Cruise: DE1202
Ship: R/V Delaware II
Dates: Feb. 2012
Chief Scientist: Jerry Prezioso
Equipment: CTD samples collected
Total number of stations: 120

Sample Collection

Locations: North Atlantic from 35.9883 N to 43.855 N and 65. 7733 W to 75.533 W.
Samplins Dates (mm/dd/yyyy): 02/06/2012 – 02/19/2012

The discrete samples were from Niskin bottles attached to a 24 bottle configured rosette.
The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
 Locations, 120 samples each 500-ml, 15 sets of duplicate samples; 29 sets of duplicates
from same depth different Niskin bottles; 4 sets of triplicates from same depth different
Niskin bottles.
Sample_ID#: 1-120
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

TAlk:
 Locations, 120 samples each 500-ml, 15 sets of duplicate samples; 29 sets of duplicates
from same depth different Niskin bottles; 4 sets of triplicates from same depth different
Niskin bottles.
Sample_ID#: 1-120
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero

Sample Analysis

DIC:
Analysis date: April 16, 17, 18 and 20, 2012
Coulometer used: AOML 4
Blanks: 20.1, 15.7, 12.0 and 18.0 counts/min
CRM # used and assigned value (include both DIC and salinity): Batch 112, c: 2011.1
µmol/kg, S: 33.305
CRM value measured: AOML 4: offset 0.11 µmol/kg (2010.99 µmol/kg), offset 1.53
µmol/kg (2009.57 µmol/kg), offset 0.95 µmol/kg (2010.15 µmol/kg) and offset 0.20
µmol/kg (2010.90 µmol/kg).
Average run time, minimum run time, maximum run time: 10, 8 and 20 min; 16, 8 and
20 min; 12, 8 and 20 min and 17, 11 and 20 min.

Analysis date: April 16, 17 and 18, 2012
Coulometer used: AOML 3
Blanks: 21.0, 12.0 and 24.6 counts/min
CRM # used and assigned value (include both DIC and salinity): Batch 112, c: 2011.1 µmol/kg, S: 33.305
CRM value measured: AOML 3: offset 1.13 µmol/kg (2009.97 µmol/kg), offset 2.07 µmol/kg (2009.03 µmol/kg) and offset 1.67 µmol/kg (2009.43 µmol/kg).
Average run time, minimum run time, maximum run time: 17, 11 and 20 min; 19, 17 and 20 min; 18, 10 and 20 min.

Reproducibility: (# samples and average difference): 15 sets of duplicate samples, average difference 2.39 µmol/kg, average STDEV of 1.69 (0.09-3.37); 29 sets of duplicates from same depth different Niskin bottles, average difference 2.18 µmol/kg, average STDEV of 1.54 (0.10-9.61); 4 sets of triplicates from same depth different Niskin bottles, average difference 2.99 µmol/kg, average STDEV 2.99 (2.19-3.99).

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

Remarks-

The volume correction was applied due to added HgCl2 (Measured DIC*1.00037).
The first CRM of each cell was used for a CRM correction.

The DIC instrument was stable: the gas loop and CRM values did not change significantly through out the life span of each cell. Also cells from separate days gave calibration values of similar magnitude. The calibration factor for AOML 3 was set manually to 1.00000 for each day.

The blanks (AOML 4) on 04-16-2012 were raised from 20.1 to 26 after the 1st sample; on 04-17-2012 were raised from 15.7 to 25 before the CRM and again to 35 after the second sample; on 04-18-2012 was raised from 12 to 26 before the CRM; on 04-20-2012 was raised from 20 to 25 before the CRM and again to 35 after the 1st samples.

The blanks (AOML 3) on 04-16-2012 were raised from 21 to 28 before the CRM and again to 35 after the 3rd sample; on 04-17-2012 were raised from 12 to 25 before the CRM and again to 35 after the 2nd sample; on 04-18-2012 were raised from 24.6 to 30 before the CRM and again to 40 after the 1st sample.

Blanks were raised due to 20 minute titrations.

On 04-18-2012 on AOML 4 a second CRM was run after the first sample because the original CRM number was entered incorrectly.

Approximately 80 mL of sample was extracted from each DIC sample bottle by syringe before DIC analysis to determine the pH.

TAlk:

The results posted are analyses from the same sample bottles used for DIC.
Analysis date: 6/28/2012 – 8/7/2013
Titration system used: Open cell
CRM analysis (values in µmol/kg):

Batch	Certified TA	Average Difference	Standard Deviation
112	2223.26	6.84	5.69
108	2218.00	8.67	1.91

Reproducibility: (# samples and average difference):
  Duplicates from same Niskin:
    15 sets, average difference 5.77 µmol/kg (range: 0.68 – 32.47)
  Duplicates from different Niskin:
    29 sets, average difference 5.66 µmol/ kg (range: 0.10 – 14.29)
  Triplicates from different Niskin:
    4 sets, average difference 3.34 µmol/kg (range: 1.76 – 5.13)

Remarks-
 Analysis of CRM batch 112 showed greater variability than batch 108. CRM bottles from batch 112 were previously analyzed on our SOMMA system and we suspect some contamination from the SOMMA sampling tubing. Batch 108 behaved much better with an overall standard deviation of 1.91 µmol/kg for 13 measurements.
Only the first CRM was used to correct the data. The second CRM served to verify that no major drift had occurred to the system.
The CRM measurement for each day was used to correct the data for that day only.

pH:

Reproducibility: (# samples and average difference):
  Duplicates from same Niskin:
    15 sets, average difference 0.005 (range: 0 – 0.011)
  Duplicates from different Niskin:
    29 sets, average difference 0.005 (range: 0 – 0.027)
  Triplicates from different Niskin:
    4 sets, average difference 0.006 (range: 0 – 0.011)

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 20.0 $^{\circ}$C and reported on the Total Scale. However, the cells were not thermostated during analysis. No correction for the addition of the dye was applied.

Comments

The latitude, longitude and salinity reported with the DIC and TAlk measurements were taken from the Niskin bottle 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 bottle number for the discrete samples.

Sample number 43 was listed as a bad sample due to a broken stopper as per the log sheet.

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 samples were run for Dr. Jon Hare of the NEFSC as part of our coastal ocean acidification monitoring project.

UPDATE JULY 2015

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Niskin information was not available on the nutrient file and merging has been done based on sample depth, assuming all Niskin bottles tripped at the same depth would have the same (or close enough) nutrient values. We have kept the salinity and temperature values used for the carbon parameter calculations. Comparison with calibrated and corrected salinity values provided by Hare's group indicate that the average salinity difference (absolute difference) between preliminary and corrected values was 0.01 ± 0.03.
The following columns have been added:
Depth_station, CTDPRS, Sigma-Theta, CTDOXYmg, CTDOXY, SILCAT, NITRIT+NITRAT, AMMONIA, and PHSPHT.