**Cruise:** HB1902
**Ship:** R/V Henry Bigelow
**Expo Code:** 33HH20190522
**Dates:** May 22$^{nd}$ – June 6$^{th}$, 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:**
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

**TAlk:**
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

## *Sample Analysis*
**DIC:**

| Instrument ID | Date | Certified CRM ($\mu$mol/kg) | CRM Value ($\mu$mol/kg) | CRM Offset ($\mu$mol/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 µmol/kg, S: 33.414
CRM values measured:  AOML 5: offset 7.60 µmol/kg (2034.81 µmol/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 µmol/kg, S: 33.414
CRM values measured:  AOML 5: offset 7.64 µmol/kg (2034.77 µmol/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 µmol/kg, S: 33.414
CRM values measured:  AOML 5: offset 9.44 µmol/kg (2032.97 µmol/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 µmol/kg, S: 33.414
CRM values measured:  AOML 6: offset 5.40 µmol/kg (2047.81 µmol/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 µmol/kg, S: 33.414
CRM values measured:  AOML 6: offset 5.82 µmol/kg (2048.23 µmol/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 µmol/kg, S: 33.414
CRM values measured: AOML 6: offset 7.26 µmol/kg (2049.67 µmol/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 µmol/kg (0.01 – 0.41) and an average STDEV of 0.13 (0.01 – 0.29).

| Instrument | Sample ID | Bottle # | DIC (µmol/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 $HgCl_2$ (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 (0.0006 – 0.0096) and an average STDEV of 0.0013 (0.0004 – 0.0068).

| Instrument | Sample ID | Bottle # | pH | Average | STDEV | Difference |
|---|---|---|---|---|---|---|
| HP Agilent 8453 | 170101 | 2 | 7.8556 | | | |
| HP Agilent 8453 | 170101 | 3 | 7.8651 | 7.8603 | 0.0068 | 0.0096 |
| HP Agilent 8453 | 290305 | 12 | 7.9190 | | | |
| HP Agilent 8453 | 290305 | 13 | 7.9196 | 7.9193 | 0.0004 | 0.0006 |
| HP Agilent 8453 | 370612 | 25 | 7.9490 | | | |
| HP Agilent 8453 | 370612 | 26 | 7.9505 | 7.9497 | 0.0010 | 0.0015 |

| | | | | | | |
|---|---|---|---|---|---|---|
| HP Agilent 8453 | 511001 | 39 | 7.8097 | | | |
| HP Agilent 8453 | 511001 | 40 | 7.8116 | 7.8106 | 0.0013 | 0.0019 |
| HP Agilent 8453 | 551105 | 45 | 7.8259 | | | |
| HP Agilent 8453 | 551105 | 46 | 7.8279 | 7.8269 | 0.0014 | 0.0020 |
| HP Agilent 8453 | 731412 | 59 | 7.9433 | | | |
| HP Agilent 8453 | 731412 | 60 | 7.9424 | 7.9429 | 0.0006 | 0.0009 |
| HP Agilent 8453 | 991602 | 69 | 7.7513 | | | |
| HP Agilent 8453 | 991602 | 70 | 7.7500 | 7.7506 | 0.0009 | 0.0013 |
| HP Agilent 8453 | 1021801 | 75 | 7.7843 | | | |
| HP Agilent 8453 | 1021801 | 76 | 7.7835 | 7.7839 | 0.0006 | 0.0008 |
| HP Agilent 8453 | 1061912 | 82 | 7.9479 | | | |
| HP Agilent 8453 | 1061912 | 83 | 7.9496 | 7.9488 | 0.0012 | 0.0017 |
| HP Agilent 8453 | 1142303 | 96 | 7.8057 | | | |
| HP Agilent 8453 | 1142303 | 97 | 7.8047 | 7.8052 | 0.0007 | 0.0010 |
| HP Agilent 8453 | 1232512 | 106 | 7.9514 | | | |
| HP Agilent 8453 | 1232512 | 107 | 7.9521 | 7.9517 | 0.0005 | 0.0007 |
| HP Agilent 8453 | 1352701 | 113 | 7.6540 | | | |
| HP Agilent 8453 | 1352701 | 114 | 7.6547 | 7.6544 | 0.0005 | 0.0007 |
| Average | | | | | 0.0013 | 0.0019 |

**pH Sample Temperature**

| Sample ID | Sample BTL # | Sample Temp. ($^0$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 $20^0$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 $25^0$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 | $|\Delta CRM|$ |
|---|---|---|---|---|---|
| 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 | |

| | 2 | 06/20/2019 | 16:51:38 | 1193 | 2198.87 | 3.32 | |

**Reproducibility:** (# samples and average difference): 12 duplicate samples were collected with an average difference μmol/kg 1.50 (0.04- 4.04) and an average STDEV of 1.06 (0.03-2.85).

| Instrument | Sample ID | Bottle # | TA (μmol/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

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.