Cruise Report 9/2/16

East Coast Ocean Acidification Cruise (ECOA-1)

R/V Gordon Gunter (R336)
17 June– 24 July, 2015

Newport, RI – Miami, FL USA
PIs Joseph Salisbury (University of New Hampshire) and Wei-Jun Cai (University of Delaware)

Chief Scientists:
Leg 1: Joseph Salisbury (University of New Hampshire)
Leg 2: Joseph Salisbury and Janet Reimer (University of Delaware)

Table of Contents

1.- Summary

This report describes the first East Coast Ocean Acidification Cruise (ECOA-1). 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, biogeochemical parameters and production rates as they relate to ocean acidification (OA) in the coastal realm. This was the third comprehensive occupation of the coastal waters, with the first occurring in 2007, and the second in 2012. The previous efforts were named the Gulf of Mexico and East Coast Carbon (GOMECC) cruises I and II. During each of these cruises key knowledge and data gaps were realized including: 1) a need to sample contributing Scotian Shelf and Labrador Slope waters, 2) a need to sample closer to the coast in order to better understand the effects of land fluxes on OA and 3) the need to characterize biological rate processes that affect distributions of carbonate parameters.

Our efforts are intended to complement mooring time series and other regional OA activities. The cruise included a series of transects complemented by lines laid out approximately parallel to the coast. A comprehensive set of underway measurements were taken between stations along the entire transect (Figure 1). Full water column CTD/rosette stations were occupied at 163 specified locations. A total of 15 scientists from UNH, UDEL, Princeton, ODU, and AOML/NOAA participated in the 34-day cruise, which departed from Newport, RI, on 19 June, and arrived on schedule in Miami, FL on 24 July. The cruise was delayed for 2 days in Newport due to the failure in the Ship's hydraulic steering mechanism. These days were lost from the mission and had a significant impact on the total number of samples retrieved in the Gulf of Maine. We also lost 2-3 days due to high sea state or unfavorably high winds. During these times the pace of underway sampling was usually accelerated.

Water samples were collected from the 24-bottle rosette at each station and analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon (DIC), total alkalinity, 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 pCO_2, DIC, pH, bio-optical properties and acoustic Doppler current profiles (ADCP). Several members of the field party posted photographs and brief descriptions of science sampling and activities on https://www.facebook.com/ECOA2015.

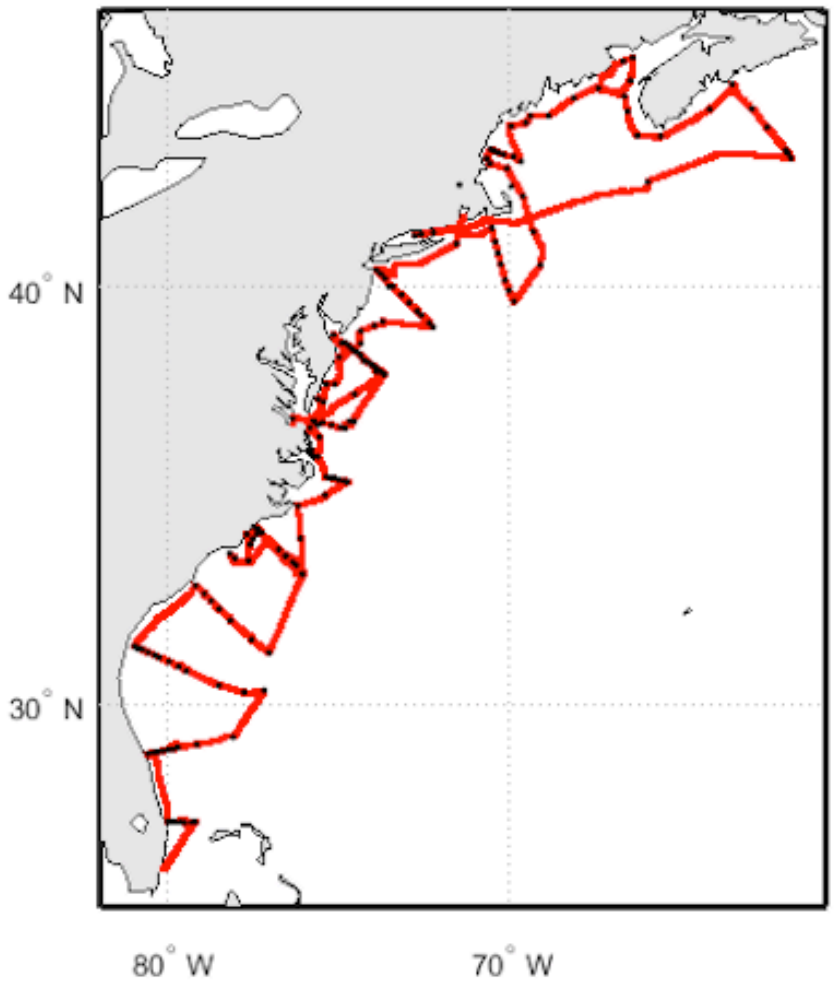

Figure 1 – Cruise track (red line) and CTD station locations (black circles)

2.- Introduction

NOAA OAP and partners conducted the first East Coast Ocean Acidification cruise (ECOA-1) Cruise (Figure 1) along the East Coast of the United States, and the Canadian Maritimes. Its purpose was to document the status of ocean acidification (OA) by collecting a comprehensive dataset over a wide range of oceanographic and biogeochemical conditions. An important secondary goal was to collect an ancillary data set, including biological rate measurements that will enable a fuller understanding of processes affecting carbonate chemistry.

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 (https://www.whitehouse.gov/sites/default/files/microsites/ostp/NSTC/iwg-oa_strategic_plan_march_2014.pdf). 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 Eastern North American 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. In addition, in coastal regions where net biological processes can dominate carbonate system variability over daily-monthly time scales, understanding the net biological rates of organic and inorganic carbon production is advised.

To address this problem, NOAA OAP, and its Marine CO_2 Programs at PMEL and AOML initiated dedicated coastal carbon research cruises for the Alaska, West, East and Gulf Coasts. 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 ECOA cruise aboard the R/V *Gordon Gunter*, is the third 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 ECOA 1 cruise was supported by the NOAA/OAR Ocean Acidification Program (OAP). Fifteen scientists representing 5 universities, NASA and 2 NOAA line offices participated on the cruise (Table 1) covering the North American continental shelf region from Miami Florida in the south to Halifax Nova Scotia in the north. The R/V *Gordon Gunter* departed Newport, RI on 19 June, 2015. The cruise completed a series of 11 transects, most intended to be 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, pCO_2, dissolved organic matter, colored dissolved organic matter, and phytoplankton pigments, 13C primary productivity and community respiration. A total of 163 stations were occupied on the cruise (Table 2). East Coast transects occupied in the previous GOMECC 2 Cruise include those identified as: 27˚ North, Georgia, Cape Hatteras, New Jersey, Line W and New Hampshire Transects. Several more transect were added to the Northeast with the goal of understanding biogeochemical characteristics of Canadian waters influencing the US East Coast.

In addition to bottle-based measurements, underway measurements of salinity, temperature, dissolved oxygen, pCO_2 (air and water), DIC, pH, fluorescence of chlorophyll and colored dissolved organic matter (CDOM), light transmittance at 660nm, and the continuous oxygen/argon ratios were measured. When we had a considerable steam between stations, samples were taken every ~ hour from the underway sampling line for discrete analyses of oxygen, inorganic nutrients, dissolved inorganic carbon, total alkalinity, pH and calcium concentration. There were 233 sets of discrete samples taken from the underway line.

Table 1 - Scientific Cruise Participants

Name (First, Last)	Title	Date Aboard	Date Disembark	Sex	Affiliation
Joe Salisbury	Chief Scientist/ CTD	6/17/15	7/24/15	M	UNH
Shawn Shellito	CTD/ cruise management/ IOP	6/17/15	7/24/15	M	UNH
Marc Emond	CTD	6/17/15	7/3/15	M	UNH
JunFang Lin	AOP	6/17/15	7/3/15	M	UMASSB
Melissa Melendez	CTD/ Pigments, DOC, POC, CDOM	6/17/15	7/24/15	F	UNH
Yuanyuan Xu	DIC/ nutrients/ underway sampling	6/17/15	7/24/15	F	UDEL
Bror Jonsson	EIMS/O2-Ar, underway DIC, triple isotopes	6/17/15	7/24/15	M	PRINCETON
Andrew Collins	pH/deck	6/17/15	7/24/15	M	UDEL
Chuck Featherstone	DIC/ nutrients/ underway sampling	6/17/15	7/24/15	M	AOML
Yafeng Zhang	sample collection	6/17/15	7/24/15	M	UDEL
Najid Hussain	TA	6/17/15	7/24/15	M	UDEL
Peter Bernhardt	NPP/N2 fix	6/17/15	7/3/15	M	ODU
Carlisle Withers	O2	6/17/15	7/3/15	F	UM/RSMAS
Yonghui Gao	EIMS/O2-Ar, underway DIC, triple isotopes	6/17/15	7/3/15	F	UDEL

Steven Gonski	pH	6/17/15	7/3/15	M	UDEL
Janet Reimier	O2 Sampling / Co-Chief Scientist (Leg 2)	7/8/15	7/24/15	F	UDEL
Andrew Joesoef	Alkalinity	7/8/15	7/24/15	M	UDEL
Baoshan Chen	pH	7/8/15	7/24/15	M	UDEL
Maria Arroyo	O2	7/8/15	7/24/15	F	UM/RSMAS
Lynn Price	NPP/N2 fix	7/8/15	7/24/15	F	ODU
Mike Ondrusek	AOP	7/8/15	7/24/15	M	NOAA/NESDIS

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
UDEL	University of Delaware
UMASSB	University of Massachusetts-Boston
UNH	University of New Hampshire
ODU	Old Dominion University
Princeton	Princeton University

3.0 Hydrography

3.1 CTD/Hydrographic Measurements

Analysts: Shawn Shellito, Joseph Salisbury (UNH)

After a thorough investigation, the wire and winch set up on the *Gunter* were considered adequate for the mission. The Gunter does not carry a survey tech so it was the responsibility of the science party to setup and integrate the CTD with the SBE11 and Seasave data acquisition system. CTD casts were limited to 1600 m due to the lack of annual maintenance on the wire. The Gunter ET determined the safe working load for the wire to be 2500 lbs. That is approximately the weight of the CTD plus 1600 m of wire paid out. The 2500 lbs. safe working load also took into consideration the lack of a tensionometer on the winch.

A total of 163 CTD/O_2/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 20 m of the bottom for the majority of casts, using a Sea-Bird SBE-911plus CTD system. Water samples for calibration of the dissolved oxygen profiles as well as 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)
1	6/20/15	01:41:30	41.30865	-70.4943	18
2	6/20/15	4:13:09	41.00191	-70.3994	43
3	6/20/15	6:07:14	40.75706	-70.3222	50
4	6/20/15	8:05:17	40.5098	-70.2356	65
5	6/20/15	10:48:57	40.14683	-70.10934	119
6	6/20/15	13:00:52	39.9227	-70.0000	472
7	6/20/15	16:03:57	39.67235	-69.84416	2210
8	6/21/15	0:18:12	40.48712	-69.07379	80
9	6/21/15	5:23:39	41.22816	-69.28466	64
10	6/21/15	10:51:37	42.00664	-69.5879	119
11	6/21/15	15:40:58	42.60296	-70.05248	125
12	6/21/15	18:55:45	42.7114	-70.5504	84
13	6/21/15	20:28:53	42.81693	-70.65348	76
14	6/21/15	22:25:34	43.01989	-70.53022	73
15	6/21/15	22:25:34	42.98014	-70.4247	110
16	6/22/15	0:55:23	42.94333	-70.2981	146
17	6/22/15	2:23:50	42.90195	-70.14686	66
18	6/22/15	04:20:51	42.86249	-69.8625	265
19	6/22/15	06:18:32	42.75337	-69.6425	271
20	6/22/15	11:14:02	42.21921	-69.91564	169
21	6/22/15	14:23:58	43.5105	-69.932	117
22	6/22/15	17:42:48	43.5784	-69.4984	158
23	6/22/15	20:42:58	43.7255	-69.365	94
24	6/23/16	00:36:25	43.7268	-68.8334	90
25	6/23/16	05:04:52	44.1012	-68.0972	101
26	6/23/16	09:15:24	44.3104	-67.378	189
27	6/23/16	15:41:55	44.4698	-66.4303	192
28	6/23/16	19:32:28	44.9449	-66.367	118
29	6/23/16	21:34:18	44.8741	-66.6442	128
30	6/24/16	10:45:29	44.1428	-66.613	100
31	6/24/16	13:22:27	43.8228	-66.5182	81
32	6/24/16	19:21:44	43.3083	-66.2342	70
33	6/24/16	23:53:35	43.2951	-65.5512	50
34	6/25/16	07:34:09	43.8629	-64.1116	154
35	6/25/16	13:51:21	44.4001	-63.458	98
36	6/25/16	19:25:49	43.8783	-62.8749	279
37	6/25/16	23:56:14	43.4833	-62.4345	81
38	6/26/16	04:11:14	42.995	-61.8815	174
39	6/26/16	05:28:24	42.937	-61.827	485
40	6/26/16	07:22:22	42.829	-61.732	1162

41	6/27/16	04:47:21	42.31205	-65.93205	234
42	6/28/16	18:57:57	42.2524	-71.4453	36
43	6/28/16	23:40:30	41.2065	-72.2138	50
44	6/29/16	02:21:03	41.1677	-72.5679	29
45	6/29/15	04:03:08	41.1409	-72.7611	41
46	6/29/15	14:43:08	40.966	-71.5303	50
47	6/30/15	07:40:05	40.375	-73.8739	21
48	6/30/15	08:56:45	40.2845	-73.7414	27
49	6/30/15	10:24:32	40.188	-73.631	34
50	6/30/15	11:49:50	40.009	-73.519	44
51	6/30/15	13:41:04	40.007	-73.3986	69
52	6/30/15	16:08:56	39.8221	-73.14621	50
53	6/30/15	18:43:00	39.6407	-72.9229	65
54	6/30/15	21:19:20	39.4541	-72.6848	85
55	6/30/15	23:00:57	39.362	-72.567	125
56	7/1/15	01:28:14	39.179	-72.331	762
57	7/1/15	03:27:52	39.0853	-72.216	1557
58	7/1/15	12:00:58	39.2185	-73.6983	44
59	7/1/15	14:07:52	39.1252	-73.9305	45
60	7/1/15	17:05:19	39.003	-74.3355	33
61	7/1/15	19:50:03	38.717	-74.338	30
62	7/1/15	22:05:00	38.559	-74.571	30
63	7/2/15	00:10:59	38.453	-74.35	39
64	7/2/15	01:41:21	38.321	-74.2316	51
65	7/2/15	03:32:11	38.2249	-73.997	72
66	7/2/15	05:20:02	38.078	-73.882	132
67	7/2/15	07:50:29	38.004	-73.647	1286
68	7/2/15	16:05:59	37.5545	-74.5197	72
69	7/8/15	17:36:24	36.9805	-76.338	14
70	7/8/15	17:36:24	36.9267	-75.7075	19
71	7/9/15	00:02:27	36.8871	-75.4569	29
72	7/9/15	01:52:28	36.8331	-75.19183	27
73	7/9/15	04:53:23	36.777	-74.925	36
74	7/9/15	07:11:49	36.7512	-74.793	60
75	7/9/15	09:26:10	36.831	-75.594	1013
76	7/9/15	13:40:37	36.921	-74.661	98
77	7/9/15	18:11:44	36.9196	-74.5335	1367
78	7/10/15	05:26:42	38.0096	-73.6524	1283
79	7/10/15	07:31:39	38.079	-73.7634	781
80	7/10/15	09:48:48	38.154	-73.877	149
81	7/10/15	11:59:28	38.218	-73.987	71
82	7/10/15	14:17:48	38.288	-74.109	59

83	7/10/15	16:45:49	38.3204	-74.234	50
84	7/10/15	18:54:58	38.4467	-74.3449	42
85	7/10/15	21:35:31	38.5197	-74.4584	41
86	7/10/15	23:23:34	38.5894	-74.5739	31
87	7/11/15	01:10:43	38.6619	-74.6936	22
88	7/11/15	02:45:00	38.734	-74.809	18
89	7/11/15	04:04:35	38.728	-74.9001	24
90	7/11/15	06:17:29	38.9146	-75.1443	21
91	7/11/15	13:08:54	38.4014	-74.9707	14
92	7/11/15	18:17:49	37.7793	-75.1005	25
93	7/11/15	20:28:14	37.7839	-75.346	14
94	7/11/15	23:57:39	37.4371	-75.5945	13
95	7/12/15	01:08:46	37.3715	-75.4333	26
96	7/12/15	04:48:29	36.926	-75.7068	15
97	7/12/15	06:29:51	36.77039	-75.8259	12
98	7/12/15	09:11:23	36.5439	-75.5468	25
99	7/12/15	12:36:04	36.0891	-75.6029	18
100	7/12/15	16:29:45	35.6107	-75.3411	31
101	7/12/15	18:24:06	35.5831	-75.2488	31
102	7/12/15	20:02:42	35.5889	-75.1215	38
103	7/12/15	22:24:30	35.5413	-74.98207	47
104	7/13/15	00:18:55	35.5086	-74.8144	120
105	7/13/15	01:44:03	35.4886	-74.7287	1692
106	7/13/15	08:15:19	35.173	-75.381	17
107	7/13/15	13:47:03	34.9109	-76.1717	12
108	7/13/15	19:36:21	34.1255	-76.1041	225
109	7/14/15	02:55:08	33.2687	-76.0384	2118
110	7/14/15	13:54:04	33.7117	-76.5402	236
111	7/15/15	01:17:15	34.2669	-77.2461	24
112	7/15/15	02:26:18	34.3515	-77.3585	18
113	7/15/15	03:29:41	34.4119	-77.4668	13
114	7/15/15	05:47:33	34.2368	-77.3815	16
115	7/15/15	08:31:00	34.231	-77.676	12
116	7/15/15	11:53:43	33.9796	-77.5797	22
117	7/15/15	17:19:36	33.5827	-77.6283	16
118	7/15/15	21:44:17	33.6446	-78.019	17
119	7/15/15	23:59:08	33.7639	-78.1804	17
120	7/16/15	09:15:33	34.1113	-77.5055	30
121	7/16/15	12:05:33	33.861	-76.7429	40
122	7/16/15	14:21:58	33.6963	-76.5454	250
123	7/16/15	17:40:20	33.554	-76.336	562
124	7/16/15	20:33:24	33.4759	-76.2243	687

125	7/17/15	00:00:33	33.2576	-76.0413	2113
126	7/17/15	17:44:00	31.3151	-77.0198	2470
127	7/17/15	23:22:52	31.6385	-77.5378	824
128	7/18/15	05:20:43	32.1146	-78.1532	500
129	7/18/15	08:33:47	32.3979	-78.4831	260
130	7/18/15	11:18:43	32.6026	-78.7209	40
131	7/18/15	13:35:52	32.7787	-78.9202	32
132	7/18/15	16:20:58	32.9818	-79.1785	16
133	7/19/15	07:41:12	31.475	-80.973	10
134	7/19/15	08:23:15	31.452	-80.928	11
135	7/19/15	09:14:08	31.4107	-80.8649	19
136	7/19/15	10:09:30	31.409	-80.864	17
137	7/19/15	12:44:25	31.393	-80.747	19
138	7/19/15	14:27:24	31.3249	-80.567	22
139	7/19/15	16:30:46	31.257	-80.384	31
140	7/19/15	17:51:30	31.1927	-80.2441	40
141	7/19/15	20:28:24	31.0911	-79.9545	48
142	7/19/15	23:01:31	30.961	-79.6699	465
143	7/19/15	02:08:29	30.8456	-79.4481	804
144	7/20/15	08:51:18	30.488	-78.504	820
145	7/20/15	14:18:34	30.318	-77.752	835
146	7/20/15	20:50:17	30.3625	-77.164	1293
147	7/21/15	08:26:04	29.171	-78.079	900
148	7/21/15	16:10:32	28.989	-79.138	803
149	7/21/15	21:47:57	28.9137	-79.6965	780
150	7/22/15	01:06:26	28.8668	-79.842	488
151	7/22/15	04:34:12	28.8492	-79.9885	231
152	7/22/15	06:12:18	28.8214	-80.1373	63
153	7/22/15	07:35:48	28.7976	-80.2841	30
154	7/22/15	08:44:03	28.7788	-80.4065	16
155	7/22/15	10:06:33	28.7529	-80.5785	14
156	7/23/15	02:23:10	26.9957	-80.0016	36
157	7/23/15	03:23:43	26.9823	-79.9283	163
158	7/23/15	04:40:53	26.9796	-79.8648	270
159	7/23/15	06:08:28	26.9795	-79.7774	400
160	7/23/15	08:06:35	26.9768	-79.6211	640
161	7/23/15	10:07:34	26.9638	-79.4965	757
162	7/23/15	14:20:22	26.9745	-79.2715	612
163	7/23/15	16:29:05	26.9777	-79.1808	453

Table 2 – CTD station locations visited during the ECOA cruise.

3.1.1 CTD Operations

CTD/rosette casts were performed with a package consisting of a 24-place, 10-liter rosette frame (AOML's yellow frame), a 24-place water sampler/pylon (SBE32) and 21, 10-liter Bullister/Niskin-style bottles. The 3 remaining positions were filled with modified 8L niskins for UNH respiration experiments. This package was deployed on all stations. Underwater electronic components for the CTD/rosette consisted of a Sea-Bird Electronics (SBE) 9 plus CTD with dual pumps and the following sensors: dual temperature (SBE3), dual conductivity (SBE4), single dissolved oxygen (SBE43), and a Simrad 807 altimeter. The other underwater electronic components involved an array of several optical sensors, consisting of a Biospherical QCP-2300 irradiance sensor, a Wet Labs ECO fluorometer, a Seapoint ultraviolet fluorometer, a Seapoint turbidity meter and a Wet Labs Beam C (turbidity) sensor. The Beam C sensor was removed for stations deeper than 600 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 and conductivity 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 *Gunter's* starboard CTD winch was used with the 24-place 10-liter rosette for all station/casts.

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 5 m for 5 minutes to remove any air bubbles from the sensor lines and to make sure the sensors were behaving appropriately. 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.

3.1.2 System Problems

During the cruise there were only two known problems with the CTD. The first originated on cast 19 (Wilkinson Basin), when the rosette evidently approached too closely to the bottom, temporarily fouling the secondary conductivity sensor. The primary unit was not affected. The secondary unit was flushed with deionized water where after it resumed normal performance. The second issue occurred on cast 105, it was noticed during the upcast that the oxygen and conductivity sensors were responding dramatically different than on the down cast. It was determined that we had a faulty pump and it was replaced. We followed up with a test cast and the conductivity sensors were reading within 0.001 of one another. We repeated the station two days later after adverse sea conditions abated.

Post cruise analysis of the CTD data determined that there was an air blockage of the primary sensors on the initial 10 – 15 m decent of casts 140 – 145. Once below this depth the air bubble was squeezed out and temp and salinity readings from the primary and secondary sensors tracked each other nicely. For these stations and station 19 secondary sensors were used for the CTD cast files. For all other casts, the primary sensors were used.

There was also a problem with the Simrad altimeter. It appears either wire angle, soft bottom, or acoustic interference with the depth finders would cause the altimeter not to find the bottom at times. In these situations max wire depth would not be greater than current depth assuring there was a safety factor for the CTD package.

3.1.3 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 7. SBE Seasave software version 7.23.2 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 above the railing, the J-frame and rosette were extended outboard, and the package quickly lowered into the water and submerged to 5 meters of wire out. At that time the package was powered on and once data was streaming into the computer a 5 minute count down was initiated to let the pumps start and for the sensors to stabilize. The CTD console operator 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 typical profiling rate was no more than 30 m/min to 100 m and then no faster than 45 m/min to bottom depth. The

exception was when performing casts in fast moving currents. At those times the first 20 m was paid out at 30 m/min and then sped up to 50 m/min. This approach helped with getting the CTD deeper before wire angle became a problem.

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 - 20 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 "bottle 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.

3.1.4 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.

3.1.5 Shipboard and Post Cruise CTD Data Processing

Shipboard CTD data processing was performed, usually at the end of each deployment, using SEABIRD SBE Data Processing version 7.22.5. The raw CTD data and bottle trips acquired by SBE Seasave on the Windows 7 workstation were processed from hex files to cnv files and then into bottle files.

Post cruise data processing was completed on a Windows 7 machine running SEABIRD SBE DATA Processing version 7.22.5 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 sensors were automatically advanced by 0.073 seconds.

- 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.

- 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.

- CELLTM - 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.

- 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.

- DERIVE - compute primary, secondary salinities, and DO concentrations.

- BINAVG - 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 non-derived conductivities and other dependent variables.

- SPLIT - separates the cast into upcast and downcast values.

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

A total of 163 casts were made.

3.1.6 CTD Calibration Procedures

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

Secondary temperature and conductivity (T2, C2) sensors served as calibration checks for the reported primary sensors. During the cruise, it was determined that the primary sensors likely had more stable behaviors during the cruise with the exceptions listed above. Dissolved O_2 check samples collected during each cast were used to calibrate the dissolved O_2 sensor.

3.1.7 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 depths (bottle trip locations) for each cast. For the entire cruise, only one set of temperature sensors were used, both tracked each other very well. Post cruise calibration of the primary sensor determined the drift since last calibration as +0.00123 Degree Celsius/year.

3.1.8 CTD Conductivity

Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities. Calibration accuracy was examined by comparing C1-C2 over a range of station numbers and depths (bottle trip locations) for each cast. For the entire cruise, only one set of conductivity sensors were used, both tracked each other very well. Post cruise calibration of the primary sensor determined the sensor drift to be 0.0008 PSU/month.

3.1.9 CTD Dissolved Oxygen

A SBE43 dissolved O_2 (DO) sensor was used on this leg (Table 4). The DO sensor was calibrated to dissolved O_2 check samples by matching the up cast bottle trips to CTD bottle samples at various depths. Post cruise calibration of the sensor determined that there was minimal drift with a slope of 1.0301 ml/L between calibrations. However we believe it is best to regress the bottle data against the profile data to achieve the best results (see 3.2).

Instrument	S/N	Stations Used	Sensor Use	Pre-Cruise Calibration	Comment
Sea-Bird SBE32 24-place Carousel Water Sampler	3260142-07163			NA	

Sea-Bird SBE9plus CTD					
Paroscientific Digiquartz Pressure Sensor	131732			23-Jan-15	
Sea-Bird SBE3plus Temperature Sensor	04981		primary	24-Feb-15	
Sea-Bird SBE3plus Temperature Sensor	04101		secondary	22-Jan-15	
Sea-Bird SBE4C Conductivity Sensor	04385		primary	10-Mar-15	
Sea-Bird SBE4C Conductivity Sensor	043151		secondary	23-Jan-15	
Sea-Bird SBE43 Dissolved Oxygen	430477		primary	25-Apr-15	
Sea-Bird SBE5T pump	05-8128		primary	NA	
Sea-Bird SBE5T pump	05-3958		secondary	NA	failed
Sea-Bird SBE5T pump	05-7588		secondary	NA	
Simrad 807 Altimeter				NA	
Wet Labs Fluorometer	FLRTD-2125			21-Dec-10	
Biospherical QCP 2300 Irraddiance	70550			24-Mar-15	
Seapoint Turbidity	14036			NA	
Seapoint Turbidity	1480			NA	
Seapoint Ultraviolet Flourometer	6201F			NA	
Wet Lab CST Beam-C	1124PR			16-Oct-14	

Table 4: Equipment used during the cruise.

3.2 Oxygen Measurements

Analysts: Carlisle Withers (RSMAS, University of Miami) and Maria Arroyo (RSMAS, University of Miami)

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

3.2.1 Equipment and Techniques

Dissolved oxygen analyses were performed with an automated oxygen titrator using amperometric end-point detection (Langdon, 2010). Sample titration, data logging, and graphical display were performed on a PC running a LabView program written by Ulises Rivero of AOML. The titrations were performed in a climate controlled lab at 23.0°C-27.9°C. The temperature-corrected molarity of the thiosulfate titrant was determined as given by Dickson (1994). Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. The whole-bottle titration technique of Carpenter (1965) with modifications by Culberson et al. (1991) was used. Four to six replicate 10 ml iodate standards were run every seven days. The reagent blank was determined as the difference between V1 and V2, the volumes of thiosulfate required to titrate 1-ml aliquots of the iodate standard, was determined at the beginning and end of the cruise.

3.2.2 Sampling and Data Processing

Dissolved oxygen samples were drawn from 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 an Oakton 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 (μmol 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 the sample was concluded using Repipetors. The flasks were then stoppered and shaken well. De-ionized water 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.

Samples plus duplicates were drawn from the full cast of 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 1100. Duplicate samples were drawn once every station. A total of 130 sets of duplicates were run. The preliminary difference between replicates averaged 0.76 μmol kg^{-1} for stations 1-68 (Leg 1) and 0.44 μmol kg^{-1} for stations 69-149 (Leg 2). Due to lack of titrants no oxygen samples were taken on Stations 150-163.

The total number of samples flagged after post-cruise quality control:
Questionable (n=40), Bad (n=97).

125 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 CO2 buoy.

3.2.3 Problems

There was a problem with the iodate dispenser on leg 1 that led to poor reproducibility of standards on leg 1 (± 6 ul vs the usual ± 1-2 ul). This was handled during the cruise by using a nominal value for the concentration of the thiosulfate. Portions of each bottle of thiosulfate were saved and later standardized post-cruise. The post-cruise determinations were completely in the line with the expected values for the standards. These post-cruise standard values were used to calculate the leg 1 discrete oxygen concentrations. A replacement iodate dispenser was brought out for leg 2 and the standardization problem was resolved.

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.

Dickson, A. G., "Determination of dissolved oxygen in seawater by Winkler titration," WHP Operations and Methods (1994a).

Langdon, C. (2010). *Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique.* The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. E. M. Hood, C. L. Sabine and B. M. Sloyan, IOCCP Report Number 14, ICPO Publication Series Number 134.

3.3 Nutrient Measurements

Analyst: Charles Fischer (AOML)

Approximately 1000 nutrient vials were taken for analysis back at AOML. Nutrient samples were collected from Niskin bottles, after at least three seawater rinses. Samples were frozen immediately and stored in a ship's freezer. Nutrient samples were analyzed at AOML nutrient lab with a SEAL Analytical AA3 continuous flow autoanalyzer using the standard and analysis protocols for the GO-SHIP repeat hydrographic program (Hydes et al., 2010).

3.3.1 Analytical Methods

Samples were analyzed for phosphate (PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-) and silicic 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 copper-coated 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 molybdic acid to form phosphomolybdic acid. This complex was subsequently reduced with hydrazine, and the absorbance of the resulting phosphomolybdous acid was measured at 836 nm (Zhang et al., 2001). Silicic acid was analyzed by reacting with ammonium molybdate in an acidic solution to form β-molybdosilicic acid, which was then reduced with ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue was measured at 660 nm (Zhang and Berberian, 1997).

3.3.2 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 andNa_2SiF_6) in deionized water using a two step dilution for phosphate and nitrate. A nitrite stock standard was prepared separately by dissolving $NaNO_2$ in distilled water. Working standards were prepared fresh daily by diluting the stock solutions in low nutrient seawater. The mixed standards were verified against CRMs.

References:

Hydes, D. J., M. Aoyama, A. Aminot, K. Bakker, S. Becker, S. Coverly, A. Daniel, A. G. Dickson, O. Grosso, R. Kerouel, J. van Ooijen, K. Sato, T. Tanhua, E. M. S. Woodward, J. Z. Zhang. Determination of Dissolved Nutrients (N, P, Si) In Seawater With High Precision And Inter-Comparability Using Gas-Segmented Continuous Flow Analysers. In The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines, IOCCP Report No. 14, ICPO Publication Series No. 134, Version 1, 2010.

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. (2001). Continuous Flow Analysis of Phosphate in Natural Waters Using Hydrazine as a Reductant. Intern. J. Environ. Anal. Chem. 80(1): 61-73.

3.4 DIC Measurements

Analysts: Charles Featherstone (NOAA/AOML) and Yuan Yuan Xu (Univ. Delaware)

Samples for total dissolved inorganic carbon (DIC) measurements were drawn according to procedures outlined in the *Handbook of Methods for CO_2 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 air bubbles. After 0.2 ml of saturated $HgCl_2$ 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 the Chem Lab on board the RV Gordon Gunter. The analysis was done by coulometry with two analytical systems (AOML3 and AOML4) used simultaneously on the cruise. Each system consisted of a CM5015 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 coulometric analysis of DIC, all carbonate species are converted to CO_2 (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved CO_2 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 CO_2 that enters the cell is determined by integrating the total change during the titration.

The coulometers were calibrated by injecting aliquots of pure CO_2 (99.99%) by means of an 8-port valve outfitted with two sample loops with known gas volumes bracketing the amount of CO_2 extracted from the seawater samples for the two AOML systems.

The stability of each coulometer cell solution was confirmed three different ways: (1) two sets of gas loops were measured at the beginning, (2) The Certified Reference Material (CRM), Batch 121, supplied by Dr. Andrew Dickson of SIO, were measured at the beginning and (3) 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 CO_2 injected was according to the CO_2 handbook (DOE 1994). The concentration of CO_2 *($[CO_2]$)* 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 (µmol/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 at the beginning of the cell. The average correction was 2.13 µmol/kg.

The systems worked well during the cruise, but they occasionally had high blanks. Normally the blank is less than 30, but we were forced to run them with blanks in the 12-38 range.

Several relatively minor problems occurred with AOML 3 during the cruise; (1) A power problem on 06/20/2015 with the coulometer was resolved by plugging several items into different outlets instead of all into the same power strip, (2) Pipette filling problem (liquid level sensor error) which started on 06/28/2015 was resolved on 07/08/2015 by replacing sample tubing and valve/inlet 13, (3) the coulometer was malfunctioning on 07/10/2015 and not responding to the computer/labview program and was switched out with an older version coulometer (AOML5), which was used for the remainder of the cruise, and (4) a field point communication error occurred on 07/16/2015 and was resolved by tightening the serial port connection to DICE 3. AOML 4 worked well during the cruise with no problems occurring.

Underway samples were collected from the flow thru system in the Chem Lab during transits between lines. Discrete DIC samples were collected approximately every hour with duplicates every fifth sample. A total of 287 discrete DIC samples including duplicates were collected while underway. The average difference for replicates of underway DIC samples was 1.31 µmol/kg and the average STDEV was 0.92 µmol/kg.

A total of 1358 samples including duplicates were analyzed for discrete dissolved inorganic carbon from 163 CTD casts. The average difference for replicates of CTD DIC

samples was 1.09 µmol/kg and the average STDEV was 0.77 µmol/kg. 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.

3.5 Total Alkalinity Measurements

Analysts: Andrew Collins and Najid Hussain

3.5.1 Determination of Total Alkalinity by Gran Titration:

Gran titration is a method that linearizes the titration curve using the following function:

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

where F is the Gran Factor, v is the volume of acid added to the sample vessel, V_0 is the sample volume, E is the electro motive force (EMF) measured, and a is the slope of electrode for pH buffers. 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.

Sampling:

Samples for TA were drawn from Niskin bottles directly into 250 ml borosilicate glass bottles using flexible silicon tubing. Coastal waters with high particulate matter were filtered using 0.45 μm filter cartridge. Bottles were rinsed at least three times with sample water and care was taken to expel all air bubbles in the sample prior to filling. Samples were stored at room temperature and were analyzed within 6 hours of collection, then bottles were cleaned and reused. No $HgCl_2$ was added to samples. Samples were brought to 22.0 ^{o}C for analysis.

3.5.2 Measurements, Precision, and Accuracy:

For each measurement 25 ml of TA sample was titrated with 0.1M HCl solution. HCl stock solution was prepared in the laboratory at the University of Delaware (UD) as 0.1M HCl in 0.5M NaCl and allowed to age and stabilize for several weeks prior to the cruise. Our experience has shown aging the acid solution for TA analysis considerably reduces the variability of the results. This TA titration system has a precision >0.1% (Cai et al. 2010). Each TA measurement was repeated until two measurements were within 0.1% of each other. The pH electrode was calibrated using pH buffers (NBS) – 4.01, 7.0, and 10.01 – and pH recalibration is carried out underway every 12 to 24 hours.

Dickson Certified Reference Material (CRM; Batch # 121) was used to test the accuracy of the method. CRM was also used to determine the concentration of the acid solution approximately every 24 hours. Calibration checks are made at least twice between calibrations by running CRM standards of the same batch but with a different bottle.

Duplicate water samples were run on an average every 15 samples, with the exception of four samples that were flagged, all other duplicates agreed within 3 uM of the respective samples with more than 80% agreeing within 2 uM. The overall determined precision of this method is within 0.1%. Samples with repeatability exceeding 0.1% have been flagged in the master data file.

Underway TA samples were collected from the ship's flow through system during longer transits between stations. A total of 1128 samples, including duplicates, were taken from Niskin bottles and 224 underway samples were analyzed.

Reference:

Cai, W.-J., X. Hu, W.-J. Huang, L.-Q. Jiang, Y. Wang, T.-H. Peng, and X. Zhang. 2010. Alkalinity distribution in the western North Atlantic Ocean margins. J. Geophys. Res. **115**, doi:10.1029/2009JC005482

3.6 Seawater pH Measurements

Analysts: Stephen Gonski, Andrew Collins, Baoshan Chen, and Najid Hussain (UDel)

Seawater pH on the concentration scale can be defined as:

$$pH = -log\left(\frac{[H^+]}{mol \cdot kg^{-1}}\right)$$

where the hydrogen ion (H) concentration (in molar units of mols·kg^{-1} SW) can be expressed as three different quantities depending on which concentration scale is being used to measure seawater pH. The most widely used concentration scale, and the one used for this cruise, is the total Hydrogen ion concentration scale or total scale, denoted pH_T, which uses a hydrogen ion concentration defined as:

$$[H^+]_T = [H^+]_F + [HSO_4^-] = [H^+]_F + \left(1 + \frac{S_T}{K_S}\right)$$

where $[H^+]_F$ is the concentration of free protons in seawater (as well as complexes with water molecules), S_T is the total sulfate concentration in seawater, and K_S is the dissociation constant bisulfate (HSO_4^-) (Zeebe & Wolf-Gladrow, 2001; Dickson et al., 2007).

Seawater pH can be measured via potentiometry using a wide array of electrodes and buffers (Zeebe & Wolf-Gladrow, 2001) or spectrophotometry using pH-sensitive colorimetric indicator dyes (Clayton & Byrne, 1993; Zhang and Byrne, 1996). The spectrophotometric pH method has been proven to yield much higher precisions (±0.0004-0.001 pH units) (Liu et al., 2006) than potentiometric pH methods that can only reach ±0.001-0.003 pH units (Millero et al., 1993). For the purposes of this cruise, and for testing a new setup, we have chosen to use a colorimetric spectrophotometric method since it is the most precise method.

3.6.1 Sampling:

Samples for pH were drawn from Niskin bottles directly into 125 ml borosilicate glass bottles with GL45 screw caps, using flexible silicon tubing. Sample water was filtered with Waltman 0.45 µm filters and bottles were rinsed at least three times with sample with care taken to expel all air bubbles prior to filling. All visible air bubbles are allowed to escape from the filter prior to filling the bottles with sample water. The silicon tubing is placed at the bottom of the bottle and is tightly pinched to stop the water flow prior to removing it. The bottles were allowed to overflow with at least one and a half volumes worth of water before the final sample is collected, leaving no headspace in the bottle. Samples were placed in a water bath at 20 or 25 °C (water bath temperature was adjusted during the cruise due to bubble formation) directly after sampling and analyzed within 2-3 hours of collection. No $HgCl_2$ was added to samples.

Apparatus & Chemicals

The design and technical details of the spectrophotometric pH system used is described in detail by Carter et al. (2013). However, the automation software addressed in Carter et al. (2013) was abandoned in favor of a semi-automated measurement program modeled after the original automation software. While minimizing operator interaction with the system when making measurements would minimize the operator-derived error associated with making seawater pH measurements at sea (Cater et al., 2013), a fully automated arrangement severely limits the troubleshooting capabilities of the operator when problems arise within the system. Therefore, a fully automated system could result in degraded repeatability or the possible loss of single or multiple water samples. A computer with syringe pump control software and the Agilent ChemStation software is used to operate the spectrophotometric pH system that consisted of: 1) a Kloehn V6 automated syringe pump equipped with a water-jacketed 25 mL syringe; 2) a 4-port distribution valve and an Agilent 8453 UV-Visible Single-Beam Spectrophotometer equipped with an Agilent long path-length cell holder; and 3) a water-jacketed 10 cm flow-through cell kept at a measurement temperature of 20.0 ± 0.1^{o}C. The temperature is regulated using a thermal bath (VWR, Scientific Product).

Purified meta-cresol purple (mCP) from Robert Byrne, of the University of South Florida, along with CO_2-free pure water (Milli-Q) is used to prepare a 0.1% purified mCP dye solution. After preparation, the pH of the dye solution was checked with a 0.2 cm cell and adjusted to the recommended 7.9 ± 0.1 using low concentration HCl and NaOH. To protect the dye from degradation by UV light and prevent gas exchange between the dye and the laboratory atmosphere, the dye solution is stored in an aluminum foil bag . Routine checks of dye pH using this method were performed at sea to ensure the dye pH remained unchanged. Deionized (DI) water and additional volumes of seawater taken directly from Niskin bottles were used during troubleshooting procedures.

3.5.2 Measurement:

The samples are placed in the thermal bath set to 20.0 ± 0.1 ^{o}C (or 25.0 ± 0.1 ^{o}C) for 30 minutes to equilibrate to the measurement temperature prior to beginning the measurement sequence. Upon reaching the measurement temperature, each bottle is placed in a thermostatted bottle holder. A 95 second equilibration time is allowed in the analysis process to ensure the sample inside the cell reaches thermal and chemical equilibrium prior to collecting the background spectrum. While waiting for the sample to equilibrate in the flow cell, the sample and dye are mixed together. 30 µL of mCP dye is used for every injection. Because the volume of dye used can vary by up to 10% between successive injections, the recommendations made by Carter et al. (2013) were followed as well as recommendations for measured absorbances used in spectrophotometric pH calculations outlined in Dickson et al. (2007). For the sample+dye mixture, the 95 second equilibration period started immediately following the conclusion of the dispensing of the sample+dye mixture. After which, a series of 3-4 spectra are collected for the sample+dye mixture in quick succession. The second rinse that is performed at the end of each analysis sequence is performed to sufficiently flush the flow cell of all the

sample+dye mixture. Measurements were taken using the tungsten lamp to prevent the degradation of the sample and the dye by UV light from the deuterium lamp.

The method of bubble control, described in Mosley et al. (2004), is employed and involves dispensing of the top and bottom 1 mL of solution during each filling cycle to waste as a means of preventing bubbles from entering the flow cell. By directing the top and bottom 1.5 mL of each syringe full of solution to waste, the transport and accumulation of bubbles inside the syringe, tubing, and flow cell is greatly reduced, which gives the operator better overall control of the system and measurements the operator makes. All samples are analyzed within two to three hours of collection. A total of 1128 samples were analyzed from Niskin bottles and 190 underway samples were analyzed.

3.5.3 Calculations:

The absorbances recorded by the Agilent ChemStation software were saved and run through an Excel Spreadsheet programmed with the necessary equations to calculate the preliminary pH values for all of the water samples run during the cruise. The calculation for determining pH_T valid over $5 \leq T \leq 35$ °C and salinity of $20 \leq S \leq 40$ developed by Liu et al. (2011) was applied to the absorbances.

$$pH_T = \log(K_2^T e_2) + \log\left(\frac{R - e_1}{1 - R \cdot \frac{e_3}{e_2}}\right)$$

where R it the ratio of absorbances measured at 578 nm and 434 nm, and e is the molar absorptivity ratio. The salinity (S), temperature (T), and temperature dependence of $K_2^T e_2$ can be expressed as:

$$-\log(K_2^T e_2) = a + \left(\frac{b}{T}\right) + c \ln T - dT$$

where the coefficients *a, b, c,* and *d* are:

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

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

$$c = 44.493382 - 0.052711S$$

$$d = 0.0781344.$$

The temperature and salinity dependence of the molar absorptivity constants (e_1, e_2, e_3) can be expressed as:

$$e_1 = -0.007762 + 4.5174 \cdot 10^{-5}T$$

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

3.5.4 Repeatability, Reproducibility, Precision, and Accuracy:

The repeatability of other published spectrophotometric pH techniques is ± 0.0004 pH units (Clayton & Byrne, 1993; Carter et al., 2013; Hammer et al., 2014). For our purposes of obtaining weather quality data we set this value at ±0.001 pH units (Tapp et al., 2000; Hammer et al., 2014). The repeatability of all of the samples run on the spectrophotometer by all operators falls within published repeatability range of ±0.0004-0.001 pH units. Reproducibility is linked to repeatability.

Determining the measurement precision involves measuring the pH from repeated injections of a single sample of a known salinity and pH (i.e. TRIS Buffer) thermostatted at a constant temperature under carefully-controlled laboratory conditions such as those described in Hammer et al. (2014). Gauging the accuracy of pH values measured at sea is usually done via tests of internal consistency with measurements of the other parameters of the marine-CO_2 system using the DIC, TA, and pCO_2 or fCO_2 measured from samples taken from the same Niskin bottle at the same time as the pH samples (Millero, 2007; Hoppe et al., 2012). Using this method, an accuracy of 0.01-0.02 pH units is routinely achieved depending on which set of K_1 and K_2 values are used (Carter et al., 2013; Hammer et al., 2014). Using purified mCP, the errors associated with dye impurities that can result in pH offsets as high as 0.01 pH units depending on the dye manufacturer (Yao et al., 2007) can be avoided, and lead to more accurate pH measurements.

References for pH

Carter BR, Radich JA, Doyle HL, Dickson AG (2013). An automated system for spectrophotometric seawater pH measurements. Limnology & Oceanography: Methods 11: 16-27.

Clayton TD, Byrne RH (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.

Dickson A, Sabine C, Christian J (eds) (2007). Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.

Hammer K, Schneider B, Kulinski K, Schulz-Bull DE (2014). Precision and accuracy of spectrophotometric pH measurements at environmental conditions in the Baltic Sea. Estuarine, Coastal, and Shelf Science: 146: 24-32.

Hoppe CJM, Langer G, Rokitta SD, Wolf-Gladrow DA, Rost B (2012). Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies. Biogeoscience Discussions 9: 1781-1792.

Liu X, Wang ZA, Byrne RH, Kaltenbacher EA, Bernstein RE (2006). Spectrophotometric Measurements of pH in-Siut: Laboratory and Field Evaluations of Instrumental Performance Environ. Sci. Technol. 40: 5036-5044.

Millero FJ, Zhang JZ, Fiol S, Sotolongo S, Roy RN, Lee K, Mane S (1993). The use of buffers to measure pH for seawater. Marine Chemistry 22: 143-152.

Mosley LM, Husheer SLG, Hunter KA (2004). Spectrophotometric pH measurement in estuaries using thymol blue and *m*-cresol purple. Marine Chemistry 91: 175-186.

Tapp M, Hunter K, Currie K, Mackaskill B (2000). Apparatus for continuous-flow underway spectrophotometric measurement of surface water pH. Marine Chemistry 72: 193-202.

Yao W, Liu X, Byrne RH (2007). Impurities in indicators used for spectrophotometric seawater pH measurements: Assessment and remedies. Marine Chemistry 107: 167-172.

Zeebe RE, Wolf-Gladrow DA (2001). CO2 in seawater: equilibrium, kinetics, isotopes. vol 65. Elsevier Science.

Zhang H, Byrne RH (1996). Spectrophotometric pH measurements of surface seawater at in-situ conditions: Absorbance and protonation behavior of thymol blue. Marine Chemistry 5: 17-25.

3.7 Respiration measurements

PI – J. Salisbury: Analyst Shawn Shellito

At 48 stations throughout the cruise respiration was measured as the net time evolution of oxygen within custom built, dark chambers (7.5 L) designed to interface with a SeaBird rosette. Each chamber contains sealed Aanderraa Oxygen Optodes, which measure oxygen and temperature at 0.2 Hz. At each station, three chambers were attached to the sampling rosette and then triggered to sample at 3 predetermined depths within the euphotic layer. During the daylight the depth of sampling usually corresponded to the depths of NPP sampling. We also sampled several stations at night when no NPP samples were taken. The chambers were brought on deck and then incubated at the temperature determined for each sample depth using CTD data. This was achieved using temperature-regulated containers into which the respiration chambers were immersed. Oxygen readings were started after temperature equilibration was achieved.

The respiration rates were calculated as the net change in the oxygen concentration (umol kg^{-1}) from the time of temperature equilibration (t_0) to t_1, t_0 +6 hours, or to the end of the incubation.

$$Net\ O_2\ uptake\ (\mu mol\ kg^{-1}h^{-1}) = \frac{[O_2(t_0)] - [O_2(t_1)]}{t_1 - t_0}$$

3.7.1 Problems

There were two basic problems encountered in the determination of respiration. The first is that the chamber temperature often did not equilibrate to a reasonable value, considered +/- 2°C of the in-situ temperature at snap depth, over the first hour. This was due to high temperatures in the lab, and also the capacity of the temperature regulation system. These data are flagged as questionable. We also had one bottle that is suspected of leaking. These data are flagged as bad data as are data that had a positive value. Data that did not show a change of +/-2 umol kg^{-1} (assumed to be the sensitivity of the optode), are flagged as questionable.

3.8 ^{13}Carbon Net Primary Production measurements

PI - Margaret Mulholland (ODU)

NPP was determined one to two times per day throughout the mixed layer using the ^{13}C method (ODU, Mulholland Lab). Bicarbonate enriched in the stable isotope ^{13}C is incorporated into the biomass of phytoplankton. This is followed by using mass spectrometry to track changes in the ^{13}C:^{12}C ratio of particles relative to that in the DIC pool. The Mulholland Lab is also analyzing for POC and ^{15}N uptake by phytoplankton.

3.9 Dissolved organic carbon (DOC), High-performance liquid chromatography (HPLC) and Colored dissolved organic matter (CDOM)

PI – Antonio Mannino (NASA Goddard)

During the cruise Melissa Melendez (UNH) sampled for CDOM, DOC HPLC pigments from all of the CTD casts. Samples were taken from the surface, at the base of the first euphotic depth 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. All samples were analyzed by Antonio Mannino's laboratory at NASA Goddard, using NASA protocols. Data from this collaborative effort are also archived on the NASA Ocean Biology Processing Group's SEABASS archive. http://seabass.gsfc.nasa.gov/wiki/article.cgi?article=System_Description

3.10 Gross Primary Production (GPP)

Analyst/lead PI: Lauren Juranek (OSU)

Gross Primary Production (GPP) is the absolute rate of assimilation of CO_2 by autotrophic organisms before including internal respiration. 140 samples were taken. This property, especially in conjunction with Net Primary Production, Net Community Production and Community Respiration, can provide insight to carbon export and phytoplankton physiology. We measured GPP using the triple-isotope method, which is based on the isotopic composition of dissolved oxygen of seawater. This method allows the estimation of integrated oceanic productivity on a time scale of weeks. The oxygen triple-isotope method is based on the fact that photosynthesis and respiration fractionates 17O and 18O differently, and hence generates differences in the ratio of 17O/16O and 18O/16O. See a full description in Barkan and Luz [2005].

150 Louwer bottles were filled at the surface and the depth of Chlorophyl maximum. The samples are being analyzed by Lauren Juranek at OSU. Stations with both NPP and or Respiration measurements were prioritized for GPP sampling.

Barkan, E. and Luz, B. (2005), High precision measurements of 17O/16O and 18O/16O ratios in H2O. Rapid Commun. Mass Spectrom., 19: 3737–3742. doi:10.1002/rcm.2250

3.11 Dissolved Calcium Measurements

PI- Wei-Jun Cai (UDEL)

Calcium (Ca) concentration of seawater samples is determined by potentiometric titration using an Ethylene Glycol Tetra Acetic Acid (EGTA) solution and a Ca-ion Selective Electrode (ISE) developed in the Cai Lab at the University of Delaware. A fixed volume of sample (1.0 ml) is diluted to 20 ml with DI water, and then 100 µL borate buffer is added and an initial EMF value from ISE is recorded. While a magnetic stirrer is constantly stirring, pre-calibrated EGTA (0.01 M) is added via a tube in volume increments such that the initial delivery is large (~200 µL) but reduces to 5 µL as the end point approaches. Following each addition, EMF is recorded after allowing voltage stabilization. Klohn pumps are used for precise sample uptake and EGTA deliveries. The volume of EGTA at the endpoint (V_E), to an accuracy of better than 1 µL, is obtained by fitting EGTA volumes and corresponding EMFs using RSpline software. The program generates dEMF/dV values for dV of 0.1 µL and determines V_E at $(dEMF/dV)_{max}$. EGTA concentration and the volume of sample taken (V_S) are used to calculate Ca concentration using the relationship:

$$[Ca] = [EGTA] * V_E/V_S$$

The sample is read multiple times to obtain two consecutive measurements that agree within 0.1% accuracy.

4.0 Underway data collection

4.1 Underway pCO_2 Analyses

Analysts: Kevin Sullivan (CIMAS/RSMAS), Charles Featherstone (NOAA/AOML) and Stephen Allen (ET RV Gordon Gunter)

During the ECOA-1 cruise, there was an automated underway pCO_2 system from AOML situated in the Chem Lab of the RV Gordon Gunter. 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 included 3 gas standards, 5 ambient air samples, and 60 headspace samples from its equilibrator every 3 hours. The concentrations of the standards range from 247 to 510 ppm CO_2 in compressed air. These field standards were calibrated with primary standards that are directly traceable to the WMO scale. A gas cylinder of ultra-high purity air was used every 18 hours to set the zero of the analyzer.

The system included an equilibrator where approximately 0.6 liters of constantly refreshed surface seawater from the bow intake was equilibrated with 0.8 liters of gaseous headspace. The water flow rate through the equilibrator was 1.5 to 3.0 liters/min.

The equilibrator headspace was circulated through a non-dispersive infrared (IR) analyzer, a LI-COR™ 7000, at 50 to 120 ml/min and then returned to the equilibrator. When ambient air or standard gases were analyzed, the gas leaving the analyzer was vented to the lab. A KNF pump constantly pulled 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 had 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 gas and marine air were dried before flushing the IR analyzer.

A custom program developed using LabView™ controlled the system and graphically displayed the air and water results. The program recorded the output of the IR analyzer, the GPS position, water and gas flows, water and air temperatures, internal and external pressures, and a variety of other sensors. The program recorded all of these data for each analysis.

The automated pCO_2 analytical system had two problems during Leg 1 of the cruise: (1) the system stopped operating on 06/20/2015 for approximately 12 hours due to a power issue with the UPS, which was corrected by setting the UPS to a more sensitive setting, and (2) the system stopped for approximately 24 hours on 06/21/2015 due to water in the headspace condensate trap, the problem was corrected by drying the trap. This failure unfortunately occurred while on station at the PMEL-UNH CO2 Buoy. The system worked well for the remainder of Leg 1 and throughout Leg 2 of this cruise.

Standard Gas Cylinders

Cylinder#	ppm CO_2
JA02267	247.72
JB03296	382.61
JB03673	510.35

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. Oxygen:Argon ratio and estimation of net community production

Analysts: Yonghui Gao, Bror Jonsson

Underway O_2/Ar ratios are measured using equilibrium inlet mass spectrometer (EIMS) and dissolved oxygen saturation (DO%) using Aanderaa oxygen optod (Model #4531). O_2/Ar ratios better reflect biological driven changes due to the similar physical characters of O_2 and Ar than the DO% method. For the EIMS water flows at a constrant rate of 100 ml min^{-1} through filters (5µm core size) and a gas-water exchange equilibrator to separate gasses. The quadrupole mass spectrometry (MQS 2000) measured O_2 and Ar ions once per second. Air was used as standard because of its stable O_2/Ar ratios, which were measured every 3 hours and lasted for 20 minutes (Cassar et al., 2009). The accuracy of this method is ± 0.02%

Reference

Cassar, N., Barnett, B. A., Bender, M. L., Kaiser, J., Hamme, R. C., and Tilbrook, B.: Continuous high-frequency dissolved O_2/Ar measurements by equilibrator inlet mass spectrometry, Anal. Chem., 81, 1855-1864, 2009.

4.3 Underway Picarro Cavity Ring-Down Spectroscopy, (DIC)

PI: Bror Jonsson

DIC was measured continuously via the underway surface water intake using a method based on dual isotope dilution and cavity ring-down spectroscopy (DID-CRDS). In this method, seawater is continuously sampled and mixed with a flow of NaH13CO3 solution that is also enriched in deuterated water. The isotopic composition of CO_2 (δ13Cspiked sample) derived from the [DIC] in the mixture, and the D/H ratio of the

mixed water (δDspiked sample), are measured by CRDS analyzers. The D/H of the water in the mixture allows accurate estimates of the mixing ratio of the sample and the spike. [DIC] of the sample is then calculated from the mixing ratio, [DI13C] of the spike, and δ13Cspiked sample. This method has shown a precision of <0.02% (±0.4 μmol kg−1 when DIC = 2000 μmol kg−1) in lab and <0.03% for 2 minute averages in shipboard tests. The system was run continuously from Newport to Miami with the exception of short interruptions due to maintenance and temporary problems with the plumbing. CRM standards were run about twice a day for calibration. We will also use the discrete underway measurements of DIC sampled by AOML for QC'ing and calibration.

Reference: Kuan, K., N. Cassar, B. Jonsson, W.J. Cai, M.L. Bender (2015) "An Ultra-high precision, High-frequency Dissolved Inorganic Carbon Analyzer based on Dual Isotope Dilution and Cavity Ring-Down Spectroscopy", Environ Sci Technol. 2015 Jul 21;49(14):8602-10. doi: 10.1021/acs.est.5b01036.

4.4 Underway pH

Analyst/lead PI: Yaunyuan Xu, Najid Hussain

Underway pH was measured by a Honeywell Durafet® III pH electrode (Martz et al. 2010). The Durafet pH sensor was placed in a flow-through cell, with a volume of ~500 mL, attached to the ship's underway seawater intake line. Observations were recorded at 30 second intervals. The raw pH output is on the NBS scale at *in situ* temperature without calibration. Spectrophotometric pH_T analyses of water discrete samples were used to calibration the raw data. pH at *in situ* SST was calculated with temperature and salinity from a SBE 21 SeaCAT thermosalinograph and TA determined from a linear relationship between salinity using CO2SYS (Lewis and Wallace 1998). The underway pH is reported on the total scale at SST with an uncertainty of ± 0.005.

References

Lewis, E., and D. Wallace. 1998. Program developed for CO2 system calculations, ORNL/CDIAC 105, Carbon Dioxide Information Analysis Center.

Martz, T. R., J. G. Connery, and K. S. Johnson. 2010. Testing the Honeywell Durafet for seawater pH applications. Limnol. Oceanogr. Methods **8**: 172–184.

5.0 Ocean Color Measurements

5.1 Apparent optical properties (AOP) and solar irradiance

Analyst/lead PI: Michael Ondrusek (NOAA NESDIS) and JunFang Lin (UMASS-Boston)

NOAA/NESDIS investigators conducted in situ optical measurements during the East Coast Ocean Acidification (ECOA) cruise to support the primary cruise objectives of improving our understanding of ocean acidification and to provide ocean color satellite

validation. JunFang Lin participated on the first leg of the ECOA 2015 cruise and Michael Ondrusek participated in the second. One of the primary validation tools used by NOAA/STAR for in situ ocean color radiance validations is a Satlantic HyperPro Profiler II (http://www.satlantic.com). We also collected solar irradiance data. The HyperPro system has a downward looking HyperOCR radiometer that measures upwelling radiance $L_u(\lambda)$ and an upward looking HyperOCI irradiance sensor to measure downwelling irradiance $E_d(\lambda)$ in the water column. In addition there is an above-water upward looking HyperOCI irradiance sensor to measure downwelling surface irradiance $E_s(\lambda)$. These measurements are used to calculate normalized water-leaving radiance $nL_w(\lambda)$ and remote sensing reflectance spectra observed by ocean color satellites. $nL_w(\lambda)$ spectra can be used to validate satellite ocean color radiances and develop ocean color derived products monitored during the ECOA investigations.

The HyperPro Profiler II is deployed in a free falling mode where it is lowered and raised in the water column while keeping it away from the ship to avoid ship shadowing. The weight is adjusted on the profiler to allow a descent rate of 0.1 to 0.3 m s^{-1}. Each HyperOCR or HyperOCI has 256 channels each with a 10 nm spectral resolution with a spectral sampling of 3.3 nm/pixel. The instruments are calibrated from 350 nm to 900 nm. The HyperOCRs have dark signal corrections using shutter dark measurements collected every 5th scan. The radiometers were calibrated before and after the cruise. The profiler is equipped with depth, temperature, tilt and two WET Labs ECO Puck Triplet sensors. One ECO Puck sensor measures fluorescence estimates of chlorophyll-a (mg m^{-3}), CDOM (ppb) and phycoerythin (ppb). The second ECO Puck sensor measures backscattering b_b (m^{-1}) at 443 nm, 550 nm, and 860 nm.

The VIIRS data was processed by NOAA MSL12. Data from this effort are archived on the NASA Ocean Biology Processing Group's SEABASS archive.
http://seabass.gsfc.nasa.gov/wiki/article.cgi?article=System_Description

The direct solar radiation was measured at each station using a Microtops II sun photometer from Solar Light Co. These measurements are used to estimate atmospheric optical thickness is used to support the atmospheric correction process. Data from this collaborative effort are archived on the NASA Ocean Biology Processing Group's SEABASS archive.
http://seabass.gsfc.nasa.gov/wiki/article.cgi?article=System_Description

5.2 Inherent Optical Property (IOP) profiles and ancillary measurements

Analyst/lead PI: Shawn Shellito and Joseph Salisbury (UNH)

IOP and ancillary measurements were collected at 103 stations during the ECOA-1 cruise. The primary instruments used were the Wetlabs™ ac-s, which measures hyperspectral absorption and attenuation from 400-730nm, and the Wetlabs ™bb-9, which measures optical backscatter at 9 wavelengths. Additionally the profiler included CTD data, oxygen and fluorescence of chlorophyll *a* and CDOM (see table below). All instruments were factory calibrated at the SeaBird™ factory prior to the ECOA cruise.

Measurements were usually taken during daylight hours (1000-1500 local), and efforts were made to have the IOP measurements coincide with AOP measurements. All data have been delivered to the NASA Ocean Biology Processing Group's SEABASS archive. http://seabass.gsfc.nasa.gov/wiki/article.cgi?article=System_Description.

UNH Inherent optical property profiler measurements

Measurement	Equipment	unit	uncertainty
Hyperspectral attenuation and absorption	Wetlab ac-s	m^{-1}	0.01%[1]
Spectral optical backscattering	Wetlab bb9	m^{-1}	0.00002[2]
salinity/ temperature/depth	SBE 49	psu/^{o}C/m	0.01%[1]
Dissolved oxygen	SBE 43	umol/kg	0.5%[1]
Stim. Fluorescence of chlorophyll a	Wetlabs ECOFL Chl	mg/ m^{-3}	0.02[2]
Flow through Fluorescence of DOM	Wetlabs ECOFL DOM	ppb QSE	0.09[2]
Flow through Beam attenuation	Wetlab Beam C	m^{-1}	0.01%[1]
Conductivity/ salinity/ temperature	Aanderra CT	psu/^{o}C	0.03%[1]

[1] Accuracy, [2] Precision

5.3 Dedicated NASA Fly over with the GCAS and GeoTASO radiometers

The NASA Langley B200 aircraft conducted overflight observations of the ECOA cruise area of operations on 9 July 2015. The aircraft carried two hyperspectral imagers, the GeoCAPE Airborne Simulator (GCAS) and the Geostationary Trace Gases and Aerosol Sensor Optimization (GeoTASO), capable of measuring scene reflected radiances from the ultraviolet to near infrared. Two four-hour flights with takeoff times of approximately 08:56 (local) and 14:23 (local) were performed off the coast of Norfolk, VA and in the Hampton Roads channel. Flight operations were originally planned at a high (28kft) and low (14kft) altitude but were modified to 11kft altitude in the morning due to a solid, low cloud deck. Afternoon observations were largely successful due to the clouds dissipating in the area of interest. Widely scattered cumulus below the aircraft and scattered cirrus above were present. Most flight operations were conducted at 19kt in order to avoid occasional clouds at the edges of the area of operations. GCAS and GeoTASO instruments operated nominally during both flight segments. In summary, the morning flight data is of questionable use for ocean color studies due to the presence of clouds and it will require intensive data analysis in order to determine its usefulness. The afternoon flight was largely successful in collecting useable data and should be the primary focus for initial data analysis. Contact Joseph Salisbury (joe.salisbury@unh.edu) for data status.

6. Gray's Reef survey

Analyst: Janet Reimer (UDel)

As part of an agreement with PMEL, the Cai laboratory group is responsible for ground truthing, or validation, of the Gray's Reef (GR) coastal $MAPCO_2$ system time series. As part of our efforts for year 2015 we have included a three to four hour station at the mooring during the ECOA cruise to obtain a full set of discrete measurements as well as

underway pCO_2, O_2/Ar, and DIC measurements. All the parameters collected during ECOA were collected at the GR mooring. Specifically, repeat measurements in triplicate were collected each hour for DIC, pH, TA, and dissolved oxygen in the surface at 17 minutes past the hour from 5 to 7 am at roughly the same time as the $MAPCO_2$ takes its measurement. For this exercise the mooring frequency was increased to once every hour, therefore we have three hours of data for validation between the mooring system, the underway system, and discrete bottle samples. Furthermore, we will have net and gross primary production, respiration, as well as particulate, dissolved, and colored organic matter. We arrived at this station pre-dawn and took a water column CTD cast collecting water at three depths. We then started our circle around the station and took a second full water column CTD cast as well as an IOP cast. In the same position as the second CTD cast we took surface water samples from the underway system for the third of the three measurements. Following the approximately bi-monthly sampling during routine maintenance work at the GR mooring (by Scott Noakes, University of Georgia) we took triplicate samples over a three to four hour period. Following the final cast we completed a circle around the mooring before leaving for the next station. Due to the size and maneuverability limitation of the ship we were not able to get closer than 0.6 nautical miles (1.1 km). Parameters measured underway are already included in the master files and upon receiving the rest of the data from the groups that will be processing data post cruise we will include all the parameters in a specific ground truthing spread sheet available to all participants including the group from NOAA PMEL.

7.0 Acknowledgements:

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