

Cruise: HB1902
Ship: R/V Henry Bigelow
Expo Code: 33HH20190522
Dates: May 22nd – June 6th, 2019
Chief Scientist: Jerry Prezioso
Equipment: CTD and TSG-Flow thru system
Total number of stations: 29
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 Henry 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:

29 locations, 123 samples each 500-ml, 12 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:

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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 5	06/12/2019	2042.41	2034.81	7.60	20.0	11

AOML 5	06/13/2019	2042.41	2034.77	7.64	20.0	8
AOML 5	06/14/2019	2042.41	2032.97	9.44	20.0	8
AOML 6	06/12/2019	2042.41	2047.81	5.40	12.0	8
AOML 6	06/13/2019	2042.41	2048.23	5.82	12.0	9
AOML 6	06/14/2009	2042.41	2049.67	7.26	12.0	8

Analysis date: 06/12/2019

Coulometer used: DICE–CM5011- AOML 5

Blanks: 20.00 counts/min

CRM # 385 was used and with an assigned value of (includes both DIC and salinity):

Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 5: offset 7.60 $\mu\text{mol/kg}$ (2034.81 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 11, 7 and 14 min.

Analysis date: 06/13/2019

Coulometer used: DICE–CM5011- AOML 5

Blanks: 20.0 counts/min

CRM # 6 was used and with an assigned value of (includes both DIC and salinity): Batch

173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 5: offset 7.64 $\mu\text{mol/kg}$ (2034.77 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 11 min.

Analysis date: 06/14/2019

Coulometer used: DICE–CM5011- AOML 5

Blanks: 20.0 counts/min

CRM # 882 was used and with an assigned value of (includes both DIC and salinity):

Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 5: offset 9.44 $\mu\text{mol/kg}$ (2032.97 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 06/12/2019

Coulometer used: DICE–CM5011- AOML 6

Blanks: 12.0 counts/min

CRM # 69 was used and with an assigned value of (includes both DIC and salinity):

Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 6: offset 5.40 $\mu\text{mol/kg}$ (2047.81 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 06/13/2019

Coulometer used: DICE–CM5011- AOML 6

Blanks: 12.0 counts/min

CRM # 319 was used and with an assigned value of (includes both DIC and salinity):

Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 6: offset 5.82 $\mu\text{mol/kg}$ (2048.23 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 7 and 14 min.

Analysis date: 06/14/2019

Coulometer used: DICE-CM5011- AOML 6

Blanks: 12.0 counts/min

CRM # 1007 was used and with an assigned value of (includes both DIC and salinity):

Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414

CRM values measured: AOML 6: offset 7.26 $\mu\text{mol/kg}$ (2049.67 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Reproducibility: (# samples and average difference): 12 duplicate samples were collected with an average difference 0.18 $\mu\text{mol/kg}$ (0.01 – 0.41) and an average STDEV of 0.13 (0.01 – 0.29).

Instrument	Sample ID	Bottle #	DIC ($\mu\text{mol/kg}$)	Average	STDEV	Difference
AOML6	170101	2	1995.45			
AOML6	170101	3	1995.40	1995.42	0.04	0.05
AOML6	290305	12	1952.28			
AOML6	290305	13	1952.63	1952.46	0.24	0.35
AOML6	370612	25	2019.11			
AOML6	370612	26	2018.77	2018.94	0.24	0.34
AOML6	511001	39	2076.52			
AOML6	511001	40	2076.34	2076.43	0.13	0.19
AOML6	551105	45	2047.75			
AOML6	551105	46	2047.34	2047.54	0.29	0.41
AOML6	731412	59	2023.83			
AOML6	731412	60	2023.78	2023.81	0.04	0.05
AOML5	991602	69	2161.61			
AOML5	991602	70	2161.98	2161.79	0.26	0.37
AOML5	1021801	75	2051.07			
AOML5	1021801	76	2051.13	2051.10	0.04	0.06
AOML5	1061912	82	2007.36			
AOML5	1061912	83	2007.37	2007.37	0.01	0.01
AOML5	1142303	96	2075.93			

AOML5	1142303	97	2076.24	2076.09	0.22	0.31
AOML5	1232512	106	1868.65			
AOML5	1232512	107	1868.64	1868.64	0.01	0.01
AOML6	1352701	113	2112.51			
AOML6	1352701	114	2112.68	2112.59	0.12	0.17
Average					0.13	0.18

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

pH:

Analysis date: 06/12/2019, 06/13/2019 and 06/14/2019
Spectrophotometer used: HP Agilent 8453

A CRM was run before pH analysis on each day
06/12/2019 Batch 169 CRM #004 = 7.8126
06/13/2019 Batch 173 CRM #810 = 7.8739
06/14/2019 Batch 173 CRM #943 = 7.8749

Reproducibility: (# samples and average difference): 12 duplicate samples were collected with an average difference 0.0019 (0.0005 – 0.0020) and an average STDEV of 0.0014 (0.0003 – 0.0014).

Instrument	Sample ID	Bottle #	pH	Average	STDEV	Difference
HP Agilent 8453	170101	2	7.85551			
HP Agilent 8453	170101	3	7.86507	7.8603	0.0068	0.0096
HP Agilent 8453	290305	12	7.91910			
HP Agilent 8453	290305	13	7.91958	7.9193	0.0003	0.0005
HP Agilent 8453	370612	25	7.94900			
HP Agilent 8453	370612	26	7.95052	7.9498	0.0011	0.0015

HP Agilent 8453	511001	39	7.80968			
HP Agilent 8453	511001	40	7.81140	7.8105	0.0012	0.0017
HP Agilent 8453	551105	45	7.82592			
HP Agilent 8453	551105	46	7.82788	7.8269	0.0014	0.0020
HP Agilent 8453	731412	59	7.94316			
HP Agilent 8453	731412	60	7.94231	7.9427	0.0006	0.0008
HP Agilent 8453	991602	69	7.75113			
HP Agilent 8453	991602	70	7.74978	7.7505	0.0010	0.0013
HP Agilent 8453	1021801	75	7.78409			
HP Agilent 8453	1021801	76	7.78328	7.7837	0.0006	0.0008
HP Agilent 8453	1061912	82	7.94783			
HP Agilent 8453	1061912	83	7.94947	7.9486	0.0012	0.0016
HP Agilent 8453	1142303	96	7.80576			
HP Agilent 8453	1142303	97	7.80484	7.8053	0.0006	0.0009
HP Agilent 8453	1232512	106	7.95137			
HP Agilent 8453	1232512	107	7.95207	7.9517	0.0005	0.0007
HP Agilent 8453	1352701	113	7.65410			
HP Agilent 8453	1352701	114	7.65473	7.6544	0.0004	0.0006
Average					0.0014	0.0019

pH Sample Temperature

Sample ID	Sample BTL #	Sample Temp. (°C)
CRM169_004	4	19.979
CRM173_810	810	19.983
CRM173_943	943	19.985
10000	1	20.003
170101	2	20.006
170101	3	19.995
170105	4	19.989
170112	5	19.995

190200	6	19.997
190201	7	19.996
190207	8	19.993
190211	9	19.988
100000	10	19.996
290301	11	19.994
290305	12	20.002
290305	13	19.993
290312	14	19.992
300400	15	20.003
300401	16	19.997
300407	17	20.002
300412	18	20.009
320501	19	19.999
320504	20	19.997
320512	21	19.992
220000	22	19.995
370601	23	19.996
370605	24	20.002
370612	25	19.995
370612	26	20.008
380701	27	20.006
380702	28	20.003
380712	29	20.012
300000	30	20.004
430801	31	20.011
430802	32	19.997
430812	33	19.998
440900	34	20.001
440901	35	19.998
440904	36	19.996
440912	37	20.005
380000	38	20.001
511001	39	20.013
511001	40	20.004
511007	41	19.997
511012	42	19.993
430000	43	19.996
551101	44	20.000
551105	45	20.000

551105	46	20.001
551112	47	20.009
601200	48	19.989
601201	49	19.993
601206	50	19.994
601210	51	19.983
520000	52	19.990
691300	53	19.991
691301	54	20.006
691305	55	19.990
691312	56	19.994
731401	57	20.004
731405	58	20.009
731412	59	20.008
731412	60	20.011
771500	61	19.992
771501	62	19.990
771505	63	19.990
771510	64	19.993
650000	65	20.007
660000	66	20.012
991600	67	20.008
991601	68	20.011
991602	69	20.015
991602	70	20.012
991612	71	20.007
1001701	72	20.015
1001704	73	20.011
1001712	74	20.016
1021801	75	20.017
1021801	76	20.008
1021803	77	20.013
1021812	78	20.013
790000	79	20.013
1061901	80	20.005
1061903	81	20.005
1061912	82	20.010
1061912	83	20.004
1072000	84	20.006
1072001	85	20.008

1072004	86	20.005
1072011	87	20.011
1092101	88	20.005
1092104	89	19.996
1092112	90	19.998
1132200	91	20.012
1132201	92	20.009
1132203	93	20.004
1132211	94	19.999
1142301	95	19.997
1142303	96	19.990
1142303	97	19.986
1142312	98	20.001
1172400	99	19.990
1172401	100	19.993
1172403	101	19.984
1172412	102	19.990
1232500	103	19.998
1232501	104	20.002
1232502	105	19.999
1232512	106	20.002
1232512	107	20.004
1080000	108	19.992
1322600	109	19.992
1322601	110	19.993
1322603	111	20.010
1322612	112	19.995
1352701	113	20.002
1352701	114	19.995
1352703	115	19.996
1352712	116	19.997
1372800	117	19.999
1372801	118	19.997
1372803	119	20.002
1372812	120	19.989
1382901	121	20.017
1382905	122	20.010
1382912	123	20.007

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°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.

Final pH results were reported at 25°C and at pH temperature analyzed in the data file.

Talk:

Analysis date: 06/18/2019, 06/19/2019 and 06/20/2019

Titration system used: Open cell

CRM Batch 169, Salinity = 33.518, cert. TA = 2207.03µmol/kg.

CRM Batch 173, Salinity = 33.414, cert. TA = 2210.77µmol/kg.

On 06/18/2019, 06/19/2019 and 06/20/2019 one CRM was analyzed before the samples and the same CRM was run at the end of analysis each day 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	06/18/2019	09:06:52	623	2208.52	
1	06/18/2019	17:23:26	623	2208.51	0.01
1	06/19/2019	08:28:11	8	2209.27	
1	06/19/2019	17:06:13	8	2209.59	0.32
1	06/20/2019	08:49:50	883	2209.53	
1	06/20/2019	16:36:54	883	2206.82	2.71
2	06/18/2019	12:07:13	78	2202.71	
2	06/18/2019	17:18:24	78	2205.00	2.29
2	06/19/2019	08:46:39	321	2203.24	
2	06/19/2019	16:59:49	321	2201.61	1.63
2	06/20/2019	08:41:23	1193	2202.19	

Reproducibility: (# samples and average difference): 12 duplicate samples were collected with an average difference $\mu\text{mol/kg}$ 1.50 (0.04- 4.04) and an average STDEV of 1.06 (0.03-2.85).

Instrument	Sample ID	Bottle #	TA ($\mu\text{mol/kg}$)	Average	STDEV	Difference
System 2	170101	2	2138.82			
System 2	170101	3	2139.63	2139.22	0.57	0.80
System 2	290305	12	2118.54			
System 2	290305	13	2117.92	2118.23	0.44	0.63
System 2	370612	25	2206.14			
System 2	370612	26	2206.23	2206.19	0.07	0.09
System 1	511001	39	2210.27			
System 1	511001	40	2207.08	2208.67	2.26	3.19
System 2	551105	45	2179.00			
System 2	551105	46	2183.04	2181.02	2.85	4.04
System 2	731412	59	2209.69			
System 2	731412	60	2209.35	2209.52	0.24	0.34
System 1	991602	69	2321.05			
System 1	991602	70	2324.60	2322.83	2.51	3.55
System 1	1021801	75	2213.89			
System 1	1021801	76	2211.67	2212.78	1.57	2.22
System 2	1061912	82	2192.17			
System 2	1061912	83	2190.23	2191.20	1.38	1.94
System 2	1142303	96	2209.32			

System 2	1142303	97	2209.36	2209.34	0.03	0.04
System 1	1232512	106	2030.03			
System 1	1232512	107	2030.68	2030.36	0.46	0.65
System 1	1352701	113	2191.17			
System 1	1352701	114	2191.71	2191.44	0.39	0.55
Average					1.06	1.50

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

Flow through (FT) samples not collected while on a CTD station were given the sample ID of the sample bottle number.

Flow through sample info such as salinity, temperature and latitude/longitude were taken from the TSG and UWpCO2 files.

Due to bottle firing error, data from the bottom and mid depths for Station 106, Cast 19 were not available. DIC, pH and TA could not be calculated for those samples.

Station 138, Cast 29, Niskin 5 mid depth temperature and salinity were not available. DIC, pH and TA could not be calculated for this sample.

Silica values were marked as bad and not reported, possibly due to changes in the laboratory and equipment used to process these samples (Dave Townsend and Maura Thomas-U of Maine).

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