**Cruise:** GU1804
**Ship:** R/V Gordon Gunter
**Expo Code:** 33GG20180822
**Dates:** August 22, 2018 – August 31, 2018
**Chief Scientist:** Harvey Walsh
**Equipment**: CTD Rosette & Ship's Flow Thru (FT)
**Total number of stations:** 23 (16 CTD and 7 FT )
**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 onboard the R/V Gordon Gunter 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, 60 samples each 500-ml, 5 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, 60 samples each 500-ml, 5 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, 60 samples each 500-ml, 5 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI:  Dr. Rik Wanninkhof
Analyzed by:  Leticia Barbero, 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 | 09/24/2018 | 2017.88 | 2020.34 | 2.46 | 12.0 | 7.0 |
| AOML 5 | 09/25/2018 | 2017.88 | 2017.18 | 0.70 | 16.0 | 7.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| AOML 6 | 09/24/2018 | 2017.88 | 2021.15 | 3.27 | 12.0 | 14.0 |
| AOML 6 | 09/24/2018 | 2017.88 | 2019.50 | 1.62 | 22.0 | 10.0 |

Analysis date:  09/24/2018
Coulometer used: DICE–CM5011- AOML 5
Blanks: 12.0 counts/min
CRM # 1036 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured:  AOML 5: offset 2.46 µmol/kg (2020.34 µmol/kg).
Average run time, minimum run time, maximum run time:  7, 7 and 8 min.

Analysis date:  09/25/2018
Coulometer used: DICE–CM5011- AOML 5
Blanks: 16.0 counts/min
CRM # 180 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured:  AOML 5: offset 0.70 µmol/kg (2017.18 µmol/kg).
Average run time, minimum run time, maximum run time:  7, 7 and 7 min.

Analysis date:  09/25/2018
Coulometer used: DICE–CM5011- AOML 6
Blanks: 12.0 counts/min
CRM # 1092 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured:  AOML 6: offset 3.27 µmol/kg (2021.15 µmol/kg).
Average run time, minimum run time, maximum run time:  14, 8 and 20 min.

Analysis date:  09/25/2018
Coulometer used: DICE–CM5011- AOML 6
Blanks: 22.0 counts/min
CRM # 486 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured:  AOML 6: offset 1.62 µmol/kg (2019.50 µmol/kg).
Average run time, minimum run time, maximum run time:  10, 7 and 15 min.

**Reproducibility:** (# samples and average difference): 5 duplicate samples were collected
with an average difference 1.02 µmol/kg (0.24 – 2.35) and an average STDEV of 0.72
(0.17 – 1.66).

| System | Sample ID | DIC | Average | Difference | STDEV |
|---|---|---|---|---|---|
| AOML5 | 230501 | 1998.66 | | | |
| AOML5 | 230501 | 1996.31 | 1997.48 | 2.35 | 1.66 |
| | | | | | |
| AOML5 | 290705 | 2152.51 | | | |

| | | | | | |
|---|---|---|---|---|---|
| AOML5 | 290705 | 2153.02 | 2152.76 | 0.51 | 0.36 |
| | | | | | |
| AOML5 | 300801 | 2180.28 | | | |
| AOML5 | 300801 | 2180.04 | 2180.16 | 0.24 | 0.17 |
| | | | | | |
| AOML5 | 511201 | 2181.59 | | | |
| AOML5 | 511201 | 2182.31 | 2181.95 | 0.72 | 0.51 |
| | | | | | |
| AOML5 | 541411 | 1899.79 | | | |
| AOML5 | 541411 | 1901.06 | 1900.43 | 1.27 | 0.90 |
| Average | | | | 1.02 | 0.72 |

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.

The blank on AOML 6 (09/25/2018) was raised from 12.0 to 22.0 after running a new CRM.

**pH:**

Analysis date: 09/24/2018 and 09/25/2018
Spectrophotometer used:  HP Agilent 8453
09/24/2018 CRM #798, Batch 150 had a pH value of 7.9412
09/25/2018 CRM #1170, Batch 150 had a pH value of 7.9420

**Reproducibility:** (# samples and average difference): 5 duplicate samples were collected with an average difference 0.0013 (0.0001 – 0.0027) and an average STDEV of 0.0009 (0.0001 – 0.0019).

| System | Sample ID | Sample Bottle # | S | t | pH | Average | Difference | STDEV |
|---|---|---|---|---|---|---|---|---|
| HP Agilent 8453 | 230501 | 92 | 32.325 | 20.061 | 7.9490 | | | |
| HP Agilent 8453 | 230501 | 93 | 32.325 | 20.067 | 7.9511 | 7.950 | 0.0021 | 0.0015 |
| | | | | | | | | |
| HP Agilent 8453 | 290705 | 100 | 35.312 | 20.04 | 7.863 | | | |
| HP Agilent 8453 | 290705 | 101 | 35.332 | 20.033 | 7.863 | 7.863 | 0.0001 | 0.0001 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| HP Agilent 8453 | 300801 | 103 | 35.034 | 20.044 | 7.762 | | |
| HP Agilent 8453 | 300801 | 104 | 35.034 | 20.045 | 7.761 | 7.762 | 0.0005 | 0.0003 |
| | | | | | | | |
| HP Agilent 8453 | 511201 | 117 | 35.031 | 20.051 | 7.762 | | |
| HP Agilent 8453 | 511201 | 118 | 35.031 | 20.067 | 7.760 | 7.761 | 0.0011 | 0.0008 |
| | | | | | | | |
| HP Agilent 8453 | 541411 | 126 | 31.297 | 20.064 | 8.054 | | |
| HP Agilent 8453 | 541411 | 127 | 31.297 | 20.068 | 8.051 | 8.053 | 0.0027 | 0.0019 |
| Average | | | | | | | 0.0013 | 0.0009 |

## Temperatures measured during pH analysis

| Sample ID | Station | Botlle # | Temp. $^0$C |
|---|---|---|---|
| CRM150_798 | CRM798 | CRM798 | 20.032 |
| CRM150_1170 | CRM 1170 | CRM 1170 | 20.055 |
| 80101 | 8 | 81 | 20.035 |
| 80102 | 8 | 82 | 20.040 |
| 80112 | 8 | 83 | 20.036 |
| 110201 | 11 | 85 | 20.050 |
| 110203 | 11 | 86 | 20.043 |
| 110210 | 11 | 87 | 20.048 |
| 150301 | 15 | 91 | 20.055 |
| 150305 | 15 | 90 | 20.051 |
| 150312 | 15 | 89 | 20.060 |
| 230501 | 23 | 92 | 20.061 |
| 230501 | 23 | 93 | 20.067 |
| 230504 | 23 | 94 | 20.061 |
| 230508 | 23 | 95 | 20.065 |
| 270601 | 27 | 96 | 20.065 |
| 270605 | 27 | 97 | 20.068 |
| 270612 | 27 | 98 | 20.058 |
| 290701 | 29 | 99 | 20.039 |
| 290705 | 29 | 100 | 20.040 |
| 290705 | 29 | 101 | 20.033 |
| 290712 | 29 | 102 | 20.045 |
| 300801 | 30 | 103 | 20.044 |
| 300801 | 30 | 104 | 20.045 |
| 300804 | 30 | 105 | 20.045 |
| 300812 | 30 | 106 | 20.046 |
| 360902 | 36 | 109 | 20.055 |
| 360905 | 36 | 110 | 20.057 |

| | | | |
|---|---|---|---|
| 360912 | 36 | 111 | 20.061 |
| 371001 | 37 | 112 | 20.058 |
| 371004 | 37 | 113 | 20.059 |
| 371012 | 37 | 114 | 20.070 |
| 511201 | 51 | 117 | 20.051 |
| 511201 | 51 | 118 | 20.067 |
| 511202 | 51 | 119 | 20.066 |
| 511211 | 51 | 120 | 20.060 |
| 521301 | 52 | 121 | 20.060 |
| 521303 | 52 | 122 | 20.065 |
| 521310 | 52 | 123 | 20.060 |
| 541401 | 54 | 124 | 20.062 |
| 541405 | 54 | 125 | 20.067 |
| 541411 | 54 | 126 | 20.064 |
| 541411 | 54 | 127 | 20.068 |
| 561501 | 56 | 128 | 20.055 |
| 561504 | 56 | 129 | 20.051 |
| 561509 | 56 | 130 | 20.048 |
| 691701 | 69 | 132 | 20.042 |
| 691703 | 69 | 134 | 20.043 |
| 691706 | 69 | 133 | 20.049 |
| 701801 | 70 | 135 | 20.048 |
| 701804 | 70 | 136 | 20.047 |
| 701811 | 70 | 137 | 20.038 |
| 721901 | 72 | 138 | 20.047 |
| 721903 | 72 | 139 | 20.037 |
| 721911 | 72 | 140 | 20.040 |
| 840000 | 84 | 84 | 20.044 |
| 880000 | 88 | 88 | 20.050 |
| 1070000 | 107 | 107 | 20.046 |
| 1080000 | 108 | 108 | 20.049 |
| 1150000 | 115 | 115 | 20.063 |
| 1160000 | 116 | 116 | 20.060 |
| 1310000 | 131 | 131 | 20.048 |

## 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 $20^0C$ at Full Scale (pH 0-14).

Samples were run on an automated system where the temperature was kept constant.

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

A CRM was run for pH before analysis of samples.

pH values are reported at $25^0C$ in the data spreadsheet.

**TAlk:**

Analysis date: 09/25/2018, 09/26/2018, 09/27/2018 and 09/28/2018
Titration system used: Open cell
CRM Batch 150, Salinity = 33.343, cert. TA = 2214.71µmol/kg.

On 09/25/2018, 09/26/2018, 09/27/2018 and 09/28/2018 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 | $\|\Delta CRM\|$ |
|---|---|---|---|---|---|
| 2 | 09/25/2018 | 13:03:03 | 180 | 2223.96 | |
| 2 | 09/25/2018 | 16:21:02 | 180 | 2223.06 | 0.90 |
| 2 | 09/26/2018 | 09:40:09 | 1216 | 2211.60 | |
| 2 | 09/26/2018 | 17:15:03 | 1216 | 2221.03 | 9.43 |
| 2 | 09/27/2018 | 11:07:17 | 616 | 2223.92 | |
| 2 | 09/27/2018 | 16:24:32 | 616 | 2224.78 | 0.86 |
| 2 | 09/28/2018 | 08:34:52 | 292 | 2215.09 | |
| 2 | 09/28/2018 | 13:40:41 | 292 | 2223.74 | 8.65 |

**Reproducibility:** (# samples and average difference): 5 duplicate samples were collected with an average difference µmol/kg 9.48 (1.45-38.04) and an average STDEV of 6.71 (1.74-26.90).

| System | Sample ID | TA | Average | Difference | STDEV |
|---|---|---|---|---|---|
| 2 | 230501 | 2181.02 | | | |
| 2 | 230501 | 2178.56 | 2179.79 | 2.47 | 1.74 |
| 2 | 290705 | 2332.78 | | | |
| 2 | 290705 | 2294.74 | 2313.76 | 38.04 | 26.90 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 300801 | 2317.70 | | | |
| 2 | 300801 | 2316.25 | 2316.97 | 1.45 | 1.03 |
| | | | | | |
| 2 | 511201 | 2303.93 | | | |
| 2 | 511201 | 2301.01 | 2302.47 | 2.92 | 2.07 |
| | | | | | |
| 2 | 541411 | 2130.40 | | | |
| 2 | 541411 | 2132.94 | 2131.67 | 2.54 | 1.80 |
| Average | | | | 9.48 | 6.71 |

## Remarks

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

The second duplicate with sample ID 290705 had a large difference which contributed to the overall high average for the difference and STDEV of all the samples.

## *Comments*

Sample bottle 121 the titration stopped mid ways thru and could not be recovered. The sample was marked 4-Bad. DIC and pH values were good.

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.

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

Final data – the sample ID number of the flow through (FT) samples is the same as the bottle number in which they were collected, example bottle 84 = sample ID of 840000.

The temperature and salinity for the FT samples were taken from the ship's TSG.