Cruise: WS20231
Ship: R/V Walton Smith
Expo Code: 33WA20200818
Funding Project Title: Surface OA Observations on Ships of Opportunity
Funding Project ID: SOOP-OA
Dates: August 18th – August 22nd, 2020
Chief Scientist: Ian Smith
Equipment: CTD and Flow-Through
Total number of stations: 45
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 Charles Featherstone. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
45 locations, 75 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:
45 locations, 75 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:
45 locations, 75 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	09/02/2020	2017.88	2021.71	3.83	25.0	8
AOML5	09/03/2020	2017.88	2018.12	0.24	20.0	10
AOML 6	09/01/2020	2017.88	2025.44	7.56	12.0	8
AOML 6	09/02/2020	2017.88	2021.99	4.11	12.0	9
AOML 6	09/03/2020	2017.88	2022.02	4.14	12.0	9

Analysis date: 09/02/2020
Coulometer used: DICE–CM5011-AOML 5
Blanks: 25.0 counts/min
CRM # 594 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 3.83 µmol/kg (2021.71 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 09/03/2020
Coulometer used: DICE–CM5011-AOML 5
Blanks: 20.0 counts/min
CRM # 1166 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 0.24 µmol/kg (2018.12 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 09/01/2019
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 1234 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 7.56 µmol/kg (2025.44 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 11 min.

Analysis date: 09/02/2019
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 9280 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 4.11 µmol/kg (2021.99 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 10 min.

Analysis date: 09/03/2019
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 862 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 4.14 µmol/kg (2022.024 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

…

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.52 (0.13-2.83) and average STDEV of 0.95 (0.09-2.00).

Sample ID	DIC (μmol/kg)	Average	Difference	STDEV
57101012	1643.29			
57101012	1643.16	1643.22	0.13	0.09
620000	1702.36			
620000	1705.19	1703.78	2.83	2.00
BG401012	2045.85			
BG401012	2044.90	2045.37	0.95	0.67
EB20101	2038.00			
EB20101	2037.19	2037.60	0.81	0.57
RP201012	2018.34			
RP201012	2016.98	2017.66	1.35	0.09
KW401012	2019.01			
KW401012	2016.65	2017.83	2.35	1.67
320000	2078.27			
320000	2076.05	2077.16	2.22	1.57
Average			1.52	0.95

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: 09/01/2020, 09/02/2020 and 09/03/2020
A CRM was analyzed before sample analysis.

09/01/2020, Batch 150, CRM #50, pH = 7.9260
09/02/2020, Batch 150, CRM #304, pH = 7.9395
09/03/2020, Batch 150, CRM #550, pH = 7.9391

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^{0}C)
CRMB150_050	50	33.343	20.123
CRMB150_304	304	33.343	20.038
CRMB150_550	550	33.343	20.048
470000	81	33.683	20.086
4901012	82	32.744	20.087
5101012	83	34.617	20.088
5401012	84	34.427	20.079
5501012	85	34.046	20.076
5601012	86	34.628	20.082
5701012	87	35.249	20.083
57101012	88	35.496	20.072
57101012	89	35.496	20.080
6001012	90	35.71	20.074
610000	91	36.176	20.078
620000	92	36.176	20.079
620000	93	36.176	20.086
6301012	94	36.784	20.075
6801012	95	35.954	20.072
GP50101	173	35.393	20.031
GP50105	174	35.941	20.034
GP501012	175	35.942	20.045
BG40101	176	35.92	20.038
BG401012	177	35.932	20.027
BG401012	178	35.932	20.023
BG30101	179	35.618	20.035
BG301012	180	35.627	20.042
BG20101	181	34.733	20.041
BG201012	182	34.798	20.051
BG10101	183	34.442	20.045
BG101012	184	31.287	20.046
EB10101	185	34.645	20.046
EB101012	186	34.647	20.045

EB20101	187	35.771	20.045
EB20101	188	35.771	20.056
EB201012	189	35.774	20.054
410000	190	32.694	20.055
390000	191	27.898	20.052
4501012	192	34.992	20.049
CAL60101	401	36.195	20.063
CAL601012	402	36.066	20.072
CAL50101	403	35.399	20.067
CAL501012	404	35.411	20.075
CAL40101	405	35.856	20.079
CAL401012	406	35.856	20.072
CAL30101	407	35.557	20.080
CAL301012	408	35.558	20.078
CAL20101	409	34.687	20.084
CAL201012	410	34.683	20.079
CAL101012	411	33.491	20.080
RP10101	412	35.127	20.076
RP101012	413	35.081	20.082
RP20101	414	35.188	20.082
RP201012	415	35.194	20.080
RP201012	416	35.194	20.098
RP30101	417	35.593	20.083
RP301012	418	35.576	20.085
RP40101	419	35.699	20.084
RP401012	420	35.705	20.083
UKOFF0000	461	36.348	20.044
UKMID0000	462	36.387	20.052
UKIN0000	463	36.444	20.057
KW10101	464	36.19	20.049
KW101012	465	36.194	20.051
KW20101	466	36.115	20.056
KW201012	467	36.116	20.063
KW40101	468	36.236	20.050
KW401012	469	36.237	20.050
KW401012	470	36.237	20.064
300101	471	35.728	20.056
3001012	472	35.922	20.057
3050000	473	36.1	20.050
310101	474	36.071	20.041
3101012	475	36.075	20.065

320000	476	35.392	20.050
320000	477	35.392	20.057
330101	478	35.018	20.040
3301012	479	35.034	20.052
340000	480	34.034	20.056

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.01564 (0.0005-0.0334) and an average STDEV of 0.01106 (0.0003-0.0236).

Instrument	Sample ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	57101012	88	8.15738			
HP Agilent 8453	57101012	89	8.15910	8.15824	0.0012	0.0017
HP Agilent 8453	620000	92	8.13575			
HP Agilent 8453	620000	93	8.15402	8.14489	0.0129	0.0183
HP Agilent 8453	BG401012	177	8.13336			
HP Agilent 8453	BG401012	178	8.09205	8.11270	0.0292	0.0413
HP Agilent 8453	EB20101	187	8.13458			
HP Agilent 8453	EB20101	188	8.13407	8.13432	0.0004	0.0005
HP Agilent 8453	RP201012	415	8.14795			
HP Agilent 8453	RP201012	416	8.14954	8.14875	0.0011	0.0016
HP Agilent 8453	KW401012	469	8.10566			
HP Agilent 8453	KW401012	470	8.07227	8.08896	0.0236	0.0334
HP Agilent 8453	320000	476	8.03000			
HP Agilent 8453	320000	477	8.04272	8.03636	0.0090	0.0127
Average					0.01106	0.01564

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: 09/03/2020 and 09/04/2020
Titration system used: Open cell
Batch 150, CRM #304 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #417 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #1108 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #928 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #550 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #234 Salinity = 33.343, cert. TA = 2214.71µmol/kg.

On 09/03/2020 CRM #304 was analyzed before sample analysis on System 1.
On 09/03/2020 CRM #417 was analyzed after sample analysis on System 1.
On 09/04/2020 CRM #1108 was analyzed before and after sample analysis on System 1.
On 09/03/2020 CRM #928 was analyzed before sample analysis on System 2.
On 09/03/2020 CRM #550 was analyzed after sample analysis on System 2.
On 09/04/2020 CRM #234 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	09/03/2020	08:50:00	304	2201.06	13.65
1	09/03/2020	18:42:46	417	2215.92	1.21
1	09/04/2020	08:23:46	1108	2214.13	0.58
1	09/04/2020	15:48:38	1108	2214.23	0.48
2	09/03/2020	13:04:23	928	2212.49	2.22
2	09/03/2020	18:33:52	550	2214.44	0.27
2	09/04/2020	08:48:23	234	2213.74	0.97
2	09/04/2020	15:40:38	234	2214.03	0.68

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.81 (0.08-1.71) and an average STDEV of 0.46 (0.06-1.21).

Station	Sample ID	TA (µmol/kg)	Average	Difference	STDEV
57.1	57101012	1927.15			
57.1	57101012	1888.27	1907.71	38.87	27.49
62	620000	2007.05			
62	620000	2006.47	2006.76	0.58	0.41
BG4	BG401012	2380.80			
BG4	BG401012	2382.12	2381.46	1.32	0.93
EB2	EB20101	2379.62			
EB2	EB20101	2379.54	2379.58	0.08	0.06
RP2	RP201012	2340.58			
RP2	RP201012	2341.58	2341.08	1.00	0.71
KW-4	KW401012	2352.03			
KW-4	KW401012	2351.87	2351.95	0.17	0.12
32	320000	2386.31			
32	320000	2388.02	2387.16	1.71	1.21
Average				0.81	0.46

Remarks

The first duplicate 57101012 was bad and not included in the overall average and STDEV of the TA duplicates. The first duplicate value was the TA value reported.

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: 09/15/2020
PI: Dr. Jia-Zhong Zhang
Analyzed by: Ian Smith

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: 09/04/2020
PI: Dr. Christopher Kelble
Analyzed by: Ian Smith

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.