Cruise: H23138
Ship: R/V Hogarth
Expo Code: 33SGDK20230518
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: May 18th-May 24th 2023
Chief Scientist: Enrique Montes
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 Tyler Christian. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

54 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:

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Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
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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	06/12/2023	2024.96	2026.68	1.72	12	8
AOML 5	06/14/2023	2024.96	2029.34	4.38	27.4	8
AOML 6	06/12/2023	2024.96	2021.98	2.98	12	11
AOML 6	06/14/2023	2024.96	2022.55	2.41	13.6	10

Analysis date: 06/12/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 490 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 1.72 µmol/kg (2026.68 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 06/14/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 27.4 counts/min
CRM # 542 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 4.38 µmol/kg (2029.34 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 06/12/2023
Coulometer used: DICE–CM5017O-AOML6
Blanks: 12 counts/min
CRM # 510 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 2.98 µmol/kg (2021.98 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 7 and 16 min.

Analysis date: 06/14/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 13.6 counts/min
CRM # 505 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 2.41 µmol/kg (2022.55 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 8 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.18 (0.05-2.98) and average STDEV of 0.83 (0.04-2.11).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
AMI90112	2098.39			
AMI90112	2097.07	2097.73	0.94	1.32
V10112	2116.51			
V10112	2114.73	2115.62	1.26	1.78
BG10112	2010.73			
BG10112	2012.46	2011.60	1.22	1.73
580112	2028.47			
580112	2025.49	2026.98	2.11	2.98
KW10112	2110.55			
KW10112	2110.61	2110.58	0.04	0.05
KW20101	2108.0			
KW20101	2107.7	2107.84	0.21	0.29
KW20112	2109.1			
KW20112	2109.0	2109.06	0.05	0.08
Average			0.83	1.18

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

Remarks

Based on the data on station KW2 and a nearby station, it was determined that two of the duplicate bottles were switched or mislabeled. The correct bottle was identified and corrected.

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: 06/12/2023 and 06/14/2023
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	1	36.731	19.949
TB40112	2	36.745	19.936
TB100101	3	36.597	19.937
TB100112	4	36.628	19.94
TB10101	5	36.953	19.941
AMI10112	6	36.699	19.949
AMI50101	7	36.601	19.941
AMI50112	8	36.635	19.934
AMI90101	9	36.481	19.932
AMI90112	10	36.580	19.933
AMI90112	11	36.580	19.94
V10112	12	37.002	19.938
V10112	13	37.002	19.94
V50101	14	36.688	19.937
V50112	15	36.750	19.942
V90101	16	36.509	19.928
V90112	17	36.551	19.934
GP50101	18	36.560	19.922
GP50112	19	36.617	19.929
BG40101	20	36.657	19.93
BG40112	21	36.720	19.932
RP40101	22	36.658	19.934
RP40112	23	36.680	19.934
BG30101	24	36.695	19.928
BG30112	25	36.717	19.937

BG20112	26	36.801	19.931
BG10112	27	36.416	19.929
BG10112	28	36.416	19.944
RP30112	29	36.541	19.951
RP20112	30	36.500	19.965
RP10112	31	35.646	19.966
CAL10112	32	33.739	19.963
CAL20112	33	36.801	19.957
CAL30101	34	36.686	19.951
CAL30112	35	36.667	19.954
CAL40101	36	36.648	19.955
CAL40112	37	36.599	19.958
CAL50101	38	36.636	19.957
CAL50112	39	36.696	19.959
330112	40	36.731	19.956
310112	81	36.672	19.923
410112	82	37.317	19.933
450112	83	37.059	19.932
490112	84	37.108	19.94
510112	85	37.268	19.942
540112	86	34.909	19.947
550112	87	36.453	19.944
560112	88	37.172	19.946
570112	89	37.466	19.941
57.10112	90	37.483	19.94
57.20112	91	37.005	19.949
57.30112	92	36.823	19.943
580112	93	36.534	19.938
580112	94	36.534	19.936
600112	95	36.943	19.94
650112	96	37.916	19.939
680112	97	37.534	19.938
160112	98	37.461	19.927
100112	99	37.546	19.936
70112	100	37.318	19.94
UK_IN0000	173	37.15	19.929
UK_MID0000	174	36.68	19.915
UK_OFF0000	175	36.72	19.926
MR0101	176	36.300	19.935
MR0112	177	36.292	19.931
20112	178	36.419	19.934

21/LK0101	179	36.494	19.934
21/LK0112	180	36.595	19.939
WS0101	181	36.537	19.948
WS0112	182	36.563	19.956
KW10112	183	36.536	19.963
KW10112	184	36.536	19.966
KW20101	186	36.469	19.948
KW20101	187	36.470	19.953
KW20112	185	36.469	19.967
KW20112	188	36.470	19.96
KW40101	189	36.412	19.955
KW40112	190	36.415	19.957
300101	191	36.499	19.953
300112	192	36.588	19.953

Reproducibility: pH @ 20^{0}C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0064 (0.0000– 0.0237) and an average STDEV of 0.0044 (0.0000 – 0.0167).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	AMI90112	10	8.115	8.115	0.0000	0.0000
HP Agilent 8453	AMI90112	11	8.115			
HP Agilent 8453	V10112	12	8.115	8.110	0.0071	0.0101
HP Agilent 8453	V10112	13	8.105			
HP Agilent 8453	BG10112	27	8.184	8.184	0.0009	0.0013
HP Agilent 8453	BG10112	28	8.185			
HP Agilent 8453	580112	93	8.064	8.063	0.0010	0.0014
HP Agilent 8453	580112	94	8.062			
HP Agilent 8453	KW10112	183	8.095	8.097	0.0021	0.0030
HP Agilent 8453	KW10112	184	8.098			
HP Agilent 8453	KW20101	186	8.077	8.089	0.0167	0.0237
HP Agilent 8453	KW20101	187	8.101			
HP Agilent 8453	KW20112	185	8.106	8.103	0.0031	0.0044
HP Agilent 8453	KW20112	188	8.101			

Average	0.0044	0.0063

Reproducibility: pH @ 25^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0062 (0.0000– 0.0235) and an average STDEV of 0.0044 (0.0000 – 0.0166).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	AMI90112	10	8.040	8.040	0.0000	0.0000
HP Agilent 8453	AMI90112	11	8.040			
HP Agilent 8453	V10112	12	8.039	8.034	0.0070	0.0100
HP Agilent 8453	V10112	13	8.029			
HP Agilent 8453	BG10112	27	8.107	8.108	0.0009	0.0013
HP Agilent 8453	BG10112	28	8.109			
HP Agilent 8453	580112	93	7.988	7.988	0.0010	0.0014
HP Agilent 8453	580112	94	7.987			
HP Agilent 8453	KW10112	183	8.020	8.021	0.0021	0.0030
HP Agilent 8453	KW10112	184	8.023			
HP Agilent 8453	KW20101	186	8.002	8.013	0.0166	0.0235
HP Agilent 8453	KW20101	187	8.025			
HP Agilent 8453	KW20112	185	8.030	8.028	0.0031	0.0043
HP Agilent 8453	KW20112	188	8.026			
Average					0.0044	0.0062

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.

Based on the data on station KW2 and a nearby station, it was determined that two of the duplicate bottles were switched or mislabeled. The correct bottle was identified and corrected.

Bottle station KW20101 is not reported as a duplicate measurement because the value of bottle #186 is very different from surrounding measurements and the expected value calculated from the other carbon parameters and considered questionable.

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: 06/13/2023 and 06/15/2023
Titration system used: Open cell
Batch 195, CRM #504 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #542 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #490 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #505 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.

On 06/13/2023 CRM #504 was analyzed before and after sample analysis on System 1.
On 06/15/2023 CRM #542 was analyzed before and after sample analysis on System 1.
On 06/13/2023 CRM #490 was analyzed before and after sample analysis on System 2.
On 06/15/2023 CRM #505 was analyzed before and after sample analysis on System 2.
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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	06/13/2023	07:52:50	504	2215.17	1.66
1	06/13/2023	17:43:49	504	2216.60	3.09
1	06/15/2023	08:25:25	542	2219.00	5.49
1	06/15/2023	17:45:32	542	2217.13	3.62
2	06/13/2023	09:22:34	490	2217.62	4.11
2	06/13/2023	17:39:03	490	2219.74	6.23
2	06/15/2023	09:41:34	505	2219.50	5.99
2	06/15/2023	17:39:14	505	2219.53	6.02

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 5.47 (0.77 – 15.12) and an average STDEV of 3.87 (0.54 – 10.69).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
AMI9	AMI90112	2409.19			
AMI9	AMI90112	2408.42	2408.8	0.54	0.77
V1	V10112	2433.88			
V1	V10112	2449.00	2441.44	10.69	15.1
BG1	BG10112	2384.83			
BG1	BG10112	2383.52	2384.17	0.93	1.32
58	580112	2313.55			
58	580112	2312.16	2312.85	0.98	1.39
KW1	KW10112	2419.98			
KW1	KW10112	2415.58	2417.78	3.11	4.41
KW2	KW20101	2426.00			
KW2	KW20101	2438.36	2432.18	8.7	12.4
KW2	KW20112	2415.75			
KW2	KW20112	2412.84	2425.6	2.05	2.90
Average				3.87	5.47

Remarks

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

Based on the data on station KW2 and a nearby station, it was determined that two of the duplicate bottles were switched or mislabeled. The correct bottle was identified and corrected.

On station ID V10112, one of the duplicates was determined to be questionable due to carbonate parameter comparison and is not included in the data. The other bottle was reported for that station as a flag 2.

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 -80^0C 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.