A. Cruise Narrative: A22_2003a (preliminary: 2003.NOV.13)

A.1 Highlights
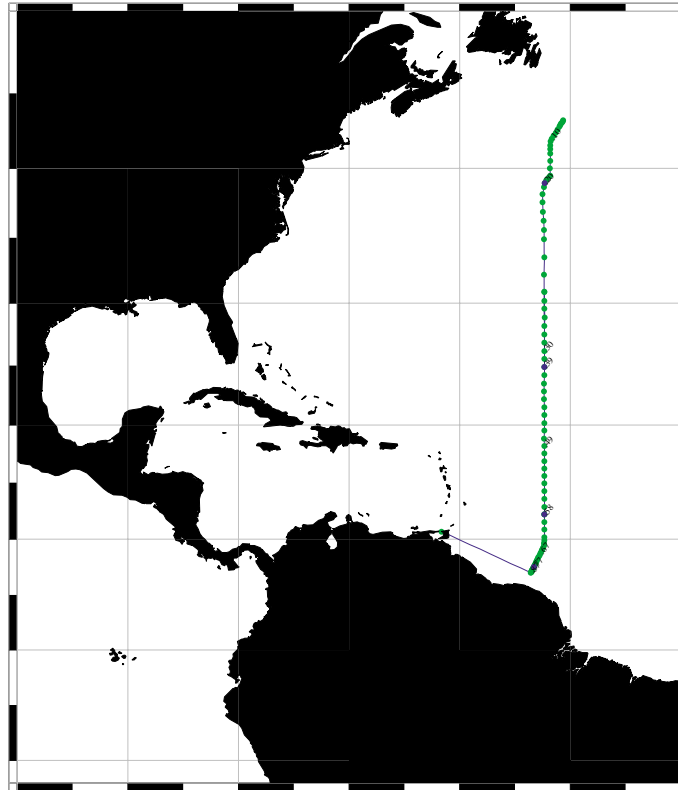
WHP Cruise Summary Information

WOCE section designation	**A22_2003a**
Expedition designation (ExpoCode)	**316N200310**
Chief Scientists and their affiliations	**Dr. Terrence M. Joyce / WHOI***
	Dr. William M. Smethie Jr. / LDEO**
Dates	2003 OCT 23 to 2003 NOV 13
Ship	*R/V* Knorr
Ports of call	Port of Spain, Trinidad - Woods Hole, Ma
Number of stations	82
Stations' Geographic boundaries	40° 0.63'N 70° 0.45'W 64° 9.37'W 11° 0.02'N
Floats and drifters deployed	3 ARGO floats deployed (one failed)
Moorings deployed or recovered	0
Contributing Authors	T. Joyce F. Delahoyde

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WHP Cruise and Data Information

Instructions: Click on headings below to locate primary reference or use naviga-
tion tools above. (Shaded headings were not available when this
report was assembled or not relevant to this cruise)

Cruise Summary Information	Hydrographic Measurements
Description of scientific program	**CTD Data**
	CTD - general
Geographic boundaries of the survey	CTD - pressure
Cruise track (figure)	CTD - temperature
Description of stations	CTD - conductivity/salinity
Description of parameters sampled	CTD - dissolved oxygen
Bottle depth distributions (figure)	
Floats and drifters deployed	**Bottle Data**
Moorings deployed or recovered	Salinity
	Oxygen
Principal Investigators for all measurements	Nutrients
Cruise Participants	CFCs
	Helium
Problems and goals not achieved	Tritium
Other incidents of note	Radiocarbon
	CO2 system parameters
Underway Data Information	Other parameters
Navigation	**DQE Reports**
Bathymetry	
Acoustic Doppler Current Profiler (ADCP)	CTD
Thermosalinograph and related measurements	S/O2/nutrients
XBT and/or XCTD	CFCs
Meteorological observations	14C
Atmospheric chemistry data	

| Acknowledgments	References	Data Processing Notes

Summary

A hydrographic survey consisting of LADCP/CTD/rosette sections and float deployments in the western North Atlantic was carried out October to November 2003. The R/V Knorr departed Port of Spain, Trinidad on 23 October 2003. A total of 82 LADCP/CTD/Rosette stations were occupied, and 3 profiling ARGO floats were deployed from 23 October - 13 November. Water samples (up to 36), LADCP and CTD data were collected in most cases to within 10 meters of the bottom. Salinity, dissolved oxygen and nutrient samples were analyzed from every bottle sampled on the rosette. The cruise ended in Woods Hole, Ma. on 13 November 2003.

Principal Investigators:

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	Robert Key	Princeton	rkey@princeton.edu
C13 profiles	Paul Quay	UofWash	pdquay@u.washington.ed

Station locations: A22_2003a • Joyce/Smethie • *RV Knorr*
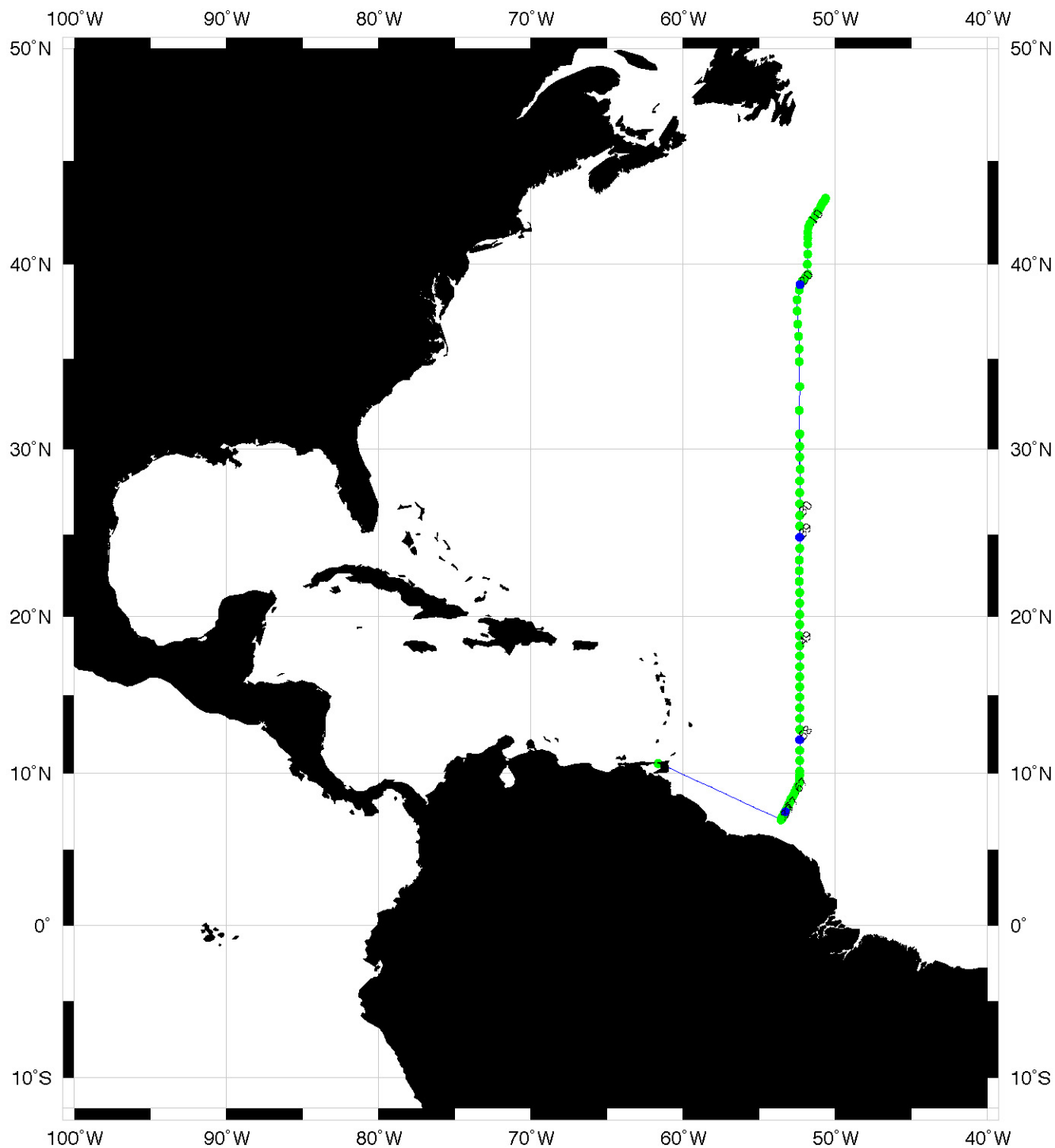
(Produced from .sum file by WHPO-SIO)

Introduction

A sea-going science team gathered from ten oceanographic institutions around the U.S. participated on the cruise. Several other science programs were supported with no dedicated cruise participant. The science party and their responsibilities are listed below:

Scientific Personnel

Name	Affiliation	Duties	E-mail
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Jules Hummon	U. Hawaii	Shipboard ADCP	
Ann McNichol	WHOI	Surface C14	
Robert Key	Princeton	Surface C14	
Paul Quay	UW	C13 profiles	
Allyn Clarke	BIO	Profiling ARGO floats	
Wilf Gardnert	AMU-CA	Transmissometer profiles	

B. Cruise Narrative
(T. Joyce/WHOI)

B.1 Freshwater front in Caribbean

A selection of data obtained with the thermosalinograph in the bow intake of the Knorr shows a strong SSS front near 12° 40'N, which is between CTD stations 8 & 9. This is the same location of a similar feature found during the cruise in 1997 along this transect, and could be a signature of the Orinoco river plume in the Caribbean. The latitude extent of the fresh water layer is larger and the near surface salinity lower in the present section, with a return to higher salinity surface water just to the south of 16°N, whereas this low salinity layer terminated just to the north of 14°N in 1997. This fresh layer is very thin, limited to the upper 20-30m. In the 1997 section, a strong surface velocity jet was associated with the front. While SADCP data on ship suggested this as present, we were unable to produce processed SADCP data at sea & this will be investigated later.
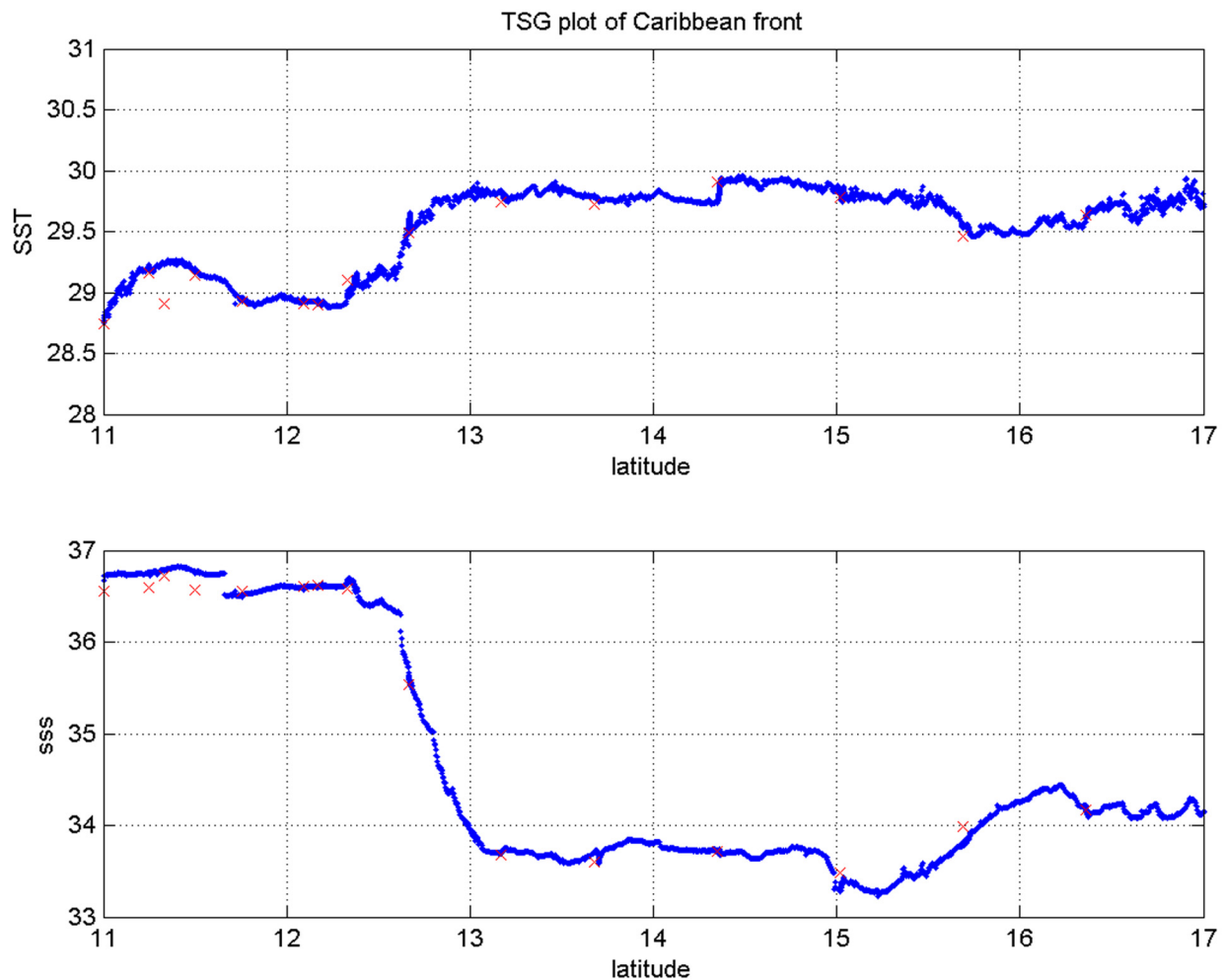
Figure B.1.1: Preliminary TSG data from the A22 section on KN173/2 using constant salinity offset based on surface Rosette samples from CTD stations.

We have been able to download a Seawiffs composite image from 24-31 October showing ocean color for the Caribbean and the north coast of Brazil. This figure follows and shows a clear Orinoco signal which is likly to be the cause of the low salinity water seen on the TSG series above as well as the high CDOM signal in the surface waters of the Caribbean. The plume from the Amazon is clearly not going into the Caribbean, but is being diverted into the interior of the tropical Atlantic by the North Equatorial Counter Current.
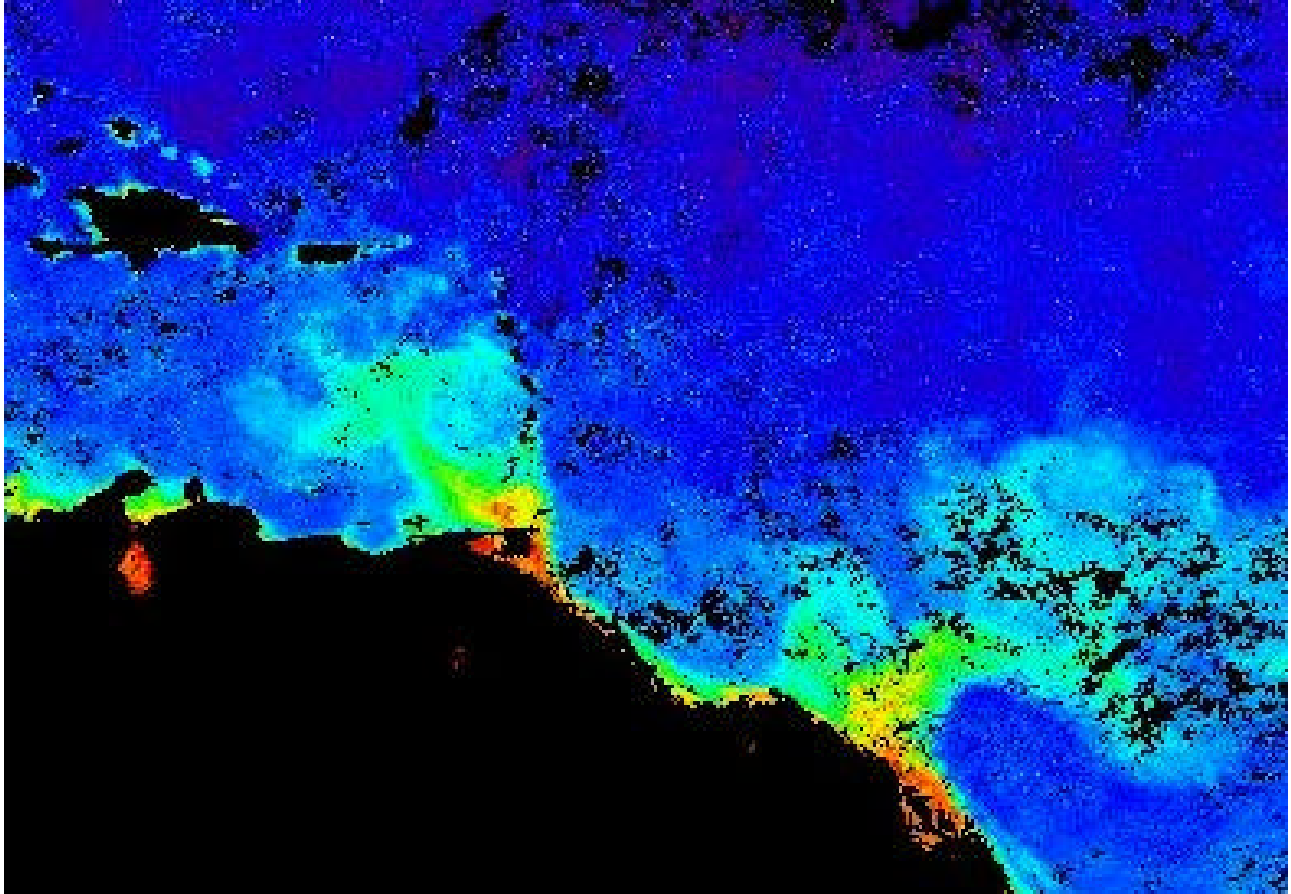

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Figure B.1.2: Seawifs image of ocean color for 24-31 October 2003 obtained with the help of Mike Caruso (WHOI) from MODIS data available from a NASA website.

B.2 Deep Water Ventilation of the Caribbean

The deepest sill into the Caribbean is the Jungfern sill with a depth of 1824m. This sill separates the Caribbean from the Virgin Island Basin, in which station 24 was taken. The sill is about 35 nm directly eastward of our section. As the deep flow is westward at 66W at the northern margin of the Caribbean, the overflow water from the N. Atlantic will be swept downstream across our section. Moored current meter observations together with hydrography done previously has indicated that occasional dense, high velocity pulses of overflow water are capable of reaching the bottom of the Caribbean after mixing and entraining ambient water. As the vertical "fall" from the sill to the bottom is over 2 km, the

resulting water, though high in oxygen initially, is highly attenuated by mixing. We have observed this newly ventilated water to be higher in salinity with a small positive temperature anomaly. Compare stations 14 & 15 in the central Caribbean with stations 17 & 18 near the northern boundary in the westward flow. Water depths for stations 17 & 18 are 4500 & 3350m, respectively, and high oxygen/ salinity anomalies of this deep ventilation appear in the lower part of the water column as revealed in the following figure, where we have plotted CTD data at 10 dbar resolution with preliminary calibrations from the water samples. Note the large anomaly at θ = 4.0 ^{o}C and again at the bottom. Silica samples collected in these anomalies confirm that high oxygen/low silica is a characteristic of the ventilation, which should also appear in the other tracers such as CFCs.
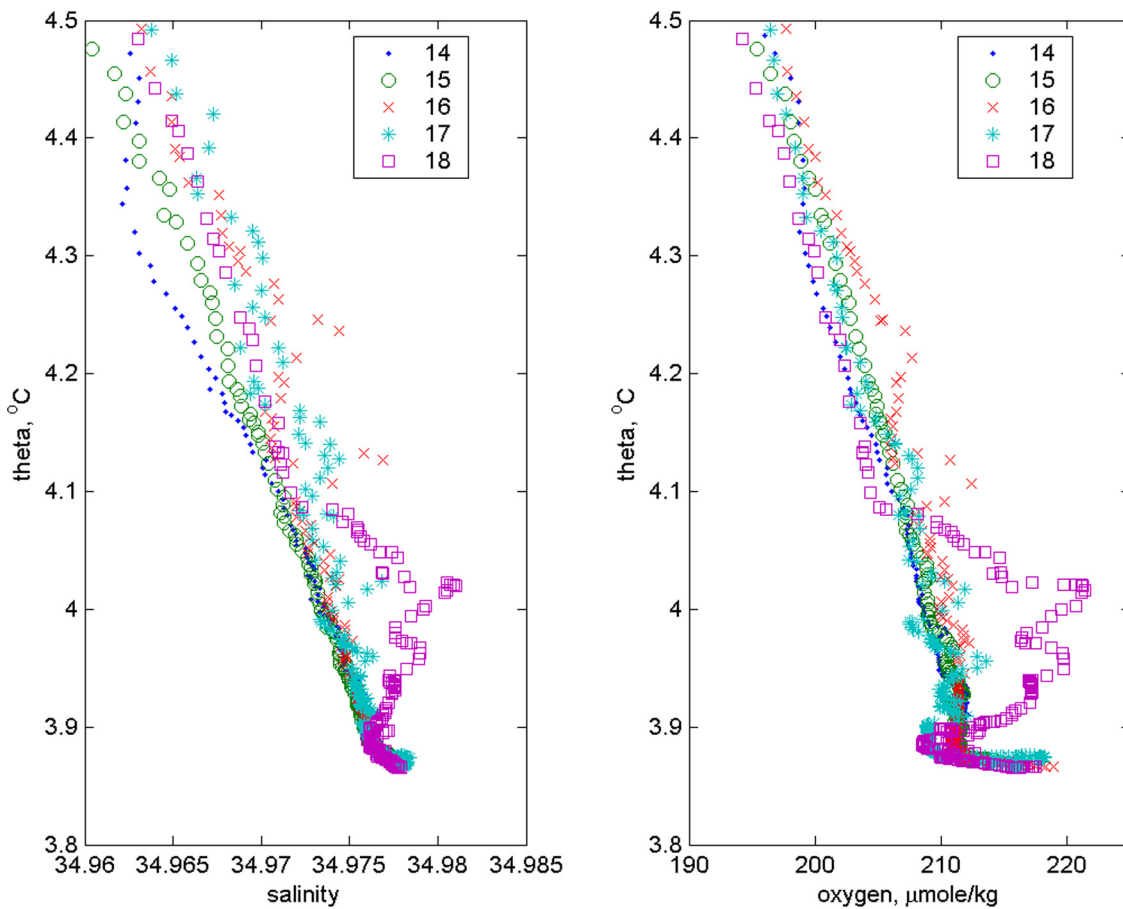

Figure B.2.1: Deep Caribbean properties from CTD data on KN173/2. Stations are identified by different colors & symbols.

The High oxygen signal θ = 4.0 $^{\circ}$C on station 18 is slightly shallower than the sill depth and could have entered the basin without mixing. However, the deeper signal on that station and is found at 3300 m depth. The bottom depth on station 17 is 4570m, where there is an oxygen signal (and silica) near the bottom and 600 m above the bottom (see following figure)
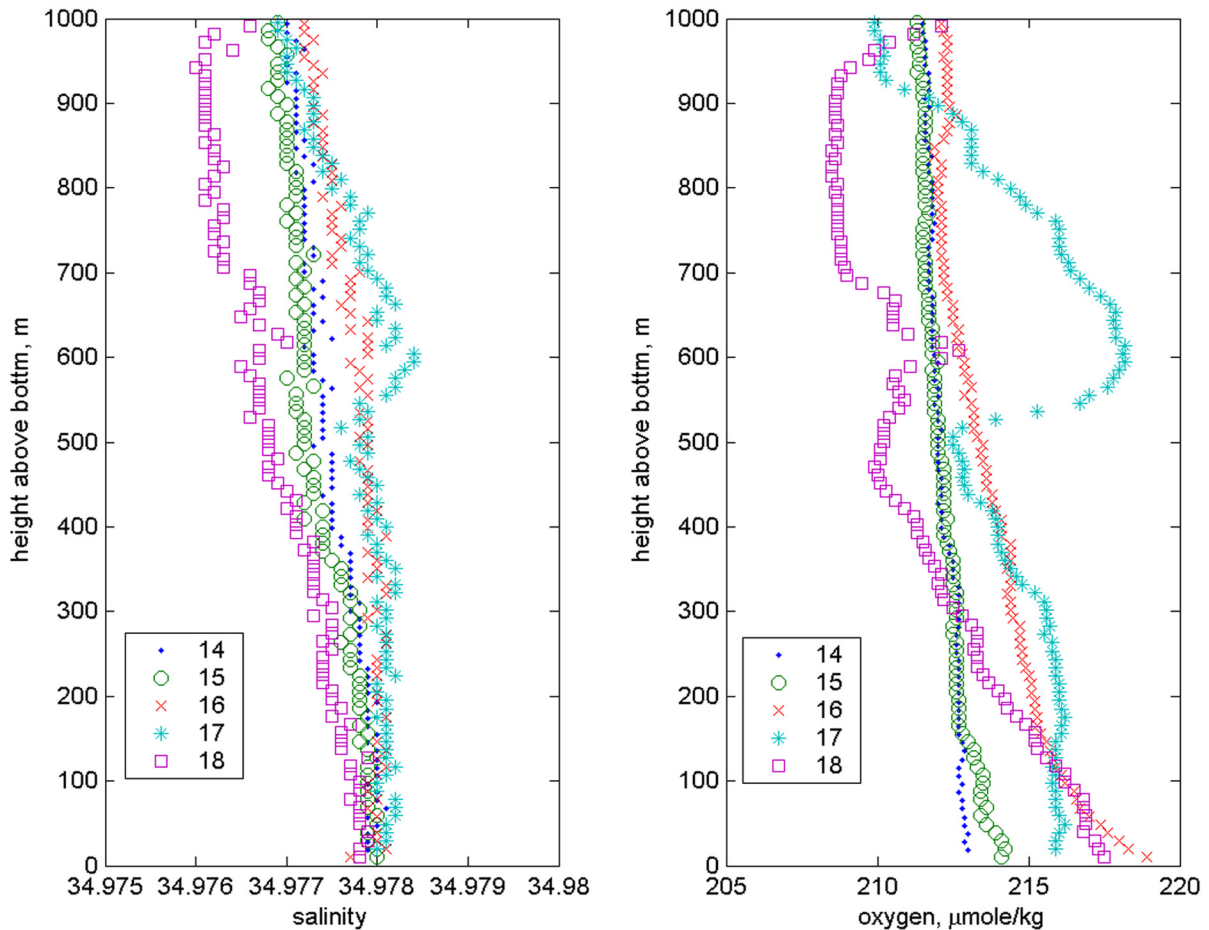

Figure B.2.2: Salinity and oxygen profiles relative to depth above bottom for the stations selected in the previous figure.

B.3 Changes in Labrador Sea Water to the north of Puerto Rico

Comparing the properties of the water column in 2003 with those measured in WOCE in 1997 on A22 reveals substantial change in the properties of the classical Labrador Sea Water. This layer, occupies a depth interval of approximately 2000-2500m. We show examples of this difference using neutral density as the ''vertical' coordinate, thus removing any signature of vertical heaving from the differences. In the first case, we plot salinity differences over much of the water column and for a close-up of the LSW. This is followed by similar plots showing differences in dissolved oxygen. Similar changes can be seen in the nutrients, CFCs, and TCO$_2$ for the classical LSW but will not be presented here.
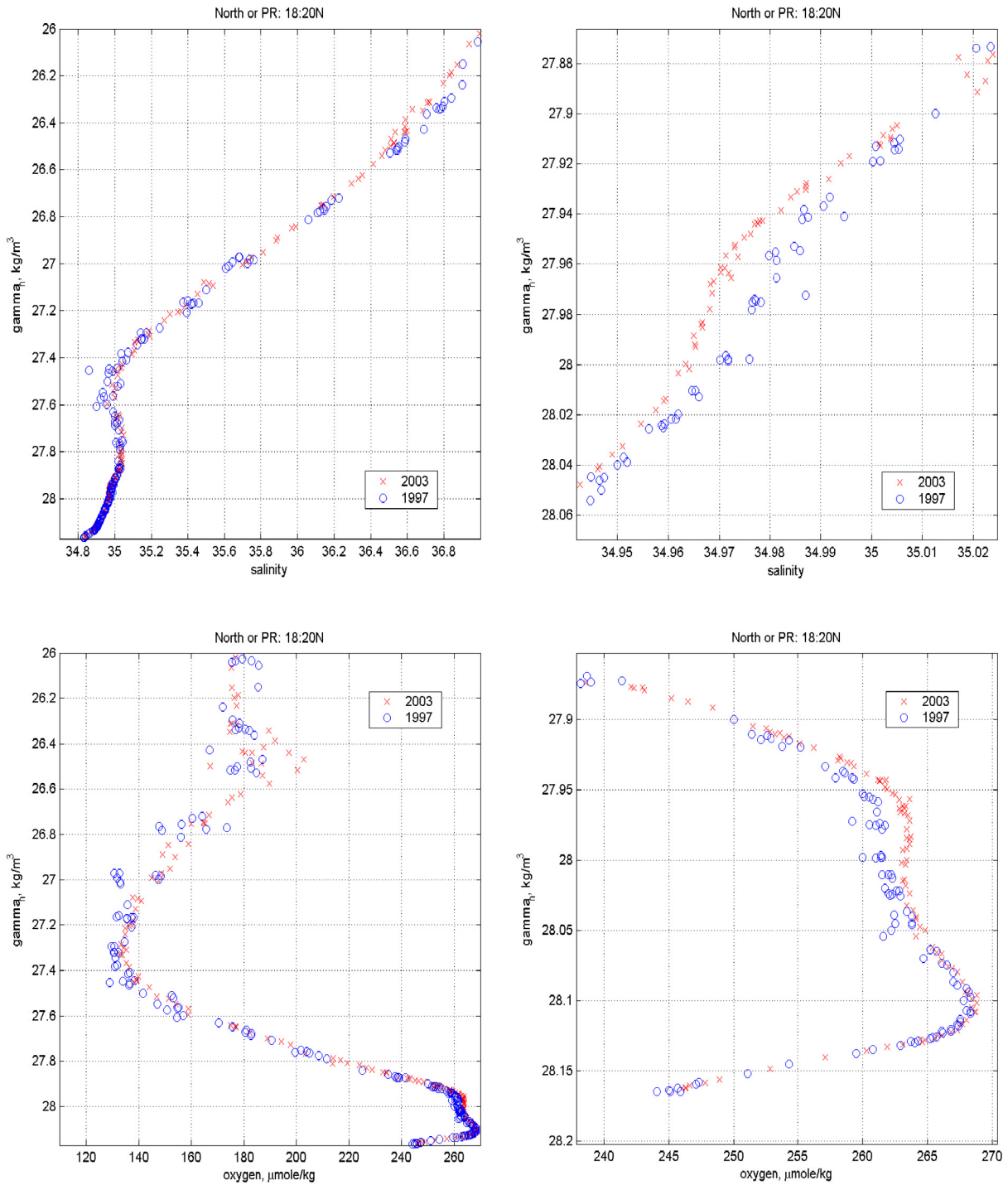
Figure B.3: Comparison of bottle measurements of salinity and oxygen from the region north of Puerto in the DWBC between 18 & 20N. Top panels for salinity and bottom for oxygen: left panels are overall & right are blowups of LSW layer.

B.4 Stratification changes in the Sargasso Sea

It is apparent that properties of the SubTropical Mode Water (eighteen degree water – EDW) have changed between 1997 and the present. This can be seen in the oxygen, nutrients and other tracers with a clear signature of lower ventilation of the density associated with the EDW. Here we show a comparison of the potential vorticity (related to the inverse of the thickness between density layers) for the EDW in the northern Sargasso Sea. We show the vertical profile of PV against both pressure and neutral density using mean CTD data between 31 and 33N. Because of our extra stations in 2003 around Bermuda, there are 7 stations in this latitude band in 2003 compared with 5 in 1997. We have used the station and pressure-averaged mean CTD data in the figure below.
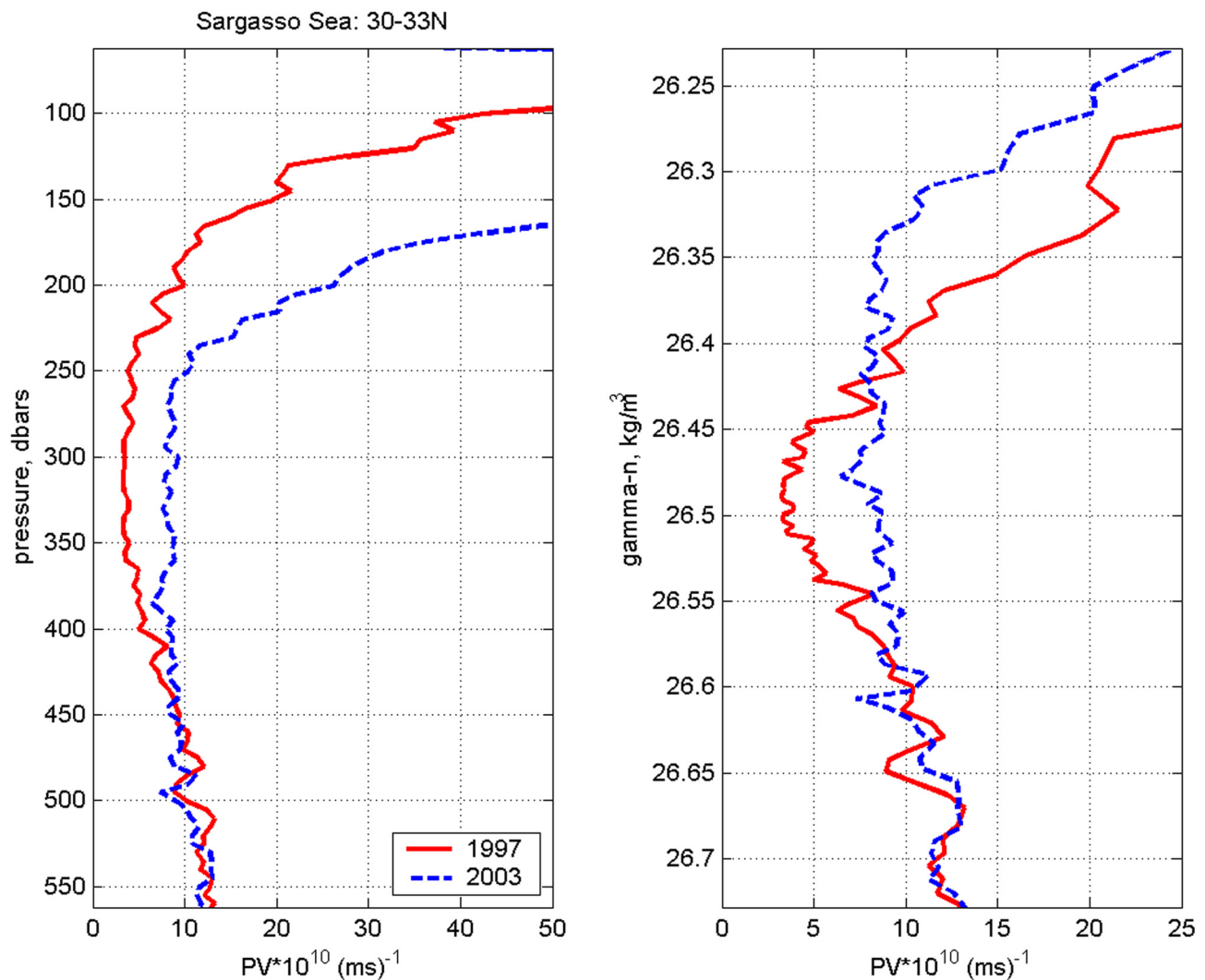

Figure B.4: Potential vorticity for the northern Sargass Sea in 1997 and 2003 from A22. Note how the PV in '97 was about half that at present and much more concentrated in a 'mode' with a density near 26.47 $_n$.

B.5 Argo Float releases

Allyn Clarke provided three Argo floats to be deployed on the section in the Northern Sargasso, Gulf Stream, and Slope Water. One of the three floats refused to initiate its pre-launch sequence when the magnet was removed, despite it responding to some rudimentary communication tests with a computer connection in the lab on Knorr. The launch sites for the two other floats are given in the table.

Float #	ARGOS ID	Latitude	Longitude	Day/time	Station #
M-106	30175	34 43.38N	66 34.20W	8 Nov. 1948Z	61
MT-115	30237	37 24.16N	68 10.02W	10 Nov. 1854Z	68

B.6 Carbon isotope sampling

Surface ^{14}C samples and three complete vertical profiles of ^{13}C were taken on the cruise for later analysis ashore at the following stations:

^{14}C surface samples on stations: 1, 4, 11, 31, 36, 41, 49, 61, 64, 68, 72, 75, 79
^{13}C full profiles on stations: 42, 56, 75

B.7 Summary

In all, 82 stations were taken, 2 more than originally planned. One station was added to the NE of Bermuda and a second was added to the DWBC crossing SE of Cape Cod. With excellent support by ship personnel, the seagoing scientific groups, and the weather, this cruise was both enjoyable and successful.

C. Description of Measurement Techniques
(F. Delahoyde/SIO)

C.1. CTD/Hydrographic Measurements Program

The basic CTD/hydrography program consisted of salinity, dissolved oxygen and nutrient measurements made from bottles taken on CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen and transmissometer from CTD profiles. A total of 88 CTD/rosette casts were made, usually to within 10 meters of the bottom. No major problems were encountered during the operation. The distribution of samples is illustrated in Figures C.1.0 - C.1.3.
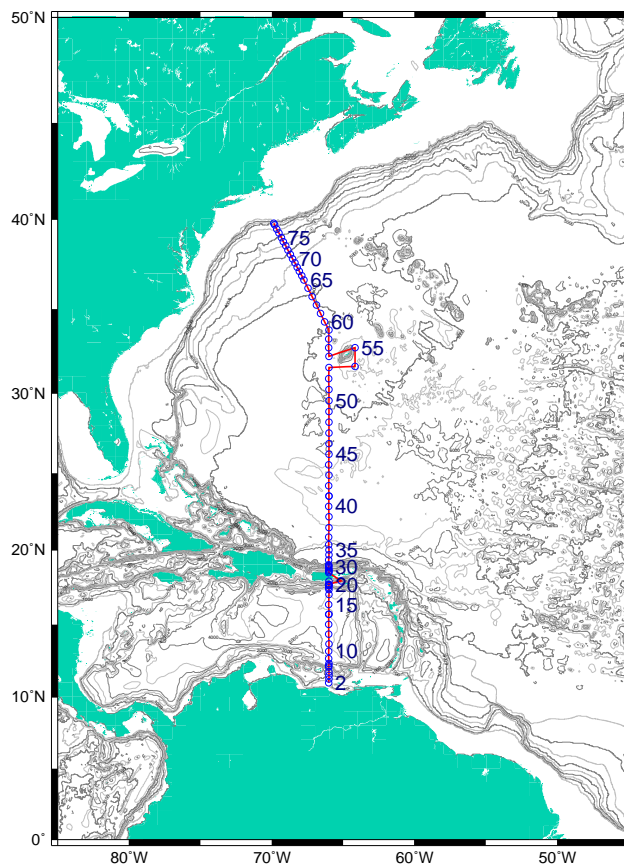
A22_2003a Cruise Track

Preliminary Cruise Report
mod. 13 November 2003

Data Submitted by:

Oceanographic Data Facility
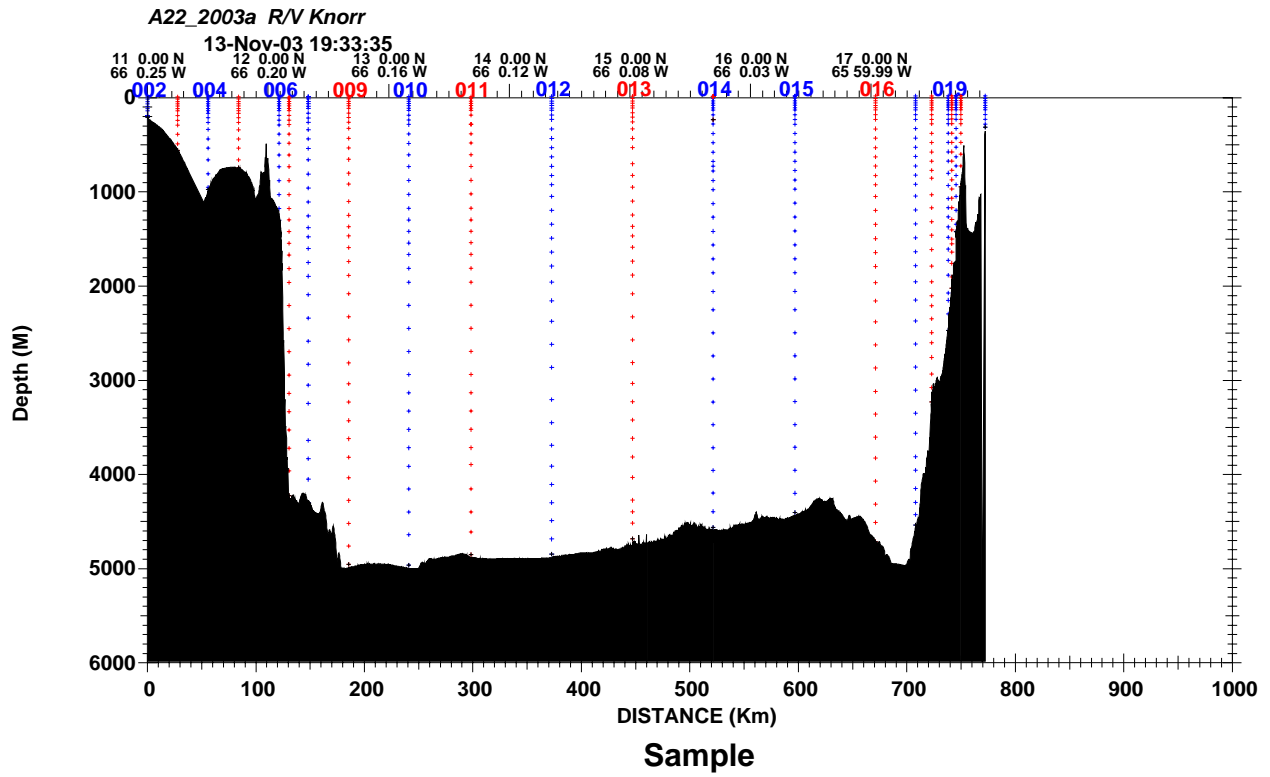Scripps Institution of Oceanography
La Jolla, Ca. 92093-0214

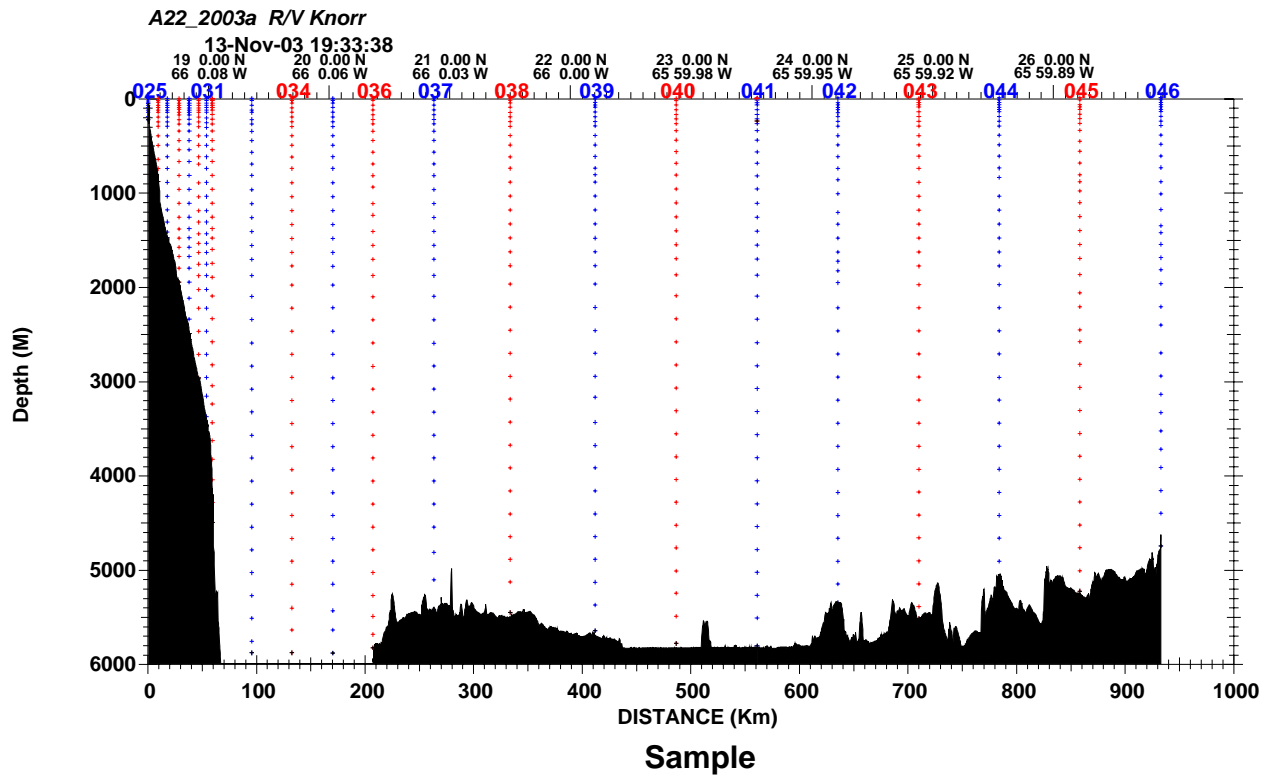**Figure C.1.0** Sample distribution, stations 1-27.
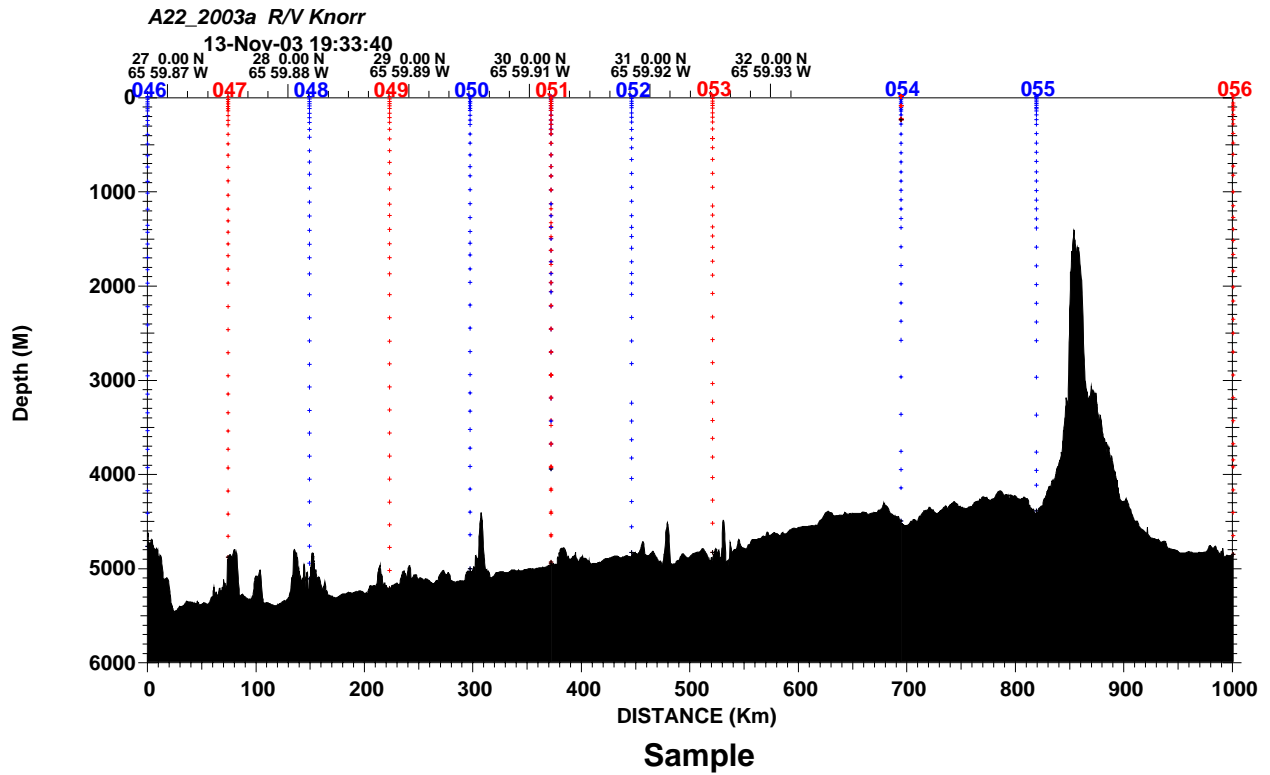

Figure C.1.1 Sample distribution, stations 27-38.

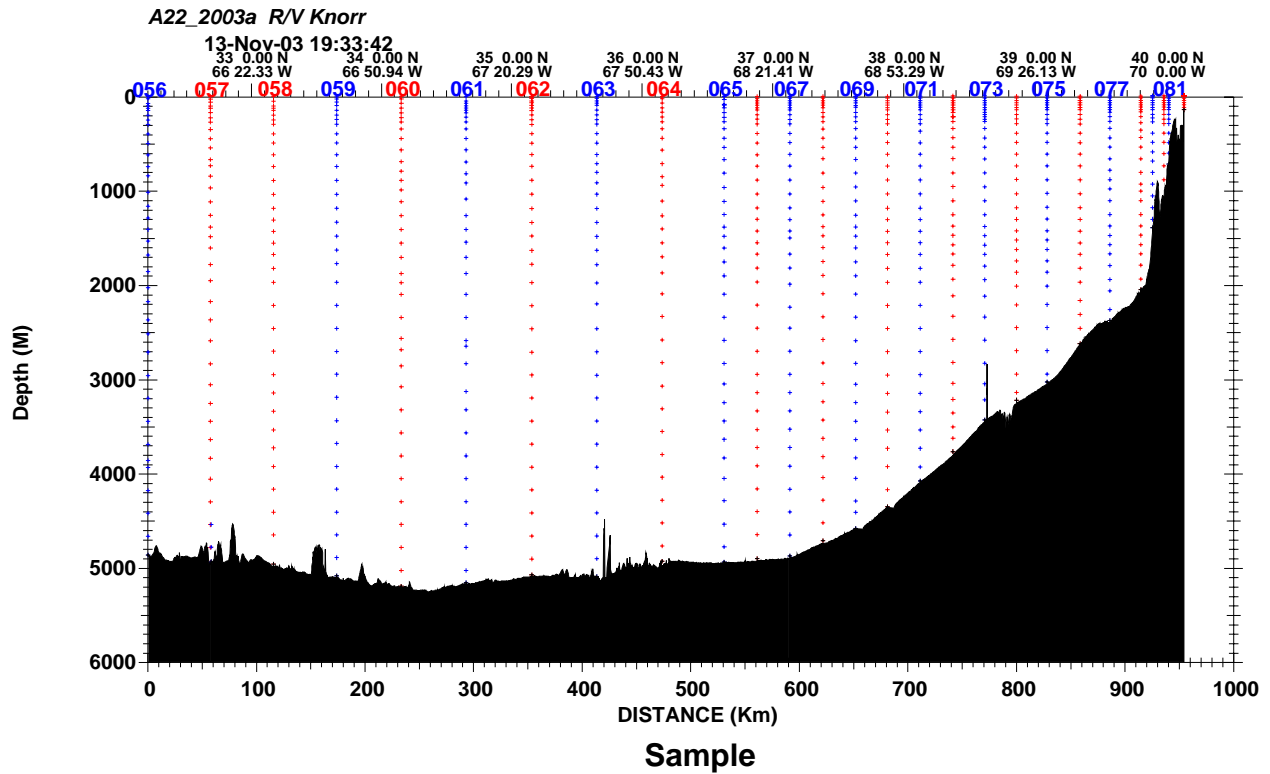**Figure C.1.2** Sample distribution, stations 38-52.

Figure C.1.3 Sample distribution, stations 52-88.

C.2. Water Sampling Package

LADCP/CTD/rosette casts were performed with a package consisting of a 36-bottle rosette frame (ODF), a 36-place pylon (SBE32) and 36 10-liter Bullister bottles (ODF). Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9plus CTD (ODF #474) with dual pumps, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star) and fluorometer (Seapoint Sensors); an SBE35RT Digital Reversing Thermometer, RDI LADCPs (Workhorse 300khz/Broadband 150khz) and a Simrad 1007 altimeter.

The CTD was mounted horizontally along one side of the bottom center of the rosette frame for casts 1/1-61/1, and vertically in an SBE CTD frame attached to the same rosette location for casts 62/1-82/1. The SBE sensors and pumps were deployed along the CTD pressure case for both horizontal and vertical mountings. The transmissometer, fluorometer and SBE35RT temperature sensor were mounted horizontally along the rosette frame adjacent to the CTD. The LADCP battery pack was mounted alongside and outboard from the CTD. The LADCPs were vertically mounted inside the bottle rings on the opposite side of the frame from the CTD and LADCP battery pack, with one set of transducers pointing down, the other up. The altimeter was mounted on the inside of support strut outboard from the LADCP battery pack.

The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable. The *R/V Knorr's* starboard-side CTD winch was used on all casts except 58/1, where the port-side winch was used. A broken sea cable conductor resulting in signal loss resulted in the premature termination of cast 57/1 (renamed 57/2) at 4600 decibars after tripping 3 bottles. One other cast (51/1, renamed 51/3) was repeated due to all bottle vents having been left open and no usable samples taken. No other casts were aborted and no other reterminations were performed on the sea cable.

The deck watch prepared the rosette 10-20 minutes prior to each cast. All valves, vents and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Once stopped on station, the LADCP was turned on and the rosette moved into position under the starboard boom via an air-powered cart and tracks. As directed by the deck watch leader, the CTD was powered-up and the data acquisition system started. Two stabilizing tag lines were threaded through rings on the rosette frame, and syringes were removed from the CTD sensor intake ports. The deck watch leader directed the winch operator to raise the package, the boom and rosette were extended outboard and the package quickly lowered into the water. The tag lines were removed and the package was lowered to 10 meters. The CTD console operator then directed the winch operator to bring the package close to the surface, pause for typically 30 seconds and begin the descent.

Each rosette cast was lowered to within 10-20 meters of the bottom (with the exception of 3 shallow incubation casts).

Each Bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette, which was used for sample identification. No bottles were changed or replaced on this leg, although parts of a few of them were replaced or repaired.

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

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

C.3.   UnderwaterElectronics Packages

CTD data were collected with a SBE9plus CTD (ODF #474). This instrument provided pressure, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star), fluorometer (Seapoint Sensors) and altimeter (Simrad 1007) channels. CTD #474 supplied a standard Sea-Bird format data stream at a data rate of 24 frames/second (fps).

Table 1.3.0: A22 Rosette Underwater Electronics.

Sea-Bird SBE32 36-place Carousel Water Sampler	S/N 0187
Sea-Bird SBE35RT Digital Reversing Thermometer	S/N 0035
Sea-Bird SBE9plus CTD	S/N09P9852-0474
Paroscientific Digiquartz Pressure Sensor	S/N 69008
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-4138 (Primary)
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-2359 (Secondary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2419 (Primary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2319 (Secondary)
Sea-Bird SBE43 DO Sensor	S/N 43-0255 (casts 2/1-37/1)
Sea-Bird SBE43 DO Sensor	S/N 43-0199 (casts 38/1-82/1)
Wetlabs C-Star transmissometer	S/N 507DR
Seapoint Sensors Fluorometer	S/N 2273
Simrad 1007 Altimeter	S/N 0201075
RDI Workhorse 300khz LADCP	S/N 3898-XR
RDI Workhorse 300khz LADCP	S/N 3898-VXR
RDI Workhorse 300khz LADCP	S/N 149
RDI Workhorse 300khz LADCP	S/N 150
RDI Workhorse 300khz LADCP	S/N 754
RDI Broadband 150khz LADCP	S/N 1546
LADCP Battery Pack	

The CTD was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed on one pump circuit and secondary temperature and conductivity on the other. The sensors were deployed horizontally for casts 2/1-61/1, and vertically for casts 62/1-82/1. The secondary temperature and conductivity sensors (T2 #2359 and C2 #2319) were used for reported CTD temperatures and conductivities on all casts, due to a down/upcast conductivity offset observed in the primary channel. The primary temperature and conductivity sensors (T1 #4138 and C1 #2419) were used for calibration checks.

The SBE9 CTD and the SBE35RT Digital Reversing Thermometer were both connected to the SBE32 36-place pylon providing for single-conductor sea cable operation. All 3 sea cable conductors were connected together to improve reliability. Power to the SBE9 CTD,SBE32 pylon, and SBE35RT was provided through the sea cable from the SBE11plus deck unit in the main lab. The Simrad altimeter and LADCP were powered by battery packs.

C.4. Navigation and Bathymetry Data Acquisition

Navigation data were acquired (at 1-second intervals) from the ship's Seanav GPS receiver by one of the Linux workstations beginning October 23. Data from the ship's Knudsen 320B/R Echosounder (12 KHz transducer) were also acquired, corrected using Carter tables [Cart80] and merged with the navigation. The Knudsen bathymetry data were noisy and subject to washing out on station when the bow thrusters were engaged.

Bathymetric data from the ship's multibeam (SeaBeam) echosounder system were also logged by the *R/V Knorr's* underway system.

C.5   Lowered Acoustic Doppler Current Profiler

Velocity profiles were obtained during the standard hydrographic casts of the Knorr A20 cruise using self contained ADCPs (Acoustic Doppler Current Profilers) attached to the CTD rosette. Dual WH300 ADCPs (RDI Instruments Inc.) were used for Stations 1 through 37 and the test station 999. A single broadband 150 khz ADCP (RDI Instruments Inc.) was used for stations 38 through 84. Lowered ADCP data for stations 85 through 88 was not collected given that these stations were too shallow to obtain meaningful information. An experimental high power version of the WH300 ADCP was used on casts 1-11 and initially exhibited promising (higher range) results. Unfortunately a failed transducer on that instrument required that it be replaced with a standard WH300 ADCP for subsequent casts.

Based on the instrument range and the magnitude of the error associated with the velocity estimates, the dual WH300 ADCPs performed well in the high back- scatter region on the northern portion of the transect. The range of these instruments declined steadily and the velocity error increased as the ship proceeded south into lower back-scatter waters, requiring the switch to the higher powered broadband 150 khz instrument after station 37. While the performance of the broadband 150 khz instrument was adequate in the low back- scatter waters of the main gyre, the range and velocity error steadily improved as the ship made progress south. Poor velocity estimates in the upper 200 meters of the water column is common when profiling with a single ADCP and is not entirely understood. This proved to be the case when the single BB150 ADCP was used during this cruise. The hull mounted ADCP data will be used to fill in for the poor surface data that was obtained while using the single BB150 ADCP. Additional post processing will be done to optimize the threshold settings that will allow our bottom tracking routines to decrease the error in the velocity estimates when the paired WH300 ADCPs were used. However, preliminary examination of the velocity profiles indicates good correlation with the geostrophic velocities computed from the temperature and salinity data.

C.6.   Real-Time CTD Data Acquisition System

CTD data acquisition system consisted of an SBE-11plus deck unit and four networked generic PC workstations running RedHat 9 Linux. Each PC workstation was configured with a color graphics display, keyboard, trackball, 60 GB disk, CD-R and CDRW drives. Two of the four systems also had 8 additional RS-232 ports via a Rocketport PCI serial controller. The systems were networked through 2 100BaseTX ether net switches which were also connected to the ship's network. These systems were available for real-time operational and CTD data displays, as well as providing for CTD and hydrographic data management and backup. Hardcopy capability was provided by a networked HP 1600CM color printer.

One of the workstations was designated the CTD console and was connected to the CTD deck unit via RS-232. The CTD console provided an interface for controlling CTD deployments as well as real-time operational displays for CTD and rosette trip data, GPS navigation, bathymetry and the CTD winch.

CTD deployments were initiated by the console watch once the ship was stopped on station. A console operations log was maintained by the watch containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. The deployment software presented the operator with a short dialog instructing them to turn on the deck unit, examine the on screen raw data display for stable CTD data and to notify the deck watch that this was accomplished. When the deck watch was ready to put the rosette over the side, the console watch was notified and the CTD data acquisition started. Time, GPS position and bottom depth were automatically logged at 1 second resolution. Both raw and processed (2 Hz time-series) CTD data were automatically backed up by one of the other workstations via ethernet. The deployment software display changed to indicate that a cast was in progress. A processed data display appeared, as did a rosette bottle trip display and control for closing bottles. Various real-time plots were then initiated to display the progress of the deployment.

Once the deck watch had deployed the rosette, the winch operator would immediately lower it to 10 meters. The CTD pumps were configured with an 8 second startup delay, and would be on by this time. The console operator would check the CTD data for proper operation, then instruct the winch operator to bring the package to the surface and then descend to a target depth (wire-out). The lowering rate was normally 60 meters/minute for this package, depending on sea cable tension and sea state.

The console watch monitored the progress of the deployment and quality of the CTD data through interactive graphics and operational displays. Additionally, the watch decided where to trip bottles on the up cast, noting this on the console log. The altimeter channel, CTD depth, wire-out and bathymetric depth were monitored to determine the distance of the package from the bottom. The on-screen winch and altimeter displays allowed the watch to refine the target wire-out relayed to the winch operator and safely approach to within 10-20 meters of the bottom.

Bottles were closed on the up cast by operating a "point and click" graphical trip control button. The data acquisition system responded with trip confirmation messages and the corresponding CTD data in a rosette bottle trip window on the display. All tripping attempts were noted on the console log. The console watch then directed the winch operator to raise the package up to the next bottle trip location. The console watch was also responsible for creating a sample log for the deployment which was used to record the correspondence between rosette bottles and analytical samples taken.

After the last bottle was tripped, the console watch directed the deck watch to bring the rosette on deck. Once on deck, the console watch terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.

C.7. CTD Data Processing

ODF CTD processing software consists of over 30 programs running in a Unix run- time environment. The initial CTD processing program (ctdrtd/ctdba) is used either in real-time or with existing raw CTD data to:

- Convert raw CTD scans into scaled engineering units, and assign the data to logical channels
- Filter various channels according to specified criteria
- Apply sensor- or instrument-specific response-correction models
- Decimate the channels according to specified criteria
- Store the output time-series in a CTD-independent format

Once the CTD data are reduced to a standard format time-series, they can be manipulated in various ways. Channels can be additionally filtered. The time- series can be split up into shorter time-series or pasted together to form longer time-series. A time-series can be transformed into a pressure-series, or into a larger-interval time-series. The pressure, temperature and conductivity laboratory calibration coefficients are applied during the creation of the initial time-series. Oxygen conversion equation coefficients and any adjustments to pressure, temperature or conductivity are maintained in separate files and are applied whenever the data are accessed.

The CTD data acquisition software acquired and processed the data in real-time, providing calibrated, processed data for interactive plotting and reporting during a cast. The 24 Hz data from the CTD were filtered, response-corrected and decimated to a 2.0 Hz time-series. Sensor correction and calibration models were applied to pressure, temperature, conductivity and O_2 .Rosette trip data were extracted from this time-series in response to trip initiation and confirmation signals. The calibrated 2.0 Hz time-series data, as well as the 24 Hz raw data, were stored on disk and were backed up via ethernet to a second system. At the end of the cast, various consistency and calibration checks were performed, and a 2-db pressure-series of the down cast was generated and subsequently used for reports and plots.

CTD data were examined graphically at the completion of deployment for potential problems. The two CTD temperature sensors were compared, intercompared with the SBE35RT Digital Reversing Thermometer and checked for sensor drift. CTD conductivity sensors were compared and monitored by examining differences between CTD values and check-sample conductivities. Additionally, deep theta-salinity comparisons were made between down and up casts as well as adjacent deployments. The CTD O_2 sensor data were calibrated to bottle check- sample data.

The minor sea cable noise problems on this cruise did not significantly affect the CTD data, being filtered out during the data acquisition. No additional filtering was done on any of the CTD data.

The initial 10 M yo in each deployment resulting from lowering then raising the package to the surface to start the pumps was removed during the generation of the 2.0 db pressure-series.

Density inversions can be induced in high-gradient regions by ship-generated vertical motion of the rosette. Detailed examination of the raw data shows significant mixing can occur in these areas because of "ship roll". To minimize density inversions, a "ship-roll" filter which disallowed pressure reversals was applied during the generation of all 2.0 db pressure-series down-cast data.

C.8.   CTD Laboratory Calibration Procedures

Laboratory calibrations of the CTD pressure, temperature and conductivity sensors were used to generate Sea-Bird conversion equation coefficients applied by the data acquisition software at sea.

Pressure calibrations were last performed on CTD #474 at the ODF Calibration Facility (La Jolla) 26 August 2003, immediately prior to A22_2003a.

The Paroscientific Digiquartz pressure transducer (S/N 69008) was calibrated in a temperature-controlled water bath to a Ruska Model 2400 Piston Gauge Pressure Reference. Calibration curves were measured at 4 temperatures from -1.38 to 29.30°C to two maximum loading pressures (1191 and 6081 decibars).

The SBE3plus temperature sensors (primary S/N 03-4138, secondary S/N 03-2359) were calibrated at SBE on 08 August 2003.

The SBE4 conductivity sensors (primary S/N 04-2419, secondaries S/Ns 04-1908, 04-2572 and 04-2319) were calibrated on 08 August 2003, 08 August 2003, 08 August 2003 and 03 May 2003 at SBE respectively..

The SBE35RT Digital Reversing Thermometer (S/N 0035) was calibrated on 27 June 2003 at SIO/ODF. Laboratory pressure, temperature and conductivity calibrations will be repeated post-cruise.

C.9. CTD Shipboard Calibration Procedures

CTD #474 was used for all A22_2003a casts, and had been used for the previous leg (A20_ 2003a, kn173-1) as well. The CTD was deployed with sensors and pumps aligned horizontally for casts 1/1-61/1, the same configuration as on the previous leg. The sensors and pumps were aligned vertically for casts 62/1- 88/1. Primary temperature and conductivity sensors served as calibration checks for the secondary temperature and conductivity. The primary sensors were not used for reported data because of a conductivity offset between down and up casts that was discovered on the previous leg. This offset was attributed to pump flow rate, a conjecture that was substantiated on this leg. The SBE35RT Digital Reversing Thermometer served as an independent temperature calibration check. In-situ salinity and dissolved O_2 check samples collected during each rosette cast were used to calibrate CTD conductivity and dissolved O_2 .

C.9.1. CTD Pressure

Pressure sensor conversion equation coefficients derived from the pre-cruise pressure calibration were applied to raw pressures during each cast. No additional adjustments were made to the calculated pressures, but a change in the on-deck pressure offset was observed when the CTD was reoriented vertically prior to cast 62/1. The offset changed from +0.1 db to +1.0 db.

Residual offsets at the beginning and end of each cast (the difference between the first/last pressures in-water and 0) were monitored during the cruise to check for shifts in the pressure calibration. All residual differences were 0.5 decibar or less prior to cast 62/1 and 1.0 decibar or less thereafter.

There was no apparent shift in pressure calibration during the cruise. This will be verified by a post-cruise laboratory pressure calibration.

C.9.2. CTD Temperature

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

Two independent metrics of calibration accuracy were examined. The primary and secondary temperatures were compared at each rosette trip, and the SBE35RT and secondary temperatures were compared at each rosette trip. These comparisons are summarized in Figures C.9.2.0 and C.9.2.1.
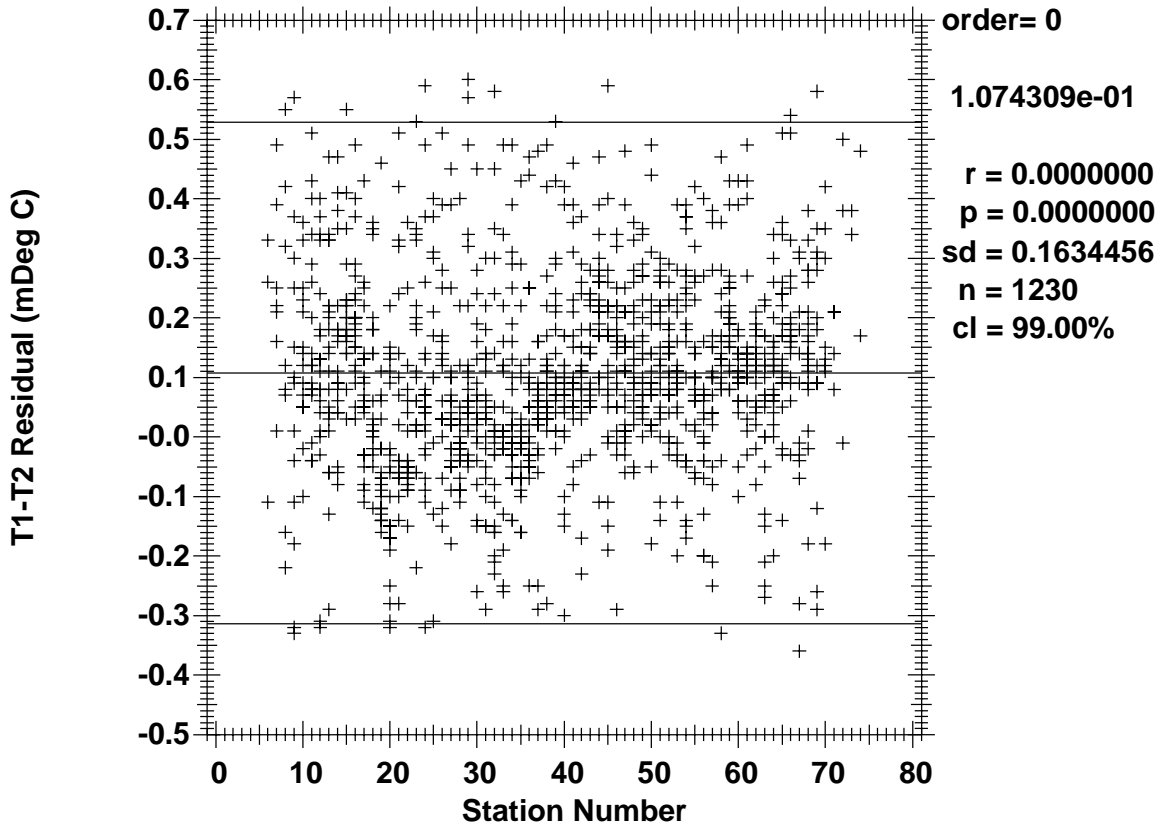
order= 0

1.074309e-01

r = 0.0000000
p = 0.0000000
sd = 0.1634456
n = 1230
cl = 99.00%

Figure C.9.2.0 Primary and secondary temperature comparison, p>1000db.

order= 0

-2.706267e-01

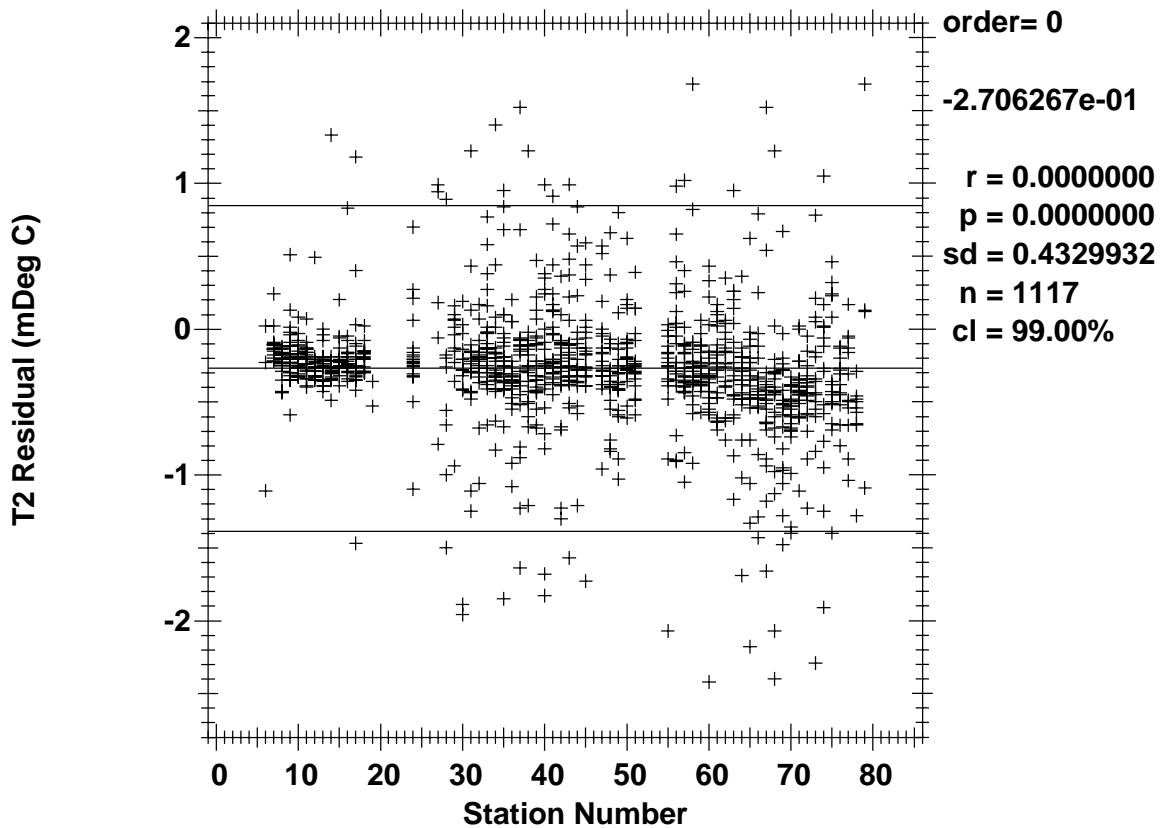r = 0.0000000
p = 0.0000000
sd = 0.4329932
n = 1117
cl = 99.00%

Figure C.9.2.1: Primary and SBE35RT temperature comparison, p>1000db.

The comparison between primary and secondary temperatures shows a small (0.00011°C) mean calibration offset, well within the reported accuracy of the SBE temperature calibrations.

The comparison between SBE35RT and T2 temperatures shows a constant offset of -0.00027°C prior to cast 62/1 and less distinct differences thereafter. This change corresponds to the change in sensor orientation and an increase in distance from the T2 pump intake to the SBE35 (from ~ 0.5 meters to ~ 0.8 meters).

C.9.3. CTD Conductivity

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

A single pair of conductivity sensors were used on A22: #2419 (primary) and #2319 (secondary). Both conductivity sensors were stable and noise-free. The primary conductivity sensor exhibited a 0.0007 mS/cm offset between down and up cast on the previous leg that was attributed to pump flow rate (and horizontal sensor alignment) and so was not used for reported CTD data on A22. This offset disappeared (cast 62/1) when the CTD was reconfigured for vertical sensor alignment. No offset was apparent in the secondary conductivity data, perhaps due to the absence of the SBE43 DO sensor in the P2 sensor circuit. Comparisons to bottle salinities to the secondary conductivity sensor showed a mean conductivity correction slope of 0.000 mS/cm and a constant offset of 0.000212 mS/cm.

The comparison of the primary and secondary conductivity sensors by station is summarized in Figure C.9.3.0.

The salinity residuals after applying the shipboard calibration are summarized in figures C.9.3.1 and C.9.3.2.

order = 0

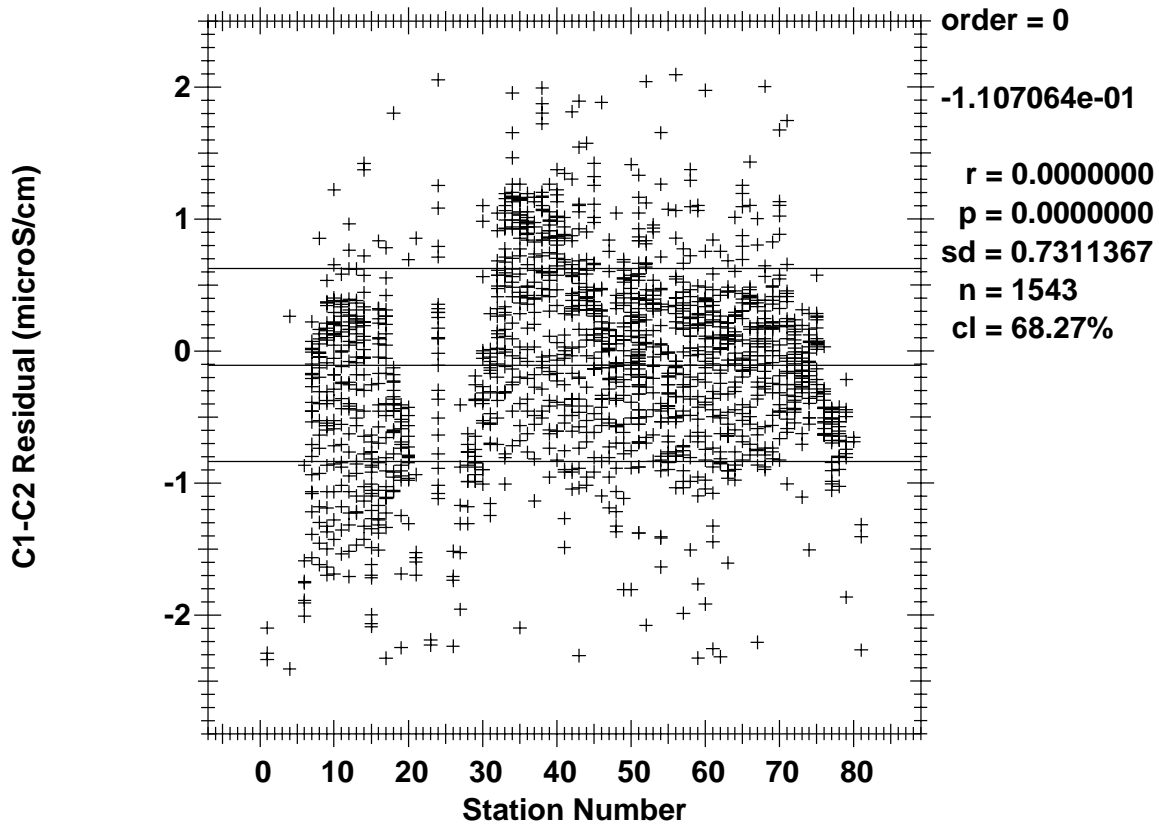-1.107064e-01

r = 0.0000000
p = 0.0000000
sd = 0.7311367
n = 1543
cl = 68.27%

Figure C.9.3.0 C1 and C2 conductivity differences by pressure, p>500db.

order = 0

2.494935e-02

r = 0.0000000
p = 0.0000000
sd = 1.4087124
n = 1382
c l = 99.00%
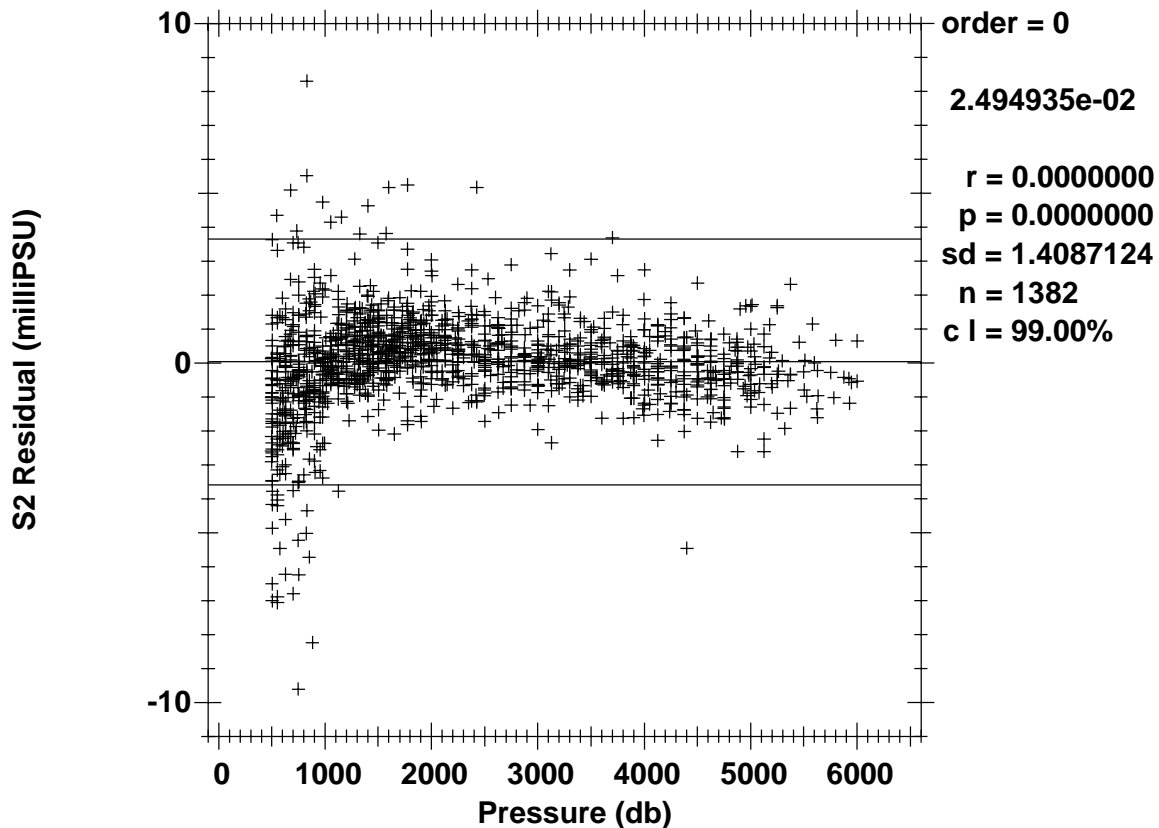
Figure C.9.3.1 C2 salinity residuals, p>500db.

order = 0

2.494935e-02

r = 0.0000000
p = 0.0000000
sd =1.4087124
n = 1382
cl = 99.00%
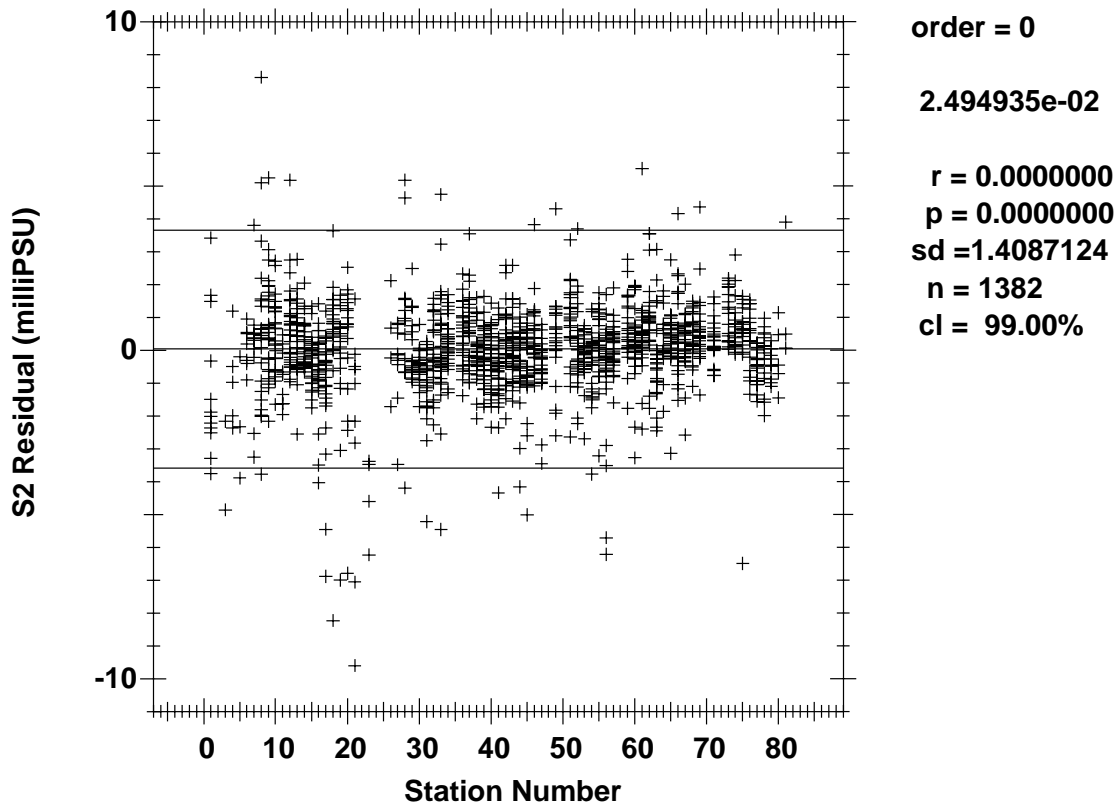
Figure C.9.3.2 C2 salinity residuals, p>500db.

order= 0

7.932707e-02

r = 0.0000000
p = 0.0000000
sd = 0.7701734
n = 639
cl = 95.00%
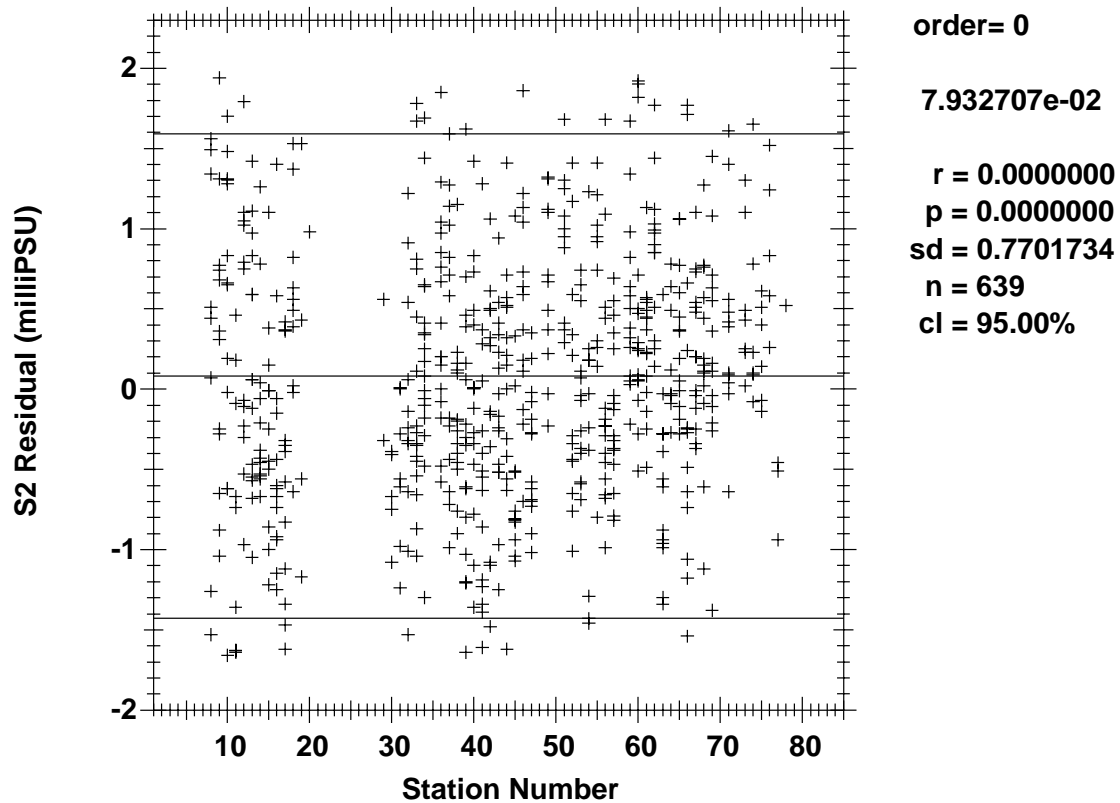
Figure C.9.3.3 C2 salinity residuals by station, p>2000db.

Excluding thermocline and gradient values (early and late stations were shallow and also excluded), Figure C.9.3.3 represents an estimate of the salinity accuracy of CTD #474. The 95% confidence limit is ±0.0015 PSU, in agreement with the generally accepted limit of repeatability for bottle salinities (±0.002PSU).

C.9.4. CTD Dissolved Oxygen

Two SBE43 dissolved O_2 (DO) sensors were used for this cruise (#43-0225 casts 1/1-37/1, #43-0199 casts 38/1-82/1). Sensor #43-0225 was replaced to determine if non-linear pressure response and hysteresis were sensor-dependent (they weren't). The sensor was plumbed into the P1/T1/C1 intake line in a horizontal configuration after C1 and before P1 (per SBE spec). This was changed to a vertical configuration prior to cast 62/1.

One characteristic of this type of sensor (membrane-covered polarigraphic oxygen detector or MPOD) is a flow dependence. Non-pumped sensors of this type exhibit a significantly decreased response at bottle stops. The pumped SBE43 reduces but does not eliminate this problem, perhaps due to pump or flow rate variations in the primary sensor circuit. DO sensor calibration to check samples is somewhat problematic as sensor data from the bottle stop does not provide a representative comparison.

The DO sensor calibration method used for this cruise was to match down-cast CTD DO data to up-cast bottle trips along isopycnal surfaces, then to minimize the residual differences between the in-situ check sample values and CTD O_2 using a non-linear least-squares fitting procedure. Since this technique only calibrates the down-cast, only the 2.0 pressure series downcast data contain calibrated CTD O_2 .

A small (<0.02 ml/l) but significant non-linearity apparent in the O_2 residuals as a function of pressure was corrected with an additional empirical 5th-order polynomial pressure correction. The explanation for this non-linearity requires further investigation.

Figures C.9.4.0, C.9.4.1 and C.9.4.2 show the residual differences between bottle and calibrated CTD O_2 for all points excluding the thermocline and surface gradients. Figure C.9.4.3 shows the residual differences for pressures > 1000 db.
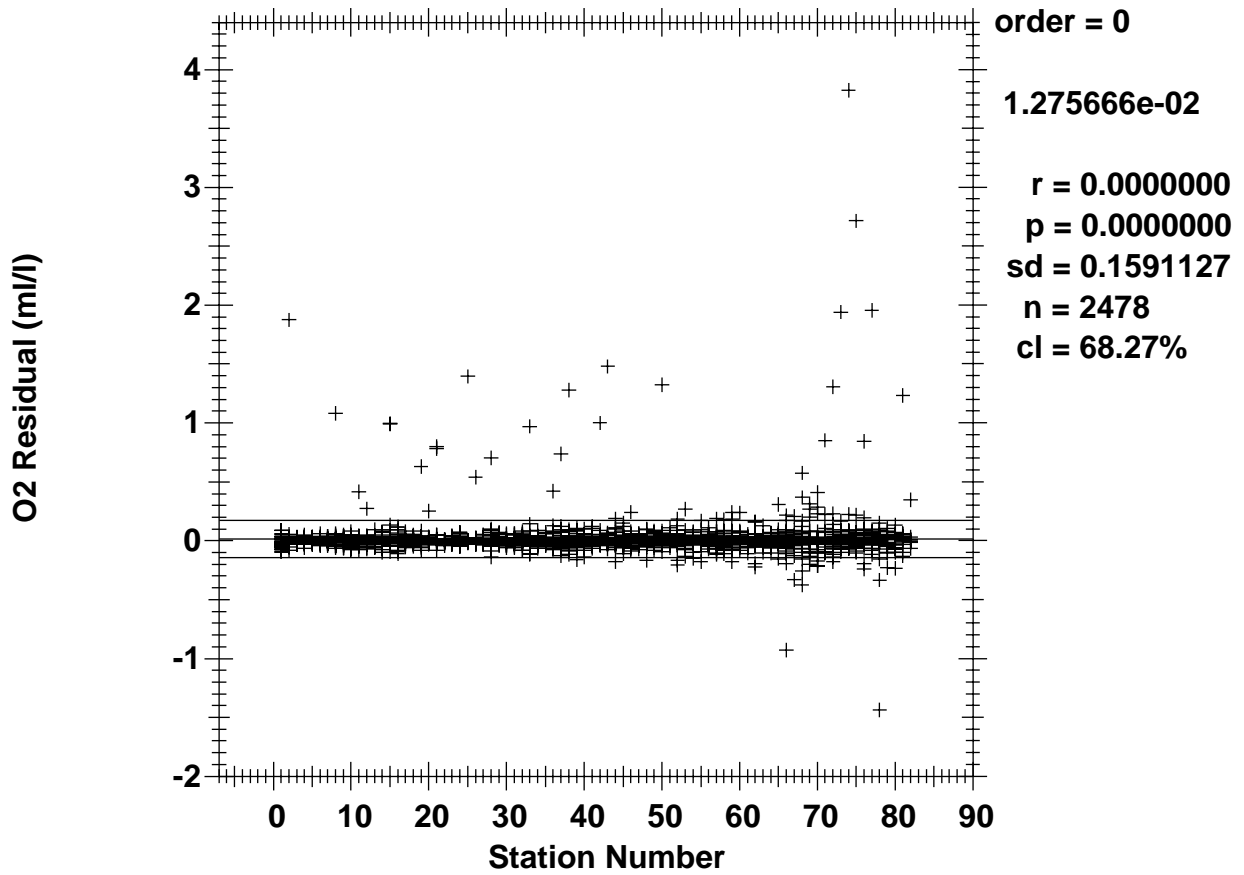
order = 0

1.275666e-02

r = 0.0000000
p = 0.0000000
sd = 0.1591127
n = 2478
cl = 68.27%

Figure C.9.4.0 O_2 residuals by station number.

order = 0

4.671717e-04

r = 0.0000000
p = 0.0000000
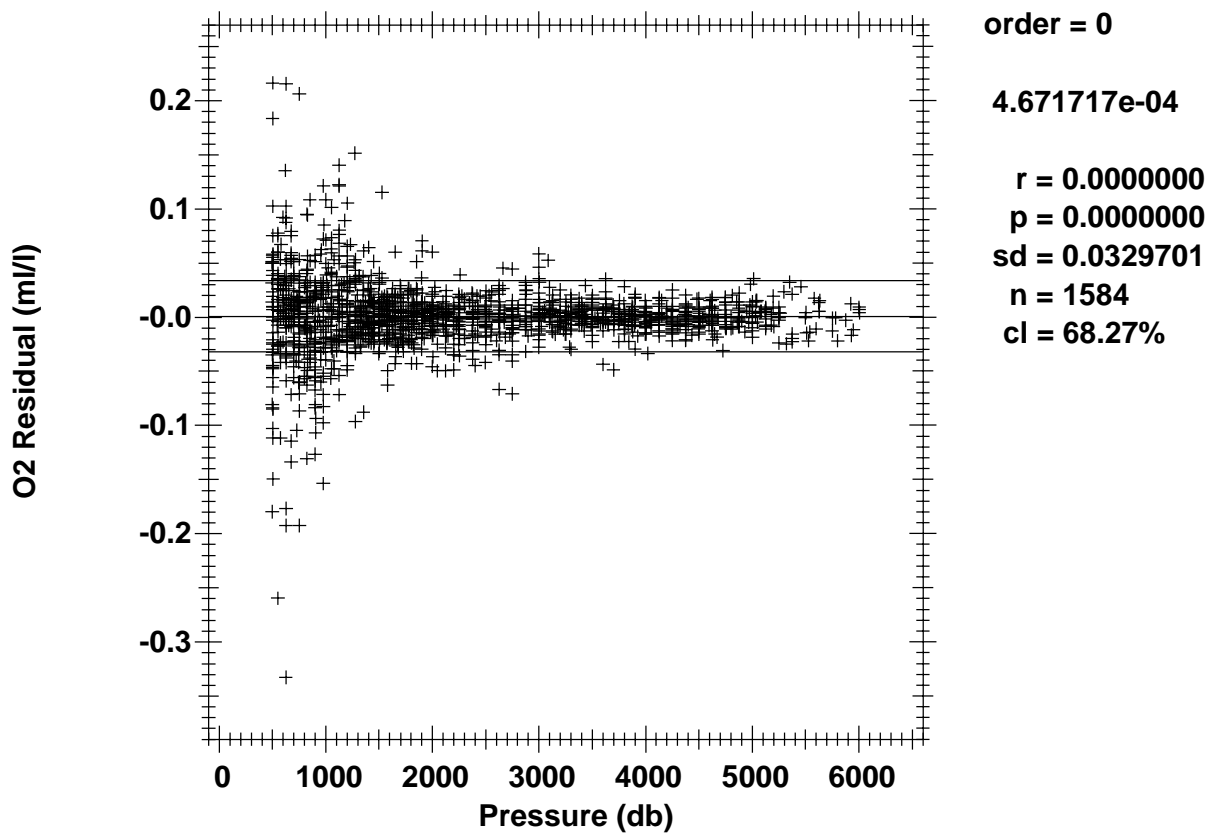sd = 0.0329701
n = 1584
cl = 68.27%

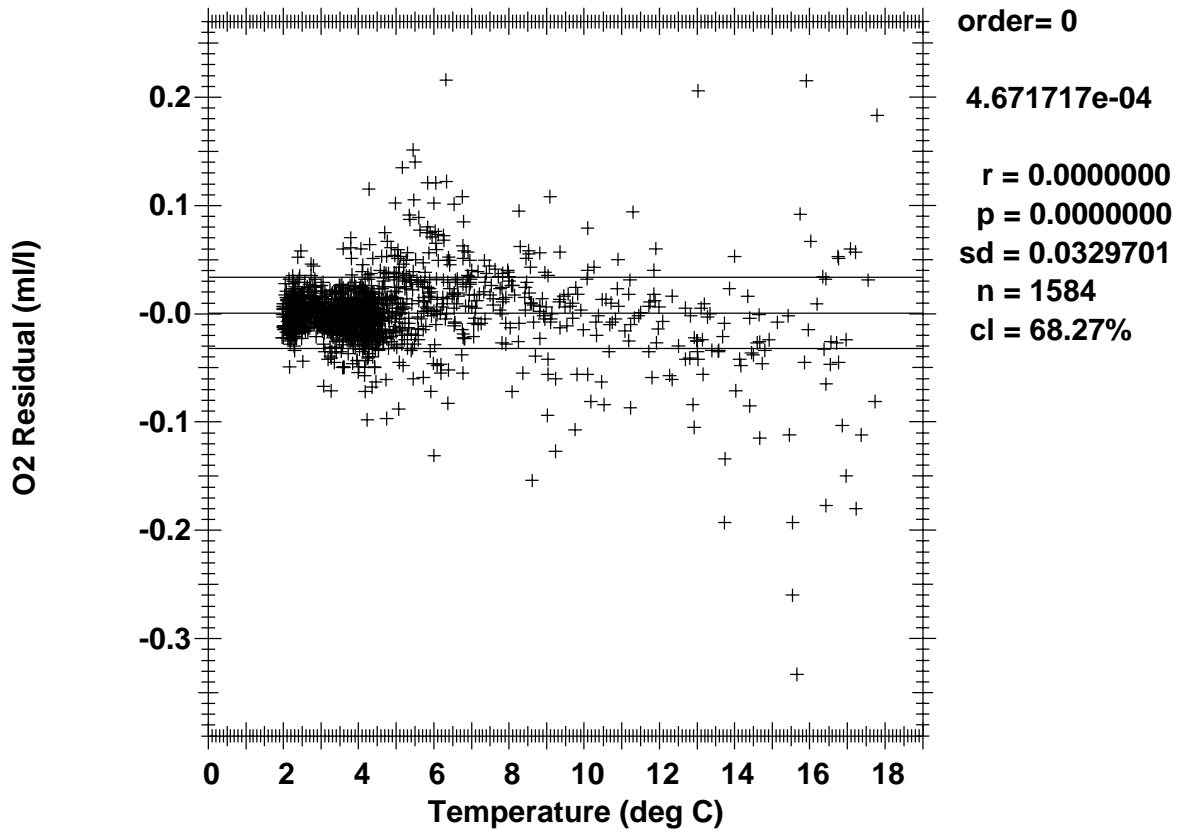**Figure C.9.4.1** O_2 residuals by pressure.
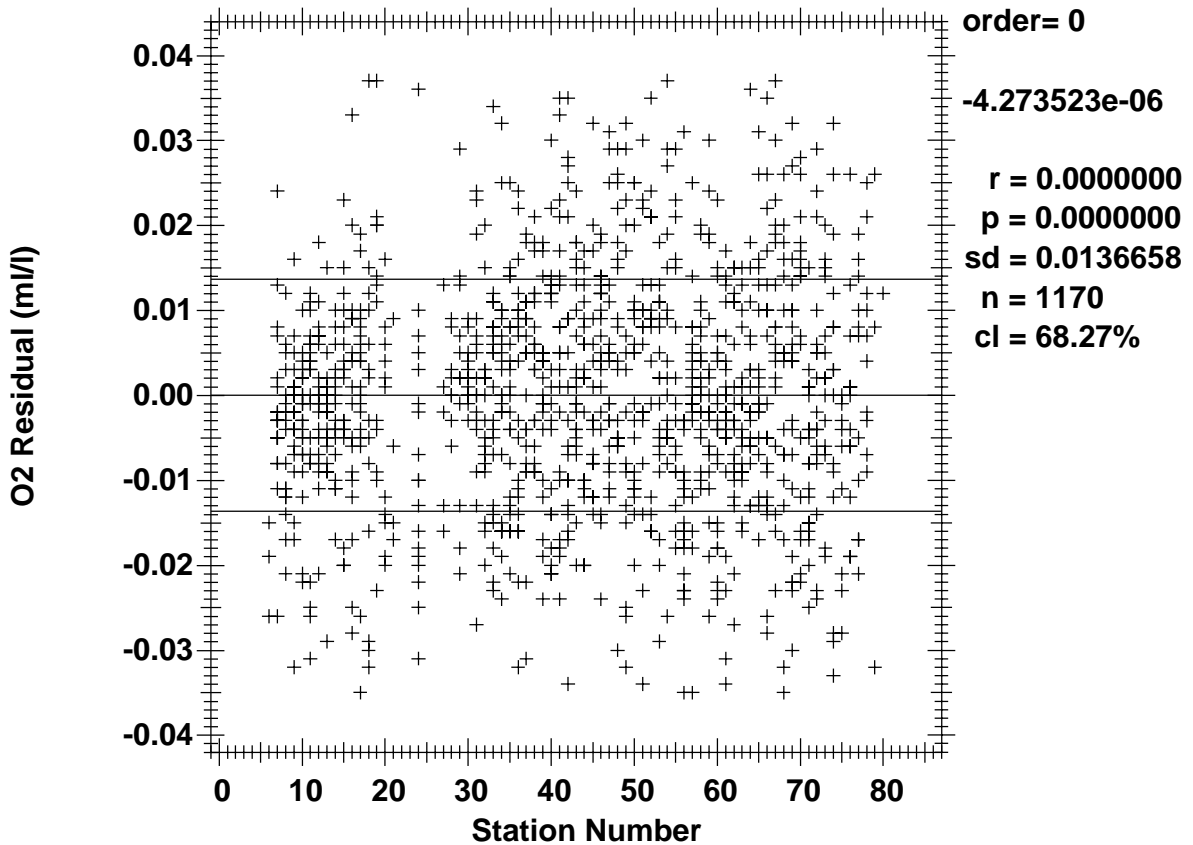
Figure C.9.4.2 O_2 residuals by temperature.

Figure C.9.4.3 O_2 residuals by station number, p>1000db.

The standard deviations of 0.033 ml/l for all oxygens and 0.014 ml/l for deep oxygens are only intended as indicators of how well the up-cast bottle O_2 and down-cast CTD O_2 match. ODF makes no claims regarding the precision or accuracy of CTD dissolved O_2 data.

The general form of the ODF O_2 conversion equation follows Brown and Morrison [Brow78] and Millard [Mill82], [Owen85]. ODF models membrane and sensor temperatures with lagged CTD temperatures. In-situ pressure and temperature are filtered to match the sensor response. Time-constants for the pressure response tp, and two temperature responses tTs and tTf are fitting parameters. The Oc gradient, dOc/dt ,is approximated by low-pass filtering 1st-order Oc differences. This gradient term attempts to correct for reduction of species other than O_2 at the sensor cathode. The time-constant for this filter, tog ,is a fitting parameter. Oxygen partial-pressure is then calculated:

$$O_{pp} = [c_1 O_c + c_2] \cdot f_{sat}(S, T, P) \cdot e^{(c_3 P_l + c_4 T_f + c_5 T_s + c_6 \frac{dO_c}{dt})} \tag{1.8.4.0}$$

where:

O_{pp}	= Dissolved O_2 partial-pressure in atmospheres (atm);
O_c	= Sensor current (μamps);
$f_{sat}(S, T, P)$	= O_2 saturation partial-pressure at S,T,P (atm);
S	= Salinity at O_2 response-time (PSUs);
T	= Temperature at O_2 response-time (° C);
P	= Pressure at O_2 response-time (decibars);
P_l	= Low-pass fi ltered pressure (decibars);
T_f	= Fast low-pass fi ltered temperature (° C);
T_s	= Slow low-pass fi ltered temperature (° C);
$\dfrac{dO_c}{dt}$	= Sensor current gradient (μamps/secs).

C.10. Bottle Sampling

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

- CFCs
- $He3$
- O_2
- DIC/Total Alkalinity
- DOC/DON/DCNS/CDOM
- Tritium
- I_{129}
- C_{13} and C_{14}
- Nutrients
- Salinity

The correspondence between individual sample containers and the rosette bottle 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 sample 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. Oxygen, nutrient and salinity analyses were performed on computer-assisted (PC) analytical equipment networked to the data processing computer for centralized data analysis.

C.11. Bottle Data Processing

Bottle data processing began with water sample drawing and continued iteratively until the data were considered to be problem-free. A sample log was made for each cast and was filled out during sample drawing, serving both as a sample inventory and as a resource for the technicians performing their analyses. Any problems observed with the rosette before or during the sample drawing were noted on this for m, including indications of bottle leaks, incorrect bottle tripping and out-of-order sample drawing. Additional information regarding bottle tripping or leak problems were reported back as water samples were analyzed.

Reported water sample values were associated with rosette bottles using cast and bottle number to make the association. Bottle integrity and tripping issues were usually resolved at this stage, sometimes resulting in changes to the CTD properties assigned to the bottle.

A quality code was associated with every reported value (as well as with every bottle and associated CTD property). The quality coding followed the coding scheme developed for the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP) [Joyc94]. Diagnostic comments from the sample log, and notes from analysts and data processors were also associated with sample values as part of the quality control procedure. Sample values and quality codes were continuously reviewed and revised to best reflect the reliability of the measurements. This included intercomparison of bottle properties, comparison to CTD profile data and comparison of properties at adjacent stations.

WHP water bottle quality code assignments were made as defined in the WOCE Operations Manual [Joyc94] with the following additional interpretations:

2	No problems noted.
3	Leaking. An air leak large enough to produce an observable effect on a sample is identified by a code of 3 on the bottle and a code of 4 on the oxygen. (Small air leaks may have no observable effect, or may only affect gas samples.)
4	Did not trip correctly. Bottles tripped at other than the intended depth were assigned a code of 4. There may be no problems with the associated water sample data.
5	Not reported. No water sample data reported. This is a representative level derived from the CTD data for reporting purposes. The sample number should be in the range of 80-99.
9	The samples were not drawn from this bottle.

WHP water sample quality flags were assigned using the following criteria:

1	The sample for this measurement was drawn from the water bottle, but the results of the analysis were not (yet) received.
2	Acceptable measurement.
3	Questionable measurement. The data did not fit the station profile or adjacent station comparisons (or possibly CTD data comparisons). No notes from the analyst indicated a problem. The data could be acceptable, but are open to interpretation.
4	Bad measurement. The data did not fit the station profile, adjacent stations or CTD data. There were analytical notes indicating a problem, but data values were reported. Sampling and analytical errors were also coded as 4.
5	Not reported. There should always be a reason associated with a code of 5, usually that the sample was lost, contaminated or rendered unusable.
9	The sample for this measurement was not drawn.

WHP water sample quality flags were assigned to the CTDSAL (CTD salinity) parameter as follows:

2	Acceptable measurement.
3	Questionable measurement. The data did not fit the bottle data, or there was a CTD conductivity calibration shift during the up-cast.
4	Bad measurement. The CTD up-cast data were determined to be unusable for calculating a salinity.
7	Despiked. The CTD data have been filtered to eliminate a spike or offset.

WHP water sample quality flags were assigned to the CTDOXY (CTD O_2)parameter as follows:

1	Not calibrated. Data are uncalibrated.
2	Acceptable measurement.
3	Questionable measurement.
4	Bad measurement. The CTD data were determined to be unusable for calculating a dissolved oxygen concentration.
5	Not reported. The CTD data could not be reported, typically when CTD salinity is coded 3 or 4.
7	Despiked. The CTD data have been filtered to eliminate a spike or offset.
9	Not sampled. No operational CTD O_2 sensor was present on this cast.

Note that CTDOXY values were derived from up-cast rosette trip values matched to the down-cast CTD pressure-series data along isopycnal surfaces. Since this property depends on CTD salinity, it is not reported if the CTD salinity is quality coded as bad or questionable.

C.12. Salinity Analysis

Equipment and Techniques A single Guildline Autosal Model 8400A salinometer (S/N 48-266) located in the forward analytical lab was used for all salinity measurements. The salinometer was modified by ODF to contain an interface for computer-aided measurement. The water bath temperature was set and maintained at a value near the laboratory air temperature. It was set to 24°C for the entire leg.

The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 16-36 hours after collection. A temperature-controlled waterbath was used to assist sample equilibration. The salinometer was standardized for each group of analyses (1-4 casts, up to~50 samples) using at least one fresh vial of standard seawater per group. A computer (PC) prompted the analyst for control functions such as changing sample, flushing, or switching to "read" mode. The salinometer cell was flushed and results were logged by the computer until two successive measurements met software criteria for consistency. These values were then averaged for a final result.

Sampling and Data Processing

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with sample 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 collecting each sample, inserts were inspected for proper fit and loose inserts were replaced to insure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run.

PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and one run at the end as an unknown was applied linearly to the data to account for any drift. The data were incorporated into the cruise database. 2493 salinity measurements were made and approximately 60 vials of standard water were used. Temperature control was somewhat problematic and several runs were rendered unusable for calibration purposes because of a lack of temperature stability. The estimated accuracy of bottle salinities run at sea is usually better than ±0.002 PSU relative to the particular standard seawater batch used.

Laboratory Temperature

The temperature in the salinometer laboratory varied from 20.9 to 25.8°C, during the cruise. The air temperature change during any single run of samples was less than ±3.0°C.

Standards

IAPSO Standard Seawater (SSW) Batches P-140 and P-141 were used to standardize all salinity measurements.

C.13. Oxygen Analysis

Equipment and Techniques

Dissolved oxygen analyses were performed with an ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC software. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 ml buret. ODF used a whole-bottle modified- Winkler titration following the technique of Carpenter [Carp65] with modifications by Culberson et al. [Culb91], but with higher concentrations of potassium iodate standard (~0.012N) and thiosulfate solution (~65 gm/l). Pre- made liquid potassium iodate standards were run at the beginning of each session of analyses, which typically included from 1 to 3 stations. Reagent/distilled water blanks were determined every other day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. The auto-titrator generally performed well.

Sampling and Data Processing

Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125ml volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample draw temperature was measured with a small platinum resistance thermometer embedded in the drawing tube. Reagents were added to fix the oxygen before stoppering. The flasks were shaken twice (10-12 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes.

The samples were analyzed within 1-6 hours of collection, then the data were incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20°C. The 20°C normalities and the blanks were plotted versus time and were reviewed for possible problems.

As samples warmed up to room temperature they would occasionally degas which would cause a noisy endpoint due to gas bubbles in the light path. 2487 oxygen measurements were made.

The blank volumes and thiosulfate normalities were smoothed (linear fits) at the end of the cruise and the oxygen values recalculated.

Volumetric Calibration

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at ODF's chemistry laboratory. This is done once before using flasks for the first time and periodically thereafter when a suspect bottle volume is detected. The volumetric flasks used in preparing standards were volume-calibrated by the same method, as was the 10 ml Dosimat buret used to dispense standard iodate solution.

Standards

Liquid potassium iodate standards were prepared and bottled in ODF's chemistry laboratory prior to the cruise. The normality of the liquid standard was determined at ODF by calculation from weight. A single standard batch was used during A22-2003a. Potassium iodate was obtained from Acros Chemical Co. and was reported by the supplier to be >99.4% pure. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

C.14. Nutrient Analysis

Equipment and Techniques

Nutrient analyses (phosphate, silicate, nitrate and nitrite) were performed on an ODF-modified 4-channel Technicon AutoAnalyzer II, generally within one hour after sample collection. Occasionally samples were refrigerated up to 4 hours at ~4°C. All samples were brought to room temperature prior to analysis.

The methods used are described by Gordon et al. [Gord92]. The analog outputs from each of the four colorimeter channels were digitized and logged automatically by computer (PC) at 2-second intervals.

Silicate was analyzed using the technique of Armstrong et al. [Arms67]. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. Tartaric acid was also added to impede PO_4 color development. The sample was passed through a 15mm flowcell and the absorbance measured at 660nm.

A modification of the Armstrong et al. [Arms67] procedure was used for the analysis of nitrate and nitrite. For the nitrate analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. Sulfanilamide was introduced to the sample stream followed by N-(1-naphthyl)ethylenediamine dihydrochloride which coupled to form a red azo dye. The stream was then passed through a 15mm flowcell and the absorbance measured at 540nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50mm flowcell was used for measurement.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms [Bern67] technique. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The reaction product was heated to ~55°C to enhance color development, then passed through a 50mm flowcell and the absorbance measured at 820nm.

Sampling and Data Processing

Nutrient samples were drawn into 45 ml polypropylene, screw-capped "oak-ridge type" centrifuge tubes. The tubes were cleaned with 10% HCl and rinsed with sample 2-3 times before filling. Standardizations were performed at the beginning and end of each group of analyses (typically one cast, up to 36 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low-nutrient seawater matrix. The secondary standards were prepared aboard ship by dilution from primary standard solutions. Dry standards were pre-weighed at the laboratory at ODF, and transported to the vessel for dilution to the primary standard. Sets of 6-7 different standard concentrations were analyzed periodically to determine any deviation from

linearity as a function of concentration for each nutrient analysis. A correction for non-linearity was applied to the final nutrient concentrations when necessary.

After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbances. Computer-produced absorbance readings were checked for accuracy against values taken from a strip chart recording. The data were then added to the cruise database.

Nutrients, reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), in situ salinity, and an assumed laboratory temperature of 25°C.

2497 nutrient samples were analyzed. The pump tubing was changed 2 times.

Standards

Primary standards for silicate (Na2 SiF6)and nitrite ($NaNO_2$)were obtained from Johnson Matthey Chemical Co.; the supplier reported purities of >98% and 97%, respectively. Primary standards for nitrate (KNO3)and phosphate (KH2 PO4)were obtained from Fisher Chemical Co.; the supplier reported purities of 99.999% and 99.999%, respectively. The efficiency of the cadmium column used for nitrate was monitored throughout the cruise and ranged from 99-100%.

No major problems were encountered with the measurements. The temperature of the laboratory used for the analyses ranged from 20.9°C to 25.5°C, but was relatively constant during any one station (±1.5°C).

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D. Dissolved Organic Matter (DOM) Projects

Cruise Participants:

Craig A. Carlson   Associate Professor   University of California Santa Barbara
Stuart Goldberg   Graduate Student   University of California Santa Barbara
Jon Klamberg   Graduate Student   University of California Santa Barbara

Project 1:   Biogeochemistry of Dissolved Organic Matter (DOM)
PIs: D. Hansell, University of Miami
               C. Carlson, University of California, Santa Barbara
Support: NSF

Project Goals

Our goal is to evaluate dissolved organic carbon and nitrogen concentrations over a variety of spatial sections of the repeat hydrography program. Funds were only available to have samples collected on the various repeat hydrography cruises. Subsequent analyses will take place back at UCSB and University of Miami laboratories. During the A22 cruise, A type casts were specifically targeted in order to overlap with the TCO_2 sampling program. Surface DOM samples were also drawn on a number of B stations. Samples were drawn at higher depth resolution for B station located at the beginning of the Sargasso Sea line and in the box around Bermuda.

Depending on the station depth, 24 - 36 Niskin bottles were sampled following directly behind the TCO_2 sample draw. Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) samples were passed through an inline filter holding a combusted GF/F filter attached directly to the Niskin for samples in the top 1000 m of each cast. This was done to eliminated particles > than 0.7 µm from the sample. Previous work has demonstrated that there is no resolvable difference between filtered and unfiltered sample in waters below 1000m at the $µmol/kg^{-1}$ resolution. The samples are stored frozen at - 20°C until analyses. All samples will be analyzed via the high temperature combustion technique on a Shimadzu TOC-V analyzer. DOC data is expected to be complete within approximately 6 months of their return to the laboratory. Additional time may be required to complete DON samples.

Project 2: **Chromophoric DOM: An Ignored PhotoactiveTracer of Geochemical Processes**
PIs: D. Siegel, University of California, Santa Barbara
N. Nelson, University of California, Santa Barbara
C. Carlson, University of California, Santa Barbara
Support: NSF (2/3) and NASA

Project Goals

Our goals are to determine chromophoric dissolved matter (CDOM) distributions over a range of oceanic regimes on meridional sections of the CO_2/CLIVAR Repeat Hydrography survey, and: to quantify and parameterize CDOM production and destruction processes with the goal of mathematically constraining the cycling of CDOM. CDOM is a poorly characterized organic matter pool that interacts with sunlight, leading to the production of climate-relevant trace gases, attenuation of solar ultraviolet radiation in the water column, and an impact upon ocean color that can be quantified using satellite imagery. We believe that the global distribution of CDOM in the open ocean is controlled by microbial production and solar bleaching in the upper water column. We are testing these hypotheses by a combination of field observation and controlled experiments. We are also interested in the deep-sea reservoir of CDOM and its origin and connection to surface waters and are making the first large-scale survey of the abundance of CDOM in the deep ocean.

Activities on A22:

We collected samples of seawater for absorption spectroscopy on one deep ocean cast (24 depths) each day. CDOM is typically quantified as the absorption coefficient at a particular wavelength or wavelength range (we are using 325 nm). We deter mined CDOM at sea by measuring absorption spectra (280-730 nm) of 0.2um filtrates using a liquid waveguide spectrophotometer with a 200cm cell. We concurrently collected samples for prokaryotic abundance and production rates, and carbohydrates to compare the distribution of these quantities to that of DOM (see above)and CDOM. In surface waters (< 300m) we are also estimating bacterial productivity of field samples by measuring the uptake of bromo-deoxyuridine (BrdU) a non radiotracer assay. On selected stations (stations 8, 18, 36, 46, 54, and 68) DNA was collected for further molecular analyses to identify community structure. This in situ prokaryotic community structure will be compared to that which developed in incubation experiments used to assess CDOM production (see below).

Because of the connections to light availability and remote sensing, we collected samples for pigment analysis (HPLC), chlorophyll a (fluorometric), and particulate absorption (spectrophotometric) when possible (ca daily). We also deployed a Satlantic free-fall profiling spectroradiometer (SPMR) to quantify the underwater light field, and we have a Satlantic surface irradiance meter continuously logging the solar spectrum during daylight hours. SPMR casts were launched from the fantail as close to local noon as possible. Details of casts times and locations are presented in table 1. Due to overcast skies SPMR casts were halted on November 9th. Fluorometric chlorophyll analysis were done at sea after 48 hour extractions.

Dates, times and locations of SPMR profiles.

Date	Time (GMT)	Station #	# of Casts
10/25/03	16:07	A22S8	3
10/26/03	16:45	A22S12	2
10/27/03	16:45	Between A22S15 &16	1
10/28/03	16:51	A22S21	2
10/29/03	17:07	A22S25	1
10/30/03	17:41	A22S33	1
11/02/03	18:18	A22S43	2
11/03/03	17:22	A22S46	2
11/05/03	16:25	A22S52	1
11/06/03	17:41	A22S55	1
11/07/03	17:14	A22S57	1

Process Experiments:

At selected stations (subtropical, and tropical stations) we collected extra seawater for a) microbial culture experiments and b) solar bleaching experiments. Water was collected from short casts within the surface 250 m from stations 14, 41, and 54. In these experiments we will examine the rate of CDOM production relative to microbial productivity in culture, and quantify the rate of solar bleaching of CDOM near the surface. Microbial Growth experiments: Three microbial cultures were conducted over the course of the cruise with water collected from 3 special shallow casts to 250 m. Experiments were conducted with water collected from stations 14, 41 and 54. Each experiment comprised of 2 to 4 different treatments of varying organic matter mixture and incubated at in situ temperatures over the course of 5-7 days. The objective was to monitor microbial biomass production, DOM consumption, shifts in the microbial community and temporal variability of CDOM throughout the microbial growth curves. Culture activity was monitored by microscopic direct counts. Preliminary results indicate that all treatments except the unamended control cultures showed significant growth. Further analyses of CDOM, DOM, molecular composition of the prokaryotic community will be conducted at UCSB. Bleaching Experiments: Two bleaching experiments were conducted at with water collected at station 14 and 54. Water was collected from surface and 250m at station14 and 100 m and 250 m at station 54. The water was then passed through an inline 0.2 µm filter. The filtrates were then placed into 24 200 ml quartz tubes and exposed with several solar spectra controlled with various screens. These time series incubations were sampled 6 times over an 8 day period. CDOM scans were completed at sea and will be further processed by N.B. Nelson back at UCSB.

Total Dissolved Inorganic Carbon (DIC)

The DIC analytical equipment was set up in a seagoing container modified for use as a shipboard laboratory. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic

Analyzer) inlet system developed by Ken Johnson (Johnson et al., 1985, 1987, 1993; Johnson, 1992) of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, all carbonate species are converted to CO_2 (gas) by addition of excess hydrogen to the seawater sample, and the evolved CO_2 gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH-. CO_2 is thus measured by integrating the total change required to achieve this. The coulometers were each calibrated by injecting aliquots of pure CO_2 (99.995%) by means of an 8- port valve outfitted with two sample loops. The instruments were calibrated at the beginning and end of each station with a set of the gas loop injections. Secondary standards were run throughout the cruise on each analytical system. These Certified Reference Materials (CRMs) are poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), which have been certified in their shore-based facility to have a known concentration of DIC. Although there were numerous small equipment problems, particularly during the first third of the cruise, the overall accuracy and precision of the at-sea analyses of the CRMs on both instruments was -0.14±0.74 µmol/kg (n=35) and 0.09±1.06 µmol/kg (n=37) for systems 1 and 2, respectively. Preliminary DIC data reported to the database have not yet been corrected to the Batch 61 CRM value, but a more careful quality assurance to be completed shore-side will evaluate the results on a per instrument basis. Samples were drawn from the Niskin-type bottles into cleaned, pre-combusted 500-mL Pyrex bottles using Tygon tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume, and care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5-mL headspace, and 0.2 mL of saturated HgCl2 solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored at room temperature for a maximum of 12 hours prior to analysis. Approximately 1640 samples were analyzed for DIC; full profiles were completed on the 'A' (even numbered) stations, with replicate samples taken from the surface, oxygen minimum, and bottom Niskin-type bottles. At a minimum, replicate surface samples were taken at every 'B' (odd numbered) station, and when time permitted, additional depths were sampled. Approximately 120 replicates were collected in total. The replicate samples were run at different times during the station analysis for quality assurance of the integrity of the coulometer cell solutions. No systematic differences between the replicates were observed and the standard deviation of the differences was approximately 1.2 µmol/kg on both systems.

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SIO Data Processing Notes

Date	Contact	Data Type	Data Status Summary
01/28/04	Diggs	BTL/SUM/DOC	Submitted

Frank,

Thanks for the A20/A22 2003 data along with the PDF documentation and the CTD 2 decibar downcast data.

You may put the files in the following location:

/usr/export/html-public/data/co2clivar/atlantic/a20/a20_2003a

Please let me know once all files have been copied into that directory. -SCD

Date	Contact	Data Type	Data Status Summary
02/09/04	Delahoyde	CTD	Submitted

They're (A20 & A22 ctd data) now in WHP format on whpo:

/usr/export/html-public/data/co2clivar/atlantic/a22/a22_2003a/original/a22-CTD/

and

/usr/export/html-public/data/co2clivar/atlantic/a20/a20_2003a/original/a20-CTD/

Let me know if you have problems.

Date	Contact	Data Type	Data Status Summary
02/12/04	Diggs	DOC	PI list

These data were provided by:

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The data included in these files are preliminary, and are subject to final calibration and processing. They have been made available for public access as soon as possible following their collection. Users should maintain caution in their interpretation and use. Following American Geophysical Union recommendations, the data should be cited as: "data provider(s), cruise name or cruise ID, data file name(s), CLIVAR and Carbon Hydrographic Data Office, La Jolla, CA, USA, and data file date." For further information, please contact one of the parties listed above or whpo@ucsd.edu. Users are also requested to acknowledge the NSF/NOAA-funded U.S. Repeat Hydrography Program in publications resulting from their use.

Date	Contact	Data Type	Data Status Summary
02/04/04	Delahoyde	DOC	Submitted chief scientist's narrative

Located chief scientist's narrative and forwarded it to J Kappa

02/13/04	Delahoyde	DOC	Updated figs for ODF ctd report
02/17/04	Kappa	DOC	Produced PDF and Text reports
			Combined ODF CTD report with Chief Scientist's Cruise Narrative. Produced PDF and TEXT versions.