Cruise: HB1803 Ship: R/V Henry Bigelow Expo Code: 33HH20180523 Dates: May 23, 2018 to June 5, 2018 Chief Scientist: Jerry Prezioso Equipment: CTD and TSG-Flow thru system Total number of stations: 23 Location: U.S. Mid-Atlantic and New England coastal region

The samples were run for Chris Melrose 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 and TSG-flow thru system onboard the R/V H. Bigelow by the survey tech Christopher Taylor. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

23 locations, 83 samples each 500-ml, 8 duplicate samples. Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone and Patrick Mears

pH:

23 locations, 83 samples each 500-ml, 8 duplicate samples. Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone and Patrick Mears

TAlk:

23 locations, 83 samples each 500-ml, 8 duplicate samples. Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Dr. Leticia Barbero, Charles Featherstone and Patrick Mears

<u>Sample Analysis</u> DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	08/08/2018	2042.41	2040.93	1.48	15.0	9

AOML 5	08/09/2018	2042.41	2043.12	0.71	12	9
AOML 6	08/08/2018	2042.41	2045.29	2.88	12	8
AOML 6	08/09/2018	2042.41	2046.69	4.28	15	9

Analysis date: 08/08/2018

Coulometer used: DICE-CM5011- AOML 5

Blanks: 15.0 counts/min

CRM # 230 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 µmol/kg, S: 33.414

CRM values measured: AOML 5: offset 1.48 µmol/kg (2040.93 µmol/kg).

Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 08/09/2018 Coulometer used: DICE–CM5011- AOML 5 Blanks: 12.0 counts/min CRM # 355 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 µmol/kg, S: 33.414 CRM values measured: AOML 5: offset 0.71 µmol/kg (2043.12 µmol/kg). Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 08/08/2018 Coulometer used: DICE–CM5011- AOML 6 Blanks: 12.0 counts/min CRM # 166 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 μmol/kg, S: 33.414 CRM values measured: AOML 6: offset 2.88 μmol/kg (2045.29 μmol/kg). Average run time, minimum run time, maximum run time: 8, 7 and 20 min.

Analysis date: 08/09/2018 Coulometer used: DICE–CM5011- AOML 6 Blanks: 15.0 counts/min CRM # 416 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 µmol/kg, S: 33.414 CRM values measured: AOML 6: offset 4.28 µmol/kg (2046.69 µmol/kg). Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference 0.26 μ mol/kg (0.02 – 0.75) and an average STDEV of 0.18 (0.01 – 0.53).

Instrument	Sample ID	DIC (umol/kg)	Average	STDEV	Difference
AOML5 AOML5	50101 50101	2063.38 2063.36	2063.37	0.01	0.02
AOML5 AOML5	110402 110402	2188.61 2189.36	2188.98	0.53	0.75

AOML5 AOML5	210501 210501	2072.78 2072.93	2072.85	0.10	0.15
AOML6 AOML6	240611 240611	2050.91 2050.77	2050.84	0.10	0.15
AOML6 AOML6	591201 591201	2042.96 2042.58	2042.77	0.27	0.38
AOML5 AOML5	721402 721402	2174.74 2174.41	2174.57	0.23	0.32
AOML5 AOML5	921703 921703	2143.59 2143.83	2143.71	0.17	0.24
AOML6 AOML6	991911 991911	2002.31 2002.25	2002.28	0.04	0.06
Average				0.18	0.26

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

<u>Remarks</u>

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 instruments were stable: the gas loop and CRM values did not change significantly throughout the life span of each cell.

pH:

Analysis date: 08/08/2018 and 08/09/2018 Spectrophotometer used: HP Agilent 8453

A CRM was run before pH analysis on each day 08/08/2018 Batch 173 CRM #110 = 7.8775 08/09/2018 Batch 173 CRM #478 = 7.8767

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference 0.09000 (0.0005 - 0.2166) and an average STDEV of 0.06000 (0.0004 - 0.1532).

	Sample					
Instrument	ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	50101	1	7.8364			
HP Agilent 8453	50101	2	7.8371	7.8367	0.0005	0.0007

HP Agilent 8453 110402 13 HP Agilent 8453 110402 14	7.7863 7.7853	7.7858	0.0008	0.0011
HP Agilent 8453 210501 16	7.8009			
HP Agilent 8453 210501 17	7.8010	7.8009	0.0001	0.0001
HP Agilent 8453 240611 23	8.0457			
HP Agilent 8453 240611 24	8.0457	8.0457	0.0001	0.0001
HP Agilent 8453 591201 41	7.9367			
HP Agilent 8453 591201 42	7.9375	7.9371	0.0005	0.0007
HP Agilent 8453 721402 49	7.8098			
HP Agilent 8453 721402 50	7.8119	7.8108	0.0015	0.0021
HP Agilent 8453 921703 60	7.8803		0.0000	
HP Agilent 8453 921703 61	7.8794	7.8798	0.0006	0.0008
HP Agilent 8453 991911 69	7.9421	7.0422	0.0004	0.0004
HP Agilent 8453 991911 70	7.9423	7.9422	0.0001	0.0001

Average

0.0005 0.0007

<u>pH Sample Temperature</u>

	Sample BTL	
Sample ID	#	Sample Temp. (⁰ C)
CRM173_110	110	20.094
CRM173_478	478	20.028
50100	5	20.029
50101	1	20.020
50101	2	20.033
50105	3	20.022
50109	4	20.029
60201	6	20.028
60209	7	20.035
60211	8	20.039
100301	9	20.032
100304	10	20.044
100312	11	20.042

110401	12	20.040
110402	13	20.032
110402	14	20.042
110412	15	20.040
210500	20	20.048
210501	16	20.039
210501	17	20.041
210507	18	20.034
210511	19	20.054
240601	21	20.023
240603	22	20.028
240611	23	20.025
240611	24	20.035
250701	25	20.024
250703	26	20.031
250711	27	20.027
350801	28	20.044
350803	29	20.032
350805	30	20.035
510900	34	20.047
510901	31	20.035
510907	32	20.034
510911	33	20.034
571001	35	20.046
571002	36	20.037
571011	37	20.033
581101	38	20.049
581105	39	20.039
581111	40	20.044
591201	41	20.050
591201	42	20.054
591206	43	20.042
591211	44	20.040
701300	48	20.041
701301	45	20.052
701302	46	20.041
701311	47	20.038
721402	49	20.034
721402	50	20.031
721405	51	20.030

721412	52	20.023
831501	53	20.037
831506	54	20.044
831511	55	20.041
911601	56	20.054
911605	57	20.056
911611	58	20.041
921700	63	20.051
921701	59	20.060
921703	60	20.043
921703	61	20.047
921711	62	20.055
941801	64	20.031
941805	65	20.034
941811	66	20.036
991901	67	20.030
991905	68	20.037
991911	69	20.058
991911	70	20.058
1012001	71	20.047
1012005	72	20.051
1012011	73	20.061
1072100	77	20.056
1072101	74	20.046
1072105	75	20.055
1072111	76	20.057
1102201	78	20.064
1102207	79	20.050
1102211	80	20.045
1112301	81	20.052
1112306	82	20.046
1112311	83	20.063

<u>Remarks</u>

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.

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

Final pH results were reported at 25^oC in the data file.

TAlk:

Analysis date: 08/15/2018 and 08/16/2018 Titration system used: Open cell CRM Batch 173, Salinity = 33.414, cert. TA = 2210.77µmol/kg.

On 08/25/2018 and 08/16/2018 one CRM was analyzed before the samples and the same CRM was run at the end of analysis each day for each system. On 08/16/2018 2 different CRMs were run from the same batch on system 1. The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on each cell. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	ТА	\DCRM
1	08/15/2018	15:25:37	1091	2211.41	
1	08/15/2018	23:42:24	1091	2213.26	1.85
1	08/16/2018	13:10:39	1227	2210.67	
1	08/16/2018	20:27:45	1192	2210.34	0.33
2	08/15/2018	13:50:39	1027	2212.44	
2	08/15/2018	23:38:48	1027	2210.00	2.44
2	08/16/2018	13:28:10	1161	2212.16	
2	08/16/2018	20:21:35	1161	2209.59	2.57

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference μ mol/kg 2.22 (0.41- 3.60) and an average STDEV of 1.57 (0.29-2.55).

System	Sample ID	Bottle #	DuplicateTA	AVG TA	Difference	STDEV
System 2	50101	1	2212.41			
System 2	50101	2	2209.04	2210.72	3.37	2.38
System 2	110402	13	2331.71			

System 2	110402	14	2332.13	2331.92	0.41	0.29
System 2	210501	16	2210.67			
System 2	210501	17	2208.75	2209.71	1.91	1.35
~						
System 1	240611	23	2306.75			
System 1	240611	24	2309.05	2307.90	2.30	1.63
System 1	591201	41	2237.13			
System 1	591201	42	2236.75	2236.94	0.38	0.27
System 1	721402	49	2337.27			
System 1	721402	50	2334.83	2336.05	2.44	1.73
System 1	921703	60	2328.63			
System 2	921703	61	2325.30	2326.96	3.33	2.36
System 2	991911	69	2186.95			
System 2	991911	70	2190.56	2188.76	3.60	2.55
Average					2.22	1.57

<u>Remarks</u>

The CRM measurement for each day was used to correct the data for that day only. Both systems worked well.

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 Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

Station 6, Niskin 9 the sample data was not reported because the sample bottle was not properly numbered and it could not be resolved by the sampler.

Salt and temperature data from the UW pCO2 files was used for the Flow-thru (FT)

samples collected.

Corresponding UW pCO2 data can be found at the following website http://www.aoml.noaa.gov/ocd/ocdweb/occ.html

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.