Cruise: WS24139
Ship: R/V Walton Smith
Expo Code: 33WA20240518
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: 05/18/2024 to 05/24/2024
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations:
Location: Southwest Florida Gulf of Mexico coastal region

Samples were collected for Dr. Leticia Barbero for the Ocean Acidification Program during the South Florida Project (SFP) water quality cruises in the SW Gulf of Mexico.

Sample Collection

The discrete samples were collected from the CTD-Niskin/rosette and Flow-Through system onboard the R/V Walton Smith by Rachel Cohn and Ian Smith. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
55 locations, 81 samples each 500-ml, 7 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone, Patrick Mears, Alison MacLeod

pH:
55 locations, 81 samples each 500-ml, 7 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone, Patrick Mears, Alison MacLeod

TAlk:
55 locations,81 samples each 500-ml, 7 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears, Alison MacLeod

Sample Analysis
DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	6/26/2024	2099.260	2099.17	0.09	12	9
AOML 5	7/1/2024	2099.260	2101.55	2.29	12	8
AOML 5	7/10/2024	2099.260	2099.18	0.08	15	9
AOML 6	6/26/2024	2099.260	2102.46	3.2	13	10
AOML 6	7/1/2024	2099.260	2102.26	3	17	10
AOML 6	7/10/2024	2099.260	2102.58	3.32	17	9

Analysis date: 6/26/2024
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 572 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 5: offset 0.09 µmol/kg (2099.17 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 15 min.

Analysis date: 7/1/2024
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 695 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 5: offset 2.29 µmol/kg (2101.55 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 7/10/2024
Coulometer used: DICE–CM5017O-AOML5
Blanks: 14.6 counts/min
CRM # 1068 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 5: offset 0.08 µmol/kg (2099.18 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 10 min.

Analysis date: 6/26/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.9 counts/min

CRM # 635 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 6: offset 3.2 µmol/kg (2102.46 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 7 and 13 min.

Analysis date: 7/1/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 16.4 counts/min
CRM # 1006 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 6: offset 3.0 µmol/kg (2102.26 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 8 and 13 min.

Analysis date: 7/10/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 16.4 counts/min
CRM # 1136 was used and with an assigned value of (includes both DIC and salinity):
Batch 188, c: 2099.26 µmol/kg, S: 33.595
CRM values measured: AOML 6: offset 3.32 µmol/kg (2102.58 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.99 (0.02-3.82) and average STDEV of 1.41 (0.02-2.70).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
160112	1768.83	1769.10	0.37	0.53
160112	1769.36			
310112	2089.48	2089.47	0.02	0.02
310112	2089.46			
550112	2306.74	2307.89	1.62	2.30
550112	2309.03			
560112	2200.18	2198.43	2.48	3.50
560112	2196.67			
CAL20112	2184.30	2182.39	2.70	3.82
CAL20112	2180.48			
TB10112	2146.9	2146.56	0.42	0.59

TB10112	2146.3			
V10112	2133.3	2132.46	1.22	1.72
V10112	2131.6			
Average			1.41	1.99

CRM, salinity and $HgCl_2$ 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.

DIC samples were analyzed on new coulometers 5017O from UIC. Inc.

pH:

Analysis date: 6/26/2024, 7/1/2024, and 7/10/2024
No CRMs were analyzed before sample analysis.

Three "Junk" samples were run from the same bottle prior to analysis to ensure the precision of the measurements are equal to or less than 0.003 TOTAL pH.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^0C)
700000	149	36.905	19.934
650112	639	37.037	19.934
300101	640	36.596	19.934
CAL20112	643	35.315	19.935
CAL10112	644	35.319	19.935
310112	649	36.433	19.935
330112	650	34.866	19.940

RP40101	663	36.535	19.929
MR0101	673	36.513	19.910
21/LK0101	677	36.515	19.913
UK IN0000	678	37.122	19.917
70112	679	37.371	19.920
UK MID0000	682	36.629	19.929
GP50101	1009	36.532	19.942
V50101	1010	36.494	19.930
AMI10112	1022	35.894	19.935
TB100101	1024	36.514	19.927
RP40112	1170	36.546	19.936
GP50112	1179	36.572	19.934
V50112	1181	36.416	19.933
TB40101	1184	36.466	19.934
100112	1226	37.514	19.922
UK OFF0000	1231	36.490	19.926
MR0112	1232	36.514	19.917
TB10112	1490	35.978	19.930
BG40101	2047	36.498	19.930
20112	2065	36.480	19.915
21/LK0112	2069	36.570	19.919
160112	2074	37.684	19.926
160112	2075	37.684	19.932
57.10112	2638	35.898	19.925
570112	2639	36.063	19.922
560112	2640	36.249	19.918
550112	2646	36.001	19.922
490112	2649	33.076	19.943
550112	2650	36.001	19.927
450112	2651	35.869	19.927
KW20112	2976	37.027	19.918
KW10112	2977	37.183	19.930
WS0101	2978	36.544	19.922
KW40101	2982	36.667	19.929
KW20101	2983	37.029	19.920
WS0112	2984	36.551	19.924
KW40112	2988	36.726	19.926
300112	2989	36.671	19.939
V90101	3311	36.468	19.937
V10112	3321	35.546	19.930
TB40112	3322	36.219	19.931

Sample ID	Bottle #	pH @20deg C	Average
TB100112	3323	36.547	19.931
TB10112	3324	35.978	19.933
BG40112	3326	36.523	19.920
510112	3655	34.376	19.918
540112	3658	35.347	19.933
560112	3661	36.249	19.933
57.20112	4565	35.865	19.926
57.30112	4567	36.694	19.928
CAL30112	4568	35.448	19.930
RP30112	4569	36.192	19.942
RP20112	4570	36.011	19.936
CAL30101	4571	35.448	19.930
CAL20112	4572	35.315	19.944
CAL40101	4573	35.932	19.933
BG30101	4709	36.410	19.936
BG10112	4710	35.200	19.939
BG30112	4712	36.408	19.941
CAL40112	4713	35.674	19.933
AMI90101	4714	35.876	19.930
AMI50112	4715	36.479	19.935
CAL50112	4716	36.495	19.927
AMI90112	4717	36.553	19.922
RP10112	4869	36.017	19.939
BG20112	4871	36.077	19.933
AMI50101	4876	36.381	19.917
410112	4877	34.800	19.925
CAL50101	5013	36.465	19.934
V90112	5017	36.558	19.931
V10112	5019	35.546	19.932
310112	6726	36.433	19.938
580112	6727	37.074	19.929
680112	6729	36.893	19.936
600112	6731	37.679	19.937

Reproducibility: pH @ 20^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0027 (0.0011– 0.0052) and an average STDEV of 0.0019 (0.0008– 0.0036).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	160112	2074	8.184	8.186	0.0018	0.0025

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	160112	2075	8.187			
HP Agilent 8453	310112	649	8.107	8.105	0.0022	0.0031
HP Agilent 8453	310112	6726	8.104			
HP Agilent 8453	550112	2646	7.981	7.980	0.0013	0.0019
HP Agilent 8453	550112	2650	7.979			
HP Agilent 8453	560112	2640	8.101	8.100	0.0023	0.0032
HP Agilent 8453	560112	3661	8.098			
HP Agilent 8453	CAL20112	643	8.026	8.029	0.0036	0.0052
HP Agilent 8453	CAL20112	4572	8.031			
HP Agilent 8453	TB10112	1490	8.065	8.065	0.0008	0.0011
HP Agilent 8453	TB10112	3324	8.066			
HP Agilent 8453	V10112	3321	8.091	8.092	0.0012	0.0017
HP Agilent 8453	V10112	5019	8.092			
Average					0.0019	0.0027

Reproducibility: pH @ 25^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0026 (0.0011– 0.0051) and an average STDEV of 0.0019 (0.0008 – 0.0036).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	160112	2074	8.108	8.110	0.0018	0.0025
HP Agilent 8453	160112	2075	8.111			
HP Agilent 8453	310112	649	8.031	8.029	0.0022	0.0031
HP Agilent 8453	310112	6726	8.028			
HP Agilent 8453	550112	2646	7.907	7.906	0.0013	0.0018
HP Agilent 8453	550112	2650	7.905			
HP Agilent 8453	560112	2640	8.026	8.024	0.0023	0.0032
HP Agilent 8453	560112	3661	8.023			
HP Agilent 8453	CAL20112	643	7.951	7.954	0.0036	0.0051

HP Agilent 8453	CAL20112	4572	7.956			
HP Agilent 8453	TB10112	1490	7.989	7.990	0.0008	0.0011
HP Agilent 8453	TB10112	3324	7.991			
HP Agilent 8453	V10112	3321	8.015	8.016	0.0012	0.0016
HP Agilent 8453	V10112	5019	8.017			
Average					0.0019	0.0026

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). The pH was reported at 20^0C and 25^0C.

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 automatic syringe before DIC analysis to determine the pH.

TAlk:
Analysis date: 6/27/2024, 6/28/2024, 7/2/2024, 7/11/2024
Titration system used: Open cell
Batch 188, CRM #572 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #821 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #855 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #1006 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #1068 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #1192 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 201, CRM #335 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 188, CRM #1136 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.
Batch 188, CRM #695 Salinity = 33.595, cert. TA = 2264.96 µmol/kg.

On 6/27/2024 CRM #572 was analyzed before and after sample analysis on System 1.
On 6/28/2024 CRM #821 was analyzed before sample analysis on System 1.
On 6/28/2024 CRM #885 was analyzed after sample analysis on System 1.
On 7/2/2024 CRM #1006 was analyzed before and after sample analysis on System 1.
On 7/11/2024 CRM #1068 was analyzed before and after sample analysis on System 1.
On 7/12/2024CRM #1192 was analyzed before sample analysis on System 1.

On 7/12/2024 CRM #335 was analyzed after sample analysis on System 1.
On 6/28/2024 CRM #821 was analyzed before sample analysis on System 2.
On 6/28/2024 CRM #885 was analyzed after sample analysis on System 2.
On 7/2/2024 CRM #695 was analyzed before and after sample analysis on System 2.
On 7/11/2024 CRM #1136 was analyzed before and after sample analysis on System 2.

The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on system 1 and 2 cells.

On 7/11/2024 on System 1 the CRM ran before the samples was used to adjust the TA values.

On 7/11/2024 on System 2 the CRM ran after the samples was used to adjust the TA values.

On 7/12/2024 on System 1 the CRM ran after the samples was used to adjust the TA values.

The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	|ΔCRM|
1	6/27/2024	09:00:45	572	2271.95	6.99
1	6/27/2024	17:18:37	572	2271.59	6.63
1	6/28/2024	09:20:35	821	2268.19	3.23
1	6/28/2024	13:00:56	885	2272.04	7.08
1	7/2/2024	09:33:23	1006	2273.42	8.46
1	7/2/2024	15:53:10	1006	2273.26	8.3
1	7/11/2024	10:18:59	1068	2265.65	0.69
1	7/11/2024	16:41:34	1068	2270.43	5.47
1	7/12/2024	10:30:49	808	2278.47	13.51
1	7/12/2024	14:03:25	808	2206.61	-0.95
2	6/28/2024	09:24:11	821	2272.18	7.22
2	6/28/2024	12:52:30	885	2274.86	9.9
2	7/2/2024	09:34:58	695	2270.77	5.81
2	7/2/2024	15:36:07	695	2272.14	7.18
2	7/11/2024	14:42:43	1136	2273.85	8.89

2	7/11/2024	16:33:52	1136	2270.06	5.1

Reproducibility: (# samples and average difference): 5 duplicate samples were collected with an average difference of 1.10 (0.21 – 1.55) and an average STDEV of 0.078 (0.15 – 1.10).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
16	160112	2110.48			
16	160112	2110.27	2110.37	0.15	0.21
31	310112	2392.27			
31	310112	2390.72	2391.50	1.10	1.55
56	560112	2507.39			
56	560112	2508.88	2508.14	1.06	1.50
TB1	TB10112	2437.21			
TB1	TB10112	2436.05	2436.63	0.82	1.16
V1	V10112	2435.23			
V1	V10112	2434.16	2434.70	0.76	1.07
Average				0.78	1.10

Remarks

The average of the CRMs were used to adjust the values of the samples for each day unless otherwise noted in the CRM information section..

It was determined using calculated TA values from DIC and pH that one of the duplicate samples associated with Sample ID 550112 and CAL20112 was bad and was not included in the statistics.

Stations 54, 55, 56, and 57 are known to have historically high TA values and should be considered normal.

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 station number, cast number and niskin number.

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

Nutrients:
Analysis Date: Will be added at a later date

Nutrient samples were analyzed using a Seal Analytical high-resolution digital colorimeter auto-analyzer 3 (AA3). A series of standards for each method were run before sample analysis to obtain a calibration curve for data reduction.
Method 353.4 was used to determine the concentration of nitrate and nitrite for each station (Zhang et al., 1997b). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of nitrate and nitrite. Samples were first passed through a copper-coated cadmium reduction column. Nitrate was reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance measured at 550 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. Nitrate concentrations are obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.
Method 365.5 was used to determine the concentration of orthophosphate for each station (Zimmermann and Keefe, 1997; Zhang et al., 2001). This method used automated colorimetric and continuous flow analysis for the determination of low-level orthophosphate concentrations. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with orthophosphate to form an antimony-phospho-molybdate complex. This complex was reduced to a blue-colored complex by ascorbic acid. The absorbance measured at 880 nm is proportional to the phosphate concentration in the sample.
Method 366.0 was used to determine the concentration of soluble silica for each station (Zhang and Berberian, 1997). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of dissolved silicate concentration. In this method, β-molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The β-molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 550 nm, is linearly proportional to the concentration of silicate in the sample.

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.

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.

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.

Operation Manual (2008), AutoAnalyzer 3 high resolution, Seal Analytical. *Publication No. MB7-31EN-02*, (February 2008).

Remarks

No remarks.

Chlorophyll and Phaeophytin:
Analysis Date: <mark>Will be added at a later date</mark>

Chlorophyll-a concentrations are determined via a standardized filtration-extraction method using a 60:40 mixture of 90% acetone and dimethyl sulfoxide. The fluorescence of each sample is measured before and after acidification in order to correct for phaeophytin on a TD-700 fluorometer. Samples are stored in the dark at -80^0C until analysis. A sample duplicate is analyzed with each sample.

Shoaf, W.T. and Lium, B.W. (1976). Improved extraction of chlorophyll-a and b from algae using dimethyl sulfoxide. Limnology and Oceanography 21: 926-928.

EPA Method 445 (1997) In vitro determination of chlorophyll-a in marine and freshwater algae by fluorescence.