

# CLIVAR P16N Leg-2

R/V *Thomas G. Thompson*, 3250TT191b

10 – 30 March 2006

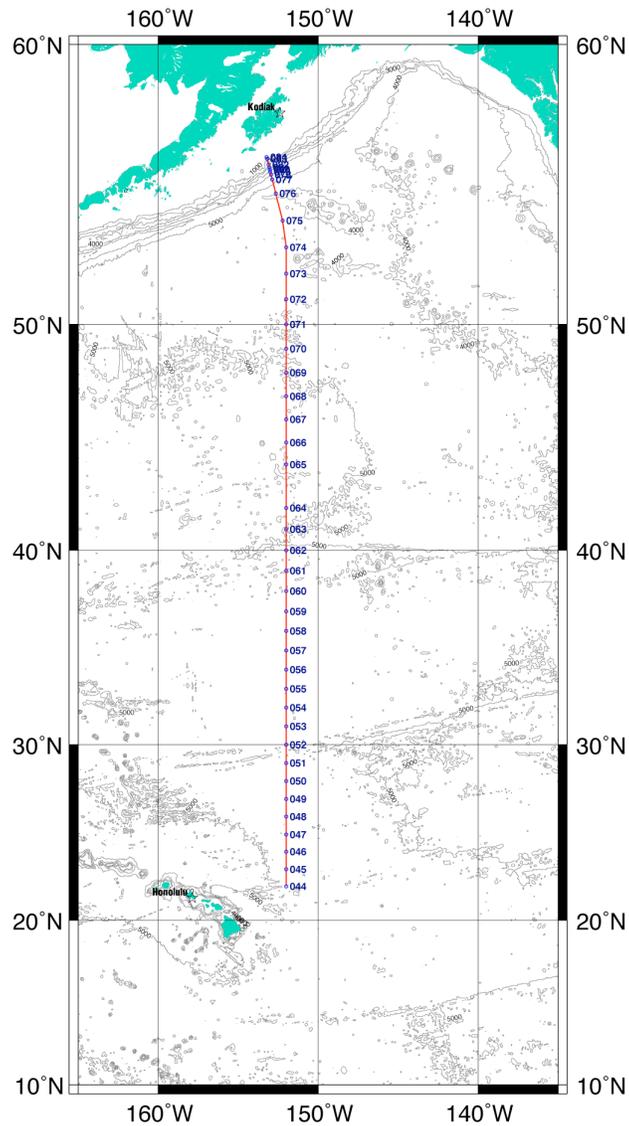
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**Cruise Report**  
**30 March 2006**

## Table of Contents

<b>1.0</b>	<b>Summary.....</b>	<b>2</b>
<b>2.0</b>	<b>Introduction.....</b>	<b>2</b>
<b>3.0</b>	<b>Description of Measurements from Vertical Profiles.....</b>	<b>4</b>
3.1	<i>CTD/Hydrographic Measurements Program.....</i>	<i>4</i>
3.2	<i>LADCP.....</i>	<i>18</i>
3.3	<i>Salinity Measurements.....</i>	<i>19</i>
3.4	<i>Oxygen Measurements.....</i>	<i>20</i>
3.5	<i>Nutrient Measurements.....</i>	<i>21</i>
3.6	<i>CFC Measurements.....</i>	<i>22</i>
3.7	<i>DIC Measurements.....</i>	<i>24</i>
3.8	<i>TA Measurements.....</i>	<i>24</i>
3.9	<i>pH Discrete Measurements.....</i>	<i>25</i>
3.10	<i>Discrete pCO<sub>2</sub>.....</i>	<i>26</i>
3.11	<i>Carbon/Oxygen Isotopes.....</i>	<i>27</i>
3.12	<i>Dissolved Organic Carbon/Dissolved Organic Nutrients .....</i>	<i>28</i>
3.13	<i>CDOM, chlorophyll, bacterial suite.....</i>	<i>28</i>
3.14	<i>Helium-tritium.....</i>	<i>28</i>
3.15	<i>Trace Metals.....</i>	<i>29</i>
3.16	<i>Optical Casts.....</i>	<i>30</i>
<b>4.0</b>	<b>Underway Measurements.....</b>	<b>30</b>
4.1	<i>USF Underway DIC/pCO<sub>2</sub>/pH .....</i>	<i>31</i>
4.2	<i>NOAA/PMEL Underway pCO<sub>2</sub>.....</i>	<i>31</i>
4.3	<i>UM Underway pH.....</i>	<i>31</i>
<b>5.0</b>	<b>Other Measurements.....</b>	<b>32</b>
5.1	<i>Net tows/Pteropods .....</i>	<i>32</i>
5.2	<i>Floats .....</i>	<i>32</i>
<b>6.0</b>	<b>Acknowledgements.....</b>	<b>32</b>
<b>7.0</b>	<b>References.....</b>	<b>32</b>

## 1.0 Summary

The R/V *Thomas G. Thompson* completed the second half of a hydrographic survey in the North Pacific Ocean, nominally along 152°W between 22°S and 55°N, from 10 - 30 March 2006. Thirty-five scientists from 11 academic institutions and two NOAA laboratories participated in the cruise. Full-depth CTD/rosette/LADCP casts were collected every 60 nautical miles. Water samples were collected from the 36-bottle rosette at each station and analyzed for salinity, nutrients, dissolved oxygen, four inorganic carbon parameters, radiocarbon, dissolved organic matter, colored dissolved organic matter, chlorofluorocarbons, helium/tritium, oxygen isotopes, chlorophyll, and a suite of bacterial measurements. Trace metal casts to 1000m were conducted at approximately every other station. Optical profiles were collected once each day. Plankton tows were conducted at about 10 stations at night. Argo floats were deployed at 8 locations. Near surface seawater and atmospheric measurements were also made along the cruise track. No major problems were encountered on the cruise and all major cruise objectives were achieved.

## 2.0 Introduction

The P16N Leg 2 cruise is the second half of a meridional hydrographic section nominally along 152°W in the Pacific Ocean. This cruise is part of a decadal series of repeat hydrography sections jointly funded by the NOAA Office of Global Programs (now the [Climate Program Office](#)) and the [National Science Foundation Division of Ocean Sciences](#) as part of the Climate Variability and Predictability Study (CLIVAR) CO<sub>2</sub> Repeat Hydrography Program (<http://ushydro.ucsd.edu>). The repeat hydrography program focuses on the need to monitor inventories of CO<sub>2</sub>, heat and freshwater and their transports in the ocean. Earlier programs under WOCE and JGOFS have provided baseline observational fields for these parameters. The new measurements will reveal much about the changing patterns on decadal scales. The program will serve as a structure for assessing changes in the ocean's biogeochemical cycle in response to natural and/or man-induced activity.

Thirty-five scientists from 11 academic institutions and two NOAA research laboratories participated in leg 2 (Table 1) covering the northern portion of the P16N line from Honolulu, HI to Kodiak, AK. The R/V *Thomas G. Thompson* departed Honolulu, HI on 10 March 2006 for the start of leg 2. Leg 1 of P16N from Papeete, Tahiti to Honolulu, HI was conducted just prior to leg 2 from 14 February – 3 March 2006. The first station of leg 2 was at 22°N, 152°W. The ship then proceeded north while we conducted a full-depth CTD/rosette/LADCP cast every 60 nautical miles to 55°N, 152°W, where we conducted a series of 8 closely-spaced stations normal to the Alaskan coast. Thirty-six 12L Niskin-type bottles were used to collect water samples from throughout the water column at each station. Each Niskin was sub-sampled on deck for a variety of analyses. Twenty projects were represented on Leg 2 of the cruise (see Table 1). A 1000 m trace metal cast was conducted approximately every other station for a total of 17 trace metal casts. The trace metal casts were conducted at approximately the same locations as the primary profiles and were either before or after the full-depth casts depending on time of day. One optical profile was collected each day on stations that occurred between 10:00 and 14:00 local time. A total of 41 stations were occupied on leg 2 (Table 2). In addition, net tows were conducted at night at about 10 stations either while steaming into a station or upon departure. As part of the Argo program, floats were deployed at about 8 locations usually upon departure from a station. Underway measurements of surface seawater properties (temperature, salinity, pCO<sub>2</sub>, ADCP) and atmospheric concentrations of CO<sub>2</sub>, CFCs, and aerosols were also made along the cruise track. The last station was completed on Wednesday, 29 March, 2006. The cruise ended in Kodiak, AK on 30 March, 2006.

Table 1. Projects and participants on P16N leg 2

Research Project	PI	Leg 2 Participant	Participant E-mail
Chief Scientist		Richard Feely (PMEL)	richard.a.feely@noaa.gov
Co-chief Scientist		Sabine Mecking (APL/UW)	smecking@apl.washington.edu
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DIC Measurements	Christopher Sabine (PMEL) Rik Wanninkhof (AOML) Richard Feely (PMEL)	Dana Greeley (PMEL) Dave Wisegarver (PMEL)	dana.greeley@noaa.gov david.wisegarver@noaa.gov
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pH Discrete Measurements (primary)	Robert Byrne (USF)	Robert Byrne (USF) Zhaohui 'Aleck' Wang (USF) Johan Schijf (USF) Ryan Bell (USF)	byrne@marine.usf.edu awang@marine.usf.edu schijf@marine.usf.edu rbell@marine.usf.edu
Discrete pCO <sub>2</sub>	Rik Wanninkhof (AOML)	Bob Castle (AOML)	robert.castle@noaa.gov
Underway DIC/pCO <sub>2</sub> /pH	Robert Byrne (USF)	Zhaohui 'Aleck' Wang (USF)	awang@marine.usf.edu
Underway pCO <sub>2</sub>	Richard Feely (PMEL)	David Wisegarver (PMEL)	david.wisegarver@noaa.gov
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Oxygen/Argon Measurements	Paul Quay (UW)	Laurie Juranek (UW)	juranek@ocean.washington.edu
Transmissometer on rosette	Wilf Gardner (TAMU)	Chantal Swan (UCSB)	swan@icess.ucsb.edu

## 3.0 Description of Measurements from Vertical Profiles

### 3.1 CTD/Hydrographic Measurements Program

The basic CTD/hydrographic measurements consisted of salinity, dissolved oxygen and nutrient measurements made from water samples taken on LADCP/CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen, transmissometer and fluorometer from CTD profiles. A total of 43 casts (78/1 and 83/1 were aborted) were conducted on leg 2, usually to within 10-20m of the bottom (Table 2). Figure 1 shows the sample locations of the discrete water samples. No major problems were encountered during the operation; however, one station was lost due to bad weather conditions.

#### 3.1.1 Water Sampling Package

CTD/rosette casts were performed with a package consisting of a 36-bottle rosette frame (PMEL), a 36-place pylon (SBE32) and 36 12-liter Niskin type Bullister bottles (PMEL). Underwater electronic components consisted of a Sea-Bird Electronics SBE9plus CTD with dual pumps, dual temperature sensors (SBE3plus), dual conductivity sensors (SBE4), a dissolved oxygen sensor (SBE43), transmissometer (Wetlabs), fluorometer (Wetlabs), load cell (PMEL), altimeter (Simrad), pinger (Benthos) and upward and downward looking LADCPs (RDI) (see table 3).

The CTD was mounted vertically in an SBE CTD frame attached to a plate welded in the center of the rosette frame, under the pylon. The SBE4 conductivity and SBE3plus temperature sensors and their respective pumps were mounted vertically as recommended by SBE. Pump exhausts were attached to inside corners of the CTD cage and directed downward. The transmissometer was mounted horizontally and the fluorometer vertically, attached to a rigid plastic screen that did not impede water flow. The altimeter was mounted on the inside of the bottom frame ring. The RDI LADCPs were mounted vertically on the top and bottom frame rings. The LADCP battery pack was mounted on the bottom of the frame.

The WetLabs UV fluorometer was designed to stimulate and measure fluorescence of CDOM. We were evaluating the use of this instrument to supplement or enhance bottle CDOM measurements, as bottle samples often do not have the depth resolution needed to resolve the observed strong near-surface gradients in CDOM concentration, and on cruises such as this we were not able to sample CDOM on every station. On three of the stations, the fluorometer was covered with duct tape to quantify the background “dark” readings for calibration purposes. This fluorometer was ganged to a WetLabs C-star 660 nm 0.1m pathlength beam transmissometer belonging to Dr. Wilf Gardner, TAMU. The transmissometer developed troubles on the upcast of station 56. The instrument remained on the CTD, but the data beyond this station may not be correctable.

The rosette system was suspended from a UNOLS-standard three-conductor (0.322”) electro-mechanical sea cable using the R/V Thompson’s forward winch on the aft starboard side. This cable replaced the 0.322” cable used on leg 1 (spooled on the aft winch) since it was found that the aft cable had flat spots in the lower layers on the drum which limited the maximum wireout to 5200m. Despite initial concerns that the weight of the 36 bottle rosette would put an extensive amount of stress on the older replacement wire, especially at deep stations and under rough seas, no significant winch or wire problems were encountered on leg 2.

Table 2. P16N leg 2 CTD rosette station locations

Sta	Date	UTC	Latitude	Longitude	Depth <sup>1</sup>	Hab <sup>2</sup>	Wire <sup>3</sup>	Pmax <sup>4</sup>
44	12 Mar 06	1330	22 0.02 N	152 0.02 W	5156	10	5188	5252
45	13 Mar 06	0058	23 0.00 N	152 0.00 W	5397	9	5546	5547
46	13 Mar 06	1347	24 0.00 N	152 0.01 W	5526	10	5628	5700
47	13 Mar 06	2350	24 59.97 N	152 0.01 W	5361	8	5417	5486
48	14 Mar 06	1131	26 0.01 N	152 0.02 W	5292	10	5381	5448
49	14 Mar 06	2114	27 0.00 N	152 0.00 W	5347	9	5396	5463
50	15 Mar 06	0828	28 0.01 N	152 0.01 W	5467	11	5547	5617
51	15 Mar 06	2012	29 0.00 N	152 0.00 W	5508	10	5655	5730
52	16 Mar 06	0708	30 0.00 N	152 0.00 W	5326	10	5417	5480
53	16 Mar 06	1644	30 59.98 N	152 0.02 W	5301	10	5578	5446
54	17 Mar 06	0327	31 59.99 N	152 0.02 W	5194	9	5288	5354
55	17 Mar 06	1342	32 59.98 N	152 0.00 W	5373	10	5451	5522
56	18 Mar 06	0002	33 59.98 N	152 0.03 W	5507	10	5643	5619
57	18 Mar 06	1040	35 0.00 N	152 0.00 W	5652	16	5739	5809
58	18 Mar 06	2107	36 0.00 N	152 0.01 W	5510	14	5575	5662
59	19 Mar 06	1048	36 59.99 N	152 0.00 W	5530	20	5603	5682
60	19 Mar 06	2302	37 59.98 N	152 0.03 W	4930	19	4988	5051
61	20 Mar 06	0953	39 0.00 N	152 0.00 W	5782	13	5862	5948
62	20 Mar 06	2018	40 0.00 N	152 0.00 W	5177	n/a	n/a	5324
63	21 Mar 06	0837	41 0.00 N	152 0.00 W	4995	20	5054	5120
64	21 Mar 06	2008	41 59.98 N	151 59.92 W	5035	21	5099	5166
65	23 Mar 06	0952	44 0.01 N	151 59.97 W	5497	22	5632	5716
66	23 Mar 06	2116	44 59.99 N	151 59.98 W	5282	19	5354	5428
67	24 Mar 06	1006	46 0.00 N	152 0.01 W	5230	20	5343	5416
68	24 Mar 06	1938	47 0.00 N	152 0.01 W	5073	15	5143	5218
69	25 Mar 06	0612	48 0.10 N	151 59.92 W	4896	22	4885	4950
70	25 Mar 06	1628	49 0.01 N	151 59.96 W	4980	10	5043	5110
71	26 Mar 06	0248	50 0.00 N	151 59.97 W	4908	21	4963	5031
72	26 Mar 06	1159	50 59.99 N	151 59.99 W	4951	9	5011	5081
73	26 Mar 06	2238	51 59.99 N	151 59.93 W	5087	12	5130	5201
74	27 Mar 06	1007	53 0.00 N	152 0.00 W	4446	11	4483	4541
75	27 Mar 06	2018	54 0.00 N	152 13.21 W	4393	19	4450	4508
76	28 Mar 06	0637	55 0.00 N	152 39.58 W	4199	19	4122	4266
77	28 Mar 06	1429	55 30.00 N	152 52.82 W	5352	19	5404	5482
78	29 Mar 06	0105	55 40.20 N	152 57.00 W	4954	16	5035	5106
79	29 Mar 06	0713	55 46.19 N	153 0.02 W	3920	13	4048	4095
80	29 Mar 06	1203	55 51.01 N	153 1.81 W	3429	20	3292	3324
81	29 Mar 06	1645	55 55.18 N	153 3.59 W	2422	10	2361	2380
82	29 Mar 06	2147	56 0.60 N	153 5.98 W	1832	20	1795	1809
83	30 Mar 06	0313	56 13.19 N	153 11.38 W	1084	20	1125	1134
84	30 Mar 06	0711	56 16.81 N	153 13.21 W	399	9	391	395

<sup>1</sup>Depth [m] is uncorrected bottom depth from shipboard Knudsen echosounder

<sup>2</sup>Height above bottom [m] at maximum pressure from Simrad altimeter

<sup>3</sup>Wire out [m] of winch cable at maximum pressure

<sup>4</sup>Maximum pressure [db] of CTD package

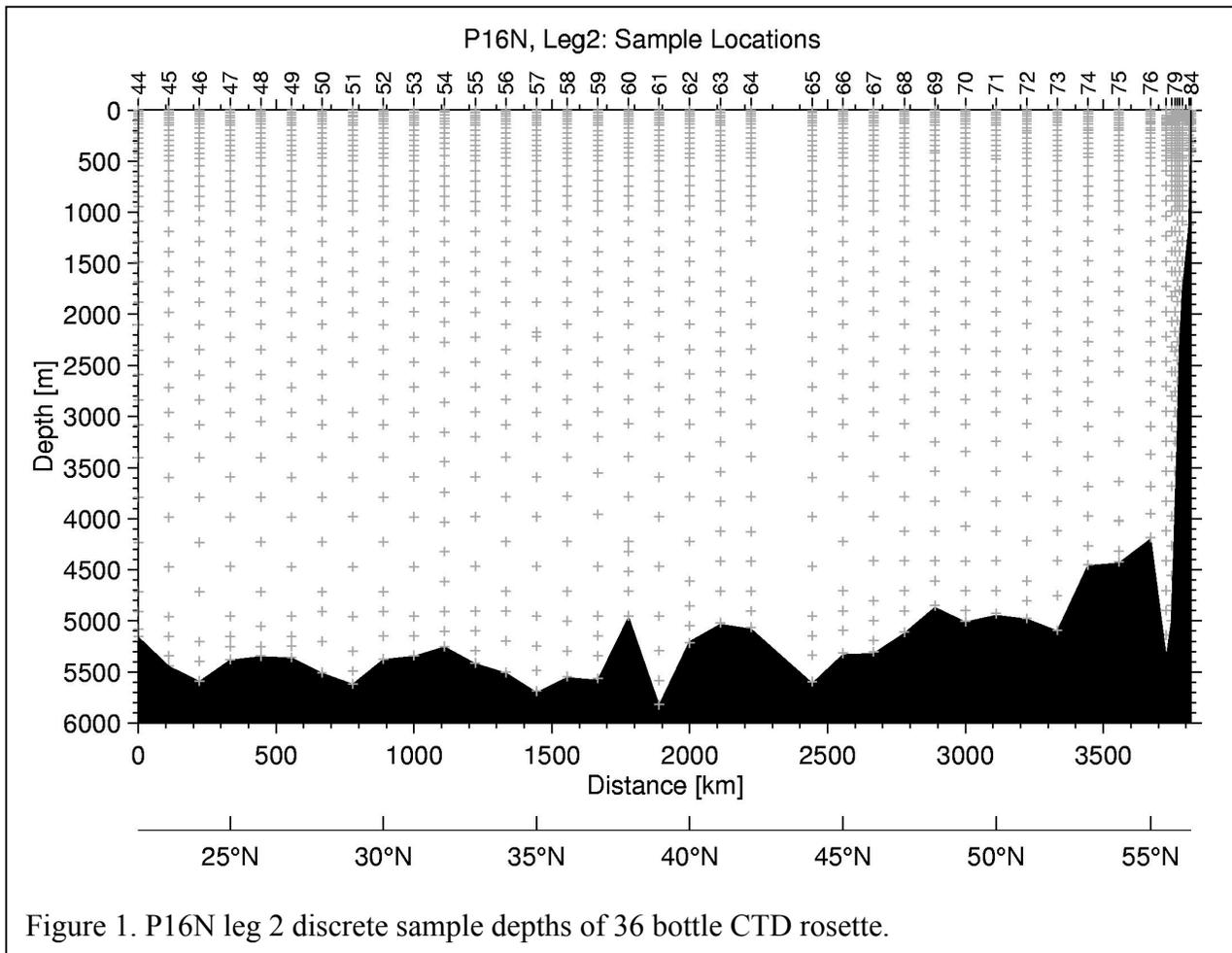


Figure 1. P16N leg 2 discrete sample depths of 36 bottle CTD rosette.

The deck watch prepared the rosette 10-15 minutes prior to each cast. The bottles were cocked and all valves, vents and lanyards were checked for proper orientation. The CTD was powered up about 10 minutes prior to station. Once stopped on station, the data acquisition system in the computer lab was started when directed by the deck watch leader. The rosette was unstrapped from its tiedown location on deck. The pinger was activated and syringes were removed from the CTD intake ports. The winch operator was directed by the deck watch leader to raise the package, the squirt boom and rosette were extended outboard and the package quickly lowered into the water. The package was lowered to at least 10 meters and held there for 1 minute after the sensor pumps had turned on. The winch operator was then directed to bring the package back to the surface (0 winch wireout) and to begin the descent.

At each station the CTD rosette was lowered to within 10-20 meters of the bottom (Table 2) depending on weather conditions and bottom slope, using both the pinger and altimeter to determine the height above bottom. During the upcast the winch operator was directed to stop the winch at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle to insure the package wake had dissipated and the bottles were flushed, then an additional 10 seconds after bottle closure to insure that stable CTD comparison data had been acquired. Once a bottle had been closed, the console operator directed the winch operator to haul in the package to the next bottle stop. Standard sampling depths that were staggered at every other station were used throughout the cruise (Figure 1).

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

Each bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette, which was used for sample identification. No bottles were replaced on this cruise, but various parts of bottles were occasionally changed or repaired.

Routine CTD maintenance included soaking the conductivity and DO sensors in dilute Triton-X solution between casts to maintain sensor stability by eliminating any accumulating biofilms. 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.

The SBE32 carousel frequently didn't release properly causing mistripped bottles. This continual problem worsened toward the end of the cruise, in spite of several repair attempts.

Two rosette casts (78/1 and 83/1) were aborted because of a sudden loss of shipboard power. The casts were brought back on deck and the ship repositioned before deploying the rosette again.

### *3.1.2 Underwater Electronics Packages*

CTD data were collected with a SBE9plus CTD (Table 3). This instrument provided pressure, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), fluorometer (Wetlabs), transmissometer (Wetlabs), load cell (PMEL) and altimeter (Simrad 807) channels. The CTD supplied a standard SBE-format data stream at a data rate of 24 frames/second.

The CTD was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed into one pump circuit and secondary temperature and conductivity into the other. The sensors were deployed vertically. The primary temperature and conductivity sensors (Table 3) were used for reported CTD temperatures and conductivities on all casts except cast 81/1 where biofouling occurred on the sensors. The secondary temperature and conductivity sensors were used in this case as well as for calibration checks otherwise.

The SBE9plus CTD was connected to the SBE32 36-place pylon providing for single-conductor sea cable operation. The sea cable armor was used for ground (return). Power to the SBE9plus CTD (and sensors), SBE32 pylon and Simrad 807 altimeter was provided through the sea cable from the SBE11plus deck unit in the main lab.

### *3.1.3 Navigation and Bathymetry Data Acquisition*

Navigation data were acquired at 1-second intervals from the ship's P-Code GPS receiver by a Linux system that provided a web-page with continuous updates to the ship's position and to the arrival times for upcoming stations throughout the cruise. Bathymetric data were collected using the Ship's 12khz Knudsen echosounder system. These data were logged using the R/V *Thompson's* DAS system as well as a direct connection to the above Linux system about half-way through leg 2. Interruptions to the acquisition of the bathymetric data occurred when the Knudsen system was switched to receive the frequency of the pinger to track the distance between the CTD rosette package and the bottom starting at about a 1000m above the bottom.

Table 3. P16N leg 2 underwater electronics

Sensor	Serial Number	Calib. Date	Calib. Facility
Sea-Bird SBE32 36-place Carousel Water Sampler	S/N 3229650-0431	N/A	N/A
Sea-Bird SBE9plus CTD	S/N 09P8431-0315	N/A	N/A
Paroscientific Digiquartz Press. Sensor	S/N 53960	25-MAY-05	SBE
Sea-Bird SBE3plus Temp. Sensor	S/N 03P-4341 (Primary)	15-NOV-05	SBE
Sea-Bird SBE3plus Temp. Sensor	S/N 03P-4335 (Secondary)	15-NOV-05	SBE
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2887 (Primary)	15-NOV-05	SBE
Sea-Bird SBE4C Conductivity Sensor	S/N 04-3068 (Secondary)	15-NOV-05	SBE
Sea-Bird SBE43 DO Sensor	S/N 43-0664	29-NOV-05	SBE
Sea-Bird SBE43 DO Sensor	S/N 43-0313	03-DEC-05	SBE
Wetlabs CDOM Fluorometer	S/N FLCDRTD-428	09-DEC-05	Wetlabs
Wetlabs CST Transmissometer	S/N CST-327DR	26-JAN-06	Wetlabs
PMEL LoadCell	S/N 1109	N/A	N/A
Simrad 807 Altimeter	S/N 98110	N/A	N/A
Benthos Pinger	S/N 1134	N/A	N/A
RDI WH300 Workhorse LADCP	LDEO #299 (Upward)	N/A	N/A
RDI WH300 Workhorse LADCP	LDEO #149 (Downward)	N/A	N/A

### 3.1.4 CTD Data Acquisition and Rosette Operation

The CTD data acquisition system consisted of an SBE-11plus (V2) deck unit and a networked generic PC workstation running Windows XP. SBE SeaSave software was used for data acquisition and to close bottles on the rosette. CTD deployments were initiated by the console watch after the ship had stopped on station. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. Once the deck watch had deployed the rosette, the winch operator would lower it to 10 meters. The CTD sensor pumps were configured with a 60 second startup delay, and were usually on by this time. The console operator checked the CTD data for proper sensor operation, waited an additional 60 seconds for sensors to stabilize, then instructed the winch operator to bring the package to the surface, pause for 10 seconds, and descend to a target depth (wire-out). The profiling rate was no more than 30m/min to 50m, no more than 45m/min to 200m and no more than 60m/min deeper than 200m varying with sea cable tension and the 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 created a sample log for the deployment which would be later used to record the correspondence between rosette bottles and analytical samples taken. The altimeter channel, CTD pressure, wire-out, pinger and bathymetric depth were all monitored to determine the distance of the package from the bottom, usually allowing a safe approach to within 10 meters. Bottles were closed on the up cast by operating an on-screen control. Bottles were tripped 30 seconds after stopping at the trip location to allow the rosette wake to dissipate and the bottles to flush. The winch operator was instructed to proceed to the next bottle stop 10 seconds after closing bottles to insure that stable CTD data were associated with the trip. After the last bottle was closed, the console operator

directed the deck watch to bring the rosette on deck. Once out of the water, the console operator terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.

### *3.1.5 CTD Data Processing*

Shipboard CTD data processing was performed automatically at the end of each deployment using SIO/ODF CTD processing software. The raw CTD data and bottle trips acquired by SBE SeaSave on the Windows XP workstation were copied onto the Linux database and web server system, then processed to a 0.5 second time series. Bottle trip values were extracted and a 2 decibar down cast pressure series created. This pressure series was used by the web service for interactive plots, sections and CTD data distribution (the 0.5 second time series were also available for distribution). During and after the deployment the data were redundantly backed up to another Linux system. CTD data were examined at the completion of each deployment for clean corrected sensor response and any calibration shifts. As bottle salinity and oxygen results became available, they were used to refine shipboard conductivity and oxygen sensor calibrations. T, S and theta-O<sub>2</sub> comparisons were made between down and up casts as well as between groups of adjacent deployments. Vertical sections of measured and derived properties from sensor data were checked for consistency. Few CTD acquisition and processing problems were encountered during P16N. A clogged bleeder valve in the primary pump circuit led to using the upcasts of 50/1 and 51/1. DO sensor offsets appearing on the downcasts during unscheduled winch stops on 60/2 and 64/1 led to replacement of the DO sensor prior to 67/1, and filtering-out the offsets. Cast 78/1 and 83/1 were aborted due to shipwide power failures. Biofouling of the primary sensors on 81/1 led to using T2 and C2 sensors for reported T and C data, and filtering the downcast O<sub>2</sub> data. A total of 43 casts were made (including 2 aborted casts) using the 36-place CTD/LADCP rosette.

### *3.1.6 CTD Sensor Laboratory and Shipboard Calibrations*

Laboratory calibrations of the CTD pressure, temperature, conductivity and dissolved oxygen sensors were performed prior to P16N. Serial numbers and calibration dates are listed in table 3. In-situ salinity and dissolved O<sub>2</sub> samples collected during each cast were used in addition to calibrate the conductivity and dissolved O<sub>2</sub> sensors.

Calibration coefficients derived from the calibration of the Paroscientific Digiquartz pressure transducer were applied to raw pressures during each cast. Residual pressure offsets (the difference between the first and last submerged pressures) were examined to check for calibration shifts. All were < 0.7dbar, and the sensor exhibited < 0.2 dbar offset shift over the period of use. No additional adjustments were made to the calculated pressures.

### *3.1.7 CTD Shipboard Calibration Procedures*

CTD 09P8431-0315 was used for all P16N casts (Table 3). The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE. The primary temperature and conductivity sensors (T1 & C1) were used for all reported CTD data on all casts except 81/1, the secondary sensors (T2 & C2) serving as calibration checks. In-situ salinity and dissolved O<sub>2</sub> check samples collected during each cast were used to calibrate the conductivity and dissolved O<sub>2</sub> sensors.

### *3.1.8 CTD Pressure*

The Paroscientific Digiquartz pressure transducer (S/N 53960) was calibrated in May2005 at SBE (Table 3). Calibration coefficients derived from the calibration were applied to raw pressures during each cast. Residual pressure offsets (the difference between the first and last

submerged pressures) were examined to check for calibration shifts. All were  $< 0.7\text{db}$ , and the sensor exhibited  $< 0.2\text{ db}$  offset shift over the period of use. No additional adjustments were made to the calculated pressures.

### 3.1.9 CTD Temperature

A single primary temperature sensor (SBE 3, S/N 03P-4341) and secondary temperature sensor (SBE 3, S/N 03P-4335) served the entire cruise (Table 3). Calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary temperatures during each cast. Calibration accuracy was monitored by comparing the primary and secondary temperatures at each rosette trip. Calibration accuracy was examined by tabulating T1-T2 over a range of pressures and temperatures (bottle trip locations) for each cast. No significant temperature or pressure slope was evident. These comparisons are summarized in Figure 2 for all stations from legs 1 and 2. Since the primary and secondary conductivity sensors had been stable, analysis of the differences between salinity calculated from sensor pairs with bottle salinities identified the drifting temperature as T2.

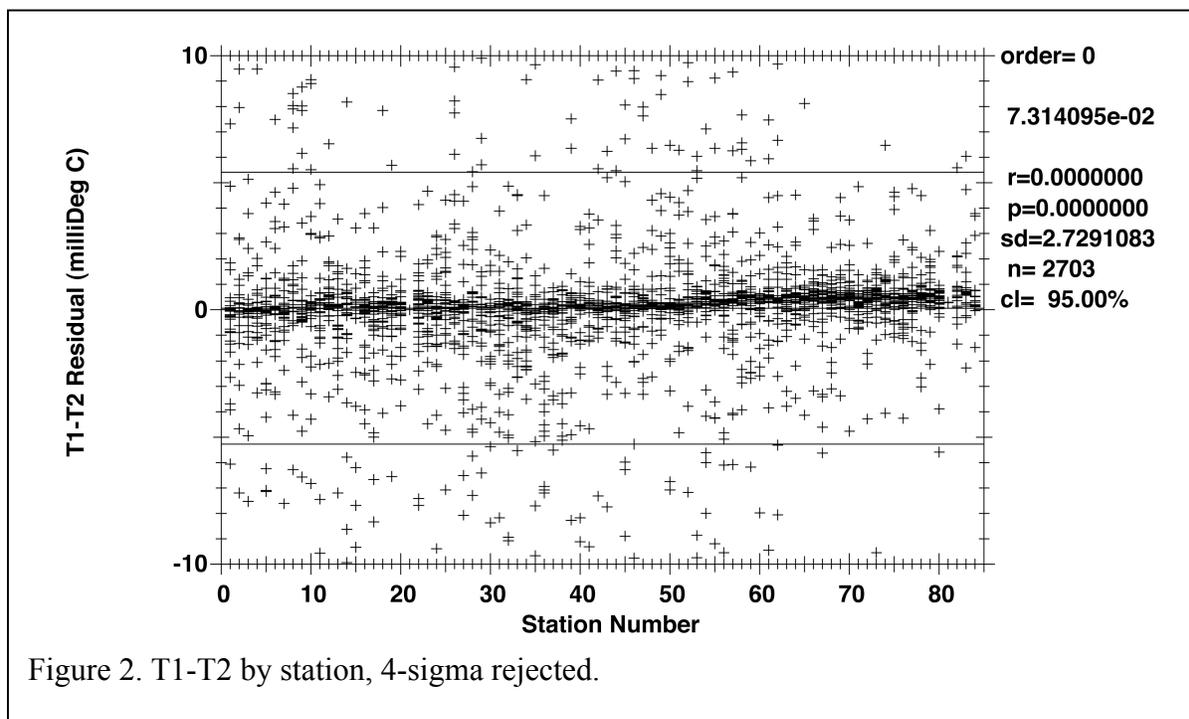


Figure 2. T1-T2 by station, 4-sigma rejected.

The 95% confidence limit for the mean of the differences is  $\pm 0.0073^{\circ}\text{C}$ . The variance is relatively high in spite of the small spatial separation of the sensors ( $< 0.5$  meters) because of package wake effects.

### 3.1.10 CTD Conductivity

A single primary conductivity sensor (SBE 4, S/N 04-2887) and secondary conductivity sensor (SBE 4, S/N 04-3068) served the entire leg (Table 3). Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities. Comparisons between the primary and secondary sensors and between each of the sensors to check sample conductivities (calculated from bottle salinities) were used to derive conductivity corrections. To reduce the contamination of the comparisons by package wake, differences between primary and secondary temperature sensors were used as a metric of

variability and used to qualify the comparisons. The coherence of this relationship is illustrated in Figure 3.

Neither of the sensors exhibited a secondary pressure response. The uncorrected comparison between the primary and secondary sensors is shown in Figure 4, and between C2 and the bottle salinities in Figure 5 for legs 1 and 2. Note that the bottle salinities were unusable for check sample purposes due to analytical temperature problems for casts 1/2-7/1.

Since C2 showed no significant conductivity slope or offset relative to bottle conductivities, and since the comparison to C1 showed only minor ( $<0.001\text{mS/cm}$ ) drift and shifts), C1 was calibrated to C2. No correction was made to C2. The comparison of the primary and secondary conductivity sensors by cast after applying shipboard corrections is summarized in Figure 6.

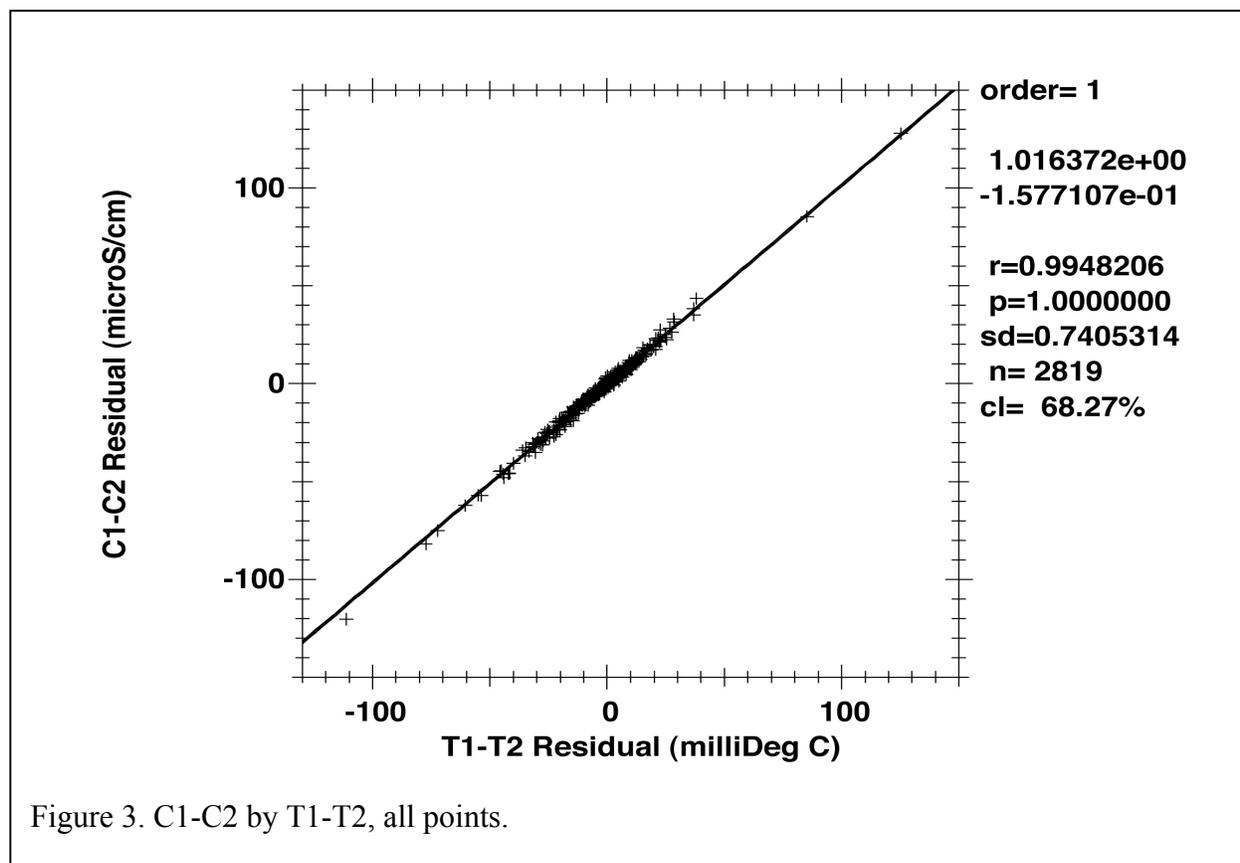


Figure 3. C1-C2 by T1-T2, all points.

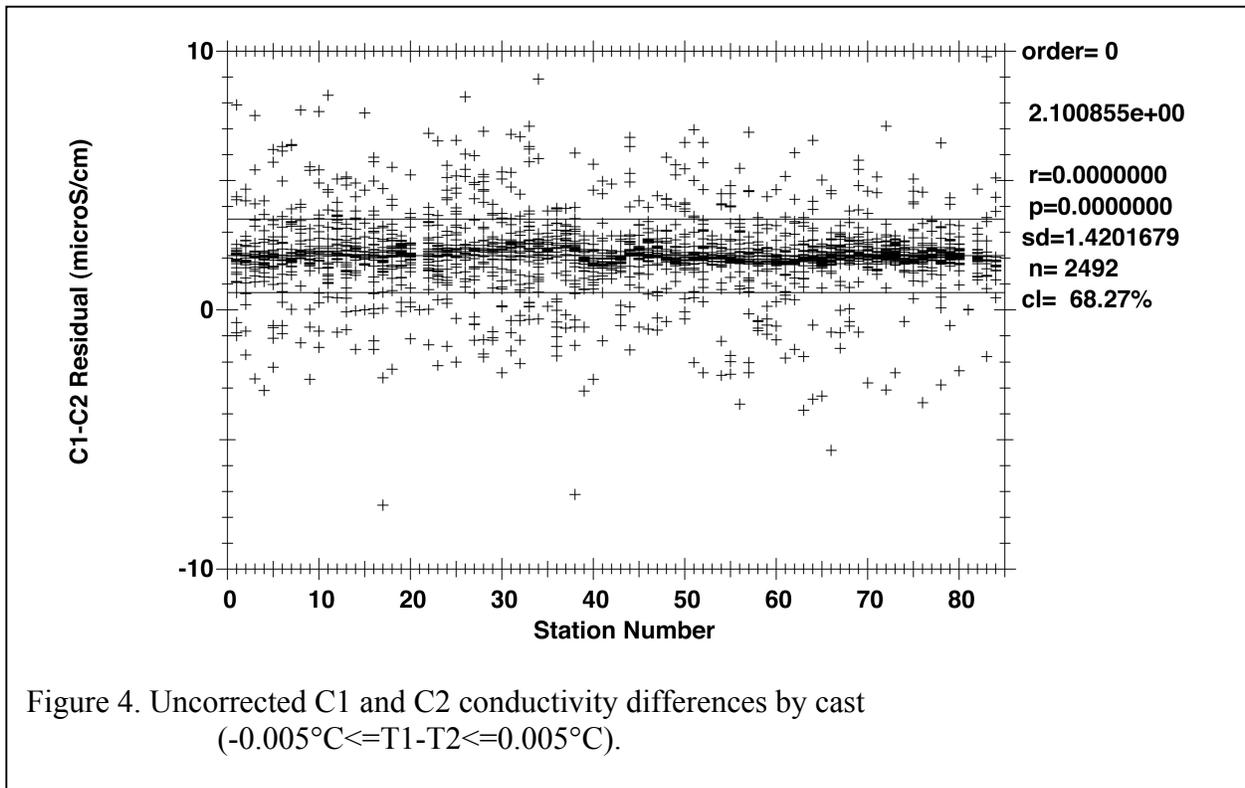


Figure 4. Uncorrected C1 and C2 conductivity differences by cast  
 $(-0.005^{\circ}\text{C} \leq T1-T2 \leq 0.005^{\circ}\text{C})$ .

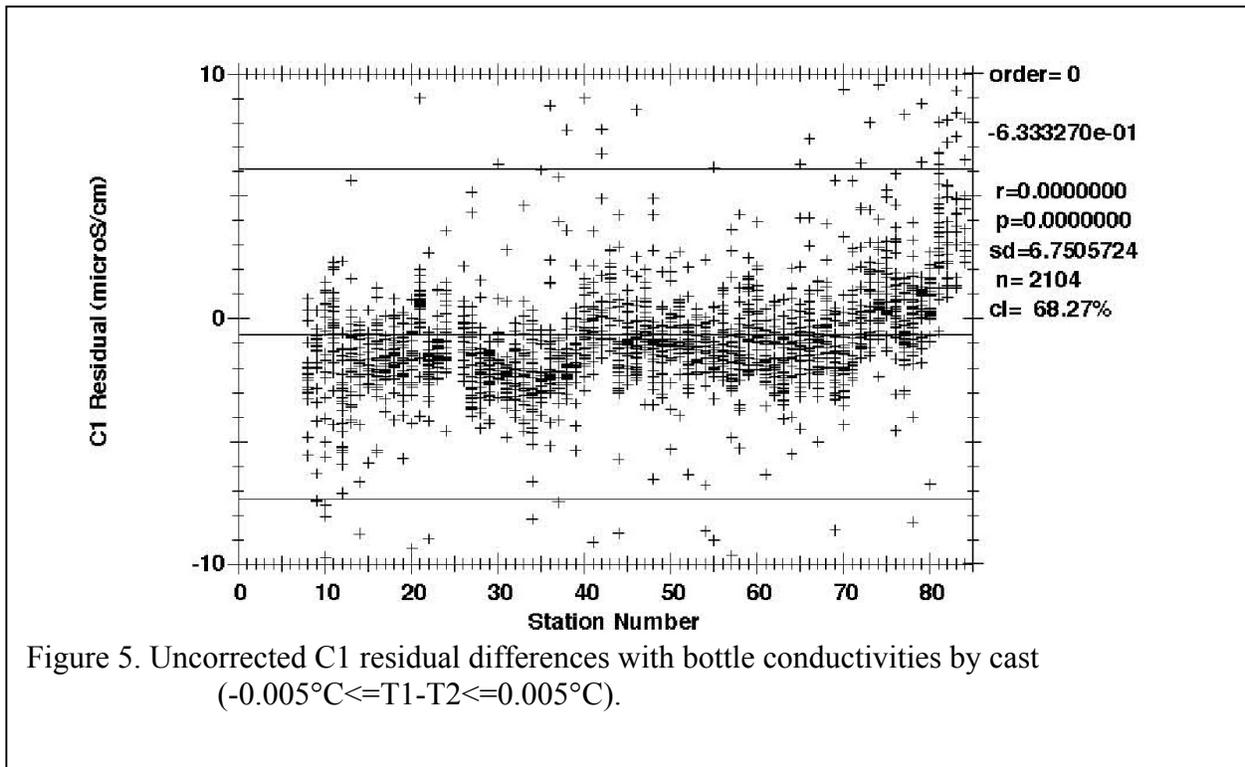
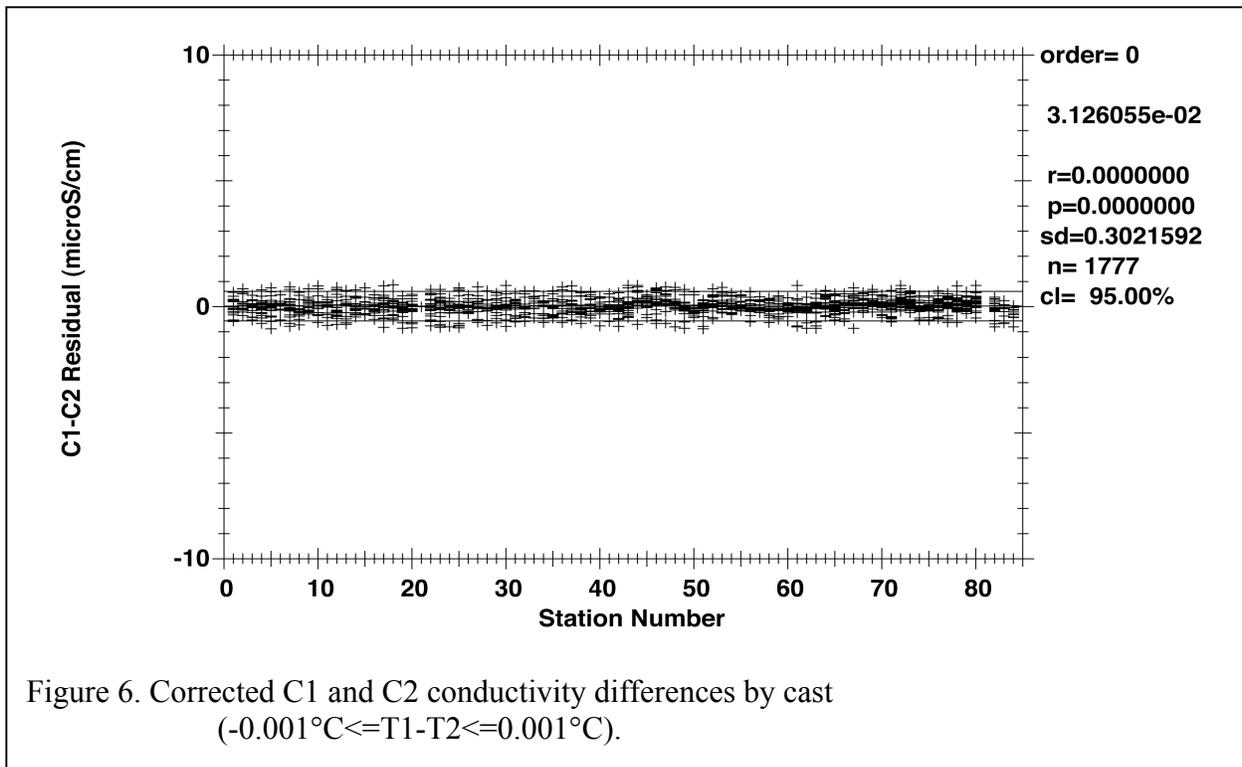
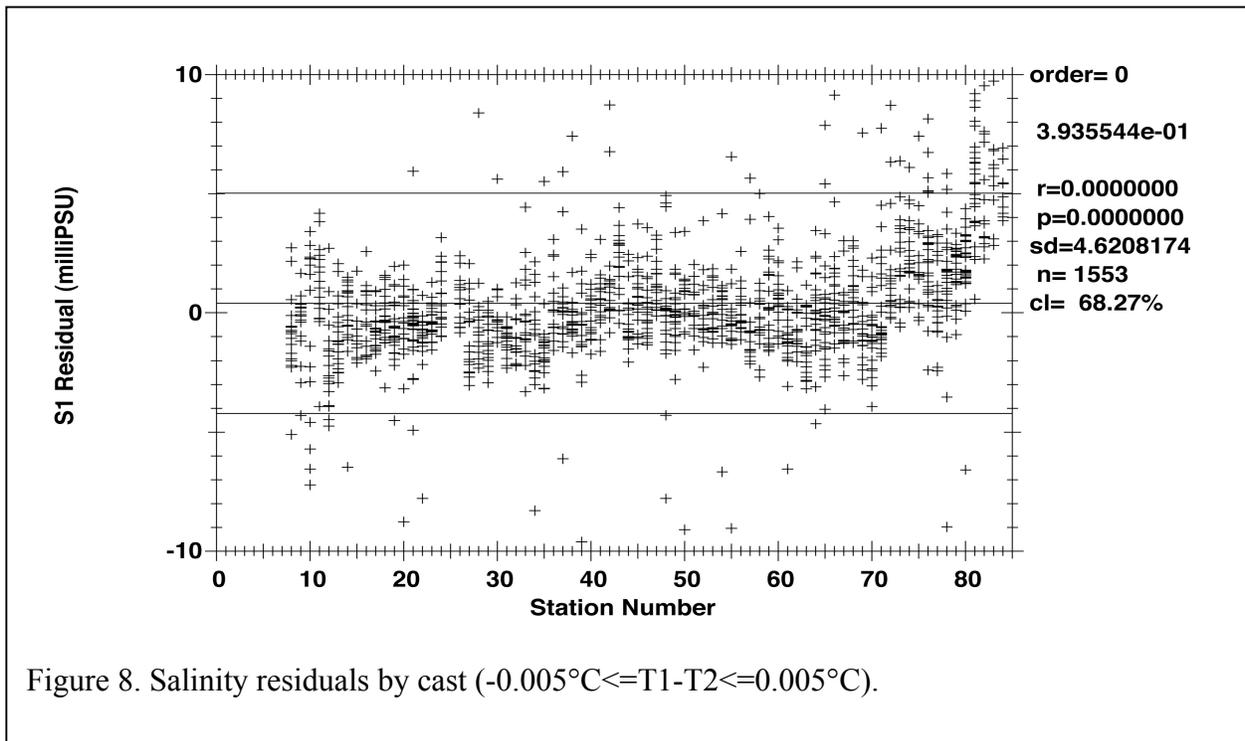
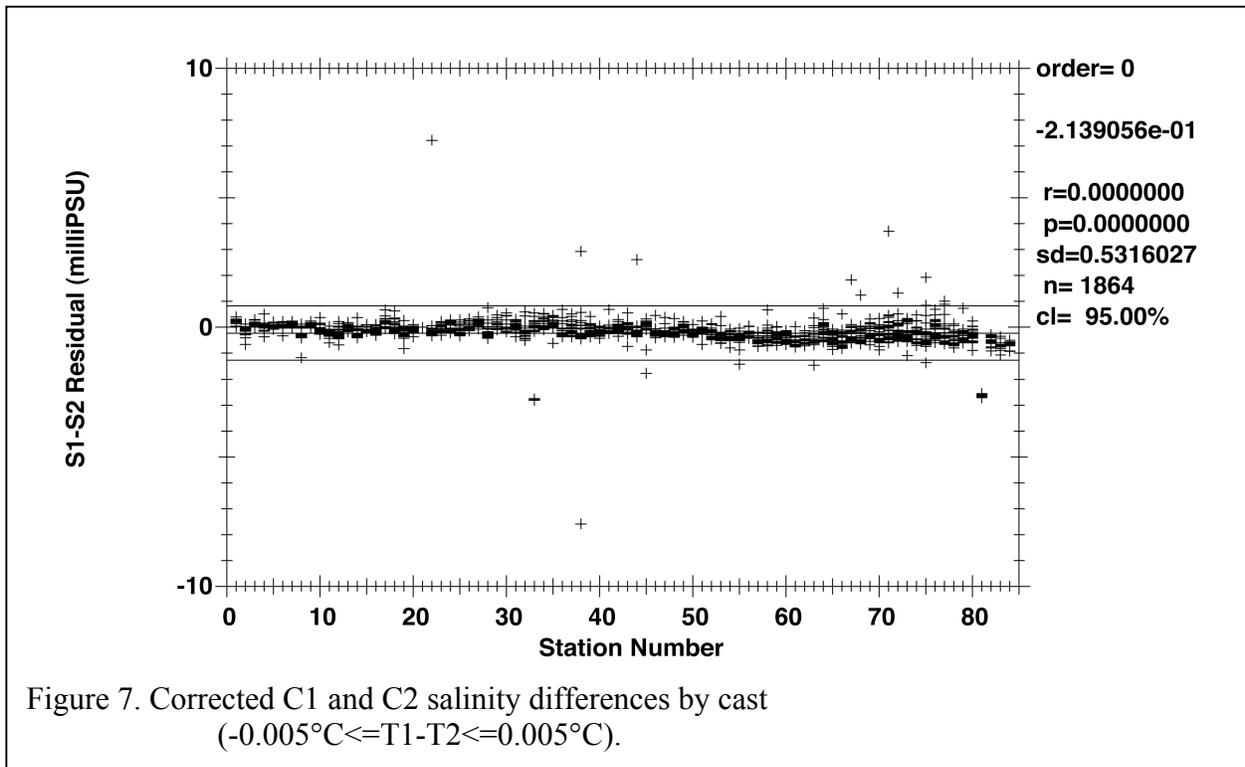


Figure 5. Uncorrected C1 residual differences with bottle conductivities by cast  
 $(-0.005^{\circ}\text{C} \leq T1-T2 \leq 0.005^{\circ}\text{C})$ .



C1 was calibrated against C2 on the previous leg, and the sensors continued to track to within  $\pm 0.74$  mS/cm over both legs. No changes in conductivity slopes or secondary responses were noted during leg 2. The bottle salinities are problematic after cast 71/1. The salinometer dial setting was changed from 525 to 545 and standard drift rates increased sharply for subsequent runs. It appears that the lab temperature was fluctuating, and the standard dial setting was changed to attempt to compensate for the fluctuation. C1-C2 differences indicate that these check samples have a mean offset of +0.002. Salinities are reported using the Practical Salinity Scale of 1978 (PSS-78). Salinity residuals after applying shipboard T1/C1 corrections are summarized in Figures 7 and 8. Figures 7 and 8 represent estimates of the salinity accuracy on P16N.



A single SBE43 dissolved O<sub>2</sub> (DO) sensor was used for most of leg 2 (S/N 43-0663). The sensor was plumbed into the primary T1/C1 pump circuit after C1. The sensor was replaced prior to cast 67/1 against a different SBE43 DO sensor (S/N 43-0313) because of offsets that began to appear after unscheduled winch stops on the downcasts of 60/2 and 64/1. The DO sensors were calibrated to dissolved O<sub>2</sub> check samples at bottle stops by calculating CTD

dissolved O<sub>2</sub> then minimizing the residuals using a non-linear least-squares fitting procedure. The fitting procedure determined the calibration coefficients for the sensor model conversion equation, and was accomplished in stages. The time constants for the exponential terms in the model were first determined for each sensor. These time constants are sensor-specific but applicable to an entire cruise. Next, casts were fit individually to check sample data. The resulting calibration coefficients were then smoothed and held constant during a refit to determine sensor slope and offset. Standard and blank values for bottle oxygen data were smoothed and the bottle oxygen recalculated prior to the final fitting of CTD oxygen. The residuals are shown in Figures 9-11.

The standard deviations of 5.63 uM/kg for all oxygens and 1.29 uM/kg for low-gradient oxygens are only presented as general indicators of goodness of fit. ODF makes no claims regarding the precision or accuracy of CTD dissolved O<sub>2</sub> data.

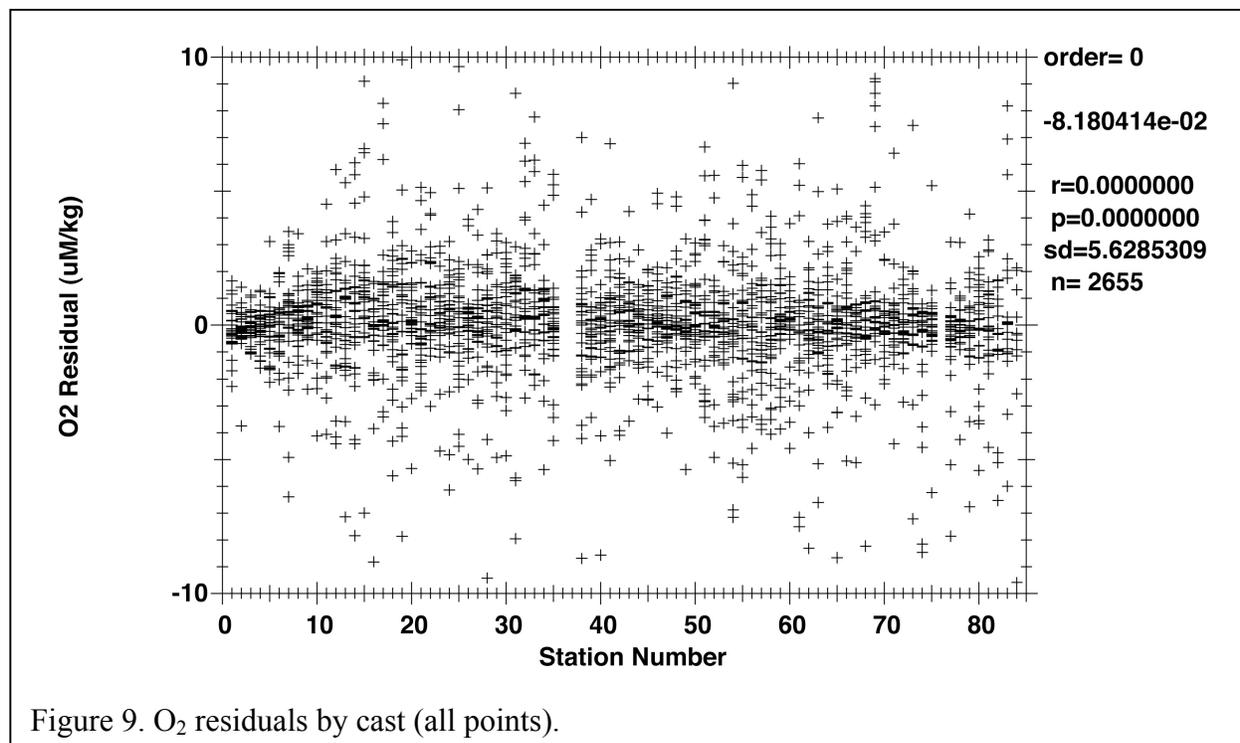
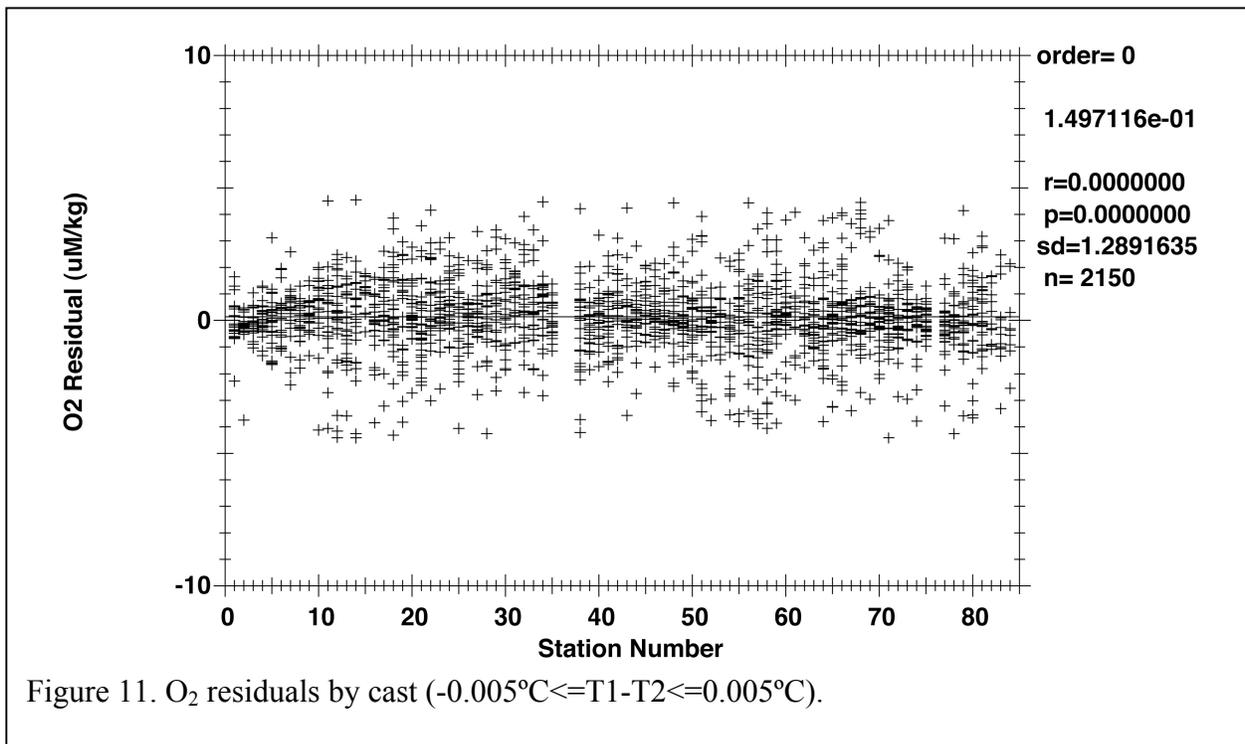
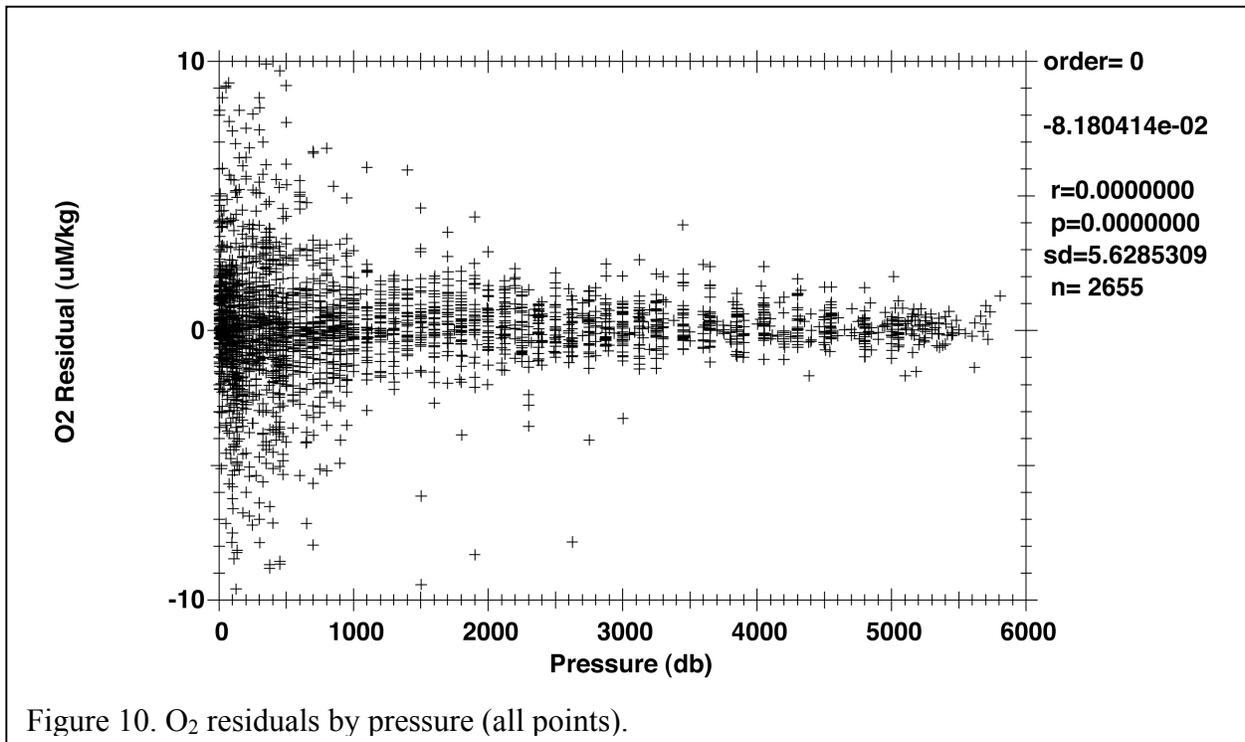


Figure 9. O<sub>2</sub> residuals by cast (all points).



The general form of the ODF O<sub>2</sub> conversion equation for Clark cells follows Brown and Morrison (1978), Millard (1982) and Owen and Millard (1985). ODF models membrane and sensor temperatures with lagged CTD temperatures and a lagged thermal gradient. In-situ pressure and temperature are filtered to match the sensor response. Time-constants for the pressure response  $\text{Tau}_p$ , two temperature responses  $\text{Tau}_T$ s and  $\text{Tau}_T$ f, and thermal gradient response  $\text{Taud}_T$  are fitting parameters. The thermal gradient term is derived by low-pass

filtering the difference between the fast response ( $T_f$ ) and slow response ( $T_s$ ) temperatures. This term is SBE43-specific and corrects a non-linearity introduced by analog thermal compensation in the sensor. The  $O_c$  gradient,  $dO_c/dt$ , is approximated by low-pass filtering 1st-order  $O_c$  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,  $\tau_{og}$ , is a fitting parameter. Dissolved  $O_2$  concentration is then calculated:

$$O_2(\text{ml/l}) = [c_1 * O_c + c_2] * f_{\text{sat}}(S, T, P) * e^{-(c_3 * P + c_4 * T_f + c_5 * T_s + c_6 * dO_c/dt)} \quad (1)$$

where:

$O_2(\text{ml/l})$	= Dissolved $O_2$ concentration in ml/l;
$O_c$	= Sensor current ( $\mu\text{amps}$ );
$f_{\text{sat}}(S, T, P)$	= $O_2$ saturation concentration at S, T, P (ml/l);
S	= Salinity at $O_2$ response-time;
T	= Temperature at $O_2$ response-time ( $^{\circ}\text{C}$ );
P	= Pressure at $O_2$ response-time (decibars);
Pl	= Low-pass filtered pressure (decibars);
$T_f$	= Fast low-pass filtered temperature ( $^{\circ}\text{C}$ );
$T_s$	= Slow low-pass filtered temperature ( $^{\circ}\text{C}$ );
$dO_c/dt$	= Sensor current gradient ( $\mu\text{amps/secs}$ );
$dT$	= low-pass filtered thermal gradient ( $T_f - T_s$ ).

### 3.1.11 Bottle Sampling

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

- o CFCs
- o He
- o  $O_2$
- o Ar and  $O_2$  isotopes
- o  $p\text{CO}_2$
- o Dissolved Inorganic Carbon (DIC)
- o pH
- o Total Alkalinity
- o C-13/C-14
- o Dissolved Organic Carbon (DOC)
- o CDOM
- o Bacterial Suite
- o Salinity
- o Nutrients
- o Tritium
- o PIC/POC

Water samples for analyses of dissolved  $\text{SF}_6$  and pteropods were collected at a few stations throughout the cruise. These samples were collected to support laboratory experiments onboard the ship.

The correspondence between individual sample containers and the rosette bottle position (1-36) 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 management.

### *3.1.12 Bottle Data Processing*

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-8.0.3) run on a Linux system. A web service (OpenAcs-5.2.2 and AOLServer-4.0.10) 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 (and any diagnostic comments) was 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) (Joyce and Corry, 1994). Various consistency checks and detailed examination of the data continued throughout the cruise.

## **3.2 LADCP**

Two RDI 300-kHz Acoustic Doppler Current Profilers (ADCPs) were mounted on the CTD frame with one transducer pointing downward and the other pointing upward. They were powered by a "DeepSea Power and Light " rechargeable sealed lead-acid battery pack. The battery was charged and the instruments activated before each cast. While on deck, the ADCPs were connected to a Macintosh computer that handled both instrument setup and data processing. Both ADCPs were set up to record single-ping beam-coordinate velocity ensembles in 10m bins. Between casts, the data from the ADCPs were downloaded and processed using the LDEO (Columbia University) processing software (Thurnherr, 2006). The processing combined CTD, GPS, and shipboard ADCP data with the data from the lowered ADCPs to produce both shear and inverse solutions of absolute velocities. The results showed weak currents in most areas, with a strong eastward surface current at station 49 (Figure 12). The strongest flow was recorded in the Alaska current, which reached a westward velocity maximum of 60 cm/s at station 80. This current was noticeable in the data from stations 78 through 82 (Figure 12).

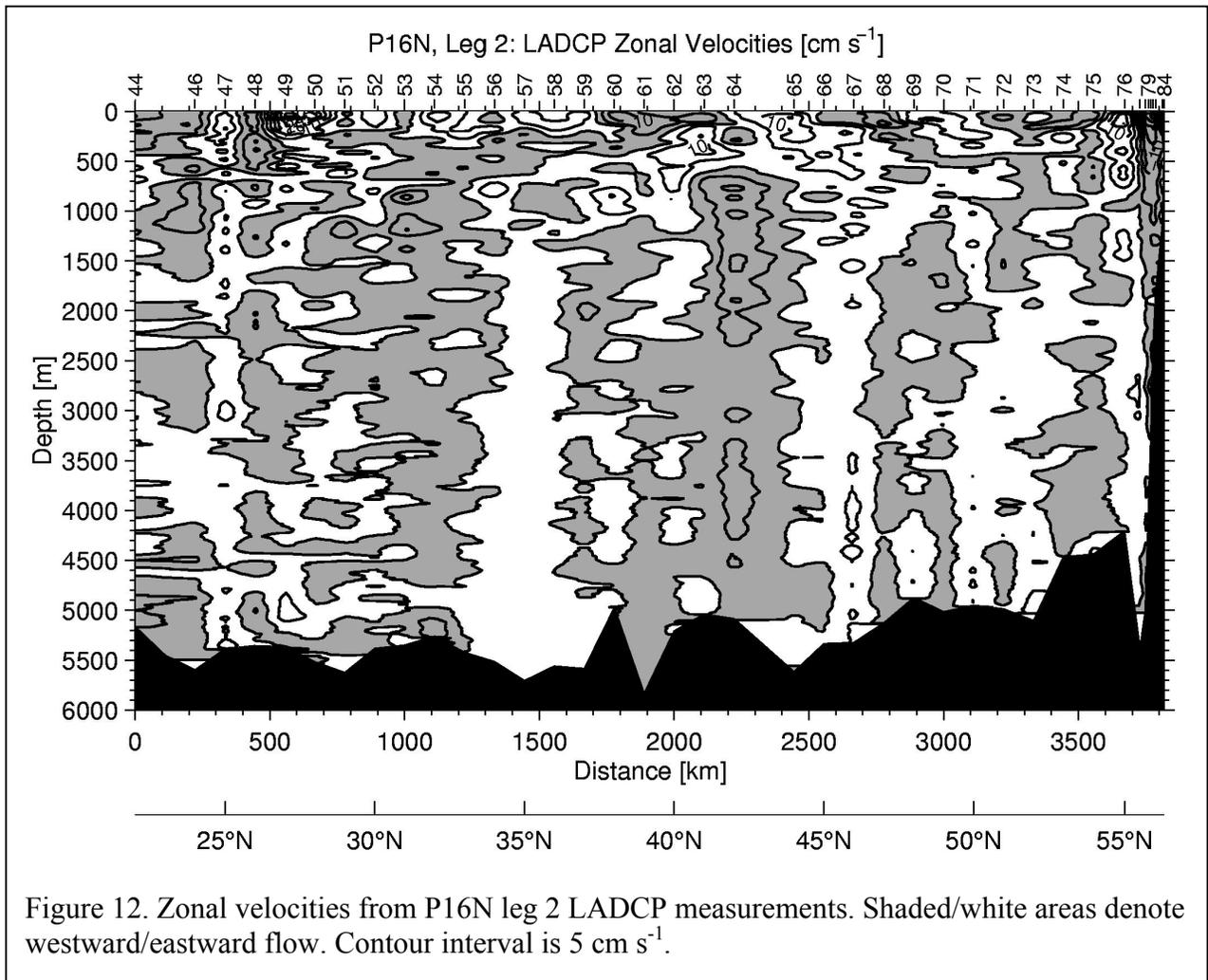


Figure 12. Zonal velocities from P16N leg 2 LADCP measurements. Shaded/white areas denote westward/eastward flow. Contour interval is  $5 \text{ cm s}^{-1}$ .

### 3.3 Salinity Measurements

A single Guildline Autosol Model 8400A salinometer (S/N 48-266), located in a container lab on the aft deck, was used for all salinity measurements. The salinometer was modified by SIO/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 ( $24^{\circ}\text{C}$ ). The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 6-8 hours after collection. The salinometers were standardized for each group of analyses (usually 1-2 casts, up to  $\sim 40$  samples) using at least two fresh vials of standard seawater per group. Salinometer measurements were made by computer, the analyst prompted by the software to change samples and flush.

3250 salinity measurements were made and approximately 200 vials of standard water (SSW) were used. 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 sample collection, inserts were inspected for proper fit and loose inserts 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 (UNESCO, 1981) was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database.

The temperature in the salinometer laboratory varied from 21 to 24°C, during the cruise. The air temperature change during any particular run varied from -1.2 to +2.2°C. Insufficient sample equilibration times were sometimes a problem as was having to collect samples on deck. The salinometer standard dial setting which had been constant for most of the cruise was changed from 525 to 545 after cast 71/1 and the standard drift rates increased sharply for subsequent runs. These runs show a mean offset of +0.002 relative to calibrated CTD conductivity. The estimated accuracy of bottle salinities run at sea is usually better than +/-0.002 relative to the particular standard seawater batch used. The 95% confidence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-145 was +/-0.010 for all salinities, and +/-0.0035 for salinities collected in low gradients. IAPSO Standard Seawater Batch P-145 was used to standardize all casts.

### ***3.4 Oxygen Measurements***

Samples were drawn from Niskin bottles into calibrated 140 ml iodine titration flasks using Tygon tubing with a Silicone adapted that fit over the petcock to avoid contamination of DOM samples. Bottles were rinsed twice and filled from the bottom, overflowing three volumes while taking care not to entrain any bubbles. The draw temperature was taken using a digital thermometer with a flexible thermistor probe that was inserted into the flask while the sample was being drawn. These temperatures were used to calculate  $\mu\text{mol kg}^{-1}$  concentrations, and a diagnostic check of bottle integrity. One-ml of  $\text{MnCl}_2$  and one-ml of  $\text{NaOH/NaI}$  were added using a Repipetor, the flask stoppered and shaken. DIW was added to the neck of each flask to create a water seal. The flasks were stored in the lab in plastic totes at room temperature for 1-2 hours before analysis. Thirty-six samples plus 1-2 duplicates were drawn from each station except the shallow coastal stations where only 15-28 samples were drawn. Total number of samples collected was 1536; total number of samples flagged after initial shipboard reduction of quality control: Questionable (QC=3): Bad (QC=4): Not reported (QC=5).

Dissolved oxygen analyses were performed with a MBARI-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365 nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by a 386 PC running the Oxygen program written by Gernot Friedrich. Thiosulfate was dispensed by a Dosimat 665 fitted with a 5.0 ml buret. The whole-bottle titration technique of Carpenter (1965) with modifications by Culberson et al. (1991) was used, but with a more dilute solution of thiosulfate ( $10 \text{ g L}^{-1}$ ). Standard curves were run each day. The reagent blank was taken to be the intercept of the standard curve and compared to the reagent blank determined by the convention two titration method. The autotitrator and Dosimat generally performed well. Endpoints were noted to be noisy during periods of particularly bad weather. Thiosulfate molarities were calculated from titration of the standard iodate solution dispensed using a calibrated Wheaton bottle top dispenser and corrected to 20°C. The 20°C molarities were plotted versus time and were reviewed for possible problems. Blank volumes and thiosulfate molarities were smoothed (linear fits) at the end of the cruise and the oxygen values recalculate. Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at AOML and corrected for the buoyancy factor. The Dosimat and Wheaton positive displacement dispenser used for dispensing the  $\text{KIO}_3$  were calibrated in the same way. Liquid potassium

iodate standard solution with a normality of 0.0100 was prepared and bottled at AOML prior to the cruise. A single batch was used during the cruise.

In addition to the photometric end-point technique, samples from several stations during leg 2 were analyzed using an amperometric detection method (Culberson and Huang, 1987) for comparison. This was done to test amperometric detection method for future standard use. The difference between the two techniques was on average  $<1 \mu\text{mol kg}^{-1}$ .

### **3.5 Nutrient Measurements**

Nutrient samples were collected from the Niskin bottles in acid washed 25-ml linear polyethylene bottles after three complete seawater rinses and analyzed within 1 hour of sample collection. Measurements were made in a temperature-controlled laboratory ( $20 \pm 2^\circ\text{C}$ ). Concentrations of nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ) and silicic acid ( $\text{H}_4\text{SiO}_4$ ) were determined using an Alpkem Flow Solution Auto-Analyzer aboard the ship. During this cruise approximately 3000 samples were analyzed along with their standards and baseline samples. The following analytical methods were employed:

#### *3.5.1 Nitrate and Nitrite*

Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm (Zhang et al., 1997). Samples for nitrate analysis were passed through a home made cadmium column (Zhang et al., 2000), which reduced nitrate to nitrite and the resulting nitrite concentration was then determined as described above. Nitrate concentrations were determined from the difference of nitrate + nitrite and nitrite.

#### *3.5.2 Phosphate*

Phosphate in the samples was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex a temperature of  $55^\circ\text{C}$ . This complex was subsequently reduced with hydrazine to form a blue complex and the absorbance was measured at 815 nm (Zhang et al., 2001).

#### *3.5.3 Silicic Acid*

Silicic acid in the sample was analyzed by reacting the aliquote with molybdate in a acidic solution to form molybdosilicic acid. The molybdosilicic acid was then reduced by  $\text{SnCl}_2$  to form molybdenum blue (Gordon et al., 1995). The absorbance of the molybdenum blue was measured at 660 nm.

#### *3.5.4 Calibration and Standards*

Stock standard solutions were prepared by dissolving high purity standard materials ( $\text{KNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{SiF}_6$ ) in deionized water. Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. The low nutrient seawater used for the preparation of working standards, determination of blank, and wash between samples was filtered seawater obtained from low-nutrient Pacific surface waters. Standardizations were performed prior to each sample run with working standard solutions. Replicates were usually collected at the deepest Niskin bottle from each cast. The relative standard deviation from the results of these replicate samples was used to estimate the overall precision obtained by the sampling and analytical procedures. The precisions of these samples were  $0.04 \mu\text{mol/kg}$  for nitrate,  $0.01 \mu\text{mol/kg}$  for phosphate and  $0.1 \mu\text{mol/kg}$  for silicic acid.

### 3.6 CFC Measurements

Samples for the analysis of dissolved CFC-11, CFC-12, and CFC-113 were drawn from 960 of the 1300 water samples collected during the expedition. Specially designed 12 liter water sample bottles were used on the cruise to reduce CFC contamination. These bottles have the same outer diameter as standard 10 liter Niskin bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples for CFC analysis were the first samples drawn from the 12-liter bottles. Care was taken to coordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, helium-3, dissolved oxygen, alkalinity and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 12-liter bottles into 100 ml precision glass syringes equipped with 3-way plastic stopcocks. The syringes were immersed in a holding bath of freshwater until analyzed.

For air sampling, a ~100 meter length of 3/8" OD Dekaron tubing was run from the main laboratory to the bow of the ship. A flow of air was drawn through this line into the CFC van 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 (100 ml min<sup>-1</sup>) of the compressed air to be directed to the gas sample valves of the CFC and SF<sub>6</sub> analytical systems, while the bulk flow of the air (>7 l min<sup>-1</sup>) was vented through the back pressure regulator. Air samples were generally analyzed when the ship was on station and the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. The pump was run for approximately 45 minutes prior to analysis to insure that the air inlet lines and pump were thoroughly flushed. The average atmospheric concentrations determined during the cruise (from a set of 5 measurements analyzed approximately once per day, n=23) were 252.9 +/- 4.4 parts per trillion (ppt) for CFC-11, 547.2 +/- 5.0 ppt for CFC-12, and 76.3 +/- 1.9 ppt for CFC-113.

Concentrations of CFC-11 and CFC-12, and CFC-113 in air samples, seawater and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988). For seawater analyses, water was transferred from a glass syringe to a fixed volume chamber (~30 ml). The contents of the chamber were then injected into a glass sparging chamber. The dissolved gases in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 minutes at 70 ml min<sup>-1</sup>. Water vapor was removed from the purge gas during passage through an 18 cm long, 3/8" diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8" OD stainless steel tube with a ~10 cm section packed tightly with Porapak N (60-80 mesh). A vortex cooler, using compressed air at 95 psi, was used to cool the trap, to approximately -20°C. After 4 minutes of purging, the trap was isolated, and the trap was heated electrically to ~100°C. The sample gases held in the trap were then injected onto a pre-column (~25 cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil C, held at 70°C) for the initial separation of CFC-12, CFC-11 and CFC-113 from other compounds. After the CFCs had passed from the pre-column into the main analytical column (~183 cm of 1/8" OD stainless steel tubing packed with Carbograph 1AC, 80-100 mesh, held at 70°C) of GC1 (a HP 5890 Series II gas chromatograph with ECD), the flow through the pre-column was reversed to backflush slower

eluting compounds. Both of the analytical systems were calibrated frequently using a standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column and EC detector were similar to those used for analyzing water samples. Two sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was ~10.5 minutes.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et. al., 2000). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater ( $\text{pmol kg}^{-1}$ ). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (UW cylinder 45191 for CFC-11: 386.94 ppt, CFC-12: 200.92 ppt, and CFC-113: 105.4 ppt) into the analytical instrument. The response of the detector to the range of moles of CFC-12 and CFC-113 passing through the detector remained relatively constant during the cruise. A thorough baking of the column and trap after a power outage during trapping of a seawater sample introduced an unknown contaminant into the column changed the response of the detector to CFC-11. Full-range calibration curves were run at intervals of 10 days during the cruise. These were supplemented with occasional injections of multiple aliquots of the standard gas at more frequent time intervals. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity. The CFC-113 peak was often on a small bump on the baseline, resulting in a large dependence of the peak area on the choice of endpoints for integration. The height of the peak was instead used to provide better precision. The precisions of measurements of the standard gas in the fixed volume ( $n=395$ ) were  $\pm 0.44\%$  for CFC-12,  $0.56\%$  for CFC-11, and  $3.0\%$  for CFC-113.

The efficiency of the purging process was evaluated periodically by re-stripping high concentration surface water samples and comparing the residual concentrations to initial values. These re-strip values were approximately  $<1\%$  for all 3 compounds. A fit of the re-strip efficiency as a function of temperature will be applied to the final data set. No correction has been applied to the preliminary data set. The determination of a blank due to sampling and analysis of CFC-free waters was hampered by a contamination peak that co-eluted with CFC-11 and varied greatly in size during this leg. The size of the peak decreased exponentially with time, but jumped to very high values ( $0.05 \text{ pmol kg}^{-1}$ ) after each of the four power outages encountered during leg 2. Further investigation needs to be done to understand the origin of this contamination. CFC-113 and CFC-12 sampling blanks were less than  $0.005 \text{ pmol kg}^{-1}$ . No sampling blank corrections have been made to this preliminary data set.

On this expedition, based on the analysis of 38 duplicate samples, we estimate precisions (1 standard deviation) of  $0.45\%$  or  $0.004 \text{ pmol kg}^{-1}$  (whichever is greater) for dissolved CFC-11,  $0.36\%$  or  $0.003 \text{ pmol kg}^{-1}$  for CFC-12 measurements, and  $0.004 \text{ pmol kg}^{-1}$  for CFC-113. A very small number of water samples had anomalously high CFC concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g. anomalous dissolved oxygen, salinity or temperature features). This suggests that these samples were probably contaminated with CFCs

during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the preliminary data, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples that were drawn from the rosette but never analyzed due to a variety of reasons (e.g. power outage during analysis).

### **3.7 DIC Measurements**

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) operated simultaneously on the cruise by Dana Greeley and David Wisegarver of PMEL. 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<sub>2</sub> (gas) by addition of excess hydrogen to the seawater sample, and the evolved CO<sub>2</sub> 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<sup>-</sup>. CO<sub>2</sub> is thus measured by integrating the total change required to achieve this.

The coulometers were each calibrated by injecting aliquots of pure CO<sub>2</sub> (99.99%) by means of an 8-port valve outfitted with two sample loops (Wilke et al., 1993). The instruments were calibrated at the beginning of each station with a set of the gas loop injections. Subsequent calibrations were run either in the middle or end of the cast if replicate samples collected from the same Niskin, which were analyzed at different stages of analysis, were different by more than 2 μmol kg<sup>-1</sup>. Secondary standards were run throughout the cruise on each analytical system; these standards are Certified Reference Materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), and their accuracy is determined shoreside manometrically. On this cruise, the overall accuracy for the CRMs on both instruments combined was 0.8 μmol/kg (n=66). Preliminary DIC data reported to the database have not yet been corrected to the Batch 73 CRM value, but a more careful quality assurance to be completed shoreside will have final data corrected to the secondary standard on a per instrument basis.

Samples were drawn from the Niskin-type bottles into cleaned, precombusted 300-mL Pyrex bottles using silicone tubing. Bottles were rinsed three times 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 6-mL headspace, and then 0.2 mL of 50% saturated HgCl<sub>2</sub> solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease.

DIC values were reported for 1324 samples or approximately 80% of the tripped bottles on this cruise (92% of the non-trace metal bottles). Full profiles were completed at stations on whole degrees, with replicate samples taken from the surface, oxygen minimum, and bottom depths. Duplicate samples were drawn from 72 bottles and interspersed throughout the station analysis for quality assurance of the coulometer cell solution integrity. The average of the absolute value of the difference between duplicates was 1.0 μmol kg<sup>-1</sup> for both systems. No systematic differences between the replicates were observed.

### **3.8 TA Measurements**

Total alkalinity (TA) measurements were made potentiometrically using closed cell systems consisting of: a ROSS 8101 glass and Orion 90-92 double junction Ag/AgCl reference

electrode monitored by an Orion 720A pH meter, Metrohm 665 Dosimat titrator that adds our 0.7M acid (0.25N HCl and 0.45M NaCl) and a system of solenoid valves that controls the rinsing and filling of the cell. The titration cell was thermostated to 25°C using a Neslab RTE 17 constant temperature bath. The titration systems are controlled programmatically using National Instrument's Labwindows/CVI environment (developed by Dr. Pierrot). A typical titration (including rinse and fill) takes about 15 minutes, using two systems a typical 36 bottle cast requires about six hours.

During the second leg of the P16N cruise, about 1444 TA samples were run between the two systems, with Dickson certified reference material (CRM) run between each station to monitor the accuracy of the instruments. If the CRM run was outside of the standard error of our systems (3  $\mu\text{mol/kg}$ ) a correction factor was applied to the reported TA (ratio of measured TA to certified TA) with the systems generally giving  $\pm 2 \mu\text{mol/kg}$ . Duplicate (same samples run on each system) and replicate (same samples run on the same system) samples were taken to assess the precision of the instruments, with duplicates giving a standard deviation of  $\pm 2.3 \mu\text{mol/kg}$  and replicate on System A giving a standard deviation of  $\pm 1.2 \mu\text{mol/kg}$  and System B giving  $\pm 1.0 \mu\text{mol/kg}$ .

### ***3.9 pH Discrete Measurements***

#### *3.9.1 UM pH*

pH measurement were made using the spectrophotometric techniques of Clayton and Byrne (1993) with m-cresol purple (mCP) indicator determined from:

$$\text{pH} = \text{pK}_{\text{ind}} + \log\left[\frac{R - 0.0069}{2.222 - 0.133R}\right] \quad (2)$$

where  $K_{\text{ind}}$  is the dissociation constant for the indicator and R (A578/A434) is the ration of the absorbance of the acidic and basic forms of the indicator corrected for baseline at 730 nm. The samples are drawn from 50cc glass syringes using a Kloehn 50300 syringe pump and injected into the 10cm optical cell. The syringe rinses and primes the optical cell with 20  $\text{cm}^3$  of sample and the software permits three minutes of temperature stabilization before a blank is measured. The automated syringe then draws 0.008  $\text{cm}^3$  of indicator and 4.90  $\text{cm}^3$  of sample and allows for five minutes of temperature stabilization. A typical pH measurement takes about 15 minutes to run, with a 36 bottle cast taking about six plus hours. Values are reported with temperature to allow the user the greatest quality in interpretation and calculation with the data, but were made near 25°C reported in the seawater scale (SWS).

During leg 2 of P16N, the pH system was converted to a flowing mode. This entailed circulating the optical cell with underway seawater for insitu pH measurements. Discrete pH samples were taken, for comparison sake, on 8 stations (about 280 samples) throughout the course of the second leg. These runs were measured at the insitu surface temperature relative to the ship's position, and reported with the temperature of the measurement. A normalization of theses pH measurement will be made once on shore to a temperature of 25°C to be consistent with the measurements made on the first leg.

#### *3.9.2 USF pH*

USF pH measurements were the primary pH measurements on leg 2. Discrete USF pH measurements were made on all water samples for which discrete DIC measurements were obtained by NOAA personnel. Measurements of discrete pH were precise, and highly effective at prompt identification of mistrips. Comparison with pH measurements obtained 15 years

earlier, using nearly identical procedures, revealed substantial decreases in pH down to approximately 500 meters along the entire transect. The observed decreases generally correlated well with observed 15-year DIC differences along the transect. USF personnel measured seawater pH using the procedures outlined in SOP 7 of DOE Handbook (1996) and in Clayton and Byrne (1993). Samples were drawn from the Niskin bottles into 10 cm glass cells using a 20cm long silicon tube. The samples were thermostated to 25°C. After a blank was taken for each sample, an aliquot of 10  $\mu$ L (early in the transect) to 20  $\mu$ L (late in the transect) of m-cresol purple indicator dye (concentration  $\sim$  10mM) was added using a Gilmont pipette. The absorbance ratio, R, of A578/A434 was then measured. The pH<sub>T</sub> on the total scale is calculated using the following equation:

$$\text{pH}_T = 1245.69/T + 3.8275 - 0.00211(35-S) + \log((R-0.00691)/(2.222-0.1331R))$$

where T is the measurement temperature (T = 273.15 + t) and S is salinity. The overall precision of pH measurements from duplicate samples was better than 0.001 pH units.

### 3.10 Discrete pCO<sub>2</sub>

Samples were drawn from the Niskin bottles into 500 ml volumetric flasks using Tygon<sup>®</sup> tubing with a Silicone adapter that fit over the petcock to avoid contamination of DOM samples. Bottles were rinsed while inverted and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at room temperature generally for no more than 5 hours.

On previous cruises with this instrument the analyses were done at 20°C. Due to the anticipated high pCO<sub>2</sub> results for analyses at 20°C of intermediate waters in the North Pacific, two water baths were used for analyses at 20°C and 12°C. There were two secondary baths to get the samples close to the analytical temperatures prior to analyses. As soon as space was available in the secondary and then primary baths, the sample flasks were moved into the more controlled temperature bath. No flask was analyzed without spending at least 2.5 hours in a bath close to the analytical temperature. The pCO<sub>2</sub> in the intermediate water in the North Pacific reaches the highest values in the world's oceans and even with samples run at 12°C some analyses would exceed the working range of the detector of about 2000 ppm. The depth interval where very high pCO<sub>2</sub> concentrations are encountered gets progressively greater going northward. Therefore no pCO<sub>2</sub> samples were taken between 700 and 1200 db at station 53 and the range progressively increased to 175 to 1500 db at station 77.

Generally when samples were taken, flasks were drawn on all the Niskins including four duplicates. Two of the duplicates were analyzed at different temperatures. Four hundred sixteen samples were collected at fourteen stations (stations 44, 47, 56, 53, 56, 59, 62, 65, 68, 70, 73, 75, 77, 80). The data from eighteen of these samples was lost due to power failures. The fifty-four pairs of duplicates include twenty-six pairs run at different temperatures. The breakdown and precision of replicates are:

Duplicates @ 12°C:	0.23+- 0.15 % N = 15
Duplicates @ 20°C:	0.17 +-0.15 % N=12 , one duplicate omitted (bad analysis)
Duplicates 12° and 20°C*:	0.64 +- 0.60 % N =25, one duplicate omitted (bad analysis)

\*for comparison of the duplicates run at 12° and 20°C the 12°C results were normalized to 20°C using the procedures and constants listed in the Appendix of Peng et al. (1987) as incorporated in the GW BASIC data reduction program.

The discrete pCO<sub>2</sub> system is patterned after the instrument described in Chipman et al. (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen et al. (1995). The major difference between the two systems is that Wanninkhof instrument uses a LI-COR® (model 6262) non-dispersive infrared analyzer, while the Chipman instrument utilizes a gas chromatograph with a flame ionization detector.

Once the samples reach the analyses temperature, a 50-ml headspace is created by displacing the water using a compressed standard gas with a CO<sub>2</sub> mixing ratio close to the anticipated pCO<sub>2</sub> of the water. The headspace is circulated in a closed loop through the infrared analyzer that measures CO<sub>2</sub> and water vapor levels in the sample cell. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differ by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 minutes. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at room pressure.

In order to maintain analytical accuracy, a set of six gas standards is run through the analyzer before and after every ten seawater samples. The cylinder serial numbers and mole fractions of CO<sub>2</sub> with balance artificial air are:

CA5998	205.1 ppm
CA5989	378.7 ppm
CA5988	593.6 ppm
CA5980	792.5 ppm
CA5984	1037.0 ppm
CA5940	1533.7 ppm

The standards were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale.

The calculation of pCO<sub>2</sub> in water from the headspace measurement involves several steps. The CO<sub>2</sub> concentrations in the headspace are determined via a second-degree polynomial fit using the nearest three standard concentrations. Corrections for the water vapor concentration, the barometric pressure, and the changes induced in the carbonate equilibrium by the headspace-water mass transfer are made. The corrected results are reported at the analytical temperature and at a reference temperature of 20°C.

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

### ***3.11 Carbon/Oxygen Isotopes***

Samples for C-14/C-13 analysis were collected in 500 ml borosilicate bottles with ground stoppers. The samples were preserved with 100 µl of saturated mercuric chloride solution. The stoppers were greased with Apezion grease and held in place with rubber bands. Samples were collected from 32 Niskin bottles on stations 46, 50, 54, 58, 64, 68, 72, 76. Short casts of 16 bottles were collected at stations 44, 48, 52, 56, 60, 62, 66, 70, 74, 77, 80, 83. Samples will be returned to the WHOI NOSAMS facility for analysis.

Samples for oxygen isotopes and oxygen:argon ratio were collected from a near-surface (15-25 m) Niskin at all stations. Another 11 stations had 5 samples collected in the upper 300m. Samples were collected in 500 ml evacuated glass sampling bottles and preserved with mercuric chloride. Samples will be returned to the University of Washington for analysis.

### ***3.12 Dissolved Organic Carbon/ Dissolved Organic Nitrogen***

Water for DOC/DON analyses were collected into 60 ml high density polyethylene (HDPE) bottles from every cast (2818 samples total). Samples from the upper 250 m were passed through GF/F filters using in-line filtration from the Niskin bottles; at greater depths the samples were whole (unfiltered) water. The samples then were frozen in a -20°C freezer room and returned to RSMAS for analysis..

### ***3.13 CDOM, chlorophyll, bacterial suite***

Samples were collected from the rosette for absorption spectroscopy on one deep ocean cast each day. CDOM is typically quantified as the absorption coefficient at a particular wavelength or wavelength range (we are using 325 nm). CDOM was determined at sea by measuring absorption spectra (280-730 nm) of 0.2µm filtrates using a liquid waveguide spectrophotometer with a 200cm cell. Samples were concurrently collected for bacterial abundance and carbohydrates to compare the distribution of these quantities to that of CDOM. In surface waters (< 300m) bacterial productivity of field samples was estimated by measuring the uptake of bromo-deoxyuridine (BrdU), a non-radioactive alternative to the standard bacterial productivity technique using tritiated thymidine. Because of the connections to light availability and remote sensing, samples were collected for chlorophyll, carotenoid, and mycosporine-like amino acid pigment analysis (HPLC), chlorophyll a (fluorometric), and particulate absorption (spectrophotometric). Large volume (ca. 2L) samples were sporadically collected for CDOM photolysis experiments back at UCSB, and occasionally large volume samples were collected for POC analysis by Dr. Gardner's lab to compare with transmissometer data. CDOM and chlorophyll a samples were analyzed at sea. The rest of the samples were prepared for later analysis.

### ***3.14 Helium-tritium***

Helium samples were collected in stainless steel containers with pneumatic valves (“bunnies”). To draw a sample, two pieces of tubing are attached to the ends of the container, and one end is attached to the spigot on the Niskin bottle. The sample is held vertically above the water level in the Niskin bottle, the valve is opened to establish flow, and the sample is lowered over a ten- to twenty-second period to establish gravity flow. The relatively slow entry of the water into the container minimizes trapped air and bubble formation. The amount of water flushed through the tube is about six volumes. During the flush period, the container is tapped to remove bubbles. The pneumatic valves are closed and the sample is stored until it can be further processed.

After all samples were collected, the helium samples were degassed and extracted into glass vials for analysis in the shore-based laboratory. In general, the extraction and degassing procedures were executed with several (~8) samples in parallel, with extraction or degassing sections coupled to a common vacuum manifold.

Tritium samples were collected in 1 liter flint glass bottles, sealed with caps fitted with high density polyethylene cones to minimize water vapor transpiration. To achieve a minimum contamination, the bottles were pretreated to remove adsorbed water. The bottles are sealed with

argon inside. After the tritium samples were collected they are sealed and returned to the shore-based laboratory for analysis.

### **3.15 Trace metals**

Hydrographic sampling for the trace elements Al and Fe was conducted during leg 2 of P16N. Samples were collected using a specially designed rosette system which consists of 12 x 12L Go-Flo bottles mounted on a powder-coated rosette frame. The package is equipped with a SeaBird SBE 911 CTD that also has an SBE 43 oxygen sensor and a Wet Labs FL1 fluorometer. The package is lowered using a Kevlar conducting cable and bottles were tripped at pre-determined depths from the ship using a deck box. Water samples were collected in the upper 1000 m at a total of 17 stations, collecting roughly 200 samples. Bad weather (high winds and rough seas) prevented us deploying at only one station (station 64, 43N). Subsamples were taken from each GoFlo bottle for at-sea analysis of salinity, nutrients, dissolved total Fe and Al (Bill Hiscock of the Measures Group), and dissolved Fe(II).

#### *3.15.1 Aerosol Sampling*

Aeolian transport and deposition of soluble aerosol Fe is believed to influence phytoplankton primary productivity in the majority of the open ocean (far from Fe inputs from rivers and coastal sediments). The purpose of the FSU aerosol sampling program is primarily to measure the concentration of total aerosol Fe, and to quantify the aerosol Fe fractions that are soluble in natural surface seawater and in ultra-pure deionized water. Additional analyses are conducted on the samples in an effort to understand the atmospheric processes that yield differences in the aerosol Fe solubility.

The aerosol sampling equipment consists of four replicate filter holders deployed on a 20' fold-down aerosol tower mounted on the forward, starboard corner of the 03 deck of the ship. One of the replicate filters (0.4  $\mu\text{m}$  Nuclepore polycarbonate track-etched) is used for total aerosol measurements (see below); one replicate filter (0.45  $\mu\text{m}$  polypropylene) is used to quantify the seawater-soluble fraction; one replicate filter (0.45  $\mu\text{m}$  polypropylene) is used to quantify the ultra-pure deionized water soluble fraction; and one replicate filter (0.45  $\mu\text{m}$  polypropylene) is used for precision (QA) tests or stored as a backup sample. Size-fractionated aerosols are also collected for 48 hour intervals starting every 3<sup>rd</sup> day using a MOUDI cascade impactor (>3.2  $\mu\text{m}$ , 1.0  $\mu\text{m}$ , 0.56  $\mu\text{m}$ , 0.056  $\mu\text{m}$ ). Air is pulled through the filters using two high-capacity vacuum pumps. The sampling is controlled by a Campbell Scientific CR10 datalogger that immediately shuts off the flow when the wind might blow stack exhaust forward towards the sampling tower, or when the wind drops below 0.5 m/s. Air flow is measured using Sierra mass-flow meters.

We have collected 24-hour integrated aerosol samples each day for the entire leg (24 days of sampling) for the following analyses:

1. Total aerosol Si, Al, Fe (to be analyzed using Energy Dispersive X-Ray Fluorescence by Dr. Joe Resing at NOAA/PMEL).
2. Seawater-soluble aerosol Al and Fe (to be run back at FSU).
3. Ultra-pure water soluble Si, Al, Ti, Fe, chloride, sulfate, nitrate, sodium (to be run back at FSU). The MOUDI size-fractionated aerosol filters are also leached with ultra-pure water for these same analyses.

#### *3.15.2 Dissolved Fe(II)*

The purpose of the dissolved Fe(II) sampling program is to study the effects of photochemical reduction and biological remineralization on the redox chemistry of iron in

seawater. Filtered samples (0.2  $\mu\text{m}$ ) are collected from the Trace Metal Go-Flo bottles immediately upon recovery into polyethylene bottles that have been pre-charged with a small amount of ultrapure 6M HCl to drop the pH to 6.0-6.2. This stabilizes the existing Fe(II) from rapid oxidation, but is not low enough to trigger thermochemical Fe(III) reduction. The samples are quickly analyzed for dissolved Fe(II) using the FeLume chemiluminescent method. Samples for dissolved Fe(II) analysis have been collected from each depth on every Trace Metal cast (17 stations, approx. 200 samples).

Additional experiments being conducted on the ship include laboratory photochemical exposure experiments to study the wavelength dependence of Fe(II) photoproduction and to quantify the maximum extent to which photochemical Fe reduction might occur in surface waters. We are also measuring  $\text{H}_2\text{O}_2$  on selected profiles since  $\text{H}_2\text{O}_2$  is known to enhance the chemiluminescent response of the Fe(II) measurement. A correction to the Fe(II) concentrations must therefore be applied, and we conducted Fe(II) and  $\text{H}_2\text{O}_2$  spike experiments to quantify the effect.

### *3.15.3 Other Sampling*

We collected archived samples from each trace metal cast (17 stations, approx. 200 samples) for FSU shore-based analysis of dissolved Fe, Ni, Cu, Zn, Cd, and Pb using isotope dilution ICPMS.

The Total Suspended Matter (TSM) from each trace metal cast was collected on 47 mm 0.4  $\mu\text{m}$  Nuclepore filters for EDXRF analysis of total particulate Si, Mn, Fe, and Al (Joe Resing, NOAA/PMEL).

We collected approximately 200 filtered seawater samples for dissolved Mn, Ga and Sc analysis by Alan M. Shiller (University of Southern Mississippi). These samples will be shipped back to USM for later shore-based analysis.

We collected approximately 100 samples for Dave Krabbenhoft (USGS, Madison) for dissolved total mercury and methyl mercury analyses. Human exposure to environmental mercury is mainly through consumption of marine fish containing methyl mercury, so these samples will help us understand the marine mercury cycle and the production of methyl mercury.

### *3.16 Optical Casts*

Once each day, an optical cast with a hand-deployed free-fall Satlantic MicroPro II multichannel UV/Visible spectroradiometer was conducted. This instrument has 14 upwelling radiance sensors and 14 downwelling irradiance sensors in wavelength bands ranging from 305 to 683 nm. The package also mounts a WetLabs chlorophyll fluorometer and scattering meter, plus ancillary sensors including X-Y tilt, internal and external temperatures. The instrument is allowed to trail away behind the port quarter, then free-falls to 150m and is hand-recovered. The radiometric data will be used to study the effects of CDOM on the underwater light environment, to validate satellite ocean radiance sensor data, and to develop new algorithms employing satellite and in situ optical sensor data to retrieve ocean properties such as CDOM light absorbance, chlorophyll concentration, and particulate backscattering.

## **4.0 Underway Measurements**

### *4.1 USF Underway DIC/pCO<sub>2</sub>/pH*

An automated CO<sub>2</sub> system analyzer was set up on board to measure underway surface seawater CO<sub>2</sub> parameters (7 samples per hour), including total CO<sub>2</sub> (DIC), pH, air and seawater pCO<sub>2</sub> at 25°C. DIC was measured by equilibrating acidified seawater across a liquid-core waveguide membrane with a known alkalinity standard solution (Byrne et al., 2002). pCO<sub>2</sub> was analyzed by equilibrating seawater or air across a liquid-core waveguide membrane with a known alkalinity standard solution. The equilibrium pH was measured, and DIC and pCO<sub>2</sub> were calculated. The assessed precisions are 2 μM for DIC, 2 ppm for pCO<sub>2</sub> and 0.001 for pH.

Underway measurements of surface pH, DIC and pCO<sub>2</sub> along the transect generally went smoothly and correlated well with discrete measurements. Underway surface pH measurements were in excellent agreement with discrete measurements, even though the procedures for the measurements had distinct differences. Underway and discrete DIC measurements were in very good agreement with the exception of one short segment of stations over an approximately two to three day period. Comparisons of USF and NOAA underway pCO<sub>2</sub> measurements were somewhat compromised by the limited flow of seawater to the PMEL underway system. Comparisons with AOML discrete measurements should eventually shed light on underway pCO<sub>2</sub> measurement issues.

#### 4.2 NOAA/PMEL Underway pCO<sub>2</sub>

The NOAA/PMEL underway surface pCO<sub>2</sub> system was started shortly after leaving Honolulu, HI. The semi-autonomous system analyzes surface water collected from the ship's uncontaminated seawater supply and marine air from the ship's bow on a repeating hourly cycle. The first quarter of each hour is devoted to calibration with four CO<sub>2</sub> standards (Feely et al., 1998). A second order polynomial calibration curve is calculated for the LiCor 6262 infrared detector. The remaining time in each hour is used to measure equilibrator air (15 min), bow air (15 min), and equilibrator air once again (15 min). The analytical precision of the system is estimated to be approximately 0.3-0.4 ppm for seawater and for air.

The underway system experienced some problems throughout cruise because of low water flow rate and air contamination in the equilibrator.

#### 4.3 UM Underway pH

pH measurement were made using the spectrophotometric techniques of Clayton and Byrne (1993) with m-cresol purple (mCP) indicator determined from:

$$\text{pH} = \text{pK}_{\text{ind}} + \log\left[\frac{R - 0.0069}{2.222 - 0.133R}\right] \quad (2)$$

where  $K_{\text{ind}}$  is the dissociation constant for the indicator and  $R$  (A<sub>578</sub>/A<sub>434</sub>) is the ration of the absorbance of the acidic and basic forms of the indicator corrected for baseline at 730 nm. The samples are drawn from a SBE 45, which measured the temperature and salinity, using a Kloehe 50300 syringe pump and injected into the 10cm optical cell. The syringe rinses and primes the optical cell with 20 cm<sup>3</sup> of sample and the software permits three minutes of temperature stabilization before a blank is measured. The automated syringe then draws 0.008 cm<sup>3</sup> of indicator and 4.90 cm<sup>3</sup> of sample and allows for five minutes of temperature stabilization. The program was set to measure an underway sample every ten minutes and reported with a timestamp (the GPS line provided by the ship was not compatible the software) that will have to be matched with the ship's GPS position. The system was stopped while on station, and restarted during the transit between stations, this yielded about 1480 samples. The values reported are with the measured temperature and are in terms of the sea water scale.

## 5.0 Other Measurements

### 5.1 Net tows/Pteropod

In an add-on project funded by the NSF Chemical Oceanography Program, V. Fabry (CSUSM), R. Byrne (USF), and J. Schijf (USF) worked on the dissolution of freshly collected pteropod shells. At about 10 stations, plankton tows were conducted in the upper 25 m at night. Pteropod shells were quickly sorted and used in dissolution experiments employing a high precision, spectrophotometric method to measure pH. The main objective of this cruise work was to test a newly constructed experimental cell. We conducted dissolution experiments at 25 stations between Honolulu and Kodiak. In addition, we conducted preliminary experiments on live pteropods at 8 stations. Samples were shipped back to CSUSM for laboratory analysis.

### 5.2 Floats

Eight Web Research Corporation APEX floats were launched for Howard Freeland of the Institute of Ocean Sciences in British Columbia. These floats are part of the Canadian Argo project and were deployed at the northern end of the P16N section to better populate this area. Floats were deployed after the completion of all station work at 31°N, 34°N, 37°N, 40°N, 44°N, 47°N, 50°N, and 55°N. Each deployment required 30 minutes of startup time to unpack, inspect, and test the float. All floats passed their self-check routines and were launched successfully. Immediately following deployment, an email was sent to Dr. Freeland to report the exact time and position of the float. Return emails from Dr. Freeland confirmed that all floats were working properly.

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