Cruise: WS23203
Ship: R/V Walton Smith
Expo Code: 33WA20230722
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: July 22nd – July 28th 2023
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 55
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:
55 locations, 80 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:
55 locations, 80 samples each 500-ml, 7 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
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TAlk:
55 locations, 80 samples each 500-ml, 7 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
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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	10/25/2023	2028.23	2029.47	1.24	16	11
AOML 5	10/30/2023	2028.23	2030.23	2.0	18	11
AOML 6	10/25/2023	2028.23	2026.94	1.29	12	10
AOML 6	10/30/2023	2028.23	2031.87	3.64	12	12

Analysis date: 10/25/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 15.8 counts/min
CRM # 093 was used and with an assigned value of (includes both DIC and salinity):
Batch 204, c: 2028.23µmol/kg, S: 33.494
CRM values measured: AOML 5: offset 1.24 µmol/kg (2029.47 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 8 and 14 min.

Analysis date: 10/30/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 17.8 counts/min
CRM # 1132 was used and with an assigned value of (includes both DIC and salinity):
Batch 204, c: 2028.23µmol/kg, S: 33.494
CRM values measured: AOML 5: offset 2.0 µmol/kg (2032.23 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 9 and 13 min.

Analysis date: 10/25/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 895 was used and with an assigned value of (includes both DIC and salinity):
Batch 204, c: 2028.23µmol/kg, S: 33.494
CRM values measured: AOML 6: offset 1.29 µmol/kg (2026.94 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 7 and 14 min.

Analysis date: 10/30/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 363 was used and with an assigned value of (includes both DIC and salinity):
Batch 204, c: 2028.23µmol/kg, S: 33.494
CRM values measured: AOML 6: offset 3.64 µmol/kg (2031.87µmol/kg).
Average run time, minimum run time, maximum run time: 12, 9 and 16 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.25 (0.18-3.73) and average STDEV of 0.88 (0.12-2.63).

Sample ID	DIC (μmol/kg)	Average	STDEV	Difference
160112	1894.45			
160112	1895.55	1895.00	0.78	1.10
CAL10112	2150.93			
CAL10112	2152.72	2151.82	1.27	1.79
V10101	2061.82			
V10101	2062.00	2061.91	0.12	0.18
AMI10112	2086.35			
AMI10112	2087.10	2086.73	0.53	0.76
TB10112	2082.25			
TB10112	2081.90	2082.08	0.24	0.34
410112	2108.40			
410112	2104.68	2106.54	2.63	3.73
57.30112	2101.48			
57.30112	2100.64	2101.06	0.6	085
Average			0.88	1.25

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: 10/25/2023 and 10/30/2023
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)
20112	401	35.989	20.041
MR0101	402	36.375	20.047
MR0112	403	35.927	20.053
UK_OFF0000	404	35.565	20.041
UK_MID0000	405	35.495	20.042
UK_IN0000	406	35.475	20.039
70112	407	36.508	20.046
100112	408	38.042	20.049
160112	409	37.080	20.05
160112	410	37.080	20.045
21/LK0101	411	36.345	20.044
21/LK0112	412	36.281	20.045
WS0101	413	36.229	20.037
WS0112	414	36.187	20.049
KW10112	415	36.855	20.045
KW20101	416	36.739	20.041
KW20112	417	36.739	20.045
KW40101	418	36.640	20.059
KW40112	419	36.678	20.057
300101	420	36.548	20.058
300112	421	36.843	20.058
310112	422	36.934	20.034
330112	423	37.156	20.043
CAL50101	424	37.043	20.053
CAL50112	425	36.972	20.048
CAL40101	426	37.070	20.042
CAL40112	427	37.066	20.057
CAL30101	428	36.877	20.055
CAL30112	429	36.825	20.044
CAL20112	430	36.502	20.055

CAL10112	431	33.151	20.05
CAL10112	432	33.151	20.049
RP10112	433	36.188	20.06
RP20112	434	36.710	20.057
RP30112	435	37.286	20.05
BG10112	436	36.932	20.053
BG20112	437	36.964	20.055
BG30112	438	37.334	20.061
RP40101	439	37.155	20.051
RP40112	440	37.192	20.053
BG40101	441	36.961	20.029
BG40112	442	37.142	20.043
GP50101	443	36.664	20.044
GP50112	444	37.003	20.069
V90101	445	36.437	20.036
V90112	446	36.770	20.049
V50101	447	36.651	20.038
V50112	448	36.706	20.04
V10101	449	37.221	20.045
V10101	450	37.221	20.051
AMI90112	451	36.395	20.046
AMI90101	452	36.157	20.052
AMI50112	453	36.564	20.052
AMI50101	454	34.749	20.048
AMI10112	455	36.669	20.039
AMI10112	456	36.669	20.05
TB40101	457	36.624	20.052
TB40112	458	34.768	20.061
TB100101	459	36.428	20.046
TB100112	460	36.030	20.061
TB10112	461	35.586	20.046
TB10112	462	35.586	20.04
410112	463	37.197	20.053
410112	464	37.197	20.048
450112	465	37.866	20.051
490112	466	34.042	20.044
510112	467	36.381	20.054
540112	468	34.388	20.049
550112	469	36.513	20.05
560112	470	37.695	20.055
570112	471	37.720	20.052

57.10112	472	37.837	20.058
57.20112	473	37.457	20.049
57.30112	474	37.679	20.049
57.30112	475	37.679	20.059
580112	476	37.258	20.05
600112	477	37.397	20.056
650112	478	37.94288	20.044
680112	479	37.83807	20.056
700000	480	37.097	20.048

Reproducibility: pH @ 20^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0013 (0.0006-0.0028) and an average STDEV of 0.0009 (0.0003-0.0020).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	160112	409	8.206			
HP Agilent 8453	160112	410	8.205	8.205	0.0010	0.0015
HP Agilent 8453	CAL10112	431	8.149			
HP Agilent 8453	CAL10112	432	8.149	8.149	0.0004	0.0006
HP Agilent 8453	V10101	449	8.131			
HP Agilent 8453	V10101	450	8.130	8.131	0.0009	0.0012
HP Agilent 8453	AMI10112	455	8.118			
HP Agilent 8453	AMI10112	456	8.118	8.118	0.0003	0.0004
HP Agilent 8453	TB10112	461	8.125			
HP Agilent 8453	TB10112	462	8.125	8.125	0.0006	0.0008
HP Agilent 8453	410112	463	8.126			
HP Agilent 8453	410112	464	8.127	8.127	0.0010	0.0015
HP Agilent 8453	57.30112	474	8.076			
HP Agilent 8453	57.30112	475	8.079	8.078	0.0020	0.0028
Average					0.0009	0.0013

Reproducibility: pH @ 25^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0013 (0.0006– 0.0028) and an average STDEV of 0.0009 (0.0003 – 0.0020).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	160112	409	8.1290			
HP Agilent 8453	160112	410	8.1276	8.1283	0.0010	0.0015
HP Agilent 8453	CAL10112	431	8.0728			
HP Agilent 8453	CAL10112	432	8.0722	8.0725	0.0004	0.0006
HP Agilent 8453	V10101	449	8.0546			
HP Agilent 8453	V10101	450	8.0534	8.0540	0.0009	0.0012
HP Agilent 8453	AMI10112	455	8.0416			
HP Agilent 8453	AMI10112	456	8.0420	8.0418	0.0003	0.0004
HP Agilent 8453	TB10112	461	8.0490			
HP Agilent 8453	TB10112	462	8.0482	8.0486	0.0006	0.0008
HP Agilent 8453	410112	463	8.0495			
HP Agilent 8453	410112	464	8.0510	8.0503	0.0010	0.0015
HP Agilent 8453	57.30112	474	8.0003			
HP Agilent 8453	57.30112	475	8.0031	8.0017	0.0020	0.0028
Average					0.0009	0.0013

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: 10/26/2023, 10/27/2023 and 10/31/2023
Titration system used: Open cell
Batch 204, CRM #093 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.
Batch 204, CRM #307 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.
Batch 204, CRM #846 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.
Batch 204, CRM #363 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.
Batch 204, CRM #895 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.
Batch 204, CRM #1132 Salinity = 33.494, cert. TA = 2205.58 μmol/kg.

On 10/26/2023 CRM #093 was analyzed before and after sample analysis on System 1.
On 10/27/2023 CRM #307 was analyzed before sample analysis on System 1.
On 10/27/2023 CRM #846 was analyzed after sample analysis on System 1.
On 10/31/2023 CRM #363 was analyzed before and after sample analysis on System 1.
On 10/26/2023 CRM #895 was analyzed before and after sample analysis on System 2.
On 10/31/2023 CRM #1132 was analyzed before and after sample analysis on System 2.

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

Cell System	Date	Time	Bottle #	TA	|ΔCRM|
1	10/26/2023	08:36:54	93	2205.58	3.46
1	10/26/2023	18:07:48	93	2199.96	2.16
1	10/27/2023	09:15:35	307	2203.91	1.79
1	10/27/2023	11:31:46	846	2201.99	0.13
1	10/31/2023	10:21:59	363	2204.31	2.19
1	10/31/2023	17:34:12	363	2206.73	4.61
2	10/26/2023	11:10:48	895	2209.57	7.45
2	10/26/2023	15:16:17	895	2206.05	3.93
2	10/31/2023	08:59:53	1132	2203.3	1.18
2	10/31/2023	17:17:03	1132	2208.13	6.01

Reproducibility: (# samples and average difference): 7 duplicate samples were collected. The average difference of 3.27(0.49 – 6.03) and an average STDEV of 2.31 (0.34 – 4.26).

Station	Sample ID	TA (umol/kg)	Average	Difference	STDEV
409	160112	2263.41			
410	160112	2266.80	2265.10	3.39	2.39
431	CAL10112	2487.89			
432	CAL10112	2491.74	2489.81	3.85	2.72
449	V10101	2408.30			
450	V10101	2406.58	2407.44	1.72	1.21
455	AMI10112	2421.41			
456	AMI10112	2415.38	2418.39	6.03	4.26
461	TB10112	2401.55			
462	TB10112	2403.37	2402.46	1.82	1.28
463	410112	2455.81			
464	410112	2450.25	2453.03	5.57	3.93
474	57.30112	2409.96			
475	57.30112	2409.47	2409.71	0.49	0.34
Average				3.27	2.31

Remarks

The average of the CRMs run before and after analysis 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.

The samples at Stations UK_MID and UK_IN were lost due to equipment malfunction.

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 provided 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 provided 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 -80^0C 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.