**Cruise:** EQNX_20160415
**Ship:** Royal Caribbean Equinox
**Expocode:** MLCE20160415
**Dates:** April 15th – April 25th, 2016
**Chief Scientist:** Dr. Denis Pierrot
**Equipment**: TSG-Flow thru system
**Total number of stations:** 36
**Location:** Ft. Lauderdale, FL to Lisbon, Portugal

## ***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:**
36 locations, 40 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

**pH:**
36 locations, 40 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

**TAlk:**
36 locations, 40 samples each 500-ml, 4 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 | 07/18/2016 | 2031.53 | 2031.26 | 0.27 | 26.0 | 15 |
| AOML 3 | 07/19/2016 | 2031.53 | 2033.04 | 1.51 | 26.0 | 14 |
| AOML 4 | 07/18/2016 | 2031.53 | 2028.56 | 2.97 | 28.0 | 13 |

Analysis date: 07/18/2016
Coulometer used: DICE–CM5015- AOML 3
Blanks: 14.4 counts/min and raised to 26.0 counts/min before CRM analysis
CRM # 1235 was used and with an assigned value of (includes both DIC and salinity):
Batch 144, c: 2031.53 µmol/kg, S: 33.571
CRM values measured: AOML 3: offset 0.27 µmol/kg (2031.26 µmol/kg).
Average run time, minimum run time, maximum run time: 15, 12 and 19 min.

Analysis date: 07/19/2016
Coulometer used: DICE–CM5015- AOML 3
Blanks: 12.0 counts/min and raised to 26.0 counts/min before CRM analysis
CRM # 1110 was used and with an assigned value of (includes both DIC and salinity):
Batch 144, c: 2031.53 µmol/kg, S: 33.571
CRM values measured: AOML 3: offset 1.51 µmol/kg (2033.04 µmol/kg).
Average run time, minimum run time, maximum run time: 14, 11 and 16 min.

Analysis date: 07/19/2016
Coulometer used: DICE–CM5015- AOML 4
Blanks: 23.9 counts/min and raised to 28.0 counts/min before CRM analysis
CRM # 236 was used and with an assigned value of (includes both DIC and salinity):
Batch 144, c: 2031.53 µmol/kg, S: 33.571
CRM values measured: AOML 4: offset 2.97 µmol/kg (2028.56 µmol/kg).
Average run time, minimum run time, maximum run time: 13, 12 and 16 min.

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples, average difference 5.00 µmol/kg (3.62-6.03), average STDEV of 3.54 (2.56-4.26).

| Instrument ID | Sample ID | Bottle # | Corrected DIC (µmol/kg) | Average | Difference | STDEV |
|---|---|---|---|---|---|---|
| AOML3 | 10000 | 1 | 2036.64 | | | |
| AOML4 | 20000 | 2 | 2042.53 | 2039.59 | 5.88 | 4.16 |
| AOML4 | 80000 | 8 | 2081.93 | | | |
| AOML3 | 90000 | 9 | 2085.55 | 2083.74 | 3.62 | 2.56 |
| AOML3 | 260000 | 26 | 2115.68 | | | |
| AOML3 | 270000 | 27 | 2109.65 | 2112.66 | 6.03 | 4.26 |
| AOML3 | 820000 | 82 | 2123.00 | | | |
| AOML3 | 830000 | 83 | 2118.53 | 2120.76 | 4.47 | 3.16 |
| Average | | | | | 5.00 | 3.54 |

CRM, salinity and HgCl2 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.

The samples were analyzed using the DICE (AOML 3 & AOML 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

**pH:**

Analysis date: 07/18/2016 and 07/19/2016
Spectrophotometer used: HP Agilent 8453

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples, average difference 0.0061 (0.0019-0.0125), average STDEV of 0.0043 (0.0013-0.0088).

| System | Sample ID | Bottle # | pH | Average | Difference | STDEV |
|---|---|---|---|---|---|---|
| HP Agilent 8453 | 10000 | 1 | 8.1387 | | | |
| HP Agilent 8453 | 20000 | 2 | 8.1405 | 8.1396 | 0.0019 | 0.0013 |
| HP Agilent 8453 | 80000 | 8 | 8.1183 | | | |
| HP Agilent 8453 | 90000 | 9 | 8.1153 | 8.1168 | 0.0030 | 0.0021 |
| HP Agilent 8453 | 260000 | 26 | 8.0382 | | | |
| HP Agilent 8453 | 270000 | 27 | 8.0312 | 8.0347 | 0.0071 | 0.0050 |
| HP Agilent 8453 | 820000 | 82 | 8.0238 | | | |
| HP Agilent 8453 | 830000 | 83 | 8.0114 | 8.0176 | 0.0125 | 0.0088 |
| Average | | | | | 0.0061 | 0.0043 |

Temperature measured during pH analysis

| Sample ID | Sample BTL # | Btl. Temp | Start Cell ($^0$C) | End Cell ($^0$C) | Differ Start to End Cell ($^0$C) |
|---|---|---|---|---|---|
| 10000 | 1 | 19.821 | 20.918 | 21.648 | 0.730 |
| 20000 | 2 | 19.802 | 20.712 | 21.509 | 0.797 |
| 30000 | 3 | 20.004 | 20.907 | 21.694 | 0.787 |
| 40000 | 4 | 20.009 | 20.949 | 21.862 | 0.913 |
| 50000 | 5 | 19.986 | 20.789 | 21.911 | 1.122 |
| 60000 | 6 | 20.303 | 20.965 | 21.582 | 0.617 |

| | | | | | |
|---|---|---|---|---|---|
| 70000 | 7 | 20.070 | 20.898 | 21.798 | 0.900 |
| 80000 | 8 | 19.958 | 20.927 | 21.926 | 0.999 |
| 90000 | 9 | 19.974 | 20.886 | 21.735 | 0.849 |
| 100000 | 10 | 19.951 | 20.828 | 21.939 | 1.111 |
| 110000 | 11 | 20.004 | 20.855 | 21.962 | 1.107 |
| 120000 | 12 | 20.068 | 20.901 | 21.736 | 0.835 |
| 130000 | 13 | 20.126 | 20.952 | 21.618 | 0.666 |
| 140000 | 14 | 20.012 | 20.961 | 21.952 | 0.991 |
| 160000 | 16 | 20.152 | 20.951 | 21.804 | 0.853 |
| 200000 | 17 | 19.960 | 20.932 | 21.922 | 0.990 |
| 170000 | 18 | 19.985 | 20.865 | 21.810 | 0.945 |
| 220000 | 19 | 20.029 | 20.986 | 21.880 | 0.894 |
| 190000 | 20 | 19.916 | 20.849 | 21.703 | 0.854 |
| 210000 | 21 | 19.964 | 20.805 | 21.714 | 0.909 |
| 230000 | 22 | 19.954 | 20.982 | 21.972 | 0.990 |
| 250000 | 23 | 20.003 | 20.987 | 21.933 | 0.946 |
| 270000 | 24 | 20.002 | 20.892 | 21.919 | 1.027 |
| 310000 | 25 | 20.024 | 20.838 | 21.796 | 0.958 |
| 240000 | 26 | 20.037 | 20.838 | 21.916 | 1.078 |
| 260000 | 27 | 19.957 | 20.808 | 21.779 | 0.971 |
| 290000 | 29 | 19.949 | 20.904 | 21.753 | 0.849 |
| 350000 | 31 | 20.109 | 21.076 | 21.963 | 0.887 |
| 370000 | 33 | 20.043 | 20.947 | 21.674 | 0.727 |
| 390000 | 35 | 20.07 | 21.054 | 21.927 | 0.873 |
| 330000 | 37 | 19.863 | 20.815 | 21.699 | 0.884 |
| 810000 | 39 | 20.131 | 20.962 | 21.896 | 0.934 |
| 820000 | 81 | 19.897 | 20.877 | 21.594 | 0.717 |
| 830000 | 82 | 18.896 | 20.695 | 21.680 | 0.985 |
| 880000 | 83 | 20.024 | 20.935 | 21.723 | 0.788 |
| 890000 | 88 | 20.045 | 20.957 | 21.826 | 0.869 |
| 900000 | 89 | 19.956 | 20.822 | 21.630 | 0.808 |
| 910000 | 90 | 20.044 | 20.862 | 21.655 | 0.793 |
| 1740000 | 91 | 19.987 | 20.818 | 21.740 | 0.922 |
| 180000 | 174 | 19.984 | 20.708 | 21.686 | 0.978 |
| Average | | 19.977 | 20.890 | 21.787 | 0.896 |

**Remarks**

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

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 $20^0$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.

**TAlk:**

Analysis date: 7/28/2016
Titration system used: Open cell
CRM Batch 120, Salinity = 33.072, cert. TA = 2208.34 µmol/kg.

On 7/28/2016 one CRM was analyzed before the samples and another CRM was run at the end of analysis for each system.
The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on each cell. The following table shows the CRM measurements for each day and cell.

| Cell System | Date | Time | Bottle # | TA | \|ΔCRM\| |
|---|---|---|---|---|---|
| 1 | 07/28/2016 | 11:26:45 | 434 | 2207.70 | |
| 1 | 07/28/2016 | 19:57:20 | 434 | 2211.51 | 3.81 |
| 2 | 07/28/2016 | 11:19:11 | 268 | 2182.56 | |
| 2 | 07/28/2016 | 19:50:56 | 268 | 2183.19 | 0.63 |

**Reproducibility:** (# samples and average difference): 4 duplicate samples were collected with an average difference 3.78 µmol/kg (0.34 – 9.89) and an average STDEV of 2.67 (0.24 – 6.99).

| System | Sample ID | TAlk | Average | Difference | STDEV |
|---|---|---|---|---|---|
| System 2 | 10000 | 2368.62 | 2373.56 | 9.89 | 6.99 |
| System 1 | 20000 | 2378.51 | | | |
| System 1 | 80000 | 2400.61 | 2401.45 | 1.68 | 1.19 |
| System 2 | 90000 | 2402.29 | | | |
| System 1 | 260000 | 2377.77 | 2376.16 | 3.21 | 2.27 |
| System 2 | 270000 | 2374.56 | | | |
| System 2 | 820000 | 2365.48 | 2365.65 | 0.34 | 0.24 |
| System 1 | 830000 | 2365.83 | | | |

| | | |
|---|---|---|
| Average | 3.78 | 2.67 |

**Remarks**

The CRM measurement for each day was used to correct the data for that day only. Both systems worked well.

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

***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.

The salinity and temperature were taken from the UW pCO2 system. The salinities were used in the DIC, Talk and pH calculations.

Corresponding UW pCO2 data can be found at the following website
http://www.aoml.noaa.gov/ocd/ocdweb/occ.html

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.