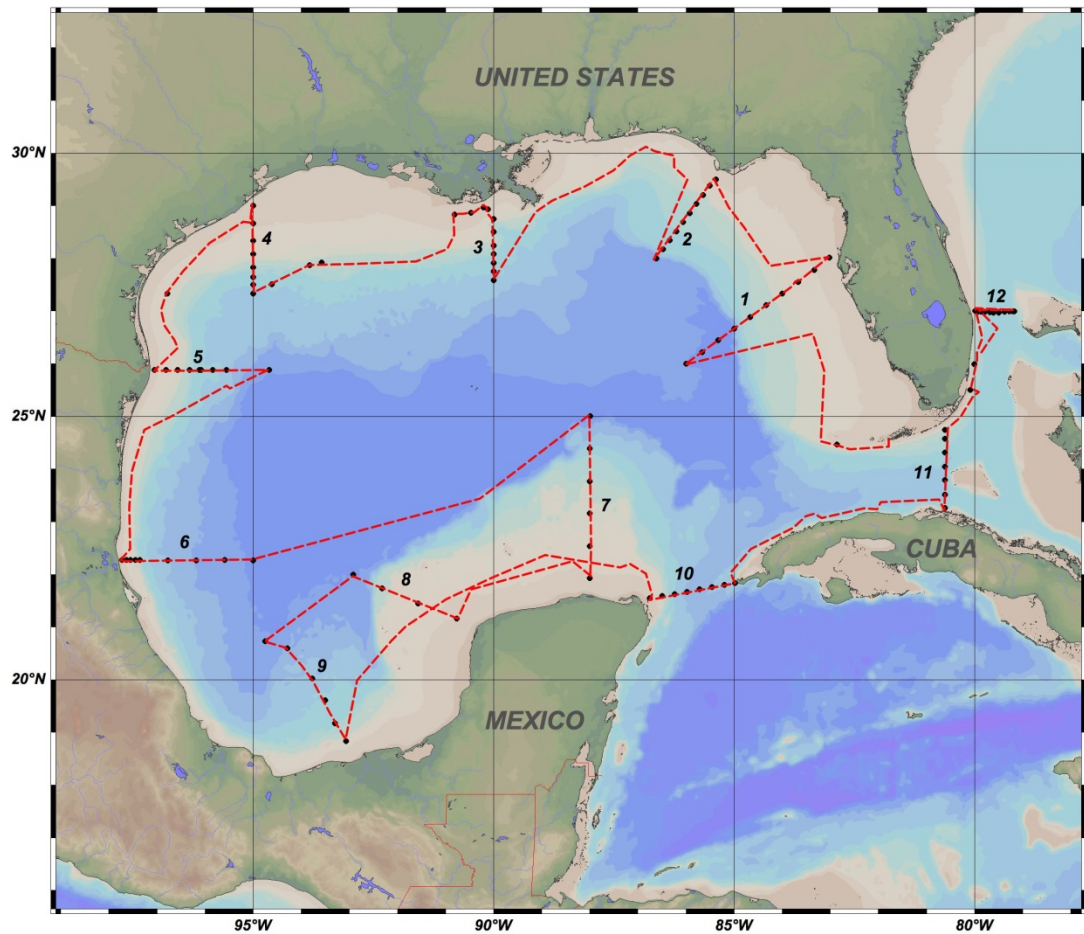# Cruise Report
(doi:10.25923/y6m9-fy08)

Third Gulf of Mexico Ecosystems and Carbon Cycle (GOMECC-3) Cruise

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Cruise Summary Information

Cruise designation	**GOMECC-3**
Expedition designation (expocode)	**33RO20170718**
Ship's cruise ID	**RB17-04**
Chief scientist	**Leticia Barbero**
Dates	**18 July-21 August 2017**
Ship	**R/V *Ronald H. Brown***
Ports of call	**Key West, FL, USA – Fort Lauderdale, FL, USA**
Geographic Boundaries	**18.2–30°N, 79–98°W**
Stations	**107**
Floats and drifters deployed	**25 CARTHE drifters deployed**

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1. GOMECC-3 Project

The third Gulf of Mexico Ecosystems and Carbon Cycle (GOMECC-3) cruise on board the R/V *Ronald H. Brown* took place from July 18–August 21, 2017. The survey of GOMECC-3 consisted of CTD/DO, rosette, LADCP, water samples, bongo-style net tows, hand-held net tows, and underway measurements. The ship departed from Key West, FL and went around the Gulf of Mexico in a counterclockwise direction, ending in Fort Lauderdale, FL.

A total of 107 stations were occupied with a CTD/DO/rosette/LADCP package. Of these stations, 104 were divided into 12 lines, and an additional three stations were occupied as part of a collaboration with the National Park Service. Four of the 12 lines were reoccupations of previous GOMECC cruises; the remaining lines were new stations occupied for the first time during this cruise. Twenty-five CARTHE drifters were deployed at stations with depths close to 50 m. Up to four bongo net tows were conducted at each of the 12 lines to collect zooplankton samples. Twenty-four hour grazing incubation experiments were performed at deep and shallow stations in eight of the lines. Profiles from hyperspectral radiometer (HyperPro-II) casts were conducted at 14 stations throughout the cruise. On one station located in the Flower Garden Banks National Marine Sanctuary, a diel station was performed. The ship stayed on site for a little over 24 hours and performed eight CTD casts and four bongo net tows (the net tows were done outside the sanctuary, at a depth of 200 m). Water samples were obtained next to a buoy equipped with ocean acidification sensors in order to provide calibration measurements for the buoy. This buoy, located in the Mississippi River outflow, is partially funded through NOAA's Ocean Acidification Program.

CTD/DO data and water samples were collected on each cast, from surface (2-5 m) to usually within 5-8 m of the bottom. Water samples were measured on board for salinity, dissolved oxygen, nutrients, dissolved inorganic carbon (DIC), pH, carbonate concentration, total alkalinity (TA), and pCO_2. Additional water samples were collected and stored for shore analyses of chlorophyll concentration, HPLC analysis, and DNA/RNA composition of eukaryote plankton communities (<200 μm).

A seagoing science team assembled from 11 different institutions and three countries participated in the collection and analysis of this data set. The programs, principal investigators, science team, responsibilities, instrumentation, analysis and analytical methods are outlined in the following cruise document.

1.1 Programs and Principal Investigators

Table 1: GOMECC-3 principal investigators.

Program	Affiliation	Principal Investigator	Email Address
CTD/DO data, salinity	AOML/NOAA	Molly Baringer	Molly.Baringer@noaa.gov
Dissolved inorganic carbon (DIC), pCO$_2$	AOML/NOAA	Rik Wanninkhof Leticia Barbero	Rik.Wanninkhof@noaa.gov, Leticia.Barbero@noaa.gov
Total alkalinity	AOML/NOAA	Rik Wanninkhof Denis Pierrot	Rik.Wanninkhof@noaa.gov, Denis.Pierrot@noaa.gov
Dissolved oxygen	AOML/NOAA RSMAS	Molly Baringer Chris Langdon	Molly.Baringer@noaa.gov, clangdon@rsmas.miami.edu
Nutrients	AOML/NOAA	Jia-Zhong Zhang	jia-zhong.zhang@noaa.gov
pH, carbonates, MICA	USF	Robert Byrne	rhbyrne@usf.edu
Underway pH	UABC	Martín Hernández Ayon	jmartin@uabc.edu.mx
Ocean color	NOAA/NESDIS	Mike Ondrusek	Michael.Ondrusek@noaa.gov
Remote sensing, particulate and CDOM absorption, pigments	USF	Chuanmin Hu David English	huc@usf.edu, denglish@mail.usf.edu
Pteropods	ECOSUR	Daniel Pech	dpech@ecosur.mx
Ichtyoplankton	CICESE USM	Sharon Herzka Frank Hernandez	sherzka@cicese.mx, frank.hernandez@usm.edu
Plankton ecology	NCSU ULL	Astrid Schnetzer Beth Stauffer	aschnet@ncsu.edu, bas1301@louisiana.edu
CARTHE drifters	RSMAS	Josefina Olascoaga	jolascoaga@rsmas.miami.edu
Transmissometry	TAMU	Wilford Gardner	wgardner@tamu.edu
LADCP	AOML/NOAA	Leticia Barbero	Leticia.Barbero@noaa.gov
SADCP	AOML/NOAA UH	Ryan Smith Julia Hummon	Ryan.Smith@noaa.gov, hummon@hawaii.edu

1.2 Participating Institutions

AOML/NOAA   – Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration
CICESE   – Ensenada Center for Scientific Research and Higher Education
ECOSUR   – Colegio de Frontera Sur
NCSU   – North Carolina State University
NOAA/NESDIS – National Oceanic and Atmospheric Administration, National Environmental Satellite, Data and Information Service
RSMAS   – Rosenstiel School of Marine and Atmospheric Science/University of Miami
TAMU   – Texas A&M University
UABC   – Universidad Autónoma de Baja California
UH   – University of Hawaii
ULL   – University of Louisiana at Lafayette
USF   – University of South Florida
USM   – University of Southern Mississippi

1.3 Science Team and Responsibilities

Table 2: GOMECC-3 cruise participants.

Duty	Name	Affiliation	Email Address
Chief Scientist/data manager/CTD watchstander	Leticia Barbero	AOML	Leticia.Barbero@noaa.gov
Co-Chief Scientist/CTD watchstander	Denis Pierrot	AOML	Denis.Pierrot@noaa.gov
CTD/LADCP/salinity	Andrew Stefanick	AOML	Andrew.Stefanick@noaa.gov
CTD/CTD processing/ salinity	James Hooper	AOML	James.Hooper@noaa.gov
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O_2	Leah Chomiak	RSMAS	l.chomiak1@umiami.edu
Nutrients	Ian Smith	AOML	Ian.Smith@noaa.gov
DIC	Patrick Mears	AOML	patrick.mears@noaa.gov
DIC	Joletta Silva	RSMAS	jsilva@rsmas.miami.edu
pCO$_2$ discrete	Kevin Sullivan	AOML	Kevin.Sullivan@noaa.gov
Alkalinity/underway pH	Linda Barranco	UABC	linda.barranco@gmail.com
Alkalinity/underway pH	Gabriela Cervantes	UABC	gabita23@gmail.com
pH/carbonate/MICA	Jon Sharp	USF	jdsharp@mail.usf.edu
pH/carbonate	Katelyn Schockman	USF	kschockman@mail.usf.edu
pH/carbonate/MICA	Ellen Hudson-Heck	USF	ehudsonheck@mail.usf.edu
pH/carbonate	Courtney Tierney	USF	chtierne@eckerd.edu
Spectral absorption and reflectance, pigments	Yingjun Zhang	USF	yingjunzhang@mail.usf.edu
Spectral absorption and reflectance, pigments	Shuangling Chen	USF	shuangling@mail.usf.edu
Spectral absorption and reflectance, pigments	Jennifer Cannizzaro	USF	jpatch@mail.usf.edu
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Plankton ecology	Mrunmayee Pathare	ULL	mgp1539@louisiana.edu
Pteropods	Lucio Lomán	Ecosur	lucioloman@gmail.com
Ichthyoplankton	Jesús Cano Compairé	CICESE	jcanocompaire@cicese.mx
Cuban National Observer	Alain Muñoz	CEAC	alainmunozcaravaca1970@gmail.com
Cuban National Observer	Jorge Luis Viamontes	GEOCUBA	vivian@geocuba.cu

2. Cruise Narrative

2.1. Summary

This report describes the third Gulf of Mexico Ecosystems and Carbon Cycle (GOMECC-3) cruise on board the R/V *Ronald H. Brown* from Key West, FL into the Gulf of Mexico and then around the coastal waters of the Gulf of Mexico in a counter-clockwise direction. The cruise took place from July 18–August 21, 2017. The effort was in support of the coastal monitoring and research objectives of NOAA'S Ocean Acidification Program. The cruise was designed to obtain a snapshot of key carbon, physical, and biogeochemical parameters as they relate to ocean acidification (OA) in the coastal realm. This was the third occupation of the Gulf of Mexico as part of the Ocean Acidification Program's monitoring efforts, with the first two occurring in 2007 and 2012, respectively.

The cruise included a series of 11 transects approximately orthogonal to the coast of the Gulf of Mexico and a 12th transect along the 27°N line, between Florida and the Bahamas, as well as a comprehensive set of underway measurements along the entire cruise track (Figure 1). In addition to these transects, three more stations were sampled as part of a collaboration with the National Park Service to monitor ocean acidification at national parks. Four parks participated in this effort: Padre Island (in Texas), Dry Tortugas, Everglades, and Biscayne (these three in Florida).

CTD/DO/LADCP/transmissometer/rosette stations were occupied at 107 specified locations. Bio-optical casts were performed once per day when the skies were clear and the ship was on station near the time of an ocean color satellite pass of the area. Underway measurements of shipboard surface acoustic Doppler current profiler (SADCP), partial pressure of carbon dioxide (pCO_2), pH, dissolved oxygen (DO), total alkalinity (TA), dissolved inorganic carbon (DIC), temperature, and salinity were performed. During the transit times from line to line, underway discrete samples for DIC, pCO_2, TA, pH, carbonates, nutrients, and dissolved oxygen (DO) were taken every 2/3 hours.

A total of 24 scientists from NOAA's AOML and multiple other universities and institutions participated in the 35-day cruise. Water samples were collected from the 24-bottle rosette at each station and analyzed for salinity, oxygen, nutrients, DIC, TA, pCO_2, pH, carbonates, chlorophyll, eukaryote plankton (<200 µm), colored dissolved organic matter (CDOM), and pigments. Automated underway systems were in operation for measuring atmospheric CO_2 and near-surface water pCO_2, DIC, pH, oxygen, and bio-optical properties.

The general GOMECC-3 cruise track followed the coast of the Gulf of Mexico going in a counterclockwise fashion. Each of the lines (transects) started as close as possible to the shore and ended at a deep station considered representative of oceanic conditions ("open ocean") (Figure 1).
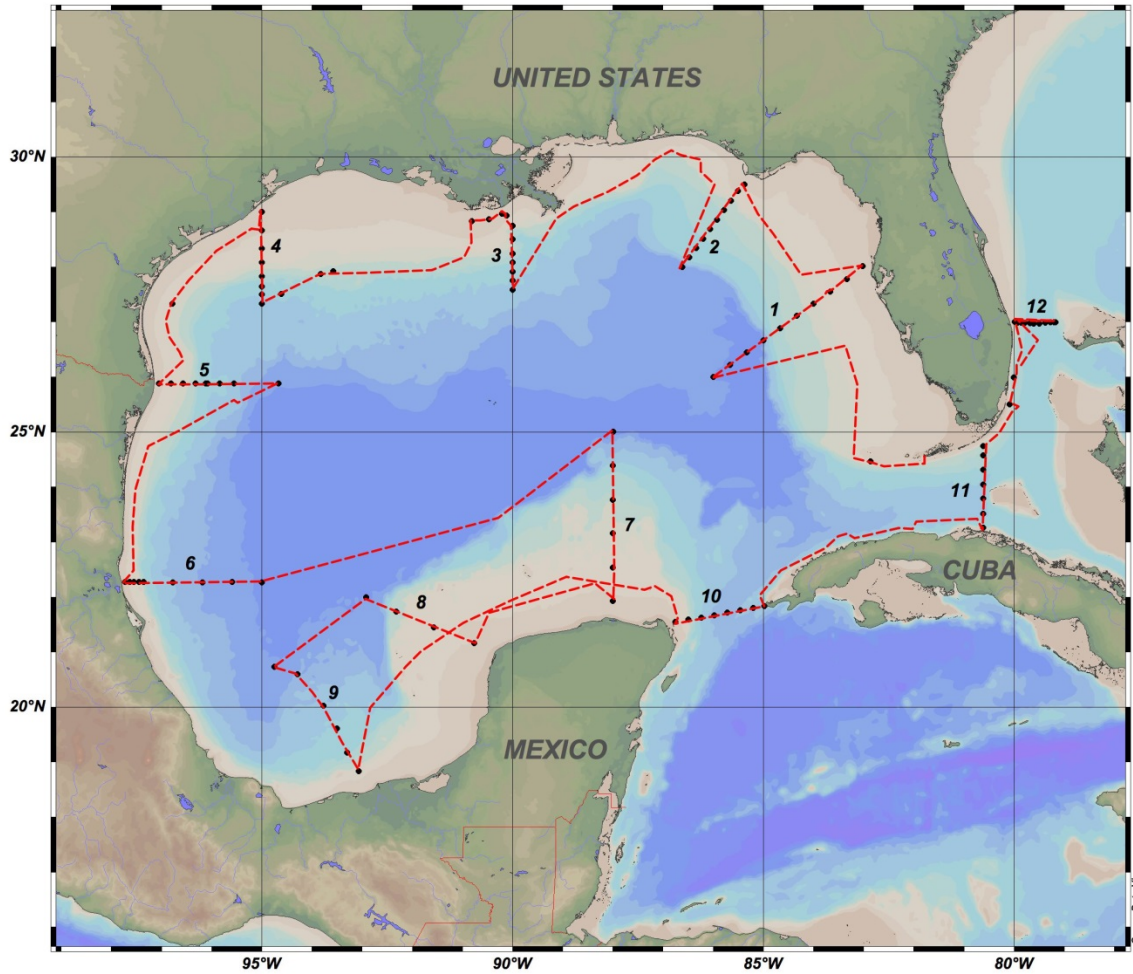
Figure 1: Cruise track (red line) and CTD station locations (black dots) visited during the GOMECC-3 cruise. The numbers identify the different transects: 1) Tampa Line, 2) Panama City Line, 3) Louisiana Line, 4) Galveston Line, 5) Brownsville Line, 6) Tampico Line, 7) Yucatan Line, 8) Veracruz Line, 9) Campeche Line, 10) Cancun Line, 11) Florida Straits Line, and 12) 27°N Line.

On all shallow stations, and depending on the strength of the local currents, the CTD/rosette was deployed to within 5-8 m of the bottom. On deep stations (1500 m depths or more), the CTD was deployed to within 10 m of the bottom. On multiple stations, several Niskin-style Bullister bottles were tripped at the chlorophyll maximum depth and at the surface in order to accommodate the water needs of the phytoplankton group and the assessment of pigments and CDOM absorptions by Dr. Hu's group. Approximately once per day, if the weather and timing were conducive to sampling, a bio-optical cast (at 14 stations in total) was performed from the aft deck. Water samples from the rosette/CTD package were collected in up to 24 11 L-Bullister bottles at all stations, providing water samples for DO, total DIC, pH, pCO$_2$, TA, nutrients, salinity, CDOM, chlorophyll-a, HPLC, and plankton community composition. Underway surface pCO$_2$, temperature, salinity, DO, multi-beam bathymetry, and meteorological measurements were collected, as well as a suite of biochemical samples for subsequent analysis.

On July 27, we performed an unscheduled stop next to the coastal Louisiana buoy located at 28.9°N, 90.5°W equipped with a pCO$_2$ system maintained by Dr. S. Howden of the University of Southern Mississippi and Dr. A. Sutton of NOAA's PMEL (https://www.pmel.noaa.gov/co2/story/Coastal+LA). This buoy is partially maintained with funds provided by NOAA's Ocean Acidification Program. We used the ship's small boat to get as close to the buoy as practical to take samples and then stayed on site for 4 hours in order to get additional calibration samples (Figure 2).
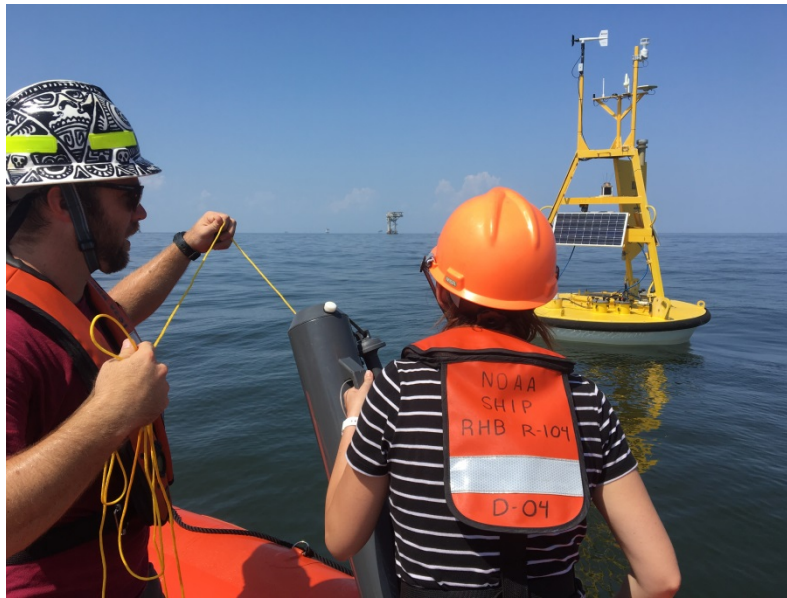
Figure 2: Water collection at a coastal LA buoy site during GOMECC-3 for data calibration.

At station 34, located in the Flower Garden Banks National Marine Sanctuary, we performed a diel station. We stayed on site for approximately 32 hours, during which time we performed eight CTD casts and four bongo net tows in order to capture diurnal variations on the physical, chemical and biological characteristics of the sanctuary.

The passage of Hurricane Franklin through the Gulf of Mexico forced a deviation from our initial cruise track (shown in Figure 3a). After finishing station 63 on Line 6 (Tampico Line), we were forced to sail eastwards at full steam for about 36 hours and wait. We arrived at 25.00°N, 88.00°W (station 64) and designed a remediation strategy consisting of reducing the number of stations in Line 7 from 9 to 6, adding a new, short line with 4 stations starting off the western tip of the Yucatan Peninsula (Line 8) and then returning west to reoccupy the line in the Bay of Campeche (Line 9, Veracruz Line). Transit speed between lines was increased from 7.5 knots to 11-12 knots. Discrete underway sampling frequency was increased from 3 to 2 hours to try to maintain the geographical spacing of the samples despite the change in cruise speed. Overall, as a result of the storm and our forced deviation from track, we lost the underway sampling of the coastal area of the Bay of Campeche, but we increased the total number of stations from 106 to 107 and increased the number of discrete underway sampling. The selected remediation strategy also allowed us to better sample the coastal area of the Yucatan Peninsula and get data before/after the passage of the storm.

No loss of operational time was experienced due to failure of the science equipment or ship's performance. The cruise objectives, as described in the project instructions (downloadable from http://www.aoml.noaa.gov/ocd/gcc/GOMECC3/) and detailed below, were achieved. Modifications to the cruise track as a result of the passage of Hurricane Franklin were satisfactory for the purpose of the cruise objectives.

2.2. Issues/Goals not Achieved

The following issues impacted operations during the cruise:

1. As indicated above, Hurricane Franklin formed in the Caribbean Sea on Sunday, August 6, 2017. We were advised that Hurricane Franklin was predicted to enter the Gulf of Mexico and would move through the Bay of Campeche at the same time as we were intending to work in the area. Figure 3a shows our position on Sunday August 6, when the decision was made to deviate from our planned track, as well as what would have been our expected time at different stations in the path of the hurricane had we not deviated. Figure 3b shows the anticipated path of the hurricane as predicted by the National Hurricane Center on Monday, August 7. At the time, we were finishing Line 6 (station 63). Based on the information available, the captain made the call for the cruise to deviate from its schedule and head northeast at top speed to reach the waters north of the Yucatan Peninsula before the hurricane arrived and then wait for it to pass. In order to recover as many of the initial stations planned as possible, while remaining in the wake of the hurricane, the following impacts/adjustments were made:

   a. Steam at top speed for approximately 36 hours from the last station in Line 6, at 22.27°N, 95°W (Figure 3a), to 25°N, 88°W (which became our first station in Line 7) and wait there for the storm to pass, then work in its wake.

   b. Loss of the surface underway sampling of the southwestern coastal region of the Gulf of Mexico (Bay of Campeche) between Line 6 and Line 9.

   c. The number of stations in Line 7 was reduced from 9 to 6 stations. However, the stations were spaced so that the 6 stations continued to cover the nearshore to open-ocean end members.

   d. A new, short line with four stations was added at the western tip of the Yucatan Peninsula to study the east-west carbonate trends along the Yucatan Peninsula.

   e. Transit speed increased from 7.5 kt to 11-12 kt between lines and increased in the underway discrete sampling frequency from 3 to 2 hours, to maintain geographical spacing between underway samples, recover time and to be able to return to Line 9 and sample those stations as initially planned.
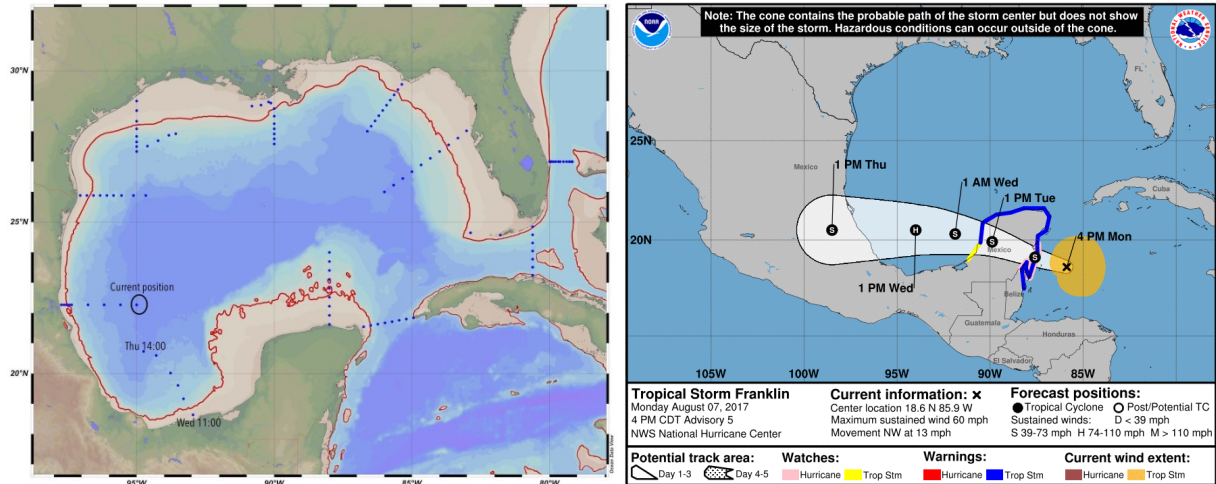
Figure 3: a) Planned stations before Franklin. b) Hurricane Franklin storm track (Credit NHC/NOAA).

2. The aft winch malfunctioned on the first station of the cruise. The readings on all the sensors in the CTD were all spiking at the same time, indicating some kind of issue with the communications cable. The CTD had to be connected to the forward winch, and cables had to be re-terminated. Overall 4 hours were lost, which were recovered quickly, putting us back on schedule. The bongo nets, which did not need a communications cable, were hooked to the aft winch and bongo deployments were done using that winch. However, as we were working on the deep station from Line 4 (station 37), the aft winch malfunctioned again, becoming non-operational. The initial evaluation of the survey tech on duty was that no more net tows would be possible for the remainder of the cruise. After evaluating options with the captain and the chief bosun, a temporary deployment system was set up using the A-Frame. This enabled net tows to continue to be performed while the engineers worked on fixing the aft winch. Overall, the winch was out of order for 2 days. On Line 4, the deep and mid-depth stations that were planned for bongo net tows were lost. To compensate, the four shallowest stations were sampled.

2.3. Communication and Outreach Activities

A number of communication and outreach activities were performed during GOMECC-3. Tweets, Facebook, and Instagram posts used the hashtags #GOMECC3, and #GulfOA. Additional recommended hashtags were used: #CO2, #oceanacidification, #ourchangingocean, #coastalacidification, #highCO2world, and #ourocean. A blog was created for the cruise with entries describing life on board, as well as explaining what we were doing and measuring: https://gomecc3.wordpress.com/. As of this version of the cruise report, the blog has had over 9000 visits. One of the cruise participants, Gabrielle Corradino, was awarded a National Geographic Explorer fellowship. As part of the award, her work during the cruise will be showcased on National Geographic's website (https://www.nationalgeographic.org/find-explorers/7C8EB2D2/gabrielle-l-corradino).
Different institutions involved in the cruise made communications and notes about the cruise, and GOMECC-3 appeared on different websites and news outlets, including

written media in Mexico and Spain. For a full list of links, please check https://www.aoml.noaa.gov/ocd/gcc/GOMECC3/.

2.4. Acknowledgments

3. Description of Measurements from Vertical Profiles

3.1. CTD/Hydrographic Measurements

Analysts: James Hooper (AOML/CIMAS), Andrew Stefanick (AOML/NOAA)
PI: Molly Baringer (AOML/NOAA)

The basic CTD measurements consisted of pressure, temperature, salinity, dissolved oxygen, and optical transmissometry (for determining the chlorophyll maximum) from CTD profiles (Table 3). A total of 114 CTD/rosette casts were made at 107 stations, usually to within 10 m of the bottom. Several shallow coastal stations were within 5 m of the bottom. Station 34 had eight repeat casts over 36 hours.

3.1.1. CTD Electronics and Water Sampling Package

CTD/rosette casts were performed with a package consisting of a 24-place, 11-liter rosette frame (AOML's pink frame), a 24-place water sampler (SBE32), and 24, 11-liter Bullister-style bottles. This package was deployed on all stations/casts. Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9 plus CTD with dual pumps and the following sensors: dual temperature (SBE3), dual conductivity (SBE4), dual dissolved oxygen (SBE43), reference temperature (SBE35), a Wet Labs CSTAR transmissometer, and a Valeport VA500 altimeter. The package also included two (an upward facing and a downward facing) TRDI 300 kHz, self-contained, lowered acoustic Doppler profilers (LADCP) (Table 3).

The CTDs supplied a standard Sea-Bird format data stream at a data rate of 24 frames/second. The SBE9 plus CTD was connected to the SBE32 24-place pylon, providing for single-conductor sea cable operation. Power to the SBE 9 plus CTD, SBE32 pylon, auxiliary sensors, and altimeter was provided through the sea cable from the SBE 911plus deck unit in the computer lab. The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable.

The CTD was mounted vertically attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3 temperature sensors and their respective pumps were mounted vertically as recommended by SBE outboard of the CTD. Primary temperature, conductivity, and dissolved oxygen were plumbed on one pump circuit and secondary temperature, conductivity, and dissolved oxygen on the other. Pump exhausts were attached to outside corners of the CTD cage and directed downward. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring. The LADCPs were vertically mounted inside the bottle rings with one 300 kHz pointing down, the other 300 kHz transducer pointing up. The ship's forward CTD winch was used with the 24-place, 11-liter rosette for all station/casts, except for station 1. Several modulo errors occurred in the first few hundred meters of station 2. The cast was aborted, and the CTD package was switched to the forward winch.

The deck watch prepared the rosette 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. The CTD was powered-up and the data acquisition system started. The CTD package was put in the water and taken down 10 m for 2-3 minutes to remove any air bubbles from the sensor lines and to make sure the sensors were behaving appropriately. After recovery of the CTD package on deck, it was brought into the staging bay for sampling at all stations except the last one. The bottles and rosette were examined before samples were taken, and anything unusual was noted on the sample log.

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

System Problems

There was spiking across all sensory channels during the downcast in the first few hundred meters of station 2. The cast was aborted, and the CTD package was switched from the aft winch to the forward winch and the problem was resolved.

Table 3: Equipment used during GOMECC-3.

Instrument	Stations	S/N	Use	Other
Sea-Bird SBE 32 24-place Carousel Water Sampler	1-107	32-1079		
Sea-Bird SBE9plus CTD	1-107	1292		
Paroscientific Digiquartz Pressure Sensor	1-107	136924		
Sea-Bird SBE3plus Temperature Sensor	1-107	4799	Primary	
Sea-Bird SBE3plus Temperature Sensor	1-107	5855	Secondary	
Sea-Bird SBE33 Reference Temperature Sensor	1-107	97		
Sea-Bird SBE4C Conductivity Sensor	1-107	4346	Primary	
Sea-Bird SBE4C Conductivity Sensor	1-107	3861	Secondary	
Sea-Bird SBE43 Dissolved Oxygen Sensor	1-107	2082	Primary	
Sea-Bird SBE43 Dissolved Oxygen Sensor	1-107	1348	Secondary	
Sea-Bird SBE5T Pump	1-107	7267	Primary	
Sea-Bird SBE5T Pump	1-107	7889	Secondary	
Valeport VA500	1-107	48591		Scale 15 Range 100
Transmissometer CSTAR	1-107	339DR		
RDI LADCP - 300 kHz Workhorse (AOML)	1-107	24472	Upward	
RDI LADCP - 300 kHz Workhorse (AOML)	1-107	1856	Downward	

3.1.2. Real-Time CTD Data Acquisition System

The CTD data acquisition system consisted of an SBE-11plus (V2) deck unit and a networked generic PC workstation running Windows located in the computer room. SBE Seasave software version 7.23.2 was used for data acquisition and to close bottles on the rosette.

The deck watch prepared the rosette typically after sampling the previous cast. All valves, vents, and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Fifteen minutes or so prior to station, the deck unit was powered on and an on-deck pre-cast pressure was obtained.

Once on station, the syringes were removed from the CTD sensor intake ports. Tag lines were necessary for deployments during this cruise, and an air tugger was used during recoveries for positioning the CTD on the platform. As soon as it was in the water, the CTD deck unit was powered on and the data acquisition system started. As directed by the deck watch leader, the CTD was taken down to 10 m for 2 minutes to remove any air bubbles from the sensor lines and to make sure the sensors were behaving appropriately. The CTD was brought back to just below the surface with the console operator hitting "Mark Scan" before beginning the descent. The profiling rate was no more than 30 m/min to 50 m, 45 m/min to 200 m, and no more than 60 m/min deeper than 200 m. Upon recovery, the CTD deck unit was turned off on deck. The rosette was brought inside the staging bay for sampling. The bottles and rosette were examined before samples were taken and anything unusual noted on the sample log.

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

On the up cast, the winch operator was directed to stop at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle using a "point and click" graphical trip button and 8 seconds after to allow the reference temperature sensor to sample. The data acquisition system responded with trip confirmation messages and the corresponding CTD data in a rosette bottle trip window on the display. All tripping attempts were noted on the console log. The console watch then directed the winch operator to raise the package up to the next bottle trip location. After the last bottle was tripped, the console watch directed the deck watch to bring the rosette on deck.

3.1.3. Shipboard CTD Data Processing

Shipboard CTD data processing was performed automatically at the end of each deployment using SEABIRD SBE Data Processing version 7.25.0.319 and AOML Matlab processing software. The raw CTD data and bottle trips acquired by SBE Seasave on the Windows workstation were copied onto the CTD processing laptop and processed

to a 1-dbar series and a 1-second time series. Bottle trip values were extracted, and a 1-decibar (dbar) down cast pressure series created. The Sea-Bird Data Processing for primary calibrated data (1 dbar averages) uses the following routines in order:

- DATCNV - converts raw data into engineering units and creates a .ROS bottle file. Both down and up casts were processed for scan, elapsed time(s), depth, pressure, t0 ITS-90 C, t1 ITS-90 C, c0 S/m, c1 S/m, salinity (PSU), salinity2 (PSU), oxygen voltage V, oxygen 2 voltage V, altimeter, oxygen μmol/kg, oxygen2 μmol/kg, oxygen ml/l, oxygen2 ml/l, oxygen dv/dt, oxygen dv/dt2, potential temperature, potential2 temperature, sigma-theta, sigma-theta2, latitude, longitude, and Voltage channel 6 (transmissometer). The scan range offset is 0 seconds, and the scan range duration is 5.5 seconds. MARKSCAN was used to determine the number of scans acquired on deck and while priming the system to exclude these scans from processing.

- ALIGNCTD - aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary and secondary conductivity are automatically advanced by 0.073 seconds and both oxygen measurements are advanced by an additional 1.073 seconds.

- BOTTLESUM - creates 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 5.5 second interval.

- WILDEDIT - computes the standard deviation of 100 point bins and then makes two passes through the data. The first pass flags points that differ from the mean by more than 2 standard deviations. A new standard deviation is computed excluding the flagged points, and the second pass marks bad values greater than 20 standard deviations from the mean. For this data set, data were kept within a distance of 100 of the mean (i.e., all data).

- FILTER - applies a low pass filter to pressure with a time constant of 0.15 seconds. In order to produce zero phase (no time shift), the filter is first run forward through the file and then run backwards through the file.

- 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.

- LOOPEDIT - removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m/s or the pressure is not greater than the previous maximum scan, the scan is omitted.

- DERIVE - uses 1 dbar averaged pressure, temperature, and conductivity to compute primary and secondary salinities.

- 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 the computed oxygen variable.

- TRANS - converts the binary data file into ASCII format.

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

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

Final calibrations are applied to de-looped data files. ITS-90 temperature, salinity, and oxygen are computed, and WOCE quality flags are created.

CTD data were examined at the completion of each deployment for clean corrected sensor response and any calibration shifts. As bottle salinity and oxygen results became available, they were used to refine shipboard conductivity and oxygen sensor calibrations. A total of 114 casts were processed.

3.1.4. CTD Calibration Procedures

Laboratory calibrations of the CTD pressure, temperature, and conductivity sensors were all performed at SBE. Secondary temperature, conductivity, and dissolved oxygen (T2, C2, and DO2) sensors served as calibration checks for the reported primary sensors. In-situ salinity and dissolved O_2 check samples collected during each cast were used to calibrate the conductivity and dissolved O_2 sensors. A reference temperature sensor was used to calibrate the temperature sensor. Sensors used during the cruise are listed in Table 3.

3.1.5. CTD Pressure

Pressure sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw pressure data during each cast. Residual pressure offsets between the first and last near surface pressures and before and after on deck pressures were examined to check for calibration shifts (see Table 4 and Figure 4). Pressure sensor s/n 1292 was used for the entirety of the cruise with an initial pressure offset of 0.47 dbar applied to the configuration file for a total offset of -0.3. On deck pressure before and after the cast was stable at -0.04 ± 0.03 dbar and -0.03 ± 0.07 dbar, respectively. Near surface pressure values at the start and end of the cast were stable at 3.02 ± 0.63 dbar and 3.02 ± 0.53 dbar, respectively.

Table 4. Near surface pressure values and scan number used to remove surface soak and on-deck values.

Station Number	Cast	Mark Scan	Start Pressure	End Pressure	Start Sfc Btl Prs	End Sfc Btl Prs
1	1	24661	0.038	0.026	2.78	2.915
2	2	16002	0.06	-0.23	2.73	2.483
3	1	22263	-0.05	-0.3	2.57	2.126
4	1	11296	-0.06	-0.3	3.67	2.729
5	1	10427	0.03	-0.2	2.07	1.852
6	1	9672	-0.036	0.06	3.44	3.463
7	1	9174	-0.041	0.02	3.04	3.138
8	1	17305	-0.04	0.06	3	2.847
9	1	8565	0.038	-0.03	3.23	2.672
10	1	9993	0	0.2	2.58	2.514
11	1	11940	0.04	0.01	2.11	2.119
12	1	28256	-0.05	-0.08	2.78	3.036
13	1	11667	0.01	-0.01	3.53	3.435
14	1	14890	-0.02	-0.02	3.53	3.622
15	1	15481	-0.05	0.02	3.74	3.158
16	1	12913	-0.03	0.01	3.67	3.84
17	1	26853	-0.05	0.03	3.58	3.503
18	1	7792	-0.05	-0.01	2.89	2.999
19	1	9987	-0.03	0	2.58	2.78
20	1	14604	-0.04	0.02	2.31	2.928
21	1	24803	-0.05	-0.015	2.5	3.304
22	1	6835	0.03	-0.05	3.73	3.471
23	1	18225	-0.05	0.03	3.77	3.574
24	1	15895	-0.03	-0.02	3.3	3.603
25	1	9483	-0.02	0.04	2.08	2.713
26	1	16196	-0.05	0.02	2.6	2.473
27	1	19396	-0.05	0	2.6	2.305
28	1	20756	0.01	-0.01	2.31	2.73
29	1	15392	-0.05	-0.03	2.47	3.271
30	1	13709	-0.03	-0.05	3.41	3.416
31	1	9654	-0.05	-0.03	3.49	3.645
32	1	18769	-0.02	-0.04	3.52	3.372
33	1	32634	-0.03	-0.03	3.57	2.352
34	1	8281	-0.04	-0.07	2.57	2.954
34	2	210404	-0.01	-0.08	2.41	2.769
34	3	14371	-0.01	-0.03	3.31	3.606
34	4	14698	-0.01	-0.05	3.28	3.476
34	5	20521	-0.04	-0.05	3.19	3.431
34	6	13653	-0.05	-0.06	2.57	2.679
34	7	15132	-0.04	-0.09	2.9	2.153
34	8	17757	-0.05	-0.07	2.68	2.187
35	1	26005	-0.04	-0.05	3.52	3.452
36	1	19703	-0.06	-0.03	3.54	3.079
37	1	17168	-0.09	-0.05	3.53	3.135
38	1	12761	-0.04	-0.05	2.67	2.243
39	1	10405	-0.1	-0.06	2.84	2.668
40	1	23151	-0.08	-0.07	2.47	2.449
41	1	21149	-0.02	-0.08	2.08	2.012
42	1	22242	0.03	-0.06	3.77	3.425
43	1	15526	-0.025	-0.08	3.83	3.827
44	1	17531	-0.07	-0.045	3.67	3.696
45	1	21941	-0.07	-0.04	3.52	3.458
46	1	24880	-0.05	-0.05	2.03	2.016
47	1	21661	-0.04	-0.06	2.23	2.147
48	1	21086	-0.03	-0.04	3.68	3.384
49	1	14232	-0.02	0.03	3.63	3.186
50	1	12356	-0.05	-0.06	3.48	3.731
51	1	17399	-0.05	-0.02	3.76	3.624

Table 4. Near surface pressure values and scan number used to remove surface soak and on-deck values.

Station Number	Cast	Mark Scan	Start Pressure	End Pressure	Start Sfc Btl Prs	End Sfc Btl Prs
52	1	18832	-0.03	-0.07	2.25	2.61
53	1	10457	-0.05	-0.02	2.56	2.637
54	1	16891	-0.02	-0.15	2.55	3.167
55	1	20734	-0.03	-0.03	2.19	2.312
56	1	37681	-0.04	-0.004	1.95	2.058
57	1	20723	-0.06	0.006	2.08	2.005
58	1	25543	-0.003	-0.06	1.87	2.133
59	1	18426	-0.02	-0.04	3.63	3.522
60	1	15168	-0.05	-0.1	3.43	3.522
61	1	22538	-0.08	-0.15	2.14	2.178
62	1	19033	-0.04	-0.2	3.14	2.799
63	1	25696	-0.02	-0.22	3.3	3.47
64	1	23561	-0.08	-0.25	3	3.059
65	1	38618	-0.07	-0.009	3.52	4.185
66	1	34133	-0.04	-0.07	5.18	2.928
67	1	20488	-0.08	-0.13	3	3.622
68	1	22877	-0.07	0.001	2.94	3.262
69	1	8321	-0.03	0.02	3.31	3.241
70	1	27884	-0.04	-0.09	2.78	3.264
71	1	11170	0.02	-0.05	4.03	3.21
72	1	31646	-0.03	0.07	3.2	2.816
73	1	24737	0.01	-0.22	2.85	2.81
74	1	23820	-0.05	-0.15	4.36	3.721
75	1	17840	-0.05	-0.11	2.86	2.72
76	1	18223	0.002	-0.03	3.08	3.617
77	1	19212	-0.03	0.07	3.46	3.382
78	1	15101	-0.04	0.007	3.71	2.712
79	1	13825	-0.04	-0.04	3.59	2.318
80	1	23130	0.001	0.05	2.49	2.352
81	1	7249	-0.04	0.0025	2.53	2.9
82	1	21936	0.04	0.0256	2.71	2.709
83	1	33513	-0.07	-0.17	2.57	2.444
84	1	19234	-0.04	-0.1547	3.43	3.353
85	1	22018	-0.05	-0.06	3.5	3.459
86	1	9486	-0.07	-0.13	3.45	3.582
87	1	13157	-0.05	0.03	2.8	2.754
88	1	16012	0.0172	0.0005	3.47	3.475
89	1	21533	0.05	-0.0222	5.62	3.394
90	1	8441	-0.05	-0.01	2.78	2.443
91	1	28659	-0.05	-0.038	2.76	2.934
92	1	21863	-0.08	-0.07	2.57	2.895
93	1	30887	0.01	0.0491	3.6	3.866
94	1	15053	-0.01	0.05	3.47	3.568
95	1	20656	-0.05	0.0044	2.55	2.548
96	1	19643	-0.05	-0.007	3.61	3.292
97	1	15968	-0.04	-0.03	3.67	3.357
98	1	8325	0.08	0.01	3.58	3.498
99	1	12323	-0.07	0.06	3.58	3.598
100	1	9742	-0.02	-0.02	3.16	3.627
101	1	17760	-0.03	0.02	2.54	2.46
102	1	51196	-0.03	-0.03	2.7	2.611
103	1	12819	-0.05	-0.03	2.64	2.625
104	1	23914	-0.03	-0.06	2.39	2.543
105	1	15729	-0.06	-0.02	2.58	2.746
106	1	10665	0.008	-0.018	2.86	2.737
107	1	17574	0.02	0.04	3.49	3.512
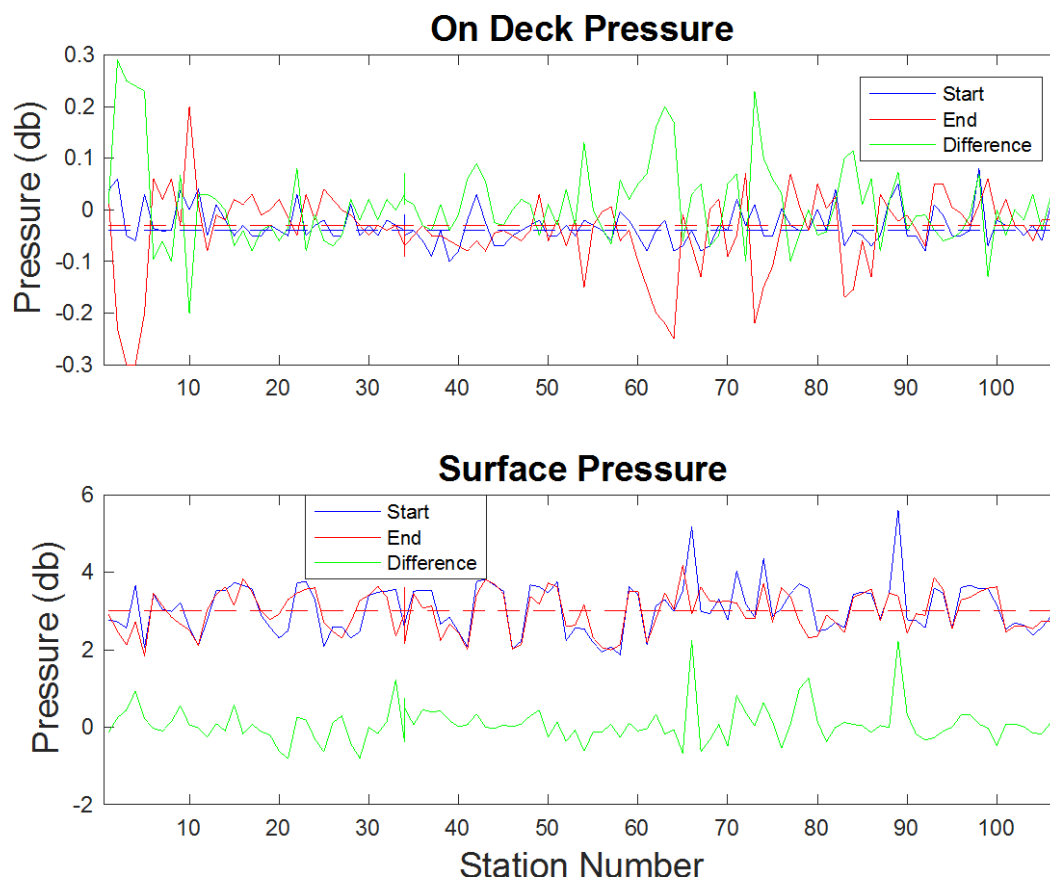
Figure 4: Near surface pressure values include on deck (top) and just below the surface (bottom) before and after each CTD cast.

3.1.6. *CTD Temperature*

Temperature sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary temperature data during each cast. Calibration accuracy was examined by comparing T1-T2 over a range of station numbers and pressures (bottle trip locations) for each cast. For the entire cruise, the same set of temperature sensors was used (Table 3). These comparisons are summarized in Figure 5, which shows a median temperature difference between the two sensors of 0.001°C and a standard deviation of 0.02°C (0.0015°C and a standard deviation of 0.0007°C below 1000 m).
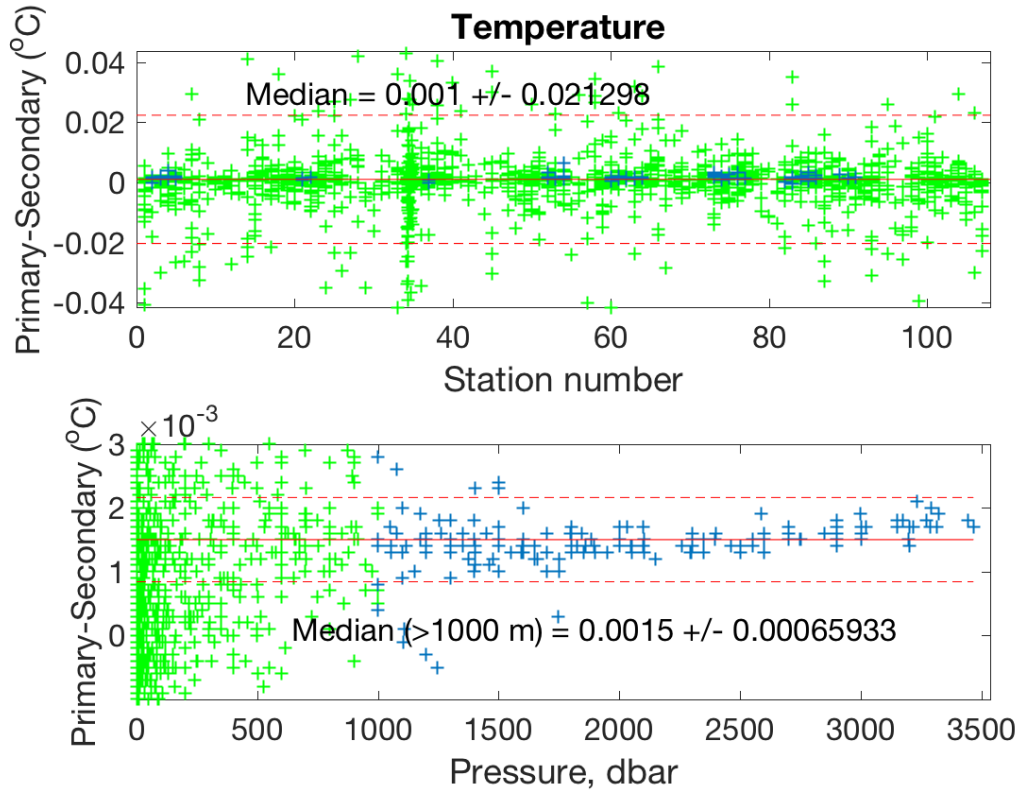
Figure 5:Uncalibrated temperature sensor differences between primary and secondary sensors.

A SBE 35RT reference temperature was used during the cruise as a check to monitor the behavior of the primary and secondary temperature sensors. This allows for corrections to be made if there is any significant pressure dependence or offset seen in the sensors throughout the cruise. Both sensors were corrected for the pressure dependencies observed in Figure 6 and Figure 7. Both temperature sensors behaved well compared to the reference temperature. The primary median difference was -0.0004°C ± 0.002°C and the secondary was 0.0005°C ± 0.0019°C, with both sensors improving with smaller differences below 1000 m.
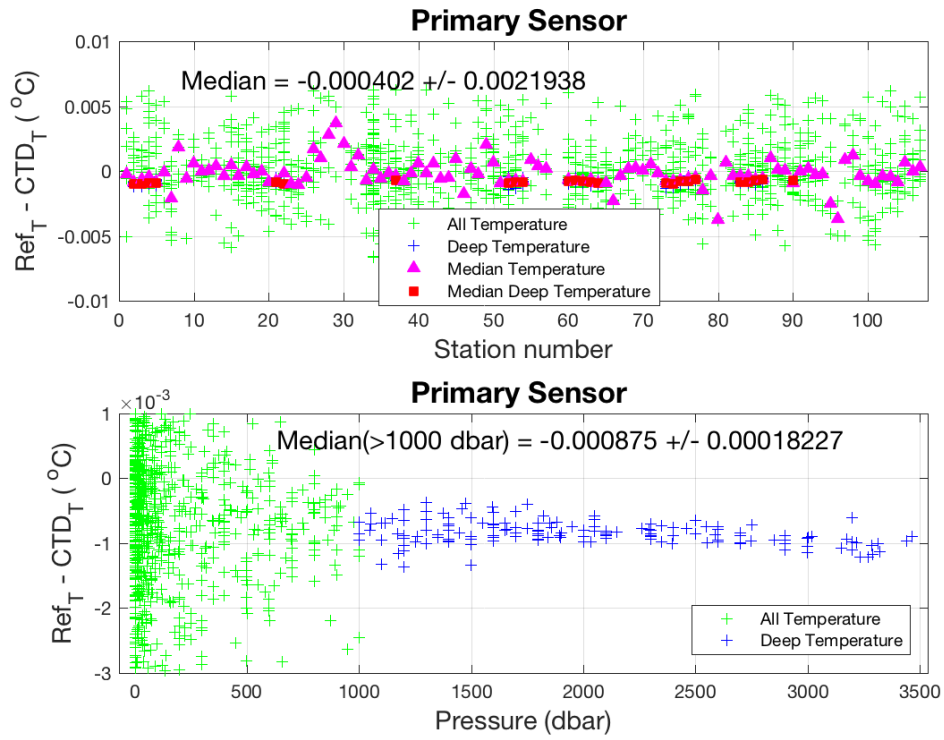
Figure 6: Uncalibrated temperature sensor differences between primary and reference temperature.
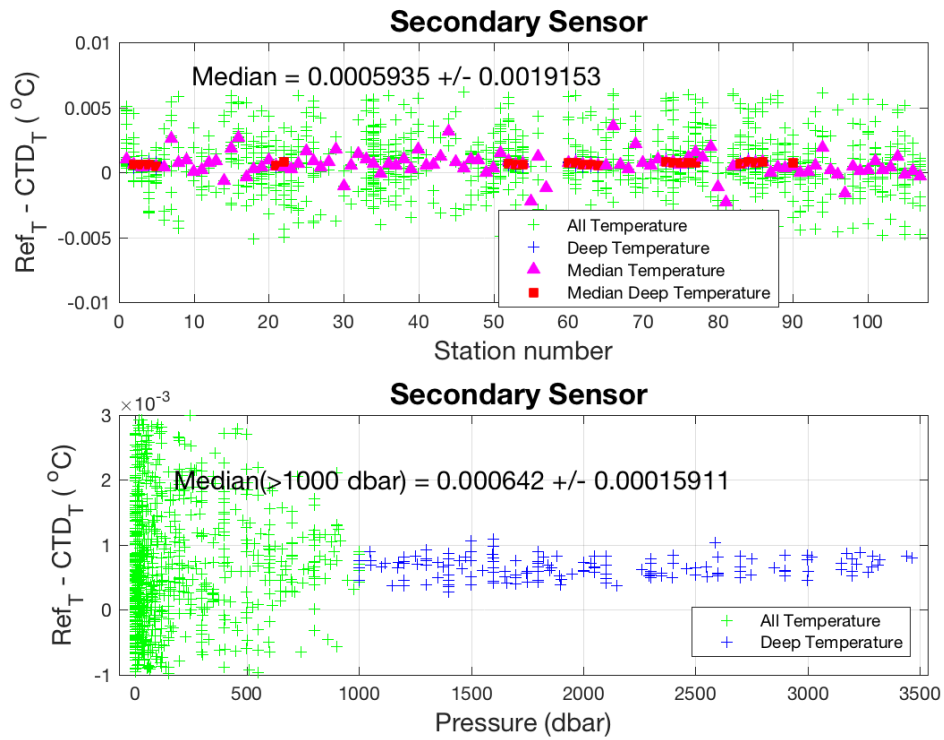
Figure 7: Uncalibrated temperature sensor differences between secondary and reference temperature.

3.1.7. CTD Conductivity

Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities. Comparisons between the primary and secondary sensors and between each of the sensors to check sample conductivities (conductivity calculated from bottle salinities) were used to derive conductivity corrections. Uncorrected C1-C2 are shown in Figure 8 to help identify sensor drift. For the entire cruise, the same set of conductivity sensors was used, no sensor needed replacement (Table 3), and both tracked each other extremely well. The two sensors show a median difference of -0.001 mS/cm and a standard deviation of 0.05 mS/cm (-0.001 mS/cm and a standard deviation of 0.0006 mS/cm below 1000 m).
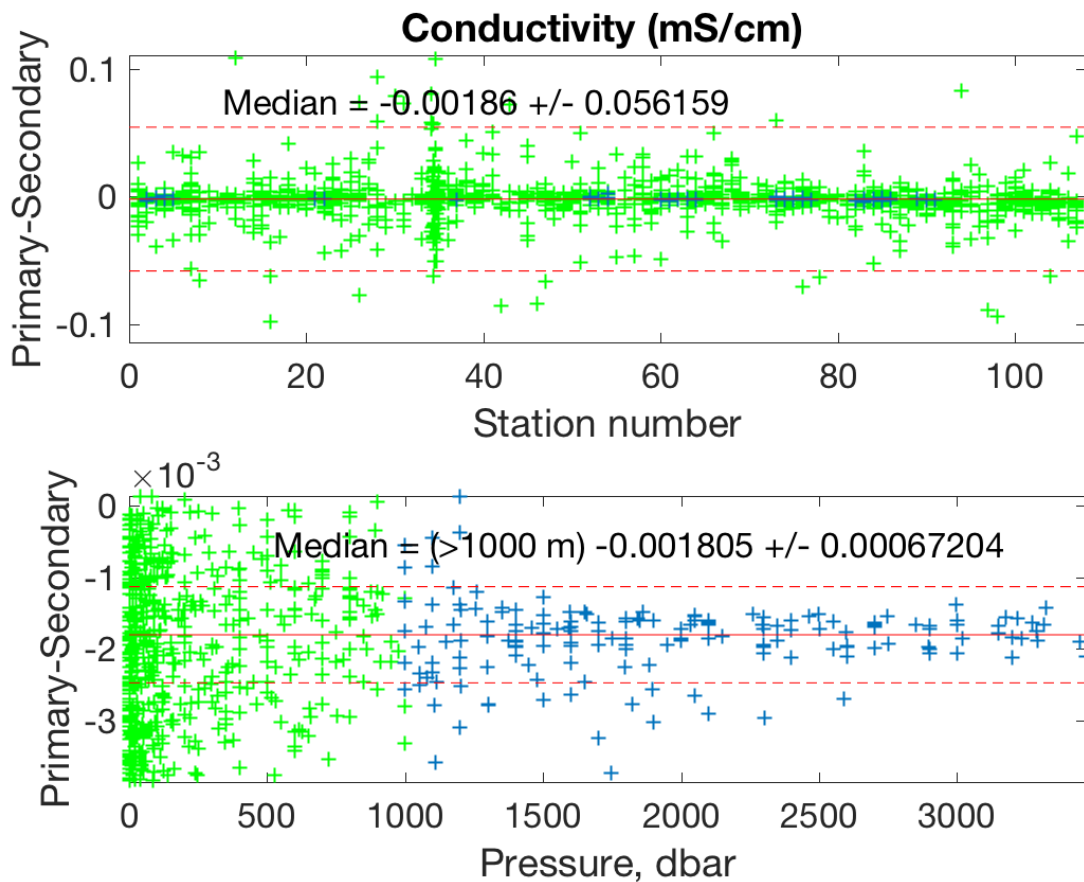
Figure 8: Uncalibrated conductivity differences between primary and secondary sensors.

3.1.8. CTD Dissolved Oxygen

Two SBE43 dissolved O_2 (DO) sensors were used on this cruise (Table 3). Both sensors tracked each other well (Figure 9). The sensors showed a median difference of 1.92 μmol/kg and a standard deviation of 0.66 μmol/kg (2.02 μmol/kg and a standard deviation of 0.32 μmol/kg below 1000 m).
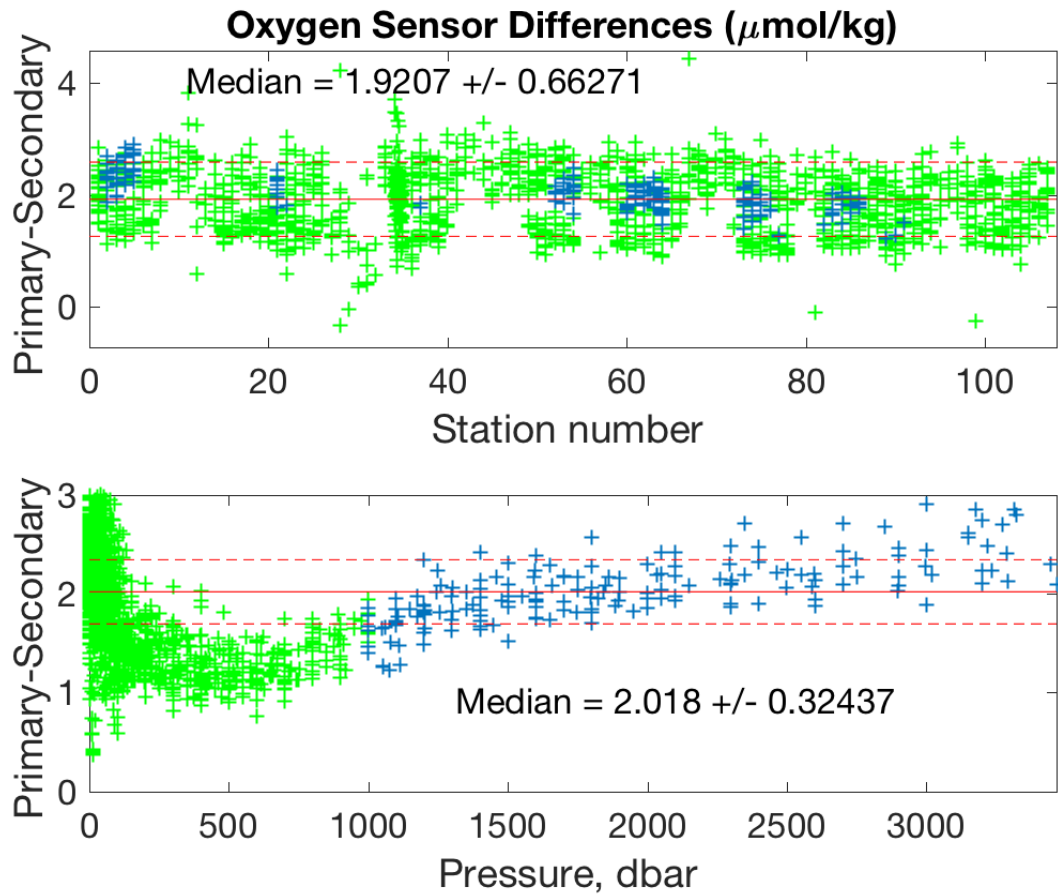
Figure 9: Uncalibrated oxygen differences between primary and secondary sensors.

3.1.9. Preliminary CTD Data Processing

Calibration of the CTD instrument was completed after a recalibration of the sensors at Seabird following the cruise. Primary uncalibrated data, as well as bottle trip depths for the main CTD lines, are shown in Figures 10 to 45.

Figure 10: Potential temperature along the Tampa Line. The black crosses represent the bottle trip depths.

Figure 11: Salinity along the Tampa Line. The black crosses represent the bottle trip depths.

Figure 12: Dissolved oxygen along the Tampa Line. The black crosses represent the bottle trip depths.

Figure 13: Potential temperature along the Panama City Line. The black crosses represent the bottle trip depths.

Figure 14: Salinity along the Panama City Line. The black crosses represent the bottle trip depths.

Figure 15: Dissolved oxygen along the Panama City Line. The black crosses represent the bottle trip depths.

Figure 16: Potential temperature along the Louisiana Line. The black crosses represent the bottle trip depths.

Figure 17: Salinity along the Louisiana Line. The black crosses represent the bottle trip depths.

Figure 18: Dissolved oxygen along the Louisiana Line. The black crosses represent the bottle trip depths.

Figure 19: Potential temperature along the Galveston Line. The black crosses represent the bottle trip depths.

Figure 20: Salinity along the Galveston Line. The black crosses represent the bottle trip depths.

Figure 21: Dissolved oxygen along the Galveston Line. The black crosses represent the bottle trip depths.

Figure 22: Potential temperature along the Brownesville Line. The black crosses represent the bottle trip depths.

Figure 23: Salinity along the Brownesville Line. The black crosses represent the bottle trip depths.

Figure 24: Dissolved oxygen along the Brownesville Line. The black crosses represent the bottle trip depths.
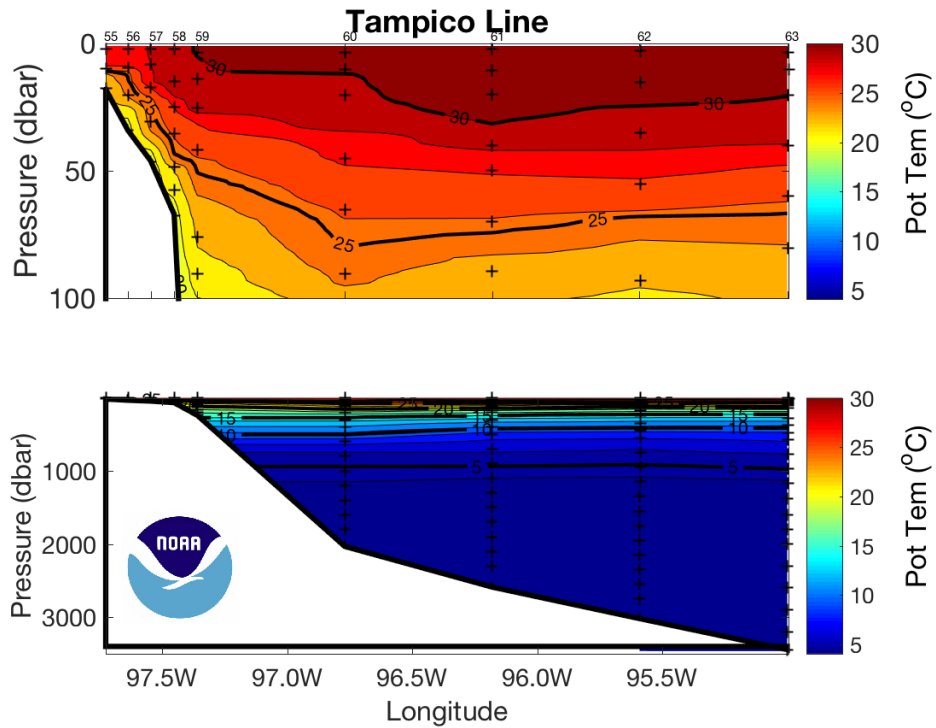
Figure 25: Potential temperature along the Tampico Line. The black crosses represent the bottle trip depths.
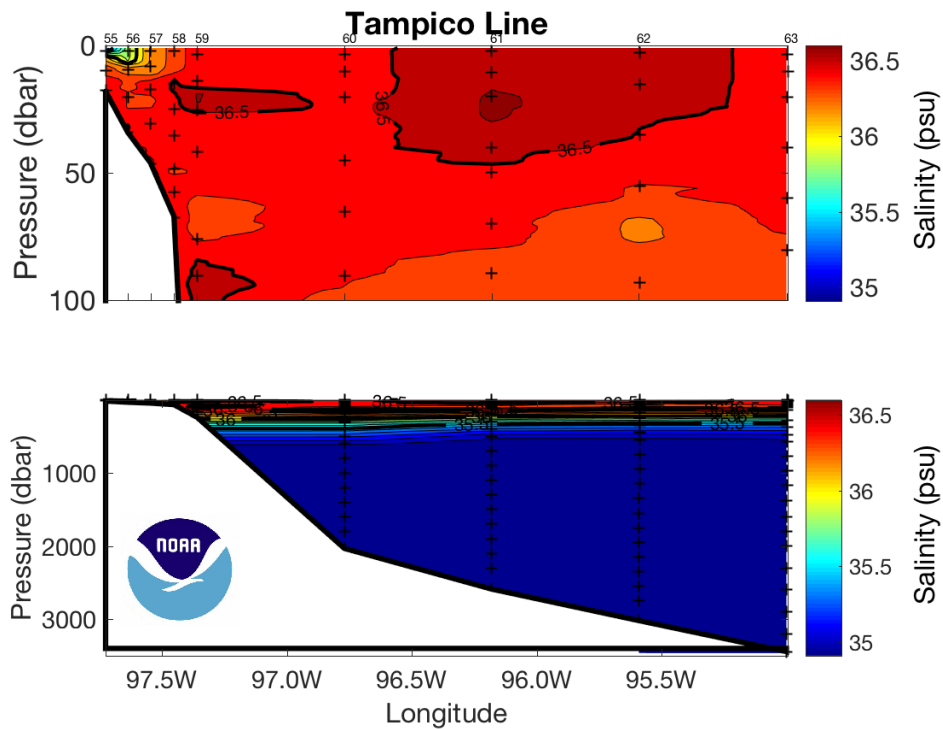
Figure 26: Salinity along the Tampico Line. The black crosses represent the bottle trip depths.
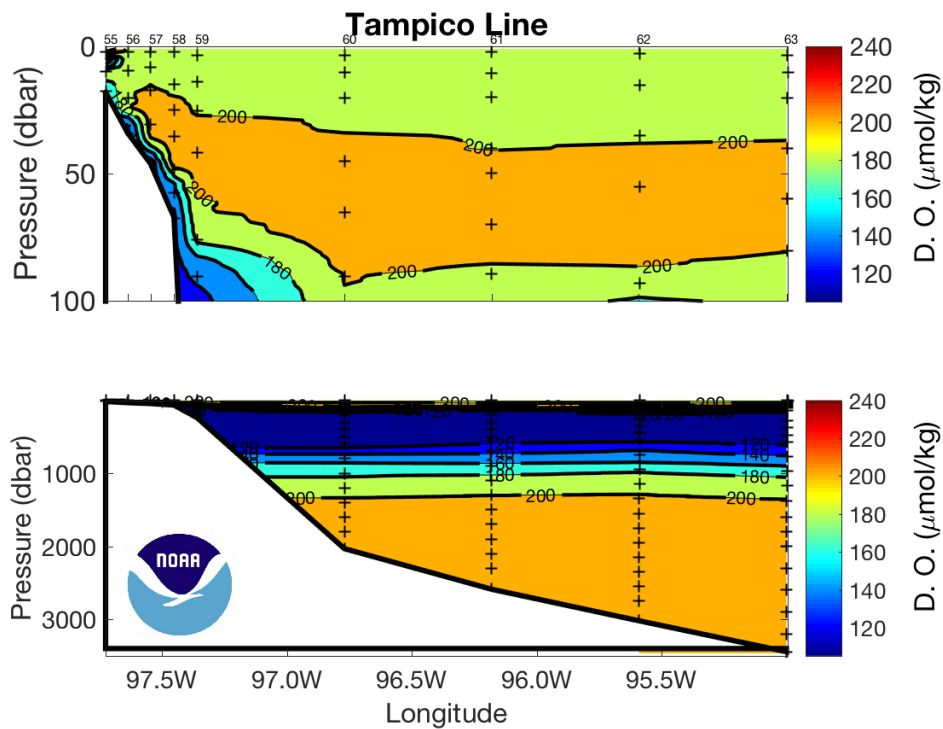
Figure 27: Dissolved oxygen along the Tampico Line. The black crosses represent the bottle trip depths.
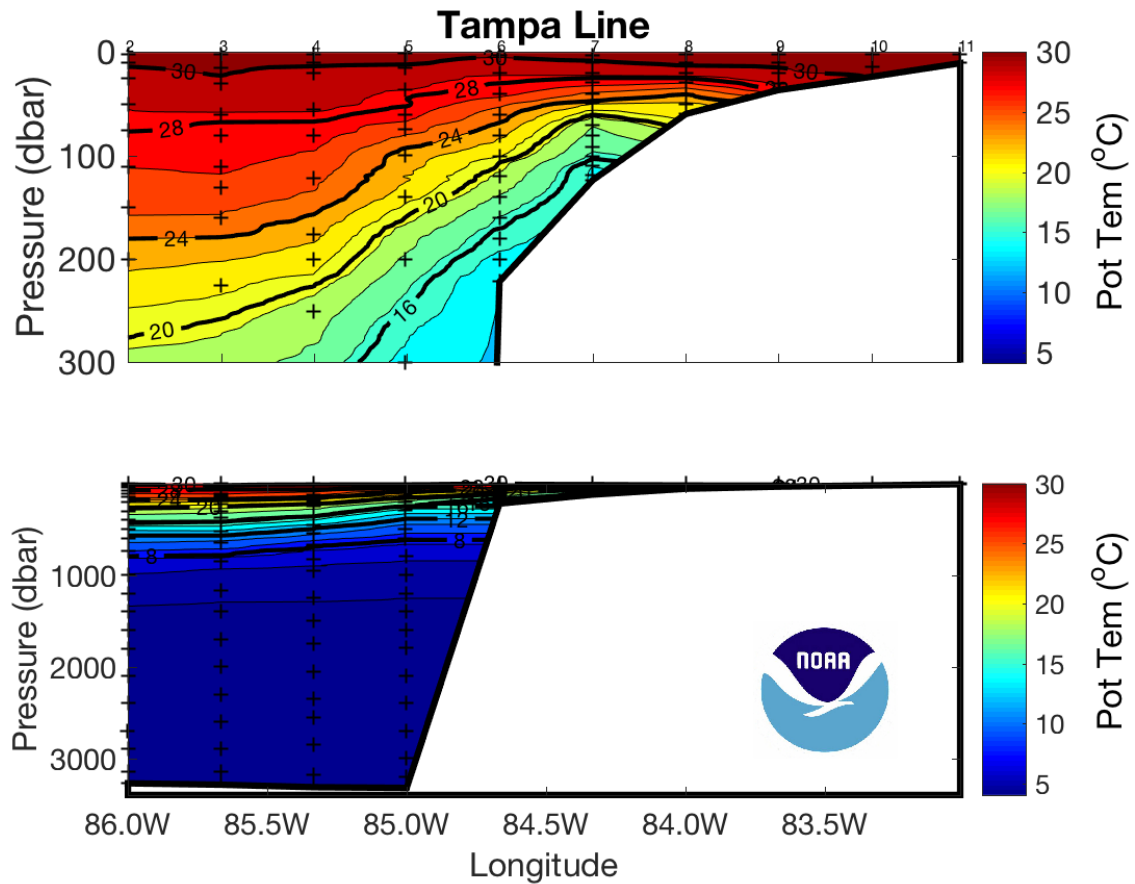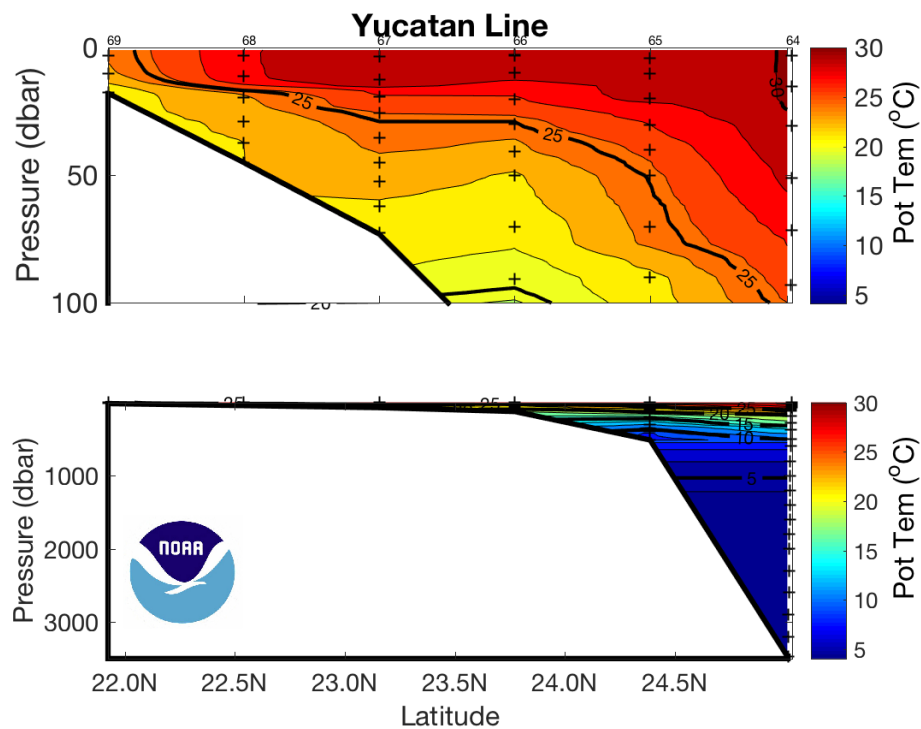

Figure 28: Potential temperature along the Yucatan Line. The black crosses represent the bottle trip depths.
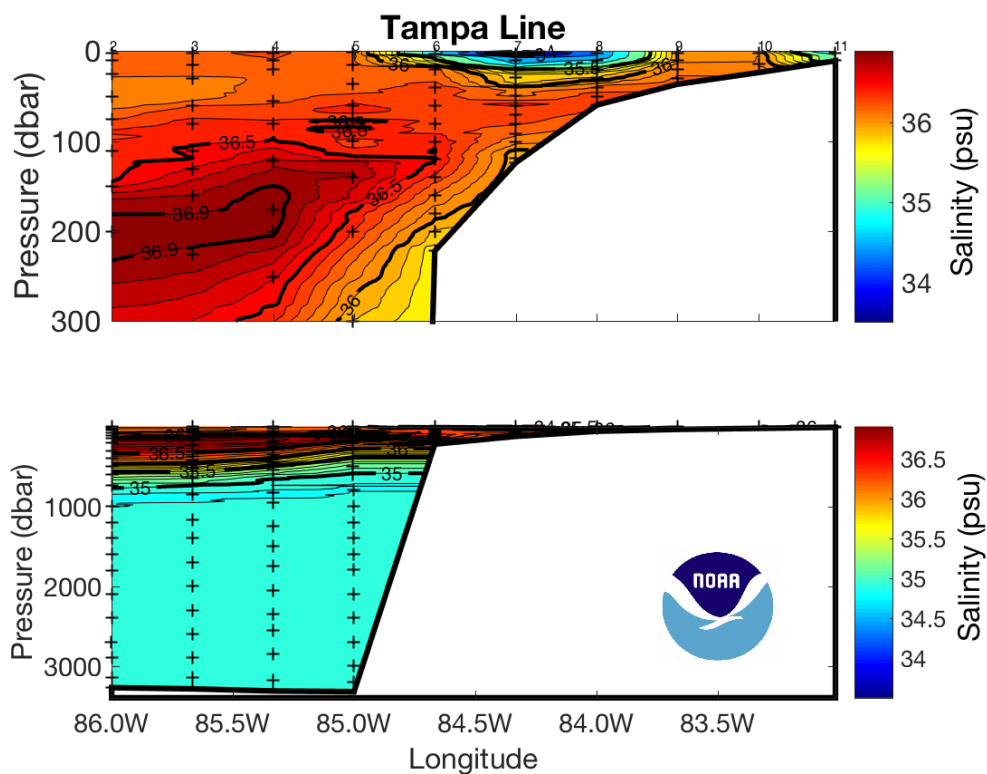
31
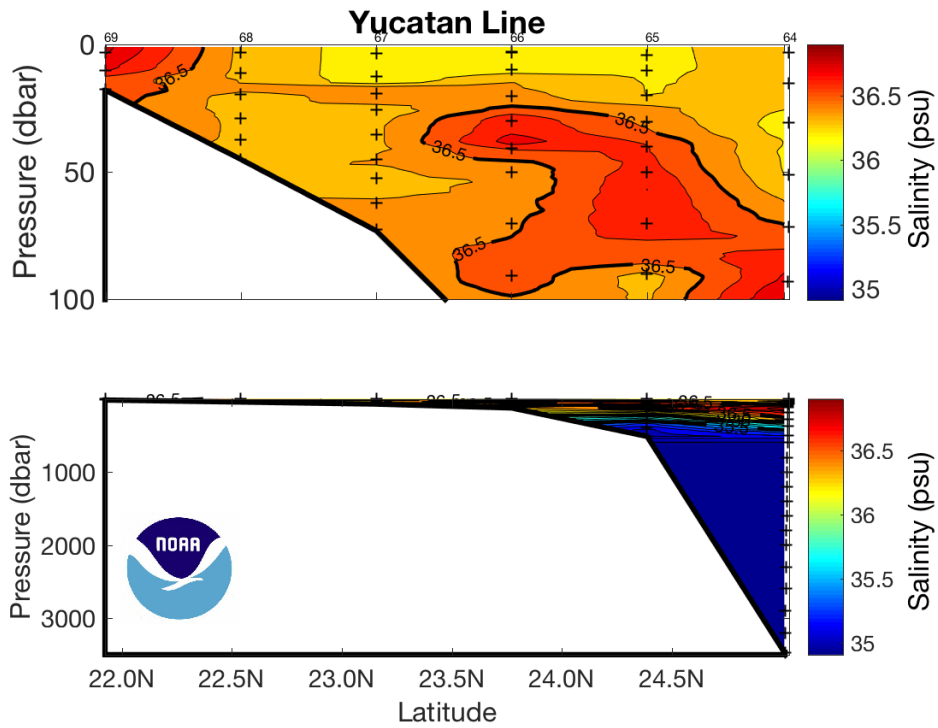
Figure 29: Salinity along the Yucatan Line. The black crosses represent the bottle trip depths.
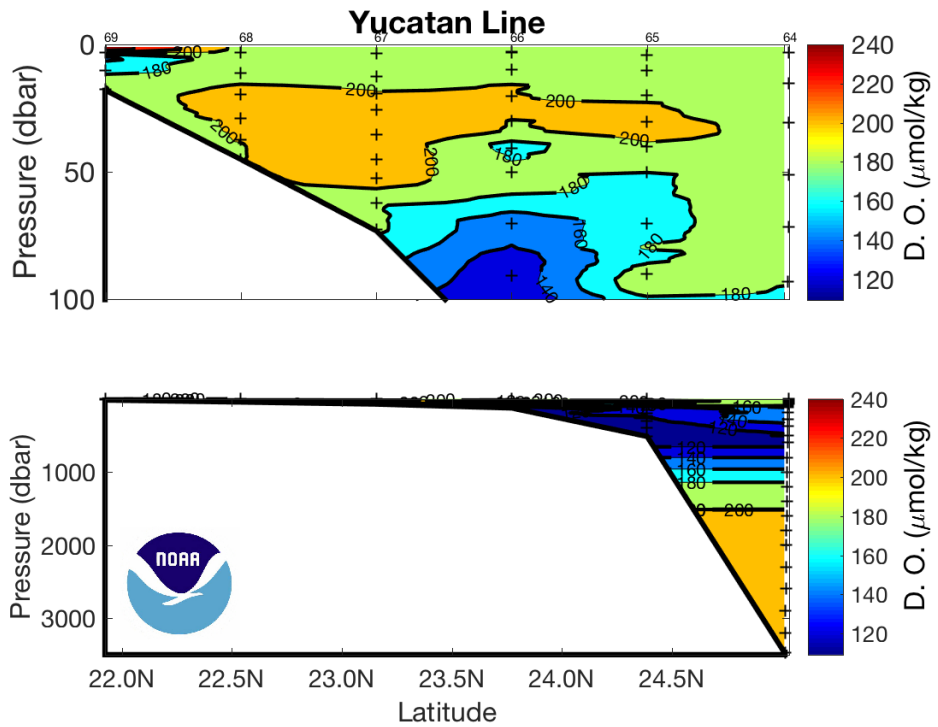
Figure 30: Dissolved oxygen along the Yucatan Line. The black crosses represent the bottle trip depths.
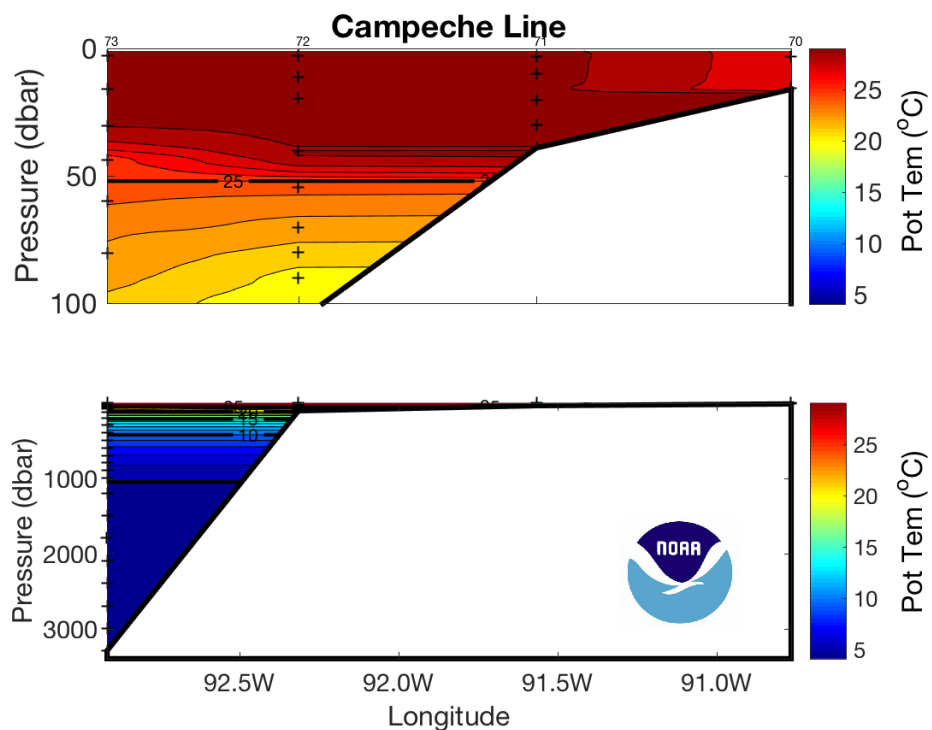
Figure 31: Potential temperature along the Campeche Line. The black crosses represent the bottle trip depths.
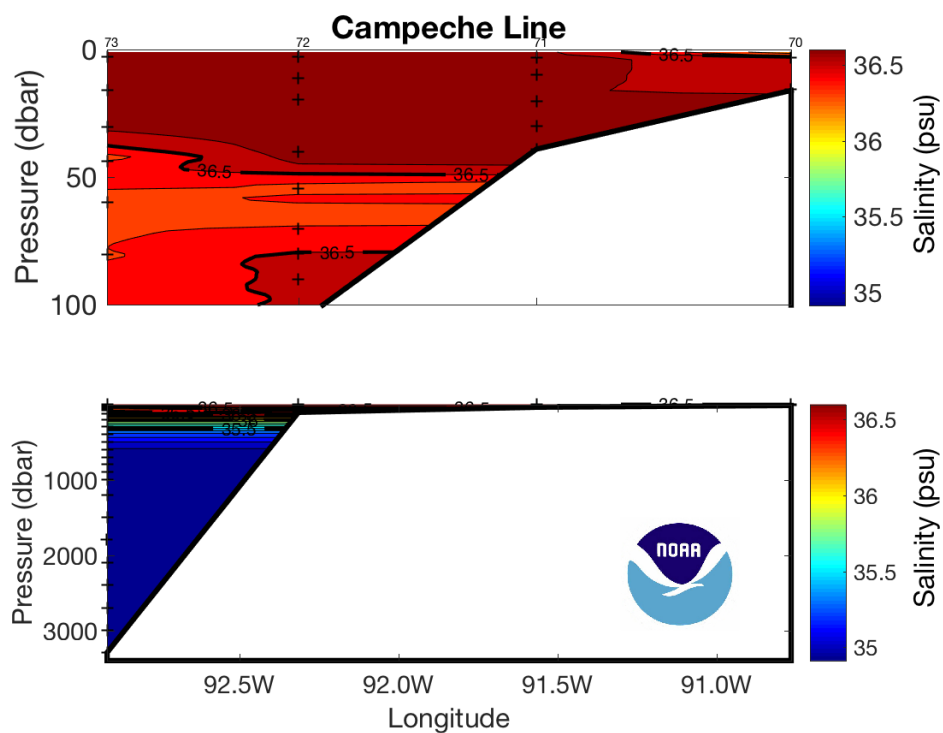
Figure 32: Salinity along the Campeche Line. The black crosses represent the bottle trip depths.
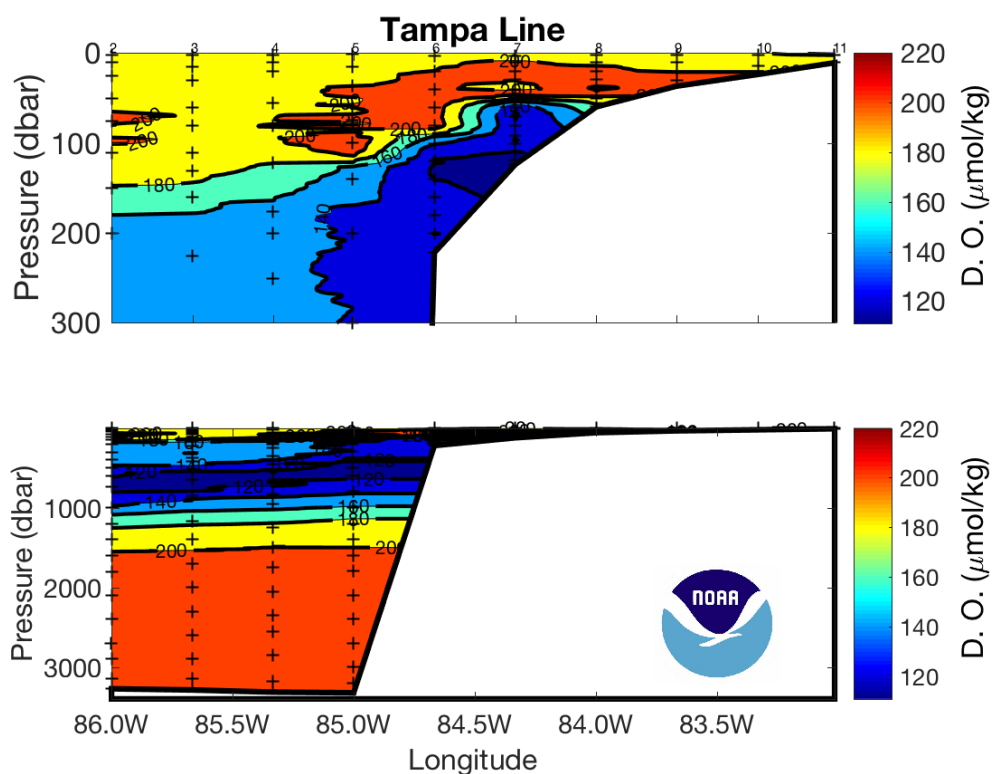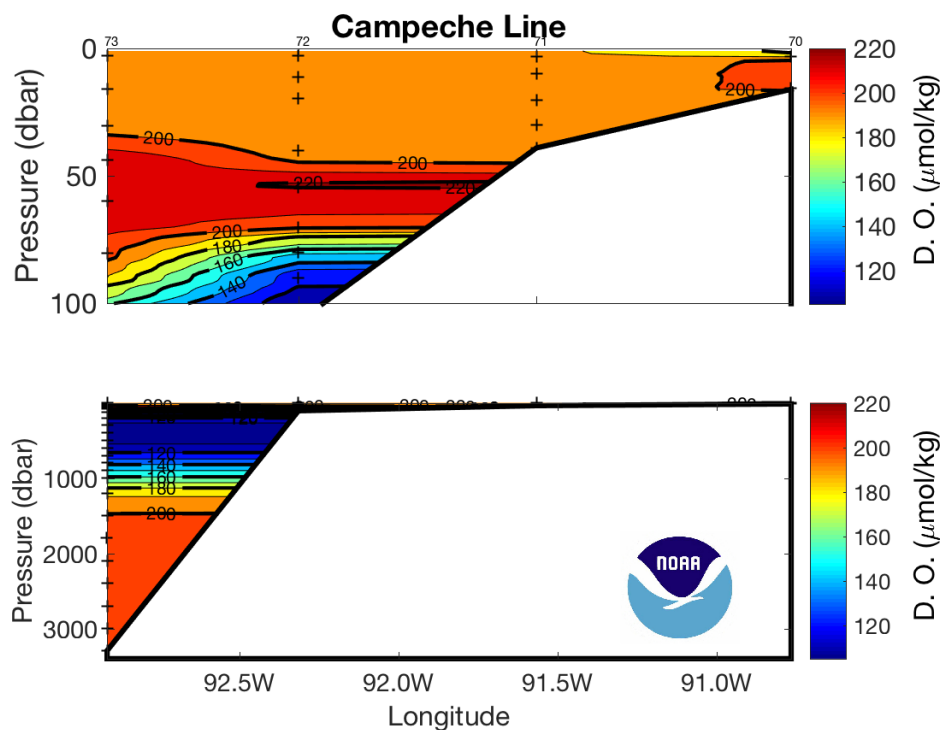
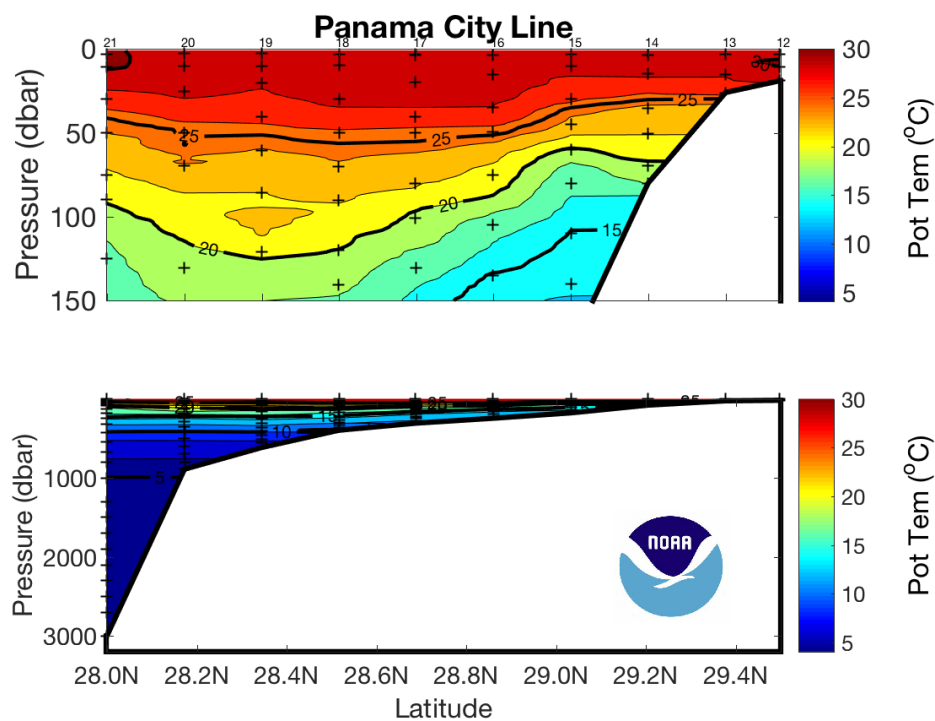*Figure 33: Dissolved oxygen along the Campeche Line. The black crosses represent the bottle trip depths.*
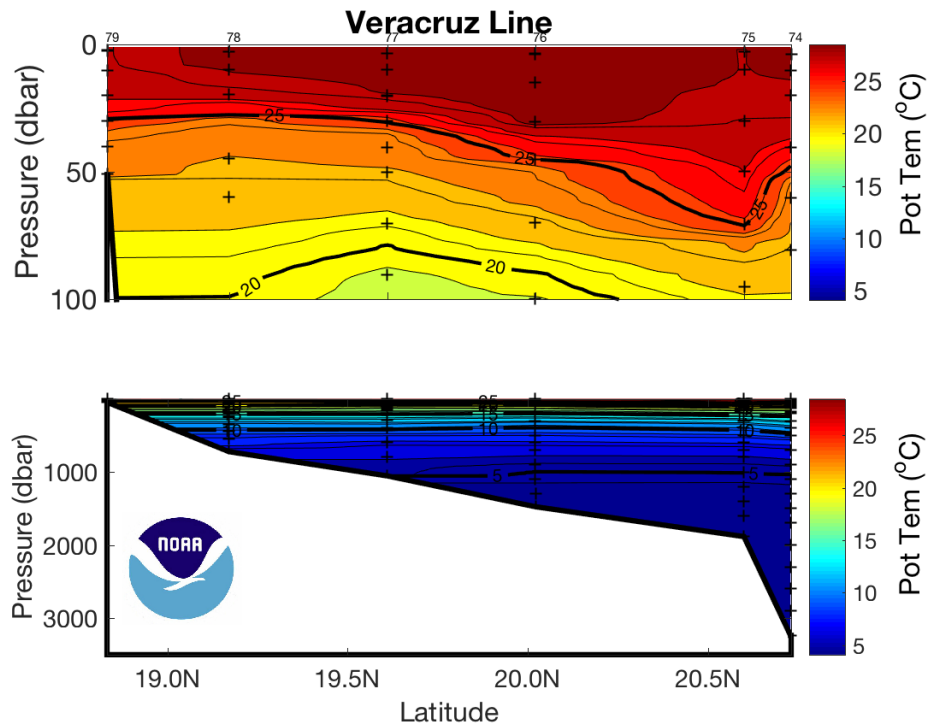
Figure 34: Potential temperature along the Veracruz Line. The black crosses represent the bottle trip depths.
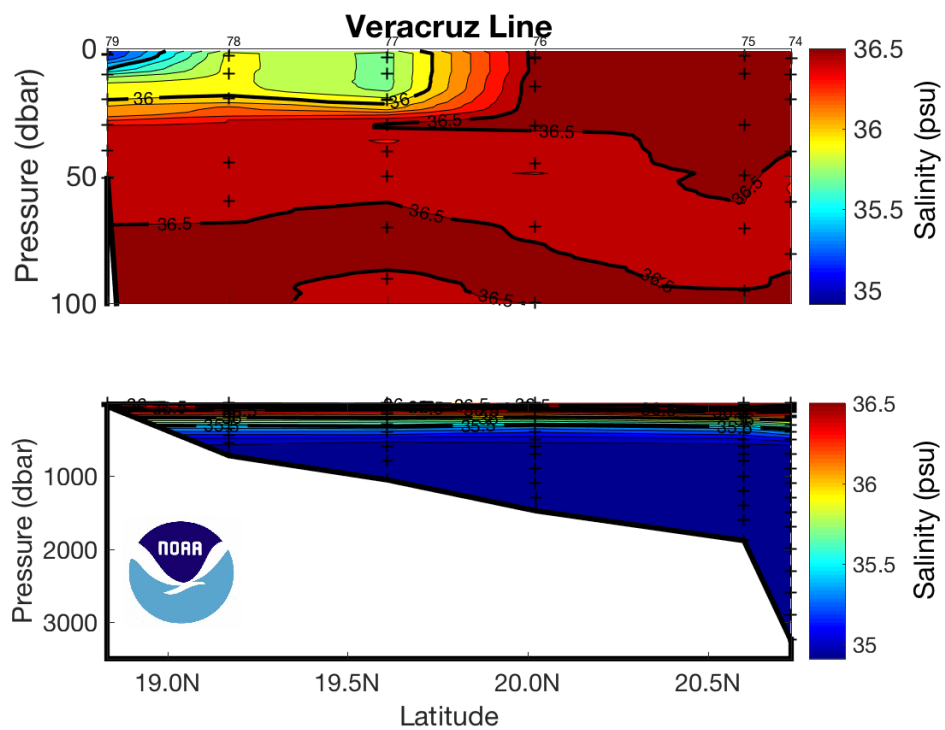
Figure 35: Salinity along the Veracruz Line. The black crosses represent the bottle trip depths.
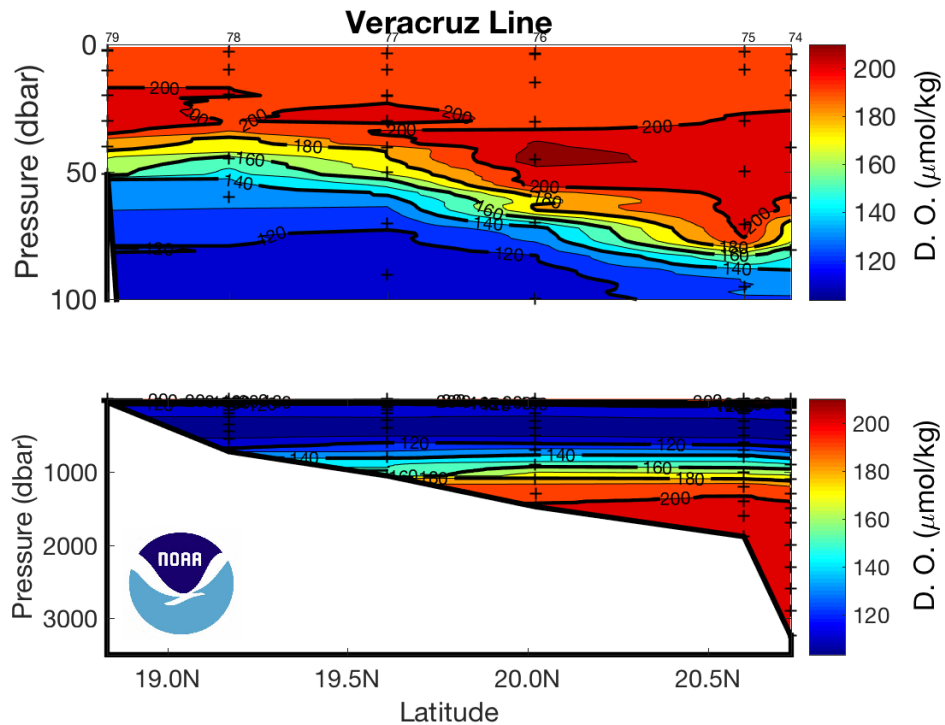
Figure 36: Dissolved oxygen along the Veracruz Line. The black crosses represent the bottle trip depths.
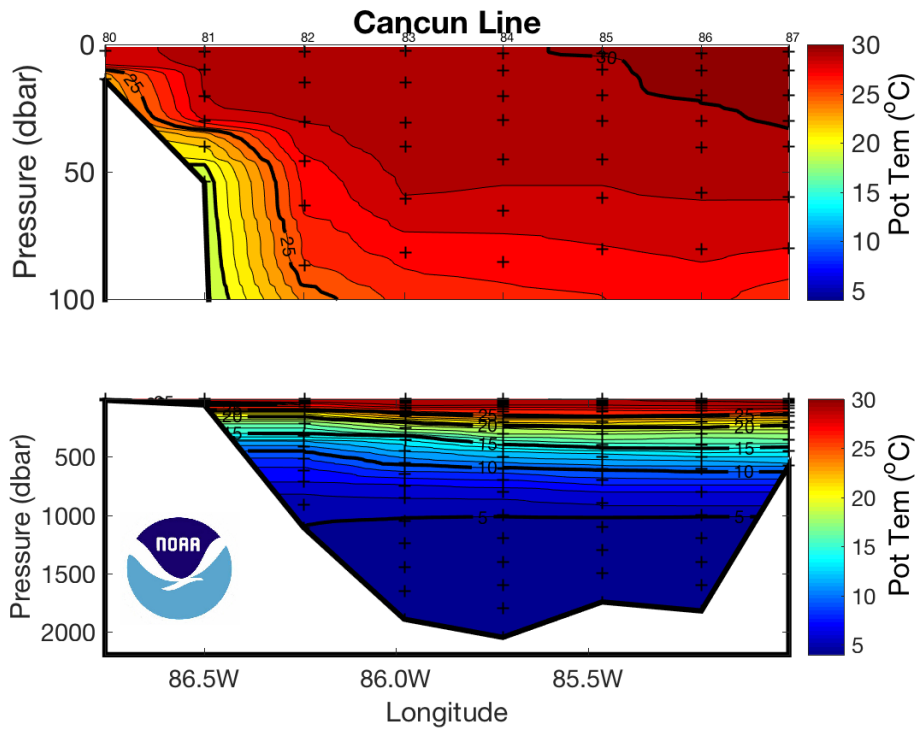
Figure 37: Potential temperature along the Cancun Line. The black crosses represent the bottle trip depths.
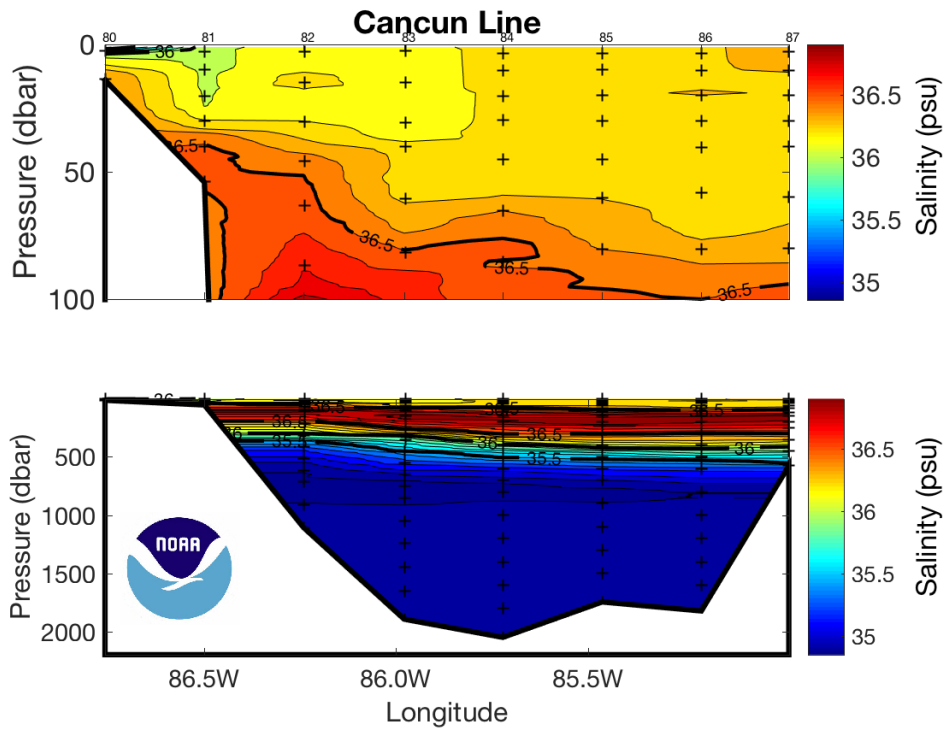
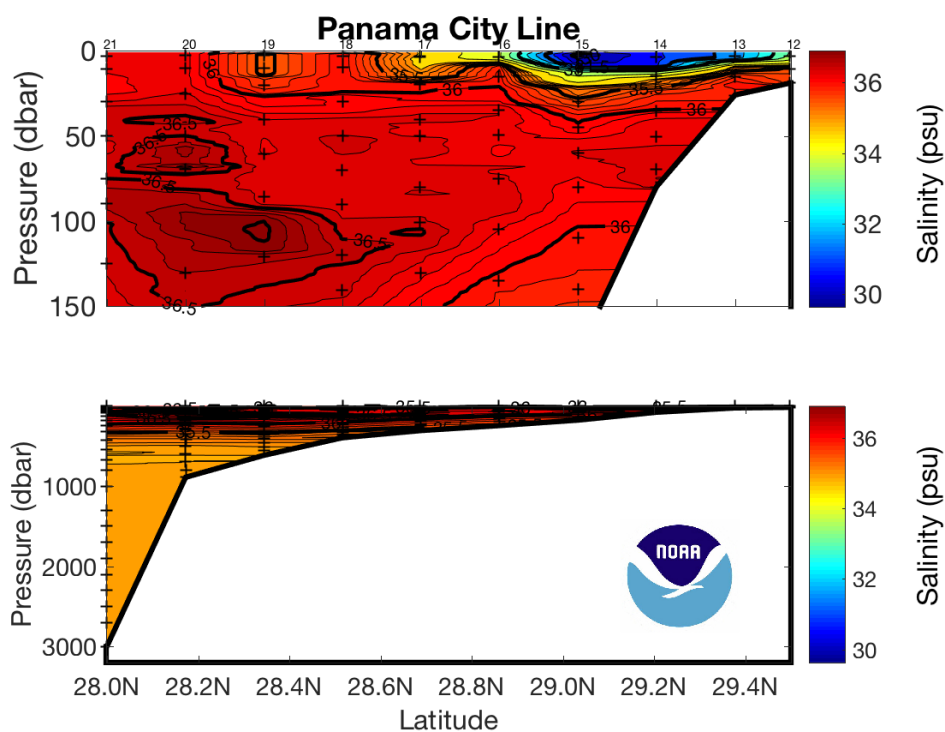

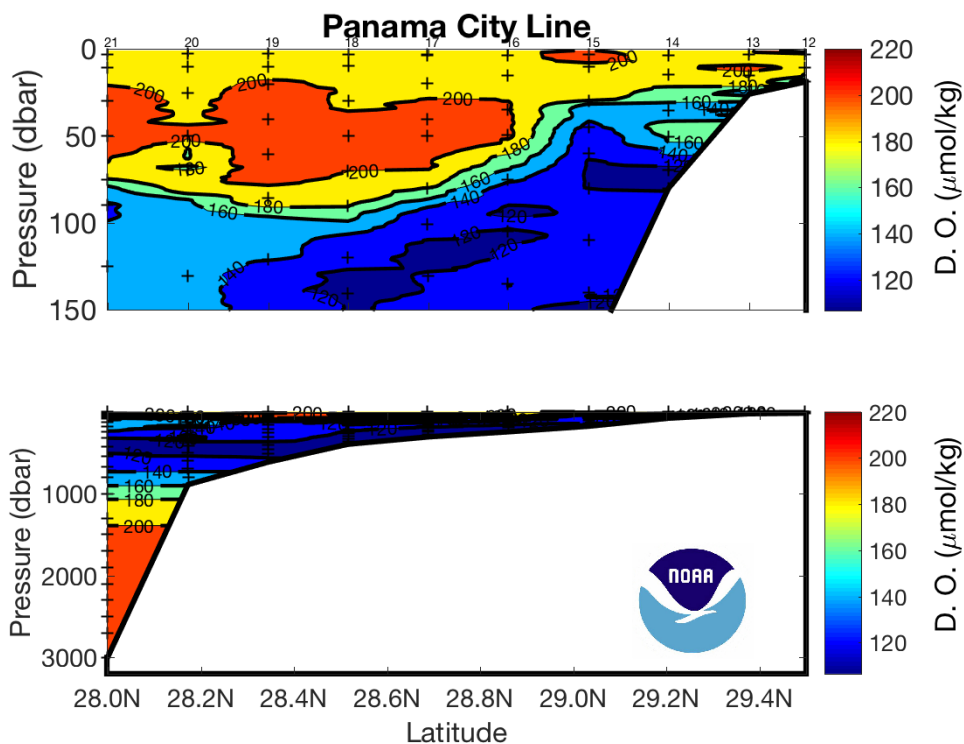*Figure 38: Salinity along the Cancun Line. The black crosses represent the bottle trip depths.*
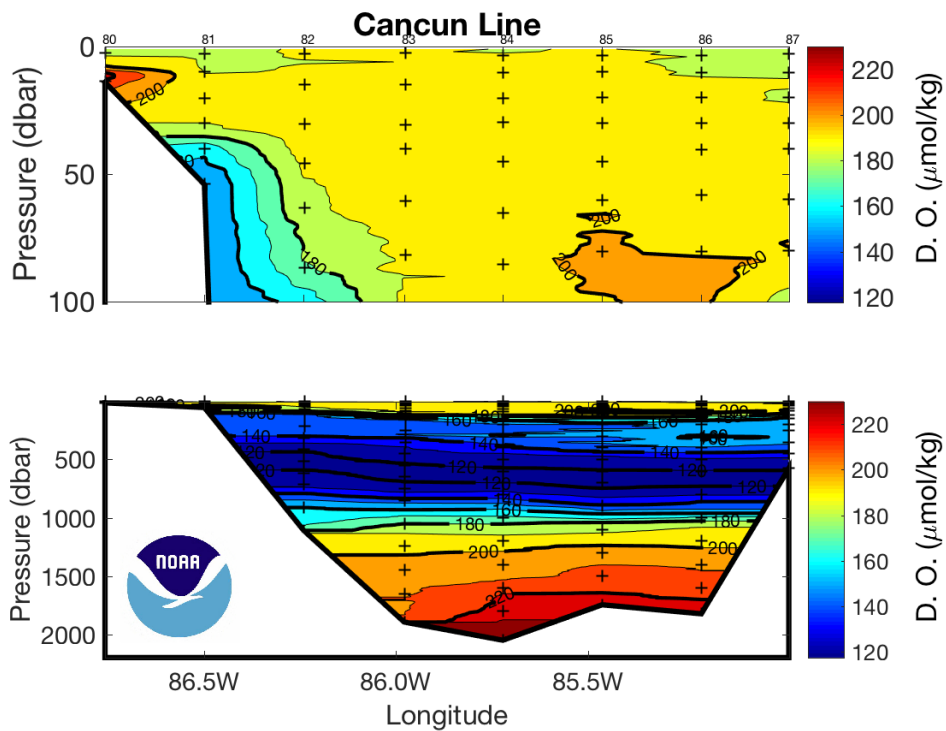
Figure 39: Dissolved oxygen along the Cancun Line. The black crosses represent the bottle trip depths.
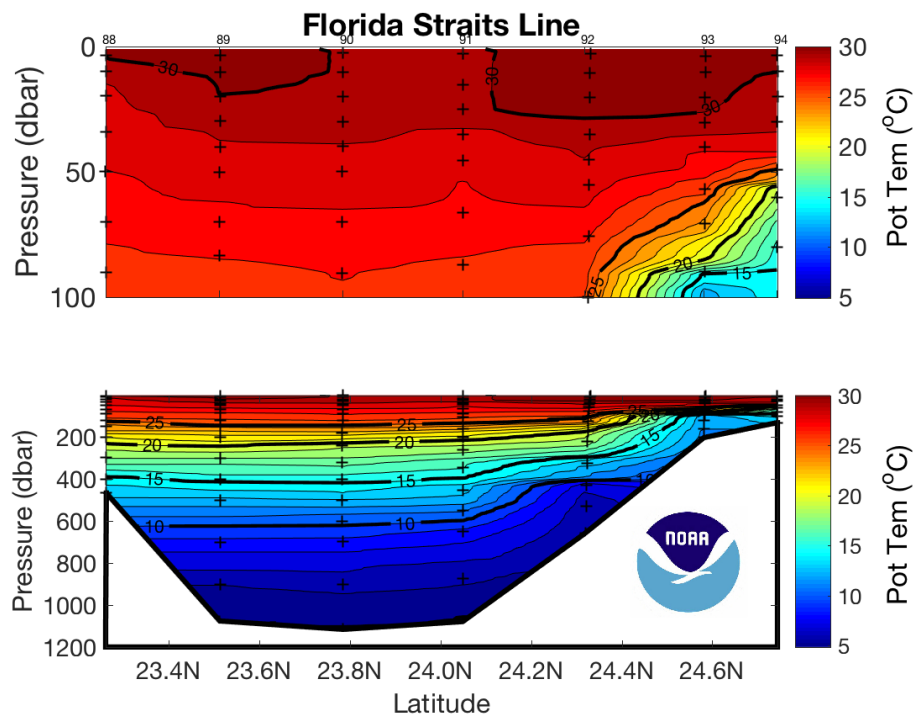
Figure 40: Potential temperature along the Florida Straits Line. The black crosses represent the bottle trip depths.
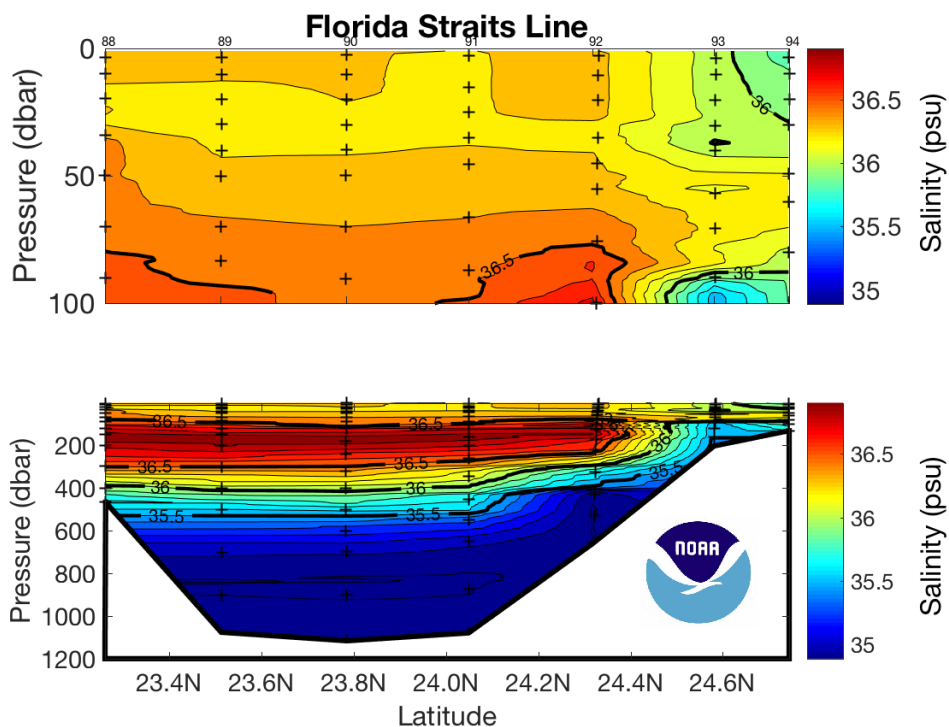
Figure 41: Salinity along the Florida Straits Line. The black crosses represent the bottle trip depths.
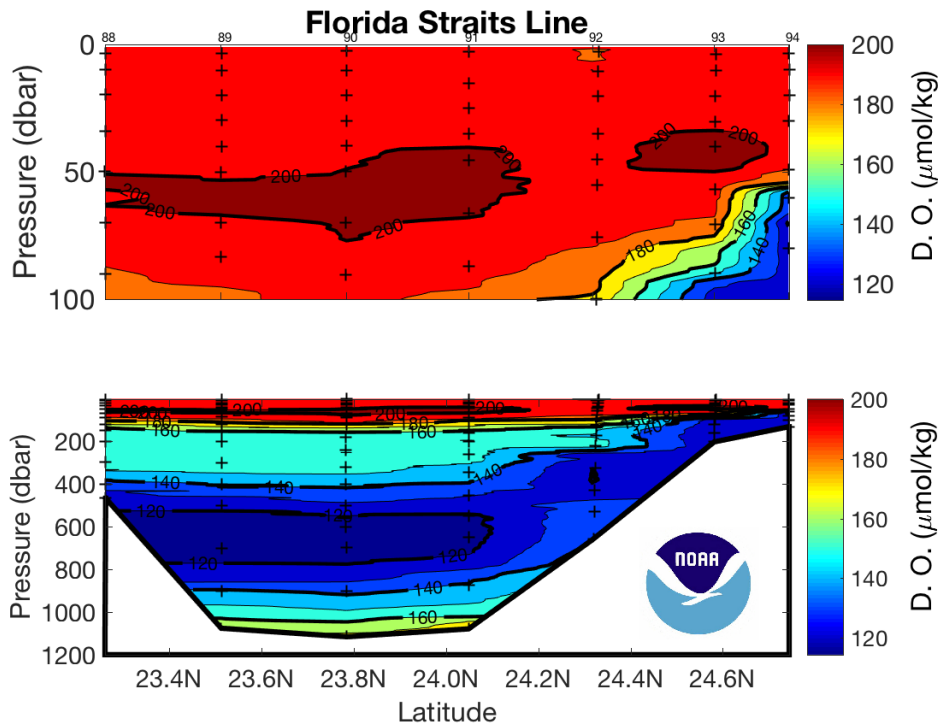
Figure 42: Dissolved oxygen along the Florida Straits Line. The black crosses represent the bottle trip depths.
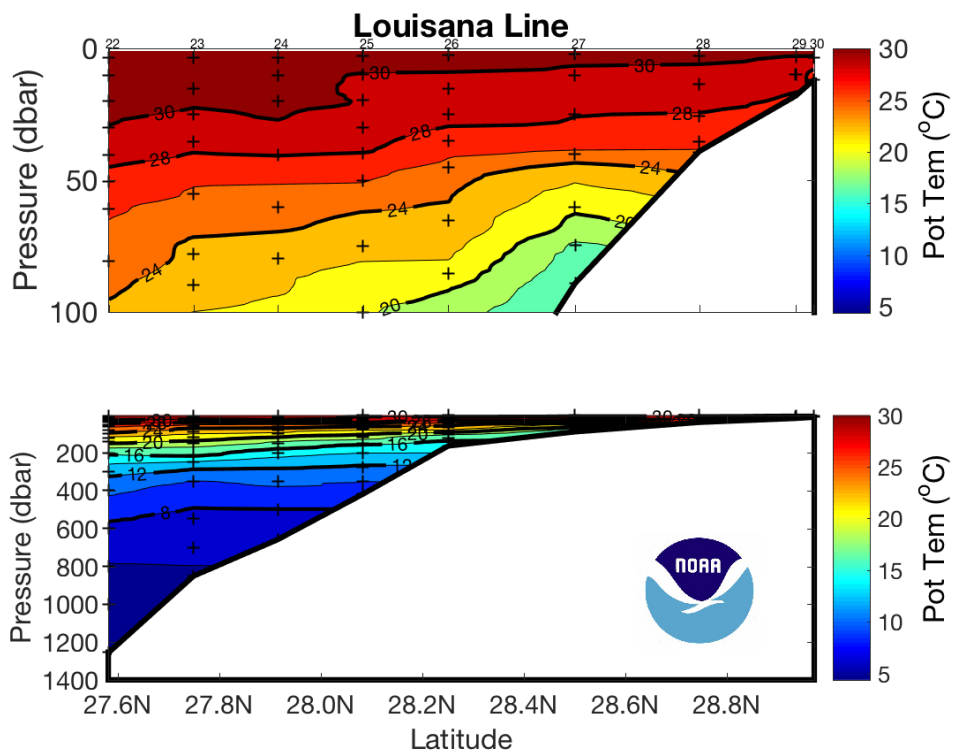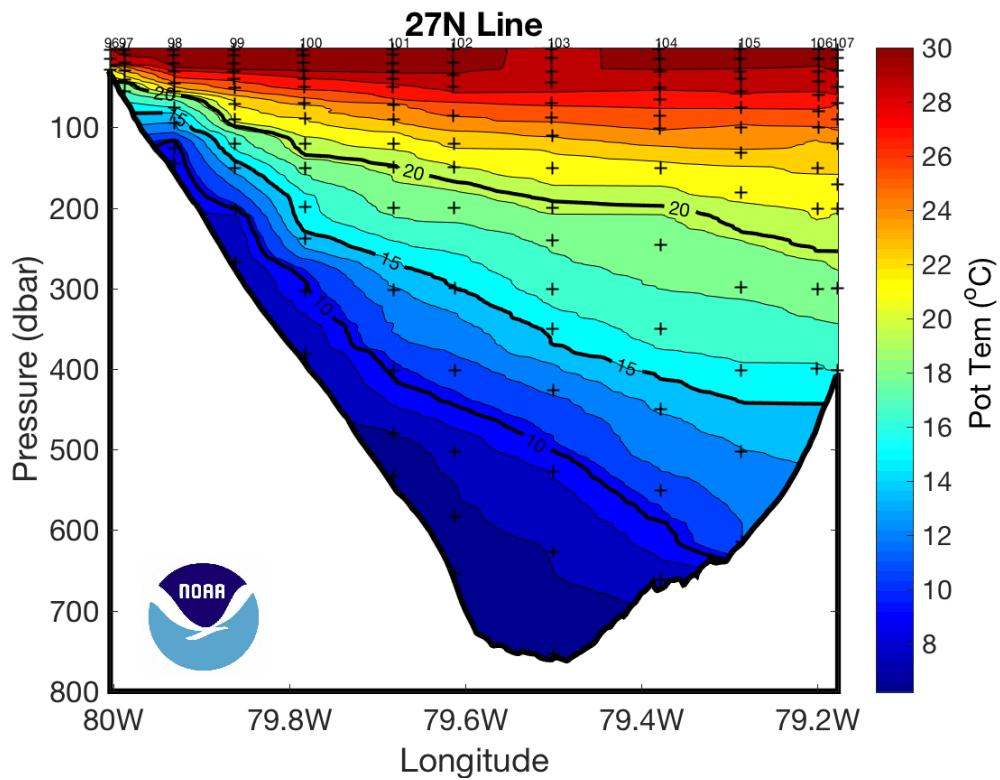
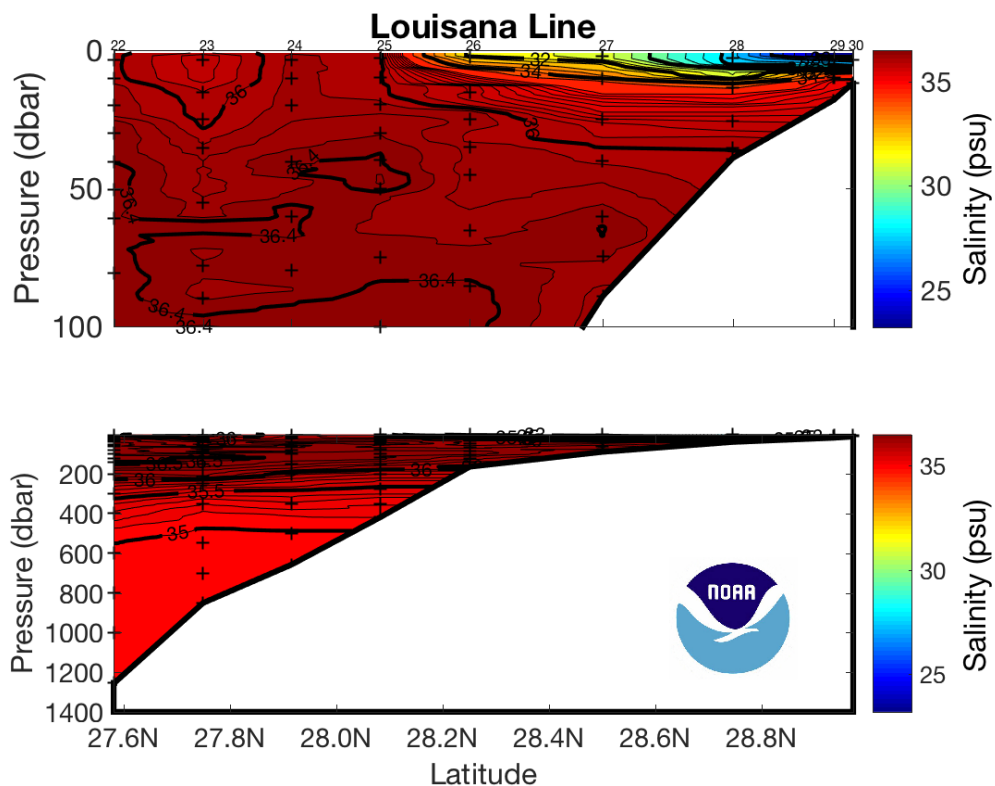*Figure 43: Potential temperature along the 27°N Line. The black crosses represent the bottle trip depths.*
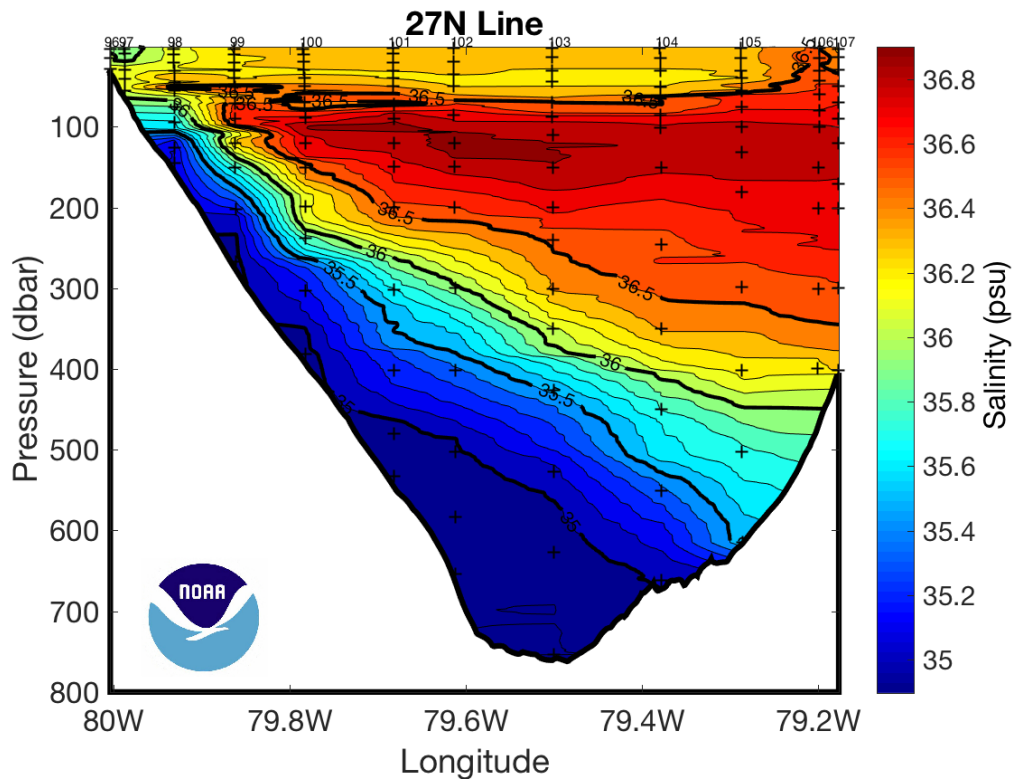
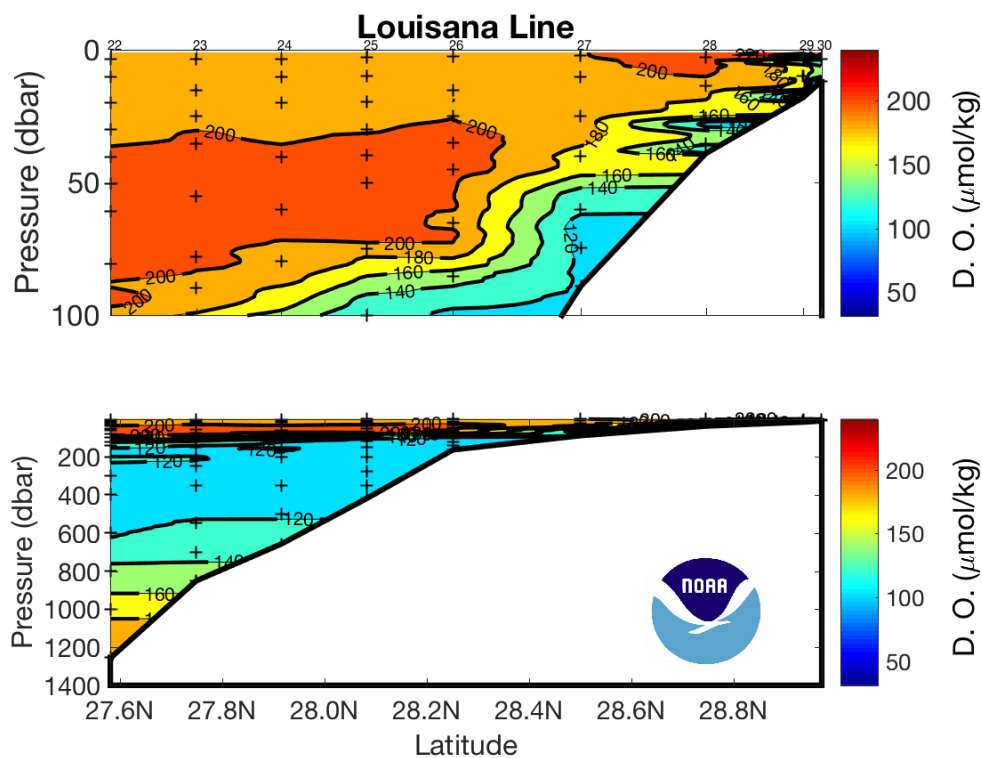*Figure 44: Salinity along the 27°N Line. The black crosses represent the bottle trip depths.*

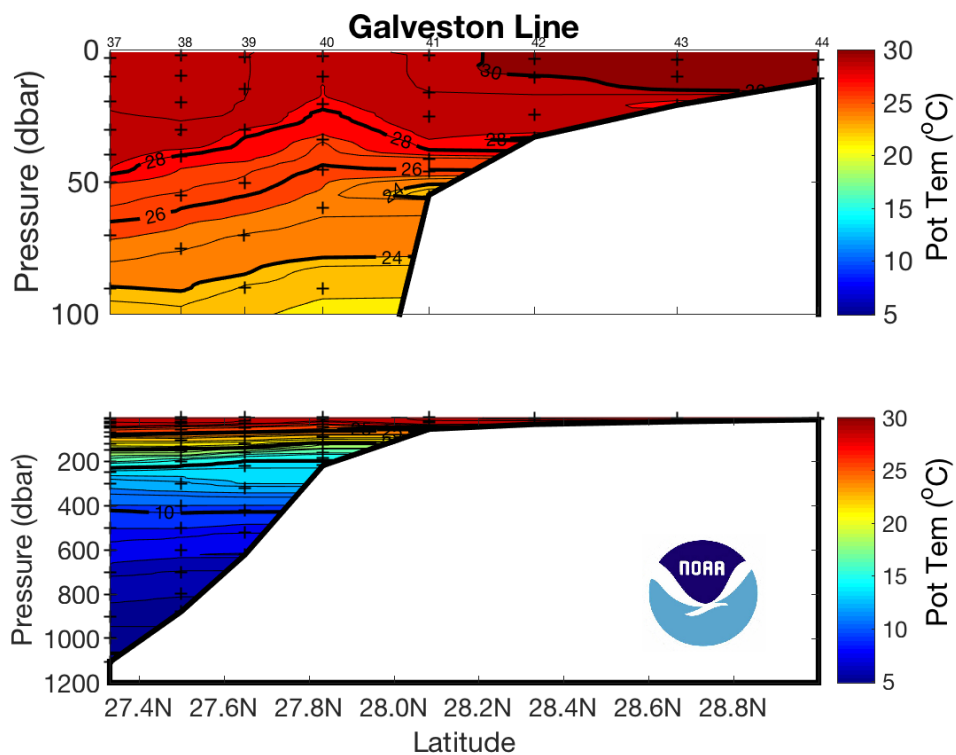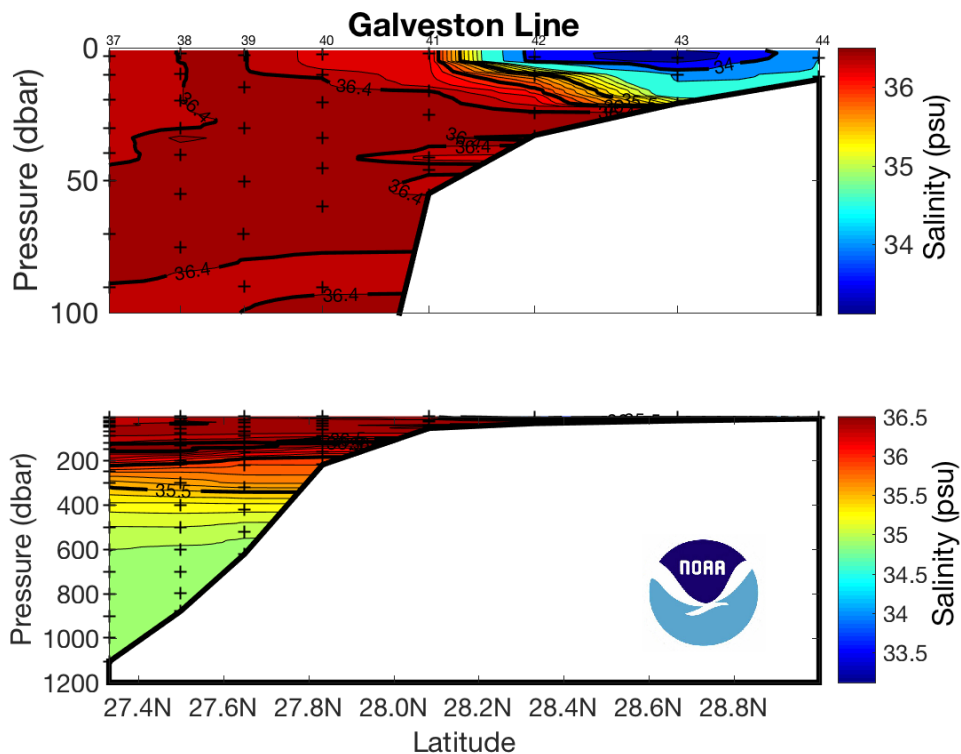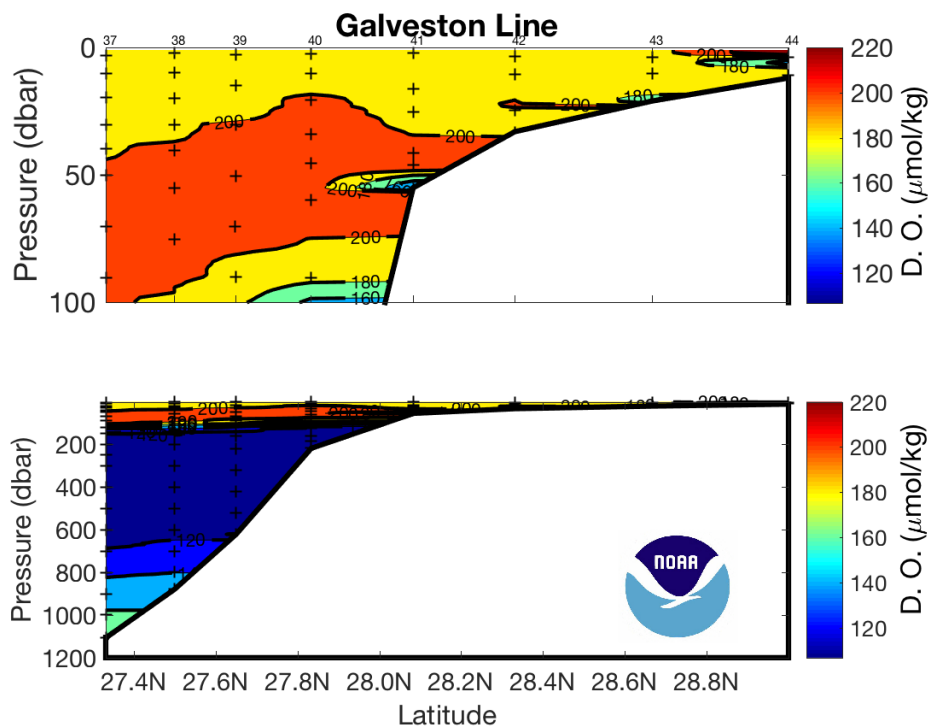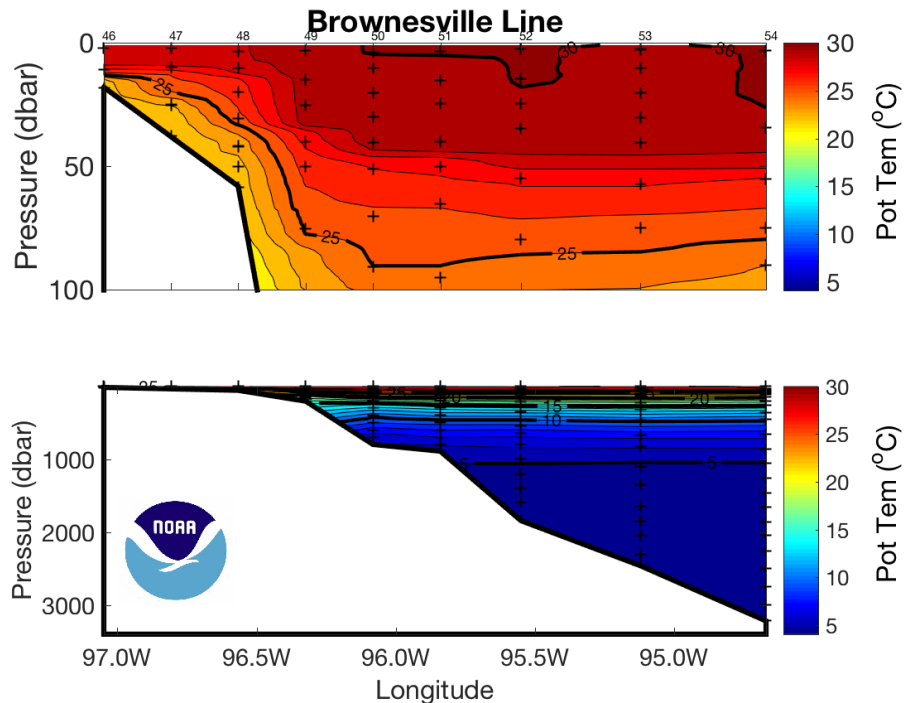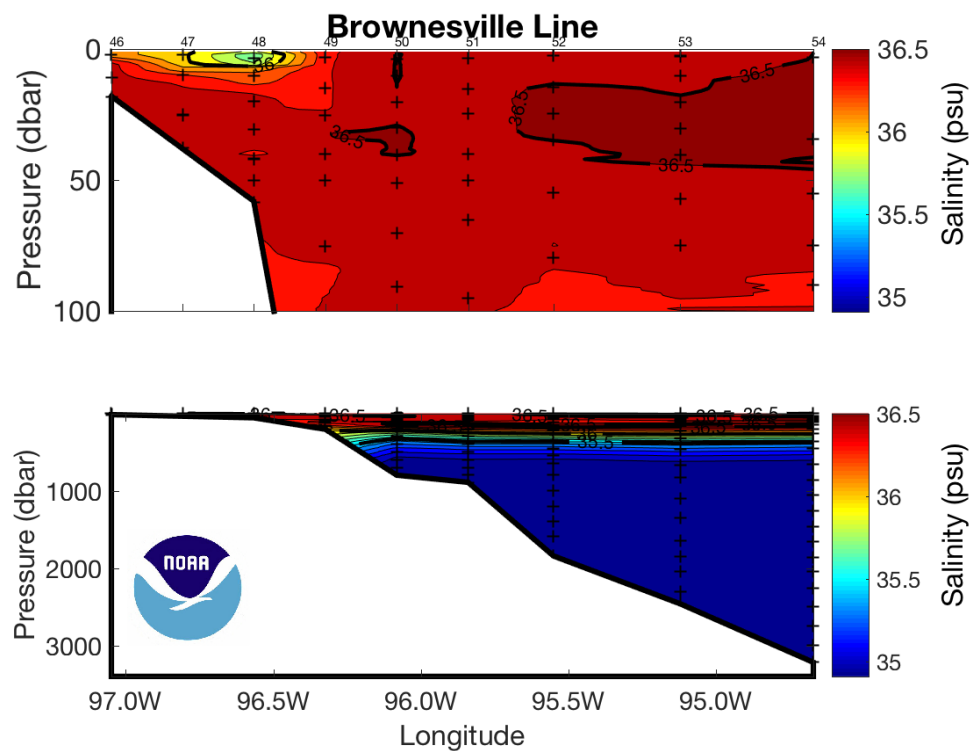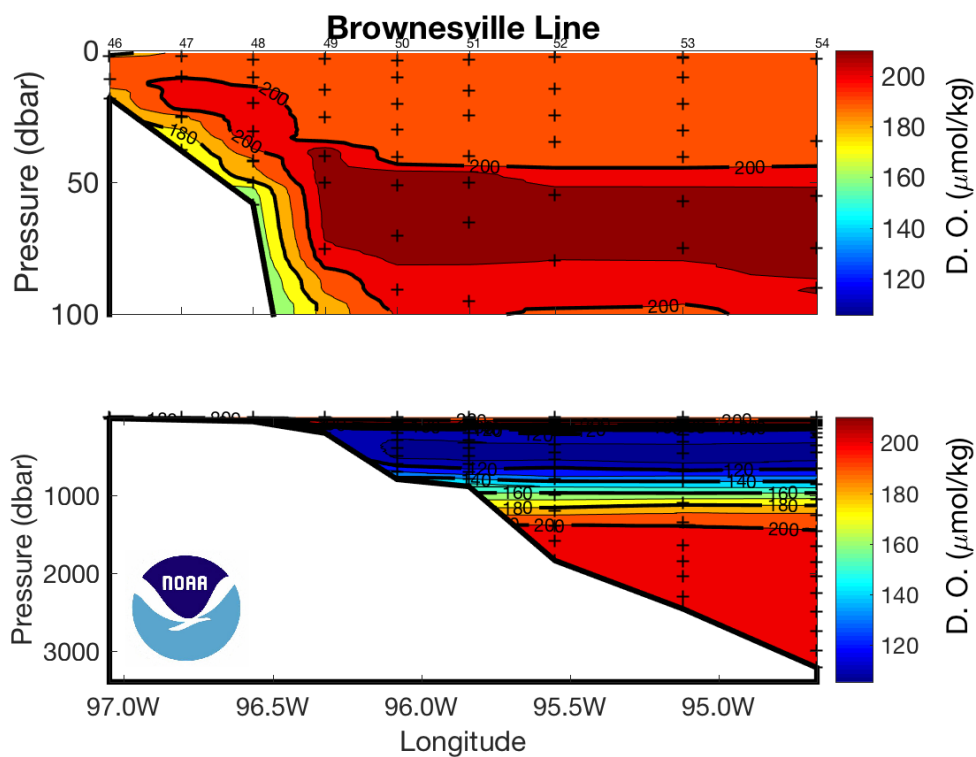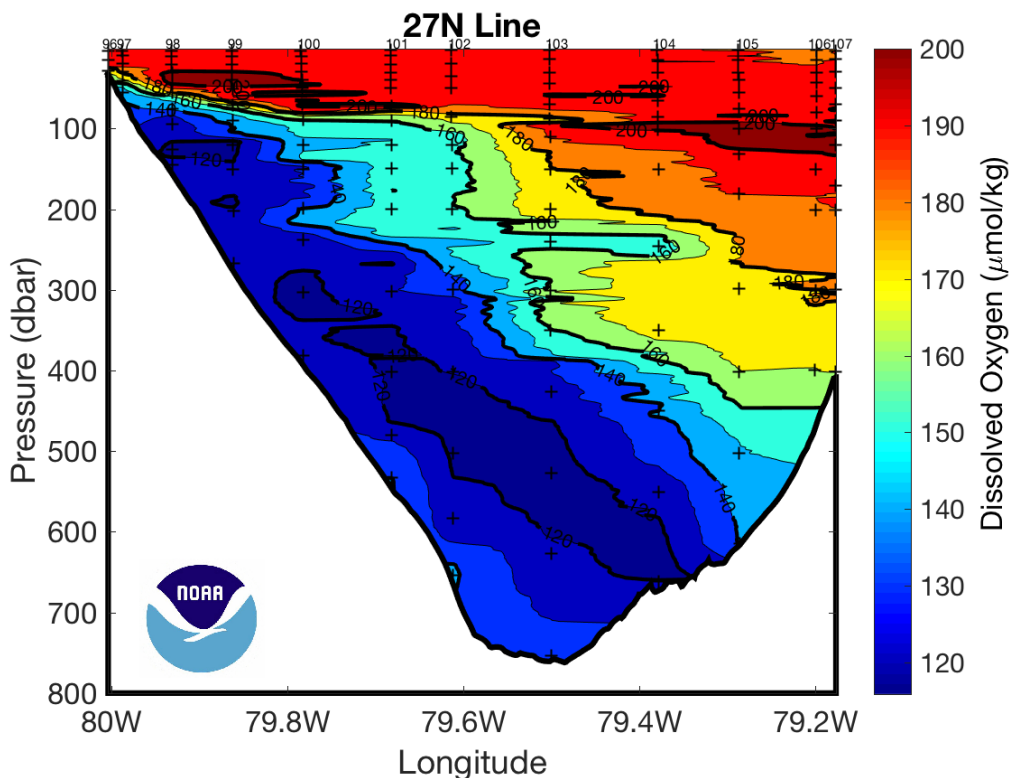*Figure 45: Dissolved oxygen along the 27°N Line. The black crosses represent the bottle trip depths.*

3.2. Acoustic Doppler Current Profiler Activities

3.2.1. Shipboard Acoustic Doppler Current Profiler (SADCP)

During the GOMECC-3 survey, the NOAA Ship *Ronald H. Brown* was equipped with a hull-mounted (or shipboard) Teledyne RD-Instruments (TRDI) 75 kHz Ocean Surveyor (OS75) acoustic Doppler current profiler (SADCP). The OS75 SADCP provided reliable coverage of upper-ocean current velocities to a depth of approximately 750 m during the cruise. In addition to a primary heading source provided by the ship's gyrocompass, the SADCP was also equipped with a secondary heading input from an Applanix POS MV directional GPS (which also provided position information to the instrument). The addition of a secondary GPS-based heading device like the POS MV allowed for improved heading accuracy when the ship was accelerating (which can impart Shuler Oscillations in the output from a traditional mechanical gyrocompass), as well as when trying to account for long-period drift over the course of an entire cruise.

SADCP data were collected using the University of Hawaii's UHDAS software package (UHDAS: University of Hawaii Data Acquisition System). The software's configuration allowed for collection of alternating narrowband (greater depth range) and broadband (greater resolution) data. Broadband data were collected with a 4-m bin length, while narrowband data were collected with a 16-m bin length. Broadband data coverage typically extended into the water column to a depth range of 270-400 m

(depending on the speed of the vessel), while narrowband data were typically collected to a depth of ~750 m (previously mentioned). The nature of the SADCP installation: including the hull depth of the transducer, the blanking distance required by the instrument (8 meters), and the bin length, results in a data gap at the surface. In some cases, this gap can be greater than the water depth in nearshore survey work, resulting in a loss of data. By collecting broadband data in addition to the narrowband data, scientists were able to collect more usable SADCP data on the shallower legs of the survey than would otherwise have been possible collecting narrowband data alone.

Following the cruise, the GOMECC-3 SADCP data set was successfully post-processed using the University of Hawaii's CODAS software package (CODAS: Common Ocean Data Access System). CODAS is the industry standard for producing the highest quality SADCP data set possible. Selected GOMECC-3 velocity sections produced from the post-processed narrowband SADCP data are shown in Figure 46.
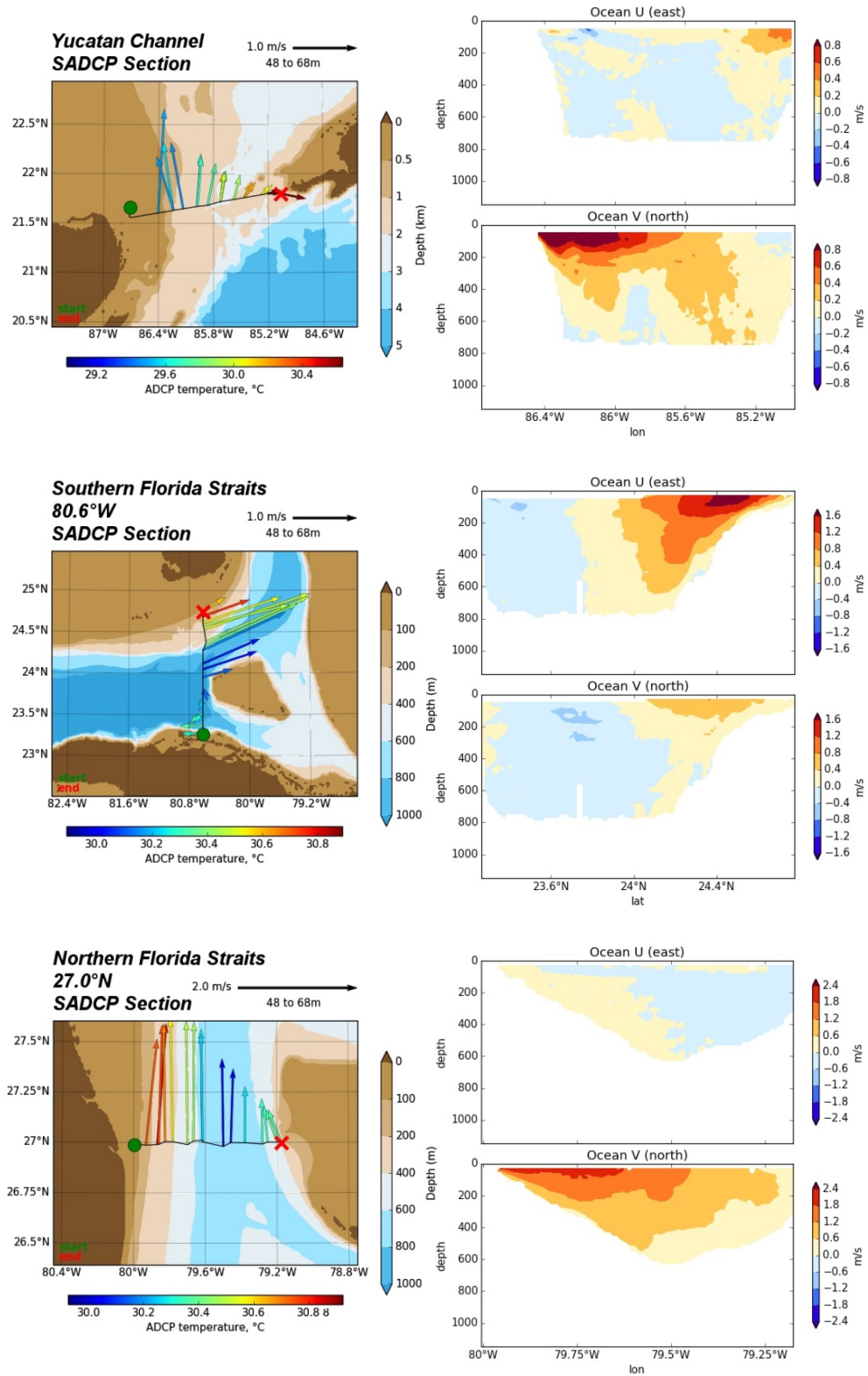
Figure 46: SADCP data from selected sections: Yucatan Channel (top), the southern Florida Straits between Cuba and Florida (at 80.6°W) (middle), and the northern Florida Straits between Florida and the Bahamas (bottom). These plots were generated from narrowband data collected from the ship's hull-mounted 75 kHz SADCP.

3.2.2. *Lowered Acoustic Doppler Current Profiler (LADCP)*

Dual, upward-facing and downward-facing, TRDI 300 kHz Workhorse (WH300) acoustic Doppler current profilers (ADCPs) were incorporated into the CTD package used during the GOMECC-3 survey. These *lowered* ADCPs (LADCP) were battery-powered and logged velocity data internally during each CTD cast. Following each cast, data were recovered from the instruments manually using a direct cable connection to an LADCP processing computer onboard the ship.

Data collected from the LADCPs were processed using v10.20 of the *Visbeck* MATLAB routines originally developed by Martin Visbeck while at Lamont-Doherty Earth Observatory (LDEO) and now maintained by Gerd Krahmann at the Helmholtz Center for Ocean Research in Kiel, Germany (part of IMF-GEOMAR). The Visbeck software suite incorporates concurrent GPS position data, as well as supplementary pressure, temperature, and salinity data from the CTD, and SADCP velocity data for the upper ocean, into the LADCP processing to produce a final LADCP ocean velocity profile for the entire depth of the cast. This method for processing LADCP data is considered the best technique for producing the most accurate LADCP velocity profiles possible. Final ocean velocity profiles were generated, at a resolution of 10 m, for each of the CTD casts conducted during the GOMECC-3 research cruise.

3.3. Discrete Salinity Sampling

A single Guildline Autosal, model 8400B (s/n 61664), located in the salinity analysis room, was used for all salinity measurements. The salinometer readings were logged on a computer using Ocean Scientific International's logging hardware and software. The Autosal's water bath temperature was set to 24°C, which the Autosal is designed to automatically maintain. The laboratory's temperature is typically set and maintained to just below 24°C to help further stabilize reading values and improve accuracy. The room temperature was monitored by a digital thermometer. The temperature was used to gauge when the Autosal room temperature was acceptable to run salts. Salinity analyses were performed after samples had equilibrated to laboratory temperature, usually at least 12 hours after collection. The salinometer was standardized for each group of samples analyzed (usually two casts and up to 52 samples) using two bottles of standard seawater: one at the beginning and end of each set of measurements. The salinometer output was logged to a computer file. The software prompted the analyst to flush the instrument's cell and change samples when appropriate. Prior to each run a sub-standard flush, approximately 200 ml, of the conductivity cell was conducted to flush out the deionized water used in between runs. For each calibration standard, the salinometer cell was initially flushed six times before a set of conductivity ratio readings was taken. For each sample, the salinometer cell was initially flushed at least three times before a set of conductivity ratio readings were taken.

IAPSO Standard Seawater Batch P-160 was used to standardize all casts.

The salinity samples were collected in 200 ml Kimax high-alumina borosilicate bottles that had been rinsed at least three times with sample water prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. Laboratory temperature was also monitored electronically throughout the cruise. PSS-78 salinity was calculated for each sample from the measured conductivity ratios (UNESCO, 1981). The offset between the initial standard seawater value and its reference value was applied to each sample. Then the difference (if any) between the initial and final vials of standard seawater was applied to each sample as a linear function of elapsed run time. The corrected salinity data was then incorporated into the cruise database. When duplicate measurements were deemed to have been collected and run properly, they were averaged and submitted with a quality flag of 6. During GOMECC-3, 679 salinity measurements were taken, including 31 duplicates, and approximately 40 vials of standard seawater (SSW) were used. Up to two duplicate samples were drawn, primarily for the deep casts (>1000 m), to determine total analytical precision.

The running standard calibration values are shown in Figure 47. Throughout the course of the cruise, the autosal standards had a range of 0.0002 in conductivity ratio (about 0.003 in salinity). The duplicates for the bottle salinity had a median of 0.0003 psu ± 0.001 psu and can be seen in Figure 48.
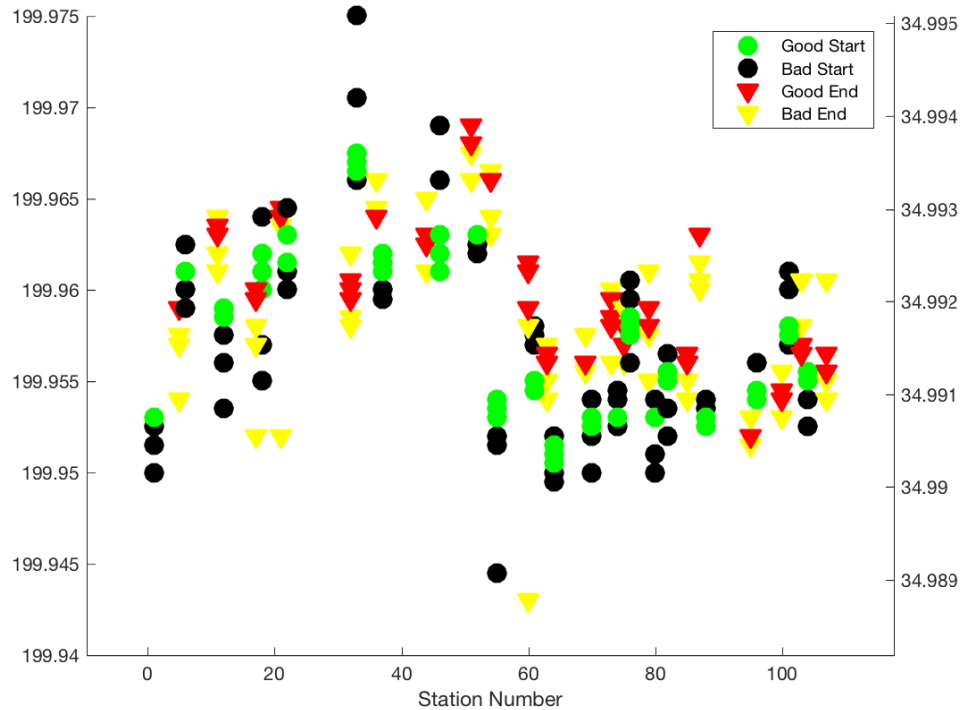
Figure 47: Standard vial calibrations throughout the cruise.
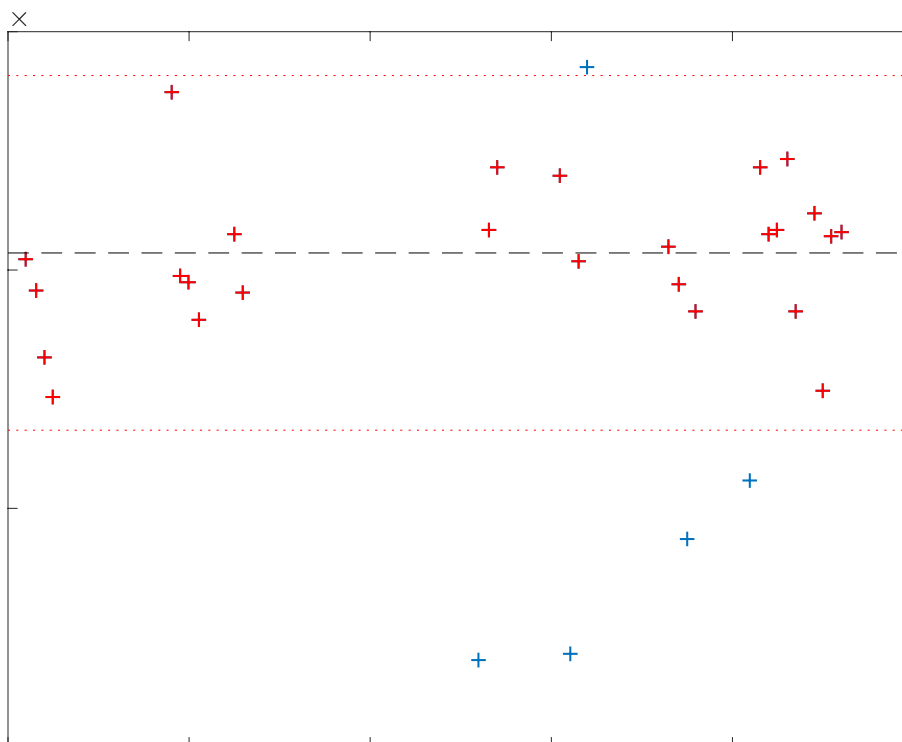
Figure 48: Duplicate bottle salinity differences. Blue colors indicate values that fall outside 2 standard deviations from the mean difference.

3.4. Dissolved Oxygen Measurements

Analysts: Emma Pontes, Leah Chomiak (RSMAS)
PIs: Molly Baringer (AOML/NOAA), Chris Langdon (RSMAS)

3.4.1. Equipment and Techniques

Dissolved oxygen analyses were performed with an automated titrator using amperometric end-point detection (Langdon, 2010). Sample titration, data logging, and graphical display were performed with a PC running a LabView program written by Ulises Rivero of AOML. 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 replicate 10 ml iodate standards were run every 2-3 days (SD <1 uL) either at the start and half waypoint of one 500 mL bottle of thiosulfate, or after 2 days (whichever came first). A 1 ml iodate standard was titrated using a volume (V1) of thiosulfate. An additional 1 ml of standard was added to the titrated sample and titrated again. The volume of thiosulfate used for the second titration was defined as V2. The reagent blank was determined as the difference between V1 and V2. This blank was determined at the beginning and end of the cruise.

3.4.2. Sampling and Data Processing

Dissolved oxygen samples were drawn from Bullister bottles into calibrated 125-150 ml iodine titration flasks using silicon tubing to avoid possible contamination of DOC and CDOM samples. Samples were drawn by counting while the flask was allowed to fill at full flow from the Bullister bottle. This count was then doubled and repeated, thereby allowing the flask to be overflowed by two flask volumes. At this point the silicone tubing was pinched to reduce the flow to a trickle. This was continued until a stable draw temperature was obtained on the Oakton meter. These temperatures were used to calculate µmol/kg concentrations, and provide a diagnostic check of Bullister bottle integrity. One (1) ml of $MnCl_2$ and 1 ml of NaOH/NaI were added immediately after drawing the sample using a Re-pipetor bottle-top dispenser. The flasks were then stoppered and shaken well. Deionized water (DIW) was added to the neck of each flask to create a water seal. A maximum of 24 samples plus two duplicates were drawn at each station, depending on that station's depth. If fewer than four Bullister bottles were tripped, only one duplicate was taken for that cast. The total number of samples collected from the rosette was 1407. During transit days (periods ranging from 12-48 hours when the ship was transiting to the next line of stations), underway samples were collected every 2-3 hours, depending on the speed of the ship. Underway samples were run when at least 10 had been collected in order to maximize chemical use and efficiency. The total number of samples collected from the underway flow-through tubing was 156. Before running a set of samples, a dummy sample was run in order to prepare the probe and ensure its proper functionality. The dummy sample consisted of tap water and was treated the same as a regular sample with the addition of the aforementioned chemicals. All samples were stored in the lab in plastic totes at room temperature for at least 30-40 minutes before analysis. The data were sent to the server immediately after analysis and additionally logged in a mass spreadsheet. Thiosulfate normality was calculated for each standardization and corrected to the laboratory temperature. This temperature ranged between 19.2 and 21.5°C, with an average temperature of 20.58°C. Thermistor failure after station 68 resulted in the use of the average thiosulfate temperature value of 20.6°C for stations 69-103. A total of 14 standardizations were performed (mean=706.120, mean SD=0.359 uL). Reagent blanks were run at the beginning of the cruise (2.1±1.0 uL) and at the end.

3.4.3. Volumetric Calibration

The dispenser used for the standard solution (SOCOREX Calibrex 520) and the burette used to dispense the thiosulfate titrant were calibrated gravimetrically just before the cruise. Oxygen flask volumes were determined gravimetrically with degassed deionized water at AOML. The correction for buoyancy was applied. Flask volumes were corrected to the draw temperature.

3.4.4. Duplicate Samples

Duplicate samples were drawn at two depths on every cast. The Bullister bottles selected for the duplicates and, hence the oxygen flasks, were changed for each cast. However, if the CTD tripped less than four Bullister bottles at a certain station, only one depth was duplicated. A total of 205 duplicates were run during the cruise. The average standard deviation of all duplicates was 0.164 µmol kg^{-1}.

3.4.5. Quality Coding

Based on preliminary quality control performed during the cruise, the following quality flags were assigned.

Quality Flag	Number	Note
2	1092	Good
3	26	Sample value low or high for profile and adjoining casts. Code questionable.
4	30	Stopper loose or bubbles noted in the flask prior to titration.
6	205	Duplicate
9	278	Not sampled

3.4.6. Problems

On station 66, the main thermistor began malfunctioning. CTD bottle temperatures were used to calculate and convert the O_2 concentration to µmol/kg for this station because of the incorrect temperatures given by the faulty thermistor. During stations 67, 68, and 69, the two remaining thermistors also stopped working properly, yielding unrealistic values such as -40°C. There were a total of four thermistors on the ship; however, one thermistor remained in the lab to constantly measure thiosulfate temperature. It was decided that the remaining functional thermistor originally kept in the lab should be used to measure water temperature from the CTD. As such, the thiosulfate temperature in the lab for the rest of the cruise (station 69 and on) was set at 20.6°C, the average thiosulfate temperature for stations 1-68.

3.4.7. Cross-Over Comparisons

None this cruise.

3.5. Nutrient Measurements

Analyst: Ian Smith (AOML/CIMAS)
PI: Jia-Zhong Zhang (AOML/NOAA)

3.5.1. Equipment and Techniques

Dissolved nutrients (phosphate, silicate, nitrate, nitrite, and ammonium) were measured using an automated continuous flow analytical system with segmented flow and colorimetric detection. The four-channel auto-analyzer used was produced by SEAL Analytical.

The major components of the nutrient system consisted of an autoXY-2 auto-sampler, two AA3 high precision peristaltic pumps, four Digital Colorimeter detectors, and custom software for digitally logging and processing the chromatograms. In addition, glass coils were used for mixing the nutrients with their appropriate reagents to produce the proper reaction for analysis. All samples were analyzed at 37°C.

Nutrient samples were collected from the Bullister bottles in 50 ml acid-washed sample bottles after three seawater rinses. Sample analysis typically began within 1 hour of sample collection after the samples had warmed to room temperature.

Detailed methodologies are described by Gordon *et al.* (1993).

3.5.2. Analytical Methods

There were 1502 samples taken at both discrete depths and from the ship's underway system and were analyzed for phosphate (PO_4^{-3}), nitrate (NO_3^-), nitrite (NO_2^-), and orthosilicic acid (H_4SiO_4). Nitrite was determined by diazotizing the sample with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm. Samples for nitrate analysis were passed through a cadmium column, which reduced nitrate to nitrite, and the resulting nitrite concentration (i.e., the sum of nitrate + nitrite which is signified as N+N) was then determined as described above. Nitrate concentrations were determined from the difference between N+N and nitrite (Zhang *et al.,* 1997). Phosphate was determined by reacting the sample with molybdic acid to form phosphomolybdic acid. This complex was subsequently reduced with hydrazine, and the absorbance of the resulting phosphomolybdous acid was measured at 820 nm (Zhang *et al.,* 2000). Silicic acid was analyzed by adding an acidic solution of ammonium molybdate to seawater to produce silicomolybic acid (Zhang and Berberian, 1997). Oxalic acid was then added to inhibit a secondary reaction with phosphate. Finally, a reaction with ascorbic acid formed the blue compound silicomolybdous acid. The color formation was detected at 660 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride by Gordon *et al.,* 1993) were employed to reduce the toxicity of our waste stream.

3.5.3. *Standards and Sampling*

A mixed stock standard consisting of silicic acid, phosphate, and nitrate was prepared by dissolving high purity standard materials (KNO_3, KH_2PO_4, and Na_2SiF_6) in deionized water using a two-step dilution for phosphate and nitrate. This standard was stored at room temperature. A nitrite stock standard was prepared about every 10 days by dissolving $NaNO_2$ in distilled water, and this standard was stored in the refrigerator.

Working standards were freshly made every day by diluting the stock solutions in low nutrient seawater. The working standard was made by the addition of 1 ml of primary nitrite standard and 20 ml of a secondary mixed standard (containing silicic acid, nitrate, and phosphate) into a 500 ml calibrated volumetric flask of Low Nutrient Seawater (LNSW).

Nutrient concentrations were reported in micromoles per kg. Lab temperatures were also recorded for each analytical run. Pump tubing was replaced twice during the cruise.

Nutrient samples were drawn into 50 ml HDPE sample bottles that had been stored in 10% HCl. The bottles were rinsed three to four times with sample before filling. Samples were then brought to room temperature prior to analysis. Samples were analyzed from deep water to the surface. Deionized Water (DIW) was used as a wash and base line carrier. LNSW was used as the medium for the working standards.

3.6. DIC Measurements

Analysts: Norris Patrick Mears (AOML/CIMAS), Joletta Silva (RSMAS)
PIs: Rik Wanninkhof (AOML/NOAA), Leticia Barbero (AOML/CIMAS)

3.6.1 *Sample Collection*

Samples for DIC measurements were drawn (according to procedures outlined in the PICES Publication, *Guide to Best Practices for Ocean CO₂ Measurements,* Dickson *et al.,* 2007) from Bullister bottles into 294 ml borosilicate glass bottles using silicone tubing. The flasks were rinsed once and filled from the bottom with care not to entrain any bubbles, overflowing by at least one-half volume. The sample tube was pinched off and withdrawn, creating a 6 ml headspace, followed by the addition of 0.2 ml of saturated $HgCl_2$ solution which acted as a preservative. The sample bottles were then sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours.

3.6.2 *Equipment*

The analysis was done by coulometry with two analytical systems (AOML 3 and AOML 4) used simultaneously on the cruise. Each system consisted of a coulometer (CM5015 UIC, Inc) coupled with a Dissolved Inorganic Carbon Extractor (DICE). The DICE system 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, 1999; Johnson, 1992).

The two DICE systems (AOML 3 and AOML 4) were set up in a seagoing container modified for use as a shipboard laboratory on the aft main working deck of the NOAA Ship *R/V Ronald H. Brown.*

3.6.3 DIC Analysis

In coulometric analysis of DIC, all carbonate species are converted to CO_2 (gas) by the addition of an 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 precisely measured current through the cell and causing the 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.

3.6.4 DIC Calculation

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 the coulometric titration (in minutes), and *K* is the conversion factor from counts to micromoles.

All DIC values were calculated to a molar weight ($\mu mol/kg$) using density obtained from the CTD's salinity and the pipette temperature. The DIC values were corrected for dilution due to the addition of 0.20 ml of saturated $HgCl_2$ used for sample preservation. The total water volume of the sample bottles was 294 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 1.07 ± 1.43 $\mu mol/kg$ for AOML 3 (n=52) and 6.66 ± 2.01 $\mu mol/kg$ for AOML 4 (n=40).

The coulometer cell solution was replaced after 21–25 mg of carbon was titrated, typically after 9–12 hours of continuous use. The blank was usually less than 30, but during the cruise samples were run with blanks in the 12–48 range.

3.6.5   *Calibration, Accuracy, and Precision*

The stability of each coulometer cell solution was confirmed three different ways.

1) Gas loops were run at the beginning of each cell.

2) CRMs supplied by Dr. A. Dickson of the Scripps Institution of Oceanography (SIO) were analyzed at the beginning of the cell before sample analysis.

3) Duplicate samples from the same Bullister bottle were measured near the beginning, middle, and end of each cell.

Each coulometer was calibrated by injecting aliquots of pure CO_2 (99.999%) by means of an 8-port valve (Wilke *et al.,* 1993) outfitted with two calibrated sample loops of different sizes (~1 ml and ~2 ml). The instruments were each separately calibrated at the beginning of each cell with a minimum of two sets of these gas loop injections.

The accuracy of the DICE measurement was determined with the use of standards (Certified Reference Materials (CRMs), consisting of filtered and UV irradiated seawater) supplied by Dr. A. Dickson of SIO. The CRM accuracy was determined manometrically on land in San Diego, and the DIC data reported to the database have been corrected to this batch 153 CRM value. The CRM certified value for this batch was 2017.95 µmol/kg. Table 5 shows a summary of the average values, standard deviation, and replicates obtained for CRMs during GOMECC-3.

The precision of the two DICE systems can be demonstrated via the replicate samples. Approximately 14% of the water samples were duplicates taken as a check of our precision. These replicate samples were interspersed throughout the station analysis for quality assurance and integrity of the coulometer cell solutions. The average absolute difference from the mean of these replicates was 1.37 µmol/kg. No major systematic differences between the replicates were observed (Table 5).

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

Calibration data during this cruise:

Table 5: Summary of CRM results during GOMECC-3. The assigned value of batch 153 CRM = 2017.95 µmol/kg.

Unit	Ave L Loop Cal Factor	Ave S Loop Cal Factor	Pipette	Avg. CRM	Std Dev	Avg. Diff. Duplicates
AOML 3	1.002350	1.003285	27.9276ml	2017.85, N= 52	1.43	1.45 ± 1.03, N=122
AOML 4	1.000212	0.998573	29.306 ml	2011.28, N = 40	2.01	1.30 ± 0.92, N=90

3.6.6 Underway DIC Samples

Underway samples were collected from the flow-through system in the Hydro Lab during transit. Discrete DIC samples were collected approximately every 3 hours for the first six transects; the time between underway samples was decreased for transit after this time due to increased ship speed to every 2 hours. A total of 172 discrete DIC samples were collected while underway, including 18 duplicates. The average difference for the 18 replicates of underway DIC samples was 2.37 µmol/kg, and the average standard deviation was 2.24 µmol/kg. Figure 49 shows preliminary surface DIC values obtained from samples collected underway and from the surface bottle of each CTD cast.
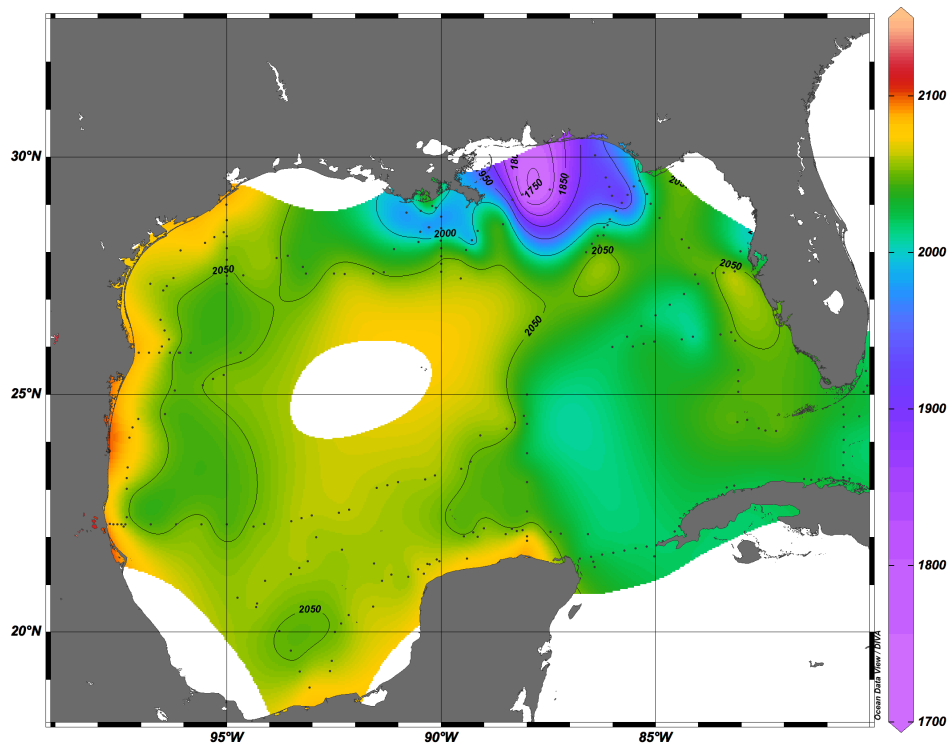
Figure 49: Preliminary surface DIC measurements collected from underway samples and from the surface bottle at each CTD cast during GOMECC-3.

3.6.7 Summary

The overall performance of the analytical equipment was good during the cruise. Early in the cruise, it was discovered that the carrier gas line connected to the auxiliary carrier gas (ACG) needle valve on AOML 4 formed a leak that required the stainless tubing to be replaced. This resulted in downtime of AOML 4 but did not affect any samples as the leak gave blanks of over 80 counts and no samples were run. At the same time a leak in the bulkhead connection between the small calibration loop was found and corrected. Shortly after, larger blanks were again detected (60-80 counts) and no leaks were found. The problem progressed and AOML 4 began to have problems filling the pipette. Water would flow through the SBE connections and into the overflow pipette, causing the water level sensor to trip before the pipette was filled. It was discovered that water was flowing through a faulty valve #2, past valve #7 and into the overflow pipette. The valve (#2) was receiving power; however, the valve movements were "sticky" and would not close with enough force to close off the tubing. In addition to replacing the valve, the tubing was also replaced. This solved the problem with high blanks.

Including the duplicates, over 1738 samples were analyzed from 114 casts and 1633 tripped Bullister bottles for dissolved inorganic carbon (DIC), which means that there was a DIC value for approximately 100% of the depths where bottles were tripped. The DIC data reported to the database directly from the ship are to be considered preliminary until a more thorough quality assurance can be completed shoreside.

3.7. Discrete pCO$_2$ Measurements

Analyst: Kevin Sullivan, Denis Pierrot (AOML/CIMAS)
PI: Rik Wanninkhof (AOML/NOAA)

3.7.1 Sampling

Samples were drawn from 11-L Bullister bottles into 500 ml glass bottles using nylon tubing with a Silicone adapter that fit over the drain cock. Bottles were first rinsed three times with ~25 ml of water. They were then filled from the bottom, overflowing a bottle volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn to allow for expansion of the water as it warmed and to provide space for the stopper and tubing of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with grease and were stored at room temperature for a maximum of 8 hours prior to analysis.

The analyses for pCO$_2$ were done with the discrete samples at 20°C. A primary water bath was kept within 0.03°C of the analytical temperature; a secondary bath was kept within 0.3°C the analytical temperature. The majority of the samples were analyzed in batches of 12 bottles, which took approximately 3.5 hours, including the six standard gases. When 12 bottles were moved into the primary water bath for analyses, the next 12 bottles were moved into the secondary water bath. No sample bottle spent less than 2 hours in the secondary water bath prior to being moved to the analytical water bath.

Duplicate samples from the same Niskin-style bottles were drawn to check the precision of the sampling and analysis. Discrete samples were collected from the underway (UW) flowing seawater line aboard the ship. The results for the UW samples compared well with the results for the autonomous UW pCO_2 instrument.

Over 1300 samples were drawn from 113 CTD casts. From the UW seawater line, 153 samples were drawn. Seventy-eight sets of duplicate bottles were drawn at numerous depths. The average relative standard error was 0.21%, while the median relative error was 0.15%.

3.7.2 *Analyzer Description*

The principles of the discrete pCO_2 system are described in Wanninkhof and Thoning (1993) and Chipman *et al.* (1993). The major difference in the current system is the method of equilibrating the sample water with the constantly circulating gas phase. This system uses miniature membrane contactors (Micromodules from Membrana, Inc.), which contain bundles of hydrophobic micro-porous tubes in polycarbonate shells (2.5 × 2.5 × 0.5 cm). The sample water is pumped over the outside of the tubing bundles in two contactors in series at approximately 25 ml/min and to a drain. The gas is recirculated in a vented loop, which includes the tubing bundles and a non-dispersive infrared analyzer (LI-COR™ model 840) at approximately 32 ml/min.

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

The instrumental system employs a large insulated cooler (Igloo Inc.) that accommodates 12 sample bottles, the miniature contactors, a water circulation pump, a copper coil connected to a refrigerated circulating water bath, an immersion heater, a 12-position sample distribution valve, two thermistors, and two miniature pumps. The immersion heater works in opposition to the cooler water passing through the copper coil. One thermistor is immersed in the water bath, while the second thermistor is in a sample flow cell after the second contactor. The difference between the two thermistor readings was consistently less than 0.02°C during sample analyses. In a separate enclosure are the 8-port gas distribution valve, the infrared analyzer, a barometer, and other electronic components. The gas distribution valve is connected to the gas pump and to six standard gas cylinders.

To ensure analytical accuracy, a set of six gas standards (ranging from 288 to 1534 ppm) was run through the analyzer before and after every sample batch. The standards were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale.

A custom program developed using LabView™ controls the system and graphically displays the CO_2 concentration, as well as the temperatures, pressures, and gas flow during the 15-minute equilibration (Figure 50). The analytical system was running well enough that the equilibration period was shortened to 12 minutes for the second half of the cruise. The CO_2 in the gas phase changes greatly within the first minute of a new sample and then goes through nearly two more oscillations. The oscillations dampen quickly as the concentration asymptotically approaches equilibrium. The flows are stopped, and the program records an average of ten readings from the infrared analyzer along with other sensor readings. The data files from the discrete pCO_2 program are reformatted so that a Matlab™ program designed for processing data from the continuous pCO_2 systems can be used to calculate the fugacity of the discrete samples at 20°C. The details of the data reduction are described in Pierrot *et al.* (2009).
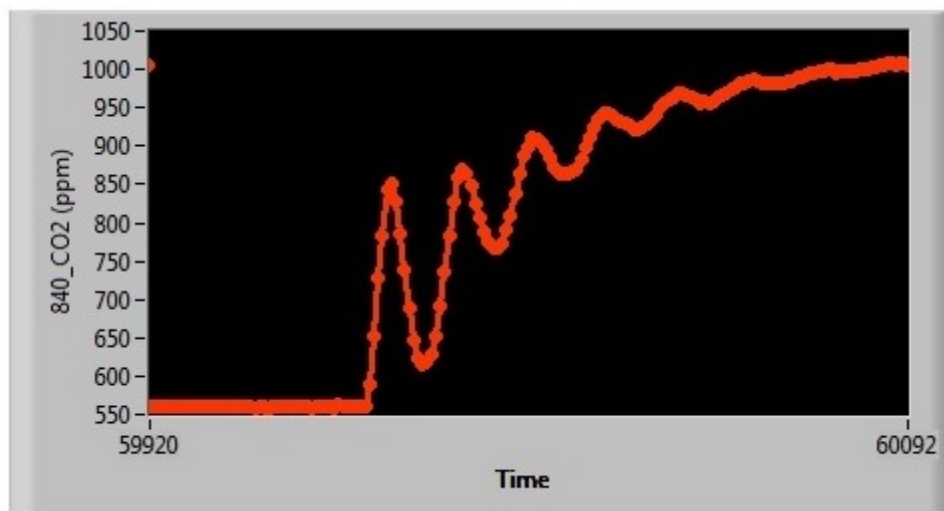
Figure 50: CO_2 oscillations at the start of the first sample in a set of twelve.

The instrumental system was originally designed and built by Tim Newberger and was supported by C. Sweeney and T. Takahashi. Their skill and generosity has been essential to the successful use and modification of this instrumental system. Denis Pierrot assisted in analyzing samples. Alain Munoz Caravaca and Leticia Barbero assisted in collecting samples.

The pressure transducer in the LICOR 840 analyzer failed on the seventh day of the cruise and resulted in a CTD cast not being sampled for discrete pCO_2. The spare LI-840 was installed and worked well throughout the rest of the cruise.

Standard Gas Cylinders	
Cylinder Number	**ppm CO_2**
JB03282	288.46
JB03268	384.14
JB03309	567.40
CA05980	792.51
CA05984	792.51
CA05940	1533.7

Figure 51 shows preliminary surface discrete pCO_2 values obtained from samples collected underway and from the surface bottle of each CTD cast.

Figure 51: Preliminary surface discrete pCO₂ measurements collected from underway samples and from the surface bottle at each CTD cast during GOMECC-3.

3.8. Total Alkalinity Measurements

Analysts: Gabriela Cervantes, Linda Barranco (UABC)
PIs: Rik Wanninkhof (AOML/NOAA), Denis Pierrot (AOML/CIMAS)

3.8.1 Alkalinity Definition

The total alkalinity of a seawater sample is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant K ≤ 10–4.5 at 25°C and zero ionic strength) over proton donors (acids with K > 10–4.5) in 1 kilogram of sample (Dickson, 1981).

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

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

3.8.2 Alkalinity Measurement System

Two titration systems were used: "System 1" used a Metrohm 765 Dosimat Titrator and an Orion 720A pH meter controlled by a personal computer (Millero *et al.,* 1993). "System 2" used a Metrohm 665 Dosimat Titrator and an Orion 2-Star pH meter. The cells consisted of a 400 ml water-jacketed glass beaker. A plexiglass reference electrode (Orion 900200) and a glass pH electrode (Orion 8101BNWP) were used to measure the e.m.f during the titration. The samples were delivered in the cells using a water-jacketed pipette, the calibrated volume of which was 185.63 ml at 25°C. A small air pump, which was also used to empty the cells after the titrations were complete, was used to pressurize and push the sample to fill the pipette. The filling and emptying of the pipette is controlled by a series of pinch valves controlled by manual electric switches. The tubing was first rinsed with small volumes of sample, then the pipette was rinsed with a full volume. The pipette was then filled again, and the volume delivered to one of the cells. Both the pipette and the cells were kept at 25 ± 0.1°C with a Neslab constant-temperature bath. The acid titrant, a 0.25175 mol/kg^{-1} HCl solution in ~0.55 molal NaCl solution, was made by Dr. Dickson of Scripps Institution of Oceanography (SIO) and stored in 1-L glass bottles, which were used to refill the acid bottles of the Dosimat when the level fell below the half mark.

The volume of HCl delivered to the cell is traditionally assumed to have a small uncertainty (Dickson, 1981) and is equated with the digital output of the titrator. Certified standard Reference Material (CRM) Batch 153 prepared by Dr. Dickson was used at sea to monitor the performance of the titrators. Roughly two CRMs a day were used to calibrate the instruments, once at the beginning of the day and once at the end. A total of 68 and 55 CRMs were run on System 1 and System 2, respectively. All TA data were corrected using the average of the before and after measured CRM values for each cell, unless one CRM measurement presented issues, in which case only the good measurement was used for the correction.

The progress of the titration is controlled by a computer program written in National Instrument's Labwindows/CVI 4.1, and the total alkalinity is computed from the titrant volume, concentration, and e.m.f. measurements using a non-linear least-squares approach that corrects for the reactions with sulfate and fluoride ions (Dickson *et al.,* 2007).

3.8.3 *Sampling*

Samples for total alkalinity measurements were taken at all GOMECC-3 stations (1-107). Two Bullister bottles at roughly each station were sampled twice for duplicate measurements. Seawater samples were drawn from the Bullister bottles on the CTD rosette with a 40-cm length of silicon tubing fitted directly over the petcock of the Bullister bottle and the other end was inserted into the bottom of a 500-ml Corning glass-stoppered sample bottle. The sample bottle was rinsed three times with approximately 300 ml of seawater. The sample bottle was slowly filled from the bottom and allowed to overflow for one volume. Once filled, the sample was poisoned with a saturated solution of mercuric chloride and the bottles were kept in a constant water bath at 25°C for at least an hour before analysis.

3.8.4 *Quality Control*

Dickson laboratory Certified Reference Material (CRM) Batch 153 were used to determine the accuracy of the total alkalinity analyses. The total alkalinity certified value for each batch is:

Batch 153: 2225.59 ± 0.77 µmol/kg

	# of CRMs measured	Average Measured Value (µmol/kg)	Standard Deviation (µmol/kg)
System 1	68	2228.28	± 1.78
System 2	55	2226.60	± 1.77

On most stations, duplicates were drawn on one Bullister bottle. The standard deviation for the duplicates measured on GOMECC-3 (for both systems) is:

Duplicate Standard Deviation: 1.04 ± 0.8 µmol kg^{-1} (n=86)

Figure 52 shows preliminary surface alkalinity values obtained from samples collected underway and from the surface bottle of each CTD cast.

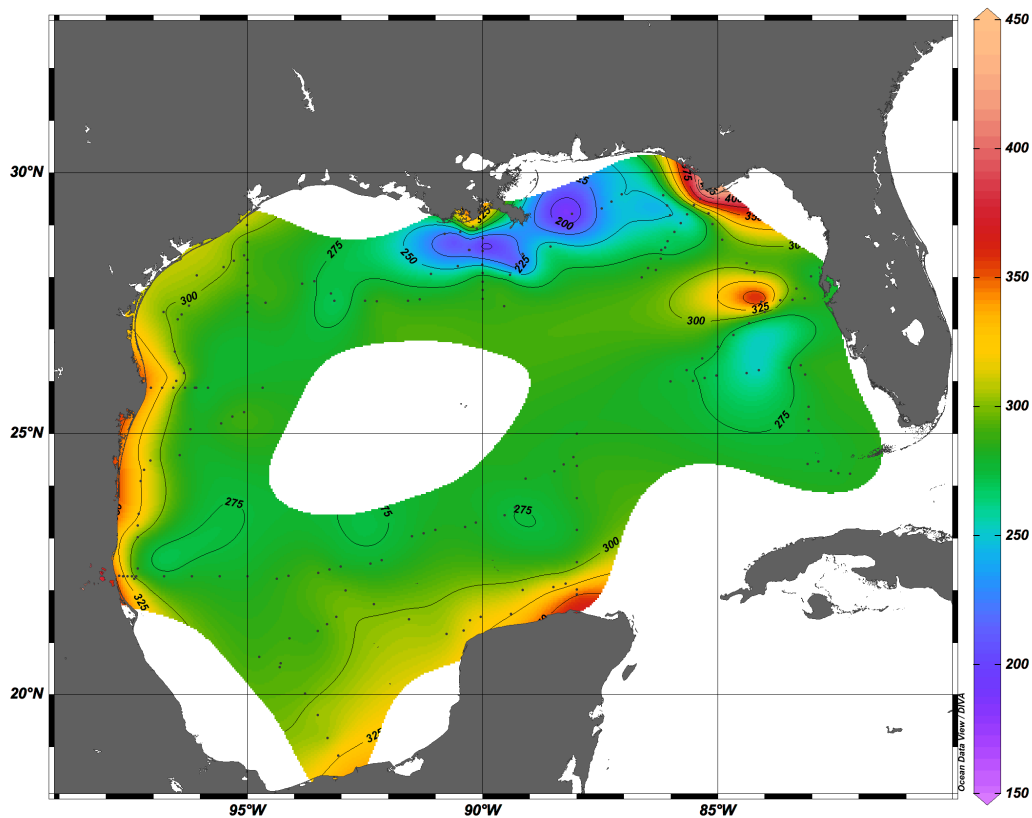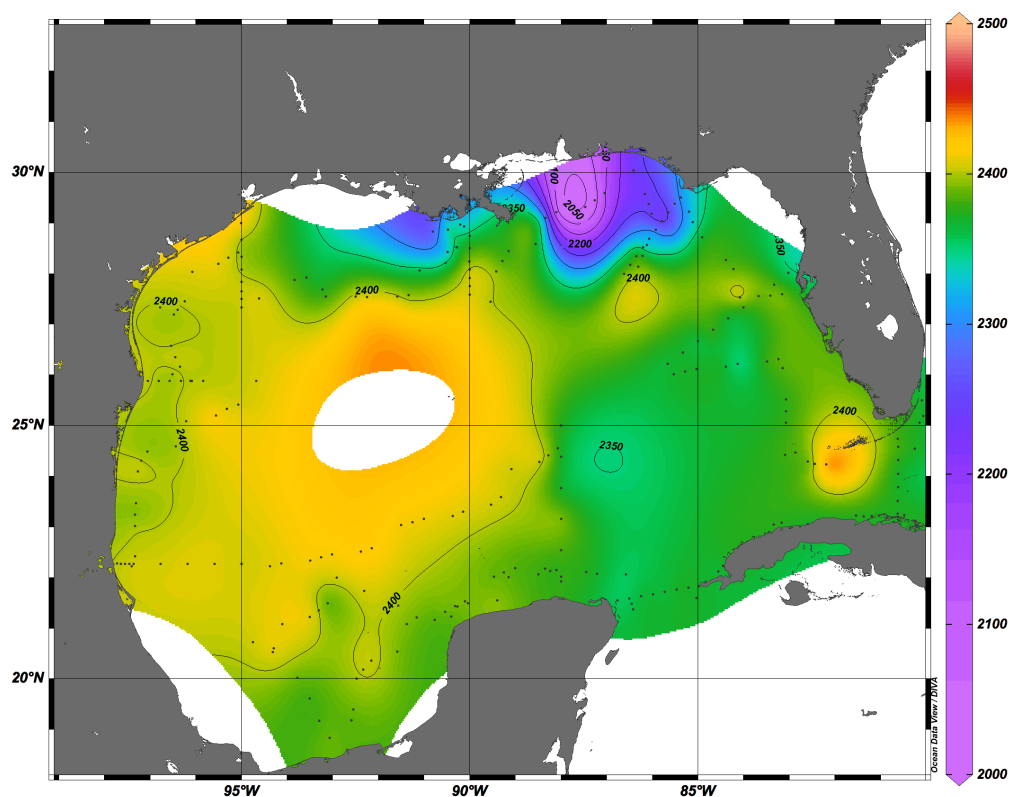*Figure 52: Preliminary surface total alkalinity measurements collected from underway samples and from the surface bottle at each CTD cast during GOMECC-3.*

3.9. Discrete pH Analyses

Analysts: Jonathan Sharp, Katelyn Schockman, Ellen Hudson-Heck, Courtney Tierney (USF)
PI: Robert H. Byrne (USF)

3.9.1 Sampling

Samples were collected for pH analysis immediately following O_2 in the rosette sampling sequence. Seawater samples were collected from Bullister bottles directly in 10-cm glass cylindrical optical cells (~30 mL volume) using a section of silicone tubing (about 15 cm long). One end of the silicone tubing was first attached to the nipple of the Bullister bottle. The nipple was pushed in to initiate flow, and the silicone tubing was squeezed to eliminate air bubbles. The other end of the silicone tubing was attached to the optical cell, which was agitated to eliminate any residual bubbles. After ~15 seconds of sample flow, the cell was capped at one end. The silicone tubing was then detached from the optical cell and, with the water still flowing, the other cap was rinsed and used to seal the optical cell. Samples collected this way are not exposed to the atmosphere, and each cell is flushed with at least three cell volumes of seawater.

The samples were collected, taken into the lab, and rinsed with tap water to eliminate salt on the outsides of the cells. The cells were dried thoroughly and the optical

windows were cleaned with Kimwipes immediately before measurement. Samples were thermostatted at 25 (±0.05) °C in a custom-made, 36-position cell warmer.

3.9.2 *Measurement and Calculation*

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

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

with R being the ratio of absorbances measured at 578 nm (λ_2) and 434 nm (λ_1), corrected for baseline changes using absorbance measured at 730 nm (λ_3): $R = (_{\lambda 2}A - _{\lambda 3}A) / (_{\lambda 1}A - _{\lambda 3}A)$. The salinity and temperature dependence of $K_2^T e_2$ is given as:

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

where

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

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

$c = 44.493382 - 0.052711\ S,$

$d = 0.0781344,$

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

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

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

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

The pH is calibration-free (no calibrations are needed). Duplicate pH samples, collected from discrete samples taken from Bullister bottles (N = 173), displayed a standard deviation of 0.001.

3.9.3   Perturbation Determination for pH

Small changes in sample pH (measurement perturbations; Clayton and Byrne, 1993) created by the addition of titrant to samples were quantified using samples collected from profiles. For each perturbation determination, ΔpH was defined as ΔpH = $\mathrm{pH_{final}} - \mathrm{pH_{initial}}$, where $\mathrm{pH_{initial}}$ is the total scale pH taken after a single titrant addition and $\mathrm{pH_{final}}$ is the total scale pH after a second titrant addition.

An equation developed using this perturbation data was used to correct pH measurements:

$$\mathrm{pH}^0 = 1.009332 \cdot \mathrm{pH} - 0.07155$$

where pH is the raw $\mathrm{pH_T}$ measurement and pH^0 is the perturbation-corrected $\mathrm{pH_T}$ measurement.

3.9.4   Quality Control

All spectrophotometric pH and $[CO_3^{2-}]_T$ (see next section) measurements were tentatively flagged if the baseline shifted more than 0.002 absorbance units. A series of five spectra were averaged for each determination, and samples were rerun if the overall standard deviations were higher than 0.0004 for pH measurements and 0.001 for $-\log[CO_3^{2-}]_T$ measurements. This process was repeated until the standard deviation of multiple readings was within 0.0004 for pH and 0.001 for carbonate. Absorbance values were saved so that the quality criteria can be evaluated in the future.

A total of 1,530 pH samples and 1,527 carbonate ion samples were collected from the 107 stations, and 154 underway samples were collected for both parameters. In the pH data set, perturbation-corrected $\mathrm{pH_T}$ measurements were reported along with their associated quality-control flags. In the $[CO_3^{2-}]_T$ data set, calculated carbonate ion concentrations and measured (uncorrected) absorbance ratios were reported, along with their associated quality-control flags. Both $\mathrm{pH_T}$ and $[CO_3^{2-}]_T$ were reported at the measurement temperature of 25°C.

3.10. Discrete Carbonate Ion Analyses

Analysts: Jonathan Sharp, Katelyn Schockman, Ellen Hudson-Heck, Courtney Tierney (USF)
PI: Robert H. Byrne (USF)

3.10.1 Sampling

The carbonate ion ($[CO_3^{2-}]_T$) samples were collected in 10-cm quartz cylindrical optical cells in the same manner as the pH samples. Samples were collected fifth in the rosette sampling sequence (following O_2, pH, pCO_2, and DIC).

3.10.2 Measurement and Calculation

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

Both the tungsten and UV lamps were turned on for carbonate ion analysis. A UV blank was taken for each sample and 20 µL of 0.022 M $PbClO_4$ were added (Acros Organics, 99% purity). Absorbances (A) were measured at two wavelengths on the Pb(II) absorbance peak ($_1\lambda = 234$ nm and $_2\lambda = 250$ nm) and at a non-absorbing wavelength ($_3\lambda = 350$ nm). Absorbance values were used to calculate absorbance ratios: R = ($_{\lambda 2}A - _{\lambda 3}A$) / ($_{\lambda 1}A - _{\lambda 3}A$) (Byrne and Yao, 2008).

The ratios were corrected for spectrophotometer wavelength offsets using the equation given in Sharp *et al.* (2017): $R^0 = R - 0.265 \cdot \Delta\lambda_{241.1}$. Corrected absorbance ratios (R^0) are calculated using an instrument-specific wavelength offset at 241.1 nm ($\Delta\lambda_{241.1}$), which was determined using SRM 2034 from the National Institute of Standards and Technology.

Carbonate ion concentrations ($[CO_3^{2-}]_T$) were then calculated using the equation:

$$-\log[CO_3^{2-}]_T = \log\left\{\frac{co_3\,\beta_1}{e_2}\right\} + \log\left\{(R^0 - e_1)\Big/\left(1 - R^0 \cdot \frac{e_3}{e_2}\right)\right\}$$

where $co_3\,\beta_1$ is the formation constant for $PbCO_3^0$ and the e_1 terms are molar absorptivity ratios. The following equation is equivalent to equation 8 of Sharp *et al.* (2017). The fitting parameters given for measurements at 25°C are:

$$\log\left\{\frac{{}_{CO_3}\beta_1}{e_2}\right\} = 6.87057 - 0.142142\,S + 0.00190892\,S^2$$

$$e_1 = 0.787458 - 0.0339648\,S + 0.000583574\,S^2$$

$$\frac{e_3}{e_2} = 2.52288 - 0.0383205\,S$$

where S is salinity. Duplicate carbonate ion samples, collected from discrete samples taken from Bullister bottles (N = 165), displayed a standard deviation of 2 μmol kg^{-1}.

3.10.3 Quality Control

All spectrophotometric pH and $[CO_3^{2-}]_T$ measurements were tentatively flagged if the baseline shifted more than 0.002 absorbance units. A series of five spectra were averaged for each determination, and samples were rerun if the overall standard deviations were higher than 0.0004 for pH measurements and 0.001 for $-\log[CO_3^{2-}]_T$ measurements. This process was repeated until the standard deviation of multiple readings was within 0.0004 for pH and 0.001 for carbonate. Absorbance values were saved so that the quality criteria could be evaluated in the future.

A total of 1,530 pH samples and 1,527 carbonate ion samples were collected from the 107 stations, and 154 underway samples were collected for both parameters. In the pH data set, perturbation-corrected pH$_T$ measurements were reported along with their associated quality-control flags. In the $[CO_3^{2-}]_T$ data set, calculated carbonate ion concentrations and measured (uncorrected) absorbance ratios were reported, along with their associated quality-control flags. Both pH$_T$ and $[CO_3^{2-}]_T$ were reported at the measurement temperature of 25°C.

3.11. Spectral Measurement of the Optical Absorption of Particulates and CDOM

Analysts: Shuangling Chen, Yingjun Zhang, Jen Cannizzaro (USF/CMS)
PIs: Mike Ondrusek (NOAA/NESDIS), Chuanmin Hu (USF/CMS)

In total, 180 water samples were collected during the cruise, with 122 samples from the surface and 58 samples from depths near changes in O_2 concentrations. From these samples, suspended particulates were collected on glass-fiber filters for spectral particulate and pigment analysis, while <200 ml of filtrate was collected from additional filtering for spectral CDOM analysis.

Sampling: Surface water samples were collected from most of the stations, either from the CTD Bullister bottles or using bucket casts. Samples from >2 m were collected from the CTD Bullister bottles. Typically, two 10-L carboys of surface water and six 1-L bottles from deeper water samples were collected for stations with a bottom depth of

≥100 m. For stations where an above-water remote sensing reflectance ($R_{rs}(\lambda)$) or HyperPro measurement was made, the surface water sample was collected near the Rrs or HyperPro measurement to permit a relation of the $R_{rs}(\lambda)$ measurement to the in situ sample.

Preparation: Both the surface water samples and deeper water samples were filtered onto GF/F glass fiber filters using a vacuum pressure of <7 in Hg. Surface water samples were usually filtered both for the particulate absorption measurements and for later HPLC phytoplankton pigment analysis. Subsurface water samples were only filtered for the particulate absorption and CDOM analysis. The volume of water filtered was varied, so that sufficient colored material was retained on the filter. The filters were kept frozen using liquid N_2 until they were analyzed. Filtrate from the particulate absorption filtration underwent additional filtration using a 0.2 μm polycarbonate filter, and ~125 ml of the subsequent filtrate was saved into a glass brown bottle for later CDOM analysis. While <1 liter of water might be filtered in turbid coastal waters, it was necessary to filter several liters (i.e., 5~9 L) for samples taken in oligotrophic waters.

Analysis: The absorption spectra of the particulate (a_p), detrital (a_d), and dissolved material (a_g) were determined in post-cruise, shore-based lab analysis. By combining the pigmented-particulate absorption spectra with a chlorophyll-a measurement, one can determine a phytoplankton specific absorption that is useful for developing primary productivity, in-water light field, and remote sensing algorithms. To measure the particulate spectral absorption, the transmission of light through a particulate laden filter was compared to a wetted blank filter. The measurement was repeated after extraction of pigments from the particles (Kishino *et al.,* 1985). This allowed the spectra to be divided into pigmented and detrital components. A chlorophyll-a concentration was also determined by fluorometric measurement (Holm-Hansen and Riemann, 1978; Welschmeyer, 1994) for each filter pad measurement.

The filtrate from the initial water sample filtration underwent an additional filtration using a 0.2 μm filter. The CDOM absorption spectra, $a_g(\lambda)$, was determined by measuring the transmission of light through this filtrate using a spectrophotometer. The $a_g(\lambda)$ spectra is usually measured from <250 nm to >600 nm, while $a_p(\lambda)$ and $a_d(\lambda)$ are measured from ~400 to 750 nm. The analysis is expected to be completed by 2019.

3.12. Plankton Community Dynamics/Trophic Interactions across Continental Margins

Analysts: Gabrielle Corradino (NCSU), Mrunmaye Pathare (ULL)
PIs: Astrid Schnetzer (NCSU), Beth Stauffer (ULL)

Our group's efforts on the GOMECC-3 cruise addressed three objectives designed to test several hypotheses about the nature and fate of organic carbon in the surface ocean across diverse oceanographic regions, variable levels of ocean acidification and eutrophication, and with complex planktonic communities:

Objective I: Characterize plankton abundances, community composition, and coherence along spatial (vertical and horizontal) gradients within the Gulf of Mexico.

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

Objective III: Assess surface-carbon allocation in response to changes in phytoplankton-grazer coupling within the Gulf of Mexico.

To address these objectives, we brought together traditional (i.e., microscopy) and modern (i.e., next generation sequencing, flow cytometry) techniques to characterize plankton community structure 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, CO2, pH, and dissolved oxygen. The data will also help elucidate how these communities are affected by environmental changes, and how this, in turn, impacts the fate of carbon from the surface ocean.

3.12.1 Methods

The CTD samples were taken from two or three depths for each pre-selected station (one nearshore, offshore, and intermediate on each transect line). The samples were filtered onto GF/Fs for DNA, RNA, and chlorophyll and stored at -20°C. The whole water preservation used lugols, formalin, and ethanol. All samples were brought back to North Carolina State University or the University of Louisiana for processing and analysis.

3.12.2 CTD Sampling

Whole seawater sampling was conducted to characterize pico-, nano-, and microeukaryote communities via microscopy and flow cytometry. Briefly, for microscopy 110 ml were preserved with ~5% Lugol's, 110 ml preserved with 1% gluteraldehyde (to identify mixotrophs), and 4 ml preserved with 1% formalin for flow cytometry. All water collected from all depths was passed through a 200 μm mesh to exclude larger zooplankton grazers and additional aliquots were further processed, as described below.

3.12.3 Chlorophyll-a and Molecular Sampling

Samples for chlorophyll quantification were filtered onto GF/F filters in duplicate with volumes of 100 ml for surface and chlorophyll max depths and 150 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 1000 and 500 ml were collected for subsequent RNA and DNA analyses, respectively. For deep sampling depths, volumes were increased for each analysis to ensure sufficient biomass. 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. The 200 µm mesh was rinsed with filtered seawater, and organisms retained on the screen were concentrated in 20 ml of filtered seawater (FSW) and ethanol (EtOH) (50/50) in cryovials.

3.12.4 Microzooplankton Dilution and Copepod Feeding Experiment

For grazing experiments, a total of 10 zooplankton tows were conducted at 10 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) were fitted with (Presense) optodes to measure oxygen concentrations and temperatures pre- and post-experiment. The on-deck incubator had ambient seawater flowing through it throughout the cruise, and light conditions were monitored using a PAR sensor several times throughout the experiments. 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.

Based on the methods of Landry *et al.* (1995), 18 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 6. 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. Undiluted bottles were prepared in quadruplicate; two each were exposed to light, while two were wrapped in black tape to provide "dark bottles." PreSense optodes in these four sets of bottles allowed for non-invasive measurement of dissolved oxygen at the start and end of grazing experiments, allowing for the calculation of primary production and respiration using the light/dark bottle approach (Holtappels *et al.,* 2014). A known quantity of the most common copepods (15-20 total), isolated from the net tow, was added to a set of light and dark bottles containing 100% FSW (Figure 53).

Table 6: Dilution and copepod addition experiment details.

Dilutions	<200 SW	FSW	N stock solution (2.5 mM)	P stock solution (1 mM)
5% × 3	100 mL	900 mL	0.5 ml	0.5 ml
20% × 3	200 mL	800 mL	0.5 ml	0.5 ml
100% × 3	1000 mL	0 mL	0.5 ml	0.5 ml
100% − dark × 3	1000 mL	0 mL	0.5 ml	0.5 ml
100% + cop	1000 mL	0 mL	0.5 ml	0.5 ml
100% + cop − dark	1000 mL	0 mL	0.5 ml	0.5 ml

Figure 53: Schematic of the microzooplankton dilution and copepod feeding experimental design.

Bottles were incubated for 24 hours at ~50% ambient light in the on-deck incubator with flowing seawater and were sampled at the beginning (T0) and end (Tf) of the experiment. T0 sampling for chlorophyll, community composition (microscopy, 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, dissolved oxygen was measured in light/dark bottles, and all bottles were sampled for chlorophyll and community composition (microscopy, flow cytometry). Filters for chlorophyll and flow cytometry analyses were stored in the freezer until shipment back to ULL; preserved samples were stored in dark boxes. Lugols- and glutaraldehyde-preserved samples were counted for auto-, hetero-, and mixotrophic microplankton in the Schnetzer lab at NCSU using inverted microscopy. Formalin-preserved samples were analyzed for picocyanobacteria, picoeukaryotes, and nanoplankton in the Stauffer lab at ULL using flow cytometry (FACSCalibur). Abundance changes and community structure shifts in bottles without grazers compared to those with grazers present (both micro-and mesozooplankton grazers) were determined to quantify and characterize plankton trophic interactions within varying regions of the Gulf of Mexico. Copepod grazing rates derived from the incubations were extrapolated to community grazing estimates based on overall copepod abundances in the tow samples at each station.

The activities conducted by the plankton group are summarized in Table 7.

Table 7: Activities conducted by the plankton group during GOMECC-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

4. Community Structure of Zooplankton and Ichthyoplankton

4.1. Biological Samples and Data Collection

Samples for the analysis of the community structure of zooplankton and ichthyoplankton were collected at 51 stations (38% over the pre-defined stations) corresponding to the following code cruise station [CTD: 2, 5, 8, 10 (*Line 1*), 13, 15, 19, 21 (*Line 2*), 22, 24, 27, 29 (*Line 3*), 34.1, 34.2, 34.3, 34.5 (*Diel station*), 41, 42, 43, 44 (*Line 4*), 47, 49, 51, 54 (*Line 5*), 57, 59, 60, 63 (*Line 6*), 64, 65, 66, 68 (*Line 7*), 71, 72, 73 (*Line 8*), 74, 76, 78, 79 (*Line 9*), 81, 82, 86, 87 (*Line 10*), 88, 90, 92, 94 (*Line 11*), 96, 99, 102, 106 (*Line 12*)]. All the tows were operated from the aft winch at the starboard side, except the stations in Lines 4 and 5, which were sampled with the manual winch trawl from the A-frame by the fantail. The original stations for Line 4 were CTD-37, 39, 40, and 44. However, upon arrival to the first of these stations the winch was damaged. The three first stations were aborted, and that is the reason why this line was shallower than the rest. Overall, the stations were located along 12 transects throughout the entire Gulf of Mexico waters, a diel station by the National Marine Sanctuary Flower Garden Banks, and adjacent waters of east Florida, ranging from shallow waters (18 m deep) to the deep water region (3426 m deep).

Samples were collected performing double-oblique tows with the vessel holding a 45° wire angle, from the surface to 200 m (or closest to the bottom at stations with depths shallower than 200 m) at a vessel speed of ca. 1.5 knots. Payout was set at 20 m/min, and there was a 1-minute stop at the bottom before heading back to the surface. The bongo net has two 60 cm diameter rings and nets with a mesh size of 335 μm. Both nets were equipped with two mechanical flowmeters (*General Oceanics 2030R*) in the net mouth. Volume filtered ranged from 44-593 m^3, but most frequently was between 300-350 m^3. The sample collected with one of the nets was fixed in 4% formalin buffered with sodium borate. The second sample was fixed in 96% ethanol for genomic analysis.

To approach the study of the zooplankton and ichthyoplankton and their relationship with environmental factors, the information about temperature, salinity, wind, and transmissometry obtained from the CTD was recorded. Besides these, we obtained information from remote sensors to analyze the relationship between sea surface height and chlorophyll-a when it was available.

4.2. Plankton Sample Processing Protocols

Bongo net samples (n=51) were collected during the GOMECC-3 cruise and preserved in formalin. These were delivered to the Fisheries Oceanography and Ecology Lab at the University of Southern Mississippi in August 2017. In collaboration with Glenn Zapfe and the NOAA SEAMAP Plankton Team, we were able to include aliquots of these samples in the SEAMAP plankton sample shipment to the Plankton Sorting and Identification Center (ZSiOP) in Szczecin, Poland. At ZSiOP, the samples were sorted for fish eggs, fish larvae, and cephalopods, and larval fish were identified to the lowest possible taxonomic level.

Below is a description of the sample processing protocols (a flow diagram is also provided in Figure 54). Decisions to aliquot samples were based on the volume of plankton in each sample, and the need to expedite sample processing so that the samples reached the other GOMECC-3 plankton collaborators in a timely manner.

1. All samples were transferred from formalin to 85% ethanol. After 2 weeks a second transfer was made into 95% ethanol.

2. All samples were then sieved through a 5-mm mesh to remove larger organisms (e.g., juvenile fishes); these specimens were retained and stored in 95% ethanol.

3. The volume of plankton (in ml) was determined for each sample using the volume displacement method described in the ICES Zooplankton Methodology Manual (2000, Eds. R. Harris, P. Wiebe, J. Lenz, H.-R. Skjoldal and M. Huntley).

4. Samples with plankton volumes >20 ml (n=24) were split to generate two 1/2 sample aliquots. One of the 1/2 aliquots was set aside for the shipment to ZSiOP; the other 1/2 aliquot was split a second time to generate two 1/4 aliquots. One of the 1/4 aliquots was shipped to the zooplankton group at ECOSUR; the other 1/4 aliquot was processed at USM for fish larvae and microplastics.

5. Samples with plankton volumes >10 ml and <20 ml (n=22) were split to generate two 1/2 aliquots. One of the 1/2 aliquots was set aside for shipment to ZSiOP; the other 1/2 aliquot was processed at USM for fish larvae and microplastics, then shipped to the zooplankton group at ECOSUR.

6. Samples with plankton volumes <10 ml (n=5) were processed at USM for fish eggs, fish larvae, cephalopods, and microplastics, then shipped to the zooplankton group at ECOSUR.

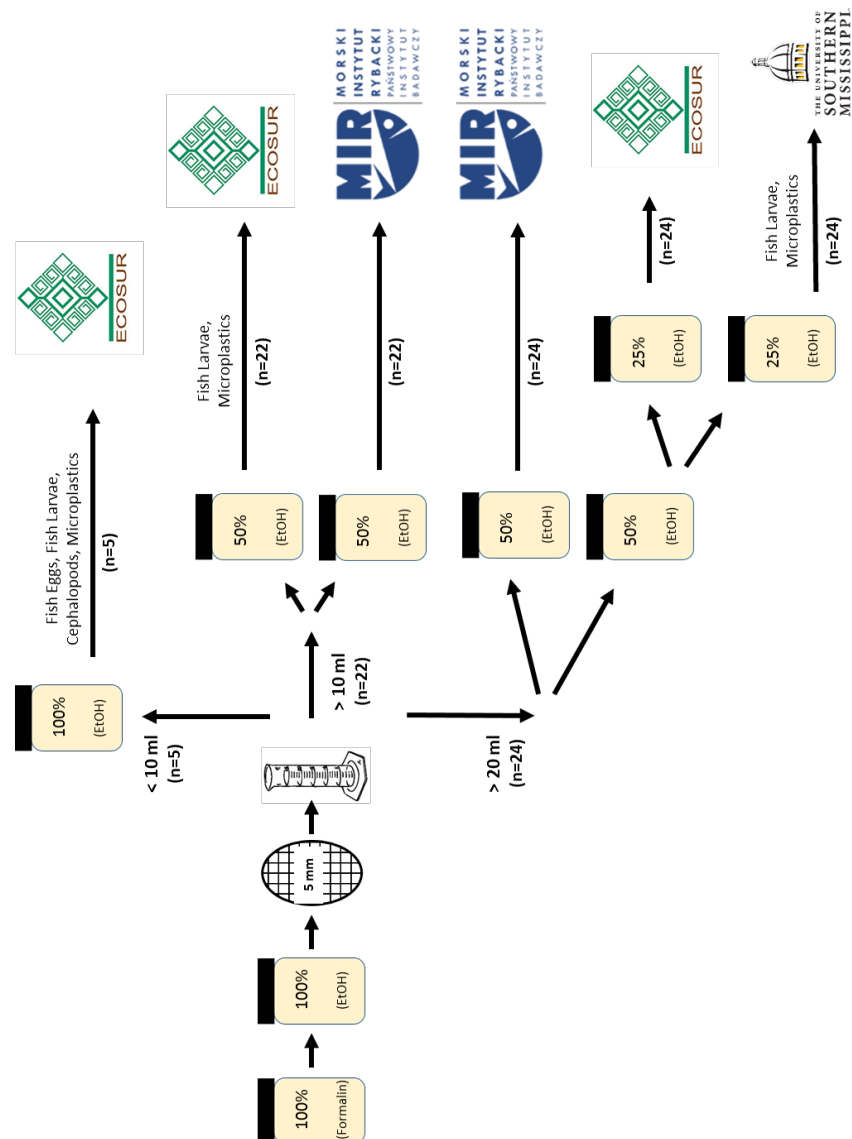7. Aliquots from 46 of the 51 samples were sent to ZSiOP in October 2017.

Figure 54: Flow diagram describing the plankton sample processing protocols.

4.3. Ichthyoplankton

Analysts: Jesús Cano Compairé (CICESE), Lucio Lomán (ECOSUR)
PIs : Sharon Herzka (CICESE), Frank Hernandez (USM)
Land-based analyst: Clarisa Galindo (CICESE)

A variety of studies have documented changes in the distribution of marine fish species in response to shifting environmental conditions attributed to climate change. Specifically, ocean acidification due to the influx of higher concentrations of CO_2 from the atmosphere into the marine environment can negatively impact fish populations by acting upon several life stages, influencing spawning grounds, recruitment, and migration patterns. The larval stage is potentially the most sensitive to acidification due to a larva's limited development, including a lack of fully functional pH regulatory system and the formation of calcareous structures (otoliths) that are part of the auditory and balance systems. In addition, most larval fishes rely on zooplankton for prey, some of which have calcareous shells (e.g., ostracods, pteropods) that are potentially sensitive to acidification impacts. Since larval fish feeding, growth, and survival is intimately linked to recruitment success, negative effects on fish larvae will adversely impact adult population size.

Most of the research that has focused on characterizing the community composition and distribution of larval fishes in the Gulf of Mexico relative to oceanographic conditions has been focused in US waters and, to a much lesser extent, on the Bay of Campeche and Yucatan Platform. Additional studies have focused on Caribbean fish species and their transport through the Yucatan Channel into the Gulf of Mexico via the Loop Current. To our knowledge, there have been no synoptic larval fish surveys with which to characterize the patterns of larval fish distribution (and hence spawning ranges) on a basinwide scale. In the long-term, this baseline information will allow for the evaluation of changes in species ranges and patterns of distribution during the larval stage.

Our objective was to characterize the abundance and distribution of larval fish in the Gulf of Mexico, Yucatan Channel, Florida Straits, and Bahamas Channel within a single season based on samples collected during the GOMECC-3 cruise. These data will be used to generate basinwide distribution maps that should be reflective of spawning regions and will provide a much-needed baseline for future studies of the effects of ocean acidification on marine fish populations within the Gulf.

We used two complementary approaches to characterize the ichthyoplankton community: traditional identification based on morphological and meristic characteristics and metagenomics. For some taxa, there are limited morphological differences between species that can render identification impossible, particularly for early larvae. Metagenomics can provide a means for identifying individuals, as long as a specific taxon has been correctly sequenced and genetic information is available. Comparison of the community composition derived through both approaches will yield a more complete characterization of the Gulf's ichthyofauna than either approach alone.

Note: At CICESE, S. Herzka and C. Galindo are participating in a 5-year extensive research project (2015-2020) in which they are sampling ichthyoplankton in the deep water region of the Gulf of Mexico and Yucatán Channel and analyzing the community composition through traditional identification and metagenomics.

Objectives

- Conduct a synoptic survey of the ichthyoplanktonic community (species composition and abundance) of the Gulf of Mexico's platform and deep water region, as well as the Yucatan Channel, Florida Straits, and Bahamas Channel by coupling traditional identification techniques and metagenomics.

- Generate basinwide distribution maps that should be reflective of spawning regions and that will provide a much-needed baseline for future studies of the effects of ocean acidification and other anthropogenic impacts (such as increasing SST) on marine fish populations within the Gulf.

4.4. Pteropods and Zooplankton Community

Analysts: Lucio Lomán (ECOSUR), Jesús Cano Compairé (CICESE)
PI: Daniel Pech (ECOSUR)

Pteropods have been commonly used as an indicator of the potential effect of ocean acidification on marine life because of their thin aragonite shells, which are extremely sensitive to changes in the aragonite ionic equilibrium of seawater. It has been documented that in undersaturated conditions of aragonite the pteropod shell can dissolve (Bednarsek *et al.,* 2016). Participation in GOMECC-3 represented an excellent opportunity to explore the potential use of pteropods as a species indicator of the current status of ocean acidification in the Gulf of Mexico. Our first approach was based on the identification and quantification of the pteropod species occurring in the sampling areas covered during the GOMECC-3 cruise. The species abundance database was used to establish potential statistical relationships between pteropod community characteristics and current pCO$_2$ levels. Furthermore, we also explored this relationship at population levels. We expected that high pCO$_2$ levels would cause a lower abundance, richness, and diversity of pteropods.

Main Goals

- Investigate the potential use of pteropods as an indicator of ocean acidification in the Gulf of Mexico.

- Evaluate the potential statistical association between the pteropod population parameters and the pCO$_2$ levels in the Gulf of Mexico.

Our approach was based on the quantification of community and population characteristics and included observing samples under a microscope and robust taxonomic work to be performed at ECOSUR facilities. We estimate at least 11 months for sample

analysis and two more months for numerical population analysis. The statistical association with pCO$_2$ levels depended on the availability of data. We also explored the relationship of pCO$_2$ levels with the zooplankton community structure.

5. Underway Measurements

5.1. Thermosalinograph Measurements

The ship has two thermosalinographs that continuously measure sea surface temperature and salinity from the seawater line. However, these data have not been traditionally quality controlled. During GOMECC-3, the AOML group led by Dr. Rik Wanninkhof undertook the task of quality controlling the data by comparing them to TSG data collected by the group's TSG connected to the underway pCO$_2$ system and the surface bottle salinity samples collected at each CTD station. The quality controlled TSG data were incorporated into the underway dataset.

5.2. Underway pCO$_2$ Analyses

Analyst: Kevin Sullivan (AOML/CIMAS)
PIs: Rik Wanninkhof (AOML/NOAA), Denis Pierrot (AOML/CIMAS)

During the GOMECC-3 cruise, there was an automated underway pCO$_2$ system from AOML situated in the hydrolab, as it has been since 2007. The design of the instrumental system is based on Wanninkhof and Thoning (1993) and Feely *et al.* (1998), while details of the instrument and its data processing are described in Pierrot *et al.* (2009).

The repeating cycle of the system includes four gas standards, five ambient air samples, and 100 headspace samples from its equilibrator within 4.8 hours. The concentrations of the standards range from 283 to 539 ppm CO$_2$ in compressed natural air. They were purchased from NOAA/ESRL in Boulder and are directly traceable to the WMO scale.

The system includes an equilibrator where approximately 0.6 liters of constantly refreshed surface seawater from the bow intake is equilibrated with 0.8 liters of gaseous headspace. The water flow rate through the equilibrator was 1.7-2.2 liters/min, which yielded a vigorous spray pattern during this cruise.

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

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

The automated pCO_2 analytical system operated well throughout the entire cruise.

Standard Gas Cylinders

Cylinder Number	ppm CO_2
CA04957	282.55
CC105863	380.22
CB09696	453.04
CB09032	539.38

Figure 55 shows raw xCO_2 measurements collected during GOMECC-3.

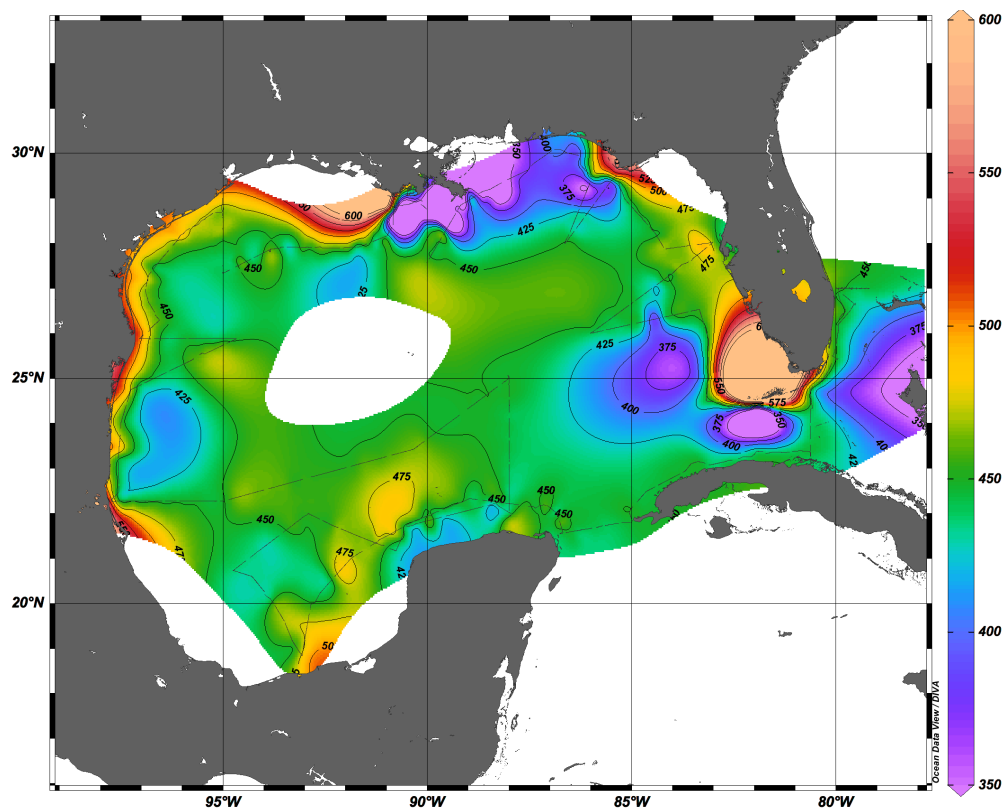*Figure 55: Raw surface xCO_2 values measured during GOMECC-3. The extrapolation method leads to some unrealistic artifacts with high values in areas where no measurements were collected (particularly the Southwest Florida Shelf and the west Louisiana shelf east of Galveston, TX).*

5.3. SeaFet System: Underway pH measurements

Analysts: Linda M. Barranco, Gabriela Cervantes (UABC)
PI: Martín Hernández Ayón (UABC)

Underwater-SeaFet System Description

The SeaFet is a system composed of two electrodes:

- A Half-cell Solid State Ion-Selective Electrode (ISE) (Thermo Orion). This electrode uses a solid membrane of silver chloride, which is an ionic conductor for silver. The silver ion develops a potential across the membrane that depends on chloride ion activity in the sample solutions.

- A non-glass pH electrode (Durafet) with an internal reference of saturated KCl. The pH measurement is based on ISFET (Ion Selective Field Effect Transistor) technology. A temperature sensor is mounted internal to the Durafet to measure process temperature and provide a signal for automatic (Nernstian) temperature compensation.

The underwater system was built by Dr. Martin Hernandez. He coupled the SeaFet sensor to an underwater cell (Provided by Todd Martz). The cell allows for the housing of the pH electrodes and the chloride electrode to be immersed in the water. This gives stability to the millivolt readings and better stability to the overall measurements.

The system was connected to the ship's underway seawater line in the Hydrolab. The flow of water passed first through MBARI's Durafet System, and then through our SeaFet System in a continuous line.

The SeaFET was started the day before the cruise began, which is considered a conditioning period. From then and until August 19, a file was downloaded daily at approximately 16:00 GMT with 24 hours of measurements.

The SeaFet system was configured with the following parameters:

- *Date:* The official time of the cruise (GMT time)
- *Deployment parameters*
  - The rate of sampling was 120 seconds, taking the average of 5 samples.
  - Battery: The battery was new with 11 V (Full charge)

The SeaFET was monitored daily. The cell was rotated occasionally to get out potential bubbles trapped in the cell.

Database

A total of 34 files were created. Each file contained 24 hours of measurements, except for the last file which contained 48 hours of measurements. The files contained the date, battery voltage, measurements from the two sensors, and the temperature.

Observations on Board

The pH sensor worked well; however, the chloride electrode data were very noisy. The sensor was changed twice, but measurements did not improve. The shape of the cell retained organic material from the seawater, therefore; the sensors tend to get dirty continuously, especially in areas near the coast. To prevent this, the cell and sensors were cleaned, but the chloride sensor response did not improve.

5.4. Multi-Parameter Inorganic Carbon Analyzer for Underway pH/TA Monitoring

Analysts: Jonathan Sharp, Katelyn Schockman, Ellen Hudson-Heck, Courtney Tierney (USF)
PI: Robert H. Byrne (USF)

We operated an underway sampling system during the GOMECC-3 cruise. The Multi-parameter Inorganic Carbon Analyzer (MICA) in a Box is a modification of previous MICA instruments; it is assembled using more affordable parts and is compact enough to fit into a small Pelican case. MICA in a Box (MIB) is designed to measure seawater pH, total alkalinity (TA), and dissolved inorganic carbon (C_T) using spectrophotometric principles.

On the GOMECC-3 cruise, MIB continuously measured seawater pH and TA. Measurements of C_T were not carried out on the cruise due to technical issues related to light attenuation within the C_T measurement cell. C_T can be calculated from the other two measured parameters. MIB was set up next to the uncontaminated seawater line in the main lab, where surface water was continuously introduced to the system. The parameters were measured spectrophotometrically by directly injecting indicator dye into the stream of underway seawater. Each parameter was paired with an optical cell where absorbances were monitored.

For pH measurements, purified meta-cresol purple (mCP) is injected into a seawater sample and a ratio calculated comparing the absorbances of the resulting acid and base peaks. Five scans are averaged per sample.

For TA measurements, bromo-cresol purple (BCP) is injected into a seawater sample. The mixture is equilibrated with standard gas of a known mole fraction of CO_2 (30%). Absorbance values of the solution are measured, and total alkalinity is calculated using measured pH and the known pCO_2 of the solution (set by the standard gas).

The peripheral parameters—temperature, salinity, and pressure—are read each time a pH scan is stored (~every 30 seconds). The most recent peripheral data is used for each TA calculation.

On GOMECC-3, an automated program ran cycles to operate the MIB continuously. The time required for each measurement cycle depended on the equilibration time and flushing time for the indicator/reference solution and samples. The chemical reaction for pH measurements was essentially instantaneous; however, the TA equilibration time was much longer (~6 min). The following sequences were used for each measurement cycle:

1. pH Measurement Cycle
   1. Flush pH reference (seawater without indicator solution).
   2. Read and store reference reading.
   3. Inject indicator; mix mCP with seawater (pH measurements); Mix BCP with seawater sampler (TA measurements).
   4. Read and store individual pH absorbance; 5 scans per sample.
   5. Read and store temperature, salinity, and pressure measurements.
   6. Compute pH using temperature, salinity, and pressure.
   7. End one measurement cycle and repeat from the beginning.

2. TA Measurement Cycle
   1. Flush TA reference (seawater without indicator solution).
   2. Read and store reference reading.
   3. Inject indicator; mix BCP with seawater.
   4. Wait 6 minutes for equilibration of seawater mixture with CO_2.
   5. Read and store individual TA absorbance; 10 scans per sample.
   6. Compute TA using the most recent temperature, salinity, and pressure measurements.
   7. End one measurement cycle and repeat from the beginning.

Over 61,000 measurements of underway pH and over 8,500 measurements of underway TA were collected by MIB during the GOMECC-3 cruise.

5.5. Flow-Through Laser Fluorometer Measurement

Analysts: Shuangling Chen, Yingjun Zhang, David English (USF/CMS)
PIs: Mike Ondrusek (NOAA/NESDIS), Chuanmin Hu (USF/CMS)

Equipment and Techniques

The WETLabs ALFA system is a device that measures the temporal and spectral fluorescence response of a water sample to pulsed laser excitation at 2 wavelengths. This ALFA system uses excitation lasers at 405 and 515 nm, intended to provide information about the fluorescence of CDOM, chlorophyll-a, and some accessory pigments. The ALFA can be operated either as a flow-through system or for the analyses of discrete samples, but collected data while plumbed into the ship's flowing seawater system for

most of this cruise. The system was installed in the hydro lab, passing ~0.5 liters of seawater per minute from the ship's flow-through system. Its purpose was to record information about the phytoplankton and CDOM fluorescence of near-surface waters several times a minute, throughout the cruise.

Analysis

This system uses a combination of a blue and green laser light to excite fluorescence in a small water sample. The subsequent spectral and temporal analysis of the fluorescent response not only provides information about chlorophyll and CDOM concentrations, but also provides information about phytoplankton health and functional types (Chekalyuk and Hafez, 2011, 2013).

Data from the system requires post-cruise processing and water sample validation. By matching the temporal measurements with the ship's position, spatial surface transects can be produced for each cruise leg.

6. Other Activities

6.1. Optical Oceanography activities

Analysts: Shuangling Chen, Yingjun Zhang, David English (USF/CMS)
PIs: Mike Ondrusek (NOAA/NESDIS), Chuanmin Hu (USF/CMS)

The USF Optical Oceanography Lab made measurements to assist in the validation of ocean color data collected by the Visible Infrared Imaging Radiometer Suite (VIIRS) instrument on the Suomi National Polar-Orbiting Partnership (Suomi NPP) satellite, as well as to enhance the optical characterization of near surface waters during the GOMECC-3 cruise. The goal of the measurements is to aid the development of remote sensing algorithms and the assessment of the spatial distributions of chlorophyll, salinity, and other components of the near-surface waters. Figure 56 is a 7-day CI (color index) composite from the MODIS satellite sensor and the GOMECC-3 cruise track.
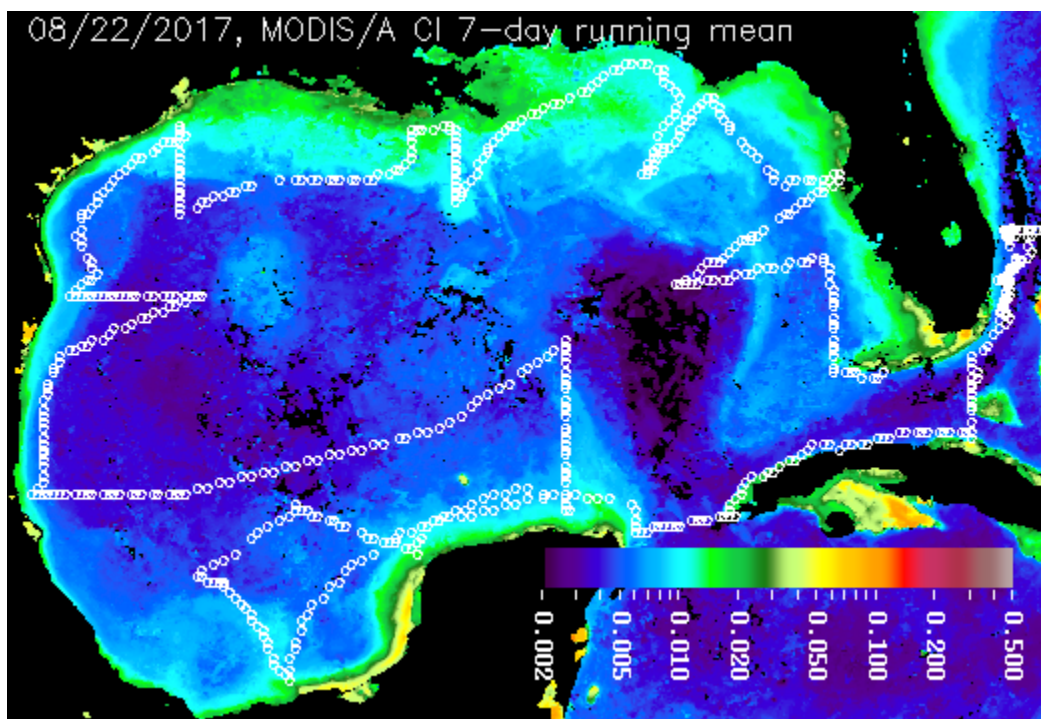
Figure 56: A 7-day composite of color index (CI) image (centered on Aug. 22, 2017) from the MODIS Aqua ocean-color sensor. The white circles show the GOMECC-3 cruise track.

In addition to the water sample absorption measurements (section 3.10) and flow-through ALFA measurements (section 5.5) collected during GOMECC-3, measurements were also made of the atmospheric aerosol optical thickness, the above-water spectral remote sensing reflectance ($R_{rs}(\lambda)$), and the measurement of multiple optical properties from near-surface profiling of upwelling radiance and downwelling irradiance.

Both the above-water $R_{rs}(\lambda)$ and the near-surface bio-optical profiles allow estimation of $R_{rs}(\lambda)$ for validation of VIIRS satellite imagery. The above-water $R_{rs}(\lambda)$ was measured using a handheld radiometer and a reference reflectance target (Mueller *et al.,* 2003). The bio-optical profiles were made by lowering a Satlantic® HyperPro-II profiling system through the surface waters. The accuracy of these measurements, as well as the aerosol optical thickness in the ozone column, improves when clear skies and suitable weather conditions are present. Their utility for validation is best when they are made near the time of surface water collection and satellite overpasses, allowing the relation of bio-optical measurements to the observed surface water properties and satellite measurements.

6.1.1 Aerosol Optical Thickness in the Ozone Column

A MicroTOPS II was used at 67 locations during GOMECC-3 to make measurements for the determination of the aerosol optical thickness at several wavelengths. These measurements are intended to aid the validation of the VIIRS ocean color satellite sensor.

Equipment and Techniques

The MICROTOPS II is a hand-held multi-band sunphotometer capable of measuring direct solar radiation within specific wavelength ranges. The instrument uses five aligned optical collimators, each with a field view of <3°. Each collimator is paired with a narrow-band interference filter and a photodiode, so that measurements are made at 305, 312, 320, 936, and 1020 nm. The measurements are made by recording energy received when these collimated detectors are aligned with the sun (Solar Light Company Inc, 2003; Morys *et al.,* 2001).

Sampling

The measurement requires a clear sky near the sun, but does not require the ship to be stationary. A measurement was collected at those stations occupied between 10 am and 5 pm (local time) with an unobscured view of the sun.

Analysis

Measurements collected by the MICROTOPS II were processed for the retrieval of aerosol optical thickness with quality control using the typical data processing routine as described in Ichoku *et al.* (2002) and Gomez-Amo *et al.* (2011) back on land.

6.1.2 Near Surface Light Field Measurements using the Satlantic HyperPro-II

The HyperPro-II system was deployed during mostly clear skies at 14 locations during the cruise.

Equipment and Techniques

The core of the Satlantic HyperPro-II system is a bio-optical profiler combining hyperspectral radiance and irradiance measurements with depth, tilt, fluorescence, optical backscattering, conductivity, and temperature measurements. Upwelling radiance ($L_u(\lambda)$) and downwelling irradiance ($E_d(\lambda)$) are measured at <5 nm increments between ~350 and 750 nm, while an above-water irradiance sensor allows comparison of the in-water light measurements to the light available above the surface. To improve the accuracy of near-surface reflectance estimates, the HyperPro-II is manually lowered from the sea surface several times during each deployment. The HyperPro's profiler descends a short distance from the ship, with the location of the deployment and profiles determined by wind and the ship's orientation relative to the sun to prevent shading of the sensors (Satlantic, 2003, 2004).

Deployment

The HyperPro-II profiler is hand deployed from the deck of the ship in such a way to avoid alteration of the observed light field. The protocols for the deployments are outlined in the instrument's documentation and previous cruise reports (Satlantic, 2003, 2004; Ondrusek *et al.,* 2016). During a typical deployment, data is logged continuously by an on-board PC during several moderately deep casts (e.g. 50~70 m), followed by multiple shallow casts (e.g., 10~15 m).

Analysis

During post-deployment processing the measurements are combined to estimate water leaving radiances, $R_{rs}(\lambda)$, and other properties used in ocean color validations (e.g., Ondrusek *et al.,* 2012).

6.1.3 Above-water $R_{rs}(\lambda)$ measurement

Above-water R_{rs} measurements were collected using a handheld radiometer at 19 locations during the cruise.

Equipment and Techniques

This $R_{rs}(\lambda)$ measurement is made from a ship's deck or airborne platform, rather than from sensors immersed in the water. A handheld radiometer measures the light reflected from the sea surface, the sky, and a gray reference plaque. The measurements are made with specific orientations relative to the sun, which vary with the environmental conditions. These measurements require direct sunlight with solar elevations >30° and are usually made under relatively clear skies since the quality of the measurements is severely degraded by the presence of clouds.

Sampling

A Panalytical ASD HandHeld2-Pro (HH2) radiometer with an 8° foreoptic was used during GOMECC-3 for the above-water Rrs measurement. The Rrs measurements were collected within the constraints recommended in the NASA Ocean Optics Protocols (Mueller *et al.,* 2003). The HH2 radiometer is turned on for 5-10 minutes before the measurements begin to attain radiometric stability. A sampling sequence that measures the radiance from a calibrated grey reference plaque the water's surface, and the skylight is repeated several times.

Analysis

Remote sensing reflectance is determined by the ratio of the water leaving radiance, $L_w(\lambda)$, to the downwelling irradiance, $E_d(\lambda)$. The $L_w(\lambda)$ value is determined by subtraction of a fraction of the measured skylight radiance from the measured water reflectance radiance. The fraction of skylight removed is variable, determined largely by wind speed, viewing angles, and orientation relative to the sun. The $R_{rs}(\lambda)$ estimate is computed during the post-processing of the individual spectral measurements and the

ancillary information about the time, location, and environmental conditions present during the measurement.

6.2. CARTHE Drifter Deployments

Drifter assembly: Alain Munoz Caravaca (CEAC), Jorge Luis Viamontes Fernandez (GEOCUBA)
Deployers: Members of the scientific party
PI: Josefina Olascoaga (RSMAS)

The Gulf of Mexico Ecosystems and Carbon Cruise (GOMECC-3; http://www.aoml.noaa.gov/ocd/gcc/GOMECC3/) led by NOAA/AOML (Leticia Barbero, PI) circumnavigated the Gulf of Mexico along the isobath of 50 m in around 35 days (18 July–21 August 2017). The GoMRI/CARTHE consortium participated in this campaign with a deployment of surface drifters.

Over the past few decades, a number of satellite-tracked surface drifters have surveyed the Gulf of Mexico. Much insight into the Gulf of Mexico's surface-ocean Lagrangian dynamics has been gained from the analysis of different subsets of the collected drifter data. A large body of the work done was dedicated to study relative dispersion statistics using pairs of drifter trajectories and their velocities in an attempt to deduce the shape of the kinetic energy wavenumber spectrum (LaCasce and Ohlmann, 2003; LaCasce, 2010; Poje *et al.,* 2014; Beron-Vera and LaCasce, 2016; Zavala-Sanson *et al.,* 2017b). Other work employed drifter trajectory data to assess the significance of transport patterns detected from altimetry-derived velocity using nonlinear dynamics tools (Olascoaga *et al.,* 2013; Beron-Vera *et al.,* 2015; Romero *et al.,* 2016). Additional work was more concerned with making practical use of the drifter data through assimilating drifter velocities into ocean general circulation models (Coelho *et al.,* 2015) and blending these velocities with altimetry-derived velocities to improve near-real-time synoptic estimates of ocean currents (Berta *et al.,* 2015). Descriptive studies were also reported highlighting preferred synoptic pathway patterns (Yang *et al.,* 1999; DiMarco *et al.,* 2005; Perez-Brunius *et al.,* 2013; Zavala-Sanson *et al.,* 2017a).

A global characterization of the Gulf of Mexico's Lagrangian dynamics has been recently carried out using probabilistic tools which enable sketching absorbing and almost-invariant sets and their corresponding basins of attraction in the phase space of a nonlinear dynamical system (Dellnitz and Junge, 1999; Froyland, 2005). Although attracting regions may be small and trap trajectories for long periods of time before eventually exiting and thus constituting almost-invariant regions, if their basins of attraction are large, they can exert great influence on the global Lagrangian dynamics. Decompositions of the surface-ocean flow into almost-invariant sets form the basis of a *dynamical geography*, where the boundaries between basins are determined by the Lagrangian circulation itself, instead of arbitrary geographical divisions. Miron *et al.* (2017) constructed the first such dynamical geography for the Gulf of Mexico, which has implications for connectivity passive tracers and potentially also active tracers (such as fish larvae) within the Gulf of Mexico.

The trivial partition of the dynamical geography has a single province covering the whole Gulf of Mexico, which is fully evacuated by tracers through the Straits of Florida after a few years. The coarsest nontrivial partition divides the Gulf of Mexico into two halves by a nearly straight boundary connecting the Mississippi River Delta and the easternmost tip of the Yucatan Peninsula. Tracers initially on the western province accumulate after a few months and for a period of a few years on the southern end of the Louisiana–Texas Shelf, while those initially on the eastern province eventually completely exit the Gulf of Mexico through the Straits of Florida after a few years. A refined partition has five coastal provinces roughly spanning the northern Florida Shelf, the southern Florida Shelf, the Louisiana-Texas Shelf, the Yucatan Shelf, and a region south of the Island of Cuba. Tracers initially within each of these provinces accumulate temporarily (from several weeks to a few months) on smaller regions contained within.

The database employed by Miron *et al.* (2017) has drifter trajectories from over 3000 deployments along the period 1994–2016. CARTHE has contributed to this database with 302 drifters from the Grand LAgrangian Experiment (GLAD) and 1002 during the LAgrangian Submesoscale ExpeRiment (LASER). The "spaghetti" plot shown in the left panel of Figure 57 reveals that the drifters sample most of the Gulf of Mexico domain (about three drifters are found per km^2 on average, ignoring time). An important exception is a region on the Yucatan Shelf, which has never been visited by any drifters. The drifter density plot in the right panel of Figure 57 shows that, ignoring time, there are 246 drifters on average per bin, with as many as 4266 drifters in some bins and a few (108) empty bins. Most of the empty bins lie on the Yucatan Shelf area.
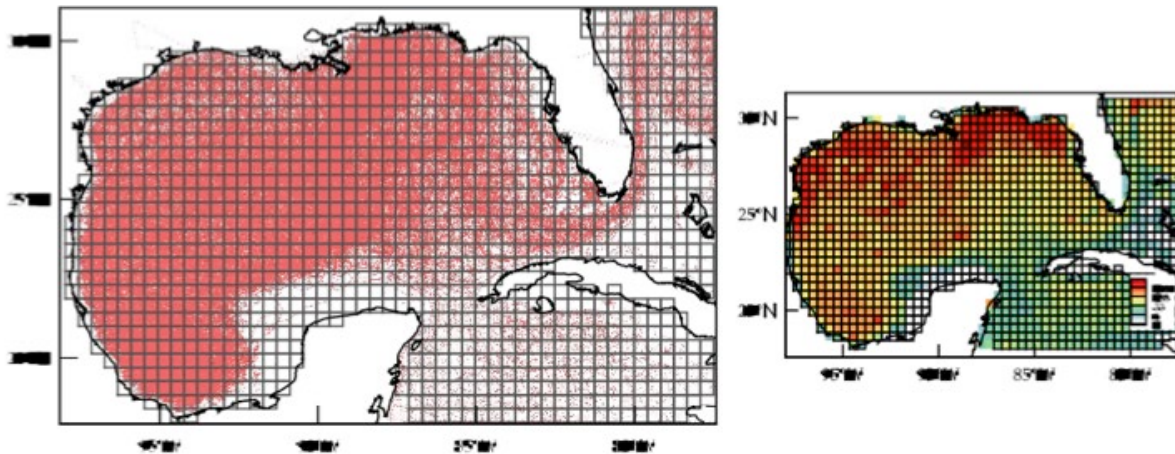

Figure 57: (left) "Spaghetti" plot of all daily satellite-tracked drifter trajectories describing the surface-ocean Lagrangian dynamics in the extended Gulf of Mexico domain. (right) Number of drifters per grid bin independent of the day over 1994–2016 subjected to a fourth-root transformation.

An important goal of the proposed drifter deployment during the GOMECC-3 cruise was to fill the noted data gap. In addition to filling this gap, some attention was paid on across shelfbreak exchange. The latter was motivated by earlier numerical work on the isolation of the Texas–Louisiana Shelf and the West Florida Shelf in connection to red tides (Olascoaga *et al.*, 2006; Olascoaga, 2010), as well as by an ongoing numerical investigation of cross-shelfbreak transport at the Texas–Mexico Shelf and the Mexican Shelf in connection for oil exploration in the Perdido Foldbelt region (Gough *et al.*, 2017).

Figure 58 shows a schematic of the 25 CARTHE drifter deployments. These are biodegradable and thus sacrificial drifters, which track currents centered 40 cm below the surface. The patented design was developed by a team of physical oceanographers and engineers at the University of Miami. The drifters were deployed (blue dots) during each of the planned CTD cruise stations (red dots) near the 50-m isobath. Additional deployments were made off CTD stations while navigating over the Campeche Bank to better sample this region.
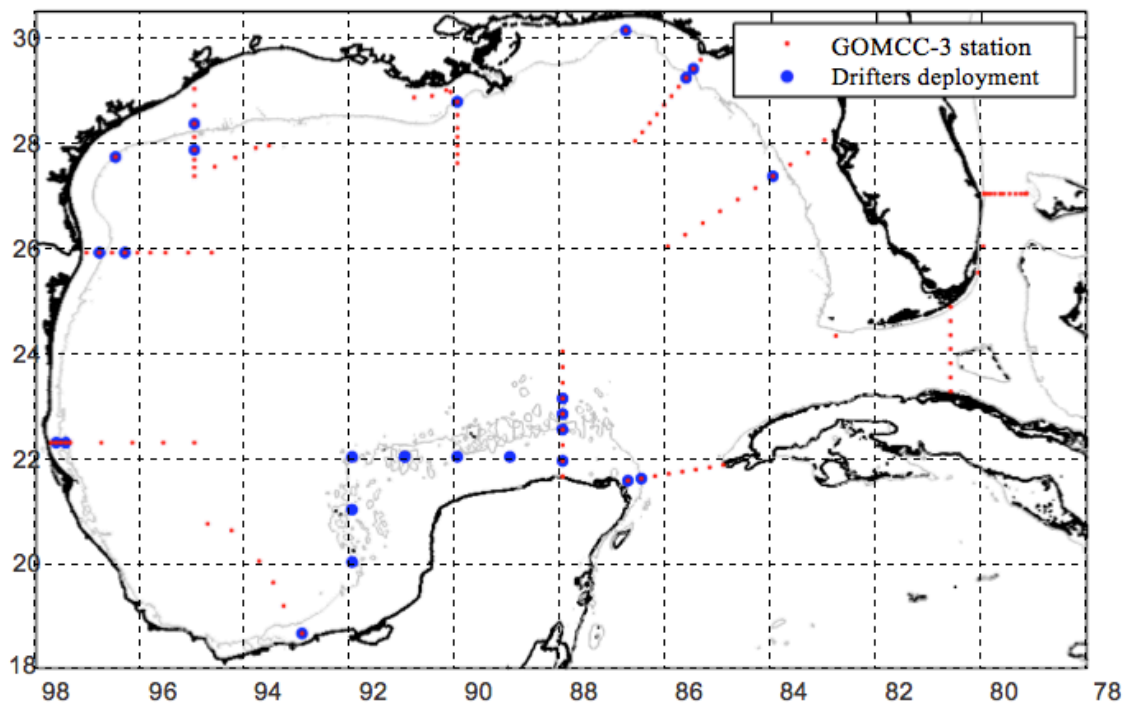

Figure 58: GOMECC-3 cruise stations (red dots) and CARTHE deployment sites (blue dots).

Table 8 shows the dates, times, and actual locations of where the CARTHE drifters were deployed.

Table 8: Date, time, and location of CARTHE drifter deployments during GOMECC-3.

Science Station	Latitude (°N)	Longitude (°E)	UTC Date	UTC time	Drifter #
Station 8	27.3198	-84.0000	Jul 22, 2017	02:42	0344
Station 13	29.3766	-85.5136	Jul 23, 2017	16:42	0500
Station 14	29.1635	-85.5566	Jul 23, 2017	18:54	0047
UW	30.0912	-86.8239	Jul 25, 2017	13:56	0480
Station 28	28.7460	-89.9969	Jul 27, 2017	13:53	0172
Station 40	27.8333	-94.9998	Jul 31, 2017	10:12	0021
Station 42	28.3333	-95.0000	Jul 31, 2017	17:35	0234
Station 45	27.3376	-96.7871	Aug 01, 2017	21:35	0232
Station 47	25.8802	-96.8085	Aug 02, 2017	14:56	0433
Station 49	25.8810	-96.3243	Aug 02, 2017	20:25	0205
Station 56	22.2708	-97.6380	Aug 05, 2017	12:39	0179
Station 58	22.2717	-97.4517	Aug 05, 2017	15:38	0458
Station 66	23.8233	-88.0000	Aug 09, 2017	03:15	0478
Station 67	23.1550	-88.0000	Aug 09, 2017	09:30	0100
Station 68	22.5407	-88.0000	Aug 09, 2017	15:59	0485
Station 69	21.9263	-88.0000	Aug 09, 2017	21:31	0248
Station 70	21.0167	-90.7700	Aug 10, 2017	14:12	0219
Station 71	21.4508	-91.5620	Aug 10, 2017	21:21	0032
Station 79	18.8350	-93.0650	Aug 13, 2017	07:50	0492
UW	20.6500	-92.2117	Aug 13, 2017	18:48	0207
UW	21.7655	-90.4539	Aug 14, 2017	04:55	0119
UW	22.2683	-89.1067	Aug 14, 2017	11:59	0474
UW	22.1824	-87.6815	Aug 14, 2017	18:49	0483
Station 80	21.5497	-86.7522	Aug 15, 2017	04:09	0493
Station 81	21.5917	-86.4917	Aug 15, 2017	06:42	0239

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