Cruise: GU1305

**Ship:** R/V Gordon Gunter

**Dates:** Nov. 13<sup>th</sup> – Nov. 25<sup>th</sup>, 2013 **Chief Scientist:** Harvey Walsh **Equipment:** CTD Rosette **Total number of stations:** 23

## Sample Collection

Locations: North Atlantic from 38.00 N to 43.7733 N and 65.77 W to 74.9617 W Samplins Dates (mm/dd/yyyy): 11/14/2013 – 11/24/2013.

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette onboard the ship by Christopher Taylor of the NE Fisheries science center. The date and time listed in the data file are UTC when each sample bottle was collected.

#### DIC:

23 locations, 75 samples each 500-ml, 7 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

## pH:

23 locations, 75 samples each 500-ml, 7 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

#### TAlk:

23 locations, 75 samples each 500-ml, 7 duplicate samples.

Sample ID#:

PI: Dr. Rik Wanninkhof

Analyzed by: Dr. Leticia Barbero and Dr. Denis Pierrot

# Sample Analysis

**DIC:** All CRMs are from batch 112: cert.S= 33.305 and cert. DIC =  $2011.09 \mu mol/kg$ .

				meas DIC	Offset	Run	Times (r	nin.)
Data	Blanks	CRM	CRM#	(1170)	1/1,~)	A ***	Min	Mov
Date	(cnts/min)	batch	CKM #	(μπс	ol/kg)	Avg	Min.	Max.
2/11/14	19.00	112	293	2011.70	0.61	13.8	11.0	20.0
2/12/14	34.80	112	818	2013.02	1.93	9.7	8	20
2/14/14	25.00	112	245	2014.04	2.95	9.6	8	15
2/18/14	23.70	112	354	2013.69	2.60	18.2	10	20
2/19/14	22.00	112	896	2011.78	0.69	16.0	9	20
2/20/14	36.00	112	29	2015.06	3.97	16.3	9	20
2/21/14	25.60	112	616	2013.31	2.22	12.0	9	14

Reproducibility: (# samples and average difference): 7 sets of duplicate samples, average difference 2.93  $\mu$ mol/kg (0.02-8.77), average STDEV of 1.90 (0.43-5.29).

Sample_ID	Bottle #	DIC	DIC_Flag	Difference	
130304	607	2014.0	2	0.2	
130304	608	2013.8	2	0.2	
200002	(22	2050.0	2		
290802	623	2050.9	2	0.0	
290802	624	2050.9	2		
391004	631	2193.0	2	0.5	
391004	632	2192.4	2	0.6	
571306	642	2052.8	3	1.9	
571306	643	2054.7	3	1.7	
711804	657	2145.0	3		Not taken
711804	658	2135.4	3	9.6	into account
782202	669	2132.3	3	1.2	
782202	670	2133.5	3	1.2	
		Without bad	average	0.8	
		replicates 657 & 658	std dev	0.8	

CRM and HgCl<sub>2</sub> correction applied

# Remarks

The volume correction was applied due to added HgCl<sub>2</sub> (Measured DIC\*1.00037).

The first CRM of each cell was used for a CRM correction (additive).

### pH:

Analysis date: Feb. 11<sup>th</sup>, 12<sup>th</sup>, 14<sup>th</sup>, 18<sup>th</sup>, 19<sup>th</sup>, 20<sup>th</sup> and 21<sup>st</sup>, 2014

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 7 sets of duplicate samples (1 bad),

average difference 0.002 (0.000-0.004)

Bottle #	pH at 20 oC	Difference	
607	7.970	0.001	
608	7.968	0.001	
623	7.915	0.003	
624	7.919	0.003	
631	7.760	0.001	
632	7.760	0.001	
642	7.853	0.000	
643	7.853		
657	7.778		
		0.004	
658	7.774		
669	7.755	0.000	
670	7.764	0.009	Not taken into account
	Average	0.002	
	Std. Dev.	0.0017	

### Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. The temperature of the pH cell was recorded before and after the absorbance measurements using a Hart Scientific Fluke 1523 reference thermometer. The pH was calculated using the average of the 2 temperatures. Samples were analyzed between 21 °C and 22 °C. They were calculated at 20 °C using CO2Sys and the DIC measurements. The average correction made is 0.025 in pH. They are reported at 20 °C on the Total Scale.

**TAlk:** The results posted are analyses from the same sample bottles used for DIC. Analysis date: 3/4/2014 - 3/6/2014

Titration system used: Open cell

CRM batch: 123, S = 33.384, certified TA = 2225.21  $\mu$ mol/kg.

System	Date	Time	Bottle #	TA	ΔCRM
1	3/4/2014	12:45:18	284	2217.91	
1	3/4/2014	19:35:49	561	2220.49	2.58
1	3/5/2014	12:35:07	843	2219.21	
1	3/5/2014	19:14:46	174	2219.41	0.2
1	3/6/2014	11:10:15	340	2221.06	
1	3/6/2014	14:36:51	622	2219.55	1.51
2	3/4/2014	12:55:36	284	2210.56	
2	3/4/2014	19:43:00	561	2212.62	2.06
2	3/5/2014	12:39:45	843	2210.87	
2	3/5/2014	19:15:49	174	2211.02	0.15
2	3/6/2014	11:37:23	340	2213.93	
2	3/6/2014	14:53:13	622	2210.24	3.69
				Average	1.70
				Std. Dev.	1.4
				Sta. Dor.	1.1

Reproducibility: (# samples and average difference): 7 sets of duplicate samples, average absolute difference 1.74 μmol/kg (0.2-4.9), Standard Deviation of 2.0.

Bottle #	System	Date	Time	S	TA	Difference	Comments
607	1	3/4/2014	14:39:19	32.897	2093.53	133.80	Low initial emf. Flag 4
608	1	3/4/2014	15:16:47	32.897	2227.33	155.00	Not used in average.
623	1	3/4/2014	18:00:22	33.404	2237.20	0.27	0
624	1	3/4/2014	18:24:18	33.404	2237.47	0.27	0
631	1	3/5/2014	13:52:06	35.346	2325.53		0
632	1	3/5/2014	14:19:32	35.346	2330.41	4.88	0
642	2	3/5/2014	15:53:19	32.687	2195.82		0
643	2	3/5/2014	16:14:05	32.687	2196.02	0.20	0
657	2	3/5/2014	18:31:34	33.947	2264.45		0
658	2	3/5/2014	18:52:04	33.947	2263.50	0.96	0
669	2	3/6/2014	13:29:43	33.734	2248.15		0
670	2	3/6/2014	13:53:19	33.734	2245.73	2.41	0

Average 1.74 Std. Dev. 2.0

#### Remarks-

Samples 614, 615 and 616 were lost and could not be run for total alkalinity.

Several samples had a low initial emf and were flagged 4.

Sample 665 was flagged 3 because the stirrer was not on for the first point in the titration. The value is probably correct despite this.

### **Comments**

The latitude, longitude, date, and time reported with the DIC, pH and TAlk measurements were taken from the sample field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data. The Niskin bottles are approximately one half meter above the CTD sensors on the rosette. Therefore, Temp and Sal are bin-averaged CTD values representing the next shallower depth from that recorded by the CTD (CTD Depth) at the time the Niskin bottles were fired with the exception of the surface values, which are the same as the CTD Depth

values (as per the log sheet).

The Sample\_ID is the sample station, cast number and Niskin bottle number for the discrete samples.

The DIC instrument was stable: CRM values did not change significantly throughout the life span of each cell.

The blank (CM5011) on 02-19-2014 was raised from 12.0 to 22.0 before running the CRM.

The blank (CM5011) on 02-20-2014 was lowered from 45.6 to 36.0 before running the CRM.

On Feb. 16<sup>th</sup> and 18<sup>th</sup>, 2014 the syringe would not fill completely with sample water. The syringe was untightened and retightened at which time the syringe began filling sample analysis was resumed on the 18<sup>th</sup>.

All samples were analyzed in duplicate and the value reported is the average of the two analyses. Samples bottles 619, 620, 640, 642, 643, 645, 654, 656 and 660 had a single analysis due to one of the two runs failing the clear and ready check. These samples did not have an averaged final result.

Sample bottles 605, 622 and 619 had an air bubble in the syringe for both analyses and the results have been marked questionable.

Approximately 80 mL of sample was extracted from each DIC sample bottle by syringe before DIC analysis to determine the pH.

The samples were run for Dr. Jon Hare of the NEFSC as part of our coastal ocean acidification monitoring project.

#### **UPDATE JULY 2015**

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Samples for carbon parameters and nutrients were drawn from different Niskin bottles, so merging has been done based on sample depth, assuming all Niskin bottles tripped at the same depth would have the same (or close enough) nutrient values. We have kept the salinity and temperature values used for the carbon parameter calculations. Comparison with calibrated and corrected salinity values provided by Hare's group indicate that the average salinity difference (absolute difference) between preliminary and corrected values was  $0.004 \pm 0.01$ .

The following columns have been added: Depth\_station, CTDPRS, Date (UTC), Sigma-Theta, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT and Niskin nuts.