**Cruise:** RAPID 3 **Ship:** R/V Pelican **Dates:** March 19<sup>th</sup> - March 23<sup>rd</sup>, 2018 **Expocode:** 32PE20180319 **Chief Scientist:** Stauffer **Equipment:** CTD **Total number of stations:** 9 **Location:** Gulf of Mexico

### Sample Collection

The discrete samples were collected from the CTD/rosette system onboard the R/V Pelican by Stauffer et al. The date and time listed in the data file are UTC when each sample bottle was collected.

### DIC:

9 locations, 9 samples each 500-ml, no duplicate samples.Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle numberPI: Dr. Rik WanninkhofAnalyzed by: Charles Featherstone and Patrick Mears

## pH:

9 locations, 9 samples each 500-ml, no duplicate samples.Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle numberPI: Dr. Rik WanninkhofAnalyzed by: Charles Featherstone and Patrick Mears

## TAlk:

9 locations, 9 samples each 500-ml, no duplicate samples.
Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero, Charles Featherstone and Patrick Mears

### <u>Sample Analysis</u> DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	08/09/2018	2042.41	2043.12	0.71	12.0	8
AOML 6	08/09/2018	2042.41	2046.69	4.28	15.0	8

Analysis date: 08/09/2018 Coulometer used: DICE–CM5011- AOML 5 Blanks: 12.0 counts/min CRM # 0355 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 µmol/kg, S: 33.414 CRM values measured: AOML 5: offset 0.71 µmol/kg (2043.12 µmol/kg). Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 08/09/2018 Coulometer used: DICE–CM5011- AOML 6 Blanks: 12.0 raised to15.0 counts/min CRM # 416 was used and with an assigned value of (includes both DIC and salinity): Batch 173, c: 2042.41 μmol/kg, S: 33.414 CRM values measured: AOML 6: offset 4.28 μmol/kg (2046.69 μmol/kg). Average run time, minimum run time, maximum run time: 8, 8 and 9 min.

**Reproducibility:** (# samples and average difference): No duplicate samples were collected.

CRM, salinity and HgCl2 correction applied: Salinity correction was applied using TSG salinity.

## <u>Remarks</u>

The volume correction was applied due to added HgCl<sub>2</sub> (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.

The blank on AOML 6 (08/09/2018) was raised from 12.0 to 15.0 before running the  $2^{nd}$  gas calibration.

# pH:

Analysis date: 08/09/2018 A CRM was analyzed before sample analysis. CRM #478, Batch 173 pH = 7.8767

Spectrophotometer used: HP Agilent 8453

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	Sample ID	Station #	Sample Bottle #	S	t			
	CRM 173-478	CRM 173	CRM 173	33.414	20.028			
	10106	1	46	36.300	20.053			
	10107	1	47	36.200	20.038			
ſ	20103	2	54	36.200	20.047			
ſ	20106	2	55	36.200	20.037			

Salinity and temperature of pH samples analyzed.

20112	2	56	36.200	20.031
30103	3	49	36.100	20.056
30108	3	50	36.400	20.054
30112	3	51	36.500	20.054
40112	4	52	36.500	20.044
60112	6	53	36.300	20.037
70106	7	44	35.000	20.039
70112	7	45	29.900	20.049
80107	8	43	34.900	20.043
90107	9	48	36.300	20.041
100108	10	41	31.000	20.047
100109	10	42	31.000	20.053

Reproducibility: (# samples and average difference): No duplicates were collected.

## <u>Remarks</u>

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  $20^{\circ}$ C at Full Scale (pH 0-14). The pH results are reported at  $25^{\circ}$ 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 automated syringe before DIC analysis to determine the pH.

## TAlk:

Analysis date: 08/17/2018 Titration system used: Open cell CRM #41 Batch 153, Salinity = 33.357, cert. TA = 2225.59µmol/kg. CRM #739 Batch 150, Salinity = 33.343, cert. TA = 2214.71µmol/kg

On 08/17/2018 CRM #41, Batch 153 was analyzed before the samples and CRM #739, Batch 150 was run at the end of analysis on system 1.

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 cell. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	$ \Delta CRM $
1	08/17/2018	09:28:20	41	2229.30	3.71
1	08/17/2018	19:57:15	739	2215.77	1.06

Reproducibility: No duplicates were collected.

## <u>Remarks</u>

### **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 Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

### UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.