

**Cruise:** PC2104  
**Ship:** R/V Pisces  
**Expo Code:** 334B20210805  
**Dates:** August 5<sup>th</sup> – August 18<sup>th</sup>, 2021  
**Chief Scientist:** Harvey Walsh  
**Equipment:** CTD Rosette & Ship's Flow Thru (FT)  
**Total number of stations:** 28  
**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 the TSG flow thru system onboard the R/V Pisces by the survey tech. The date and time listed in the data file are UTC when each sample bottle was collected.

#### **DIC:**

28 locations, 99 samples each 500-ml, 15 duplicate samples.

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

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone, Dr. Denis Pierrot and Dr. Leticia Barbero

#### **pH:**

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#### **TAlk:**

28 locations, 99 samples each 500-ml, 15 duplicate samples.

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

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone, Dr. Denis Pierrot, Dr. Leticia Barbero and Dismey Sosa-Rodriguez

### **Sample Analysis**

#### **DIC:**

Instrument ID	Date	Certified CRM ( $\mu\text{mol/kg}$ )	CRM Value ( $\mu\text{mol/kg}$ )	CRM Offset ( $\mu\text{mol/kg}$ )	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	08/24/2021	1952.65	1952.91	0.26	19.5	9

AOML 5	12/08/2021	1952.65	1949.03	3.62	24.2	8
AOML 6	08/24/2021	1952.65	1956.79	4.14	12.0	8
AOML 6	11/17/2021	1952.65	1954.83	2.18	12.0	7
AOML 6	12/08/2021	1952.65	1950.24	2.41	24.0	8
AOML 6	12/09/2021	1952.65	1954.35	1.70	20.0	9

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Analysis date: 08/24/2021

Coulometer used: DICE-CM5011- AOML 5

Blanks: 19.5 counts/min

CRM # 937 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 5: offset 0.26  $\mu\text{mol/kg}$  (1952.91  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 9, 7 and 13 min.

Analysis date: 12/08/2021

Coulometer used: DICE-CM5011- AOML 5

Blanks: 24.2 counts/min

CRM # 691 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 5: offset 3.62  $\mu\text{mol/kg}$  (1949.03  $\mu\text{mol/kg}$ ).

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

Analysis date: 08/24/2021

Coulometer used: DICE-CM5017O- AOML 6

Blanks: 12.0 counts/min

CRM # 818 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 4.14  $\mu\text{mol/kg}$  (1956.79  $\mu\text{mol/kg}$ ).

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

Analysis date: 11/17/2021

Coulometer used: DICE-CM5017O- AOML 6

Blanks: 12.0 counts/min

CRM # 82 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 2.18  $\mu\text{mol/kg}$  (1954.83  $\mu\text{mol/kg}$ ).

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

Analysis date: 12/08/2021

Coulometer used: DICE-CM5017O- AOML 6

Blanks: 24.0 counts/min

CRM # 392 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 2.41  $\mu\text{mol/kg}$  (1950.24  $\mu\text{mol/kg}$ ).

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

Analysis date: 12/09/2021

Coulometer used: DICE-CM5017O- AOML 6

Blanks: 20.0 counts/min

CRM # 205 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 1.70  $\mu\text{mol/kg}$  (1954.35  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

**Reproducibility:** (# samples and average difference): 15 duplicate samples were collected with an average difference 0.84  $\mu\text{mol/kg}$  (0.04-2.12) and an average STDEV of 0.59 (0.06-3.00).

Instrument	Sample ID	Bottle #	DIC	Average	STDEV	Difference
			( $\mu\text{mol/kg}$ )			
AOML5	241401	170	2186.63			
AOML5	241401	171	2185.99	2186.0	0.46	0.65
AOML5	241403	168	2200.45			
AOML5	241403	169	2202.21	2202.2	1.24	1.76
AOML5	241412	166	1983.66			
AOML5	241412	167	1982.85	1982.9	0.57	0.81
AOML6	792501	241	2116.76			
AOML6	792501	242	2115.91	2115.9	0.60	0.85
AOML6	792503	239	2111.13			
AOML6	792503	240	2111.94	2111.9	0.57	0.81
AOML6	792512	238	2010.55			
AOML6	792512	237	2010.89	2010.9	0.24	0.34
AOML5	842601	202	2181.39			
AOML5	842601	207	2181.45	2181.4	0.04	0.06
AOML5	842603	203	2179.61			
AOML5	842603	206	2180.78	2180.8	0.83	1.17
AOML5	842612	204	1922.55			
AOML5	842612	205	1921.95	1921.9	0.42	0.60
AOML6	942901	211	2070.84			
AOML6	942901	212	2071.17	2071.2	0.23	0.33

AOML6	942903	213	2069.11			
AOML6	942903	214	2069.83	2069.8	0.51	0.73
AOML6	942912	215	2067.77			
AOML6	942912	216	2068.34	2068.3	0.40	0.57
AOML6	1213701	141	2052.4			
AOML6	1213701	146	2049.4	2049.4	2.12	3.00
AOML6	1213703	143	2047.5			
AOML6	1213703	144	2047.8	2047.8	0.20	0.29
AOML6	1213712	145	2009.0			
AOML6	1213712	142	2008.4	2008.4	0.43	0.60
Average					0.59	0.84

CRM, salinity and HgCl<sub>2</sub> 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.

#### **pH:**

Analysis date: 08/24/2021, 11/17/2021, 12/08/2021 and 12/09/2021

Spectrophotometer used: HP Agilent 8453

No CRMs run.

**Reproducibility:** pH at 20<sup>0</sup>C (# samples, average difference, average STDEV): 15  
duplicate samples were collected with an average difference 0.00356 (0.00007 – 0.01726)  
and an average STDEV of 0.00252 (0.00005 – 0.02441).

Instrument	Sample ID	Bottle #	pH @20 <sup>0</sup> C	Average	STDEV	Difference
HP Agilent 8453	241401	170	7.781341			
HP Agilent 8453	241401	171	7.756930	7.76914	0.01726	0.02441
HP Agilent 8453	241403	168	7.744848			
HP Agilent 8453	241403	169	7.746451	7.74565	0.00113	0.00160

HP Agilent 8453	241412	166	8.102440			
HP Agilent 8453	241412	167	8.100831	8.10164	0.00114	0.00161
HP Agilent 8453	792501	241	7.786029			
HP Agilent 8453	792501	242	7.788301	7.78717	0.00161	0.00227
HP Agilent 8453	792503	239	7.786700			
HP Agilent 8453	792503	240	7.786497	7.78660	0.00014	0.00020
HP Agilent 8453	792512	237	7.935685			
HP Agilent 8453	792512	238	7.933101	7.93439	0.00183	0.00258
HP Agilent 8453	842601	202	8.092245			
HP Agilent 8453	842601	207	8.089825	8.09104	0.00171	0.00242
HP Agilent 8453	842603	203	7.761040			
HP Agilent 8453	842603	206	7.763111	7.76208	0.00146	0.00207
HP Agilent 8453	842612	204	7.759278			
HP Agilent 8453	842612	205	7.759209	7.75924	0.00005	0.00007
HP Agilent 8453	942901	211	7.805220			
HP Agilent 8453	942901	212	7.804850	7.80504	0.00026	0.00037
HP Agilent 8453	942903	213	7.805396			
HP Agilent 8453	942903	214	7.804268	7.80483	0.00080	0.00113
HP Agilent 8453	942912	215	7.808526			
HP Agilent 8453	942912	216	7.806353	7.80744	0.00154	0.00217
HP Agilent 8453	1213701	143	7.897545			
HP Agilent 8453	1213701	146	7.891976	7.89476	0.00394	0.00557
HP Agilent 8453	1213703	141	7.906038			
HP Agilent 8453	1213703	144	7.899780	7.90291	0.00443	0.00626
HP Agilent 8453	1213712	142	7.981830			
HP Agilent 8453	1213712	145	7.981121	7.98148	0.00050	0.00071
Average					0.00252	0.00356

Temperatures measured during pH analysis.

Sample ID	Sample BTL #	Salinity	Analysis T (°C)
111101	157	32.1024	19.851
111107	158	31.4129	19.839
111112	159	30.2050	19.884
141201	160	32.7815	19.878
141203	161	32.3992	19.906
141212	162	31.2350	19.900
231301	165	35.6011	19.926
231303	164	35.7617	19.977
231312	163	32.8079	19.962
241401	170	35.0642	19.927
241401	171	35.0642	20.036
241403	168	35.3053	19.949
241403	169	35.3053	19.866
241412	166	33.8584	19.920
241412	167	33.8584	19.937
321501	174	35.0735	20.016
321503	173	35.2707	20.005
321512	172	35.2804	20.055
331601	177	35.7534	19.848
331603	176	36.1089	19.997
331612	175	34.7465	20.023
351701	180	33.4326	19.868
351703	179	33.2521	19.878
351712	178	32.4866	19.853
441801	184	35.0582	19.917
441804	183	35.3652	19.898
441812	182	35.1374	19.878
451901	186	35.1561	19.914
451903	185	35.5963	19.927
451912	181	35.3234	19.970
532001	187	35.3234	19.935
532003	188	32.6725	19.927
532012	189	32.4677	19.920
572101	190	32.5642	19.937
572105	191	32.5641	19.889
572109	192	32.5633	20.002

602201	195	32.7357	20.005
602205	194	32.6234	19.991
602209	193	32.1453	20.029
732301	198	35.0699	19.941
732303	197	35.3780	19.941
732312	196	35.6010	20.018
752401	201	35.2560	19.935
752403	200	34.8794	19.933
752412	199	32.4413	19.940
792501	241	33.4099	19.956
792501	242	33.4099	19.968
792503	239	33.3308	19.969
792503	240	33.3308	19.973
792512	237	32.4649	19.971
792512	238	32.4649	19.977
842601	205	32.3262	19.938
842601	204	32.3262	19.947
842603	203	35.1640	19.934
842603	206	35.1640	19.946
842612	202	35.1322	19.930
842612	207	35.1322	19.961
862701	210	34.8773	19.960
862703	209	33.9301	19.945
862712	208	32.3264	19.953
892801	245	34.7434	19.969
892804	244	33.8800	19.968
892812	243	32.4665	19.963
942901	211	32.5888	19.935
942901	212	32.5888	19.931
942903	213	32.5864	19.942
942903	214	32.5864	19.943
942912	215	32.5771	19.956
942912	216	32.5771	19.952
953001	246	33.6744	19.963
953003	247	33.4705	19.942
953012	248	32.7467	19.956
973101	219	33.2747	19.970
973103	218	32.9464	19.950
973112	217	32.7467	19.951
1063201	222	34.2962	19.958
1063203	221	33.4583	19.955

1063212	220	31.9815	19.952
1083301	249	32.6367	19.956
1083303	250	32.4162	19.958
1083312	251	31.3342	19.960
1113401	252	32.4301	19.958
1113403	253	32.4294	19.962
1113412	254	31.4262	19.964
1123501	255	32.3463	19.971
1123503	256	32.3363	19.971
1123512	137	31.6737	19.964
1133601	138	32.4652	19.950
1133603	139	32.4552	19.935
1133612	140	31.4317	19.934
1213701	143	33.2619	19.934
1213701	146	33.2619	19.939
1213703	141	33.2538	19.933
1213703	144	33.2538	19.929
1213712	142	33.3547	19.935
1213712	145	33.3547	19.924
1394001	225	32.6519	19.949
1394006	224	32.6632	19.947
1394012	223	32.3634	19.943

### **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).

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.

pH values are reported at 20<sup>0</sup>C and 25<sup>0</sup>C.

### **Talk:**

Analysis date: 08/25/2021, 11/22/2021 and 12/09/2021

Titration system used: Open cell

CRM Batch 178, Salinity = 33.782, cert. TA = 2216.53  $\mu$ mol/kg.



System 1:

On 08/25/2021 CRM #937 was run before analysis and CRM #818 was run at the end of analysis.

On 11/22/2021 CRM #82 was run before analysis and at the end of analysis.

On 12/09/2021 CRM #691 was run before analysis and at the end of analysis.

System 2:

On 08/25/2021 CRM #937 was run before analysis and CRM #818 was run at the end of analysis.

On 11/22/2021 CRM #20 was run before and after analysis.

On 12/09/2021 CRM #392 was run before analysis and at the end of analysis.

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	Difference
1	08/25/2021	10:34:54	937	2225.14		8.61
1	08/25/2021	18:02:01	818	2220.65	4.49	4.12
1	11/22/2021	09:48:06	82	2216.92		0.39
1	11/22/2021	17:33:11	82	2218.21	1.29	1.68
1	12/09/2021	09:44:20	691	2212.40		4.13
1	12/09/2021	17:52:38	691	2211.86	0.54	4.67
2	08/25/2021	10:04:30	937	2206.89		9.64
2	08/25/2021	17:18:30	818	2209.00	3.89	7.53
2	11/22/2021	13:18:14	20	2219.40		2.87
2	11/22/2021	17:46:09	20	2222.82	3.42	6.29
2	12/09/2021	09:52:55	392	2215.63		0.90
2	12/09/2021	17:51:49	392	2215.70	0.13	0.83

**Reproducibility:** (# samples and average difference): 15 duplicate samples were collected with an average difference  $\mu\text{mol/kg}$  3.46 (0.27-16.34) and an average STDEV of 2.45 (0.19-11.55).

Station	Sample ID	Bottle #	TA (umol/kg)	Average	STDEV	Difference
24	241401	170	2313.5			
24	241401	171	2313.9	2313.7	0.31	0.44

24	241403	168	2311.6			
24	241403	169	2328.0	2319.8	11.55	16.34
24	241412	166	2260.3			
24	241412	167	2259.6	2259.9	0.48	0.67
79	792501	241	2242.0			
79	792501	242	2238.7	2240.3	2.36	3.34
79	792503	239	2237.20			
79	792503	240	2236.37	2236.8	0.58	0.82
79	792512	238	2191.0			
79	792512	237	2190.2	2190.6	0.54	0.76
84	842601	202	2315.63			
84	842601	207	2315.36	2315.5	0.19	0.27
84	842603	203	2317.7			
84	842603	206	2318.7	2318.2	0.70	1.00
84	842612	204	2189.2			
84	842612	205	2187.6	2188.4	1.12	1.59
94	942901	211	2200.2			
94	942901	212	2199.0	2199.6	0.88	1.24
94	942903	213	2197.4			
94	942903	214	2199.3	2198.4	1.37	1.93
94	942912	215	2200.4			
94	942912	216	2199.0	2199.7	0.95	1.34
121	1213701	141	2226.3			
121	1213701	146	2222.3	2224.3	2.81	3.97
121	1213703	143	2234.7			
121	1213703	144	2224.2	2229.5	7.40	10.46
121	1213712	145	2231.1			

121	1213712	142	2223.4	2227.3	5.46	7.73
Average					2.45	3.46

### **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.

Temperature and salinity from surrounding stations was used for 3 samples that did not have a CTD temp/salt value. These were used to calculate DIC, pH and TA for those sample bottles. Sample ID 973112 (Btl #217), 1123501 (Btl #255) and 1133601 (Btl #138).

There were several sample bottles switched after looking at the values of the duplicates. Below lists what was switched;

#### **Station 84**

842601 sample bottle 205 switched with sample bottle 207  
842601 original sample bottle 202 ok  
842603 original sample bottle 203 ok  
842603 original sample bottle 206 ok  
842612 sample bottle 207 switched with sample bottle 205  
842612 original sample bottle 204 ok

#### **Station 121**

1213701 sample bottle 146 ok  
1213701 sample bottle 141 switched with sample bottle 145  
1213703 sample bottle 143 ok  
1213703 sample bottle 144 ok  
1213712 sample bottle 142 ok  
1213712 sample bottle 145 switched with sample bottle 141