

Cruise: PC1607
Ship: R/V Pisces
Expo Code: 334B20160807
Dates: 08/07/2016 – 08/19/2016
Chief Scientist: Harvey Walsh
Equipment: CTD Rosette
Total number of stations: 19
Location: US Mid-Atlantic coastal region (ECOMON cruise)

The samples were run for Dr. 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 Pisces by Christopher Taylor. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

19 locations, 64 samples each 500-ml, 9 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

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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 3	09/19/2016	2002.61	1998.97	3.64	26.0	16
AOML 3	09/20/2016	2002.61	2003.23	0.62	28.0	20
AOML 3	09/21/2016	2002.61	2002.10	0.51	28.0	19
AOML 3	09/21/2016	2002.61	2006.09	3.48	40.0	19

AOML 3	09/22/2016	2022.04	2018.40	3.64	50.0	17
AOML 4	09/19/2016	2002.61	1999.05	3.56	28.0	19
AOML 4	09/20/2016	2002.61	2000.99	1.62	28.0	19
AOML 4	09/21/2016	2002.61	1998.36	4.25	28.0	18
AOML 4	09/21/2016	2002.61	2005.55	2.94	39.0	18
AOML 4	09/22/2016	2022.04	2019.36	2.68	48.0	15

Analysis date: 09/19/2016

Coulometer used: DICE –CM5015- AOML 3

Blanks: 26.0 counts/min

CRM # 657 was used and with an assigned value of (includes both DIC and salinity):

Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072

CRM values measured: AOML 3: offset 3.64 $\mu\text{mol/kg}$ (1998.97 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 16, 13 and 20 min.

Analysis date: 09/20/2016

Coulometer used: DICE –CM5015- AOML 3

Blanks: 28.0 counts/min

CRM # 597 was used and with an assigned value of (includes both DIC and salinity):

Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072

CRM values measured: AOML 3: offset 0.62 $\mu\text{mol/kg}$ (2003.23 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 20, 20 and 20 min.

Analysis date: 09/21/2016

Coulometer used: DICE –CM5015- AOML 3

Blanks: 28.0, 40.0 counts/min

CRM # 804 was used and with an assigned value of (includes both DIC and salinity):

Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072

CRM values measured: AOML 3: offset 0.51 $\mu\text{mol/kg}$ (2002.10 $\mu\text{mol/kg}$).

CRM # 1091 was used and with an assigned value of (includes both DIC and salinity):

Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072

CRM values measured: AOML 3: offset 3.48 $\mu\text{mol/kg}$ (2006.09 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 19, 16 and 20 min.

Analysis date: 09/22/2016

Coulometer used: DICE –CM5015- AOML 3

Blanks: 50.0 counts/min

CRM # 341 was used and with an assigned value of (includes both DIC and salinity):

Batch 123, c: 2022.04 $\mu\text{mol/kg}$, S: 33.384

CRM values measured: AOML 3: offset 3.64 $\mu\text{mol/kg}$ (2018.40 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 17, 12 and 20 min.

Analysis date: 09/19/2016

Coulometer used: DICE –CM5015- AOML 4

Blanks: 28.0 counts/min

CRM # 919 was used and with an assigned value of (includes both DIC and salinity):

Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072

CRM values measured: AOML 4: offset 3.56 $\mu\text{mol/kg}$ (1999.05 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 19, 16 and 20 min.

Analysis date: 09/20/2016
Coulometer used: DICE –CM5015- AOML 4
Blanks: 28.0 counts/min
CRM # 863 was used and with an assigned value of (includes both DIC and salinity):
Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072
CRM values measured: AOML 4: offset 1.62 $\mu\text{mol/kg}$ (200.99 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 19, 19 and 20 min.

Analysis date: 09/21/2016
Coulometer used: DICE –CM5015- AOML 4
Blanks: 28.0, 39.0 counts/min
CRM # 1032 & 321 were used and with an assigned value of (includes both DIC and salinity): Batch 120, c: 2002.61 $\mu\text{mol/kg}$, S: 33.072
CRM values measured: AOML 4: offset 4.25 $\mu\text{mol/kg}$ (1998.36 $\mu\text{mol/kg}$) and offset 2.94 $\mu\text{mol/kg}$ (2005.55 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 18, 12 and 20 min.

Analysis date: 09/22/2016
Coulometer used: DICE –CM5015- AOML 4
Blanks: 48.0 counts/min
CRM # 232 was used and with an assigned value of (includes both DIC and salinity):
Batch 123, c: 2022.04 $\mu\text{mol/kg}$, S: 33.384
CRM values measured: AOML 4: offset 2.68 $\mu\text{mol/kg}$ (2019.36 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 15, 12 and 20 min.

Reproducibility: (# samples and average difference): 9 sets of duplicate samples, average difference 4.41 $\mu\text{mol/kg}$ (1.35-9.56), average STDEV of 3.12 (0.96-6.76).

Sample		DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
Instrument	ID				
AOML3	190504	2021.81			
AOML3	190504	2020.46	2021.14	1.35	0.96
AOML3	200601	2110.28			
AOML3	200601	2108.04	2109.16	2.24	1.58
AOML3	200611	1924.16			
AOML3	200611	1925.51	1924.84	1.35	0.96
AOML4	391004	2127.58			
AOML4	391004	2133.38	2130.48	5.80	4.10
AOML4	591211	1951.92			
AOML4	591211	1946.77	1949.35	5.16	3.65
AOML4	631411	2012.63			

AOML4	631411	2017.03	2014.83	4.39	3.11
AOML3	1081902	2111.96			
AOML3	1081902	2108.77	2110.37	3.19	2.26
AOML3	1081906	2087.84			
AOML3	1081906	2081.23	2084.54	6.61	4.68
AOML3	1081910	1982.53			
AOML4	1081910	1972.97	1977.75	9.56	6.76
Average				4.41	3.12

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.

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

The bottle for sample ID #841603 was cracked and the DIC was calculated using the measured pH and Alkalinity with the CO₂sys version 2.2 program. The samples were marked as questionable (3).

There was a total of 28 samples that had 20 minute titrations for DIC analysis most having 3 to 4 endpoints. A total of 3 samples were marked questionable.

The blank on AOML 3 (09/19/2016) was raised from 12.9 to 26.0 before running the CRM.

The blank on AOML 4 (09/19/2016) was raised from 17.4 to 28.0 before running the CRM.

The blank on AOML 3 (09/20/2016) was raised from 14.8 to 28.0 before running the CRM.

The blank on AOML 4 (09/20/2016) was raised from 12.0 to 28.0 before running the CRM.

The blank on AOML 3 (09/21/2016) was raised from 16.4 to 28.0 before running the

CRM. Raised blank to 40.0 after sample bottle 16 and ran another CRM

The blank on AOML 4 (09/21/2016) was raised from 22.0 to 28.0 before running the CRM. Raised blank to 39 after sample bottle 35 and ran another CRM

The blank on AOML 3 (09/22/2016) was raised from 40.0 to 50.0 before running the CRM.

The blank on AOML 4 (09/22/2016) was raised from 34.8 to 48.0 before running the CRM.

pH:

Analysis date: 09/19/2016, 09/20/2016, 09/21/2016 and 09/22/2016

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 9 sets of duplicate samples, average difference 0.0070 (0.0001-0.0261), average STDEV of 0.0049 (0.0001-0.0184).

Instrument	Sample_ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	190504	13	7.8649			
HP Agilent 8453	190504	14	7.8683	7.8666	0.0024	0.0035
HP Agilent 8453	200601	16	7.7285			
HP Agilent 8453	200601	17	7.7198	7.7241	0.0062	0.0088
HP Agilent 8453	200611	19	8.0615			
HP Agilent 8453	200611	20	8.0554	8.0584	0.0043	0.0061
HP Agilent 8453	391004	30	7.6345			
HP Agilent 8453	391004	31	7.6084	7.6215	0.0184	0.0261
HP Agilent 8453	591211	38	8.0640			
HP Agilent 8453	591211	39	8.0639	8.0639	0.0001	0.0001
HP Agilent 8453	631411	45	8.0900			
HP Agilent 8453	631411	46	8.0886	8.0893	0.0010	0.0014
HP Agilent 8453	1081902	59	7.7307			
HP Agilent 8453	1081902	60	7.7294	7.7300	0.0009	0.0013
HP Agilent 8453	1081906	61	7.7801			
HP Agilent 8453	1081906	62	7.7787	7.7794	0.0009	0.0013

HP Agilent 8453	1081910	63	7.9444			
HP Agilent 8453	1081910	64	7.9588	7.9516	0.0102	0.0144

Average				0.0049	0.0070
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Temperature measurements made during pH analysis

Sample ID	Sample BTL #	BTL Temp (°C)	Start Cell (°C)	End Cell (°C)	Differ Start to End Cell (°C)
30101	1	19.865	20.845	21.871	1.026
30104	2	19.96	21.127	21.928	0.801
30107	3	19.929	20.904	21.818	0.914
40201	4	19.888	20.635	21.419	0.784
40207	5	19.981	20.849	21.550	0.701
40208	6	19.857	20.777	21.643	0.866
50301	7	19.742	19.972	20.053	0.081
50304	8	19.658	19.920	20.017	0.097
50309	9	19.637	19.984	20.214	0.230
60401	10	19.755	20.095	20.502	0.407
60411	11	19.774	20.376	20.651	0.275
190501	12	19.83	20.359	20.702	0.343
190504	13	19.714	20.042	20.387	0.345
190504	14	19.725	19.991	20.207	0.216
190511	15	19.798	20.320	20.588	0.268
200601	16	19.834	20.300	20.642	0.342
200601	17	19.725	20.085	20.215	0.130
200605	18	19.724	19.918	20.239	0.321
200611	19	19.737	19.912	20.341	0.429
200611	20	19.79	20.044	20.410	0.366
210701	21	19.83	20.756	21.806	1.050
210703	22	19.964	20.924	21.918	0.994
210711	23	19.989	20.918	21.672	0.754
320801	24	19.944	20.659	21.317	0.658
320802	25	20.05	20.692	21.482	0.790
320811	26	19.599	19.835	20.144	0.309
330903	27	19.683	19.867	20.162	0.295
330911	28	19.667	19.926	20.187	0.261
391001	29	19.862	20.277	20.543	0.266
391004	30	19.911	20.381	20.659	0.278
391004	31	19.979	20.695	20.859	0.164
391011	32	19.636	19.987	20.410	0.423
431101	33	19.875	20.170	20.538	0.368

431109	34	19.853	20.294	20.551	0.257
431111	35	19.713	20.048	20.326	0.278
591201	36	19.718	20.138	20.368	0.230
591204	37	19.757	19.897	20.204	0.307
591211	38	19.85	19.980	20.370	0.390
591211	39	19.985	20.208	20.614	0.406
621302	40	19.896	20.154	20.422	0.268
621304	41	19.807	20.815	21.822	1.007
621311	42	19.924	20.914	21.763	0.849
631402	43	20.153	20.894	21.610	0.716
631403	44	20.108	20.803	21.532	0.729
631411	45	19.993	20.759	21.351	0.592
631411	46	19.812	20.628	21.018	0.390
691501	47	19.692	20.202	20.743	0.541
691504	48	19.873	20.418	20.777	0.359
691511	49	19.882	20.438	20.897	0.459
841602	50	19.942	20.679	21.206	0.527
841603	51	19.915	20.490	20.941	0.451
841611	52	19.728	20.209	20.658	0.449
931701	53	19.866	20.812	21.611	0.799
931705	54	19.917	20.835	21.558	0.723
931711	55	20.111	20.723	21.249	0.526
1071801	56	20.182	20.718	21.349	0.631
1071806	57	20.055	20.714	21.186	0.472
1071811	58	19.888	20.647	21.296	0.649
1081902	59	19.587	20.195	20.656	0.461
1081902	60	19.878	20.785	21.174	0.389
1081906	61	19.88	20.635	21.025	0.390
1081906	62	20.204	21.287	21.840	0.553
1081910	63	19.705	20.368	20.727	0.359
1081910	64	19.913	20.354	20.872	0.518
Average		19.855	20.431	20.919	0.488

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 20⁰C 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 date: 9/27/2016, 9/28/2016, 8/12/2016 and 9/29/2016

Titration system used: Open cell

CRM Batch 123, Salinity = 33.384, cert. TA = 2225.21 $\mu\text{mol/kg}$.

On 9/27, 9/28 and 9/29/2016 one CRM was analyzed before the samples and another 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\text{CRM}
1	09/27/2016	09:56:05	624	2214.29	2.97
1	09/27/2016	15:54:42	452	2217.26	
1	09/28/2016	08:51:57	66	2213.95	1.11
1	09/28/2016	16:05:56	120	2215.06	
1	09/29/2016	09:22:15	1000	2213.73	1.68
1	09/29/2016	12:59:33	508	2215.41	
2	09/27/2016	11:07:35	670	2224.65	20.73
2	09/27/2016	15:36:30	731	2245.38	
2	09/28/2016	09:03:29	945	2224.98	0.79
2	09/28/2016	16:01:04	397	2224.19	
2	09/29/2016	09:56:08	784	2223.62	0.41
2	09/29/2016	13:20:48	11	2224.03	

Reproducibility: (# samples and average difference): 9 sets of duplicate samples, average difference 2.03 (0.23-3.92), average STDEV of 1.43 (0.18-2.77).

System	Bottle #	Sample ID	Talk	Average	Difference	STDEV
System 2	13	190504	2180.11	2179.74	0.73	0.52
System 2	14	190504	2179.37			
System 1	16	200601	2210.20	2210.43	0.47	0.31
System 1	17	200601	2210.64			

System 1	19	200611	2149.18	2150.62	2.88	2.00
System 1	20	200611	2152.00			
System 1	30	391004	2194.72	2194.85	0.23	0.18
System 1	31	391004	2194.98			
System 2	38	591211	2184.76	2186.60	3.68	2.60
System 2	39	591211	2188.43			
System 1	45	631411	2281.24	2281.04	0.37	0.30
System 1	46	631411	2280.82			
System 1	59	1081902	2206.70	2207.74	2.10	1.46
System 1	60	1081902	2208.76			
System 2	61	1081906	2194.74	2192.75	3.92	2.77
System 2	62	1081906	2190.81			
System 1	63	1081910	2138.87	2140.82	3.86	2.74
System 1	64	1081910	2142.74			
Overall Average					2.03	1.43

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 Niskin bottles are approximately one half meter above the CTD sensors on the rosette. Therefore, Temp and Sal are bin-averaged CTD values representing the next shallower depth from that recorded by the CTD (CTD Depth) at the time the Niskin bottles were fired with the exception of the surface values, which are the same as the CTD Depth values (as per the log sheet).

The Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

This carbon dataset has been merged with nutrient data from the same cruise, provided by Dr. Chris Melrose's group. Where samples for carbon parameters and nutrients were drawn from different Niskin bottles, merging has been done based on sample depth, assuming all Niskin bottles tripped at the same depth would have the same nutrient values.

The following columns have been imported from the nutrients file:

Date.UTC, Depth_station, Depth_sampling, CTDPRS, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT

An additional column named Niskin_nuts has been added to reflect the niskin that nutrient samples were drawn from (which sometimes is different from the niskin used for carbon samples).

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.