Cruise: HB1202

**Ship:** R/V H. Bigelow **Dates:** June 2012

Chief Scientist: Jerry Prezioso Equipment: CTD rosette Total number of stations: 18

# Sample Collection

Locations: North Atlantic from 35.9933 N to 42.2283 N and 65.4317 W to 75.5217 W. Samplins Dates (mm/dd/yyyy): 06/02/2012 – 06/13/2012

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette and the flow-through system 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:

18 locations, 38 samples each 500-ml, 4 sets of duplicate samples. Sample ID#: Composed of the station, cast and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

#### TAlk:

18 locations, 38 samples each 500-ml, 4 sets of duplicate samples. Sample\_ID#: Composed of the station, cast and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Dr. Leticia Barbero

Nutrients:

## Sample Analysis

#### DIC:

Analysis date: August 20<sup>th</sup> and 21<sup>st</sup>, 2012

Coulometer used: AOML 4 Blanks: 28.0 and 25.0 counts/min

CRM # 1002 and 0890 were used and with an assigned value of (include both DIC and

salinity): Batch 112, c: 2011.09 µmol/kg, S: 33.305

CRM value measured: AOML 4: offset 3.78  $\mu$ mol/kg (2007.31  $\mu$ mol/kg) and offset 2.37

µmol/kg (2008.72 μmol/kg).

Average run time, minimum run time, maximum run time: 10, 8 and 17 min; 9, 8 and 11

min.

Analysis date: August 20<sup>th</sup>, 2012

Coulometer used: AOML 3 Blanks: 35 counts/min

CRM # 0577 was used and with an assigned value of (include both DIC and salinity):

Batch 112, c: 2011.09 μmol/kg, S: 33.305

CRM value measured: AOML 3: offset 0.6 µmol/kg (2010.41 µmol/kg). Average run time, minimum run time, maximum run time: 18, 14 and 20 min.

Reproducibility: (# samples and average difference): 4 sets of duplicate samples, average difference 2.04 µmol/kg (0.70-4.03), average STDEV of 1.44 (0.50-2.85).

		Corr.			
System	ID	DIC	Avg	Difference	STDEV
AOML3	771512	2047.874	2049.89	4.03	2.85
AOML4	771512	2051.904			
AOML3	781612	2019.477	2019.83	0.70	0.50
AOML4	781612	2020.18			
AOML4	891707	2010.821	2012.17	2.70	1.91
AOML4	891707	2013.518			
AOML4	961810	2011.399	2011.04	0.71	0.50
AOML4	961810	2010.685			
Overall				2.04	1.44

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 correction).

#### TAlk:

The results posted are analyses from the same sample bottles used for DIC.

Analysis date: 10/28/2013 – 10/29/2013

Titration system used: Open cell

CRM analysis (values in µmol/kg):

Each day, a CRM was analyzed before (CRM-1) and after (CRM-2) the samples.

CRM analyzed: Batch 112, Salinity = 33.305, cert. TA = 2223.26 µmol/kg.

			SYSTEM 1			SYSTEM 2		
CRM	Date	Bottle	meas. TA	Avg (cert	Diff	meas.	Avg (cert	Diff
CIXIVI	Date	#	ilicas. 1A	meas.) TA	(1-2)	TA	meas.) TA	(1-2)
1	10/28/13	923	2219.44	4.37	1.09	2220.15	3.80	1.38
2	10/28/13	881	2218.35	4.37	1.09	2218.77	3.80	1.30
1	10/29/13	544	2221.42	2.59	1.49	2223.96	0.36	2.12
2	10/29/13	38	2219.93	2.39	1.49	2221.84	0.30	2.12

# Reproducibility:

Sample					Bottle	meas.		
ID	Salinity	System	Date	Time	#	TA	Difference	
771512	35.2	system1	10/29/13	14:54:20	82	2301.54	4.16	
	33.2	system2	10/29/13	15:18:27	83	2305.7	4.10	
781612	32.94	system1	10/29/13	16:26:44	88	2194.04	-15.51	
781012	32.74	system2	10/29/13	16:27:27	87	2178.53	-13.31	
		. 1	10/20/12	17 10 04	02	2164.02		
891707	32.7	system1	10/29/13	17:12:04	92	2164.02	-4.15	
0,1,0,	52.7	system2	10/29/13	17:36:26	93	2159.87	20	
		gygtom 1	10/29/13	19:21:34	96	2143.05		
961810	32.4	system1					-36.16	
		system2	10/29/13	19:22:22	95	2106.89		

#### Remarks-

All the CRM batch 112 analyzed were brand new bottles so no contamination from the SOMMA system was possible. The precision of the CRM measurements were within 2.0  $\mu$ mol/kg.

Only the first CRM was used to correct the data. The second CRM served to verify that no major drift had occurred to the system.

The CRM measurement for each day was used to correct the data for that day only. Two duplicates showed larger difference than expected ( $\sim 15~\mu mol/kg$  and  $\sim 36~\mu mol/kg$ ). Since these duplicates show very good reproducibility in both DIC and pH measurements, we suspect contamination from the SOMMA system. The samples have been analyzed more than a year after the DIC and pH measurements, which were made at the same time. In view of the duplicates' results, we estimate that the possibility of contamination increases the uncertainty of our TA measurements to about +/- 30  $\mu mol/kg$ .

pH:

Reproducibility: (# samples and average absolute difference):

Duplicates from same Niskin:

4 sets, average difference 0.006 (range: 0.002 - 0.009)

Sample ID	Salinity	Bottle #	pH <sub>T</sub> (20°C)	Absolute Difference
771512	35.2	82 83	8.068 8.059	0.009
781612	32.94	88 87	7.949 7.951	0.002
891707	32.7	92 93	7.931 7.934	0.003
961810	32.4	96 95	7.904 7.895	0.009

#### Remarks-

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. pH samples were analyzed at 20.0 °C and reported on the Total Scale. However, the cells were not thermostated during analysis. No correction for the addition of the dye was applied.

# **Comments**

The latitude, longitude and salinity reported with the DIC and TAlk measurements were taken from the Niskin bottle field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data.

The DIC instruments were stable: the gas loop and CRM values did not change significantly through out the life span of each cell. Also cells from separate days gave calibration values of similar magnitude.

The blanks (AOML 4) on 08-20-2012 were raised from 24.8 to 28 before the 1<sup>st</sup> gas loop calibration; on 08-21-2012 were raised from 17.5 to 25 before the 1<sup>st</sup> gas loop calibration.

The blanks (AOML 3) on 08-20-2012 were raised from 30.9 to 35 before the 1<sup>st</sup> gas loop calibration.

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

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 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. Niskin information for the nutrients was not available and 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  $0.01 \pm 0.02$ .

The carbon parameters for sample 771504 had to be recalculated because the salinity was wrong (off by 0.5 salinity units). The correct salinity has been added to the salinity column

The following columns have been added:

Date\_UTC, Depth\_station, CTDPRS, Sigma-Theta, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, and PHSPHT.