Cruise: H23314
Ship: R/V W.T. Hogarth
Expo Code:33SGDK20230909
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: September 9th - September 22nd, 2023
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 52
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 lead by Dr. Chris Kelble.

Sample Collection

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

DIC:

52 locations, 76 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 and Alison MacLeod

pH:

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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	12/6/2023	2043.33	2045.95	2.62	12	9
AOML 5	12/11/2023	2040.33	2042.93	2.6	30	8
AOML 6	12/6/2023	2043.33	2040.83	2.5	15	12
AOML 6	12/11/2023	2040.33	2039.35	0.98	12	10

Analysis date: 12/6/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 624 was used and with an assigned value of (includes both DIC and salinity):
Batch 202, c: 2040.33 µmol/kg, S: 33.237
CRM values measured: AOML 5: offset 2.62 µmol/kg (2045.95 µmol/kg).
Average run time, minimum run time, maximum run time: 8.5, 7 and 10 min.

Analysis date: 12/11/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 30.0 counts/min
CRM # 247 was used and with an assigned value of (includes both DIC and salinity):
Batch 207, c: 2043.33 µmol/kg, S: 33.356
CRM values measured: AOML 5: offset 2.6 µmol/kg (2042.93 µmol/kg).
Average run time, minimum run time, maximum run time: 7.5, 7 and 8 min.

Analysis date: 12/6/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 14.8 counts/min
CRM # 1217 was used and with an assigned value of (includes both DIC and salinity):
Batch 202, c: 2040.33 µmol/kg, S: 33.237
CRM values measured: AOML 5: offset 2.5 µmol/kg (2040.83 µmol/kg).
Average run time, minimum run time, maximum run time: 14.8, 9 and 18 min.

Analysis date: 12/11/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 545 was used and with an assigned value of (includes both DIC and salinity):
Batch 207, c: 2043.33 µmol/kg, S: 33.356
CRM values measured: AOML 6: offset 0.98 µmol/kg (2039.35 µmol/kg).
Average run time, minimum run time, maximum run time: 10.2, 9 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.57 (0.20-1.56) and average STDEV of 0.57 (0.14-1.11).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
AMI10112	2082.77	2083.17	0.56	0.80
AMI10112	2083.57			
BG10112	2080.44	2080.71	0.38	0.54
BG10112	2080.98			
RP10112	2083.55	2084.14	0.83	1.18
RP10112	2084.73			
CAL50112	2071.18	2071.38	0.30	0.42
CAL50112	2071.59			
680112	1864.07	1863.29	1.11	1.56
680112	1862.51			
160112	2112.01	2111.91	0.14	0.20
160112	2111.81			
KW10112	2008.75	2008.28	0.65	0.92
KW10112	2007.82			
Average			0.57	0.80

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: 12/6/2023 and 12/11/2023
No CRMs were analyzed before sample analysis.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^{0}C)
TB40101	401	36.789	8.094399
TB40112	402	36.654	8.084397
TB10112	403	34.868	8.066728
TB100101	404	36.536	8.12463
TB100112	405	36.321	8.130926
AMI90101	406	36.481	8.130578
AMI90112	407	35.930	8.146749
AMI50101	408	36.635	8.081902
AMI50112	409	36.431	8.084211
AMI10112	410	34.887	8.084038
AMI10112	411	34.887	8.083597
V10112	412	35.37	8.076381
V50101	413	37.259	8.112261
V50112	414	36.426	8.125368
V90101	415	36.598	8.120561
V90112	416	35.848	8.148202
GP50101	417	37.018	8.118232
GP50112	418	36.360	8.133453
BG40101	419	37.114	8.128831
BG40112	420	36.676	8.131182
RP40101	421	37.101	8.122012
RP40112	422	36.260	8.130359
BG30101	423	37.750	8.103967
BG30112	424	36.829	8.124098
BG20112	425	35.401	8.030971
BG10112	426	35.458	8.005222
BG10112	427	35.458	8.004388
RP30112	428	36.331	8.104995
RP20112	429	35.101	8.045866
RP10112	430	35.599	8.056678

RP10112	431	35.599	8.056028
CAL10112	432	34.000	7.999526
CAL20112	433	34.433	8.03279
CAL30101	434	36.740	8.051544
CAL30112	435	35.636	8.077919
CAL40101	436	37.643	8.09871
CAL40112	437	36.448	8.131267
CAL50101	438	37.446	8.110809
CAL50112	439	36.110	8.140415
CAL50112	440	36.110	8.138987
330112	441	35.956	8.033175
310112	442	36.444	8.095896
410112	443	36.098	7.990343
450112	444	35.927	8.006416
490112	445	34.907	7.977312
510112	446	36.473	7.994656
57.10112	447	36.692	8.018668
570112	448	36.183	7.977235
560112	449	35.512	7.94436
550112	450	34.503	7.916923
540112	451	32.508	7.802156
57.20112	452	36.876	8.030984
57.30112	453	36.667	8.115463
580112	454	36.982	8.078295
600112	455	35.302	7.971391
650112	456	38.495	8.153188
680112	457	39.631	8.131661
680112	458	39.631	8.132513
700000	459	38.814	7.986497
MR0101	460	36.107	8.14444
MR0112	461	36.110	8.143194
UK_IN0000	462	34.393	8.043155
UK_MID0000	463	36.275	8.130452
UK_OFF0000	464	36.120	8.147414
70112	465	36.142	8.076698
100112	466	36.621	7.996272
160112	467	35.967	8.02759
160112	468	35.967	8.026088
21/LK0101	469	36.171	8.142517
21/LK0112	470	36.179	8.145207
WS0101	471	36.174	8.139956

WS0112	472	36.174	8.139349
KW10112	473	36.330	8.038936
KW10112	474	36.330	8.037352
KW20101	475	36.810	8.10923
KW20112	476	37.275	8.116788

Reproducibility: pH @ 20^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0012 (0.000– 0.002) and an average STDEV of 0.0008 (0.000 – 0.001).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	AMI10112	410	8.084	8.084	0.000	0.000
HP Agilent 8453	AMI10112	411	8.084			
HP Agilent 8453	BG10112	426	8.006	8.005	0.001	0.001
HP Agilent 8453	BG10112	427	8.005			
HP Agilent 8453	RP10112	430	8.057	8.057	0.000	0.000
HP Agilent 8453	RP10112	431	8.057			
HP Agilent 8453	CAL50112	439	8.141	8.140	0.001	0.002
HP Agilent 8453	CAL50112	440	8.140			
HP Agilent 8453	680112	457	8.132	8.133	0.001	0.001
HP Agilent 8453	680112	458	8.133			
HP Agilent 8453	160112	467	8.028	8.028	0.001	0.002
HP Agilent 8453	160112	468	8.027			
HP Agilent 8453	KW10112	473	8.040	8.039	0.001	0.002
HP Agilent 8453	KW10112	474	8.038			
Average					0.0008	0.0012

Reproducibility: pH @ 25^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0011 (0.000-0.002) and an average STDEV of 0.0008 (0.000-0.001).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	AMI10112	410	8.009	8.009	0.000	0.000
HP Agilent 8453	AMI10112	411	8.009			
HP Agilent 8453	BG10112	426	7.931	7.931	0.001	0.001
HP Agilent 8453	BG10112	427	7.930			
HP Agilent 8453	RP10112	430	7.982	7.982	0.000	0.000
HP Agilent 8453	RP10112	431	7.982			
HP Agilent 8453	CAL50112	439	8.065	8.064	0.001	0.002
HP Agilent 8453	CAL50112	440	8.064			
HP Agilent 8453	680112	457	8.057	8.057	0.001	0.001
HP Agilent 8453	680112	458	8.057			
HP Agilent 8453	160112	467	7.953	7.953	0.001	0.002
HP Agilent 8453	160112	468	7.952			
HP Agilent 8453	KW10112	473	7.965	7.964	0.001	0.002
HP Agilent 8453	KW10112	474	7.963			
Average					0.0008	0.0011

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^{0}C at Full Scale (pH 0-14). The pH was reported at 20^{0}C and 25^{0}C.

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: 12/7/2023, 12/8/2023 and 12/12/2023

Titration system used: Open cell
Batch 202, CRM #1717 Salinity = 33.356, cert. TA = 2215.13 µmol/kg.
Batch 207, CRM #607 Salinity = 33.273, cert. TA = 2199.32 µmol/kg.
Batch 207, CRM #899 Salinity = 33.273, cert. TA = 2199.32 µmol/kg.
Batch 207, CRM #545 Salinity = 33.273, cert. TA = 2199.32 µmol/kg.
Batch 207, CRM #318 Salinity = 33.273, cert. TA = 2199.32 µmol/kg.
Batch 207, CRM #1204 Salinity = 33.273, cert. TA = 2199.32 µmol/kg.

On 12/8/2023 CRM #318 was analyzed before and after sample analysis on System 1.
On 12/12/2023 CRM #247 was analyzed before sample analysis on System 1.
On 12/12/2023 CRM #1204 was analyzed after sample analysis on System 1.
On 12/7/2023 CRM #1717 was analyzed before and after sample analysis on System 2.
On 12/8/2023 CRM #607 was analyzed before sample analysis on System 2.
On 12/8/2023 CRM #899 was analyzed after sample analysis on System 2.
On 12/8/2023 CRM #545 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 2 cells. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	|ΔCRM|
1	12/8/2023	11:06:40	318	2200.27	0.95
1	12/8/2023	17:19:13	318	2195.76	3.56
1	12/12/2023	09:47:58	247	2198.19	1.13
1	12/12/2023	16:43:09	1204	2202.4	3.08
2	12/7/2023	16:05:03	1717	2213.66	1.47
2	12/7/2023	18:27:03	1717	2215.78	0.65
2	12/8/2023	10:32:54	607	2194.00	5.32
2	12/8/2023	17:05:18	899	2199.48	0.16
2	12/12/2023	09:32:24	545	2196.2	3.12
2	12/12/2023	16:29:44	545	2196.4	2.92

Reproducibility: (# samples and average difference): 7 duplicate samples were collected, two duplicate pairs were discarded due to being significantly different from calculated TA values using the other carbonate parameters. The average difference of 7.72(3.19 – 15.07) and an average STDEV of 5.46 (2.26 – 10.65).

Sample ID	Bottle #	TA umol/kg	Average	STDEV	Difference
AMI10112	410	2378.80	2376.20	3.68	5.21
AMI10112	411	2373.59			
BG10112	426	2320.83	2318.72	2.99	4.22
BG10112	427	2316.61			
CAL50112	439	2395.21	2387.68	10.65	15.07
CAL50112	440	2380.15			
160112	467	2387.07	2381.61	7.72	10.92
160112	468	2376.15			
KW10112	473	2276.81	2275.22	2.26	3.19
KW10112	474	2273.63			
Average				5.46	7.72

Remarks

The average of the CRMs were used to adjust the values of the samples for each day.

Samples taken around Shark River, (Stations 54, 55, 56, 57) have high TA values that are a consistent feature present in past cruises and should be considered real features.

One sample from Station 680112 and one sample from Station RP10112 were determined to be bad based on carbon parameter comparisons and calculations. Those samples are not included in the final data and the statistics.

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: To 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: To be added at a later date

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^{0}C 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.