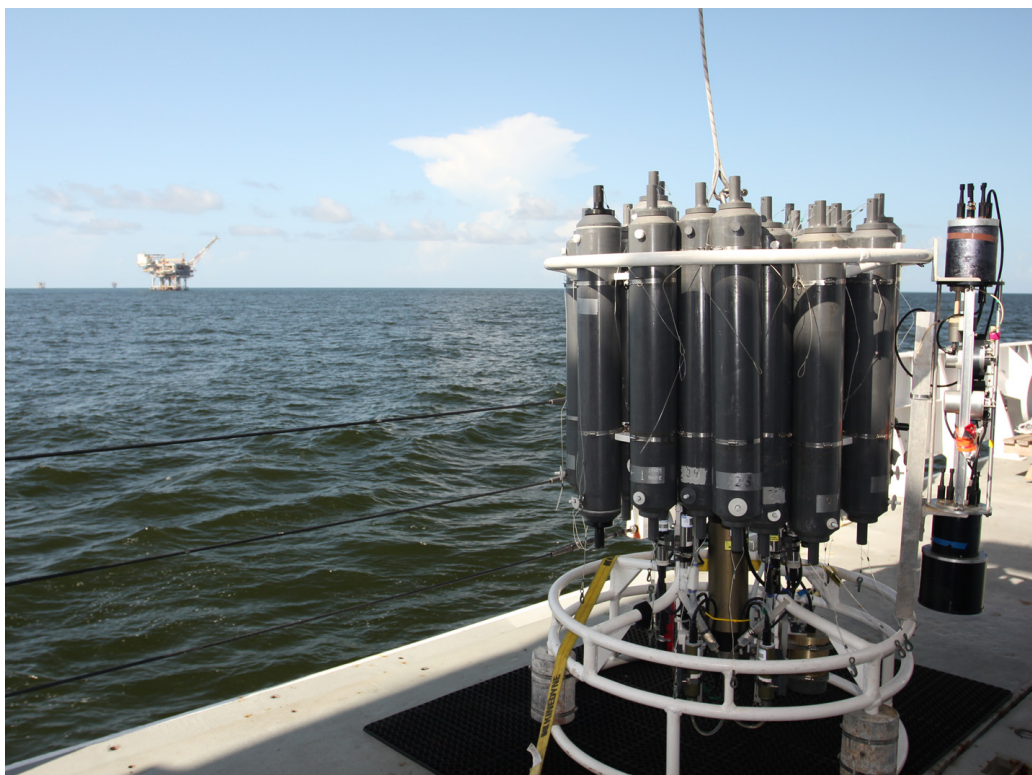


Cruise Report

Gulf of Mexico and East Coast Carbon Cruise #2 (GOMECC-2)



**R/V Ronald H. Brown, RB-12-03
21 July – 13 August, 2012**

Miami, FL – Boston, MA USA

Chief Scientists: Rik Wanninkhof, Michelle Wood and Leticia Barbero

NOAA Atlantic Oceanographic and Meteorological Laboratory

Table of Contents

1.- SUMMARY	3
2.- INTRODUCTION	4
3.- DESCRIPTION OF MEASUREMENTS FROM VERTICAL PROFILES.....	7
3.1 CTD/HYDROGRAPHIC MEASUREMENTS	7
3.2 DISCRETE SALINITY MEASUREMENTS.....	35
3.3 OXYGEN MEASUREMENTS	36
3.4 NUTRIENT MEASUREMENTS	38
3.5 DIC MEASUREMENTS.....	40
3.6 DISCRETE PCO ₂ MEASUREMENTS.....	42
3.7 TOTAL ALKALINITY MEASUREMENTS.....	45
3.8 PH AND CARBONATE MEASUREMENTS.....	47
3.9 PHYTOPLANKTON COMMUNITY DISTRIBUTION ACROSS THE CONTINENTAL MARGINS.....	51
3.10 DISSOLVED ORGANIC CARBON (DOC) AND COLORED DISSOLVED ORGANIC MATTER (CDOM)....	53
4.- UNDERWAY MEASUREMENTS.....	54
4.1 UNDERWAY PCO ₂ ANALYSES.....	54
4.2 AMMONIA UNDERWAY MEASUREMENTS	55
4.3 UNDERWAY MEASUREMENTS OF PCO ₂ , TCO ₂ , AND PH USING A MULTI-PARAMETER INORGANIC CARBON ANALYZER (MICA).....	58
4.4 OCEAN COLOR MEASUREMENTS	59
5.- OTHER MEASUREMENTS	61
5.1 PH PROFILER.....	61
5.2 ABOVE-WATER REFLECTANCE MEASUREMENTS.....	62
6.- ACKNOWLEDGEMENTS:	66

Leticia Ba
Deleted:

1.- Summary

This report describes the second Gulf of Mexico and East Coast Carbon (GOMECC-2) Cruise on board the R/V *Ronald H. Brown* from Miami, into the Gulf of Mexico and then along the East US coast to Boston. The effort was in support of the coastal monitoring and research objectives of the NOAA Ocean Acidification Program (OAP). The cruise was designed to obtain a snapshot of key carbon, physical, and biogeochemical parameters as they relate to ocean acidification (OA) in the coastal realm. This was the second occupation, with the first occurring in 2007, and complement mooring time series and other regional OA activities. The cruise included a series of 8 transects approximately orthogonal to the Gulf of Mexico and Atlantic coasts and a comprehensive set of underway measurements along the entire transect (Figure 1). Full water column CTD/rosette stations were occupied at 93 specified locations. A total of 22 scientists from AOML and other NOAA line offices and universities participated on the 24-day cruise which departed from Miami, FL on 21 July, and arrived on schedule in Boston, Massachusetts on 13 August. Water samples were collected from the 24-bottle rosette at each station and analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon (DIC), total alkalinity, partial pressure of carbon dioxide ($p\text{CO}_2$), pH, dissolved organic matter, colored dissolved organic matter, and phytoplankton pigments. Underway systems were in operation for measuring atmospheric CO_2 and near-surface water $p\text{CO}_2$, DIC, pH, ammonia (NH_3), and bio-optical properties. An *in situ* spectrophotometric pH profiler was used with the CTD to measure pH profiles to a depth of 1000m. During the transit in the Gulf of Mexico, the ship encountered a catastrophic auxiliary generator failure, which was dealt with in a professional fashion. No loss of operational time was experienced due to the failure. All cruise objectives described in the project instructions (downloadable from <http://www.aoml.noaa.gov/ocd/gcc/GOMECC2/>) and detailed below were achieved.

Madalyn Meaker, from the University of Southern Mississippi, wrote a blog about her experience onboard during the cruise. A copy of this blog has been archived at the cruise website cited above.

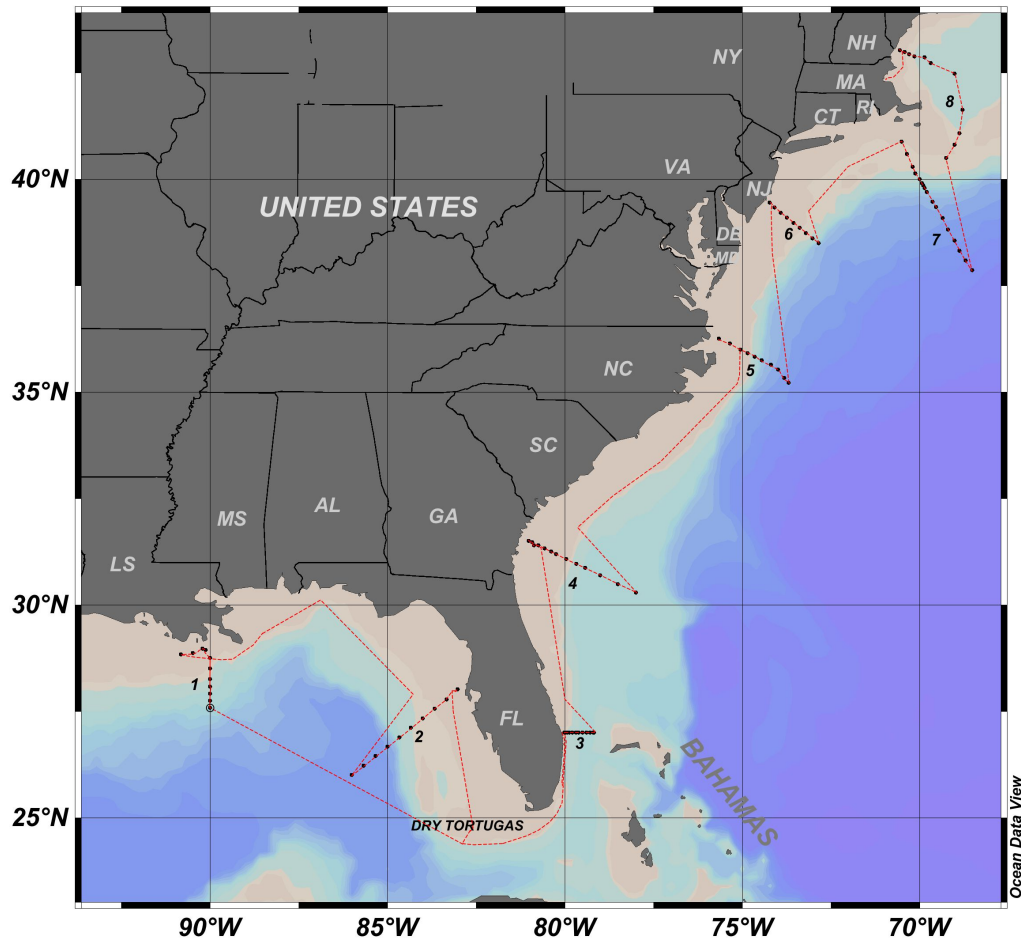


Figure 1 – Cruise track (red line) and CTD station locations (black circles) visited during the GOMECC-2 cruise. The numbers identify the different transects: 1) Louisiana Line, 2) Tampa Line, 3) 27 N Line, 4) Georgia Line, 5) Cape Hatteras Line, 6) New Jersey Line, 7) Line W, and 8) New Hampshire Line.

2.- Introduction

NOAA conducted the second Gulf of Mexico and East Coast Carbon (GOMECC-2) Cruise (Figure 1) along the coast of the Gulf of Mexico and the Atlantic coast to study ocean acidification (OA) processes in the coastal zone over a wide range of oceanographic, and biogeochemical conditions. The coastal ocean is emphasized in NOAA OA monitoring and research as it is believed to be particularly vulnerable to ocean acidification processes and contains many ecosystems of great socioeconomic values (REF- OA plan). It is a conduit for transport of terrestrial material from the land to the open ocean and its specific biological productivity is on average about three times larger than the average open-ocean values. It is also the region where the interior ocean interacts with the bottom boundary, leading to enhancements of many chemical, biological and physical processes in mid-water regions of the ocean. These processes contribute to the large variability encountered and associated with ecosystem stress. The major goal of the cruise was to identify the magnitude and controls of ocean acidification

in the U.S. coastal regime, along with their magnitudes, and scales of biogeochemical parameters impacting ocean acidification. The coastal zone must be well quantified regarding carbon speciation in order to make reasonable projections of future levels of ocean acidification.

To address this problem, the PMEL and AOML Marine CO₂ Programs have initiated dedicated coastal carbon research cruises for the West, East and Gulf Coasts of the USA. This program is designed to establish baseline observational fields for carbon system parameters, provide comparative data for observations from other projects, and develop a set of hydrographic transects of full water column measurements to be re-occupied over time for studies of inter-annual changes in physical, chemical and biological characteristics of the coastal ocean as they impact ocean acidification.

This GOMECC-2 cruise aboard the R/V *Ronald H. Brown*, is the second of what were originally planned to be a biennial sequence of observations and studies of carbon and related biogeochemical parameters in the dynamic coastal ocean region above/adjacent to the continental shelf along the coast of the Gulf of Mexico and East coast of the North American continent. Data from this cruise will provide a robust observational framework to monitor long-term ocean acidification trends on inter-annual timescales, and determine the temporal variability of the inorganic carbon system and its relationship to biological and physical processes in the coastal ocean and their capacity to withstand the onset of ocean acidification.

The GOMECC RB-12-03 cruise was supported by the NOAA/OAR Ocean Acidification Program (OAP). Twenty-four scientists representing 6 universities and 2 NOAA line offices participated on the cruise (Table 1) covering the Gulf of Mexico and eastern North American continental shelf region from the Florida Keys in the south to Portsmouth, NH in the north. The R/V *Ronald H. Brown* departed Miami, FL on 21 July, 2012. The cruise completed a series of 8 transects approximately orthogonal to the coast (Figure 1). Full water column CTD/rosette stations were occupied at specified locations along each of these transects. Twenty-four 10L Niskin-type bottles were used to collect water samples from throughout the water column at each station. Each Niskin-type bottle was sub-sampled on deck for a variety of analyses, including salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, pCO₂, dissolved organic matter, colored dissolved organic matter, and phytoplankton pigments. A total of 93 stations were occupied on the cruise (Table 2) in 8 transects identified as Louisiana, Tampa, 27° North, Georgia, Cape Hatteras, New Jersey, Line W and New Hampshire Transects. In addition, underway measurements of salinity, temperature, dissolved oxygen, pCO₂ (air and water), total carbon, pH, ammonia, fluorescence, light transmittance, and colored dissolved organic matter fluorescence were made. Samples were taken every two-hours from the underway sampling line for discrete analyses of oxygen, inorganic nutrients, dissolved inorganic carbon, total alkalinity, pCO₂ and pH.

For several CTD stations with depth less than 1000 m, an *in situ* spectrophotometric pH profiler was installed on the CTD/rosette for measuring pH profiles. To provide comparison and calibration of autonomous measurements made by

sensors installed in the coastal CO₂ buoys, the ship sailed closely to Gray's Reef Buoy in Georgia coast. In addition to underway measurements, CTD casts were taken for discrete measurements of DIC, TA, and pCO₂ near these coastal observation moorings. The cruise ended in Boston, MA on 13 August, 2012.

Name (First, Last)	Title	Date Aboard	Date Disembark		Affiliation
Rik Wanninkhof	Chief Scientist	7/20/2012	7/30/2012*	M	AOML
Michelle Wood	Chief Scientist	7/30/2012*	8/13/2012	F	AOML
Leticia Barbero	Co-Chief Scientist	7/20/2012	8/13/2012	F	AOML/CIMAS
James Hooper	CTD	7/20/2012	8/13/2012	M	AOML/CIMAS
Andrew Stefanick	CTD/Watch	7/20/2012	8/13/2012	M	AOML
Kyle Seaton	CTD/Watch	7/20/2012	7/30/2012*	M	AOML
Erik Valdes	CTD/Watch	7/30/2012*	8/13/2012	M	AOML/CIMAS
Carolina Mor	O ₂	7/20/2012	8/13/2012	F	RSMAS
Hernan Garcia	O ₂	7/20/2012	8/13/2012	M	NODC
Charles Fischer	Nutrients	7/20/2012	8/13/2012	M	AOML
Esa Peltola	DIC	7/20/2012	8/13/2012	M	AOML
Charles Featherstone	DIC	7/20/2012	8/13/2012	M	AOML
Kevin Sullivan	pCO ₂ discrete	7/20/2012	8/13/2012	M	AOML/CIMAS
Andrew Margolin	pCO ₂ discrete	7/20/2012	8/13/2012	M	RSMAS
Wei-Jen Huang	Alkalinity	7/20/2012	8/13/2012	M	UGA
Andrew Joesoef	Alkalinity	7/20/2012	8/13/2012	M	UGA
Sherwood Liu	UWpH/DiscpH	7/20/2012	8/13/2012	M	USF
Yong-Rae Kim	UWpH/DiscpH	7/20/2012	8/13/2012	M	USF
Regina Easley	UWpH/DiscpH	7/20/2012	8/13/2012	F	USF
Mark Patsavas	UWpH/DiscpH	7/20/2012	8/13/2012	M	USF
Bo Yang	UWpH/DiscpH	7/20/2012	8/13/2012	M	USF
Sumit Chakraborty	Pigments	7/20/2012	8/13/2012	M	UMASSD
Madalyn Meaker	Pigments	7/20/2012	8/13/2012	F	USM
Marc Emond	DOC/Chl/Colr	7/20/2012	8/13/2012	M	UNH

Table 1 - Scientific Cruise Participants

* disembarked/embarked in an at ship to shore transfer near Miami

Affiliations:

NODC	NOAA/NESDIS – National Ocean Data Center
AOML	Atlantic Oceanographic and Meteorological Laboratory
RSMAS	Rosenstiel School of Marine and Atmospheric Science/University of Miami
UGA	University of Georgia
UMASSD	University of Massachusetts-Dartmouth
UNH	University of New Hampshire
USF	University of South Florida
USM	University of Southern Mississippi
CIMAS	Cooperative Institute of Marine and Atmospheric Sciences/University of Miami

3.- Description of Measurements from Vertical Profiles

3.1 CTD/Hydrographic Measurements

Analysts: James Hooper and Erik Valdes (CIMAS/RSMAS), Kyle Seaton, and Andrew Stefanick (NOAA/AOML)

A total of 93 CTD/O₂/Optics stations were conducted during the cruise (Table 2, Figure 1). At each station, profiles of temperature, salinity (conductivity), and dissolved oxygen concentration were collected from the surface to within approximately 5 m of the bottom for cast shallower than 100 m and 10 m of the bottom deeper than 100 m casts, using a Sea-Bird SBE-911plus CTD system. Water samples for calibration of the salinity and dissolved oxygen profiles as well all the other parameters sampled on this cruise were collected using a 24-bottle Rosette system containing 10-liter Niskin bottles.

Station #	Date	Time	Latitude, N	Longitude, E	Bottom Depth (m)
0	7/22/12	19:30	25.188	-84.640	1786
1	7/24/12	0:30	27.582	-89.998	1263
2	7/24/12	3:19	27.750	-90.000	856
3	7/24/12	6:30	27.584	-90.000	667
4	7/24/12	9:16	28.083	-89.998	435
5	7/24/12	11:55	28.250	-89.983	172
6	7/24/12	15:00	28.500	-89.998	98
7	7/24/12	17:27	28.748	-89.998	48
8	7/24/12	19:51	28.934	-90.123	26
9	7/24/12	21:13	28.979	-90.211	19
10	7/24/12	23:47	28.869	-90.476	21
11	7/25/12	3:34	28.835	-90.809	17
12	7/27/12	9:09	25.983	-85.983	3243
13	7/27/12	14:22	26.217	-85.667	3254
14	7/27/12	18:49	26.433	-85.333	3285
15	7/27/12	23:24	26.663	-85.003	3293
16	7/28/12	4:02	26.890	-84.000	230
17	7/28/12	6:51	27.112	-84.334	135
18	7/28/12	9:30	27.317	-83.983	72
19	7/28/12	11:56	27.533	-83.667	48
20	7/28/12	14:18	27.767	-83.333	32
21	7/28/12	17:35	28.017	-83.031	16
22	7/30/12	18:59	26.997	-80.003	42
23	7/30/12	20:15	27.000	-79.986	67
24	7/30/12	21:47	26.989	-79.931	159
25	7/30/12	23:24	26.979	-79.865	276
26	7/31/12	1:34	26.980	-79.781	404
27	7/31/12	3:47	26.973	-79.686	554

28	7/31/12	6:18	26.969	-79.620	653
29	7/31/12	8:36	26.965	-79.499	780
30	7/31/12	11:14	26.975	-79.383	700
31	7/31/12	13:58	26.978	-79.282	628
32	7/31/12	4:28	26.980	-79.200	509
33	7/31/12	19:02	26.987	-79.174	431
34	8/1/12	22:13	31.480	-80.975	17
35	8/1/12	22:57	31.464	-80.921	18
36	8/2/12	0:06	31.406	-80.867	23
37	8/2/12	4:41	31.396	-80.742	24
38	8/2/12	6:05	31.325	-80.566	26
39	8/2/12	7:23	31.254	-80.386	35
40	8/2/12	8:40	31.194	-80.245	39
41	8/2/12	10:39	31.083	-79.958	50
42	8/2/12	12:47	30.953	-79.677	470
43_2	8/2/12	18:50	30.854	-79.442	807
44	8/2/12	22:58	30.674	-79.007	812
45	8/3/12	3:02	30.491	-78.500	819
46	8/3/12	7:03	30.288	-77.998	813
47	8/5/12	5:19	36.252	-75.655	26
48	8/5/12	8:34	36.142	-75.349	32
49	8/5/12	8:34	36.142	-75.349	32
50	8/5/12	12:41	35.904	-74.821	310
51	8/5/12	14:59	35.833	-74.647	1645
52	8/5/12	17:59	35.734	-74.458	1948
53	8/5/12	21:48	35.602	-74.215	2687
54	8/6/12	1:47	35.482	-74.008	3036
55	8/6/12	5:31	35.318	-73.831	3386
56	8/6/12	9:19	35.212	-73.697	3590
57	8/7/12	12:15	39.449	-74.222	17
58	8/7/12	13:57	39.439	-74.091	25
59	8/7/12	15:55	39.216	-73.914	36
60	8/7/12	17:30	39.097	-73.733	39
61	8/7/12	19:00	38.977	-73.556	50
62	8/7/12	20:41	38.858	-73.380	68
63	8/7/12	22:09	38.737	-73.197	96
64	8/7/12	23:40	38.615	-73.022	1422
65	8/8/12	2:24	38.496	-72.843	2395
66	8/8/12	23:39	40.899	-70.320	43
67	8/9/12	2:01	40.594	-70.360	60
68	8/9/12	5:15	40.290	-70.201	92
69	8/9/12	6:54	40.141	-70.115	120
70	8/9/12	8:40	40.012	-69.988	154
71	8/9/12	10:33	39.882	-69.908	720
72	8/9/12	12:56	39.851	-69.901	1002
73	8/9/12	15:40	39.792	-69.852	1493
74	8/9/12	18:48	39.699	-69.799	2082

75	8/9/12	22:12	39.477	-69.605	2402
76	8/10/12	1:42	39.352	-69.539	2493
77	8/10/12	5:48	39.087	-69.354	2989
78	8/10/12	10:09	38.817	-69.199	3243
79	8/10/12	14:24	38.557	-68.010	3476
80	8/10/12	18:53	38.323	-68.870	3818
81	8/10/12	23:26	38.091	-68.700	4100
82	8/11/12	4:54	37.861	-68.517	4382
83	8/12/12	2:51	40.511	-69.235	73
84	8/12/12	6:19	40.815	-69.009	76
85	8/12/12	8:59	41.079	-68.867	75
86	8/12/12	13:31	41.626	-68.783	157
87	8/12/12	20:46	42.479	-69.008	227
88	8/13/12	2:06	42.728	-69.686	302
89	8/13/12	4:21	42.861	-69.863	257
90	8/13/12	6:48	42.890	-70.141	62
91	8/13/12	8:28	42.938	-70.297	137
92	8/13/12	10:26	42.998	-70.420	105
93	8/13/12	12:27	43.032	-70.548	50

Table 2 – CTD station locations visited during the GOMECC-2 cruise.

3.1.1 CTD Operations

The basic CTD measurements consisted of salinity and dissolved oxygen measurements made from water samples taken on CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen, pH, and several optical parameters from CTD profiles. A total of 94 CTD/rosette casts were made, usually to within 10 m of the bottom. The bottle distributions of water samples taken are shown in Figures 2-9.

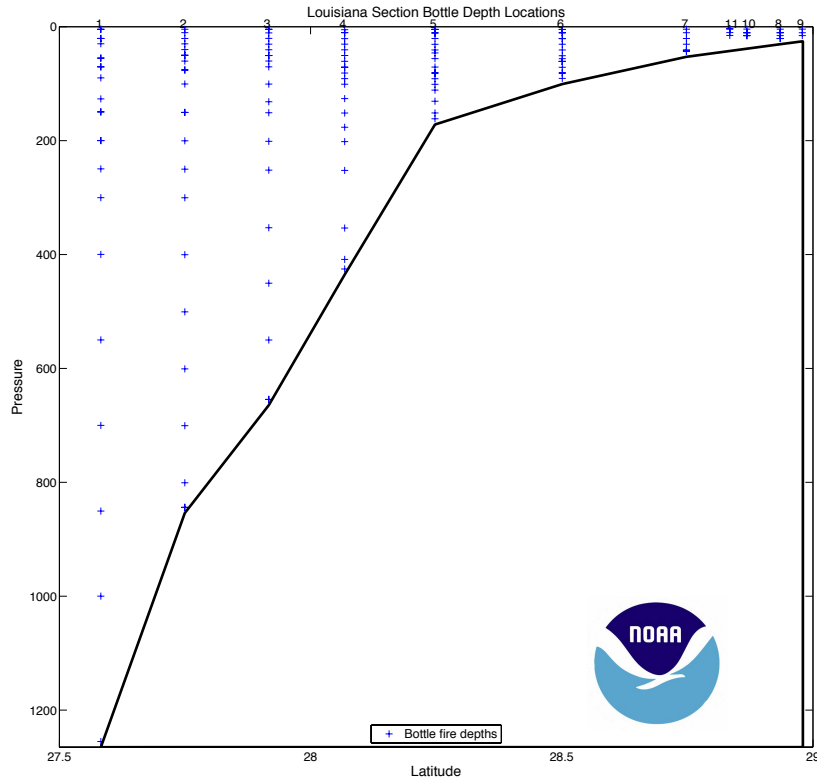


Figure 2 - Bottle locations for the Louisiana line, south of New Orleans, LA in the northern Gulf of Mexico.

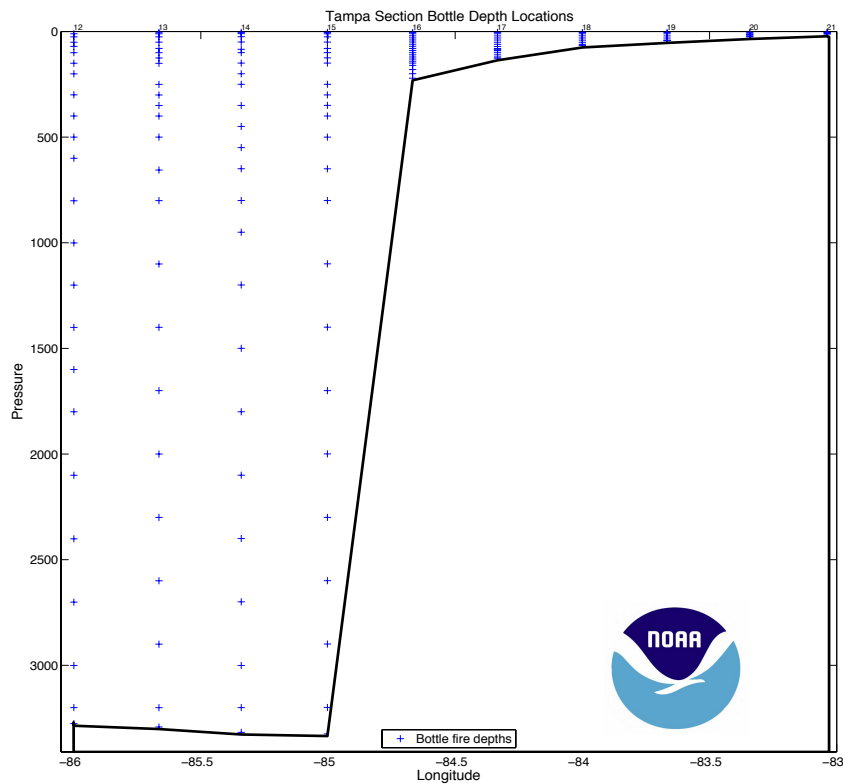


Figure 3 - Bottle locations for the Tampa line, west of Tampa, FL in the eastern Gulf of Mexico.

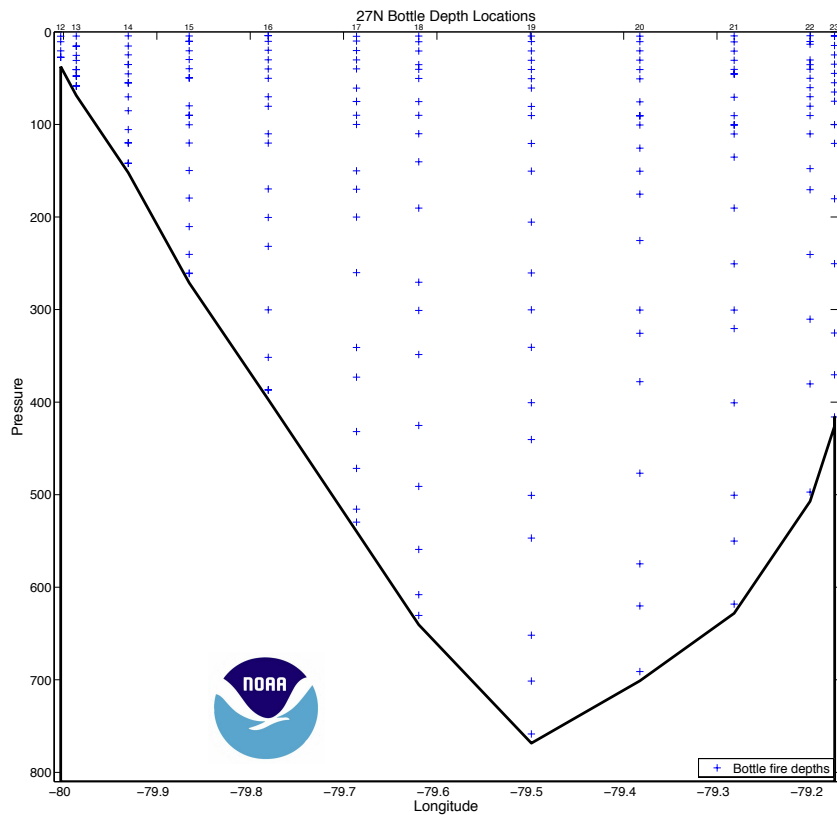


Figure 4 - Bottle locations for the 27° North line in the Florida Straits.

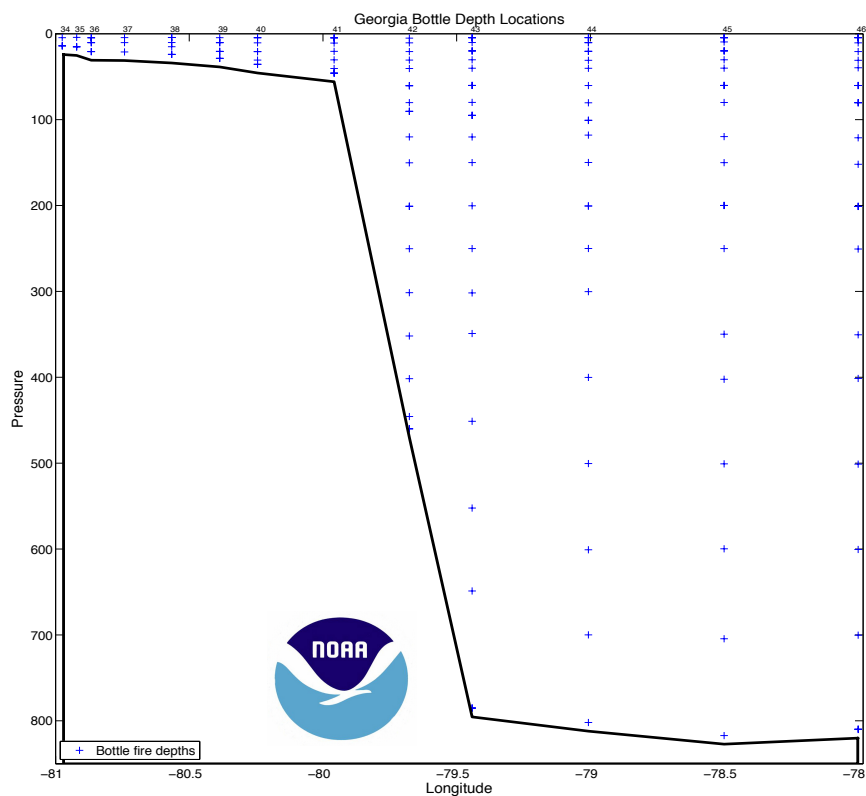


Figure 5 - Bottle locations for the Georgia line, off the East Coast of Georgia in the western North Atlantic.

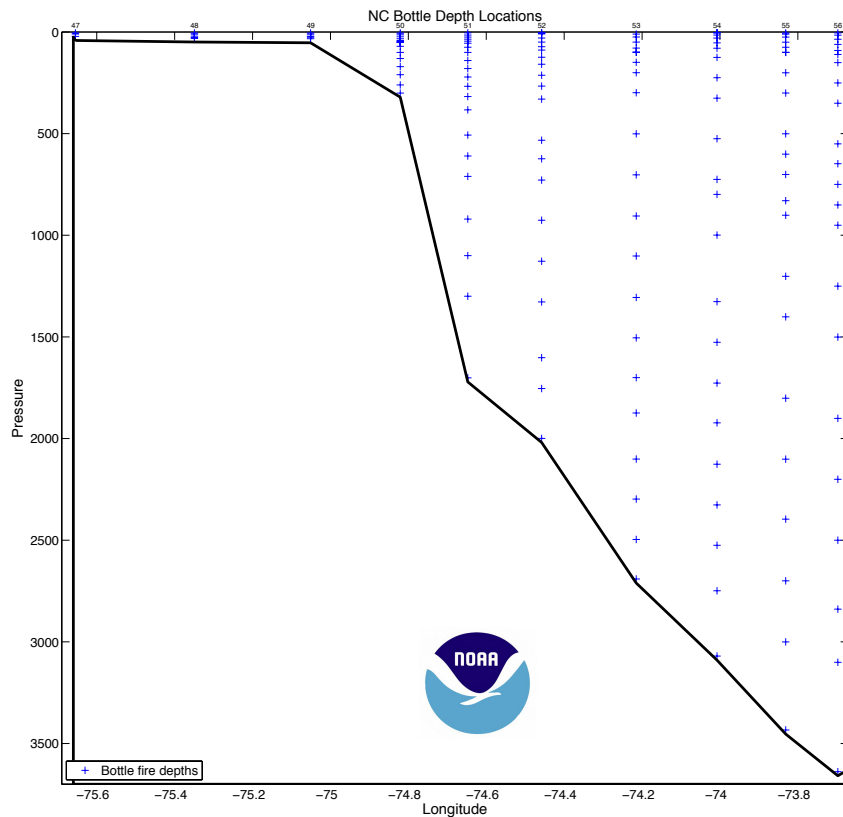


Figure 6 - Bottle locations for the Cape Hatteras line, off the East coast of North Carolina in the western North Atlantic

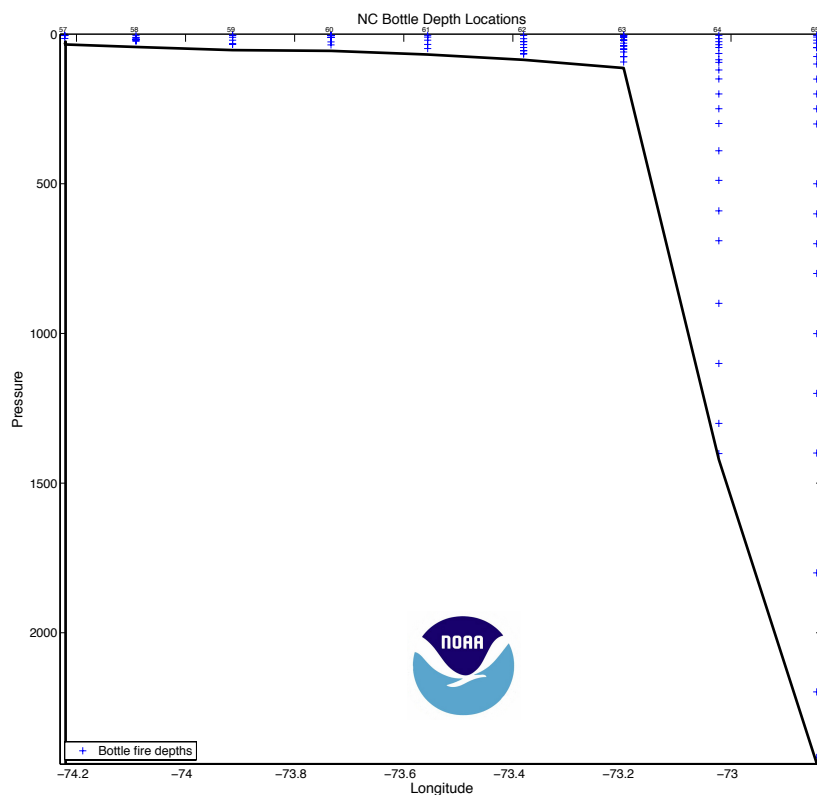


Figure 7 - Bottle locations for the New Jersey line in the western North Atlantic.

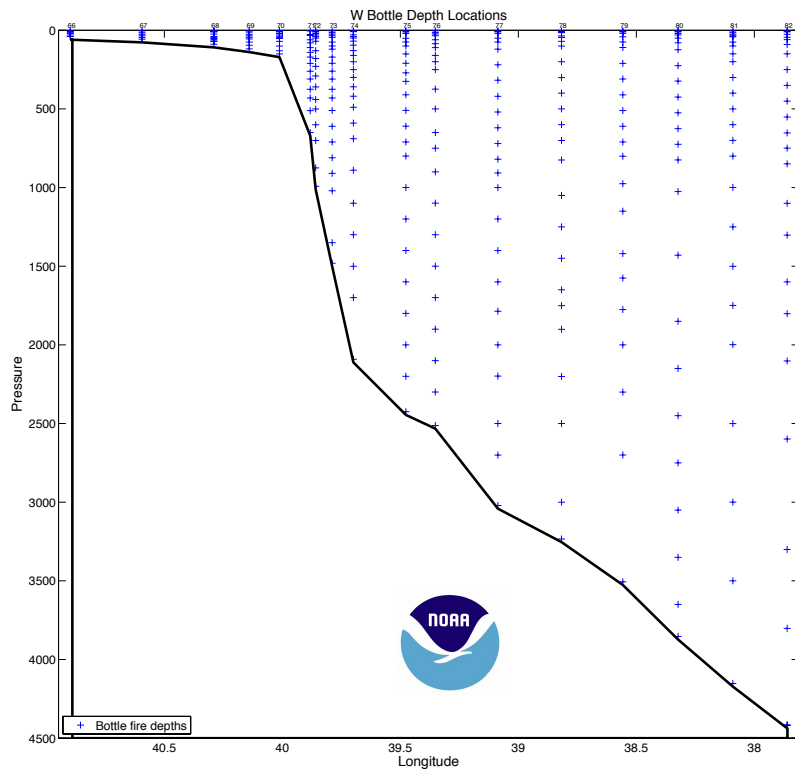


Figure 8 - Bottle locations for the W line, off the East coast of Massachusetts in the western North Atlantic.

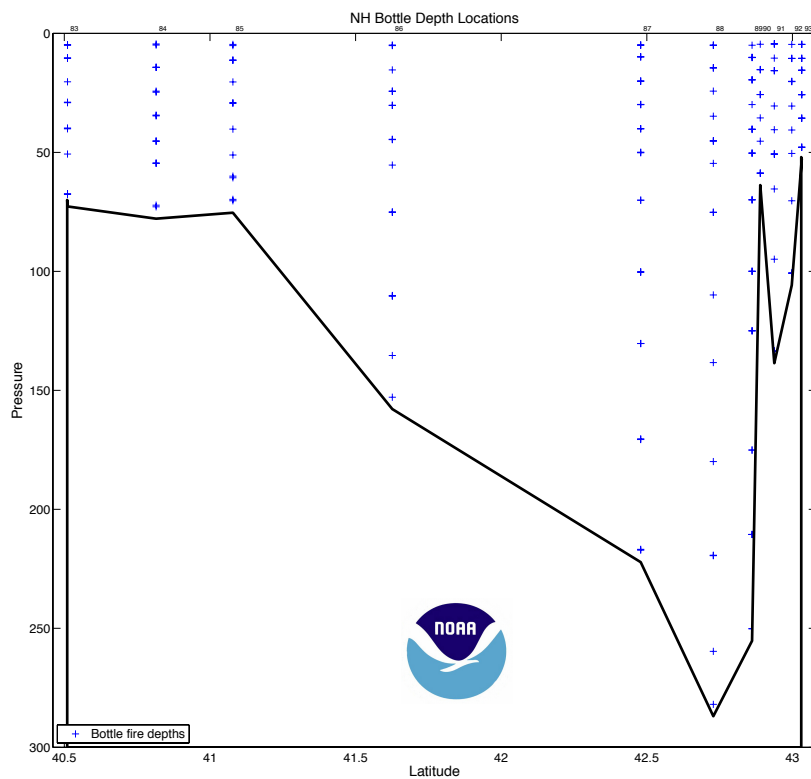


Figure 9 - Bottle locations for the New Hampshire line, off the East coast of Cape Cod and New Hampshire in the western North Atlantic.

i. CTD Electronics and Water Sampling Package

CTD/rosette casts were performed with a package consisting of a 24-place, 10-liter rosette frame (AOML's white frame), a 24-place water sampler/pylon (SBE32) and 24, 10-liter Bullister/Niskin-style bottles. This package was deployed on all stations/casts. Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9 plus CTD with dual pumps and the following sensors: dual temperature (SBE3), dual conductivity (SBE4), dual dissolved oxygen (SBE43), and a Simrad 807 altimeter. The other underwater electronic components involved an array of several optical sensors, consisting of a Biospherical QSP-2300 irradiance sensor, a Wet Labs ECO fluorometer, a Seapoint ultraviolet fluorometer, a Seapoint chlorophyll fluorometer, and a Seapoint turbidity meter. There was also a pH sensor attached to the CTD frame on the outside. The pH sensor and irradiance sensor were removed for stations deeper than 1000 m.

The CTDs supplied a standard Sea-Bird format data stream at a data rate of 24 frames/second. The SBE9plus CTD was connected to the SBE32 24-place pylon providing for single-conductor sea cable operation. Power to the SBE9plus CTD, SBE32 pylon, auxiliary sensors, and altimeter was provided through the sea cable from the SBE11plus deck unit in the computer lab. The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable.

The CTD was mounted vertically attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3 temperature sensors and their respective pumps were mounted vertically as recommended by SBE outboard of the CTD. The CTD was outfitted with dual pumps. Primary temperature, conductivity, and dissolved oxygen were plumbed on one pump circuit and secondary temperature, conductivity and dissolved oxygen on the other. Pump exhausts were attached to outside corners of the CTD cage and directed downward. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring.

The R/V *Brown's* aft CTD winch was used with the 24-place 10-liter rosette for all station/casts. During the deployment of the CTD at station 43, the aft winch experienced very high modulo errors, ~100, as it was being put into the water. After the CTD was brought back on deck, it was determined that there was corrosion on the tips of the grounding wires. They were replaced and no further problems were recorded.

The deck watch prepared the rosette typically within a few minutes prior to each cast. All valves, vents, and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Once on station, the syringes were removed from the CTD sensor intake ports. As directed by the deck watch leader, the CTD was powered-up and the data acquisition system started. The CTD package was put in the water and taken down to 10 m for 2-3 minutes to remove any air bubble from the sensor lines and to make sure the sensors were behaving appropriately. On the casts where the pH and irradiance sensors were attached, depths < 1000m, the pH was turned on manually during the package preparation and then, when the depths allowed, the package was soaked at 20 m for 5 minutes to allow the pH to acclimate.

The rosette was left on deck for sampling. The bottles and rosette were examined before samples were taken, and anything unusual, such as open or leaking bottles, was noted on the sample log.

Routine CTD maintenance included soaking the conductivity and DO sensors in a solution of de-ionized water as recommended by Sea-Bird between casts to maintain sensor stability. Rosette maintenance was performed on a regular basis. O-rings were changed as necessary and bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

a. System Problems

With the addition of the optical sensors, ‘y’ cables had to be used to attach all the sensors to the CTD. The test cast showed an issue with the ‘y’ cable attaching the two oxygen sensors. Kyle Seaton was able to repair the ‘y’ cable and the rest of the casts proceeded with dual oxygen sensors. Later in the cruise around station 49 it was discovered that one of one of the other ‘y’ cables, attaching the irradiance and Chlorophyll sensor, had been malfunctioning. The irradiance sensor hadn’t been recording meaningful data. This problem was never resolved and the sensor remained off the rest of the cruise.

There were also problems with the Seasave software communicating with the water sampler (carousel). Bottles were firing out of order or misfiring. On station 43, the Seabird water sampler (s/n 328531-0031) failed, and would no longer communicate with the deck unit. This was replaced with the backup water sampler (s/n 328531-0032), which has also shown issues communicating with the deck unit. Bottles would not record when they ‘tripped’. This problem was not resolved and the cruise finished with the back up water sampler. As of September 06, 2012, issues have been detected in the stations listed in the table below (Table 3):

Station #	Niskin bottle	Issue
1	10	Recorded as 8
1	21	Recorded as 17
4	21	Recorded as 17
18	10	Recorded as 8
20	10	Recorded as 12
22	5	Recorded as 1
42	18	Recorded as 16
53	10*	No registered firing at console but was fired
53	16*	No registered firing at console but was fired
83	11	Recorded as 15

Table 3: Stations where CTD software issues have been detected.

*These depths ended up getting a duplicate niskin fired because it was thought that they were not actually triggered. As a result there were no bottles available for the two surface trips.

Instrument	S/N	Stations Used	Sensor Use	Pre-Cruise Calibration	Comment
Sea-Bird SBE32 24-place Carousel Water Sampler	328531 - 0031	0-42			Failed at station 43
Sea-Bird SBE32 24-place Carousel Water Sampler	328531 - 0032	43-93			
Sea-Bird SBE9plus CTD	0957				
Paroscientific Digiquartz Pressure Sensor	115173	0-93		07/01/09	
Sea-Bird SBE3plus Temperature Sensor	2946	0-93	Primary	06/26/12	
Sea-Bird SBE3plus Temperature Sensor	1701	0-93	Secondary	07/10/12	
Sea-Bird SBE4C Conductivity Sensor	1387	0-93	Primary	06/22/12	
Sea-Bird SBE4C Conductivity Sensor	1346	0-93	Secondary	06/03/12	
Sea-Bird SBE43 Dissolved Oxygen	0140	0-93	Primary	07/10/12	
Sea-Bird SBE43 Dissolved Oxygen	2085	0-93	Secondary	03/30/12	
Sea-Bird SBE5T Pump	0140	0-93	Primary		
Sea-Bird SBE5T Pump	2085	0-93	Secondary		
Simrad 807 Altimeter	9811860	0-93			
Wet Labs Fluorometer	2088	0-93			
Biospherical QSP2300 Irradiance	70275				Not responsive; Bad cable
Seapoint Turbidity	1573	0-93			
Seapoint Ultraviolet Fluorometer	6201	0-93			
Seapoint Chlorophyll Fluorometer	2770	0-93			

Table 4: Equipment used during the cruise.

ii. Real-Time CTD Data Acquisition System

The CTD data acquisition system consisted of an SBE-11plus (V1) deck unit and a networked generic PC workstation running Windows 2000. SBE Seasave software version 7.21d was used for data acquisition and to close bottles on the rosette.

The console watch initiated CTD deployments after the ship stopped on station. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments.

The deck watch leader directed the winch operator to raise the package, the squirt boom and rosette were extended outboard, and the package quickly lowered into the water and submerged to 10 meters of wire out. No tag lines were necessary for either deployments or recoveries during this cruise. The CTD sensor pumps were configured with a 60 second startup delay. The CTD console operator waited for the CTD sensor pumps to turn on, waited an additional 60 seconds for sensors to stabilize (all together about 2 minutes), then directed the winch operator to bring the package close to the surface, pause for typically 10 seconds, hitting “Mark Scan” and begin the descent. The profiling rate was no more than 30 m/min to 50 m, no more than 45 m/min to 200 m, and no more than 60 m/min deeper than 200 m depending on sea cable tension and the sea state. On the shallow stations, < 1000 m, when the pH sensor was attached the profiling rate was no more than 30 m/min down to 500 m. After that profiling rates could return to normal.

The console watch monitored the progress of the deployment and quality of the CTD data through interactive graphics and operational displays. Additionally, the watch created a sample log for the deployment that would be later used to record the correspondence between rosette bottles and analytical samples taken. The altimeter channel, CTD pressure, wire-out and bathymetric depth were all monitored to determine the distance of the package from the bottom, usually allowing a safe approach to within 10 m.

On the up cast, the winch operator was directed to stop at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle using a “point and click” graphical trip button. The data acquisition system responded with trip confirmation messages and the corresponding CTD data in a rosette bottle trip window on the display. All tripping attempts were noted on the console log. The console watch then directed the winch operator to raise the package up to the next bottle trip location.

After the last bottle was tripped, the console watch directed the deck watch to bring the rosette on deck. Once on deck, the console watch terminated the data acquisition, turned off the deck unit, and assisted with rosette sampling.

iii. Navigation and Bathymetry Data Acquisition

Navigation data were acquired by the database workstation at 1-second intervals from the ship's Trimble PCODE GPS receiver beginning. The ship conducted nearly continuous operations of Bathy2000 3.5 kHz depth estimation and Seabird 12 kHz depth data streams recorded in the SCS system. In addition, the multibeam system was used primarily during transits and the deeper stations.

iv. Shipboard CTD Data Processing

Shipboard CTD data processing was performed automatically at the end of each deployment using SEABIRD SBE Data Processing version 7.21h and AOML Matlab processing software. The raw CTD data and bottle trips acquired by SBE Seasave on the Windows 2000 workstation were copied onto the CTD-PROC workstation, and processed to a 1-dbar series and a 1-second time series. Bottle trip values were extracted and a 1-decibar (dbar) down cast pressure series created.

The Sea-Bird Data Processing for primary calibrated data (1 dbar averages) uses the following routines in order:

- DATCNV - converts raw data into engineering units and creates a .ROS bottle file. Both down and up casts were processed for scan, elapsed time (s), pressure, t0 ITS-90 (°C), t1 ITS-90 (°C), c0 (mS/cm), c1 (mS/cm), and oxygen voltage (V), oxy voltage 2, altimeter, optical sensor, oxygen (umol/kg) and oxygen 2 (umol/kg). Optical sensor data were not carried through the processing stream. MARKSCAN was used to determine the number of scans acquired on deck and while priming the system to exclude these scans from processing.
- ALIGNCTD - aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary and secondary conductivity were automatically advanced by 0.073 seconds. Align adjusted these advances to 0.006 for the primary sensor and +0.063 for the secondary sensor (stations 8-59) and 0.083 for stations 0-7 (primary sensor).
- BOTTLESUM - created a summary of the bottle data. Bottle position, date, and time were output automatically. Pressure, temperature, conductivity, salinity, oxygen voltage and preliminary oxygen values were averaged over a 2 second interval.
- WILDEDIT - computes the standard deviation of 100 point bins, and then makes two passes through the data. The first pass flags points that differ from the mean by more than 2 standard deviations. A new standard deviation is computed excluding the flagged points and the second pass marks bad values greater than 20 standard deviations from the mean. For this data set, data were kept within a distance of 100 of the mean (i.e., all data).

- FILTER - applies a low pass filter to pressure with a time constant of 0.15 seconds. In order to produce zero phase (no time shift), the filter is first run forward through the file and then run backwards through the file.
- CELLM - uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. In areas with steep temperature gradients the thermal mass correction is on the order of 0.005 PSS-78. In other areas the correction is negligible. The value used for the thermal anomaly amplitude (alpha) was 0.03°C. The value used for the thermal anomaly time constant (1/beta) was 7.0°C.
- LOOPEDIT - removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m/s or the pressure is not greater than the previous maximum scan, the scan is omitted.
- DERIVE - uses 1 dbar averaged pressure, temperature, and conductivity to compute primary and secondary salinities.
- BINAVERAGE - averages the data into 1 dbar bins. Each bin is centered on an integer pressure value, e.g., the 1 dbar bin averages scans where pressure is between 0.5 dbar and 1.5 dbar. There is no surface bin. The number of points averaged in each bin is included in the data file.
- STRIP - removes the computed oxygen variable.
- TRANS - converts the binary data file into ASCII format.
- SPLIT - separates the cast into upcast and downcast values.

Package slowdowns and reversals owing to ship roll can move mixed water in tow to in front of the CTD sensors and create artificial density inversions and other artifacts. In addition to Seasoft module LOOPEDIT, a program computes values of density locally referenced between every 1 dbar of pressure to compute N^2 and linearly interpolates temperature, conductivity, and oxygen voltage over those records where N^2 is less than or equal to -1×10^{-5} per s^2 . These data were retained but flagged as questionable in the final WOCE formatted files.

Final calibrations are applied to “de-looped” data files. ITS-90 temperature, salinity, and oxygen are computed, and WOCE quality flags are created. ASCII files are converted to WOCE format for submission to the GOMECC-2 science group.

CTD data were examined at the completion of each deployment for clean corrected sensor response and any calibration shifts. As bottle salinity and oxygen results became available, they were used to refine shipboard conductivity and oxygen sensor calibrations.

A total of 94 casts were made (including 1 test cast).

v. CTD Calibration Procedures

Pre-cruise laboratory calibrations of the CTD pressure, temperature, and conductivity sensors were all performed at SBE. The calibration dates are listed in Table 4.

Secondary temperature, conductivity and dissolved oxygen (T2, C2 and DO2) sensors served as calibration checks for the reported primary sensors. During the cruise, it was determined that the primary sensors likely behaved more stably during the cruise.

In-situ salinity and dissolved O₂ check samples collected during each cast were used to calibrate the conductivity and dissolved O₂ sensors.

Only two sets of sensor combinations were used during the cruise as listed in Table 4.

vi. CTD Pressure

Pressure sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw pressure data during each cast. Residual pressure offsets (the difference between the first and last submerged pressures) were examined to check for calibration shifts (see Figure 10 and Table 5). On deck pressure before the start of each cast was recorded and is plotted in Figure 10. The on deck pressure before and after the cast were stable at 1.67 +/- 0.081 db, and 1.68 +/- 0.087 db respectively.

Near surface pressure values (which are taken as the near-surface pressure at the markscan and the last fired bottle pressure) showed relatively small variability (4.41 +/- 0.40 db before and 4.54 +/- 0.33 db after).

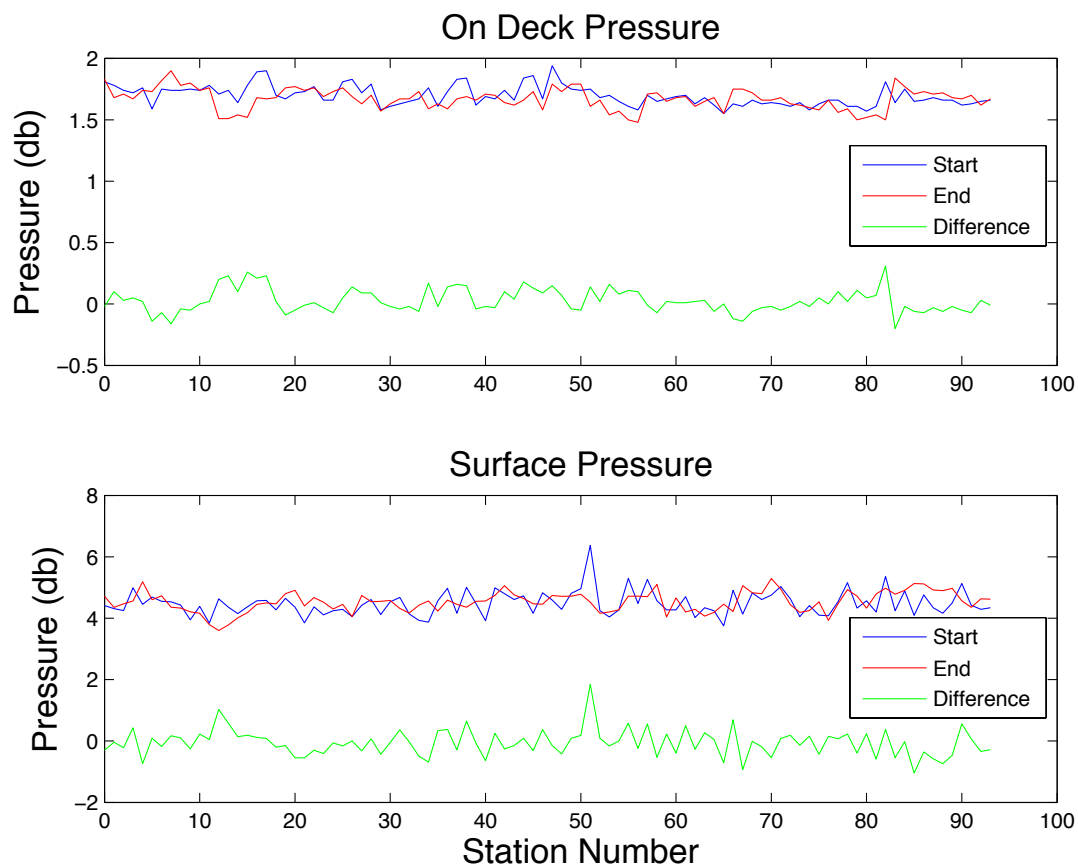


Figure 10: Near Surface pressure values include on deck (top) and just below the surface (bottom) before and after each CTD cast.

station	mark scan	start pr	end pr	start sfc btl prs	end sfc btl prs
0	8700	1.81	1.83	4.41	4.71
1	8215	1.78	1.68	4.31	4.35
2	9022	1.74	1.71	4.25	4.47
3	14168	1.72	1.67	4.99	4.56
4	26084	1.76	1.74	4.45	5.19
5	18453	1.59	1.73	4.69	4.60
6	14066	1.75	1.82	4.55	4.73
7	12147	1.74	1.90	4.53	4.36
8	18301	1.74	1.78	4.43	4.33
9	10369	1.75	1.80	3.95	4.21
10	9352	1.74	1.74	4.39	4.16
11	10596	1.78	1.76	3.84	3.79
12	19149	1.71	1.51	4.63	3.60
13	7906	1.74	1.51	4.36	3.78
14	20163	1.64	1.54	4.15	4.01

15	8744	1.78	1.52	4.37	4.18
16	13132	1.89	1.68	4.57	4.45
17	12566	1.90	1.67	4.58	4.50
18	9012	1.70	1.68	4.27	4.47
19	10828	1.67	1.76	4.65	4.80
20	7950	1.72	1.77	4.36	4.91
21	19132	1.73	1.74	3.85	4.40
22	17852	1.77	1.76	4.37	4.67
23	15630	1.66	1.69	4.11	4.52
24	14414	1.66	1.73	4.24	4.30
25	14304	1.81	1.76	4.29	4.45
26	16065	1.83	1.69	4.05	4.05
27	17029	1.72	1.63	4.42	4.74
28	17046	1.79	1.70	4.61	4.54
29	18271	1.58	1.57	4.12	4.55
30	13936	1.61	1.63	4.53	4.58
31	16504	1.63	1.67	4.68	4.32
32	20640	1.65	1.67	4.14	4.17
33	12942	1.67	1.73	3.93	4.42
34	4133	1.76	1.59	3.87	4.56
35	11844	1.61	1.63	4.57	4.23
36	9398	1.73	1.59	4.97	4.59
37	9570	1.83	1.67	4.16	4.45
38	9111	1.84	1.69	5.01	4.36
39	12997	1.62	1.66	4.48	4.55
40	16273	1.69	1.71	3.92	4.56
41	14271	1.67	1.70	4.99	4.74
42	18499	1.74	1.64	4.80	5.06
43_2	15811	1.66	1.62	4.61	4.76
44	10899	1.84	1.66	4.73	4.64
45	16171	1.86	1.73	4.16	4.47
46	12026	1.67	1.58	4.83	4.46
47	10761	1.94	1.79	4.59	4.74
48	15186	1.80	1.73	4.29	4.71
49	17387	1.75	1.79	4.81	4.72
50	13396	1.74	1.79	4.96	4.78
51	10254	1.75	1.61	6.37	4.52
52	13618	1.68	1.66	4.25	4.16
53	7345	1.70	1.54	4.04	4.20
54	9012	1.65	1.57	4.27	4.27
55	7599	1.61	1.50	5.30	4.72
56	7176	1.58	1.48	4.48	4.72
57	9914	1.70	5.26	1.71	4.70
58	8995	1.65	1.72	4.57	5.10
59	12408	1.67	1.65	4.27	4.04
60	10407	1.69	1.68	4.27	4.66
61	10896	1.70	1.69	4.70	4.20
62	6043	1.63	1.61	4.02	4.29
63	7531	1.68	1.65	4.34	4.07

64	7542	1.62	1.68	4.24	4.19
65	8089	1.55	1.55	3.75	4.46
66	9254	1.63	1.75	4.91	4.22
67	11154	1.61	1.75	4.13	5.06
68	13254	1.66	1.72	4.82	4.83
69	13224	1.63	1.66	4.61	4.80
70	11980	1.64	1.66	4.75	5.29
71	11003	1.63	1.68	5.03	4.95
72	14490	1.61	1.63	4.63	4.44
73	7303	1.64	1.62	4.05	4.19
74	8053	1.58	1.60	4.41	4.25
75	8220	1.63	1.58	4.10	4.53
76	8733	1.66	1.66	4.08	3.93
77	7949	1.66	1.56	4.54	4.47
78	8003	1.61	1.59	5.16	4.93
79	7801	1.61	1.50	4.33	4.72
80	7817	1.57	1.52	4.57	4.33
81	6973	1.61	1.54	4.20	4.79
82	11129	1.81	1.50	5.36	4.98
83	13452	1.64	1.84	4.24	4.78
84	11531	1.75	1.77	4.89	4.91
85	13407	1.65	1.71	4.09	5.13
86	14483	1.66	1.73	4.76	5.12
87	23001	1.68	1.71	4.34	4.92
88	12181	1.66	1.72	4.16	4.90
89	15578	1.66	1.68	4.50	4.97
90	12767	1.62	1.67	5.13	4.57
91	13320	1.63	1.70	4.42	4.35
92	13128	1.65	1.62	4.29	4.63
93	13252	1.66	1.67	4.34	4.62

Table 5: Near surface pressure values and scan number used to remove surface soak and on-deck values.

vii. CTD Temperature

Temperature sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary temperature data during each cast. Calibration accuracy was examined by comparing T1-T2 over a range of station numbers and pressures (bottle trip locations) for each cast. For the entire cruise, only one set of temperature sensors were used, both tracked each other extremely nicely. These comparisons are summarized in Figure 11, which shows a median temperature difference between the two sensors of 0.0006 °C and a pseudo standard deviation of 0.006 °C.

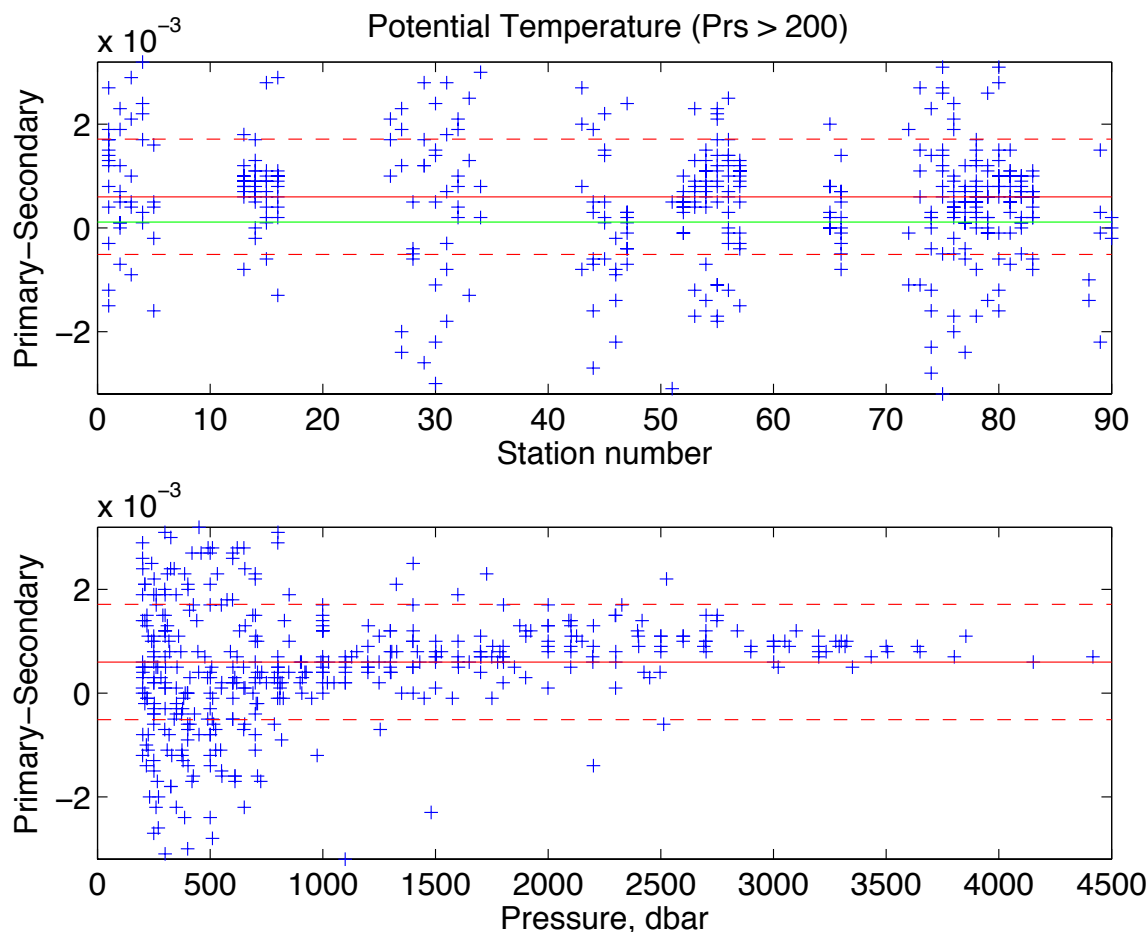


Figure 11: Uncalibrated potential temperature sensor differences (in 10^{-3} dbar) between primary and secondary sensors for pressures ≥ 200 db.

viii. CTD Conductivity

Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities. Comparisons between the primary and secondary sensors and between each of the sensors to check sample conductivities (conductivity calculated from bottle salinities) were used to derive conductivity corrections. Uncorrected C1-C2 are shown in Figure 12 to help identify sensor drift. For the entire cruise, only one set of conductivity sensors were used, both tracked each other extremely nicely. The two sensors show a median difference of 0.00092 S/m and a pseudo standard deviation of 0.00064 S/m.

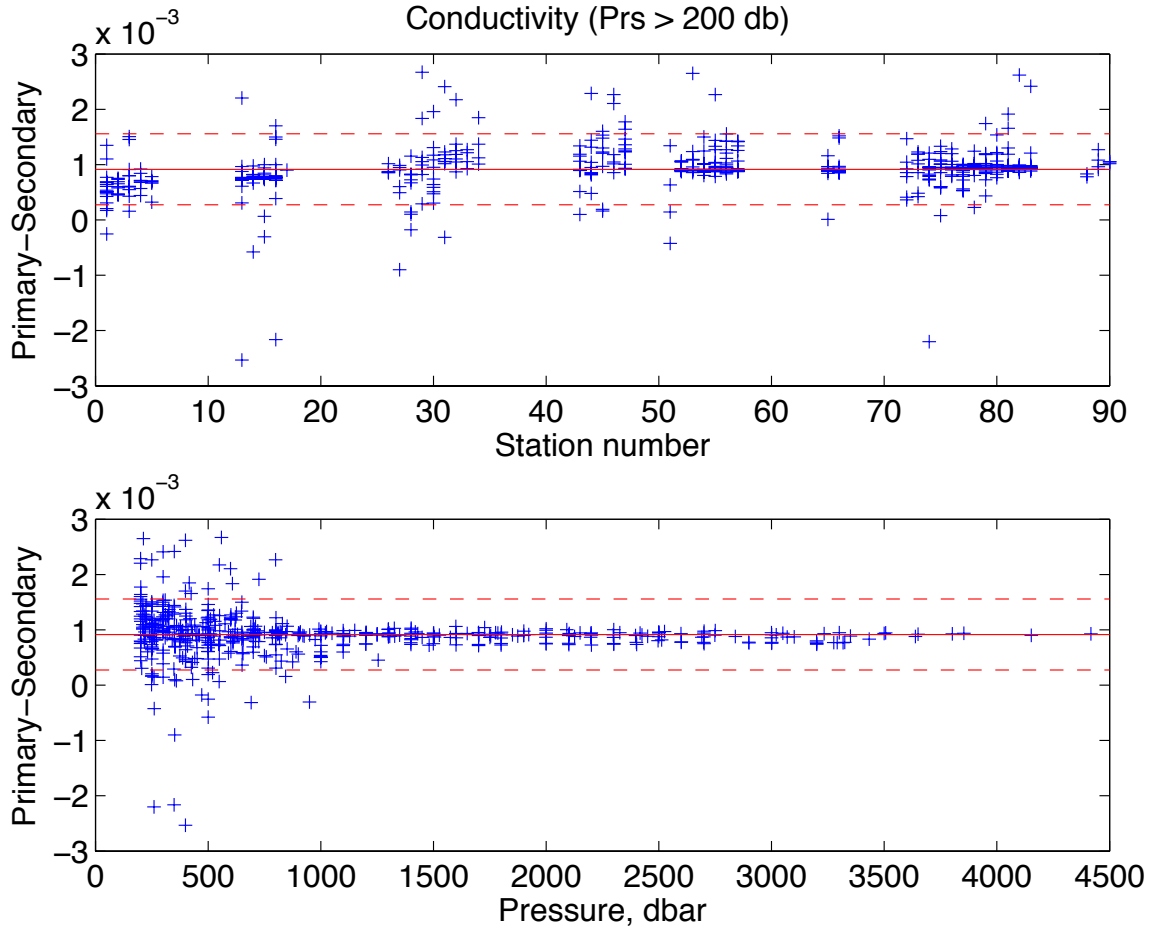


Figure 12: Uncalibrated conductivity differences (in 10^{-3} S/m) between primary and secondary sensors for pressures ≥ 200 db.

ix. CTD Dissolved Oxygen

Two SBE43 dissolved O_2 (DO) sensors were used on this leg (Table 4). Both sensors tracked each other very well, with no noted problems. The DO sensors were calibrated to dissolved O_2 check samples by matching the up cast bottle trips to down cast CTD data along isopycnal surfaces, calculating CTD dissolved O_2 , and then minimizing the residuals using a non-linear least-squares fitting procedure. The fitting determined calibration coefficients for the sensor model conversion equation and proceeded in a series of steps. Each sensor was fit in a separate sequence. The first step was to determine the time constants for the exponential terms in the model. These time constants are sensor-specific but applicable to an entire cruise. Once the time constants had been determined, casts were fit individually to O_2 check sample data. The resulting calibration coefficients were then smoothed and held constant during a refit to determine sensor slope and offset. Calibration accuracy was examined by comparing O1-O2 over a range of station numbers and pressures (bottle trip locations) for each cast. For the entire cruise,

only one set of oxygen sensors were used, both tracked each other extremely nicely (Figure 13). The two sensors show a median difference of $-2.96 \mu\text{mol/kg}$ and a pseudo standard deviation of $1.21 \mu\text{mol/kg}$.

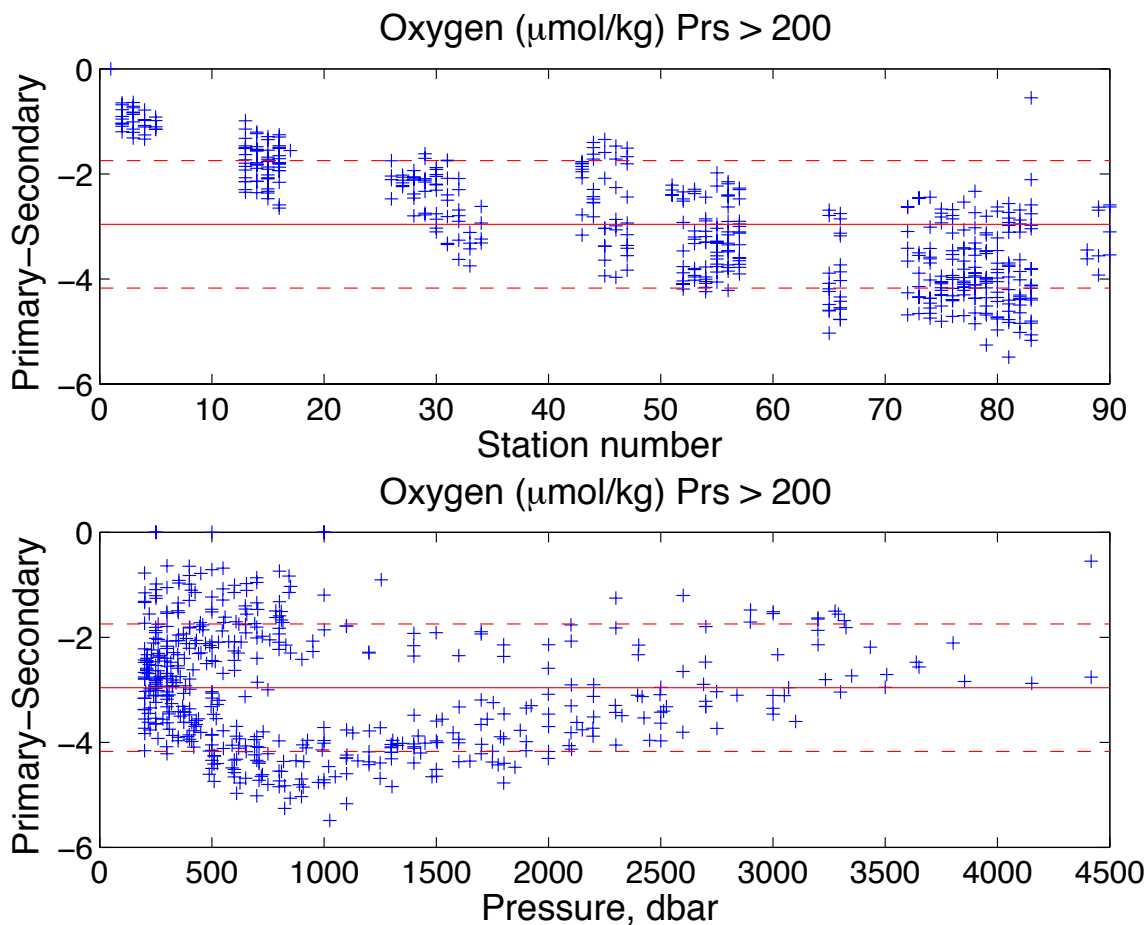


Figure 13: Uncalibrated oxygen differences between primary and secondary sensors for pressures ≥ 200 db.

x. Preliminary CTD Data Processing

The calibration of the CTD instruments will be completed after a recalibration of the sensors at Seabird following the cruise. Secondary, uncalibrated data is shown in Figures 14 to 29.

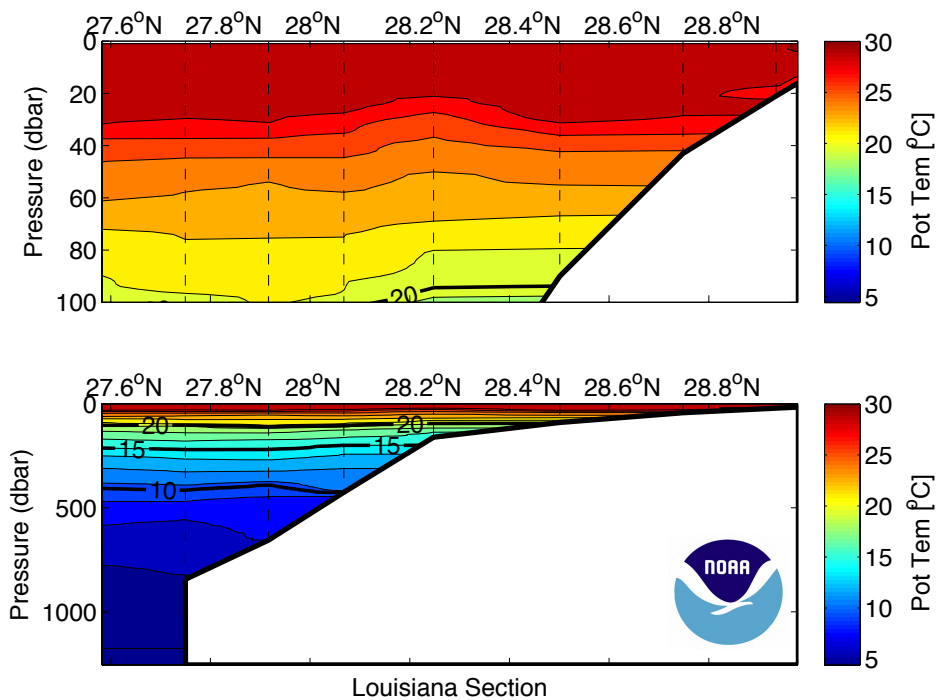


Figure 14: Potential temperature along the Louisiana section.

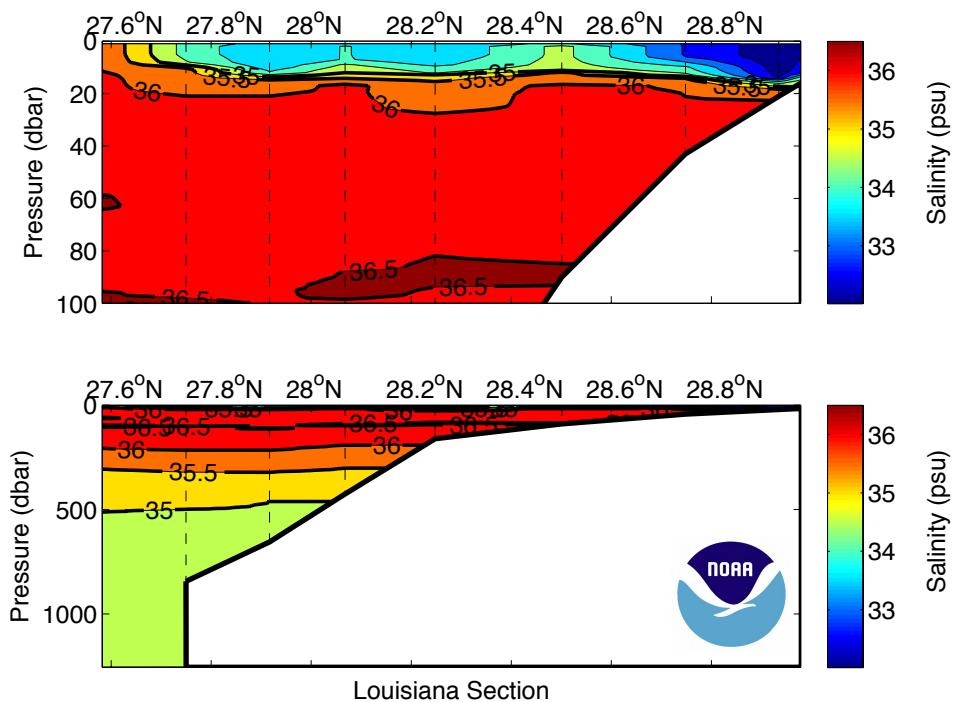


Figure 15: Salinity along the Louisiana section.

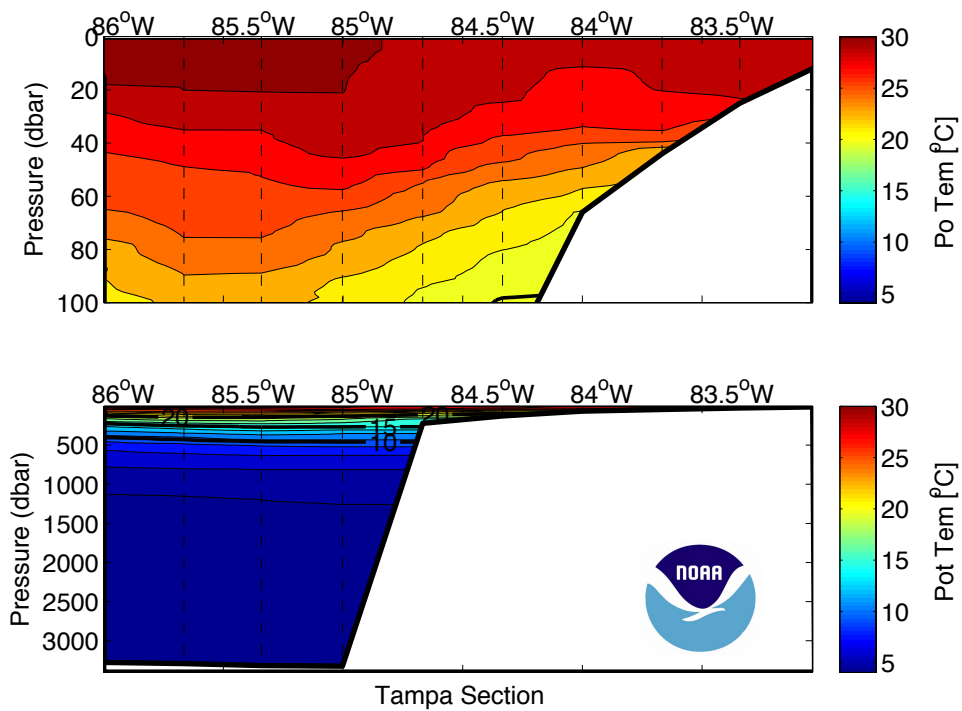


Figure 16: Potential temperature along the Tampa section.

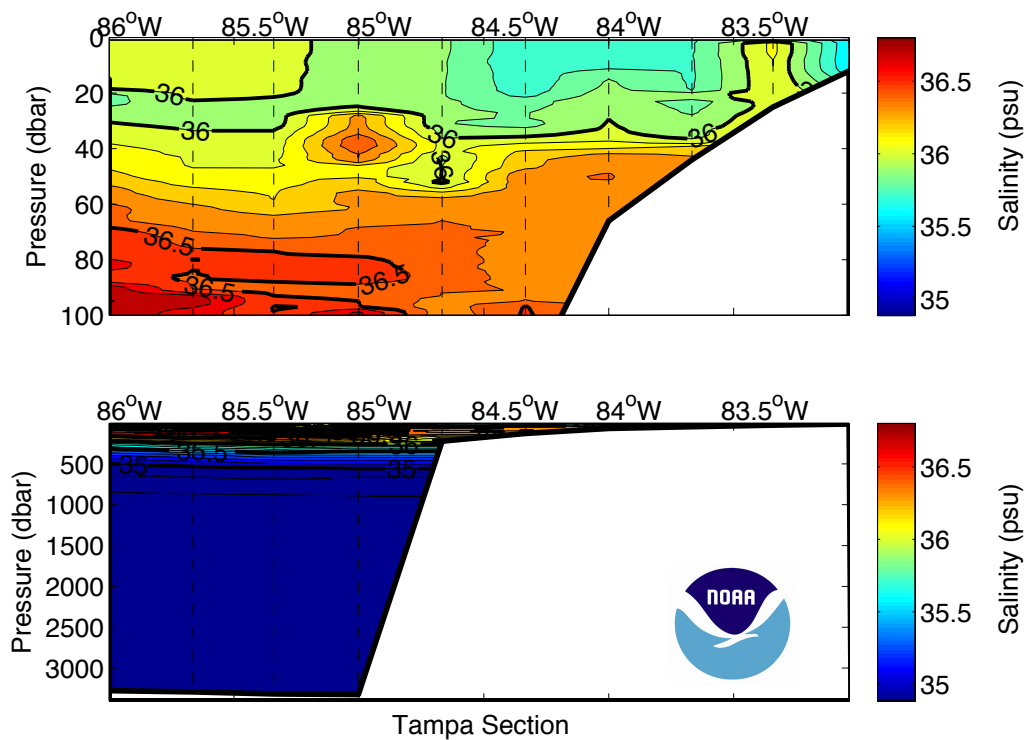


Figure 17: Salinity along the Tampa section.

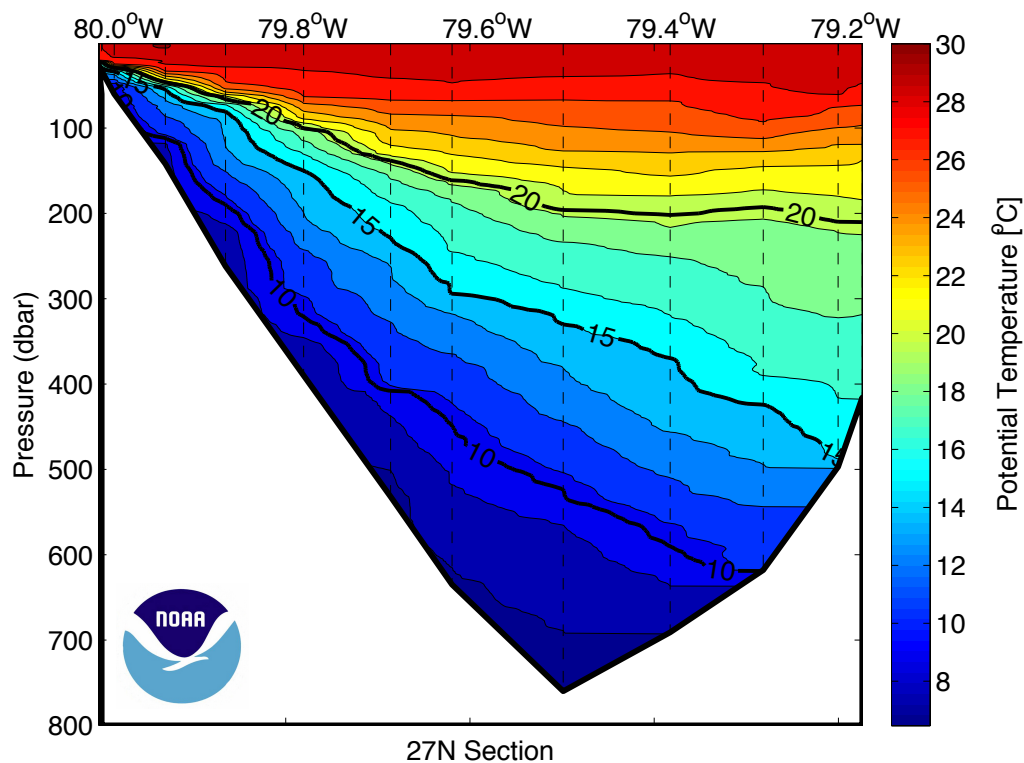


Figure 18: Potential temperature along the 27°N section.

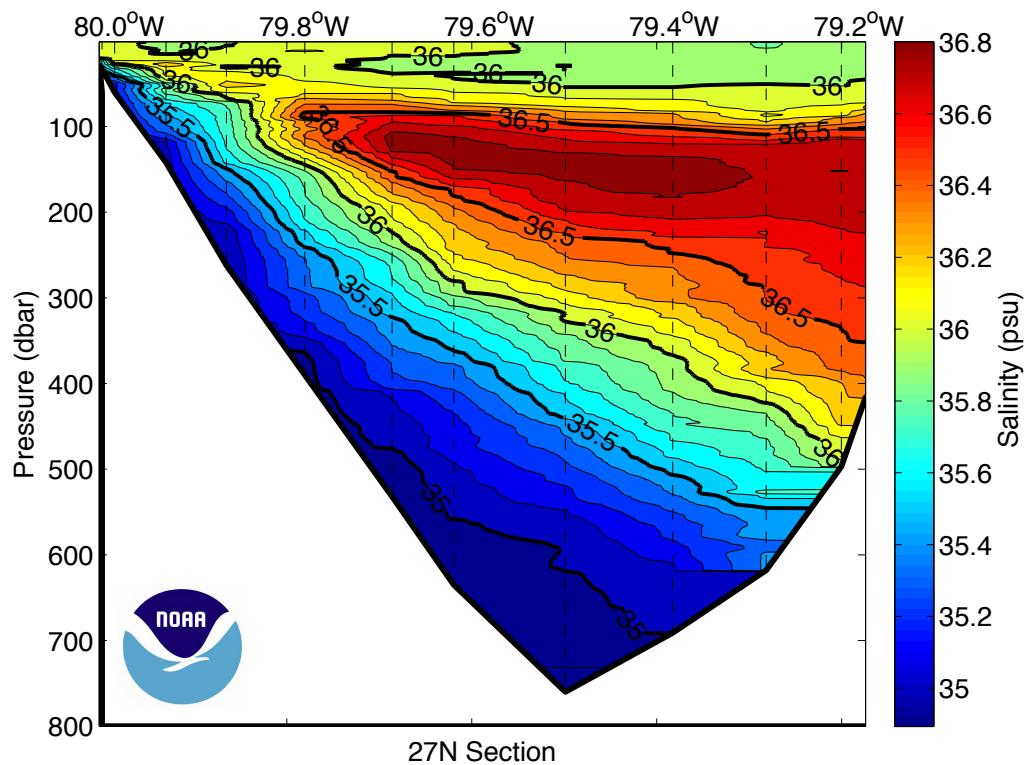


Figure 19: Salinity along the 27°N section.

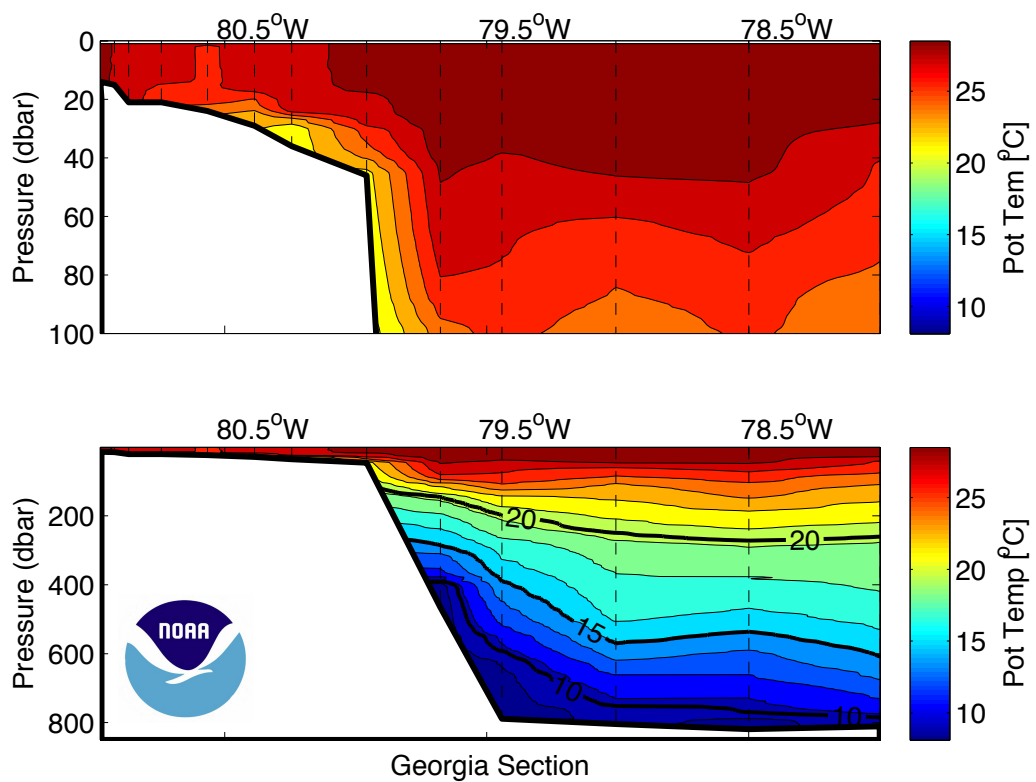


Figure 20: Potential temperature along the Georgia section.

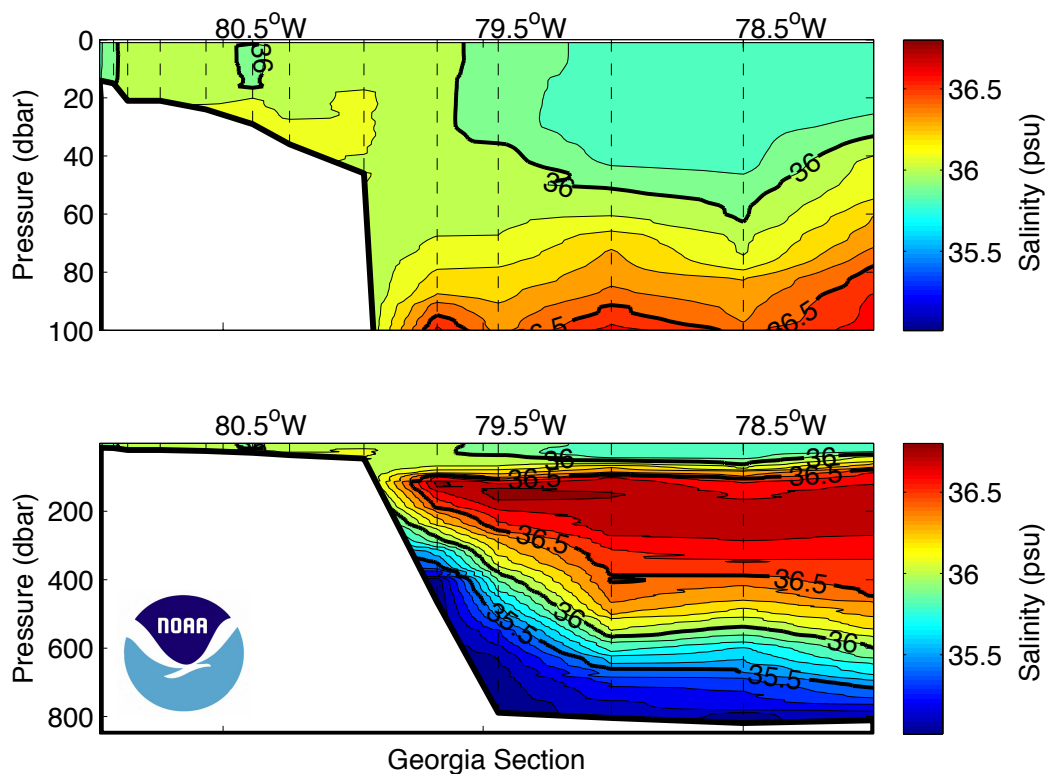


Figure 21: Salinity along the Georgia section.

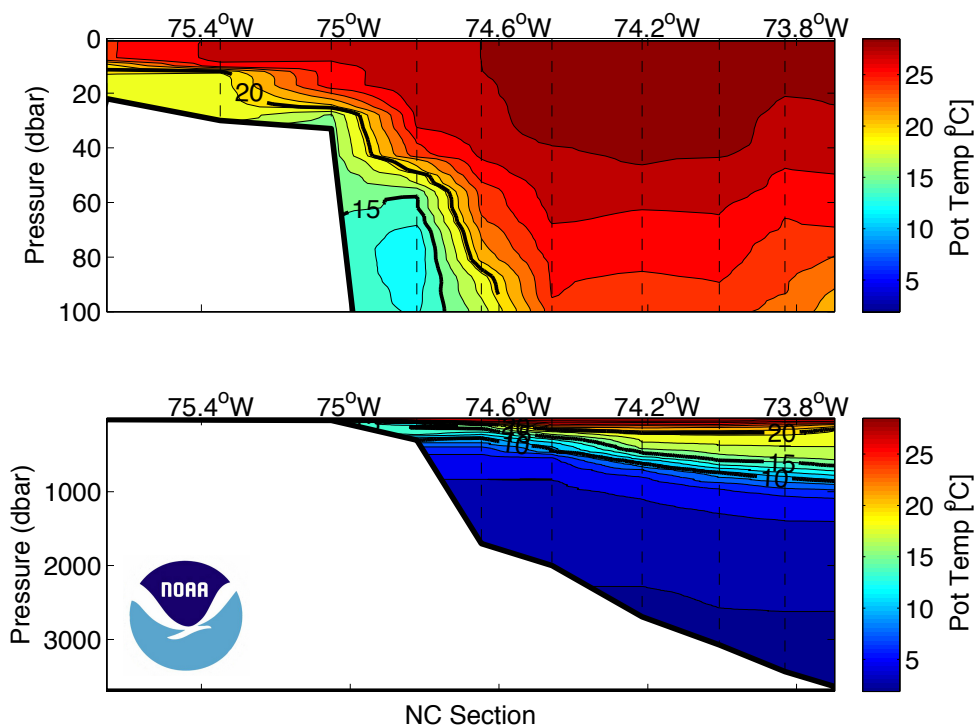


Figure 22: Potential temperature along the Cape Hatteras section.

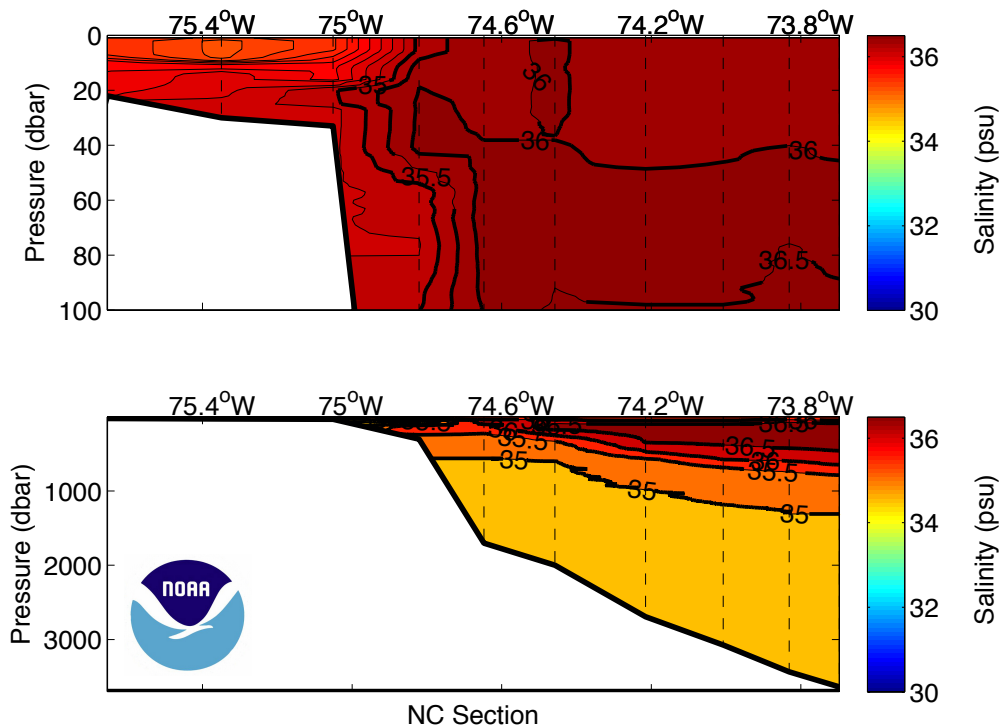


Figure 23: Salinity along the Cape Hatteras section.

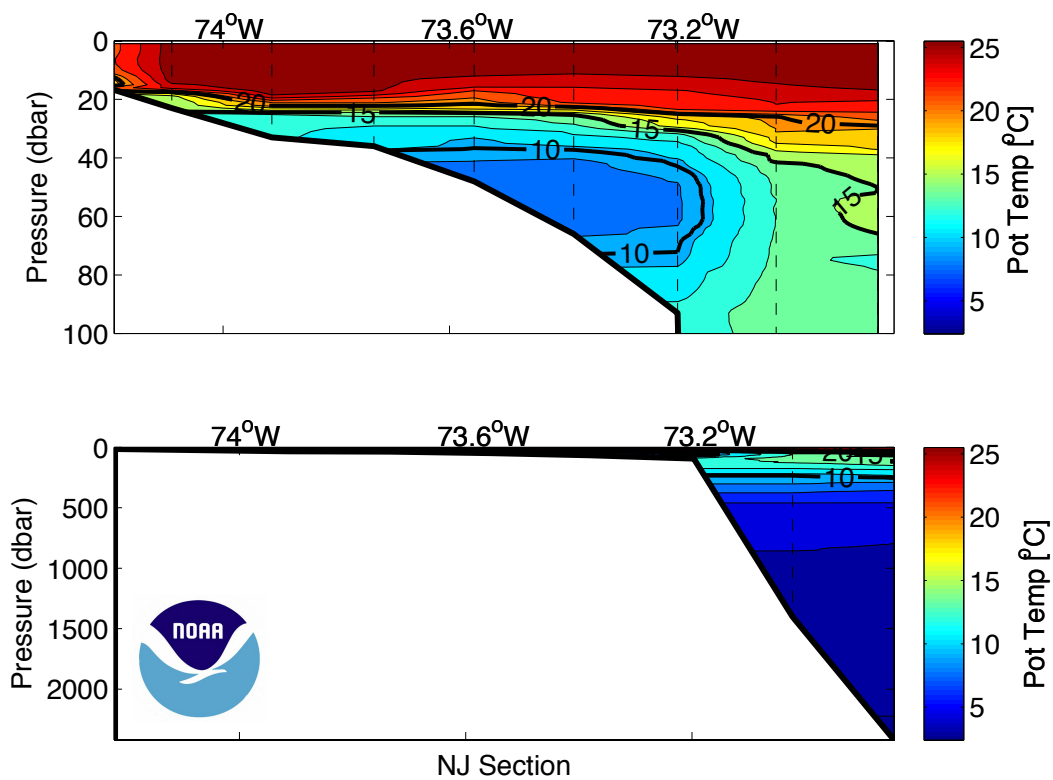


Figure 24: Potential temperature along the New Jersey section.

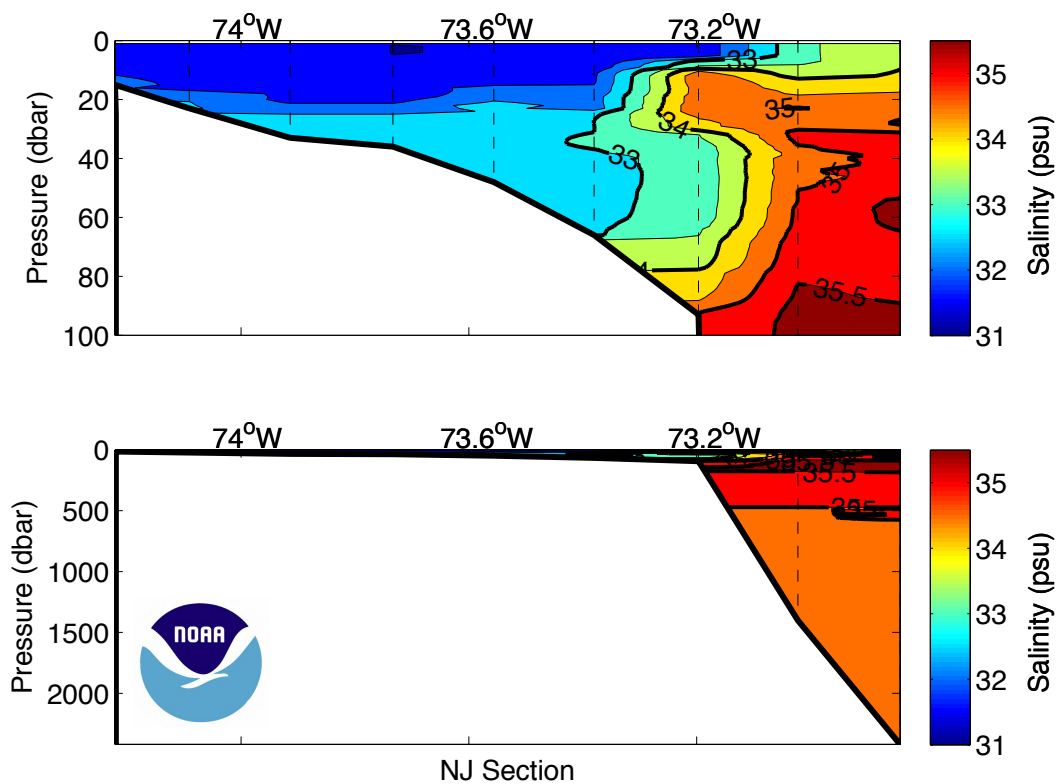


Figure 25: Salinity along the New Jersey section.

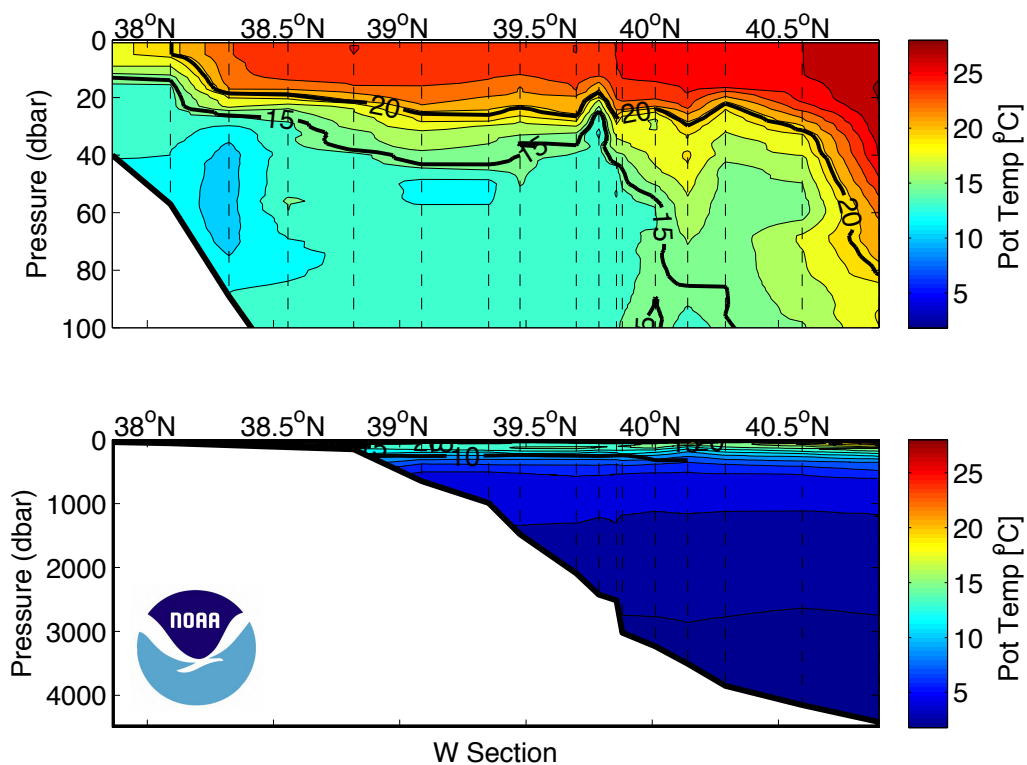


Figure 26: Potential temperature along the Line W section.

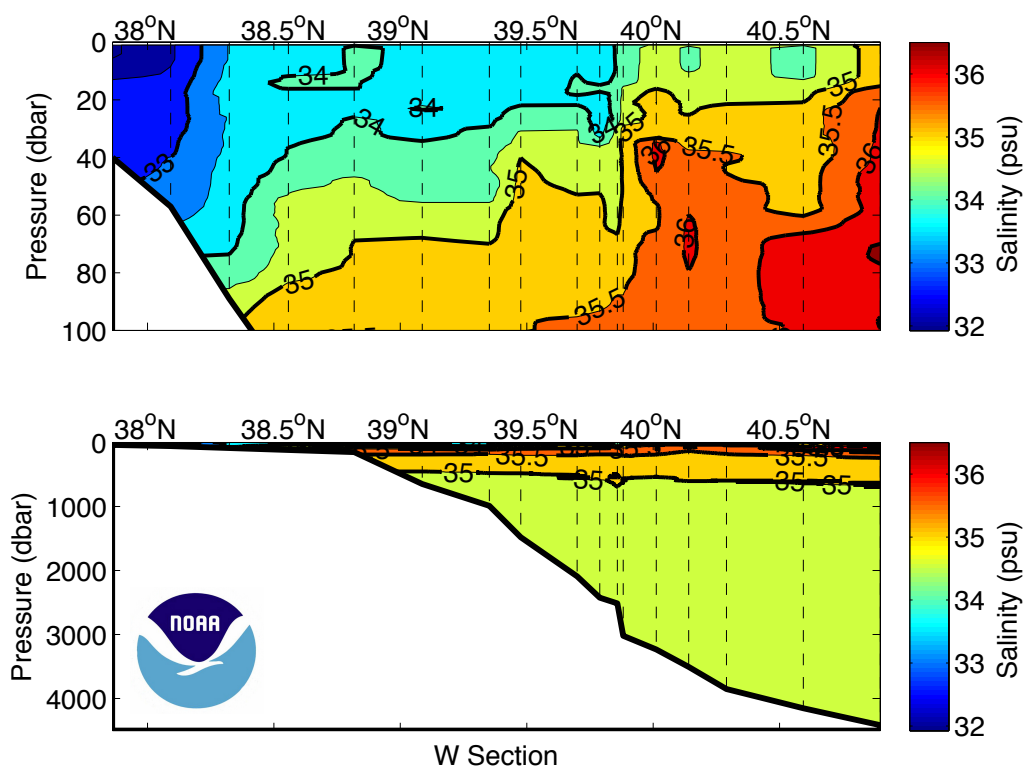


Figure 27: Salinity along the Line W section.

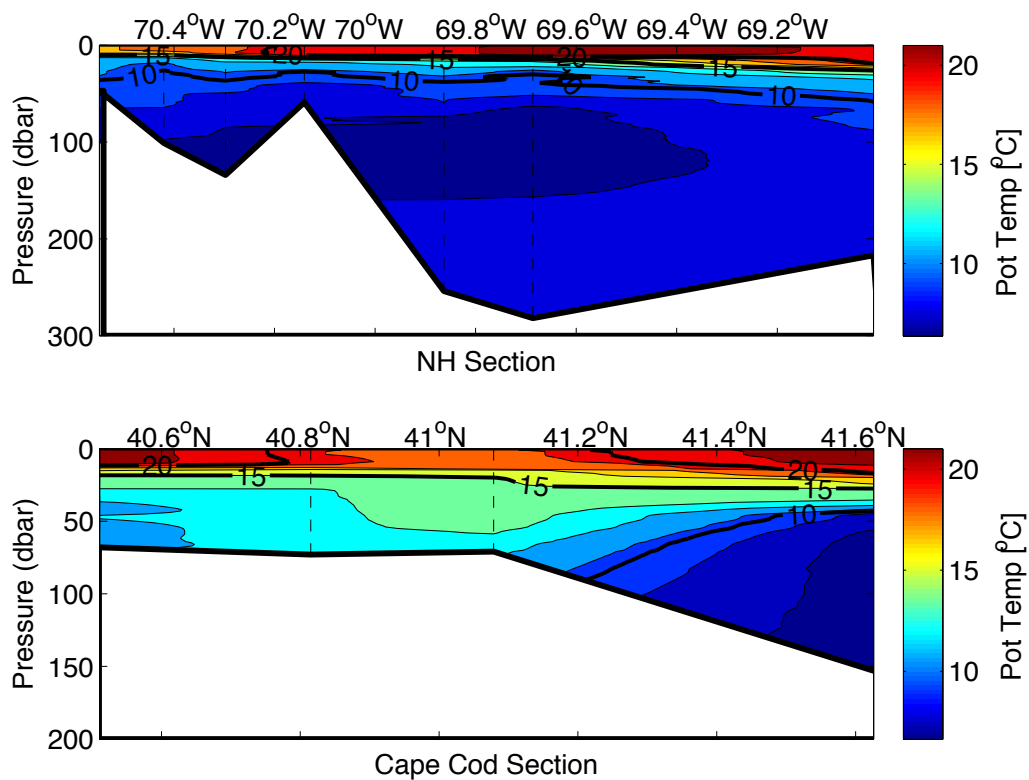


Figure 28: Potential temperature along the New Hampshire section.

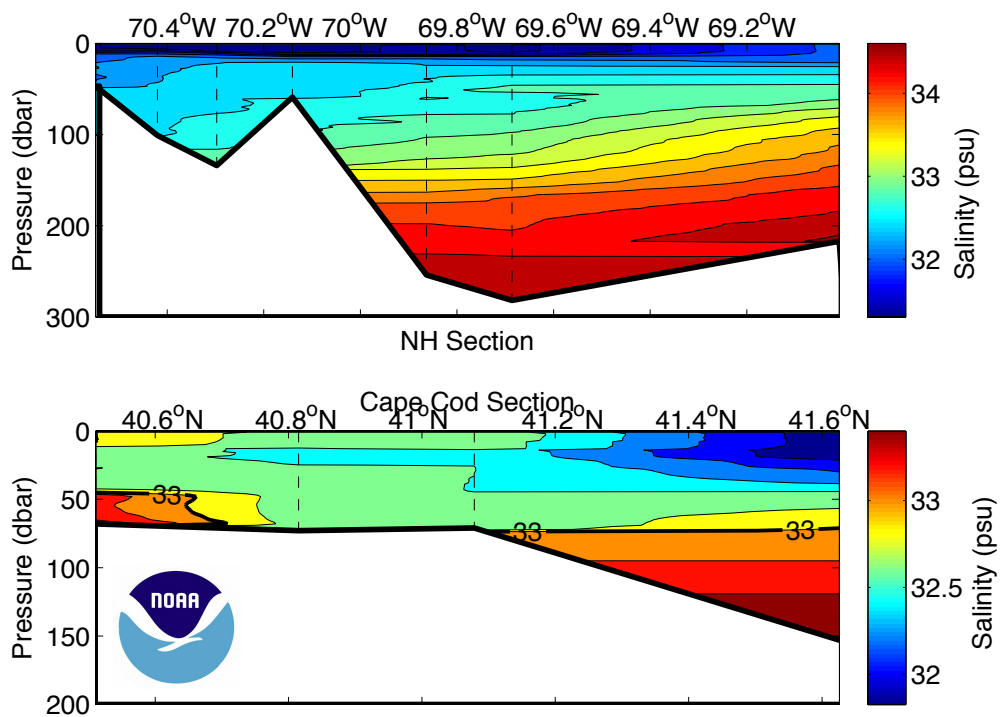


Figure 29: Salinity along the New Hampshire section.

3.2 Discrete Salinity Measurements

Analysts: Erik Valdes (CIMAS/RSMAS), Kyle Seaton, and Andrew Stefanick (NOAA/AOML)

A single Guildline Autosol, model 8400B salinometer (S/N 60843, nicknamed Josey), located in the salinity analysis room, was used for all salinity measurements. The autosol was the same one used for the spring 2012 WBTS cruise (it was filled, powered on and ready to go). The salinometer readings were logged on a computer using Ocean Scientific International's logging hardware and software. The Autosol's water bath temperature was set to 24°C, which the Autosol is designed to automatically maintain. The laboratory's temperature was also set and maintained to just below 24°C, to help further stabilize reading values and improve accuracy. Salinity analyses were performed after samples had equilibrated to laboratory temperature, usually at least 24 hours after collection. The salinometer was standardized for each group of samples analyzed (usually 2 casts and up to 50 samples) using two bottles of standard seawater: one at the beginning and end of each set of measurements. The salinometer output was logged to a computer file. The software prompted the analyst to flush the instrument's cell and change samples when appropriate. For each sample, the salinometer cell was initially flushed at least 3 times before a set of conductivity ratio readings were taken.

IAPSO Standard Seawater Batch P-154 was used to standardize all casts.

The salinity samples were collected in 200 ml Kimax high-alumina borosilicate bottles that had been rinsed at least three times with sample water prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. Laboratory temperature was also monitored electronically throughout the cruise. PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The offset between the initial standard seawater value and its reference value was applied to each sample. The difference (if any) between the initial and final vials of standard seawater was then applied to each sample as a linear function of elapsed run time. The corrected salinity data was then incorporated into the cruise database. When duplicate measurements were deemed to have been collected and run properly, they were averaged and submitted with a quality flag of 6. On GOMECC-2, 1139 salinity measurements were taken and approximately 60 vials of standard seawater (SSW) were used. A duplicate sample was drawn from each cast to determine total analytical precision.

The running standard calibration values are shown in Figure 30. Through the course of the 24-day cruise, the autosol standards changed by 0.0001 in conductivity ratio (about 0.008 in salinity).

- a. Recommend that in the future we bring a UPS clean power supply/conditioner. We discovered that we thought the room was equipped

with clean power, but it is not. A UPS/power conditioner should help reduce electrical noise.

- b. Recommend that all AOML salinity bottles be renamed following PMEL convention of 1-24, 101-124, 201-224, etc. This should reduce errors and issues on incomplete cast sampling issues, etc.

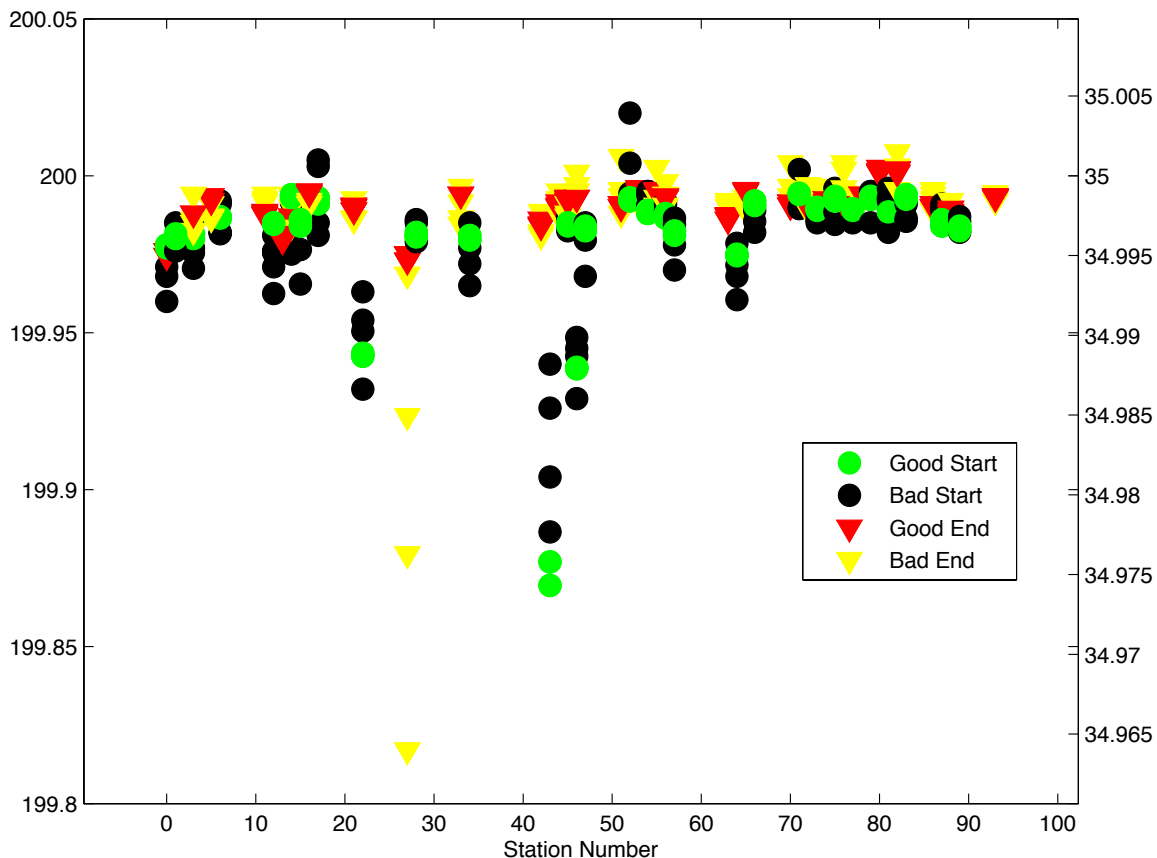


Figure 30: Salinity standard vial calibrations throughout the cruise.

3.3 Oxygen Measurements

Analysts: Hernan Garcia (NODC) and Carolina Mor (MBF/RSMAS, University of Miami)

Data oversight: Chris Langdon, (MBF/RSMAS, University of Miami)

Samples were drawn from all casts and all Niskin bottles into volumetrically calibrated 125 ml iodine titration flasks using Tygon tubing with a silicone adaptor that fit over the petcock to avoid contamination of DOC samples. Bottles were rinsed three times and filled from the bottom, overflowing three volumes while taking care not to

entrain any bubbles. The draw temperature was taken using a digital thermometer with a flexible thermistor probe that was inserted into the flask while the sample was being drawn during the overflow period. These temperatures were used to calculate micromole/kg ($\mu\text{mol kg}^{-1}$) concentrations, and a diagnostic check of Niskin bottle integrity. One ml of MnCl_2 and one ml of NaOH/NaI were added immediately after drawing of the sample was concluded using a Repipetor, the flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. The flasks were stored in the lab in plastic totes at room temperature for at least 1 hour before analysis. Twenty-four samples plus duplicates were drawn from each station except the shallow coastal stations where fewer samples were drawn depending on the depth or as directed by the chief scientist. The total number of hydrocast samples collected was 1578. A total of 82 sets of duplicates were run. The preliminary difference between replicates averaged $0.2 \mu\text{mol kg}^{-1}$ for stations 1-93. The total number of samples flagged after initial shipboard reduction of quality control: Questionable (n=51): Not reported (n=2).

200 additional discrete oxygen samples including duplicates were drawn from the ship's uncontaminated seawater line along the cruise track at specific times for the purpose of checking the calibration of the UNH Aanderra Optode oxygen sensor and for comparison with the oxygen sensor on the UGA CO_2 buoy.

Dissolved oxygen analyses were performed with an automated oxygen titrator using amperometric end-point detection (Langdon 2010). The titration of the samples and the data logging and graphical display was performed on a PC running a LabView program written by Ulises Rivero of AOML. The titrations were performed in a climate controlled lab at 18.5°C - 20°C . Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. Tests in the lab were performed to confirm that the precision and accuracy of the volume dispensed were comparable or superior to the Dosimat 665. The whole-bottle titration technique of Carpenter (1965) with modifications by Culberson et al. (1991) was used. Four to three replicate 10 ml iodate standards were run 13 times during the cruise. The reagent blank was determined at the beginning and end of the cruise. 1 ml of iodate standard was titrated using a volume (V1) of thiosulfate. An additional 1 ml of standard was added to the titrated sample and titrated again. The volume of thiosulfate used for the second titration was defined as V2. The reagent blank was determined as the difference between V1 and V2.

References

- Carpenter, J.H. (1965). *The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method*. Limnol. Oceanogr. 10: 141-143
- Culberson, C.H. and Huang, S. (1987). *Automated amperometric oxygen titration*. Deep-Sea Res. 34: 875-880.
- Culberson, C.H.; Knapp, G.; Stalcup, M.; Williams, R.T. and Zemlyak, F. (1991). *A comparison of methods for the determination of dissolved oxygen in seawater*. WHP Operations and Methods.
- Langdon, C. (2010). *Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique*. The GO-SHIP Repeat Hydrography Manual:

3.4 Nutrient Measurements

Analyst: Charles J. Fischer (NOAA/AOML)

3.4.1 Equipment and Techniques

Nutrient samples were collected from Niskin bottles, after at least three seawater rinses. Sample analysis typically began within a few hours of sample collection after the samples had warmed to room temperature. Those samples not analyzed within 3 hours were refrigerated for later analysis. Nutrients were analyzed with a continuous flow analyzer (CFA) using the standard and analysis protocols for the WOCE hydrographic program as set forth in the manual by L.I. Gordon, *et al.* (1993). In addition, nutrient samples were collected from the ship's underway system at selected intervals.

3.4.2 Analytical Methods

1333 samples were taken at discrete depths and from the ship's underway system. They were analyzed for phosphate (PO_4^{-3}), nitrate (NO_3^{-}), nitrite (NO_2^{-}) and orthosilicic acid (H_4SiO_4). Nitrite was determined by diazotizing the sample with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm. Samples for nitrate analysis were passed through a cadmium column, which reduced nitrate to nitrite, and the resulting nitrite concentration (i.e. the sum of nitrate + nitrite which is signified as N+N) was then determined as described above. Nitrate concentrations were determined from the difference of N+N and nitrite (Zhang et al., 1997). Phosphate was determined by reacting the sample with molybdcic acid to form phosphomolybdcic acid. This complex was subsequently reduced with hydrazine, and the absorbance of the resulting phosphomolybdous acid was measured at 710 nm (Zhang et al., 2000). Silicic acid was analyzed using Zhang and Berberian (1997). The sample is reacted with ammonium molybdate in an acidic solution to form molybdosilicic acid. The molybdosilicic acid was then reduced with ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue was measured at 660 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride by Gordon et al.) was to reduce toxicity of our waste stream.

Temperatures in the ship's main laboratory fluctuated with temperatures ranging from 19°C to 22°C; however, temperatures were generally stable during an individual analytical run. During the cruise, pump tubes were changed as needed.

3.4.3 Standardization

A mixed stock standard consisting of silicic acid, phosphate and nitrate was prepared by dissolving high purity standard materials (KNO_3 , KH_2PO_4 and Na_2SiF_6) in deionized water using a two step dilution for phosphate and nitrate. This standard was stored at room temperature. A nitrite stock standard was prepared dissolving NaNO_2 in distilled water, and this standard was stored in the ship's refrigerator. Working standards were prepared fresh daily by diluting the stock solutions in low nutrient seawater. The mixed standards were verified against commercial standards (Wibby Environmental), and in-lab standards.

3.4.4 Problems

Due to problems with the NO_2 detector, NO_2 measurements were not possible for stations 12 – 21. There were also continuing problems with the AUFS settings for NO_2 , but was corrected during data processing.

References:

- Gordon, L.I., Jennings Jr., J.C., Ross, A.A. and Krest, J.M. (1993). *A suggested protocol for the continuous automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic program and the Joint Global Ocean Fluxes Study*. WOCE Operations Manual, vol. 3: The Observational Programme, Section 3.2: WOCE Hydrographic Programme, Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1; WOCE Report No. 68/91. November 1994, Revision 1, Woods Hole, MA., USA, 52 loose-leaf pages.
- Zhang, J.-Z. and Berberian G.A. (1997). *Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis*. EPA Method 366.0. National Exposure Research Laboratory Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Zhang, J.-Z., Ortner, P.B., Fischer, C.J. (1997). *Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis*. EPA Method 353.4. National Exposure Research Laboratory Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Zhang, J.-Z., Fischer, C.J., Ortner, P.B. (2000). *Continuous Flow Analysis of Phosphate in Natural Waters Using Hydrazine as a Reductant*. Intern. J. Environ. Anal. Chem. 80(1): 61-73.

3.5 DIC Measurements

Analysts: Esa Peltola and Chuck Featherstone (NOAA/AOML)

Samples for total dissolved inorganic carbon (DIC) measurements were drawn according to procedures outlined in the *Handbook of Methods for CO₂ Analysis* (DOE 1994) from Niskin bottles into cleaned 294-ml glass bottles. Bottles were rinsed and filled from the bottom, leaving 6 ml of headspace; care was taken not to entrain any bubbles. After 0.2 ml of saturated HgCl₂ solution was added as a preservative, the sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours prior to analysis.

The DIC analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (AOML3 and AOML4) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a Dissolved Inorganic Carbon Extractor (DICE) inlet system. DICE was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA (Johnson et al. 1985, 1987, 1993, and 1999; Johnson 1992). In the coulometric analysis of DIC, all carbonate species are converted to CO₂ (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved CO₂ gas is swept into the titration cell of the coulometer with pure air or compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. In this process, the solution changes from blue to colorless, triggering a current through the cell and causing coulometrical generation of OH⁻ ions at the anode. The OH⁻ ions react with the H⁺, and the solution turns blue again. A beam of light is shone through the solution, and a photometric detector at the opposite side of the cell senses the change in transmission. Once the percent transmission reaches its original value, the coulometric titration is stopped, and the amount of CO₂ that enters the cell is determined by integrating the total charge during the titration.

The coulometers were calibrated by injecting aliquots of pure CO₂ (99.99%) by means of an 8-port valve outfitted with two sample loops with known gas volumes bracketing the amount of CO₂ extracted from the water samples for the two AOML systems.

The stability of each coulometer cell solution was confirmed three different ways: two sets of gas loops were measured at the beginning; also the Certified Reference Material (CRM), Batches 112 and 120, supplied by Dr. A. Dickson of SIO, were measured at the beginning; and the duplicate samples at the beginning, middle, and end of each cell solution. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9–12 hours of continuous use.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes. The weights with the appropriate densities were used to determine the volume of the pipettes.

Calculation of the amount of CO₂ injected was according to the CO₂ handbook (DOE 1994). The concentration of CO₂ ($[CO_2]$) in the samples was determined according to:

$$[CO_2] = Cal.factor * \frac{(Counts - Blank * Run Time) * K \mu mol/count}{pipette volume * density of sample}$$

where *Cal. Factor* is the calibration factor, *Counts* is the instrument reading at the end of the analysis, *Blank* is the counts/minute determined from blank runs performed at least once for each cell solution, *Run Time* is the length of coulometric titration (in minutes), and *K* is the conversion factor from counts to micromoles.

The instrument has a salinity sensor, but all DIC values were recalculated to a molar weight ($\mu\text{mol/kg}$) using density obtained from the CTD's salinity. The DIC values were corrected for dilution by 0.2 ml of saturated HgCl_2 used for sample preservation. The total water volume of the sample bottles was 288 ml (calibrated by Esa Peltola, AOML). The correction factor used for dilution was 1.0007. A correction was also applied for the offset from the CRM. This additive correction was applied for each cell using the CRM value obtained in the beginning of the cell. The average correction was 2.3 $\mu\text{mol/kg}$.

While both systems worked very well during the cruise, they occasionally had high blanks. Normally the blank is less than 30, but we were forced to run them with blanks in the 12-45 range.

Other problems were relatively minor. The Midas failed shortly after the cruise began so compressed Nitrogen was used for sample analysis. Communication errors between the instruments and their controlling laptop computers occurred several times. Coulometer AOML 5 was replaced with Coulometer AOML 3 on DICE 3 the second to last day during the GOM line of stations.

Underway samples were collected from the flow thru system in the Wet Lab during transits between station lines. Discrete DIC samples were collected every two hours with duplicates every fourth sample. A total of 143 discrete DIC samples including duplicates were collected while underway.

A total of 1159 samples including duplicates were analyzed for discrete dissolved inorganic carbon from 93 CTD casts. The total dissolved inorganic carbon data reported to the database directly from the ship are to be considered preliminary until a more thorough quality assurance can be completed shore side.

References

- DOE (U.S. Department of Energy). (1994). *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater*. Version 2.0. ORNL/CDIAC-74. Ed. A. G. Dickson and C. Goyet. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Johnson, K.M., Körtzinger, A.; Mintrop, L.; Duinker, J.C.; and Wallace, D.W.R. (1999). *Coulometric total carbon dioxide analysis for marine studies: Measurement and*

- internal consistency of underway surface TCO₂ concentrations*. Marine Chemistry 67:123–44.
- Johnson, K.M., Wills, K.D.; Butler, D.B.; Johnson, W.K.; and Wong, C.S. (1993). *Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated gas extraction*.
- Johnson, K.M. (1992). *Operator's Manual: Single-Operator Multiparameter Metabolic Analyzer (SOMMA) for Total Carbon Dioxide (CT) with Coulometric Detection*. Brookhaven National Laboratory, Brookhaven, N.Y.
- Johnson, K.M.; Williams, P.J.; Brandstrom, L.; and McN. Sieburth, J. (1987). *Coulometric total carbon analysis for marine studies: Automation and calibration*. Marine Chemistry 21:117–33.
- Johnson, K.M.; King, A.E.; and McN. Sieburth, J. 1985. *Coulometric TCO₂ analyses for marine studies: An introduction*. Marine Chemistry 16:61–82.

3.6 Discrete pCO₂ Measurements

Analysts: Kevin Sullivan (CIMAS/RSMAS), Andrew Margolin (MAC/RSMAS University of Miami)

3.6.1 Sampling:

Samples were drawn from 10-L Niskin bottles into 500 ml glass bottles using Tygon© tubing with a Silicone adapter that fit over the drain cock to avoid contamination of DOM samples. Bottles were rinsed twice, the second time while inverted. They were filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper and tubing of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of twelve hours prior to analysis.

The analyses for pCO₂ were done with the discrete samples at 20°C. A primary water bath was kept within 0.03°C of the analytical temperature; a secondary bath was kept within 0.15°C the analytical temperature. The majority of the samples were analyzed in batches of twelve bottles, which with standards took approximately 2.5 hours. When twelve bottles were moved into the primary water bath for analyses, the next twelve bottles were moved into the secondary water bath. No sample bottle spent less than one hour in the secondary water bath prior to being moved to the analytical water bath.

Significant effort was made to sample every depth on every cast; however, the relatively slow analysis required skipping some depths from some stations that were close to each other. Duplicate samples from the same Niskin were drawn regularly to check the precision of the sampling and analysis. Discrete samples were collected from the underway (UW) flowing sea water line aboard the ship. The UW samples will be

compared to the results for the autonomous pCO₂ instrument. Some discrete UW samples were collected as a station was being completed. Generally, these UW samples were well less than 1% different than the samples collected from the top Niskin.

Approximately one thousand two hundred samples were drawn at ninety-two stations. Over one hundred and thirty samples were collected from the UW seawater line, mostly during the transits between stations. More than fifty sets of duplicate bottles were drawn at numerous depths. The average relative error of these duplicate pairs was 0.18%, while the median relative error was 0.11%.

3.6.2 Analyzer Description:

The principles of the discrete pCO₂ system are described in Wanninkhof and Thoning (1993) and Chipman et al. (1993). The major difference in the current system is the method of equilibrating the sample water with the constantly circulating gas phase. This system uses miniature membrane contactors (Micromodules from Memrana, Inc.), which contain bundles of hydrophobic micro-porous tubes in polycarbonate shells (2.5 x 2.5 x 0.5 cm). The sample water is pumped over the outside of the tubing bundles in two contactors in series at 25 ml/min. The gas is recirculated through the inside of the tubing and through a non-dispersive infrared analyzer, LI-COR© (model 840) at 13-14 ml/min.

The flow rates of the water and gas are chosen with consideration of competing concerns. Faster water and gas flows yield faster equilibration. A slower water flow would allow collection of smaller sample volume; while a slower gas flow would minimize the pressure increase in the contactor. Additionally, the flow rates are chosen so that the two fluids generate equal pressures at the micro-pores in the tubes to avoid leakage into or out of the tubes. A significant advantage of this instrumental design is the complete immersion of the miniature contactors in the constant temperature bath. Also in the water bath are coils of stainless steel tubing before the contactors that ensure the water and gas enter the contactors at the known equilibration temperature.

The instrumental system employs a large insulated cooler (Igloo Inc.) that accommodates twelve sample bottles, the miniature contactors, a water stirrer, a copper coil connected to a Neslab© water bath, an immersion heater, a 12-position sample distribution valve, two thermistors, and two miniature pumps. The immersion heater works in opposition to the cooler water passing through the copper coil. One thermistor is immersed in the water bath, while the second thermistor is in a sample flow cell after the second contactor. The difference between the two thermistor readings was consistently less than 0.01°C. In a separate enclosure are the 8-port gas distribution valve, the infrared analyzer, a barometer, and other electronic components. The gas distribution valve is connected to the gas pump and to six standard gas cylinders.

To ensure analytical accuracy, a set of six gas standards (ranging from 248 to 1534 ppm) was run through the analyzer before and after every sample batch. The

standards were obtained from Scott-Marín and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale.

A custom program developed using LabView™ controls the system and graphically displays the CO₂ concentration as well as the temperature and pressure during the 10-minute equilibration. The CO₂ in the gas phase changes greatly within the first minute of a new sample and then goes through nearly two more oscillations. The oscillations dampen quickly as the concentration asymptotically approaches equilibrium. The flows are stopped, and the program records an average of ten readings from the infrared analyzer along with other sensor readings. The data files from the discrete pCO₂ program are reformatted so that a Matlab program designed for processing data from the underway pCO₂ systems can be used to calculate the fugacity of the discrete samples at 20°C. The details of the data reduction are described in Pierrot, et.al. (2009).

The instrumental system was designed and built by Tim Newberger and was supported by C. Sweeney and T. Takahashi. Their skill, assistance, and generosity were essential to the successful use of this instrumental system during this cruise. No instrumental problems occurred during the cruise.

Standard Gas Cylinders:

Cylinder#	ppm CO ₂
JA02280	248.73
JB03268	384.14
JB03309	567.40
CA05980	792.51
CA05984	1036.95
CA05940	1533.7

References

- Chipman, D.W.; Marra, J.; and Takahashi, T. (1993). *Primary production at 47°N and 20°W in the North Atlantic Ocean: A comparison between the 14C incubation method and mixed layer carbon budget observations*. Deep-Sea Res., II, v. 40, pp. 151-169.
- Wanninkhof, R.; and Thoning, K. (1993). *Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods*. Mar. Chem., v. 44, no. 2-4, pp. 189-205.
- Pierrot, D.; Neill, C.; Sullivan, K.; Castle, R.; Wanninkhof, R.; Luger, H.; Johannessen, T.; Olsen, A.; Feely, R.A.; and Cosca, C.E. (2009). *Recommendations for autonomous underway pCO₂ measuring systems and data-reduction routines*. Deep-Sea Res., II, v. 56, pp. 512-522.

3.7 Total Alkalinity Measurements

Analysts: Andrew Joesoef and Wei-Jen Huang (UGA)

3.7.1 Alkalinity Definition:

The definition of total alkalinity used is the proton acceptors – proton donors. In order to define the acceptors and the donors, *zero level of protons* was defined ($pK_{zlp} = 4.5$ is adapted from Dickson 1981). Thus, when

$pK \leq pK_{zlp}$: acids are proton donors;

$pK > pK_{zlp}$: base formed from weak acids are proton acceptors.

By Dickson's definition, total alkalinity, (TA), is expressed as:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - [HNO_2]$$

Wolf-Gladrow (2007) derived Dickson's expression from electro neutrality, the explicitly conservative form of total alkalinity or TA_{ec} , as:

$$TA_{ec} = [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] + \dots - [Cl^-] - [Br^-] - [NO_3^-] - \dots + TPO_4 + TNH_3 - 2TSO_4 - THF - THNO_2$$

Where,

$$TPO_4 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$TNH_3 = [NH_3] + [NH_4^+]$$

$$TSO_4 = [SO_4^{2-}] + [HSO_4^-]$$

$$THF = [F^-] + [HF]$$

$$THNO_2 = [NO_2^-] + [HNO_2]$$

3.7.2 Principle of titration

The precision of alkalinity determination was improved by using a potentiometric titration with a glass electrode (Dyrssen 1965, Dyrssen and Sillen 1967). The Gran method (Gran, 1952) was used to determine the end point.

3.7.3 Determination of Total Alkalinity by Gran Titration:

The Gran titration essentially linearizes the titration curve using the following function:

$$F = (v + V_0) * 10^{E/a}, \text{ where}$$

F = Gran Factor, v = volume of acid added to the sample vessel, V_0 = sample volume, E = electric motive force (EMF) measured, and a = slope of electrode.

On the $v - F$ diagram a linear regression can be used to determine the intercept on the x-axis, which is the second end point of titration.

Principle of pH glass electrode:

The pH electrode is the core of the total alkalinity measurement. The main function of the glass electrode is to measure the voltage contributed by $[H^+]$ between the interior (reference electrode) and exterior (solution) of the electrode.

3.7.4 Equipment

TA was measured by Gran titration (Gran, 1952) using the open cell method with a semi-automatic titration system (AS-ALK2, Apollo Scitech), consisting of two KloehnTM syringe pumps (module #50300) of 1 ml and 25 ml respectively, a pH meter (AR15, Accumet Research), and a ROSS combination pH glass electrode (Orion 8102BN, Thermo Scientific). Throughout the entire cruise, the TA samples, the HCl solution, and the syringes of the KloehnTM pumps were all water-jacketed at 22 ± 0.1 °C maintained by a thermal bath (VWR, Scientific Product).

3.7.5 Sampling

During this GOMECC2 cruise (7/21 – 8/13, 2012), 1039 TA samples were collected, including 980 TA samples from 87 stations along with 8 transects, and 59 samples from the underway system. All of the samples were measured in 48 hours except 86 samples were poisoned with 40 μ l saturated $HgCl_2$ for later, post-cruise analysis at the UGA lab.

TA samples were taken by 250ml narrow-ground neck, borosilicate glass bottles from Niskin bottles after removing air bubbles from the sampling tubing. Each glass bottle was rinsed three times and then filled from the bottom (overflow of half of bottle volume seawater was allowed). One ml headspace was left for those post-cruise-analysis samples and no headspace was left for those measured on board.

Furthermore, 223 DIC samples and 226 Ca^{2+} samples were collected in 60 ml borosilicate glass vials and 100 ml borosilicate glass bottles (Pyrex 7740), respectively. They were shipped back to UGA lab and analyzed.

3.7.6 Measurements, Precision, and Accuracy:

For each measurement, 25 ml of TA sample was titrated with an HCl solution (0.1 M HCl and 0.5 M NaCl). This TA titration system has a precision of better than 0.1 % (Cai et al. 2010). pH electrode was calibrated with pH buffer (NBS) 4.01, 7.00, and 10.01 and recalibration was done every 12 to 24 hours.

All the TA values were directly measured with reference to Certified Reference Material (CRM, batch#114). System (titrator and electrode) stability was also checked along with the sample run using the CRM seawater every 12 hours or when necessary. Ten duplicated samples were sampled during this cruise. The precision of this method is better than 0.1% and accuracy is 0.1%.

References:

- Dickson A.G. (1981). *An exact definition of total alkalinity, and a procedure for the estimation of alkalinity and total inorganic carbon from titration data*. Deep-Sea Res. 28, 609-623.
- Dickson A.G. (1992). *The development of the alkalinity concept in marine chemistry*. Marine chemistry 40:1-21-2, 49-63.
- Gran G. (1952). *Determination of the equivalence point in potentiometric titrations. Part II*. The analyst, 77, 661-671.
- Bates, R.G. *Determination of pH. Theory and Practice. A Wiley-Interscience Publication*, Second Edition.
- Wolf-Gladrow, D.A. et al. (2007). *Total alkalinity: The explicit conservative expression and its application to biogeochemical process*.

3.8 pH and carbonate measurements

Analysts: Xuewu [Sherwood] Liu, Regina Easley, Mark Patsavas, Bo Yang and Yong-Rae Kim (USF)

3.8.1 Discrete pH Measurements

Sampling

Samples were collected for pH analysis immediately following O₂ in the Niskin/Rosette sampling sequence. Seawater samples were collected from the Niskin bottles directly in 10-cm cylindrical optical cells (~30 mL volume) using a section of silicone tubing (about 15 cm long). One end of the silicone tubing was attached to the optical cell and the other end was attached to the nipple of the Niskin bottle. The Niskin bottle nipple was pushed in to initiate flow and the silicone tubing was squeezed to eliminate air bubbles. The optical cell was agitated to eliminate bubbles and, after 15 seconds of sample flow, the cell was capped at one end. The silicone tubing was then detached from the optical cell and, with the water still flowing, the cap was rinsed and used to seal the optical cell. Samples collected this way were not exposed to the atmosphere, and each cell was flushed with approximately three cell volumes of seawater.

The samples were collected, taken into the lab, and rinsed with tap water to get rid of salt outside of the cells. The cells were dried and the optical windows were cleaned with Kimwipes. Samples were thermostatted at 25 (±0.05) °C in a custom made 36-position cell warmer.

Measurement and Calculation

The pH_T of each sample was determined on an Agilent 8453 spectrometer setup with a custom-made temperature-controlled cell holder. Only the tungsten lamp was turned on. The UV lamp was turned off to prevent photodegradation of organic matter in the samples by UV light. A custom macro program running on Agilent ChemStation was used to guide the measurements and data processing. The macro automated the procedures of sample input, blank and sample scans, quality control, and data archiving. The quality control steps included checking the baseline shift after dye injection and monitoring the standard deviation of multiple scans. Absorbance blanks were taken for each sample and 10 microliters (μl) of purified m-cresol purple (10 mmol kg^{-1}) were added for the analysis. pH_T (total scale) was calculated according to Liu et al. (2011):

$$\text{pH}_T = -\log(K_2^T e_2) + \log \left(\frac{R - e_1}{1 - R \frac{e_3}{e_2}} \right) \quad (1)$$

with R being the ratio of absorbances measured at 578 nm (λ_2) and 434 nm (λ_1): $R = \lambda_2 A / \lambda_1 A$. The salinity and temperature dependence of $K_2^T e_2$ is given as:

$$-\log(K_2^T e_2) = a + (b / T) + c \ln T - dT \quad (2)$$

where

$$a = -246.64209 + 0.315971S + 2.8855 \times 10^{-4} S^2$$

$$b = 7229.23864 - 7.098137S - 0.057034S^2$$

$$c = 44.493382 - 0.052711S$$

$$d = 0.0781344$$

and the temperature and salinity dependence of e_1 and e_3/e_2 are given by:

$$e_1 = -0.007762 + 4.5174 \times 10^{-5} T \quad (3)$$

$$e_3 / e_2 = -0.020813 + 2.60262 \times 10^{-4} T + 1.0436 \times 10^{-4} (S - 35) \quad (4)$$

These equations are applicable for samples between temperature ($278.15\text{K} \leq T \leq 308.15\text{K}$) and salinity ($20 \leq S \leq 40$). In all of our measurements at sea $T = 298.15\text{K}$.

The pH is calibration-free (no calibrations are needed). Duplicate pH samples were collected from underway samples ($N = 105$) and from discrete samples taken from the Niskin bottles ($N = \sim 60$) with a precision equal to ± 0.0004 .

3.8.2 Direct Carbonate Ion ($[CO_3^{2-}]$) Measurements

Sampling

The carbonate ion samples were sampled into quartz cells in the same manner as the pH samples. After the pH samples were taken, the quartz cells were attached to the silicone tubing to collect samples for carbonate ion concentration measurements.

Measurement and Calculation

The carbonate ion concentration of each sample was determined on an Agilent 8453 spectrometer setup with a custom-made temperature-controlled cell holder. A custom macro program was used to guide the measurements and data processing in a similar manner as was done for pH measurements.

Samples were analyzed on an Agilent 8453 spectrophotometer. A UV blank was taken for each sample and 20 microliters (μ l) of 0.022 M $PbClO_4$ were added (Acros Organics, Lot A0301399 – 99% purity). Absorbances, A , were measured at two wavelengths (${}_1\lambda = 234$ nm and ${}_2\lambda = 250$ nm), along with the absorbance at a non-absorbing wavelength (350 nm). Carbonate ion concentrations were calculated using equation:

$$-\log[CO_3^{2-}]_T = \log\{({}_{CO_3}\beta_1)/(e_2)\} + \log\{(R - e_1)/(1 - Re_3/e_2)\} \quad (5)$$

where ${}_{CO_3}\beta_1$ is the $PbCO_3^0$ formation constant, e_i are molar absorptivity ratios, and $R = {}_{250}A/{}_{234}A$ (Byrne and Yao, 2008). Equation 5 is equivalent to equation 20 of Byrne and Yao (2008). The fitting parameters given for measurements at 25 °C were:

$$\log\{({}_{CO_3}\beta_1)/(e_2)\} = 6.087 - 8.495 \times 10^{-2}S + 9.360 \times 10^{-4}S^2 \quad (6)$$

$$e_1 = 0.2215 - 5.554 \times 10^{-4}S + 8.440 \times 10^{-5}S^2 \quad (7)$$

$$(e_3/e_2) = 3.061 - 8.730 \times 10^{-2}S + 9.363 \times 10^{-4}S^2 \quad (8)$$

where S is salinity. Duplicate carbonate ion samples were collected from underway samples ($N = 105$) and from discrete samples taken from the Niskin bottles ($N = \sim 80$).

3.8.3 Spectrophotometric Quality Control

All spectrophotometric pH and CO_3^{2-} measurements were tentatively flagged if the baseline shifted more than 0.002 absorbance units for pH and 0.004 absorbance units for carbonate ion measurements. A series of at least three spectra were averaged for each determination and samples were rerun if the overall standard deviations were higher than 0.0004 for pH measurements and 0.002 for carbonate ion measurements. This process was repeated until the standard deviation of multiple readings was within 0.0004 for pH

and 0.002 for carbonate. Absorbance values were saved so that the quality criteria can be evaluated in the future.

A total of 1308 pH samples and 1312 carbonate ion samples were collected from the 93 stations, and 225 underway samples were collected for both parameters.

3.8.4 Perturbation Determinations

Small changes in sample pH and carbonate ion concentrations (measurement perturbations; Clayton and Byrne (1993)) created by addition of titrants to samples were quantified using samples collected from profiles. For each perturbation determination, ΔR was defined as $\Delta R = R_{\text{initial}} - R_{\text{final}}$, where R_{initial} is the absorbance ratio taken after a single titrant addition and R_{final} is the R-ratio after a second titrant addition.

3.8.5 Data Processing

Final reported pH data includes the perturbation correction. The values for the CO_3^{2-} data do not include the perturbation correction and will be updated accordingly. Data for directly measured carbonate are reported in terms of both concentrations and the R-Ratios taken at 250 nm and 234 nm. Following redetermination of the fitting parameters in equations 2–4, the raw data can subsequently be evaluated to provide more accurate assessments of carbonate ion concentrations. Data for both $[\text{CO}_3^{2-}]$ and pH are reported at the analysis temperature of 25 °C.

References

- Byrne, R.H.; & Yao, W. (2008). *Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb(II) complexation*. Marine Chemistry, 112(1-2), 128-135.
- Clayton, T.D.; & Byrne, R.H. (1993). *Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results*. Deep Sea Research Part I: Oceanographic Research Papers, 40(10), 2115-2129. doi: 10.1016/0967-0637(93)90048-8
- Liu, X.; Patsavas, M.C.; & Byrne, R. H. (2011). *Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements*. Environmental Science & Technology, 45(11), 4862-4868. doi: 10.1021/es200665d

3.9 Phytoplankton community distribution across the continental margins.

Shipboard Analysts: Sumit Chakraborty and Madalyn Meaker (USM)

Shoreside support: PI : Steven E. Lohrenz (UMass),

Shoreside Analyst and Data Manager: Sumit Chakraborty (USM)

Objectives:

Our primary objective was to complement the GOMECC2 cruise objectives to characterize carbon and ocean acidification properties in the coastal margin with observations of phytoplankton taxonomy and community structure across large spatial and environmental gradients. Our other objectives were to provide in situ observations of optical properties in support of ocean color algorithm validation for Visible Infrared Imaging Radiometer Suite (VIIRS).

Additionally, data collected during this cruise will help us to assess or validate pigment (HPLC) derived phytoplankton community structure with other approaches like traditional microscopy and more modern techniques such as flow cytometry and DNA analysis.

Sampling and Methods:

3-4 L of seawater was drawn from the 10 L Niskin bottles into pre-clean (with de-ionized water) carboys for every station. Samples were collected from a variety of depths, a maximum of 6 within the top 200 m of the water column. Sampling was based on the fluorescence profile at each station.

Phytoplankton pigments:

During the cruise, seawater (2-4 L) for pigment analysis was collected at selected depths (based on the fluorescence profile) from 10 L Niskin bottles on a rosette and was immediately filtered onto *Whatman* 47mm GF/F filters using a vacuum pump <0.5 atm. The filters were blotted dry and frozen in 2 ml cryotubes in liquid nitrogen till analysis on land. The phytoplankton pigment analysis will follow the method described in Van Heukelem and Thomas (2001). Details of analysis precision will be provided during data submission. QA-QC protocols for pigments analysis will follow the steps mentioned in Hooker et al. (2005).

Microscopy:

125 ml of seawater samples were collected into amber bottles pre-fixed with Lugol's iodine. At most stations samples were collected at the surface (4 m) and at the chlorophyll max or at bottom (for shallow stations). Samples were stored in the dark at lab temperatures.

Flow Cytometry:

Approximately 2 ml of seawater were collected in cryovials and were fixed using a mixture of glutaraldehyde + formaldehyde (final concentration of 1% by volume). Samples were incubated at room temperature for about 15 minutes and then stored in liquid N₂.

DNA analysis:

150-1000 ml of seawater were filtered onto a 25 mm Milipore Isopore HAWP 0.45 µm filter. Special care was taken to avoid contaminations; forceps were sanitized before use with ethanol for every sample. Filters were folded and stored in cryotubes in liquid N₂.

Discrete samples were also collected for particulate absorption (a_p) and total suspended solids (TSS) from the flow through of the UNH optics tank.

TSS (Total suspended solids):

About 500-4000 ml of seawater were filtered onto 0.7 µm (nominal size) GF/F filters. Pre-weighted and combusted GF/F's were used for the collection of the TSS samples. Special care was taken to avoid sea-salt retention in the filters; sample filters were rinsed several times with deionized water to remove sea salt. The dry mass of particles collected on the filters will be measured with an OHAUS Discovery microbalance (resolution 0.0001 mg). TSS samples were collected in conjunction with particulate organic carbon (POC) samples, POC samples collected during GOMECC2 will be analyzed at the UNH lab (P.I: Joe Salisbury).

Particulate absorption (a_p):

A seawater volume of 500-3500 ml, depending on the amount of particles present, was filtered onto a 25 mm Whatman GF/F glass-fiber filter at low vacuum. Immediately following filtration the filters were stored in liquid N₂ until laboratory analysis. The absorption spectrum of the particles ($a_p(\lambda)$) retained on the filter will be measured with a benchtop spectrophotometer (Cary 100) using the quantitative filter pad technique (Lohrenz et al. 2003); a clear GF/F filter soaked in filtered seawater (0.2 µm) will be used as a reference blank. The spectrophotometer (Cary 100) equipped with a 60 nm integrating sphere, absorbance will be measured between 300-800 nm. Following the measurements of $a_p(\lambda)$, absorption coefficients of non-algal particles (NAP), $a_{NAP}(\lambda)$ will be determined, after pigment extraction from the filters by hot methanol for 30 min. The extracted filters will be rinsed with MilliQ water to ensure removal of the biliproteins and the excess methanol and finally rinsed with filtered seawater (0.2 µm). Correction of pathlength amplification will be made according to Lohrenz (2000). Final estimates will be made on all spectra after subtracting the mean absorption values between 750 and 800 nm. Phytoplankton absorption coefficients will be determined by $a_{\phi}(\lambda) = a_p(\lambda) - a_{NAP}(\lambda)$.

A non-linear exponential function will be fitted to all NAP spectra to determine the spectral slope coefficient of NAP (S_{NAP})

$$a_{\text{NAP}}(\lambda) = a_{\text{NAP}}(\lambda_r) \exp^{(-S_{\text{NAP}}(\lambda - \lambda_r))}$$

where λ_r is the absorption at the reference wavelength. The fit will be performed according to Babin et al. (2003) and on raw data (i.e. not log-transformed). Each fitted curve will be individually checked for quality QA-QC. This be reported at the time of data submission.

Number of samples collected: 380 pigment samples from 91 CTD cast, 160 for each (DNA, flow cytometry and microscopy), 85 each for TSS and a_p , were collected during GOMECC2.

References:

- Babin, M.; Stramski, D.; Ferrari, G.M.; Claustre, H.; Bricaud, A.; Obolensky, G.; and Hoepffner, N. (2003). *Variations in the light absorption coefficients of phytoplankton, nonalgal particles, and dissolved organic matter in coastal waters around europe*. Journal of Geophysical Research C: Oceans 108:4-1
- Hooker, S.B.; VanHeukelem, L.; Thomas, C.S.; Claustre, H.; et al. (2005). *The second sea-wifs hplc analysis round-robin experiment (seaharve-2)*.
- Lohrenz, S.E. (2000). *A novel theoretical approach to correct for pathlength amplification and variable sampling loading in measurements of particulate spectral absorption by the quantitative filter technique*. Journal of Plankton Research 22:639-657
- Lohrenz, S.E.; Weidemann, A.D.; and Tuel, M. (2003). *Phytoplankton spectral absorption as influenced by community size structure and pigment composition*. Journal of Plankton Research 25:35-61
- Van Heukelem, L.; and Thomas, C.S. (2001). *Computer-assisted high-performance liquid chromatography method development with applications to the isolation and analysis of phytoplankton pigments*. Journal of Chromatography A 910:31-49

3.10 Dissolved organic carbon (DOC) and colored dissolved organic matter (CDOM)

DOC sampling

Analyst: Andrew Margolin (MAC/RSMAS, University of Miami)

Samples for DOC analysis were collected on all sections except for the Louisiana and 27° North sections. Samples were collected at ~50 m intervals in the top 200 m, ~100 m intervals between 200 and 1000 m, and at all depths > 1000 m. Forty mL of unfiltered seawater were collected into PC bottles, frozen upright in the onboard walk-in

freezer at -16°C (3°F), and stored frozen for shipment. In total, 598 samples for DOC analysis were collected. These are complementary to the samples collected by UNH for DOC/CDOM/Chl_a analysis. At stations where DOC samples were collected for both RSMAS and UNH analyses, duplication occurred at the surface and bottom depths. At shallow stations (water depths ~50 m), DOC samples were not collected by RSMAS since they were collected by UNH. Samples will be analyzed in Dr. Dennis Hansell's lab at RSMAS by Andrew Margolin and Dr. Wenhao Chen over the next few months.

CDOM and DOC sampling

Shipboard analyst: Marc Emond (UNH) See section 4.4

4.- Underway Measurements

4.1 Underway pCO₂ Analyses

Analysts: Kevin Sullivan (CIMAS/RSMAS), Jonathan Shannahoff, Chief Survey Technician *R H Brown*

During the GOMECC cruise, there was an automated underway pCO₂ system from AOML situated in the hydrolab, as it has been since 2007. The design of the instrumental system is based on Wanninkhof and Thoning (1993), and Feely et al. (1998), while the details of the instrument and of the data processing are described in Pierrot, et.al. (2009).

The repeating cycle of the system includes 4 gas standards, 5 ambient air samples, and 66 headspace samples from its equilibrator within 3.3 hours. The concentrations of the standards range from 285 to 546 ppm CO₂ in compressed natural air. They were purchased from NOAA/ESRL/GMD in Boulder and are directly traceable to the WMO scale.

The system includes an equilibrator where approximately 0.6 liters of constantly refreshed surface seawater from the bow intake is equilibrated with 0.8 liters of gaseous headspace. The water flow rate through the equilibrator was 1.0 - 1.5 liters/min, which is slightly lower than usual because of the greater demand for underway water during this cruise.

The equilibrator headspace is circulated through a non-dispersive infrared analyzer (IR), a LI-COR™ 6262, and then returned to the equilibrator. When ambient air or standard gas is analyzed, the gas leaving the analyzer is vented to the lab. A KNF pump constantly draws 6-8 liter/min of marine air through 100 m of 0.95 cm (= 3/8") OD Dekoron™ tubing from an intake on the bow mast. The intake has a rain guard and a

filter of glass wool to prevent water and larger particles from contaminating the intake line and reaching the pump. The headspace and marine air gases are dried before flushing the IR analyzer.

A custom program developed using LabView™ controls the system and graphically displays the air and water results. The program records the output of the infrared analyzer, the GPS position, water and gas flows, water and air temperatures, internal and external pressures, and a variety of other sensors. The program records all of this data for each analysis.

The automated pCO₂ analytical system operated well throughout the entire cruise.

Standard Gas Cylinders

Cylinder#	ppm CO ₂
CA06709	284.75
CA02813	363.24
CA07921	423.57
CA07931	545.88

References

- Pierrot, D.; Neill, C.; Sullivan, K.; Castle, R.; Wanninkhof, R.; Luger, H.; Johannessen, T.; Olsen, A.; Feely, R.A.; and Cosca, C.E. (2009). *Recommendations for autonomous underway pCO₂ measuring systems and data-reduction routines*. Deep-Sea Res., II, v. 56, pp. 512-522.
- Feely, R.A.; Wanninkhof, R.; Milburn, H.B.; Cosca, C.E.; Stapp, M.; and Murphy, P.P. (1998). *A new automated underway system for making high precision pCO₂ measurements onboard research ships*. Analytica Chim. Acta, v. 377, pp. 185-191.
- Wanninkhof, R., and Thoning, K. (1993). *Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods*. Mar. Chem., v. 44, no. 2-4, pp. 189-205.

4.2 Ammonia Underway Measurements

Shipboard Analyst: Charles Fischer (NOAA/AOML)

Shoreside support: Natchanon Amornthammarong, (CIMAS/RSMAS)

Introduction

A portable ammonium analyzer was developed and used to measure ammonium in the marine environment. The analyzer incorporates an improved LED photodiode-based fluorescence detector (LPFD). This system is more sensitive and considerably smaller than previous systems and incorporates a pre-filtering subsystem enabling

measurements in turbid sediment-laden waters. Over the typical range for ammonium in marine waters (0-10 micromolar, μM), response is linear ($r^2 = 0.9930$) with a S/N ratio > 3 and a limit of detection of 10 nanoM. Reproducibility is 0.3% ($n=10$) at an ammonium level of 2 micromolar. Results from automated operation in 15-min cycles over 16 days had good overall precision ($n = 660$, RSD = 3%). The system was field tested at three shallow South Florida sites.

Experimental Section

Reagents

Reagent 1 (R1) was prepared by dissolving 2.01 g of *o*-phthaldialdehyde (OPA, P1378, Sigma) in 200 mL of methanol and made up to 1 L with deionized water. The concentration of OPA is 15 milliM.

Reagent 2 (R2) was prepared by dissolving 1.26 g of sodium sulfite (1-3922, J.T. Baker Chemical) in 5 milliM formaldehyde (HCHO) solution. The solution is 10 milliM sulfite in 5 milliM HCHO.

Stock Standard: A 0.1 M NH_4Cl stock solution was prepared by dissolving 5.35 g ammonium chloride (12125-02-9, Aldrich) in 1 L deionized water.

All chemicals were reagent grade. Acidic traps (made of acid-washed silica) were used to protect reagents and standard solutions from possible atmospheric ammonia contamination. Exposure of reagents and standards to ambient air was minimized to avoid such contamination⁽¹⁾.

Portable Fluorometric Analyzer

All components of the instrument were housed in a metal case (12.7cm x 22.9cm x 43.2cm). The fluidic system is shown in Figure 31. It consists of one syringe pump (P/N 54023, Kloehe, NV) equipped with an eight-way distribution valve. The syringe pump is equipped with a 5-mL capacity zero dead volume syringe. The details of this pump, its configuration and mode of operation were described in our previous work⁽²⁾. In order to completely and rapidly mix the solutions; the syringe itself serves as the primary mixing chamber, and a 5 mL pipette tip as the secondary mixing chamber. Mixing is complete in 5 cycles⁽³⁾. The mixed solution is held in the syringe for 3 more minutes during which 1-sulfonatoisoindole is formed. The syringe pump then pushes the solution into the LED photodiode-based fluorescence detector (LPFD) to obtain a response signal. Last, the system is cleaned by deionized water (DIW), which is pumped through the syringe, the pipette tip, and the detector 3 times before the system is ready to take another measurement. The cleaning steps reduce contamination from previous samples and minimize carryover. A small amount of the new sample is disposed as waste prior to the next measurement.

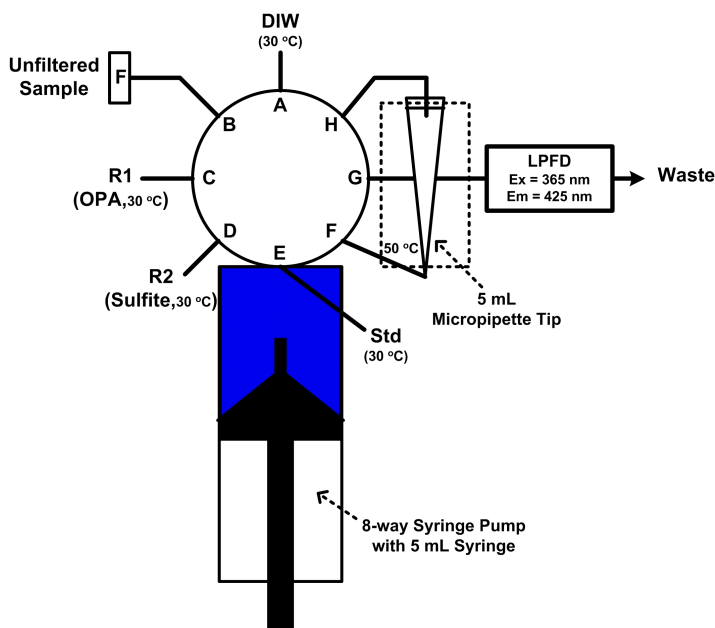


Figure 31: The components of the portable ammonium analyzer: DIW, deionized water; Std, standard solution; F, passive filter 0.45 μm ; LPFD, LED-photodiode-based flow-through fluorescence detector. DIW, R1, R2 and Std solutions were temperature-controlled at 30 $^{\circ}\text{C}$.

Underway method.

For operating as an underway system, the port B is connected with a filter and put inside a small cup where the seawater continuously overflows all the time.

Data processing.

After each run, the peak information was processed with Microcal Origin Pro 7.0 and Excel to get the peak height of each peak. Ammonia concentrations were reported in micromoles per liter, and then converted to micromoles per kilogram.

Approximately 1400 underway samples (the sampling rate is 4 times/hour) were analyzed during the GOMECC cruise. Detection limit for this cruise is 10 nanoM (nmol/L). No replications for these samples were made.

Problems.

After the power outage during the first week of the cruise, the ammonia system was malfunctioning. It was still able to run for about a week after that, and then the syringe pump stopped working. We are not certain that the power outage caused the problems.

References:

- ⁽¹⁾Amornthammarong, N.; Jakmunee, J.; Li, J.; and Dasgupta, P.K. (2006). Anal. Chem. 78, 1890 - 1896.
- ⁽²⁾Amornthammarong, N.; Ortner, P.B.; and Zhang, J.-Z. (2010). Talanta. 81, 1472-1476.
- ⁽³⁾Amornthammarong, N.; Zhang, J.-Z.; and Ortner, P.B. (2011). Anal. Methods. 3, 1501-1506.

4.3 Underway Measurements of pCO₂, TCO₂, and pH using a Multi-parameter Inorganic Carbon Analyzer (MICA)

Shipboard Analysts: Xuewu [Sherwood] Liu, Regina Easley, Bo Yang, Mark Patsavas, (USF)

The USF automated Multi-parameter Inorganic Carbon Analyzer (MICA) was used to simultaneously measure underway surface sea water DIC and pH during the GOMECC II cruise. The MICA instrument was set up in the wet lab alongside NOAA's underway pCO₂ system. MICA generally takes 4 parameters (pCO₂ in air and water, DIC and pH). Considering the shipboard NOAA pCO₂ set up for the GOMECC II cruise, only the DIC and pH channels were configured for use on GOMECC II. The instrument was set up with dual DIC and pH channels. Combined with NOAA's pCO₂ underway data, underway observations of pCO₂, DIC and pH_T were collected at high resolution.

In contrast to the GOMECC I cruise, purified m-cresol purple was used as the pH indicator (Liu et al. 2011) on the GOMECC II expedition. The indicator was directly injected into a stream of underway seawater, and absorbances were monitored spectrophotometrically.

For DIC measurements, Teflon AF 2400 (DuPont) was used as both a CO₂ permeable membrane and a long liquid-core waveguide (LCW) (Wang et al., 2007). DIC measurements were obtained using acidified seawater samples to convert all carbonate species to CO₂ before analysis.

All channels were thermostated in a Lauda E100 water bath that was set to 25 ± 0.05°C. All samples, reference and indicator solutions were also temperature pre-equilibrated in the water bath at 25°C using PEEK and glass coils. All measurements, as well as calibrations, were conducted at 25 ± 0.05°C.

A program ran cycles to operate the MICA continuously. The time required for each measurement cycle depended on the equilibration time and flushing time for the indicator/reference solution and samples (~2 minutes). The chemical reaction for pH measurements was essentially instantaneous. The following sequence was used during each measurement cycle:

1. Flush pH reference (sea water samples without indicator solution).
2. Flush reference for DIC.
3. Read and store reference readings.
4. Flush indicator solutions for seawater *DIC*; mix mCP with sea water samples (pH measurements); acidify DIC samples.
5. Wait 5 minutes for pre-equilibration of DIC channel.
6. Read and store measurements every minute.
7. Repeat these steps 30 times.
8. End one measurement cycle and repeat from the beginning.

During measurements, seawater flowed continuously through the channels.

The precisions of parameters were determined as follows:

pH	± 0.001
DIC	$\pm 2 \mu\text{mol/kg}$

Over 20,000 pairs of underway pH and DIC were collected during the GOMECC II cruise.

References

- Liu, X., Patsavas, M.C., & Byrne, R.H. (2011). *Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements*. Environmental Science & Technology, 45(11), 4862-4868. doi: 10.1021/es200665d
- Wang, Z.A., et al., (2007). *Simultaneous spectrophotometric flow-through measurements of pH, carbon dioxide fugacity, and total inorganic carbon in seawater*. Analytica Chimica Acta, 596(1): p. 23-36.

4.4 Ocean Color Measurements

Shipboard Analyst: Marc Emond (UNH)

Shoreside support: J. Salisbury, P.I.; Shawn Shellito, equipment and Chris Hunt, data analysis (UNH). Antonino Mannino from NASA Goddard is a collaborator.

Tank measurements:

We operated an underway, continuous seawater system comprised of a 120 liter tank containing 6 sensors. The sensors are listed in Table 6. The residence time of

seawater in the tank was 6-10 minutes. The data (along with GPS) were logged throughout the cruise for 10 minutes each ½ hour, at a rate of 1Hz. The tank was cleaned and the ac-9 calibrated every 1-3 days depending on visual water quality.

Tank Instrument	Measurement	Manufacturer	units
ac-9	Attenuation and absorption at 9 l	WetLabs	m ⁻¹
Oxygen optode	Oxygen (concentration and saturation %)	Aanderraa	micromol kg ⁻¹ ; %
FLNTU	Turbidity and chlorophyll fluorescence	WetLabs	NTU/ mg liter ⁻¹ chlorophyll
FDOM	Fluorescence of dissolved organic matter	WetLabs	QSE
ISUS	UV absorption (l); nitrate	Satlantic	m ⁻¹ ; micromol L ⁻¹
Aanderraa CT	salinity	Aanderraa	psu
Aanderraa CT	temperature	Aanderraa	degrees C
Profiling Instruments	Measurement	Manufacturer	units
CHL sensor ¹	Fluorescence of chlorophyll	WetLabs	mg liter ⁻¹ chlorophyll
FDOM sensor	Fluorescence of dissolved organic matter	Seapoint	QSE
Turbidity meter	turbidity	Seapoint	NTU

Table 6: Tank and Profiling instruments for ocean color measurements.

¹The profiling chlorophyll fluorescence sensor is property of AOML

Preliminary viewing of the first 9 days of tank data (except the ISUS), show that the optical instruments were responding as expected to surface features (e.g. low salinity; high attenuation, thermal fronts). The data show little influence of excessive bubbles, but do show a response in SST of <0.2 °C each time the tank is switched on. The tank had seawater coming in continuously, but a seabird pump was used to pull the tank water through the ac-9, pulling from the bottom of the instrument and exiting closer to the top. Each time the pump inside the tank was switched on, a slight increase in the temperature was observed, which leveled out shortly afterward. We believe that removing the first 1-3 minutes of data each time the tank is switched on will filter out this effect. Data processing, filtering and application of calibration information to the ac-9 instrument is scheduled to take place in October.

Profiling measurements:

We also provided optical instruments that were attached to the CTD (see Table 6). A Biospherical scalar irradiance sensor failed to provide data and was removed from the CTD a week into the deployment. Viewing of several profiles taken during the first week of the cruise shows good optical responses in f-chl, f-dom and turbidity to the vertical structure in the water column. F-dom demonstrates an expected response to salinity (e.g. increasing with decreasing salinity). However the scaling of the f-dom sensor was set to

expect a very large range of salinity (i.e. 10-37psu), thus its sensitivity is somewhat less than desired in regions of low fdom variability. Profiling data are scheduled to be checked for quality in October.

Bottle Samples:

During the cruise Marc Emond sampled for CDOM and DOC from all of the CTD casts. Samples were taken from the surface, near bottom (isopycnal), and where applicable at a second depth in the mixed layer. The samples were run through 47mm GFF filters and separated into 2 or 3 (depending on depth) 40ml vials for DOC and one 125ml bottle for CDOM. The DOC vials were frozen and the CDOM bottles refrigerated. DOC and CDOM samples will be analyzed by Antonio Mannino's laboratory at NASA Goddard. Additionally, samples for POC were taken several times per day from the outflow of the tank. These were filtered using precombusted GFF filters by colleague Sumit Chakraborty (USM). The filters were stored in liquid nitrogen and brought back to UNH where a subset of samples will be analyzed.

5.- Other Measurements

5.1 pH profiler

Analysts: Xuewu [Sherwood] Liu, Regina Easley, Mark Patsavas, Bo Yang and Yong-Rae Kim (USF)

During the GOMECC II cruise, USF scientists deployed their Spectrophotometric Elemental Analysis System (SEAS), an *in-situ* pH profiler, to obtain high resolution pH profiles. In contrast to the GOMECC I cruise, purified m-cresol purple (1.5 milliM) prepared in 0.7 m NaCl was used as the indicator stock solution. Running at 1 Hz, the instrument provided pH measurements with a frequency comparable to those for O₂, fluorescence and CTD data.

The rosette setup

During the cruise the pH profiler was deployed at hydrocast stations shallower than 1000 meters. The SEAS II instrument, measuring 130 cm tall and 18 cm in diameter, was installed via attachment to the rings of the Rosette frame (extending outside the Rosette frame). The instrument was powered by a nickel metal hydride (NiMH) battery pack which enabled measurements for a maximum of 8 hours. A Falmouth 2-inch Micro CTD (MCTD-MBP-D) was connected directly to SEAS II in order to obtain concurrent salinity, depth, and temperature data for pH calculations. The internal clock was set to

GMT time. The instrument and Micro CTD were removed from the Rosette for casts with bottom depths greater than 1000 m.

At each station, SEAS was powered up prior to the cast. The instrument was lowered to 20 meters to collapse bubbles in the pH cell. Seawater was then flushed for 5 minutes through the instrument prior to take a nine-wavelength reference scan. The dye pump was then turned on for 60 seconds in order to achieve a uniform mixture of seawater and dye prior to sample collection. There was an approximate 11 second delay between the sample intake and optical cell measurements. The profile data were subsequently uploaded from the instrument once the package was retrieved.

Profiles of pH were obtained on 57 of the hydro-casts conducted during the cruise. The vertical resolution of the profiled pH was better than 1 meter. The overall precision of the method was 0.001 pH units.

5.2 Above-Water Reflectance Measurements

P.I.: Anne Michelle Wood (AOML), Joe Salisbury (UNH), Bob Arnone (NRL)

Shipboard Analysts: Marc Emond (UNH), Sumit Chakraborty (USM), and A. Michelle Wood (AOML)

Shoreside Support: Sherwin Ladner (NRL)

Above-water hyperspectral reflectance measurements were collected at twenty-two stations along the cruise track (Table 7), usually under clear or only partly cloudy skies. Measurements were taken between 0900-1100 or 1500-1700 (local time) for preferred sun angle. Data were collected with an ASD, Inc. Field Spec 2 handheld spectroradiometer adapted for a 10-degree field-of-view and a spectralon 10% grey card as reference. Water and sky conditions at each station were recorded photographically and descriptively. These data were specifically collected as part of an ongoing AOML/Naval Research Laboratory (NRL) collaboration in support of the calibration and validation of the VIIRS sensor on the new National Polar Orbiting Satellite and as a complement to data on apparent and inherent optical properties and pigments being collected for GOMECC-II (see preliminary report from UNH and USM). Sampling sites included eight stations in the Gulf of Mexico and fourteen along the Atlantic east coast. Throughout the cruise, near-real time support was provided by NRL in the form of composite satellite imagery showing ocean color and temperature from either the NPP satellite or MODIS Aqua (Figures 32 and 33).

ASD Station	GOMECC-II Station	Date	Time (Local)	Time (UTC)	Latitude (N)	Longitude (W)	Water Depth (m)	Cloud %
1	asds*	7/22/12	1612	2012	25° 11.29'	84° 38.39'	1785	30
2	8	7/24/12	1600	2000	25° 56.08'	90° 07.37'	26	10
3	8	7/24/12	1606	2006	25° 56.08'	90° 07.37'	26	10
4	asds	7/26/12	1615	2015	25° 58.41'	84° 22.02'	65.4	<10
5	13	7/27/12	935	1335	26° 13.35'	85° 39.88'	3257	15
6	14	7/27/12	1645	2045	26° 26.40'	85° 19.74'	3286	15
7	asds	7/28/12	1100	1500	27° 46.80'	83° 19.75'	25	10
8	asds	7/28/12	1515	1915	24° 21.99'	84° 34.66'	53	2
9	22	7/30/12	1510	1910	27° 00.12'	80° 00.19'	58	<10
10	31	7/31/12	1104	1504	27° 00.17'	79° 16.89'	617	20
11	33	7/31/12	1523	1923	26° 59.38'	79° 10.45'	470	15
12	asds	8/1/12	1526	1926	31° 14.43'	80° 37.22'	23	0
13	43_2	8/2/12	1551	1951	30° 52.44'	79° 25.51'	788	<10
14	asds	8/3/12	1555	1955	31° 56.83'	79° 28.70'	60	<15
15	asds	8/4/12	1522	1922	35° 02.32'	75° 18.79'	72.2	40
16	50	8/5/12	935	1335	35° 54.25'	74° 49.26'	304	15
17	52	8/5/12	1530	1930	35° 46.61'	74° 25.70'	2000	20
18	59	8/7/12	1215	1615	39° 12.90'	73° 54.88'	30	80
19	asds	8/7/12	1614	2014	38° 53.87'	73° 26.34'	56	>90
20	asds	8/8/12	1515	1915	40° 37.12'	71° 10.34'	x	>90
21	74	8/9/12	1650	2050	39° 42.04'	69° 47.84'	x	30
22	asds	8/13/12	950	1350	42° 58.51'	70° 28.89'	90	0

Table 7: Above water reflectance measurements

*asds=ASD Stop while ship in transit

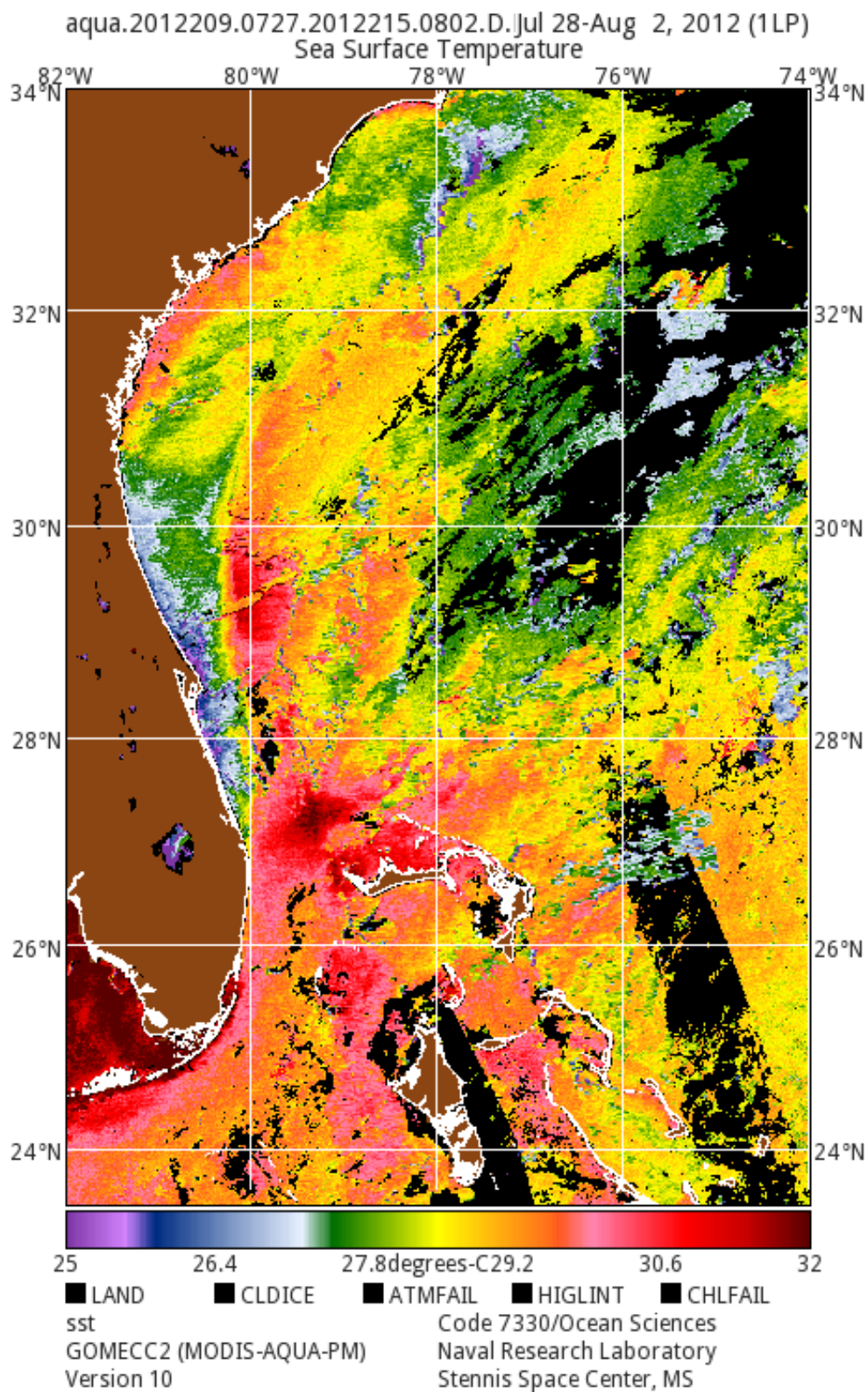
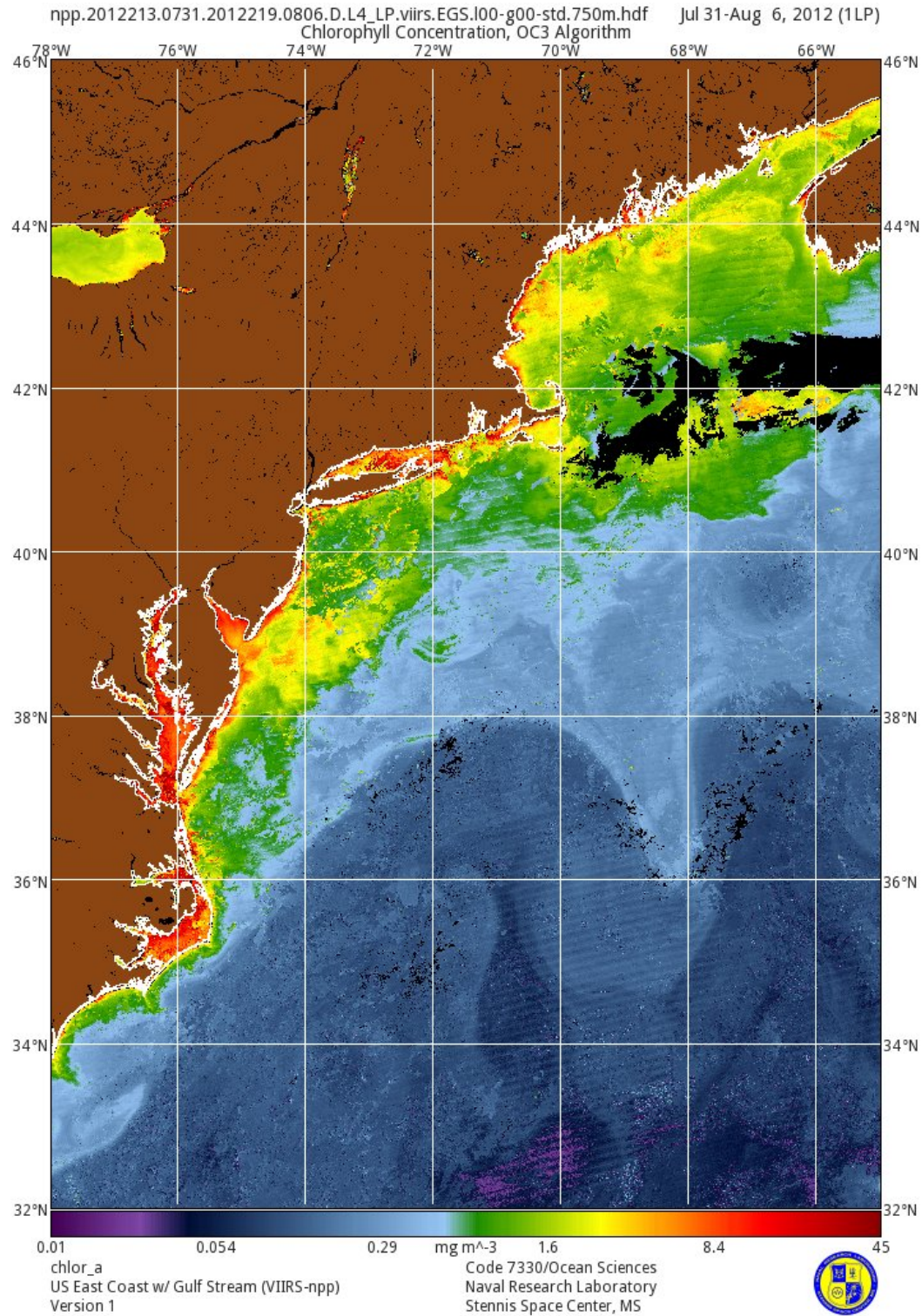


Figure 32: MODIS AQUA Sea Surface Temperature composite for July 28-Aug 2, 2012, showing strong upwelling along the north Florida coast. GOMECC-II underway sampling along the 50m contour probably sampled the eastern edge of this feature. (Processing courtesy Sherwin Ladner, NRL/SSC).



6.- Acknowledgements:

The scientific party of the NACP GOMECC-2 cruise would like to express sincere thanks to Captain, officers and the crew of the R/V *Ronald H. Brown* for their assistance in carrying out this cruise. Support from the NOAA Ocean Acidification Program is gratefully acknowledged.