

Cruise: GU1401 , EcoMon
Ship: R/V Gordon Gunter
Dates: March 1st, 2014 – March 8th, 2014
Expocode: 33GG20140301
Chief Scientist: Jerry Prezioso
Equipment: CTD Rosette
Total number of stations: 19
Location: Northeast Coast and Gulf of Maine

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

Sample Collection

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

DIC:

19 locations, 64 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone and Bob Castle

pH:

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Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Leticia Barbero and Denis Pierrot

Sample Analysis

DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	05/22/14	2016.65	2025.40	8.75	16.0	10
AOML 3	05/23/14	2016.65	2026.98	10.33	24.0	9

AOML 3	05/24/14	2016.65	2026.29	9.64	25.0	10
AOML 4	05/22/14	2016.65	2019.55	2.90	18.0	13
AOML 4	05/23/14	2016.65	2019.60	2.95	28.3	12
AOML 4	05/24/14	2016.65	2020.96	4.31	24.0	16

Analysis date: 05/22/2104

Coulometer used: AOML 3

Blanks: 16.0 counts/min

CRM # 0537 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 3: offset 8.75 $\mu\text{mol/kg}$ (2025.40 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 05/22/2104

Coulometer used: AOML 4

Blanks: 18.0 counts/min

CRM # 0223 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 4: offset 2.90 $\mu\text{mol/kg}$ (2019.55 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 13, 11 and 16 min.

Analysis date: 05/23/2014

Coulometer used: AOML 3

Blanks: 24.0 counts/min

CRM # 1015 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM value measured: AOML 3: offset 10.33 $\mu\text{mol/kg}$ (2026.98 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 13 min.

Analysis date: 05/23/2014

Coulometer used: AOML 4

Blanks: 28.3 counts/min

CRM # 0651 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 4: offset 2.95 $\mu\text{mol/kg}$ (2019.60 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 12, 9 and 16 min.

Analysis date: 05/24/2014

Coulometer used: AOML 3

Blanks: 25.0 counts/min

CRM # 0184 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM value measured: AOML 3: offset 9.64 $\mu\text{mol/kg}$ (2026.29 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 05/24/2014

Coulometer used: AOML 4

Blanks: 24.0 counts/min

CRM # 0464 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 4: offset 4.31 $\mu\text{mol/kg}$ (2020.96 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 16, 12 and 20 min.

Reproducibility: (# samples and average difference): 4 sets of duplicate samples, average difference 7.73 $\mu\text{mol/kg}$ (2.58 – 15.37), average STDEV of 5.5 (1.8 – 10.9).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML3	90306	7	2125.6			
AOML3	90306	8	2141.0	2133.3	15.37	10.9
AOML4	320710	23	2108.5			
AOML4	320710	24	2116.7	2112.6	8.26	5.8
AOML4	471510	46	2076.9			
AOML3	471510	47	2072.2	2074.5	4.70	3.3
AOML4	561905	62	2087.3			
AOML3	561905	63	2089.9	2088.6	2.58	1.8
				Average	7.73	5.5

CRM, salinity and HgCl₂ correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl₂ (Measured DIC*1.00037).

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

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

The blank (AOML 3) on 05-22-2014 was raised from 12.0 to 16.0 before running the CRM.

The blank (AOML 3) on 05-23-2014 was raised from 19.2 to 24.0 before running the CRM.

The blank (AOML 3) on 05-24-2014 was raised from 12.0 to 25.0 before running the CRM.

The blank (AOML 4) on 05-22-2014 was raised from 12.0 to 18.0 before running the CRM.

The blank (AOML 4) on 05-24-2014 was raised from 13.3 to 24.0 before running the CRM.

The glass stopper for bottle #10 broke while trying to open it, sample tube was held in the sample bottle during analysis by hand. A black rubber stopper was used to cap the bottle for later alkalinity analysis.

Replaced (AOML 3) the blue fitting to pump 8 due to a crack and leakage of acid, this occurred at the end of analyzing samples.

pH:

Analysis date: May 22nd, 23rd and 24th, 2014

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 2 sets of duplicate samples, average difference 0.0003 (0.0003-0.0004), average STDEV of 0.0002 (0.0002-0.0003).

Instrument	Sample_ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	90306	7	7.9121			
HP Agilent 8453	90306	8	7.8999	N/A*	N/A*	N/A*
HP Agilent 8453	320710	23	7.7809			
HP Agilent 8453	320710	24	7.7647	N/A*	N/A*	N/A*
HP Agilent 8453	471510	46	7.7619			
HP Agilent 8453	471510	47	7.7622	7.7620	0.0002	0.0003
HP Agilent 8453	561905	62	7.7724			
HP Agilent 8453	561905	63	7.7728	7.7726	0.0003	0.0004
Average					0.0002	0.0003

*No average, difference or STDEV was calculated for the first two sets of duplicates due to the incorrect amount of dye added to bottles 7 and 23 during pH analysis.

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 20⁰C at Full Scale (pH 0-14).

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

The incorrect amount of dye was added to sample bottles 1 – 7 and 23 for pH, sample bottles 1-6 were re-analyzed using the correct amount of dye. Sample bottles 7 and 23 were not re-analyzed since DIC had already been run.

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

Talk:

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

Analysis dates: 06/02/2014 – 06/04/2014

Titration system used: Open cell

CRM batch: 123, S = 33.384, certified TA = 2225.21 μ mol/kg

2 CRM samples were run daily on each cell, before and after the seawater samples. The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the 2 CRMs run on each cell. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	\u0394CRM
1	6/2/2014	13:01:02	121	2215.65	
1	6/2/2014	20:01:19	394	2217.41	1.76
1	6/3/2014	14:19:27	946	2222.74	
1	6/3/2014	21:05:15	681	2215.78	946 was not used in the calculations
1	6/4/2014	12:19:11	394	2215.21	
1	6/4/2014	17:41:44	997	2213.95	1.26
2	6/2/2014	14:38:09	889	2210.75	
2	6/2/2014	19:59:09	889	2208.35	2.40
2	6/3/2014	15:15:28	946	2209.99	
2	6/3/2014	20:59:07	681	2204.73	5.26

2	6/4/2014	13:04:56	732	2207.69	
2	6/4/2014	17:51:16	997	2206.70	0.99
				Average	1.63
				Std. Dev.	2.54

Reproducibility: 4 sets of duplicate samples were run in the same cell, with an average absolute difference of 1.10 $\mu\text{mol/kg}$ (0.09-1.84), and a Standard Deviation of 0.7.

Bottle #	System	Date	Time	S	TA	Difference	Comments
7	1	6/2/2014	16:07:29	35.218	2312.78		0
8	1	6/2/2014	17:01:03	35.218	2311.62	1.16	0
23	1	6/3/2014	15:42:16	33.372	2223.99		0
24	1	6/3/2014	16:07:07	33.372	2225.83	1.84	0
46	1	6/4/2014	12:52:22	32.532	2184.74		0
47	1	6/4/2014	13:39:37	32.532	2186.04	1.30	0
62	1	3/6/2014	16:58:56	32.892	2196.59		0
63	1	3/6/2014	17:21:40	32.892	2196.50	0.09	0
						Average	1.10
						Std. Dev.	0.7

Remarks

The two systems behaved well during the analyses. On June 3rd, the value for the first CRM used on system 1 was considered suspicious based on the normal values obtained for CRMs from batch 123 and was not used for the correction of samples run on system 1 on that day.

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.

UPDATE JULY 2015

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Where samples for carbon parameters and nutrients were drawn from different Niskin bottles, 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 ± 0.01 .

The carbon parameters for sample 360802 had to be recalculated because the salinity was wrong (off by 4.2 salinity units).

The following columns have been added:

Date.UTC, Depth_station, Depth_sampling, CTDPRS, Sigma-Theta, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT and Niskin_nuts

UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.