# CRUISE REPORT: A16N\_2003a (Updated MAY 2012)



#### HIGHLIGHTS A.

#### **Cruise Summary Information** A.1.

	WOCE section designation			<b>3</b> a		
Expeditio	Expedition designation (ExpoCodes)			806_01		
				806_02		
	Chief Sc	ientist	John Bulli	ster / PM	EL	
	Co-Chief Sc	ientist	Nicolas Gi	ruber / UC	CLA	
		Dates	2003 JUN	04 - 2003	AUG 11	
		Ship	R/V RONA	LD H. BRO	OWN	
	Ports	of call	Reykjavik,	Iceland to	Natal, Br	azil
				63	° 17.58' N	1
Sta	tion geographic boun	daries	29° 0	0.00' W		19° 59.99' W
				6	5° 0.64' S	
	St	ations	150			
			6 ALACE	profiling fl	loats,	
]	Floats and drifters deployed			lrifters and	l	
				Explorer flo	oats	
Mooi	ings deployed or reco	overed	0			
	Con	tributi	ng Authors			
E. Peltola,	R. Wanninkhof,	R. F	Feely,	R. Castle,		D. Greeley,
JZ. Zhang,	F. Millero,	N.C	Gruber,	J. Bulliste	er,	T. Graham
	John L. I	Bulliste	r (NOAA-P	'MEL)		
	7600 Sand Point W	ay N.E	. • Seattle, W	/A 98115 •	• USA	
Tel: 206-5	Tel: 206-526-6741 • Fax: 206-526-6744 • e-mail: John.L.Bullister@noaa.gov				a.gov	
	Nicol	as Gru	ber (UCLA	)		
Institute of	Institute of Geophysics and Planetary Physics & Dept. of Atmospheric Sciences					
	5853 Slichter Hall • L	los Ang	geles, CA 90	095-1567	USA	
Tel: 310	Tel: 310-825 4772 • Fax: 310-206-3051 • e-mail: ngruber@jgpp.ucla.edu					

#### **Cruise and Data Information**

Links to select locations. Shaded items are not relevant to this cruise or were not available when this report was compiled

Cruise Summary Information	Hydrographic Measurements
Description of Scientific Program	CTD Data:
Geographic Boundaries	Acquisition
Cruise Track (Figure): PI CCHDO/WHPO	Processing
Description of Stations	Calibration
Description of Parameters Sampled	Salinities
Bottle Depth Distributions (Figure)	Oxygens
Floats and Drifters Deployed	Bottle Data
Moorings Deployed or Recovered	Oxygen
	Nutrients
Principal Investigators for All Measurements	Carbon System Parameters
Cruise Participants	Helium Tritium
	Radiocarbon
Problems and Goals Not Achieved	CFCs
Other Incidents of Note	
Underway Data Information	References
Navigation Bathymetry	Nutrients
Acoustic Doppler Current Profiler (ADCP)	CFCs
Thermosalinograph & Related Measurements	Carbon System Parameters
XBT and/or XCTD	
Meteorological Observations	Acknowledgments
Atmospheric Chemistry Data	General
	CO <sub>2</sub> Report

**Data Processing Notes** 



Cruise track for the Atlantic Ocean A16N\_2003a cruise in June-August 2003



## Station Locations for A16N\_2003 • Bullister/Gruber • R/V RONALD H. BROWN

(Produced from .sum file by CCHDO/WHPO)

#### **SUMMARY:**

A hydrographic survey consisting of a meridional CTD/rosette section in the North Atlantic, nominally along 20°W from 63°N to 6°S was carried out on NOAA ship *Ronald H. Brown* (NOAA Cruise RB-03-04) during July-August 2003 The expedition has been assigned the ExpoCode 33RO200306\_01. This 2003 section repeated the A16N section occupied during the World Ocean Circulation Experiment (WOCE) period, hence this cruise is also designated A16N\_2003. This was also a repeat of a NOAA cruise in 1993, during which a full suite of inorganic carbon, hydrographic and CFC measurements were made.

This cruise was the first in a decadal series of repeat hydrography sections jointly funded by NOAA's Office of Global Programs (OGP) and the US National Science Foundation (NSF) as part of the CLIVAR/CO<sub>2</sub>/hydrography/tracer program. The program focuses on the need to monitor inventories of CO<sub>2</sub>, tracers, heat and freshwater and their transports in the ocean. Earlier programs under the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) have provided a baseline observational field for these parameters.

A total of 150 full water column CTD/rosette stations were occupied, . Water samples (up to 34 at each station), LADCP, CTD and bio-optical data were collected on most casts to within ~20 m of the bottom. Salinity, dissolved oxygen, and nutrient samples were analyzed from every bottle sampled. Other parameters were sampled at a lower density, including a suite of carbon parameters (dissolved inorganic carbon-DIC, total alkalinity- Talk, pH and partial pressure of  $CO_2$ . pCO<sub>2</sub>), chlorofluorocarbons (CFCs), dissolved organic carbon (DOC), <sup>3</sup>He-tritium, and carbon isotopes. In addition to the CTD/rosette casts, separate trace metal casts were made at stations along the section, nominally at 60 nautical mile spacing.

Measurements of near surface seawater properties (temperature, salinity, and pCO<sub>2</sub>), as well as atmospheric measurements (CO<sub>2</sub>, CFCs, aerosols) were made along the cruise track. Six ALACE-type profiling floats were deployed along the section, along with 6 surface drifters and 3 special 'Carbon Explorer' profiling floats designed to measure particulate inorganic carbon (PIC).

This report describes the participants, scientific programs, and sampling details. Additional information on analytical methodologies are included in separate reports appended to this file. Further information and copies of the data from this cruise can be found at

http://sts.ucsd.edu/cruise/a16n/hydro/

#### ACKNOWLEDGMENTS:

The successful completion of the cruise relied on dedicated assistance from many individuals on shore and on the expedition. Funded investigators in the project and members of the Repeat Hydrography Oversight Committee, with Lynne Talley and Richard Feely as co-chairs, were instrumental in planning and executing the cruise. Officers and crew of the *Ronald H. Brown* exhibited a high degree of professionalism and assistance to accomplish the mission.

The U.S. CLIVAR/CO<sub>2</sub> Repeat Hydrography Program is jointly sponsored by the National Science Foundation's Physical and Chemical Oceanography Programs, and NOAA's Office of Climate Observation, with contributions from the National Aeronautics and Space Administration and the Department of Energy. In particular, we wish to thank program managers Eric Itsweire (NSF/OCE), Don Rice (NSF/OCE), Mike Johnson (NOAA/OCO), and Kathy Tedesco (NOAA/OGP) for their moral and financial support in the effort.

#### A.2. INTRODUCTION:

NOAA ship *Ronald H. Brown* departed Reykjavik Iceland on 19 June 2003. There was a port stop in Funchal Madeira from 10-15 July 2005. The cruise ended in Natal, Brazil on 11 Aug 2005. A sea-going science team from 14 institutions in the U.S. participated on the cruise. Several other science programs were supported with no dedicated cruise participants.

#### **Participating Institutions:**

AOML	NOAA-Atlantic Ocean Marine Laboratory
FSU	Florida State University
Hawaii	University of Hawaii
LDEO	Lamont-Doherty Earth Observatory, Columbia University
LBNL	Lawrence-Berkeley National Laboratory
NOAA	National Oceanic and Atmospheric Agency
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences, University of Miami
PMEL	NOAA-Pacific Marine Environmental Laboratory
SIO	Scripps Institution of Oceanography, University of California, San Diego
TAMU	Texas A&M University
UCLA	University of California, Los Angeles
UW	University of Washington
UCB	University of California, Berkeley
UCI	University of California, Irvine
WHOI	Woods Hole Oceanographic Institution

#### A.3. CTD/HYDROGRAPHIC MEASUREMENT PROGRAM:

Chief Scientists:	John Bullister & Nicolas Gruber
Survey Department:	CST Jonathan Shannahoff
CTD Personnel:	Regina Cesario, Elena Brambilla, Nicole Lovenduski, Kristy McTaggart
Final Processing:	Kristy McTaggart

A total of 150 CTD/rosette casts were made, usually to within 20 m of the bottom. Most of the casts were performed with a package consisting of a 36-position, 12-liter rosette frame designed at PMEL, a 36-place pylon (SBE32) and 34 12-liter 'Bullister' bottles. Two of the 36 bottle positions (positions 34 and 36) on the rosette frame were not available because of interference with the LADCP instruments mounted on the rosette frame. Because of inclement weather or winch/wire problems, a smaller 24-place 3-liter foul weather rosette package also designed at PME was deployed at 14 stations (Stations 35-42, 102-103, and 142-143). Water samples were collected from every bottle for analysis of salinity, dissolved oxygen, and nutrients. The distribution of water sample bottles is illustrated in the following figure.



The basic CTD measurements were of pressure, temperature, salinity, and dissolved oxygen. Additional optical sensors were attached to the large rosette frame. Underwater electronic components on the 36 position frame consisted of a Sea-Bird Electronics (SBE) 9 plus CTD with dual pumps and the following sensors: dual temperature (SBE3plus), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs SeaStar), turbidity (Seapoint Sensors), and

PIC (Wetlabs). The other underwater electronic components consisted of RDI LADCPs, a Simrad or Benthos altimeter, and a pinger. A detailed description of the sensors on the two (large and small) rosette frames is provided in the CTD section below.

The CTD was mounted vertically in an SBE CTD frame attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3plus temperature sensors and their respective pumps were mounted vertically as recommended by SBE. The entire cage assembly was mounted on the bottom ring of the rosette frame, offset from center to accommodate the pylon, and also secured to frame struts at the top. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring. The transmissometer, turbidity and PIC sensors were mounted horizontally along the rosette frame adjacent to the CTD. The LADCPs were vertically mounted inside the bottle rings on the opposite side of the frame from the CTD.

The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electromechanical sea cable. A load cell was installed between he rosette frame hanger and the sea cable to monitor the CTD/rosette package weight during casts. The load cell data stream was transmitted via the CTD unit and monitored in real time in the CTD lab.

The *R/V Brown's* forward CTD winch was used during the cruise,

The deck watch prepared the rosette within 40 minutes prior to each cast. All valves, vents, and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Once stopped on station, the LADCP was turned on and syringes were removed from the CTD sensor intake ports. As directed by the deck watch leader, the CTD was powered-up and the data acquisition system started. Two stabilizing taglines were threaded through rings on the rosette frame. The deck watch leader directed the winch operator to raise the package, the squirt boom and rosette were extended outboard, and the package quickly lowered into the water. The tag lines were removed and the package was lowered to 10 m. The CTD console operator waited for the CTD sensor pumps to turn on, waited an additional 60 seconds for sensors to stabilize, then directed the winch operator to bring the package close to the surface, pause for typically 10 seconds, and begin the descent.

Each rosette cast was usually lowered to within 20 m of the bottom, using the altimeter and pinger to determine a safe distance.

On the up cast, the winch operator was directed to stop at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle, then an additional 10 seconds after receiving the trip confirmation before directing the winch to proceed to the next bottle stop.

Sampling depths and the total number of bottles tripped on each cast were adjusted depending the overall water depth. Typically all 34 bottles were closed for casts deeper than ~3000 m. Sample spacing was closer in the upper water column, with typically ~20 bottles closed in the upper 1000 meters of the water column. The bottle depths were staggered to reduce data contouring artifacts (see sample distribution figure).

Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks to attach tag lines for added safety and stability. The rosette was left outside on deck for sampling. The bottles and rosette were examined before samples were taken, and anything unusual noted on the sample log.

Each bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette, which was used for sample identification.

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

#### A.4. BOTTLE SAMPLING:

#### A.4.1. Bottle Sampling Procedures

A station log sheet was maintained in the CTD lab for each sample team to indicate their sampling plans for the upcoming  $\sim$ 10-20 stations. This allowed groups which did not sample every station fully to better co-ordinate sampling plans with other groups. Planned deployments of floats at upcoming stations were also entered in this table.

At each station, a sample log sheet was prepared prior to the arrival of the case on deck. Each sampling group filled out a column on this log sheet, indicating which rosette bottles were to be sampled, and the ID numbers of their individual sample containers. At the end of each rosette deployment, water samples were drawn from the bottles in the order listed below. This log also included any comments or anomalous conditions noted about the rosette and bottles. One member of the sampling team was designated the "sample cop," whose responsibility was to maintain this log sheet, check the correspondence between individual sample containers and the rosette bottle as the samples were drawn, and insure that sampling progressed in the proper drawing order.

Normal bottle sampling practice included initially pushing in the drain valve petcock prior to opening the air vent screw. The release of any water from the petcock indicated an air leak. This observation, together with other diagnostic comments (e.g., "lanyard caught in lid," "valve left open") that might later prove useful in determining sample integrity, were routinely noted on the sample log and are included below.

Once individual samples had been drawn and properly prepared, they were distributed for analysis.

### Sampling and Analyses of Bottle Data

The order of drawing samples was: CFCs, helium isotopes ( ${}^{3}$ He), oxygen (O<sub>2</sub>), hydrochlorofluorocarbon (HCFCs), pCO<sub>2</sub>, DIC, pH, TAlk, radiocarbon (DI ${}^{14}$ C), tritium, DOC, particulate inorganic/organic carbon (PIC/POC), salinity, and nutrients. Sampling of the 34 bottles on the package took about 1.5 hours. The samples analyzed for gases were sampled first and usually drawn within an hour of the rosette reaching the deck. The deepest bottle was sampled first and bottles were sampled sequentially to the surface bottle. Care was taken to coordinate the sampling to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, CFCs,  ${}^{3}$ He, dissolved oxygen, and HCFC samples were collected within several minutes of the initial opening of each bottle.

Oxygen, nutrient, and salinity samples were taken from all bottles. For the other parameters, not all stations or all bottles were sampled. Full profiles were typically collected at every other station for CFCs, DIC, pH, and TAlk, with partial sampling for DOC. The intermediate stations were typically only partially sampled for CFCs, DIC, pH, Talk, HCFC, PIC/POC. Discrete pCO<sub>2</sub>

profiles were obtained at every two degrees. <sup>3</sup>He, DI<sup>14</sup>C, and tritium were sampled at coarser intervals. A complete listing of the samples collected is available at:

http://whpo.ucsd.edu/data/CO2clivar/atlantic/a16/a16n\_2003a/index.htm

To allow direct comparison, CFCs were usually drawn from the same bottles as DIC and Talk . <sup>3</sup>He and tritium were typically drawn from the same bottles as CFCs. For casts where many parameters were sampled, water levels in some of the 12 liter bottles occasionally were very low by the time the salinity and nutrients were drawn. This was particularly true for the deepest two bottles and the shallowest two bottles that were often used for duplicate sampling for parameters with large water requirements such as DIC and TAlk.

Because of the small volume ( $\sim$  3 liters) of the sample bottles on the smaller rosette, not all parameters could be drawn from these bottles. On these casts, water for DIC and Talk was collected in the same sample bottle to conserve water and some parameters (e.g. helium and tritium) were not sampled from the same bottles as the carbon parameters.

#### A.4.2. Problems

There were relatively few bottle misfires or leaking bottles on the 36 position rosette frame. Several of the release pins on the 24 position small volume rosette did not function reliably and a number of bottles did not close on these casts. Sample bottles that did not close or bottles that had obvious leaks while on deck were noted on the sample log sheets. Typically, no water samples were not drawn from leaky bottles. Notes made on the sample log sheet s concerning bottle/rosette problems are listed below:

Station	Cast	Bottles	Problem
1	1	2,11	leaky air vent screw
1	1	11	not enough water for salt sample
2	1	11	leaky air vent screw
9	1	1-3	winch problem, had to re-lower package after 1-3tripped. Did not sample
			these
9	1	16	stopcock pushed in
9	1	22	leaky air vent
13	1		Deck was washed with cleaning agent containing phosphate possible
			contamination of surface nutrient samples
21	1		light rain during sampling
23	1	4	bottom endcap did not close
25	1	6	did not close properly
26	1		rain during sampling
29	1	12	lanyard trapped under hose clamp
32	1	1-17	wire spooling problem, re-lowered after closing, did not sample these bottles
33	1	33	lanyard hang up on hose clamp
35	2	6	leaker (small rosette)
35	2	1, 9, 24	did not close
36	1	1,8,9,15	did not close (small rosette)
37	2	9,19	did not close (small rosette)
37	2	20	no water for nutrient sample
38	1	1,9,19	did not close (small package)
39	1	1,5,9	did not close (small package)
40	1	5,9	did not close (small package)

Station	Cast	Bottles	Problem
41	1	1,8,9,15	did not close (small package)
41	2	9,15	did not close (small package)
42	1	9,15	did not close (small package)
42	1	23	no water for salt, nutrients
50	1	25	stopcock pushed in
56	1	1-9	winch problem, had to re-lower package after 1-9closed
58	1	1-9	winch problem, had to re-lower package after 1-5closed
61	2	9	closed while package still moving
65	1	11	closed while package still moving
74	1	35	only enough water to partially fill salt bottle
76	1	4	bottom cap lanyard broken, possible early closure
89	1	21	stopcock pushed in
90	1	13	air vent open
93	1	12-36	lost communication with package, cast aborted
99	1	30	lanyard hang up
101	1		wire problems, replaced sheave after this station
102	2	5	did not close (small rosette)
102	2	6	leak around bottom O-ring
102	2	19	stopcock pushed in
103	1	5,8	did not close (small rosette)
103	1	19	stopcock pushed in
110	2	35	no water for nutrient
114	1	33	no water for nutrient; sampled while raining
122	2	33	no water for nutrient, salt
123	1	1	stopcock pushed in
133	1	35	not closed, lanyard hang-up
140	1	15	did not close- pylon problem
142	1	5,9,16	did not close (small rosette)
143	1	8,9,17	did not close (small rosette)
149	1	1	stopcock pushed in

#### Hydrowire And Winch Problems:

On the RB-03-04 cruise, a new hydrowire was provided on the forward CTD hydro winch. Levelwind problems were encountered on this winch early on the cruise. Because the new hydrowire was shipped to the RH Brown already spooled on a drum, there was uncertainty if the deeper layers of wire on the drum had been spooled under tension, which is essential for proper performance. Some time was lost during the up-casts on Leg 2 due to level-wind problems and 'nesting' of the wire as it was wound onto the winch, and a small number of water samples were compromised because the CTD/rosette package had to be re-lowered at depth to correct severe level-wind and nesting problems. Water samples were not drawn from these compromised bottles. Near the end of Leg 2 and during Leg 3, the winch operators became proficient in stopping the winch as necessary during upcasts and manually adjusting the clutch/level-wind mechanism as each layer of wire was spooled on the drum. This reduced these problems significantly, but was labor intensive.

The General Oceanics sheave for the hydrowire was replaced after station 101. For at least several stations prior to its replacement, the hydrowire was observed to be pulling strongly to one side and wearing a groove into the side of the sheave. On the casts immediately before 101, the sheave began to vibrate excessively. The sheave was turned 180 degrees before station 101, and another cast was attempted. On the return to deck after cast 101, hockles and birdcages were observed in the upper part of the wire. Some un-twisting of the wire strands may also have occurred at a significant distance down the wire. About 500 meters of hydrowire were cut from the spool and the wire re-terminated after this cast,. Since no equivalent replacement for this sheave was available on board, a smaller diameter sheave was substituted. Such smaller sheaves may place significantly greater stress on the hydrowire.

Short circuits or wire breaks occurred in 2 of the 3 conducting wires in the hydrowire during Leg 3, leaving only 1 conducting wire (and the steel armor of the hydrowire) available for the last  $\sim$ 40 stations on the second leg. A failure of the last remaining conducting wire would have required an unknown amount of hydrowire to be cut off, or resorting to use of the other hydrowinch.

#### A.4.3. Bottle Data Processing:

Water samples collected and properties analyzed shipboard were managed centrally in a relational database run on a Linux workstation.

The sample log (and any diagnostic comments) was entered into the database once sampling was completed. WOCE/CLIVAR quality flags associated with sampled properties were set to indicate that the property had been sampled, and sample container identifications were noted where appropriate (e.g., oxygen flask number).

Most samples were analyzed on board with the exception of <sup>3</sup>He, DI<sup>14</sup>C, tritium, DOC, CDOM, and PIC/POC that were sampled and preserved for shore-based analysis. Descriptions of sampling and analysis procedures, as well as the relevant statistics on data quantity and quality are included in individual sections below.

The results of individual shipboard analyses were then uploaded through the website as results became available. These results included a quality code associated with each measured value and followed the coding scheme developed for the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP) (Joyce, 1994).

Various consistency checks and detailed examination of the data continued throughout the cruise. Post cruise data processing and quality checking is discussed in the individual sections below.

#### Trace Metal Casts:

In addition to the 150 CTD/rosette casts, separate trace metal casts were made at along the section, nominally at 60 mile spacing.

Trace metal casts were made at stations:

4,5,9,10,13,17,19,23,26,28,31,33,35,42,44,46,48,50,53,55,57,59,61,63,65,67,69,70,72,74,7 6,78,80,82,84,86,88,90,92,94,96,98,100,102,104,106,108,110,112,114,116,118,120,122,12 4,126,129,132,135,138,141,142,144,146,148

Because of possible contamination problems in sampling for iron and aluminum, these samples were collected using a special trace metal clean CTD/rosette, bottles, wire and winch system. In addition to trace metal samples, samples were collected from each bottle for the analysis of salinity and nutrients. The CTD/rosette package was deployed off the stern A-Frame using a custom built winch with ~1500 m of Kevlar coated cable provided by the trace metal investigators. Bottles were closed during the up-cast without stopping the winch, to minimize possible contamination of the samples from the rosette frame and instruments.

There were a number of problems with the trace metal winch, particularly with its ability to lift the package out of the water when the bottles were full. On a number of casts, member of the scientific party and crew manually assisted in pulling on the wire to help lift the trace metal rosette package out of the water and onto the deck.

#### A.4.4 Underway Measurements:

Near surface seawater measurements of temperature, salinity, pCO<sub>2</sub> and ADCP measurements were made continuously along the cruise track. Copies of these data are available in digital format from the CCHDO and from the Chief Scientist.

Weather observations (ship position, cloud cover and type, visibility, wind speed and direction, sea state, wave height and direction, surface water temperature, atmospheric pressure, and wet and dry bulb air temperature) were recorded manually at hourly intervals by the bridge and during each hydrocast. Copies of these data log sheets are available from the Chief Scientist.

Float Type	Serial#	Time	Date (GMT)	Lat	Lon
Carbon Explorer	2122	0042	22 June 2005	60°00'N	20°00'W
Carbon Explorer	1	1822	28 June 2005	47°00'N	20°00'W
Carbon Explorer	2	1829	28 June 2005	47°00'N	20°00'W
Drift Buoy	39149	0027	24 July 2005	19°00'N	29°00'W
Drift Buoy	39148	1409	24 July 2005	18°00'N	29°00'W
Profiling Float	205	1143	26 July 2005	15°00'N	29°00'W
Drift Buoy	39152	0300	27 July 2005	14°00'N	29°00'W
Drift buoy	39150	1752	27 July 2005	13°00'N	29°00'W
Profiling Float	202	0052	28 July 2005	12°30'N	29°00'W
Drift buoy	39151	0902	28 July 2005	12°00'N	29°00'W
Drift buoy	35691	0050	20 July 2005	11°00'N	29°00'W
Profiling Float	188	1549	29 July 2005	10°00'N	29°00'W
Profiling Float	189	0957	31 July 2005	7°30'N	27°15'W
Profiling Float	175	2310	1 Aug 2005	5°00'N	26°00'W
Profiling Float	209	0901	3 Aug 2005	2°40'N	25°00'W

#### Float Deployment:

#### A.4.5. Samples Preserved For Shore-Side Analysis

#### **DOC** Sampling

Principal Investigator:	Dennis Hansell	U. Miami, RSMAS		
	4600 Rickenbacker Causeway			
	Miami, FL 33149			
	dhansell@rsmas.miami.ed	lu		
Sampler:	Stacy Brown	U. Miami		

Seawater samples were taken directly from the Niskin Bottles into the 60 ml precleaned bottles for deeper than 200 m. Samples from the up 200 m were collected by in-line filtration through a GF/F filter. All samples were kept in frozen before analysis.

### <sup>14</sup>C Sampling

Principal Investigator:	Ann McNichol	WHOI
Samplers:	John Bullister	NOAA-PMEL
	Nicolas Gruber	UCLA

Seawater was drawn directly from the Niskin bottles into 500-ml glass bottles after about 250 ml overflow of the water. Samples were then poisoned with 100  $\mu$ l saturated HgCl<sub>2</sub> solution and sealed by greased stoppers. Bottles with samples are kept in cases for shipping back to WHOI.

### Reference:

Measuring <sup>14</sup>C in Seawater TCO<sub>2</sub> by Accelerator Mass Spectrometry, WHOI in WHP Operation and Methods-July, 2003.

### Helium and Tritium Sampling

Principal Investigator:	Peter Schlosser	Lamont-Doherty Earth Observatory
	Palisades NY 10964	
	schlosser@ldeo.columbia.e	du
Samplers :	Brent Turrin	LDEO (Leg 2)
-	Anthony Dachille	LDEO (Leg 3)

Sampling of helium isotope (<sup>3</sup>He) and tritium involved separate containers for <sup>3</sup>He and tritium. Seawater for <sup>3</sup>He analysis was sampled into re-useable stainless steel tubes of 90-ml in volume. Tritium was sampled into 1 liter brown glass bottles. The <sup>3</sup>He samples were taken first and care was made to rid the vessel of air bubbles by hitting them with a stick and opening and closing the two valves at each end of the tube. Tritium was sampled by rinsing the bottles twice and filling with water up to the curve at the top of the bottle to allow room to allow for thermal expansion.

The He extraction was done on ship on a vacuum extraction system supplied by WHOI (W. Jenkins and D. Lott).

#### **B.** CTD DATA

Chief Scientists:	John Bullister & Nicolas Gruber
Survey Department:	CST Jonathan Shannahoff
CTD Personnel:	Regina Cesario, Elena Brambilla, Nicole Lovenduski, Kristy McTaggart
Final Processing:	Kristy McTaggart

#### B.1. Acquisition

During this cruise, 150 stations were occupied in the North Atlantic from 63N to 5S primary along 20W at 30nm spacing, and 152 CTDO profiles were collected. All profiles were to within 10m of the bottom, ranging from about 200m to nearly 6000m.

Three underwater package configurations were used during this cruise. The primary package was a new 36-position stainless steel frame mounted with 34 12-liter Niskin bottles, Sea-Bird carousel, load cell, altimeter, pinger, LADCP, and optical sensors. The Sea-Bird CTDO sensors were a 9plus CTD s/n 315; primary TC sensors s/n 4193, 1180; secondary TC sensors s/n 1455, 354; and SBE 43 oxygen sensors s/n 315, 313, or 312.

During bad weather or while testing a deteriorating winch cable, a small 24-position stainless steel frame was employed. This bad weather frame was mounted with 24 4-liter Niskin bottles, AOML-owned Sea-Bird carousel, load cell, altimeter, and pinger. The Sea-Bird CTDO sensors were a 9plus CTD s/n 209; primary TC sensors s/n 1370, 1434; secondary TC sensors s/n 1460, 1177; and SBE 43 oxygen sensors s/n 313 or 312.

The third configuration was comprised of the primary package with the bad weather CTD and sensors, and used after the primary CTD s/n 315 blew the power supply at station 142. Sea-Bird configuration files were named a16n\_1.con, a16n\_2.con, and a16n\_3.con, respectively. N.B., The pre-cruise pressure calibration offset for CTD s/n 315 was amended by +1 dbar in a16n\_1.con.

Data were acquired at full 24 Hz resolution through a Sea-Bird 11plus deck unit and the ship's dedicated PC using Seasave software version 5.28c. Analog data were archived onto VCR tapes, although likely unrecoverable. Fortunately, no real-time data were lost. Digital backups were made to Zip disks and CDs.

The discrete sample database, maintained by Frank Delahoyde at sea, totals 4824 records. The only instance of rosette misfire identified was during station 119, where two bottles closed at 1400 dbar; the following 6 bottle closures were offset by one; and no sample was collected at 600 dbar.

#### **B.2.** Processing

The reduction of profile data began with a standard suite of processing modules using Sea-Bird Seasoft software DOS version 4.249 in the following order:

DATCNV converts raw data into engineering units and creates a bottle range file. Both down and up casts were processed for scan, elapsed time(s), pressure, t0, t1, c0, c1, and oxygen voltage. Optical sensor data were carried through for casts using the primary package. MARKSCAN was used to skip over scans acquired on deck and while priming the system.

- ALIGNCTD aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary conductivity is automatically advanced in the deck unit by 0.073 seconds. On the primary package, the additional alignment of primary sensor s/n 1180 was -0.040 seconds (net alignment 0.033 seconds), and the total alignment for secondary sensor s/n 354 was 0.089 seconds. On the bad weather package, the additional alignment of primary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment of primary sensor s/n 1434 was 0.010 seconds (net alignment 0.063 seconds), and the total alignment for secondary sensor s/n 1177 was 0.089 seconds as it was then being plumbed with the optical sensors in the primary frame. It was not necessary to align temperature or oxygen.
- ROSSUM averages bottle data over an 8-second interval as specified in the range file, and derives salinity, theta, sigma-theta, and oxygen (µmol/kg).
- WILDEDIT makes two passes through the data in 100 scan bins. The first pass flags points greater than 2 standard deviations; the second pass removes points greater than 20 standard deviations from the mean with the flagged points excluded. Data were kept within 100 of the mean (i.e. all data).
- FILTER applies a low pass filter to pressure with a time constant of 0.15 seconds. In order to produce zero phase (no time shift) the filter is first run forward through the file and then run backwards through the file. Mistakenly, a time constant of only 0.03 seconds was used for this cruise, of small consequence.
- CELLTM uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. In areas with steep temperature gradients the thermal mass correction is on the order of 0.005 PSU. In other areas the correction is negligible. The value used for the thermal anomaly amplitude (alpha) was 0.03. The value used for the thermal anomaly time constant (1/beta) was 7.0. Mistakenly, the secondary sensors of either CTD were not corrected for this effect.
- LOOPEDIT removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m/s or the pressure is not greater than the previous maximum scan, the scan is omitted.
- BINAVG averages the data into 1 db bins. Each bin is centered on an integer pressure value, e.g. the 1 db bin averages scans where pressure is between 0.5 db and 1.5 db. There is no surface bin.
- DERIVE uses 1 db averaged pressure, temperature, and conductivity to compute salinity, theta, sigma-theta, and dynamic height.
- TRANS converts the data file from binary to ASCII format.

Package slowdowns and reversals owing to ship roll can move mixed water in tow to in front of the CTD sensors and create artificial density inversions and other artifacts. In addition to Seasoft module LOOPEDIT, MATLAB program deloop.m computes values of density locally referenced between every 1 dbar of pressure to compute N^2 and linearly interpolates temperature,

conductivity, and oxygen voltage over those records where N^2 is less than or equal to -1e-5 per s^2. MATLAB program calctd\_1k.m or calctd\_2k.m or calctd\_3k.m applies final calibrations to temperature and conductivity, and computes salinity and calibrated oxygen. Program cnv\_eps1.f and cnv\_eps2.f computes ITS-90 temperature, theta, sigma-t, sigma-theta, and dynamic height; creates WOCE quality flags, and converts the ASCII data files into NetCDF format for PMEL's database. Program wocelst\_ox.F converts the NetCDF files into WOCE format for submission to the WHPO, and creates WOCE .SUM files, one for each leg of the cruise.

#### **B.3.** Salinities

Primary TC data were selected from the primary package. These data were used to calibrate stations 1-34, 43-101, and 104-141. Secondary TC data were selected from the bad weather package. These data were used to calibrate stations 35-42, 102-103, and 142-150. Note that stations 144-150 used bad weather CTD s/n 209 in the primary package.

Samples were collected by the CTD watchstander. A duplicate sample was collected from the deepest bottle. Salinity analysis was performed by Greg Johnson on leg 1, and Dave Wisegarver on leg 2. Analysis was done on the ship's autosalinometer using Ocean Scientific ACI2000 interface and IAPSO standard seawater batch P143 dated February 2003. The bath temperature was set to 24C. The ambient room temperature should be within 1 degree of the bath temperature, preferably cooler. Samples were left to equilibrate in the Autosal lab space for a minimum of 8 hours before analysis. The Autosal was standardized once a day.

Sample salinities used to calibrate CTD conductivity sensors were obtained from the Data Manager at sea. However, salinity data were re-evaluated post-cruise and a linear drift correction between standardizations was applied. The final data set was produced at PMEL in December 2003.

#### B.4. Oxygens

#### SBE 43 oxygen sensor s/n 315

was used on the primary package for stations 1-60. It had a noticeable trend from the onset but it wasn't confirmed until sample oxygens were reviewed. Sensor s/n 315 was swapped out for sensor s/n 313 prior to station 61. Sea-Bird has suggested that this membrane could've been frozen or torn before the cruise.

SBE 43 oxygen sensor s/n 313

was used first on the bad weather package for stations 35-42 before going on the primary package prior to station 61. Starting at station 94, s/n 313 was not responding well to the new oxygen minimum below the thermocline. It was swapped out for sensor s/n 312 prior to station 122.

#### SBE 43 oxygen sensor s/n 312

was used first on the bad weather package for stations 102-103. It was moved to the primary package prior to station 122 and used for the remainder of the cruise.

Sample oxygens used to calibrate these sensors were obtained from the Data Manager at sea. However, oxygen data were re-evaluated post-cruise and the final data set was produced at AOML in September 2004.

#### **B.5.** Bottle Data

Seasoft module ROSSUM created a bottle data file for each cast. These files were appended using program sbecal1k.f for primary sensor data or sbecal2k.f for secondary sensor data. Program addsalk3.f matched sample salinities to CTD salinities by station/sample number. MATLAB calibration programs were used to determine best fit groupings. The final results were a second order polynomial fit for stations 1-100 using the primary sensor pair; a third order polynomial fit for stations 101-141 using the primary sensor pair; a linear fit for stations 35-42 and stations 102-103 using the secondary sensor pair; and a linear fit with a station dependent slope for stations 142-150 using the secondary sensor pair.

[sta,slope,bias,newbotco,newctdco	]=calcos2(stat,cond,pres,botc,2.8,1,100);
number of points used	2427
total number of points	2815
% of points used in fit	86.22
fit standard deviation	0.001952
fit bias	0.0015337094
min fit slope	0.99993324
max fit slope	0.99997466
[sta,slope,bias,newbotco,newctdco]	]=calcos3(stat,cond,pres,botc,2.8,101,141);
number of points used	1039
total number of points	1312
% of points used in fit	79.19
fit standard deviation	0.0018
fit bias	-0.004654759
min fit slope	1.000081
max fit slope	1.0001403
[sta,slope,bias,newbotco,newctdco]	]=calcos0(stat,cond,pres,botc,2.8,35,42);
number of points used	184
total number of points	202
% of points used in fit	91.09
fit standard deviation	0.001569
fit bias	0.00067359131
min fit slope	1.0000342
max fit slope	1.0000342
[sta,slope,bias,newbotco,newctdco	]=calcos0(stat,cond,pres,botc,2.8,102,103);
number of points used	42
total number of points	44
% of points used in fit	95.45
fit standard deviation	0.00243
fit bias	-0.0086599793
min fit slope	1.0003549
max fit slope	1.0003549
[sta,slope,bias,newbotco,newctdco]	]=calcos1(stat,cond,pres,botc,2.8,142,150);
number of points used	232
total number of points	279
% of points used in fit	83.15
fit standard deviation	0.001669
fit bias	-0.0027190403
min fit slope	1.0000403
max fit slope	1.0000991

Program addoxyk3.f matched sample oxygens to CTD oxygens by station/sample number. Because of sensor hysteresis, MATLAB programs matched upcast oxygens to downcast oxygens by sigma-2. Coefficients were determined using run\_oxygen\_cal\_1.m and saved in final.mat.

Temperature viscous and drift corrections, conductivity coefficients, and oxygen coefficients were applied to the bottle data file using calclo\_k.m. Quality flags for sample salinities were determined using MATLAB program sflag.m. Of the 4676 sample salinities, 0.6% were flagged as bad and 1% were flagged as questionable. Final CTDO bottle data, a16n\_allo.flg, were given to John Bullister to incorporate into the master data file. For PMEL's database, individual bottle files for each cast were created in NetCDF format using clb\_epso.f.

#### C. BOTTLE SAMPLING:

#### C.1. Inorganic Nutrients (Phosphate, Nitrate, Nitrite and Silicate)

Samplers and Analysts:	Leg 1	Calvin Mordy
		David Wisegarver
	Leg 2	Charlie Fischer
		Jia-Zhong Zhang
Data Reduction:		Calvin Mordy

#### Equipment and Techniques

Concentrations of dissolved nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>) and silicic acid (H<sub>4</sub>SiO<sub>4</sub>) were measured using an automated continuous flow analyzer with a segmented flow and colorimetric detection. The four-channel autoanalyzer was customized using components from various systems. The major components were an Alpkem 301 sampler, one 24 channel Ismatek peristaltic pump and three ThermoSeparation monochrometers (for silicic acid, nitrate, and nitrite), one Technicon AAII pump and detector (for phosphate), and custom software for digitally logging and processing the chromatographs. Glass coils and tubing from the Technicon Autoanalyzer II were used for analysis of phosphate, and micro-coils from Alpkem were used for the other three analyses. Pump tubes were changed 4 times during the expedition, although some of the tubes were changed more frequently as part of troubleshooting.

#### Chemistry

#### Nitrite

Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm (Zhang et al., 1997a). Samples for nitrate analysis were passed through a cadmium column, which reduced nitrate to nitrite. Total nitrite, mostly from reduction of nitrate with a small amount of nitrite present in the original samples, was then determined as described above. Nitrate concentrations in seawater samples were calculated by difference.

#### Phosphate

Phosphate in the samples was determined by reacting with molybdenum (VI) in an acidic medium to form a phosphomolybdate complex. This complex was subsequently reduced with hydrazine at a temperature of 55°C to form phosphomolybdenum blue (Zhang et al., 2001). An AAII detector with an 880 nm filter was used to measure the absorbance during the cruise.

#### Silicic acid

Silicic acid was analyzed by reacting with molybdate in acidic solution to form  $\beta$ -molybdosilicic acid. The  $\beta$ -molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue (Zhang et al., 1997b). The absorbance of the molybdenum blue was measured at 660 nm.

#### Sampling and Standards

Nutrient protocols closely followed the methods of Gordon et al. (1993). Samples were drawn in 40 ml HDPE Boston Round sample bottles that had been stored in 10% HCl and rinsed 4-5 times with sample before filling. Samples were usually analyzed 2-3 hours after sampling. A replicate was

always drawn from the deep bottle for analysis with samples from the subsequent station for comparison. All samples were brought to room temperature prior to analysis. A separate analytical run was conducted at each station (except for the most shallow stations). The sequence of a typical analytical run for a station was 1) blanks, 2) working standards, 3) the working standard from the previous station, 4) deep water from the previous station, 5) samples analyzed from deep to surface, 6) replicate analysis of the four deepest samples and problem samples (if any), 7) working standards, and 8) blanks. The blanks were deionized water, and the standards were simply a "zero" standard of Low Nutrient Seawater (LNSW), and a high standard of spiked LNSW. Linearity of the autoanalyzer was checked every ten days, and corrections for non-linearity were applied to the phosphate data.

The high standard was made from the addition of 1 ml of primary nitrite standard and 20 ml of a secondary mixed standard (containing silicic acid, nitrate, and phosphate) in 500 ml of Low Nutrient Sea Water using pre-calibrated Eppendorf pipettes and volumetric flasks.

Dry standards were pre-weighed at PMEL, and dissolved to prepare primary standards at sea. Silicic acid (Na2SiF6, >98%) and nitrate (KNO3, 99.99%) were from Aldrich, phosphate (KH2PO4, 99.99%) and nitrite (NaNO2, 98.2%) were from Baker. The secondary mixed standard was prepared by additions of the nitrate and phosphate primary standards to the silicic acid primary standard in deionized water.

After each run, the electronic chromatograph was scrutinized to ensure proper selection of individual peak heights. The peak height data was inserted into Microsoft Excel worksheets and the concentrations were calculated after factoring the baseline drift, carryover corrections, refractive index, and standard drift. Quality control plots were maintained of the baseline, matrix, carryover, standard factor, old standard, and station- to-station variability of the deep water replicate.

Nutrient concentrations were reported to the shipboard data manager in micromole per liter. Measurements were made in a temperature-controlled bioanalytical laboratory ( $20 \pm 2^{\circ}$ C), and the laboratory temperature during analysis was reported to facilitate unit conversion to a micromole per kg basis.

#### Problems

During the cruise, several detectors had to be replaced. During the first 25 stations, the data acquisition system was not working, and the peaks were read from chart recorders.

After installation of Lachat Cd Column at Station 84, the NO3 carryover correction immediately increased from about 1% to 3%, followed by a steady increase to about 6% at Station 135, and then an exponential increase to about 14% at Station 150. Carryover corrections were substantial for samples collected in the nutricline, and corrections for stations 149 and 150 were closely examined. The first of the deep water replicates analyzed at the end of the run always had the largest carryover correction. This "dummy" deep sample (bottle 1) was used to wash out the previous low nutrient surface sample before analysis of bottles 2, 3 and 4. The carryover correction for the dummies from Stations 149 and 150 were  $\sim$ 4 M, and this brought the concentrations to within 0.2 M of the initial bottle 1 measurement. Although substantial, this suggests that the correction was appropriate and the error in the correction was minimal. Samples of greatest concern were at the base of the mixed layer (i.e. Sta. 149, bottle 31) where carryover corrections of 1.0 and 0.8 (stations 149 and 150 respectively) were applied to give concentrations of 0.0 and 0.1 M – the same as observed for the upper 3 bottles. (Stations were measured deep to shallow; therefore, samples at the top of the

nutricline have the largest relative carryover correction.) A check of the bottle temperature and salinity data suggests that these samples were indeed from the upper mixed layer.

Another problem was a dramatic ( $\sim$ 30%) drop in the nitrite standard factor from Station 84 to Station 111. The standard factor immediately recovered after making a new nitrite primary standard. The nitrite standard has been known to decay with time, especially if not stored in the refrigerator. The standard concentration of nitrite was recalculated for these stations based on comparisons of the decaying standard factors with standard factors from Stations 25-83 and 112-150.

#### Number of Samples, Replicates and Precision

A replicate sample was almost always drawn from the deepest bottle, and most replicate analyses were conducted on the four deepest bottles. A few replicate analyses were conducted for samples in the upper water. The precision of phosphate, silicic acid and nitrate was within 1% of full scale.

	Phosphate	Silicic Acid	Nitrate	Nitrite
Number of Samples	5368	5369	5369	5369
Number of Replicates	499	500	490	n/a
Average Standard Deviation ( M)	0.006	0.064	0.062	n/a
Percent Deviation	0.5%	0.5%	0.3%	n/a

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#### C.2. CHLOROFLUOROCARBON (CFC) MEASUREMENTS

Principal Investigators: John L. Bullister, NOAA-PMEL John.L.Bullister@noaa.gov Mark J. Warner, University of Washington mwarner@ocean.washington.edu

Samplers and Analysts: Mark J. Warner, University of Washington Eric Wisegarver, University of Washington esw@u.washington.edu

Samples for the analysis of dissolved CFC-11, CFC-12 and CFC-113 were drawn from ~2,421 of the ~4,923 water samples collected during the expedition. Specially-designed 12-liter 'Bullister' sample bottles were used on the cruise to reduce CFC contamination. These bottles have the same outer diameter as standard 10 liter Niskin bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples for CFC analysis were the first samples drawn from the 12-liter bottles. Care was taken to coordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, <sup>3</sup>He, and HCFC samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 12-liter bottles into 100 ml precision glass syringes equipped with two-way metal stopcocks. The syringes were immersed in a holding tank of clean surface seawater until analyzed.

For air sampling, a ~100 m length of 3/8" OD Dekaron tubing was run from the main laboratory to the bow of the ship. A flow of air was drawn through this line into the main laboratory using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm. Using a backpressure regulator. A tee allowed a flow (100 cc min<sup>-1</sup>) of the compressed air to be directed to the gas sample valves of the CFC analytical system, while the bulk flow of the air (>7000 cc min<sup>-1</sup>) was vented through the backpressure regulator. Air samples were only analyzed when the relative wind direction was within 60° of the bow of the ship to reduce the possibility of shipboard contamination. The pump was run continuously to insure that the air inlet lines and pump were thoroughly flushed. Analysis of ~ 190 bow air samples was performed along the cruise track. At each location, replicate measurements were made to increase the precision.

Concentrations of CFC-11 and CFC-12 in air samples, seawater, and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988). For seawater analyses, water was transferred from a glass syringe to a fixed volume chamber (~30 ml). The contents of the chamber were then injected into a glass-sparging chamber. The dissolved gases in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 minutes at ~70 ml min<sup>-1</sup>. Water vapor was removed from the purge gas during passage through an 18 cm long, 3/8" diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8" OD stainless steel tube with a ~10 cm section packed tightly with Porapak N (60-80 mesh), held at ~ -20°C in a cryogenic bath. After 4 minutes of purging, the trap was isolated, and the trap was heated electrically to  $\sim 100^{\circ}$ C. The sample gases held in the trap were then injected onto a precolumn ( $\sim 25$  cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil C, held at 70°C) for the initial separation of CFC-12, CFC-11, and CFC-113 from later eluting compounds. After these CFCs had passed from the pre-column into the main analytical column ( $\sim 183$  cm of 1/8" OD stainless steel tubing packed with Carbograph 1AC, 80-100 mesh, held at 70°C) of the GC (a Shimadzu Mini-2 gas chromatograph with ECD)

The analytical system was calibrated frequently, using a standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column, and EC detector were similar to those used for analyzing water samples. Two sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was ~11 minutes.

Concentrations of the CFCs in air, seawater samples, and gas standards are reported relative to the SIO98 calibration scale (Cunnold *et. Al.*, 2000). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg<sup>-1</sup>). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (PMEL cylinder 34603) into the analytical instrument. The response of the detector to the range of moles of CFC passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at intervals of 14 days during the cruise. These were supplemented with occasional injections of multiple aliquots of the standard gas at more frequent time intervals. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity.

The efficiency of the purging process was evaluated periodically by re-stripping high concentration surface water samples and comparing the residual concentrations to initial values. These re-strip values were approximately 0.8% for CFC-11, 0.2% for CFC-12 and 0.0% for CFC-113. Corrections for the efficiency were applied to the final data set.

On this expedition, based on the analysis of ~100 duplicate samples, we estimate precisions (1 standard deviation) of 1% or 0.004 pmol kg<sup>-1</sup> (whichever is greater) for dissolved CFC-11, 1% or 0.004 pmol kg<sup>-1</sup> for CFC-12 measurements and 2% or 0.009 pmol kg<sup>-1</sup> for CFC-113

A small number of water samples had anomalously high CFC concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the preliminary data, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples which were drawn from the rosette but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel). A total of 35 analyses of CFC-11, 24 analyses of CFC-12 and 5

analyses of CFC-113 were assigned a quality flag of 3. A total of 16 analyses of CFC-11, 13 analyses of CFC-12 and 17 analysis of CFC-113, were assigned a quality flag of 4.

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Date	Time	CFC-11	CFC-12	CFC-113
YYYYMMDD	HHMM	(ppt)	(ppt)	(ppt)
20030619	0829	254.0	534.2	79.4
20030619	0841	254.1	533.1	78.9
20030619	0853	253.3	532.7	78.9
20030619	0905	253.1	532.4	78.8
20030619	0917	252.7	532.6	78.8
20030619	1825	252.2	527.4	78.6
20030619	1837	251.5	528.9	77.9
20030619	1849	252.6	528.6	78.3
20030619	1901	252.5	528.2	78.3
20030619	1913	251.4	528.3	78.6
20030620	0121	251.8	526.8	78.9
20030620	0133	251.6	527.0	77.2
20030620	0145	250.8	525.6	79.0
20030620	0157	251.1	527.4	78.3
20030620	0209	251.2	527.3	78.5
20030620	1458	250.1	514.4	76.2
20030620	1510	250.7	514.6	76.3
20030620	1522	250.4	513.2	75.7
20030623	0730	251.8	511.6	75.0
20030623	0742	250.2	511.8	75.1
20030623	0754	252.1	512.2	75.9
20030623	0806	250.2	511.0	75.9
20030626	0352	253.1	540.7	81.8
20030626	0404	253.8	541.0	81.5
20030626	0416	253.4	539.9	80.8
20030626	0428	253.9	539.7	81.5
20030627	0456	253.1	541.7	80.2
20030627	0508	252.8	541.8	80.4
20030627	0520	252.2	541.0	79.8
20030627	0532	252.3	540.8	80.4
20030628	0702	251.7	541.1	80.7
20030628	0714	252.5	539.9	81.4
20030628	0726	250.8	539.0	81.2
20030628	0738	251.7	540.7	81.4
20030629	0026	251.5	540.4	81.3
20030629	0038	249.8	540.9	82.6
20030629	0050	250.0	540.0	79.8
20030629	0102	252.3	543.0	80.3
20030629	1000	251.0	545.6	82.5
20030629	1012	252.4	542.6	82.2
20030629	1024	252.9	542.9	81.1
20030629	1036	252.9	547.1	81.5
20030629	1048	252.7	543.1	80.9
20030630	0007	251.9	543.2	80.5
20030630	0019	253.1	543.9	80.9
20030630	0031	252.4	540.2	81.3

Date	Time	CFC-11	CFC-12	CFC-113
YYYYMMDD	ннмм	(ppt)	(ppt)	(ppt)
20030630	00/13	251.8	544 1	81 1
20030630	0045	251.0	542.3	80.0
20030630	1206	252.9	5/13/2	80.0
20030630	1200	252.4	541.4	80.9
20030630	1218	251.9	539.6	80.3
20030630	1230	251.0	5417	80.3
20030030	0/10	251.9	541.7	80.4
20030702	0410	252.2	543.5	80.0 81.1
20030702	0422	252.4	542.8	81.0
20030702	0434	253.4	543.8	81.0
20030702	0440	255.5	541.9	80.3
20030703	0718	255.1	545.5	<u> </u>
20030703	0730	254.7	546.6	<u>81.2</u>
20030703	0742	255.0	545.0	80.7
20030703	0734	254.4	545.9	70.5
20030703	02255	252.6	545.0	<u> </u>
20030703	2243	255.0	545.5	80.2
20030703	2237	254.2	545.0	80.0
20030703	2309	254.5	543.1	80.4
20030703	2321	255.6	543.0	80.4 80.2
20030704	1030	253.0	544.5	80.2
20030704	1708	252.9	544.1	81.0
20030704	1720	252.8	543.7	81.0
20030704	1/32	255.5	544.5	80.8
20030705	0911	233.3	543.9	80.8
20030705	0923	255.7	542.8	80.7
20030705	0933	254.0	543.5	80.4
20030703	0947	255.5	543.9	80.0
20030706	0032	254.4	542.8	80.9
20030706	0104	252.8	540.7	/9.0
20030706	0110	252.3	540.8	80.2
20030706	0128	255.8	542.8	80.7
20030700	0140	253.1	540.0	80.2
20030707	0/31	253.9	541.2	80.4
20030707	0803	253.9	544.1	00.4
20030707	0013	233.0	542.0	01.U 20 4
20030707	1429	233.0	542.3	00.4
20030708	1428	204./ 252.2	543.5 543.0	01.4
20030708	1440	233.3 252.9	544.0	<u>80./</u>
20030708	1432	252.0	541.0	02.4
20030708	1304	233.2 252.2	541.2	00.0 70.9
20030709	2213	252.2	541.2	/ 7.0
20030709	2227	231.3 252.2	541.5	70.4
20030709	2239	252.5	544.1	/ 7.4
20030709	1020	231.3	543.0	00.1
20030/19	1020	250.8	541.0 541.0	0U.3 91.2
20030/19	1032	231.3	341.0	01.2

Date	Time	CFC-11	CFC-12	CFC-113
YYYYMMDD	HHMM	(ppt)	(ppt)	(ppt)
20030719	1044	253.3	540.2	80.5
20030719	1056	252.8	543.0	80.7
20030720	0053	253.2	541.6	80.3
20030720	0105	252.6	541.5	81.1
20030720	0117	251.4	542.3	80.9
20030720	0129	252.5	542.2	80.8
20030720	0141	253.1	540.6	79.8
20030721	0644	250.7	542.7	80.4
20030721	0656	251.6	543.5	80.7
20030721	0708	251.4	543.3	81.4
20030721	0720	249.9	542.3	81.0
20030721	2214	251.2	542.3	81.4
20030721	2226	251.5	540.9	80.7
20030721	2238	250.4	541 9	81.0
20030721	2250	252.2	540.8	80.6
20030721	2302	250.3	542.4	81.6
20030722	1417	250.5	541.6	80.3
20030722	1429	251.7	540.3	81.0
20030722	1441	253.3	539.6	80.4
20030722	1453	253.5	542.0	80.3
20030723	2158	250.6	541.5	81.2
20030723	2130	253.1	540.3	80.1
20030723	2210	252.5	542.7	81.7
20030723	2222	252.0	542.7	81.0
20030723	2234	252.0	541.7	81.1
20030725	0253	251.3	542.2	81.1
20030725	0305	252.0	541.8	81.7
20030725	0317	252.0	541.6	81.0
20030725	0329	252.7	541.5	81.6
20030725	0341	252.2	541.5	81.0
20030728	0715	251.1	543.8	81.0
20030728	0727	231.1	546.0	81.3
20030728	0739	250.0	545.6	81.8
20030728	0751	250.0	544 7	81.2
20030728	2248	250.2	543 5	81.2
20030728	2300	249.9	540.5	81.6
20030728	2312	2504	540.8	81.0
20030728	2374	251.6	541.4	80.3
20030730	0229	251.0	540.2	81.1
20030730	0241	252.8	540.3	80.9
20030730	0253	250.0	541.5	81.2
20030730	0305	251.0	541.2	80.7
20030731	0017	252.7	541.2	81.0
20030731	0029	250.7	541.8	82.1
20030731	0041	250.8	541.5	81.8
20030731	0053	252.0	540.3	81.5

Date	Time	CFC-11	CFC-12	CFC-113
YYYYMMDD	HHMM	(ppt)	(ppt)	(ppt)
20030731	1703	252.4	540.2	81.2
20030731	1715	251.5	540.4	81.7
20030731	1727	249.6	540.1	80.9
20030731	1739	249.2	540.2	81.3
20030731	1751	250.3	539.8	80.8
20030801	2133	249.9	540.5	81.8
20030801	2145	250.9	540.6	81.4
20030801	2157	250.1	541.2	80.0
20030801	2209	250.1	544.1	80.8
20030801	2221	250.3	539.9	81.2
20030803	0350	250.7	541.2	81.9
20030803	0402	250.7	539.1	79.9
20030803	0414	250.7	540.7	81.3
20030803	0426	251.7	540.4	80.5
20030803	1833	250.6	542.1	81.5
20030803	1845	252.1	541.9	80.4
20030803	1857	251.2	542.7	81.1
20030803	1909	252.0	539.3	80.1
20030804	1020	252.0	539.9	81.5
20030804	1032	251.7	540.9	80.9
20030804	1044	251.4	540.8	81.0
20030804	1056	252.7	541.0	80.9
20030805	0235	251.7	543.3	81.0
20030805	0247	251.2	543.1	81.6
20030805	0259	252.4	541.4	81.5
20030805	0311	250.4	541.8	81.8
20030806	1418	251.7	541.0	80.2
20030806	1442	251.2	539.9	81.7
20030806	1454	251.6	538.6	80.1
20030807	0446	249.3	539.4	80.8
20030807	0458	252.1	540.7	80.5
20030807	0510	249.5	540.1	80.6
20030807	0522	249.6	538.3	80.2
20030808	0445	252.7	541.0	80.0
20030808	0457	250.8	541.0	81.2
20030808	0509	250.6	540.7	80.3
20030808	0521	249.5	540.8	80.5
20030808	1749	250.9	541.3	81.0
20030808	1801	252.1	541.3	81.4
20030808	1813	251.6	541.1	80.1
20030808	1825	250.7	539.4	81.5

## C.3. CO<sub>2</sub> STUDIES ON A REPEAT HYDROGRAPHY CRUISE IN THE ATLANTIC OCEAN: CO<sub>2</sub> CLIVAR SECTION A16N\_2003A DURING JUNE-AUGUST, 2003

E. Peltola, R. Wanninkhof, R. Feely, R. Castle, D. Greeley, J.-Z. Zhang, F. Millero, N. Gruber, J. Bullister and T. Graham (Atlantic Oceanographic and Meteorological Laboratory)

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#### Abstract

This report presents methods, analytical and quality control procedures performed during A16N cruise, which took place from June 4 to August 11, 2003 aboard the NOAA Ship RONALD H. BROWN under auspices of the National Oceanic and Atmospheric Administration (NOAA). The first hydrographic leg (June 19-July 10) was from Reykjavik to Funchal, Madeira along the 20° W meridian and the second leg (July 15-August 11) continued operations from Funchal to Natal, Brazil on a track southward and ending at 6° S, 25° W. The research was the first in a decadal series of repeat hydrography sections jointly funded by NOAA-OGP and NSF-OCE as part of the CLIVAR/CO<sub>2</sub>/hydrography/tracer program. Samples were taken from up to 34 depths at 150 stations.

The data presented in this report includes the analyses of water samples for: dissolved inorganic carbon (DIC), fugacity of  $CO_2$  (f $CO_2$ ), Total Alkalinity (TA), pH, nitrate (NO<sub>3</sub>), nitrite (NO<sub>2</sub>), phosphate (PO<sub>4</sub>), silicate (SiO<sub>4</sub>) and dissolved oxygen (O<sub>2</sub>).

#### C.3.1. INTRODUCTION

The A16N\_2003a cruise from Reykjavik, Iceland to Natal, Brazil was the first in a series of repeat hydrography cruises to measure decadal changes in circulation, heat and fresh water budgets, and carbon inventory in the ocean. The cruises repeat a sub-set of the World Ocean Circulation Experiment/World Hydrographic Program (WOCE/WHP) lines occupied in each major ocean basin in the 1990ties.

The program is driven by the need to monitor the changing patterns of carbon dioxide  $(CO_2)$  in the ocean and provide the necessary data to support continuing model development that will lead to improve forecasting skill for oceans and global climate. The WOCE/JGOFS survey during the 1990s has provided a full depth, baseline data set against which to measure future changes. By integrating the scientific needs of programs requiring measurement of the full water column, major synergies and cost savings are achieved. These measurements are of importance both for major research programs, such as CLIVAR and the U.S. GCRP Carbon Cycle Science Program (CCSP), and for operational activities such as GOOS and GCOS. As outlined in the program documentation

one component of a global observing system for the physical climate/ $CO_2$  system should include periodic observations of hydrographic variables,  $CO_2$  system parameters and other tracers. The large-scale observation component of the CCSP has a need for systematic observations of the invasion of anthropogenic carbon in the ocean superimposed on a variable natural background. The five topic areas that the  $CO_2/CLIVAR$  repeat hydrography program addresses are:

- A. Carbon system studies
- B. Heat and freshwater storage and flux studies
- C. Deep and shallow water mass and ventilation studies
- D. Calibration of autonomous sensors
- E. Data for model calibration

Further descriptions of the repeat hydrography program can be found at:

http://ushydro.ucsd.edu/

Details of the A16N\_2003a cruise can be found in the cruise instructions posted at the website of PMEL: http://www.pmel.noaa.gov/CO<sub>2</sub>/a16n/

and the repeat hydrography website:

#### http://ushydro.ucsd.edu/

The latter website also serves the full dataset from the cruise. The A16N\_2003a cruise involved efforts of a dozen investigators whose names and project are listed in Table 1. The cruise was executed under leadership of Dr. John Bullister who served as chief scientist and Dr. Niki Gruber who was co-chief scientist. A full list of personnel on the cruise is given in Table 2. A list of participating institutions is in Table 3.

The cruise consisted of a transit leg from Charleston to Reykjavik on which limited surface water observations were taken. Surface water  $pCO_2$  measurements for the transit and the hydrography legs can be found at www.aoml.noaa.gov/ocd/gcc. The first hydrographic leg was from Reykjavik to Funchal, Madeira along the 20° W meridian and the second leg continued operations from Funchal to Natal, Brazil on a track southward and ending at 6° S, 25° W (see Figure 1).

This data report focuses on the measurement of dissolved inorganic carbon (DIC), fugacity of CO<sub>2</sub> (fCO<sub>2</sub>), Total Alkalinity (TA), pH, nitrate (NO3), nitrite (NO2), phosphate (PO4), silicate (SiO4) and dissolved oxygen (O2).

Methodology, instrumentation and standardization of these parameters improved significantly during the WOCE/JGOFS era. Notable developments include release of manuals detailing the analytical methods and operating protocols (DOE, 1994; http://cdiac.esd.ornl.gov/oceans /handbook.html). Certified Reference Materials (CRM) are now available for DIC and TA, which are run interspersed with samples to determine calibration offsets. On this cruise the TA values were adjusted accounting for the small difference between the CRMs run at sea and the certified value determined at SIO. For DIC there were problems with the gas loop calibrations attributed to inaccurate temperature sensors. The reference materials were therefore used as primary calibration for both DIC and TA..

Instrumentation improved as well in the last decade. Alkalinity measurements can be done with better precision through automation and close checks of the response of electrodes. Burettes are independently calibrated, and the preparation of titrant (hydrochloric acid) undergoes improved

quality control and standardization (Millero et al., 1998). Measurement of pH is now done at extreme precision with spectrophotometric methods (Byrne and Breland, 1989). The DIC measurements are done by coulometry, a precise integrative method. During the A16\_2003a cruise we utilized two single operator multi-parameter metabolic analyzers (SOMMAs) (Johnson et al., 1999) for analyses, which facilitated a sample throughput of up to 80 samples per day. The fCO<sub>2</sub> measurements were done with an equilibration system described in Wanninkhof and Thoning, (1993). For this cruise we changed the data reduction and calculation routines. Comparison of data with a cruise along a similar transect in 1993 shows a appreciable bias between results that is detailed in the section describing the pCO<sub>2</sub> analyses. Oxygen measurements were performed by Winkler titrations (Carpenter, 1965) with photometric endpoint detection (Friederich et al., 1984). The titrator worked well but there were issues with errors in bottle volumes and problems with pipettes used to generate standard curves. Extensive post-cruise trouble shooting and bottle volume re-determination were necessary to reduce the data.

The data underwent carefully quality assurance and quality control (QA/QC) both during the cruise and post-cruise. Precision of measurements was determined from duplicate sampling and comparison of deep-water data where little variability is expected. Outliers in the data were flagged based on several methods utilizing prior knowledge of the trends and known relationships between parameters. Depth profiles for each parameter were scrutinized for outliers. When deviations were observed, it was assessed if other parameters showed deviations. Inorganic carbon system parameters were linked through physical chemical properties and by knowledge of two of the four parameters, the other two can be calculated provided silicate, phosphate, temperature and salinity of the sample are known. These so-called over-determinations or internal consistency calculations were used to assess the difference between calculated and measured values. When the difference exceeded 10 µmol kg-1 for the measured TA and the TA calculated from DIC and pH or fCO<sub>2</sub>, the three parameters were scrutinized and compared with other methods to assess if the datum should be labeled as questionable. Other techniques described in detail below include regional multi-linear regressions (MLR) between the inorganic carbon parameters and physical and chemical parameters known to correlate with them (for instance DIC = f(T, S, AOU, Si, PO4)). Again the differences between measured and calculated parameters are inspected. Finally the parameters were plotted against latitude for narrow depth intervals. Since changes along depth horizons are usually gradual, anomalies can be easily spotted and flagged.

This report describes the analytical procedures, calculations, and assessment of precision for DIC, TA, fCO<sub>2</sub>, and pH. This is followed by a description of the QA/QC methods based on internal consistency of these parameters and the MLR technique. The final section describes the procedures for measurement of nutrients and oxygen, and details the issues encountered during the cruise.

#### C.3.2. DATA COLLECTION AND ANALYTICAL METHODS

#### C.3.2.1. Total Dissolved Inorganic Carbon (DIC)

The DIC analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (AOML-1 and AOML-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Kenneth Johnson (Johnson et al., 1985, 1987, 1993; Johnson, 1992) formerly

of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, all carbonate species are converted to  $CO_2$  (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved  $CO_2$  gas is swept into the titration cell of the coulometer with compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH-.  $CO_2$  is thus measured by integrating the total charge required to achieve this.

The coulometers were calibrated by injecting aliquots of pure CO<sub>2</sub> (99.995%) by means of an 8port valve outfitted with two sample loops that had been calibrated by Kelly Brown, CCN Consulting (Wilke, 1993). However, due to large temperature variation the calibration factors obtained from gas loop measurements were of poor quality. Instead of using an average of the small and large loop values, we used a constant value for each analyzer throughout the entire cruise. The constant calibration value used for AOML-1 was 1.00532 and for AOML-2 1.00650. The CO<sub>2</sub> gas volumes bracketed the amount of CO<sub>2</sub> extracted from the water samples for the two AOML systems. All DIC values were corrected for dilution by 0.2 ml of HgCl<sub>2</sub> used for sample preservation. The total water volume of the sample bottles was 540 ml. The correction factor used for dilution was 1.00037. A correction was also applied for the offset from the Certified Reference Material (CRM) Batch 59, supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). This correction was applied for each cell using the CRM value obtained in the beginning of the cell. To check the stability of the coulometer and coulometer solutions, the CRMs were measured at the beginning, middle, and end of each coulometer cell solution. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9-12 hours of continuous use. Sample titration times were 9-16 minutes.

Samples were drawn from the "Niskin" bottles into cleaned, precombusted 540-ml Pyrex bottles using Tygon tubing according to procedures outlined in the Handbook of Methods for CO<sub>2</sub> Analysis (DOE, 1994). Bottles were rinsed once and filled from the bottom, overflowing half a volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5-ml headspace, and 0.2 ml of saturated HgCl<sub>2</sub> 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.

Replicate seawater samples were taken from the surface, 1000 m, and bottom "Niskin" sample bottles and run at different times during the cell. The first replicate of the surface water was used at the start of the cell with fresh coulometer solution, the second surface replicate and the first one of the 1000 replicates were run in the middle of the cell after about 12 mg of C were titrated. The second one of the 1000 m replicates and the first one of the bottom replicates were run at the end of the cell after about 25 mg of C were titrated, while the second one of the bottom replicate samples was run using a new coulometer cell solution, see. No systematic difference between the replicates was observed. The trends do not suggest any systematic dependency of results with amount of carbon titrated for a particular cell. The results of the duplicate samples have been presented in Figure 2, and Table 4 and 5.

#### Calculations

Calculation of the amount of  $CO_2$  injected was according to the Department of Energy (DOE)  $CO_2$  handbook [DOE, 1994].
The concentration of  $CO_2$  ([CO<sub>2</sub>]) 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 that were fixed for this cruise because of malfunctioning of gas loops, "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 of the solution, "Run Time" is the length of coulometric titration (in minutes), and K is the conversion factor from counts to  $\mu$ mol which is dependent on the slope and intercept relation between instrument response and charge. For a unit with Ecal slope of 1 and intercept of 0, the constant is 2.0728 \* 10<sup>-4</sup>.

The blank values for AOML1 were in the range of 12.0-33.3 counts/min with an average value of 19.6 counts/min and a standard deviation of 6.8 counts/min. For AOML2 they were in the range of 12.0-30.0 counts/min with an average value of 21.7 counts/min and a standard deviation of 6.1 counts/min.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes prior to the cruise. The weights with the appropriate densities were used to determine the volume of the pipettes (AOML1: 28.726 cm<sup>3</sup> @ 19.96°C, AOML2: 22.623 cm<sup>3</sup> @ 22.63°C). Calculation of pipette volumes, density, and final CO<sub>2</sub> concentration were performed according to procedures outlined in the DOE CO<sub>2</sub> handbook (DOE, 1994).

#### C.3.2.2. Fugacity of CO<sub>2</sub> (fCO<sub>2</sub>)

#### Instrumentation

The fugacity of  $CO_2$  was measured on the A16N\_2003a cruise at a constant temperature of 20°C by equilibrating a 500-ml water aliquot in a volumetric flask with a closed headspace. The headspace is circulated through a non-dispersive infrared detector that measures both  $CO_2$  and  $H_2O$  levels. The analytical instrumentation is detailed in Wanninkhof and Thoning (1993) and is the same as the setup used in the N.Atl-93 cruise that occupied the same cruise line in 1993 (Castle et al., 1998).

The system is patterned after that of Chipman *et al.* (1993) with modifications as presented in Wanninkhof and Thoning (1993). In short, in the system a 500-ml water sample is equilibrated at ambient pressure with an 80-ml headspace in a thermostatted volumetric flask. The headspace is circulated through a non-dispersive infrared analyzer, NDIR, LICOR model 6262. Upon equilibration the circulation flow is stopped and 30 readings of  $H_2O$  content and  $CO_2$  content in the cell are taken over a 30-second interval and averaged. The system is a dual channel system where one equilibration occurs while circulating through the NDIR and a second flask is equilibrated offline. Once the first sample is analyzed the second flask is switched in line with the NDIR and the residual air in the NDIR is equilibrated with the second flask content. The second equilibration phase through the NDIR takes less time as a large part of the headspace already is equilibrated offline. The two-channel configuration decreases the total analysis time to about 20 minutes for two samples.

The system is calibrated after every eight samples with six gaseous standards traceable to the manometrically determined values of C. D. Keeling of Scripps Institute of Oceanography. The mole fractions of the standards used during the A16N2003a cruise were:

Tank number	mole fraction
CA05989	378.7 ppm
CA05980	792.5 ppm
CA05984	1036.9 ppm
CA05940	1533.7 ppm
CA05988	593.6 ppm
CA05998	205.1 ppm

The standards are also used as the headspace gas for the equilibration. Since the mole fractions of the gases in the headspace prior to equilibration are known, the small perturbation of the  $fCO_2$  in the water during the equilibration process can quantitatively be accounted for. The headspace gas is selected such that it is close the anticipated water value thereby minimizing the correction.

#### Data Reduction

The calculation of the fCO<sub>2</sub> involves several steps including the conversion of the NDIR output to an equivalent dried mole fraction of CO<sub>2</sub>, the correction for the perturbation of the fCO<sub>2</sub> in water by equilibration, and the small adjustment from the measurement temperature to 20°C. For the reduction of the A16N\_2003a fCO<sub>2</sub> we made an important adjustment in procedures. On previous cruises, the calibration of the samples that were run at 100 % water vapor pressure (@ 20°C) to the standards that are dry was done through an empirical algorithms created by running standards both wet and dry. For this cruise we relied on the internal correction from wet to dry mole fraction of CO<sub>2</sub> provided by the LI-COR 6262. This change is based on testing by our group and other investigators that showed that the correction provided by the instrument is of high quality and subject to less uncertainty than our empirical corrections. Since this is a fundamental change in our procedures we describe the old and new routine in detail below including comparison of the results.

The correction from detector output to (dry) mole fraction of  $CO_2$ ,  $XCO_2$  in the headspace was previously done by measuring the voltage output of the  $CO_2$  and  $H_2O$  channel. An empirical algorithm between dry standards and standards saturated with water vapor at 20°C was created of the form:

$$MVCO_2(dry) = MVCO_2 (wet) + A + B^*MVCO_2(wet) + C^*(MVCO_2(wet))^2$$

Where MV is the millivolt output of the  $CO_2$  channel and  $MVCO_2$  (wet) is the milli-volt value measured for the equilibrated headspace of the sample. From this algorithm the (water saturated) headspace gas is corrected to the dry state such that the samples can be directly related to the standard. The next step is the convert the  $MVCO_2(dry)$  of the sample to a  $XCO_2$  by creating a curve of  $MVCO_2(dry)$  vs.  $XCO_2$  using the standards preceding and following the samples. For each sample the three standards closest to the samples are selected and a second-order polynomial was created of  $MVCO_2$  vs.  $XCO_2$  by averaging the appropriate standards preceding and following the sample. The second- order polynomial is then used to calculate the  $XCO_2$  of the sample.

Following this step the fCO<sub>2</sub> in the headspace is calculated according to:

$$fCO_2 = XCO_2 (1-pH_2O) * 0.9966$$

Where pH<sub>2</sub>O is the water vapor pressure @  $20^{\circ}$ C (= 0.0226 atm) and 0.9966 is the conversion factor from pCO<sub>2</sub> to fCO<sub>2</sub> @  $20^{\circ}$ C.

The next step is the correction for change in the  $fCO_2$  in the water sample due to exchange of  $CO_2$  with the headspace during equilibration. This step is accomplished by using the mass balance criteria that the total amount of carbon in the headspace and water is conserved and by using the fact that the TA remains unchanged during equilibration. The DIC of the sample (determined independently) and the headspace gas concentration prior to equilibration along with the volume of water and headspace are used to calculate the total amount of carbon in the system. From the change in headspace  $CO_2$  before versus after equilibration the change the DIC in the water can then be determined. From this change and the TA (calculated from DIC and  $fCO_2$  after equilibration), the  $fCO_2$  in the water before equilibration can then be determined.

The final step is to correct the fCO<sub>2</sub> from analysis temperature to 20°C. The water samples are always equilibrated within 0.1°C of 20°C such that this correction is less than 0.4 % of the value. The correction for perturbation of the fCO<sub>2</sub> in the water during equilibration and the temperature correction to 20°C are performed using the carbonate dissociation constants and the temperature dependence of the constants and the calculation routines described in (Peng et al., 1987)

For A16N\_2003a the correction from the moist gas of the sample to an equivalent dry concentration was performed utilizing the internal correction routine built into the Li-6262 analyzer. This internal algorithm has been extensively checked by others and our tests showed that the correction was robust as well. The important advantage of this internal correction is that in our previous data reductions we assumed that the algorithm between wet and dry created in laboratory tests before the cruise or after the cruise does not change appreciably over time. This has proven not always to be the case. Secondly, the water vapor level measured during the standard runs can be appreciable despite absence of water vapor in the compressed gas standards since it takes a long time for the water vapor introduced by the equilibration of the samples to be flushed from the system. Therefore we see a decreasing trend of water vapor level when the six samples are run consecutively (see Figure 3).

The modified data reduction routine uses the  $XCO_2(dry)$  calculated by the detector for both standards and samples. A second-order polynomial fit is created between the actual mole fraction of  $CO_2$  in the standard and the instrument value. This standardization accounts instrument drifts over time. The detector was zeroed and spanned for  $CO_2$  every day while the water vapor channel was spanned right before the first leg and before the second leg. Standardizing the water vapor channel is difficult because of the "stickiness" of the water vapor leading to lags and very slow response times. A polynomial is created for the three standards closest to the sample by averaging the pertinent standards before and after the sample. The other steps of correcting for small temperature deviations of the water bath from 20°C and correction to  $fCO_2$  prior to equilibration are identical to the procedures outlined above.

The new correction routine results in small differences in values for calculated  $fCO_2$  compared to the previous data reduction routine. Table 6 shows a comparison for station 45. The values using the new reduction are systematically about 2 µatm lower than the old reduction method. The table also gives the results of two different water vapor correction algorithms. One empirical correction was established before the cruise and one determined from running wet vs. dry standards after the cruise. The results show differences in the range from 7 to 17 µatm.

#### Quality Control

During the cruise a total of 1515 Niskin samples were analyzed for  $fCO_2$ , compared to 2500 DIC samples. This was because only one full-time and a part -time operator were available for the work while two full-time analysts were involved in DIC analysis. A summary of the analysis statistics is given in Table 7.

The precision of the results is based on comparison of duplicate values and is estimated to be  $2 \mu atm$  or 0.3 % based on the results in Table 8. There is no apparent trend in imprecision with depth or absolute concentration when comparing absolute difference. The relative (%) difference is slightly higher for lower fCO<sub>2</sub> values found near the surface.

#### Deep-water comparison with the 1993 cruise (NAtl-93) and crossover with 1999 cruise (24N).

The A16N\_2003a cruise overlapped or intersected with two previous cruises that were sampled by our group. The NAtl-93 cruise (Castle et al., 1998) followed the same track and was occupied during the summer of 1993 but it was run from South to North. A 24- bottle rosette was used such that fewer depth samples were obtained and the spacing of the stations was nominal 1 degree compared to 1/2 degree spacing on the 2003 occupation.

The 24N-98 cruise was run in February and intersected the A16N\_2003a cruise near 24° N, 26.5° W. In the comparison we make the assumption that changes in deep water are negligible over the time period. The crossover with the 24 N cruise is shown in Figure 4. The fCO<sub>2</sub> shows a consistent offset with the 2003 data being about 18  $\mu$ atm higher than the 1998 data. For the comparison with the 1993 data we looked at the deep water offset in the deep water for stations spaced about 5 degrees apart (Figure 5). Again a systematic bias is observed with the 2003 data being higher. The magnitude of the bias however is about 10  $\mu$ atm. The cause of these offsets is disconcerting and attributed to the water vapor correction. However, the exact reason or possible corrections is not readily apparent.

The surface water  $fCO_2$  levels are measured with a different system in underway mode near sea surface temperature and offer an independent assessment of agreement of  $fCO_2$  values. However, the temperature correction has some uncertainties which complicate the comparison. For the comparison the  $fCO_2(20)$  values are corrected to SST as determined by the thermosalinograph using the empirical correction of  $\partial fCO_2/\partial T = 0.0423^{\circ}C^{-1}$  and by using the temperature dependence of the dissociation constant and using the thermodynamic equations. The results are shown in Figure 6 and show average differences of:

# $-3.30 \pm 4.9 \ \mu atm \ (n=76) \ for \ fCO_2(UW) - fCO_2(disc)Mehr$ and -6.66 $\pm 4.1 \ \mu atm \ (n=76) \ for \ fCO_2(UW) - fCO_2(disc) 4.23\%$ .

In case of  $fCO_2(UW)$ -  $fCO_2(disc)Mehr$ , the  $fCO_2(20)$  are normalized to sea surface temperature using the Mehrbach constants as refit by Dickson and Millero. For  $fCO_2(UW)$ - $fCO_2(disc)4.23\%$ ., the  $fCO_2(20)$  are normalized to SST using the empirical relationship of  $0.0423^{\circ}C^{-1}$ . Again our temperature corrected discrete data are on average higher than the underway measurements. The differences  $CO_2(UW)$ - $fCO_2(disc)Mehr$  and  $fCO_2(UW)$ - $fCO_2(disc)4.23\%$  are plotted against temperature in Figure 7. There is a slight trend with temperature for the adjustments using the Mehrbach constants. Also, near 20°C when the adjustment is small the comparison shows that the discrete data is systematically higher. For the range from 18 to 22°C the difference is -5.1 ± 4.9µatm ( n=76) and -6.7 ± 4.1 µatm ( n=76) for  $fCO_2(UW)$ - $fCO_2(disc)Mehr$  and  $fCO_2(UW)$ - fCO<sub>2</sub>(disc)4.23% very similar to the average difference over the entire temperature range suggesting that the systematic offset is not attributable to the temperature correction alone.

#### C.3.2.3. Total Alkalinity (TA)

Seawater samples were drawn from the "Niskin" bottles with a 40-cm length of silicon tubing. One end of the tubing was fit over the petcock of the "Niskin" bottle and the other end was inserted into the bottom of a 500-ml Corning glass-stoppered sample bottle. The sample bottle was rinsed three times with approximately 300 ml of seawater. The sample bottle was slowly filled from the bottom. Once filled, the sample bottles were kept in a constant water bath at 25°C for half-hour before analysis.

The titration system used to determine TA consisted of a Metrohm 665 Dosimat titrator and an Orion 720A pH meter controlled by a personal computer (Millero et al., 1993). The acid titrant, in a water-jacketed burette, and the seawater sample, in a water-jacketed cell, were kept at  $25\pm0.1^{\circ}$ C with a Neslab constant-temperature bath. The Plexiglas water-jacketed cells were similar to those used by Bradshaw et al. (1988), except that a larger volume (200 ml) was used to increase the precision. The cells had fill and drain valves with zero dead-volume to increase the reproducibility of the cell volume.

The HCl solutions used throughout the cruise were made, standardized, and stored in 500 cm<sup>3</sup> glass bottles in the laboratory for use at sea. The 0.23202 M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater ( $\approx 0.7$  M). The acid was standardized using a coulometric technique by the Univ. of Miami and by Dr. Dickson of Scripps Institution of Oceanography (SIO). The two standardization techniques agreed to +/-0.0001 N.

The volume of HCl delivered to the cell is traditionally assumed to have a small uncertainty (Dickson, 1981) and is equated with the digital output of the titrator. Calibrations of the Dosimat burettes with Milli Q water at 25°C indicated that the systems deliver 3.000 ml (the value for a titration of seawater) to a precision of 0.0004 ml. This uncertainty resulted in an error of 0.4  $\mu$ mol/kg in TA.

The titrators were calibrated in the laboratory before the cruise. Certified standard Reference Material (CRM) **Batch 59** prepared by Dr. Dickson was used at sea to monitor the performance of the titrators. All TA data have been corrected based on CRM values for each cell and each leg. (Millero et al, 2000), see Table 9.

### С.3.2.4. рН

Seawater samples were drawn from the "Niskin" bottles with a 20-cm length of silicon tubing. One end of the tubing was fit over the petcock of the "Niskin" bottle and the other end was attached over the opening of a 10-cm glass spectrophotometric cell. The spectrophotometric cell was rinsed three to four times with a total volume of approximately 200 ml of seawater; the Teflon endcaps were also rinsed and then used to seal a sample of seawater in the glass cell. While drawing the sample, care was taken to make sure that no air bubbles were trapped within the cell. The sample cells were kept in a waterbath at 20°C for a half an hour before analysis.

Seawater pH was measured using the spectrophotometric procedure (Byrne, 1987) and the indicator calibration of Clayton and Byrne (1993). The indicator was an 8.0-mM solution of m-cresol purple sodium salt ( $C_{21}H_{17}O_5Na$ ) in MilliQ water.

The absorbance measurements were made using a Varian Cary 2200 spectrophotometer. The temperature was controlled to a constant temperature of  $25^{\circ}$ C with an Endocal RTE 8DD refrigerated circulating temperature bath that regulates the temperature to  $\pm 0.01^{\circ}$ C. The temperature was measured using a Guildline 9540 digital platinum resistance thermometer.

### C.3.2.5 Oxygen

#### Method

The analytical method for dissolved oxygen in seawater during A16N 2003a cruise was based on automated Winkler titration by Williams and Jenkinson (1982) and modified by Friederich et al. (1991). Dissolved oxygen samples were withdrawn from 10-L Niskin bottles to 145-ml Pyrex brand iodine flasks (Corning 5400, Corning, New York, USA). The exact volume of each flask at room temperature had been gravimetrically calibrated with its ground glass stopper following standard procedures (DOE, 1994; WHP Operations and methods, 1991). One ml of manganese chloride reagent and one ml of alkaline iodide reagent were added to each sample in the iodine flasks and its stopper was placed in the bottle neck. The bottles were shaken vigorously for about one minute to completely fix oxygen with manganese hydroxide. In this method, dissolved oxygen in the sample reacts with manganese hydroxide to form Mn(OH)<sub>3</sub> precipitate. Particulate Mn(OH)<sub>3</sub> dissolve upon the acidification and resulting Mn<sup>3+</sup> oxidize iodide to iodine in acidic solution. The liberated iodine complex with excess iodide forming I<sub>3</sub> and the latter is titrated with a sodium this ulfate solution that is standardized by a primary standard potassium iodate. The complex  $I_3$ has a maximum absorbance at 352 nm and change in absorbance of I<sub>3</sub> at 352 nm is used to detect the end point. A custom-build automated oxygen titrator with MS DOS interfacing software was used to determine dissolved oxygen concentrations in the samples.

A total of 5011 seawater samples were taken from 150 stations and analyze for dissolved oxygen concentrations. At the beginning of cruise, a test CTD cast was made by sampling 20 Niskin bottles from same depth (170 m). Analysis of these samples was listed in Table 10 and indicate a precision of 0.3 micromole/L. Throughout the cruise duplicate samples from same Niskin bottle were collected at each station to estimate the precision of overall measurement (sampling and analysis). Analyses of 300 replicate samples listed in Table 11 indicated that the precision of shipboard automated Winkler titration is 0.29 including all outliers and 0.24 micromole/L excluding the outliers. Analysis of outliers indicated that most outliers in duplicate analysis were due to errors in the volumes of oxygen bottles if it is not a problem with Niskin bottles or sampling error. The outliers in vertical profiles of oxygen were also used to identify the bottles that might have errors in volumes. Total of 33 sample bottles were recalibrated and 11 of them had volume errors greater than 0.3 ml (Table 12). This accounts about 5 % of sample bottles used during the A16N cruise. The volumes of such identified questionable oxygen bottles were recalibrated after the cruise and dissolved oxygen concentrations were recalculated for those samples using correct volumes.

The primary iodate standard solution was prepared from high purity reagent grade  $KIO_3$  (Mallinckrodt, USA), pre-dried in an oven at 110°C for overnight and cooled in a desiccator before weighing. The thiosulfate solution was prepared from reagent grade  $Na_2S_2O_3 \cdot 5H_2O$  (Mallinckrodt,

USA). During the cruise, total of 25 bottles of thiosulfate solutions (1 liter each) were consumed for oxygen analyses. Each new bottle of thiosulfate solution was first standardized by the primary standard KIO<sub>3</sub> solution before using it for sample titration. Standardizations of the thiosulfate solutions were performed by titration of known amounts of KIO<sub>3</sub> solution (usually 2, 4, 6, and 8 ml). Regression analysis of four titration points generates a slope (factor) and an intercept (blank) from which sample concentration are calculated. Extending KIO<sub>3</sub> solution to 20 ml produced essentially the same calibration curve as shown in the thiosulfate bottle 21 in Table 13. Each bottle of thiosulfate usually lasts for 2 to 3 days of sample titration. The thiosulfate bottle 24 had replicate standardization. The thiosulfate bottle 19 was standardized at the beginning and the end of its life span to check its stability during storage. All the replicate analyses produced acceptable results within uncertainty of standardization as shown in Table 13. It should be pointed out that at beginning of cruise there are several standardizations with lower slopes and larger intercepts as shown in Figure 8. These were attributed to malfunction of titration system used during that period. When system is functioning properly it produced slopes within 1% of the theoretical value of 24.818 and intercepts less than  $\pm 0.01$  as shown in most part of cruise in Figure 8.

At the beginning of leg 2 (from stations 72 to 79) a problematic automatic pipette was used to deliver the  $KIO_3$  standard solution for standardization of thiosulfate solution in bottle 14. An unusually high slope was observed and this pipette was not used in subsequent analyses. Shipboard and post cruise comparison indicated that there is an error in volume delivery of this automatic pipette. Dissolved oxygen concentrations from station 72 to 79 have been corrected for errors in volume delivery of iodate solution by this automatic pipette used in the standardization of thiosulfate solution. A correction factor (1.0153) was estimated based on post-cruise recalibration of the automatic pipette as shown in Table 14 and was applied to data from station 72 to 79.

Since the Dosimat titrators have demonstrated high precision and accuracy (0.05 and 0.2% at delivery of 10ml solution, respectively) in volume delivery of titrants, we recommend use a Dosimat or similar positive displacement burette to quantitatively dispense the iodate standard solution in the future cruises. This procedure can improve the accuracy of shipboard oxygen analysis.

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Figure 1: Cruise track for the Atlantic Ocean A16N\_2003a cruise in June-August 2003



	Average	Sluev
Surface Water	1.0	0.9
1000 m	1.2	0.8
Deep Water	1.4	0.9

Figure 2: DIC duplicates



**Figure 3:** Change in water vapor concentration (in millivolts) when a set of 6 (dry) standards are run showing that some residual water vapor remains in the lines after water samples are equilibrated . Water samples which show an H<sub>2</sub>O response of about 2200 mV.



**Figure 4:** Comparison of fCO<sub>2</sub> (20) profiles for a crossover location between a cruise in 1998 and the A16N\_2003a cruise

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Figure 5: Comparison of deep-water fCO<sub>2</sub> values for a cruise in 1993 and the A16N\_2003a cruise at a depth range of 4000 to 5000 m



**Figure 6:** Comparison of underway  $fCO_2$  measurements (line) with the discrete samples normalized to the same temperature as the underway measurements using an empirical relationship of 4.23 % °C<sup>-1</sup> (diamonds) and the constants of Mehrbach (open squares).



**Figure 7:** Difference in underway  $fCO_2$  measurements and with the discrete samples normalized to the same temperature as the underway measurements using an empirical relationship of 4.23 % °C<sup>-1</sup> (open squares) and the constants of Mehrbach (solid squares).



**Figure 8:** Shipboard standardization of thiosulfate solution during A16N\_2003a cruise: slopes in the upper panel and intercepts in the lower panel.



## Table 1: Principal Investigators

Project	Name	Institution
CTD	Gregory Johnson	PMEL
Salinity	Gregory Johnson	PMEL
CTD/O2	Gregory Johnson	PMEL
Chlorofluorocarbons (CFCs)	John Bullister	PMEL
Chlorofluorocarbons (CFCs)	Mark Warner	UW
HCFs	Shari Yvon-Lewis	AOML
Total CO <sub>2</sub> (DIC), pCO <sub>2</sub>	Richard Feely	PMEL
Total CO <sub>2</sub> (DIC), pCO <sub>2</sub>	Richard Wanninkhof	AOML
Nutrients	Calvin Mordy	PMEL
Nutrients	Jia-Zhong Zhang	AOML
Dissolved Oxygen	Jia-Zhong Zhang	AOML
Helium/tritium	Peter Schlosser	LDEO
Total Alkalinity	Frank Millero	Miami
pH	Frank Millero	Miami
Trace Metals	Christopher Measures	Hawaii
Trace Metals	William Landing	FSU
Aerosols	William Landing	FSU
ADCP	Eric Firing	Hawaii
ALACE Float deployment	Breck Owens	WHOI
ALACE Float deployment	Silvia Garzoli	AOML
PIC/POC	Jim Bishop	LBNL
DOC	Dennis Hansell	Miami
13-C, 14-C	Ann McNichol	WHOI
Alkyl Nitrate	Eric Saltzman	UCI
Bathymetry	Ship personnel	
Underway thermosalinograph	Ship personnel	

			Leg			
Position	Name	Institution	Nationality	0	1	2
Chief Scientist	John Bullister	PMEL	US		*	*
Co-Chief Scientist	Nicolas Gruber	UCLA	Swiss		*	*
Data Manager	Frank Delahoyde	SIO	US		*	*
Grad Student	Nicole Lovenduski	UCLA	US			*
Grad Student	Elena Brambilla	SIO	Italy		*	
Grad Student	Regina Cesario	UW	US		*	
CTD Data Processor	Kristene McTaggart	PMEL	US		*	*
ET	Douglas Anderson	AOML	US		*	
ET	David Bitterman	AOML	US			*
LADCP	Julia Hummon	UH	US		*	*
Salinity	Gregory Johnson	PMEL	US		*	
Salinity	David Wisegarver	PMEL	US			*
02	George Berberian	AOML	US		*	*
Nutrients	Jia-Zhong Zhang	AOML	US			*
Nutrients	David Wisegarver	PMEL	US		*	
Nutrients	Charles Fischer	AOML	US			*
Nutrients	Calvin Mordy	UW-JISAO/PMEL	US		*	
CFC	Mark Warner	UW	US		*	*
CFC	Eric Wisegarver	PMEL	US		*	*
Helium/Tritium	U	LDEO			*	*
HCFC	Shari Yvon-Lewis	AOML			*	*
Alkalinity & pH	Xiaorong Zhu	UM	China		*	*
Alkalinity & pH	Taylor Graham	UM	US	*	*	
Alkalinity & pH	Mike Trapp	UM	US			*
Alkalinity & pH	Vanessa Koehler	UM	US	*	*	*
Alkalinity & pH	William Hiscock	UM	US	*	*	
Alkalinity & pH	David Sergio Valdes	UM	Mexico			*
Alkalinity & pH	Denis Pierrot	UM	France	*		
DIC1	Esa Peltola	AOML	US		*	*
DIC2	Robert Castle	AOML	US		*	*
pCO <sub>2</sub>	Dana Greeley	PMEL	US		*	*
pCO <sub>2</sub>	Kevin Sullivan	UM-CIMAS/AOML	US	*		
Trace Metal	Chris Measures	UH	Chile		*	*
Trace Metal	Rodrigo Torres	WHOI	US	*	*	*
Trace Metal	Matt Brown	UH		*		
Aerosol	William Landing	FSU	US	*	*	*
Aerosol	Clifton Buck	FSU	US	*	*	*
Aerosol	Erik Kvaleberg	FSU	Norway	*		
Aerosol	Anthony Arguez	FSU	US	*		
POC/PIC	lim Rishon	LBNL	US		*	
POC	Alexev Mishonov	TAMU	Ukraine		*	
DOC	Stacy Brown	UM	US		*	
Alkyl Nitrate	Elizabeth Dahl	UCI				
CIRIMS-IR-SST	Trina Litchendorf	UW	US	*		
		1	~~	L. C. C.	I	

#### Table 2: Cruise Personnel

The Chief Survey Technician aboard the *R/V Ronald Brown* for the cruise was Jonathan Shannahoff.

## **Table 3:** Participating Institutions

Institution		Address
NOAA, Atlantic Oceanographic and	AOML	4301 Rickenbacker Causeway,
Meteorological Laboratory		Miami, FL 33149-1098
Florida State Univ.	FSU	0102 OSB, West Call Street
Department of Oceanography		Tallahassee, FL 32306
EO Lawrence Berkeley National Laboratory	LBNL	1 Cyclotron Road
		Berkeley, California 94720
The Lamont-Doherty Earth Observatory	LDEO	61 Route 9W
		Palisades, NY 10964-1000
NOAA, Pacific Marine Environmental	PMEL	7600 Sand Point Way NE
Laboratory		Seattle, WA 98115-0070
Scripps Institution of Oceanography	SIO	8602 La Jolla Shores Drive
		La Jolla, CA. 92037
Texas A&M Univ., Department of Oceanography	TAMU	College Station, TX 77843-3146
Univ. of California, Irvine, Earth System Science	UCI	Irvine, CA 92697-3100
Univ. of California, Institute of Geophysics and	UCLA	5853 Slichter Hall,
Planetary Physics & Dept. of Atmospheric Sci		Los Angeles, CA 90095-1567
Univ. of California, San Diego	UCSD	9500 Gilman Drive
		La Jolla, CA 92093 - 0214
Univ. of Hawaii, Department of Oceanography,	UH	1000 Pope Rd, Marine Sci. Bldg,
Univ. of Hawaii at Manoa		Honolulu, HI 96822
Univ. of Miami	UM	4301 Rickenbacker Causeway,
		Miami, Florida 33149
Univ. of Miami/Cooperative Institute for	UM-CIMAS	4301 Rickenbacker Causeway,
Marine and Atmospheric Studies		Miami, Florida 33149
Univ. of Washington	UW	Box 357940, Seattle,
		WA 98195-7940
Univ. of Washington/Joint Institute for	UW-JISAO	Box 357940, Seattle,
Study of the Atmosphere and Ocean		WA 98195-7940
Woods Hole Oceanographic Institution	WHOI	Co-op Building, MS #16
		Woods Hole, MA 02543

#### **Table 4:** Dissolved Inorganic Carbon Duplicate Statistics

	BB	BM	ME	BE	DC	DI	BEBE	MM	EE	Deleted
Average:	0.8	1.3	1.2	1.3	1.4	0.7	-	1.3	1.0	
Stdev:	0.80	0.94	0.57	1.27	0.86	0.42	-	1.01	0.30	
Number:	94	39	13	8	56	3	0	6	3	64
Total:	286									

#### **Duplicate Statistics:**

BB The duplicate samples were measured back-to-back

BM One duplicate was measured in the beginning and the other one in the end of the cell

ME One duplicate was measured in the middle and the other one in the end of the cell

BE One duplicate was measured in the beginning and the other one in the end of the cell

DC The duplicates were run on a same instrument, but on different cells

DI The duplicates were run on different instruments

BEBE Both duplicates were measured in the beginning of the cell, but not back-to-back

MM Both duplicates were measured in the middle of the cell, but not back-to-back

EE Both duplicates were measured in the end of the cell, but not back-to-back

Station#	Cast#	Bottle#	Pressure/db	DIC µmol/kg	Stdev
1	1	1	200	2145.9	0.38
1	1	11	2	2099.3	1.71
2	1	1	553	2157.6	0.36
2	1	18	2	2105.8	0.86
3	1	1	1,009	2157.6	1.23
5	1	1	1,816	2161.5	0.81
5	1	8	1,000	2157.2	1.23
6	1	29	2	2085.1	1.11
7	1	29	2	2079.5	0.15
8	1	30	2	2068.8	0.52
10	1	32	2	2064.4	0.16
11	1	12	1.051	2168.3	0.72
11	1	33	3	2064.7	1.19
12	1	32	2	2062.6	0.25
13	1	33	2	2063.3	0.86
15	1	1	1.647	2161.9	0.50
15	1	27	2	2090.1	0.60
16	1	1	1.168	2172.1	0.70
17	1	21	2	2082.7	0.87
19	1	1	1 464	2159.3	1 70
21	1	26	9	2088.8	0.54
22	1	25	6	2083.1	0.17
23	1	1	1 418	2160.7	0.05
24	1	31	3	2088 7	0.02
25	1	1	2,706	2190.1	0.01
25	1	26	125	2128.7	0.03
25	1	32	2	2080.1	1.84
26	1	33	3	2090.8	0.22
27	1	1	3 812	2203.2	0.18
27	1	13	1 050	2166.7	0.80
29	1	14	1 100	2172.0	0.51
29	1	35	20	2086 3	1 75
30	1	33	2	2082.2	0.74
31	1	1	4 472	2204.0	1 60
31	1	13	1 050	2180.3	0.49
32	1	35	2	2075.3	0.98
33	1	1	4.482	2201.4	0.27
33	1	14	1.002	2177.5	0.49
34	1	33	3	2072.3	0.60
36	1	24	8	2079.6	0.34
41	1	20	1.001	2180.5	0.13
41	2	24	4	2069 7	0.50
42	1	23	25	2070 1	0.05
43	1	1	4 066	2197.4	0.75
43	1	14	1 003	2182.1	1 45
43	1	35	4	2070.2	0.25
-J	1	55	Т	2070.2	0.40

 Table 5: Dissolved Inorganic Carbon (DIC) Duplicates

	115
44 2 32 3 2067	.4 0.03
45 1 1 5.240 2200	0.0 0.53
45 1 14 1,001 2184	.3 1.73
45 1 35 3 2067	0.68
46 1 33 3 2067	2.01
47 1 1 2,458 2169	0.3 1.26
47 1 10 1.049 2192	2.6 1.47
47 1 31 3 2068	0.28
48 2 30 3 2070	0.7 0.49
49 1 1 4,775 2197	.9 1.64
51 1 15 1.046 2190	0.3 0.05
51 1 35 3 2069	0.7 2.05
52 1 1 4,734 2198	3.0 1.72
52 1 33 4 2069	0.9 0.91
53 1 1 4.826 2201	.0 1.04
53 1 14 900 2179	03 110
$\frac{1}{53}$ $\frac{1}{1}$ $\frac{32}{19}$ $\frac{19}{2066}$	0.53
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2 1.82
<u>55</u> 2 1 5218 2200	0.6 0.14
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.0 - 0.11
$\frac{1}{55}$ $\frac{1}{2}$ $\frac{1}{30}$ $\frac{92}{92}$ $\frac{2099}{2099}$	$\frac{1}{0.15}$
$\frac{55}{55}$ 2 35 4 2085	9 0.29
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.2
$\frac{57}{57}$ 2 35 4 2086	4 0.60
$\frac{57}{58}$ $\frac{1}{1}$ $\frac{35}{35}$ $\frac{4}{4}$ 2092	6 2.11
<u>59 1 15 1051 2194</u>	2 1 71
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 1 04
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\frac{1}{6}$ 0.32
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5 0.26
61 2 17 992 2185	0.20
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9 0.67
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\frac{1}{4}$ 0 30
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.1 0.71
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0 0 01
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 0.93
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 1.43
65 1 1 5.343 2198	0.36
<u>65 1 33 3 2109</u>	1.39
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5 0.78
67 2 1 5.252 2200	0.5 0.72
<u>67 2 17 951 2190</u>	0.2 1.62
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 1 84
68   1   17   942   2186	1.0
68   1   35   3   2100	0.62
<u>69 1 1 5317 2199</u>	0.7 2.33
69   1   14   1.002   2187	.6 0.54

**Table 5:** Dissolved Inorganic Carbon (DIC) Duplicates (continued)

Station#	Cast#	Bottle#	Pressure/db	DIC µmol/kg	Stdev
69	1	35	4	2101.5	0.27
70	1	33	3	2103.2	0.02
71	1	1	5.332	2199.4	0.99
71	1	17	951	2186.6	0.59
71	1	35	3	2103.0	0.17
72	2	1	5.332	2198.1	0.41
72	2	17	950	2188.8	0.57
72	2	31	65	2095 3	0.92
72	2	35	3	2109.7	1.77
74	1	1	5.275	2199.4	1.87
74	1	14	1.000	2191.4	0.40
74	1	35	4	2111.0	1.54
75	1	35	3	2111.9	0.63
76	1	1	5.306	2198.7	0.80
76	1	13	1.050	2197.3	1.86
76	1	35	4	2112.4	0.05
78	2	1	5.329	2193.8	1.01
78	2	35	3	2103.6	0.05
79	1	35	3	2109.9	0.55
80	1	14	1 000	2196.4	0.57
80	1	35	3	2108.1	0.17
81	1	35	4	2096 7	0.65
82	2	1	5.491	2201.1	0.17
82	2	17	949	2195.7	0.52
82	2	35	4	2100.5	0.04
83	1	35	4	2101.6	0.36
84	1	1	5.551	2202.9	0.88
84	1	17	950	2205.3	0.90
84	1	35	4	2102.1	1.65
85	1	35	4	2097.5	1.73
86	1	35	3	2100.1	0.09
87	1	35	4	2082.8	0.56
88	2	1	5.528	2201.2	0.34
88	2	17	949	2209.3	0.59
88	2	35	4	2086.0	1.88
89	1	35	3	2083.5	0.72
90	1	1	5.125	2198.7	1.31
90	1	14	1 000	2209.0	2.12
91	1	35	3	2065.0	0.53
92	1	1	4.874	2201.0	1.05
92	1	12	1.050	2208.2	1.57
92	1	35	4	2064.0	2.10
94	2	1	4.632	2200.6	0.55
94	2	33	3	2062.8	0.29
95	1	35	4	2064 9	0.47
96	1	1	4.612	2202.5	2.00
20	-	-	.,012		00

**Table 5:** Dissolved Inorganic Carbon (DIC) Duplicates (continued)

Station#	Cast#	Bottle#	Pressure/db	DIC µmol/kg	Stdev
96	1	15	950	2216.7	1.24
96	1	35	3	2055.3	0.08
97	1	33	3	2063.7	0.82
98	2	13	1,000	2211.4	0.77
98	2	33	4	2035.1	0.49
100	2	1	3,892	2203.1	0.68
100	2	12	1,050	2220.2	0.19
100	2	33	4	2048.2	0.14
101	1	35	3	2035.8	0.09
104	2	1	5,534	2207.5	1.41
104	2	20	548	2240.9	0.10
104	2	35	3	2040.4	0.24
105	1	35	3	2025.6	0.54
106	2	1	5,796	2198.2	1.94
106	2	35	4	2026.5	0.21
107	1	35	3	2013.5	0.20
108	1	1	5 798	2199.3	0.69
108	1	15	749	2238.0	1.96
108	1	35	3	2018.2	0.69
109	1	35	3	2028.2	0.04
110	2	1	6 071	2198.1	0.01
110	2	35	3	2026.0	0.03
111	1	35	3	2019.1	0.03
112	1	1	5 446	2201.7	0.23
112	1	17	950	2226.5	0.64
112	1	35	3	2004.8	1.92
112	1	35	3	1977.0	0.73
114	1	1	5 296	2205.2	0.96
114	1	14	1 001	2203.2	0.50
114	1	33	20	1978 5	0.50
116	2	1	5 162	2206.6	2 36
116	2	20	424	2200.0	0.18
116	2	35	3	1955.0	0.10
117	1	35	4	1953.3	0.52
118	2	1	4 422	2193.1	2 31
118	2	13	1,000	2195.1	0.83
118	2	33	3	1954.8	0.05
110	1	35	3	1951.0	0.10
120	1	1	4 358	2193.9	1.04
120	1	20	449	2238.3	0.26
120	1	35	<u></u>	1944 9	1.08
120	1	35	3	1948 3	0.28
121	2	1	4 577	2197.4	0.20
122	2	13	1 051	2177.4	0.03
122	2	33	1,031	1986 5	0.30
122	1	35	10	1987.8	1 40
143	1	55	4	170/.0	1.40

**Table 5:** Dissolved Inorganic Carbon (DIC) Duplicates (continued)

Station#	Cast#	Bottle#	Pressure/db	DIC µmol/kg	Stdev
124	1	1	4,088	2195.7	0.12
124	1	35	3	1987.2	0.63
125	1	35	3	1986.0	0.96
126	2	18	550	2218.4	1.62
126	2	33	10	1986.7	0.26
127	1	35	3	1989.8	0.16
128	1	1	3,803	2191.6	0.97
129	1	1	3,932	2194.4	2.15
129	1	13	999	2217.2	0.09
129	1	35	4	1987.8	2.23
130	1	35	3	1995.2	0.45
131	1	1	3,678	2191.5	1.51
132	1	1	3,358	2186.2	1.64
132	1	12	1,052	2212.8	0.68
132	1	33	3	2038.5	1.27
133	1	33	19	2042.0	0.33
134	1	35	4	2043.1	0.28
135	1	1	3,231	2185.0	1.00
135	1	12	1,000	2216.5	0.06
135	1	33	4	2044.8	0.15
136	1	32	3	2044.9	0.02
137	1	33	3	2048.5	1.54
138	2	1	3,187	2182.0	0.95
138	2	11	1,049	2214.8	1.10
138	2	32	3	2049.6	0.21
141	1	1	5,019	2257.0	1.09
141	1	15	1,000	2216.5	0.56
141	1	35	3	2040.2	0.80
144	2	1	5,410	2257.3	0.23
144	2	14	1,050	2215.4	0.10
144	2	35	3	2037.1	0.59
146	1	17	1,000	2215.3	0.21
146	1	35	4	2024.2	2.17
148	2	1	5,807	2255.9	0.61
148	2	17	950	2215.0	1.66
148	2	35	4	2017.4	0.31
150	1	18	1,000	2214.9	0.72
150	1	35	4	2020.1	0.58

 Table 5: Dissolved Inorganic Carbon (DIC) Duplicates (continued)

Keyfield	Lat(N)	pressure	fCO <sub>2</sub> (20) (final)	fCO <sub>2</sub> (20) (cruise)	fCO <sub>2</sub> (20) (newH <sub>2</sub> O)
45101	43	5239.7	762.9	765.80	745.8
45102	43	4994.3	765.7	768.80	748.5
45103	43	4499.7	769.5	771.45	751.7
45104	43	3983.9	768.5	770.30	751.8
45106	43	3001.5	758.4	760.50	742.1
45108	43	2000.5	755.2	756.60	738.6
45109	43	1800.0	761.4	762.90	745.3
45111	43	1401.5	746.0	747.80	729.8
45112	43	1200.0	728.4	730.10	712.9
45114	43	1001.0	724.1	725.70	708.1
45115	43	900.3	728.7	730.40	713.2
45116	43	800.7	712.4	714.00	696.6
45117	43	699.6	712.3	713.80	696.9
45118	43	601.3	687.2	689.00	672.7
45119	43	501.0	635.2	637.20	621.3
45121	43	401.1	576.8	578.60	563.8
45123	43	299.7	556.3	557.90	543.4
45125	43	201.0	510.7	512.10	499.1
45127	43	151.0	507.8	509.00	495.7
45129	43	99.7	494.1	495.30	482.3
45130	43	79.6	486.6	487.80	474.8
45131	43	60.0	482.2	483.40	471.7
45132	43	39.5	450.7	451.80	440.2
45133	43	19.9	381.9	384.20	374.2
45135	43	3.4	374.7	375.30	365.6

**Table 6:** Comparison of results of different water vapor correction routines

 $fCO_2(20)(final)$  final data reduction using the detector  $XCO_2$  (dry) output

 $fCO_2(20)$ (cruise) data reduction on cruise using an empirical water vapor correction

fCO<sub>2</sub>(20)(new H<sub>2</sub>O) data reduction in Jan 2004 using an empirical water vapor correction that was determined post-cruise

**Table 7:** Analysis statistics for fCO<sub>2</sub>(20)

Total number of stations	150
Total number of stations sampled for fCO <sub>2</sub> (full depth)	67
Total number of Niskin bottles tripped	4823
Total number of Niskin bottles sampled for fCO <sub>2</sub>	1522
Number of duplicates	140
Number of bad values	6
Number of questionable values	48

Key number	Depth	Dif. (uatm) %	Dif.	Ave.	# samples	Comment
1101	200.1	44	0.7	644	2	B
1111	200.1	4	0.8	503.1	2	B
5108	999.7	5	0.7	718.9	2	B
9112	1199.8	4.8	0.6	781	2	В
9133	20.5	0.4	0.1	435.8	2	C
10131	19.8	0.3	0.1	409.0	4	A & B, 4 bottles
13105	2101	4.6	0.6	758	2	В
17103	799.7	4.2	0.6	749.6	2	В
18125	3.1	2.5	0.6	453.45	2	В
25106	1700.4	0	0.0	770.8	2	С
25107	1500.5			770.8	1	B, 1 dup bad
26135	2.3	3.6	0.8	453.2	2	B
28235	2.2			424.4	1	B, 1 dup bad
33102	4000.4	1.7	0.2	775.15	2	B
33135	2.5			384	1	B, 1 dup bad
41121	893.9	2.8	0.4	737.9	2	С
43105	3000.8	1.3	0.2	760.15	2	В
45103	4499.7	1.8	0.2	769.5	2	В
45125	201	0.8	0.2	510.7	2	В
45133	19.9	3.2	0.8	381.9	2	В
47103	1999.7	4.2	0.6	751.2	2	В
47113	748.8	3.5	0.5	707.85	2	В
49111	1199.7	2.2	0.3	701.3	2	В
49126	149.4			507.7	1	B, 1 dup bad
49132	20.3	3.9	1.0	371.75	2	В
51113	1457.1	0.5	0.1	750.05	2	В
51135	2.9	2.9	0.8	356.8	2	В
52133	3.6			358.9	1	B, 1 dup bad
53112	1099.9	2.5	0.3	715.4	2	В
53120	400.3	6.4	1.1	571.9	2	В
54104	4304.7	0.5	0.1	762.5	2	В
54111	1437.6	2.5	0.3	715.4	4	A & B, 2 bottles dup
54135	2.8			357.3	1	B, 1 dup bad
56133	3.2	3.3	0.9	359.7	2	В
57205	2492.3	3.3	0.4	745.0	2	В
57221	398.7	1.4	0.2	597.1	2	В
61204	4297.4	1.9	0.2	763.2	2	В
61215	1300.5	2.9	0.4	740.4	2	В
61230	100.7	1.6	0.4	409.8	2	В
63202	4999.8	1.7	0.2	765.4	2	B
63214	1050.6	1.4	0.2	725.8	2	В
65102	5001.8	2.4	0.3	765.4	2	В
65108	2000.5	3.8	0.5	735	2	В
65114	1099.3	0.6	0.1	766.9	2	В
67203	4707.3	3.4	0.4	770	2	В
67216	1100.5	1.5	0.2	729.1	2	В
67218	800	3.3	0.5	732.2	2	В

**Table 8:** Table of pCO<sub>2</sub> duplicate values

Key number	Depth	Dif. (µatm) %	Dif.	Ave.	# samples	Comment
69104	4000.4	2.5	0.3	765.3	2	В
69106	2999.5	0	0.0	757.1	2	В
69112	1199.3	2.7	0.4	739.3	2	В
71107	3349.7			761.5	1	B, 1 dup bad
71110	2650.8	1.8	0.2	751	2	B
71113	1750	0	0.0	731.2	2	В
72207	3549.7	0.3	0.0	760.5	2	В
72210	2650.2	0.2	0.0	750.8	2	В
72213	1749	1	0.1	733.7	2	В
74103	4500.1	0.1	0.0	766.4	2	В
74107	2500.1	4.6	0.6	752.2	2	В
75135	3.2	0.9	0.3	331.3	2	В
76103	4244.4			760.2	1	B, 1 dup bad
76107	2248.6	1.9	0.3	749.4	2	В
76110	1499.2	1.2	0.2	764.5	2	В
78202	5000	3.4	0.4	765.1	2	В
78206	2998.9	0.3	0.0	755.9	2	В
80102	4150	7.1	0.9	758.3	2	В
80106	2949.8	0.3	0.0	755.1	2	В
80110	1750.6	0.8	0.1	762.8	2	В
80126	190	0.3	0.1	420.1	2	В
82203	4747.8	1.3	0.2	766.4	2	В
82207	3549	0	0.0	761.6	2	В
84102	5299.6	2	0.3	770.5	2	В
84106	3799.5	0.6	0.1	768.1	2	В
84112	1899.2	0.6	0.1	765	2	В
84116	1099.9	0.4	0.0	897.9	2	В
86101	5611.2	1.8	0.2	766.1	2	В
86105	4399.6	2.1	0.3	765.6	2	В
88204	4449.5	0.3	0.0	766.5	2	В
88206	3849	1.7	0.2	763.0	2	В
88217	949.2	1.9	0.2	1002.1	2	В
90105	3499.8	3.9	0.5	761.6	3	A & B
90115	898.3	3.3	0.3	1078.4	2	В
94203	4002	0.4	0.1	764.8	2	В
94206	2499.6	0.9	0.1	764.45	2	В
94215	799.2			1151.3	1	B, 1 dup bad
96103	4150.3	0.7	0.1	766.95	2	В
96106	3250.3	0.9	0.1	765.55	2	В
98203	3997.9			770.4	1	B, 1 dup bad
98205	2996.7			757.4	1	B, 1 dup bad
100204	2797.3			756.4	1	B,1 dup bad
100206	2200	0.4	0.1	762.5	2	В
100214	849.5	3.7	0.3	1183.9	2	В
104205	4147.9	2.1	0.3	779.15	2	В
104207	3548.8	1.8	0.2	760.9	2	B
104213	1748.6	0.8	0.1	791.7	2	В

 Table 8: Table of pCO2 duplicate values, continued

Key number	Depth	Dif. (µatm) %	Dif.	Ave.	# samples	Comment
106206	3998.4	0.6	0.1	777	2	В
106209	2798.8	1.8	0.2	757.5	2	В
108112	1299.2	2.6	0.3	947.7	2	В
108135	2.7	2.3	0.8	285.25	2	В
110205	4400.3	1.2	0.2	777.9	2	В
110212	1899.9	1.8	0.2	763.4	2	В
110226	199.4	8.3	0.8	1048.7	2	В
112105	4148	0.4	0.1	770.6	2	В
112120	550.1	1.6	0.1	1433	2	В
112133	14.5	1.6	0.6	277.8	2	В
114103	4500.9	3.2	0.4	776.2	2	В
114110	1600.6	0	0.0	804.7	2	В
116203	4249.5	0.4	0.1	776.1	2	В
116207	2249.5	0.7	0.1	755.3	2	В
116216	749.2	2.8	0.2	1336.6	2	В
118203	3999.4	3.9	0.5	771.6	2	В
118211	1199.5	5	0.5	1053.1	2	В
118224	199.6	5.2	0.6	873.7	2	В
118233	3.2	0.6	0.2	252.3	2	С
118235	3.1	1.6	0.6	252.6	2	В
120103	3599.9	0.4	0.1	775	2	В
120108	2000			767.1	1	B, 1 dup bad
120129	99.3	0	0.0	596.1	2	В
122204	2999.6	0.2	0.0	769.8	2	В
122212	1149.3	2.9	0.3	1037.1	2	В
124105	2401.5	1.7	0.2	760.0	2	В
124123	300.6	2.2	0.2	1099.6	2	В
126203	3398.7	0	0.0	774.1	2	В
126208	1899.2	0	0.0	758.3	2	В
126225	185.5	3	0.4	855.2	2	В
129103	3098.8	2.7	0.4	770.75	2	В
130116	747.7	0.7	0.1	1177.2	2	В
130125	184.6	5	0.6	815.6	2	В
130129	90.4	6	0.8	756.8	2	В
131113	1049.3	1	0.1	1090.7	2	A & B,1 dup bad
129133	19.6	0.7	0.3	267.05	2	В
132103	2900.3	0.8	0.1	768.2	2	В
132115	750.7	2.5	0.2	1185.1	2	В
132130	50.4	0.4	0.1	323.4	2	В
133133	19.1	1.1	0.4	313.3	2	B
135105	1899.3	1.6	0.2	757.4	2	В
135114	799.4	0.2	0.0	1177.5	2	В
135128	79.6	1.5	0.4	419.25	2	B
138203	2599.7	2.4	0.3	765.1	2	В
138207	1599.3	0.9	0.1	780.0	2	В
138231	10	0.2	0.1	318.7	2	В
141104	3999.6	1.5	0.2	799.75	2	В

Table 8:	Table of	pCO <sub>2</sub> duplicate	values, continued
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Key number	Depth	Dif. (µatm) %	Dif.	Ave.	# samples	Comment
141114	1199.6			1016.4	1	B, 1 dup bad
141126	219.8	2.2	0.2	933.8	2	В
144203	4599.9	2.1	0.2	962.55	2	В
144209	1899.6	0	0.0	750.2	2	В
146103	4898.9	5.5	0.6	993.05	2	В
146110	2800	0.7	0.1	764.85	2	В
146126	199.8	0	0.0	910.2	2	В
148203	4998.7	2.3	0.2	1001.15	2	В
148220	548.4	3.8	0.3	1238.8	2	В
150133	25.7	1.1	0.4	293.15	2	В
	Average	2.0	0.3			
	Stdev	1.7	0.3	-		

Table 8:	Table of	pCO <sub>2</sub> dup	licate values,	continued
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Values were labeled questionable or bad based on the quality control procedures listed below.

A =from same sample bottle

B = from same Niskin

C = from different Niskins sampled at same depth

	TA μmol/kg	DIC kg/kg	pH (total scale) @ 25°C	<b>Total Runs</b>
Leg 1				
System 1	$2222.2 \pm 3.6$	$2015.0 \pm 3.7$	$7.891 \pm 0.007$	15
System 2	$2224.2 \pm 3.2$	$2017.7 \pm 3.4$	$7.893 \pm 0.007$	17
Leg 2				
System 1	$2222.5 \pm 4.5$	$2012.1 \pm 2.4$	$7.895 \pm 0.009$	16
System 2	$2222.9 \pm 3.8$	$2016.1 \pm 4.1$	$7.890 \pm 0.009$	15
Manual Sys	$2217.2 \pm 2.1$	$2013.4 \pm 0.5$	$7.888 \pm 0.006$	3
Both Legs				
System 1	$2222.4 \pm 3.8$	$2013.6 \pm 3.4$	$7.891 \pm 0.011$	33
System 2	$2223.6 \pm 3.5$	$2017.0 \pm 3.8$	$7.891 \pm 0.008$	30
Manual Sys	$2217.2 \pm 2.1$	$2013.4\pm0.5$	$7.888 \pm 0.006$	3
All Systems	$2222.7 \pm 3.6$	$2015.2 \pm 3.5$	$7.891 \pm 0.009$	66
<b>Certified Values</b>				
CRM Batch 59	2220.98	2007.1	7.895a	
			7.9674 +/- 0.0005b	19
TRIS			$8.0855 \pm 0.0003a$	19

# **Table 9:** Total Alkalinity (TA) Certified Reference Material Measurements (DIC and pH values have been calculated from TA titrations)

<b>Correction Factor</b>				
Leg 1				
System 1	0.9994	0.9961	0.004	
System 2	0.9980	0.9947	0.002	
Leg 2				
System 1	0.9988	0.9975	0.000	
System 2	0.9991	0.9958	0.005	
Manual Sys	1.0017	0.9969	0.007	

Station	Niskin Bottle	Depth (m)	DO (µm)		
test	1	170	277.2		
test	2	170	277.2		
test	3	170	276.9		
test	4	170	277.1		
test	5	170	276.8		
test	6	170	276.8		
test	7	170	277.1		
test	8	170	276.8		
test	9	170	276.7		
test	10	170	277.4		
test	11	170	277.6		
test	12	170	274.5*		
test	13	170	277.9		
test	14	170	277.2		
test	15	170	277.3		
test	16	170	276.8		
test	17	170	277.4		
test	18	170	276.9		
test	19	170	277		
test	20	170	276.8		
	Average				
		STDV	0.03		

Table 10: Replicate analyses of dissolved oxygen concentration from the test CTD cast

\* Outlier in replicate analyses not included in the average and possibly due to errors in bottle volumes or sampling.

Station	Sample	Replicate 1	Replicate 2	Replicate 3	<b>Replicate 4</b>
1	1	276.1	266.8*		
1	4	279.1	279.4		
1	8	266.7	289.2		
1	11	297.2	296.1		
2	2	262.8	262.2		
2	18	297.2	302.7*	297.4	
4	1	287.1	161.1*		
5	4	277.3	266.3*		
5	25	276.2*	279.9		
6	1	302.1*	288.1		
6	12	245.4	245.3		
7	8	250.4	249.9		
7	14	269.9*	261.1		
10	6	286.6	286		
10	32	306.3	306.8		
11	4	286.2	286.5		
11	35	307.6	308.3	307.6	
12	23	273.1	273.4		
14	3	277.5	278		
14	32	275.1	275.6		
15	7	232.4	232.1		
15	27, 28	274.3	275.6		
16	2	241.1	241.6		
16	24	279.8	279.9		
19	4	264	264.5		
19	26, 27	274.6	281.7*		
20	4	231.1*	227.4		
20	17	258	257.8		
21	25, 26	275.5	275.1		
24	7	265.7	265.1		
24	25	259	259.3		
25	5	284.3	284.3		
25	20	241	241		
25	28	263.8	264.4		
26	33, 35	268.3	267.9		
28	2	243.7	244.2		
30	9	275.6	276.6		
30	31	271.9	271.7		
32	27	194	194.2		
34	33, 35	269.6	270.2		
40	1	270.2*	246.5		
43	6	268.8	268.6		
43	17	196.5	192.9		
44	7	263.9	264.1		
45	2	247	246.9		
45	35	248.7	249.4		

 Table 11: Replicate analyses of dissolved oxygen concentration (µmol/L) by Winkler titration from same Niskin bottle or different bottles at same depth

Station	Sample	Replicate 1	Replicate 2	Replicate 3	Replicate 4
46	10	208.2	208.4		
47	7	229.7	229.9		
47	31, 32	247.1	247		
49	33	240	239.8		
51	15	195.5	195.9		
51	32	278.3	278.6		
52	11	200.4	200.1		
52	32	240.2	240.4		
53	33, 35	237.9	237.7		
54	14	190.1	191.5		
54	31	261.4	261.4		
55	7	251.2	250.6		
55	31	260	259.9		
57	6	264.9	265.4		
57	33	238.1	237.8		
60	1	250.9	250.8	250.8	
60	11, 15	248.1	247.7	246.3	247.3
60	13	218.7	216.1	216.9	
60	29	236	235.5	235.4	
61	1	258.9	253.3*		
61	2	253.1	251.7		
61	5	251.7	252	252.6	
61	7	252.9	253.1		
62	1	250.9	251		
62	3	251	250.8		
62	5	250.8	250.7		
62	7	251	251.5		
63	8	261	260.9	261.5	
63	13	190.1	190.1	190	
63	17	187.9	187.6	187.9	
63	24	212.6	212.8	212.5	
63	29	234.3*	240	241.6	
63	33	242.3	242.2		
64	4	251.4	250.8		
64	12	186.8	182.4*		
65	1	251.1	251		
64	30	237.6	237.8		
65	4	251.8	251.6		
65	17	170.6	170.6		
66	3	251.6	251.4		
66	9	247.4	246.8		
66	15	181.1	181	180.8	
66	28	228.2	228.8		
67	7	251.2	250.8	251.1	
67	20	191.6	191.5	191.6	
68	1	251.6	251.8		

 Table 11: Replicate analyses of dissolved oxygen concentration (µmol/L) by Winkler titration from same Niskin bottle or different bottles at same depth (continued)

Station	Sample	Replicate 1	Replicate 2	Replicate 3	Replicate 4
68	3	251.6	251.9		
68	7	251.3	251.5		
68	16	189.5	189.7		
68	25	209.5	209.4		
68	33	226.2	226.1		
69	1	251.1	251.3		
69	3	251.5	251.3		
69	5	250.9	250.6		
69	16	180.9	181.3		
69	33	229.8	229.8		
70	9	246.1	245.8		
70	12, 13	192.2	191.3		
70	22	213.5	213.1		
71	1	251.6	251.9		
71	5	251.4	251.6		
71	18	169.8	170		
71	30	242.8	242.9		
72	12	246.3	246		
72	28	217	217.1		
73	1	246.5	246.6		
73	3	246.9	246.6		
73	5	245.9	246.2		
73	16	161.8	162.4		
73	33	213.8	213.8		
74	1	246.1	246.3		
74	4	247.3	247		
74	17	171.6	171.6		
74	21	195.4	195		
74	33	214	214.1		
74	35	213.6	213.8		
75	1	246.4	246.4		
75	5	246.9	246.6		
76	1	246.6	246.7		
76	4	247	246.8		
76	18	182.5	182.3		
77	1	247.3	246.4		
77	5	246.8	247		
77	23	197.8	197.4		
78	4	246.4	246.8		
78	10	214.2	214.4		
79	1	246.3	246.8		
79	5	246.1	246		
79	18	154*	158.2		
79	33	212.7	212.5		
80	3	249.2	249.3		
80	14	161.4	161.1		

 Table 11: Replicate analyses of dissolved oxygen concentration (µmol/L) by Winkler titration from same Niskin bottle or different bottles at same depth (continued)
Station	Sample	Replicate 1	Replicate 2	Replicate 3	Replicate 4
80	32	229.9	229.7		
81	1	249.3	249.6		
81	2	249.6	249.8		
82	2	249.8	249.6		
82	28	213	212.6		
83	1	249.3	249		
83	5	249.3	248.9		
83	18	132.2	132.2		
84	3	238.4*	249.3		
84	15	181.4	181.6		
85	1	248.6	249.2		
85	2	248.8	249.2		
86	1	249.7	248.8		
86	5	249.2	248.8		
86	19	131.2	130.8		
87	1	254.6	254.2		
87	19	130	130.3		
88	1	254.5	254		
88	16	173	172.8		
89	1	253.8	253.5		
89	3	252.3	253.8		
89	5	252.2	251.9		
89	16	133	131.7		
90	2	253.3	253.8		
90	18	116.2	115.7		
91	1	252.9	252.4		
91	18	94.7	95.2		
92	1	251.9	251.8		
92	2	251.7	252		
92	18	110.9	110.3		
92	33	215.7	215.8		
94	2	249	249.3		
94	14	117.9	117.5		
95	1	256.4*	245.3		
95	6	243.2	243.4		
95	23	74	73.9		
96	2	243.5	243.2		
96	22	70.5	70.8		
96	32	220.8	220.2		
97	2	246.8	246.9		
97	18	93.2	96*		
98	2	245.9	249.2*		
98	19	81	80.6		
98	32	209	209		
99	2	248.1	248		
99	21	94.8	95		

Station	Sample	<b>Replicate 1</b>	Replicate 2	<b>Replicate 3</b>	<b>Replicate 4</b>
99	23	94	93.9		
100	2	250.5	250.7		
100	22	76.5	76.2		
100	32	211.2	211		
101	1	250.9	251.2		
101	19	71.6	71.6		
104	2	252	251.9		
104	23	72.9	72.9		
104	33	206.7	206.7		
105	1	253.1	253.3		
105	4	250.1	249.9		
105	25	79.3	79.7		
106	2	253.9	253.6		
106	22	59.5	59.5		
106	33	206.8	206.6		
107	1	252	252.2		
107	18	70.3	70.2		
107	32	206.6	206.2		
108	2	253.4	254.2		
108	21	51	51.2		
108	32	211.6	211.8		
109	2	254.1	254.4	254.2	
109	14	225.3	225.5		
109	22	50.4	51.7		
110	2	254.4	254.5		
110	21	51.4	51		
111	4	250.7	250.8		
111	24	67.7	67.5		
111	30	83.3	83.7		
112	4	253.6	254.5		
112	24	96.2	96.4		
112	32	179.8	179.9		
113	5	254.3	254		
113	1/	92.7	92.7		
113	23	89.6	89.5		
114	6	255.5	255.9		
114	25	102.5	102.1		
114	32	186.4	186.5		
115		249	249.2		
115	21	04.0	04.5		
115	33	205.5	205.2		
110	2	252.1	252.2		
110	20	//.0	//.5		
110	32	207.9	207.8		
	4	259.6	259.9		
117	22	63.7	63		

Station	Sample	<b>Replicate 1</b>	Replicate 2	Replicate 3	<b>Replicate 4</b>
118	2	257	257.1		
118	19	62.6	62.2		
118	33	206.8	206.9		
119	1	254.8	254.7		
119	22	55.6	55.4		
119	35	206.6	206.9		
120	4	254.8	255.1		
120	24	140	140.3		
120	33	205.4	205.1		
121	3	255.2	255.1		
121	19	70	69.9		
121	33	206.7	206.5		
122	2	255.4	255.3		
122	18	87.8	87.6		
122	33	209.1	209		
123	1	252	252		
124	3	255.6	256		
124	28	137.2	137.4		
124	30	205.5	205.8		
125	1	253	253.4		
125	19	112.8	113.8		
125	35	255	254.7		
123	17	131.6	131.8		
123	29	155.3	155.1		
126	4	256.2	256.3		
126	13	160.7	161		
126	26	98.7	98.1		
127	4	257	257.4		
127	28	99.4	98.9		
127	33	209.2	209.1		
128	2	259.3	259.1		
128	16	153.7	153.9		
128	28	96.7	96.3		
129	3	255	255		
129	19	136.7	136.9		
129	32	207.2	207.5		
130	1	253.6	253.4		
130	35	213.5	213.2		
131	3	257.6	258		
131	26	108.5	108.7		
131	33	212.3	212.4		
132	4	253.6	253.3		
132	19	121.5	121		
132	28	132.5	132.5		
133	1	261.2	261		
133	23	105.4	105.3		

Station	Sample	Replicate 1	<b>Replicate 2</b>	Replicate 3	<b>Replicate 4</b>
133	32	204.6	204.8		
134	1	257.9	257.7		
134	23	96.8	96.6		
134	35	210.5	210.3		
135	6	245.9	245.9		
135	20	116.9	116.6		
135	33	208.8	208.8		
136	1	256.6	256.2		
136	8	229.2	229.6		
136	26	175.7	175.5		
137	2	256.9	257.2		
138	20	83.2	83		
138	31	208.9	209.1		
139	2	232.5	232.2		
139	23	95.8	95.6		
140	3	240.9	241.2		
140	23	70.1	70.3		
140	31	207.3	207.5		
137	24	113.4	113.3		
137	32	209.3	209.5		
138	2	255.8	256		
141	3	236.2	236.3		
141	15	166.4	166.7		
141	32	209.1	209.2		
143	13	158.7	158.9		
144	2	230.2	230.3		
144	15	158.9	158.8		
144	31	169.2	169.5		
145	1	228	228.1		
145	23	104.3	104.7		
145	35	212.9	212.7		
146	4	234.1	234.3		
146	16	174.5	174.3		
146	25	101.8	101.9		
147	4	233.2	233.6		
147	28	106.3	106.3		
147	33	209.7	209.7		
148	1	228.6	229.2		
148	23	90.7	90.6		
148	33	210.3	210		
149	2	228.9	228.6		
149	24	86.5	86.2		
149	35	208.4	208.4		
150	3	231.1	231.2		
150	24	85.9	86.2		
150	31	205.6	205.6		

Bottle	Old Volume	New Volume	Difference
1	145.853	145.610	-0.243
2	145.200	145.209	0.009
3	145.318	149.967	4.649
4	143.917	143.908	-0.009
5	139.471	138.748	-0.723
6	145.464	145.470	0.006
7	145.443	145.441	-0.002
8	152.778	152.796	0.018
9	142.276	146.019	3.743
10	145.662	145.666	0.004
11	143.687	143.643	-0.044
12	145.292	147.003	1.711
13	142.335	142.307	-0.028
14	141.151	145.220	4.069
15	145.456	145.507	0.051
16	145.908	145.897	-0.011
17	145.645	145.644	-0.001
18	144.759	144.734	-0.025
19	142.898	142.913	0.015
20	143.300	143.310	0.010
21	146.299	141.180	-5.119
22	144.406	147.777	3.371
23	145.704	148.320	2.616
24	141.570	152.070	10.500
25	145.085	145.109	0.024
26	145.599	145.606	0.007
27	147.751	146.772	-0.979
28	144.469	144.459	-0.010
29	147.404	147.396	-0.008
30	146.101	146.131	0.030
31	146.039	146.004	-0.035
32	145.111	145.152	0.041
33	145.501	145.501	0.000
34	146.663	146.678	0.015
35	143.309	143.347	0.038
36	147.371	147.429	0.058
37	146.290	150.489	4.199
38	140.623	144.152	3.529
39	146.959	151.425	4.466
40	144.179	144.183	0.004
41	139.747	141.192	1.445
42	143.726	150.186	6.460
43	146.369	146.369	0.000
44	142.137	142.137	0.000
45	142.478	142.478	0.000
46	143.805	143.805	0.000
47	143.494	143.500	0.006

**Table 12:** After cruise recalibration of the volumes (cm<sup>3</sup>) of the oxygen bottles

Bottle	Old Volume	New Volume	Difference
40			
48	145.665	142.890	-2.775
49	144.254	144.254	0.000
50	145./15	141.225	-4.490
51	14/.80/	14/.809	0.002
52	146.055	146.055	0.000
53	143.431	143.431	0.000
54	143.34/	145.342	1.995
	144.658	144./15	0.057
50	146.009	146.032	0.023
59	142.60/	144.083	1.4/0
50	145.371	145.572	0.001
	144.344	144.343	-0.001
60	145.292	145.244	-0.048
62	140.185	140.139	-0.026
62	142.781	142.780	0.005
63	144.319	144.307	-0.012
64	144.039	144.042	0.003
65	145.511	149.030	4.319
60	144.080	144.155	0.075
<u> </u>	143.908	145.892	-0.010
60	137.380	140.308	8.982
	145.505	145.559	0.034
70	145.275	143.270	0.003
/1	140.390	140.3//	-0.019
72	145.002	145.555	-0.04/
73	145.019	145.027	0.008
74	140.027	140.034	0.007
75	144.237	144.230	-0.001
70	144.955	144.030	-0.079
78	140.340	140.332	0.012
70	143.397	143.331	-0.040
80	142.704	145.421	1 380
81	140.007	143.227	-1.380
82	147.642	147.013	-0.131
83	140.024	143 503	6 / 17
83	149.920	143.303	-7.458
<u> </u>	143 718	143 666	-0.052
<u> </u>	145 6/1	145 552	-0.032
87	143 796	143.654	-0.009
88	140.322	140.321	0.001
<u> </u>	138 752	138 633	_0 110
09	138.785	138.658	-0.117
01	145 587	142 2/10	_3 338
02	144 516	142.249	-3.330
02	151 851	149 504	-2.112
 Q/	145 714	145 720	0.006
74	173./14	173.740	0.000

**Table 12:** After cruise recalibration of the volumes (cm<sup>3</sup>) of the oxygen bottles (continued)

Bottle	Old Volume	New Volume	Difference
95	149.465	149.364	-0.101
96	151.184	148.882	-2.302
97	144.609	144.592	-0.017
98	152 251	152 200	-0.051
99	144 545	144 552	0.007
100	147 346	147 187	-0.159
101	139,500	139 479	-0.021
102	149 319	149 298	-0.021
103	147 485	147 484	-0.001
104	138 295	138 310	0.015
105	139.030	139.035	0.005
106	144 610	144 606	-0.004
107	148 793	148 778	-0.015
108	146 952	146 951	-0.001
100	149 911	149 928	0.017
110	146 285	142 968	-3 317
111	149.657	141 784	-7 873
112	142 400	143 215	0.815
112	143 206	143 217	0.011
114	139 272	139.267	-0.005
115	139.648	139.631	-0.017
116	141 125	141 138	0.013
117	141 218	142 124	0.906
118	147 477	147 484	0.007
119	148 834	148 847	0.013
120	147.002	147.023	0.021
120	144 803	144 080	-0 723
122	141.945	141.949	0.004
123	143.415	143.134	-0.281
124	145.482	144.116	-1.366
125	145.685	145.706	0.021
126	144.523	144.527	0.004
127	145.756	145.780	0.024
128	140.523	140.521	-0.002
129	143.820	143.811	-0.009
130	145.730	138.828	-6.902
131	145.849	145.855	0.006
132	145.156	145.146	-0.010
133	145.696	145.673	-0.023
134	143.807	143.807	0.000
135	148.692	148.692	0.000
136	141.083	141.083	0.000
137	143.675	143.675	0.000
138	145.247	145.247	0.000
139	144.459	144.459	0.000
140	143.336	143.336	0.000
141	143.962	143.971	0.009

**Table 12:** After cruise recalibration of the volumes (cm<sup>3</sup>) of the oxygen bottles (continued)

Bottle	Old Volume	New Volume	Difference
142	144.590	142.608	-1.982
143	145.759	145.776	0.017
144	137.683	145.339	7.656
145	145.356	145.346	-0.010
146	142.249	142.273	0.024
147	145.810	145.800	-0.010
148	144.984	144.954	-0.030
149	146.996	146.998	0.002
150	145.100	145.094	-0.006
151	142.395	142.369	-0.026
152	144.586	144.983	0.397
153	147.093	147.102	0.009
154	145.219	142.119	-3.100
155	150.067	150.055	-0.012
156	138.514	143.383	4.869
157	148.070	144.191	-3.879
158	145.740	145.788	0.048
159	143.852	143.853	0.001
160	145.975	145.999	0.024
161	144.786	144.785	-0.001
162	144.560	144.304	-0.256
163	146.144	146.096	-0.048
164	144.518	144.296	-0.222
165	144.623	144.514	-0.109
166	141.617	141.524	-0.093
167	144.192	144.162	-0.030
168	145.917	145.651	-0.266
169	145.682	145.604	-0.078
170	146.535	146.342	-0.193
171	139.221	139.144	-0.077
172	150.611	150.569	-0.042
173	145.165	145.101	-0.064
174	145.379	145.303	-0.076
175	144.814	144.744	-0.070
176	141.770	141.687	-0.083
177	143.827	143.722	-0.105
178	145.031	144.941	-0.090
179	145.668	143.528	-2.140
180	147.606	147.524	-0.082

**Table 12:** After cruise recalibration of the volumes (cm<sup>3</sup>) of the oxygen bottles (continued)

Thio Bottle	Standard File	Starting Station	Ending Station	Intercept	Slope	Remarks
1	2	1	4	-0.004	24.743	
2	6	4	8	0.1515	24.585	
3	7	7	15	0.1155	23.87	
4	9	16	18	0.0885	24.635	
5	10	19	23	0.1117	24.312	
6	11	24	29	0.05	24.96	
7	15	30	37	0.143	24.495	
8	16	37	46	0.1255	24.135	
9	17	46	50	0.0405	24.845	
10	18	51	58	0.0072	24.988	
11	21	59	61	0.0042	25.075	
12	22	62	65	-0.0015	25.005	
13	23	66	71	-0.0025	24.87	
14	24	72	79	-0.01	25.355	Digital Pipette
15	25	80	86	-0.0007	24.97	
16	26	87	92	0.008	24.755	
17	27	93	97	0.002	24.735	
18	30	98	98	0.0045	24.92	
19	30G	98	106	0.0057	24.873	
19				0.001	24.89	End of the Bottle
20	31G	107	115	0.002	24.88	
21				0.0096	24.719	5-20ml KIO <sub>3</sub>
21	32G	116	123	0.0043	24.747	2-16ml KIO <sub>3</sub>
22	33G	124	131	0.0056	24.757	
23	35G	132	140	0.0097	24.753	
24	36G	141	148	0.0063	24.682	
24				0.009	24.685	Repeat
25	37G	149	150	0.007	24.697	
25	38			0.007	24.678	
25	39			0.0039	24.649	
			Average	0.03015	24.7421	

 Table 13: Shipboard standardization of thiosulfate solution during A16N\_2003a cruise

**TABLE 14:** Post cruise comparison of volume delivery of a manual and the problematic automatic pipette used for stations 72-79 by standardization of KIO<sub>3</sub> solution with same batch Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The correction of 1.01531 was applied to all samples in this station range.

Run	Automatic Factor	Intercept	r2	Manual Factor	Intercept	r2	Ratio
1	25.050	-0.0023	1.0000	24.577	0.0127	1.0000	
2	25.035	-0.0008	1.0000	24.690	0.0057	1.0000	
3	25.017	-0.0005	1.0000	24.685	0.0040	1.0000	
4	25.205	-0.0052	1.0000	24.673	0.0050	1.0000	
5	25.067	0.0012	1.0000	24.687	0.0063	1.0000	
6	24.990	0.0022	1.0000	24.690	0.0070	1.0000	
7	25.112	-0.0030	1.0000	24.670	0.0065	1.0000	
8	25.047	0.0030	1.0000	24.700	0.0060	1.0000	
9	25.290	-0.0063	1.0000	24.685	0.0075	1.0000	
10	24.910	0.0040	1.0000	24.658	0.0075	1.0000	
11	24.861	0.0050	1.0000	24.697	0.0065	1.0000	
12				24.693	0.0083	1.0000	
AVE	25.05309	-0.0002		24.67542	0.0069		1.015306
STD	0.120788	0.0037		0.03323	0.0022		
RSD	0.5%			0.1%			

#### APPENDIX

WOCE quality flag definitions for water bottles

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Flag	Definition
1	Bottle information unavailable
2	No problems noted
3	Leaking
4	Did not trip correctly
5	Not reported
7	Unknown problem
9	Samples not drawn from this bottle

WOCE water quality flag definitions

Flag	Definition
1	Sample drawn but analysis not received
2	Acceptable measurement
3	Questionable measurement
4	Bad measurement
5	Not reported
6	Mean of replicate measurements
9	Sample not drawn for measurement

Date	Contact	Data Type	Data TypeData Status Summary				
04/01/03	Swift	CTD/BTL	List	of cruise p	arameters		
	Here is the c	urrent parameter list	for th	ne 2003 A1	6N son-of-	WOCE cru	ise.
	Kristin Sanb preparations samples gen from the CT	oorn of ODF gave n for the bottle data erate many individua D computer. An f be	ne the proce al par fore a	e list. She essing on rameters. A value indi	has been that cruise an asterisk cates it's a	working wi . Of course after a valu flag.	th Bob Williams on e some of the water ae indicates it comes
	stnnbr btlnbr lat year* second* ctdtmp* pic* scatter* cfc11 cfc13 hcfc22 ch3cl ch3br aomlcfc11 hcfc141b ch3i aomlcfc13 aomlcfc13 aomlcfc13 aomlcfc13 aomlcfc13	castno (bottle serial number (decimal degrees) month* (decimal seconds) ctdoxy* (Bishop particulate i (Bishop particulate i (Bishop scatter meter fcfc11 fcfc13 (AOML HCFC-22) (methyl chloride) (MOML HCFC-22) (methyl bromide) (AOML cfc-11) (AOML HCFC-1411 (methyl iodide) (AOML cfc13) (AOML ccl4) ftcarbn fpco2 fphspht fhel3	r) norga er) b)	sampno lon day* ctdprs* fctdoxy anic carbon sigma0* cfc12 ccl4 fhcfc22 fch3cl fch3br faomlcfc1 fhcfc141b fch3i faomlcfc1 faomlcfc1 faomlcfc1 faomlcfc1	(niskin nu (decimal hour* ctdsal* trans* )) theta* fcfc12 fcc14 1 3 4 fnitrat fsilcat ftritum	umber + cas degrees) min* fctdsal (Bishop t Bishop t nitrit oxygen alkali	stno*100) ranmissometer) fnitrit foxygen falkali
	There appea apparently d	tpn doc tdoc don tdon ear to be two different CFC groups working at the same time on A16N, e					time on A16N, each
08/27/03	Bullister	CTD/BTL/SUM	Rav	v shipboard	l prelim dat	a available	via ftp
	You have my should inclu- and will be u	have my permission to obtain the data from Frank and post them at the website. You id include the caveats that these data are the raw shipboard version, are still preliminary vill be updated.					
09/14/03	Bullister	DOC	Sub	mitted			
	This is from Brown). It's post-cruise r doc with the	s is from John Bullister and is the project instructions document for A16N_2003a (Ron wn). It's the closest thing that he had to cruise docs, but he's working on a preliminary t-cruise report. When he completes the work-in-progress, we should replace the new with the one he's working on now.					
09/08/03	McTaggart	CTD	Sub	mitted avai	ilable on N	OAA ftp sit	te
	A16N prelin ftp.pmel.noa	ninary CTD data fil a.gov under /ctd/woc	es in e/a16	WOCE fo	ormat are 1	ready for y	ou on our FTP site:
09/08/03	Diggs	CTD	Dat	a retrieved	from NOA	A ftp site	
	I have receive	ad wave files and are	ahaa	ling that	0.1.0 <b>r</b>		

I have received your files and am checking them over.

Date	Contact	Data	Туре	Da	ata Status	Summary				
09/10/03	Delahoyd	BTL/S	SUM	B	ГL Paramet	ers Submit	ted:			
	BTLNBR OXYGEN TCO2	CTDRA SILCAT TALK	W CTD NITH PH	PRS RAT	CTDTMP NITRIT PCO2	CTDSAL PHSPHT	CTDOX CFC-11	Y TH CF	IETA FC-12	SALNTY CFC113
	These data v	vere prov	ided by:							
	Param./Program Chief ScientistName John Bullister-PMEL John Bullister-PMEL giohnson@pmel.noaa.gov mordy@pmel.noaa.gov thisterEmail bullister@pmel.noaa.gov mordy@pmel.noaa.gov thisterNutrientsCalvin Mordy-PMEL Jia-Zhong Zhang-AOMLbullister@pmel.noaa.gov mordy@pmel.noaa.govTCARBN, pCO2Dick Feely- PMEL Rik Wanninkhof-AOMLfeely@pmel.noaa.gov rik.wanninkhof@noaa.govCFCJohn Bullister-PMEL bullister-PMELbullister@pmel.noaa.gov rik.wanninkhof@noaa.govCFCMark Warner-UW Mark Warner-UWmwarner@ocean.washington.edu syvon@aoml.noaa.govHe/TrPeter Schlosser peters@ldeo.columbia.edu amcnichol@whoi.edu14C/13CAnn McNichol WHOI maintain caution in their interpretation and use. Following the collection. Users should maintain caution in their interpretation and use. Followin American Geophysical Union recommendations, the data should be cited as: "da provider(s), cruise name or cruise ID, data file name(s), CLIVAR and Carbon Hydrograph Data Office, La Jolla, CA, USA, and data file date." For further information, please conta one of the parties listed above or whpo@ucsd.edu. Users are also requested to acknowled the NSF/NOAA-funded U.S. Repeat Hydrography Program in publications resulting fro their use.						ibration and lowing their Following d as: "data ydrographic ease contact cknowledge sulting from			
	A16N water	property	codes for	WOC	CE ".sum" f	ile "PROP	ERTIES"	colun	nn:	
	<u>Code</u> <u>Pro</u>	<u>perty</u>	<u>Code</u> I	Prope	<u>rty Co</u>	<u>de</u> <u>Prop</u>	<u>erty</u> <u>C</u>	ode	<u>Prop</u>	<u>erty</u>
	1 Sali	nity	8 (	CFC-1	2 2:	5 PCO	2	101	PIC	
	$\begin{array}{ccc} 2 & 02 \\ 2 & SIO \end{array}$	2	9 1 10 I	ritiur	n $20$	D PH	112	102	Al Ea	
	$\begin{array}{c} 3 \\ 4 \\ 10^{\circ} \end{array}$	5 R	10 f	1e 1e114(	$\frac{2}{3}$	7 CFC DON	-115 [	103	re AlkN	103
	5 NO2	2	12 C	lel130	2 4(	POC	1	105	Carb	ohydrates
	6 PO4	- •	23 1	CO2	4.	B DOC		106	CDO	M
	7 CFC	C-11	24 7	TALK	100	) HCF	Cs			
09/26/03	McTaggart	CTD		Su	bmitted					
	There is a /ctd/woce/a	file fo 6n. It's o	or you c called a16	on ou n_allo	or anonym a.clb and it	ous FTP is the pre	site, ftp liminary o	.pme calibr	l.noaa. ated d	gov, under iscrete CTD

There is a file for you on our anonymous FTP site, ftp.pmel.noaa.gov, under /ctd/woce/a16n. It's called a16n\_allo.clb and it is the preliminary calibrated discrete CTD measurements and associated sample salinities and oxygens. In generating this file, I found an error I had made in applying the preliminary calibrations to the profile data. The .ctd files now on our FTP site are correct and should be downloaded again. I apologize for this oversight. And I changed the expocode in the header to be a 13-character string instead of a 12-character string as it is on the WHPO website (e.g. suffix '\_01' instead of '\_1').

Date	Contact	Data Type	Data Status Summary				
09/29/03	Diggs	CTD	Website Updated; CTD submitted and online				
	CTD data reca	alibrated. Updated v	versions of the ctd and ctd- exchange on website.				
10/03/03	Johnson	CTD/BTL	Defined ctd/nuts/O2 PIs				
	For A16N ple for nutrients,	ase keep me (Grego and Zhang for bottle	bry Johnson) as PI for CTD/O2 and S, but Mordy & Zhang e O2.				
10/20/03	Diggs	CTD/SUM/BTL	Website Updated with Formatted files				
	CTD, SUM, E	BTL available along	with Exchange formatted versions on WHPO website.				
10/23/03	Diggs	CTD/BTL	Website Updated; Citation added to files				
	Repackaged a new citation f	Ill zip files (WOCE	E CTD, Exchange CTD, and WOCE Bottle w/ SUM) with n Talley and Swift).				
10/29/03	Diggs	SUM/CTD/BTL	Updated archive citations				
	Updated all c Exchange for each station fr	titations (00_READ matted bottle file. E om updated summa	DME files) embedded in each zip archive as well as the Bottle Exchange updated to reflect accurate ExpoCodes for ary file.				
10/24/03	Kappa	DOC	Cruise Report PDF & ASCII versions Updated				
	added links fr Data Processi	om TOC to text in PDF version made a text version added these WHPO-SIC ng Notes					
11/03/03	Coartney	Cruise Report	Website Updated; New PDF & ASCII docs online				
01/30/04	Diggs	CTD/BTL/SUM	Website Updated; line identifiers changed				
	Corrected all	cruise line identifier	rs to A16N (from A16N_2003A) as per Jim Swift's request.				
02/20/04	Kappa	Cruise Report	Updated PDF & ASCII versions made				
06/11/04	Diggs	CTD	Website Updated; missing files added				
	A transmissio WHPO. Alise checked them checks out.	ssion error occurred from PMEL to SIO, resulting in only 80 files being at the alison MacDonlad from WHOI noticed the problem. I re-ftp'd the files, format nem, convert them to Exchange, and put all of the ftp files back on the website. All t					
10/27/04	Hansell	DOC/TDN	Submitted data & sampling procedures report				
	The data dispo The file forma The archive ty The data type	isposition is: Public rmat is: Plain Text (ASCII) e type is: NONE - Individual File /pe(s) is: Bottle Data (hyd)					
	<ul> <li>Dissolved Organic Carbon</li> <li>Total Dissolved Nitrogen for A16N2003 Line</li> <li>Documentation</li> </ul>						
	The file conta • Cast Nu • Station • Bottle†	ins these water sam umber (CASTNO) Number (STATNO Number (BTLNBR	ple identifiers:				
	• Sample	Number (SAMPNO)(next page)					

10/27/04       Hansell       DOC/TDN       Submitted data & sampling procedures report (cont.)         HANSELL, DENNIS would like the following action(s) taken on the data:       • Merge Data         • Place Data Online       • Place Data Online         12/10/04       Kozyr       Cruise Report       Submitted CO2 report         I am attaching here 3 files with reports on measured carbon fields. You will have to decid what and how much information you need for cruise report.         12/10/04       Kozyr       CO2       Submitted: TCARBN, ALKALI, pH, and pCO2         I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruis for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         This is information regarding line A16N_2003a       ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11       From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov       Institution:       CDIAC/ORNL
HANSELL, DENNIS would like the following action(s) taken on the data:         • Merge Data         • Place Data Online         12/10/04       Kozyr         Cruise Report       Submitted CO2 report         I am attaching here 3 files with reports on measured carbon fields. You will have to decide what and how much information you need for cruise report.         12/10/04       Kozyr       CO2         Submitted: TCARBN, ALKALI, pH, and pCO2         I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruise for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         This is information regarding line A16N_2003a       ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11       From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov       Institution:       CDIAC/ORNL
<ul> <li>Merge Data         <ul> <li>Place Data Online</li> </ul> </li> <li>12/10/04 Kozyr Cruise Report Submitted CO2 report         <ul> <li>I am attaching here 3 files with reports on measured carbon fields. You will have to decid what and how much information you need for cruise report.</li> </ul> </li> <li>12/10/04 Kozyr CO2 Submitted: TCARBN, ALKALI, pH, and pCO2         <ul> <li>I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruis for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.</li> </ul> </li> <li>12/10/04 Kozyr CO2 Submitted         <ul> <li>This is information regarding line A16N_2003a</li> <li>ExpoCode: 33RO200306_01 33RO200306_02</li> <li>Cruise Date: 2003/06/19 - 2003/08/11</li> <li>From: KOZYR, ALEX</li> <li>Email address: kozyra@ornl.gov</li> <li>Institution: CDIAC/ORNL</li> </ul> </li> </ul>
12/10/04       Kozyr       Cruise Report       Submitted CO2 report         I am attaching here 3 files with reports on measured carbon fields. You will have to decide what and how much information you need for cruise report.         12/10/04       Kozyr       CO2       Submitted: TCARBN, ALKALI, pH, and pCO2         I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruise for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         This is information regarding line A16N_2003a       ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11       From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov       Institution:       CDIAC/ORNL
Image: Indepine the indepine the point of the point
what and how much information you need for cruise report.         12/10/04       Kozyr       CO2       Submitted: TCARBN, ALKALI, pH, and pCO2         I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruiss for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         12/10/04
12/10/04       Kozyr       CO2       Submitted: TCARBN, ALKALI, pH, and pCO2         I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruis for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         12/10/04       Kozyr       CO2       Submitted         12/10/04       Kozyr       CO2       Submitted         This is information regarding line       A16N_2003a         ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11         From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov         Institution:       CDIAC/ORNL
I have just submitted the final TCARBN, TALK, pH, and pCO2 data for A16_2003 cruis for merging into the hydrographic data file. Could you with the new numbers. Please, let m know if you have any questions regarding the data.         12/10/04       Kozyr       CO2       Submitted         This is information regarding line A16N_2003a       ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11       From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov       Institution:       CDIAC/ORNL
12/10/04KozyrCO2SubmittedThis is information regarding line A16N_2003aExpoCode:33RO200306_01 33RO200306_02Cruise Date:2003/06/19 - 2003/08/11From:KOZYR, ALEXEmail address:kozyra@ornl.govInstitution:CDIAC/ORNL
This is information regarding line A16N_2003aExpoCode:33RO200306_01 33RO200306_02Cruise Date:2003/06/19 - 2003/08/11From:KOZYR, ALEXEmail address:kozyra@ornl.govInstitution:CDIAC/ORNL
ExpoCode:       33RO200306_01 33RO200306_02         Cruise Date:       2003/06/19 - 2003/08/11         From:       KOZYR, ALEX         Email address:       kozyra@ornl.gov         Institution:       CDIAC/ORNL
Cruise Date:2003/06/19 - 2003/08/11From:KOZYR, ALEXEmail address:kozyra@ornl.govInstitution:CDIAC/ORNL
InominicINOP IN, ALLAEmail address:kozyra@ornl.govInstitution:CDIAC/ORNL
Institution: CDIAC/ORNL
Country: USA
The file: a16n 2003 carbn final.txt - 308958 bytes
Has been saved as:
20041210.063700_KOZYR_A16N_2003_a16n_2003_carbn_final.txt
In the directory: 20041210.063700_KOZYR_A16N_2003
The data disposition is: Public
The bottle file has the following parameters: TCARBN, TALK, PCO2, PH The file format is: WOCE Format (ASCII)
The archive type is: NONE - Individual File
The data type(s) is: Bottle Data (hyd)
The file contains these water sample identifiers:
• Cast Number (CASTNO) • Station Number (STATNO)
• Bottle Number (BTLNBR)
• Sample Number (SAMPNO)
KOZYR, ALEX would like the following action(s) taken on the data: Merge Data
Any additional notes are:
• This is the final bottle TCARBN, TALK, pH, and pCO2 data. I have
<ul> <li>merged these numbers from two different files I received from</li> <li>PMEL and AOML CO2 measurement groups. New quality flags were</li> </ul>
• assigned according to QA-QC work. Please let me know if you need
• more information on these data.

Date	Contact	Data Type	Data Status Summary					
12/10/04	Anderson	CO2	Website Updated OnLine					
	Copied files s	ubmitted by A. Koz	cyr from INCOMING to					
	/a16n_200	3a/original_data/20	041210_KOZYR_A16N_2003.					
	I will merge in	Il merge into online file.						
12/17/04	Bullister	Cruise Report	Submitted Final cruise report					
12/29/04	Mordy	NUTs	Submitted by Calvin Mordy					
	This is inform	ation regarding line	ion regarding line A16N_2003a					
	ExpoCode:	StypeCode:         33RO200306_01_02           Truise Date:         2003/06/04 - 2003/08/11						
	From:: MORDY, CALVIN							
	Email address: Calvin.W.Mordy@noaa.gov Institution: NOAA/PMEL							
	Country.	USA						
	The file: A16 $2004122$	9 N-Apr14nuts-subm 9 134359 MORDY	Alted xis - 120/296 bytes has been saved as: Alter Alter Alter April 4 nuts-submitted xis					
	in the dir	rectory: 20041229.1	134359_MORDY_A16N					
	The data dispo Public	e data disposition is:						
	The bottle file has the following parameters:							
	The file forma	SILCAI, NIIKAI, NIIKII, PHSPHI e file format is:						
	MS Exce	MS Excel (Binary)						
	The archive ty NONE -	/pe is: Individual File						
	The data type Bottle Da	(s) is: ata (hyd)						
	The file contains these water sample identifiers:							
	Cast Number (CASTNO)     Station Number (STATNO)							
	• Station • Bottle I	Number (BTLNBR)	·)					
	MORDY, CA	LVIN would like th	ne following action(s) taken on the data:					
	• Merge	Data						
	• Place L • Update	Parameters						
	Any additiona	al notes are:						
	• Data ar	e provided in µmole	e/l and μmole/kg.					
	• The lab also pr	temperature and the ovided.	e CID bottle salts that were used in the unit conversion are					
12/30/04	Bullister	Cruise Report	Submitted Oxygen Data Report					
	The cruise we	did was A16N_200	03 (not p16n_2003).					
	I forwarded Jim Swift's directive (see next message) to all the investigators on A16N_2003 last February, advising them to forward data and documentation directly to the CCHDO- WHPO. I'll send out another reminder. <i>(next page)</i>							

Date	Contact	Data Type	Data Status Summary			
12/30/04	Bullister	Cruise Report	Submitted Oxygen Data Report (continued)			
	In addition to the carbon data and documentation, I have copies here of the revised CTD and bottle salinity data from Kristy McTaggart, revised CFC data from our group, revised oxygen data (and documentation) from Z.Zhang, and revised nutrient data from Calvin Mordy. I can send you these individual files as attachments to the next message. I have merged all of these revised data files into Frank Delahoyde's A16n2003 shipboard file to create a master data file in the .sea format. I can also sent this to you. Unfortunately, I am heading out tomorrow for the A16S cruise and can't do much more before I leave. I will have all the a16n2003 data with me on the cruise and should be able to answer questions by e-mail					
	My address should be:john.bullister.atsea@rbnems.ronbrown.omao.noaa.gov					
01/18/05	Anderson	CO2	Website Updated, data OnLine			
	File Jan. 18, 2 a16n_2003a 3 Merged the ca his email belo Date Fri, From: Alex Subject: A22 To: Sari Thank you ver Could you ch TCO2), ALKA any changes in four paramete but in reality v	2005 33RO200306_01 arbon data (TCO2, w into online file. 14 Jan 2005 14:18: ander Kozyr <kozy 2003 Alkalinity d lee Anderson <saril ry much Sarilee. Di eck A16N_2003a f ALI, pH, and pCO2 n your files. When rs, because from th we PIs changed som</saril </kozy 	TALK, PH, and PCO2) sent by A. Kozyr Dec. 10, 2004 re Made new exchange and netcdf files. 05 -0500 yra@ornl.gov> ata lee@minerva.ucsd.edu> d you make a new exchange file as well? files? I've sent the final carbon-related data (TCARBN (or 2) for this section on 12/10/2004 to WHPO but did not see you merge these data, please make sure that you merge all he first look it seems like TCARBN and pH are the same, he numbers and flags for both.			
02/14/05	Kappa	Cruise Report	Replaced "Cruise Instructions"			
	The bulk of this cruise report was submitted by Alex Kozyr on 12/10/04. It includes sections on: • TCARBN • Fugacity of CO2 • ALKALI • pH • Nutrients • Oxygen • Figures • Tables					
	Both the PDF and ASCII cruise reports also contain the WHPO/CCHDO summary pages and these Data Processing Notes. Figures are found only in the PDF version. The PD version also has links from text to figures and tables, PDF bookmarks and PDF thumbnails.					
03/10/05	McTaggart	CTD	Submitted Data Processing Report			
	Attached is th data last Nov nutrients etc. a	e CTD documentat rember. He said and submitted to W	ion file I gave to John Bullister along with the CTD bottle it was incorporated into a document with oxygens and HPO.			

Data	Processing	Notes
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Date	Contact	Data Type	Data Status Summary			
03/15/05	Kappa	CTD	Added CTD Data Processing report			
	Added CTD I	Data Processing Rep	oort to Cruise report			
05/19/05	Locarnini	CTD	Data Update: oxy values corrected			
	Please, notice CASTNO 1, a	ase, notice that all CTD dissolved oxygen values for 33RO200306, STNNBR 018, STNO 1, are equal to 0.0 (Zero) and have a Quality Flag equal to 2 (Two).				
06/21/05	Anderson	TOC/TDN	Data, Exchange, and NetCDF files online			
	a16n_2003a 2	33RO200306_01 an	nd 33RO200306_02			
	Merged the D by Dennis H	OOC (dissolved orga Hansell on Oct. 27, 2	anic carbon) and TDN (total dissolved nitrogen) submitted 2004.			
	Many values	of -9.00 had flag of	2 or 3, I changed the flags for values of -9.00 to 9.			
	There was one	e level that was not	in the online file and therefore was not merged, see below.			
	STNNBR (	CASTNO SAMPNO	BTLNBR DOC DOCF TDN TDNF			
	150 1	kg/kg k	33 66 2			
	Made new exe	change and NetCDF	F files. Sarilee Anderson			
08/29/05	Kozyr	DOC/TDN	Submitted Final Data			
	I tried to submit some files to CCHDO through your web site, but it would not work, it would ask me to complete the form, but form was completely completed :-) and I did not know what it wanted from me. So, the attached file is the final and public DOC and TDN data measured during the A16N_2003a cruise (33RO200306_01_02). Could you please merge these data and their quality flags into the main hydrographic files. Please, let me					
09/06/05	Anderson	DOC/TDN	Data Online; No exchange file yet			
	Merged the fi into the online Was not able TDN.	Merged the final DOC and TDN data submitted by Alex Kozyr (see B.Key 8/26/05 email) into the online file. No apparent problems. Was not able to make the exchange file Program needs to be modified to accept DOC and TDN				
09/22/05	Bullister	Cruise Report	Submitted cruise report and cfc report			
	I was the Chi 33RO200306	ef Scientist on the 1_01).	repeat hydrography cruise A16N_2003a (Cruise ExpoCode			
	I did a quick currently at th	c check to compare the web site:	e the shipboard data file from A16N_2003a to the files			
	http://whpo.ue	csd.edu/data/CO2cl	ivar/atlantic/a16/a16n_2003a/index.htm			
	I think the b fctdoxy), diss versions.	I think the bottle hydro values (ctdprs, ctdtmp, ctdsal, salnty, ctdoxy, fctdsal, fsalnty, fctdoxy), dissolved oxygen, nutrients, and CFCs have not been updated from the shipboard versions				
	Last year I asl	ked the individual P	I's to send their updated A16N_2003a data to the <i>(next page)</i>			

Date	Contact	Data Type	Data Status Summary					
09/22/05	Bullister	BTL	Submitted updated BTL files (continued)					
	CCHDO offic updated hydro important to g	e directly, as per b, oxygen, nutrient et the updated version	Jim Swift's instructions. I also sent copies I had of the and CFC data to the office some time ago I think it is ions of the data merged into your web site files					
	In the next me	essage I will attach t	the following files:					
	a16n_allo.f	lg	g					
	(revised data, prej	bottle file of ctdpr pared by Kristy Mc	s, ctdtmp, ctdsal, salnty, ctdoxy, fctdsal, fsalnty, fctdoxy Taggart at PMEL)					
	A16NBottl	eOxygenFinal_may	221_2004.xls					
	in per lite	er units)	a oxygen data, from Jia-Znong Znang at AOML; data are					
	A16NBottl	eOxygenFinal_may	21_2004working.txt.sent toWOCE*					
	(ASCII ver	sion of oxygen dat	ta I extracted from above Excel spreadsheet. I changed 5					
	A16nuts-api	14.xls (Excel sp	readsheet of revised nutrient data from Calvin Mordy at					
	PMEL; d	lata are in per liter units)						
	• A16nuts-apr	14working.txt						
	(ASCII v per liter u	version of revised nutrient data I extracted from above spreadsheet; data are in units)						
	• a16n2003_c	fc.dat						
	(ASCII li	isting of revised CF	g of revised CFC data from John Bullister; data are in per kg units)					
	flag changes	5	he flag changes I applied to the master bottle data file I keep here at stly change the parameter flags for samples where the fbtlnbr is 3, 4					
	(a file de PMEL. or 9)	scribing the flag ch These mostly chang						
	I would be ext you have into the v	tremely grateful if y any questions or c web site version of t	ely grateful if you could let me know that you have received these files, i questions or comments on the files, and when the data have been merge site version of the A16N 2003a data set					
09/23/05	Locarnini	CTDOXY	Update Needed					
	Please, notice CASTNO 1, a	that all CTD distrete equal to 0.0 (Zer	solved oxygen values for 33RO200306, STNNBR 018, o) and have a Quality Flag equal to 2 (Two).					
09/23/05	Anderson	CTDOXY	Data values corrected as per Locarnini					
	Station 18 oxy	gens were all 0.0, b	but the Q flag was 2					
	<ul> <li>I changed</li> <li>Made new</li> </ul>	the flags to 9 for al $\frac{1}{2}$	l oxygens cted stall 18 and made a new exchange file					
	I was unable t	o make a NetCDF f	ile at this time					
09/26/05	Mordy	Cruise Report	and Nutrients report submitted					
	Here is a more	e informative version	on of the A16N cruise report for nutrients					
10/12/05	Kappa	Cruise Report	Updated w/ new Chi Sci, PI reports					
	<ul> <li>John Bull:</li> <li>Mordy's n</li> </ul>	ister's cruise summa	ary, OXY and CFC reports,					
	• K. McTag	gart's CTD report,	and					
	• NOAA/P	MEL CO <sub>2</sub> report; ar	nd					
	<ul> <li>expanded</li> </ul>	• expanded CCHDO data processing notes.						

Date	Contact	Data Type	Data Status Summary					
10/27/05	Bullister	BTL	Final data submitted					
	Updates prelim	m data files, see 9/22/	05 Updates prelim data files, see 9/22/05					
10/28/05	Bishop	Transmisometer	Data availability: 1/2006					
	I am responsi records during those for A10 sucessive yea NOAA related	ble for the data and i g A16N. FYI, results 6N. I estimate comp rs when funding did d work had to stop.	it's final workup. There were significant data dropouts in s from A16S should be available about the same time as eletion to be approximately January 2006. We had two not appear as expected (this year a 4 month gap) and all					
10/28/05	Anderson	BTL	Updating files from Bullister					
	I am working yesterday.	on merging, updatin	g the a16n_2003a line using the files the Bullister sent					
12/12/05	Smith	MET	Submitted					
	Hello John,I j A16N cruise	ust wanted to let you from the Ronald Brow	know that we received the meteorological data from your vn's					
	The data unde Brown meteor	erwent quality contro rology data at:	at FSU and are available as part of a larger set of Ron					
	http:	//www.coaps.fsu.edu/	r/RVSMDC/cgi-bin/nonwoce-ship.cgi?id=WTEC					
01/09/06	KappaCruise ReportUpdatedAdded Chief Scientist ReportDeleted redundant Oxygen ReportUpdated these Data Processing Notes							
01-30-06	0-06       Jim Bishop       Transmissometer       Submitted       raw data only         A16N_2003 & A16S_2005 wil be completed together       All I can do is work forward on this. A16N and A16S data will be completed together, after Ocean Sciences.         The rew data are on line at SIO							
05-10-06	Iohn L. Rullister	Cruise Report	To go online OK'd by Bullister					
	Thanks for sending	g the file. I read through	it and it looks OK.					
05-22-06 / I	5       Alexander Kozyr       DOC       Submitted       None         I submitted the DOC data from P02_2004 and A16N_2005 using CCHDO submission page. I received the A20 and A22 DOC data files from you, so I guess you have these files, but I did not see the DOC numbers for these cruises were merged at CCHDO yet.         Here are attached 3 files for DOC data from P02_2004, A16N_2003, and A16S_2005 cruises. Please, let me know if you received these files OK and when are you planning to merge these data.							
09-06-06	Sarilee Anderson	DOC/TDN	Website Updated: Data OnLine; no exchange					
	Sept. 6, 2006 Merged the final I No apparent probl Was not able to m	DOC and TDN data subr ems. ake the exchange file. P	nitted by Alex Kozyr (see B.Key 8/26/05 email) into the online file. rogram needs to be modified to accept DOC and TDN.					

Date	Contact	Data Type	Data Status	Summary			
11-15-06	Alexander Kozyr	CO2	status summary	None			
03-02-07	Alexander Kozyr Here are the latest A16N_2003: TCO2 - OK; TALK - OK; pCO2 - OK; pH - OK; DOC, DTN - data Wilford Gardner File: a16n1POC_s Name: Gardner, W Institute: Texas Ac Country: USA Expo:33RO2003_ Date: 06/2003 Action:Merge Dat Notes: These are POC and	CO2 update on the Carbon were not merged in C <u>POC/PON</u> ubmission-redo2.xls T /ilford D &M University 01 Line: A16N a,Place Data Online d PON bottle data	status summary Data status at CCH CHDO exchange fi Submitted 'ype: Excel Status:	None IDO and CDIAC. le. None Public			
00.00.07		mcoming_data/2007	1307.070010_A10F				
05-26-07	pH data for A16N_2003 have major problems and will be revised. I am going to put a note on a web that nobody should use pH numbers at this time. Could you do the same, please? I will send you new numbers as soon as I get the new file from Frank Millero.						
10-04-07	Alexander Kozyr	CO2/PH	Submitted	New params: FCO2, FCO2_TMP, PH_SWS, PH_TMP			
	Type: Status: public Name: Kozyr, Alex Institute: CDIAC/ORNL Country: USA Expo:33RO200306_01 Line: A16N_2003a Date: 2003-06-04 Action:Merge Data, Place Online, Updated Parameters Notes:Please, replace all carbon-related parameters with these ones in the attached file. Note that PCO2 was replaced with FCO2 and extra column for FCO2_TMP, also PH was replaced with PH_SWS (pH on the sea water scale) with extra column for PH_TMP. Please, let me know when the data in this file will be merged with the master file at CCHDO						
01-02-08	Alexander Kozyr	CO2	Submitted	Replaces all previous CO2 data			
	Please, replace all carbon-related parameters with these. Note that PCO2 was replaced with FCO2 and extra column for FCO2_TMP, also PH was replaced with PH_SWS (pH on the sea water scale) with extra column for PH_TMP.						
08-06-08	Wilf Gardner Attached are two f your revised file w been posted as cas have any other dat they were associat in yellow or by a c	POC/PON iles - a revision of the ve have indicated what t 2. Most of the others a. They were taken on ed. You can add these lifferent font color in t	Submitted file you sent and th to do with each fil are in-line samples station as indicated or ignore them as y he other attached fi	Revision of 7/7/08 data file ne file we sent in with the data for the bottles. In e. As you suspected, many of them should have s (inflow) or bucket samples for which you don't d by the same lat-lon as the stations with which you wish. The stations in question are highlighted ile.			

Date	Contact	Data Type	Data Status	Summary				
07-07-08	Danie Bartolocci	POC/PON	Website Updated	Sumbitted by Wilf Gardner				
	Notes on Completed WOCE Bottle file:							
	Created exchange file with no apparent errors. File named a16n_2003a_hy1.csv							
	Following parameters were not recognized nor included in the exchange file: FCO_TMP PH_SWS PH_SWS_FLAG_W PH_TMP POC POC_FLAG_W PON PON_FLAG_W TDN_FLAG_W TDN_FLAG_W The exchange conversion code changed FCO2 to PCO2 during conversion. This was edited back in file. Checked file with JOA, which also calls FCO2 by another parameter name, however this appears to be a JOA bug and FCO2 values appear accurate.							
	Created netcdf files with no apparent errors. Zipped file is named a16n 2003a nc hyd.zip							
07-08-08	Danie Bartolocci     CO2     Website Updated     Submitted by Alex Kozyr       2008.07.08 DBK     V     V     V							
	Merge notes for m	erging Alex Kozyr's fi	nal carbon data into	the a16_2003a bottle file.				
	Data submitted by Alex on 10.05.2007. File named a16n_2003a_final_Carbon.csv contained the following parameters: FCO2,FCO2_TMP,PH_SWS_25C,PH_TMP,TALK,TALK_FLAG_W,TCO2,DOC,TDN and their associated quality flags.							
	Instructions as per Notes: Please, repl replaced with FCC water scale) with e with the master fil	Alex's web submission lace all carbon-related 22 and extra column fo extra column for PH_T e at CCHDO.	n entry were: parameters with the r FCO2_TMP, also MP. Please, let me	ese ones in the attached file. Note that PCO2 was PH was replaced with PH_SWS (pH on the sea know when the data in this file will be merged				
	MERGE NOTES: Original file was .csv and had to be converted to fixed width in order to use merge software mrgsea.							
	mrgsea did not accept FCO2_TMP as an integer for merging. This parameter was edited to a floating point number with precision of 1 (f8.1).							
	PH_SWS missing	values of -999.0000 ar	e larger than the w	oce format allows and were edited to -9.0000.				
	All parameters me were unrecognized	rged without problems 1.	or errors. Ran woo	eevt with no errors, however some parameters				
	I							

Date	Contact	Data Type	Data Status	Summary				
07-09-08	Danie Bartolocci	DELC14/13	Website Updated	Sumbitted by Bob Key				
	2008.07.09 DBK							
	Merging notes for C14/13 into a16n_2003a bottle file.							
	file submitted by Bob Key on 2008.06.26 called A16N.2003.CIsotopes.csv contains: DELC14,C14ERR,DELC13 and associated errors All parameters merged with no apparent errors. Checked the format of the file using woccvt. No errors were reported.							
	Bottle file still nee	ds PON/POC data mer	ged.					
07-14-08	Shari Yvon Lewis	HCFC	Submitted	HCFC-22.HCFC142b.HCFC141b				
07-14-08	Shari Yvon Lewis	CH3	Submitted	CH3Cl CH3Br CH3I				
12-12-08	Chris Measures	BTL	Submitted	Updated Fe/Al params				
	Status: nublic							
	Action: Updated P	arameters						
	Notes: These are t	he shorebased correcte	d values of the shir	board generated trace elements Fe and Al. They				
	are in tab delimite	text the output from a	an ODV file contai	ning location station bottle cast information etc				
	Quality flags are a	ssigned using the ODV	7  mapping  0 = good	1=unknown $4=$ questionable $8=$ bad				
	Quality hugs are a	ssigned using the obt	mapping o good					
08-07-09	Chris Measures	Tracers	Submitted	AL/FE/MAN				
	the data are public							
	parameter names a	ind units						
	Station number							
	Cast number + bot	tle number						
	Aluminum (unit: n	M)						
	Flag							
	Iron (unit: nM)							
	Flag							
	Manganese (unit: 1	nM)						
	Flag							
07-31-10	Carolina Berys	CH3	Website Update	Available under 'Preliminary/Unprocessed'				
	A16N MeX HY1	.csv submitted by Shar	ri Yvon Lewis on 2	008-07-14 available under				
	'Preliminary/Unpre	ocessed', unprocessed l	by CCHDO.					
08 02 10	Carolina Barys	POC/PON	Website Undate	Available under 'Preliminary/Unprocessed'				
08-02-10	alén1POC submi	1/100/10 m	websile Opuale mitted by Danie Ki	needeon behalf of Wilf Gardner on 2008 08 06				
	available under 'Pr	eliminary/Unprocesse	d' upprocessed by	CCHDO POC/PON data not merged in Exchange				
	file these data are	merged in WOCE for	nat file	eenbo. 10e/100 data not merged in Exchange				
	ine, mese data are		nat me.					
09-21-10	Carolina Berys	CDOM	Website Update	Available under 'as received'				
	File a16ncdom_final.txt containing CDOM data submitted by Norm Nelson on 2005-04-20, resubmitted by email from Susan Piercy on behalf of Norm Nelson on 2010-09-21, available under 'as received', unprocessed							
	by CCHDO.							
09-21-10	Carolina Berys	CDOM	Submitted	resubmission of text file				
	Action: Merge Da	ta						
	Notes: CDOM data submitted by Norm Nelson on 2005-04-20, resubmitted by email from Susan Piercy on							
	behalf of Norm Ne	elson on 2010-09-21.						

Contact	Data Type	Data Status	Summary										
Alex Kozyr	Carbon	Submitted	Final data to go online										
I've just discovered that the CCHDO Exchange file for the a16n_2003a cruise 33RO200306, does not have PH, PH_TMP, PH_FLAG, FCO2_TMP, and TDN data. I'vesend the final carbon data file with all these data to CCHDO on 10.05.2007, according to my notes. Attached is the final a16n_2003a_final_Carbon.csv data file for your use. Please merge the data into CCHDO Exchange file.													
Carolina Berys	CO2	Website Updated	Exchange, NetCDF files online										
<ul> <li>2011-08-24</li> <li>A16N 2003 ExpoCode 33RO200306_01</li> <li>WOCE to Exchange conversion notes C Berys</li> <li>Converted WOCE bottle file to Exchange using hyd_to_exchange.rb (J Fields)</li> <li>The following changes were made to the WOCE bottle file:</li> <li>FCO_TMP changed to FCO2TMP</li> <li>FCO2TMP units changed from 'ITS-90' to 'DEG C'</li> <li>PH_TMP units changed from 'ITS-90' to 'DEG C'</li> <li>NOTE: Units for PON and POC are 'UMOL/L' which does not match the value in the parameter descrip table 'UG/KG'.</li> </ul>													
							All comment lines from original file copied back into new file following merge						
							NetCDF bottle file created using exbot_to_netcdf.pl (S Diggs), files zipped						
NetCDF and Exchange files opened in JOA with no apparent problems													
Working directory: /data/co2clivar/atlantic/a16/a16n_2003a/original/20110823_carbon_cberys													
Carolina Berys	CDOM	Website Updated	Updated NetCDF, Exchange, WOCE files online										
2011-11-22 A16N 2003 ExpoCode 33RO200306_01 merge notes - CDOM													
a16ncdom_final.txt submitted by Norm Nelson on 2005-04-20, resubmitted by email from Susan Piercy behalf of Norm Nelson on 2010-09-21, containing CDOM data merged into online file us merge_exchange_bot.rb (J Fields)													
The following parameters were added: CDOM325 CDOM325 FLAG W													
CDOM340 CDOM340_FLAG_W													
CDOM380 CDOM380_FLAG_W CDOM412 CDOM412_FLAG_W													
							CDOMSL CDOMSL_FLAG_W						
CDOMSN CDOMSN_FLAG	_W												
	Contact Alex Kozyr I've just discovere PH, PH_TMP, PH to CCHDO on 10. file for your use. F Carolina Berys 2011-08-24 A16N 2003 Expoo WOCE to Exchan Converted WOCE The following cha FCO_TMP change FCO2TMP units ch NOTE: Units for I table 'UG/KG'. All comment lines NetCDF bottle file NetCDF and Exch Working directory /data/co2clivar/atl Carolina Berys 2011-11-22 A16N 2003 Expoo C BerysSUBMISS a16ncdom_final.tb behalf of Norm merge_exchange_ The following par CDOM325 CDOM325 CDOM340 CDOM340_FLAC CDOMSL_FLAG CDOMSN_FLAG	ContactData TypeAlex KozyrCarbonI've just discovered that the CCHDO ExcPH, PH_TMP, PH_FLAG, FCO2_TMP, to CCHDO on 10.05.2007, according to 1file for your use. Please merge the data inCarolina BerysCO22011-08-24A16N 2003 ExpoCode 33RO200306_01WOCE to Exchange conversion notes CConverted WOCE bottle file to ExchangeThe following charges were made to theFCO_TMP changed to FCO2TMPFCO2TMP units changed from 'ITS-90' toNOTE: Units for PON and POC are 'UMtable 'UG/KG'.All comment lines from original file copNetCDF bottle file created using exbot_tNetCDF and Exchange files opened in JCWorking directory:/data/co2clivar/atlantic/a16/a16n_2003a/Carolina BerysCDOM2011-11-22A16N 2003 ExpoCode 33RO200306_01C BerysSUBMISSIONa16ncdom_final.txt submitted by Normbehalf of Norm Nelson on 2010-0merge_exchange_bot.rb (J Fields)The following parameters were added:CDOM325CDOM325CDOM380CDOM380CDOM380CDOM380CDOM380CDOM380CDOM380CDOMS1CDOMS1CDOMSNCDOMSNCDOMSN_FLAG_W	ContactData TypeData StatusAlex KozyrCarbonSubmittedI've just discovered that the CCHDO Exchange file for the aPH_TMP, PH_FLAG, FCO2_TMP, and TDN data. I'veto CCHDO on 10.05.2007, according to my notes. Attachedfile for your use. Please merge the data into CCHDO ExchanCarolina BerysCO2Website Updated2011-08-24A16N 2003 Expo⊂de 33RO200306_01WOCE to Exchange conversion notes C BerysConverted WOCE bottle file to Exchange using hyd_to_excThe following changes were made to the WOCE bottle file:FCO_TMP changed to FCO2TMPFCO2TMP units changed from 'ITS-90' to 'DEG C'PH_TMP units changed from 'ITS-90' to 'DEG C'NOTE: Units for PON and POC are 'UMOL/L' which does table 'UG/KG'.All comment lines from original file copied back into new fileNetCDF bottle file created using exbot_to_netcdf.pl (S DiggNetCDF and Exchange files opened in JOA with no apparentWorking directory:/data/co2clivar/atlantic/a16/a16n_2003a/original/20110823_Carolina BerysCDOMWebsite Updated2011-11-22A16N 2003 Expo⊂de 33RO200306_01 merge notes - CDOC BerysSUBMISSIONa16ncdom_final.txt submitted by Norm Nelson on 2005-0behalf of Norm Nelson on 2010-09-21, containingmerge_exchange_bot.rb (J Fields)The following parameters were added:CDOM325CDOM380CDOM380CDOM380CDOM380CDOMSN_CDOMSNCDOMSN_FLAG_WCDOMSN <td< th=""></td<>										

The following changes were made to the submission file: added parameter mnemonics and units added cast 1 to all stations in accordance with sum file changed bottle numbers to 3 digits with leading zeros

Date	Contact	Data Type	Data Status	Summary			
11-22-11	Carolina Berys	CDOM	Website Updated	Updated NetCDF, Exchange, WOCE files online			
	ORIGINAL						
	The following changes were made to the original Exchange Bottle file:						
	DEPTH units changed from "" to "METERS"						
	CTDRAW units changed from "" to "DBAR" NOTE: PON and PON have units "UMOL/L" which do not match the expected "UG/KG"						
	MERGED FILE						
	All comment lines from original file copied back in following merge						
	NetCDF bottle file created using exbot_to_netcdf.pl (S Diggs)						
	WOCE bottle file created using exchange_to_wocebot.rb (J Fields)						
	Exchange and NetCDF files opened in JOA with no apparent problems						
	Working directory						
	/data/co2clivar/atlantic/a16/a16n_2003a/original/2011_11_21_cdom_chervs/						
05.04.10							
05-04-12	Jerry Kappa	CrsKpt	Website Updated	new PDF & TXT versions online			
	Additions/changes include:						
	• New CFC report						
	New Summary/Introduction						
	<ul> <li>New sections on Dissolved Organic Carbon, 14C &amp; Helium/Tritium</li> </ul>						
	Expanded Nutrients report						

• expanded data processing notes