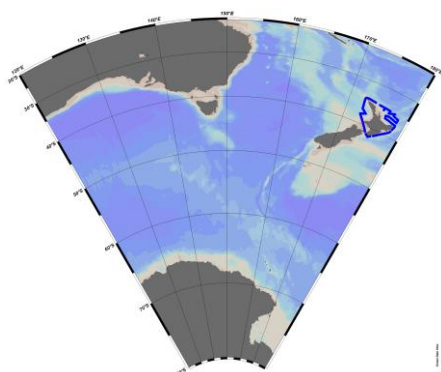
**Expocode**          61TG20240904

| | | | |
|---|---|---|---|
| **Departed:** | Wellington, New Zealand | 05 September 2024 | (NZST) |
| **Arrived:** | Wellington, New Zealand | 13 September 2024 | (NZST) |
| **Data start**: | 05 September 2024 | 03:09:52 | (UTC) |
| **Data end:** | 13 September 2024 | 0:49:10 | (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**
Andrew Marriner (NIWA)

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

**Acknowledgment**
This data was collected with funding from the Atmosphere and Climate Centre, NIWA, New Zealand. Post-processing software courtesy Denis Pierrot, NOAA

**Distribution statement**
Data, products and services from NIWA are provided "as is" without any warranty as to fitness for a particular purpose.

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

van de Velde, S., and A Marriner, (2024) Underway $CO_2$ data for RV *Tangaroa* voyage TAN2409

**$CO_2$ 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 2.5 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 | 3488 | 327.53 |
| 3 | 3742 | 414.35 |
| 4 | 3765 | 438.69 |

**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 hull 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 0.5°C. 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 | $\mu$atm | fugacity of carbon dioxide at surface water salinity and temperature |
| 17 | fCO2_ATM_interpolated | $\mu$atm | fugacity of $CO_2$ in the atmosphere, with values linearly interpolated to the times shown |
| 18 | dfCO2 | $\mu$atm | Difference between fCO2SW and fCO2ATM |
| 19 | WOCE-QC_FLAG | | WOCE quality control flag:<br>2 = Good<br>3 = Questionable<br>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. Data with $\Delta T$ > bulk $\Delta T \pm 0.3$ °C are flagged 3.

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 $\pm 2\sigma$ 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):

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

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 $\delta$ 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:**

**References**

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**Questions and comments:**

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