Cruise: Equinox 0315

**Ship:** Equinox

Expo Code: MLCE20150306

Dates: March 6<sup>th</sup> – March 11<sup>th</sup>, 2015 Chief Scientist: Dr. Denis Pierrot Equipment: TSG-Flow thru system

**Total number of stations: 19** 

Location: Ft. Lauderdale, FL and the US, Virgin Islands

# **Sample Collection**

The discrete samples were collected from the TSG-flow thru system onboard the ship of opportunity Royal Caribbean Equinox by Dr. Denis Pierrot. The date and time listed in the data file are UTC when each sample bottle was collected.

#### DIC:

19 locations, 19 samples each 500-ml, 6 duplicate samples.

Sample ID#: 301, etc.; Sample bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

### pH:

19 locations, 19 samples each 500-ml, 6 duplicate samples.

Sample\_ID#: 301, etc.; Sample bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

#### TAlk:

19 locations, 19 samples each 500-ml, 6 duplicate samples.

Sample ID#: 301, etc.; Sample bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Dr. Leticia Barbero 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 3	03/24/2015	2016.65	2017.60	0.95	15.2	13

Analysis date: 03/24/2015

Coulometer used: DICE-CM5015- AOML 3

Blanks: 15.2 counts/min

CRM # 0793 was used and with an assigned value of (includes both DIC and salinity): Batch 129, c:  $2016.65 \mu mol/kg$ , S: 33.361

CRM values measured: AOML 3: offset 0.95 µmol/kg (2017.60 µmol/kg). Average run time, minimum run time, maximum run time: 13, 8 and 20 min.

**Reproducibility:** (# samples and average difference): 6 sets of duplicate samples, average difference 6.01 μmol/kg (0.65-12.21), average STDEV of 4.25 (0.46-8.63).

Instrument ID	Sample ID	Bottle #	Corrected DIC (µmol/kg)	Average	Difference	STDEV
 AOML3	1	1	2047.81	<u> </u>		
AOML3	2	2	2045.96	2046.89	1.85	1.31
AOML3	6	6	2069.12			
AOML3	7	7	2074.75	2071.93	5.63	3.98
AOML3	12	12	2052.74			
AOML3	13	13	2040.54	2046.64	12.21	8.63
AOMI 2	1.4	1.4	2046.04			
AOML3 AOML3	14 15	14 15	2046.04 2037.81	2041.93	8.23	5.82
AOML3	16	16	2025.35			
AOML3	17	17	2032.85	2029.10	7.51	5.31
AOML3	18	18	2030.73			
AOML3	19	19	2030.08	2030.40	0.65	0.46
Average					6.01	4.25

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

### Remarks

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. End blank (AOML 3 = 27.5).

The samples were analyzed using the DICE (AOML 3) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

Duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

# pH:

Analysis date: 03/24/2015

Spectrophotometer used: HP Agilent 8453

**Reproducibility:** (# samples and average difference): 6 sets of duplicate samples, average difference 0.0052 (0.0002-0.0106), average STDEV of 0.0037 (0.0001-0.0075).

	Bottle	Sample				
System	#	ΙĎ	рН	Average	Difference	STDEV
HP Agilent 8453	1	1	8.1261			
HP Agilent 8453	2	2	8.1331	8.1296	0.0070	0.0050
HP Agilent 8453	6	6	8.1625			
HP Agilent 8453	7	7	8.1519	8.1572	0.0106	0.0075
HP Agilent 8453	12	12	8.1566			
HP Agilent 8453	13	13	8.1613	8.1590	0.0047	0.0033
HP Agilent 8453	14	14	8.1610			
HP Agilent 8453	15	15	8.1612	8.1611	0.0002	0.0001
HP Agilent 8453	16	16	8.1583			
HP Agilent 8453	17	17	8.1534	8.1558	0.0049	0.0035
HP Agilent 8453	18	18	8.1568			
HP Agilent 8453	19	19	8.1609	8.1589	0.0041	0.0029
Average					0.0052	0.0037

# 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<sup>0</sup>C at Full Scale (pH 0-14).

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 syringe before DIC analysis to determine the pH.

Duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

#### TAlk:

The results posted are analyses from the same sample bottles used for DIC and pH.

Analysis dates: 03/25/2015 Titration system used: Open cell

CRM batch: 129, S = 33.361, certified TA = 2237.32  $\mu$ mol/kg

2 CRM samples were run on each cell, before and after the seawater samples. The TA for the water samples was corrected using the averaged ratios between the certified and measured values of the 2 CRMs run on each cell. The following table shows the CRM measurements for each cell.

Cell Syster	m Date	Time	Bottle #	TA	\Delta CRM
1	3/25/2015	11:58:09	201	2219.28	
1	3/25/2015	16:38:22	795	2222.28	3.00
2	3/25/2015	12:08:25	201	2211.12	
2	3/25/2015	16:38:54	795	2214.66	3.54
				Average	3.27
				Std. Dev.	0.38

**Reproducibility:** 5 sets of duplicate samples were run in the cell 1 and one set of duplicates was run on cell 2, with an average absolute difference of 1.68  $\mu$ mol/kg (0.03 – 2.96), and a Standard Deviation of 1.06. The duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

Bottle #	System	Date	Time	S	TA	Difference	Comments
1	2	3/25/2015	12:39:09	36.38	2378.04	1.67	
2	2	3/25/2015	13:01:10	36.36	2379.71		
6	1	3/25/2015	12:16:44	36.66	2398.27	0.03	
7	1	3/25/2015	12:40:53	36.66	2398.30		
12	1	3/25/2015	13:03:00	36.14	2369.52	2.96	
13	1	3/25/2015	13:25:40	36.17	2372.48		
14	1	3/25/2015	13:52:44	36.13	2370.84	2.70	
15	1	3/25/2015	14:17:48	36.16	2373.54		
16	1	3/25/2015	14:41:17	35.88	2354.90	1.48	

17	1	3/25/2015	15:04:36	35.88	2356.38	
18	1	3/25/2015	15:26:18	35.89	2355.31	1.26
19	1	3/25/2015	15:55:31	35.88	2356.57	

Average	1.68
Std. Dev.	1.06

# Remarks

The two systems behaved well during the analyses.

Duplicates were sampled from the ships TSG flow thru system 1 to 3 minutes apart.

## **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 May 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. The ship code in the Expocode was corrected (EQNX => MLCE). Additionally, pH results were recalculated to 20 and 25 degrees Celsius.