Cruise: HB1701, EcoMon Ship: Henry B. Bigelow Expo Code: 33HH20170211 Dates: February 11-23, 2017

Chief Scientist: Dr. Jerry Prezioso

**Equipment**: CTD and TSG-Flow thru system

**Total number of stations: 27** 

Location: U.S. Mid-Atlantic and New England coastal region

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 the TSG-flow thru system and the CTD/Rosette onboard the Henry B. Bigelow by Chris Taylor. The date and time listed in the data file are UTC when each sample bottle was collected.

#### DIC:

27 locations, 102 samples each 500-ml, 10 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:

27 locations, 102 samples each 500-ml, 10 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:

27 locations, 102 samples each 500-ml, 10 duplicate samples.

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

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

## 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	03/06/2017	2016.35	2014.71	1.64	28.0	13
AOML 4	03/06/2017	2016.35	2015.90	0.45	28.0	13
AOML 3	03/07/2017	2016.35	2017.03	0.68	28.0	12

AOML 4	03/07/2017	2016.35	2015.58	0.77	28.0	12
AOML 3	03/08/2017	2016.35	2018.09	1.74	28.0	16
AOML 4	03/08/2017	2016.35	2015.39	0.96	28.0	12

Analysis date: 03/06/2017

Coulometer used: DICE-CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 38 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 µmol/kg, S: 33.361

CRM values measured: AOML 3: offset 1.64 µmol/kg (2014.71 µmol/kg). Average run time, minimum run time, maximum run time: 13, 8 and 20 min.

Analysis date: 03/06/2017

Coulometer used: DICE-CM5015- AOML 4

Blanks: 13.2 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 801 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 μmol/kg, S: 33.361

CRM values measured: AOML 4: offset 0.45 µmol/kg (2015.90 µmol/kg). Average run time, minimum run time, maximum run time: 13, 9 and 19 min.

Analysis date: 03/07/2016

Coulometer used: DICE-CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 761 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 µmol/kg, S: 33.361

CRM values measured: AOML 3: offset 0.68 µmol/kg (2017.03 µmol/kg). Average run time, minimum run time, maximum run time: 12, 9 and 16 min.

Analysis date: 03/07/2017

Coulometer used: DICE-CM5015- AOML 4

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 343 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 µmol/kg, S: 33.361

CRM values measured: AOML 4: offset 0.77 µmol/kg (2015.58 µmol/kg). Average run time, minimum run time, maximum run time: 12, 10 and 16 min.

Analysis date: 03/08/2016

Coulometer used: DICE-CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 98 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 µmol/kg, S: 33.361

CRM values measured: AOML 3: offset 1.74 µmol/kg (2018.09 µmol/kg). Average run time, minimum run time, maximum run time: 16, 12 and 20 min.

Analysis date: 03/08/2017

Coulometer used: DICE-CM5015- AOML 4

Blanks: 17.6 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 924 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.35 µmol/kg, S: 33.361

CRM values measured: AOML 4: offset 0.96 µmol/kg (2015.39 µmol/kg). Average run time, minimum run time, maximum run time: 12, 9 and 18 min.

**Reproducibility:** (# samples and average difference): 10 sets of duplicate samples, average difference 2.91  $\mu$ mol/kg (1.25 – 5.13), average STDEV of 2.06 (0.83 – 3.63).

Instrument ID	Sample ID	Bottle #	Corrected DIC (µmol/kg)	C Average	Difference	STDEV
AOML3	100103	2	2082.42	11101450	Difference	SIBLY
AOML3	100103	3	2084.58	2083.50	2.16	1.53
11011120	100100	J	20000	2002120		1100
AOML3	180311	10	2093.90			
AOML3	180311	11	2095.77	2094.83	1.87	1.32
AOML 3	240411	14	2114.10			
AOML 3	240411	15	2108.96	2111.53	5.13	3.63
AOML 3	340501	16	2205.82			
AOML 3	340501	17	2207.07	2206.45	1.25	0.88
AOML 4	500811	28	2080.78			
AOML 4	500811	29	2085.14	2082.96	4.36	3.08
AOML 4	581102	37	2205.97			
AOML 4	581102	38	2208.98	2207.48	3.01	2.13
AOML 4	661301	43	2187.96			
AOML 4	661301	44	2192.88	2190.42	4.92	3.48
AOML 4	811502	50	2095.51			
AOML 4	811502	51	2094.35	2094.93	1.17	0.83
AOML 4	841605	55	2076.61			
AOML 4	841605	56	2078.46	2077.54	1.85	1.31
AOML 4	971811	63	2069.83			
AOML 4	971811	64	2066.48	2068.16	3.36	2.37
					• • • • • • • • • • • • • • • • • • • •	
Average					2.91	2.06

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

## 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.

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

The samples were analyzed using the DICE (AOML 3 & AOML 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

# pH:

Analysis date: 03/06/2017, 03/08/2017 & 03/09/2017

Spectrophotometer used: HP Agilent 8453

**Reproducibility:** (# samples and average difference): 10 sets of duplicate samples, average difference 0.004 (0.002-0.008), average STDEV of 0.003 (0.001-0.006).

System	Sample	Sample	S	t	pН	Average	Difference	STDEV
	<b>Bottle</b> #	ID						
HP Agilent 8453 HP Agilent	2	100103	34.0242	20.489	7.913			
8453	3	100103	34.0242	20.572	7.911	7.912	0.002	0.001
HP Agilent								
8453 HP Agilent	11	180311	34.4633	20.427	7.930			
8453	10	180311	34.4633	20.260	7.933	7.932	0.003	0.002
HP Agilent								
8453 HP Agilent	14	240411	34.5741	20.662	7.902			
8453	15	240411	34.5741	20.007	7.907	7.904	0.006	0.004
HP Agilent								
8453 HP Agilent	16	340501	35.1015	21.202	7.707			
8453	17	340501	35.1015	21.156	7.698	7.702	0.008	0.006
HP Agilent								
8453 HP Agilent	28	500811	32.8389	20.508	7.800			
8453	29	500811	32.8389	20.298	7.805	7.803	0.005	0.004

HP Agilent 8453	37	581102	35.3428	20.686	7.7281			
HP Agilent 8453	38	581102	35.3428	21.130	7.7205	7.724	0.008	0.005
HP Agilent								
8453 HP Agilent	43	661301	35.3465	20.506	7.759			
8453	44	661301	35.3465	20.539	7.757	7.758	0.002	0.001
HP Agilent								
8453	50	811502	33.1930	20.618	7.797			
HP Agilent 8453	51	811502	33.1930	20.364	7.801	7.799	0.004	0.003
HP Agilent								
8453 HP Agilent	55	841605	33.1118	20.376	7.851			
8453	56	841605	33.1118	20.342	7.853	7.852	0.002	0.002
HP Agilent								
8453 HP Agilent	63	971811	31.8676	20.775	7.728			
8453	64	971811	31.8676	20.516	7.736	7.732	0.008	0.006

0.004

0.003

Temperature measured during pH analysis

Average

Sample ID	Sample BTL #	BTL Temp (°C)	Start Cell (°C)	End Cell (°C)	Differ Start to End Cell (°C)
301	301	19.729	20.016	20.654	0.638
302	302	19.834	20.243	20.754	0.511
303	303	19.719	19.832	20.057	0.225
304	304	19.824	20.034	20.333	0.299
305	305	19.829	20.283	20.568	0.285
306	306	19.843	20.057	20.356	0.299
307	307	19.818	20.023	20.477	0.454
308	308	19.838	20.186	20.440	0.254
309	309	19.856	20.152	20.315	0.163
310	310	19.932	20.094	20.242	0.148
311	311	19.754	20.115	20.546	0.431
312	312	19.901	20.216	20.802	0.586
313	313	19.687	19.959	20.250	0.291
314	314	19.821	20.105	20.449	0.344
315	315	19.831	20.123	20.493	0.370

316	316	19.909	20.167	20.482	0.315
317	317	19.88	20.046	20.356	0.310
318	318	19.802	20.150	20.337	0.187
319	319	19.842	20.138	20.294	0.156
320	320	19.888	20.088	20.313	0.225
100101	1	19.703	20.170	20.648	0.478
100103	2	19.762	19.869	20.489	0.620
100103	3	19.885	20.162	20.572	0.410
100107	4	19.836	20.178	20.573	0.395
170202	5	19.882	20.020	20.445	0.425
170205	6	20.138	20.371	20.795	0.424
170209	7	19.906	20.146	20.437	0.291
180301	8	19.741	19.997	20.301	0.304
180307	9	19.755	20.015	20.334	0.319
180311	11	19.817	20.056	20.427	0.371
180311	10	19.864	20.002	20.260	0.258
240401	12	19.783	19.847	19.998	0.151
240404	13	19.755	19.831	20.032	0.201
240411	14	19.914	20.180	20.662	0.482
240411	15	19.714	19.862	20.007	0.145
340501	16	19.704	20.153	21.202	1.049
340501	17	19.794	20.218	21.156	0.938
340502	18	20.053	20.167	20.590	0.423
340511	19	19.706	20.187	20.600	0.413
350601	20	19.697	20.102	20.860	0.758
350604	21	19.694	20.075	20.277	0.202
350611	22	19.395	19.689	20.402	0.713
380701	23	19.7	19.901	20.234	0.333
380703	24	19.764	20.189	20.607	0.418
380705	25	19.794	20.101	20.560	0.459
500801	26	19.696	19.979	20.364	0.385
500808	27	19.717	20.026	20.346	0.320
500811	28	19.694	20.032	20.508	0.476
500811	29	19.761	19.996	20.298	0.302
560902	30	19.788	19.923	20.106	0.183
560906	31	19.768	19.895	20.257	0.362
560911	32	19.701	19.896	20.216	0.320
571001	33	19.755	19.939	20.073	0.134
571004	34	19.675	19.989	20.168	0.179
571011	35	19.570	19.831	20.141	0.310
581101	36	19.802	20.015	20.964	0.949
581102	37	19.702	19.954	20.686	0.732
581102	38	19.766	20.373	21.130	0.757

581111	39	19.896	19.875	20.606	0.731
651201	40	19.793	19.864	20.940	1.076
651202	41	20.01	20.436	21.529	1.093
651211	42	19.816	20.265	20.953	0.688
661301	43	19.708	20.064	20.506	0.442
661301	44	19.796	20.023	20.539	0.516
661304	45	19.905	20.228	20.661	0.433
661311	46	20.050	20.202	20.664	0.462
741401	47	19.822	20.269	20.684	0.415
741404	48	19.801	20.163	20.817	0.654
741409	49	19.767	20.170	20.511	0.341
811502	50	19.768	20.146	20.618	0.472
811502	51	19.765	20.012	20.364	0.352
811503	52	19.749	20.029	20.435	0.406
811507	53	19.781	19.928	20.313	0.385
841601	54	19.776	19.925	20.235	0.310
841605	55	19.881	19.998	20.376	0.378
841605	56	19.876	20.151	20.342	0.191
841611	57	19.720	19.898	20.194	0.296
951701	58	19.789	19.877	20.282	0.405
951702	59	19.759	19.680	20.379	0.699
951711	60	19.816	20.130	20.485	0.355
971801	61	19.740	20.151	20.359	0.208
971804	62	19.720	20.029	20.111	0.082
971811	63	19.711	19.945	20.775	0.830
971811	64	19.832	20.360	20.516	0.156
1021901	65	19.592	19.942	20.467	0.525
1021903	66	19.739	20.019	20.535	0.516
1021911	67	19.763	19.968	20.342	0.374
1032001	68	19.876	20.063	20.342	0.279
1032006	69	19.715	19.980	20.429	0.449
1032011	70	19.698	19.878	20.272	0.394
1102101	71	19.715	20.168	20.514	0.346
1102104	72	19.891	20.006	20.495	0.489
1102111	73	19.712	20.150	20.410	0.260
1112201	74	19.762	19.930	20.209	0.279
1112204	75	19.617	19.894	20.121	0.227
1112211	76	19.788	20.148	20.513	0.365
1132301	77	19.727	19.854	20.390	0.536
1132305	78	19.720	20.003	20.902	0.899
1132311	79	19.685	20.122	20.709	0.587
1142401	80	19.735	20.095	20.901	0.806
1142404	81	19.838	20.093	20.666	0.573

1142411	82	19.766	19.876	20.265	0.389	
Average		19.785	20.053	20.480	0.427	

### 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<sup>0</sup>C 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.

#### TAlk:

Analysis dates: 03/13/2017, 03/14/2017, 03/16/2017, -3/17/2017, 03/21/2017 and 03/22/2017

Titration system used: Open cell

CRM Batch 129, Salinity = 33.361, cert. TA =  $2237.32 \mu mol/kg$ . CRM Batch 144, Salinity = 33.571, cert. TA =  $2238.60 \mu mol/kg$ .

On 03/13/2017, 03/14/2017, 03/16/2017, 03/17/2017, 03/21/2017 and 03/22/2017 one CRM was analyzed before the samples and another CRM or same CRM was run at the end of analysis for each system.

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 #	TA	ΔCRM
1	03/14/2017	09:51:37	225	2218.88	_
1	03/14/2017	15:30:05	225	2218.41	0.47
1	03/17/2017	09:34:27	762	2222.71	
1	03/17/2017	15:29:03	762	2227.04	4.33
1	03/21/2017	11:30:12	1095	2219.53	
1	03/21/2017	15:52:16	1095	2218.93	0.60
1	03/22/2017	08:34:23	347	2215.66	
1	03/22/2017	10:14:13	347	2221.18	5.52
2	03/13/2017	10:15:23	873	2225.92	

2	03/13/2017	16:40:17	873	2228.28	2.36
2	03/14/2017	09:20:40	163	2232.70	
2	03/14/2017	15:36:30	163	2228.25	4.45
2	03/16/2017	09:17:38	102	2229.04	
2	03/16/2017	15:35:02	102	2227.38	1.66
2	03/17/2017	09:06:12	288	2227.07	
2	03/17/2017	15:39:02	288	2233.93	6.86
2	03/21/2017	10:59:06	975	2228.87	
2	03/21/2017	15:49:31	975 975	2229.58	0.71
_					
2	03/22/2017	08:03:35	583	2229.15	
2	03/22/2017	10:06:50	583	2230.07	0.92

**Reproducibility:** (# samples and average difference): 9 duplicate samples were collected with an average difference 4.70  $\mu$ mol/kg (1.67 – 9.30) and an average STDEV of 3.32 (1.18 – 6.57).

System	Bottle #	Sample ID	TAlk	Average	Difference	STDEV
System 2	10	180311	2282.28	2283.12	1.67	1.18
System 2	11	180311	2283.95			
System 2	14	240411	2299.92	2296.11	7.63	5.39
System 2	15	240411	2292.30	2290.11	7.02	0.09
System 2	16	340501	2308.90	2313.45	9.11	6.44
System 2 System 2	17	340501	2318.01	2313.73	<i>7.</i> 11	0.44
System 1	20	500011	2211.01	2213.03	4.04	2.05
System 1 System 1	28 29	500811 500811	2215.05	2213.03	4.04	2.85
•					4 =0	4.00
System 2	37	581102	2330.18	2329.28	1.79	1.26
System 2	38	581102	2328.39			
System 2	43	661301	2328.21	2329.21	2.01	1.42
System 2	44	661301	2330.22			
System 2	50	811502	2227.21	2228.31	2.20	1.56

System 2	51	811502	2229.41			
System 2	55	841605	2217.54	2219.83	4.57	3.23
System 2	56	841605	2222.12			
System 1	63	971811	2168.22	2163.57	9.30	6.57
System 1	64	971811	2158.92			
Overall						
Average					4.70	3.32

## Remarks

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 bottle number for the discrete flow thru samples.

The salinity and temperature were taken from the UW pCO2 system for the flow thru samples. The salinities were used in the DIC, Talk and pH calculations.

Corresponding UW pCO2 data can be found at the following website <a href="http://www.aoml.noaa.gov/ocd/ocdweb/occ.html">http://www.aoml.noaa.gov/ocd/ocdweb/occ.html</a>

Duplicate bottle #3 was broken and sample lost for alkalinity, so 9 duplicates for alkalinity and 10 for DIC and pH.

This carbon dataset has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group from NESFC.

The following columns have been imported from the nutrients file:

Date\_UTC, Depth\_station, Depth\_sampling, CTDPRS, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT

### 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.