Cruise: H24062
Ship: R/V Hogarth
Expo Code: 33SGDK20240302
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: 03/02/2024 to 03/08/2024
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 54
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 Hogarth by Rachel Cohn and Ian Smith. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

54 locations, 78 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

pH:

54 locations, 78 samples each 500-ml, 7 duplicate samples.
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TAlk:

54 locations, 78 samples each 500-ml, 7 duplicate samples.
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PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears

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	07/31/2024	2048.19	2049.09	0.9	12	9
AOML 5	08/05/2024	2048.19	2047.19	1.0	19	9
AOML 5	08/07/2024	2048.19	2049.57	1.38	12	9
AOML 5	08/12/2024	2048.19	2048.98	0.79	13	9
AOML 6	08/05/2024	2048.19	2045.09	3.1	12	8
AOML 6	08/07/2024	2048.19	2049.36	1.17	12	9
AOML 6	08/12/2024	2048.19	2047.9	0.29	12	8
AOML 6	08/14/2024	2046.37	2044.83	1.54	12	8

Analysis date: 07/31/2024
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 578 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 5: offset 0.9 µmol/kg (2049.09 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 13 min.

Analysis date: 08/05/2024
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 693 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 5: offset 1.0 µmol/kg (2047.19 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 14 min.

Analysis date: 08/07/2024
Coulometer used: DICE–CM5017O-AOML5
Blanks: 12.0 counts/min
CRM # 1042 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 5: offset 1.38 µmol/kg (2049.57 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 08/12/2024
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 1224 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 5: offset 0.79 µmol/kg (2048.98 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 20 min.

Analysis date: 08/05/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.4 counts/min
CRM # 987 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 6: offset 3.1 µmol/kg (2045.09 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

Analysis date: 08/07/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 1101 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 6: offset 1.17 µmol/kg (2049.36 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 12 min.

Analysis date: 08/12/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 1189 was used and with an assigned value of (includes both DIC and salinity):
Batch 201, c: 2048.19 µmol/kg, S: 33.302
CRM values measured: AOML 6: offset 0.29 µmol/kg (2047.9 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 13 min.

Analysis date: 08/14/2024
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 214 was used and with an assigned value of (includes both DIC and salinity):
Batch 210, c: 2046.37 µmol/kg, S: 33.231
CRM values measured: AOML 6: offset 1.54 µmol/kg (2046.37 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 13 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.37 (0.55-3.64) and average STDEV of 0.97 (0.39-2.57).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
AMI90101	2094.67	2096.49	2.57	3.64
AMI90101	2098.31			
AMI90112	2091.72	2092.33	0.86	1.22
AMI90112	2092.94			
BG20112	2141.85	2141.57	0.39	0.55
BG20112	2141.30			
310112	2123.11	2123.67	0.79	1.12
310112	2124.24			
57.30112	2120.70	2121.59	1.26	1.78
57.30112	2122.48			
20112	2042.29	2041.84	0.64	0.90
20112	2041.38			
KW10112	2084.84	2083.53	1.86	2.63
KW10112	2082.21			
Average			0.97	1.37

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: 07/31/2024, 8/05/2024, 8/07/2024, and 8/12/2024
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 0.003pH.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^{0}C)
TB40101	21	36.027	19.922
TB40112	22	35.243	19.927
TB100101	23	36.528	19.926
TB100112	24	36.538	19.928
TB10112	25	34.698	19.925
AMI10112	26	34.268	19.915
AMI50101	27	36.315	19.921
AMI50112	28	36.150	19.93
AMI90101	29	36.513	19.921
AMI90101	30	36.513	19.919
AMI90112	31	36.516	19.93
AMI90112	32	36.516	19.913
V10112	33	34.093	19.913
V50101	34	36.443	19.92
V50112	35	36.132	19.921
V90101	36	36.507	19.919
V90112	37	36.450	19.932
GP50101	38	36.384	19.928
GP50112	39	36.397	19.929
BG40101	40	36.173	19.933
BG40112	41	36.044	19.945
RP40101	42	36.032	19.937
RP40112	43	35.853	19.944
BG30101	44	35.594	19.953
BG30112	45	35.376	19.919
BG20112	46	34.534	19.912
BG20112	47	34.534	19.916
BG10112	48	33.360	19.919

RP30112	49	35.432	19.92
RP20112	50	34.438	19.921
RP10112	51	33.582	19.93
CAL10112	52	33.807	19.928
CAL20112	53	34.393	19.934
CAL30101	54	35.027	19.937
CAL30112	55	34.509	19.941
CAL40101	56	35.542	19.945
CAL40112	57	35.195	19.962
CAL50101	58	35.791	19.943
CAL50112	59	35.915	19.956
330112	60	34.412	19.964
310112	61	35.716	19.918
310112	62	35.716	19.924
410112	63	34.216	19.92
450112	64	34.305	19.923
490112	65	30.813	19.918
510112	66	33.067	19.922
540112	67	30.532	19.923
550112	68	31.946	19.925
560112	69	32.752	19.928
570112	70	33.631	19.925
57.10112	71	35.018	19.929
57.20112	72	35.667	19.929
57.30112	73	35.716	19.92
57.30112	74	35.716	19.919
580112	75	36.472	19.92
600112	76	35.698	19.921
650112	77	31.510	19.922
680112	78	34.047	19.939
700000	79	33.546	19.924
160112	80	34.680	19.924
WS0101	81	36.205	19.917
WS0112	82	35.860	19.918
21/LK0101	83	36.381	19.922
21/LK0112	84	35.439	19.933
100112	85	32.028	19.907
70112	86	35.902	19.913
MR0101	87	36.363	19.904
MR0112	88	36.323	19.925
20112	89	35.471	19.898

20112	90	35.471	19.931
KW10112	91	36.406	19.929
KW10112	92	36.406	19.904
KW20101	93	36.499	19.934
KW20112	94	36.413	19.918
KW40101	95	36.505	19.939
KW40112	96	36.480	19.925
300101	97	36.392	19.928
300112	98	36.268	19.918

Reproducibility: pH @ 20^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0030 (0.0001– 0.0066) and an average STDEV of 0.0021 (0.0001 – 0.0047).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	AMI90101	29	8.0899	8.090	0.0001	0.0001
HP Agilent 8453	AMI90101	30	8.0897			
HP Agilent 8453	AMI90112	31	8.0944	8.092	0.0027	0.0038
HP Agilent 8453	AMI90112	32	8.0906			
HP Agilent 8453	BG20112	46	7.9877	7.987	0.0006	0.0008
HP Agilent 8453	BG20112	47	7.9868			
HP Agilent 8453	310112	61	8.0262	8.027	0.0010	0.0014
HP Agilent 8453	310112	62	8.0276			
HP Agilent 8453	57.30112	73	7.9997	7.998	0.0018	0.0025
HP Agilent 8453	57.30112	74	7.9972			
HP Agilent 8453	20112	89	8.1962	8.193	0.0039	0.0054
HP Agilent 8453	20112	90	8.1908			
HP Agilent 8453	KW10112	91	7.9965	8.000	0.0047	0.0066
HP Agilent 8453	KW10112	92	8.0031			
Average					0.0021	0.0030

Reproducibility: pH @ 25^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0029 (0.0001– 0.0065) and an average STDEV of 0.0021 (0.0001 – 0.0046).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	AMI90101	29	8.0143	8.014	0.0001	0.0001
HP Agilent 8453	AMI90101	30	8.0141			
HP Agilent 8453	AMI90112	31	8.0188	8.017	0.0027	0.0038
HP Agilent 8453	AMI90112	32	8.0150			
HP Agilent 8453	BG20112	46	7.9132	7.913	0.0006	0.0008
HP Agilent 8453	BG20112	47	7.9123			
HP Agilent 8453	310112	61	7.9513	7.952	0.0010	0.0014
HP Agilent 8453	310112	62	7.9526			
HP Agilent 8453	57.30112	73	7.9250	7.924	0.0018	0.0025
HP Agilent 8453	57.30112	74	7.9226			
HP Agilent 8453	20112	89	8.1197	8.117	0.0038	0.0054
HP Agilent 8453	20112	90	8.1143			
HP Agilent 8453	KW10112	91	7.9219	7.925	0.0046	0.0065
HP Agilent 8453	KW10112	92	7.9284			
Average					0.0021	0.0029

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: 8/01/2024, 8/06/2024, 8/08/2024, and 8/13/2024
Titration system used: Open cell
Batch 201, CRM #693 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #754 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #1042 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #1224 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #808 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #987 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 201, CRM #1101 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.
Batch 210, CRM #136 Salinity = 33.231, cert. TA = 2220.62 µmol/kg.
Batch 210, CRM #214 Salinity = 33.231, cert. TA = 2220.62 µmol/kg.

On 8/6/2024 CRM #693 was analyzed before sample analysis on System 1.
On 8/6/2024 CRM #754 was analyzed after sample analysis on System 1.
On 8/8/2024 CRM #1042 was analyzed before and after sample analysis on System 1.
On 8/13/2024 CRM #1224 was analyzed before and after sample analysis on System 1.
On 8/15/2024 CRM #136 was analyzed before and after sample analysis on System 1.
On 8/1/2024 CRM #808 was analyzed before and after sample analysis on System 2.
On 8/6/2024 CRM #987 was analyzed before and after sample analysis on System 2.
On 8/8/2024 CRM #1101 was analyzed before and after sample analysis on System 2.
On 8/15/2024 CRM #214 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. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	|ΔCRM|
1	8/6/2024	09:41:14	693	2222.45	14.89
1	8/6/2024	16:00:36	754	2213.69	6.13
1	8/8/2024	08:27:42	1042	2214.45	9.87
1	8/8/2024	14:08:38	1042	2216.42	10.64
1	8/13/2024	08:52:04	1224	2214.02	7.91
1	8/13/2024	16:02:57	1224	2213.88	8.42
1	8/15/2024	09:40:32	136	2223.27	-0.37
1	8/15/2024	15:33:52	136	2219.91	2.96
2	8/1/2024	09:00:14	808	2218.69	11.13

2	8/1/2024	15:22:18	808	2217.31	9.75
2	8/6/2024	10:27:05	987	2220.38	12.82
2	8/6/2024	15:34:55	987	2218.54	10.98
2	8/8/2024	08:47:49	1101	2216.67	9.11
2	8/8/2024	13:52:48	1101	2215.52	7.96
2	8/15/2024	09:45:04	214	2226.43	5.81
2	8/15/2024	14:49:53	214	2224.77	4.15

The acid was replaced on system 1 prior to running on 8/15/2024.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.43 (0.45 – 3.47) and an average STDEV of 1.01 (0.32 – 2.45).

Station	**Sample ID**	**TA (umol/kg)**	**Average**	**STDEV**	**Difference**
AMI9	AMI90101	2396.50			
AMI9	AMI90101	2398.95	2397.73	1.73	2.45
AMI9	AMI90112	2396.43			
AMI9	AMI90112	2395.13	2395.78	0.92	1.3
BG2	BG20112	2368.68			
BG2	BG20112	2368.23	2368.45	0.32	0.45
31	310112	2385.48			
31	310112	2386.54	2386.01	0.75	1.06
57.3	57.30112	2367.89			
57.3	57.30112	2365.99	2366.94	1.34	1.89
2	20112	2410.04			
2	20112	2413.50	2411.77	2.45	3.47
Average				1.01	1.43

Remarks

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

It was determined using calculated TA values from DIC and pH that one of the duplicate samples associated with Sample ID KW10112 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: Will 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.