Cruise: HB1301 Legs 1 and 2
Ship: R/V Henry B. Bigelow
Dates: 03/04/2013-04/05/2013
Expocode: 33HH20130314
Chief Scientist: John Galbraith – Leg1 and Pete Chase – Leg 2
Equipment: Ships Flow-thru system
Total number of stations: 16

Sample Collection

The discrete samples were collected from the ships flow-thru system by Amanda Andrews survey tech on board R/V H. Bigelow. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
16 locations, 16 samples each 500-ml, No duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:
16 locations, 16 samples each 500-ml, No duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

TAlk:
16 locations, 16 samples each 500-ml, No duplicate samples.
Sample_ID#:
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero

Sample Analysis

DIC:
Analysis date: April 30th, 2013
Coulometer used: AOML 3
Blanks: 32.1 and 25 counts/min
CRM # 0061 was used and with an assigned value of (includes both DIC and salinity):
Batch 112, c: 2011.09 µmol/kg, S: 33.305
CRM value measured: AOML 3: offset 0.20 µmol/kg (2011.29 µmol/kg).
Average run time, minimum run time, maximum run time: 17, 11 and 20 min.

Analysis date: April 30th, 2013
Coulometer used: AOML 4

Blanks: 24 counts/min
CRM # 0013 was used and with an assigned value of (includes both DIC and salinity):
Batch 112, c: 2011.09 µmol/kg, S: 33.305
CRM values measured: AOML 4: offset 1.3 µmol/kg (2009.79 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 9 and 12 min.

Reproducibility: (# samples and average difference): No duplicates were collected.

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.

pH:
Analysis date: April 30th, 2013
Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): No duplicates were collected

Sample ID	Sample BTL #	Temp. Sample Bottle (0^C)	Temp. pH Cell Start (0^C)	Temp. pH Cell End (0^C)	Differ of Sample Btl to Start of Cell	Diff Start to End of Cell
230000	551	19.829	19.992	20.332	0.163	0.340
320000	552	20.190	20.402	21.225	0.212	0.823
410000	553	20.114	20.366	21.182	0.252	0.816
510000	554	19.993	20.317	20.957	0.324	0.640
620000	555	19.942	20.396	21.544	0.454	1.148
730000	560	19.887	20.206	21.046	0.319	0.840
820000	556	19.924	20.193	21.077	0.269	0.884
940000	557	19.913	20.090	20.576	0.177	0.486
1090000	558	19.874	19.877	20.084	0.003	0.207
1170000	559	20.280	20.503	21.216	0.223	0.713
1260000	561	20.156	20.388	21.145	0.232	0.757
1370000	562	20.029	20.416	21.222	0.387	0.806
1510000	563	20.059	20.411	21.078	0.352	0.667
1710000	564	19.970	20.432	21.129	0.462	0.697
1820000	565	19.981	20.386	21.032	0.405	0.646
1900000	566	19.840	20.379	20.883	0.539	0.504
STDEV		0.131	0.177	0.366	0.135	0.225
Average		19.999	20.297	20.983	0.298	0.686

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 the temperature listed in the Temp. pH Cell Start column of the table above at Full Scale.

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

TAlk:
The results posted are duplicate analyses from the same sample bottles used for DIC.
Analysis date: 10/21/2013 and 10/28/2013
Titration system used: Open cell
CRM Batch 112, Salinity = 33.305, cert. TA = 2223.26 µmol/kg.

On 10/21 one CRM was analyzed before the samples. On 10/28, a CRM was analyzed before (CRM-1) and after (CRM-2) the samples.
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	10/21/2013	17:02:00	653	2221.85	
1	10/28/2013	13:20:46	923	2219.44	
1	10/28/2013	21:12:12	881	2218.35	1.09
2	10/21/2013	15:32:37	653	2221.01	
2	10/28/2013	14:45:08	923	2220.15	
2	10/28/2013	21:29:03	881	2218.77	1.38

Reproducibility: No duplicates were collected.

Remarks-

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

Nutrients:

Nutrient samples were collected from the flow-thru system on the R/V H. Bigelow immediately after the collection of the DIC/pH/Talk sample by survey tech. Amanda Andrews. Samples were collected in labeled 50 mL polypropylene acid washed tubes. Samples were preserved by adding 1 to 2 drops of chloroform and freezing.

Sample analysis was conducted at the NOAA-Atlantic Oceanographic & Meteorological Lab (AOML) by Dr. Jia-Zhong Zhang and Charles Fischer using a Seal Analytical Auto Analyzer 3. The methods used for the nutrient analyses are listed below;

Zhang, J-.Z. and Berberian, G.A. (1997). Determination of dissolved silicate in estuarine and coastal waters by gas segmented flow colorimetric analysis, U.S. Environmental Protection Agency, (EPA Method 366.0), EPA-600-R-97-072.

Zhang, J-.Z., Fischer, C.J. and Ortner, P.B. (2001). Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant. Intern. J. Environ. Anal. Chem. 80(1): 61-73.

Zhang, J.-Z., Ortner, P.B. and Fischer, C.J. (1997b). Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. U.S. Environmental Protection Agency (EPA Method 353.4), EPA-600-R-97-072.

Zhang, J.-Z., Ortner, P.B., Fischer, C.J and Moore, L.D. (1997a). Determination of ammonia in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. U.S. Environmental Protection Agency (EPA Method 349.0), EPA-600-R-97-072.

Zimmermann, C.F., and C.W. Keefe (1997). Determination of orthophosphate in estuarine and coastal waters by automated colorimetric analysis. U.S. Environmental Protection Agency (EPA method 365.5), EPA-600-R-97-072.

Station ID	Date	Time	Si (μM)	NO_2 (μM)	NO_3+NO_2 (μM)	NO_3 (μM)	NH_4 (μM)	PO_4 (μM)
230000	3/17/2013	2053	1.9	0.21	6.58	6.37	0.27	0.52
320000	3/18/2013	1730	2.1	0.20	1.52	1.32	1.01	0.24
410000	3/19/2013	1751	1.0	0.02	0.12	0.10	0.00	0.03
510000	3/20/2013	1700	0.5	0.04	0.13	0.10	0.15	0.24
620000	3/21/2013	1612	0.4	0.06	0.06	0.00	0.13	0.29
820000	3/23/2013	1620	0.5	0.09	5.03	4.94	0.08	0.49
940000	3/24/2013	1840	2.4	0.19	7.95	7.76	0.14	0.57
1090000	3/27/2013	135	0.1	0.02	2.43	2.41	0.18	0.27
1170000	3/27/2013	1759	0.6	0.08	4.44	4.36	0.10	0.49
730000	3/22/2013	1712	0.1	0.06	0.08	0.02	1.24	0.18

1260000	3/28/2013	1606	0.9	0.12	8.91	8.80	0.08	0.66
1370000	3/29/2013	1626	1.0	0.03	3.64	3.61	0.32	0.28
1510000	3/30/2013	1635	1.0	0.08	4.34	4.25	0.91	0.53
1710000	4/1/2013	1745	0.0	0.04	1.30	1.26	0.34	0.37
1820000	4/2/2013	1640	4.2	0.21	6.97	6.76	1.59	0.69
1900000	4/3/2013	1740	7.3	0.21	11.38	11.17	0.24	0.80

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. Salinity and temperature values were taken from the ships TSG 15 second bin-averaged data. The salinity value used in the DIC data reduction was the average of the four salinity values recorded by the ships TSG at the time the flow-thru sample was collected. This was done to achieve a salinity value with four decimal places.

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

The DIC instruments were stable: the gas loop and CRM values did not change significantly through out the life span of each cell. AOML 3 had a high blank (63.1 counts/min) at the end of sample analysis on 04/30/2013. The last four samples had 20 minute titrations with jumpy counts indicating a possible leak. A leak was detected from valve 8 at the end of sample analysis. This is the pump that controls the release of the acid into the stripper, it is possible the final sample bottle #566 did not acquire enough acid during analysis.

The blank (AOML 3) on 04-30-2013 was lowered from 32.1 to 25.0 before the analysis of sample bottle #553.

The blank (AOML 4) on 04-30-2013 was raised from 14.2.0 to 24.0 before the analysis of CRM #0013.

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

Nutrient samples are being collected on the R/V H. Bigelow to compare and correct the nitrate values being collected by the Satlantic Ultraviolet Nitrate Analyzer (SUNA), which has been mounted and attached to the ships flow-thru system to monitor real-time nitrate levels.

The samples were run as part of our coastal ocean acidification monitoring project.

Cruise: HB1301 Legs 3 and 4
Ship: R/V Henry B. Bigelow
Dates: 04/11/2013 – 05/09/2011
Expocode: 33HH20130314
Chief Scientist: Jakub Kircun – Leg 3 and Heath Cook – Leg 4
Equipment: Ships Flow-thru system
Total number of stations: 19

Sample Collection

The discrete samples were collected from the ships flow-thru system by Amanda Andrews survey tech onboard the R/V H. Bigelow. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
19 locations, 19 samples each 500-ml, No duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:
19 locations, 19 samples each 500-ml, No duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

TAlk:
No alkalinity samples were run on these legs

Sample Analysis

DIC:
Analysis date: May 22nd, 2013
Coulometer used: AOML 3
Blanks: 18.5 and 30 counts/min
CRM # 0446 was used and with an assigned value of (includes both DIC and salinity):
Batch 112, c: 2011.09 µmol/kg, S: 33.305
CRM value measured: AOML 3: offset 3.27 µmol/kg (2007.82 µmol/kg).
Average run time, minimum run time, maximum run time: 17, 14 and 20 min.

Analysis date: May 22nd, 2013
Coulometer used: AOML 4
Blanks: 14.2 and 25 counts/min
CRM # 0713 was used and with an assigned value of (includes both DIC and salinity):
Batch 112, c: 2011.09 µmol/kg, S: 33.305

CRM values measured: AOML 4: offset 1.87 µmol/kg (2012.96 µmol/kg).

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

Reproducibility: (# samples and average difference): No duplicates were collected.

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.

pH:
Analysis date: May 22nd, 2013
Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): No duplicates were collected

Sample ID	Sample BTL #	Temp. Sample Bottle (0^C)	Temp. pH Cell Start (0^C)	Temp. pH Cell End (0^C)	Differ of Sample Btl to Start of Cell	Diff Start to End of Cell
5310100	531	20.173	20.620	21.920	0.447	1.300
5320100	532	20.408	21.080	22.160	0.672	1.080
5330100	533	19.919	20.820	22.085	0.901	1.265
5340100	534	19.967	20.621	21.685	0.654	1.064
5350100	535	19.886	20.610	22.240	0.724	1.630
5360100	536	19.951	20.947	22.515	0.996	1.568
5370100	537	19.987	20.898	22.483	0.911	1.585
5380100	538	19.948	20.718	22.346	0.770	1.628
5390100	539	19.882	20.920	22.645	1.038	1.725
5400100	540	20.242	20.930	22.584	0.688	1.654
5410100	541	20.066	20.825	21.909	0.759	1.084
5420100	542	19.915	20.465	21.855	0.550	1.390
5430100	543	19.924	20.756	22.121	0.832	1.365
5440100	544	19.862	20.699	22.235	0.837	1.536
5450100	545	19.886	20.639	22.364	0.753	1.725
5460100	546	20.024	20.714	22.467	0.690	1.753
5470100	547	19.996	20.859	22.356	0.863	1.497
5480100	548	19.898	20.740	22.379	0.842	1.639
5500100	550	19.866	20.545	21.995	0.679	1.450
STDEV		0.144	0.157	0.269	0.146	0.224
Average		19.989	20.758	22.229	0.769	1.470

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 the temperature listed in the Temp. pH Cell Start column of the table above at Full Scale.

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

Nutrients:

Nutrient samples were collected from the flow-thru system on the R/V H. Bigelow immediately after the collection of the DIC/pH/Talk sample by survey tech. Amanda Andrews. Samples were collected in labeled 50 mL polypropylene acid washed tubes. Samples were preserved by adding 1 to 2 drops of chloroform and freezing.

Sample analysis was conducted at the NOAA-Atlantic Oceanographic & Meteorological Lab (AOML) by Dr. Jia-Zhong Zhang and Charles Fischer using a Seal Analytical Auto Analyzer 3. The methods used for the nutrient analyses are listed below;

Zhang, J-.Z. and Berberian, G.A. (1997). Determination of dissolved silicate in estuarine and coastal waters by gas segmented flow colorimetric analysis, U.S. Environmental Protection Agency, (EPA Method 366.0), EPA-600-R-97-072.

Zhang, J-.Z., Fischer, C.J. and Ortner, P.B. (2001). Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant. Intern. J. Environ. Anal. Chem. 80(1): 61-73.

Zhang, J.-Z., Ortner, P.B. and Fischer, C.J. (1997b). Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. U.S. Environmental Protection Agency (EPA Method 353.4), EPA-600-R-97-072.

Zhang, J.-Z., Ortner, P.B., Fischer, C.J and Moore, L.D. (1997a). Determination of ammonia in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. U.S. Environmental Protection Agency (EPA Method 349.0), EPA-600-R-97-072.

Zimmermann, C.F., and C.W. Keefe (1997). Determination of orthophosphate in estuarine and coastal waters by automated colorimetric analysis. U.S. Environmental Protection Agency (EPA method 365.5), EPA-600-R-97-072.

Station ID	Date	Time	Si (µM)	NO$_2$ (µM)	NO$_3$+NO$_2$ (µM)	NO$_3$ (µM)	NH$_4$ (µM)	PO$_4$ (µM)
5310100	4/11/2013	0:30	2.7	0.15	5.82	5.66	0.48	0.75
5320100	4/11/2013	18:14	0.9	0.13	2.15	2.01	0.29	0.48
5330100	4/12/2013	18:44	0.9	0.09	4.93	4.85	0.84	0.60
5340100	4/13/2013	0:31	6.0	0.18	5.70	5.52	0.07	0.69
5350100	4/15/2013	19:07	4.7	0.22	3.38	3.16	4.74	0.56

5360100	4/14/2013	17:25	6.0	0.15	5.41	5.25	0.37	0.66
5370100	4/16/2013	19:30	6.3	0.10	4.09	3.99	0.43	0.64
5380100	4/20/2013	1:36	1.4	0.11	5.06	4.95	0.49	0.68
5390100	4/21/2013	15:46	1.3	0.12	4.54	4.43	0.48	0.58
5400100	4/22/2013	17:46	4.6	0.14	3.22	3.09	0.33	0.61
5410100	4/23/2013	19:15	5.7	0.14	4.81	4.67	0.30	0.71
5420100	5/1/2013	18:20	3.6	0.05	0.05	0.00	0.32	0.27
5430100	5/2/2013	17:18	0.3	0.01	0.01	0.00	0.19	0.20
5440100	5/3/2013	16:17	0.4	0.04	0.10	0.06	0.17	0.24
5450100	5/4/2013	20:10	0.4	0.02	0.02	0.00	0.23	0.17
5460100	5/6/2013	16:47	5.2	0.01	0.01	0.00	0.31	0.33
5470100	5/7/2013	18:00	3.4	0.01	0.01	0.00	0.30	0.22
5480100	5/9/2013	0:29	2.4	0.01	0.01	0.00	0.42	0.12
5500100	5/5/2013	16:25	0.8	0.04	0.31	0.27	0.69	0.29

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. Salinity and temperature values were taken from the ships TSG 15 second bin-averaged data. The salinity value used in the DIC data reduction was the average of the four salinity values recorded by the ships TSG at the time the flow-thru sample was collected. This was done to achieve a salinity value with four decimal places.

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

The DIC instruments were stable: the gas loop and CRM values did not change significantly through out the life span of each cell. AOML 3 had a high blank (53.1 counts/min) at the end of sample analysis on 05/22/2013.

The blank (AOML 3) on 05-22-2013 was raised from 18.5 to 30.0 before the analysis of CRM #0446.

The blank (AOML 4) on 05-22-2013 was raised from 14.2 to 25.0 before the analysis of CRM #0713.

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

Nutrient samples are being collected on the R/V H. Bigelow to compare and correct the nitrate values being collected by the Satlantic Ultraviolet Nitrate Analyzer (SUNA), which has been mounted and attached to the ships flow-thru system to monitor real-time nitrate levels.

The samples were run as part of our coastal ocean acidification monitoring project.

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.