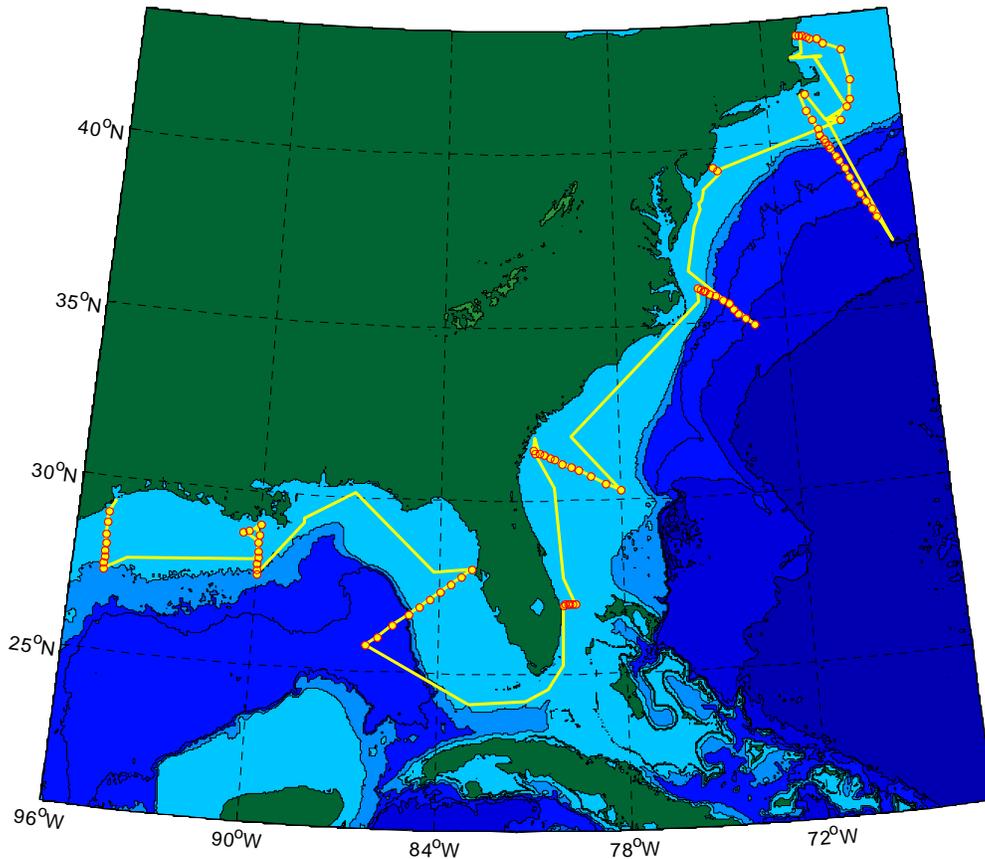


Gulf of Mexico and East Coast Carbon Cruise (GOMECC)



R/V Ronald H. Brown, RB-07-05

10 July – 4 August, 2007

Galveston, TX – Boston, MA USA

Chief Scientists: Tsung-Hung Peng and Chris Langdon

NOAA Atlantic Oceanographic and Meteorological Laboratory

Cruise Report

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1. Summary

We completed the first North American Carbon Program (NACP) Gulf of Mexico and East Coast Carbon (GOMECC) Cruise on board the R/V *Ronald H. Brown* from Galveston in the northern Gulf of Mexico to Boston on the East coast. The cruise was designed to obtain a snapshot of concentrations and fluxes of key carbon, physical, and biogeochemical parameters in the coastal realm. The program is in support of the North American Carbon Program (NACP) that has as overriding goal to constrain fluxes of carbon over North America and adjacent seas. Full scale repeat occupations are planned every two years to complement mooring time series and other regional activities. The cruise included a series of 9 transects approximately orthogonal to the Gulf of Mexico and Atlantic Coast and a comprehensive set of underway measurements along the entire transect (Figure 1). Full water column CTD/rosette stations were occupied at 90 specified locations. A total of 29 scientists from AOML and other government agencies and universities participated on the 26-day cruise which departed from the Galveston, Texas on 10 July, and arrived on schedule in Boston, Massachusetts on 4 August. Water samples were collected from the 24-bottle rosette at each station and analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, pCO₂, dissolved organic matter, colored dissolved organic matter, particulate organic carbon, halocarbons, alkyl nitrates, CO and phytoplankton pigments. Underway systems were in operation for measuring atmospheric CO₂ and near-surface water pCO₂, DIC, halocarbons, pH, NH₃, CO and bio-optical properties. An *in situ* spectrophotometric pH profiler was used with the CTD to measure pH profiles to a depth of 1000m. Air-sea fluxes of CO₂ and ozone were also measured using eddy correlation methods. In the midst of a CTD cast along the New Jersey transect, the ship encountered generator cooling problem and needed to go into Boston harbor for emergency repairs. As a result, only two stations of the 10 scheduled stations along the New Jersey transect were occupied. After repair of the ship's generator science was resumed July 30 starting at the northern most stations and working backwards through Gulf of Maine and MVCO stations as far as time would allow. All major cruise objectives were achieved.

2. Introduction

In support of the interagency North American Carbon Program (NACP) of the Climate Cycle Science Program (CCSP), NOAA conducted the NACP Gulf of Mexico and East Coast Carbon (GOMECC) Cruise (Figure 1) along the coast of Gulf of Mexico and Atlantic coast to study carbon cycle processes in the coastal zone over a wide range of oceanographic, atmospheric, and biogeochemical conditions. The coastal ocean plays a critical role in the North American carbon cycle and global carbon dynamics. It is a conduit for transport of terrestrial material from the land to the open ocean and its specific biological productivity is on average about three times larger than the average open-ocean values. It is also the region where the majority of the interior ocean interacts with the bottom boundary, leading to enhancements of many chemical, biological and physical processes in mid-water regions of the ocean. The coastal regions have large air-sea fluxes both into and out of the ocean. To date, the net magnitude and direction of the

flux still have large uncertainties. Globally, net CO₂ fluxes as large as 1 Pg C/year, or about 60% of the oceanic uptake, have been hypothesized for this region of the oceans. The large flux is due, in part, from the coastal pump hypothesis in which the coastal margin sink is enhanced by net offshore carbon transport. The uncertainty in coastal ocean flux would be reduced with comprehensive measurements of CO₂ and related controlling parameters and yields significant improvements in the understanding of carbon sources and sinks on the continental shelf. The major goal of the cruise was to identify the sources and sinks of CO₂ in the U.S. coastal regime, along with their magnitudes, scales of variability, and controls on CO₂ fluxes. The coastal zone must be well quantified regarding carbon sources and sinks in order to make reasonable projections of future atmospheric CO₂ levels.

To address this problem, the PMEL/AOML Marine CO₂ Program has initiated a coastal carbon studies component to the U.S. North American Carbon Program to apply a variety of approaches for studying the carbon cycle (e.g. survey cruises, underway surface observations, and moorings) in the coastal region to study the invasion and transport of anthropogenic CO₂ and other tracers in coastal ocean waters. This program is designed to establish baseline observational fields for carbon system parameters, provide comparative data for observations from other projects, and develop a set of hydrographic transects of full water column measurements to be re-occupied over time for studies of inter-annual changes in physical, chemical and biological characteristics of the coastal ocean.

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

Table 1. Scientific Cruise Participants

	<i>Name</i>	<i>Affiliation</i>	<i>Citizenship</i>	<i>Function</i>
1	Peng, Tsung-Hung	NOAA/AOML	US	Chief Scientist
2	Langdon, Chris	RSMAS/UM	US	Chief Scientist
3	Fonseca, Carlos	NOAA/AOML	Brazil	CTD
4	Langdon, Brian	NOAA/AOML	US	CTD/watch
5	Seaton, Kyle	NOAA/AOML	US	CTD/watch
6	Berberian, George	NOAA/AOML	US	O ₂
7	Featherstone, Chuck	NOAA/AOML	US	O ₂
8	Fischer, Charlie	NOAA/AOML	US	Nutrients
9	Amornthammarong, Natchanon	NOAA/AOML	Thailand	Nutrients
10	Peltola, Esa	NOAA/AOML	US	DIC
11	Castle, Bob	NOAA/AOML	US	DIC
12	Hu, Xiping	UGA	China	Alk
13	Huang, Wei-Jen	UGA	Taiwan	Alk
14	Sullivan, Kevin	NOAA/AOML	US	pCO ₂

15	Plagge, Amanda	UNH	US	DOC/Chl/color
16	St. Louis, Jennifer	UNH	US	DOC/Chl/color
17	Salisbury, Joe	UNH	US	DOC/Chl/color
18	Liu, Xue wu (Sherwood)	USF	US	UW pH/Profile
19	Easley, Regina	USF	US	UW pH/Profile
20	Wang, Zhaohui (Aleck)	USF	China	UW pH/Profile
21	Otto, Bill	UC/ESRL	US	Micromet Fluxes
22	Lang, Eva	UC	Germany	Ozone fluxes
23	Chakraborty, Sumit	USM	India	Pigments
24	Yvon-Lewis, Shari	TAM	US	HCFC
25	O'Hern, Julia	TAM	US	HCFC
26	Dahl, Elizabeth	Loyola	US	Alkyl Nitrates
27	Murawski, Kevin	Loyola	US	Alkyl Nitrates
28	Reader, Heather	UGA	Canada	Photochemistry
29	Graustein, Meg	UConn	US	Carbon fluxes

The GOMECC RB-07-05 cruise was supported by the NOAA Global Carbon Cycle (GCC) program. Twenty-nine scientists representing 9 universities and 2 government research laboratories participated on the cruise (Table 1) covering the Gulf of Mexico and eastern North American continental shelf region from Florida Keys in the south to Portsmouth, NH in the north. The R/V *Ronald H. Brown* departed Galveston, TX on 10 July, 2007. The cruise completed a series of 9 transects approximately orthogonal to the coast (Figure 1). Full water column CTD/rosette stations were occupied at specified locations along each of these transects. Twenty-four 10L Niskin-type bottles were used to collect water samples from throughout the water column at each station. Each Niskin-type bottle was sub-sampled on deck for a variety of analyses, including salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, pCO₂, dissolved organic matter, colored dissolved organic matter, particulate organic carbon, halocarbons, alkyl nitrates, CO, and phytoplankton pigments. A total of 90 stations were occupied on the cruise (Table 2) in 9 transects identified as Galveston, Louisiana, Tampa, 27North, Savannah, Cape Hatteras, New Jersey, MVC0 and Portsmouth Transect. In addition, underway measurements of salinity, temperature, dissolved oxygen, pCO₂ (air and water), total carbon, pH, ammonia, fluorescence, light transmittance, and colored dissolved organic matter fluorescence were made. For each CTD station with depth less than 1000 m, an *in situ* spectrophotometric pH profiler was installed on the CTD/rosette for measuring pH profiles. Measurements of air-sea fluxes of ozone and CO₂ by eddy correlation method were carried out simultaneously at bow section. To provide comparison and calibration of remote measurements made by sensors installed in the coastal CO₂ buoys and observation tower, the ship sailed closely to Savannah Buoy in Georgia coast, Martha's Vineyard Coastal Observatory (MVCO), and UNH Buoy in the Gulf of Maine. In addition to underway measurements, CTD casts were taken for discrete measurements of DIC, TA, and pCO₂ near these coastal observation moorings. The cruise ended in Boston, MA on 4 August, 2007.

3. Description of Measurements from Vertical Profiles

Station	Latitude			Longitude			Depth (m)
1	29	0.00	N	95	0.00	W	18
2	28	40.00	N	95	0.00	W	27
3	28	20.00	N	95	0.00	W	35
4	28	5.00	N	95	0.00	W	55
5	27	50.00	N	95	0.00	W	217
6	27	40.00	N	95	0.00	W	632
7	27	30.00	N	95	0.00	W	890
8	27	20.00	N	95	0.00	W	1115
9	28	47.59	N	90	33.30	W	17
10	28	50.67	N	90	20.24	W	16
11	29	3.12	N	89	59.34	W	15
12	28	45.00	N	90	0.00	W	49
13	28	30.00	N	90	0.00	W	98
14	28	15.00	N	90	0.00	W	175
15	28	5.00	N	90	0.00	W	434
16	27	55.00	N	90	0.00	W	665
17	27	45.00	N	90	0.00	W	835
18	27	35.00	N	90	0.00	W	1263
19	28	0.00	N	83	0.00	W	16
20	27	46.67	N	83	20.00	W	29
21	27	33.33	N	83	40.00	W	43
22	27	20.00	N	84	0.00	W	65
23	27	6.67	N	84	20.00	W	126
24	26	53.33	N	84	40.00	W	219
25	26	40.00	N	85	0.00	W	3294
26	26	20.50	N	85	30.50	W	3266
27	26	0.00	N	86	0.00	W	3238
28	25	45.43	N	86	20.77	W	3196
29	27	0.00	N	79	59.20	W	59
30	27	0.00	N	79	56.00	W	150
31	27	0.00	N	79	52.00	W	293
32	27	0.00	N	79	47.00	W	405
33	27	0.00	N	79	41.00	W	542
34	27	0.00	N	79	37.00	W	639
35	31	24.08	N	80	52.14	W	13

36	31	28.01	N	80	55.29	W	15
37	31	23.78	N	80	44.58	W	23
38	31	19.46	N	80	33.87	W	26
39	31	15.15	N	80	23.15	W	31
40	31	11.70	N	80	14.58	W	37
41	31	4.80	N	79	57.44	W	45
42	30	57.90	N	79	40.31	W	511
43	30	52.02	N	79	25.80	W	790
44	30	41.52	N	79	0.00	W	801
45	30	29.45	N	78	30.00	W	812
46	30	17.37	N	78	0.00	W	804
47	36	0.00	N	75	3.00	W	45
48	35	57.90	N	74	57.20	W	71
49	35	55.00	N	74	51.00	W	110
50	35	53.90	N	74	47.45	W	921
51	35	50.00	N	74	39.00	W	1665
52	35	45.00	N	74	27.00	W	2080
53	35	38.50	N	74	11.00	W	2667
54	35	31.60	N	73	59.00	W	3080
55	35	20.00	N	73	49.00	W	3385
56	35	13.00	N	73	41.00	W	3602
57	35	2.00	N	73	24.00	W	3991
58	34	52.50	N	73	7.00	W	4774
59	39	28.08	N	74	14.33	W	17
60	39	20.35	N	74	5.05	W	30
61	43	2.30	N	70	38.50	W	28
62	43	1.30	N	70	33.60	W	97
63	42	59.64	N	70	25.32	W	114
64	42	56.38	N	70	17.53	W	151
65	42	53.34	N	70	8.48	W	71
66	42	51.68	N	69	51.68	W	269
67	42	43.73	N	69	41.09	W	292
68	42	28.72	N	69	0.42	W	230
69	41	37.57	N	68	46.94	W	168
70	41	4.82	N	68	52.32	W	86
71	40	50.88	N	69	1.00	W	96
72	40	30.20	N	69	17.51	W	74
73	41	19.13	N	70	33.60	W	23
74	40	51.16	N	70	32.09	W	61

75	40	35.64	N	70	22.14	W	71
76	40	17.40	N	70	12.00	W	95
77	40	8.46	N	70	6.96	W	124
78	40	0.00	N	70	0.00	W	164
79	39	54.36	N	69	55.80	W	752
80	39	47.00	N	69	51.18	W	1632
81	39	42.00	N	69	48.00	W	2118
82	39	28.62	N	69	38.34	W	2439
83	39	21.00	N	69	32.22	W	2532
84	39	5.22	N	69	21.24	W	3025
85	38	49.20	N	69	12.00	W	3268
86	38	33.48	N	69	0.60	W	3494
87	38	19.32	N	68	52.14	W	3830
88	38	5.40	N	68	42.00	W	4095
89	37	51.60	N	68	30.90	W	4382
90	37	37.26	N	68	22.00	W	4597

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

3.1.1 Standards and Pre-Cruise Calibrations

The CTD/O₂ system is a real-time data acquisition system with the data from a Sea Bird Electronics, Inc. (SBE) 9plus underwater unit transmitted via a conducting cable to a SBE 11plus deck unit. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format. The deck unit decodes the serial data and sends it to a personal computer for display and storage in a disk file using Sea-Bird Seasave software.

The SBE 911plus system transmits data from primary and auxiliary sensors in the form of binary numbers equivalent to the frequency or voltage outputs from those sensors. These are referred to as the raw data. The SBE software performs the calculations required to convert raw data to engineering units.

The SBE 911plus system is electrically and mechanically compatible with the standard, unmodified carousel water sampler, also made by Sea-Bird Electronics, Inc. A modem and carousel interface allows the 911plus system to control the operations of the carousel directly without interrupting the flow of data from the CTD.

The SBE 9plus underwater unit is configured with dual standard modular temperature (SBE 3) and conductivity (SBE 4) sensors, which are mounted near the lower end cap. The conductivity cell entrance is co-planar with the tip of the temperature sensor probe. The pressure sensor is mounted inside the underwater unit main housing. A centrifugal pump module flushes water through sensor tubing at a constant rate independent of the CTD's motion to improve dynamic performance. Single dissolved

oxygen sensor is added to the pumped sensor configuration following the primary temperature-conductivity (TC) pair. A Seapoint transmissometer and fluorometer and a pH profiler developed by the University of South Florida (USF) were also mounted on the CTD package. For the bottom approaches a Simrad 12 kHz and a Benthos 12 kHz altimeters were used. The Simrad altimeter offers us a better range (approximately 130 meters off bottom) although in locations with strong currents the tilt angle caused on the CTD frame compromises its proper operation. On these location the Benthos altimeter were used but the range decreases to order 50 meters of bottom.

3.1.2.1 Conductivity

The flow-through conductivity-sensing element is a glass tube (cell) with three platinum electrodes. The resistance measured between the center electrode and the end electrode pair is determined by the cell geometry and the specific conductance of the fluid within the cell, and controls the output frequency of a Wein Bridge circuit. The sensor has a frequency output of approximately 3 to 12 kHz corresponding to conductivity from 0 to 7 Siemens/meter (0 to 70 mmho/cm). The SBE 4 has a typical accuracy/stability of ± 0.0003 S/m and resolution of 0.00004 S/m at 24 scans per second.

Two conductivity sensors were used during the GOMECC cruise, serial numbers (s/n) 3338 and 1374. Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASAVE® using the configuration file:

s/n 3338	s/n 1374
June 22, 2007	February 28, 2007
$G = -9.97145386$	$G = -3.96228321$
$H = 1.54092348$	$H = 4.83436925e-01$
$I = -1.73104395e-03$	$I = -2.22089905e-05$
$J = 2.24116667e-04$	$J = 2.79996287e-05$
$ctcor = 3.2500e-06$	$ctcor = 3.2500e-06$
$cpcor = -9.5700e-08$	$cpcor = -9.5700e-08$

Conductivity calibration certificates show an equation containing the appropriate pressure-dependent correction term to account for the effect of hydrostatic loading (pressure) on the conductivity cell:

$$C(\text{Siemens / meter}) = \frac{(g + h \cdot f^2 + i \cdot f^3 + j \cdot f^4)}{[10 \cdot (1 + ctcor \cdot t + cpcor \cdot p)]}$$

where g , h , i , j , $ctcor$, and $cpcor$ are the calibrations coefficients shown above, f is the instrument frequency (kHz), t is the water temperature (degrees Celsius), and p is the water pressure (dbar). SEASAVE® automatically implements this equation.

3.1.2.2 Temperature

The temperature-sensing element is a glass-coated thermistor bead, pressure protected by a stainless steel tube. The sensor output frequency ranges from 5-13 kHz corresponding to temperature from -5 to 35 °C. The output frequency is inversely proportional to the square root of the thermistor resistance, which controls the output of a patented Wein Bridge circuit. The thermistor resistance is exponentially related to temperature. The SBE 3 thermometer has a typical accuracy/stability of ±0.004°C per year and resolution of 0.0003 °C at 24 samples per second. The SBE 3 thermometer has a fast response time of 0.070 seconds.

The two temperature sensors used during GOMECC cruise were s/n 2946 and 1701. Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASAVE® using the configuration file:

s/n 2946 February 2, 2007	s/n 1701 May 31, 2007
$g = 4.34401539e-03$	$g = 4.79081039e-03$
$h = 6.39150582e-04$	$h = 6.54310139e-04$
$I = 2.14174643e-05$	$i = 1.87197540e-05$
$j = 1.84514287e-06$	$j = 1.04900676e-06$
$f_0 = 1000.0$	$f_0 = 1000.0$

Temperature (ITS-90) is computed according to:

$$T(^{\circ}C) = \frac{1}{\left\{ g + h \cdot \left[\ln\left(\frac{f_0}{f}\right) \right] + i \cdot \left[\ln^2\left(\frac{f_0}{f}\right) \right] + j \cdot \left[\ln^3\left(\frac{f_0}{f}\right) \right] \right\}} - 273.15$$

where g , h , i , j and f_0 are the calibration coefficients above and f is the instrument frequency (kHz). SEASAVE® automatically implements this equation and converts between ITS-90 and IPTS-68 temperature scales as desired.

3.1.2.3 Pressure

The Paroscientific series 4000 Digiquartz high pressure transducer uses a quartz crystal resonator whose frequency of oscillation varies with pressure induced stress measuring changes in pressure as small as 0.01 parts per million with an absolute range of 0 to 10,000 psia (0 to 6885 dbar). Repeatability, hysteresis and pressure conformance are 0.002% FS. The nominal pressure frequency (0 to full scale) is 34 to 38 kHz. The nominal temperature frequency is 172 kHz + 50 ppm/°C.

The pressure sensor utilized during the GOMECC cruise was s/n 50363. Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASAVE® using the configuration file:

s/n 50363
August 8, 2005
$c_1 = -4.698871e+04$
$c_2 = 6.928599e-01$
$c_3 = 1.264330e-02$
$d_1 = 3.832000e-02$
$d_2 = 0.0$
$t_1 = 2.996944e+01$
$t_2 = -1.348850e-05$
$t_3 = 3.953500e-06$
$t_4 = 2.102830e-09$
$t_5 = 0.0$

Pressure coefficients are first formulated into:

$$c = c_1 + c_2 \cdot U + c_3 \cdot U^2$$

$$d = d_1 + d_2 \cdot U$$

$$t_0 = t_1 + t_2 \cdot U + t_3 \cdot U^2 + t_4 \cdot U^3 + t_5 \cdot U^4$$

Where U is temperature in degrees Celsius. Pressure is computed according to:

$$P(\text{psia}) = c \cdot \left(1 - \frac{t_0^2}{t}\right) \cdot \left[1 - d \cdot \left(1 - \frac{t_0^2}{t}\right)\right]$$

Where t is pressure period (μs). SEASAVE® automatically implements this equation.

3.1.2.4 Oxygen

The SBE 43 dissolved oxygen sensor uses a membrane polarographic oxygen detector (MPOD). Oxygen sensors determine the dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane. By knowing the flux of oxygen and the geometry of the diffusion path, the concentration of oxygen can be computed. The permeability of the membrane to oxygen is a function of temperature and ambient pressure. In order to minimize the errors in the oxygen measurement due the temperature differences between the water and the oxygen sensor, a temperature compensation is calculated using a temperature measured near the active surface of the sensor. The interface electronics output voltages proportional to the

temperature-compensated oxygen current. Initial computation of dissolved oxygen in engineering units is done in the software. The range for dissolved oxygen is 120% of surface saturation in all natural waters, fresh and salt and the nominal accuracy is 2% of saturation.

Oxygen sensor 0703 was used during the GOMECC cruise. The following oxygen calibrations were entered into SEASAVE® using the configuration file:

s/n 0703
June 20, 2007
<i>Soc</i> = 4.0350e-01
<i>Boc</i> = 0.0
<i>Offset</i> = -0.4806
<i>tcor</i> = 0.0006
<i>pcor</i> = 1.35e-04
<i>tau</i> = 0.0

Dissolved oxygen concentration is calculated according to:

$$O(ml/l) = \left\{ Soc \cdot \left[(V + Offset) + \left(tau \cdot \frac{dV}{dt} \right) \right] + Boc \cdot e^{(-0.03T)} \right\} \cdot e^{(tcor \cdot T + pcor \cdot P)} \cdot OXSAT(T, S)$$

Where *Soc*, *Boc*, *Offset*, *tcor*, *pcor*, and *tau* are the calibration coefficients above and *V* is the instrument voltage (V) and *dV/dt* (V/s) is the slope of the voltage. *T*, *S* and *P* are the temperature, salinity and pressure measured by the CTD and OXSAT is the oxygen saturation value calculated according to:

$$A1 = -173.4292 \quad A2 = 249.6339 \quad A3 = 143.3483 \quad A4 = -21.8492$$

$$B1 = -0.033096 \quad B2 = 0.014259 \quad B3 = -0.00170$$

$$OXSAT(\theta, S) = \exp \left\{ A1 + A2 \cdot \left(\frac{100}{\theta} \right) + A3 \cdot \ln \left(\frac{\theta}{100} \right) + A4 \cdot \left(\frac{\theta}{100} \right) + S \cdot \left[B1 + B2 \cdot \left(\frac{\theta}{100} \right) + B3 \cdot \left(\frac{\theta}{100} \right)^2 \right] \right\}$$

Where θ is the absolute temperature (K). SEASAVE® automatically implements this equation.

3.1.3 Data Acquisition

CTD/O₂ measurements were made using a SBE 9plus CTD with dual sensor configuration. Each set of sensors included a temperature, conductivity, and for the primary T-C set a dissolved oxygen sensor was added. The sets were placed as mirror images to each other mounted low in the CTD main housing with the intakes approximately 6-8 inches apart. The TC pairs were monitored for calibration drift and shifts by examining the differences between the two pairs on each CTD and comparing CTD salinity values with bottle salinity measurements.

AOML's SBE 9plus CTD/O₂ s/n 09P10779-0363 (sampling rate 24Hz) was mounted in a 24-position frame and employed as the primary package. Auxiliary sensors included a Seapoint transmissometer and fluorometer, a USF pH profiler and Simrad/Benthos altimeter. Water samples were collected using a SBE bottle carousel and 10-liter Niskin bottles. In order to accommodate the pH profiler for the casts shallower than 1000m, one of the Niskin bottles was removed.

The package entered the water from the starboard side of the ship and was held within 5 –10 meters of the surface for 1 minute in order to activate the pump and 3 more minutes after the pumps starts in order to purge the air from the system. The package was brought back to the surface and then lowered at a rate of 30m/min to 50 m, 45 m/min between 50 and 100m and 60 m/min generally to within 20 meters of the bottom for most of the casts, slowing on the approach. For stations shallower than 1000 m due in order to have a better resolution for the pH profiler the package was lowered at 20 m/min. The altimeter monitored the position of the package relative to the bottom.

Upon completion of the cast, sensors were flushed repeatedly and stored with a deionized water solution in the plumbing. Niskin bottles were then sampled for all the parameters described on the introduction of this report.

A SBE 11plus deck unit received the data signal from the CTD. Digitized data were forwarded to a personal computer equipped with Seasave acquisition and processing software SBEDDataProc. Preliminary temperature, salinity, and oxygen profiles were displayed in real time. Raw data files were archived to the CTD processing computer removable drives as well to compact discs.

3.1.3.1 Data Acquisition/System Problems

Data acquisition problems incurred during the cruise was due to data flow interruption to the carousel but these problems did not compromise the data sampling or the CTD data. We had fire problems in the carousel position #14, we believe due to the lack of using on this position once our upward looking LADCP took the position of bottle #14 for the most of our field season. After replacing the carousel the problem was gone. The Niskin bottles starting show also some minor problems, after a very busy CTD operations season. Some leakages on the bottom cap and on the peacocks but everything was clearly recorded and repaired or replaced in the later casts. The performance of the sensors was outstanding. The transmissometer and the fluorometer did not work because of an improper cable configuration and unfortunately we could not solve this problem.

3.1.3.2 Salinity Analyses

Bottle salinity analyses were performed in the ship's temperature-controlled salinity laboratory using a Guildline Model 8400B inductive autosalinometer, and a dedicated PC. Software allowed the user to standardize the autosalinometer. IAPSO Standard Seawater was used as the standard. The autosal was standardized before each case of samples was analyzed, or every 24 samples.

Duplicate samples were taken on several casts. Bottle salinities were compared with preliminary CTD salinity values to monitor CTD conductivity cell performance and drift. The expected precision of the autosalinometer is 0.001 PSS, with an accuracy of ± 0.003 PSS. Due to a broken temperature control switch of the air condition inside the autosalinometer room, in the beginning of the cruise it was not possible to keep control of the temperature on that room. As a consequence we had a huge variability of the data for the first 18 stations and a large amount of the data was flagged as bad or questionable. Among 1028 salinity samples, 226 samples were flagged as questionable or bad.

3.1.4. At Sea Processing of CTD data

SBEDataProc[®] consists of modular menu driven routines for acquisition, display, processing, and archiving of oceanographic data acquired with SBE equipment. The software is designed to work with a PC with Windows[®] operational system. Raw data are acquired from the instruments and are stored unmodified. The conversion module DATCNV uses the instrument configuration and pre-cruise factory calibration coefficients to create a converted engineering unit data file that is utilized by all SBEDataProc[®] post processing modules. Unless otherwise noted, all calibration parameters given are factory default values recommended by Sea Bird Electronics, Inc. The following is the SBEDataProc[®] processing module sequence and specifications used in the reduction of CTD/O₂ data from this cruise:

- DATCNV converted the raw data to pressure, temperature, conductivity, oxygen voltage. MARKSCAN was used to skip over scans acquired on deck and while priming the system under water. MARKSCAN values were entered at the DATCNV menu prompt. DATCNV also extracted bottle information where scans were marked with a bottle confirmation bit during acquisition.
- ALIGNCTD aligns conductivity, temperature and oxygen in time relative to pressure to ensure that all calculations are made using measurements from the same parcel of water, which minimizes salinity spiking and density errors. The SBE 11plus deck unit has factory settings to advance the primary conductivity cell; therefore, ALIGNCTD was not performed on this cell. The secondary conductivity cell, however, is not advanced in the deck unit and so was advanced 0.073 seconds in the ALIGNCTD module. Since the SBE3 temperature sensor response is fast, (0.06 seconds), it is not necessary to advance temperature relative to pressure. Oxygen sensors were not advanced in ALIGNCTD.

- ROSSUM created a summary of the bottle data. Bottle position, date, and time were output automatically. Pressure, temperature, conductivity, salinity, oxygen voltage, time rate of change of oxygen voltage, and preliminary oxygen values were averaged over a 2 second interval from 5 to 3 seconds prior to the confirm bit. ROSSUM computed potential temperature and sigma-theta.
- WILDEDIT marked extreme outliers in the data files. The first pass of WILDEDIT obtained an accurate estimate of the true standard deviation of the data. The data were read in blocks of 3000 scans. Data greater than two standard deviations were flagged. The second pass computed a standard deviation over the same 3000 scans excluding the flagged values. Values greater than 20 standard deviations were marked as bad values.
- FILTER performed a low pass filter on pressure data with a time constant of 0.15 seconds. In order to produce no time shift, the filter first runs forward through the data file and then runs backwards through the data file.
- CELLTM uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. Both conductivity cells are epoxy coated and therefore the thermal anomaly amplitude (α) and the time constant ($1/\beta$) were 0.03 and 9.0 respectively for each sensor.
- DERIVE was used to re-compute the time rate of change of oxygen voltage (dv/dt) and oxygen (ml/l and $\mu mol/kg$) with a time window size of 2 seconds.
- LOOPEDIT marks data scans where the CTD package was moving less than a minimum velocity of 0.25 m/s or travelling backwards due to ship roll.
- BINAVG averages the data into 1 decibar (dbar) pressure bins starting at 1 dbar with no surface bin. The center value of the first bin was set to equal the bin size. The bin minimum and maximum values are the center value \pm half the bin size. Scans with pressure values greater than the minimum and less than or equal to the maximum were averaged. Scans were interpolated so that a data record exists for every decibar. The number of points averaged in each bin was added to the variables listed in the data file.
- DERIVE recomputed salinity and calculates other oceanographic parameters (e.g. density, etc.).
- STRIP removed scan number from the data files.
- TRANS converted the data file format from binary to ASCII format.

3.1.4.1. CTD Pressure

Pressure sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw pressure data during each cast. Residual pressure offsets (the difference between the first and last submerged pressures) were examined to check for calibration shifts, all were <0.5 db. The average value for the on deck pressure (1.3 dbar) was applied as a offset for the pressure sensor. No additional adjustments were made to the calculated pressures.

3.1.4.2. CTD Temperature

Temperature sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary temperature data during each cast.

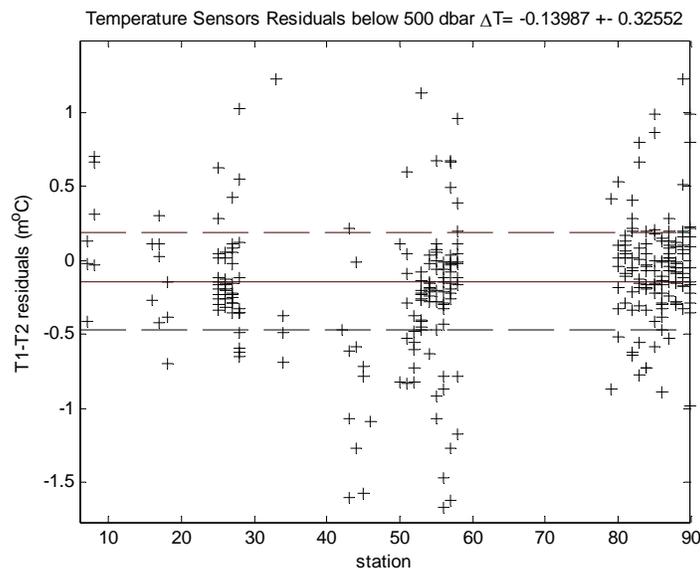


Figure 4.2.1 T1-T2 by station, p > 500 db.

Calibration accuracy was examined by tabulating the difference between the temperature measured by the primary sensor (T1) and the secondary sensors (T2) over a range of pressures (bottle trip locations) for each CTD station. These comparisons are summarized in Figure 4.2.1 and Figure 4.2.2.

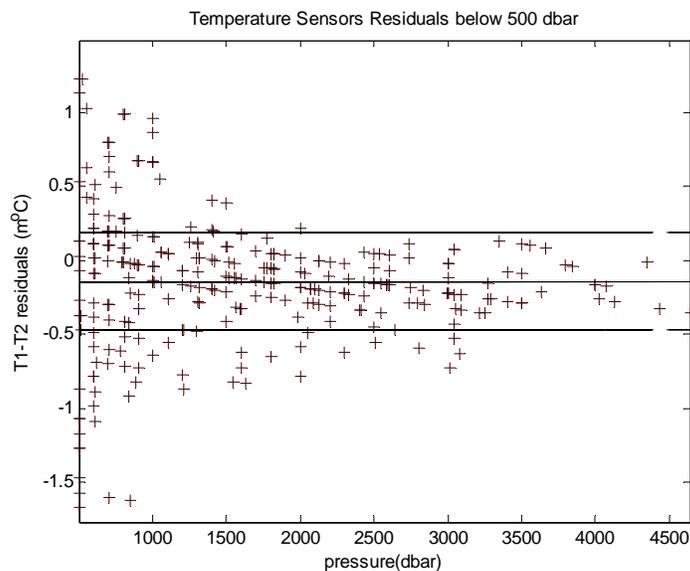


Figure 4.2.2. T1-T2 by pressure

The good performance of the CTD sensors can be observed by the small average differences between them, a small offset also can be observed on the Figure 4.2.2 indicating a potential calibration drift.

3.1.4.3 CTD Conductivity

Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities.

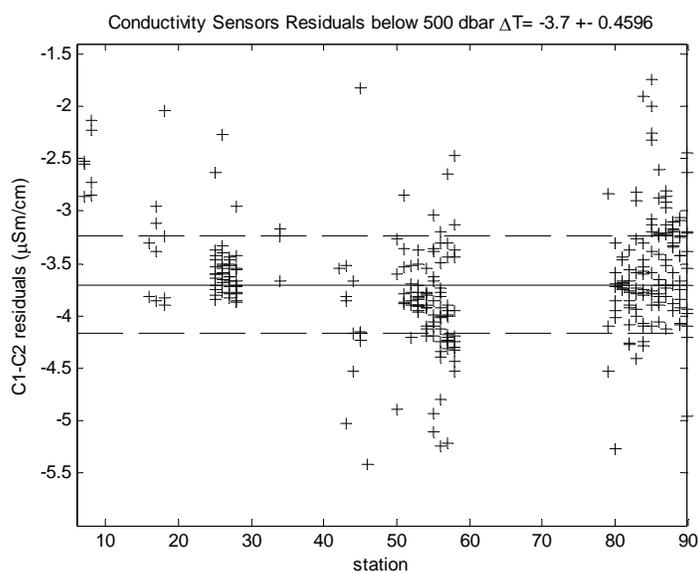


Figure 4.3.1. Uncorrected C1-C2 by station

Comparisons between the primary (C1) and secondary (C2) 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 and bottle C-C1 were first examined to identify sensor drift (Figures 4.3.1 and 4.3.2).

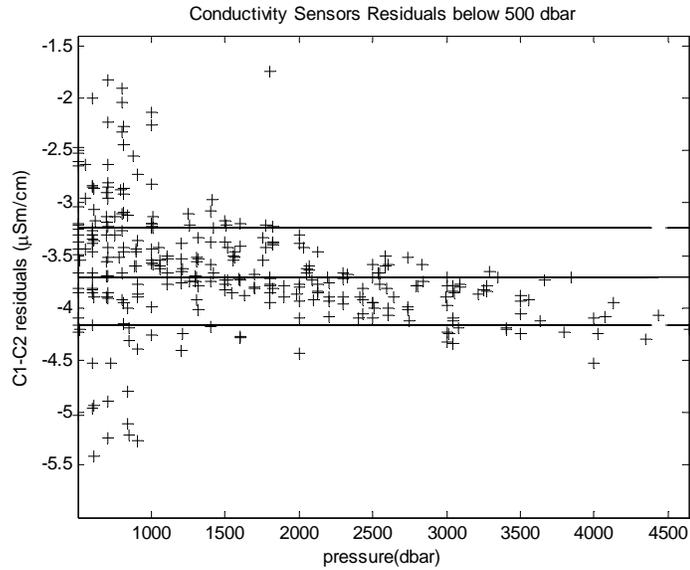


Figure 4.3.1. Uncorrected C1-C2 by pressure

Preliminary conductivity calibrations were performed using a linear regression between the CTD sensors and the salinity samples the results can be observed on the figure 4.3.2

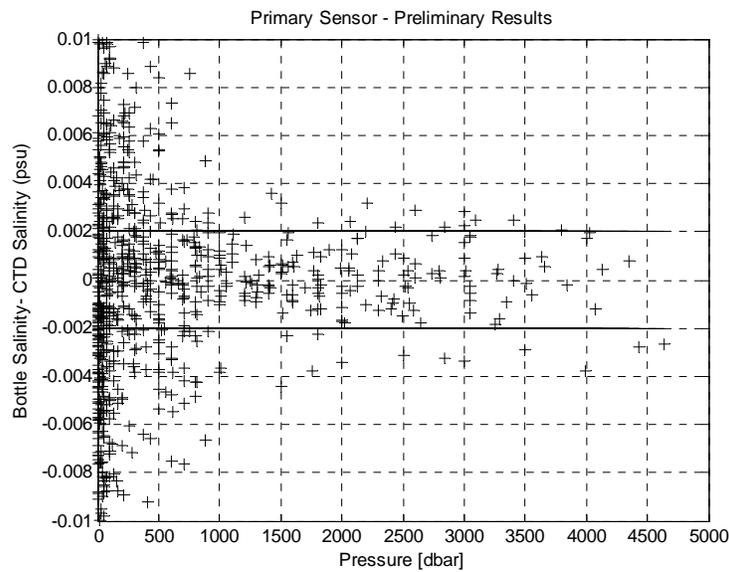


Figure 4.4.2. Salinity residuals by pressure, all pressures.

3.1.4.4. CTD Dissolved Oxygen

A SBE43 dissolved O₂ (DO) sensors was used on this leg; S/N 43-0703. The sensor behaved very well.

The DO sensors were calibrated to dissolved O₂ check samples by matching the up cast bottle trips to down cast CTD data along neutral density surfaces, calculating CTD dissolved O₂, and then minimizing the residuals using a non-linear least-squares fitting procedure. The fitting determined calibration coefficients for the sensor model conversion equation. The residuals are shown in Figures 4.4.1 -4.42.

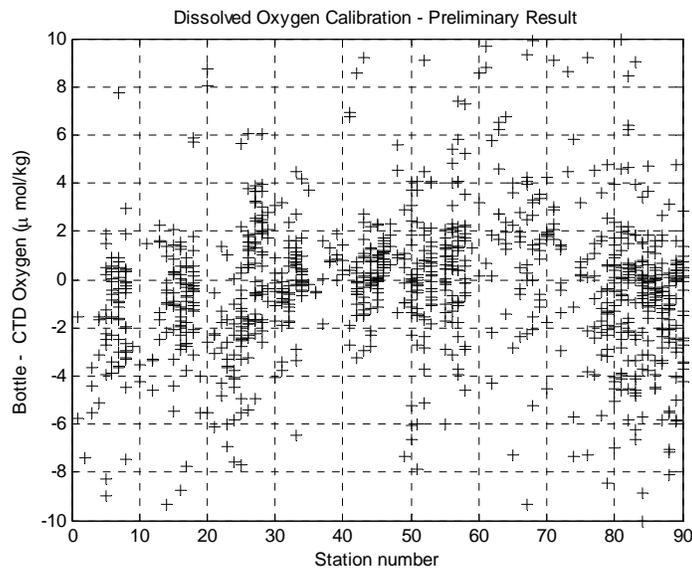


Figure 4.4.1. O₂ residuals by station, all pressures.

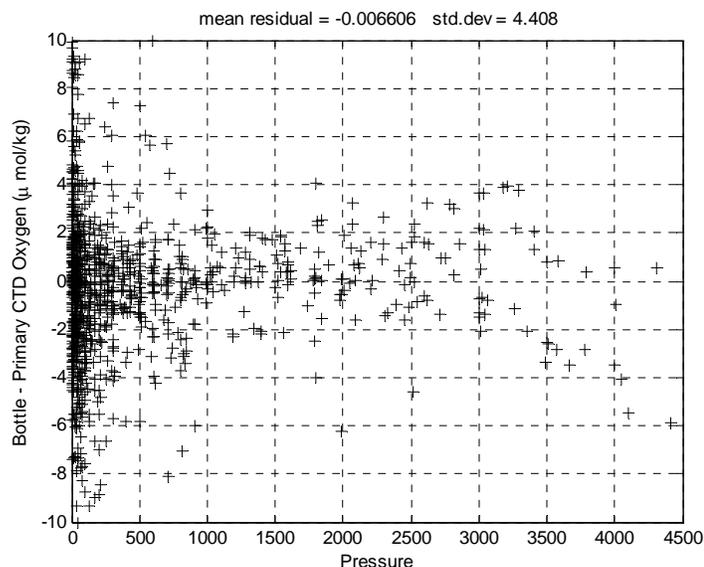


Figure 4.4.2. O₂ residuals by pressure, all pressures.

3.2 Oxygen Measurements

Analysts: George Berberian and Charles Featherstone, NOAA/AOML

Data Reduction: Chris Langdon University of Miami

Samples were drawn from all casts and all Niskin bottles into calibrated 125 ml iodine titration flasks using Tygon tubing with a silicone adaptor that fit over the petcock to avoid contamination of DOC samples. Bottles were rinsed three times and filled from the bottom, overflowing three volumes while taking care not to entrain any bubbles. The draw temperature was taken using a digital thermometer with a flexible thermistor probe that was inserted into the flask while the sample was being drawn during the overflow period. These temperatures were used to calculate $\mu\text{mol kg}^{-1}$ concentrations, and a diagnostic check of Niskin bottle integrity. One-ml of MnCl_2 and one-ml of NaOH/NaI were added immediately after drawing the sample was concluded using a Repipetor, the flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. The flasks were stored in the lab in plastic totes at room temperature for 1-2 hours before analysis. Twenty-four samples plus two duplicates were drawn from each station except the shallow coastal stations where fewer samples were drawn depending on the depth. Total number of samples collected was 1247. A total of 133 sets of duplicates were run. The difference between replicates averaged $1.3 \mu\text{mol kg}^{-1}$ for stations 1-45. The mixing time between additions by the titrator was increased from 4 to 8 s. This improved the reproducibility significantly. The difference between replicates for stations 46-90 averaged $0.4 \mu\text{mol kg}^{-1}$. The total number of samples flagged after initial shipboard reduction of quality control: Questionable (QC=34): Not reported (QC=1).

Additional oxygen samples were drawn from the ship's uncontaminated seawater line for comparison for the purpose of checking the calibration of the UNH Aanderra Optode oxygen sensor and for comparison with the oxygen sensor on the UGA CO₂ buoy.

Dissolved oxygen analyses were performed with an automated oxygen titrator using amperometric end-point detection (Culberson and Huang 1987). This was the first full cruise performed by AOML using this system. The titration of the samples and the data logging and graphical display was performed on a PC running a program written by Ulises Rivero of AOML. The titrations were performed in a climate controlled lab at 18.5°C-20°C. Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. Tests in the lab were performed to confirm that the precision and accuracy of the volume dispensed were comparable or superior to the Dosimat 665. The whole-bottle titration technique of Carpenter (1965) with modifications by Culberson et al. (1991) was used. Four replicate 10 ml iodate standards were run every 24 hours. The reagent blank determined as the difference between V1 and V2, the volumes of thiosulfate required to titrate 1 ml aliquots of the iodate standard, was determined at the beginning and end of the cruise. This method was found during pre-cruise testing to produce a more reproducible blank value than the value determined as the intercept of a standard curve. The temperature corrected molarity of the thiosulfate titrant was determined as given in Dickson (1994).

References

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- Culberson CH, Huang S (1987) Automated amperometric oxygen titration. *Deep-Sea Res.* 34: 875-880.
- Culberson CH, Knapp G, Stalcup M, Williams RT, Zemlyak F (1991) A comparison of methods for the determination of dissolved oxygen in seawater. *WHP Operations and Methods*.
- Dickson, A. G. (1994). "Determination of dissolved oxygen in seawater by Winkler titration." *WHP Operations and Methods*.

3.3 Nutrient Measurements

Analysts: Charles J. Fischer and Natchanon Amornthammarong, NOAA/AOML

Equipment and Techniques

Dissolved nutrients (phosphate, silicate acid, nitrate, and nitrite) were measured using automated continuous flow analysis with a segmented flow and colorimetric detection. The four channel autoanalyzer was customized using components from various systems. The major components were a WESTCO CS-9000 sampler, two peristaltic pumps, four Perstorp monochrometers and custom software for digitally logging and processing the chromatograms. Micro-coils from Alpkem were used for the analysis of the nutrients.

The detailed methods were described by Gordon et al. (1992). Pump tubes were changed twice during this expedition.

Silicic acid was analyzed using a modification of Armstrong et al. (1967). An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybic acid. Oxalic acid was added to inhibit a secondary reaction with phosphate. Finally, the reaction with ascorbic acid formed the blue compound silicomolybdous acid. The color formation was detected using a 6mm flowcell at 660 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride by Gordon et al.) was to reduce toxicity of our waste stream.

Nitrate and Nitrite analysis were also a modification from Armstrong et al. (1967). Nitrate was reduced to nitrite in a cadmium column, formed into a red azo dye by complexing nitrite with sulfanilamide and N-1-naphthylethylenediamine and the color formation was detected at 540 nm. The same technique was used to measure nitrite (excluding the reduction step).

Phosphate analysis was based on a technique by Bernhart and Wilhelms (1967). An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdate acid, and this was reduced to the blue compound phosphomolybdous acid following the addition of hydrazine sulfate. The color formation was detected at 799 nm.

Sampling and Standards

Nutrient samples were drawn from all casts and all Niskin bottles in 40ml HDPE sample bottles that had been stored in 10% HCl and rinsed 4-5 times with sample before filling. A replicate was always drawn from the deep Niskin bottle for analysis. All samples were brought to room temperature prior to analysis. Each analytical run consisted of blanks, old working standards, samples analyzed from deep to surface, replicate analysis of four new standards and finishing again with blanks. The blanks were deionized water, and the standards were simply a “zero” standard in Low Nutrient Seawater (LNSW), and a high standard.

The high standard was made from the addition of 1ml of primary nitrite standard and 20 ml of a secondary mixed standard (containing silicic acid, nitrate, and phosphate) in 500ml of LNSW. A new high standard was prepared for each analytical run.

Dry standards were pre-weighed at AOML and dissolved into primary standards at sea. The mixed standard was prepared by the additions of the nitrate and phosphate primary standards during the preparation of the silicic acid primary standard.

After each run, the electronic chromatograph was scrutinized to ensure proper selection of individual peak heights. The peak information was inserted into Microsoft Excel and

the concentrations were calculated after factoring the baseline drift, carryover corrections, refractive index, and standard drift.

Nutrient concentrations were reported in micromoles per liter, and then converted to micromoles per kilogram. The lab temperature was recorded for each analytical run.

Approximately 1000 samples were analyzed during the GOMECC cruise.

Reference:

Armstrong, F.A.J., Stearns, C.R. and Strickland, J.D.H. (1967) The measurement of upwelling and subsequent biological processes by means of the Technicon AutoAnalyzer and associated equipment. *Deep-Sea Res.* 14:381-389.

Bernhard, H. and Wilhelms, A. (1967) The continuous determination of low level iron, soluble phosphate and total phosphate with AutoAnalyzer. *Technicon Symposia, I.* pp.385-389.

Gordon, L.I., Jennings Jr., J.C., Ross, A.A. and Krest, J.M. (1993) A suggested protocol for the continuous automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic program and the Joint Global Ocean Fluxes Study, WOCE Operations Manual, vol. 3: The Observational Programme, Section 3.2: WOCE Hydrographic Programme, Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1; WOCE Report No. 68/91. November 1994, Revision 1, Woods Hole, MA., USA, 52 loose-leaf pages.

3.4 DIC Measurements

Analyst: Esa Peltola and Robert Castle, NOAA/AOML

Samples for total dissolved inorganic carbon (DIC) measurements were drawn according to procedures outlined in the *Handbook of Methods for CO₂ Analysis* (DOE 1994) from 9.8-L Niskin bottles into cleaned 294-mL glass bottles. Bottles were rinsed and filled from the bottom, leaving 6 mL of headspace; care was taken not to entrain any bubbles. After 0.2 mL of saturated HgCl₂ solution was added as a preservative, the sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours prior to analysis.

DIC samples were collected from variety of depths with one to three replicate samples per cast. Typically the replicate seawater samples were taken from the surface and and/or bottom Niskin bottles and run at different times during the cell. No systematic difference between the replicates was observed.

The DIC analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two newly developed analytical systems (AOML3 and AOML4) used simultaneously on the cruise. Each system consisted of a coulometer

(UIC, Inc.) coupled with a Dissolved Inorganic Carbon Extractor (DICE) inlet system. DICE was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA (Johnson et al. 1985, 1987, 1993, and 1999; Johnson 1992). This was the first at-sea operation of the systems for AOML. In the coulometric analysis of TCO₂, all carbonate species are converted to CO₂ (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved CO₂ gas is swept into the titration cell of the coulometer with pure air or compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. In this process, the solution changes from blue to colorless, which triggers a current through the cell and causes coulometrical generation of OH⁻ ions at the anode. The OH⁻ ions react with the H⁺, and the solution turns blue again. A beam of light is shone through the solution, and a photometric detector at the opposite side of the cell senses the change in transmission. Once the percent transmission reaches its original value, the coulometric titration is stopped, and the amount of CO₂ that enters the cell is determined by integrating the total charge during the titration.

The coulometers were calibrated by injecting aliquots of pure CO₂ (99.995%) by means of an 8-port valve outfitted with two sample loops with known gas volumes bracketing the amount of CO₂ extracted from the water samples for the two AOML systems.

The stability of each coulometer cell solution was confirmed three different ways: the Certified Reference Material (CRM), Batch 80, supplied by Dr. A. Dickson of SIO, was measured at the beginning; gas loops in the beginning and at the end; and the duplicate samples at the beginning, middle, and end of each cell solution. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9–12 hours of continuous use.

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

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

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

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

The instrument has a salinity sensor, but all DIC values were recalculated to a molar weight (μmol/kg) using density obtained from the CTD's salinity sensor. The DIC values were corrected for dilution by 0.2 mL of saturated HgCl₂ used for sample preservation. The total water volume of the sample bottles was 288 mL (calibrated by Esa Peltola, AOML). The correction factor used for dilution was 1.0007. A correction was also applied for the offset from the CRM. This correction was applied for each cell using the CRM value obtained in the beginning of the cell. The results underwent initial quality

control on the ship using property plots: DIC-Depth, DIC-Potential Temperature, DIC-Salinity, DIC-O₂, DIC-NO₃; DIC-SiO₃, DIC-PO₄, and DIC-TALK.

The overall performance of the instruments was good during the cruise. A coulometer stopped counting during station 25 runs and it was replaced. A computer ran out of virtual memory during station 27 and it also had serial communication problems during station 24 and 32 runs. A total of 971 samples were measured. The average difference of replications is 1.0 umol/kg.

Reference

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3.5 Discrete pCO₂ Measurements

Analysts: Kevin Sullivan, NOAA/AOML, Kevin.Sullivan@noaa.gov

Principal Investigator: Rik Wanninkhof, NOAA/AOML, Rik.Wanninkhof@noaa.gov

Sampling:

Samples were drawn from 10-l Niskin bottles into 500 ml volumetric flasks using Tygon® tubing with a Silicone adapter that fit over the petcock to avoid contamination of DOM samples. Bottles were rinsed while inverted and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were

sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at room temperature generally for no more than 6 hours.

The analyses for pCO₂ were done with the discrete samples at 20°C. In addition to the primary water bath, which maintained the analytical temperature within 0.1°C, there was a secondary bath to get the samples close to the analytical temperature. As soon as space was available in the secondary and then primary baths, the sample flasks were moved into the more controlled temperature bath. No flask was analyzed without spending at least 2 hours in a bath close to the analytical temperature.

Significant effort was made to sample as often as possible with priority given to the shallow stations. With few exceptions, if discrete pCO₂ analysis was done on a station, samples were drawn at all depths. Duplicate samples from the same Niskin were drawn regularly to check the precision of the sampling and analysis.

Eight hundred twelve samples were drawn at seventy-two of the ninety stations. On two short transects (27North, New Jersey) all stations were sampled. On five transects (Galveston, Louisiana, Tampa, Savannah, Portsmouth) only one station was not sampled. On the other two transects (Cape Hatteras, MVCO) there were numerous stations deeper than 2000 meters that generated possible samples faster than could be sampled and analyzed. This extensive coverage was only possible because occasionally Bob Castle drew samples while the primary analyst, Kevin Sullivan, slept.

Thirty-four sets of duplicate flasks were drawn at numerous depths. The average relative standard deviation of these thirty-four pairs was 0.19%. The analytical system processed two sample flasks at a time. There were eleven discrete samples drawn from the underway seawater line to pair with an odd sample from the Niskin and for comparison to the ship's underway pCO₂ instrument.

Analyzer Description:

The discrete pCO₂ system is patterned after the instrument described in Chipman et al. (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen et al. (1995). The major difference between the two systems is that Wanninkhof instrument uses a LI-COR® (model 6262) non-dispersive infrared analyzer, while the Chipman instrument utilizes a gas chromatograph with a flame ionization detector.

Once the samples reach the analytical temperature, a 50-ml headspace is created by displacing the water using a compressed standard gas with a CO₂ mixing ratio close to the anticipated pCO₂ of the water. The headspace is circulated in a closed loop through the infrared analyzer that measures CO₂ and water vapor levels in the sample cell. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differ by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 minutes. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at room pressure.

In order to maintain analytical accuracy, a set of six gas standards (ranging from 206 to 1534 ppm) is run through the analyzer before and after no more than every ten seawater samples. 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.

The calculation of pCO₂ in water from the headspace measurement involves several steps. The CO₂ concentrations in the headspace are determined via a second-degree polynomial fit using the nearest three standard concentrations. Corrections for the water vapor concentration, the barometric pressure, and the changes induced in the carbonate equilibrium by the headspace-water mass transfer are made. The corrected results are reported at the analytical temperature of 20°C.

No instrumental problems occurred during the cruise. The relatively time-consuming analyses and the presence of only one analyst limited the spatial coverage. Sampling and analyses focused on precision and accuracy rather than high throughput.

Standard Gas Cylinders:

Cylinder#	ppm CO ₂
CA05998	205.07
CA05989	378.71
CA05988	593.64
CA05980	792.51
CA05984	1036.95
CA05940	1533.7

References

Chen, H., R. Wanninkhof, R.A. Feely, and D. Greeley, 1995:
Measurement of fugacity of carbon dioxide in sub-surface water: An evaluation of a method based on infrared analysis. NOAA Technical Memorandum, ERL AOML-85, 54 pp.

Chipman, D.W., J. Marra, and T. Takahashi, 1993:
Primary production at 47°N and 20°W in the North Atlantic Ocean: A comparison between the 14C incubation method and mixed layer carbon budget observations. Deep-Sea Res., II, v. 40, pp. 151-169.

Wanninkhof, R., and K. Thoning, 1993:
Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods. Mar. Chem., v. 44, no. 2-4, pp. 189-205.

3.6 TA Measurements

Analyst: Xinping Hu and Wei-Jen Huang, UGA

Alkalinity Definition:

In 19 century, total alkalinity has been defined as the number of equivalents of strong acid required to neutralize 1 dm³ (or 1 kg) of seawater to the endpoint corresponding to the formation of carbonic acid from bicarbonate (Sverdrup, Johnson and Fleming, 1942).

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

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

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

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

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

Peng et al. (1987) defined alkalinity by a similar expression. The only different is that the zero level of protons of phosphoric is H₃PO₄.

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

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

Where,

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

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

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

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

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

This definition is very clear and gives a total concept of species to total alkalinity instead of each of them.

Principle of titration

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

1. Determination of Total Alkalinity by Gran Titration:

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

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

F = Gran Factor, v = volume of acid added to the sample vessel, V₀ = sample volume, E = electric motive force (EMF) measured, and a = slope of electrode.

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

2. Principle of pH glass electrode:

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

pH electrode was calibrated with pH buffer (NBS) 4.01, 7.00, and 10.01 and recalibration was done every 24 hours.

Equipments – Auto-titration system

The system is made up by three parts: 1) titrator, 2) software and computer, and 3) thermostat. The titrator includes two digital pumps (pump A and pump B), a pH meter and a RossTM pH combination electrode (Thermo), a stirring plate. Software controls the titration process by interfacing the computer with the pumps and the pH meter through serial ports. The titration vessel, reagent (HCl), seawater sample were all kept at constant temperature in respective water jackets maintained by the thermostat at 22.2 ± 0.1 °C during this cruise.

Sampling

During this cruise (7/10 – 8/4, 2007), 957 TA samples were collected from 87 stations along with 9 transects, 6 samples from a buoy station and 11 samples from the underway system. Besides, 1 Savannah River water TA sample was measured. These samples were kept in 4°C walk-in refrigerator (if necessary) and were measured in 48 hours.

TA samples were taken by 250ml narrow ground neck Pyrex bottles from Niskin bottles after removing air bubbles from the sampling tubing. Each glass bottle was rinsed three times using half of the bottle volume sample seawater and then filled from the bottom; overflow of half of bottle volume seawater was allowed. No headspace was left after the stopper was replaced. Duplicated sampling for one depth was done for every four stations.

Besides, 117 DIC samples (from the Savannah transect) and 408 Ca^{2+} samples were collected by 125ml narrow ground neck Pyrex bottles and 60 ml glass bottles and were kept in 4°C walk-in refrigerator. They will be shipped back to UGA lab and analyzed.

Precision and Accuracy:

TA samples were taken by 250ml narrow ground neck Pyrex bottles from Niskin bottles after removing air bubbles from the sampling tubing. Each glass bottle was rinsed three times using half of the bottle volume sample seawater and then filled from the bottom; overflow of half of bottle volume seawater was allowed. No headspace was left after the stopper was replaced. Duplicated sampling for one depth was done for every four stations.

Every sample was titrated at least twice. Certified Reference Material (CRM), Batch 80, supplied by Dr. A. Dickson of SIO, was used to determine HCl concentration before the measurements. System (titrator and electrode) stability was also checked along with the sample run using the CRM seawater every 12 hours. Duplicated samples and replicated measurements of the same sample show no significant difference. The precision of this method is better than 0.1% and accuracy is 0.1%.

Reference:

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3.7 Halocarbon/Alkyl Nitrate Depth Profiles and Saturation Anomalies

Samplers and Analysts

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Samplers:	Julia O’Hern (12 midnight – 12 noon) johern@ocean.tamu.edu Shari Yvon-Lewis (12 noon – 12 midnight)
Analysts:	Julia O’Hern (12 midnight – 12 noon) Shari Yvon-Lewis (12 noon – 12 midnight)
Data Reduction:	Shari Yvon-Lewis

Objectives

We have 3 major objectives 1) assessment of the sources and emission of selected very short lived halocarbons in the coastal ocean, 2) measuring the flux of alkyl nitrates from the coastal ocean, and 3) determination of CFC and HCFC tracers at depth in the coastal ocean. Biogenic very-short-lived halocarbons are potentially significant sources of bromine to the stratosphere. Recent results suggest that coastal emissions of these gases may be up to 5 times the amount emitted by the global open ocean. The data collected during this cruise will help us to assess the impact of coastal emission on the global budgets of these gases. Additionally, we will be examining the emission of alkyl nitrates from the coastal ocean and their subsequent impact on ozone in the coastal marine boundary layer.

Sampling

Depth profile samples were drawn from 9-L Niskin bottles into 100 mL ground glass syringes. The syringes have polycarbonate Luer tipped stopcocks. The Luer tips are inserted directly into the petcocks. The syringes are rinsed twice with full 100 mL volumes of water. Bubbles are carefully flushed out, and the third fill is the final sample. The syringes are wrapped with a stiff rubber band to maintain pressure on the plunger and sample reducing the potential for outgassing in the syringes. Storage of the samples is kept to a minimum (< 12 hours). They are stored vertically in buckets in the climate controlled cold-room (~4 °C). The cold temperature minimizes the chemical degradation of some of the species being measured. After the cold room chiller unit was broken, the samples were kept only as cold as the ice in the room could keep them. One gas chromatograph with a mass spectrometer and a purge and trap is dedicated to analyzing the discrete depth profile samples.

Saturation anomaly measurements include air samples from the bow and samples drawn from equilibrator headspace. An acrylic Weiss-type equilibrator was used, with seawater obtained from the ship's flow-through pumping system. The equilibrator showers seawater through a headspace containing continuously recirculating air [*Butler et al.*, 1988 and *Johnson*, 1999]. Samples of this headspace are drawn off periodically for analysis. One gas chromatograph with a mass spectrometer is dedicated for alternately analyzing air and equilibrator samples.

There was not enough time to complete setting up the instruments and getting them going properly before beginning transect #1 (Galveston Transect). The depth profile samples collected from that transect are not included in the totals given below. The underway instrument was also not ready until transect #2 (Louisiana Transect).

Total number of casts sampled: 68

Total number of depth profile samples collected: 428

Total number of air samples: 336

Total number of equilibrator samples: 336

Typically we analyze each sample (discrete seawater, air, and equilibrator headspace) for 21 chemical species (HCFC-22, CFC-12, HCFC-142b, Halon-1211, CFC-11, HCFC-141b, CFC-113, CH₃CCl₃, CCl₄, C₂Cl₄ (PCE), CH₃Cl, CH₃Br, CH₃I, CH₂Cl₂, CH₂Br₂, CHCl₃, CHBr₃, CH₂ONO₂, C₂H₄ONO₂, i-C₃H₆ONO₂, n-C₃H₆ONO₂).

Analyzer Descriptions

Depth Profile Instrument

The halocarbon measurement system was described in *Yvon-Lewis et al.* (2004). There have been a couple of modifications since to facilitate analysis of alkyl nitrates and to improve performance. The measurements were made with a laboratory-built, automated purge and trap system coupled to a gas chromatograph (GC, HP5890 series II) with mass spectrometer (MS, HP5973) (Figure 1). The autosampler allows us to load all of the depth profile samples directly into gas tight glass bulbs (each with a measured

volume including tubing of ~70mL) kept in a temperature-controlled cooler at approximately 8 °C. Almost the entire 100+ mL of seawater in the syringe is flushed through the bulb and tubing.

The computer switches purge valve #2 (PV2), a Valco loop selection valve (VICI Metronics, TX) with 34 ports and 16 positions, from bulb to bulb allowing the humidified helium purge gas stream to push each sample from the bulb into the temperature-controlled (50 °C) sparger. The purge gas passes through the bulb on its way to the sparger and will pick up any trace amounts of the gases left in water along the walls and any of the trace gases that may have undergone some degassing while sitting in the bulb prior to sampling. In this way, we maximize sample recovery and preconcentration on the first cryotrap. The dried (Nafion PD-100T-24SS, PermaPure Inc.) sparger effluent passes over a Unibeads 1S packed trap (3.175 mm OD, 1.6 mm ID) at -80°C and into a calibrated, evacuated stainless steel flask. The change in flask pressure and the flask temperature are recorded electronically. For a calibration run the pressure in the flask is used to determine the exact volume of the whole air standard that passed over the cryotrap. GC valve #1 (GCV1) is switched from load to transfer, and the primary trap is then flash heated (200°C, 3 min.). The sample is focussed on a second Unibeads 1S packed trap (1.59 mm OD, 0.5 mm ID) at -80°C. GC valve #2 (GCV2) is switched from backflush to inject, the focussing trap is flash heated (200°C, 3 min.) and the sample is injected onto the analytical column (0.25 mm ID x 5m pre- and 55m main, DB-VRX; J&W). The pre-column is backflushed at 10 min. after injection to prevent accumulation of the heavier compounds on the column between runs. The GC is temperature programmed to start at 30°C and end at 210°C.

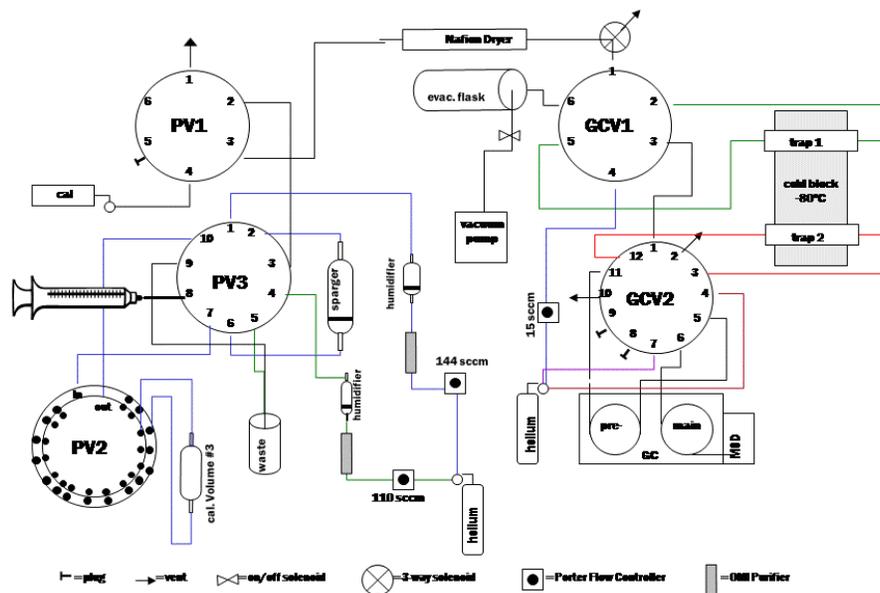


Figure 1. Schematic of the automated purge and trap GCMS system. There are 16 calibrated sample bulbs attached to PV2, however to reduce clutter in the diagram only calibrated sample bulb # 3 is shown.

Each sample, blank and standard is analyzed simultaneously for all of the compounds, HCFC-22, CFC-12, HCFC-142b, CFC-11, HCFC-141b, CFC-113,

CH₃CCl₃, CCl₄, PCE, CH₃Cl, CH₃Br, CH₃I, CH₂Cl₂, CH₂Br₂, CHCl₃, CHBr₃, methyl nitrate, ethyl nitrate, isopropyl nitrate, and n-propyl nitrate. The mass spectrometer is programmed to record signals from specific sets of masses over predetermined intervals (i.e. single ion monitoring, SIM). In this way, the mass spectrometer is extremely selective and can detect only the compound of interest at any given time reducing the potential for co-elution contamination of the signal

Calibration

Purge valve #1 (PV1) is used to switch between the humidified purge helium and the calibration gas streams before they enter the rest of the purge system. The calibration gases are from secondary standard cylinders filled with coastal Miami air. These whole air standards (1 dry acculife treated cylinders and 1 wet electropolished 34L flask) have been calibrated using NOAA/CMDL halocarbon standards and alkyl nitrate standards from lab of Dr. Eric Saltzman (Univ. of California Irvine). During a calibration run, the calibration gas flows into the nafion dryer instead of the sparger effluent, however PV2 is kept in the position of the last sample, which has already been analyzed so the sample bulb is empty. The number of moles of gas that pass over the trap is calculated from the known volume of the evacuated flask and the recorded temperature and pressure of the flask. The dry mole fractions of the halocarbons and alkyl nitrates in the calibration gas are used to determine the number of moles of each compound in each calibration run, sample and blank. After a calibration run and before the next sample run, the entire flow path is flushed with the humidified helium. Blanks are run in the same way as calibration runs except that PV1 is in position to allow the humidified helium to flow through the system not the calibration gas. Every fifth injection is a standard. This allows for tracking drift in the detector's response for each compound.

Data Processing

As mentioned above, every fifth injection is a calibration gas standard. The two standards were swapped periodically during the cruise. The standard or reference gases are used to determine the response factors (response per mole of analyte) for the mass spectrometer for each compound. Any drift or degradation in signal over time corrected for by interpolating the response factors between reference runs. The interpolated response factor is then used with the observed sample response (blank corrected) to determine the moles of analyte present in that sample. Blanks are run every fifth injection just prior to the reference run. The blank response for a specific compound in any given sample is determined by interpolating between blanks. The 2 reference gas tanks will be recalibrated after the cruise to determine if there was any drift in their concentrations over time.

Saturation Anomaly Instrument

Underway atmospheric and equilibrator head space samples were collected. An acrylic Weiss-type equilibrator was used, with seawater obtained from the ship's flow-through pumping system. The equilibrator showers seawater through a headspace containing continuously recirculating air [Butler *et al.*, 1988 and Johnson, 1999]. A second GCMS was connected to the stream select valve that allows it to cycle between the calibration standard and various sources of air such as air and equilibrator headspace (Figure 2). This provided continuous underway saturation data and allows for a comparison between observed saturation and calculated saturation from solubility equations. The precision for air measurements has been determined in the lab through repeated analysis of a single ambient level whole air standard (Table 1).

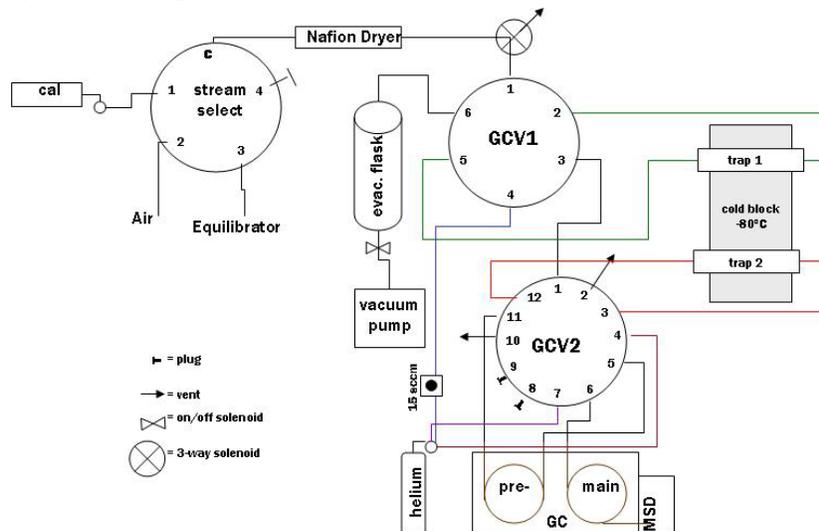


Figure 2. Schematic of GCMS instrument plumbed for analysis of air and equilibrator headspace samples.

Table 1. Precision estimates for each compound.

Compound	Seawater Precision (surface replicate pairs)	Instrument Precision (whole air – Figure 2)
HCFC-22	3.4% (n=10 pairs)	0.38% (n=23)
HCFC-142b		1.4% (n=11) preliminary
CH ₃ Cl	4.4% (n=10 pairs)	0.40% (n=23)
CH ₃ Br	14.5% (n=10 pairs)	0.67% (n=23)
CFC-11	4.2% (n=9 pairs)	0.23% (n=23)
HCFC-141b		3.0% (n=10) preliminary
CFC-113	7.6% (n=10 pairs)	8.22% (n=23)
CH ₃ I	2.6% (n=10 pairs)	2.27% (n=23)
CH ₃ CCl ₃	2.6% (n=10 pairs)	3.08% (n=23)
CCl ₄	2.3% (n=10 pairs)	0.60% (n=23)

Calibration and data processing for this instrument are essentially the same as discussed above for the depth profile instrument. The calibration cylinders are swapped between the 2 instruments daily during the cruise.

References

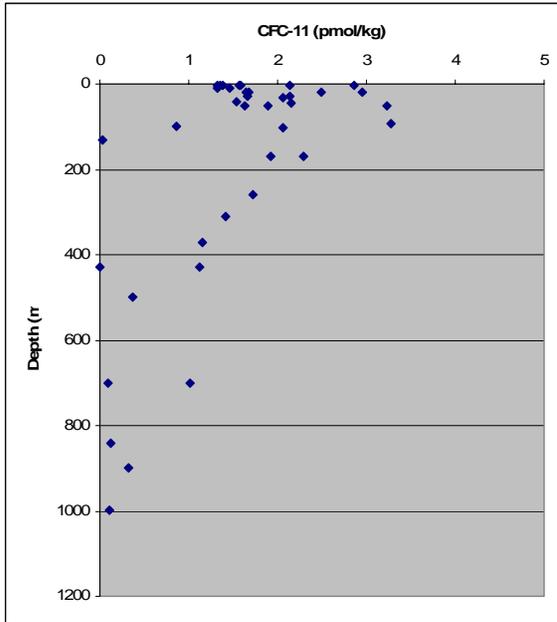
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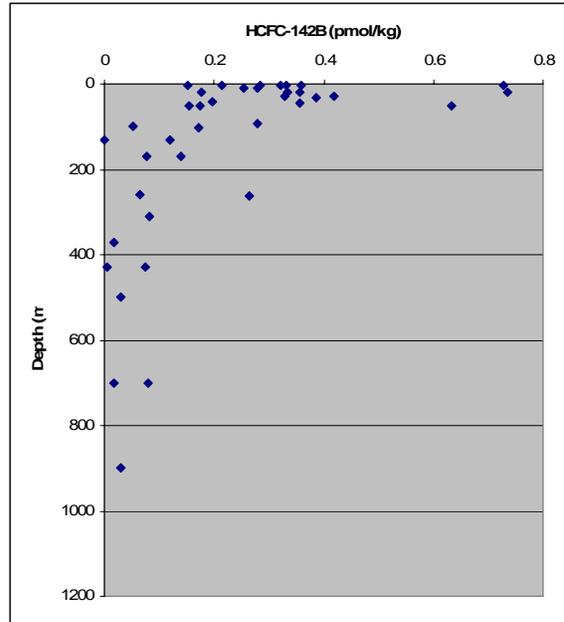
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Preliminary Results:

a)



b)



c)

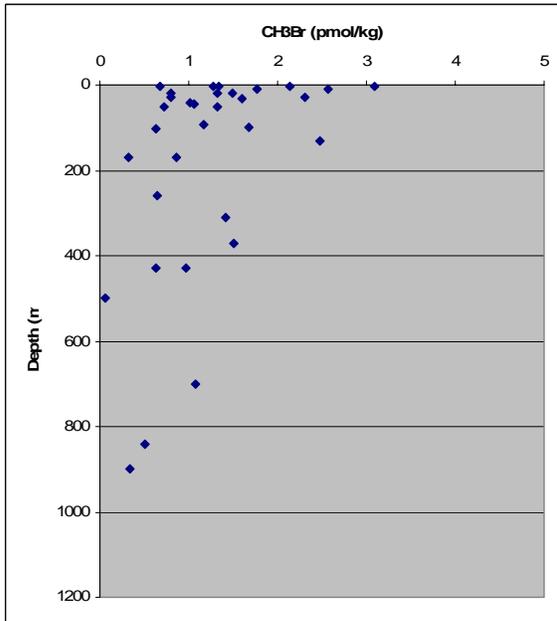


Figure 3. Preliminary depth profiles of CFC-11 (a), HCFC-142B (b), and CH₃Br (c) from transect 2.

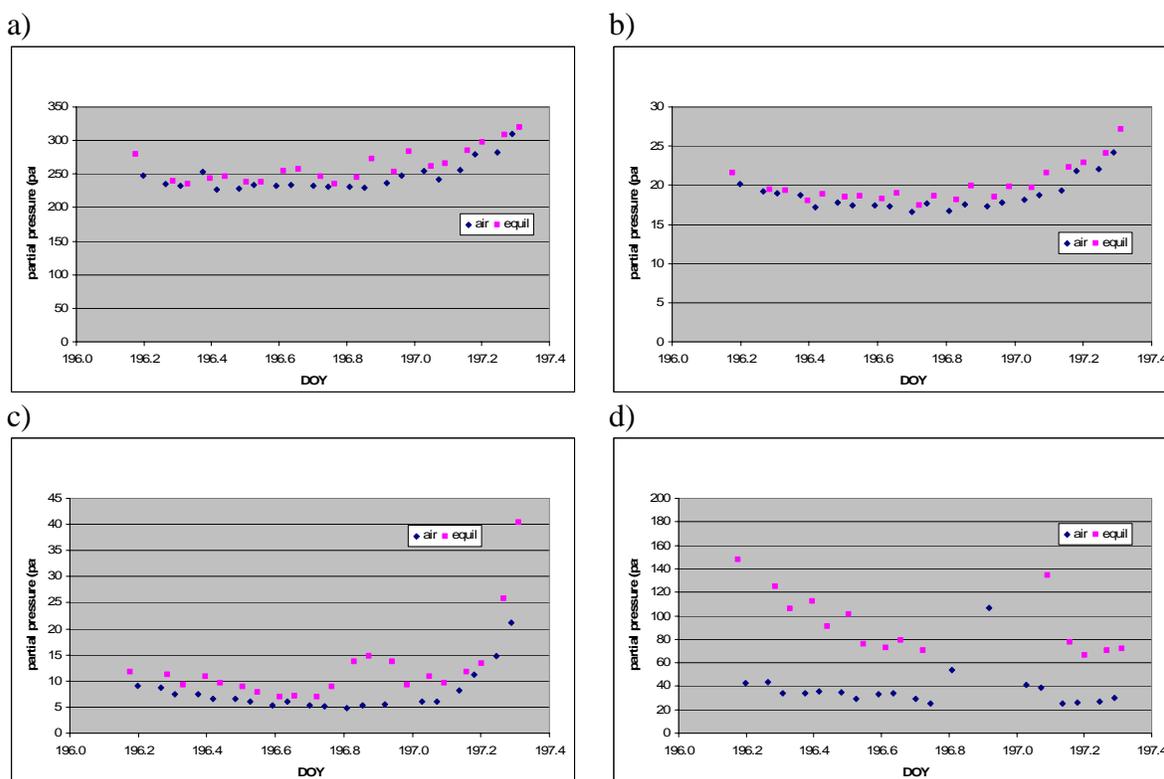


Figure 4. Preliminary air and equilibrator data for CFC-11 (a), HCFC-142B (b), CH₃Br (c), and CHBr₃ (d).

4. Underway Measurements

4.1 Underway pCO₂ Analyses

Analysts: Bob Castle and Kevin Sullivan, NOAA/AOML

PI: Rik Wanninkhof, NOAA/AOML, Rik.Wanninkhof@noaa.gov

During the GOMECC cruise there were two automated underway pCO₂ systems from AOML situated in the hydrolab. The first system has been collecting data on the R/V Ronald Brown since 1999. The second system was newly designed and built, and was installed just before this cruise. If the performance of the second system proves to be acceptable over several cruises, it will replace the first system on the R/V Ronald Brown.

The first system runs on an hourly cycle during which 3 gas standards, 3 ambient air samples, and 8 headspace samples from its equilibrator are analyzed. The second system runs 3 gas standards, 5 ambient air samples, and 55 headspace samples from its equilibrator in 2.6 hours. Both systems used the same gas standards, with concentrations of 289.06, 370.90, and 411.42 ppm CO₂ in compressed natural air. The standard gases

were purchased from NOAA/ESRL in Boulder and are directly traceable to the WMO scale.

Both systems include an equilibrator where surface seawater from the bow intake is equilibrated with headspace. One of the major differences between the systems is the size of the equilibrator. The approximate volumes of the enclosed headspace and water in the first system are 17 and 12 liters, respectively; while for the second system enclosed water was about 0.6 liters and the headspace was 0.8 liters. The approximate water flow rates were 9 liters per minute in the first system and 2 liters per minute in the second system.

On both systems, the equilibrator headspace is circulated through a non-dispersive infrared analyzer (IR) and then returned to the equilibrator. On the first system the analyzer is a LI-COR™ 6251; the second system includes a LI-COR™ 6262 analyzer. When ambient air or standard gas is analyzed the exit of the analyzer is vented to the lab rather than connected to the equilibrator. Both systems employ KNF pumps to draw marine air from separate intakes on the bow mast through 100 m of 0.95 cm (= 3/8") OD Dekoron™ tubing at a rate of 6-8 l/min. A filter of glass wool at each intake prevents particles from entering the gas streams. Both air inlet lines are constantly being flushed.

Both systems dry the environmental samples prior to analyses. Both systems first employ chilled condensers to remove water vapor. Following the condensers, the first system has a column of magnesium perchlorate while the second system has two PermaPure Naphion drying tubes to present environmental samples to the analyzers with very little water vapor. The LI-COR™ 6262 internally compensates for any residual water vapor in the sample gas streams.

Custom developed programs run under LabView™ control the systems and graphically display the air and water results. The programs record the output of the infrared analyzers, the water flow, the gas flows, the equilibrator temperature, the barometric pressure, the GPS position, and a variety of other sensors. The programs write all of this data to disk at the end of each measurement phase. The details of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1998).

The first analytical system operated throughout the entire cruise with no problems. The gas flow sensors on the second system were not responsive at the start of the cruise. Replacement gas flow sensors were brought out from Georgia and installed after 12.5 days of data collection. During that initial period, the gas flows were set and checked with a bubble flow meter and ball rotameter. The second analytical system had a low response for the first day. After the soda lime and magnesium perchlorate in the reference scrubber canister were replaced the response matched the first system very well. Over the course of the cruise, the response of the second system has slowly drifted up. Since the changes in response of the analyzer equally influence the standards and samples, the final calculated CO₂ concentrations should agree very well. The patterns of changes in water and air concentrations in the two systems were the same.

Standard Gas Cylinders

Cylinder#	ppm CO ₂
CA06745	289.06
CA05398	370.90
CA05344	411.42

References

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy, 1998: A new automated underway system for making high precision pCO₂ measurements onboard research ships. *Analytica Chim. Acta*, v. 377, pp. 185-191.

Ho, D.T., R. Wanninkhof, J. Masters, R.A. Feely, and C.E. Cosca, 1997: Measurement of underway fCO₂ in the eastern equatorial Pacific on NOAA ships *Baldrige* and *Discoverer*. NOAA Data Report, ERL AOML-30, 52 pp.

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4.2 Ammonia Underway Measurements

Analyst: Natchanon Amornthammarong, NOAA/AOML

Introduction

The most common technique used to measure ammonia in seawater is the indophenol blue method (Berthelot reaction)^{1,2}. However, there are reports of difficulties³⁻⁵ with the technique because of highly susceptible to contamination and lack of sensitivity (LOD 0.6 μM). An ammonia electrode was found easy to operate⁶, but requires long equilibration times and provides low sensitivity (LOD 0.2 μM). To increase the sensitivity, a solvent extraction method⁷ was developed, but the procedure is time consuming and labor intensive. In addition, a long-path liquid waveguide capillary cell⁸ was using to improve the sensitivity (LOD 5 nM), but the problems of the indophenol blue have not been solved such as interferences and refractive index (especially measuring in seawater). In 1971, a fluorescent reaction was developed by Roth⁹ for ammonia or primary amino acid with *o*-phthaldialdehyde (OPA) and mercaptoethanol to produce strongly fluorescent compounds, which has been broadly used in measurement of amino acids. Other dialdehydes were also developed for the same purpose¹⁰⁻¹². In 1989, Dasgupta¹³ reported that using sulfite instead of mercaptoethanol provides higher sensitivity for ammonia measurement and greater selectivity over amino acids. The OPA-sulfite-NH₃ reaction has been modified for ammonia determination in seawater^{14,15}. Recently, Dasgupta¹⁶ reported a new version of ammonia determination in atmospheric,

which can improve reagent stability that makes no need reagent replacement for at least two weeks. Moreover, the sensitivity has also been increased. Besides, this technique has no problems about refractive index and much less interference effect than the indophenol blue method.

Experimental Section

Flow Injection Analysis (FIA) technique is simply used for this work as shown in Figure 1. A peristaltic pump P (Ismatec) is used to pump water W (160 $\mu\text{L}/\text{min}$) as carrier through an electromechanically actuated six-port injection valve IV (V-1541-DC, Upchurch). The injection loop constituted a 1.0 x 1220 mm PTFE tube (Zeus Industrial Products, NJ); the measured injection volume was 958 μL , which is enough to get a flat-top peak for every concentrations. The sample or standard solution S is aspirated from an auto-sampler A (ASX-510HS, CETAC) by the pump P through the injection valve IV. The sulfite solution R2 merges with the OPA reagent stream R1 and merges again with the carrier stream. Then, the reaction stream passes through a heated reaction coil (65 $^{\circ}\text{C}$, 1.0 x 2000 mm) prior to entry into the fluorescence detector FL (F1080, Hitachi). To obtain data from the detector FL, automate the injection valve IV and control the auto-sampler, simple software was developed by LabVIEW programming.

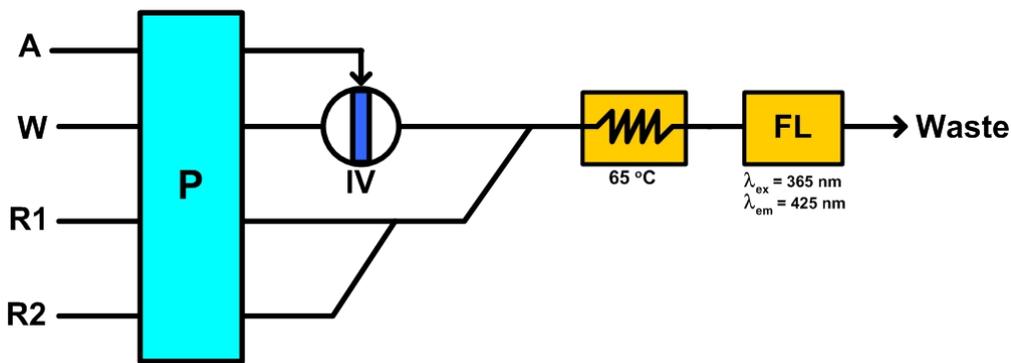


Figure 1. Flow Injection Analyzer for ammonia determination: A, Auto-sampler; W, Water; S, Sample/Standard; P, Peristaltic Pump; R1, Phthaldialdehyde (OPA) solution; R2, Sulfite in formaldehyde solution; FL, Fluorescent Detector; and IV, Injection Valve.

Underway method.

For operating as an underway mode, the autosampler A would be changed to connect with a U-pipe sampling system where the seawater continuously overflows all the time.

Sampling and Standards

Nutrient samples were drawn in 40ml HDPE sample bottles that had been stored in 10% HCl and rinsed 4-5 times with sample before filling. A replicate was always drawn from the deep Niskin bottle for analysis. All samples were brought to room temperature prior

to analysis. The blanks were deionized water, and the standards were simply 500 nM NH_4^+ in deionized water.

Data processing.

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

Approximately 2,445 underway samples (the sampling rate is 7.5 times/hour) and 1,096 Niskin samples were analyzed during the GOMECC cruise. Detection limit for this cruise is 15 nM (nmol/L). No replication for these samples were made.

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4.3 Underway Measurements of pCO_2 , TCO_2 , and pH using Multi-parameter Inorganic Carbon Analyzer (MICA)

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Data Reduction: Zhaohui Aleck Wang (awang@marine.usf.edu)

Equipment and Analytical Techniques: Multi-parameter Inorganic Carbon Analyzer, USF:

The USF automated Multi-parameter Inorganic Carbon Analyzer (MICA) was used to simultaneously measure underway surface sea water $p\text{CO}_2$, TCO_2 , pH, and air $p\text{CO}_2$. The resulting data can be compared to measurements either from the AOML underway LiCOR $p\text{CO}_2$ system (surface sea water $p\text{CO}_2$ and air XCO_2) or discrete surface sampling (surface sea water TCO_2) to evaluate performance.

The technical details and performance evaluation of the MICA can be referred to Wang et al. (2007). The system consists of three sea water channels (surface sea water $p\text{CO}_2$, TCO_2 , and pH) and an air channel (atmospheric $p\text{CO}_2$). All measurements (four channels) are based on the same spectrophotometric principles. The system can operate continuously with a sampling frequency of ~ 7 per hour. For each sample, all four parameters are measured and recorded simultaneously.

Spectrophotometric pH measurements are based on the method described in Clayton and Byrne (1993), but use thymol blue as the pH indicator (Zhang and Byrne, 1996; Wang et al., 2007). Indicator thymol blue is directly injected into a stream of underway sea water and changes of absorbances are monitored by a spectrophotometer.

In sea water/air $p\text{CO}_2$ and sea water TCO_2 measurements, Teflon AF 2400 (DuPont) is used as both a CO_2 permeable membrane and a long liquid-core waveguide (LCW) (Wang et al., 2007). For the sea water/air $p\text{CO}_2$ measurements, phenol red is used as the indicator, while bromocresol purple is used as the indicator in TCO_2 measurements. During each CO_2 measurement, the indicator solution in each of two CO_2 channels is motionless inside the LCW. The sea water or air samples are directed to flow outside the LCW. After CO_2 molecules equilibrate with the LCW's internal solution through diffusion, its equilibrium pH is measured by absorbance ratios. $p\text{CO}_2$ is then derived from this equilibrium pH. For TCO_2 measurements, sea water samples are first acidified to convert all carbonate species of sample water to CO_2 before measurements.

For each of the three indicators used, three wavelengths are chosen for measurement of absorbances. Two wavelengths assess the absorbance peaks of acid and base forms of the indicator, while a third wavelength serves as a reference wavelength. Absorbances vary at the acid and base wavelengths in response to pH changes, but not at the reference wavelength. Absorbance ratios between acid and base wavelengths are

calculated, and used to evaluate CO₂ system parameters. The wavelengths chosen for the four channels are listed in Table 1.

Table 1. Wavelengths used for spectrophotometric determination of inorganic carbon species.				
Channel	Indicator	Acid Wavelength	Base Wavelength	Reference Wavelength
Sea water and air <i>p</i> CO ₂	Phenol red	434 nm	558 nm	700 nm
TCO ₂	Bromcresol purple	432 nm	589 nm	700 nm
pH	Thymol blue	435 nm	596 nm	730 nm

Four Ocean Optic 2000 spectrophotometers are used to detect the light signals of the four channels. The light assemblies, spectrophotometers, and optical cells are connected through optic fibers. The light assembly of each channel consists of a high-temperature tungsten lamp with blue and short-pass filters in order to achieve an improved balance of spectral intensity between 430 and 700 nm.

The optical cells of the *p*CO₂ and DIC channels are custom-machined from PEEK rods. The center piece of the optical cell has a 27 mm O.D. and a 2 mm I.D. with a length of 15 cm. The Teflon AF 2400 LCW is held inside this center piece. The center piece has a sample inlet and outlet, and two optical fibers that connect the optical cell with the light source and spectrophotometer are inserted into the ends of the LCW through two custom-made PEEK connectors. The ends of the LCW are sealed by two O-rings housed inside the connectors. The PEEK connectors allow both reagent and light to pass through the LCW. The pH optical cell is also machined from a PEEK rod, but does not require special connectors since no LCW is used.

The indicator solution for *p*CO₂ measurements consists of 2 μM phenol red in 225 μmol kg⁻¹ total alkalinity (Na₂CO₃) and 0.2 μM sodium lauryl sulfate solutions. For TCO₂ measurements, the indicator solution is made of 2 μM bromcresol purple in 1000 μmol kg⁻¹ total alkalinity (Na₂CO₃) and 0.2 μM sodium lauryl sulfate solutions. The reference solutions of the *p*CO₂ and TCO₂ measurements are made similarly without indicator. For pH measurements, thymol blue solution is made in Milli-Q water with a concentration of 1.5 mM. The R ratio of thymol blue solution is adjusted (R~0.77) to minimize the magnitude of indicator-induced pH perturbations. All indicator and reference solutions are stored in gas-impermeable laminated bags.

Indicator and reference solutions are pumped through separate lines into their respective channels by digital peristaltic pumps. Surface sea water is pumped on board by a shipboard pumping system. It first flows through a SBE 49 CTD that records salinity and temperature. Sea water samples are then pumped through three sea water channels (*p*CO₂, TCO₂, and pH). Before entering the TCO₂ channel, sea water samples are acidified with ~3 N HCl using another peristaltic pump. The mixing ratio is

approximately ~700 (sea water to HCl). An in-line mixing coil is used to facilitate mixing. Thymol blue is mixed with sea water samples for pH measurement with a mixing ratio of ~700 (sea water to thymol blue), and the final thymol blue concentration in sample water is ~ 2 μM . Such a low indicator concentration results in insignificant pH perturbation (< 0.001 pH units) due to indicator addition. An in-line mixing coil is also used in this case. Air samples are drawn from a shipboard air sample line set up for the LiCOR IR underway $p\text{CO}_2$ measurement. The air flow rate is controlled at 30 ml/min using a gas flow controller. Atmospheric pressure is recorded by a barometer.

All channels are thermostated in a Lauda E100 water bath that is set to $25 \pm 0.1^\circ\text{C}$. All samples, reference and indicator solutions are also temperature pre-equilibrated in the water bath to 25°C through PEEK, glass or copper coils. All measurements, as well as calibrations, are taken at this temperature.

All units of the system are connected to a custom-made electronic motherboard and controlled by a PC. The interface program runs cycles to operate the MICA continuously. The time required for each measurement cycle depends on the equilibration time (7 minutes for the $p\text{CO}_2$ and TCO_2 channels) and flushing time for the indicator/reference solution and samples (~2 minutes). Chemical reaction for pH measurements is instantaneous. The following sequence is taken during a measurement cycle:

1. Flush pH reference (sea water samples without indicator solution).
2. Flush reference for sea water $p\text{CO}_2$, air $p\text{CO}_2$, and TCO_2 .
3. Read and store reference readings.
4. Flush indicator solutions for sea water $p\text{CO}_2$, air $p\text{CO}_2$, and TCO_2 ; mix thymol blue with sea water samples (pH measurements); acidify TCO_2 samples.
5. $p\text{CO}_2$ and TCO_2 equilibration (7 minutes).
6. Read and store measurements.
7. Repeat Step 4-6 five times.
8. End of one measurement cycle and repeat from the beginning.

During measurements, the sea water and air samples are continuously flowing through the channels.

Standards:

Two $p\text{CO}_2$ channels were calibrated before the cruise against five standard CO_2 gases (XCO_2 257, 302, 354, 404, 501 μatm , Airgas). These are initially calibrated against a high-accuracy air-balanced CO_2 standard ($454.77 \pm 0.04 \mu\text{atm}$, Cylinder No. 05507) obtained from the Climate Monitoring Division of Earth System Research Laboratory (ESRL) of NOAA at Boulder, CO. These calibrations are conducted using a Li-COR 7000 $\text{CO}_2/\text{H}_2\text{O}$ analyzer with a precision better than $\pm 1.0 \mu\text{atm}$. TCO_2 was also calibrated before the cruise using a Certified Reference Material (CRM). Thymol blue has been previously calibrated for sea water pH measurements (Zhang and Byrne, 1996). During the cruise, CO_2 gas standards and CRM were used periodically to check the pre-cruise

calibration consistency for CO₂ and TCO₂ measurements, and re-calibration was performed if necessary.

Data Processing:

The absorbance ratio R for each measurement (all four parameters) is given as:

$$R = (A_2 - A_{\text{ref}}) / (A_1 - A_{\text{ref}})$$

where A₁ and A₂ are the peak absorbance at acid and base wavelengths, respectively; and A_{ref} is the absorbance at the reference wavelength. For all four parameters measured, R is used to calculate pH via the following equation:

$$\text{pH} = \log \left(\frac{R - \epsilon_{2(\text{HA})} / \epsilon_{1(\text{HA})}}{\epsilon_{2(\text{A})} / \epsilon_{1(\text{HA})} - R \cdot \epsilon_{1(\text{A})} / \epsilon_{1(\text{HA})}} \right) - \text{pK}_{\text{a}2}$$

where $\epsilon_{1(\text{HA})}$ and $\epsilon_{2(\text{HA})}$ are the molar absorptivities of the acid form (HA⁻) of indicator at two peak-absorbance wavelengths; $\epsilon_{1(\text{A})}$ and $\epsilon_{2(\text{A})}$ are the molar absorptivities of the A²⁻ (fully unprotonated) form of indicator at two peak-absorbance wavelengths; and K_{a2} is the second dissociation constant of the indicator used. Molar absorptivities and K_{a2} for all indicators are determined in the laboratory at 25°C before the cruise. They are treated as constants since we only measure samples at 25°C.

From the above equations, pH can be directly calculated from absorbance ratios. Sea water/air pCO₂ and TCO₂ are calculated by referencing R to their respective standards.

Our sea water/air pCO₂ measurements reflect pCO₂ at 25°C with 100% water vapor content. Our results can be corrected for temperature, water vapor and pressure to compare with the AOML LiCOR underway pCO₂ measurement.

The precisions of all parameters measured, estimated by replicate measurements, are given as follows:

pH	± 0.001
Seawater or air pCO ₂	± 1 µatm
TCO ₂	± 1-3 µmol/kg

Details on the mathematical treatment and calculation procedure can be found in Wang et al. (2007).

Problems:

During the first few days of the cruise, there was a bubble issue in the two CO₂ channels. We modified the plumbing and solved the problem. The pH sample line had some fouling issue during the cruise, which was controlled by periodic acid plus detergent rinses. All channels generally performed well throughout the cruise.

Results:

All measured parameters were consistent and agreed well with other underway or discrete surface measurements. Figure 1A shows the comparison between the USF underway TCO_2 measurements (blue diamonds) and the AOML discrete TCO_2 measurements from surface Niskin bottle samples (pink squares). The UGA discrete TA measurements (yellow triangles) are also plotted. Figure 2B shows the comparison of the USF (red diamonds) and AOML (blue circles) underway measurements of surface $p\text{CO}_2$. All $p\text{CO}_2$ data have been corrected to in-situ temperature and 100% water vapor contents. Figure 2C shows the USF underway measurements of surface pH at 25°C.

GOMECC Underway and Surface Measurements

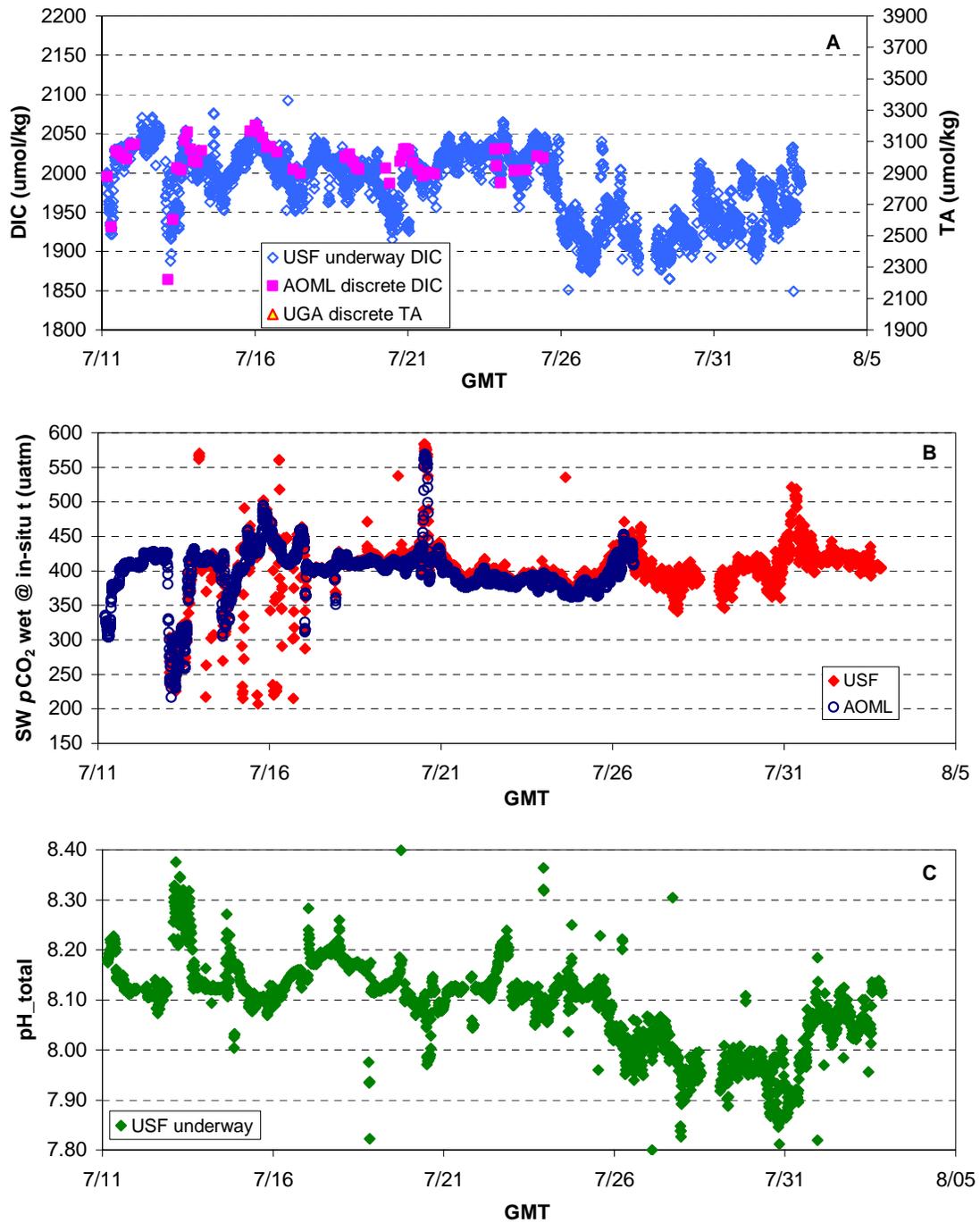


Figure 1.

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- Zhang, H.; Byrne, R. H. 1996. Spectrophotometric pH measurements of surface seawater at in-situ conditions: absorbance and protonation behavior of thymol blue. *Mar. Chem.*, 52, 17-25.

4.4 Ocean Color Measurements

Analysts: Meg Graustein (UCONN), Jennifer St.Louis, Amanda Plagge (UNH)

PI: Joe Salisbury (PI, UNH), Penny Vhalos (PI, UCONN)

The UNH-UCONN measurement/sampling efforts are nearly complete. The ship is ahead of schedule and we are planning our conclusion with a surface survey around the UNH-PMEL buoy in the Gulf of Maine.

Underway sampling:

An integrated suite of underway surface parameters were measured using the ship's uncontaminated seawater supply. Approximately 6 liters per minute were diverted to flow sequentially through a 'bio-optics' sensor suite, consisting of an Anderra Thermosalinograph, an Anderra dissolved oxygen sensor, a Satlantic ISUS Nitrate sensor and WetLabs 'Eco-triplet' product consisting of: fluorescence of colored organic; stimulated chlorophyll fluorescence and particle scattering at 660nm. The flow data were monitored and most sensors provided a reasonable range of data. Sensors were "blanked" periodically with DI water. Corrections for sensor drift will be applied at UNH. Periods when sensors apparently failed were logged and the logs will be used to cull the data.

Discrete samples:

Dissolved Organic Carbon

DOC samples were collected using two slightly different sampling protocols for investigators (Joe Salisbury (UNH) and Penny Vlahos (UCONN)). Approximately 250 samples were collected for the UNH lab and 150 samples for the UCONN. Samples were taken at the surface, 10m, below the thermocline and at the bottom. Nitrile gloves were worn and either silicon tubing was used to draw samples, or samples were drawn directly from the Niskin nipple into triple rinsed polycarbonate or glass bottles. Samples for UCONN were filtered using a nominal 0.7 μm pore size glass fibre filter (GFF) into acid washed 60 ml glass bottles with Teflon caps. UNH samples were filtered with a

peristaltic pump with silica tubing through a Whatman 0.2 μm Polycap AS filter at low pressure. All UNH samples were frozen immediately after collection. UCONN samples were fixed with phosphoric acid and refrigerated in the ship's cooler. Analysis will occur at the respective labs (below). For analysis the samples are thawed and acidified (UNH), then sparged with oxygen to remove inorganic carbon. The organic carbon is combusted and converted to carbon dioxide, which is measured by a non-dispersive infrared detector. UNH samples will be analyzed either by the Wm. MacDowell Lab at UNH or the Craig Carlson Lab, University of California Santa Barbara, UCSB. The UCONN samples will be run at Vlahos Lab.

Colored Dissolved Organic Matter (CDOM)

Approximately 250 CDOM samples were collected. They were filtered using the Whatman 0.2 μm Polycap AS (same filter and procedure as the DOC samples above) into a 125 ml amber glass bottle and refrigerated immediately. Three depths were typically sampled; surface, below the mixed layer and (less often) within the mixed layer. Analysis will be completed the University of Georgia by Heather Reader, using a dual beam spectrophotometer.

Methane

Methane was drawn from the Texas A&M equilibrator under pressure via a needle, into clean, evacuated and sealed 100ml glass bottles. Approximately 300 surface samples were taken along the cruise track. Methane will be analyzed at Dr. Ruth Varner's Lab (UNH) using a Gas Chromatograph.

DIC

Periodic underway samples were taken for dissolved inorganic carbon. Approximately 100 samples were collected. We typically did not sample on stations where the AOML group provided coverage. The purpose of these sampling efforts were to collect underway surface data in interesting low-salinity or high chlorophyll regions not captured on the transect stations. Duplicate samples were drawn from the underway outflow into 20ml Teflon-capped glass bottles, poisoned with 0.1 μM saturated HgCl_2 and refrigerated. Samples will be analyzed at the J. Salisbury Lab (UNH) using an Apollo Scientific DIC analyzer based on Li-COR IR detector technology.

¹³DIC

Samples were taken for ¹³DIC at the surface, 10m below the thermocline and at the bottom at odd-numbered stations. These will be analyzed at the Vhalos Lab UCONN using a mass spectrometer.

POC

Meg Graustein of UCONN took particulate organic carbon samples (surface, 10m, below the thermocline and bottom) at every other station. Water was sampled via silicon tubing into triple-rinsed glass bottles. Between 80 and 200ml were filtered through pre-

combusted Whatman GFF 0.45nm filters. The filters were taken off of the filtering apparatus, folded into quarters, wrapped in aluminum foils and frozen. The samples will be analyzed post-cruise at the Vhalos Lab (UCONN).

Large Volume Air sampling:

We collected air samples during steam time from one transect to another to map out atmospheric concentrations of Currently Used Pesticides and Perfluorinated organic compounds. A large volume air sampler was fitted with a pre-combusted 0.45 nominal GFF for particulates and a poly-urethane foam plug impregnated with C-18. During these sampling periods we collected 4 L of surface water from the in-line pumping system to extract for the same compounds in near surface waters and determine potential fluxes.

5. Other Measurements

5.1 pH profiler

Analysts: Sherwood Liu, Aleck Wang, and Regina Easley (USF)

Equipment and Analytical Techniques:

pH is one of the four carbon system parameters that are used to characterize the ocean carbon system and is the master variable for many chemical and physical processes. During the GOMECC cruise, USF scientists deployed their Spectrophotometric Elemental Analysis System (SEAS), an *in-situ* pH profiler, to get real-time pH profiles. The *in-situ* spectrophotometric measurements of seawater pH using sulfonephthalein indicators were based on the characterization of Thymol blue by Zhang and Byrne (1996).

$$pH_T = pK_2 + \log((R - e_1)/(e_2 - Re_3))$$

where $pH_T = -\log[H^+]_T$, $[H^+]_T = [H^+] + [HSO_4^-]$, $K_2 = [H^+][I^{2-}]/[HI]$ and $R = \frac{596 A_{435}}{435 A_{596}}$ (where λA is absorbance at wavelength λ), and

$$pK_2 = 4.706 S/T + 26.3300 - 7.17218 \log T - 0.017316 S$$

$$e_1 = -0.00132 + 1.600 \times 10^{-5} T$$

$$e_2 = 7.2326 - 0.0299717 T + 4.600 \times 10^{-5} T^2$$

$$e_3 = 0.0223 + 0.0003917 T$$

The instrument provided high frequency pH readings comparable to O₂, fluorescence and CTD data.

The Spectrophotometric Elemental Analysis System II (SEAS) developed at the University of South Florida, Center for Ocean Technology, is capable of performing high resolution *in situ* colorimetric analysis (Adornato et al, 2007). The instrument casing

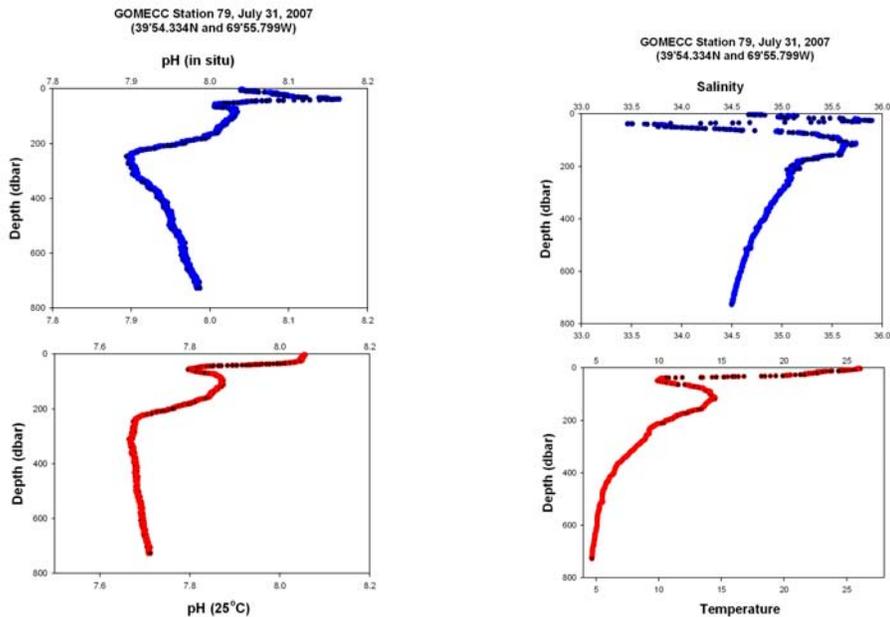
made from anodized aluminum limits the instrument to casts up to 1000 m. Electronic components include an Ocean Optics USB2000 spectrometer and an internal FLASH memory capable of storing 8000 lines of data. The optical cell consisted of a 10-cm PEEK cell (Liu et al. 2006). Each data line includes pertinent information such as a time stamp, intensities at nine specified wavelengths, peripheral measurements, and calculated values such as pH.

The Rosette Setup

During the cruise the pH profiler was deployed at all hydrocast stations above 1000 meters. The SEAS II instrument, measuring 130 cm tall and with an 18 cm diameter, was installed on the rosette frame by occupying one of the sample bottle positions. The instrument was powered by a nickel metal hydride (NiMH) battery pack which enabled it to be operated for a maximum of 8 hours. A communication cable was connected via analog port between SEAS and the main computer to allow a real-time data stream to the main control computer. A Falmouth 2-inch Micro CTD (MCTD-MBP-D) was connected directly to SEAS in order to obtain a concurrent set of salinity, depth, and temperature data for the pH calculation. The internal clock was set to GMT time. The instrument and Micro CTD were removed from the rosette for casts with bottom depths greater than 1000 m.

Once mounted on the rosette frame, analysts communicated to the instrument via an Ethernet connection. At each station, SEAS was powered up 15 – 20 minutes prior to each cast. During this time, the lamp warmed up and the sample line was flushed with surface seawater. The mission was initiated upon receiving a signal from the deck watch operator prior to the lowering of the package into the water. The mission parameters specified that there will be an initial 100 second period where the lamp will continue warming. Seawater was then flushed for 2 minutes through the instrument prior to taking a nine-wavelength reference scan at a depth of either 5 m for shallow stations and 10 m for deeper stations. The dye pump was then turned on for 60 seconds in order to achieve a uniform mixture of seawater and dye prior to sample collection. There is an approximate 6 second delay between the sample intake and the optical cell. The profile data was subsequently uploaded from the instrument once the package was retrieved via the Ethernet connection.

Of the 90 hydro-casts conducted during the cruise, 65 pH profiles were obtained, yielding detailed pH data at resolution better than 1 meter. The overall precision of the method is 0.001. Surface seawater values were compared to those taken using the underway system.



References:

Adornato, Lori, Kaltenbacher, E., Greenhow, D. and Byrne, R. H., 2007. High-resolution *in situ* analysis of nitrate and phosphate in the oligotrophic ocean. *Environmental Science and Technology*, 41, 4045 – 4052.

Liu, Xuewu, Wang, Z. A., Byrne, R. H., Kaltenbacher, E. A., and Bernstein, R. E., 2006. Spectrophotometric measurements of pH in-situ: Laboratory and field evaluations of instrumental performance. *Environmental Science and Technology*, 40, 5036 – 5044.

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5.2 Incubation Studies of Alkyl Nitrate Production

Samplers and Analysts

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Samplers: Kevin Murawski (0900 – 1800) kwmurawski@loyola.edu

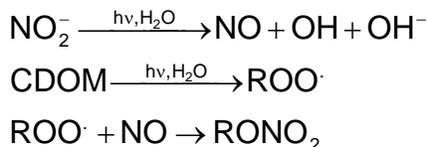
Analysts: Elizabeth Dahl (1800 – 0900)
Kevin Murawski - Nitrite
Elizabeth Dahl – Alkyl Nitrates
Data Reduction: Elizabeth Dahl

Objectives

The major goal of this project was to observe the photochemical production of methyl, ethyl and propyl nitrates in filtered and unfiltered surface water samples. The goal of this study is three-fold: 1) to determine if photochemistry production can account for coastal ocean alkyl nitrate levels 2) to determine if biology may play a role in alkyl nitrate production 3) to determine if monitoring of alkyl nitrate formation may indicate the relative formation of methyl, ethyl and propyl peroxy radicals from CDOM. The oceans have previously been shown to be the major source of low molecular weight alkyl nitrates to the troposphere. In the troposphere, alkyl nitrates are part of the reactive nitrogen pool and play a role in the NO_x/ozone cycle.

Experiment

Unfiltered surface samples were collected from 9-L Niskin bottles into a 1000 mL glass bottle. Filtered samples were filtered directly from the Niskin bottles into a 1000 mL glass bottle through Millipore 0.2 um polycap filters to remove all particulates and organisms. The samples were aliquoted into 200 mL volumetric flasks – 5 filtered and 5 unfiltered samples. Four of the samples were spiked with increasing levels of nitrite resulting in a range of nitrite concentrations from 0-4 uM, with the lowest concentration being due to ambient nitrite. The addition of nitrite promotes the formation of alkyl nitrates from the reaction of alkyl peroxy and NO radicals. The full reaction mechanism is shown below.



The aliquoted samples were drawn into 100 mL glass syringes (Popper) fitted with polycarbonate Luer tipped stopcocks. The syringes with the highest nitrite concentration for filtered samples and unfiltered samples were analyzed as T0 for alkyl nitrates and all of the syringes were placed into the deck incubator. The deck incubator is a translucent plastic container with deck seawater flowing into the incubator to maintain temperature. An underwater temperature and illuminance monitor (HOBO) was placed in the incubator as well with the syringes. The nitrite concentration was determined in each sample via a colorimetric technique using a UV/Vis spectrophotometer (Ocean Optics).

Analysis for alkyl nitrates was done before and after incubation using a purge and trap GC-MS instrument. This instrument is described in detail by Dahl [2005]. The major limitation to the instrument as a seagoing instrument is the use of liquid nitrogen for trapping analytes. One hundred liters is the typical use of the instrument for one

month of analyses. Liquid nitrogen was stored in the main laboratory in long life dewars. We discovered after the first week of the cruise that one of the dewars was not filled completely. As a result of this we limited experiments in the middle of the cruise so as to cover the widest range of water samples possible for the course of the cruise.

Incubations were carried out using waters from nine stations during the cruise with at least one station from each transect. Concentrations for alkyl nitrates during the incubation experiments will be determined post cruise after calibration of the standards used during the cruise. The results of a typical incubation are shown in Figure 1. Alkyl nitrate peak area showed an increase with increasing nitrite concentration. This increase appears to be linear at low nitrite concentrations, but starts to 'roll over' at higher nitrite concentrations, presumably as the reaction becomes limited by availability of alkyl peroxy radicals. This is similar to results observed previously in laboratory and open ocean studies. From observed peak areas, it is clear that methyl nitrate production was much higher than that of the ethyl or propyl nitrates. Early estimates indicate by as much as 5-10 times. Ethyl nitrate and isopropyl nitrate production cannot be estimated relative to each other without further analysis and standardization. N-propyl nitrate production was very low in all of the experiments, which is also similar to what has previously been observed in laboratory and open ocean experiments.

Once alkyl nitrate concentrations have been determined, it will be possible to determine the production rates of the alkyl nitrates and the relative production of the alkyl nitrates with respect to each other. This should provide an estimate as to the relative availability of alkyl peroxy radicals from CDOM. Presumably we should be able to use alkyl nitrate production to determine if the radical production from CDOM varies by location. Preliminary results from this cruise appear to indicate that there is a difference between alkyl nitrate production in the Gulf of Mexico and off the east coast of the U.S. It is expected that once data analysis is complete, the data set will provide a lot of interesting information about oceanic alkyl nitrate production with regard to oceanic alkyl nitrate concentrations (determined by S.A. Yvon-Lewis during this study) and CDOM chemistry.

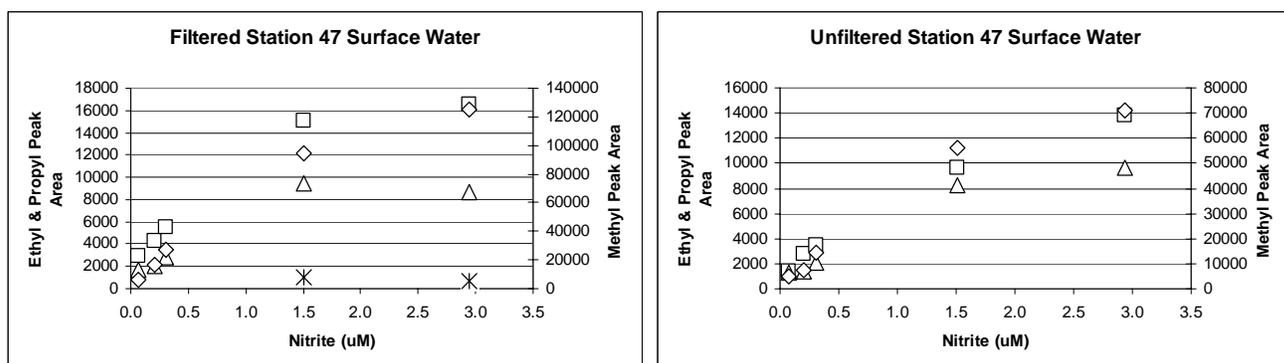


Figure 1: Results of a typical incubation experiment showing alkyl nitrate peak area as a function of nitrite concentration. Note that the ethyl and propyl nitrates are plotted on the left y-axis, and methyl nitrate is on the right y-axis. □ Methyl nitrate ◇ Ethyl nitrate * n-Propyl nitrate △ Isopropyl nitrate

References

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5.3 Apparent Quantum Yields of Carbon Monoxide Production in Surface Waters

Samplers and Analysts

PI: Bill Miller, Dept of Marine Sciences, University of Georgia, Athens, GA 30602
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Sampler:	Heather Reader	hereader@uga.edu
Analyst:	Heather Reader	
Data Reduction:	Heather Reader	

Objectives:

Carbon monoxide is a trace gas that is supersaturated in the surface ocean compared to the atmosphere (1). Surface concentrations of carbon monoxide exhibit a strong diurnal variation (1). This diurnal variation is due to strong photoproduction in the daytime, with a daily maximum occurring in the late afternoon (1), and bacterial consumption and flux out of the water at night (1). Our objectives on the GOMECC cruise were to characterize the apparent quantum yields of carbon monoxide in the surface waters, along the Gulf of Mexico, and up the East Coast. Carbon monoxide surface concentrations were also measured, with an initial attempt at using an underway equilibrator system, and later a syringe-headspace equilibration method.

Sampling

In order to characterize the production of carbon monoxide in the surface water, samples of water were taken from the surface Niskin bottles at representative stations on each transect. These generally corresponded with the nearest to shore station, the station closest to the shelf break, and then the furthest station out. Each sample was filtered directly into a 2.5 L polycarbonate bottles, using a 0.2 μm nylon cartridge filter. These samples will be used to determine the apparent quantum yield of carbon monoxide production along the length of the GOMECC cruise. The water samples were kept in the cold room in coolers at 4°C, until the condensing unit broke. At this time, the coolers were packed with ice, and the samples were kept at ~ 0°C.

An underway equilibrator system was set up, in an attempt to measure surface concentrations of CO. A mercuric oxide-based Reactive Gas Detector on a Gas Chromatograph was used to determine the concentration of CO in samples of air. Around

Station 58, it was determined that the underway equilibrators were not an appropriate system for the underway measurement of CO. This was determined by comparing the underway equilibrators measurements to a syringe head-space equilibration from the surface Niskin bottle. Because CO is very insoluble in seawater, the syringe sample was taken from the Niskin immediately after the rosette was brought on deck, and other sampling from the bottle occurred afterwards. Once it was determined that the underway system would not be a suitable way to measure carbon monoxide concentrations, an attempt was made to collect as many surface syringe equilibrators samples as possible. These were done by drawing off 80 mL of water from the Niskin bottle into a gas tight syringe, and then adding 20 mL of CO-free air in and shaking for 2.5 minutes. The headspace was then extracted and injected into the GC.

Total Number of Samples Taken:

Photochemistry samples (to be analyzed in Athens): 25
Surface CO concentrations: 30

UV Profiles

An attempt was made to take a UV profile once a day near to local noon. Using a Satlantic Micropro Apparent Optical Profiler (AOP), deployed off of the stern of the ship, several casts of downwelling irradiance were measured at each spot sampled. This data will be used in conjunction with the apparent quantum yield data to attempt to predict the production of CO in the surface ocean.

Total Number of Samples Taken:

Profiles: 15

Data Processing

All data will be processed at the University of Georgia, in Athens.

References

1. Xie, H. et al. 2001. A Simple Automated Continuous Flow Equilibration Method for Measuring Carbon Monoxide in Seawater. Environmental Science and Technology. 35 1475-1480.

5.4 Relating phytoplankton pigment distribution and abundance to air-sea flux of carbon dioxide in continental margin waters

Analyst: Sumit Chakraborty (USM)
PI : Steven Lohrenz (USM)

Scientific objective:

Carbon dioxide (CO₂) is the major currency during biological production or destruction of organic matter (OM) and is the dominant greenhouse gas. CO₂ flux between the atmosphere and the ocean is a key component in global carbon cycle models. Despite their relatively small surface area, ocean margins may have a significant impact on global biogeochemical cycles, and potentially, in the global air-sea fluxes of CO₂. The current lack of knowledge and understanding of biogeochemical processes occurring at the ocean margins has left them largely ignored in most of the previous global assessments of the oceanic carbon cycle. Recent observations of the net coastal air-sea CO₂ fluxes are available only for a limited number of regions and times, and these studies highlight the diverse and dynamic nature of coastal ecosystems. More comprehensive information about carbon fluxes in margins is critical for comprehensive assessments of their contribution to overall global carbon budgets.

The pigment analyses will provide information about phytoplankton abundance and taxonomic composition in relationship to other measured variables including CTD, partial pressure of carbon dioxide, total alkalinity, pH, total dissolved inorganic carbon, and nutrients. In addition, colleagues from the University of New Hampshire will be conducting measurements of optical properties.

Novel approaches are needed to expand the temporal and spatial coverage in margin environments. This study will provide information about key variables that can be used to implement satellite-based approaches for estimating pCO₂ distributions as has been done successfully in other studies.

Improved assessments on air-sea fluxes of carbon dioxide are essential to provide boundary constraints on North American continental margin fluxes. Carbon fixation by phytoplankton is a critical factor influencing surface pCO₂ and this study will contribute information about phytoplankton pigments to an extensive database of information over a large range of coastal water mass types conditions. Such information should help to refine models estimating North American carbon fluxes and improve their performance for predicting change and management strategies.

Sampling and Analysis:

Water samples were taken from the Niskin bottles in the upper 100 meters and were filtered using Whatman GF/F filters. The filters were stored in Liq N₂. The filters will be taken back and in lab HPLC (High Performance Liquid Chromatography) analysis will be conducted for phytoplankton pigment analysis. The analysis will follow the procedures outlined in the handbook "*Ocean Optics Protocols For Satellite Ocean Color Sensor Validation, Revision 5, Volume V: Biogeochemical and Bio-Optical Measurements and Data Analysis Protocol*" *HPLC Phytoplankton Pigments: Sampling, Laboratory Methods, and Quality Assurance Procedures* (Bidigare et.al. 2003)

Total Number of cast sampled: 49

Total number of samples: 147

5.5 Ocean Color, DOC, DIC, NO₃ (UConn)

Cruise Participant: Meg Graustein (UConn) meg_graustein@hotmail.com

PI: Penny Vlahos

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Objectives

Water Sampling

We sampled for DIC-C13 in surface waters to enhance the surface CO₂ studies and identify zones where surface CO₂ may have a significant biological signal.

Dissolved organic carbon samples were taken at 4 to 5 depths at 5 stations along each transect to further enhance carbon studies by constraining the DOC gradients. The gradients in DOC are often of equal order of magnitude as DIC and therefore lend useful insight to spatial distribution patterns.

Large Volume Air sampling:

We collected air samples during steam time from one transect to another to map out atmospheric concentrations of Currently Used Pesticides and Perfluorinated organic compounds. A large volume air sampler was fitted with a pre-combusted 0.45 nominal GFF for particulates and a poly-urethane foam plug impregnated with C-18. During these sampling periods we collected 4 L of surface water from the in-line pumping system to extract for the same compounds in near surface waters and determine potential fluxes.

Sampling

Water samples were taken at every other station from the surface and bottom for DIC analysis. The water sample was collected directly from the Niskin bottle into a 40 mL pre-combusted vial which was filled to the top. One to two drops of mercuric chloride was added to the sample and then it was placed in the climate controlled cold-room. After the cold-room chiller unit was broken the samples were kept in coolers with ice. The analysis of the samples will take place post-cruise.

Water was taken at every other station at surface, 10m, below the thermocline, and bottom for DOC measurements. 100 mL bottles were rinsed three times with water from the Niskin and then filled. The sample was then filtered into a 40 mL pre-combusted vial through a 25mm GFF under vacuum and acidified with phosphoric acid. The samples were then refrigerated in the climate controlled cold room. After the cold-room chiller unit was broken the samples were kept in coolers with ice. The analysis of the samples will take place post-cruise. The GFFs were taken off of the filtering apparatus, folded into quarters, wrapped in aluminum foils and frozen. The samples will be analyzed post-cruise at UCONN.

The air sampler was mounted on the O3 deck amidships. Samples were taken during the transits between sampling transects while the ship was continuously underway. Eight air samples were collected during the cruise transits. During each transit 4L of surface water was collected from the in-line system and placed in the climate controlled cool room. Analysis of all samples will be done post cruise.

Total number of casts sampled: 53
Total number of depth profiles sampled: 182
Total number of DOC samples collected: 171
Total number of DIC samples collected: 107
Total number of POC samples collected: 114
Total number of DOC blanks collected: 18
Total number of POC blanks collected: 7
Total number of samples collected (including blanks): 417

Total number of air samples: 11
Total number of air sample blank: 4
Total number of 4L water samples collected: 8

6. Flux Measurements

ESRL/PSD, CU Boulder, LDEO were three of several institutions participating in the Gulf Of Mexico East Coast Carbon (GOMECC) cruise. As part of this cruise, we were interested in studying 2 things: 1) Direct measurements of air-sea gas transfer, 2) Measurement of Ozone flux by eddy correlation. Below is general plan for the 2 areas of interest:

6.1 Direct measurements of air-sea gas transfer

Principal investigator: C. Fairall (ESRL), D. Helmig (UC Boulder), W. McGillis (LDEO)

Cruise participants: William Otto (ESRL), Kathrin Lang (UC Boulder)

Summary of scientific objectives:

- 1) Characterize the near-surface meteorological variables
- 2) Determine meteorological surface forcing variables (friction velocity, stability)
- 3) Perform direct eddy correlation measurements of the air sea fluxes of CO₂ and Ozone

Sampling and Analysis: The ESRL seagoing air-sea flux system was operated for the entire cruise. The system was enhanced with two additional fast gas sensors – the CU/INSTAAR (Helmig) fast ozone sensor and the LDEO/ESRL ruggedized unattended fast CO₂ sensor. The systems runs automatically and collect data at approximately 10Hz and 1-min resolution (depending on the sensors). Data was acquired and archived using the ESRL DAS in the Science lab. Some processing was done at sea for quality control.

6.2 Measurement of Ozone flux by eddy correlation

Principal investigator: Chris Fairall (ESRL), Detlev Helmig (UC Boulder)

Cruise participants: Kathrin Lang (UC Boulder), William Otto (ESRL)

Summary of scientific objectives: These measurements will be used to assess the ozone deposition velocity in the Gulf of Mexico. With this data set, we will analyze the ozone fluxes and the dependencies on physical, chemical and biological conditions encountered during the cruise. The goal is to have a better understanding of the mechanisms driving the ozone deposition into the oceans. Thus, we can incorporate these data into atmospheric chemistry transport models.

Sampling and Analyses: PSD and INSTAAR groups measured ozone concentration with a fast-response instrument using the chemiluminescence principle. NO is mixed with the sampled Ozone in a reaction chamber. A photomultiplier is used to count the photons emitted during the chemical reaction.

The device is included in the flux system of PSD. By combining sonic anemometer data and ozone data, we can assess the ozone flux, and get the deposition velocity.

The PSD flux system has a majority of the sensors for the flux system are located on the jack staff. Additional sensors in other locations include: floating SST sensor (Sea snake) on a horizontal pole off the port side; Downward IR and Solar flux radiometers on a vertical pole on the 02 deck; fast ozone system is in a rectangular container on the forward 02 deck. A sampling line is run from the sensor on 03 to the jack staff. A second box containing pumps is mounted on 03. The CO₂ system consists of two Licor-7500 units enclosed in ventilated tubes. The ventilation pump is located with the Ozone system. Computers are located in the Science Lab.

GOMECC cruise began on Galveston, Texas on July 10, 2007. The research ship, Ronald H. Brown, pulled out of Galveston harbor at 18:30 and headed to Station 1 in the Gulf of Mexico. The NOAA/PSD ship-based turbulent flux system was in continuous operation from the start of the GOMECC cruise. Along with the flux package, there are continuous measurements of solar radiation, atmospheric water vapor, and cloud base height. Data analysis will be done post cruise. Another instrument to be used in conjunction with the flux measurements was a fast response ozone instrument operated by University of Colorado. It was hoped that during the cruise preliminary ozone fluxes could be calculated, but it was not done.

Thunderstorm and lightning near the ship a night before July 19 between 10-12 PM (July 20 between 2-4 UTC) may have damaged some of the electronics of flux in the bow open area. The morning after the thunderstorm, it was discovered that the serial data transmission had failed. This transmission is to the computer that was recording and storing the data. Over the next 4 days multiple solutions were suggested and tried. Finally, another computer with the LabView software was modified to do the data transmission, and the problem was solved. The Ozone measurements were running normally by July 25. We want to thank Mana for his invaluable help in reprogramming computer that runs the ozone instrument and sends the data to the flux data acquisition system.

The ship-based turbulent flux system was in continuous operation from the start of the GOMECC cruise. Data analysis during the cruise has not been possible because of the

problems that have occurred with the fast response ozone instrument. Ozone is one of the main flux of interest during this cruise. This analysis will have to be done post cruise.

In the interest for better results, Bill Otto requested that the transit from Savannah to Wilmington, NC, would be changed. The transit was changed to closer to shore and the ship doing this section at 10 knots to help increase the resolution of the data used in the flux calculations and lessen the amount of corrections. Also, going into a region of increased ozone will improve the accuracy of the ozone measurements. This change will facilitate a better flux calculation.

On the morning of July 25 during a future cruise plan meeting, Bill Otto presented a preferred route along the coast for the flux measurements for the New Jersey transit. As a result, the transit line was changed much closer to the shore.

The PSD DAS system recorded and stored 25 days of data July 11, 2007 to August 4, 2007.

Ozone fluxes: *Cruise Participant*: Bill Otto; PI: Detlev Helmig, Chris Fairall
Instrumentation: fast response chemiluminescence instrument, pumps

Goal was to determine the ozone uptake to the ocean by eddy covariance techniques. Therefore an instrument was developed which measures the ozone concentration based on a chemiluminescence reaction of ozone with nitric oxide.

New to the system compared to previous cruises was that we added a system for a better determination of the lag time and a drying cycle to dry the sample air and to avoid the Webb correction in the analysis.

The instrument was located on the second deck and the sample tube was running to the upper mast where also a sonic was located for measuring the wind velocity.

The instrument was running continuously for about 7 days when after a storm a fuse and the data transfer to another computer broke. The fuse was easily replaced but the data transfer remained a problem. Finally, after 5 days a solution was found and since then the instrument was running without any problems. For these 5 days no continuous data but pieces are available.

About the quality of the data nothing can be said so far as the analysis will be done within the next weeks.

6.3 Direct measurements of the air-sea CO₂ transfer

Cruise Participant: Meg Graustein (UCONN), meg_graustein@hotmail.com

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PI: James Edson

Objectives

The overall objective of our research is to provide accurate measurements of CO₂ flux using the direct covariance technique. These fluxes will be used to improve parameterizations of the gas transfer velocity. This would improve indirect estimates of the flux from measurements of CO₂ concentration in the bulk seawater and air, the latter used to estimate the surface concentration by accounting for solubility. However, direct estimates of the CO₂ flux is made difficult by the low signal to noise ratio encountered by commercially available infrared gas analyzers (IRGA). This is a result of instrumental noise caused by, e.g., moisture contamination of the signal and motion induced noise; as well as the low signal that results from the small gradient of CO₂ in the atmospheric surface layer.

Therefore, the objective in our participation in the GOMECC cruise was two-fold:

1. To test a new system designed to quantify the system noise so it can be removed in post-processing from the measurements of atmospheric CO₂. This system is being readied for the upcoming Southern Ocean GASEX cruise that will also be deployed on the R/V Brown. This was our primary objective and we greatly appreciate the opportunity to deploy this system on the R/V Brown during GOMECC.
2. To use these measurements to provide direct flux estimates for the GOMECC investigations.

Although we have not begun our initial analysis, it appears that the CO₂ systems provided sufficient data to meet objective 1. The standard open path IRGA and at least one of the two prototype IRGA systems worked during the cruise. Unfortunately, we experienced problems with the sonic anemometer system about halfway through the cruise, which is required to provide the velocity estimates needed to compute the fluxes. Therefore, it will be difficult to meet objective 2, particularly during the second half of the cruise. We may be able to merge our CO₂ measurements with the sonic system operated by Chris Fairall's group. We will be able to make a better assessment of the situation after we have completed our initial analysis.

Problems encountered

The data acquisition program would only log data from two of the IRGA at one time, so the IRGA systems were cycled on and off so that only two were running at any given time. From July 10 to July 20, 2007 data was collected from the sonic anemometer and two IRGA systems. On July 20 from 0200-0400 UTC the ship went through a lightning storm. During this time the sonic anemometer signal was lost and no data was being collected. Diagnostic tests were performed and it was discovered that there were no problems with the power supply to the sonic anemometer. The head of the sonic

anemometer was replaced with a spare but this did not fix the problem. The cylinder of the sonic anemometer was then also replaced and once again this did not fix the problem. The IRGA systems continued to run and log data for the last two weeks of the trip when the sonic anemometer was not working.

7. Acknowledgements:

The scientific party of the NACP GOMECC cruise would like to express sincere thanks to Captain Gary Patrae and all of the crew of the R/V *Ronald H. Brown* for their assistance in carrying out this cruise.