Description of Underway pCO_2 System and data collected onboard the container ship *Natalie Schulte* from October 2010 through June 2012.

Under the support of NOAA's Climate Program Office (CPO), the Pacific Marine Environmental Laboratory (PMEL) is collaborating with other NOAA investigators and academic partners to document ocean carbon sources and sinks by outfitting research ships and commercial vessels with automated carbon dioxide sampling equipment to analyze the carbon exchange between the ocean and atmosphere. From the fall of 2010 through the spring of 2012, PMEL deployed an underway pCO_2 system on the Hamburg Sud container ship *Natalie Schulte*. The *Natalie Schulte* regularly traveled between Long Beach, California, and New Zealand, an important and dynamic equatorial Pacific region for sea surface flux of CO_2.

This report documents the underway pCO_2 measurements collected during 9 transits across the Pacific from March 2011 through June 2012. Two additional transits from October and December, 2010, are published in DOI 10.3334/CDIAC/OTG.VOS_NATALIE_SCHULTE_LINES.

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Ship Name: Natalie Schulte
Call Sign: C4AJ2
Country: Germany

Ship Owner: Schulte Thomas Reederei

Spatial and Temporal Coverage:
See table below for details on each cruise.

Cruises included in DOI 10.3334/CDIAC/OTG.VOS_NATALIE_SCHULTE_LINES:

Cruise Name	Data File Name	Start Date	End Date	Start Port	End Port	Ship Rider	Gas standards			
							Standard 1	Standard 2	Standard 3	Standard 4
NS_2010_09	NS2010_09.csv	1-Oct-10 15:43:28	13-Oct-10 23:30:04	Long Beach, CA	New Zealand	Carrie Wolfe SCMI	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2010_11	NS2010_11.csv	25-Nov-10 21:20:44	8-Dec-10 22:41:29	Long Beach, CA	New Zealand	Nancy Williams Univ. of Wash	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm

Cruises included in this report:

Cruise Name	Data File Name	Start Date	End Date	Start Port	End Port	Ship Rider	Gas standards			
							Standard 1	Standard 2	Standard 3	Standard 4
NS_2011_03	NS2011_03.csv	22-Mar-11	31-Mar-11	Long Beach, CA	New Zealand	Geoff Lebon Univ. of Wash	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2011_05	NS2011_05.csv	13-May-11	2-Jun-11	Long Beach, CA	Australia	John Akl CSIRO	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2011_07	NS2011_07.csv	9-Jul-11	20-Jul-11	Long Beach, CA	New Zealand	Sylvia Univ. of Wash	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2011_09	NS2011_09.csv	2-Sep-11	14-Sep-11	Long Beach, CA	New Zealand	John Akl CSIRO	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2011_11	NS2011_11.csv	29-Oct-11	9-Nov-11	Long Beach, CA	New Zealand	Geoff Lebon Univ. of Wash	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2012_01	NS2012_01.csv	24-Jan-12	5-Feb-12	New Zealand	Long Beach, CA	Carrie Wolfe SCMI	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2012_02	NS2012_02.csv	16-Feb-12	29-Feb-12	Long Beach, CA	New Zealand	Geoff Lebon Univ. of Wash	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2012_04	NS2012_04.csv	16-Apr-12	3-May-12	Long Beach, CA	Australia	John Akl CSIRO	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm
NS_2012_06	NS2012_06.csv	8-Jun-12	21-Jun-12	Long Beach, CA	New Zealand	Carrie Wolfe SCMI	LL70585 299.64 ppm	LL154364 398.47 ppm	LL154368 511.8 ppm	LL70568 601.75 ppm

Location of data: www.pmel.noaa.gov/co2/

Experiment Name: pCO_2 on Ships

Sponsor: NOAA Climate Program Office/Climate Observation Division

Name/Model of pCO2 System: GO8050, built by General Oceanics.

Method Description:
Equilibrator type/specifications: Showerhead, volume of ~0.5 L with a headspace of ~ 0.8 L.
Water Flow rate: 3.5 L/minute
Headspace gas flow rate: 60 ml/minute
Measurement method: Infrared absorption of dried gas.
CO_2 Sensor: Licor 7000, Serial # IRG4-0560
Resolution/Uncertainty: ± 2 µatm for equilibrator measurements, ± 0.1 ppm for atmospheric measurements.

Temperature and salinity measurements:
Equilibrator Temperature: Hart Scientific model 1521 digital thermometer, serial number A77488, with an NIST traceable model 5610 thermistor probe, serial number A690613. Accurate to ± 0.01°C.
Sea Surface Temperature: A Seabird SBE 48 Hull mounted temperature probe, serial number 480024, was installed on hull approximately 10m below the sea surface. The SBE 48 was calibrated annually, with a reported accuracy of ± 0.01°C. Temperature was also measured at the seawater intake with a Seabird SBE 21 sensor. Accuracy: ± 0.01°C, Precision: ± 0.001°C.
Salinity: A Seabird SBE 45 thermosalinograph, serial number 4548581-0238, was mounted next to the underway pCO_2 system in the engine room. The unit was calibrated annually and provided salinity accurate to 0.1.

Pressure measurements: Pressure inside the equilibrator was measured with a Setra 239 differential pressure transducer, accurate to ± 0.15 hPa. The equilibrator was passively vented to a secondary equilibrator, and the Licor sample output was vented to the laboratory when CO2 measurements were made, thus equilibrator headspace pressure was assumed to be laboratory pressure. Pressure in the laboratory was measured with a GE Druck barometer with an accuracy of ± 0.01 %fs. A Druck barometer was also placed on the flying bridge of the ship for atmospheric pressure measurements.

Standard gases:
Standard gases are supplied by NOAA's Climate Monitoring Diagnostics Laboratory in Boulder, CO, and are directly traceable to the WMO scale. Any value outside the range of the standards should be considered approximate, although the general trends should be indicative of the seawater chemistry. See attached table for standard concentrations for each cruise.

Sampling Cycle:
The system runs a full cycle in approximately 6 hours. The cycle starts with 4 standard gases, then measures two cylces of 6 atmospheric samples followed by 60 surface water measurements. Each new gas is flushed through the Licor Analyzer for 3 minutes prior to a 10 second reading from the analyzer during which the sample cell is open to the atmosphere. Subsequent samples of the same gas are flushed through the Licor Analyzer for 180 seconds prior to a stop-flow measurement.

Units:
All xCO_2 values are reported in parts per million by volume (ppmv) and fCO_2 values are reported in microatmospheres (µatm) assuming 100 % humidity at the equilibrator temperature.

Calculations:
The measured xCO_2 values are linearly corrected for instrument response using the standard measurements.

Mixing ratios of dried equilibrated headspace and air are converted to fugacity of CO_2 in surface seawater and water saturated air in order to determine the fCO2. For ambient air and equilibrator headspace the fCO_2a, or fCO_2eq is calculated assuming 100% water vapor content:

$$fCO_2a/eq = xCO_2a/eq(P-pH_2O)\exp(B_{11}+2d_{12})P/RT$$

where fCO2a/eq is the fugacity in ambient air or equilibrator, pH_2O is the water vapor pressure at the sea surface temperature, P is the barometric pressure, T is the SST or equilibrator temperature (in K) and R is the ideal gas constant ($82.057\ cm^3 \cdot atm \cdot deg^{-1} \cdot mol^{-1}$). The exponential term is the fugacity correction where B_{11} is the second virial coefficient of pure CO_2

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E\text{-}5\ T^3$$

and $d_{12} = 57.7 - 0.118\ T$

is the correction for an air-CO_2 mixture in units of $cm^3 \cdot mol^{-1}$ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO_2 due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.2 °C warmer than sea surface temperature. The empirical temperature correction from equilibrator temperature to SST is outlined in Weiss et al. (1982).

$$\Delta\ln(fCO_2)=(Teq-SST)(0.0317-2.7851E\text{-}4\ Teq - 1.839E\text{-}3\ \ln(fCO_2eq))$$

where $\Delta\ln(fCO_2)$ is the difference between the natural logarithm of the fugacity at Teq and SST, and Teq is the equilibrator temperature in degrees C.

A detailed description of calculations and QC procedures can be found in Pierrot et al. (2009).

File Format

	COLUMN HEADER	DESCRIPTION
1.	GROUP/SHIP:	PMEL/Natalie Schulte
2.	CRUISE_ID:	NS_<Year>_<month>
3.	JD_GMT:	Decimal year day
4.	Date_DDMMYYYY	Date in the format DDMMYYYY
5.	TIME_HH:MM:SS:	GMT HH:MM:SS
6.	LAT_DEC_DEGREE:	Latitude in decimal degrees (negative values are in southern hemisphere).
7.	LONG_DEC_DEGREE:	Longitude in decimal degrees (negative values are in western latitudes).
8.	xCO2W_PPM:	Mole fraction of CO_2 (dry) in the headspace equilibrator at equilibrator temperature (Teq) in parts per million. Water comes from bow intake 5m below the water line.

9	xCO2A_PPM:	Mole fraction of CO_2 in air in parts per million.
10	xCO2A_INTERPOLATED_PPM:	xCO_2atm_ppm averaged linearly to match up with measurements xCO_2eq_ppm
11	PRES_EQUIL_hPa:	Barometric pressure in the equilibrator
12	PRES_SEALEVEL_hPa:	Barometric pressure in the atmosphere
13.	EqTEMP_C:	Temperature in the equilibrator water.
14.	SST(TSG)_C:	Temperature from the ship's bow intake.
15.	SAL(TSG)_PERMIL:	Thermosalinograph salinity
16.	fCO2W@SST_uATM:	Fugacity of CO_2 in sea water in microatmospheres calculated as outlined in the DOE Handbook.
17.	CO2A_uATM:	Fugacity of CO_2 in air in microatmospheres
18.	dfCO2_uatm:	Sea water fCO_2 - air fCO_2 in microatmospheres.
19.	QC_FLAG:	Quality control flag 2 = Good value 3 = Questionable value 4 = Bad value
20.	QC_SUBFLAG:	Descriptive quality control flag used when a value receives a "3" QC flag 1 = Outside of Standard Range 2 = Questionable/interpolated SST 3 = Questionable EQU temperature 4 = Anomalous ΔT (EqT – SST)($\pm$ 1°C) 5 = Questionable Sea Surface Salinity 6 = Questionable pressure 7 = Low EQU gas flow 8 = Questionable air value 9= Interpolated standard value 10 = Other, see metadata

References

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