GO-SHIP CLIVAR A16S

NOAAS Ronald H. Brown
23 December 2013 – 05 February 2014
Recife, Brazil – Punta Arenas, Chile

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Preliminary Cruise Report

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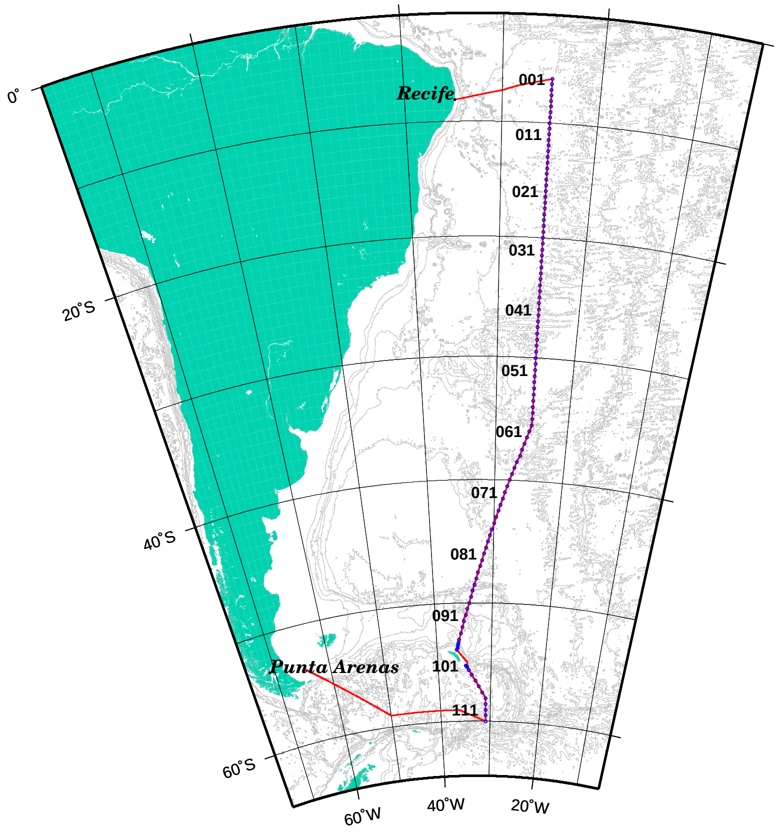
GO-SHIP CLIVAR A16S Cruise Track

Introduction

The GO-SHIP CLIVAR/CO_2 cruise in the South Atlantic on NOAA ship *Ronald H. Brown* was successfully completed over the period from 23 December 2013 to 05 February 2014. This cruise is part of a decadal series of repeat hydrography sections jointly funded by NOAA-CPO/COD and NSF-OCE as part of the GO-SHIP (Global Ocean Ship-Based Hydrographic Investigations Program) CLIVAR/CO_2/hydrography/tracer program (http://ushydro.ucsd.edu). The goal of this effort is to occupy a set of hydrographic transects over the global ocean with full water column measurements to study physical and hydrographic trends and variability over time.

The A16S cruise began in Recife, Brazil and ended in Punta Arenas, Chile. Many academic institutions and two NOAA research laboratories participated in the cruise. The A16S section ran due south along 25°W from approximately 6°S to 35°S, and then transited in a Southwest direction to South Georgia Island at 54°S, 36°W. The last part of the section crossed the Scotia Sea with a terminus at 60°S, 31°W. This is a repeat of the section previously occupied by the U.S. in 1989 and 2005. A total of 113 full water column CTD/O_2/LADCP/rosette casts were completed along the A16S section at 30 nautical mile (nm) (54 km) spacing, with closer spacing at the basin boundaries near South Georgia. Measurements taken from the instrument package include temperature, salinity, oxygen, currents (LADCP), micro-turbulence structure (Chipod), particles (transmissometer), and colored dissolved organic matter, CDOM (fluorometry). Approximately 2700 Bullister bottle samples were collected on these casts and analyzed for a variety of parameters including salinity, dissolved oxygen, nutrients, chlorofluorocarbons (CFCs), SF_6, dissolved inorganic carbon (DIC), alkalinity, pCO_2, pH, carbon isotopes (^{14}C DIC), dissolved organic carbon (DOC), $^{18}O/^{16}O$, helium, tritium, density, and trace metals.

Underway data collection included upper-ocean current measurements from the shipboard ADCP, surface oceanographic (proxi-chlorophyll by fluorometry, temperature, salinity, CO_2) and meteorological parameters from the ship's scientific seawater supply, bathymetric data and atmospheric measurements of CO_2, CFCs, and SF_6.

Data from this cruise are available from CCHDO at:

http://cchdo.ucsd.edu/data_access/show_cruise?ExpoCode=33RO20131217

Acknowledgements

The successful completion of the cruise relied on the dedicated assistance from many individuals on shore and on the NOAA ship *Ronald H. Brown*. Funded investigators in the project and members of the GO-SHIP CLIVAR/CO_2 program were instrumental in the successful planning and executing of the cruise. All of the participants showed dedication, cooperation and camaraderie during their 45 days at sea. Officers and crew of the *Ronald H. Brown* exhibited a high degree of professionalism and assistance in accomplishing the mission and made us feel at home during the voyage. Commanding officer Joseph Pica oversaw a smoothly running ship and engaged with the scientific party. Operations officer Paul Chamberlain was an excellent liaison before, during, and after the cruise to accommodate all scientific operations and scheduling. Survey Technicians Darcy Balcarce, Jonathan Shannahoff and Electronics Technician Clay Norfleet contributed to the success of this cruise through their able deck handling, stewardship of shipboard scientific gear and expert instrument and infrastructure troubleshooting experience. All officers, deck crew, engineers, and galley staff contributed to the success of this long cruise that occurred over the holiday season. Their sacrifice, assistance and good cheer are gratefully acknowledged.

The U.S. GO-SHIP Repeat Hydrography/CO_2 Program is sponsored by the NOAA Climate Observation Division of the Climate Program Office (COD/CPO) and the National Science Foundation. In particular, we wish to thank program managers David Legler and Joel Levy (NOAA/CPO), and Eric Itsweire and Don Rice (NSF/OCE), for their insights, moral and financial support.

Clearance was requested and granted from the sovereign nations of the United Kingdom and Argentina for research conducted in their declared territorial waters. Their permission to execute the research effort in the waters surrounding South Georgia Island/Isla Georgia del Sur was critical for the repeat occupation and is greatly appreciated.

Background

The CLIVAR Repeat Hydrography Program focuses on the need to monitor inventories of CO_2, tracers, heat and freshwater and their transports in the ocean. Earlier programs under WOCE and JGOFS provided a baseline observational field for these parameters. The new measurements reveal much about the changing patterns on decadal scales. The program serves as a backbone to assess changes in the ocean's biogeochemical cycle in response to natural and/or man-induced activity. Global changes in the ocean's transport of heat and freshwater, which can have a significant impact on climate, can be followed through these long-term measurements. The CLIVAR/CO_2 Repeat Hydrography Program provides a robust observational framework to monitor these long-term trends. These measurements are in support of:

- Model calibration and testing
- Carbon system studies
- Heat and freshwater storage and flux studies
- Deep and shallow water mass and ventilation studies
- Calibration of autonomous sensors

This program follows the invasion of anthropogenic CO_2 and transient tracers into intermediate and deep water on decadal timescales and determines the variability of the inorganic carbon system and its relationship to biological and physical processes. More details on the program can be found at the website: http://ushydro.ucsd.edu. Specific information about this cruise can be found at:

http://www.aoml.noaa.gov/ocd/gcc/A16S_2014/

Thanks to science participant Rachel Shelley for her informal "blogs" that recount cruise/port highlights. A link to this blog can be found on the cruise website.

GO-SHIP CLIVAR A16S Participating Institutions

Abbreviation	Institution
AOML	Atlantic Oceanographic and Meteorological Laboratory - NOAA
RSMAS	Rosenstiel School of Marine and Atmospheric Science/University of Miami
PMEL	Pacific Marine Environmental Laboratory - NOAA
FSU	Florida State University
SIO	Scripps Institution of Oceanography/University of California at San Diego
UH	University of Hawaii at Manoa
UCSB	University of California Santa Barbara
UT	University of Texas at Austin
WHOI	Woods Hole Oceanographic Institution
PU	Princeton University
OSU	Oregon State University
LDEO	Lamont-Doherty Earth Observatory/Columbia University

Principal Programs of GO-SHIP CLIVAR A16S

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CTDO	NOAA/PMEL NOAA/AOML	Gregory Johnson Molly Baringer	Gregory.C.Johnson@noaa.gov Molly.Baringer@noaa.gov
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Measurement Program Summary

NOAA Ship *Ronald H. Brown* departed Recife, Brazil, after a 2-day delay waiting for the arrival of two drums of conducting cable for the CTD winch, early morning on 23 December 2013 and arrived in Punta Arenas, Chile on 5 February 2014. A total of 113 stations were occupied during the A16S cruise which was run from north to south. The stations encompassed 113 CTD/O_2/LADCP/rosette casts and 58 trace metal casts. Fourteen Argo floats were deployed during the cruise. CTD/O_2 data, LADCP data, Chipod data, and 24 water samples were collected on the main CTD casts. Twelve samples were collected on most trace metal casts. With the use of the main rosette equipped with an altimeter, each cast came to within 8-20 meters of the bottom (see Appendix). The trace metal casts went to a depth of approximately 1000 meters. For all occupied stations, a 24-position, 11-liter Bullister bottle rosette frame (NOAA/AOML white frame) was used. A dedicated winch, 12-position rosette with 10-liter GO-FLO bottles, a white specially coated Rosette frame and special cable, to avoid trace metal contamination, supplied by UH/FSU was used every other station for trace metals. Salinity and nutrient samples were collected and analyzed on all the water samples collected from the CTD and trace metal casts. Detailed sample collection from the trace metal casts is outlined in the Trace Metals section describing the UH/FSU trace metal analytical program. The distribution of the Bullister bottle samples during the course of the cruise can be seen in Figures 1.1 and 1.2 below.

1. CTD Data Acquisition and Rosette Operation

CTD Underwater Package

Sea-Bird instrumentation was mounted in a white 24-position aluminum frame with 24, 11-liter PMEL Bullister bottles and PMEL 24-position carousel combination s/n 3210881-0053 (pylon) and s/n 3232696-0471 (tripping mechanism). Sea-Bird sensors on the package included AOML's 9plus CTD s/n 09P54833-0957 and shared TCO (temperature, conductivity, oxygen) sensors: primary TCO s/n 03-02/F-1370, 04C-3860, 43-0664 with 05T-1227; and secondary TCO s/n 03-02-1710, 04C-1467, 43-1890 with 05T-0819. Equal distance between the temperature sensors was PMEL's SBE 35RT internally recording reference temperature sensor s/n 54996-0072. Also mounted on the underwater package was a Metrox load cell s/n 8756, Kongsberg altimeter s/n 1108078 and battery pack, UH's 150 kHz downward looking LACDP and battery pack, TAMU's Cstar transmissometer s/n CST-327DR, UCSB's Wetlabs CDOM fluorometer s/n FLCDRTD-3117, and 5 Chipod sensors and battery pack. There was no room to mount a pinger.

The underwater package was electrically terminated to the new 0.322" cable on the aft winch using hot glue in heat shrink. A grounding strap was necessary at the winch to prevent acquisition alarms and errors. A strand of armor was not used in the electrical termination as recommended by Sea-Bird.

CTD Data Acquisition

The CTD data acquisition system consisted of the ship's SBE-11*plus* (V2) deck unit s/n 11P9852-0367 and a networked Dell Optiplex 755 PC workstation running Windows XP Professional. SBE Seasave v.7.21d software (c.2011) was used for data acquisition and to close bottles on the rosette. Real-time digital data were backed up by the data manager, and raw data files were archived immediately after each cast on a thumb drive as well as on Survey and PMEL networked PCs. No real-time data were lost during this cruise.

CTD deployments were initiated by Survey after the Bridge advised that the ship was on station. The computer console operator maintained a CTD Cast log recording position and depth information at the surface, depth, and end of each cast; a record of every attempt to close a bottle, and any pertinent comments.

After the underwater package entered the water, the winch operator would lower it to 15 meters and hold. After a 60-second startup delay, the pumps turned on. The console operator watched the CTD data for reasonable values, waited three minutes at the soak depth for sensors to stabilize, instructed the winch operator to bring the package to the surface, paused for 20 seconds, and began the descent to a target depth approximately 10 meters above the sea floor. The descent rate was nominally 30 m/min to 50 m, 45 m/min to 200 m, and 60 m/min deeper than 200 m. These rates could vary depending on sea cable tension and the sea state.

The console operator monitored the progress of the deployment and quality of the CTD data through interactive graphics and operational displays. The Chief or co-Chief created a sample log for the cast that would be used to record the water samples taken from each Bullister bottle. The altimeter channel, CTD depth, wire-out, and EM122 bathymetric depth were all monitored to determine the distance of the package from the bottom allowing a safe approach to within 10 meters.

Bottles were closed on the upcast through the software, and were tripped 30 seconds after stopping at a bottle depth to allow the rosette wake to dissipate and the bottles to flush. The winch operator was instructed to proceed to the next bottle stop 15 seconds after closing bottles to ensure that stable CTD and reference temperature data were associated with the trip.

Near the surface, Survey directed the winch to stop the rosette just beneath the surface. After the surface bottle was closed, the package was recovered. Once on deck, the console operator terminated data acquisition, turned off the deck unit, and assisted with rosette sampling.

At the end of each cast, primary and secondary CTDO sensors were flushed with a solution of dilute Triton-X in de-ionized water using syringes fitted with tubing. The syringes were left attached to the temperature ducts between casts, with the temperature and conductivity sensors immersed in the rinsing solution to guard against airborne contaminants. The transmissometer windows were cleaned and capped after each cast with the same solution to prevent salt buildup. The base of the fluorometer was also cleaned but not capped after each cast.

Acquisition Problems

During the test cast, the primary conductivity sensor failed on the downcast and was replaced prior to the first station with new 04C sensor s/n 3860.

During cast 7 and thereafter, the fluorometer developed a positive offset and noisy excursions below about 3000 dbar. The connection at the fluorometer as well as the y-cable between the optical sensors were tested and found not to be the problem. AOML's FLRTD-2088 was used without issue on casts 11 and 12 to further confirm the problem was with the UCSB sensor.

Kongsberg altimeter s/n 078 was replaced with s/n 080 after the signal went full scale near the bottom of cast 8. Prior to cast 14, the Kongsberg altimeter battery s/n 01 was replaced with s/n 02 after corrosion and severe pitting was found at the connector. The battery charger was also investigated and the metal case was left open to facilitate air ventilation. The altimeter battery was charged every day rather than every other day because it seemed not to hold a charge as long as expected. The lithium batteries likely need to be replaced after several years of use now.

The carousel trigger mechanism s/n 471 was replaced with s/n 163 prior to cast 31 after bottle 18 failed to close for the third time. The carousel pylon s/n 53 was replaced with s/n 163 prior to cast 45 after bottle 18 failed to close another four times.

The transmissometer window caps were left on during cast 41.

During cast 48, within the top 200 db of the upcast, the bottle firing software did not increment properly. As a result, Niskins 21-24 didn't close and the bottle data for Niskins 20, 21, and 23 were bad, and no reference temperature data were captured at those three depths. CTD data for Niskins 22 and 24 were good but there were no water samples taken. Shutting down the acquisition computer and rebooting fixed the problem, and it was done every other day after that.

Secondary oxygen sensor s/n 1890 was replaced with s/n 0154 prior to cast 81. The Secondary TCO sensors were slimed during cast 80 at 1600 dbar on the downcast, and secondary oxygen didn't recover so it was replaced with AOML s/n 154 prior to cast 81. After vigorous flushing with dilute Triton-X solution, temperature and conductivity differences remained the same. The new oxygen differences were even better than before.

At the bottom of cast 87/2, modem errors prevented bottles from being fired through the software or through the deck unit. Carousel s/n 163 was found to be at fault and was replaced with s/n 471. The station was reoccupied successfully as cast 87/3.

During cast 113/1, modulo errors indicative of data dropouts began on the downcast and increased significantly at depth. Communication was lost to the carousel so the cast was aborted. After exhaustive troubleshooting, including a new electrical termination, a second cast 113/3 was successfully collected, along with water samples. This cast still contained several modulo errors, which was believed to be caused by the wire since there was only a few meters cut off of it during termination. The top ~20 meters are usually discaded during retermination, getting rid of the section that is repeatedly strained over the block during deployments and recoveries.

CTD Data Processing

The reduction of profile data began with a standard suite of processing modules using Sea-Bird Data Processing Version 7.21d software in the following order:

- DATCNV converts raw data into engineering units and creates a .ROS bottle file. Both down and up casts were processed for scan, elapsed time(s), pressure, t0, t1, c0, c1, oxvo1, oxvo2, ox1 and ox2. Optical sensor data were converted to voltages and also carried through the processing stream. MARKSCAN was used to skip over scans acquired on deck and while priming the system under water.

- ALIGNCTD aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary and secondary conductivity were automatically advanced in the V2 deck unit by 0.073 seconds. No further alignment was warranted. It was not necessary to align temperature or oxygen.

- BOTTLESUM averages burst data over an 8-second interval (± 4 seconds of the confirm bit) and derives both primary and secondary salinity, potential temperature (θ), and potential density anomaly (σ_θ). Primary and secondary oxygen (in μmol/kg) were derived in DATCNV and averaged in BOTTLESUM, as recommended recently by Sea-Bird.

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

- CELLTM uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. In areas with steep temperature gradients the thermal mass correction is on the order of 0.005 PSS-78. In other areas the correction is negligible. Nominal values of 0.03 and 7.0 s were used for the thermal anomaly amplitude (α) and the thermal anomaly time constant (β^{-1}), respectively, as suggested by Sea-Bird.

- LOOPEDIT removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m/s or the pressure is not greater than the previous maximum scan, the scan is omitted.
- DERIVE uses 1-dbar averaged pressure, temperature, and conductivity to compute primary and secondary salinity, as well as more accurate oxygen values.
- BINAVG averages the data into 1-dbar bins. Each bin is centered on an integer pressure value, e.g. the 1-dbar bin averages scans where pressure is between 0.5 dbar and 1.5 dbar. There is no surface bin. The number of points averaged in each bin is included in the data file.
- STRIP removes oxygen that was derived in DATCNV.
- TRANS converts the binary data file 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 the square of the buoyancy frequency, N^2, and linearly interpolates temperature, conductivity, and oxygen voltage over those records where N^2 is less than or equal to $-1x10^{-5} m/s^2$. Some profiles failed the criteria in the top 5-13 dbars. These data were retained by program deloop_post.m and will be flagged as questionable in the final WOCE formatted files.

Program calctd.m reads the delooped data files and applies preliminary calibrations to temperature, conductivity, and oxygen; and computes calibrated salinity.

Pressure Calibration

Pre-cruise pressure calibrations did not account for the 2.4 dbar mean offset that existed with CTD s/n 0957. This offset was not applied during data acquisition but was removed prior to preliminary salinity and oxygen calibrations during the cruise. The ship's barometric pressure record will be evaluated post-cruise and may be used to correct the CTD pressure sensor.

On-deck pressure readings prior to each cast were examined and remained within 0.5 dbar of their offsets. Differences between first and last submerged pressures for each cast were also examined and the residual pressure offsets were also less than 0.5 dbar.

Temperature Calibration

A viscous heating correction of -0.0006°C was applied at sea as recommended by Sea-Bird prior to preliminary salinity and oxygen calibrations. Data from the SBE 35 reference temperature sensor will be evaluated post-cruise and used to correct SBE 3 temperature sensor data.

Conductivity Calibration

Seasoft module BOTTLESUM creates a sample file for each cast. These files were appended using program sbecal.f. Program addsal.f matched sample salinities to CTD salinities by station/sample number.

For primary conductivity sensor s/n 3860, a quadratic station-dependent slope and a single conductivity bias (calcos2.m) produced the best fit to sample data for stations 1-113:

- number of points used: 2183
- total number of points: 2635
- % of points used in fit: 82.81%
- fit standard deviation: 0.001132
- fit bias: 8.8273645×10^{-6}
- min fit slope: 1.000012
- max fit slope: 1.0000472

Likewise, for secondary conductivity sensor s/n 1467, a quadratic station-dependent slope and a single conductivity bias (calcos2.m) produced the best fit to sample data for stations 1-113:

- number of points used: 2224

• total number of points:	2636
• % of points used in fit:	84.37%
• fit standard deviation:	0.001197
• fit bias:	9.7364833×10^{-4}
• min fit slope:	0.99995337
• max fit slope:	1.0000123

Conductivity calibrations were applied to profile data using program calctd.m and to burst data using calclo.m. CTD-bottle conductivity differences plotted against station number (Figure 1.1) and pressure (Figure 1.2) allow a visual assessment of the success of the fits.

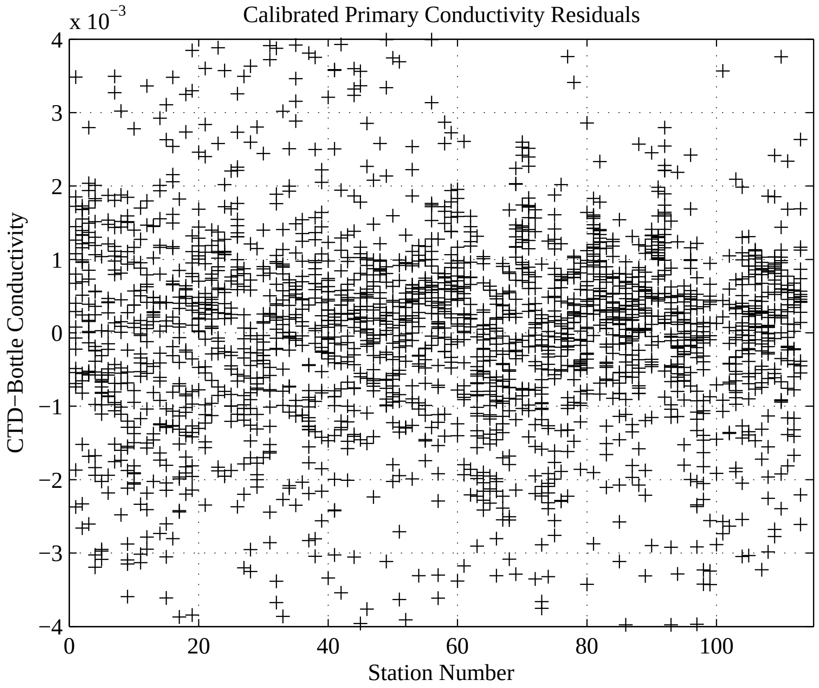

Figure 1.1 A16S CTD-bottle conductivity differences versus station.

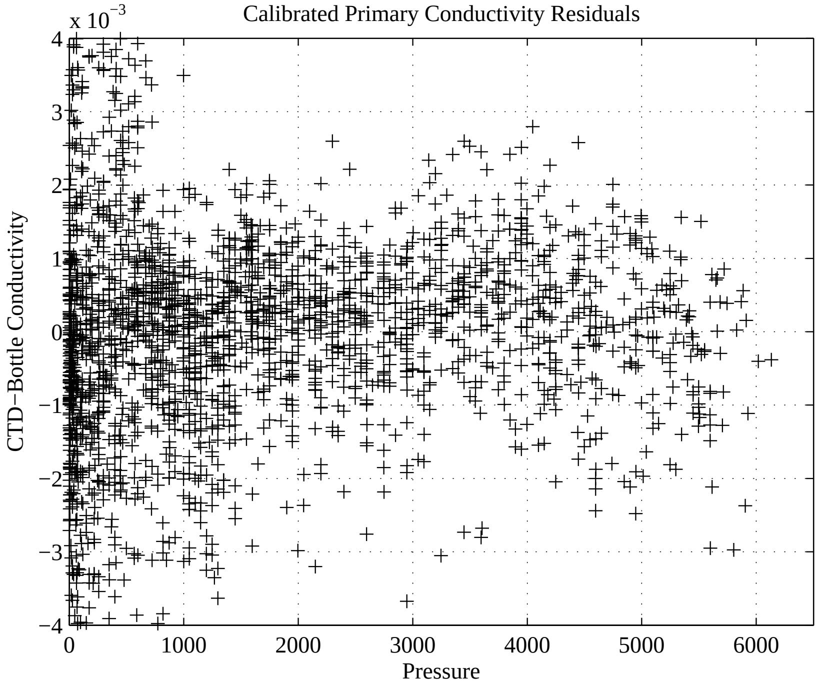

Figure 1.2 A16S CTD-bottle conductivity differences versus pressure.

Oxygen Calibration

A hybrid of the Owens-Millard (1985) and Murphy-Larson (revised 2010) oxygen sensor modeling equations was used to calibrate the SBE-43 oxygen sensor data from this cruise. The equation has the form

$$\mathrm{Ox} = \mathrm{Soc} \times [\mathrm{V} + \mathrm{V_{off}} + \tau^{\mathrm{D1\times P+D2\times T}} \frac{\mathrm{dV}}{\mathrm{dt}}] \times \frac{\mathrm{Os}^{\mathrm{T\times T_{cor} P\times P_{cor}}}}{273.15 + \mathrm{T}}$$

Where Ox is the CTD oxygen (μmol/kg), Soc is the oxygen signal slope, V is the measured oxygen voltage (in volts), $\frac{\mathrm{dV}}{\mathrm{dt}}$ is the temporal gradient of the oxygen voltage (in volts/s estimated by running linear fits made over 5 seconds), P is the CTD pressure (in dbar), T is the CTD temperature (in °C), and Os is the oxygen saturation computed from the CTD data following Garcia & Gordon (1992). Oxygen sensor hysteresis was improved by matching upcast bottle oxygen data to downcast CTD data by potential density anomalies referenced to the closest 1000-dbar interval using program match_sgn.m. We used the values provided by SBE for each sensor for the constants D1($1.9263e^{-4}$) and D2 ($-4.6480e^{-2}$) to model the pressure and temperature dependence of the response time for the sensor. For each group of stations fit we determined values of Soc (sometimes station dependent),$\mathrm{V_{off}}$, τ, $\mathrm{T_{cor}}$, and $\mathrm{P_{cor}}$ by minimizing the residuals between the bottle oxygen and CTD oxygen by minimizing the residuals between the bottle oxygen and CTD oxygen. W (listed in the tables below) represents fitting switches. If the switches are set to 0,0 the fit is a regular L2 (least squares) norm for the entire group. If the switches are set to 1,0 the fit is a regular L2 norm for the entire group but with a slope that is a linear function of station number. If the switches are set to 2,0 the program first fits the entire group, then goes back and fits a slope and bias to individual stations, keeping the other parameters at the group values. If the switches are set to 0,1 the fit is a regular L2 norm for the entire group but it is weighted by the nominal oxygen bottle spacing, thus fitting the deep portion of the water column better.

Program addsal.f matched bottle sample oxygen values to CTD oxygen values by station/sample number. Program run_oxygen_cal_ml.m was used to determine calibration coefficients for two station groupings for primary oxygen sensor s/n 664 owing to a fouling event and determined by visual inspection:

Stns	Start Soc	Voff	Tau	Tcor	Pcor	Points Used	StdDev	W
1-79	0.4960	-0.5128	7.8554	-0.0011	0.0404	24 ea 83.3%	1.2185	2 0
80-113	0.5172	-0.5110	8.2289	-0.0026	0.0390	24 ea 91.7%	1.0956	2 0

Secondary oxygen sensor s/n 1890 was used for casts 1-80 but did not recover from the fouling event mentioned above. One overall calibration for this sensor was determined by visual inspection:

Stns	Start Soc	Voff	Tau	Tcor	Pcor	Points Used	StdDev	W
1-79	0.4557	-0.5440	8.7838	-0.0003	0.0412	24 ea 91.7%	0.7663	2 0

Secondary oxygen sensor s/n 154 was used for casts 81-113. One overall calibration for this sensor was determined by visual inspection:

Stns	Start Soc	Voff	Tau	Tcor	Pcor	Points Used	StdDev	W
81-113	0.5004	-0.5099	9.9546	-0.0033	0.0403	24 ea 100.0%	1.6904	2 0

Oxygen calibration coefficients were applied to profile data using program calctd.m, and to burst data using calclo.m.

Primary sensor CTD - bottle oxygen differences plotted against station number (Figure 1.3) and pressure (Figure 1.4) allow a visual assessment of the success of the fits

Despiking

Profile 10 was edited after DATCNV to remove three bad 24-Hz records around 57 dbar down and 175 dbar up.

Profile 80 went through some biomass around 1600 dbar down rendering the secondary conductivity and oxygen data unusable.

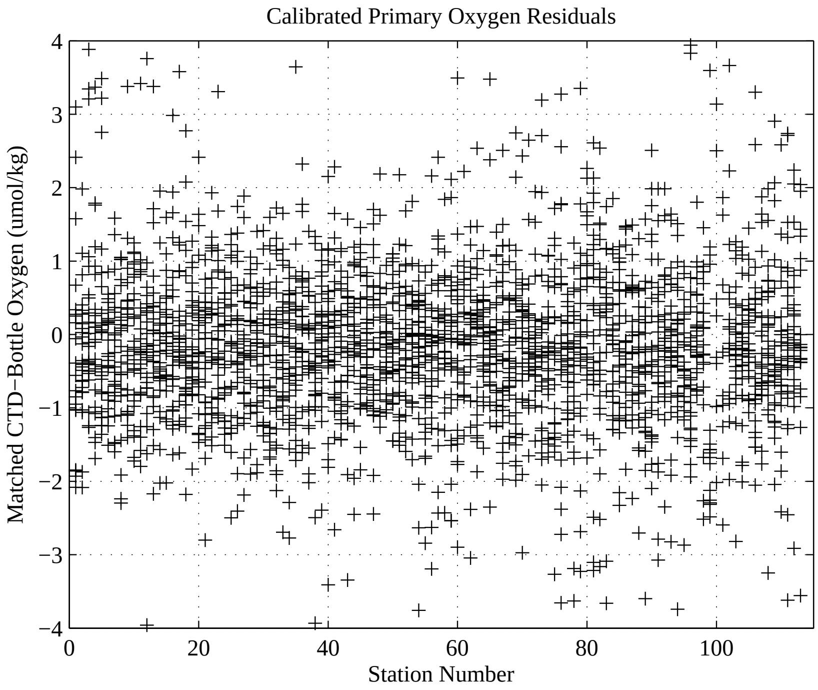

Figure 1.3 A16S CTD-bottle oxygen differences versus station.

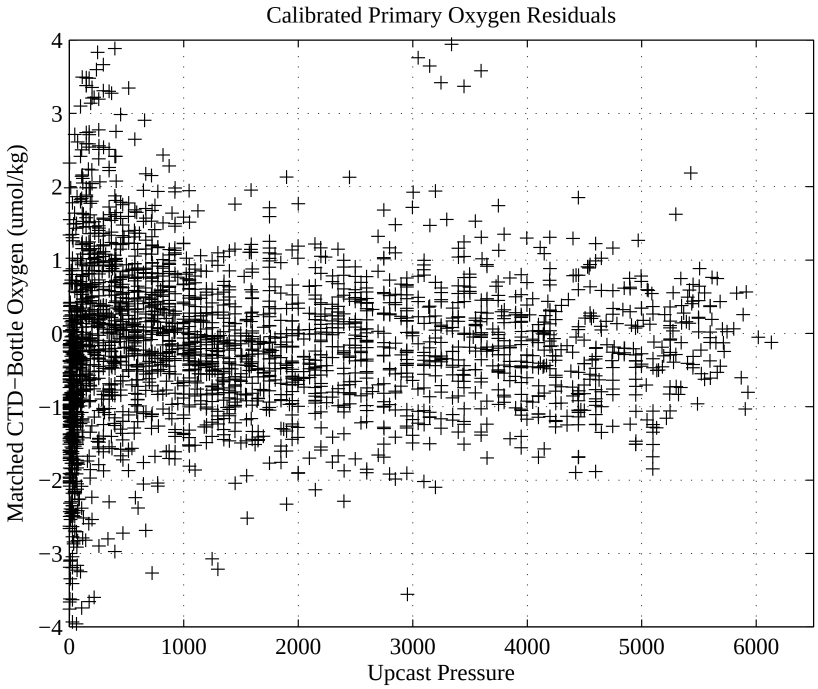

Figure 1.4 A16S CTD-bottle oxygen differences versus pressure.

Bottle Sampling and Data Processing

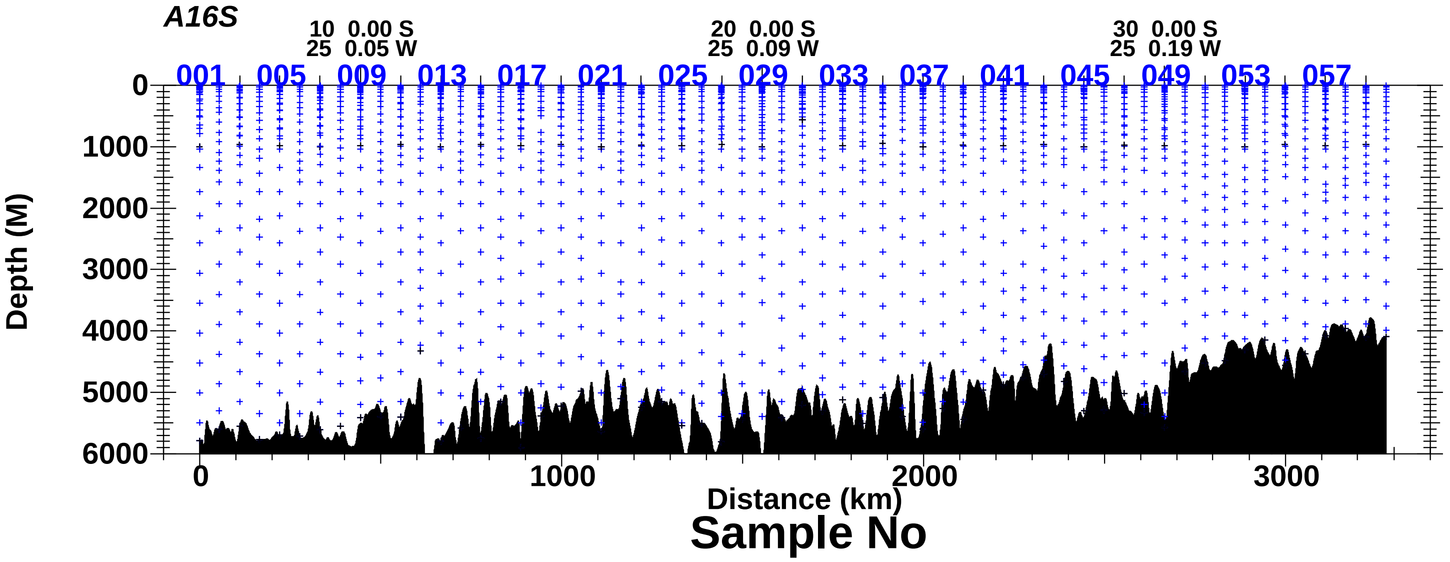

Figure 1.1 A16S Sample distribution, stations 1-60.

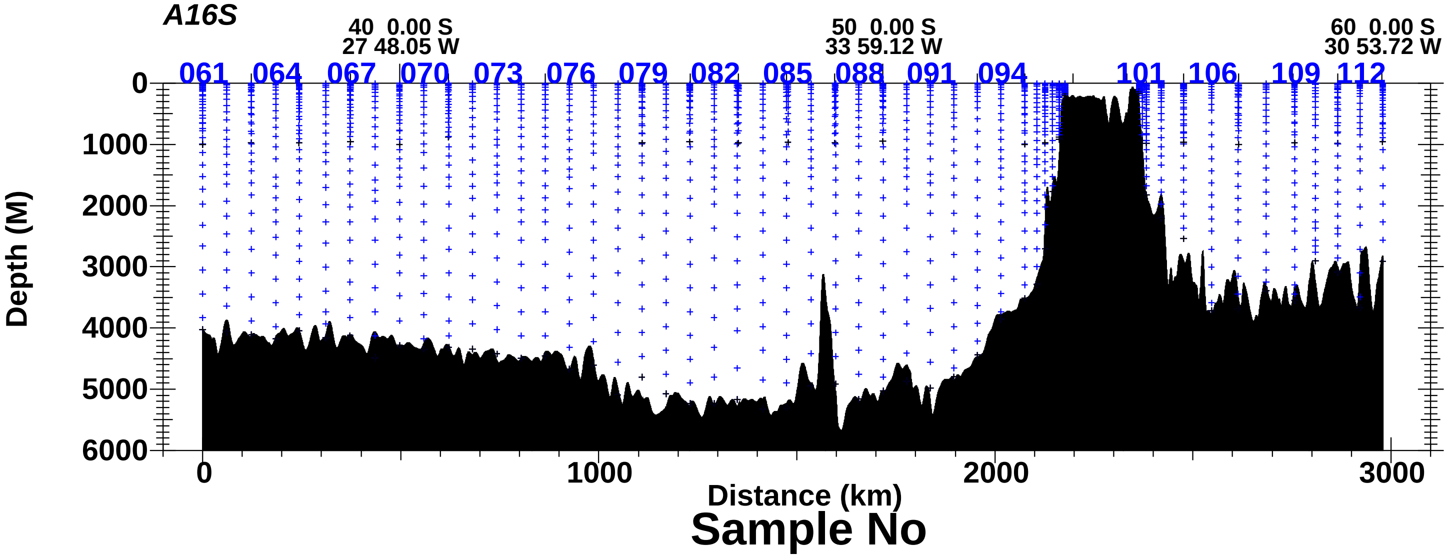

Figure 1.2 A16S Sample distribution, stations 61-113.

Water Sampling

The NOAA Ship *Ronald H. Brown* has two Markey DESH-5 winches. The Forward winch was used for all stations on A16S. All rosette casts were lowered to within 8-20 meters of the bottom, using both the altimeter to determine distance. Details of these bottom approaches can be found in the Appendix.

We utilised a sample plan to stagger sample depths for all stations throughout A16S. Staggering sample depths was to avoid spatial aliasing within this sample data set.

The 24-place SBE32 carousel had few bottle lanyard or mis-tripped bottle problems. Rosette maintenance was performed on a regular basis. O-rings were changed and lanyards repaired as necessary. Bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed. Periodic leaks were noted on sample logs. Log notes were cross referenced with sample data values and quality coded. Log notes, mis-trips, bottle lanyard issues and associated quality codes can be found in Appendix.

Bottle Sampling

At the end of each rosette deployment water samples were drawn from the bottles in the following order:

- Chlorofluorocarbons (CFCs)
- Helium ^{3}He
- Dissolved Oxygen O_2
- Dicrete pCO_2
- Dissolved Inorganic Carbon (DIC)
- pH (sw25)
- Total Alkalinity (TAlk)
- ^{14}C DIC
- Dissolved Organic Carbon (DOC)
- Oxygen Isotopes $^{18}O/^{16}O$
- Tritium
- Nutrients
- Density
- Salinity

The correspondence between individual sample containers and the rosette bottle position (1-24) from which the sample was drawn was recorded on the sample log for the cast. 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 sole responsibility was to maintain this log and insure that sampling progressed in the proper drawing order.

Normal sampling practice included opening the drain valve and then the air vent on the bottle, indicating an air leak if water escaped. 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. Drawing oxygen samples also involved taking the draw temperature from the bottle. The temperature was noted on the sample log and was sometimes useful in determining leaking or mis-tripped bottles.

Once individual samples had been drawn and properly prepared, they were distributed for analysis. On-board analyses were performed on computer-assisted analytical equipment networked to the data processing computer for centralized data management.

Bottle Data Processing

Shipboard CTDO data were re-processed automatically at the end of each deployment using SIO/ODF CTD processing software v.5.2.0. The raw CTDO data and bottle trips acquired by SBE SeaSave on the Windows XP workstation were copied onto the Linux database and web server system. Pre-cruise calibration data were applied to CTD Pressure, Temperature and Conductivity sensor data, then the data were processed to a 0.5-second time series. A 1-decibar down-cast pressure series was created from the time series; CTDO data from downcasts were matched along isopycnals to upcast trips and extracted, then fit to bottle O_2 data at trips. The pressure series data were used by the web service for interactive plots, sections and on-board CTDO data distribution; the 0.5 second time series data were also available for distribution through the web service.

CTDO data at bottle trips were extracted and added to the bottle database to use for CTD Pressure, Temperature and Salinity data in the preliminary bottle files. Downcast CTDO data, matched to upcast bottle trips along isopycnals, were used for preliminary bottle file CTDO data. When final CTDO data are submitted, the NOAA/PMEL final PTSO data will replace the preliminary SIO/ODF CTD data in the bottle files.

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-8.1.23-6.el5_8) run on a CentOS-5.9 Linux system. A web service (OpenACS-5.3.2-3 and AOLServer-4.5.1-1) front-end provided ship-wide access to CTD and water sample data. Web-based facilities included on-demand arbitrary property-property plots and vertical sections as well as data uploads and downloads.

The Sample Log information (and any diagnostic comments) were entered into the database once sampling was completed. Quality flags associated with sampled properties were set to indicate that the property had been sampled, and sample container identifications were noted where applicable (e.g., oxygen flask number).

Analytical results were provided on a regular basis by the various analytical groups and incorporated into the database. 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) [Joyc94].

Various consistency checks and detailed examination of the data continued throughout the cruise. A summary of Bottle Data Quality Codes and sampling comments are included in the Appendix.

Analytical Problems

Few bottle problems occured during A16S. Those that occured are noted in the quality table in the Appendix. More specific details on analysis problems can be found in the various water property sections below.

2. Salinity

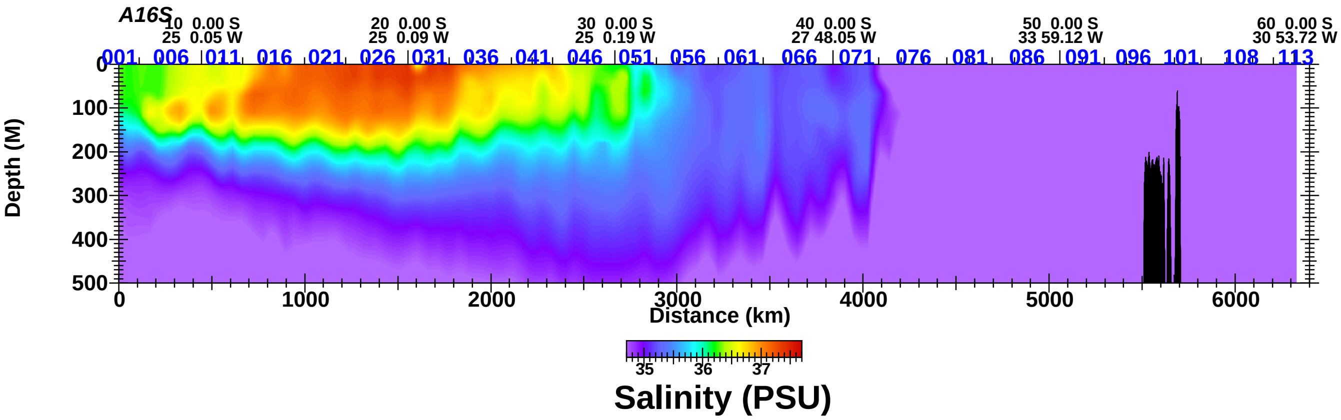

Figure 2.1 A16S shallow salinities for stations 1-113.

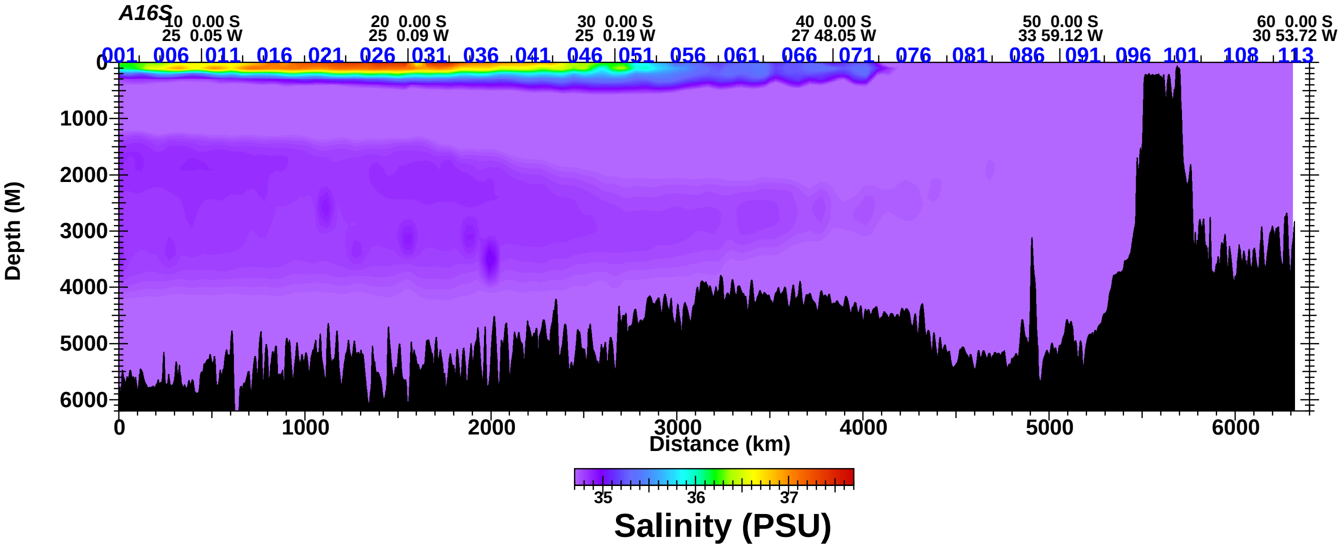

Figure 2.2 A16S all salinities for stations 1-113.

Equipment and Techniques

A single Guildline Autosal, model 8400B salinometer (S/N 60843, nicknamed Joysey), located in salinity analysis room, was used for all salinity measurements. The autosal was recently calibrated on 7/20/2013 before the previous expedition, A16N. The salinometer readings were logged on a computer using Ocean Scientific International's logging hardware and software. The Autosal's water bath temperature was set to 24°C, which the Autosal is designed to automatically maintain. The laboratory's temperature was also set and maintained to just below 24°C, to help further stabilize reading values and improve accuracy. Salinity analyses were performed after samples had equilibrated to laboratory temperature, usually at least 12 hours after collection. The salinometer was standardized for each group of samples analyzed (usually 2 casts and up to 52 samples) using two bottles of standard seawater: one at the beginning and end of each set of measurements. The salinometer output was logged to a computer file. The software prompted the analyst to flush the instrument's cell and change samples when appropriate. Prior to each run a sub-standard flush, approximately 200 ml, of the conductivity cell was conducted to flush out the DI water used in between runs. For each calibration standard, the salinometer cell was initially flushed 6 times before a set of conductivity ratio reading was taken. For each sample, the salinometer cell was initially flushed at least 3 times before a set of conductivity ratio readings were taken.

IAPSO Standard Seawater Batch P-154 was used to standardize all casts.

Sampling and Data Processing

The salinity samples were collected in 200 ml Kimax high-alumina borosilicate bottles that had been rinsed at least three times with sample water prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. Laboratory temperature was also monitored electronically throughout the cruise. PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The offset between the initial standard seawater value and its reference value was applied to each sample. Then the difference (if any) between the initial and final vials of standard seawater was applied to each sample as a linear function of elapsed run time. The corrected salinity data was then incorporated into the cruise database. When duplicate measurements were deemed to have been collected and run properly, they were averaged and submitted with a quality flag of 6.

On A16S, approximately 3450 salinity measurements were taken, including 219 duplicates, and approximately 112 vials of standard seawater (SSW) were used. Up to two duplicate sample, one for shallow casts, was drawn from each cast to determine total analytical precision.

The running standard calibration values and duplicates are below. Through the course of the 45 day cruise, the autosal standards changed by 0.00014 in conductivity ratio (about 0.005 in salinity). The duplicates taken during the cruise showed a median precision of 0.0001 ± 0.0007 psu.

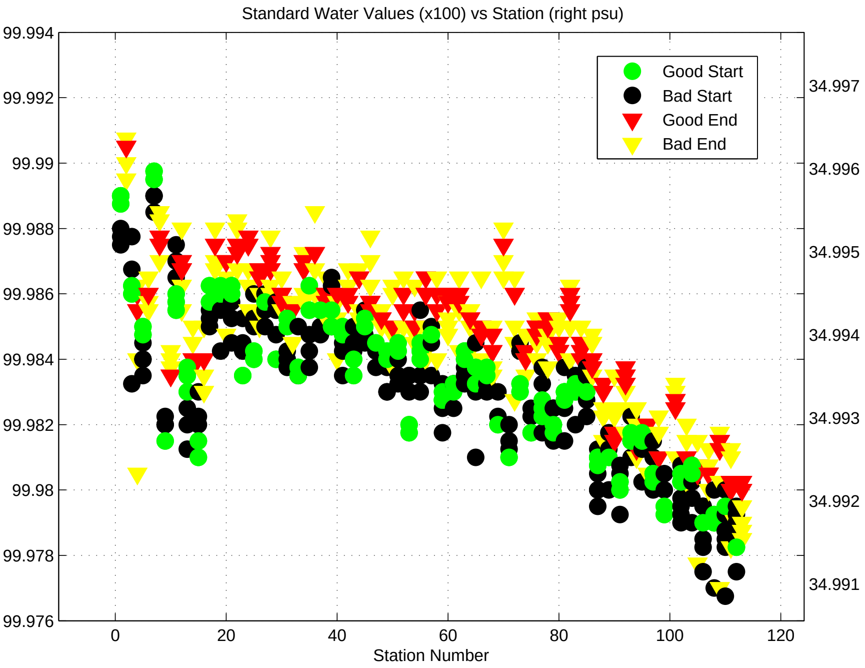

Figure 2.1 A16S SSW values for stations 1-113. The good and bad starts represent the QC'd calibration standards at the beginning and end of each run used to calculate and apply the drift correction.

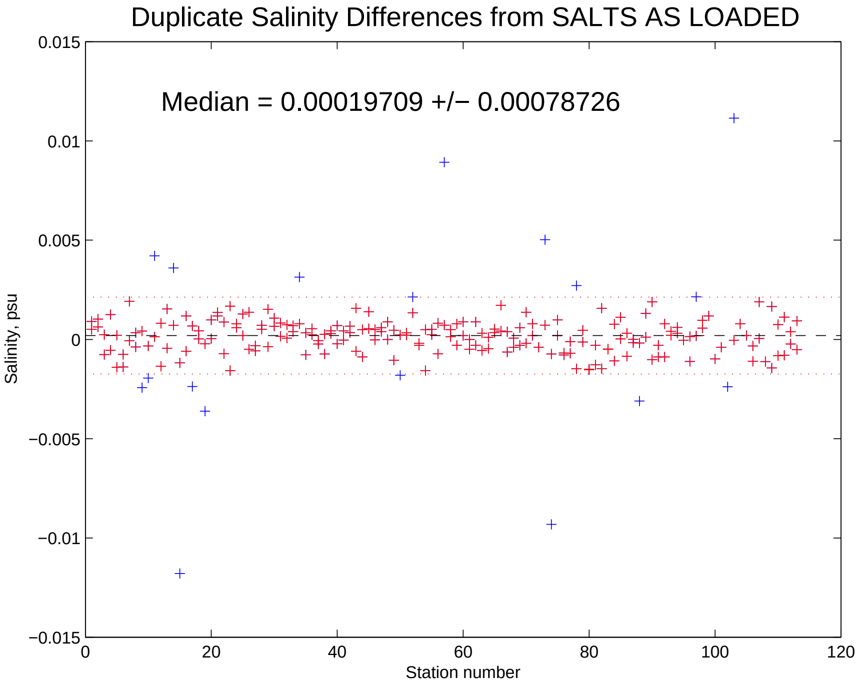

Figure 2.2 A16S salinity duplicates for stations 1-113.

3. Oxygen Analysis

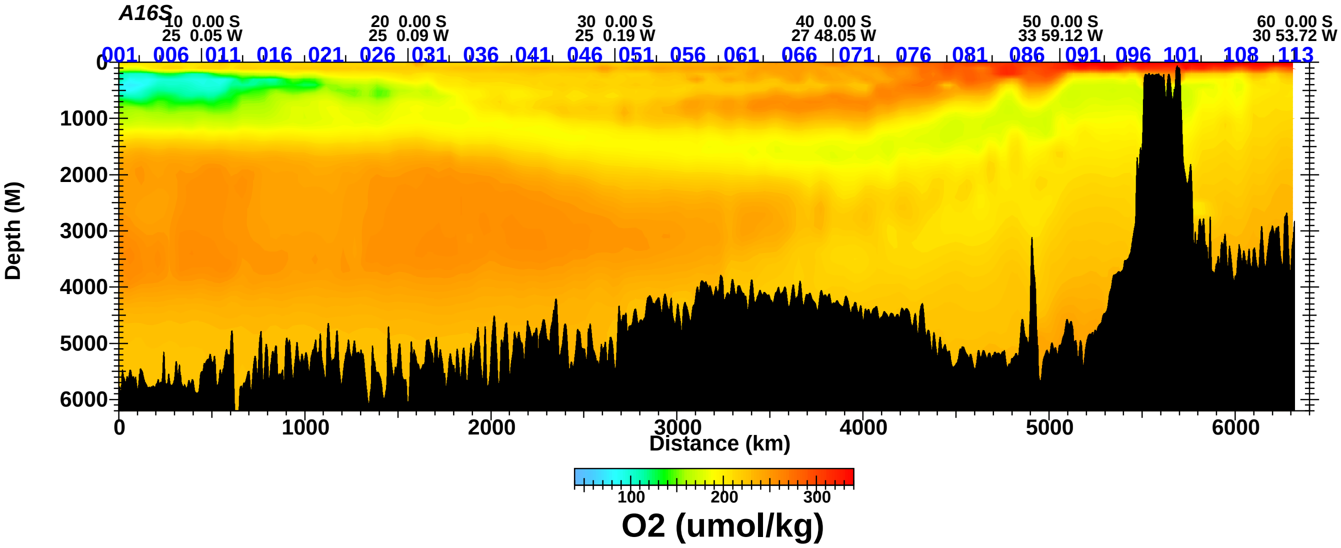

Figure 3.1 A16S stations 1-113

Equipment and Techniques

Dissolved oxygen analyses were performed with an automated titrator using amperometric end-point detection [Lang10]. Sample titration, data logging, and graphical display were performed with a PC running a LabView program written by Ulises Rivero of AOML. Lab temperature was maintained at 19.2-22.7°C. The temperature-corrected molarity of the thiosulfate titrant was determined as given by [DOE94]. Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. The whole-bottle titration technique of Carpenter [Carp65], with modifications by Culberson et al. [Culb91], was used. Three to four replicate 10 ml iodate standards were run every 3-4 days (SD<1 uL). Standards prepared with KIO_3 solution prepared at AOML before the cruise were compared with standards prepared using KIO_3 certified reference material (OSIL iodate standard). The KIO_3 solutions from Guildeline were certified to be 1.667 millimolar (0.0100 N). A total of three standards were prepared using AOML (0.0100 N) KIO_3 solutions and three using the OSIL certified iodate solution (bottles 26017 and 26012), with a mean and S.D. of 707.77±0.47 uL and 706.21±0.11 uL, respectively. The reagent blank determined as the difference between V1 and V2, the volumes of thiosulfate required to titrate 1-ml aliquots of the iodate standard, was determined at the beginning, middle and end of the cruise. A new step in the technique was to leave the probes soaking in 10% HNO_3 between stations. This seemed to keep the response of the detector constant over time (minimal changes in titration slope).

Sampling and Data Processing

Dissolved oxygen samples were drawn from Bullister bottles into calibrated 125-150 ml iodine titration flasks using silicon tubing to avoid contamination of DOC and CDOM samples. Samples were drawn by counting while the flask was allowed to fill at full flow from the Bullister. This count was then doubled and repeated thereby allowing the flask to be overflowed by two flask volumes. At this point the silicone tubing was pinched to reduce the flow to a trickle. This was continued until a stable draw temperature was obtained on the Oakton meter. These temperatures were used to calculate μmol/kg concentrations, and provide a diagnostic check of Bullister bottle integrity. 1 ml of $MnCl_2$ and 1 ml of NaOH/NaI were added immediately after drawing the sample using a Re-pipetor. The flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. 24 samples plus two duplicates were drawn at each station. The total number of samples collected from the rosette was 2866.

The samples were stored in the lab in plastic totes at room temperature for 1 hour before analysis. The data were incorporated into the cruise database shortly after analysis.

Thiosulfate normality was calculated for each standardization and corrected to the laboratory temperature. This temperature ranged between 19.2-22.7°C.

Reagent blanks were run at the beginning (2.6±0.7 μL), middle (2.5±0.4 μL) and end of the cruise (3.9±0.8 μL).

Volumetric Calibration

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

Duplicate Samples

Duplicate samples were drawn at two depths on every cast, with the exception of a very shallow cast where a duplicate was drawn at one depth only. The Bullisters selected for the duplicates and hence the oxygen flasks were changed for each cast. A total of 225 sets of duplicates were run. The average standard deviation of all sets was 0.19 μmol/kg.

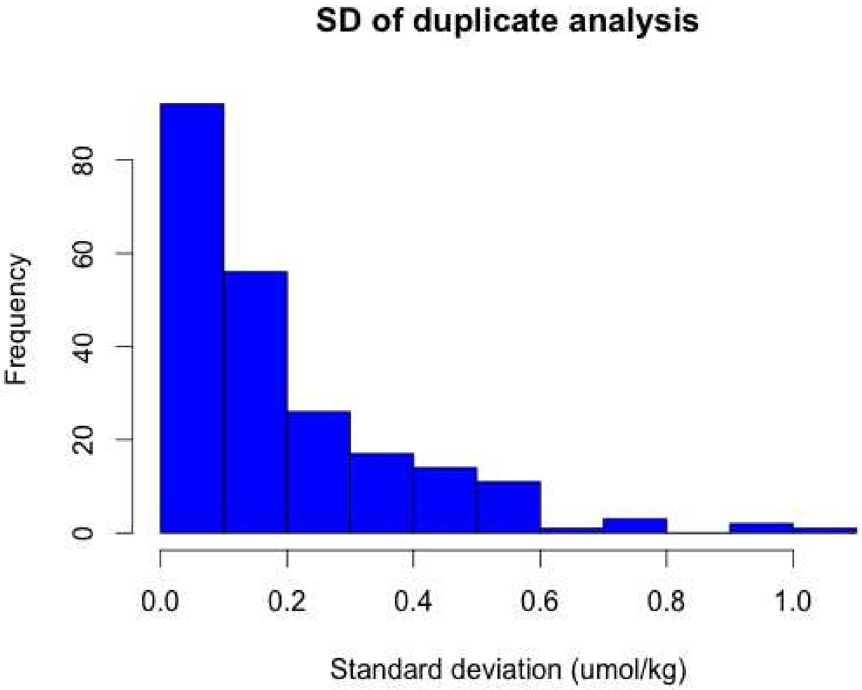

Figure 3.2 Standard deviation of duplicate oxygen analyses performed during A16S. Median was 0.13 μmol/kg, IQR was 0.06-0.28 μmol/kg, n=223.

Problems

One flask was replaced with a different flask from a separate set due to poor fitting of the stopper. At each filling of the NaI/NaOH reagent, the dispenser was rinsed out with DIW to prevent sticking. None of these problems ever rose to the point that the errors exceed 1 μmol/kg.

Assigned quality codes along with comments can be found in the Appendix.

4. Nutrients

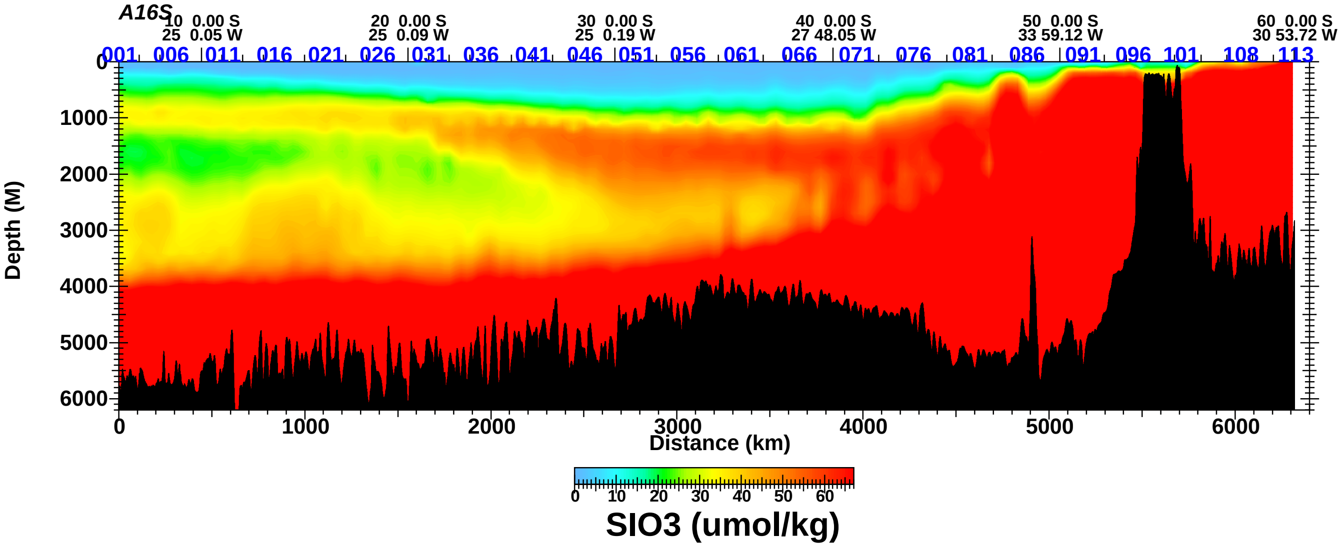

Figure 4.1 A16S silicate stations 1-113

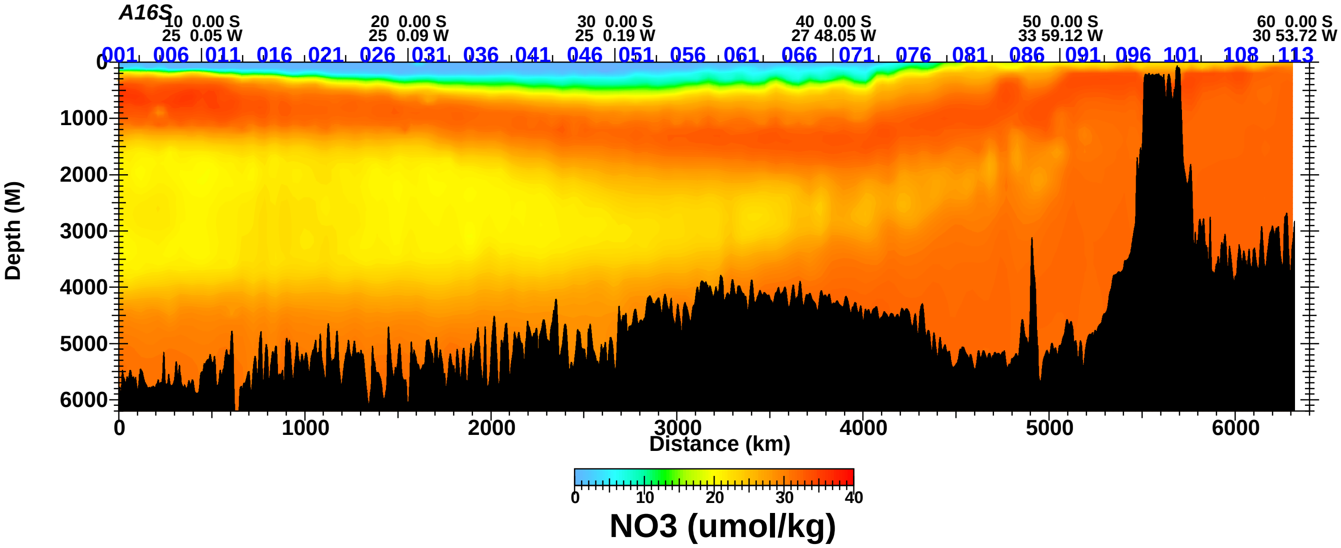

Figure 4.2 A16S nitrate stations 1-113

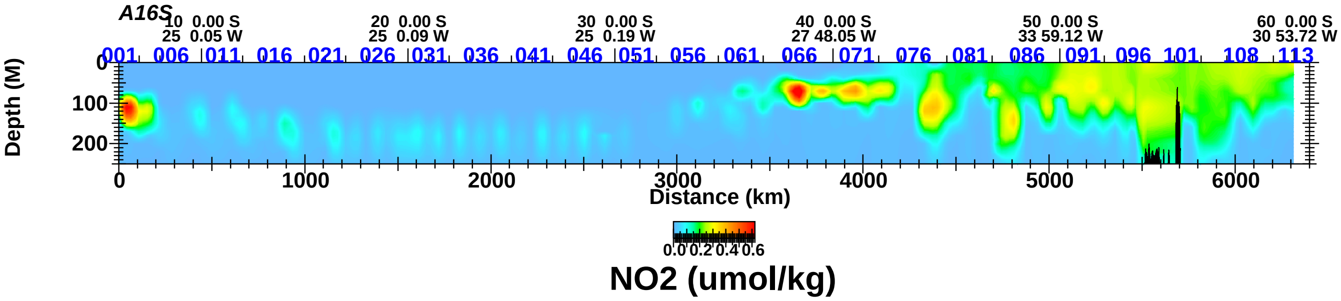

Figure 4.3 A16S nitrite for stations 1-113

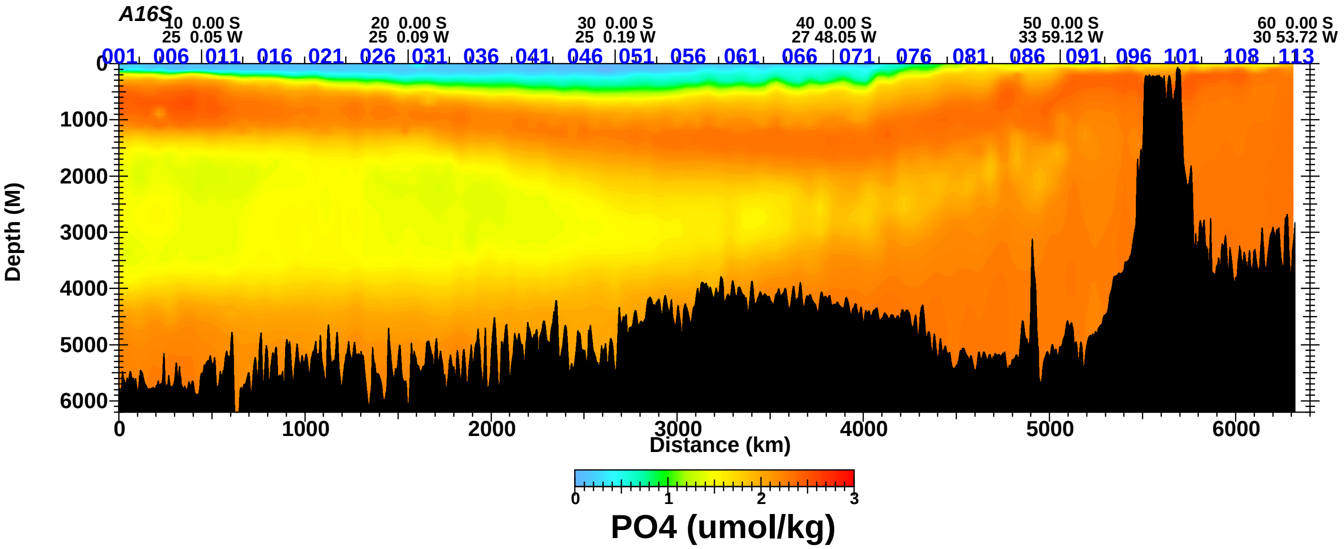

Figure 4.4 A16S phosphate stations 1-113

Equipment and Techniques

Dissolved nutrients (phosphate, silicate, nitrate and nitrite) were measured by using an automated continuous flow analytical system with segmented flow and colormetric detection. The four channel auto-analyzer was customized with various components from other systems.

The major components of the nutrient system consisted of an Alpkem auto-sampler, (model 301), two peristaltic pumps, four Lab Alliance monochrometer detectors (model 500) and custom software for digitally logging and processing the chromatograms. In addition, glass coils were used for the mixing of the nutrients.

Detailed methodologies are described by [Gord94]

Silicic acid was analyzed using a modification of [Arms67]. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybic acid. Oxalic acid was then added to inhibit a secondary reaction with phosphate. Finally, a reaction with ascorbic acid formed the blue compound silicomolybdous acid. The color formation was detected at 814 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride by [Gord94] were employed to reduce the toxicity of our waste steam.

Nitrate and Nitrite analyses were also a modification of [Arms67]. Nitrate was reduced to nitrite via a copperized cadmium column to form a red azo dye by complexing nitrite with sulfanilamide and N-1-naphthylethylenediamine (NED). Color formation was detected at 540 nm. The same technique was used to measure nitrite, (excluding the reduction step).

Phosphate analysis was based on a technique by [Bern67]. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdate acid. This was reduced to the blue compound phosphomolybdous acid following the addition of hydrazine sulfate. The color formation was detected at 819 nm.

Sampling and Standards

Nutrient samples were drawn in 30ml HDPE Nalgene sample bottles that had been stored in 10% HCl. The bottles are rinsed 3-4 times with sample prior to filling. A replicate was normally drawn from the deep Niskin bottle at each station for analysis to reduce carry over. Samples were then brought to room temperature prior to analysis. Fresh mixed working standards were prepared before each analysis. In addition to the samples, each analysis consisted of 4 replicate standards, 3 deionized water (DIW) blanks and 3 Matrix blanks placed at the beginning and then repeated at the end (with the addition of a fourth Matrix Blank) of each run. Also, one mixed working standard from the previous analytical run was used at the beginning of the new run to determine differences between the two standards. Samples are analyzed from deep water to the surface. Low Nutrient Seawater (LNSW) was used as a wash, base line carrier and medium for the working standards.

The working standard was made by the addition of 0.2 ml of primary nitrite standard and 15.0 ml of a secondary mixed standard (containing silicic acid, nitrate, and phosphate) into a 500ml calibrated volumetric flask of LNSW. Working standards were prepared daily.

Dry standards of a high purity were pre-weighed at PMEL. Nitrite standards were dissolved at sea. The secondary mixed standard was prepared by the addition of 30ml of a nitrate - phosphate primary standard to the silicic acid standard. Nutrient concentrations were reported in micromoles per liter. Lab temperatures were recorded for each analytical run. All the pump tubing was replaced at least three times during the A16S cruise.

Approximately 3252 samples were analyzed.

5. Chlorofluorocarbons (CFCs) and Sulfur Hexafluoride (SF_6)

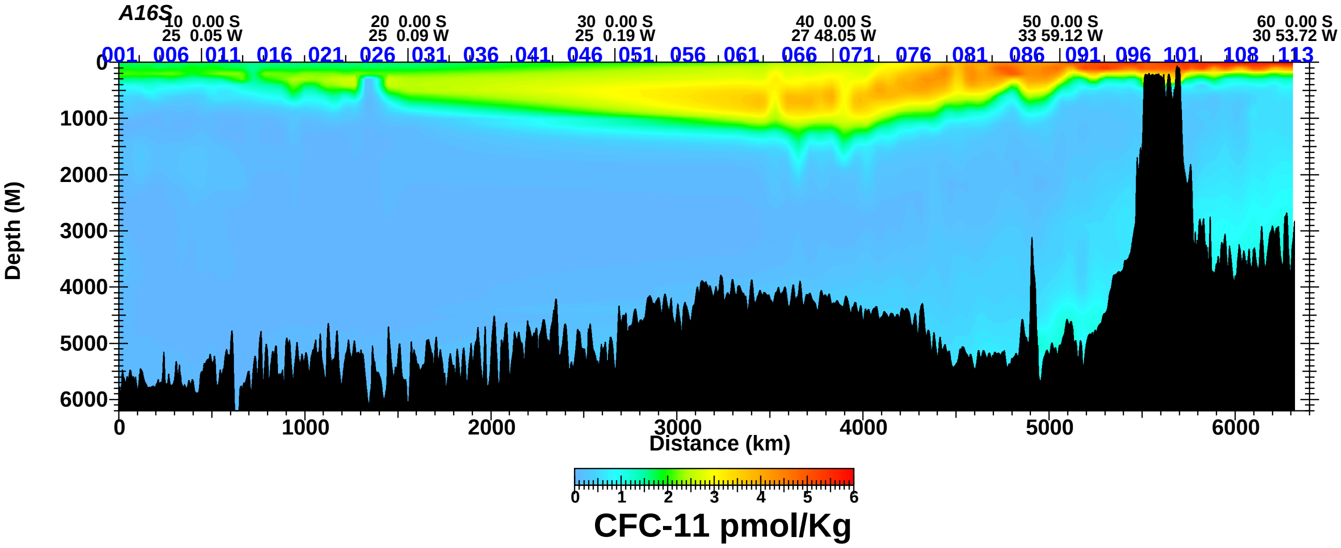

Figure 5.1 A16S stations 1-113

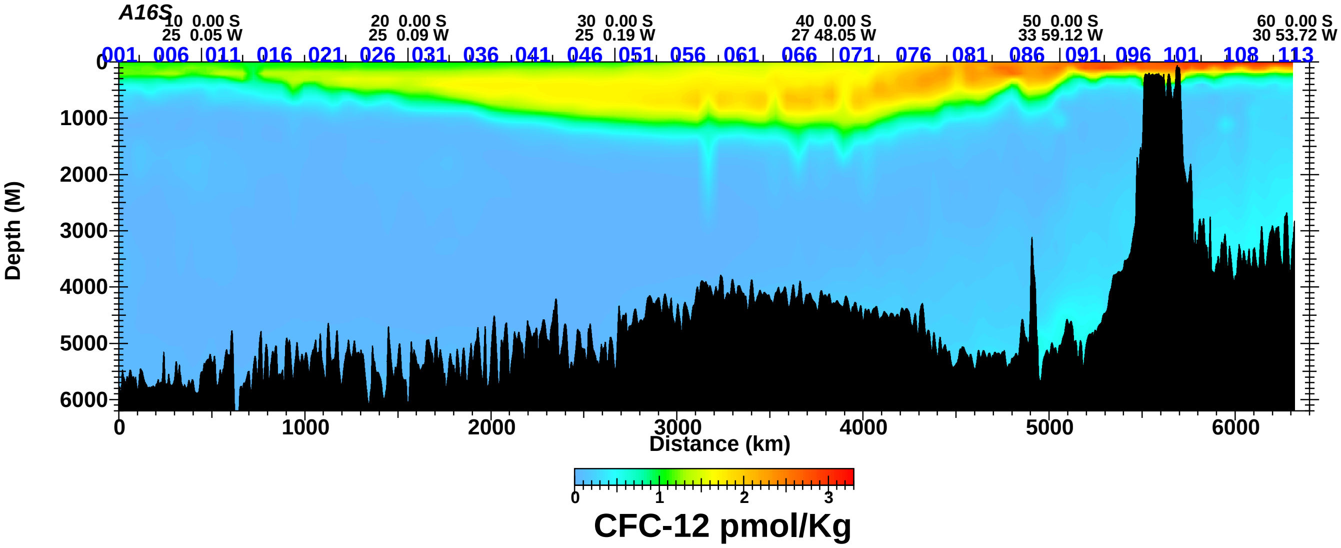

Figure 5.2 A16S stations 1-113

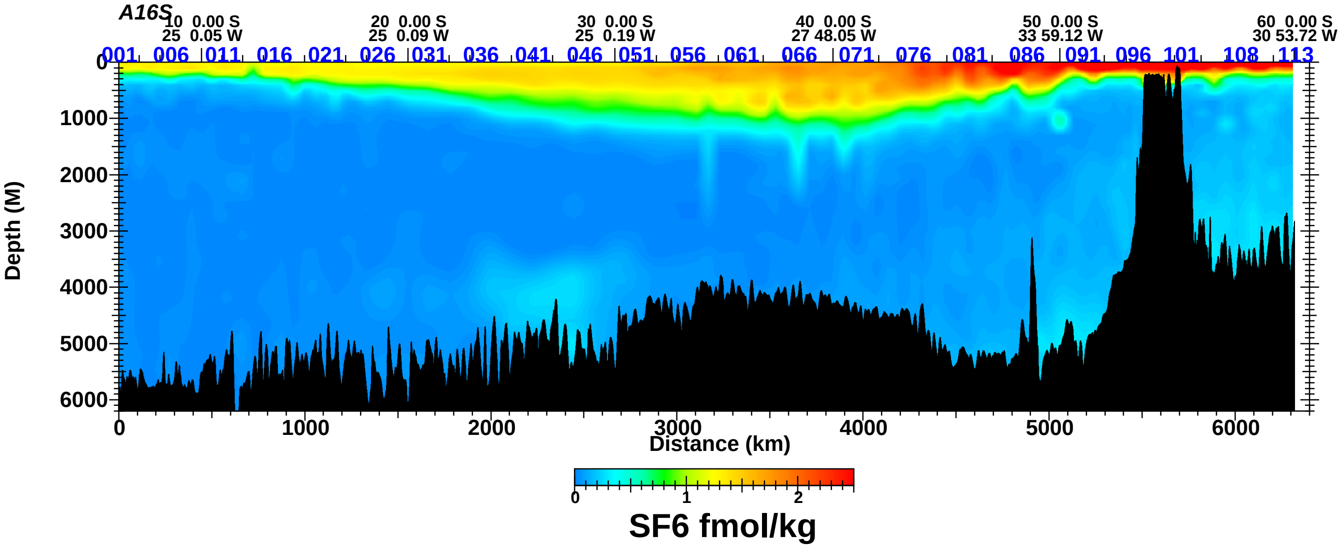

Figure 5.3 A16S stations 1-113

A PMEL analytical system [Bull08] was used for CFC-11, CFC-12, sulfur hexafluoride (SF_6) and nitrous oxide (N_2O) analyses on the 2013 CLIVAR A16S expedition. Aproximately 1850 samples of dissolved CFC-11, CFC-12, and SF_6 ('CFC/SF_6') were analysed. In general, the analytical system performed well for CFC-12, SF_6 and nitrous oxide during the cruise. There were some analytical problems with CFC-11. Typical dissolved SF_6 concentrations in modern surface water are approximately 1-2 fmolkg^{-1} seawater (1 fmol= femtomole = 10^{-15} moles), approximately 1000 times lower than dissolved CFC-11 and CFC-12 concentrations. The limits of detection for SF_6 were approximately 0.03 fmol kg^{-1}. SF_6 measurements in seawater remain extremely challenging. Improvements in the analytical sensitivity to this compound at low concentrations are essential to make these measurements more routine on future CLIVAR cruises.

Water samples were collected in bottles designed with a modified end-cap to minimize the contact of the water sample with the end-cap O-rings after closing. 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 collected for dissolved CFC-11, CFC-12 and SF_6 analysis were the first samples drawn from the bottles. Care was taken to coordinate the sampling of CFC/SF_6 with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. Samples easily impacted by gas exchange (dissolved oxygen, ^{3}He, DIC and pH) were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC/SF_6 samples were drawn directly through the stopcocks of the bottles into 250 ml precision glass syringes equipped with three-way plastic stopcocks. The syringes were immersed in a holding tank of clean surface seawater held at ~10°C until 20 minutes before being analyzed. At that time, the syringe was place in a bath of surface seawater heated to 30°C.

For atmospheric sampling, a ~75 m length of 3/8" OD Dekaron tubing was run from the CFC van located on the fantail 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 back pressure regulator. A tee allowed a flow of ~100 ml/min of the compressed air to be directed to the gas sample valves of the CFC/SF_6 analytical systems, while the bulk flow of the air (>7 l/min) was vented through the back-pressure regulator. Air samples were analyzed only when the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. Analysis of bow air was performed at ~18 locations along the cruise track. At each location, at least five air measurements were made to determine the precision of the measurements.

Analysis

Concentrations of CFC/SF_6 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[Bull88] and

Bullister and Wisegarver [Bull08], as outlined below. For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume ˜200 ml). The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF_6 free purge gas through the sparging chamber for a period of 6 minutes at ~200 ml/min. Water vapor was removed from the purge gas during passage through a Nafion drier. Carbon dioxide was removed with an 18 cm long, 3/8" diameter glass tube packed with Ascarite and a small amount of magnesium perchlorate desiccant. The sample gases were concentrated on a cold-trap consisting of a 1/16" OD stainless steel tube with a 2.5 cm section packed tightly with Porapak Q (60-80 mesh), a 15 cm section packed with Carboxen 1000 and a 2.5 cm section packed with MS5A. A Neslab Cryocool CC-100 was used to cool the trap to ~-70°C. After 6 minutes of purging, the trap was isolated, and it was heated electrically to ~175°C. The sample gases held in the trap were then injected onto a precolumn (~61 cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil B, held at 80°C) for the initial separation of CFC-12, CFC-11, SF_6 and CCL_4 from later eluting peaks. After the SF_6 and CFC-12 had passed from the pre-column and into the second precolumn (25 cm of 1/8" O.D. stainless steel tubing packed with MS5A, 80°C) and into the analytical column #1 (174 cm of 1/8" OD stainless steel tubing packed with MS5A + 60 cm Porasil C held at 80°C), the outflow from the first precolumn was diverted to the second analytical column (180 cm 1/8" OD stainless steel tubing packed with Porasil B, 80-100 mesh, held at 80°C). The gases remaining after CCl_4 had passed through the first pre-column, were backflushed from the pre column and vented. After CFC-12 had passed through the second pre-column, a flow of Argon-Methane (95:5) was used to divert the N_2O to a third analytical column (30 cm of MS5A, 150°C). Column #3 and the second pre-column were held in a Shimadzu GC8 gas chromatograph with an electron capture detector (ECD) held at 330°C. Columns #1, #2, and the first precolumn were in another Shimadzu GC8 gas chromatograph with ECD. The outflow from column #2 was directed to a Shimadzu Mini-2 gas chromatograph (no column) with the ECD held at 250°C.

The analytical system was calibrated frequently using a standard gas of known CFC/SF_6 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 ECD were similar to those used for analyzing water samples. Four 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/SF_6 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 CFC-11 and CFC-12 in air, seawater samples, and gas standards are reported relative to the SIO98 calibration scale [Prin00] , [Bull10]. Concentrations of SF_6 in air, seawater samples, and gas standards are reported relative to the SIO-2005 calibration scale[Bull10]. 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) and SF_6 concentrations in fmol/kg. CFC/SF_6 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 WRS72611) into the analytical instrument. The response of the detector to the range of moles of CFC/SF_6 passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at intervals of 4-5 days during the cruise. 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 purging efficiency was estimated by re-purging a high-concentration water sample and measuring this residual signal. At a flow rate of 200 cc/min for 6 minutes, the purging efficiency for both SF_6 and CFC gases was > 99%. The efficiency for N_2O was about 97%.

On this expedition, based on the analysis of more than 190 pairs of duplicate samples, we estimate precisions (1 standard deviation) of about 1% or 0.002 pmol/kg (whichever is greater) for dissolved CFC-12 and CFC-11 measurements. The estimated precision for SF_6 was 2% or 0.02 fmol kg-1, (whichever is greater). Overall accuracy of the measurements (a function of the absolute accuracy of the calibration gases, volumetric calibrations of the sample gas loops and purge chamber, errors in fits to the calibration curves and other factors) is estimated to be about 2% or 0.004 pmol/kg for CFC11 and CFC-12 and 4% or 0.04 fmol/kg for SF_6).

A small number of water samples had anomalously high CFC-12 and/or SF_6 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/SF_6 during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the data file, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). Less than 2% of samples were flagged as bad or questionable during this voyage. 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, etc).

During the cruise an analytical problem developed with the analysis of CFC-11. After numerous attempts to solve the problem, it was determined that the calibration loop used for monitoring the stability of the detector, was producing large and variable responses. A second large loop was created and its volume crudely determined using CFC-12 and nitrous oxide. It is believed this determination of the volume is within about 2% of the true volume, and will require a robust calibration upon its return in the laboratory. However, using this loop allowed the measurements of CFC-11 to continue. The worst of the problems occurred between stations 30 and 60 and these data were flagged as questionable.

A significant number of samples in the deep (>3000 m) Brazil Basin between about 20°S and 33°S had anomalously high SF_6 concentrations relative to the CFC-11 and CFC-12 concentrations. These high SF_6 concentrations occurred in a coherent pattern in the water column over more than 20 stations and are thought to be due to earlier deliberate deep SF_6 tracer release experiments in this region[Rye12].

6. Discrete pCO_2

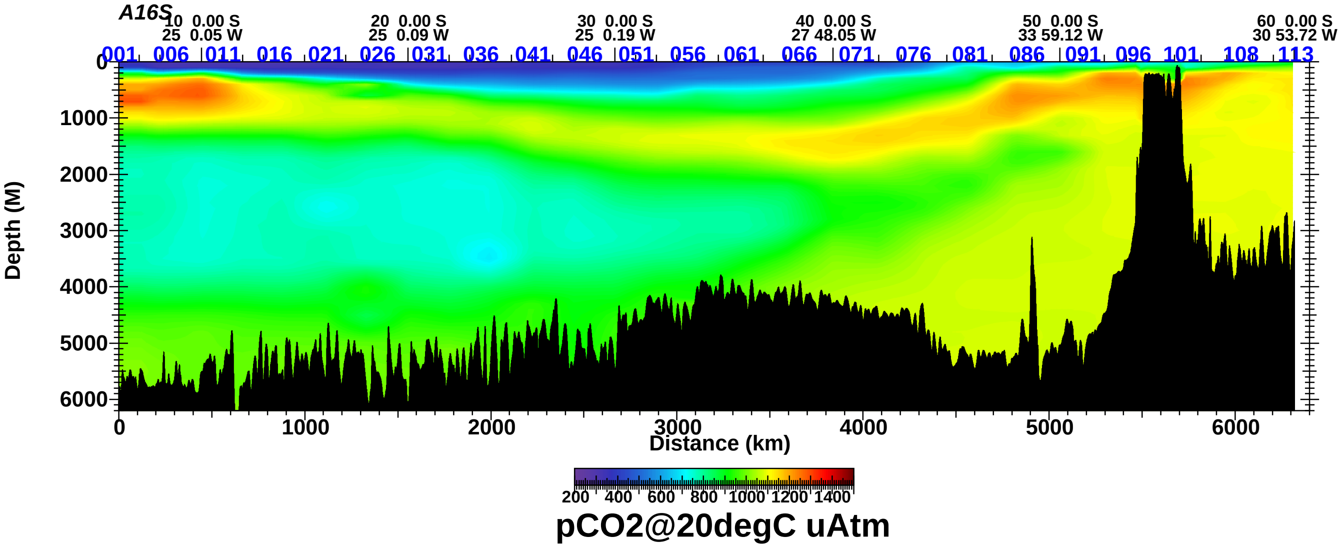

Figure 6.1 A16S stations 1-113

Sampling

Samples were drawn from 11-L Bullister bottles into 500 ml glass bottles using Tygon tubing with a Silicone adapter that fit over the spigot to avoid contamination of DOM samples. Bottles were rinsed twice with about 200 ml of seawater. Then they were filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water were withdrawn to allow for expansion of the water as it warms and to provide space for the stopper and tubing of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with grease (Down Corning silicone high vacuum grease) and were stored at room temperature for a maximum of twelve hours prior to analysis.

The analyses for pCO_2 were done with the discrete samples at 20°C. A primary water bath was kept within 0.03°C of the analytical temperature; a secondary bath was kept within 0.3°C of the analytical temperature. The majority of the samples were analyzed in batches of twelve bottles with 17 minute run time, which with standards took approximately 4 hours. When twelve bottles were moved into the primary water bath for analyses, the next twelve bottles were moved into the secondary water bath. Sample bottles spent at least two hours in the secondary water bath prior to being moved to the analytical water bath. A spot check indicated that bottom water samples (approx 2°C) reached a temperature of 18.6-18.8°C after 2.5 hours in the pre-bath.

The sampling focus was on drawing full casts every 2 degrees in latitude. Duplicate samples from the same Niskin were drawn to check the precision of the sampling and analysis. Some discrete samples were collected from the underway (UW) flowing sea water line aboard the ship. The UW samples will be compared to the results from the autonomous pCO_2 instrument. Most discrete UW samples were collected as a station was being completed.

Over 700 samples were drawn at 113 stations. About 28 duplicate samples were collected from the UW seawater line. More than 140 sets of duplicate bottles were drawn at various depths. The average relative deviation (= $\frac{\text{Max} - \text{Av}}{\text{Av} \times 100}$) of these duplicate pairs was 0.3%, while the median relative error was 0.1%.

Analyzer Description

The principles of the discrete pCO_2 system are described in [Wann93] and [Chip93]. The major difference in the current system is the method of equilibrating the the warter sample by passing it once through the equilibriation module into a drain, with the constantly circulating gas phase. This system uses miniature membrane contactors (Micromodules from Membrana, Inc.), which contain bundles of hydrophobic micro-porous tubes in polycarbonate shells (2.5 x 2.5 x 0.5 cm). The sample water is pumped for 17 minutes over the outside of the tubing bundles in two contactors in series at approximately 20 ml/min, with a total of 350 ml of the 550 ml of the bottle used. The gas is recirculated in a vented loop, which includes the tubing bundles and a non-dispersive infrared analyzer (LI-COR $^{\text{TM}}$ model 840) at approximately 24 ml/min. There was a slight draw into the vent of 0-1 ml/min based on the fluctuations of an Aalborg electronic flow meter on the vent line.

The flow rates of the water (20 ml/min) and gas (24 ml/min) for the A16S cruise are chosen with consideration of competing concerns. This optimization differs for different cruises. Faster water and gas flows yield faster equilibration. A slower water flow would allow collection of smaller sample volume; plus a slower gas flow would minimize the pressure increase in the contactor. Additionally, the flow rates are chosen so that the two fluids generate equal pressures at the micro-pores in the tubes to avoid leakage into or out of the tubes. A significant advantage of this instrumental design is the complete immersion of the miniature contactors in the constant temperature bath. Also in the water bath are coils of stainless steel tubing before the contactors that ensure the water and gas enter the contactors at the known equilibration temperature.

The instrumental system employs a large insulated cooler (Igloo Inc.) that accommodates twelve sample bottles, the miniature contactors, a water stirrer, a copper coil connected to a refrigerated circulating water bath, an immersion heater, a 12-position sample distribution valve, two thermistors, and two miniature pumps. The immersion heater works in opposition to the cooler water passing through the copper coil. One thermistor is immersed in the water bath, while the second thermistor is in a sample flow cell after the second contactor. The difference between the two thermistor readings was consistently less than 0.05°C. In a separate enclosure are the 8-port gas distribution valve, the infrared analyzer, a barometer, and other electronic components. The gas distribution valve is connected to the air-circulation pump and to six standard gas cylinders.

The instrumental system was designed and built by Tim Newberger and was supported by C. Sweeney and T. Takahashi. Their skill, assistance, and generosity were essential to the successful use of this instrumental system during this cruise.

Standardization

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

Standard Gas Cylinders

Cylinder	ppm CO_2
JB03282	288.46
JB03268	384.14
JB03309	567.40
CA05980	792.51
CA05984	1036.95
CA05940	1533.7

Data Processing

A custom program developed using LabView ^{TM} controls the system and graphically displays the CO_2 concentration as well as the temperature and pressure during the equilibration step of the process. The CO_2 in the gas phase changes greatly during the first minute of a new sample and then goes through several more oscillations. The oscillations dampen quickly as the concentration asymptotically approaches equilibrium. The flows are stopped after 17 minutes, and the program records an average of ten readings from the infrared analyzer along with other sensor readings. The data files from the discrete pCO_2 program are reformatted so that a Matlab program designed for processing data from the continuous pCO_2 systems can be used to calculate the fugacity of the discrete samples at 20°C. The details of the data reduction are described in [Pier09].

Problems

There were several issues with the system that had remained on the ship after A16N and did not get its usual pre-cruise check and refurbishment.

During the first run at the test station water got into the Nafion drier and IR possibly due to a blocked distribution valve. The Nafion drier was replaced. The IR did not respond except to the highest standard. The IR (Li-840) flow cell was removed following downloaded instructions and it was discovered that the bottom half of the gold mirrored cell was lightly coated with salt. It was cleaned with acetone and DI water and dried. The zero and span software was downloaded but because of interface issues only the CO_2 channel was spanned and not the H_2O channel which was unresponsive and showed a reading of about 8 mmol/mol throughout the cruise, irrespective if sample or standard was run.

On several occasions the head of the 8-position gas distribution valve came loose and the gas flow was interrupted. Initially it was thought that the valve was clogged and cleaning was attempted. The distribution valve was cleaned once and then replaced. To get enough torque on the hex screw on the collar of the head securing it to the valve body, a small hole was drilled in the enclosure to be able to use a long allen wrench.

The water pump had issues starting to pump water from sample bottles and priming was required to start the flow. The pump was replaced mid-cruise and this solved the problem. Samples did not reach full equilibrium in the first stations, regardless of increasing the equilibration time. As the cruise progressed, the equilibration achieved decreased from 99% to 96%. The membrane modules were cleaned with acid to improve performance and when that didn’t work, they were replaced. After replacement of the modules, equilibration (> 99.7 %) was achieved before the end of the equilibration time.

In the last stations, a decrease of up to 6 ppm in the measurements was sometimes observed in the last minutes of the equilibration period. For some samples the sinusoidal response observed for the first 6 minutes reappeared suddenly around 10 minutes.

During the cruise, the laptop controlling the analytical system suffered occasional crashes (blue screen of death). The error message indicated the problem was with a memory overload or interaction with the keyspan in the system. Rebooting the computer every 24 samples seemed to decrease the frequency of the crashes.

The response to all standards decreased appreciably (by about 80 ppm for the 1533 ppm standard) in the last week of the cruise but relative response remained unaffected.

Tests

Several tests were performed during the cruise in part to facilitate post-cruise data reduction.

A test was run to evaluate the difference in CO_2 measurements when the six standard gases were wetted by bubbling through a small volume of acidified DI water versus running them dry. No significant differences were observed.

To check for possible gas loss during equilibration through the Nafion drier and/or the vent, a duplicate sample was run with the regular N_2 gas through the nafion drier. The air circulation loop vent line was placed in the N_2 flow, such that N_2 would enter the vent. Then for the next duplicate the N_2 was replaced by the 1533 ppm std. No difference was seen indicating the integrity of the air circulation loop.

During the cruise we tested the preservation of the water samples with and without preservative (mercuric chloride) and with and without grease on the stopper. Samples were stored up to 48 hours and analyzed later. No significant difference was observed between the greased/poisoned and ungreased/non-poisoned samples.

Post cruise data reduction

The data supplied are preliminary and represent the $pCO_2(20)$ values as calculated by the data acquisition program, developed by Tim Newberger using the preceding standards and water bath temperature readings by the thermistors that appear very precise but biased high by 0.3°C compared to a Fluke/Hart thermometer. The water channel was not functioning.

For final data reduction the thermistors need to be calibrated in the lab, the response of the detector needs to be compared with current setting and after spanning and zeroing both CO_2 and H_2O channels. The response of equilibration needs to be determined from the RAW files that log data for each run at 1-second intervals and data has to be adjusted. These RAW files will also be used to pick the plateau in concentrations for the samples where concentrations changed in the last 5 minutes as the correct value.

Undwerway pCO_2 Analysis

During the A16S cruise, there was an automated underway pCO_2 system from AOML situated in the hydrolab, as it has been since 1997. The current design of the instrumental system is based on [Wann93], and Feely et al. [Feel98], while the details of the instrument and of the data processing are described in Pierrot, et.al. [Pier09].

The repeating cycle of the system includes 4 gas standards, 5 ambient air samples, and 66 headspace samples from its equilibrator within 3.3 hours. The concentrations of the standards range from 285 to 546 ppm CO_2 in compressed natural air. They were purchased from NOAA/ESRL in Boulder and are directly traceable to the WMO scale.

The system includes an equilibrator where approximately 0.6 liters of constantly refreshed surface seawater from the bow intake is equilibrated with 0.8 liters of gaseous headspace. The water flow rate through the equilibrator was 1.5 - 2.0 liters/min, which yielded a vigorous spray pattern during this cruise.

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

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

Standard Gas Cylinders

Cylinder	ppm CO_2
JB03282	288.46
JB03268	384.14
JB03309	567.40
CA05980	792.51
CA05984	1036.95
CA05940	1533.7

Problems

The system ran very well during the cruise and only two problems were encountered. During the start of the cruise the circulation gas was high and variable at about 120 ml/min. This did not seem to affect the CO_2 values. Flow was decreased to 80 ml/min and flows were steadier. On Jan. 22nd, the uncontaminated seawater line pump was turned off for about 12 hours after the strainer became clogged twice with salps.

7. Dissolved Inorganic Carbon (DIC)

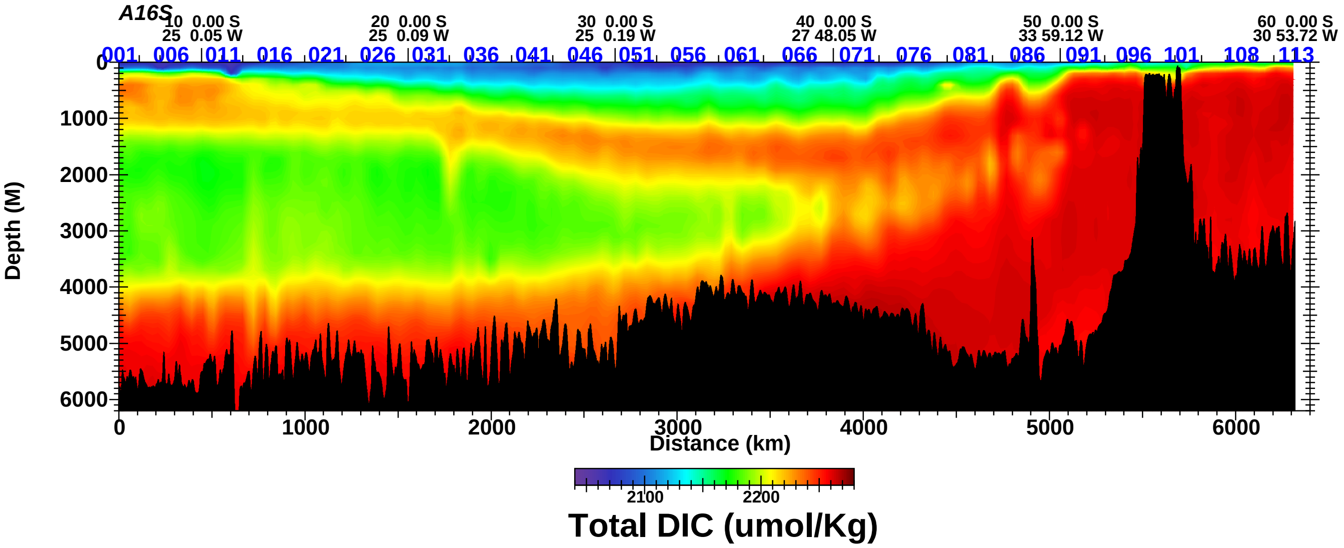

Figure 7.1 A16S stations 1-113

Sampling

Samples for TCO_2 measurements were drawn according to procedures outlined in the *Handbook of Methods* for CO_2 Analysis [DOE94] from Bullister bottles into cleaned 294-ml glass bottles. Bottles were rinsed and filled from the bottom, leaving 6 ml of headspace; care was taken not to entrain any bubbles. After 0.2 ml of saturated $HgCl_2$ solution was added as a preservative, the sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours prior to analysis.

TCO_2 samples were collected from a variety of depths with one to three replicate samples. Typically the replicate seawater samples were taken from the surface, around 1000 m, and bottom Bullister bottles and run at different times during the cell. No systematic difference between the replicates was observed.

Analysis

The TCO_2 analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (AOML3 and AOML4) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a Dissolved Inorganic Carbon Extractor (DICE) inlet system. DICE was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA [John85] [John87] [John92] [John93] [John99]. In the coulometric analysis of TCO_2, all carbonate species are converted to CO_2 (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved CO_2 gas is swept into the titration cell of the coulometer with pure air or compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. In this process, the solution changes from blue to colorless, triggering a current through the cell and causing coulometrical generation of OH^- ions at the anode. The OH^- ions react with the H^+, and the solution turns blue again. A beam of light is shone through the solution, and a photometric detector at the opposite side of the cell senses the change in transmission. Once the percent transmission reaches its original value, the coulometric titration is stopped, and the amount of CO_2 that enters the cell is determined by integrating the total charge during the titration.

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

The stability of each coulometer cell solution was confirmed three different ways: two sets of gas loops were measured at the beginning; also the Certified Reference Material (CRM), Batch 129, supplied by Dr. A. Dickson of SIO, was measured at the beginning; and the duplicate samples at the beginning, middle, and end of each cell solution. The coulometer cell solution was replaced after 25-30 mg of carbon was titrated, typically after 9-12 hours of continuous use.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes. The weights with the appropriate densities were used to determine the volume of the pipettes. Calculation of the amount of CO_2 injected was according to the CO_2 handbook (DOE 1994). The concentration of CO_2 ($[CO_2]$) in the samples was determined according to:

$$[CO_2] = \mathrm{Cal.\,Factortime}\ \frac{(\mathrm{Counts} - \mathrm{Blank} \times \mathrm{RunTime}) \times \mathrm{K}}{\mathrm{PipetteVolume} \times \mathrm{SampleDensity}}$$

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

All TCO_2 values were recalculated to a molar weight (μmol/kg) using density obtained from the CTD's salinity. The TCO_2 values were corrected for dilution by 0.2 ml of saturated $HgCl_2$ used for sample preservation. The total water volume of the sample bottles was 288 ml (calibrated by Esa Peltola, AOML). The correction factor used for dilution was 1.0007. A correction was also applied for the offset from the CRM. This correction was applied for each cell using the CRM value obtained in the beginning of the cell. The average correction was -3.22 μmol/kg for AOML 3 and 1.57 for AOML 4. The average difference of the duplicates was 1.58 μmol/kg for AOML 3 and 1.57 for AOML 4. The results underwent initial quality control on the ship using TCO_2-pressure profiles and TCO_2-NO_3 and TCO_2-pH plots.

Analytical Problems

In general, both systems worked well. One solenoid valve failed and was replaced. Two cell caps went bad and a new one was constructed. On station 34, the calibration factor was unusually high after running 3 gas loops. The CRM value was very good with the high calibration factor, but later comparisons with NO_3 and pH showed that all analyses for this station are likely bad. This anomalous calibration factor did not recur during the cruise. The total dissolved inorganic carbon data reported to the database directly from the ship are to be considered preliminary until a more thorough quality assurance can be completed shore side.

8. pH

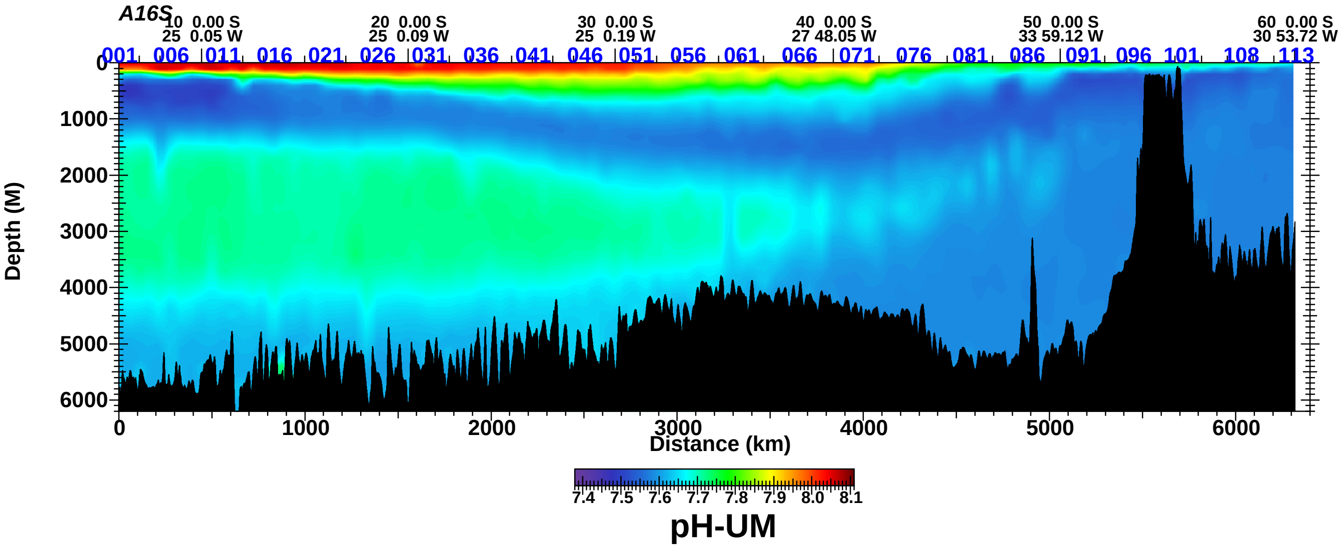

Figure 8.1 pH (sea water at 25 C) on A16S stations 1-113

Sampling

Samples were collected in 50ml borosilicate glass syringes rinsing 2 times and thermostated to 25°C before analysis. Two duplicates were collected from each station. Samples were collected on the same Bullister bottles as total alkalinity and dissolved inorganic carbon in order to completely characterize the carbon system. One sample per station was collected and analyzed with double the amount of indicator in order to correct for pH changes as a result of adding the indicator, this correction has not been applied to the preliminary data. All data should be considered preliminary.

Analysis

pH (umol/kg seawater) on the seawater scale was measured using a Agilent 8453 spectrophotometer according to the methods outlined by [Clay93] An RTE10 water bath maintained spectrophotometric cell temperature at 25.0°C. A 10cm flow through cell was filled automatically using a Kloehn 6v syringe pump. The sulfonephthalein indicator m-cresol purple (mCP) was also injected automatically by the kloehn 6v syringe pump into the spectrophotometric cells, and the absorbance of light was measured at three different wavelengths (434 nm, 578 nm, 730 nm). The ratios of absorbances at the different wavelengths were input and used to calculate pH on the total and seawater scales, incorporating temperature and salinity into the equations. The equations of [Dick87] , Dickson and Riley [Dick79] , and Dickson [Dick90] were used to convert pH from total to seawater scales. Salinity data were obtained from the conductivity sensor on the CTD. These data were later corroborated by shipboard measurements. Temperature of the samples was measured immediately after spectrophotometric measurements using a Guildline 9540 digital platinum resistance thermometer.

Reagents

The mCP indicator dye was a concentrated solution of approx. 2.0 mM. Unpurified indicator was used purchased from Alpha-Aeser.

Standardization

The precision of the data can be accessed from measurements of duplicate samples, certified reference material (CRM) Batch 129 (Dr. Andrew Dickson, UCSD) and TRIS buffers. The measurement of CRM and TRIS was alternated at each station. The mean and standard deviation for the CRMs was 7.9125± 0.0033 (n=58) and 8.0879±0.0035 (n=40) for TRIS buffer. TRIS bottles 6 and 7 were high by approximately 0.01 relative to all measurements on both A16N and A16S and have thus been excluded.

Data Processing

Addition of the indicator affects the pH of the sample, and the degree to which pH is affected is a function of the pH difference between the seawater and indicator. Therefore, a correction is applied for each batch of dye. One sample from each station was measured twice, once normally and a second time with double the amount of indicator. The change in the ratio is then plotted versus the change in the isobestic point to develop an empirical relationship for the effect of the indicator on the pH. A preliminary correction based on the measurements of A16N has been applied to this data. . The mean and standard deviation of the duplicates was 0.0004 ± 0.0017 (N = 198). The preliminary quality control is shown in the Appnedix Table.

Problems

The only major problem that occurred was on station 108 when the water bath failed and was unable to cool. The variability in the temperature of the water bath showed increased variability the few days before it failed, but was still within the acceptable range. The water bath was quickly replaced and no samples were lost.

9. Total Alkalinity

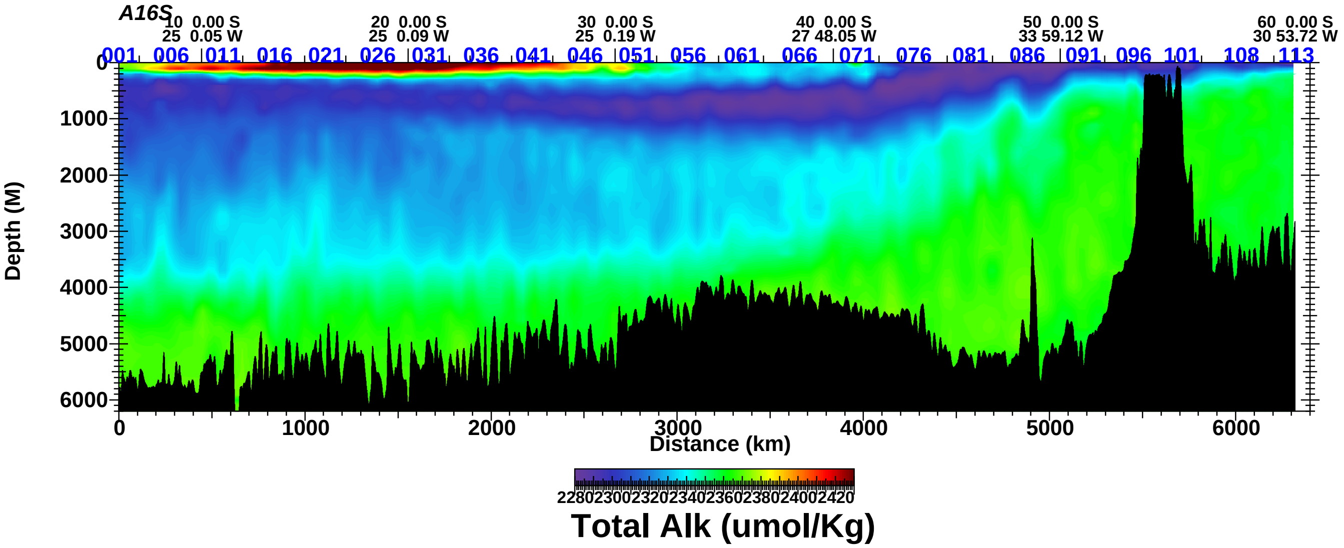

Figure 9.1 A16S stations 1-113

Sampling

At each station total alkalinity (TA) samples were drawn from Bullister bottles into 500 ml borosilicate flasks using silicone tubing that fit over the stopcock. Bottles were rinsed a minimum of three times, then filled from the bottom and allowed to overflow half of the bottle volume. The sampler was careful not to entrain any bubbles during the filling procedure. Approximately 15 ml of water was withdrawn from the flask by halting the sample flow and removing the sampling tube, thus creating a reproducible headspace for thermal expansion during thermal equilibration. The sample bottles were sealed at a ground glass joint with a glass stopper. The samples were then thermostated at 25°C before analysis. Three duplicates were collected at each station. Samples were collected from the same Bullister bottles as pH or dissolved inorganic carbon (DIC) in order to completely characterize the carbon system.

Analyzer Description

The sample TA was then evaluated from the proton balance at the alkalinity equivalence point, 4.5 at 25°C and zero ionic strength. This method utilized a multi-point hydrochloric acid titration of seawater [Dick81]. The instrument program used a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TA, DIC, and pH from the potentiometric titration data. The program was patterned after those developed by[Dick81], [Joha82], and [DOE94]. The least-squares algorithm of the potentiometric titrations not only gave values of TA but also those of DIC, initial pH as calculated from the initial EMF, the standard potential of the electrode system (E0), and the first dissociation constant of CO_2 at the given temperature and ionic strength (pK_1). Two titration systems, A and B were used for TA analysis. Each of them consisted of a Metrohm 765 Dosimat titrator, an Orion 720A or 720A+, pH meter and a custom designed plexiglass water-jacketed titration cell[Mill93]. The titration cell allowed for the titration to be conducted in a closed system by incorporating a 5 ml ground glass syringe to allow for volume expansion during the acid addition. The seawater samples were temperature equilibrated to a constant temperature of 25± 0.1°C with a water bath (Neslab, RTE-10). The electrodes used to measure the EMF of the sample during a titration were a ROSS glass pH electrode (Orion, model 810100) and a double junction Ag, AgCl reference electrode (Orion, model 900200). The water- jacketed cell was similar to the cells used by [Brad88] except a larger volume (~ 200 ml) was employed to increase the precision. Each cell had a fill and drain valve which increased the reproducibility of the volume of sample contained in the cell. A typical titration recorded the stable solution EMF (deviation less than 0.09 mV) and added enough acid to change the voltage a pre-assigned increment (13 mV). A full titration (25 points) took about 20 minutes. A 6 port valve (VICI, Valco EMTCA-CE) allowed 6 samples to be loaded into the instrument and successively measured.

Reagents

A single 50-l batch of ~0.25 m HCl acid was prepared in 0.45 m NaCl by dilution of concentrated HCl, AR Select, Mallinckrodt, to yield a total ionic strength similar to seawater of salinity 35.0 (I = 0.7 M). The acid was standardized by a coulometric technique [Mari68][Tayl59] , and verified with alkalinity titrations on seawater of known alkalinity. The calibrated molarity of the acid used was 0.24361 ±0.0001 N HCl. The acid was stored in 500-ml glass bottles sealed with Apiezon L grease for use at sea.

Standardization

The reproducibility and precision of measurements were checked using low nutrient surface seawater, used as a substandard, and Certified Reference Material (CRM) from Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California. The CRM was utilized to account for instrument drift over the duration of the cruise and to maintain measurement precision. One CRM was measured on each instrument every other station as well as the low nutrient surface. Duplicate analysis provided additional quality assurance. Three duplicates were taken, in which 2 samples were taken from the same Bullister bottle, at each station. The duplicates were then analyzed on system A, system B, or split between systems A and B. This provided a measure of the precision on the same system and between systems. Laboratory calibrations of the Dosimat burette system with water indicated the systems delivered 3.000 ml of acid (the approximate value for a titration of 200 ml of seawater) to a precision of ±0.0004 ml, resulting in an error of ±0.3 μmol/kg in TA.

Data Processing

Measurements on CRM batches 129 were made. The difference between the measured and certified values on system A is 1.87 ± 2.85 (N=55) and on B is 2.73 ± 3.45 (N=55). Part way through the cruise a noticeable decrease in precision of the CRMs occurred. It was determined to be caused by using old CRMs from DIC, the use of which was immediately stopped. These old CRMs have not yet been excluded from the data analysis; this is the reason for the high standard deviation of the CRMs and will be improved when they are excluded during final data analysis. Six different batches of low nutrient surface water were used. All had standard deviations between 0.5 and 2.5μmol/kg.

A total of 306 sets of duplicates were analyzed. The preliminary mean and standard deviations for both run on system A is 0.04 ± 1.84 (N = 103), for both run on system B is -0.13 ± 1.75 (N = 93), and for one on each system (A-B) is 2.04 ± 278 (N = 98).

Problems

The only major problem occurred on station 105 when the computer for system B irreparably crashed. It was quickly replaced and only resulted in the loss of one sample.

10. Dissolved Organic Carbon (DOC)

DOC and Total Dissolved Nitrogen (TDN) samples were taken from every Bullister bottle at every other station (odd stations). 1368 samples were taken from 57 stations in total. Samples from depths of 250m and shallower were filtered through GF/F filters using in-line filtration. Samples from deeper depths were not filtered. High-density polyethylene 60 ml sample bottles were pre-cleaned with 10% HCl and rinsed with Mili-Q water. Filters were combusted a 450°C overnight. Filter holders and silicone tube were cleaned with 10% HCl and rinsed with Mili-Q water before sampling. Bottles were rinsed three times with the seawater before collecting 50-60 ml of sample at each Bullister bottle. Samples were kept frozen in coolers inside the ship's freezer. Frozen samples will ship back to Miami in four coolers for laboratory analysis. Gloves were used during all process of collection and storage.

11. Carbon Isotopes in seawater ($^{14/13}C$)

A total of 576 samples were collected from 25 stations. In addion, surface samples were also collected from 14 stations. Seven stations were partially sampled (16 samples) while the rest were full cast (24 samples). Duplicates were collected at almost all stations. Samples were collected in 500 ml airtight glass bottles. Using silicone tubing, the flasks were rinsed 2 times with the seawater from the correspondent Niskin bottle. While keeping the tubing at the bottom of the flask, the flask was filled and flushed by allowing it to overflow one and a half times its full volume. Once the sample was taken, a small amount (about 30 cc) of water was removed to create a headspace and 200 l of 50% saturated mercuric chloride solution was added in the sampling bay.

In order to avoid contamination, gloves were used during all collection, handling, and storage processes. Sample handling was done on a clean table covered with new aluminum foil for each batch.

After all samples were collected from a station the glass stoppers were dried and greased with Apiezon-M grease to ensure an air tight seal. The stoppers were secured with a rubber band which wrapped over over the entire bottle. The samples were stored in AMS crates or boxes inside the ship's main laboratory during the cruise. The samples will be shipped to WHOI for analysis.

The radiocarbon/DIC content of seawater (DI^{14}C) is measured by extracting the inorganic carbon as CO_2 gas, converting the gas to graphite, then counting the number of ^{14}C atoms in the sample directly using an accelerator mass spectrometer (AMS).

Radiocarbon values will be reported as ^{14}C using established procedures modified for AMS applications. The $^{13}C/^{12}C$ of the CO_2 extracted from seawater is measured relative to the $^{13}C/^{12}C$ a CO_2 gas standard calibrated to the PDB standard using an isotope radio mass spectrometer (IRMS) at NOSAMS.

Problems

16 boxes of pre-cleaned bottles got wet with rainwater in Recife, Brazil prior to leaving. Samples were collected in 10 of these boxes making sure that bottles were clean and dry and not affected by the rain water at all.

12. Tritium, Helium and ^{18}O

Helium samples were taken from designated Niskins in 90 cc 316 type stainless steel gas tight vessels with valves. The samples were then extracted into aluminum silicate glass storage vessels within 24 hours using the at sea gas extraction system. The helium samples are to be shipped to the Lamont-Doherty Earth Observatory of Columbia University Nobel Gas Lab for mass spectrometric measurements. A corresponding one-liter water sample was collected from the same Niskin as the helium sample in a preprocessed glass bottle for degassing back at the shore based laboratory and subsequent tritum determination by ^{3}He in-growth method. ^{18}O samples were collected and shipped to LDEO for analysis.

During A16S, 18 stations were sampled, collecting 346 samples for tritium, 414 samples for helium and 254 samples for ^{18}O analysis. No duplicate samples were taken.

13. Density

Sampling

Over the course of A16S, 5 stations were sampled (stations 19, 43, 67, 85 and 111), for a total of 111 density samples. Each Niskin was sampled using a 150 ml HDPE bottle. The bottles were rinsed 3 times, allowed to fill until overflowing, capped, and sealed with Parafilm. This procedure leaves as little head space as possible to minimize evaporation until analysis.

Analyzer Description

The sealed samples will be shipped to the Millero Lab at RSMAS in Miami where the salinity will be re-measured on a salinometer (Guildline Portosal), and the density will be measured using an Anton-Paar DMA 5000 densitometer.

14. LADCP

System Configuration

A single downward-facing WH150-kHz LADCP (serial number 16283) was secured with brackets to a metal plate mounted on 24-bottle CTD rosette frame. The ADCP was positioned to avoid interference with the rosette frame. The instrument was connected to a NOAA 48-Volt rechargeable lead-acid battery pack mounted in the center of the rosette via a NOAA custom star cable assembly typically used for configurations consisting of both upward and downward looking ADCPs. Since only one ADCP was used in this configuration, the unused cable connectors were covered with dummy caps. On deck, the rosette was moved into and out of a sheltered sampling hanger atop a platform mounted on two tracks.

The power supply and data transfer was handled independently from any CTD connections. While on deck, a communications and power cable was connected to a cable in the sampling hangar that ran into the hydro lab on the NOAA Ship Ronald H. Brown. This cable connected to a NOAA battery charger located in the Hydro lab for power and an acquisition computer via USB connection for data download. The LADCP and CTD acquisition computer clocks both used NTP to stay in sync with the ship clock and to assure that the absolute time recorded by the CTD and LADCP were the same.

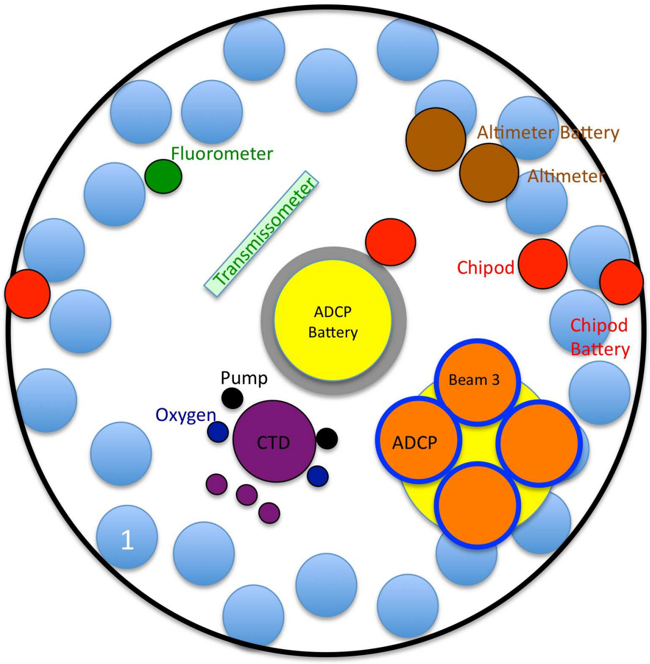

Figure 14.1 Cross-sectional diagram (looking down) of CTD rosette showing relative position and orientation of ADCP.

LADCP Operation

Operational LADCP scripts, written in python by Eric Firing and the group at the University of Hawaii, were used for instrument control and data transmission. The command file used in communication with the LADCP is shown below:

```
• CR1         # factory defaults
• PS0         # Print system serial number and other info.
• WM15        # sets LADCP mode; WB -> 1, WP -> 001, TP -> 000100, TE -> 00000100
• TC2         # 2 ensembles per burst
• TB          00:00:02.80
• TE          00:00:01.20
• TP          00:00.00
• WN40        # 40 cells, so blank + 320 m with 8-m cells
• WS0800      # 8-m cells
• WT1600      # 16-m pulse
• WF1600      # Blank, 16-m
• WV330       # 330 is max effective ambiguity velocity for WB1
• EZ0011101   # Soundspeed from EC (default, 1500)
```

• EX00100	# No transformation (middle 1 means tilts would be used otherwise)
• CF11101	# automatic binary, no serial
• LZ30,230	# for LADCP mode BT; slightly increased 220->230 from Dan Torres
• CL0	# don’t sleep between pings (CL0 required for software break)

This command file was sent to the instrument prior to each cast. Communication between the computer and the instrument was then terminated, the battery charger was turned off, the power cable was disconnected, and all connections were sealed with dummy plugs and secured.

After the CTD was brought back on deck after a cast, the data and the power supply cable was rinsed with fresh water and reconnected to the computer and battery charger. The data acquisition was terminated, the battery was charged, and the data were downloaded using the LADCP software. The battery charger remained on from the time of data download until the time the instrument was prepared for the next cast.

Log files were kept for each cast to ensure that all the steps were completed and a data acquisition log was maintained during the cruise to summarize the data collected and document any special situations in the data collection or processing.

Data Processing

Within 10 hours after each cast, the data were preliminarily processed using Lamont-Doherty Earth Observatory (LDEO) LADCP software for data processing in Matlab [Thur08]. Ancillary data were downloaded including the CTD profile and timeseries, and the shipboard ADCP data. These data were used in conjunction with the LADCP data to produce both shear and inverse solutions for the absolute velocities. The preliminary processing produced velocity profiles, rosette frame angular movements, and Matlab files. Section plots of U and V were produced and were made available on the cruise website on the local network.

The data acquisition log summarizes errors in the data processing. A common error was "Increased error because of shear-inverse difference." This was common in the early casts during the cruise and was presumably due to a lack of scatterers in the water column at these lower latitudes. Occasionally there were errors indicating a U and/or V bottom track bias. In all but one instance, this was resolved by setting p.btrack_mode=0 in the matlab script set_cast_params.

Problems

Prior to starting casts, LADCP battery problems were indicated by faint pinging that terminated prematurely during deck tests. The battery was swapped out for another NOAA battery, and the star cable was also replaced with a brand new cable. All problems were resolved with deck testing prior to the test cast, which preceded the first station.

Data collection was largely routine and problem free until cast 93. When this cast came up, the data processing indicated that one of the beams had failed. There was a severe drop in voltage and corresponding increase in current evident near the bottom of the cast. In the sampling hangar, the top of the ADCP was removed and the inside of the instrument was inspected. There was no indication of leaking or corrosion and all connections were secure. The o-rings were replaced and the instrument re-sealed. The instrument remained on the rosette for the duration of the cruise and continued to collect data from the 3 remaining beams.

Summary and Preliminary Results

Data were successfully collected on all 113 stations sampled during the cruise. Issues with the CTD led to repeat casts on two stations (87 and 113) and LADCP data were collected on both the problematic and repeat casts in each case.

Latitude-depth sections of measured zonal (U) and meridional (V) velocities are shown in Figure 14.2 and 14.3. Stations 1-60 followed the 25 West line of longitude (Figure 14.2), and Stations 60-113 were between 25 and 36.5 South (Figure14.3).

Currents were much stronger in the southern part of the transect. Note the difference in scale between Figures 14.2 and 14.3. Much of the northern portion of the transect (Figure 14.2) is in the subtropical gyre and was characterized by weaker currents and fewer scatterers in the water column.

Strong currents extending from the surface to the full ocean depth are observable at around 47 degrees South. This may correspond with the southern boundary of the South Atlantic Current.

The Antarctic Circumpolar Current is observable heading East at the end of the transect, below South Georgia Island.

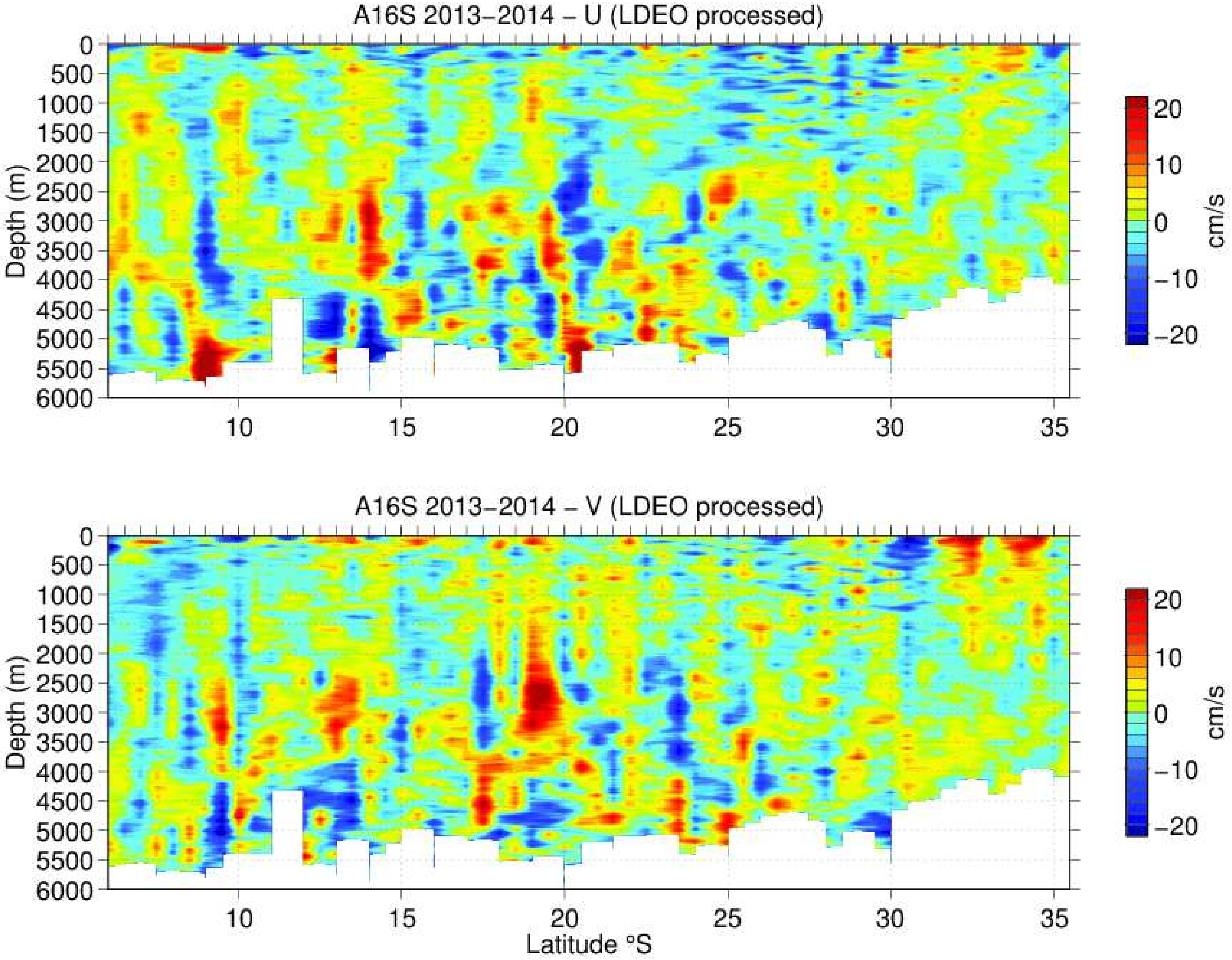

Figure 14.2 Zonal (U, upper) and meridional (V, lower) velocities measured from Stations 1-60.

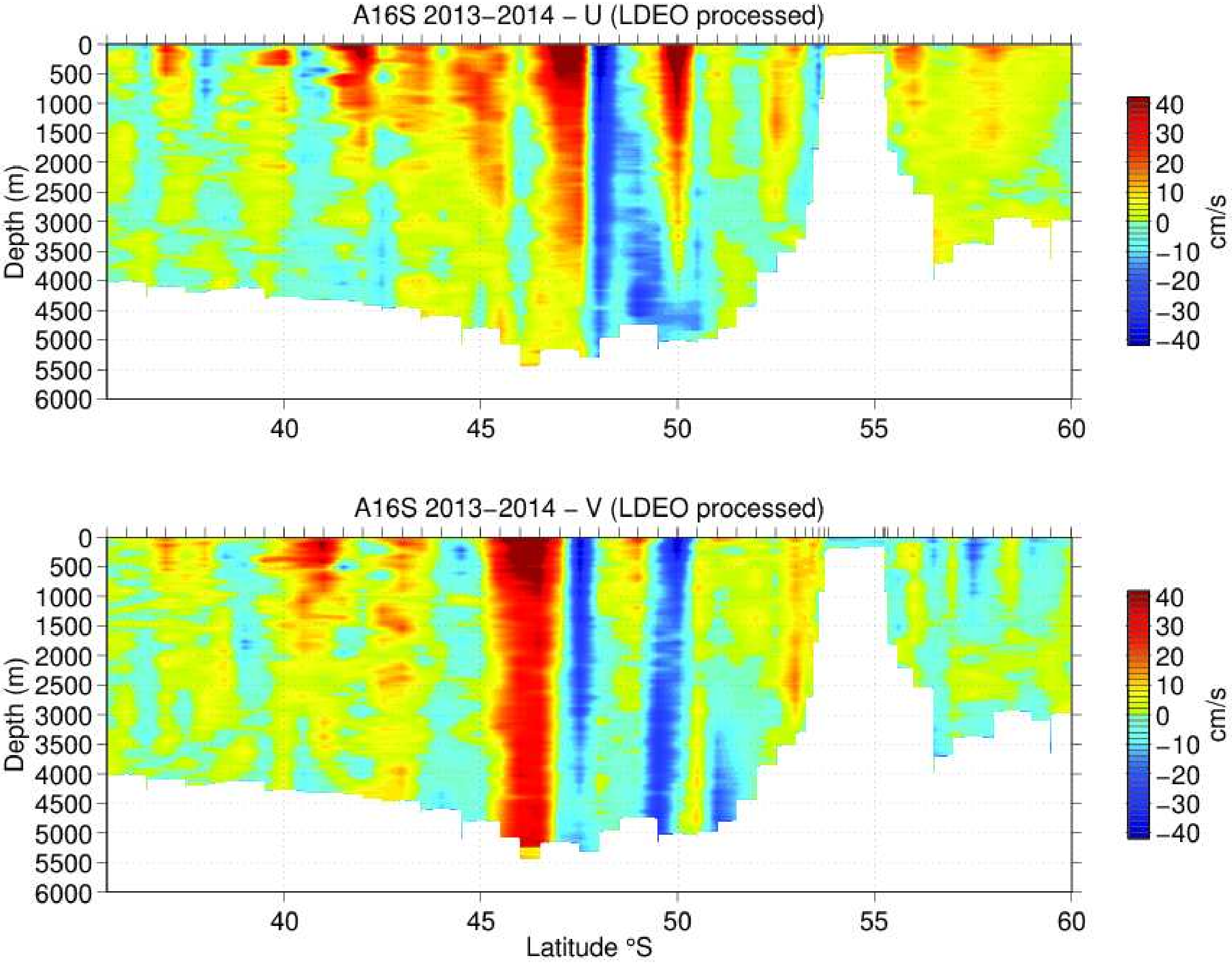

Figure 14.3 Zonal (U, upper) and meridional (V, lower) velocities measured from Stations 60-113.

SADCP

Sampling

The *Ronald H. Brown* has a permanently mounted 75 kHz acoustic Doppler current profiler (Teledyne RDI) for measuring ocean velocity in the upper water column. The ADCP is a Phased Array instrument, capable of pinging in broadband mode (for higher resolution), narrowband mode (lower resolution, deeper penetration), or interleaved mode (alternating). On this cruise, data were collected with 8m broadband pings and 16m narrowband pings. The depth range achieved depends on weather (bubbles), installation (eg. ship noise), scattering levels, and other factors. Data were recorded during the entire cruise.

Processing

Specialized software developed at the University of Hawaii has been installed on the Brown for the purpose of ADCP acquisition, preliminary processing, and figure generation during each cruise. The acquisition system ("UHDAS", University of Hawaii Data Acquisition System) acquires data from the ADCPs, gyro heading (for reliability), Mahrs and POSMV headings (for increased accuracy), and GPS positions from various sensors. Single-ping ADCP data are automatically edited and combined with ancillary feeds, averaged, and disseminated via the ship's web, as regularly-updated figures on a web page and as Matlab and netCDF files.

Summary

Shipboard ADCP data were collected for the duration of A16S. The ADCP system and data were monitored remotely. There were no changes or errors noted, beyond a continuing 15 percent failure level of the POSMV. Although the Mahrs and the POSMV are supposed to be accurate, neither is perfect and post-processing of the ADCP data will be necessary to obtain best accuracy for data while the ship is steaming. When the ship speed is near zero, heading errors do not cause significant errors in ocean velocity. Therefore the automated at-sea product should be good enough for preliminary use while the ship is on station.All in all, the instrument, ancillary devices, and acquisition system performed reasonably well.

15. Chipod

System Configuration and Sampling

Three Chipods were mounted on the CTD rosette frame to measure temperature (T), its time derivative (T_t), and acceleration at 50, 100, and 50 Hz, respectively. One Chipod-CTD has two T/T_t sensors, looking upward, and three-dimensional accelerator. Two RBR-Chipods, one looking upward and the other looking downward, are a combination of RBR Duo, which measurs T and pressure at 1 Hz, and Chipod with one T/T_t sensor and one horizontal accelerator. Figure 15.1 shows details of the configuration of the Chipods and sensors. Three upward looking T/T_t sensors were positioned above the Niskin bottles by 8.25 inches and above the bottom of the CTD rosette frame by 82.25 inches using a unistrut in order to avoid false turbulence, which might be generated by the movement of the rosette frame during the upcast. The upward looking Chipod-RBR was assembled lower than the neighboring upward looking T/T_t sensors to avoid possible disturbances by its position due to the rotation of the CTD frame, and collected data from cast 12 onward. The downward looking T/T_t sensor was placed on the LADCP battery pack above the bottom of the CTD frame by 2 inches toward the center of the CTD rosette to avoid picking up false signals due to turbulence from the LADCP modules and/or CTD system during the downcast.

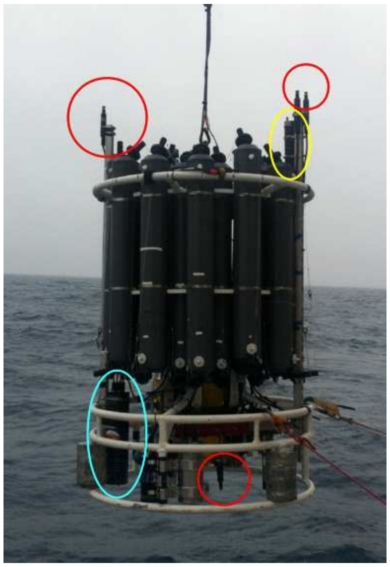

Figure 15.1 Chipod configuration on the rosette. The red, cyan, and yellow circles show the positions of T/T_t sensors, Chipod-CTD, and upward looking RBR-Chipod, respectively. The downward looking RBR-Chipod is not seen in this photo.

Data Processing

To derive profiles of turbulent kinetic energy dissipation (ε) and thermal variance dissipation (X), Chipod T/T_t records first need to be aligned to pressure. Since Chipod does not have a pressure sensor, double-integration of vertical acceleration, thus displacement of the unit, has to be fit to pressure from CTD to align T/T_t to pressure. Then, ε and X as a function of pressure can be estimated by fitting the vertical temperature gradient (T_z) spectrum, which can be computed from T_t and Chipod descent rate, to the theoretical temperature gradient spectrum, which requires buoyancy frequency and T_z, by using an iterative procedure suggested by [Moum09].

Problems

In the first thee casts, 0.3 sec interval noise was found in the signal from the secondary Chipod-CTD T_t sensor, which disappeared after the sensor cable was replaced. From station 90 onward, T/T_t sensor malfunction occurred when the package was submerged in cold water (< -0.15°C), and the T/T_t signals drifted with significant noise.

Summary

Figure 15.2 shows a comparison of upward looking Chipod-CTD (red) and downward looking RBR-Chipod data. In the top panel, all T signals represent the temperature variation during the entire cast. The RBR-Chipod T_t signal (black line in the bottom panel) shows a distinct transition between the downcast and the upcast, which occurred at ~11:27 AM. Compared to the downcast T_t signal, the upcast signal shows more noise, which seems linked to a significant disturbance by the ascending CTD structure, i.e., 24 Bullister bottles, CTD and LADCP instruments, and the frame. The upward looking T_t signals (blue and red lines) do not show such distinct changes at the transition that may be related to the rotation of the CTD frame during the cast. The LADCP heading record shows the CTD rosette rotating much faster during the upcast compared to the downcast at most stations. Such spinning of the CTD frame implies the revolution of T_t sensors around the winch cable. Thus, false turbulence might be generated by the sensor protector and/or any structure nearby while the CTD frame is rotating due to the position of the sensors (see Figure 15.1), and measured by the sensors, yielding noise in the signal. However, the downward looking sensor, which is placed in the center of the CTD frame, may not be affected significantly by the spinning of the CTD frame. Moreover, the rotation rate of the CTD frame during the downcast is less than that during the upcast.

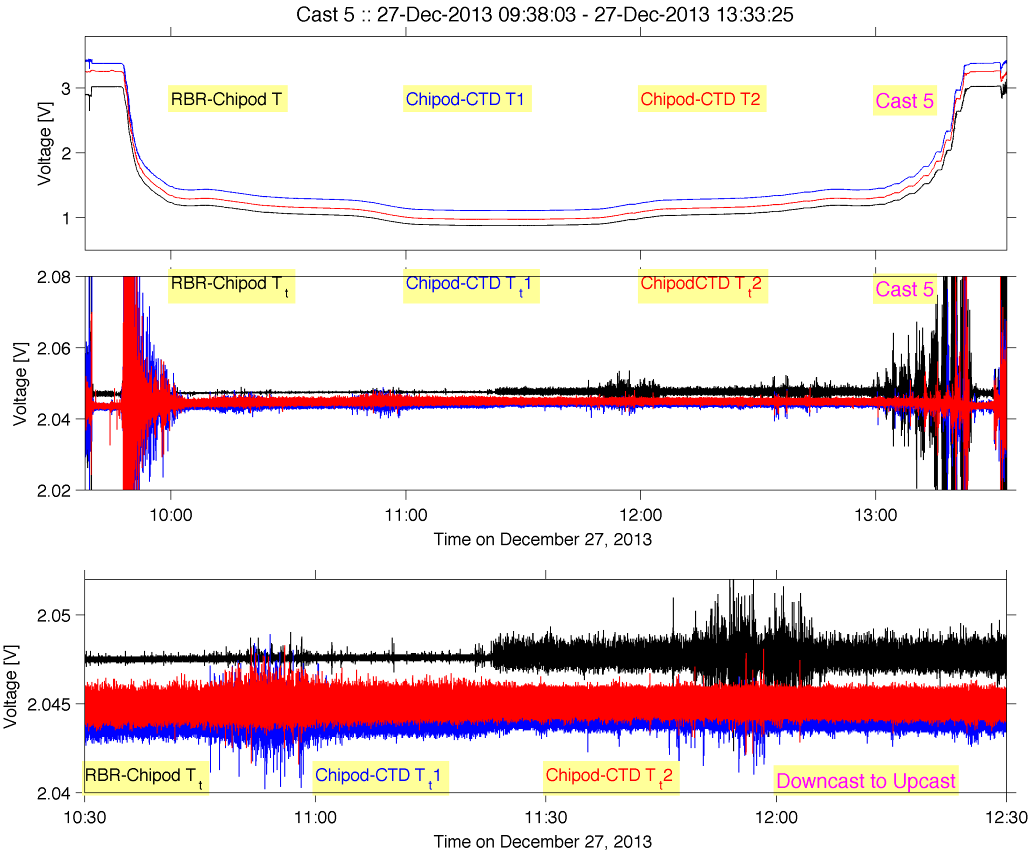

Figure 15.2 An example profile of Chipod-CTD and RBR-Chipod data. The blue and red lines indicate the first and secondary upward looking Chipod-CTD T/T_t , and the black line shows the downward looking RBR-Chpod T/T_t at station 5

16. Trace Metal Program

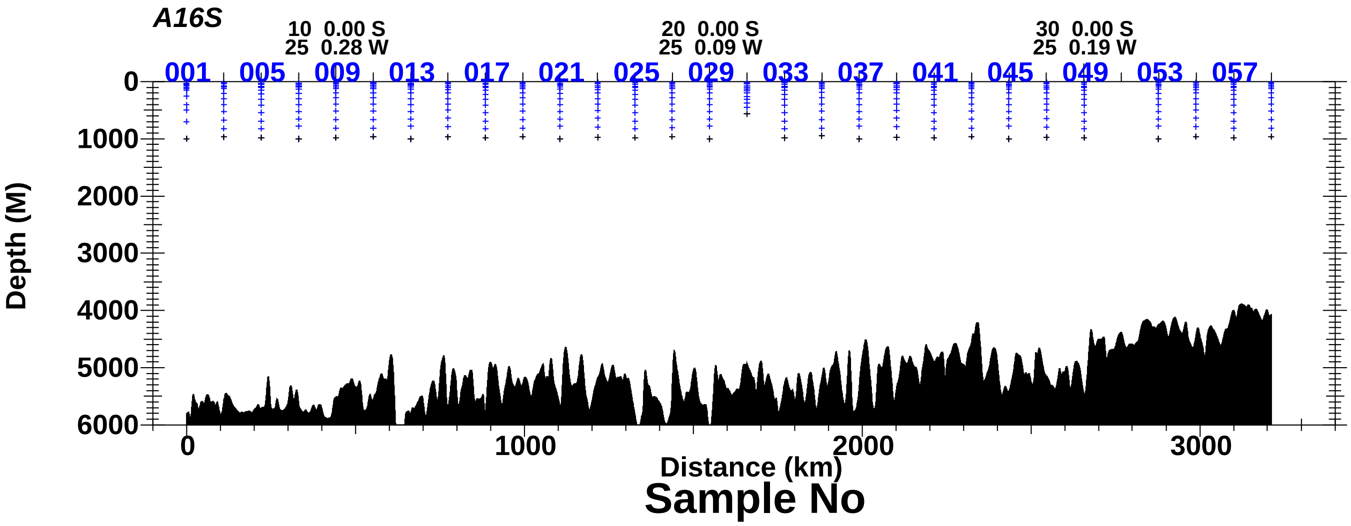

Figure 16.1 A16S Sample distribution for stations 1-60

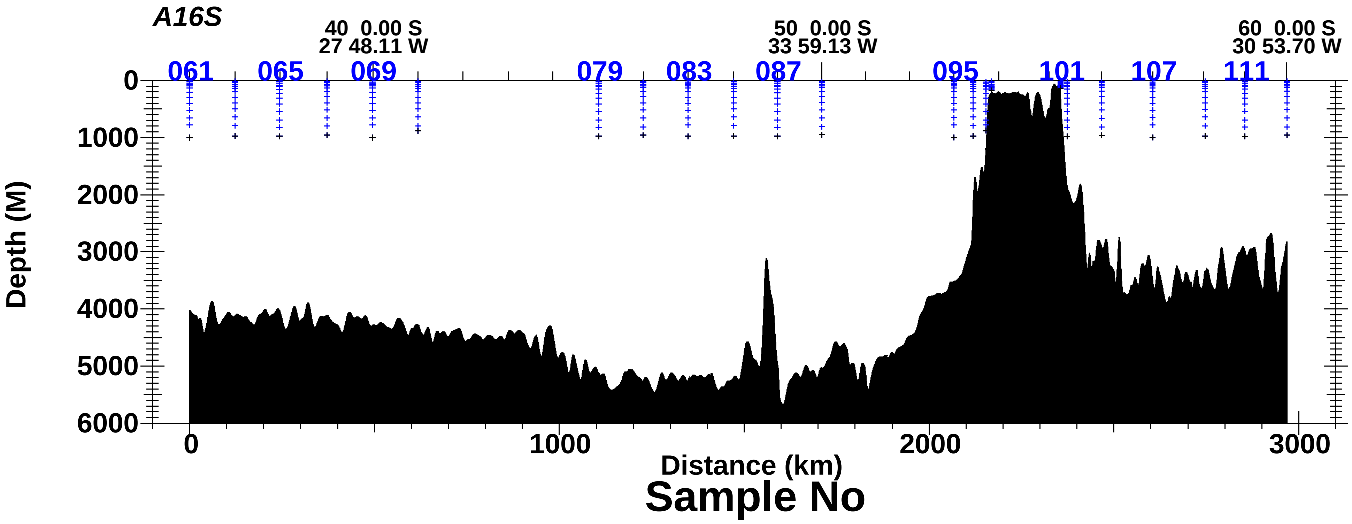

Figure 16.2 A16S Sample distribution for stations 61-113

Water Column Sampling

627 water-column trace metal samples were collected at 53 stations and a test station using a dedicated trace-element rosette with 12 Teflon-coated, 12 L General Oceanics GO-FLO bottles[Meas08] modified with the addition of curved Teflon tubing from the sample valve reaching the bottom of the bottle (for quantitative suspended matter sampling). Bottles were conditioned for 24 hours with sub-surface (approx. 1000 m) seawater collected during the test cast. Sub-sampling was conducted in a clean van. Bottles were first sub-sampled for unfiltered seawater samples (nutrients and salinity) then pressurized with filtered, compressed air. Filtered trace metal sub-samples were collected by filtration through acid-washed 0.4 μm polycarbonate track-etched 47 mm filters in polypropylene filter holders.

Filtered subsamples collected in acid-washed 125 ml LDPE bottles were acidified to 0.024M HCl and analyzed shipboard for dissolved Al and Fe using flow injection analyses[Resi94][Meas95]. Replicate samples were collected at all depths for post-cruise analysis at FSU. Total suspended matter samples on 0.4 μm, 47 mm PCTE filters were rinsed immediately after collection with 15-20 ml DI water (adjusted to pH 8 with dilute ammonia) and stored for post-cruise analysis at FSU.

Several planned stations (73,75,77, 91 & 93) were not sampled as a result of high winds and large swells that made launching from the stern A frame imprudent. Generally most samples were collected as planned, but on a few occasions bottles were found not to have tripped correctly as a result of a lanyard catching on various parts of the system. Initial problems with the signals from the SBE T probe were diagnosed as a problem of the probe itself, which was replaced with a spare at Stn 007. This probe had not been calibrated since its original use in 2004 and gave relatively high readings using the old calibration factors. It will be recalibrated after the cruise. The SBE O_2 sensor started giving problems at station 021 and attempts to fix this by changing cables etc did not solve the problem. As there was no spare it was left on the rosette but the data are not correct.

Preliminary values for dissolved Al concentrations are shown in Figure 16.3 High surface values reflecting the influence of the Saharan plume and gyre transport systems are evident in the surface waters to approximately 18°S. Continuing south, values decrease throughout the upper 1,000m. A small maximum between 200 and 400m between 32 and 41°S appears to be related to mode water formation. To the south of this latitude surface waters are extremely low reflecting the lack of aerosol inputs to the surface waters of this region. Both surface and sub-surface Al values increase again to the south of South Georgia Island in the tectonically active East Scotia Basin.

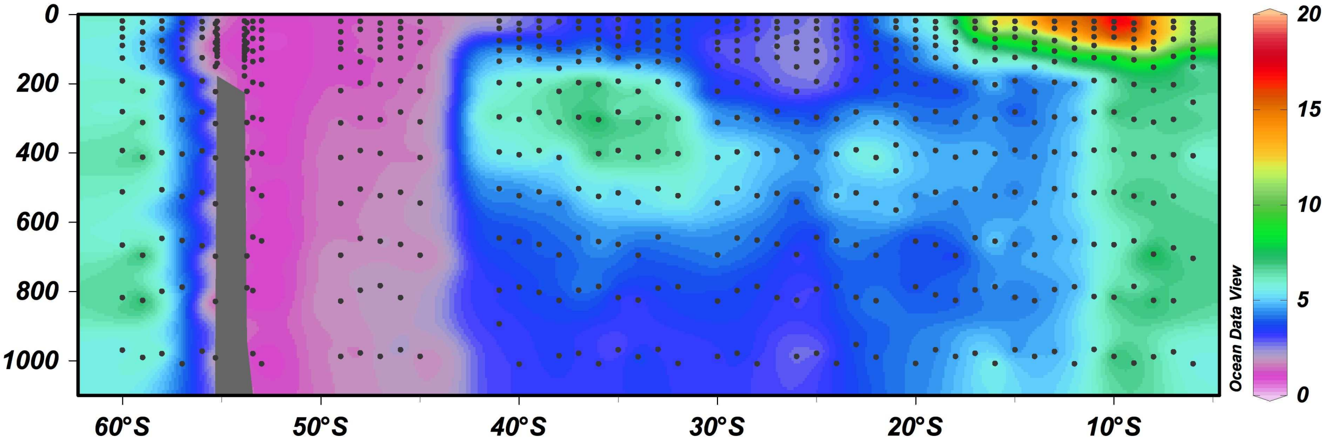

Figure 16.3 A16S Stations 1-113. Preliminary shipboard FIA dissolved Al in the top 1000 m.

Aerosol Samples

Aerosol samples (representing 25 separate deployment intervals) were collected using a Tisch-5170VBL High Volume sampler onto 12 Whatman-41 (W41) mixed cellulose ester filters over 24-48 hour sampling periods. The sampler was automatically activated only when the wind was within 60° of either side of the bow (away from ship exhaust). Throughout the cruise, 1 or 3 replicates were processed for instantaneously soluble elements[Buck06] and frozen for subsequent analysis at FSU. The remaining subsamples were stored frozen to be digested and analyzed for major and trace elements including Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb and others (FSU).While no samples were analyzed at sea, the filters were visually inspected for some indication of the composition of the aerosols collected. Filters from Stations 1-18 were colored grey, indicating a primarily anthropogenic composition, possibly biomass burning. The filters for the remainder of the cruise were only lightly loaded.

Rain Samples

Rainwater was collected using a trace element-clean funnel and bottle system in a tall bucket in an NCON automated wet deposition collector, where falling rain triggers a sensor to open the lid automatically. A minimum of 40 ml of rainwater is necessary to adequately sample a rain event for unfiltered and filtered trace elements, as well as major anions. Nine rain samples were collected of varying volumes (5-390 ml). There were no rain events north of 21.5°S. In addition, two snow samples were collected (57 and 60°S), with sufficient volume to allow both filtered and unfiltered sub-samples and an aliquot for major anion determination to be taken. Trace elements and major anions will be determined in the home laboratory.

Argo FloatDeployments

Fourteen Argo profiling CTD floats were deployed during this cruise at the request of WHOI and PMEL groups. These floats are part of the Argo array, a global network of over 3000 profiling floats. The floats are designed to sink to a depth of 1000m. They then drift freely at depth for ten days, before sinking to 2000m and then immediately rising to the surface, collecting CTD data as they rise. Conductivity (salinity), temperature, and pressure are measured and recorded at various levels (about 73 levels for Navis and every 2 decibars for the SOLOs) during each float ascent. At the surface, before the next dive begins, the acquired data is transmitted to shore via satellite, along with a location estimate taken while the float sits at the surface. The typical life time of the floats in the water is about four years. All Argo float data is made publicly available on the web in real-time at http://www.usgodae.org/argo/argo.html.

All SOLO floats were checked on the ship and started at least 8 hours before deployment, by passing a magnet over the ’reset’ area on the float. The Navis floats were preprogrammed and did not require this before deployment. Each float’s startup time was logged. When in position, each Navis float was launched by carefully lowering it into the water using a hand- held line strung through the deployment collar. Each SOLO float was deployed in the protective box the float shipped with. Deployments were done after the completion of the CTD station nearest to the requested deployment location, immediately after the ship had turned, and begun its course to the next station and had reached a speed of approximately one knot. All fourteen floats were deployed successfully. An e-mail report was sent to WHOI or PEML, depending on who provided the float, to report the float ID number, float start time, exact float deployment time, location, wind speed, wind direction, sea state and deployer’s name(s). The following table shows the location of each Argo Float deployment made on GO-SHIP CLIVAR/CO_2.

Number	Latitude	Longitude	Time(GMT)	Serial Number
1	lat: -06.00	lon: -25.00	07:19	WHOI_S2A-7190
2	lat: -08.00	lon: -25.00	14:38	WHOI_S2A-7191
3	lat: -10.00	lon: -25.00	19:55	WHOI_S2A-7192
4	lat: -12.00	lon: -25.00	00:13	WHOI_S2A-7198
5	lat: -14.00	lon: -25.00	08:09	WHOI_S2A-7182
6	lat: -17.00	lon: -25.00	04:15	WHOI_SOLO-1-1157
7	lat: -20.00	lon: -25.00	01:35	WHOI_SOLO-1-IR-1107
8	lat: -24.00	lon: -25.00	13:20	WHOI_SOLO-1-1159
9	lat: -38.00	lon: -26.55	19:00	PMEL_NAVIS-280
10	lat: -40.00	lon: -27.80	01:33	WHOI_SOLO-1-1163
11	lat: -42.00	lon: -29.03	07:14	PMEL_NAVIS-281
12	lat: -44.00	lon: -30.27	01:53	PMEL_NAVIS-163
13	lat: -46.00	lon: -31.52	08:57	WHOI_SOLO-1-1168
14	lat: -48.00	lon: -32.75	16:53	PMEL_NAVIS-285

References

Arms67.

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

Bern67.

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

Brad88.

Bradshaw, A. L. and Brewer, P. G., "High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration, 1: Presence of unknown protolyte(s)?," *Mar. Chem.,* 23, pp. 69-86 (1988).

Buck06.

Buck, C. S., Landing, W. M., Resing, J. A, and Lebon, G. T., "Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise.," Geochemistry, Geophysics, Geosystems (2006).

Bull10.

Bullister, J. L. and Tanhua, T., "Sampling and measurement of chlorofluorocarbons and sulfur hexafluoride in seawater," *GO-SHIP Repeat Hydrography Manual,* 134, pp. http://www.go-ship.org/HydroMan.html (2010).

Bull88.

Bullister, J. L. and Weiss, R. F., "Determination of CC13F and CC12F2 seawater and air," *Deep-Sea Res.,* 25, pp. 839-853 (1988).

Bull08.

Bullister, J. L. and Wisegarver, D. P., "The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater," *Deep-Sea Res.,* 55, pp. 1063-1074 (2008).

Carp65.

Carpenter, J. H., "The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method," *Limnology and Oceanography,* 10, pp. 141-143 (1965).

Chip93.

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

Clay93.

Clayton, T. D. and Byrne, R. H., "Spectrophotometric seawater pH measurements: Total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results," *Deep-Sea Res.,* 40, pp. 2315-2329 (1993).

Culb91.

Culberson, C. H., Knapp, G., Stalcup, M., Williams, R. T., and Zemlyak, F., "A comparison of methods for the determination of dissolved oxygen in seawater," Report WHPO 91-2, WOCE Hydrographic Programme Office (Aug. 1991).

Dick81.

Dickson, A. G., "An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total CO_2 from titration data," *Deep-Sea Res., Part A,* 28, pp. 609-623 (1981).

Dick90.

Dickson, A. G., "Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K," *Deep-Sea Res., Part A,* 37, 5, pp. 755-766 (1990).

Dick87.

Dickson, A. G. and Millero, F. J., "A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media," *Deep-Sea Res., Part A,* 34, 10, pp. 1733-1743 (1987).

Dick79.

Dickson, A. G. and Riley, J. P., "The estimation of acid dissociation constants in seawater media from potentiometric titration with strong base, 1: The ionic product of water-KSUS-w," *Mar. Chem.,* 7, 2, pp. 89-99

(1979).

DOE94.

DOE, (U.S. Department of Energy), *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater. Version 2.0. ORNL/CDIAC-74,* Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1994).

Feel98.

Feely, R. A., Wanninkhof, R., Milburn, H. B., Cosca, C. E., Stapp, M., and Murphy, P. P., “A new automated underway system for making high precision pCO_2 measurements onboard research ships,” *Analytica Chim. Acta,* 377, pp. 185-191 (1998).

Gord94.

Gordon, L. I., Jennings, J. C., Jr., Ross, A. A., and Krest, J. M., “A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study.,” WHP Operations and Methods, Manual 91-1, WOCE Hydrographic Program Office (Nov. 1994).

Joha82.

Johansson, O. and Wedborg, M., “On the evaluation of potentiometric titrations of seawater with hydrochloric acid,” *Oceanologica Acta,* 5, pp. 209-218 (1982).

John92.

Johnson, K. M., *Operator’s Manual: Single-Operator Multiparameter Metabolic Analyzer (SOMMA) for Total Carbon Dioxide (CT) with Coulometric Detection,* Brookhaven National Laboratory, Brookhaven, N.Y. (1992).

John85.

Johnson, K. M., King, A. E., and Sieburth, J. McN., “Coulometric TCO_2 analyses for marine studies: An introduction,” *Marine Chemistry,* 16, pp. 61-82 (1985).

John99.

Johnson, K. M., Körtzinger, A., Mintrop, L., Duinker, J. C., and Wallace, D. W. R., “Coulometric total carbon dioxide analysis for marine studies: Measurement and internal consistency of underway surface TCO_2 concentrations,” *Marine Chemistry,* 67, pp. 123-44 (1999).

John87.

Johnson, K. M., Williams, P. J., Brandstrom, L., and Sieburth, J. McN., “Coulometric total carbon analysis for marine studies: Automation and calibration.,” *Marine Chemistry,* 21, pp. 117-33 (1987).

John93.

Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., and Wong, C. S., *Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated gas extraction* (1993).

Joyc94.

Joyce, T., ed. and Corry, C., ed., “Requirements for WOCE Hydrographic Programme Data Reporting,” Report WHPO 90-1, WOCE Report No. 67/91 ., pp. 52-55, WOCE Hydrographic Programme Office, Woods Hole, MA, USA (May 1994, Rev. 2).

Lang10.

Langdon, C., “Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique,” *The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines*, p. 134 (2010).

Mari68.

Marinenko, G. and Taylor, J. K., “Electrochemical equivalents of benzoic and oxalic acid,” *Anal. Chem.*, 40, pp. 1645-1651 (1968).

Meas08.

Measures, C. I., Landing, W. M., Brown, M. T., and Buck, C. S., “A commercially available rosette system for trace metal-clean sampling.,” Limnol. Oceanogr. Methods 6, pp. 384-394 (2008).

Meas95.

Measures, C. I., Yuan, J., and Resing, J., “Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection.," Limnol. Oceanogr. Methods 50, pp. 384-394 (1995).

Mill93.
Millero, F. J., Zhang, J-Z., Lee, K., and Campbell, D. M., "Titration alkalinity of seawater," *Mar. Chem.,* 44, pp. 153-165 (1993b).

Moum09.
Moum, J. N. and Nash, J. D., "Mixing measurements on an equatorial ocean mooring," *Journal of Atmospheric and Oceanic Technology,* 12, pp. 346-366 (2009).

Pier09.
Pierrot, D., Neill, C., Sullivan, K., Castle, R., R.Wanninkhof, Luger, H., Johannessen, T., Olsen, A., Feely, R. A., and Cosca, C. E., "Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines.," *Deep-Sea Res,* II, pp. 512-522 (2009).

Prin00.
Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch, A., "A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE," *J. Geophys. Res.,* 105, pp. 17,751-17,792 (2000).

Resi94.
Resing, J. A and Measures, C. I., "Fluorometric determination of dissolved Al in seawater by flow injection analysis with in-line preconcentration.," Anal. Chem. 66, pp. 4105-4111 (1994).

Rye12.
Rye, C. D., Messias, M-J, Ledwell, J. R., Watson, A. J., Brousseau, A., and King, B. A., " Diapycnal diffusivities from a tracer release experiment in the deep sea, integrated over 13 years.," *J. Geophys. Res.,* 39, p. L04603 (2012).

Tayl59.
Taylor, J. K. and Smith, S. W., "Precise coulometric titration of acids and bases," *J. Res. Natl. Bur. Stds.,* 63, pp. 153-159 (1959).

UNES81.
UNESCO, "Background papers and supporting data on the Practical Salinity Scale, 1978," UNESCO Technical Papers in Marine Science, No. 37, p. 144 (1981).

Wann93.
Wanninkhof, R. and Thoning, K., "Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods.," *Mar. Chem.,* 44, 2-4, pp. 189-205 (1993).

APPENDIX

Cast Bottom Data

For each station/cast the following table shows the following information for the bottom of each cast, respectively:

- Station/Cast Number
- GMT Date and Time
- Latitude and Longitude
- Bathymetric Depth (meters)
- Distance Above Bottom (via Altimeter reading, meters)
- CTD Pressure of deepest bottle tripped (decibars)

A ’-999’ for any of these values indicates either an instrument error or data was not given.

A16S Cast bottom data

SSS/CC	Date & Time	Latitute & Longitude	BathyDepth	DAB	CTDPres
1/2	2013-12-26 04:58:50	6 0.0984 S,24 59.9886 W	5809	9.4	5905.6
2/1	2013-12-26 12:15:32	6 29.8620 S,24 59.9934 W	5628	9.6	5715.5
3/2	2013-12-26 21:01:15	6 59.9298 S,25 0.2556 W	5578	15	5661.5
4/1	2013-12-27 04:02:41	7 29.9802 S,25 0.0006 W	5795	9	5885.9
5/2	2013-12-27 11:23:58	7 59.9364 S,24 59.9550 W	5709	-999	5805.4
6/1	2013-12-27 19:19:59	8 29.9904 S,24 59.9970 W	5739	10	5829.6
7/2	2013-12-28 03:13:05	8 59.9514 S,25 0.0042 W	5691	10.3	5720.5
8/1	2013-12-28 10:00:19	9 30.0366 S,24 59.8086 W	5783	9.3	5661
9/2	2013-12-28 17:46:44	10 0.0216 S,25 0.0078 W	5406	-999	5517.7
10/1	2013-12-29 00:22:35	10 29.9880 S,24 59.9898 W	5427	10.5	5495.8
11/1	2013-12-29 07:09:43	10 59.9406 S,24 59.9934 W	5417	-999	5507.1
12/1	2013-12-29 14:25:33	11 29.9892 S,24 59.9892 W	4331	10.5	4397.2
13/2	2013-12-29 21:59:57	11 59.9052 S,24 59.9916 W	5808	-999	5914.3
14/2	2013-12-30 05:37:46	12 30.0318 S,25 0.0078 W	5587	8.9	5686.7
15/1	2013-12-30 12:32:21	12 59.9544 S,24 59.9802 W	5778	-999	5870.6
16/1	2013-12-30 20:50:18	13 30.0006 S,25 0.0198 W	5158	10.4	5250.1
17/2	2013-12-31 05:48:23	14 0.0090 S,25 0.0090 W	5922	-999	6019.5
18/1	2013-12-31 12:53:30	14 30.0270 S,25 0.0492 W	5405	10	5487.7
19/2	2013-12-31 20:43:47	15 0.0024 S,25 0.0066 W	5247	10	5322.9
20/1	2014-01-01 03:27:02	15 29.9646 S,24 59.9940 W	4995	10.5	5072
21/1	2014-01-01 10:29:02	16 0.0288 S,25 0.0900 W	5657	11.1	5746.5
22/1	2014-01-01 18:18:12	16 30.0204 S,25 0.0042 W	5118	10.7	5193.8
23/2	2014-01-02 02:11:55	16 59.9988 S,25 0.0024 W	5279	9.9	5342.9
24/1	2014-01-02 09:08:07	17 30.1356 S,25 0.0006 W	5172	10.1	5246.3
25/2	2014-01-02 16:59:18	18 0.0198 S,25 0.0042 W	5564	10.8	5649.6
26/1	2014-01-03 00:00:17	18 30.0138 S,25 0.0048 W	5471	10.1	5613.8
27/1	2014-01-03 07:06:04	18 59.8368 S,25 0.1008 W	5816	9.8	5929
28/1	2014-01-03 14:58:28	19 30.0300 S,25 0.0036 W	5460	10.5	5550.7
29/2	2014-01-03 23:13:30	19 59.9676 S,24 59.8722 W	6028	10.3	6133.8
30/1	2014-01-04 06:17:40	20 30.0072 S,25 0.0042 W	5433	10	5521.8
31/1	2014-01-04 13:03:41	21 0.1134 S,25 0.2466 W	5231	10	5301.6
32/1	2014-01-04 21:06:23	21 30.0306 S,25 0.0084 W	5330	11.5	5416.1
33/2	2014-01-05 05:23:16	21 59.9874 S,25 0.0078 W	5133	10.2	5217.1
34/1	2014-01-05 12:27:52	22 29.9958 S,24 59.9934 W	5533	10.5	5616
35/2	2014-01-05 20:18:03	22 59.9598 S,24 59.9802 W	5114	-999	5178.8
36/1	2014-01-06 03:10:19	23 30.0096 S,25 0.0126 W	5435	11.9	5503.2

SSS/CC	Date & Time	Latitute & Longitude	BathyDepth	DAB	CTDPres
37/1	2014-01-06 10:17:16	23 59.9946 S,25 0.0114 W	5619	10.9	5706.5
38/1	2014-01-06 17:55:02	24 30.0018 S,25 0.0012 W	5217	10	5367.8
39/2	2014-01-07 01:42:07	25 0.0318 S,25 0.0216 W	5430	9	5551.3
40/1	2014-01-07 08:19:06	25 29.7648 S,25 0.2832 W	4981	9.8	5058.6
41/2	2014-01-07 15:48:08	26 0.0054 S,25 0.0078 W	4897	-999	4966.9
42/1	2014-01-07 22:13:32	26 30.0666 S,25 0.0834 W	4765	9.5	4837.4
43/2	2014-01-08 05:50:35	26 59.9868 S,25 0.0090 W	4721	10.4	4784.9
44/1	2014-01-08 12:05:41	27 30.0426 S,25 0.2964 W	4848	9.2	4911
45/2	2014-01-08 19:37:29	28 0.0030 S,25 0.0126 W	5323	-999	5403.5
46/1	2014-01-09 02:14:57	28 30.0300 S,25 0.1230 W	5307	10.3	5392.2
47/1	2014-01-09 08:47:36	28 59.9610 S,25 0.1062 W	5031	-999	5107.5
48/1	2014-01-09 16:33:32	29 30.0180 S,25 0.0006 W	5348	8.4	5431.1
49/2	2014-01-10 00:19:16	30 0.0144 S,24 59.8512 W	5593	-999	5688.5
50/1	2014-01-10 06:56:31	30 30.0216 S,24 59.9772 W	4675	10.3	4741.1
51/1	2014-01-10 13:06:29	31 0.1992 S,25 0.0342 W	4537	10.2	4602.2
52/1	2014-01-10 20:31:04	31 30.0216 S,25 0.0204 W	4494	10.3	4561.4
53/2	2014-01-11 03:49:37	32 0.0288 S,25 0.0066 W	4321	9.6	4382.9
54/1	2014-01-11 10:05:38	32 30.0210 S,24 59.9718 W	4158	12.1	4218
55/2	2014-01-11 17:22:01	33 0.0060 S,25 0.0018 W	4586	-999	4643.6
56/1	2014-01-11 23:48:09	33 29.8098 S,24 59.9100 W	4388	8.6	4446.9
57/2	2014-01-12 07:12:56	34 0.0138 S,25 0.0282 W	4079	10.2	4140.2
58/1	2014-01-12 13:19:39	34 29.9802 S,24 59.9598 W	3973	9.2	4022
59/2	2014-01-12 20:31:05	34 59.8614 S,24 59.9916 W	4115	-999	4171
60/1	2014-01-13 03:11:22	35 29.9928 S,25 0.0030 W	4113	11.8	4162.3
61/1	2014-01-13 10:04:30	36 0.0006 S,25 18.0090 W	4039	10.3	4098.6
62/1	2014-01-13 17:57:07	36 29.9940 S,25 36.0090 W	4093	9.9	4140.3
63/2	2014-01-14 01:59:39	36 59.9628 S,25 53.9634 W	4126	10.5	4182.9
64/1	2014-01-14 09:19:19	37 29.9634 S,26 12.0150 W	4195	9.3	4251.2
65/2	2014-01-14 17:15:01	38 0.0000 S,26 26.3244 W	4068	-999	4117.3
66/1	2014-01-15 01:25:04	38 29.9178 S,26 52.0212 W	4173	10.6	4233.9
67/1	2014-01-15 08:52:40	38 59.6754 S,27 9.6684 W	4138	-999	4197.7
68/1	2014-01-15 16:19:26	39 30.0066 S,27 29.0928 W	4502	9.2	4568.9
69/2	2014-01-15 23:46:46	39 59.9148 S,27 48.0090 W	4301	8.1	4360.6
70/1	2014-01-16 06:22:31	40 29.9760 S,28 6.0354 W	4360	10	4429
71/2	2014-01-16 14:00:22	41 0.7140 S,28 24.2910 W	4328	10.5	4396.2
72/1	2014-01-16 21:00:14	41 30.0186 S,28 42.9426 W	4355	10.6	4427
73/1	2014-01-17 05:15:59	41 59.9922 S,29 1.9680 W	4437	12.6	4507
74/1	2014-01-17 14:24:56	42 30.0288 S,29 20.8440 W	4506	9.7	4580.3
75/1	2014-01-18 08:40:21	43 0.2556 S,29 38.6556 W	4479	14.1	4542.5
76/1	2014-01-18 16:51:51	43 29.9814 S,29 57.7998 W	4689	-999	4763.1
77/1	2014-01-19 00:04:17	44 0.0888 S,30 15.8160 W	4620	9.8	4692
78/1	2014-01-19 07:01:36	44 30.0048 S,30 34.9896 W	5106	9.9	5202.5
79/1	2014-01-19 13:53:46	45 0.0012 S,30 54.2496 W	4817	12	4899.9
80/1	2014-01-19 22:03:57	45 29.4738 S,31 11.1168 W	5094	10.8	5181.4
81/2	2014-01-20 06:51:58	45 59.9454 S,31 30.7794 W	5262	8.8	5346
82/1	2014-01-20 14:26:11	46 29.9196 S,31 48.4728 W	5240	-999	5343.7
83/1	2014-01-20 21:53:32	46 59.9550 S,32 7.4442 W	5179	16.3	5276.8
84/1	2014-01-21 06:47:25	47 30.5040 S,32 27.4422 W	5352	25.5	5438.9
85/1	2014-01-21 13:44:46	48 0.4248 S,32 46.6032 W	5325	27.1	5418.2
86/1	2014-01-21 21:50:55	48 30.1992 S,33 4.0284 W	4961	17	5048.7
87/3	2014-01-22 13:37:33	49 0.3876 S,33 22.1406 W	4940	85.3	5014.2
88/1	2014-01-22 20:54:52	49 30.2460 S,33 40.3404 W	5176	-999	5273

SSS/CC	Date & Time	Latitute & Longitude	BathyDepth	DAB	CTDPres
89/2	2014-01-23 05:18:37	50 0.0462 S,34 0.0090 W	5043	9.9	5132.5
90/1	2014-01-23 12:24:07	50 30.0756 S,34 17.8866 W	4892	10.8	4969.8
91/1	2014-01-23 19:55:51	51 0.0264 S,34 36.8706 W	5000	9.8	5089.7
92/1	2014-01-24 13:09:57	51 29.9664 S,34 55.8840 W	4816	9.8	4897.6
93/1	2014-01-24 20:24:02	52 0.0018 S,35 13.9800 W	4453	16.4	4528.6
94/1	2014-01-25 03:20:40	52 29.9886 S,35 33.0000 W	3868	18	3928.3
95/1	2014-01-25 09:35:15	53 0.0564 S,35 50.8296 W	3526	8.7	3575.8
96/1	2014-01-25 15:24:46	53 15.4182 S,36 1.6608 W	3295	-999	3339.7
97/1	2014-01-25 19:26:51	53 25.9002 S,36 6.9132 W	2716	14.4	2746.1
98/1	2014-01-25 23:44:27	53 35.6526 S,36 12.6408 W	1779	-999	1796.6
99/2	2014-01-26 03:12:01	53 44.4006 S,36 14.5884 W	923	10.5	923.8
100/2	2014-01-26 05:49:12	53 51.0132 S,36 22.9896 W	219	10.2	209.8
101/1	2014-01-26 17:37:54	55 13.8114 S,34 44.2662 W	177	15.4	170.4
102/1	2014-01-26 19:34:02	55 16.0608 S,34 37.7562 W	941	11.7	945
103/2	2014-01-26 22:50:10	55 19.7742 S,34 31.7706 W	1836	9	1849.4
104/1	2014-01-27 03:11:56	55 35.9640 S,34 10.9590 W	2210	15.3	2234.7
105/1	2014-01-27 08:22:58	55 59.9526 S,33 37.9692 W	2552	-999	2577.4
106/1	2014-01-27 15:48:24	56 30.0036 S,32 56.8896 W	3719	10.2	3778.3
107/1	2014-01-27 22:32:00	56 59.9250 S,32 17.2584 W	3703	15.9	3753.9
108/1	2014-01-28 06:35:50	57 29.9832 S,31 35.9508 W	3399	10.7	3439
109/1	2014-01-28 13:13:06	58 1.6848 S,30 54.7092 W	3554	-999	3607.3
110/1	2014-01-28 20:05:32	58 30.0612 S,30 55.7736 W	2926	15.9	2949.3
111/2	2014-01-29 02:44:31	58 59.9448 S,30 55.4226 W	3093	11	3141.3

A16S Trace Metals Cast bottom data

SSS/CC	Date & Time	Latitute & Longitude	BathyDepth	CTDPres
1/1	2013-12-26 02:29:07	6 0.0690 S,25 0.1380 W	5799	1022.6
3/1	2013-12-26 18:12:12	7 0.0108 S,25 0.1446 W	5580	986
5/3	2013-12-27 14:00:38	7 59.9718 S,24 59.9328 W	5708	1001.3
7/1	2013-12-28 00:47:40	9 0.0060 S,25 0.1788 W	5619	1019.9
9/1	2013-12-28 15:29:05	9 59.9952 S,25 0.1188 W	5426	999.3
11/2	2013-12-29 09:41:36	11 0.0510 S,24 59.9412 W	5417	980.3
13/1	2013-12-29 19:37:47	11 59.9886 S,25 0.0510 W	5808	1020.2
15/2	2013-12-30 15:06:39	12 59.9892 S,24 59.8344 W	5779	977.6
17/1	2013-12-31 02:22:45	14 0.0486 S,25 0.0390 W	5927	1000.2
19/1	2013-12-31 18:29:26	15 0.0210 S,25 0.0768 W	5272	979.8
21/2	2014-01-01 12:59:43	16 0.0648 S,24 59.9946 W	5667	1020.4
23/1	2014-01-01 23:51:50	17 0.0270 S,25 0.0336 W	5245	990.3
25/1	2014-01-02 14:42:19	18 0.1080 S,25 0.0228 W	5558	999.7
27/2	2014-01-03 09:37:10	18 59.8398 S,25 0.0072 W	5799	981.3
29/1	2014-01-03 20:42:29	20 0.0804 S,24 59.9682 W	6035	1021.8
31/2	2014-01-04 15:26:31	21 0.0672 S,25 0.1434 W	5217	582
33/1	2014-01-05 03:04:48	21 59.9970 S,25 0.0054 W	5093	1002.2
35/1	2014-01-05 18:02:49	22 59.8734 S,25 0.2676 W	5099	979.9
37/2	2014-01-06 12:43:48	23 59.9820 S,24 59.8920 W	5626	1022
39/1	2014-01-06 23:21:43	24 59.9946 S,25 0.0708 W	5468	989.9
41/1	2014-01-07 13:36:42	26 0.0054 S,25 0.2442 W	4894	1000.6
43/1	2014-01-08 03:36:13	26 59.9658 S,25 0.2460 W	4767	979.6
45/1	2014-01-08 17:16:37	27 59.9148 S,25 0.2160 W	5316	1025.1
47/2	2014-01-09 11:05:26	28 59.9262 S,25 0.0522 W	5027	986.1
49/1	2014-01-09 22:00:03	30 0.2010 S,25 0.0366 W	5606	998.1
53/1	2014-01-11 01:50:51	31 59.7330 S,25 0.0840 W	4326	1021.5
55/1	2014-01-11 15:16:57	32 59.8302 S,24 59.8932 W	4622	978.2
57/1	2014-01-12 05:15:33	34 0.0810 S,24 59.9250 W	4027	1002.7
59/1	2014-01-12 18:36:47	35 0.1392 S,24 59.9250 W	4112	979.8
61/2	2014-01-13 12:08:34	36 0.1674 S,25 18.0360 W	4037	1021.5
63/1	2014-01-14 00:02:22	36 59.7768 S,25 53.7684 W	4119	991.6
65/1	2014-01-14 15:13:57	37 59.5920 S,26 26.1432 W	4069	1001
67/2	2014-01-15 11:01:24	38 59.8662 S,27 9.7398 W	4136	980.7
69/1	2014-01-15 21:51:23	39 59.8692 S,27 47.9166 W	4299	1022.4
71/1	2014-01-16 11:49:57	41 0.3744 S,28 24.7746 W	4340	912.2
79/2	2014-01-19 16:22:57	44 59.9262 S,30 53.8440 W	4843	1172.1
81/1	2014-01-20 04:31:36	45 59.5356 S,31 30.6702 W	5254	978.1
83/2	2014-01-21 00:25:53	47 0.4320 S,32 5.7234 W	5167	994.4
85/2	2014-01-21 16:17:32	48 0.4320 S,32 48.3606 W	5346	990.5
87/1	2014-01-22 03:38:27	48 59.9646 S,33 22.5834 W	4751	1002.7
89/1	2014-01-23 02:56:19	50 0.3960 S,33 59.3682 W	5045	964.5
95/2	2014-01-25 11:34:24	52 59.9700 S,35 50.8830 W	3526	1022.1
97/2	2014-01-25 21:10:46	53 26.0052 S,36 7.2600 W	2622	991.7
99/1	2014-01-26 02:12:12	53 44.4018 S,36 14.3940 W	935	895.2
100/1	2014-01-26 05:16:04	53 50.9706 S,36 22.3068 W	225	181.6
101/2	2014-01-26 18:09:22	55 13.8822 S,34 44.3514 W	177	146.5
103/1	2014-01-26 21:34:48	55 19.7382 S,34 31.6104 W	1847	1002.8
105/2	2014-01-27 10:06:02	55 59.9844 S,33 38.1882 W	2548	993.4
107/2	2014-01-28 00:44:58	56 59.6286 S,32 17.3688 W	3687	1021.1
109/2	2014-01-28 15:19:43	58 1.7472 S,30 54.6936 W	3553	992.7

SSS/CC	Date & Time	Latitute & Longitude	BathyDepth	CTDPres
111/1	2014-01-29 01:00:07	59 0.0240 S,30 55.1250 W	3095	1009.4

Bottle Data Quality Code Summary and Comments

This section contains WOCE quality codes [Joyc94] used during this cruise, and remarks regarding bottle data.

A16S Water Sample Quality Code Summary

Property	1	2	3	4	5	6	7	8	9	Total
Bottle	0	3210	36	24	8	0	0	0	6	3284
Al	15	582	4	13	0	4	0	0	0	618
CFC-11	0	1285	374	5	38	0	0	0	2	1704
CFC-12	0	1659	3	2	38	0	0	0	2	1704
SF$_6$	0	1655	7	2	38	0	0	0	2	1704
cf ^{13}C/ ^{14}C	1703	0	0	0	0	0	0	0	0	1703
density	113	0	0	0	0	0	0	0	0	113
Fe	15	579	10	10	0	4	0	0	0	618
^{3}He	414	0	0	0	0	0	0	0	0	414
Ammonium	3261	0	0	0	0	0	0	0	0	3261
^{18}O	254	0	0	0	0	0	0	0	0	254
O$_2$	0	2634	0	5	3	0	0	0	0	2642
ph	0	2008	10	62	14	200	0	0	2	2296
pCO$_2$	0	687	2	3	4	1	0	0	0	697
DIC	0	1941	4	9	3	317	0	0	1	2275
tAlk	0	1923	20	33	12	306	0	0	2	2296
^{13}C/ ^{14}C	524	0	0	0	0	0	0	0	0	524
Tritium	346	0	0	0	0	0	0	0	0	346
Nitrate	0	2588	0	1	2	661	0	0	9	3261
Nitrite	0	2567	0	1	2	682	0	0	9	3261
Phosphate	0	2588	1	1	2	660	0	0	9	3261
Silicic Acid	0	2602	0	1	2	647	0	0	9	3261
sAlt	0	3030	0	0	0	201	0	0	4	3235

Quality evaluation of data included comparison of bottle salinity and bottle oxygen data with CTDO data using plots of differences; and review of various property plots and vertical sections of the station profiles and adjoining stations. Comments from the Sample Logs and the results of investigations into bottle problems and anomalous sample values are included in this report. Sample number in this table is the cast number times 100 plus the bottle position number.

Table 16.3 A16S Bottle Quality Codes and Comments

Station /Cast	Sample Number	Property	Quality Code	Comment
001/02	201	Bottle	3	Bottle leaking.
001/02	206	Bottle	3	Bottle leaking.
001/02	206	Dissolved O2	4	Bottle value low for CTD up and down profile.
001/02	207	Bottle	3	Bottle leaking. Loose o-ring.
002/01	101	Bottle	3	Bottle leaking.
002/01	104	Total Alkalinity	9	Sample not drawn.
002/01	104	pH	9	Sample not drawn.
002/01	122	Bottle	3	Bottle leaking due to open vent.
003/02	201	Bottle	3	Bottle leaking.
004/01	109	Bottle	3	Spigot leaking.

Station /Cast	Sample Number	Property	Quality Code	Comment
004/01	124	Dissolved O2	5	Sample lost.
005/02	201-224	Bottle	4	All Bottletles offset by one position.
005/02	214	Bottle	4	Both Nutrients and Oxygen values are off. Likely mistrip.
005/02	214	Dissolved O2	4	Bottle value high for CTD up and down profile.
006/01	106	Bottle	3	Lanyard caught in top cap. Leaking (air in sample).
007/02	215	Bottle	3	Vent valve was open.
008/01	108	Salinity	9	Sample not taken.
009/02	109	Bottle	4	Bottle did not close. No samples.
009/02	109	Bottle	4	Bottle did not close. No samples.
009/02	109	Salinity	4	Bottle did not close. No samples.
010/01	117	Bottle	3	Vent valve was open.
011/01	101	Bottle	3	Vent valve was open.
015/01	121-124	Bottle	2	Incinerator burning. Possible carbon contamination.
021/01	101-106	Bottle	2	No gloves worn during sampling.
021/01	108	Bottle	3	Vent valve was open.
021/01	108	Dissolved O2	4	Bottle value low for CTD up and down profile.
021/01	115	Bottle	3	Major Bottletle leak.
021/01	116	Bottle	3	Major Bottletle leak.
022/01	118	Bottle	5	Niskin didn’t close.
025/02	213	Bottle	3	Slight leak. Bottle dripping.
027/01	101	Bottle	3	Vent valve was open.
028/01	102	Total CO2	2	DIC Bottletle 303 is greaseless, without HgCl 2.
028/01	104	Total CO2	2	DIC Bottletle 304 is greaseless, without HgCl 2.
029/02	206	Bottle	3	Spigot leaking.
029/02	206	Dissolved O2	4	Bad oxygen value. Likely due to leak.
029/02	206	Total Alkalinity	9	No sample taken due to the leak.
029/02	206	Total CO2	9	No sample taken due to the leak.
029/02	206	pH	9	No sample taken due to the leak.
029/02	206	pcDissolved O2	9	No sample taken due to the leak.
029/02	212	Salinity	9	No water left for sample.
029/02	217	Salinity	9	No water left for sample.
029/02	218	Bottle	5	Bottle did not close.
030/01	118	Bottle	5	Bottle did not close. Carousel head changed after sampling.
030/01	124	Bottle	3	Bad Leak.
035/02	206	Bottle	3	Lanyard caught in top cap.
035/02	208	Bottle	3	Lanyard caught in top cap.
036/01	101	Bottle	3	Bottle leaking.
037/01	106	Bottle	3	Lanyard from Niskin 5 caught in top cap.
037/01	106	Dissolved O2	4	Oxygen low. Likely due to leak.
041/02	218	Bottle	5	Niskin didn’t close.
042/01	118	Bottle	5	Niskin didn’t close.
043/02	218	Bottle	5	Niskin didn’t close.
044/01	118	Bottle	5	Niskin didn’t close.
048/01	120-124	Bottle	5	Niskin didn’t close. Computer error.
051/01	106	Bottle	3	Bad leak.
051/01	115	Bottle	2	Hands without gloves sampled.
051/01	123	Bottle	2	Blackish residue on niskin nipple.
061/01	101	Bottle	2	No gloves worn by 1 person.
061/01	102	Bottle	2	No gloves worn by 1 person.
061/01	122	Bottle	3	Lanyard caught in Bottletom cap. Leaking bottle.
069/02	215	Bottle	3	Lanyard caught in top cap. Possible leak.

Station /Cast	Sample Number	Property	Quality Code	Comment
070/01	118	Bottle	3	Leaking.
072/01	122	Bottle	3	Lanyard caught in cap. Leaking.
072/01	122	Dissolved O2	5	Sample lost.
075/01	122	Bottle	3	Lanyard caught in bottle top cap. Leaking.
076/01	122	Bottle	3	Lanyard caught in bottle top cap. Leaking.
083/01	116	Dissolved O2	5	Sample lost.
091/01	122	Bottle	3	Lanyard caught in Bottletom cap. Leaking.
093/01	118	Bottle	3	Leaking.
094/01	101	Bottle	5	Niskin didn’t close but pin tripped.
095/01	118	Bottle	3	Major leak.
099/02	101	Bottle	5	Niskin didn’t close but pin tripped.
103/02	218	Bottle	3	Leaking.
107/01	121	Bottle	3	Bottle hit during recovery. Leaking.
109/01	122	Bottle	3	Lanyard caught in Bottletom cap. Leaking.
111/02	218	Bottle	3	Leaking.
112/01	118	Bottle	3	Leaking.
112/01	122	Bottle	3	Leaking with vent closed.
113/03	313	Bottle	2	Cigarette smoke.
113/03	314	Bottle	2	Cigarette smoke.

References

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Joyce, T., ed. and Corry, C., ed., “Requirements for WOCE Hydrographic Programme Data Reporting,” Report WHPO 90-1, WOCE Report No. 67/91 ., pp. 52-55, WOCE Hydrographic Programme Office, Woods Hole, MA, USA (May 1994, Rev. 2).