East Coast Ocean Acidification Cruise (ECOA-3)

Prepared by Shawn Shellito and Sophie Alpert
with contributions from all cruise participants.

R/V Ronald H. Brown (RB-22-2)
EXPOCODE: 33RO20220806
Project ID: OAP1812-1527
8 August – 23 September, 2022

Portland, ME – 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: Wei-Jun Cai (University of Delaware)
Co-Chief Scientist:
Leg 1: Shawn Shellito
Leg 2: Shawn Shellito

Project Summary

Section Name	*2022 East Coast Ocean Acidification (ECOA)*
Expocode	33RO20220806
Vessel	RV Ronald H. Brown
Leg 0	
Chief Scientist Leg 0	Charles Featherstone
Leg 1	
Chief Scientist Leg 1	Joe Salisbury
Co-Chief Scientist Leg 1	Shawn Shellito
Leg 2	
Chief Scientist Leg 2	Wei-Jun Cai
Co-Chief Scientist Leg 2	Shawn Shellito
Loading	*08/02/2022 to 08/04/2022*
Transit (Leg 0)	08/05/2022 to 08/08/2022
ECOA Leg 1 Dates	08/08/2022 to 08/29/2022
ECOA Leg 2 Dates	09/05/2022 to 09/23/2022
Ports of call	*Loading: Newport, RI,* ECOA Leg 0: Newport, RI, to Portland, ME, ECOA Leg 1: Portland, ME, to Newport, RI, ECOA Leg 2: Newport, RI, to Port Everglades, FL,
Stations occupied	2 test station Leg 0 126 CTD stations Leg 1 102 CTD stations Leg 2

Cruise Metrics

Measurement	Leg 1	Leg 2	Total	Objectives*
Days at Sea	22	19	41	41
AOP	51	35	86	60
Bongo	39	33	72	100
CTD	126	102	228	200
Drifter	4	1	5	2
IOP	19	12	31	N/A
Lander	17	9	26	20
Box Core (attempts)	54	0	54	20
Discrete niskin samples	954	783	1737	N/A
Distance (nm)	3330	2690	6020	N/A

*Please see Section 2.2 for additional information

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1. Summary

This report describes the third East Coast Ocean Acidification Cruise (ECOA-3). 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 and production rates as they relate to ocean acidification (OA) in the coastal realm. This was the fifth comprehensive occupation of the eastern coastal waters of the U.S., with the first occurring in 2007, the second in 2012, the third in 2015, the fourth in 2018, and this effort in 2023. The previous efforts were named the Gulf of Mexico and East Coast Carbon cruises I and II (GOMECC I and II), along with the first two ECOA cruises (ECOA 1 and 2). 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, 3) the need to sample deeper into waters to compare results with past open ocean data for better quantification of anthropogenic CO_2 accumulation rates in coastal waters, and 4) the need to perform ancillary measurements such as biological and denitrification rates 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 24 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 228 specified locations. Many of the stations occupied were stations on prior ECOAs, or in some cases the GO-SHIP cruise A22. A total of 47 scientists from 9 Universities and 5 Federal Agencies participated in the 41-day cruise, which departed from Portland, ME on the 8th of August, and arrived on schedule in Port Everglades, FL on the 23rd of September.

Water samples were collected from the 24-bottle rosette at each station and analyzed for oxygen, salinity, nutrients, dissolved inorganic carbon, 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, pH, bio-optical properties, and acoustic Doppler current profiles (ADCP).

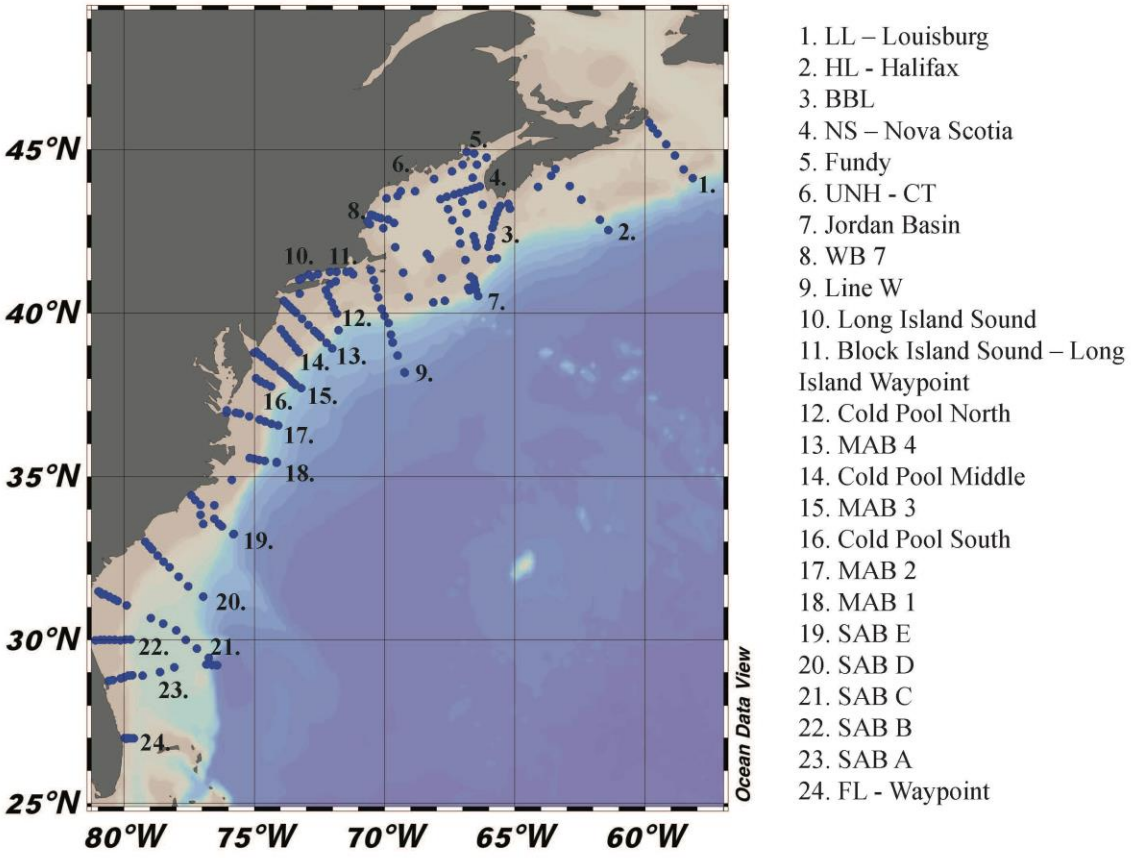

Figure 1 – ECOA-3 CTD stations

2. Introduction

2.1 Background

NOAA OAP and partners conducted the second East Coast Ocean Acidification cruise (ECOA-3) 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 and denitrification 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 value (NOAA OA Research Plan 2020 – 2029). 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 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 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 *Ronald H. Brown* is the fifth of a planned 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 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-3 cruise was supported by the NOAA/OAR Ocean Acidification Program (OAP). Forty-seven scientists representing 9 universities and 5 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 *Ronald H. Brown* departed Portland, ME on the 8th of August 2022. The cruise completed a series of 24 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 oxygen, salinity, nutrients, dissolved inorganic carbon (DIC), total alkalinity (TA), pCO_2, dissolved organic matter (DOM), colored dissolved organic matter (CDOM, and phytoplankton pigments. A total of 228 stations were occupied on the cruise (Table 4). East Coast transects occupied in both ECOA 1 & 2 were revisited as well as several more transects that were added to the Northeast with the goal of understanding biogeochemical characteristics of Canadian-sourced 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 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 2 hours from the underway-sampling line for discrete analyses of oxygen, DIC, TA, pCO_2 and pH. There were 128 sets of discrete samples taken from the underway line.

Table 1: ECOA-3 principal investigators

Program	Affiliation	Principal Investigator	Email Address
CTD/DO data, salts	UNH	Shawn Shellito Joe Salisbury	Shawn.Shellito@unh.edu Joe.Salisbury@unh.edu
DIC, underway pCO2	AOML/NOAA	Rik Wanninkhof Leticia Barbero	Rik.Wanninkhof@noaa.gov Leticia.Barbero@noaa.gov
DIC, TA, pH, d13C Underway pH	UDel	Wei-Jun Cai	Wcai@udel.edu
Ocean Color (AOP)	NOAA/NESDIS	Mike Ondrusek	Michael.Ondrusek@noaa.gov
Nutrients	UNH	Joe Salisbury	Joe.Salisbury@unh.edu
Ocean Color (IOP)	UNH	Joe Salisbury	Joe.Salisbury@unh.edu
CDOM, DOC, pigments	UNH NASA	Joe Salisbury Antonio Mannino	Joe.Salisbury@unh.edu Antonio.Mannino-1@nasa.gov
Sediment Collection Denitrification Rates	UConn	Craig Tobias Sam Siedlecki	Craig.Tobias@uconn.edu Samantha.Siedlecki@uconn.edu
O2/Ar	UDel	Wei-Jun Cai Elliott Roberts	Wcai@udel.edu ElliottR@udel.edu
Nets/Pteropods	NOAA/NFSC	Chris Melrose	Chris.Melrose@noaa.gov
Respiration Rates	UNH	Kai Ziervogel	Kai.Ziervogel@unh.edu
Phytoplankton assemblages	LEDO	Joaquim Goes	jig@ldeo.columbia.edu
Dissolved Oxygen	RSMAS	Chris Langdon	clangdon@rsmas.miami.edu
Lander	UNH	Joe Salisbury	Joe.Salisbury@unh.edu
Plankton ecology	NCSU ULL	Astrid Schnetzer Beth Stauffer	aschnet@ncsu.edu beth.stauffer@louisiana.edu

Participating Institutions

Primary:

UNH	University of New Hampshire
UDel	University of Delaware

Additional information:

OAP	NOAA/OAR/Ocean Acidification Program
LDEO	Lamont-Doherty Earth Observatory – Columbia Climate School
NOAA/AOML	NOAA Atlantic Oceanographic and Meteorological Laboratory
NOAA/OAP	NOAA Ocean Acidification Program
NOAA/NESDIS	NOAA National Environmental Satellite, Data, and Information Service
NOAA/NFSC	NOAA National Fisheries Science Center
Northeast	Northeastern University
RSMAS	Rosenstiel School of Marine and Atmospheric Science/University of Miami
UConn	University of Connecticut – Avery Point Marine Sciences
UCSD	University of California San Diego
ULL	University of Louisiana at Lafayette
NCSU	North Carolina State University
NASA	NASA Goddard

Table 2: ECOA-3 Cruise Participants - Personnel/Science Party: name, title, gender, affiliation, and nationality.

Name (First, Last)	Title	Date Aboard	Date Disembark	Leg	Gender	Affiliation	Nationality
Shawn Shellito	Co-Chief Scientist/CTD	8/8/2022	9/23/2022	both	M	UNH	USA
Charles Featherstone	DIC	8/8/2022	9/23/2022	both	M	AOML	USA
Patrick Mears	DIC	8/8/2022	9/23/2022	both	M	AOML	USA
Najid Hussain	TA	8/8/2022	9/23/2022	both	M	UDel	USA
Emma Thibodeau	Underway TA/Salinity	8/8/2022	9/23/2022	both	F	UNH	USA
Xinyu Li	pH	8/8/2022	9/23/2022	both	F	UDel	PRC
Bo Dong	pH	8/8/2022	9/23/2022	both	M	UDel	PRC
Zhentao Sun	d13C	8/8/2022	9/23/2022	both	M	UDel	PRC
Allison Black	birder	8/8/2022	9/23/2022	both	F	NOAA	USA
Carly Daiek	IFCB/NCP	9/5/2022	9/23/2022	both	F	UNH	USA
Elliott Roberts	TA	8/8/2022	9/23/2022	both	M	UDel	USA
Jennifer Acosta	phyto-structure	8/8/2022	9/23/2022	both	F	LDEO	USA
Joseph Salisbury	Chief Scientist	8/8/2022	8/29/2022	1	M	UNH	USA
Terence O'Brien	CTD/Other	8/8/2022	8/29/2022	1	M	UNH	USA
Astrid Zapata	Respiration	8/8/2022	8/29/2022	1	F	UNH	USA/PR
Lydia Pinard	Respiration	8/8/2022	8/29/2022	1	F	UNH	USA
Zoe Kendall	Respiration	8/8/2022	8/29/2022	1	F	UNH	USA
Joaquim Goes	phytoplankton structure	8/8/2022	8/29/202	1	M	LDEO	USA
Craig Tobias	Sediments	8/8/2022	8/29/2022	1	M	UConn	USA
Sam Siedlecki	Sediments	8/8/2022	8/29/2022	1	F	UConn	USA
Halle Berger	Sediments	8/8/2022	8/29/2022	1	F	UConn	USA

Alexandra Frenzel	Sediments	8/8/2022	8/29/2022	1	F	UConn	USA
Michael Ondrusek	AOP	8/8/2022	8/29/2022	1	M	NESDIS	USA
Chris Langdon	O2	8/8/2022	8/29/2022	1	M	RSMAS	USA
Skylar Rodriguez	O2	8/8/2022	8/29/2022	1	M	OAP	USA
Jordan Watson	TA	8/8/2022	8/29/2022	1	M	UDel	USA
Zhanxian Ouyang	d13C	8/8/2022	8/29/2022	1	M	UDel	PRC
Chris Taylor	CTD/zoo-plankton	8/8/2022	8/29/2022	1	M	NOAA	USA
Wei-Jun Cai	Chief Scientist	9/5/2022	9/23/2022	2	M	UDel	USA
Wu Zelun	TA	9/5/2022	9/23/2022	2	M	UDel	PRC
Marc Emond	CTD/Other	9/5/2022	9/23/2022	2	M	UNH	USA
Liza Wright-Fairbanks	filtration	9/5/2022	9/23/2022	2	F	OAP	USA
Amanda Jacobsen	CTD/zoo-plankton	9/5/2022	9/23/2022	2	F	OAP	USA
Dwight Gledhill	O2	9/5/2022	9/23/2022	2	F	OAP	USA
Clara Gramazio	O2	9/5/2022	9/23/2022	2	F	RSMAS	USA
Kai Ziervogel	Respiration	9/5/2022	9/23/2022	2	M	UNH	USA
Charles Kovach	AOP	9/5/2022	9/23/2022	2	M	NESDIS	USA
Sierra Kehoe	nutrients	9/5/2022	9/23/2022	2	F	UNH	USA
Sophie Alpert	filtration	9/5/2022	9/23/2022	2	F	UNH	USA
Lucy Roussa	HABs	9/5/2022	9/23/2022	2	F	NCSU	USA
Maya Lombardi	Protists	9/5/2022	9/23/2022	2	F	LSU	USA
Kaitlen Lang	nutrients	9/5/2022	9/23/2022	2	F	NOAA	USA
Jingui Wu	Phytoplankton structure	9/5/2022	9/23/2022	2	F	LDEO	USA

2.2 Measurement Objectives Pass/Fail

Table 3 lists the pre-cruise objectives we were striving to accomplish on ECOA-3. The majority of these objectives were met though the hard work of both the scientist on board and the ship's crew as well as the good fortune of no positive covid tests and the calm seas.

2.2.1 Problems/Objectives not accomplished

Even though we had overwhelming good seas there were still several stations (192 & 193) on transect SAB A where CTDs could not be performed because of the combination of wind and current. The projected forecast had the winds persisting throughout the evening into the following day, so it was decided to skip these stations and to continue offshore to the 5000-meter station (199) before Hurricane Fionna arrived on site. Several other stations (166b, 170, & 171) had to be shifted out of line with the rest of stations in transect SAB E because of ongoing live fire drills being carried out at those locations. The four stations in the Bahamian waters on transect SAB A seemed promising at the beginning of the cruise through the work of the State Department but at the last minute the Bahamian government requested a document to be signed by the Chief Scientist that would hold him solely responsible damages and fines. It was agreed by all US parties that this was unacceptable, and these stations had to be dropped.

Both the number of Bongo net tows and core stations were lower than expected. This was partially due to the ship's decision to interrupt Leg 2 and take on fuel in Mayport FL on September 15th (ultimately got pushed to the 16th so we could complete transect SAB D). This date caused us to push the pace on the first leg and try to get several transects from the second leg done so the steam to Mayport would be a minimum. This kept the number of bongo stations lower than anticipated and the coring attempts at the coring stations to 2 sometimes 3 max. An added complexity to the coring operations was when the decision was made to only core during hours the bosun was on shift. If coring continues, it would be wise to solve this problem so coring could happen day or night.

Table 3: ECOA-3 Measurement Objectives

METRIC	UNITS	OBJECTIVE	ACCOMPLISHED
Days at sea	QUANTITY	41	41
Number of CTD casts to collect discrete carbonate parameters	QUANTITY	200	228
Ocean Acidification cross-shelf transects	QUANTITY	16	24
Bongo net tows will be performed at select stations to sample for biological species	QUANTITY	100	72
Benthic Lander Deployments	QUANTITY	20	26
NOAA Global Drifter Program - Drifter	QUANTITY	2	5
Sediment cores will be collected at stations in US and Canadian coastal areas	QUANTITY	20	20
IOP and AOP stations for satellite calibrations	QUANTITY	60	86
Surface water measurements will be taken from the scientific seawater line during the entire cruise	PASS/FAIL	PASS	PASS
Number of stations in Bahamian waters	QUANTITY	4	0

2.3 Communication and Outreach

Liza Wright-Fairbanks, a Knauss Fellow, posted photographs and descriptions of science sampling and activities on NOAA's OAP Instagram account throughout the cruise: https://www.instagram.com/noaaoceanacidification/.
In addition to the social media communication Leticia Barbero (AOML) and Eva DiDonato (National Park Service) arranged for outreached OA coastal sampling at the following national parks when the Brown was passing by offshore: Acadia, Cape Cod National Seashore, Fire Island, Gateway, Assateageue Island, Cape Lookout National Seashore, Cumberland Island National Seashore, Timucuan, and Cape Canaveral.

3. Description of Measurements from Vertical Profiles

3.1 CTD/Hydrographic Measurements

Analysts: Shawn Shellito, Marc Emond, Joseph Salisbury (UNH)
PI: Shawn Shellito

A total of 228 CTD/O_2/Optics stations were conducted during the cruise (Table 4, 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 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.

Table 4: CTD station locations visited during the ECOA-3 cruise.

Station #	Date	Time	Latitude	Longitude	Bottom Depth (m)
1	8/8/22	22:35	43.5109	-69.9292	110
2	8/9/22	2:03	43.5808	-69.5008	149
3	8/9/22	5:00	43.7225	-69.3681	88
4	8/9/22	9:18	43.7299	-68.8272	116
5	8/9/22	19:28	44.1019	-68.0987	105
6	8/9/22	23:16	44.3325	-67.4128	108
7	8/10/22	2:21	44.5372	-67.0060	60
8	8/10/22	5:48	44.9260	-66.8505	99
9	8/10/22	8:14	44.8784	-66.5530	106
10	8/10/22	11:49	44.7590	-66.0848	109
11	8/10/22	14:56	44.5368	-66.4465	203
12	8/10/22	20:55	44.1414	-66.6160	95
13	8/10/22	23:33	43.8704	-66.3452	63
14	8/11/22	1:29	43.8193	-66.5274	97
15	8/11/22	3:11	43.7864	-66.6609	105
16	8/11/22	5:09	43.7397	-66.8548	156
17	8/11/22	7:49	43.6820	-67.1009	135
18	8/11/22	9:46	43.6239	-67.3225	212
19	8/11/22	12:11	43.5561	-67.6126	246
20	8/11/22	14:05	43.4879	-67.8562	293
21	8/11/22	20:32	43.4104	-67.0080	213
22	8/12/22	0:30	43.3096	-66.2348	74
23	8/12/22	4:59	43.3409	-65.2523	100
24	8/12/22	11:58	43.8652	-64.1100	152
25	8/12/22	15:55	44.1986	-63.6037	137
26	8/12/22	19:18	44.4030	-63.4331	83
27	8/13/22	0:48	43.8854	-62.8857	266
28	8/13/22	4:47	43.4764	-62.4502	84
30	8/13/22	13:31	42.8508	-61.7342	1020
31	8/13/22	18:38	42.5341	-61.4066	2785
32	8/14/22	12:09	44.1262	-58.1722	833
33	8/14/22	15:34	44.3935	-58.5104	64
34	8/14/22	20:46	44.8187	-58.8528	213
35	8/14/22	23:39	45.1558	-59.1824	100
36	8/15/22	2:58	45.4884	-59.5181	143
37	8/15/22	4:56	45.6596	-59.7095	126
38	8/15/22	7:13	45.8284	-59.8415	89
39	8/16/22	8:36	43.1988	-65.1826	156

40	8/16/22	11:34	43.2824	-65.5503	42
41	8/16/22	13:12	43.1590	-65.6360	75
42	8/16/22	14:36	43.0421	-65.6901	117
43	8/16/22	17:38	42.9018	-65.7563	140
44	8/16/22	20:07	42.7621	-65.8010	100
45	8/16/22	21:51	42.6078	-65.8549	87
46	8/17/22	1:08	42.3241	-65.9178	227
47	8/17/22	3:43	42.1628	-65.9532	224
48	8/17/22	5:55	42.0262	-66.0038	100
49	8/17/22	9:57	41.6744	-65.6949	1425
50	8/17/22	12:34	41.6484	-65.9211	126
51	8/17/22	16:35	42.0433	-66.4617	89
52	8/17/22	18:28	42.1907	-66.5057	211
53	8/17/22	22:13	42.3525	-66.5739	305
54	8/18/22	3:02	43.0560	-66.8487	161
55	8/18/22	7:32	43.1854	-67.5693	194
56	8/18/22	10:15	42.8369	-67.3929	199
57	8/18/22	13:10	42.5129	-67.1298	330
58	8/18/22	17:28	42.1245	-67.0847	63
59	8/18/22	23:32	41.6225	-66.8971	66
60	8/19/22	2:49	41.1121	-66.7018	81
61	8/19/22	4:48	41.0381	-66.5800	88
62	8/19/22	6:40	40.9495	-66.5645	118
63	8/19/22	9:47	40.8887	-66.5507	440
64	8/19/22	13:48	40.8466	-66.5352	1060
65	8/19/22	16:28	40.6868	-66.4846	1473
66	8/19/22	20:35	40.5289	-66.4131	2331
67	8/20/22	0:02	40.6984	-66.7476	492
68	8/20/22	2:18	40.7711	-66.7810	205
69	8/20/22	6:54	40.3704	-67.6789	462
70	8/20/22	10:32	40.3289	-68.1300	1039
71	8/20/22	18:41	41.0640	-67.8114	53
72	8/21/22	0:03	41.6623	-68.2437	32
73	8/21/22	2:08	41.8146	-68.3679	207
74	8/21/22	10:48	42.7519	-69.6387	268
75	8/21/22	12:40	42.8604	-69.8626	274
76	8/21/22	16:37	42.8993	-70.1376	62
77	8/21/22	18:17	42.9422	-70.2935	142
78	8/21/22	21:06	42.9823	-70.4226	108
79	8/21/22	22:45	43.0138	-70.5238	75
80	8/22/22	0:30	42.8201	-70.6566	72
81	8/22/22	1:58	42.7154	-70.5560	80
82	8/22/22	4:49	42.6036	-70.0516	110
83	8/22/22	9:51	42.0122	-69.5935	219
84	8/22/22	17:34	41.2334	-69.2907	64

85	8/22/22	23:19	40.4901	-69.0739	78
86	8/23/22	14:23	38.1874	-69.2487	3779
87	8/23/22	22:03	38.7050	-69.4962	3290
88	8/24/22	3:33	39.0909	-69.6668	2840
89	8/24/22	7:19	39.3397	-69.7545	2517
90	8/24/22	11:54	39.6911	-69.8440	2118
91	8/24/22	16:04	39.9174	-70.0004	458
92	8/24/22	19:30	40.1377	-70.1052	122
93	8/24/22	23:51	40.4874	-70.2380	68
94	8/25/22	2:07	40.7566	-70.3240	48
95	8/25/22	4:16	41.0045	-70.4094	40
96	8/25/22	7:04	41.3044	-70.5201	12
97	8/25/22	11:02	41.1847	-71.1969	46
98	8/25/22	12:45	41.2683	-71.3146	38
99	8/25/22	14:11	41.2629	-71.4563	34
100	8/25/22	17:55	41.2566	-72.1038	42
101	8/25/22	23:12	41.1750	-72.9039	16
103	8/26/22	1:54	41.0234	-73.2796	37
104	8/26/22	3:44	41.0624	-73.1749	23
105	8/26/22	6:18	41.1167	-72.7944	23
106	8/26/22	8:06	41.1844	-72.5652	22
107	8/26/22	11:40	41.2626	-71.8478	29.9
109	8/26/22	18:15	40.9759	-71.8697	25
110	8/26/22	19:56	40.8912	-72.0820	32
111	8/26/22	21:34	40.7018	-72.2539	47
112	8/26/22	22:59	40.5372	-72.1556	56
113	8/27/22	1:01	40.3304	-72.0277	63
114	8/27/22	2:46	40.1494	-71.9358	78
115	8/27/22	4:15	39.9827	-71.8312	96
116	8/27/22	12:33	40.5926	-73.2523	15
117	8/27/22	16:03	40.3757	-73.8654	23
118	8/27/22	17:26	40.2840	-73.7540	30
119	8/27/22	19:13	40.1944	-73.6378	35
120	8/27/22	20:25	40.0981	-73.5138	46
121	8/27/22	21:40	40.0081	-73.3967	74
122	8/27/22	23:31	39.8240	-73.1624	47
123	8/28/22	1:19	39.6374	-72.9223	65
124	8/28/22	3:19	39.4550	-72.6895	85
125	8/28/22	4:51	39.3630	-72.5670	128
126	8/28/22	6:29	39.2717	-72.4496	150
127	8/28/22	9:15	39.0887	-72.2177	1486
128	8/28/22	12:25	38.9238	-72.0053	2483
128B	8/28/22	19:03	39.4763	-71.7705	1427
124_2	9/7/22	5:46	39.4534	-72.6903	85
126_2	9/7/22	8:21	39.2740	-72.4514	140

127_2	9/7/22	11:47	39.0889	-72.2169	1508
129	9/7/22	20:11	39.5008	-73.9701	25
130	9/7/22	21:48	39.3500	-73.8360	38
131	9/7/22	23:33	39.2140	-73.7002	43
132	9/8/22	1:57	39.0826	-73.5595	50
133	9/8/22	4:08	38.9325	-73.4170	60
134	9/8/22	6:02	38.8025	-73.2829	69
135	9/8/22	14:41	37.7062	-73.1943	2600
136	9/8/22	18:45	37.8136	-73.4300	2057
137	9/8/22	21:42	37.8897	-73.5370	1834
138	9/9/22	0:27	38.0044	-73.6488	1250
139	9/9/22	2:53	38.0779	-73.7640	883
140	9/9/22	5:01	38.1517	-73.8814	120
141	9/9/22	6:41	38.2251	-73.9973	74
142	9/9/22	8:56	38.3703	-74.2287	57
143	9/9/22	10:11	38.4436	-74.3450	33
144	9/9/22	11:45	38.5169	-74.4601	34
145	9/9/22	14:02	38.6612	-74.6912	19
146	9/9/22	15:20	38.7348	-74.8092	20
147	9/9/22	16:48	38.8185	-74.9198	12
148	9/9/22	18:33	38.7849	-75.0033	19
149	9/9/22	23:53	38.0020	-74.9370	24.6
150	9/10/22	1:21	37.9098	-74.7731	30
151	9/10/22	3:11	37.8343	-74.5644	55
152	9/10/22	5:17	37.7494	-74.3493	71
153	9/10/22	14:00	36.9494	-76.0607	13
153_2	9/10/22	18:25	37.0214	-76.0596	15
154	9/10/22	21:29	36.9504	-75.7169	17
155	9/10/22	22:34	36.9194	-75.5496	21
156	9/11/22	0:37	36.8430	-75.1879	28
157	9/11/22	2:54	36.7382	-74.7941	65
158	9/11/22	5:15	36.6787	-74.5804	1233
159	9/11/22	8:30	36.6124	-74.3443	1897
160	9/11/22	12:03	36.5643	-74.0914	2400
161	9/11/22	22:51	35.4151	-74.1516	2960
163	9/12/22	4:04	35.4799	-74.6072	2117
164	9/12/22	6:34	35.5011	-74.8194	109
164B	9/12/22	8:07	35.5349	-75.0143	42
165	9/12/22	9:39	35.5687	-75.1855	35
166	9/12/22	16:18	34.8962	-75.8625	25
166B	9/12/22	22:31	34.1228	-76.5345	38
167	9/13/22	3:21	34.4171	-77.4222	14
168	9/13/22	4:45	34.2783	-77.2578	23
169	9/13/22	6:11	34.1347	-77.0737	30
170	9/13/22	8:39	33.8300	-77.0655	35

171	9/13/22	11:01	33.5430	-76.9575	53
172	9/13/22	13:43	33.7103	-76.5374	240
173	9/13/22	15:30	33.5481	-76.3577	548
174	9/13/22	18:30	33.4670	-76.2424	680
175	9/13/22	22:56	33.2391	-75.8030	3020
176	9/14/22	15:14	31.3223	-76.9651	2483
177	9/14/22	20:06	31.6320	-77.5386	815
177B	9/14/22	23:07	31.9296	-77.9006	660
178	9/15/22	3:02	32.2162	-78.2600	375
179	9/15/22	5:47	32.3902	-78.4825	265
180	9/15/22	8:11	32.5796	-78.7049	43
181	9/15/22	10:08	32.7730	-78.9182	32
182	9/15/22	11:24	32.8682	-79.0271	23
183	9/15/22	12:51	33.0055	-79.1845	12
186	9/16/22	2:00	31.4070	-80.8671	20
186_2	9/17/22	12:20	31.4026	-80.8656	17
185	9/17/22	15:13	31.4649	-80.9215	16
184	9/17/22	16:03	31.4816	-80.9767	15
187	9/17/22	17:55	31.3969	-80.7453	23
188	9/17/22	19:52	31.3245	-80.5668	26
189	9/17/22	21:13	31.2560	-80.3862	33
190	9/17/22	22:34	31.1934	-80.2446	37
191	9/18/22	1:00	31.0569	-79.8983	125
194	9/18/22	8:17	30.6635	-78.9695	805
195	9/18/22	12:01	30.4934	-78.5020	813
196	9/18/22	15:41	30.2925	-77.9989	808
197	9/18/22	19:22	30.0033	-77.6361	832
197B	9/18/22	23:06	29.7339	-77.2022	920
198	9/19/22	4:24	29.4541	-76.7461	3627
199_2	9/19/22	11:36	29.2201	-76.4438	5000
199B	9/19/22	16:18	29.2317	-76.6250	5020
200	9/19/22	18:28	29.2436	-76.8395	1390
201	9/20/22	1:40	29.1678	-78.0763	891
202	9/20/22	5:47	29.0168	-78.6251	864
203	9/20/22	10:43	28.9051	-79.2961	800
204	9/20/22	13:50	28.9072	-79.6877	785
205	9/20/22	17:40	28.8926	-79.8333	500
206	9/20/22	20:22	28.8555	-79.9843	240
207	9/20/22	22:05	28.8231	-80.1347	68
209	9/21/22	1:05	28.7509	-80.5785	18
208	9/21/22	2:40	28.7756	-80.4317	23
215	9/21/22	9:53	30.0036	-79.7536	874
216	9/21/22	12:08	30.0081	-79.9494	555
217	9/21/22	14:01	29.9896	-80.1490	340
218	9/21/22	16:00	29.9989	-80.3582	44

219	9/21/22	18:26	29.9994	-80.5537	40
220	9/21/22	20:20	29.9989	-80.7510	34
221	9/21/22	22:07	29.9989	-80.9114	26
222	9/21/22	23:56	29.9936	-81.1044	17
210	9/22/22	21:44	26.9974	-79.9809	80
211	9/22/22	23:03	26.9804	-79.9209	175
212	9/23/22	0:48	26.9966	-79.8605	278
213	9/23/22	2:58	26.9826	-79.7785	400
213B	9/23/22	5:32	26.9848	-79.6875	539
214	9/23/22	7:52	26.9840	-79.6249	630

3.1.1 CTD Operations

CTD/rosette casts were performed with a package consisting of a 24-place, 10-liter rosette frame, a 24-place water sampler/pylon (SBE32) and 24, 10-liter Niskin-style bottles. 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), dual dissolved oxygen (SBE43), and a Valeport VA500 altimeter. A replicate CTD was on loan from NOAA PMEL but was not used. The other underwater electronic components involved an array of several optical sensors, consisting of a Biospherical QCP-2300 irradiance sensor, a Seapoint chlorophyll fluorometer, and a Seapoint ultraviolet fluorometer.

The CTD 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 horizontally attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3 temperature sensors and their respective pumps were mounted horizontally and plumbed as recommended by SBE outboard of the CTD. The Primary temperature, conductivity, and dissolved oxygen were plumbed on one pump circuit and secondary temperature and conductivity on the other. Pump exhausts were facing upwards at a slight angle to assure bubbles would exit the pump. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring. The R/V *Brown's* forward starboard CTD winch was used with the 24-position 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. Deck hands preferred that the CTD/Rosette be put in the water first before being powered-up. Once the CTD was powered the data acquisition system, Seasave V7, would be started. The CTD package was then put in the water and

taken down to a depth of 10 m for 5 minutes to remove any air bubbles from the sensor lines. At the end of the cast the CTD was powered off before being put back on deck. Once on deck 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.

3.1.2 System Problems

During the cruise there were three known problems with the CTD. The first originated on station 039 when it was decided to replace the primary oxygen sensor as it was not tracking closely with the secondary and had to be replaced by a recently calibrated spare carried by the ship. The second issue happened on station 045 when our secondary oxygen sensor started to drift, and we replaced it with another recently calibrated sensor carried by the ship. The third issue happened after station 191 when it was noticed that the primary temperature sensor had stopped working after the cast was completed. The sensor was also replaced by a recently calibrated ship based spare.

Post-cruise analysis of the CTD data determined that even though two different temperature sensors had been used for the primary set of sensors, overall, these 2 sensors performed as good, if not better than, the secondary sensors for the temperature and salinity measurements. After post-cruise CTD oxygen comparison to discrete Winkler samples, it was determined the oxygen sensor from the primary set of sensors performed better than the secondary set (See section 3.2).

In addition to the CTD problems there were several instances when the Brown's winch would overheat and become immobilized at depth for a short period of time. Depending on the length of time, we would either continue with the cast or come back to the surface and repeat the cast.

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. SBE Seasave software version 7.26.7.107 was used for data acquisition and to trip (close) Niskin sampling bottles on the rosette. The CTD 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 would direct the winch operator to raise the package up and outboard with the J-frame. Once overboard, the CTD/rosette would then be quickly lowered into the water and submerged to 10 meters. 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 and wait while the cast was restarted to remove soak data. Once data was streaming again, the descent would begin. The typical profiling rate was no more than 30 m/min to 100 m, no faster than 45 m/min to 50 m, and no more than 60m/min to the bottom.

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 5 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. However, before being brought on deck the console watch terminated the data acquisition and turned off the deck unit. Once on deck and secured, sampling of the rosette would begin.

3.1.4 Navigation and Bathymetry Data Acquisition

Navigation data were acquired by the database workstation at 1-second intervals from the ship's Furuno GP150 P-Code GPS receiver. The ship conducted nearly continuous operations of bathymetric mapping with the EK60-18Hz and depth estimations with the ship's Seabeam/Kongsberg EM122 system. All data were recorded into the ships SCS system.

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 7.26.7.129. 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 7.26.7 The Sea-Bird Data Processing for primary calibrated data (1-meter 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).

- 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 correct sensor response and any calibration shifts.

A total of 228 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. 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 were more stable during the cruise with the exceptions listed above. Dissolved O_2 check samples collected during each cast were used to check 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, three conductivity sensors were used, all three tracked each other very well. These comparisons are summarized in Figure 2, which shows a median temperature difference between the two sensors of 0.001 degree C.

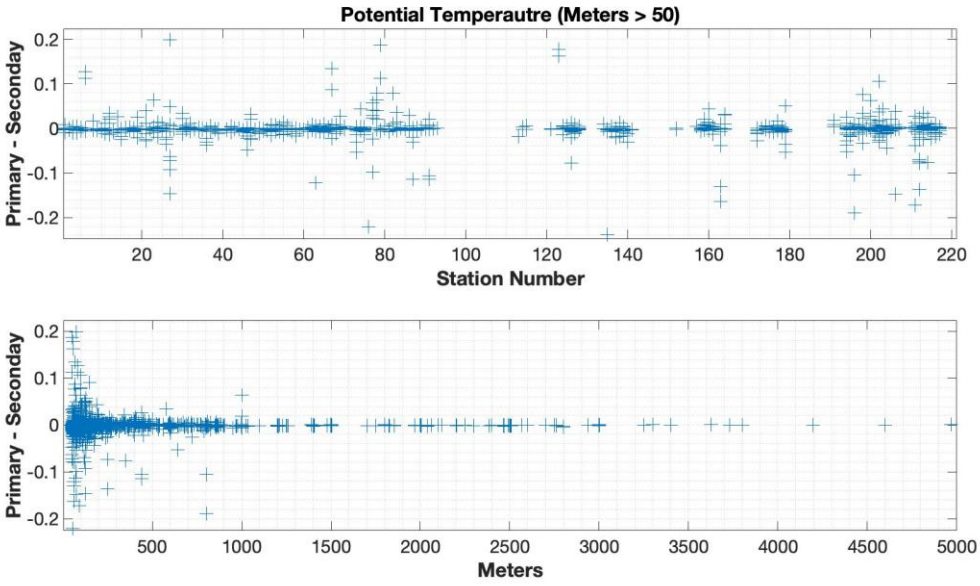

Figure 2: Uncalibrated potential temperature sensor differences between the primary and seconday sensors for depth greater the 50 meters.

3.1.8 CTD Salinity

Salinity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivity data during each cast. Calibration accuracy was examined by comparing S1-S2 over a range of station numbers and depths (bottle trip locations) for each cast. There was a consistent offset of +0.0336 between sensors. If that offset was added to S2 it would give a median salinity difference between sensors of 0.0002 PSU. For the entire cruise, only one set of temperature sensors were used, both tracked each other very well. These comparisons are summarized in Figure 3.

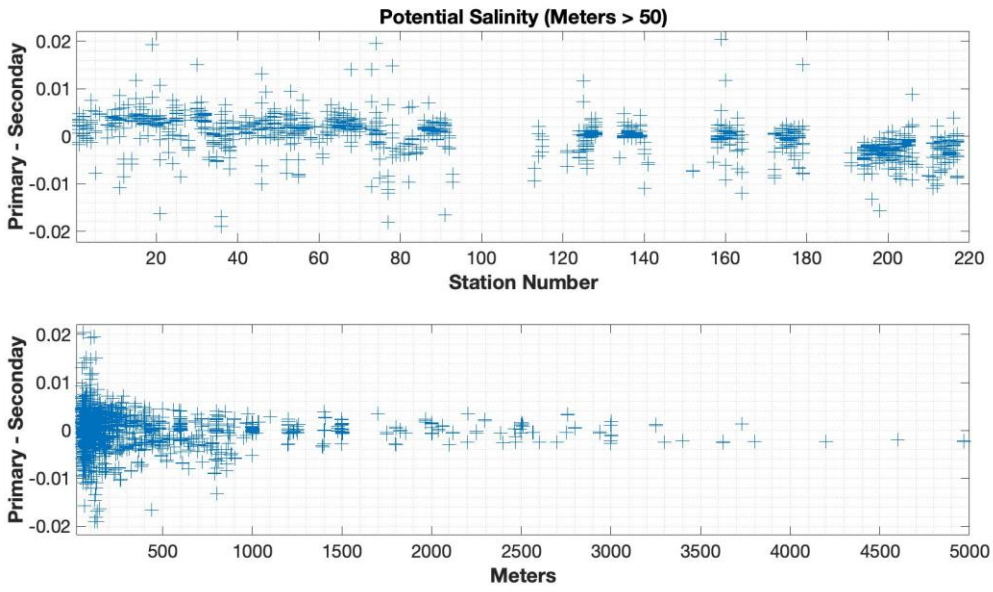

Figure 3: Uncalibrated salinity differences between primary and secondary sensor for depths> 50m.

3.1.9 CTD Dissolved Oxygen

Two SBE43 dissolved O_2 (DO) sensors were used on this cruise. Both sensors tracked each other well. Calibration accuracy was examined by comparing O1-O2 over a range of station numbers and depths (bottle trip locations) for each cast. These comparisons can be seen in Figure 4, which shows a median oxygen difference of 3.00 umol/kg. Oxygen data was post processed by merging downcast CTD/O2 sensor data with up-cast Winkler O2 data based on potential density. A non-linear least square regression equation is then used to correct the CTD/O2 sensor based on the Winkler data. Please see section 3.2 for further information.

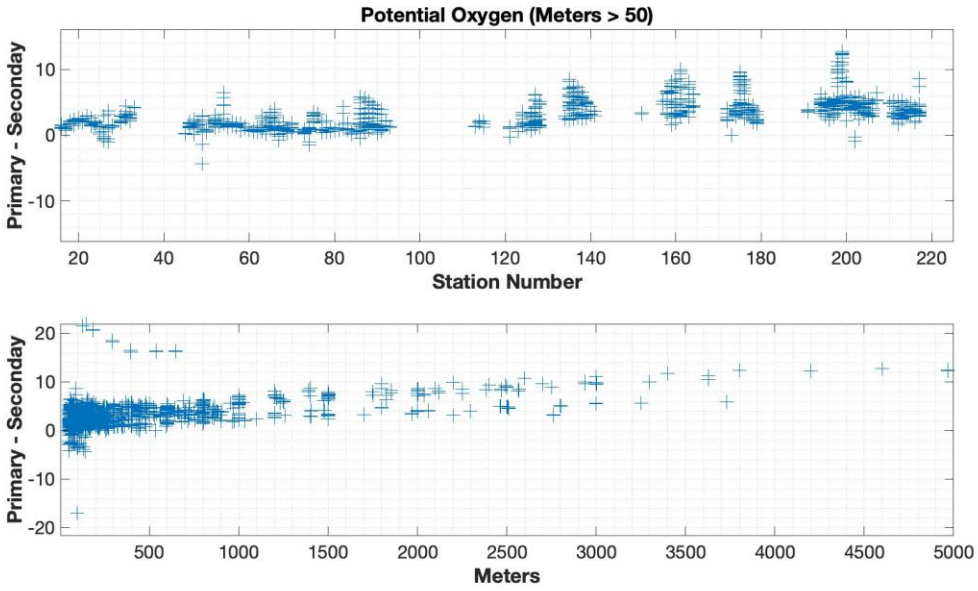

Figure 4: Uncalibrated oxygen differences between primary and secondary sensors for depths greater than 50 meters

Table 5: Equipment used during the cruise. Calibration and post calibration files available from Shawn Shellito UNH (shawn.shellito@unh.edu)

Instrument	S/N	Stations	Use	Comment
Sea-Bird SBE32 24-place Carousel Water Sampler	32-07163	1-222		
Sea-Bird SBE9plus CTD	09-1338	1-222		
Paroscientific Digiquartz Pressure Sensor	131732	1-222		
Sea-Bird SBE3plus Temperature Sensor	04981	1-191	primary	
Sea-Bird SBE3plus Temperature Sensor	0749	1-222	secondary	
Sea-Bird SBE3plus Temperature Sensor	4410	192-222	primary	Replaced after cast #195
Sea-Bird SBE4C Conductivity Sensor	04385	1-222	primary	
Sea-Bird SBE4C Conductivity Sensor	2653	1-222	secondary	
Sea-Bird SBE43 Dissolved Oxygen	0385	1-39	primary	Replaced after cast #39
Sea-Bird SBE43 Dissolved Oxygen	3669	1-45	secondary	Replaced after cast #45
Sea-Bird SBE43 Dissolved Oxygen	3778	39-222	primary	
Sea-Bird SBE43 Dissolved Oxygen	4178	46-222	secondary	

Seapoint Fluorometer	SCF-2770	1-222		
Seapoint CDOM	SUVF-6201	1-222		
Valeport VA500	24466	1-222		
Biospherical QCP 2300 Irradiance	70550	1-222		

Date will be archived at OCADS/NCEI

3.2 Oxygen Measurements

Analysts: Chris Langdon (MBF/RSMAS, University of Miami), Skylar Rodriguez (RSMAS, University of Miami), Dwight Gledhill (NOAA-OAP), and Clara Gramazio (RSMAS, University of Miami)

PI: 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 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.

Samples plus duplicates were drawn from the full cast of each station except as directed by the chief scientist. The total number of hydrocast samples collected was 1718. 35 duplicate samples were drawn.

128 additional discrete oxygen samples including duplicates were drawn from the ship's uncontaminated seawater line along the cruise track at specific times.

3.2.3 Steps to QC CTD/Oxygen data

The below steps were used to calibrate the CTD sensor and QC the winkler data.

- Merge down cast CTD/O2 sensor data (volts) with up-cast Winkler O2 data based on potential density
- Use non-linear least square regression to solve for the coefficients in the equation that minimizes the residual difference (SBE O2- Winkler O2)
- Oxygen, umol/kg = Soc(V+Voff)*Oxsat(T,S)*exp(Pcor*P)*exp(Tcor*T) (modified Owen-Millard 1990 eqn)
- Look at the Winkler-corrected CTD/O2 residuals and remove outliers > 5 umol/kg
- Refit the CTD/O2 volts with the modified up-cast Winkler O2 data
- Recompute residuals and consider deleting outlying Winklers > 3 umol/kg
- Repeat until RMSE is minimized
- Typically, CTD/O2 can be calibrated to within ±1-3 umol/kg of the Winkler data

ECOA-3 CTD/O2 had a final fitting error of ±1.75 umol/kg

The total number of samples flagged after post-cruise quality control:
Questionable (n=369), Bad (n=4).

Figures 5 & 6

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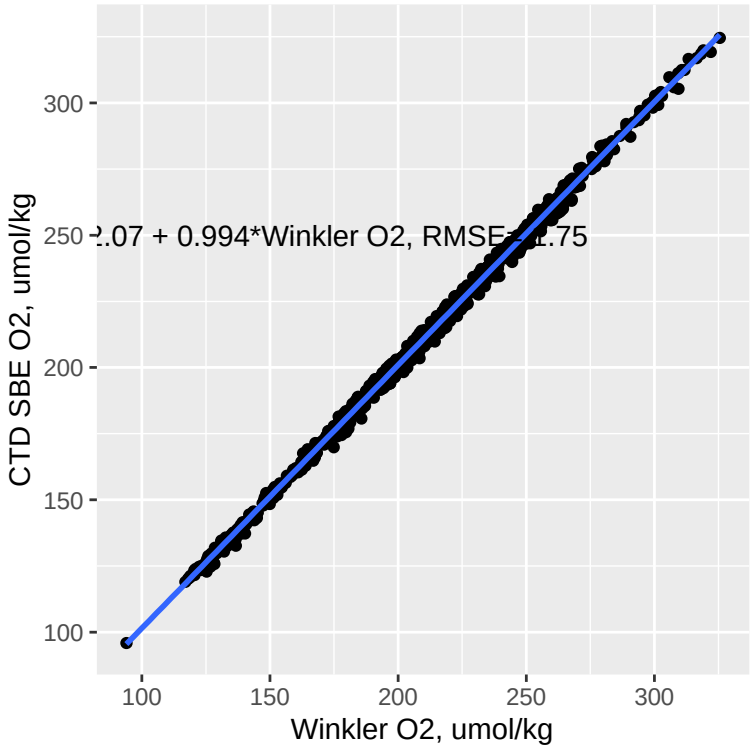

Figure 5: RMSE minimized Winkler-corrected CTD/O2 by Winkler. Final fitting error of ±1.75 umol/kg.

Figure 6: Winkler-corrected CTD/O2 by Winkler for Station 198.

3.3 Nutrient Measurements

Analysts: Susan Becker and Joe Becker (Scripps Institution of Oceanography)
Sampling: Sophie Alpert, Emma Thibodeau, Sierra Kehoe, and Kaitlen Lang
PI: Joe Salisbury

Nitrate, nitrite, phosphate, silica, and ammonium are major inorganic nutrients that control oceanic primary production and carbon exports. Together with the measurements of inorganic carbon parameters, the observations will be used to estimate the effect of riverine input, air-sea CO_2 gas exchange, biological productivity and lateral carbon exchange on the coastal carbon dynamics.

Approximately 986 nutrient vials were taken for analysis at the Scripps Institution of Oceanography. Nutrient samples were collected starting with the deepest Niskin bottle. A 60ml syringe and plunger were rinsed three times with the desired seawater. The plunger was then filled with the sample seawater, and a filter head (0.45micron disc) was attached. A small volume of seawater would then be dispensed into a cleaned acid washed, 20ml scintillation vial, the cap would then be replaced, and the vial shaken. After shaken several times the water would be discarded from the vial. This process would be repeated two more times. After the vial and cap had been rinsed, filtered seawater would slowly be dispensed into the sample vial. The total volume needed was only 10ml (the

vial would not exceed ¾ full). The filter did not need to be changed in between depths, only between stations or once clogged. After collecting each sample, the vials were immediately placed into a freezer and kept frozen until analysis.

3.3.1 Analytical Methods

The samples were analyzed at the Oceanographic Data Facility at Scripps Institution of Oceanography for nitrate, phosphate, silica, nitrite, and ammonium using a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3) according to the procedures described by Gordon et al. (1992), Hager et al. (1972), and Atlas et al. (1971).

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3.4 DIC Measurements

Analysts: Charles Featherstone (NOAA/AOML) and Patrick Mears (NOAA/AOML)
PIs: Rik Wanninkhof and Leticia Barbero (AOML/CIMAS)

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 CTD Lab on board the *R/V Ronald H. Brown*. 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 #188 and #195, 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 HgCl2 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.

Underway samples were collected from the flow thru system in the CTD Lab during transits between lines. Discrete DIC samples were collected approximately every two hours with duplicates every fifth sample. A total of 128 discrete DIC samples including duplicates were collected while underway.

A total of 1777 samples including duplicates were analyzed for discrete dissolved inorganic carbon from 228 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.

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3.5 Total Alkalinity Measurements

Analysts: Najid Hussain, Elliott Roberts, Jordan Watson, and Zelun Wu (UDel)
PI: Wei-Jun Cai (UDel)

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 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 average every 15 samples. 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 1780 samples, including duplicates, were taken from Niskin bottles and 128 underway samples were analyzed.

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3.6 Seawater pH Measurements

Analysts: Xinyu Li and Bo Dong (UDel)
PI: Wei-Jun Cai (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.

3.6.2 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 (Manufacturer, Part #). 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.

3.6.3 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 1781 samples were analyzed from Niskin bottles and 128 underway samples were analyzed.

3.6.4 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:

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

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

3.6.5 Repeatability, Reproducibility, Precision, and Accuracy

Duplicate water samples were collected 230 times throughout the cruise. 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 climate 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.

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3.7 DIC and δ^{13}C-DIC Measurements

Analysts: Zhentao Sun (UDel), Zhangxian Ouyang (UDel), and Wei-Jun Cai (UDel)
PI: Wei-Jun Cai (UDel)

Discrete CTD samples for DIC and δ^{13}C-DIC measurements were sampled from Niskin bottles at a variety of depths with one to two duplicates according to procedures outlined in the *PICES Special Publication, Guide to Best Practices for Ocean CO_2 Measurements*.

Pre-combusted (550 ℃ for 4 h) 250 mL borosilicate glass bottles were rinsed three times before being filled from the bottom, with at least half the bottle volume of overflow. 1 mL of water was extracted to allow thermal expansion and 50 μL of saturated $HgCl_2$ solution was added to poison biological activities. Sample bottles were then sealed with Apiezon-L grease and stoppers were fixed with rubber bands and clips. The samples were either stored at room temperature for at least 24 hours until water temperature approaches room temperature before onboard analysis or stored in coolers for transporting back home. Underway samples for DIC and δ^{13}C-DIC analyses were collected every 2 hours from the flow-through system in the Hydro Lab during transits between stations. Underway samples were stored at room temperature for about 5 hours before onboard analysis.

The DIC/δ^{13}C-DIC analytical equipment was set up in the Bio Lab on the first leg and the Main Lab on the second leg. The analysis was conducted with one analytical system (Unit #1) during Leg 1, and one additional analytical system (Unit #2) were used during Leg 2. Each system consisted of a G2131-i Isotope and Gas Concentration cavity ring-down spectroscopy (CRDS) Analyzer (Picarro, USA) coupled with an AS-D1 δ^{13}C-DIC Analyzer (Apollo Scitech, USA) for sample injection, CO_2 extraction, instrument control, and data acquisition in DIC and δ^{13}C-DIC measurements. The principle of this system was described by Su et al. (2019) and Deng et al. (2022).

For each measurement, 6.5 mL of water sample and 1.6 mL of phosphoric acid (2% vol./vol. H_3PO_4 with 7% wt./vol. NaCl) were drawn by the multi-valve pump coupled with a 10 mL syringe. The sample was injected and acidified in the reactor, converting all carbonate species to CO_2, which was then sent to the CRDS analyzer using CO_2-free compressed air at a 60 mL/min flow rate. The CO_2 concentration and δ^{13}C-CO_2 were concurrently measured via the CRDS, with data recorded at approximately a 1 Hz frequency for about 500 seconds. The analytical cycle would complete when the CO_2 concentration fell beneath a predetermined threshold (i.e., the deviation between 15 successive data points of CO_2 reading was less than 5 ppm above the initial baseline) or if the change dipped below a preset threshold (i.e., the standard deviation of CO_2 for 15 consecutive data points was less than 0.16 ppm). The net integration area for DIC is computed by integrating the area beneath the CO_2 concentration curve over the baseline. The δ^{13}C-DIC, defined as per mil deviations from the reference standard Vienna PeeDee Belemnite (V-PDB), is ascertained as the CO_2-weighted average of δ^{13}C-CO_2 data, applying a cutoff of 400 ppm to avoid high noise at reduced CO_2 signals. Each sample was subjected to a minimum of two and up to four consecutive measurements to achieve the preset relative standard deviation (RSD) of 0.1% for DIC and 0.06 for δ^{13}C-DIC. All measurements were carried out in a temperature-regulated environment (T = 20 ± 2 °C), with temperature variations documented using a thermometer. All DIC values were converted to a molar weight (μmol/kg) using density derived from the recorded temperature during measurements and the CTD salinity.

In order to determine the DIC concentration and δ^{13}C-DIC values, three batches of homemade $NaHCO_3$ solutions with different δ^{13}C values were used as reference standards, which were calibrated every 3 days against the Certified Reference Material

(CRM) provided by Dr. Andrew Dickson of the Scripps Institute of Oceanography. Throughout the analytical period, homemade standards were sub-sampled into 12-ml glass vials weekly and then sent to the UC Davis Stable Isotope Facility for δ^{13}C-DIC analysis. In their approach, DIC in water was converted to headspace CO_2 using phosphoric acid and analyzed using headspace equilibration technique with a Thermo Scientific GasBench II and Thermo Finnigan Delta Plus XL isotope-ratio mass spectrometer (IRMS). The δ^{13}C-DIC values, obtained through Gasbench-IRMS method at the facility, were utilized to calibrate the CRDS measurements of δ^{13}C-DIC.

The DIC concentrations were determined by daily measurements of three volumes (5.5/6.5/7.5 mL) of a pre-calibrated $NaHCO_3$ solution (SB-1). These measurements established a standard curve relating the net integration area to DIC mole amounts. The DIC concentration of a sample was then derived from this standard curve and the known injected sample volume (6.5 mL). The accuracy of measurements was validated by incorporating the other two pre-calibrated $NaHCO_3$ solutions, SB-2 and SB-3, along with the CRM (Batch #188 and #195) into the analysis sequence every 8 samples. SB-2 and SB-3 were used not only as quality checks for DIC measurement but also to correlate the δ^{13}C-DIC values provided by the CRDS Analyzer with those determined by the UC Davis Stable Isotope Facility. Time-based linear corrections were first applied to the δ^{13}C-DIC values based on two adjacent measurements of the house standards to mitigate any potential influence from instrumental drift. The δ^{13}C-DIC value of each sample was then determined based on a three-point calibration curve established by the time-corrected δ^{13}C-DIC values of three house standards. In this way, the measurements of house standards can be considered as quality checks for δ^{13}C-DIC because they were not involved in the establishment of the standard curve used for their own calibration.

During the cruise, 1972 discrete CTD samples, including 186 duplicates, were collected from 228 full water column stations. Additionally, 126 underway samples, 20 samples from the Niskin bottles on the lander, and 3 samples from the Gray's Reef mooring were gathered. Of these, 1665 samples underwent analysis onboard, while the remaining 456 samples were transported back to the laboratory for subsequent analysis using Unit #1 within a month.

In the overall assessment, the mean relative standard deviations (RSD) for DIC of house standards replicates and CRMs are within 0.09%, and the mean standard deviations (SD) for δ^{13}C-DIC are within 0.06‰. The mean relative accuracy for DIC of CRMs is 0.07%. Additionally, the average offset of house standards and CRMs in δ^{13}C-DIC, relative to the Gasbench-IRMS results from the UC Davis Stable Isotope Facility, is within 0.02‰. The mean RSD of the sample duplicates is 0.08% for DIC, and the mean SD is 0.04‰ for δ^{13}C-DIC.

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3.8 Respiration/Bacteria Activity

Analyst: Kia Ziervogel, UNH
Sampling: Astrid Zapata, Lydia Pinard, and Zoe Kendall (UNH)

3.8.1 Sampling

Seawater samples used to determine Electron transport system (ETS) activity were collected at 90 stations. ETS is used to estimate community respiration (R) These stations were sampled during daylight hours. Water samples were taken from 10 L Niskin bottles at the surface, chlorophyll maximum and 1% light level, and were transferred into plastic carboys in order to facilitate subsampling. A majority of the stations were not deep-water stations, so the depths sampled were generally above 200 m. Most surface samples were sampled at 2-3 m and a majority of the chlorophyll maximum samples were taken between 10 and 50 m. It is also important to note that the 1% light level was approximated at each station and may not be exact. 500 mL to over 1,000 mL of seawater were filtered through a GF/F placed on top of a 0.4 µm filter, to separate our size classes of microbes. The filters were separately wrapped in aluminum foil and immediately stored in liquid nitrogen until assayed at the University of New Hampshire several months later.

3.8.2 Analysis

ETS activity was determined both for the GF/F filter and the 0.4µm filter from each station. Three solutions were used for analysis. The first was a substrate made from NADH and NADPH (in a 3:1 ratio) and sodium succinate (these three components act as electron donors in the analysis), and a trace amount of Triton, all dissolved in a phosphate buffer. The phosphate buffer was made using Triton, PVP, MgSO4•7H20, and a trace amount of NaCN. Sodium cyanide was only added to the PO4 buffer in the first batch made, and in subsequent solutions it was excluded, as it was deemed unnecessary and a potential health hazard. The third solution needed for analysis was a 4 mM INT solution, made from INT (described below) and milli-Q water. This acted as the artificial electron acceptor in the analysis.

Each filter was cut in half, and using a tissue grinder, homogenized in 3 ml phosphate buffer for two minutes. During this time the sample was kept on ice to maintain the same temperature as it had been stored in. The homogenate liquid was transferred to a centrifuge tube and centrifuged for at least 5 minutes at 2000 rpm. In the case of the GF/F filters, which broke down more easily than the 0.4µm filters, the samples were usually centrifuged a second time to ensure all filter pieces settled to the bottom. The homogenate liquid was

then carefully poured into a 15 ml glass tube and the total recovered volume was recorded. A plastic cuvette was prepared with 0.5 ml of the homogenate, 0.5 ml INT solution, and 1 ml substrate. Immediately after adding the substrate, the absorbance was measured on a spectrophotometer set to 490 nm. The absorbance was recorded a total of 5 times within a 10-minute period (approximately every two minutes) to observe the change in activity over time.

ETS was converted to R based on a ratio determined by Packard and Williams (1981) where R/ETS = 0.25 ± 0.05. A temperature correction was then applied to R values using the Q10 method from Apple et al., 2006 using the equation: R2 = R1(Q10) (T2-T1)/10, where R1 was the uncorrected R value, T2 was the temperature, in Kelvin, of the seawater from when the sample was collected, T1 was the temperature when the assay was performed and was constant at 293.15 K, and Q10 was assumed to be 2.2 based on the calculations performed by Apple et al. (2006).

3.8.3 Preliminary Results

During the ECOA-3 cruise, we applied the INT assay in surface waters along the cruise track. At selected sites we compared rates of INT reduction with O_2 consumption measured in dark bottles using the Winkler method (in collaboration with the Langdon lab). The resulting relationship between the two methods illustrated in Figure 4a, allows us to express INT reduction rates in units of O_2 respiration. This work is part of a current graduate student project in the Ziervogel lab which focuses on the relative contribution of planktonic size classes to overall NCR along the ECOA cruise track (Figure 4b).

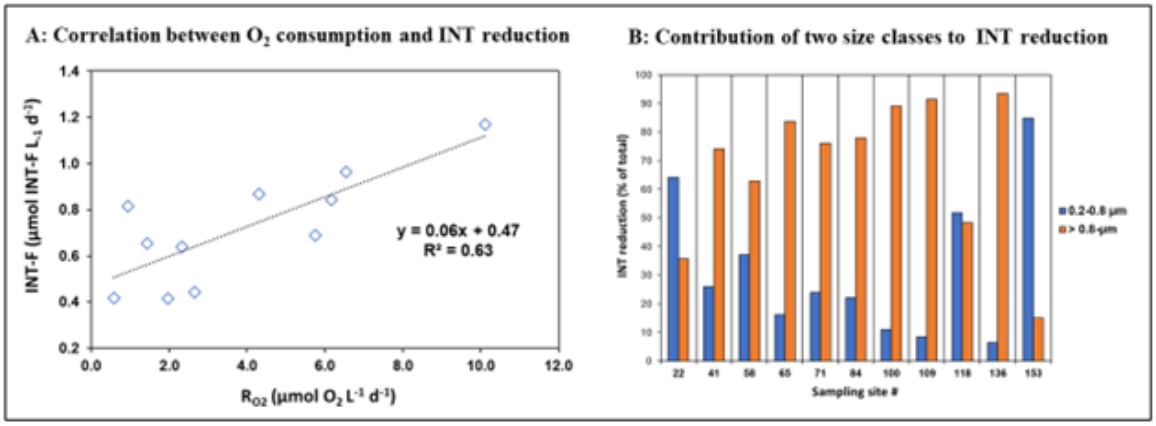

Figure 7: Preliminary results from a subset of INT reduction rates.

Date will be archived at OCADS/NCEI

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

Analysts: NASA Goddard Ocean Ecology Lab
Sampling: Emma Thibodeau and Sophie Alpert
PI: Antonio Mannino

The primary objective was to characterize carbon and ocean acidification properties in the coastal margin with observations of phytoplankton community structure across large spatial and environmental gradients. Water samples were taken from 10 L Niskin bottles at the surface, chlorophyll maximum and 1% light level, and were transferred into plastic carboys in order to facilitate subsampling. In the case of HPLC and POC sample seawater was immediately filtered onto Whatman 47mm GF/F filters using a vacuum pump <0.5 atm and then placed in foil and stored in LN2. 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). POC analysis will follow methods described in Hedges and Stem (1984). DOC and CDOM sample seawater was filtered 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. TSM sample 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. Samples were frozen until the end of the cruise and then dried when back in the lab.

Data from this collaborative effort are also archived on the NASA Ocean Biology Processing Group's SEABASS archive.

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4. Underway data collection

4.1 Underway pCO_2 Analyses

Analysts: Kevin Sullivan (CIMAS/RSMAS) and Patrick Mears (CIMAS/RSMAS)
PI's: Rik Wanninkhof (NOAA/AOML) and Denis Pierrot

During the ECOA-3 cruise, there was an automated underway pCO_2 system from AOML situated in the CTD Lab of the RV Ron Brown (Figure 6). 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.

4.1.1 Additional Information Leg 1

The pCO2 analytical system performed well for most of this cruise. The measured SSTemperature by the ship's SBE38 sensor and SSSalinity by AOML's SBE45 sensor were adjusted using relationships between the UW sensors and the in-situ CTD sensors. The regression equations and estimates of the error in the adjusted values are listed below. More data and discussion of the adjustments are in the supplemental metadata file. SST(adjusted) = 1.01557 *SBE38-Temp - 1.95588 ; standard deviation of the differences between the CTD SST and the SST(adjusted) is +/- 0.189 degree Celsius (n=82). The offset between the SBE38 and SBE45's in the Hydro lab was steady for nearly all of the cruise, but on two occasions (17:03 on 7 Aug and 10:50 on 29 Aug) there was a minor though sudden change in the offset. The CTD casts used to adjust the SBE38 SST data were between these two discontinuities; and the offset between the SST(adjusted) and the equilibrator temperature for this majority of the cruise was 0.277 (+/-0.283) degree Celsius. For the short intervals before the first discontinuity and after the second discontinuity the SST was estimated by subtracting 0.277 from the equilibrator temperature. SSS(adjusted) = 1.022388 *TSG-Salt - 0.20566 ; standard deviation of the differences between the CTD salinities and the SSS(adjusted) is +/- 0.0648 (n=79).

Original Data Location:
https://www.aoml.noaa.gov/ocd/ocdweb/brown/brown_2022.html. Full unprocessed data files from analytical instrument including flow information plus meteorological and TSG data at time of sampling can be obtained upon request.

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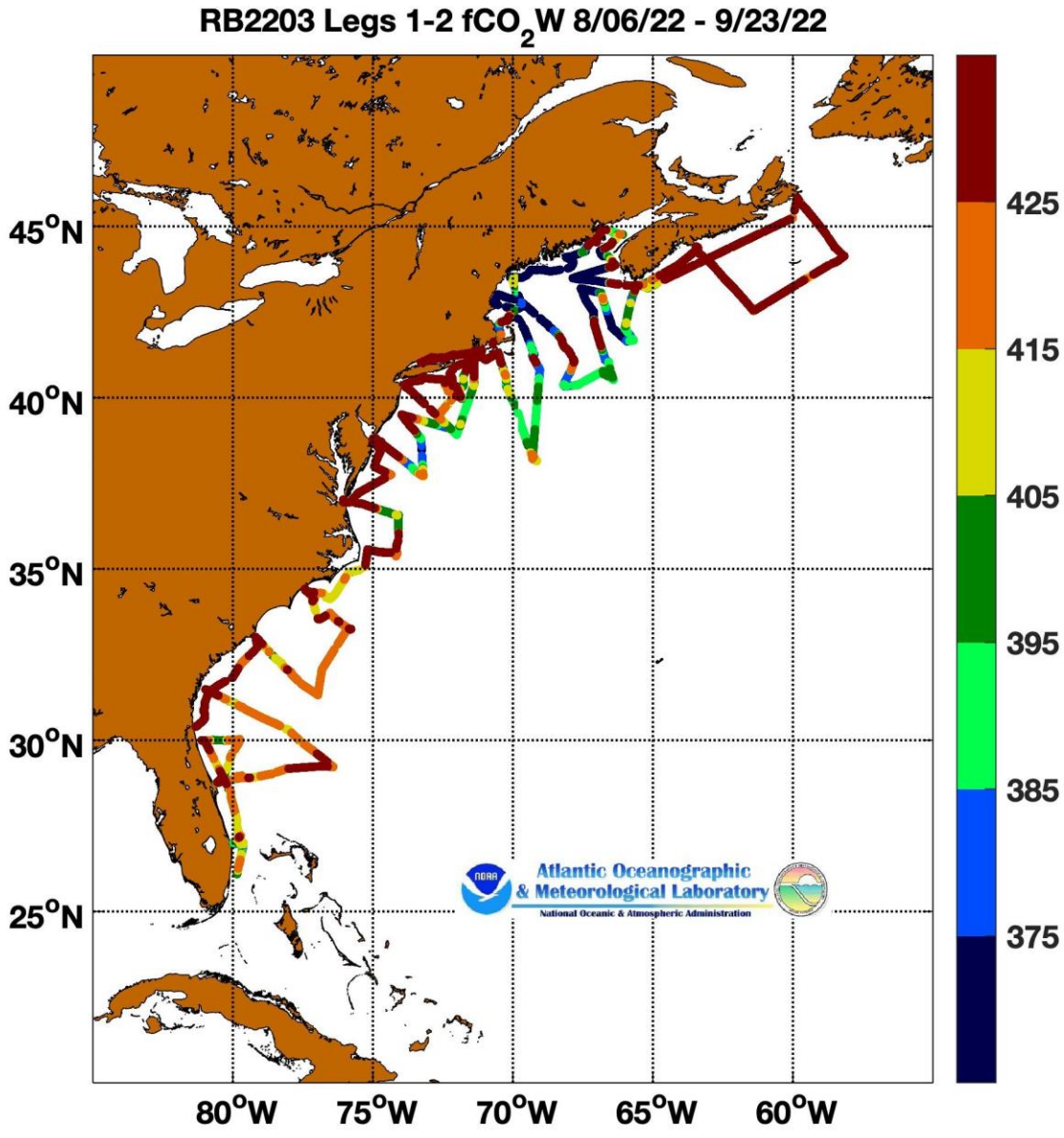

Figure 8: fCO2 readings from Legs 1 and 2 of ECOA-3

4.2. Oxygen:Argon ratio and estimation of net community production

Analysts: Drs. Elliott Gareth Roberts, Zhangxian Ouyang, and Najid Hussain (UDel)

PI: Dr. Wei-Jun Cai (UDel)

4.2.1 Equipment and Techniques

Due to the similar solubility characteristics of oxygen (O_2) and argon (Ar), the ratio of their concentrations reflects biologically driven changes better than examining oxygen saturation (O_2 %) due to the removal of the physical contribution to O_2 %. As such, the O_2/Ar determines the net community productivity (NCP), the net metabolic status between photosynthesis and respiration (Cassar et al., 2009). The ratio was measured via equilibrator inlet mass spectrometry (EIMS; Cassar et al., 2009). Surface water was pumped through the system at ~100mL min^{-1} through two filters (one coarse and one fine) to remove particulates. Afterward, the water flows through Tygon silver antimicrobial tubing and a gas-permeable membrane contactor cartridge (MicroModule 0.75×1). The equilibrated gas in the headspace was sent to a quadrupole mass spectrometer (Pfeiffer Prisma model QMG 220) for measurement. See Ouyang et al. (2020) and Cassar et al. (2009) for more details. An Aanderaa optode (model 4531A) was also used to measure the surface underway O_2 % to be used solely as a QC/QA check for O_2/Ar fluctuations.

4.2.2 Sampling and Data Processing

The O_2/Ar ratio was recorded every two seconds, then averaged into two-minute intervals. O_2 % was measured every 30 seconds. O_2 % magnitude and trends were compared with O_2/Ar ratio magnitude and trends as part of the quality check. The quality assessment also includes (but is not limited to): only including data with a stable total pressure (~10^{-6}), splicing instrument noise (such as when the instrument is stabilizing after a reboot), and flagging data with abnormal peaks.

4.2.3 Calibration

Underway seawater O_2/Ar measurements were calibrated with ambient air every three to six hours for 20 minutes. Ambient air was used as the calibration standard due to the stable O_2/Ar concentrations. The standard deviation of the air standards was ±0.26% after QC/QA. The optode was calibrated before this expedition with 0 and 100% O_2-saturated water according to the manufacturer's instructions.

4.2.4 Problems

The EIMS exhibited instrument noise throughout the cruise entirety. Since the mass spectrometer was exemplary during this expedition, the data was acceptable also after QC/QA. For 2nd leg, the unit was replaced with another model in an attempt to reduce the amount of instrument noise.

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RB2203 Legs 1-2 O_2/Ar ratio 8/06/22 – 9/23/22

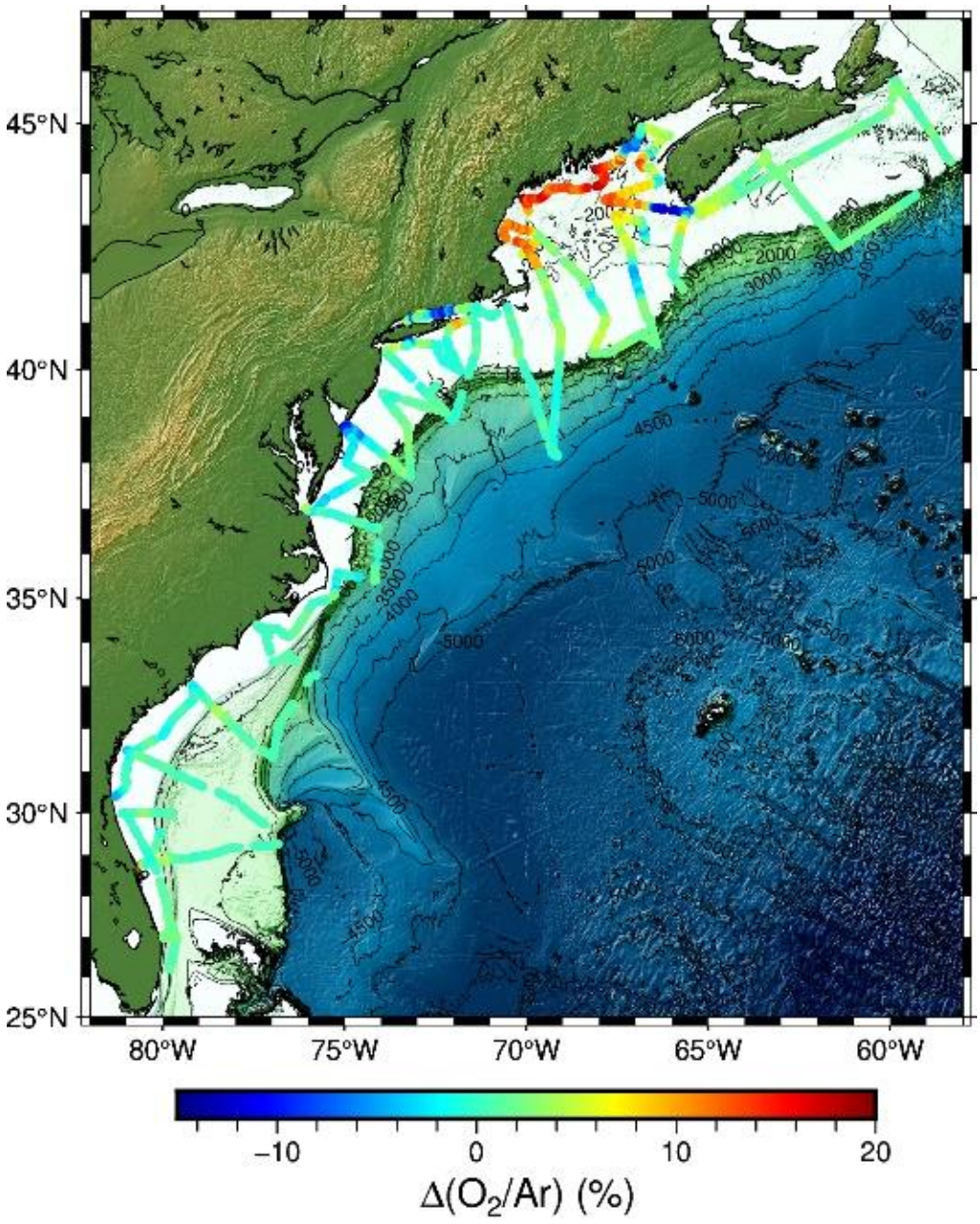

Figure 8: O_2/Ar ratio readings from Legs 1 and 2 of ECOA-3

4.3 Underway TA

Analysts: Chris Hunt and Emma Thibodeau
PI: Chris Hunt

UNH provided a Contros HydroFIA TA instrument for ECOA-3. The TA instrument was connected to the ship's underway water supply. The TA measurement is made via a single addition of calibrated hydrochloric acid titrant and pH indicator (bromo-cresol green), followed by spectrophotometric measurement of the acidified sample pH (Hunt et al. 2021, Seelmann et al. 2019). Underway water was filtered through a 0.22 um continuous-flow filter, which requires a flow of 1-2 l/minute. The instrument is calibrated with certified reference material (CRM), which is preserved with mercuric chloride. Calibration waste was stored shipboard (as well as the CRM waste from discrete TA and DIC measurements made by other investigators). The instrument requires approximately 1m of bench space, a 110V power connection, and underway water (Figure 2). The instrument is controlled by a laptop computer, and an internet connection as well as position, salinity and temperature data from the ship's data system are desired. The internet connection made remote monitoring by a tech possible while the cruise was underway.

4.4 Underway pH

Analysts: Xinyu Li and Bo Dong

Underway pH was measured by a Honeywell Durafet® III pH electrode (Martz et al. 2010) on both legs of the ECOA-2 cruise. 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. Once final QA/QC is complete data will be submitted to NCEI.

References

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4.5 Underway Phytoplankton Community Measurements

Analysts: Joaquim Goes, Jennifer Acosta, Jingui Wu, and Kali Mckee (LDEO)
PI: Joaquim Goes

The LDEO group undertook high-resolution measurements of chlorophyll, phytoplankton functional types, phytoplankton size classes and phytoplankton photosynthetic efficiencies in near surface (~5m) seawater samples that was pumped continuously through the *R/V* uncontaminated flow-seawater through system. Additionally, samples from the three depths were filtered for Chl *a* analysis in a Trilogy Fluorometer.

4.5.1 Stations Discrete Samples

Water samples were collected from a total of 145 stations at 2 to 3 depths along the cruise track (Table 1). At each station seawater samples were obtained from 3 depths in the water column.

i. Fluorescence based estimates of Chl-*a* [Holm-Hansen and Riemann, 1978].
ii. Counting, imaging and size estimations of phytoplankton and other detrital particles using a Fluid Imaging Technologies, Inc., FlowCAM [Jenkins et al., 2016).
iii. Estimates of phycobilipigments at select stations using a fluorescence technique.
iv. Fluorescence based estimates of Chl-*a*, CDOM, Phycobilipigments and variable fluorescence (F_v/F_m), a measure of phytoplankton photosynthetic efficiency, using a WET Labs Advanced Laser Fluorometer (ALF) [Chekalyuk et al., 2012; Goes et al., 2014].
v. Measurements of F_v/F_m and the functional absorption cross-section of Photosystem II (σ_{PSII}) and Electron Transport Rates (*ETR*) in a mini-Fluorescence Induction and Relaxation (FIRe)® Fast Repetition Rate Fluorometer (FRRF) [Gorbunov and Falkowski, 2004].

4.5.2 Underway Flow-through Measurements

Between stations, a suite of four instruments, an Automated Laser Fluorometer (ALF), a FlowCAM, a bbe Moledanke and a Fluorescence Induction and Response (FIRe) were connected to the ship's seawater flow-through system [Jenkins et al., 2016] to make continuous measurements as follows:

i. <u>Automated Laser Fluorescence (ALF) measurements of phytoplankton groups</u>

The ALF combines high-resolution spectral measurements of blue (405 nm) and green (532 nm) laser-stimulated fluorescence with spectral deconvolution techniques to quantify the following:

- fluorescence of Chl-*a* (peak at 679 nm),
- three phycobilipigment types: Phycoerythrin-1 (PE-1; peak at 565 nm), Phycoerythrin-2 (PE-2; peak 578 nm) and Phycoerythrin-3 (PE-3; peak at 590 nm),
- CDOM (peak at 508 nm)
- F_v/F_m,

All fluorescence values obtained are normalized to the Raman spectra of seawater and generally expressed as relative fluorescence units (RFU), whereas F_v/F_m is unitless. PE-1 type pigments are associated with blue water or oligotrophic cyanobacteria with high phycourobilin/phycoerythrobilin (PUB/PEB) ratios, PE-2 type phytoplankton with low PUB/PEB ratios are generally associated with green water cyanobacteria that usually thrive

in coastal mesohaline waters, and PE-3 attributable to eukaryotic photoautotrophic cryptophytes [Chekalyuk et al., 2014; Goes et al., 2014a,b, Wei et al., 2022]. RFU values for Chl-*a* can be converted into mg m^{-3} Chl-*a* values using least square regressions of acetone or HPLC measured Chl-*a* with RFU values for Chl-*a* measured in an ALF.

ii. FlowCAM based phytoplankton identification, cell counts and cell sizes

The FlowCAM particle imaging system used for this cruise was equipped with a 4X objective (UPlan FLN, Olympus®) and a 300 µm FOV flow cell. The system was to the ships seawater flow-through system to obtain continuous measurements of phytoplankton functional types, detrital particles and, particle size distribution of both phytoplankton and of detrital particles. The 4X objective and the 300 µm FOV flow cell combination used helped ensure that the liquid passing through the flow cell was entirely encompassed within the camera's field of view. were classified to the genus level using the Visual Spreadsheet program (v. 2.2.2, Fluid Imaging) [Goes et al, 2014a, b; Jenkins et al., 2016].

iii. Fluorescence Induction and Relaxation (FIRe) measurements of photosynthetic competency

The FIRe instrument used during the cruise provides a comprehensive suite of photosynthetic and physiological characteristics of photosynthetic organisms [Gorbunov and Falkowski, 2004; Bibby et al., 2008]. This technique provides a set of parameters that characterize photosynthetic light-harvesting processes, photochemistry in PSII (σ_{PSII}), phytoplankton variable fluorescence (*Fv/Fm*) and the photosynthetic ETR. All optical measurements by the FIRe are sensitive, fast, non-destructive, and can be done in real time and in situ and can provide an instant measure of the photosynthetic efficiency of the cells [Wei et al., 2022].

iv. bbe Moldeanke AlgaeOnlineAnalyser - a fluorescence system that allows for continuous in-water measurements of major phytoplankton groups (diatoms+dinoflagellates, cyanobacteria, cryptophytes) based on the pigment composition of the cell [Richardson et al., 2010].

The use of these four instruments in tandem allowed for continuous in-water measurements of phytoplankton community composition, phytoplankton size, phycobilipigment types and photosynthetic efficiency of phytoplankton along the cruise track. With the exception of a few breaks during stations and for reconditioning, the instruments were operated over the entire cruise track, providing several thousand fluorescence-based measurements of Chl-*a*, CDOM, PE-1, PE-2, PE-3, F_v/F_m and σ_{PSII}, *p* (a measure of electron transport between the PSII and PSI. Continuous flow through measurements of phytoplankton species distribution and cell size distribution along the cruise track will provide useful information for interpreting the optical measurements for phytoplankton functional types (PFTs) over the study area.

Preliminary plots generated using high-resolution data collected by one of the flow-through instruments the ALFA used in flow-through mode, are shown below in Figs1a-e. These plots are examples the synoptic distribution of phytoplankton biomass, phytoplankton functional types, phytoplankton photo-physiology and CDOM that will result from this data collected on board.

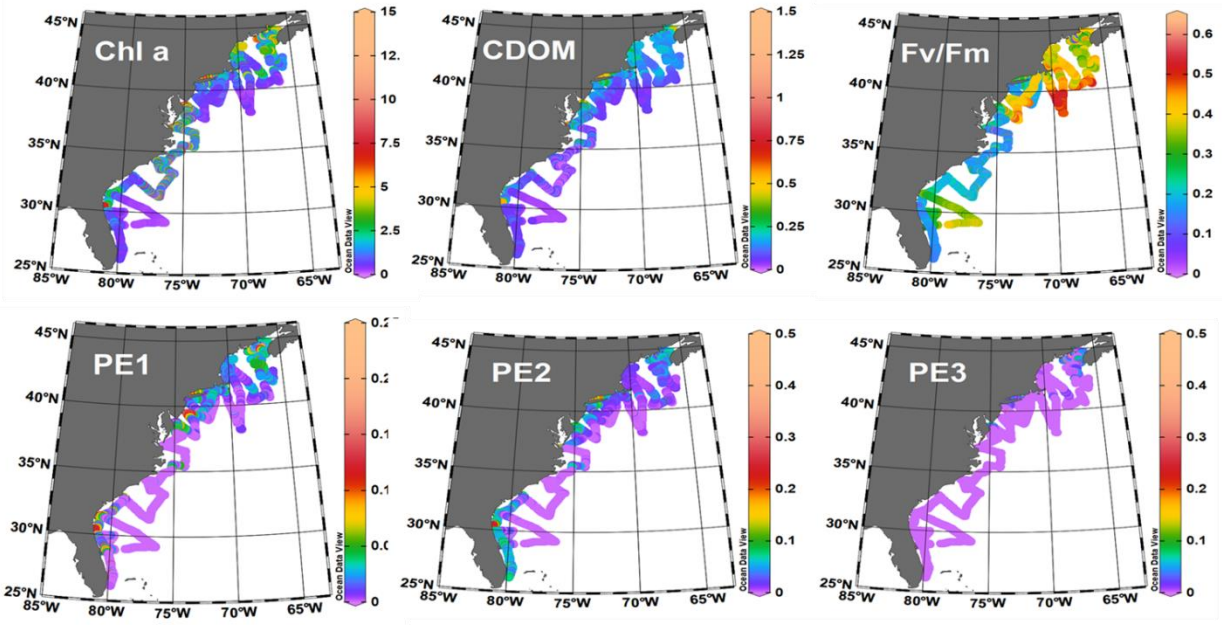

Fig. 9 Distribution of a) Chl a, b) CDOM c) PE1 - blue water cyanobacteria, d) PE-2, Coastal water cyanobacteria and e) PE3- Cryptophytes along the cruise track during ECOA-3

We anticipate completing the analysis of these datasets within the next six months. Some of the datasets that have been analyzed will be submitted immediately after they have been QC'd.

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4.6 Underway Phytoplankton Monitoring

Analysts: Carly Daiek (WHOI)
PI: Michael Brosnahan (WHOI)

An imaging flow cytobot was deployed on Leg 1. The flow cytobot was plumbed into the ships underway system and continuously imaged and counted phytoplankton cells from the surface water throughout the entire first leg.

Underway data can be found here: https://habon-ifcb.whoi.edu/ecoa

5. Ocean Color Measurements

5.1 Apparent optical properties (AOP) and solar irradiance

Analysts: Michael Ondrusek (NOAA NESDIS) and Charles Kovach (NOAA NESDIS)

NOAA/NESDIS investigators conducted in situ optical measurements during the ECOA-2 cruise to support the primary cruise objectives of improving our understanding of ocean acidification and to provide ocean color satellite validation. 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 Lu(λ) and an upward looking HyperOCI irradiance sensor to measure downwelling irradiance Ed(λ) in the water column. In addition there is an above-water upward looking HyperOCI irradiance sensor to measure downwelling surface irradiance Es(λ) . These measurements are used to calculate normalized water-leaving radiance nLw(λ) and remote sensing reflectance spectra observed by ocean color satellites. nLw(λ)

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 one WET Labs ECO Puck Triplet sensor. The ECO Puck sensor measures fluorescence estimates of chlorophyll-a (mg m-3), and backscattering bb (m−1) at 440 nm, and 532 nm,

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.

https://seabass.gsfc.nasa.gov/archive/NOAA_NESDIS/ondrusek/ECOA/ECOA-3/archive

5.2 Inherent Optical Property (IOP) profiles and ancillary measurements

Analysts: Shawn Shellito (UNH)
PI: Joseph Salisbury (UNH)

IOP and ancillary measurements were collected at 31 stations throughout ECOA-3. The primary instruments used were are 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). All instruments were factory calibrated at the SeaBird™ factory prior to the ECOA-2 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 will be delivered to the NASA Ocean Biology Processing Group's SEABASS archive.

Table 6: 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/ºC/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]

[1] Accuracy, [2] Precision

6. Community Structure of Phytoplankton and Zooplankton

6.1 Biological Samples and Data Collection

Analysts: Chris Taylor and Amanda Jacobsen
PI: Chris Melrose (NOAA/NFSC)

Zooplankton, ichthyoplankton (larval fish and eggs), and cephalopod samples to determine taxon specific abundances using bongo nets were collected at 72 stations. All the tows were operated from the aft winch at the starboard side. Bongo operations were kept to "night-time" due to the high demand of the aft winch during day-light hours for both Lander and IOP profiles. Overall, the stations were located along the entire East Coast and Gulf of Maine.

A package (Figure 1) consisting of a 61 cm, 333 µm bongo net frame with flow meters, depressor weight, a Sea-Bird Electronics SBE-19plus CTD, and a smaller 20 cm bongo net frame mounted above will be towed in an oblique profile at between 1.5-2 kts. Vessel speed should be adjusted during the bongo tow to maintain a 45º wire angle in order to uniformly sample throughout the water column. The maximum tow depth will be 200m or to within 5-10 meters of the seafloor, whichever is shallower. The tow should be performed using conducting wire from a hydrographic winch so that real time telemetry from the CTD can be used to guide the tow profile. Tows should be performed from the side of the vessel to avoid propeller wash and wake effects. The 61 cm bongo net samples will be preserved using formaldehyde, and the 20 cm samples will be preserved using ethanol to facilitate genetic identification of taxa.

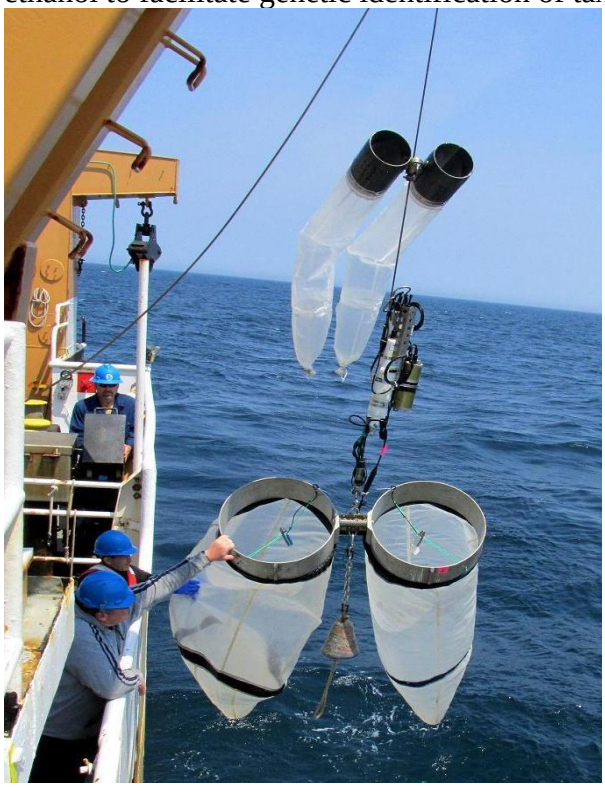

Figure 9: A standard 61 cm bongo net frame with SBE-19plus CTD and a 20cm bongo net frame mounted above and depressor weight mounted below.

6.1.1 Pteropods

Starting in 2021, funded by NOAA OAP, the NEFSC has been subsampling pteropods from bongo nets for optical analysis of shell transparency as an indicator of biological OA exposure, using methods developed by Dr. Amy Maas at the Bermuda Institute of Ocean Science (BIOS). Whenever pteropods are encountered, we will sample 10-20 individuals for analysis.

Pteropods are collected either using feather forceps, or by plastic pipette to minimize damage. These shells are then placed in glass vials and dried in an oven at sea to preserve them for analysis. In the laboratory, the shells are placed in 8% hypochlorite bleach solution for 72 hrs to remove soft tissue and allow for the dissolution of any trapped bubbles. Individuals are then imaged under a standard light stereo-microscope. Using the free ImageJ software, the background light is measured relative to the shell to determine the relative transparency.

6.2. Plankton Community Dynamics/Trophic Interactions across Continental Margins

Analysts: Lucy Roussa (NCSU) and Maya Lombardi (ULL)
PIs: Astrid Schnetzer (NCSU) and Beth Stauffer (ULL)
Our group's efforts on the ECOA cruise addressed three objectives designed to test several hypotheses about the nature and fate of organic carbon in the surface ocean. These objectives include understanding carbon fate and flux across diverse oceanographic regions, variable levels of ocean acidification and eutrophication, and with complex planktonic communities:

Objective I: Characterize plankton abundances, community composition, and diversity with depth and along environmental gradients along the East Coast.

Objective II: Quantify the impact of micro- and metazoan grazing on plankton communities along distinct environmental gradients along the East Coast.

Objective III: Assess carbon flow from pico- to microplankton and from micro- to mesozooplankton at selected coastal stations.

To address these objectives, we brought together traditional (i.e., on-deck incubation approaches) and modern (i.e., next generation sequencing, flow cytometry) techniques to characterize plankton community structure along with paired, quantitative micro- and mesozooplankton grazing experiments throughout the study region. Data generated on this cruise will provide new insights into how plankton communities and interactions within those populations change along gradients of temperature, salinity, CO_2, pH, and dissolved oxygen. The data will also help elucidate how these communities are affected

by environmental changes, and how those effects, in turn, impact the fate of carbon from the surface ocean.

Methods

The CTD samples were taken from 2-3 depths for each pre-selected station (one nearshore, offshore, and intermediate on approximately every other transect line). The samples were filtered onto GF/Fs for DNA and chlorophyll and stored at -20°C. The whole water preservation used acid Lugol's, formalin, and ethanol. All samples were brought back to NCSU or the UL Lafayette for processing and analysis.

CTD Sampling

Whole seawater sampling was conducted to characterize pico-, nano-, and microeukaryote communities via flow cytometry (pico-, nano-) and automated imaging analyses (FlowCam; primarily micro-). Briefly, for FlowCam analyses ~250 ml were preserved with ~5% Lugol's, and 4 ml preserved with 1% formalin for flow cytometry. Water collected for molecular analyses was size-fractionated to collect varying assemblage members (<20 and <200 µm size ranges), and surface water for feeding experiments was passed through a 200 µm mesh to exclude larger zooplankton grazers and additional aliquots were further processed, as described below.

Chlorophyll-*a* and Molecular Sampling

Samples for chlorophyll-*a* quantification were filtered onto GF/F filters in duplicate with volumes of 100 ml for surface and chlorophyll max depths and 150-200 ml for deeper stations. Water was additionally screened through a 20 µm Nitex to allow for the determination of chlorophyll-a concentrations due to microeukaryotes in the < 20 µm and 20–200 µm size ranges. Aliquots of 400 and 800 ml were collected for subsequent DNA analyses from high biomass (surface and chlorophyll maximum) and low biomass depths, respectively. Samples were stored in the ship's freezer at -20°C for the duration of the cruise and shipped to the laboratory on dry ice for analysis.

Microzooplankton Dilution and Copepod Feeding Experiment

For grazing experiments, a total of 7 zooplankton tows were conducted at different stations. The zooplankton sample was split using a Folsom plankton splitter and grazers for the experiments picked using a dissecting scope. Polycarbonate bottles (1 L), including varying dilutions of prey and grazer assemblages, were transferred into an on-deck incubator that had ambient seawater flowing through it throughout the cruise. A neutral density screen was used to ensure that the bottles were exposed to 50% of the natural light, simulating irradiances at 2 m depth. Temperature and light conditions were monitored throughout the experiments.

Based on the methods of Landry et al. (1995), 15 bottles were prepared with the following concentrations of seawater collected from the CTD at 2 m or with a bucket from the surface. Particle-free FSW from each station was prepared using a 0.2 µm capsule filter and used as diluent according to Table 7. Nitrate ($NaNO_3$) and phosphate (Na_2HPO_4) were added to each bottle at final concentrations of 5 µM N and 0.5 µM P. All bottles were prepared in triplicate. A known quantity of the most common copepods (~10-20 total), isolated from the net tow, was added to triplicate bottles containing 100% FSW (Figure 13).

Table 7: Experimental details for microzooplankton and copepod grazing incubations.

Bottle #s	Dilutions	<200 SW	FSW	N stock solution (10 mM)	P stock solution (1 mM)
1-3	5% x3	50 mL	950 mL	0.50 ml	0.50 ml
4-6	20% x3	200 mL	800 mL	0.50 ml	0.50 ml
7-9	100% x3	1000 mL	0 mL	0.50 ml	0.50 ml
10-12	100% +Cops x3	1000 mL	0 mL	0.50 ml	0.50 ml
13-15	100% No Nuts x3	1000 mL	0 mL	--	--

Bottles were incubated for 24 hours and were sampled at the beginning (T0) and end (Tf) of the experiment. T0 sampling for chlorophyll-*a*, community composition (FlowCam, flow cytometry), and zooplankton community structure was done on the original source water (WSW). Copepods were removed from each bottle at Tf and preserved for taxonomic identification and biomass calculations and all bottles were sampled for chlorophyll-*a* and community composition (FlowCam, flow cytometry). Filters for chlorophyll-*a* and flow cytometry analyses were stored in the freezer until shipment back to UL Lafayette; preserved samples were stored in dark boxes. Lugols- and glutaraldehyde-preserved samples will be counted for auto-, hetero-, and mixotrophic microplankton in the Schnetzer lab at NCSU using inverted microscopy. Formalin-preserved samples will be analyzed for picocyanobacteria, picoeukaryotes, and nanoplankton (auto- and heterotrophic) in the Stauffer Lab at UL Lafayette using flow cytometry (Guava easyCyte).

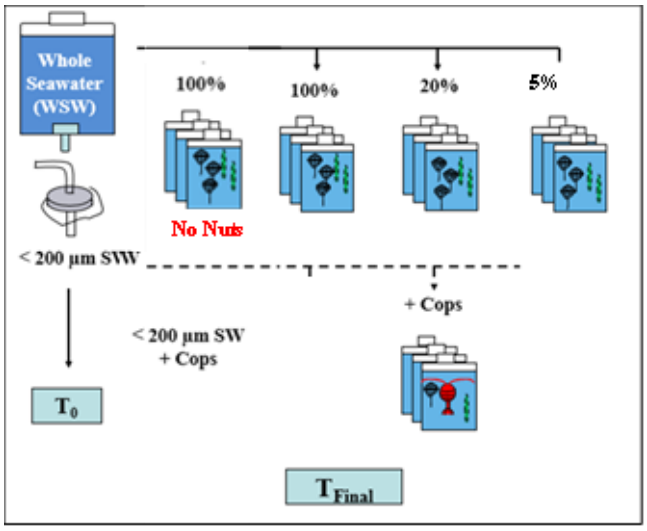

Figure 13: Schematic of the microzooplankton dilution and copepod feeding experimental design

Abundance changes in dilution series will be used to calculate microzooplankton community grazing rates. Abundance changes and community structure shifts in bottles without grazers will be compared to those with mesozooplankton grazers present to calculate copepod ingestion rates. Using overall copepod abundances observed in the tow samples at each station, the ingestion rates derived from the incubations will be

extrapolated to community grazing estimates. Together, these rates of microzooplankton and copepod consumption will allow us to quantify and characterize plankton trophic interactions and the flow of carbon through microbial versus classical (e.g., more efficient) food web pathways along the East Coast.

Table 8: Activities conducted by the plankton group during ECOA-3.

	Sampling Method	Number of Samples
CTD: 30 CTD with diel samples included	Whole water preservation	Lugols = 30 Form = 60 Ethanol = 30
	DNA Filters	90
	RNA Filters	90
	Chla Filters	60
Grazing: 10 Experiments, 24 hours each	Chla Filters	26
	Whole water preservation	Glutaraldehyde = 10 Lugols = 20 Form = 260 Ethanol = 60
	Presense	12 optodes measured pre/post
	Pre-weighed mesh screens	20
Underway	DNA	44

7. Benthic Operations

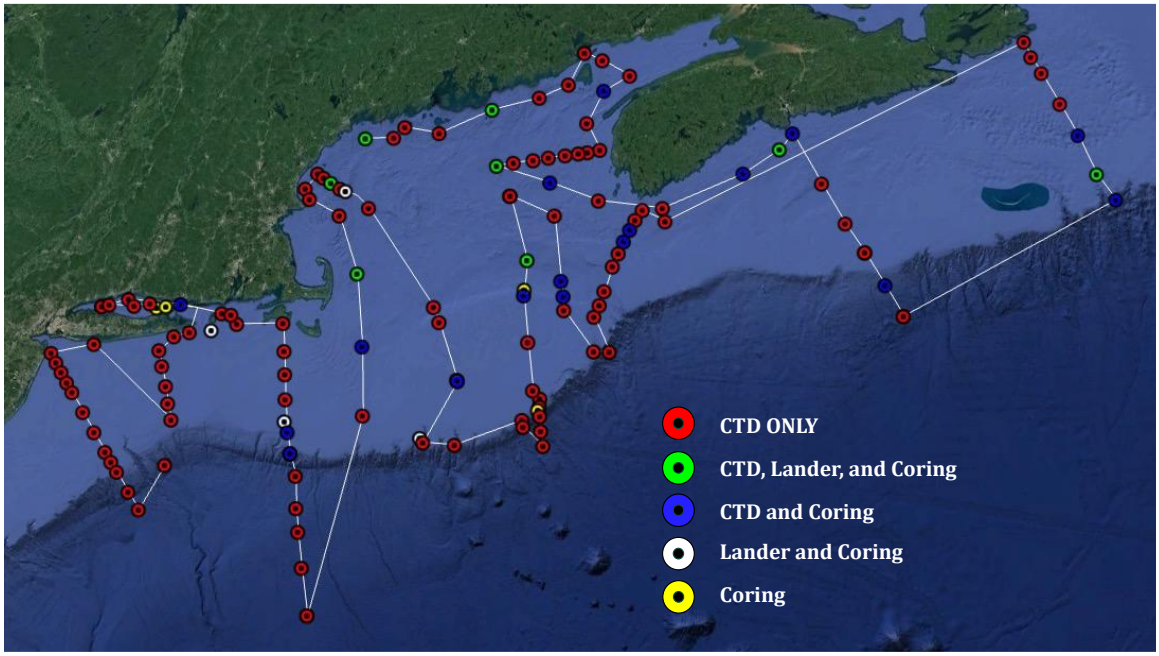

Figure 10: Leg 1 of ECOA showing the variety of station activities.

7.1. Biological Samples and Data Collection

Analysts: Shawn Shellito and Marc Emond
PI: Joe Salisbury (UNH)

7.1.1 Benthic lander

A benthic lander system was successfully deployed on ECOA-3 (Figure 11). The lander was designed to sit on the bottom and sample. It is a low-cost low-risk option to get CTD and bottom water while safeguarding the CTD/Rosette. Constructed for and operated on the 2022 ECOA-3 cruise, the lander can operate at depths up to 350 m, and is equipped with sensors to measure pressure, temperature, salinity, oxygen, stimulated fluorescence (chlorophyll), and pH (SeaBird SBE 27). The lander is currently configured with three 4l Niskin bottles, for a total sample volume of 12 l. The lander required approximately 2 m^2 of deck space. It also required enough space in the CTD control room for a rack-mountable deck box and a laptop computer. The deck box is for both power and communication to the lander, while the computer is for controlling and logging data. The lander was deployed off the aft winch (opposite winch of the CTD/Rosette). Its connection to the hydrowire was configured so that it was swappable with any other piece of equipment being deployed (on ECOA-3 the lander shared a wire with Bongo nets which had a SBE19 CTD attached and the IOP package). The lander was deployed as a CTD but when approaching the bottom, the lander operator gave off depth readings to the winch operator from the lander's Valeport VA500 altimeter, which has a resolution of several centimeters. The winch operator slowed wire payout as the lander approached the

bottom, and once on the bottom the all-stop command was given. At that time, the winch operator stopped payout to prevent “bird-nesting” the wire. The Niskin bottles on the lander were tripped and the lander was brought back to the surface for recovery and water sampling.

7.1.2 Known Problems

There was interference in the data stream once the ships hydraulics were powered up. This made processing the cast next to impossible because of various bad data lines but we were still able to operate the system and sample water as needed. It is believed that there was ground loop signal that was the cause of the problem.

Figure 11: Benthic lander being recovered.

7.2 Updating and expanding our knowledge of critical fluxes at the sediment/water interface for the carbon cycle on the NE shelf of the US

Analysts: Alexandra Frenzel and Halle Berger (UConn)
PI: Craig Tobias and Sam Siedlecki (UConn)

7.2.1 Statement of the Problem/Motivation

Over recent decades, the combination of fossil fuel emission, deforestation, and cement production have imparted large physical and biogeochemical modifications on the world's oceans [*Le Quéré et al.* 2018; *Gattuso et al.* 2015]. The oceans have gotten warmer, salinity distributions have been altered with density structures and stratification patterns modified [*Talley et al.* 2016]. In addition, biogeochemical alterations are co-occurring, including oxygen declines, changes in productivity, and increased dissolved inorganic carbon content due to uptake of anthropogenic carbon dioxide – which alters the pH and mineral saturation state through a process called ocean acidification [*Doney* 2010; *Bopp et al.* 2013]. Recently, the partial pressure of carbon dioxide (pCO_2) in coastal shelf waters has been shown to lag the rise in atmospheric CO_2, unlike the open ocean [*Laruelle et al. 2018*]. Some regions amplified the global uptake, while others did not keep up with the atmosphere or dampened the global signal. For example, over the past 15 years, waters in the Gulf of Maine have taken up CO_2 at a rate significantly slower than that observed in the open oceans due to a combination of the extreme warming experienced in the region and an increased presence of well-buffered Gulf Stream water [*Salisbury and Jönsson* 2018].

The intrusion of anthropogenic CO_2 is not the only mechanism that can reduce Ω_{arag} within coastal surface waters. Local processes like freshwater delivery, eutrophication, water column metabolism, and sediment interactions that drive variability on regional scales can also modify spatial variability in Ω_{arag} [*Feely et al.* 2008; 2018; *Siedlecki et al.* 2017; *Qi et al.* 2017; *Pilcher et al.* 2018]. Sedimentary processes like denitrification and the dissolution of calcium carbonate ($CaCO_3$) minerals acts as a negative feedback mechanism on acidification. Observation-based estimates indicate significant, anthropogenic CO_2-driven $CaCO_3$ dissolution on the seafloor at various locations in the deep ocean, particularly in the northern Atlantic [*Sulpis et al.* 2018]. This dissolution is expected to increase over the next few decades but is sensitive to the rate of meridional overturning circulation [*Perez et al.* 2018]. Observations of $CaCO_3$ cycling on productive, shallow shelf systems such as the GoME in the NW Atlantic are poorly studied even though these systems often support rich planktonic and benthic $CaCO_3$-bearing communities, including economically important species such as scallops [*Gledhill et al.* 2015] and the sediments consist of up to 40% $CaCO_3$ in some regions [*Trumbull,* 1972]. Currently, the ROMS implementation of COBALT being used for several NOAA OAP funded projects on the east coast of the US assumes the flux of calcium carbonate minerals and organic material are reflected back to the overlying water column. This is a common assumption in models and is similar to what the Fennel et al. (2006; 2008) formulation assumes for all carbon and nitrogen constituents. As suggested by the review of Soetaert et al. (2000) for applications focused on water column processes, the pulses of organic material that reach the sediment interface are returned slowly back to the water column as opposed to being instantly remineralized. Sensitivity of these simulated fluxes can be compared against the limited observations in the region *[e.g. Salisbury et al. 2012; Jahnke et al. 2005; Anderson et al. 1994],* but more spatial and temporal coverage of the shelf as most samples were taken on the slope previously– especially given recent warming trends – would help constrain the model.

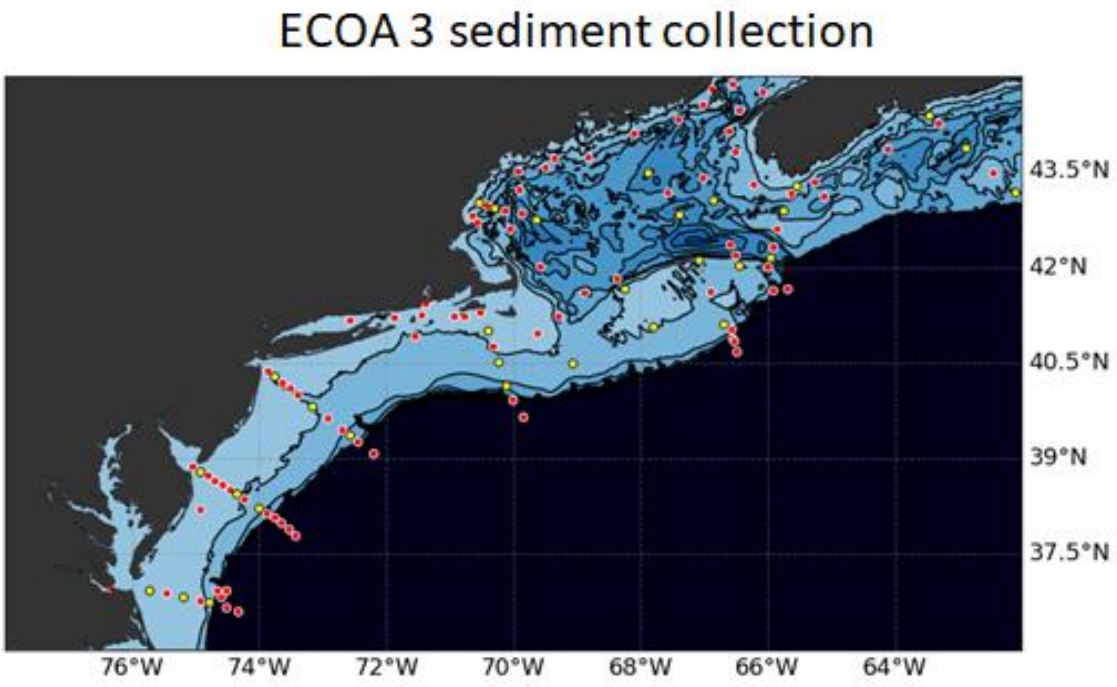

Figure 12: ECOA2 stations from the Northeast shelf region are plotted in red and the proposed sediment collection sites (30) are plotted in yellow.

7.2.2 Sampling Procedures

Sampling On Station – At target stations sediment was collected with either a box core or a Smith MacIntyre grab. Box core sampling was estimated to take about 30 min per shelf station. The sampling area of the grab was no less than 200 cm^2 with a minimum collected sediment thickness of 10 cm. The grab / box core was sub-cored immediately on deck – 8 to 10 2"-diameter cores. Cores were immediately transferred to the lab. Five liters of bottom water was also collected from the Niskin rosette into a small carboy and transferred to the lab.

7.2.3 Core Incubations – in the Lab

Staging the Incubations - Bottom water was 1 – 2μm filtered in the lab into a collapsible cubetainer. Core headspace was filled with filtered bottom water and capped with stirring tops. Cores were then loaded into incubation buckets (IBs). Each IB is a five-gallon bucket (one per station) where cores were arranged around a central magnetic stirrer. Half of the cores (4) were dedicated to detecting isotopic changes in DIC resulting from mineralization (DIC Cores). Half of the cores (4) were dedicated to measuring denitrification (DENIT Cores). Two core tubes were filled with bottom water and serve as bottom water-only controls used for both DIC and DENIT. These tubes were measured on the final incubation time point. Two core tubes were filled with bottom water and processed immediately to serve as bottom water-only 'time initial' controls for both DIC and DENIT Cores. Each IB has inflow and outflow port connected to a water chiller that recirculates a water bath at bottom water temperature. Each incubation occurred onboard in the lab and took approximately 48 hours each.

DENIT Cores - Each of the DENIT Cores is spiked with $^{15}NO_3^-$ solution to a final concentration of 50μM. DENIT Cores were sacrificed along a time series over 48 hours at intervals guided by O_2 loss measured in the DIC cores. Sacrificing a DENIT Core consists of: 1) inverting the core to mix sediment + water; 2) allowing the core to settle for ½ hour; 3) gravity feed sampling the water into 12 ml Exetainers + $ZnCl_2$ preservative, storage in refrigerator. 4) remaining water (200ml) is filtered and frozen. DIC Cores – DIC Core incubations were handled as To, T_{final} incubations n=4. The T_{final} DIC cores will be sampled when dissolved oxygen reaches 30% of its initial value or at 48 hours whichever comes first. O_2 monitoring in the DIC Cores is accomplished with O_2 active film dots affixed to the inner wall of the core tubes. DIC Core sampling consists of: 1) removing top; 2) gravity feed sampling of overlying water into a fraction for DIC concentration and a fraction for DIC isotopes – each preserved with $HgCl_2$; 3) Collection of 10 ml overlying water for nutrient analyses; 4) Extruding the core and collecting / freezing the top 2 cm of sediment for %C, C:N, and % carbonate analysis. Extra sediment will be available for carbonate mineralogy if that is desired.

7.2.4 Analysis – Determination of Rates

Denitification rates are calculated from a linear regression of the time series increases in the N2 mass 29 and 30 isotopologues. Isotope pairing equations presented in Steingruber et al. (2001) and Nielsen (1992) are used to calculate coupled and direct denitrification rates. The net $d^{13}C$ of the carbon source (i.e. indications of carbonate dissolution) contributing to DIC evolved during incubations are derived from two endmember isotope mixing equation using DIC concentrations and $d^{13}C$-DIC values at the start and end of incubations (n=4; Berelson et al., 2019).

7.2.5 Known Problems

The decision was made by the ships command to limit coring to day-time operations only. This decision limited the overall number of cores that were collected and added an extra level of complexity when planning the daily schedule.

Berelson, W. M. et al. (2019) 'Benthic fluxes from hypoxia-influenced Gulf of Mexico sediments: Impact on bottom water acidification', Marine Chemistry, 209, pp. 94–106. doi: https://doi.org/10.1016/j.marchem.2019.01.004.

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Nielsen, L.P. (1992). *Denitrification in sediment determined from nitrogen isotope pairing*. FEMS Microbiol. Ecol 86: 357-362.

Steingruber, S.M., Friedrich, J., Gachter, R., and B. Wehrli. (2001). *Measurement of Denitrification in Sediments with the ^{15}N Isotope Pairing Technique*. Appl Environ Microbiol.

7.3 $CaCO_3$ Polymorph Mineralogy of Georges Bank Sediments

PI: Justin Ries (Northeastern)

7.3.1 Statement of the Problem/Motivation

Calcifying marine organisms inhabiting Georges Bank produce their shells and skeletons from different types, or polymorphs, of $CaCO_3$, most commonly aragonite, high-Mg calcite, and/or low-Mg calcite. These mineralogical differences in shell and skeletal composition can yield a comparable range of polymorph mineralogies in the carbonate sediments that are ultimately deposited on the Bank. These polymorphs differ greatly in their solubility in seawater and, therefore, in their potential response to future CO_2-induced ocean acidification. Aragonite (produced by organisms such as clams and corals) is more soluble than low-Mg calcite, with the solubility of calcite increasing with its Mg-content, which can range from 5 to 15 mol% in some modern calcite-secreting marine organisms inhabiting Georges Bank (e.g., lobsters, coralline red algae, echinoderms). Sediments composed of the more soluble forms of $CaCO_3$ (aragonite, high-Mg calcite) will be more susceptible to dissolution as the ocean acidifies with increasing atmospheric pCO_2.

7.3.2 Sampling Procedures

Approximately 200 sediment samples were obtained by the UCONN box core across the study sites at Georges Bank (10 samples at each of 20 sites). Samples were immediately refrigerated/frozen. Analysis will be carried out at Northeastern.

7.3.3 Lab Analysis

The relative abundance of the $CaCO_3$ polymorphs within these sediment samples shall be determined via powder x-ray diffraction (XRD). Sediment samples will be mixed with 95% ethanol and gently ground for two minutes to a fine powder using an agate mortar and pestle. The slurry will be injected into a 1 cm x 1 cm x 10 µm reservoir on a glass slide and allowed to dry overnight. Ries will quantify the polymorph mineralogy of the carbonate samples using a *Rigaku Miniflex* X-ray diffractometer at Northeastern's Marine Science Center. The proportion of aragonite-to-calcite will be calculated from the ratio of the area under the primary aragonite peak [d(111): 3.39 Å; $2\theta = 26.3^{o}$] to the area under the primary calcite peak [d(104): 2.98-3.03 Å; $2\theta = 29.5\text{-}30.0^{o}$], using standardized mixtures for calibration (precision and accuracy = 3%). The Mg-content of the calcitic portions of the skeletons will be calculated from the d-spacing of the calcite crystal lattice (determined from 2Θ-shift of the primary calcite peak), using five calcite standards of known Mg-composition between 0 and 25 mol% $MgCO_3$. Analyses of the Mg-content of calcite by XRD will intermittently be compared with LA-ICP-MS measurements of calcite Mg/Ca for validation purposes. Sediment polymorph compositions shall be mapped across the bank with color-coded contours to illustrate the relative susceptibility of Georges Bank sediments to dissolution as a result of future CO_2-induced ocean acidification

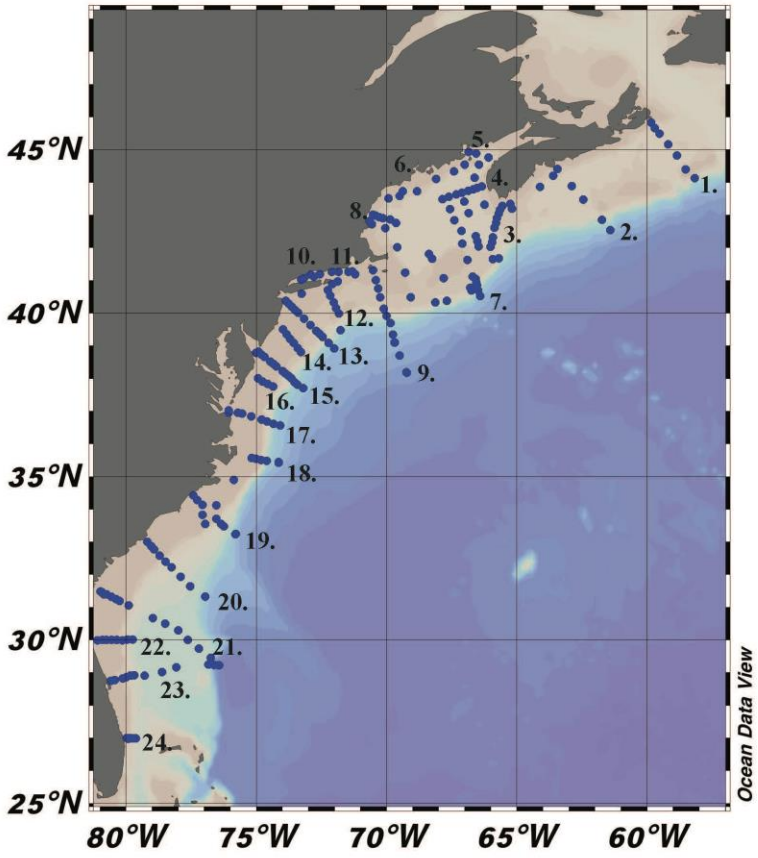
8. Other Activities

8.1 Drifter Deployments

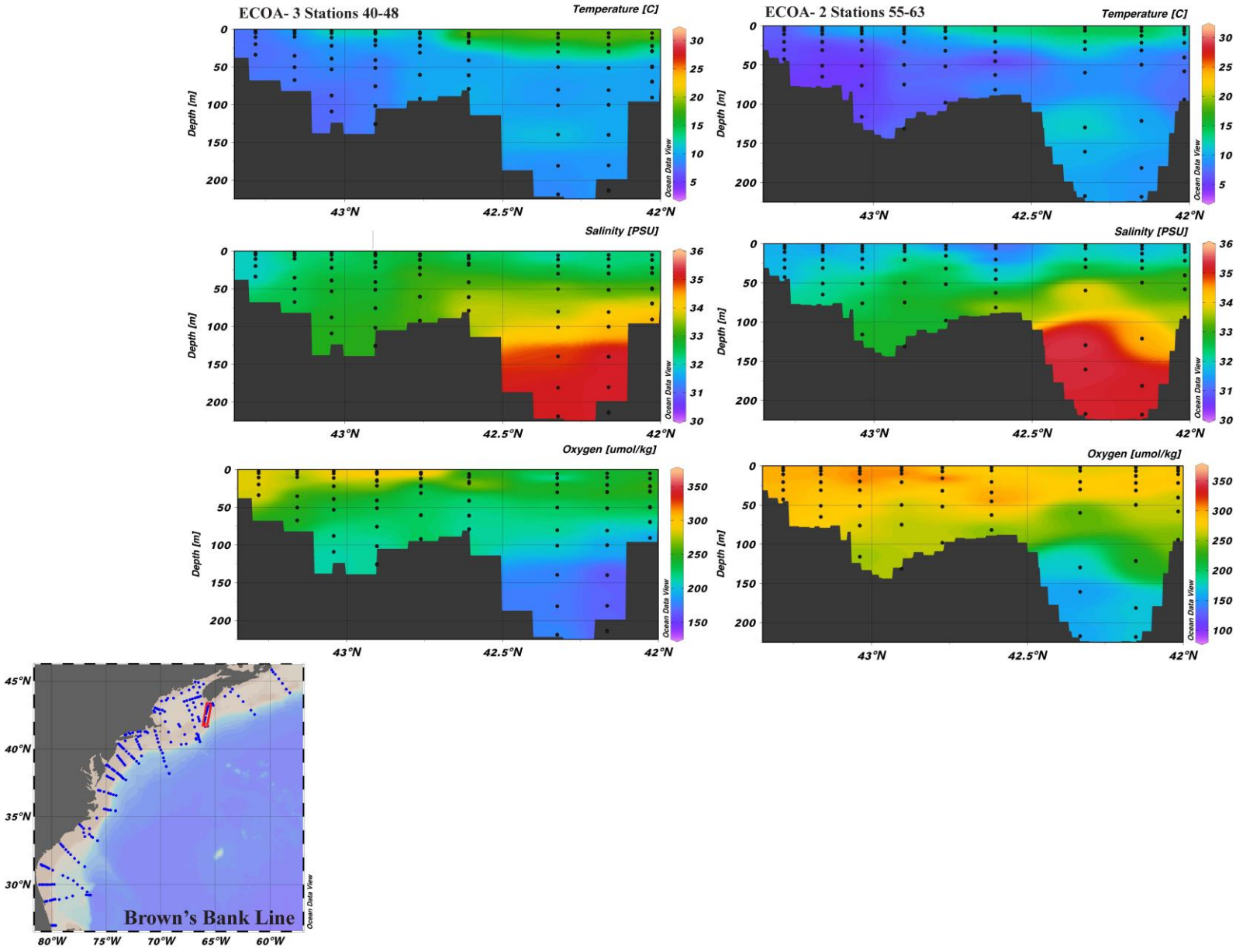
PI: Joseph Sienkiewicz (NOAA)

Five drifters were deployed throughout the cruise. These drifters were part of the NOAA Global Drifter Program. The program uses satellite tracked surface drifting buoys for a globally dense set of in-situ observations of surface currents.

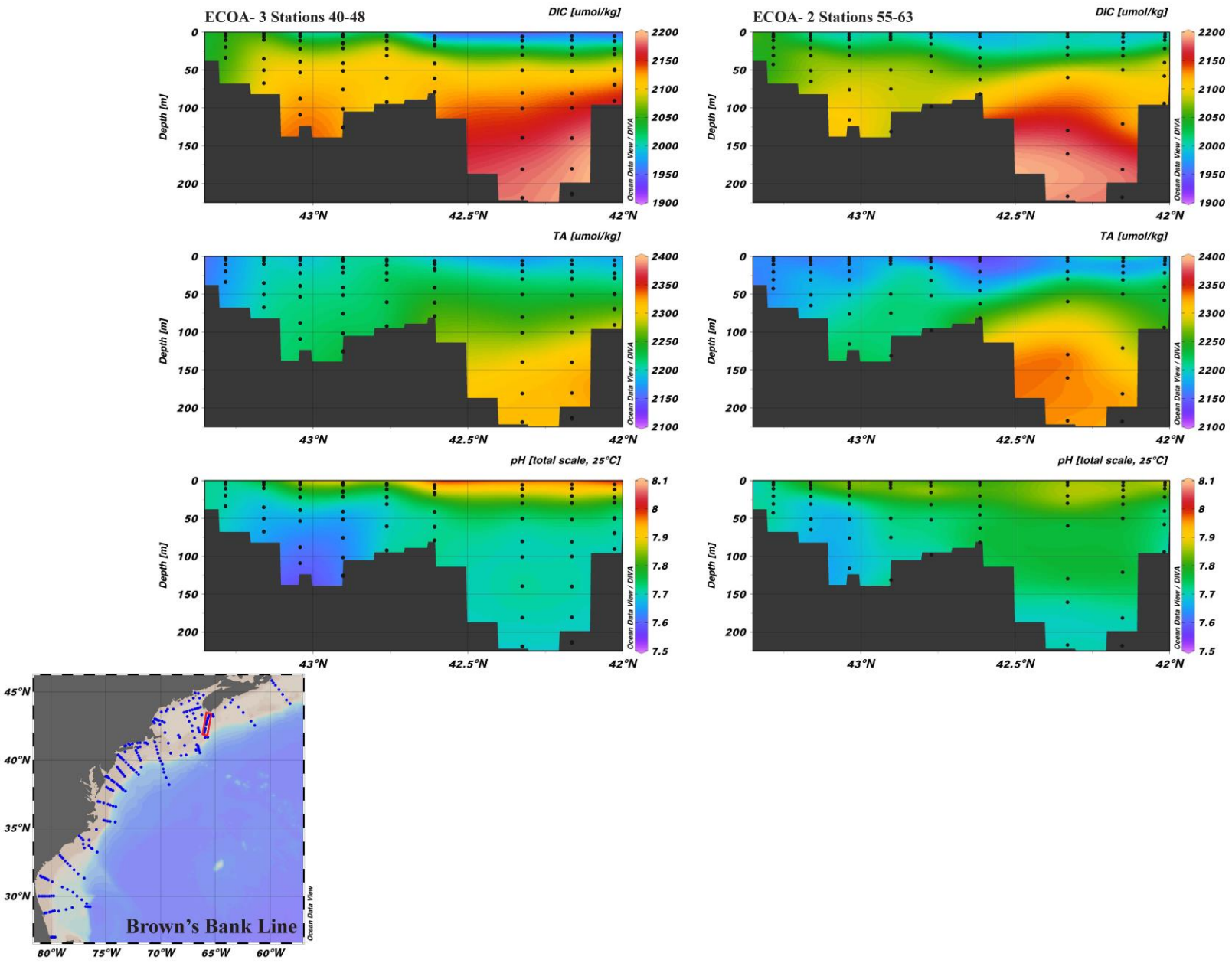
9. Supplementary Information



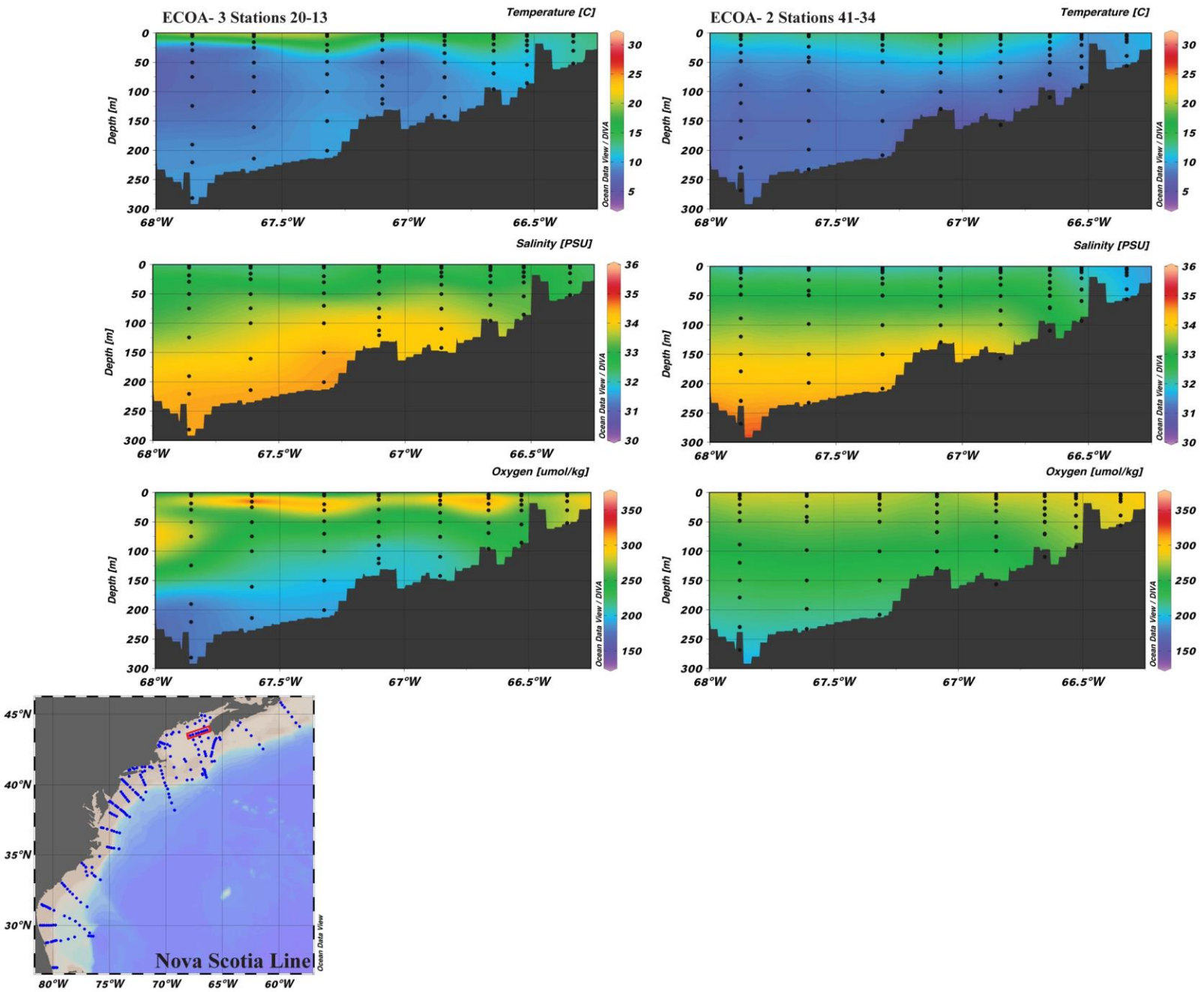
S1 ECOA-3 CTD stations



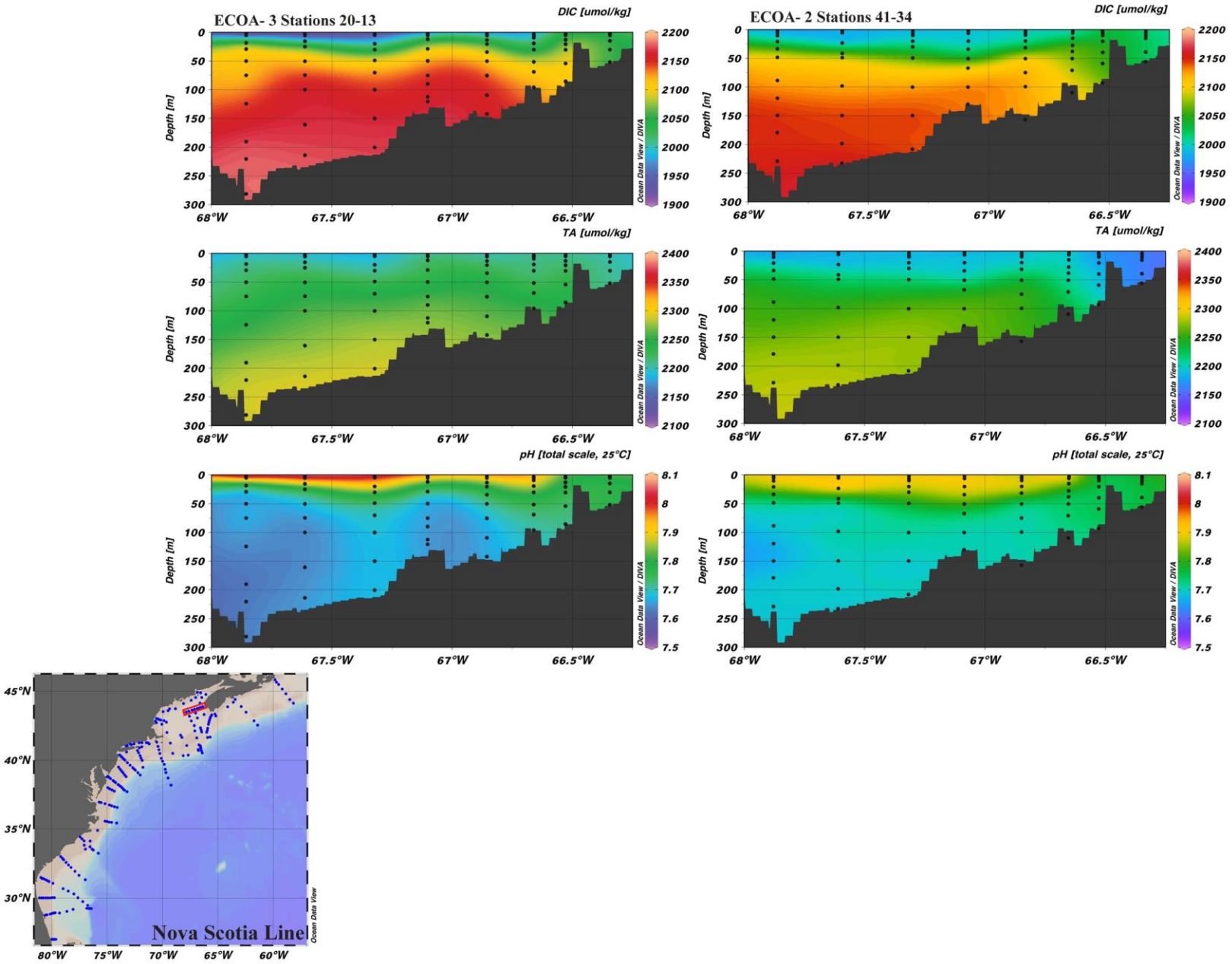
S2 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the Brown's Bank Line transect from ECOA-3 (stations 40-48) and ECOA-2 (stations 55-63). Black dots representing bottle trip depths from each station's CTD cast.



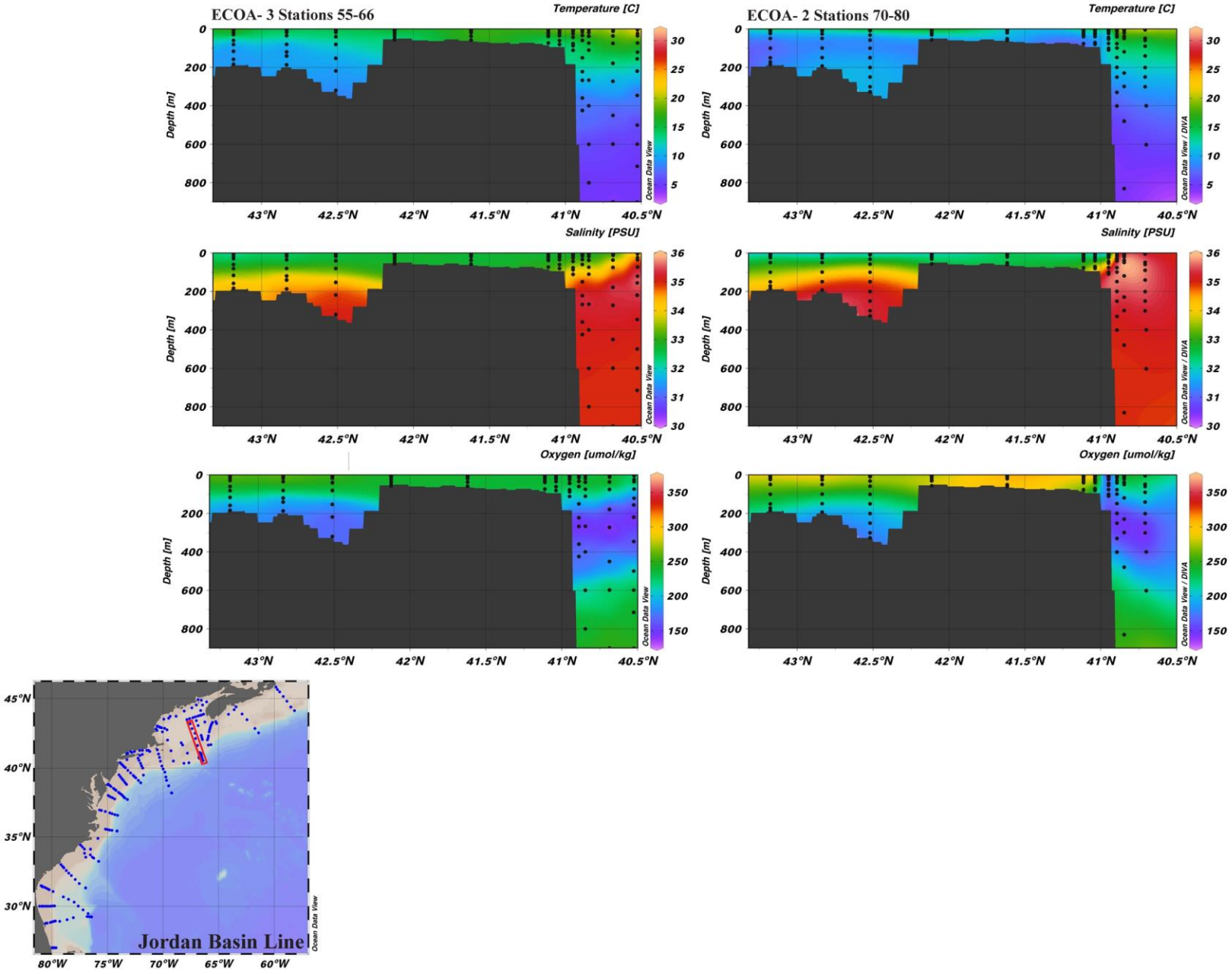
S3 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg),, pH (total scale, 25°C) at the Brown's Bank Line transect from ECOA-3 (stations 40-48) and ECOA-2 (stations 55-63). Black dots representing bottle trip depths from each station's CTD cast.



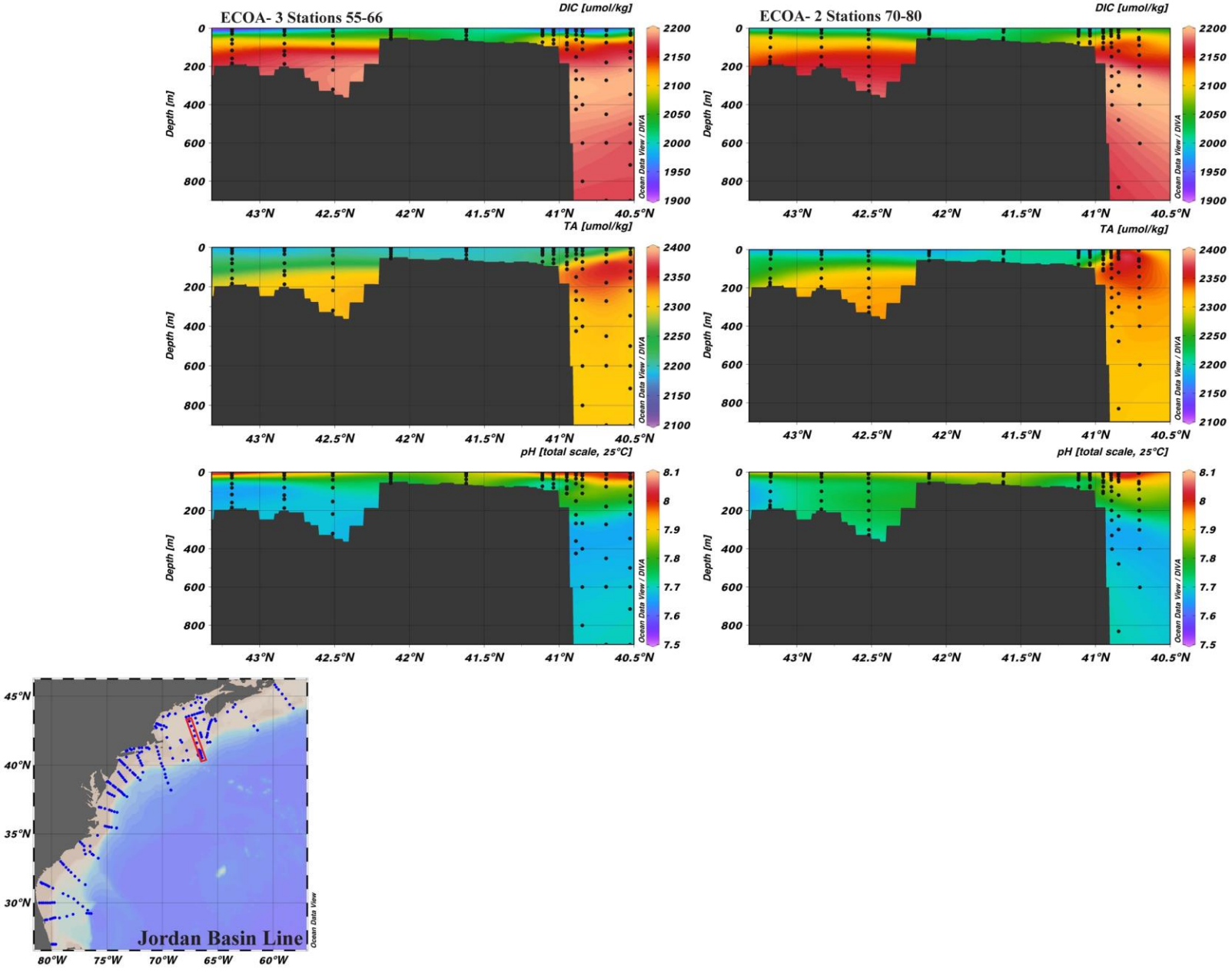
S4 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the Nova Scotia Line transect from ECOA-3 (stations 20-13) and ECOA-2 (stations 41-34). Black dots representing bottle trip depths from each station's CTD cast.



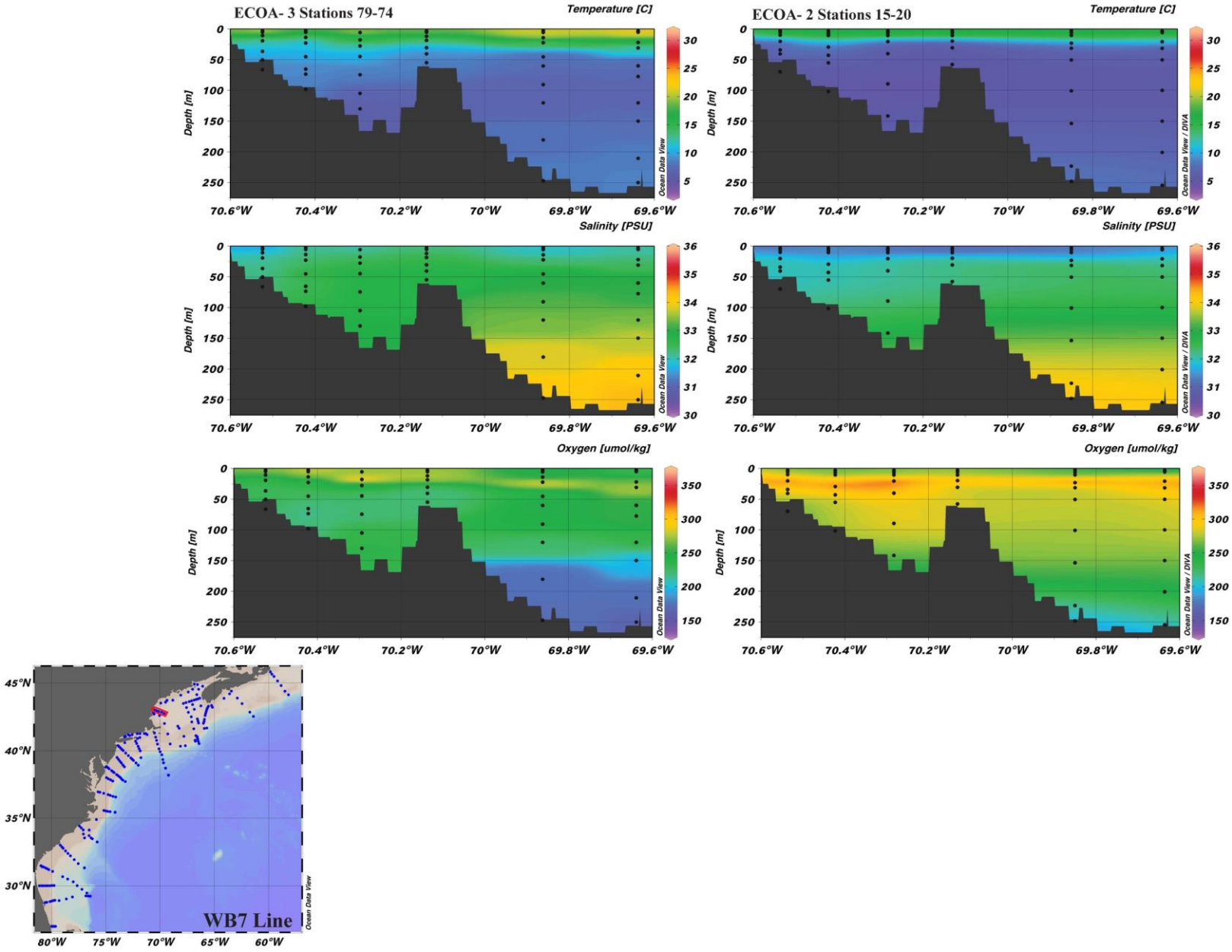
S5 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the Nova Scotia Line transect from ECOA-3 (stations 20-13) and ECOA-2 (stations 41-34). Black dots representing bottle trip depths from each station's CTD cast.



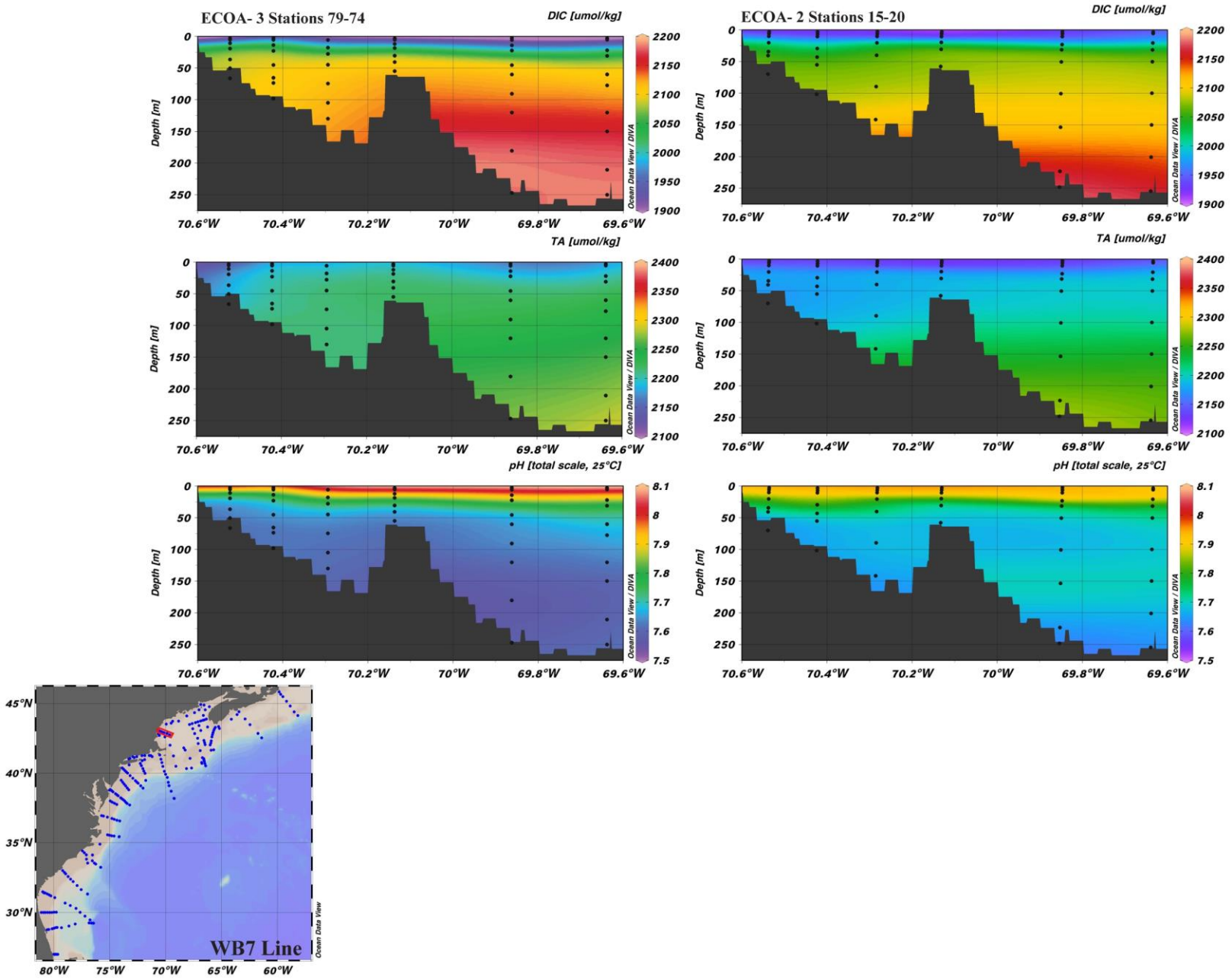
S6 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the Jordan Basin Line transect from ECOA-3 (stations 55-66) and ECOA-2 (stations 70-80). Black dots representing bottle trip depths from each station's CTD cast.



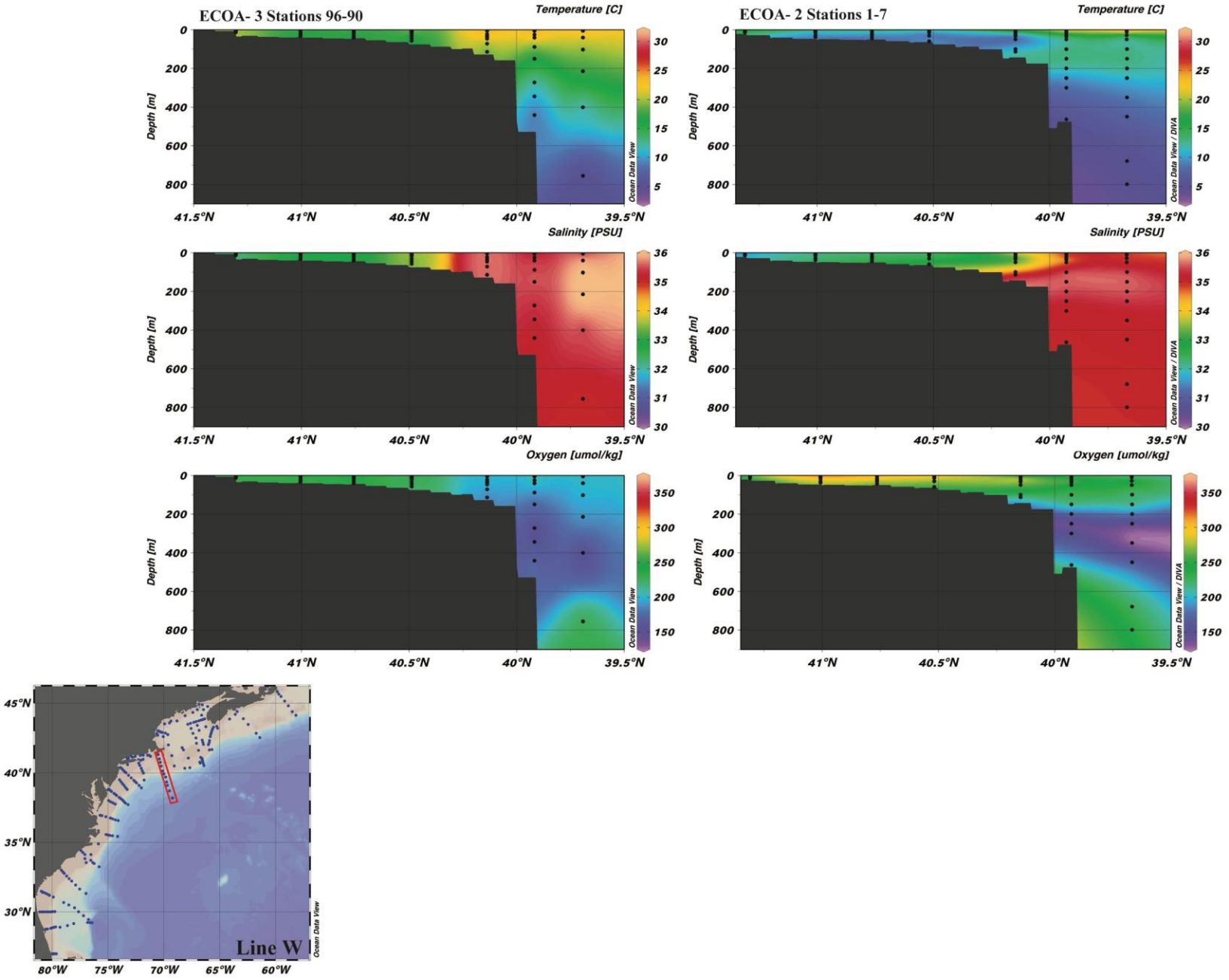
S7 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the Jordan Basin Line transect from ECOA-3 (stations 55-66) and ECOA-2 (stations 70-80). Black dots representing bottle trip depths from each station's CTD cast.



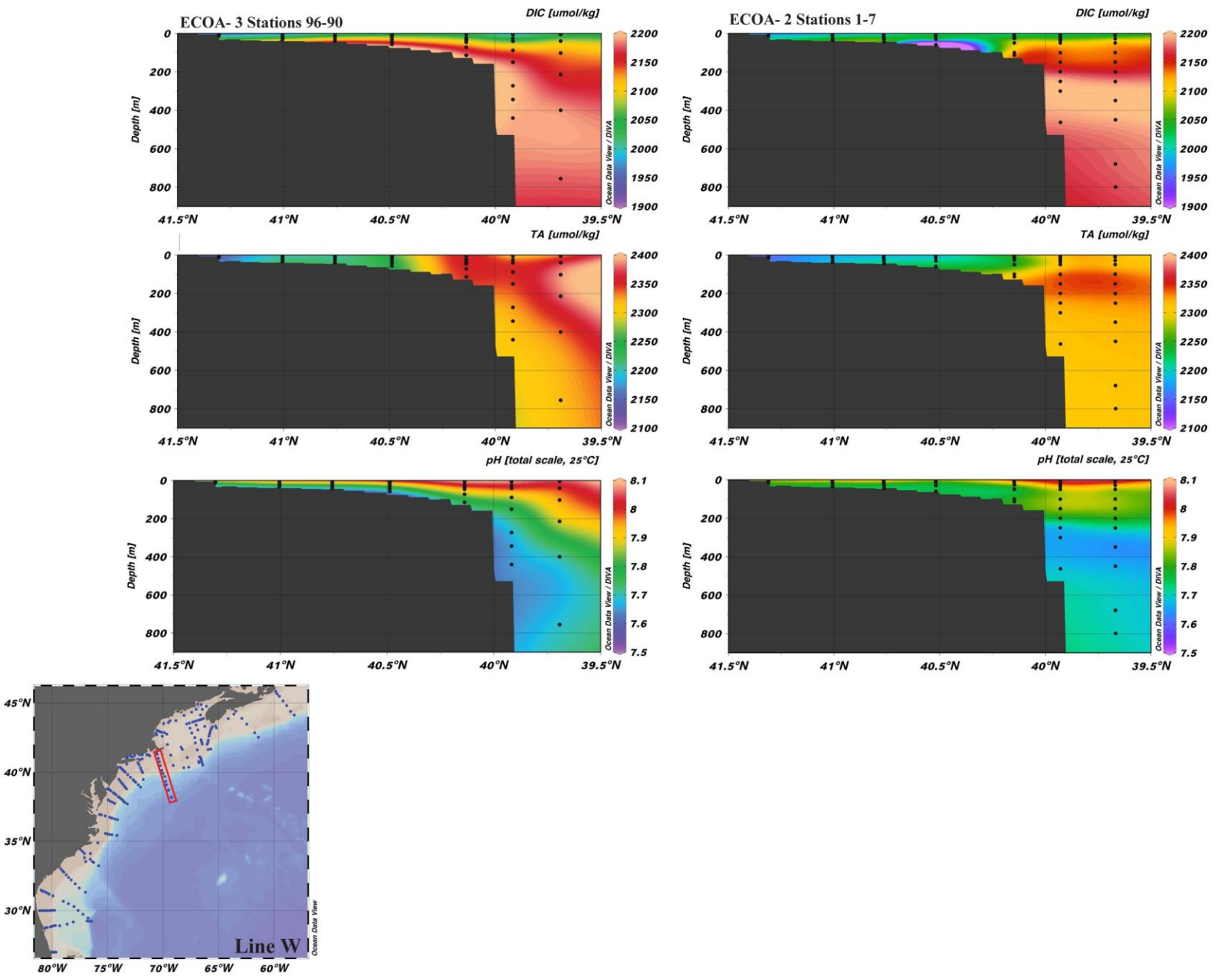
S8 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the WB7 Line transect from ECOA-3 (stations 79-74) and ECOA-2 (stations 15-20). Black dots representing bottle trip depths from each station's CTD cast.



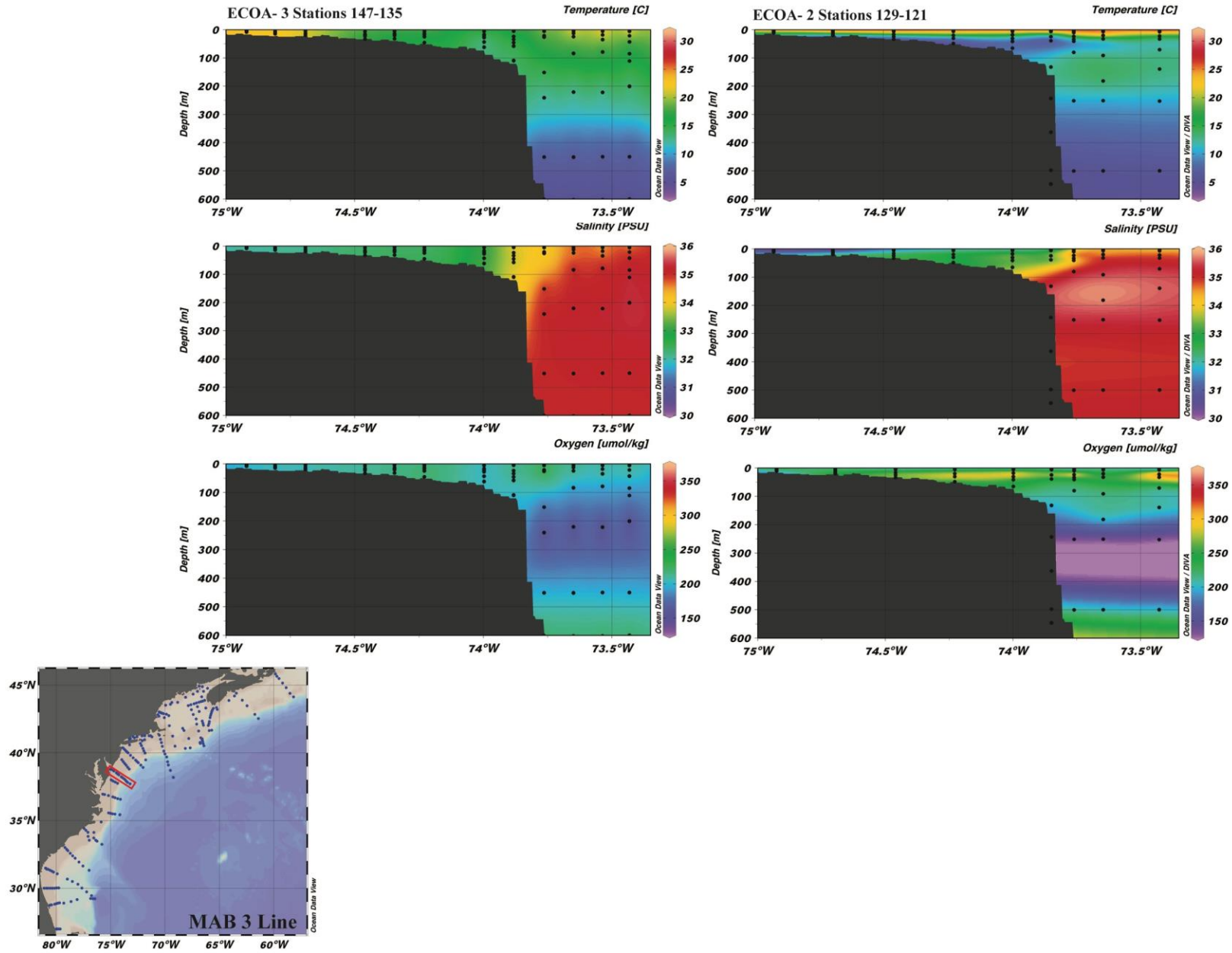
S9 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the WB7 Line transect from ECOA-3 (stations 79-74) and ECOA-2 (stations 15-20). Black dots representing bottle trip depths from each station's CTD cast.



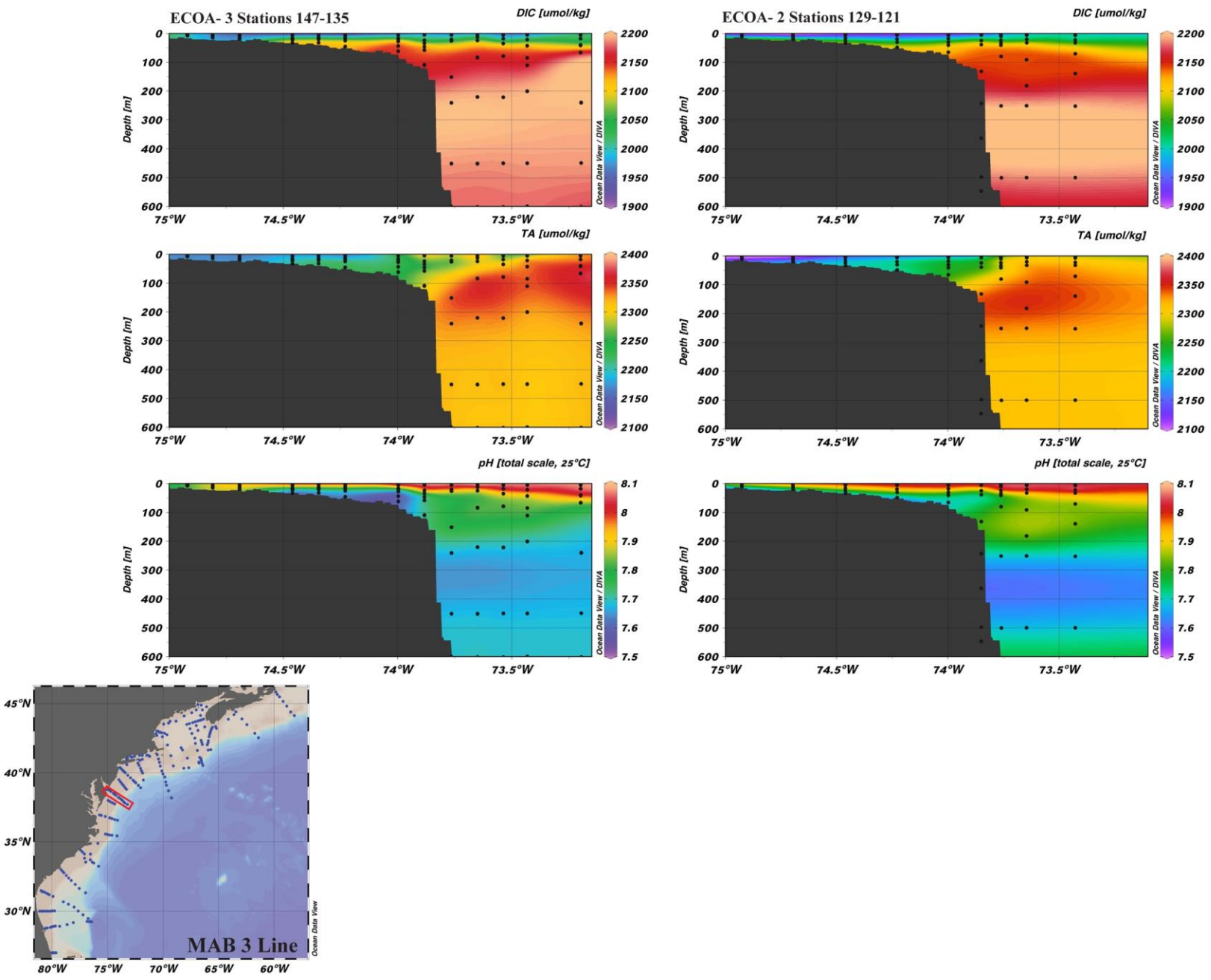
S10 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the Line W transect from ECOA-3 (stations 96-90) and ECOA-2 (stations 1-7). Black dots representing bottle trip depths from each station's CTD cast.



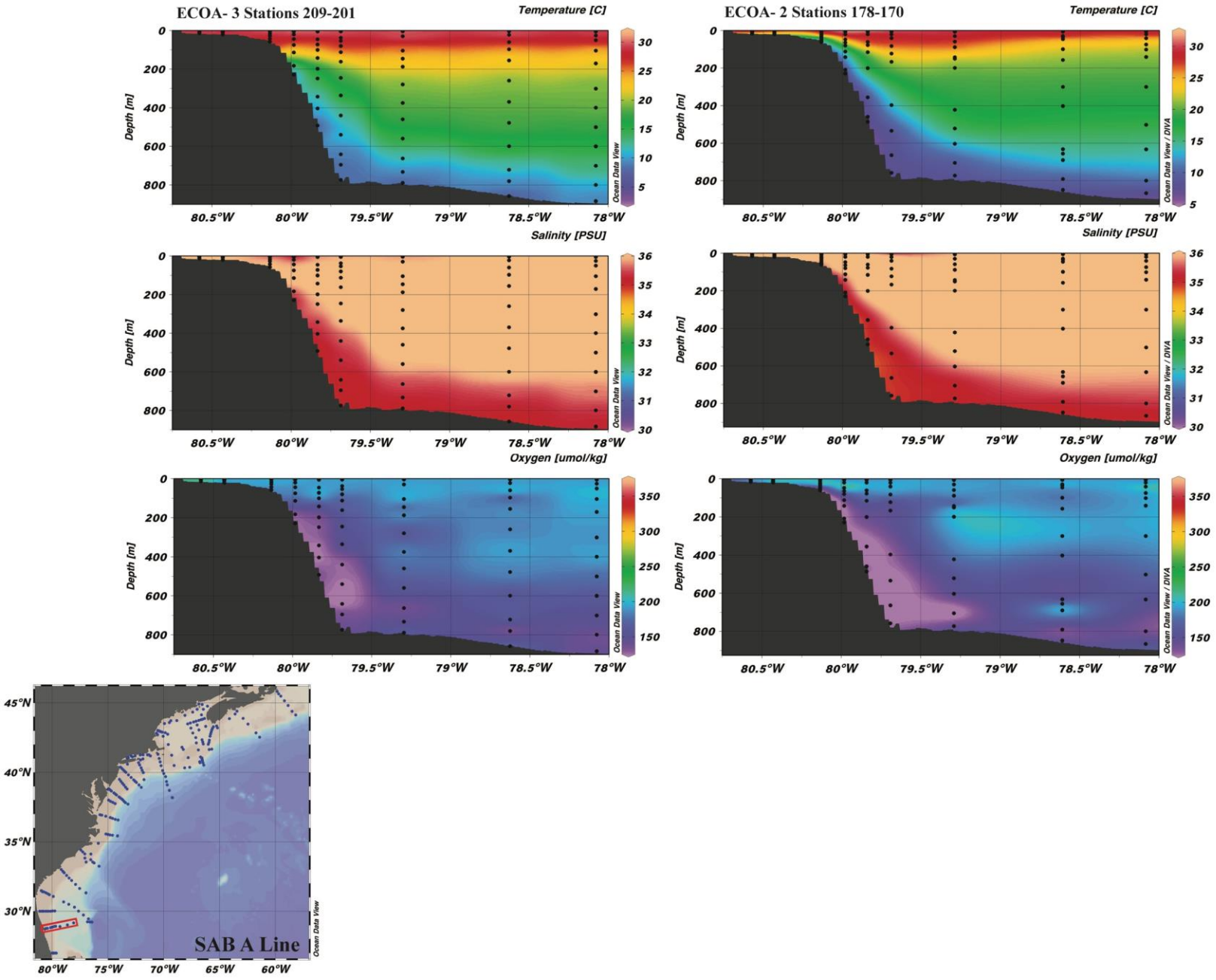
S11 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the Line W transect from ECOA-3 (stations 96-90) and ECOA-2 (stations 1-7). Black dots representing bottle trip depths from each station's CTD cast.



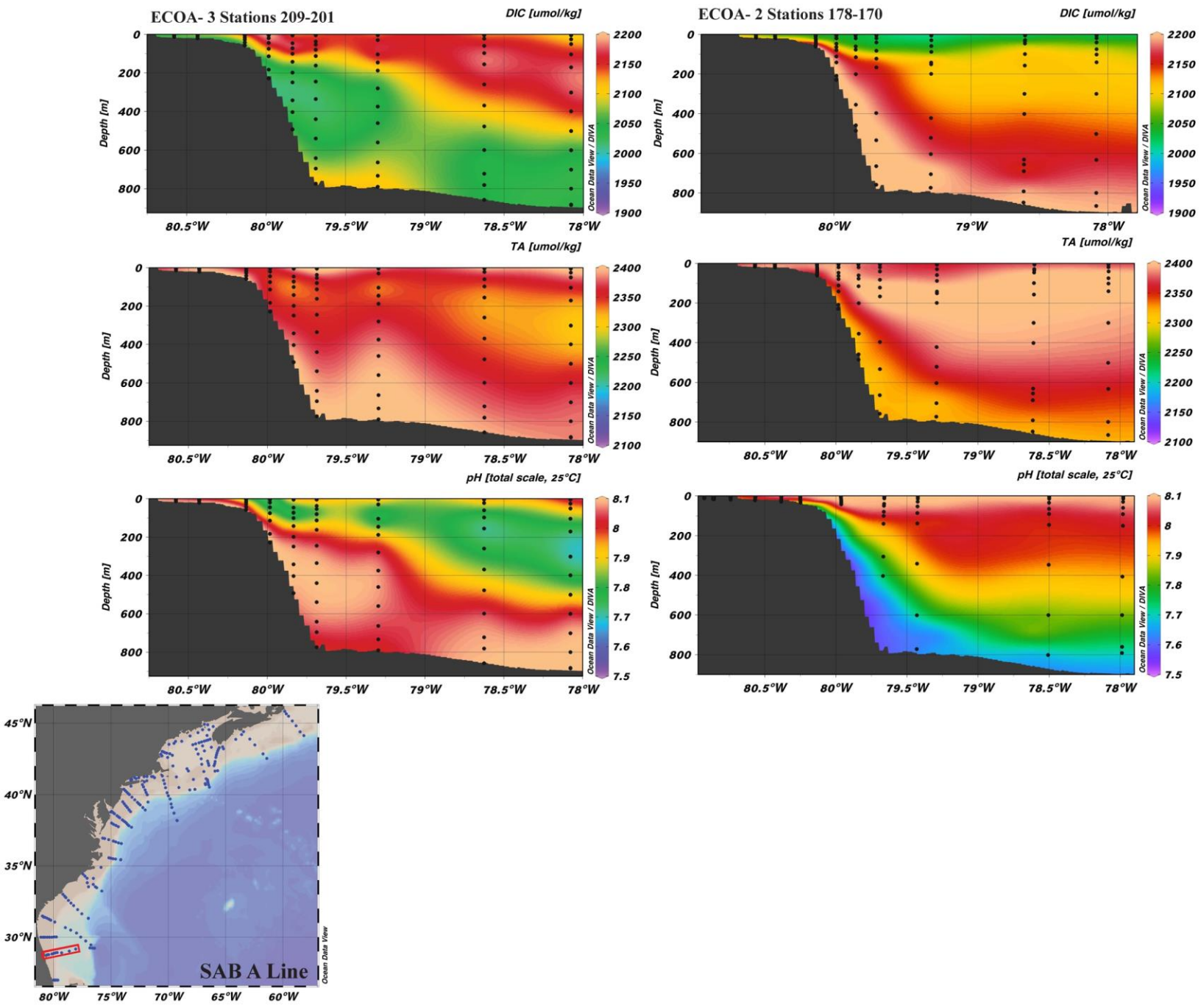
S12 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the MAB 3 Line transect from ECOA-3 (stations 147-135) and ECOA-2 (stations 129-121). Black dots representing bottle trip depths from each station's CTD cast.



S13 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the MAB 3 Line transect from ECOA-3 (stations 147-135) and ECOA-2 (stations 129-121). Black dots representing bottle trip depths from each station's CTD cast.



S14 Comparison of temperature (°C), salinity (PSU), and oxygen (µmol/kg) at the SAB A Line transect from ECOA-3 (stations 209-201) and ECOA-2 (stations 178-170). Black dots representing bottle trip depths from each station's CTD cast.



S15 Comparison of carbonate parameters DIC (µmol/kg), TA (µmol/kg), and pH (total scale, 25°C) at the SAB A Line transect from ECOA-3 (stations 209-201) and ECOA-2 (stations 178-170). Black dots representing bottle trip depths from each station's CTD cast.