Cruise: WS20278
Ship: R/V Walton Smith
Expo Code: 33WA20201005
Dates: October 5th – October 12th, 2020
Chief Scientist: Ian Smith
Equipment: CTD and Flow-Through (FT)
Total number of stations: 39
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/rosette and Flow-Through system onboard the R/V Walton Smith by Ian Smith and Patrick Mears. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
39 locations, 73 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 and Patrick Mears

pH:
39 locations, 73 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 and Patrick Mears

TAlk:
39 locations, 73 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 and 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	10/19/2020	2017.88	2019.42	1.54	20.0	10

AOML5	10/20/2020	2017.88	2019.80	1.92	15.0	8
AOML 6	10/19/2020	2017.88	2025.34	7.46	12.0	9
AOML 6	10/20/2020	2017.88	2023.30	5.42	15.0	9

Analysis date: 10/19/2020
Coulometer used: DICE–CM5011-AOML 5
Blanks: 20.0 counts/min
CRM # 493 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured: AOML 5: offset 1.54 µmol/kg (2019.42 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 7 and 19 min.

Analysis date: 10/20/2020
Coulometer used: DICE–CM5011-AOML 5
Blanks: 15.0 counts/min
CRM # 427 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured: AOML 5: offset 01.92 µmol/kg (2019.80 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 10/19/2020
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 799 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured: AOML 6: offset 7.46 µmol/kg (2025.34 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

Analysis date: 10/20/2020
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 15.0 counts/min
CRM # 163 was used and with an assigned value of (includes both DIC and salinity):
Batch 150, c: 2017.88 µmol/kg, S: 33.343
CRM values measured: AOML 6: offset 5.42 µmol/kg (2023.30 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.62 (0.18-6.05) and average STDEV of 1.14 (0.13-4.28).

Sample ID	DIC (µmol/kg)	Average	Difference	STDEV
330000	1996.7			
330000	1994.5	1995.6	2.19	1.55

RP101012	2016.4			
RP101012	2016.8	2016.6	0.41	0.29
BG40101	2004.7			
BG40101	2004.6	2004.7	0.18	0.13
V50101	2026.7			
V50101	2026.0	2026.3	0.78	0.55
AMI50101	2019.4			
AMI50101	2018.3	2018.9	1.13	0.80
AMI901012	2034.2			
AMI901012	2034.8	2034.5	0.59	0.42
5501012	1798.6			
5501012	1792.6	1795.6	6.05	4.28
Average			1.62	1.14

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 on AOML 6 were analyzed on a new coulometer 5017-O from UIC. Inc.

pH:

Analysis date: 10/19/2020 and 10/20/2020
A CRM was analyzed before sample analysis.
10/19/2020, Batch 150, CRM #1047, pH = 7.939812
10/20/2020, Batch 150, CRM #116, pH = 7.938969

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^{0}C)
CRM150_1047	1047	33.343	20.058
CRM150_116	116	33.343	20.008
UKOFF0000	1	35.494	20.097
UKMID0000	2	35.232	20.099
UKIN0000	3	35.207	20.092
300101	4	35.795	20.092
3001012	5	36.781	20.086
310101	6	35.672	20.083
3101012	7	35.405	20.081
320000	8	34.195	20.084
330000	9	34.195	20.095
330000	10	34.195	20.090
CAL101012	11	31.700	20.098
CAL30101	12	34.886	20.089
CAL301012	13	34.976	20.100
CAL50101	14	35.320	20.092
CAL501012	15	35.322	20.090
CAL60101	16	35.623	20.099
CAL60105	17	35.621	20.093
CAL601012	18	35.597	20.090
RP10101	19	33.019	20.078
RP101012	20	32.761	20.089
RP101012	21	32.761	20.091
RP20101	22	34.761	20.079
RP201012	23	33.254	20.076
RP30101	24	34.647	20.090
RP301012	25	34.536	20.096
RP40101	26	35.102	20.100
RP401012	27	35.109	20.094
GP50101	28	35.639	20.081
GP50105	29	35.642	20.087
GP501012	30	35.651	20.088
BG40101	31	35.229	20.081
BG40101	32	35.229	20.087
BG401012	33	35.232	20.088
BG30101	34	35.037	20.090
BG301012	35	34.837	20.098
BG20101	36	34.586	20.096

BG201012	37	33.652	20.084
V90101	38	35.820	20.094
V901012	39	35.758	20.092
V50101	40	35.254	20.090
V50101	421	35.254	20.096
V50105	422	35.183	20.036
V501012	423	34.499	20.035
V30101	424	35.030	20.046
V301012	425	34.487	20.057
V10101	426	33.764	20.062
V101012	427	33.696	20.061
AMI10101	428	34.142	20.030
AMI101012	429	34.137	20.031
AMI50101	430	35.852	20.043
AMI50101	431	35.852	20.054
AMI50105	432	35.859	20.054
AMI501012	433	35.800	20.071
AMI70101	434	35.792	20.059
AMI70105	435	35.761	20.059
AMI701012	436	35.793	20.064
AMI90101	437	35.864	20.059
AMI90105	438	35.729	20.074
AMI901012	439	35.728	20.073
AMI901012	440	35.728	20.078
TB100101	441	35.719	20.071
TB100105	442	35.665	20.063
TB1001012	443	35.650	20.055
TB30101	444	34.554	20.075
TB301012	445	34.544	20.069
TB10101	446	33.481	20.066
TB101012	447	33.438	20.058
4101012	448	32.901	20.069
5401012	449	33.778	20.082
5501012	450	35.274	20.086
5501012	451	35.274	20.081
5601012	452	35.510	20.086
5701012	453	36.016	20.061
5101012	454	34.606	20.068
5710101	455	36.056	20.076
57101012	456	36.064	20.087
5720101	457	35.841	20.083

57201012	458	35.841	20.071
5730101	459	35.840	20.094
57301012	460	36.030	20.072

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00079 (0.0004-0.0017) and an average STDEV of 0.00056 (0.0002-0.0012).

Instrument	Sample ID	Bottle #	pH @20 ^{0}C	Average	STDEV	Difference
HP Agilent 8453	330000	9	8.158750			
HP Agilent 8453	330000	10	8.160440	8.15960	0.0012	0.0017
HP Agilent 8453	RP101012	20	8.137798			
HP Agilent 8453	RP101012	21	8.137025	8.13741	0.0005	0.0008
HP Agilent 8453	BG40101	31	8.135837			
HP Agilent 8453	BG40101	32	8.135485	8.13566	0.0002	0.0004
HP Agilent 8453	V50101	40	8.101205			
HP Agilent 8453	V50101	421	8.099820	8.10051	0.0010	0.0014
HP Agilent 8453	AMI50101	430	8.146817			
HP Agilent 8453	AMI50101	431	8.147310	8.14706	0.0003	0.0005
HP Agilent 8453	AMI901012	439	8.163682			
HP Agilent 8453	AMI901012	440	8.163284	8.16348	0.0003	0.0004
HP Agilent 8453	5501012	450	8.028386			
HP Agilent 8453	5501012	451	8.028819	8.02860	0.0003	0.0004
Average					0.00056	0.00079

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.

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: 10/21/2020 and 10/22/2022
Titration system used: Open cell
Batch 150, CRM #163 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #977 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #116 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #681 Salinity = 33.343, cert. TA = 2214.71µmol/kg.

On 10/21/2020 CRM #163 was analyzed before and after sample analysis on System 1.
On 10/22/2020 CRM #977 was analyzed before and after sample analysis on System 1.
On 10/21/2020 CRM #116 was analyzed before and after sample analysis on System 2.
On 10/22/2020 CRM #681 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	10/21/2020	09:03:26	163	2215.62	2.26
1	10/21/2020	18:14:28	163	2217.64	0.24
1	10/22/2020	08:54:43	977	2214.75	3.13
1	10/22/2020	15:52:18	977	2222.17	4.29
2	10/21/2020	13:00:29	116	2215.94	1.94
2	10/21/2020	17:46:38	116	2214.76	3.12
2	10/22/2020	08:23:09	681	2209.49	8.39
2	10/22/2020	16:05:39	681	2210.57	7.31

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 3.43 (1.35-7.75) and an average STDEV of 2.42 (0.95-5.48).

Station #	Sample ID	TA (µmol/kg)	Average	Difference	STDEV
33	330000	2313.96			
33	330000	2312.53	2313.25	1.43	1.01
RP1	RP101012	2316.19			
RP1	RP101012	2320.35	2318.27	4.16	2.94
BG4	BG40101	2323.39			
BG4	BG40101	2322.04	2322.71	1.35	0.95
V5	V50101	2326.45			
V5	V50101	2322.70	2324.57	3.76	2.66
AMI5	AMI50101	2353.75			
AMI5	AMI50101	2357.14	2355.44	3.39	2.40
AMI9	AMI901012	2382.45			
AMI9	AMI901012	2380.28	2381.36	2.17	1.53
55	5501012	2026.15			
55	5501012	2033.90	2030.02	7.75	5.48
Average				3.43	2.42

Remarks

None

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: 10/19/2020

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: 10/22/2020

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.