Cruise: PC1207 Ship: R/V Pisces

Dates: 27 October- 14 November, 2012

Expocode: 334B20121026 Chief Scientist: Jerry Prezioso Equipment: CTD rosette Total number of stations: 15

Sample Collection

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette onboard the ship by Christopher Taylor of the NE Fisheries science center. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

15 locations, 51 samples each 500-ml, 6 sets of duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

pH:

15 locations, 51 samples each 500-ml, 6 sets of duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone

TAlk:

15 locations, 51 samples each 500-ml, 6 sets of duplicate samples.

Sample ID#:

PI: Dr. Rik Wanninkhof

Analyzed by: Dr. Leticia Barbero

<u>Sample Analysis</u>

DIC:

Analysis date: January 10th and 11th, 2013

Coulometer used: AOML 4

Blanks: 26.7 and 20.0 counts/min

CRM # 0575 and 1053 were used and with an assigned value of (includes both DIC and

salinity): Batch 112, c: 2011.09 µmol/kg, S: 33.305

CRM values measured: AOML 4: offset 1.85 µmol/kg (2009.24 µmol/kg) and offset

2.44 μmol/kg (2008.65 μmol/kg).

Average run time, minimum run time, maximum run time: 11, 8 and 20 min; 9, 8 and 11

min.

Analysis date: January 10th and 11th, 2013

Coulometer used: AOML 3

Blanks: 29.7 and 30.0 counts/min

CRM # 0391 and 0663 were used and with an assigned value of (includes both DIC and

salinity): Batch 112, c: 2011.09 μmol/kg, S: 33.305

CRM values measured: AOML 3: offset 1.49 μ mol/kg (2009.60 μ mol/kg) and offset 0.41 μ mol/kg (2010.68 μ mol/kg).

Average run time, minimum run time, maximum run time: 16, 11 and 20 min; 14, 12 and 16 min.

Reproducibility: (# samples and average difference): 6 sets of duplicate samples, average difference 3.40 µmol/kg (0.87-8.77), average STDEV of 2.40 (0.62-6.20).

		0				Sample Start	Time
Cuatana	ID	Corr.	A	Difference	CTDEV	Time	Difference
System	ID	DIC	Avg	Difference	STDEV	(hr:min)	(hr:min)
AOML3	581403	2182.73	2187.12	8.77	6.20	11:25	08:57
AOML4	581403	2191.50				20:22	
AOML4	1142901	2056.54	2059.12	5.16	3.65	10:58	09:00
AOML4	1142901	2061.70				19:58	
AOML3	170305	1991.21	1992.11	1.80	1.27	15:33	03:13
AOML3	170306	1993.01				18:46	
AOML4	1002809	2077.29	2078.68	2.78	1.97	13:13	04:22
AOML4	1002812	2080.07				19:35	
, (O.I.) .	.0020.2	2000.01					
AOML4	1373203	2059.27	2059.78	1.02	0.72	18:14	00:19
AOML4	1373204	2060.29	2000.70	1.02	0.7.2	18:33	
/ CIVIL-I	1070204	2000.20					
AOML3	1483307	2064.99	2065.43	0.87	0.62	10:19	00:53
AOML4	1483308	2065.86	2000.40	0.01	0.02	09:26	
AOIVIL4	1400000	2005.00				00.20	
0				2.40	0.40		
Overall				3.40	2.40		

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 CRM offset (certified – measured values) was added to the sample measurements.

pH:

Reproducibility: (# samples and average difference): 6 sets of duplicate samples, average difference 0.0073 (0.0001-0.0169), average STDEV of 0.0052 (0.0001-0.0108). The first two sets of duplicates were drawn from the same niskin; the next four sets of duplicates were drawn from different niskins at the same depth.

Instrument	Sample ID	Bottle #	pH@20deeg	Average	STDEV	Difference
Same niskin	Same depth					
HP Agilent 8453	581403	512	7.7648			
HP Agilent 8453	581403	513	7.7479	7.7564	0.0120	0.0169
HP Agilent 8453	1142901	8	7.9202			
HP Agilent 8453	1142901	9	7.9049	7.9125	0.0108	0.0153
Different niskin	Same depth					
HP Agilent 8453	170305	509	7.9651			
HP Agilent 8453	170306	510	7.9588	7.9619	0.0045	0.0063
HP Agilent 8453	1002809	6	8.0542			
HP Agilent 8453	1002812	7	8.0577	8.0560	0.0024	0.0034
HP Agilent 8453	1373203	19	7.8822			
HP Agilent 8453	1373204	20	7.8823	7.8823	0.0001	0.0001
HP Agilent 8453	1483307	523	7.9423			
HP Agilent 8453	1483308	524	7.9441	7.9432	0.0013	0.0018
			Average		0.0052	0.0073

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 °C and reported on the Total Scale. However, the cells were not thermostated during analysis.

TAlk:

The results posted are analyses from the same sample bottles used for DIC. Analysis date: 7/2 - 7/26 2013

Titration system used: Open cell

CRM # used and assigned value:

Date	Date Batch		Certified TA	S	Measured TA
7/2/13	108	316	2218.00	33.224	2212.79
7/2/13	108	316	2218.00	33.224	2214.32
7/5/13	108	544	2218.00	33.224	2215.17
7/5/13	108	544	2218.00	33.224	2217.43
7/9/13	108	623	2218.00	33.224	2214.12
7/9/13	108	623	2218.00	33.224	2214.01
7/25/13	108	1005	2218.00	33.224	2211.48
7/25/13	108	1005	2218.00	33.224	2209.67
7/26/13	108	395	2218.00	33.224	2211.68
7/26/13	112	198	2223.26	33.305	2222.27

Reproducibility: No samples were measured twice.

Remarks-

The CRM measurements were averaged on a per day basis to correct the sample values. Each sample was corrected according to:

$$TA(final) = TA(meas) * CRM(cert.)/CRM(meas)$$

Reproducibility of junks was good.

The difference between CRMs run at beginning and end of analyses was less than 2 μ mol/kg off except when a previously opened CRM from batch 112 was used.

Comments

The latitude, longitude and salinity reported with the DIC, pH 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 station, cast number and Niskin bottle number for the

discrete samples.

The DIC instruments were 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. AOML 3 had a high blank (152 counts/min) at the end of sample analysis on 01/10/2013. The last four samples had 20 minute titrations with jumpy counts indicating a possible leak.

The blank (AOML 4) on 01-11-2013 was raised from 12.0 to 20.0 before the 1st gas loop calibration.

The blank (AOML 3) on 01-11-2013 was raised from 28.0 to 30.0 before the 1st gas loop calibration.

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

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 AUGUST 2015

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Where samples for carbon parameters and nutrients were drawn from different Niskin bottles, 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 ± 0.01 .

The following columns have been added:

Date_UTC, Depth_station, Depth_sampling, CTDPRS, Sigma-Theta, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT and Niskin_nuts

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.