Cruise: WS21151
Ship: R/V Walton Smith
Expo Code: 33WA20210531
Funding Project Title: Near-Shore Carbonate Sampling
Funding Project ID: Near-Shore-OA
Dates: May 31st – June 6th, 2021
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 Alex Fine. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
57 locations, 83 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Denis Pierrot and Charles Featherstone

pH:
57 locations, 83 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Denis Pierrot Charles Featherstone

TAlk:
57 locations, 83 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero, Dismey Sosa-Rodriguez and Charles Featherstone

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	06/21/2021	1952.65	1953.72	1.07	15.0	7
AOML 5	06/22/2021	1952.65	1953.65	1.00	15.0	7
AOML 6	06/21/2021	1952.65	1953.07	0.42	12.0	9
AOML 6	06/22/2021	1952.65	1955.90	3.25	15.0	8

Analysis date: 06/21/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 15.0 counts/min
CRM # 927 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 5: offset 1.07 µmol/kg (1953.72 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 10 min.

Analysis date: 06/22/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 15.0 counts/min
CRM # 1110 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 5: offset 1.00µmol/kg (1953.65 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 10 min.

Analysis date: 06/21/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 443 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 6: offset 0.42 µmol/kg (1953.07 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 16 min.

Analysis date: 06/22/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 15.0 counts/min
CRM # 992 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 6: offset 3.25 µmol/kg (1955.90 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 1.44 (0.09-2.96) and average STDEV of 1.02 (0.07-2.10).

Sample ID	DIC (µmol/kg)	Average	Difference	STDEV
KW401012	2088.60			
KW401012	2088.99	2088.8	0.40	0.28

GP501012	2102.32			
GP501012	2102.99	2102.7	**0.67**	0.47
BG301012	2105.16			
BG301012	2106.86	2106.0	**1.70**	1.20
V901012	2084.10			
V901012	2084.00	2084.0	**0.09**	0.07
TB40101	2096.52			
TB40101	2099.35	2097.9	**2.83**	2.00
5701012	2353.56			
5701012	2350.59	2352.1	**2.96**	2.10
Average			1.44	1.02

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: 06/21/2021 and 06/22/2021
No CRMs was 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)
201012	1	36.431	20.173
MR0101	2	36.380	20.190

MR01012	3	36.482	20.202
UK-OFF0000	4	36.480	20.207
UK-MID0000	5	36.455	20.242
UK-IN0000	6	36.655	20.234
701012	7	37.349	20.247
1001012	8	36.925	20.244
1601012	9	37.583	20.273
21-LK0101	10	36.493	20.265
21-LK01012	11	36.478	20.270
WS0101	12	36.513	20.272
WS01012	13	36.514	20.274
KW101012	14	36.013	20.263
KW20101	15	36.033	20.246
KW201012	16	36.034	20.265
KW40101	17	36.122	20.268
KW401012	18	36.122	20.262
KW401012	19	36.122	20.253
300101	20	36.219	20.268
3001012	21	36.223	20.195
3101012	22	36.333	20.196
320000	23	36.221	20.221
3301012	24	36.184	20.233
CAL60101	178	36.330	20.333
CAL601012	179	36.370	20.676
CAL50101	25	36.380	20.236
CAL501012	26	36.387	20.237
CAL40101	27	36.356	20.246
CAL401012	28	36.358	20.254
CAL30101	29	36.356	20.264
CAL301012	30	36.355	20.250
CAL201012	31	36.405	20.269
CAL101012	32	35.039	20.262
RP101012	33	35.319	20.264
RP201012	34	35.482	20.274
RP301012	35	35.745	20.258
RP40101	36	36.204	20.263
RP401012	37	36.204	20.257
GP50101	38	36.229	20.255
GP501012	39	36.219	20.254
GP501012	40	36.219	20.254
BG40101	81	36.172	20.571

BG401012	82	36.205	20.531
BG30101	83	36.029	20.595
BG301012	84	36.021	20.766
BG301012	85	36.021	20.666
BG201012	87	35.925	20.360
BG101012	88	35.667	20.603
V101012	89	36.128	20.706
V50101	90	36.252	20.839
V501012	91	36.314	20.816
V90101	92	36.672	20.852
V901012	93	36.421	20.875
V901012	94	36.421	20.979
AMI90101	95	36.181	21.031
AMI901012	96	36.250	19.391
AMI50101	97	36.295	20.512
AMI501012	98	36.317	20.634
AMI101012	99	36.063	20.641
TB101012	100	35.230	20.721
TB40101	173	36.242	20.547
TB40101	174	36.242	20.557
TB401012	175	36.321	20.607
TB100101	176	36.035	20.954
TB1001012	177	36.208	19.803
4101012	180	36.499	20.808
4501012	181	36.242	20.954
4901012	182	34.955	20.832
5101012	183	36.238	20.893
5401012	186	35.354	20.139
5501012	185	34.927	21.022
5601012	184	35.369	20.947
5701012	187	35.870	20.416
5701012	188	35.870	20.571
57.101012	189	36.332	20.621
57.201012	190	36.186	20.702
57.301012	191	36.179	20.767
5801012	192	36.154	20.826
6001012	193	36.471	20.258
6501012	194	39.919	20.251
6801012	195	37.930	20.254
700000	196	38.302	20.259

Reproducibility: pH @ 20^0C (# samples and average difference): 6 duplicate samples were collected with an average difference of 0.00293 (0.0002 – 0.0082) and an average STDEV of 0.00207 (0.0001 – 0.0058).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	KW401012	18	8.1061878			
HP Agilent 8453	KW401012	19	8.1053932	8.10579	0.0006	0.0008
HP Agilent 8453	GP501012	39	8.1273431			
HP Agilent 8453	GP501012	40	8.1190969	8.12322	0.0058	0.0082
HP Agilent 8453	BG301012	84	8.1638399			
HP Agilent 8453	BG301012	85	8.1625914	8.16322	0.0009	0.0012
HP Agilent 8453	V901012	93	8.1223192			
HP Agilent 8453	V901012	94	8.1234376	8.12288	0.0008	0.0011
HP Agilent 8453	TB40101	173	8.1239377			
HP Agilent 8453	TB40101	174	8.1179437	8.12094	0.0042	0.0060
HP Agilent 8453	5701012	187	8.0704101			
HP Agilent 8453	5701012	188	8.0706122	8.07051	0.0001	0.0002
Average					0.00207	0.00293

Reproducibility: pH @ 25^0C (# samples and average difference): 6 duplicate samples were collected with an average difference of 0.00291 (0.0002 – 0.0082) and an average STDEV of 0.00205 (0.0001 – 0.0058).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	KW401012	18	8.0304926			
HP Agilent 8453	KW401012	19	8.0297078	8.03010	0.0006	0.0008
HP Agilent 8453	GP501012	39	8.0514400			
HP Agilent 8453	GP501012	40	8.0432649	8.04735	0.0058	0.0082
HP Agilent 8453	BG301012	84	8.0876186			
HP Agilent 8453	BG301012	85	8.0863817	8.08700	0.0009	0.0012
HP Agilent 8453	V901012	93	8.0464819			

HP Agilent 8453	V901012	94	8.0475903	8.04704	0.0008	0.0011
HP Agilent 8453	TB40101	173	8.0480695			
HP Agilent 8453	TB40101	174	8.0421313	8.04510	0.0042	0.0059
HP Agilent 8453	5701012	187	7.9948254			
HP Agilent 8453	5701012	188	7.9950163	7.99492	0.0001	0.0002
Average					0.00205	0.00291

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: 06/23/2021 and 06/24/2021
Titration system used: Open cell
Batch 178, CRM #443 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #927 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #1110 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #992 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

On 06/23/2021 CRM #443 was analyzed before sample analysis on System 1 and 2.
On 06/23/2021 CRM #927 was analyzed after sample analysis on System 1 and 2.
On 06/24/2021 CRM #1110 was analyzed before sample analysis on System 1 and 2.
On 06/24/2021 CRM #992 was analyzed after sample analysis on System 1 and 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	$|\Delta CRM|$
1	06/23/2021	11:07:51	443	2219.96	3.43
1	06/23/2021	19:22:06	927	2218.80	2.27

1	06/24/2021	09:19:13	1110	2224.53	8.00
1	06/24/2021	15:29:45	992	2222.67	6.14
2	06/23/2021	10:07:16	443	2214.62	1.91
2	06/23/2021	18:55:26	927	2214.47	2.06
2	06/24/2021	08:51:12	1110	2214.58	1.95
2	06/24/2021	15:23:02	992	2210.67	5.86

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 5.15 (0.78 – 13.33) and an average STDEV of 3.64 (0.55 – 9.42).

Station	Sample ID	TA (umol/kg)	Average	Difference	STDEV
KW4	KW401012	2391.8			
KW4	KW401012	2388.3	2390.0	3.49	2.47
GP5	GP501012	2427.4			
GP5	GP501012	2424.6	2426.0	2.76	1.95
BG3	BG301012	2453.5			
BG3	BG301012	2451.3	2452.4	2.24	1.59
V9	V901012	2399.5			
V9	V901012	2400.3	2399.9	0.78	0.55
TB4	TB40101	2411.3			
TB4	TB40101	2419.6	2415.5	8.27	5.85
57	5701012	2662.5			
57	5701012	2675.8	2669.2	13.33	9.42
Average				5.15	3.64

Remarks

Sample bottle #28 was marked 4 because the sample titration finished to early and gave a high TA value.

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: 06/15/2021 and 06/16/2021

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).

Chlorophyll and Phaeophytin:
Analysis Date: 06/18/2021 and 06/19/2021

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.