

# **Description of Underway pCO<sub>2</sub> System onboard the OOCL Ship *Tianjin* from September 2008 through February 2010**

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. During the summer of 2008, PMEL deployed an underway pCO<sub>2</sub> system on the Orient Overseas Container Line (OOCL) container ship *Tianjin*. The OOCL *Tianjin* regularly travels between Hong Kong and Long Beach, California, an important North Pacific sink region for atmospheric CO<sub>2</sub>. Data were collected to determine how ocean circulation and biological photosynthesis interact to control the rate of exchange of carbon dioxide gas between the atmosphere and North Pacific Ocean.

This report documents the underway pCO<sub>2</sub> measurements collected during 8 transits across the North Pacific from September 2008 through February 2010.

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## **Ship Name:** OOCL Tianjin

Call Sign: VRAR7

Country: China

Ship Owner: Orient Overseas Container Line

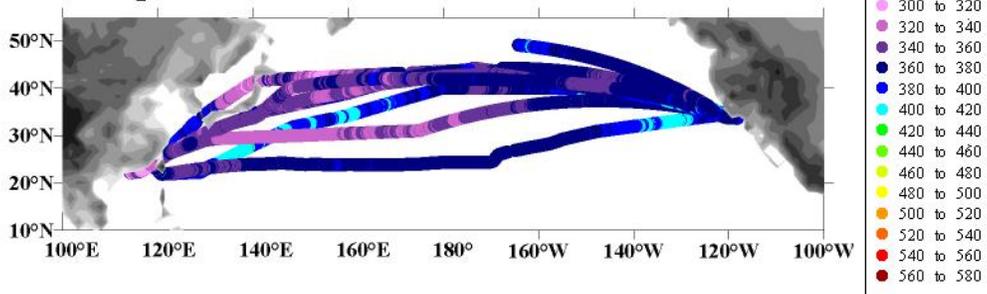
## **Temporal Coverage:**

8 cruises in the North Pacific from Hong Kong to Long Beach, California.  
See table below for details on each cruise.

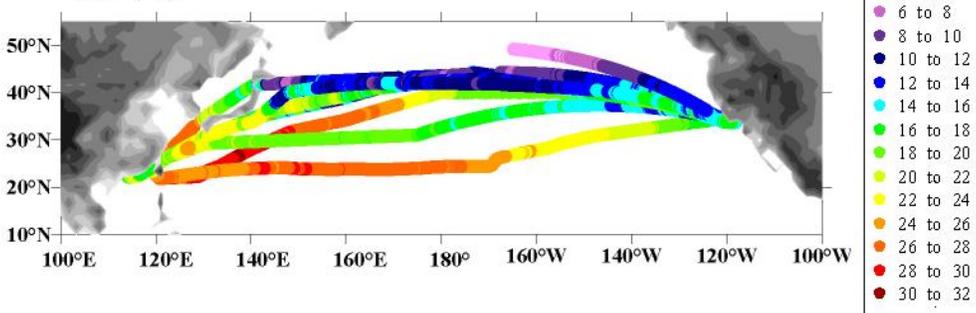
Cruise Name	Data File Name	Start Date	End Date	Start Port	End Port	Ship Rider	Gas standards			
							Standard 1	Standard 2	Standard 3	Standard 4
OOCL_TJ_2008_09	TJ2008_09.csv	19-Sep-08	29-Sep-08	Long Beach, CA	Hong Kong	Geoff Lebon NOAA/PMEL	LL70570 248.49 ppm	LL55879 351.07 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2008_10	TJ2008_10.csv	6-Oct-08	15-Oct-08	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL55879 351.07 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2008_11	TJ2008_11.csv	12-Nov-08	11-Dec-08	Hong Kong	Hong Kong	Yong-Min Liu and Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL55879 351.07 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2009_01	TJ2009_01.csv	19-Jan-09	30-Jan-09	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL81353 347.22 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2009_03	TJ2009_03.csv	31-Mar-09	11-Apr-09	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL81353 347.22 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2009_10	TJ2009_10.csv	30-Oct-09	7-Nov-09	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL81353 347.22 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2009_12	TJ2009_12.csv	2-Dec-09	12-Dec-09	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL81353 347.22 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm
OOCL_TJ_2010_02	TJ2010_02.csv	18-Feb-10	21-Feb-10	Hong Kong	Long Beach, CA	Deirdre Lockwood Univ. of Wash	LL70570 248.49 ppm	LL81353 347.22 ppm	LL55872 403.63 ppm	LL55877 483.45 ppm

## OOCL Tianjin, September 2008 through February 2010

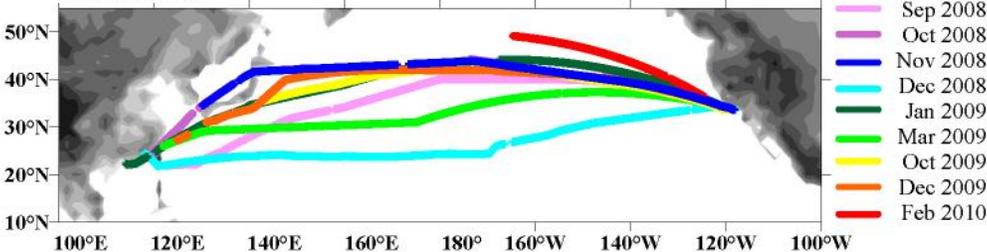
fCO<sub>2</sub>sw [µatm]



SST (°C)



Track Lines



**Location of data:** [www.pmel.noaa.gov/co2/](http://www.pmel.noaa.gov/co2/)

**Experiment Name:** Underway measurement of atmospheric and surface water pCO<sub>2</sub>

**Name/Model of pCO<sub>2</sub> 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<sub>2</sub> Sensor: Licor 7000, Serial # IRG4-0586

Resolution/Uncertainty: 0.3 µatm for equilibrator measurements, 0.2 µatm for atmospheric measurements.

**Temperature and salinity measurements:**

Equilibrator Temperature: Hart Scientific model 1521 digital thermometer, serial number A68850, with an NIST traceable model 5610 thermistor probe, serial number A690607. Accurate to ± 0.01°C.

Sea Surface Temperature: A Seabird SBE 48 Hull mounted temperature probe, serial number 480028, was installed on hull approximately 5m below the sea surface. The SBE 48 was calibrated annually, with a reported accuracy of ± 0.01°C.

Salinity: A Seabird SBE 45 thermosalinograph, serial number 4548581-0238, was mounted next to the underway pCO<sub>2</sub> 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 CO<sub>2</sub> measurements were made, thus equilibrator headspace pressure was assumed to be laboratory pressure. Pressure in the laboratory was measured with a GE Druck barometer, serial number 3054512, with an accuracy of ± 0.01 %fs.

**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 3 hours. The cycle starts with 4 standard gases, then measures three cycles of 20 surface water measurements followed by 6 atmospheric samples. Each new gas is flushed through the Licor Analyzer for 4 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 30 seconds prior to a stop-flow measurement.

**Units:**

All xCO<sub>2</sub> values are reported in parts per million by volume (ppmv) and fCO<sub>2</sub> values are reported in microatmospheres (µatm) assuming 100 % humidity at the equilibrator temperature.

**Calculations:**

The measured xCO<sub>2</sub> 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<sub>2</sub> in surface seawater and water saturated air in order to determine the fCO<sub>2</sub>. For ambient air and equilibrator headspace the fCO<sub>2a</sub>, or fCO<sub>2eq</sub> is calculated assuming 100% water vapor content:

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

where fCO<sub>2a/eq</sub> is the fugacity in ambient air or equilibrator, pH<sub>2</sub>O 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<sup>3</sup>·atm·deg<sup>-1</sup>·mol<sup>-1</sup>). The exponential term is the fugacity correction where B<sub>11</sub> is the second virial coefficient of pure CO<sub>2</sub>

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

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

is the correction for an air-CO<sub>2</sub> mixture in units of cm<sup>3</sup>·mol<sup>-1</sup> (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO<sub>2</sub> 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).

$$\Delta\ln(fCO_2)=(T_{eq}-SST)(0.0317-2.7851E-4 T_{eq} - 1.839E-3 \ln(fCO_{2eq}))$$

where Δln(fCO<sub>2</sub>) is the difference between the natural logarithm of the fugacity at T<sub>eq</sub> and SST, and T<sub>eq</sub> 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

	<b>COLUMN HEADER</b>	<b>DESCRIPTION</b>
1.	GROUP/SHIP:	PMEL/OOCL_Tianjin
2.	CRUISE_ID:	Tian_<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 <sub>2</sub> (dry) in the headspace equilibrator at equilibrator temperature (T <sub>eq</sub> ) in parts per million. Water comes from bow intake 5m below the water line.
9	xCO2A_PPM:	Mole fraction of CO <sub>2</sub> in air in parts per million.
10	xCO2A_INTERPOLATED_PPM:	xCO <sub>2</sub> atm_ppm averaged linearly to match up with measurements xCO <sub>2</sub> eq_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 <sub>2</sub> in sea water in microatmospheres calculated as outlined in the DOE Handbook.
17.	CO2A_uATM:	Fugacity of CO <sub>2</sub> in air in microatmospheres
18.	dfCO2_uatm:	Sea water fCO <sub>2</sub> - air fCO <sub>2</sub> 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 $\Delta T$ (EqT - SST)( $\pm 1^\circ\text{C}$ ) 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

DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon

- dioxide system in sea water; version 2. A.G. Dickson and C. Goyet, eds., ORNL/CDIAC-74.
- Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy (1998). A new automated underway system for making high precision pCO<sub>2</sub> measurements onboard research ships, *Analytica Chim. Acta*, 377, 185-191, 1998.
- Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessen, A. Olsen, R. A. Feely, C. E. Cosca (2009). Recommendations for autonomous underway pCO<sub>2</sub> measuring systems and data-reduction routines. *Deep Sea Research Part II: Topical Studies in Oceanography*, Volume 56, Issues 8-10, Pages 512-522.
- Wanninkhof, R. and K. Thoning (1993) Measurement of fugacity of CO<sub>2</sub> in surface water using continuous and discrete sampling methods. *Mar. Chem.* 44(2-4): 189-205.
- Weiss, R. F. (1970) The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research* 17: 721-735.
- Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203-215.
- Weiss, R. F., R. A. Jahnke and C. D. Keeling (1982) Seasonal effects of temperature and salinity on the partial pressure of CO<sub>2</sub> in seawater. *Nature* 300: 511-513.

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