Cruise: WS23061
Ship: R/V Walton Smith
Expo Code: 33WA20230302
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: March 2nd – March 9th, 2023
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 57
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:

57 locations,82 samples each 500-ml, 7 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Alison MacLeod

pH:

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Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by 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	5/3/2023	2024.96	2029.22	4.26	13	9
AOML 5	5/8/2023	2024.96	2027.91	2.95	20	10
AOML 5	5/10/2023	2024.96	2027.88	2.92	12	11
AOML 6	5/3/2023	2024.96	2036.62	11.66	16	13
AOML 6	5/8/2023	2024.96	2041.35	16.39	12	12
AOML 6	5/10/2023	2024.96	2036.14	11.18	17	12

Analysis date: 5/3/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.8 counts/min
CRM # 513 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 4.26 µmol/kg (2029.22 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 5/8/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 19.2 counts/min
CRM # 468 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 2.95 µmol/kg (2027.91 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 8 and 11 min.

Analysis date: 5/10/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 552 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 2.92 µmol/kg (2027.88 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 8 and 20 min.

Analysis date: 5/3/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 15.6 counts/min
CRM # 498 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 6: offset 11.66 µmol/kg (2036.62µmol/kg).

Average run time, minimum run time, maximum run time: 13, 10 and 16 min.
Analysis date: 5/8/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 610 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 6: offset 16.39 µmol/kg (2041.35µmol/kg).
Average run time, minimum run time, maximum run time: 12, 8 and 18 min.

Analysis date: 5/10/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 16.6 counts/min
CRM # 597 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 6: offset 11.18 µmol/kg (2036.14µmol/kg).
Average run time, minimum run time, maximum run time: 12, 9 and 15 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.77 (0.06-1.29) and average STDEV of 0.54 (0.02-0.91).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
V10112	2200.8			
V10112	2201.2	2200.97	0.27	0.38
AMI10112	2144.4			
AMI10112	2143.4	2143.88	0.73	1.03
490112	2604.5			
490112	2603.2	2603.81	0.91	1.29
CAL10112	2322.1			
CAL10112	2321.1	2321.58	0.73	1.03
TB100112	2114.9			
TB100112	2115.0	2114.94	0.02	0.03
TB10112	2159.6			
TB10112	2159.0	2159.30	0.45	0.64
KW10112	2107.5			
KW10112	2108.5	2108.01	0.71	1.00

Average	0.54	0.77

CRM, salinity and $HgCl_2$ correction applied: Salinity correction was applied using TSG salinity.

Remarks

On the AOML-6 system for all runs, it was later discovered that there was a leak in the gas loop. This created incorrect gas loop coefficients and the DIC data and the inter comparison of carbon parameters confirms this. All DIC values that were ran on that system has been flagged 3. Duplicates run on this system are still averaged but reported as flag 3.

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: 5/3/2023, 5/8/2023 and 5/10/2028
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)
21/LK0101	189	36.408	19.907
21/LK0112	190	36.347	19.913
RP30112	401	36.041	19.914
BG10112	402	34.815	19.917
BG20112	403	35.567	19.914
BG30101	404	36.142	19.914
BG30112	405	36.188	19.913
RP40101	406	36.374	19.91
RP40112	407	36.400	19.907
BG40101	408	36.399	19.911
BG40112	409	36.435	19.908
GP50101	410	36.387	19.919

GP50112	411	36.454	19.921
V90101	412	36.412	19.918
V90112	413	36.413	19.922
V50101	414	36.395	19.917
V50112	415	36.416	19.921
V10112	416	35.254	19.892
V10112	417	35.254	19.9
AMI10112	418	35.497	19.899
AMI10112	419	35.497	19.911
AMI50101	420	36.428	19.913
550112	421	33.804	19.912
540112	422	33.546	19.906
510112	423	35.662	19.91
490112	424	33.377	19.906
490112	425	33.377	19.902
450112	426	35.578	19.911
410112	427	35.398	19.914
310112	428	36.153	19.921
330112	429	35.703	19.921
CAL50112	430	36.250	19.923
CAL50101	431	36.246	19.924
CAL40101	432	36.012	19.926
CAL40112	433	36.011	19.911
CAL30101	434	35.732	19.919
CAL30112	435	35.747	19.915
CAL20112	436	35.555	19.911
CAL10112	437	35.090	19.915
CAL10112	438	35.090	19.92
RP10112	439	35.335	19.924
RP20112	440	35.562	19.915
20112	441	36.102	19.908
MR0101	442	36.248	19.919
MR0112	443	36.115	19.915
UK OFF0000	444	36.027	19.919
UK MID0000	445	36.092	19.911
UK IN0000	446	36.230	19.913
70112	447	35.585	19.919
100112	448	36.107	19.919
160112	449	36.411	19.913
700000	450	35.623	19.916
680112	451	36.049	19.883

650112	452	34.414	19.873
640112	453	34.332	19.87
600112	454	35.673	19.901
580112	455	36.115	19.905
57.30112	456	35.916	19.908
57.20112	457	36.016	19.906
57.10112	458	35.264	19.911
570112	459	33.781	19.913
560112	460	33.646	19.918
AMI50112	461	36.433	19.886
AMI90101	462	36.347	19.874
AMI90112	463	36.409	19.883
TB100101	464	36.301	19.901
TB100112	465	36.390	19.903
TB100112	466	36.390	19.911
TB40101	467	36.422	19.911
TB40112	468	36.427	19.914
TB10112	469	35.563	19.912
TB10112	470	35.563	19.921
300101	471	36.21619	19.921
300112	472	36.2875	19.935
KW40101	473	36.022	19.927
KW40112	474	36.023	19.928
KW20101	475	35.856	19.921
KW20112	476	35.852	19.917
KW10112	477	35.819	19.919
KW10112	478	35.819	19.92
WS0101	479	36.427	19.921
WS0112	480	36.248	19.92

Reproducibility: pH @ 20^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0019 (0.0003– 0.004) and an average STDEV of 0.0014 (0.0003 – 0.0027).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	V10112	416	7.985	7.986	0.0014	0.0020
HP Agilent 8453	V10112	417	7.987			
HP Agilent 8453	AMI10112	418	8.039	8.040	0.0015	0.0021
HP Agilent 8453	AMI10112	419	8.041			
HP Agilent 8453	490112	424	8.062	8.061	0.0003	0.0005
HP Agilent 8453	490112	425	8.061			
HP Agilent 8453	CAL10112	437	7.894	7.895	0.0020	0.0028
HP Agilent 8453	CAL10112	438	7.897			
HP Agilent 8453	TB100112	465	8.100	8.099	0.0027	0.0038
HP Agilent 8453	TB100112	466	8.097			
HP Agilent 8453	TB10112	469	8.054	8.054	0.0003	0.0005
HP Agilent 8453	TB10112	470	8.054			
HP Agilent 8453	KW10112	477	8.049	8.048	0.0012	0.0017
HP Agilent 8453	KW10112	478	8.047			
Average					0.0014	0.0019

Reproducibility: pH @ 25^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0019 (0.0004-0.0038) and an average STDEV of 0.0013 (0.0003-0.0027).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	V10112	416	7.910	7.911	0.0014	0.0020
HP Agilent 8453	V10112	417	7.912			
HP Agilent 8453	AMI10112	418	7.964	7.965	0.0015	0.0021
HP Agilent 8453	AMI10112	419	7.966			
HP Agilent 8453	490112	424	7.986	7.986	0.0003	0.0004
HP Agilent 8453	490112	425	7.985			
HP Agilent 8453	CAL10112	437	7.821	7.822	0.0019	0.0028
HP Agilent 8453	CAL10112	438	7.823			
HP Agilent 8453	TB100112	465	8.025	8.023	0.0027	0.0038
HP Agilent 8453	TB100112	466	8.021			
HP Agilent 8453	TB10112	469	7.978	7.979	0.0003	0.0005
HP Agilent 8453	TB10112	470	7.979			
HP Agilent 8453	KW10112	477	7.974	7.973	0.0012	0.0017
HP Agilent 8453	KW10112	478	7.972			
Average					0.0013	0.0019

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: 5/4/2023, 5/9/2023, and 5/11/2023
Titration system used: Open cell
Batch 195, CRM #513 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #610 Salinity = 33.485, cert. TA = 2213.51 µmol/kg..
Batch 195, CRM #597 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #498 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #481 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #552 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.

On 5/4/2023 CRM #513 was analyzed before and after sample analysis on System 1.
On 5/9/2023 CRM #610 was analyzed before and after sample analysis on System 1.
On 5/11/2023 CRM #597 was analyzed before and after sample analysis on System 1.
On 5/4/2023 CRM #498 was analyzed before and after sample analysis on System 2.
On 5/9/2023 CRM #481 was analyzed before and after sample analysis on System 2.
On 5/11/2023 CRM #522 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	5/4/2023	10:16:40	513	2213.82	0.31
1	5/4/2023	15:41:51	513	2211.65	1.86
1	5/9/2023	13:06:00	610	2211.76	1.75
1	5/9/2023	17:02:58	610	2212.21	1.3
1	5/11/2023	09:33:11	597	2211.27	2.24
1	5/11/2023	14:48:23	597	2212.2	1.31
2	5/4/2023	10:01:20	498	2220.44	6.93
2	5/4/2023	15:49:00	498	2218.94	5.43
2	5/9/2023	10:29:52	481	2216.05	2.54
2	5/9/2023	16:53:22	481	2224.35	10.84
2	5/11/2023	09:14:42	552	2214.96	1.45
2	5/11/2023	14:42:21	552	2213.63	0.12

Reproducibility: (# samples and average difference): 7 duplicate samples were collected. The average difference of 5.01(1.01 – 10.87) and an average STDEV of 3.54 (0.72 – 7.69).

Station ID	Bottle #	TA (umol/kg)	Averaged TA	Difference	Standard Deviation
V10112	416	2441.8	2443.25	2.93	2.07
V10112	417	2444.7			
AMI10112	418	2418.2	2413.28	9.87	6.98
AMI10112	419	2408.3			
490112	424	2902.2	2899.28	5.79	4.09
490112	425	2896.4			
CAL10112	437	2526.7	2521.29	10.87	7.69
CAL10112	438	2515.9			
TB100112	465	2395.9	2395.39	1.13	0.79
TB100112	466	2394.8			
TB10112	469	2413.1	2414.79	3.41	2.41
TB10112	470	2416.5			
KW10112	477	2379.9	2379.44	1.01	0.72
KW10112	478	2378.9			
Average				5.01	3.54

Remarks

On 5/9/2023 on System 2, the beginning CRM was used to adjust the values. The average of the CRMs were used to adjust the values of the samples for the other days for both systems.

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.

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.