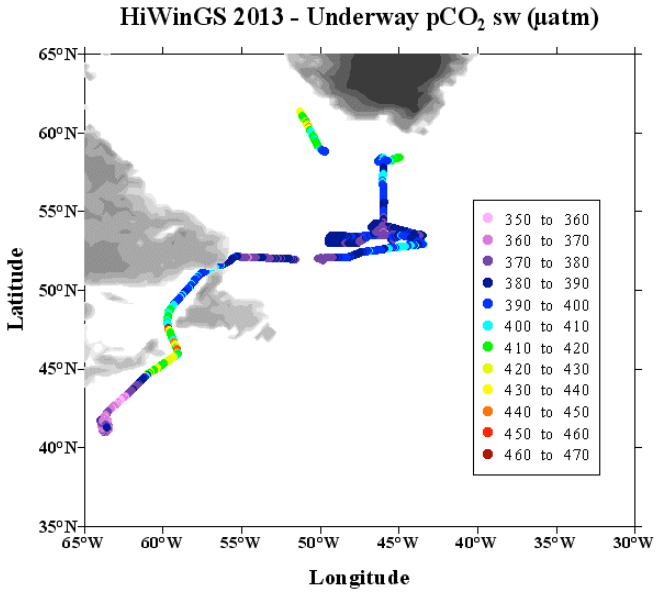
Underway pCO_2 collected on the R/V *Knorr* from October 10 through November 15, 2013 during the HiWinGS (KN213-03) cruise

In October 2013, the Pacific Marine Environmental Laboratory (PMEL) installed an underway pCO2 system on board the R/V *Knorr* to collect surface and atmospheric pCO2 during the High Wind Gas Exchange Study (HiWinGS). This study took place in the North Atlantic Ocean from October 10 to November 15, 2013.



Ship Name: R/V Knorr
Call Sign: KCEJ
Country: United States
Ship Owner: The R/V *Knorr* is owned by the U.S. Navy and operated by Woods Hole Oceanographic Institution for the ocean research community.

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Temporal Coverage:
October 10 to November 15, 2013

Geographic Coverage/Ports: Nuuk Greenland to Woods Hole, Massachusetts

Experiment Name: High Wind Gas Exchange Study (HiWinGS)

Name/Model of pCO_2 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 # IRG4-0586
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 132061, with an NIST traceable model 5610 thermistor probe, serial number B180905. Accurate to ± 0.01°C.
Sea Surface Temperature and Salinity were measured with a Seabird thermosalinograph maintained by the ship.

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, serial number 3392232, 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.
Serial numbers and concentrations of standards used on the *R/V Knorr* HiWinGS cruises:

LL70570	248.49 ppm
LL81353	347.2 ppm
LL55878	405.96 ppm
LL83529	552.53 ppm

Sampling Cycle:
The system runs a full cycle in approximately 5 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 saturation water vapor pressure at the equilibrator or SST temperature, P is the barometric pressure in the equilibrator or at the sea surface, 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 tubing within the ship to the instrumentation in the lab. The water in the equilibrator was 0.5 to 2.5 °C warmer than sea surface temperature. The empirical temperature dependence from equilibrator temperature to SST is outlined in Takahashi et al. (1993).

$$fCO2\ wet/sst = fCO2\ wet/Teq \exp\{0.0423(SST - Teq)\}$$

where SST is the sea-surface temperature in the same units as Teq.

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/RV Knorr
2.	CRUISE_DESIGNATION:	HiWinGS_2013
3.	JD_GMT:	Decimal year day
4.	DATE_MM_DD_YYYY	Date in the format MM/DD/YYYY
5.	DATE_DDMMYYYY	Date in the format DDMMYYYY
6.	TIME_HH_MM_SS:	UTC HH:MM:SS
7.	LAT_DEC_DEGREE:	Latitude in decimal degrees (negative values are in southern hemisphere).
8.	LONG_DEC_DEGREE:	Longitude in decimal degrees (negative values are in western latitudes).
9.	xCO2W_PPM:	Mole fraction of CO_2 (dry) in the equilibrator headspace at equilibrator temperature (Teq) in parts per million. Water comes from bow intake 5m below the water line.
10.	xCO2A_PPM:	Dry mole fraction of CO_2 in air in parts per million.
11.	xCO2A_INTERPOLATED_PPM:	xCO_2atm_ppm interpolated linearly to match up with measurements of xCO_2eq_ppm.
12.	PRES_EQUIL_hPa:	Barometric pressure in the equilibrator.
13.	PRES_SEALEVEL_hPa:	Barometric pressure in the atmosphere.
14.	EqTEMP_C:	Temperature in the equilibrator water.

15.	SST_TSG_C:	Temperature from the ship's bow intake.
16.	SAL_TSG_PERMIL:	Thermosalinograph salinity.
17.	fCO2W_SST_uATM:	Fugacity of CO_2 in sea water in microatmospheres calculated as outlined in the DOE Handbook.
18.	fCO2A_uATM:	Fugacity of CO_2 in air in microatmospheres
19.	dfCO2_uATM:	Sea water fCO_2 - air fCO_2 in microatmospheres.
20.	pCO2W_SST_uATM:	p CO_2 in sea water in microatmospheres, no fugacity correction.
21.	pCO2A_uATM:	pCO_2 in air in microatmospheres.
22.	dpCO2_uATM:	Sea water pCO_2 - air pCO_2 in microatmospheres.
23.	QC_FLAG:	Quality control flag 2 = Good value 3 = Questionable value 4 = Bad value

References

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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_2 measurements onboard research ships, Analytica Chim. Acta, 377, 185-191, 1998.

Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessesn, A. Olsen, R. A. Feely, C. E. Cosca (2009). Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. Deep Sea Research Part II: Topical Studies in Oceanography, Volume 56, Issues 8-10, Pages 512-522.

Takahashi,T., Olafsson,J., Goddard,J.G., Chipman,D.W., Sutherland, S.C., 1993. Seasonal variation of CO2 and nutrients in the high-latitude surface oceans—a comparative study.Global Biogeochemical Cycles 7(4), 843–878.

Wanninkhof, R. and K. Thoning (1993) Measurement of fugacity of CO_2 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_2 in seawater. Nature 300: 511-513.