# A. Cruise Narrative P16C



# A.1. Highlights

# WHP Cruise Summary Information

WOCE Line	P16C
EXPOCODE	31WTTUNES_3
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Ship	R/V Thomas Washington
Number of Stations	148
	18° 53'N
Geographic boundaries	150° 28'W 155°39'W
	17° 30'S
Floats deployed	12 ALACE floats
Drifters deployed	7 surface drifters
Moorings deployed or recovered	0
Ports of Call	Papeete, Tahiti to Honolulu, Hawaii
Cruise Dates	August 31 to October 1, 1991

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# **Station locations for P16C**



Produced from .sum file by WHPO-SIO

#### A.2. Cruise Summary

#### A.2.a. Cruise Track

R/V T. Washington departed Papeete, Tahiti for its third consecutive WOCE leg on Aug. 31, 1991. Stations were numbered consecutively from the beginning of the R/V Washington work on P17C, starting off the coast of California in May, 1991. The first station on Leg 3 (P16C) was numbered 221 and was a reoccupation of the last station on Leg 2 (P16S), which was numbered 220.

All stations were to the bottom and consisted of a rosette/CTD cast. Basic station spacing was 30 nm, closing to 20 nm for the large (36 10-liter bottle) rosette between 3S and 3N. A small rosette, with 11 1.7-liter bottles and a different CTD (WHOI's CTD 9), was alternated with the large rosette stations between 3S and 3N, to obtain CTD station spacing of 10 nm.

In Fig. A.2.1, +'s are standard CTD/36-bottle rosette stations, triangles are CTD/36-bottle rosette stations with large volume sampling, and asterisks are CTD/11-bottle rosette stations with mounted ADCP (non-WOCE measurement).

On 25 days a separate JGOFS bio-optics station was made within several hours of noon (Fig. A.2.2). These stations extended to 200 m.

## A.2.b. TOTAL NUMBER OF STATIONS AND STATION TYPE

(Fig. A.2.3 and A.2.4)

106 CTD/36-bottle rosette stations 18 CTD/11-bottle rosette/LADCP stations (non-WOCE) 8 Large volume sampling (Gerard barrel) stations 25 200-meter bio-optics stations (JGOFS)

Sampling was done primarily with a 36-place double-ring rosette with mounted CTD (WHOI CTD 10), transmissometer, and pinger. CTD data consisted of pressure, temperature, conductivity, oxygen and transmissometry. All profiles were full water column depth. Water samples were collected for analyses of salt, oxygen, silica, phosphate, nitrate and nitrite on all stations and of CFC-11, CFC- 12, helium-3, helium-4, tritium, AMS C14, alkalinity, and total dissolved inorganic carbon on selected stations. Water sample depths are shown in Fig. A.2.3.

A small rosette with 11 1.7 liter bottles and WHOI CTD 9, a pinger and an Acoustic Doppler Current Profiler was used on alternate stations between 3S and 3N, to produce a station spacing of 10 nm. CTD data consisted of pressure, temperature, conductivity and oxygen. Water sampling was limited to salinity and oxygen for calibration of the CTD. All profiles were full water column depth. Water sample depths are included in Fig. A.2.3.

Large-volume sampling was made with use of 270-liter Gerard barrels for analyses of C14, salinity, oxygen and silica on 8 stations. All profiles consisted of at least 2 9 barrel casts and covered the full water column. Water sample depths are shown in Fig. A.2.4.

Bio-optics stations consisted of a profile using a spectral radiometer package (MER) which measured pressure, temperature, conductivity, fluorescence, transmission, downwelling irradiance, upwelling radiance and photosynthetically-available radiation. A water sample was collected at 200 m and a separate bucket sample at the surface; both were filtered to be run later for chlorophyll, pigments and absorption spectra.

Underway measurements included Acoustic Doppler Current Profiling, pCO2, pN2O, and surface temperature. Underway bathymetry was collected every 2 minutes from the center beam output of the Washington's Seabeam system and merged with GPS navigation.

# A.2.c. FLOATS AND DRIFTERS DEPLOYED (Fig. A.2.5)

12 ALACE floats deployed (plus) 7 surface drifters deployed (asterisk)

## A.2.d. MOORING DEPLOYMENTS OR RECOVERIES

None

## A.2.e. INTERLABORATORY COMPARISONS

No interlaboratory comparisons were made per se on P16C, but water sample results were compared with preliminary data acquired on P16S, with final data from the Oceanographer Transport of Equatorial Waters (TEW) cruise at 12S and from the Moana Wave cruise at 10N. Comparisons of P16C salinity, oxygen, silica and nitrate with data from these three cruises are shown in Figs. A.2.6-8. Phosphates from all three comparisons are shown in Fig. A.2.9. No data from P16C were excluded, despite some obvious errors.

The P16S cruise, with chief scientist J. Swift of SIO, immediately preceded P16C on the same vessel. CTD and salinity/oxygen/nutrient analyses were carried out by SIO's Oceanographic Data Facility. In an attempt to produce data sets from P16S and P16C which are compatible without further adjustments by the data user, the same nutrient standards and same nutrient autoanalyzer were used on the two cruises (as well as on the preceding P17C/S). Different standard sea waters (SSW's) were used for salinity measurements on the two legs: P114 on Leg 2 for stations 124-140, P108 on Leg 2 for stas 141-220, and P114 on Leg 3. P108 and P114 were checked against each other at the beginning of P16C and P114 was found to be about 0.0015 psu higher than P108. A comparison of both SSW's against a common standard will be made sometime in the next year (Mantyla, personal communication). ODF used traditional Winkler titration for oxygen and WHOI used a new automated titration system with the same chemistry and measurement on an aliquot drawn from the sample bottle.

Fig. A.2.6 shows properties from the last five stations of P16S and the first five stations of P16C. Stations 220 (P16S) and 221 (P16C) were at the same location. Although the rest of the stations are not co-located, agreement of the properties (such as silica) indicates that the same deep water was sampled in both groups of stations. In Fig. A.2.6, it is seen that the salinities from P16C are about 0.003-0.004 psu higher than from P16S and noisier; about half of the offset is accounted for by the difference in SSW. Oxygen, silica and phosphate agree well. Nitrate is higher on P16C than on P16S by about .6 umol/l (1.7%). Post-cruise processing of the nutrient values may change the relative offsets of the two data sets.

The TEW cruise, with principal investigator Stan Hayes, occurred in summer, 1987, on the NOAA ship Oceanographer. The cruise track was roughly zonal, along 12S. Technical support was from NOAA/PMEL (CTD, salinity, freon), Duke (nutrients), and Bigelow Laboratory/U. Washington (oxygen). A data report is now available (Mangum et al., 1991). This is considered a "pre-WOCE" cruise and will not be duplicated in WOCE. Figs. A.2.7 and A.2.9 show P16C salinity 0.004 psu lower, oxygen 0.05 ml/l higher (1.3%), silica in the same range, nitrate 0.9 umol/l higher (2.5%), and phosphate in the same range. (Units of ml/l were used for oxygen because the TEW oxygen data available were in these units.)

A zonal section at 10N on R/V Moana Wave, with principal investigator John Toole, used technical support from WHOI for salinity, oxygen and CTD, and from Oregon State University for nutrients. This cruise is also considered "pre-WOCE" and will not be duplicated. A data report is currently being printed. Fig. A.2.8 and A.2.9 show P16C salinity and oxygen in the same range, silica 4 umol/l higher (3%), nitrate 0.8 umol/l lower (2.3%), and phosphate 0.1 umol/l lower (4%).

Thus the P16S and P16C data sets are indeed closer to each other in more parameters than is P16C with either TEW or the Moana Wave cruise. Also, with the exception of the high Moana Wave phosphates, the differences are almost within the WHP specifications. Scatter in the TEW data is the highest, in all parameters except possibly silica. However, given the expectation and planning to make sure that the P16S and P16C data sets would be as compatible as if the same technical groups had produced both, it was hoped that the differences in salinity and nitrate would have been smaller. If due to differences in techniques, it is hoped that these will be resolved prior to the next set of US WOCE cruises in 1992.

John Bullister	CFC	NOAA/PMEL	johnb@noaa.pmel.gov
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Stuart Smith	Bathymetry	SIO	ssmith@ucsd.edu
Lynne Talley	CTD/hydrography	SIO	Italley@ucsd.edu
Lynne Talley	Underway temperature	SIO	Italley@ucsd.edu
John Toole	CTD/hydro support	WHOI	jtoole@whoi.edu
Ray Weiss	underway pCO2 and pN2O	SIO	rfweiss@ucsd.edu

# A.3. LIST OF PRINCIPAL INVESTIGATORS

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## A.4. SCIENTIFIC PROGRAMME AND METHODS

#### A.4.a. NARRATIVE

#### A.4.a.1. UPPER OCEAN STRUCTURE

Data from the upper 1000 meters extends the large data set collected in 1979-1980 between Tahiti and Hawaii. The principal features on P16C in the surface dynamic height relative to 1000 meters are a very broad South Equatorial Current, from 20S to 2 30'S, the signature of the westward Equatorial Current, a weak eastward flow at 2N, and then a very strong North Equatorial Countercurrent and pronounced North Equatorial Current. The preliminary dynamic height difference across the NECC yields an approximate velocity of 85 cm/sec which is about twice what was usually reported for the shuttle (e.g. Wyrtki and Kilonsky, 1984; Taft and Kovala, 1981). The NEC is of course broader and preliminary dynamic height yields an average of about 15-20 cm/sec.

The upper ocean potential density section shows the familiar Equatorial Undercurrent, Equatorial Intermediate Current and North and South Subsurface Countercurrents (Tsuchiya Jets). The latter are pycnostads centered at 26.5-26.6 sigma theta. Just poleward of and slightly deeper than these are another pair of pycnostads, centered at 26.8-26.9 sigma theta, and located between 5-10N and 5-10S. As far as we know, these have not been pointed out before although they are apparent in sections in the data reports from the Norpax shuttle.

The salinity structure of the upper 1000 meters is well-described by the Norpax shuttle. The southern salinity maximum of the upper 200 meters surfaces between 13 30'S and 15S and extends northward above the Tsuchiya jet, where it is extremely thin and centered at 24.0-25.0 sigma theta. The northern salinity and southern salinity maxima meet between 7 and 8N. The North Pacific Intermediate Water is found at the northern end of the section and terminates abruptly and spectacularly at 16 30'N where it is chopped off from below by higher salinity water from the south and then disappears at the next station to the south. The Antarctic Intermediate Water is weakly present up to 14 30'N.

The lowest bottle oxygen measured in the oxygen minimum was 0.16 ml/l, at 320 meters at 9 30'N, the northern edge of the NECC.

#### A.4.a.2. INTERMEDIATE DEPTH OXYGEN AND NUTRIENT STRUCTURE (1000- 3500 meters)

Interesting geostrophic shear was found at 2000-3500 m between 9S and the southern end of the section at 17 30'S in the form of a bowl in isopycnals, with the lowest point at 14-15S. A similar phenomenon is found north of the equator, with the bowl at 2000- 3500 m between 3N and the northern end of the section at Hawaii (18N) and the lowest point at 9-10S. There may be some interesting stacked jets at the equator, but further work with the data will be necessary to confirm them. Both the preliminary geostrophic shear and

lowered ADCP showed greatly decreased vertical wavelength at the equator compared with just a few degrees on either side.

The bowl-shaped isopycnals were accompanied by very clear property signatures, particularly in oxygen for which we had continuous CTD profiles. Oxygen profiles centered at 12S below about 1500 meters developed a layered structure, with one pronounced layer of roughly uniform oxygen roughly between 2000 and 3000 meters. At 12S, this developed into a slight oxygen minimum. North of the equator, in a band from about 2N to 10N, a weaker version of the oxygen layer was also found. A positive thermal anomaly was also associated with the oxygen layer with maximum anomalies at 12S and 8N (G. Johnson, personal communication). Johnson has also found silica anomalies on the relevant isotherms at the same locations. The location of the layer and its lateral center is therefore on the equatorward side of the isopycnal bowl found in each hemisphere. The low oxygen in the layer suggests an eastern source. This depth range is of course that expected for the well-defined helium plumes which originate on the East Pacific Rise (Lupton and Craig, 1981); the cause of the focusing of the helium signatures into distinct plumes north and south of the equator is unknown, although hydrothermal forcing has been suggested (Speer, 1989).

## A.4.a.3. ABYSSAL FLOW INDICATIONS

Just north of the Tahitian chain a very clear signature of a deep boundary current was found banked to the south against the islands. Just south of the equator, where the ocean bottom rises slightly, a clear spreading of isopycnals and isotherms indicating a deep flow was also found. Isopycnal analysis suggests westward flow at the equator just above the bottom especially based on silica. The lowered ADCP data confirm this direction.

The Clarion Fracture Zone and deep basin just north of it contained bottom waters of the same properties found south of the equator and not in between (high density, oxygen; low silica, phosphate, nitrate, potential temperature, and salinity). There was strong deep geostrophic shear in the deep basin also, all suggestive of the eastward flow of waters expected from the western Pacific into the eastern Pacific south of Hawaii.

Strong geostrophic shear was also found in the Hawaiian Trough, banked against Hawaii.

#### A.4.b. SMALL VOLUME AND LARGE VOLUME SAMPLE LOCATIONS

(Figs. A.2.3 and A.2.4)

## A.5. MAJOR PROBLEMS ENCOUNTERED ON THE CRUISE

There were no major problems resulting in shortfalls in numbers, spacing, or coverage of the stations.

## A.5.a. WATER SAMPLE ANALYSES

A full listing of all data of questionable values, including problems with bottle tripping and leaking, is appended as section D.

#### TRIPPING PROBLEMS:

There were no notable problems with the large rosette used on most stations. Bottles on the small rosette for the additional small volume equatorial stations were hard to configure, resulting in loss of about 10% of the few samples collected there. Failure to switch to inner pylon on the large rosette at sta. 287 resulted in a lack of water samples above 500 meters.

#### SALINITY:

Salinity analyses were noisy, on the order of 0.003- 0.004 psu in the deep water, throughout much of the cruise. They were also 0.003-0.004 psu higher than those of leg 2; a preliminary at-sea comparison of the standard sea waters used for the two groups of stations indicated that the P16C salinities should be 0.001psu higher than those of leg 2. The remaining discrepancy is unaccounted for as of now; a second comparison of the SSW's will be made before looking into other possibilities. In order to reduce the noise level, various attempts were made in education of those drawing the water samples and the autosalinometer was changed before station 247.

#### NUTRIENTS:

Difficulties were encountered with some nitrate and phosphate measurements on stations 226 to 244. Replicate samples using different sample tubes and water out of different Niskins indicated that the problem was with the sampling tubes used to collect water from the rosette sampler. All tubes were thoroughly cleaned with HCl before sta. 245, solving the problem. With the exception of occasional random problems, all data from stations 221-225 and 246-326 appear acceptable.

In an attempt to ensure that nutrient data from all three WOCE legs would be compatible despite the different lead analysis groups, the same equipment and standards were used on all three legs. Silica and phosphate values from legs 2 and 3 are consistent with each other. However, nitrate on leg 3 is systematically 1-2 umoles/liter higher than on leg 2, apparently due to different calibration procedures.

## LARGE VOLUME SAMPLING:

Tripping problems were encountered on several large volume stations, necessitating a third or fourth Gerard cast in order to get a full profile. In general, problems of this sort were less common than on the first two legs, due to the good weather we enjoyed.

## A.5.b. CTD

A full description of the CTD calibration is in section B.4. The full CTD package consisted of pressure, temperature, redundant temperature, oxygen, an oxygen pump, and a transmissometer. The CTD wire had three conductors. Two separate CTD's were used: the primary CTD (WHOI #9) was used for most stations and the secondary CTD (WHOI #10) for just the odd-numbered stations from 251 to 285. This second CTD was mounted on a smaller rosette package and was used in order to halve the station spacing across the equator. A lowered acoustic doppler current profiler was also mounted on the smaller package.

The first 4 stations were noisy in pressure, oxygen and salinity. Oxygen calibration for stations 222-226 was not possible.

One of the three conductors in the conducting wire shorted to ground during sta. 234, so 9 bottles did not close. The short was measured to be at 5288m from the CTD, so cutting the wire was not an option. The CTD/rosette package was reconfigured for use with 2 conductors and used that way throughout the remainder of the cruise.

The wire was reterminated prior to station 259 and prior to station 303.

Bottom contact was made at stations 242, 245, and 288, causing a conductivity calibration shift at 245. The rosette package hit the side of the ship at 233, but there was no shift in CTD calibration.

The CTD conductivity sensor failed on station 294, necessitating a switch to a new cell.

Due to these and a problem with an apparent conductivity hysteresis, calibrating this CTD data set presented more problems than usual. Nevertheless, all but just a few of the stations in the final data set contain full profiles of data within WHP accuracy standards.

# A.6. List of Cruise Participants

Lynne Talley	Chief scientist	SIO	Italley@ucsd.edu
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Peter Guenther	carbon dioxide analyses	SIO	pguenther@ucsd.edu
Kyung-Ryul Kim	helium-3 sampling	SIO	
Leonard Lopez	large volume marine tech.	SIO/ODF	leo@odf.ucsd.edu
Gene Pillard	resident technician	SIO/MTG	
Jim Wells	marine tech.	SIO/ODF	jwells@ucsd.edu
Gary Bond	CTD/hydro group leader	WHOI	
George Knapp	oxygen analyses	WHOI	gknapp@whoi.edu
Peter Landry	CTD/hydro electronics tech.	WHOI	
Carol MacMurray	CTD/hydro processor	WHOI	
Mike Mathewson	helium-3, tritium	WHOI	
Ed Peltzer	carbon dioxide analyses	WHOI	
Bob Stanley	salinity analyses	WHOI	
Joe Jennings	nutrient analyses	OSU	
Hernan Garcia	nutrient analyses	OSU	
Frank Bahr	ADCP	U.Hawaii	
Dave Wisegarver	CFC sampling and analyses	NOAA/PMEL	
Tracy McCallister	CFC sampling and analyses	NOAA/PMEL	
Carol Knudson	bio-optics stations	LDEO	knudson@ldeo.columbia.edu



Figure A.2.1: Cruise track for WOCE P16C (31wttunes3), R/V T. Washington, 31 Aug 1991 - 1 Oct 1991.
(a) Rosette/CTD station (circle). Large volume plus large rosette/CTD station (+).
(b) Equatorial stations. Regular rosette stations with CTD10 (circles).
LADCP rosette stations with CTD9 (+).



Figure A.2.2: JGOFS bio-optical stations on P16C.



Figure A.2.3: Small volume (10 liter) water samples on P16C.



Figure A.2.4: Large volume (Gerard) water samples on P16C.



Figure A.2.5: ALACE float (circles) and surface drifter (+) deployments on P16C.



Figure A.2.6: (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate all vs. potential temperature, from P16S stations 216-220 (solid, R/V T. Washington, 8/91, 31wttunes2) and from P16C stations 221-225 (x's, R/V T. Washington, 9/91), near 18S.



Figure A.2.7: (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate, all vs. potential temperature, from TEW stations 2-4 (solid) and P16C stations 228-232 (triangles), at 12S. The TEW stations were collected in June, 1987.



Figure A.2.8: (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate, all vs. potential temperature, from Moana Wave stations 128-131 (solid) and P16C stations 298- 302 (triangles), at 10N. The Moana Wave stations were collected in April, 1989.



Figure A.2.9: Phosphate vs. potential temperature, from (a) P16S stations 217-220 and P16C stations 221-224 near 18S, (b) TEW stations 2-4 and P16C stations 228-232 at 12S, (c) Moana Wave stations 128-131 and P16C stations 298-302 at 10N.

## B. DESCRIPTION OF MEASUREMENT TECHNIQUES AND CALIBRATIONS

#### **B.1. NAVIGATION AND BATHYMETRY**

#### GPS navigation.

Underway bathymetry was logged using the centerbeam from the R/V Washington's Seabeam system. The data were acquired by George Bouchard (shipboard computer technician), who merged them with the GPS navigation. The data were quality-controlled and archived by Stuart Smith of the Geological Data Center at SIO. GPS

## **B.2. ACOUSTIC DOPPLER CURRENT PROFILER (ADCP)**

Text to be supplied by Eric Firing (U. Hawaii).

#### B.3. THERMOSALINOGRAPH AND UNDERWAY DISSOLVED GASES

A thermosalinograph with Falmouth Scientific sensors was operated on P16C and the two preceding WOCE legs on the R/V Washington. This effort was unfunded and was therefore was accorded very low priority compared with the CTD operation. The system was set up by Robert Williams of SIO's Oceanographic Data Facility. He also operated the system on the second of the WOCE legs. Peter Salameh of SIO did an initial cleanup of the data for all three legs.

Temperature, conductivity and oxygen sensors were located in the ship's main laboratory in the principal clean seawater supply. There was a steady flow of water past the sensors through most of the three legs. An additional temperature sensor was mounted in the bow inlet, at 3-5 meters depth.

#### Temperature:

Both temperature sensors were calibrated at SIO's Oceanographic Data Facility (ODF) before the cruise, in May 1991. The laboratory temperature sensor (serial number 1321) was broken when it was being removed at the end of the third leg, and so there was no post-cruise calibration. Its temperature offset was approximately 0.005 C high compared with the laboratory standard.

The bow temperature sensor (serial number 1322) was calibrated at ODF after the third leg, in February 2-5 1992. Its temperature had increased by about 0.2C between the preand post-cruise calibrations. Its pre-cruise calibration showed it to be about 0.01 C high compared with the laboratory standard.

Both sensors functioned well throughout the three legs. The average temperature difference between the two sensors for P17C was 0.081 C, with the laboratory sensor being warmer as expected.

#### Conductivity:

There were no laboratory conductivity calibrations. No log was maintained for the sensors and no bottle salinity check samples were collected for calibration during P17C. On the second leg, a brief log was maintained and a number of check samples were collected. The sensor failed 11 days into the second leg, and no conductivity was measured for the remainder of that leg or P16C.

Data for pCO2 and pN2O were taken underway with a shipboard gas chromatograph. Data were reported to CDIAC in Oak Ridge, Tennessee

#### B.4 XBT's

None

## **B.5 METEOROLOGICAL OBSERVATIONS**

Meteorological observations where taken at each station. Information taken at each station included dominant wave direction, wind speed and direction, atmospheric pressure, air temperature, weather, clouds and visibility.

## C. HYDROGRAPHIC MEASUREMENTS

A detailed list of flagged discrete data, including the reasons for problems, is provided in section D. Additional comments on some bottle salinities are included in the CTD calibration sections.

## C.1 CTD DATA COLLECTION AND PROCESSING

(Maggie Cook - WHOI; Lynne Talley - SIO)

CTD data on P16C were collected and calibrated by the WHOI CTD group. The CTD hardware technicians were Gary Bond and Peter Landry and the shipboard CTD software technician was Carol MacMurray. The shorebased CTD processor was Maggie Cook.

106 rosette/CTD stations were occupied to the bottom along 151°W between 17.5°S and 19°N (Table 1). Basic station spacing was 30 nm with a 36 bottle 10-liter rosette package; spacing closed to 20 nm between 3°S and 3 N. The backup CTD instrument, fit with a small rosette package (11 1.7-liter bottles), was alternated with the large package between 3°S and 3 N, to obtain CTD station spacing of 10 nm near the equator. Stations were numbered consecutively (starting with the first leg [P17C] of the R/V Washington work which began off the coast of California in May 1991). The first station on this leg (P16C), was station 221; it was a reoccupation of the last station (220) of Leg 2 (P16S) and a continuation of the P16 line to the north. Final CTD data are 2 db averaged pressure,temperature,salinity, oxygen profiles.

Two EG&G/Neil Brown Instrument Systems (NBIS) CTD/O2 (conductivity, temperature, depth, oxygen) profilers were employed on this cruise. WHOI CTD #10 (serial # 3448) with the large rosette package served as the primary instrument, being used for all stations 222 to 250, even stations from 252 to 284, and all stations from 286 to 326. On most stations 36 bottles were used, giving 36 calibration points. CTD 10's conductivity cell was changed prior to station 295. CTD #9 (serial #01-2405-01) with the small rosette package and lowered acoustic doppler current profiler acted as the secondary instrument. It was used for odd stations from 251 to 285, with a maximum of 11 calibration points for each cast.

Both CTD's were equipped with sensors to measure pressure, sea water temperature (two channels) conductivity, and dissolved oxygen concentration. Both were modified to employ titanium strain gauge pressure sensors (Millard, Bond and Toole, 1992). In addition, an interface for an externally mounted transmissometer was added to the CTD's at the request of investigators from Texas A & M.

The accuracy of the final data set hinges on the calibrations of these sensors. Both laboratory measurements and water sample data obtained at sea were used to calibrate sensors. General information on CTD calibration and data processing procedures can be found in the reports of Fofonoff, Hayes and Millard (1974), Millard and Galbraith (1982), and Millard and Yang (1993).

Laboratory calibrations, performed before and after this three leg cruise aboard the R/V Thomas Washington, provide the sole correction information for the CTD pressure and temperature sensors. These temperature and pressure calibrations are used to scale the 2 db data profiles as well as the CTD component of the rosette water sample data files.

The CTD instruments and secondary thermometers were calibrated at the WHOI Calibration Laboratory. The laboratory maintains primary temperature standards at the triple point of water and the melting point of gallium, thereby spanning most of the oceanographic temperature range. Weights certified periodically at the Massachusetts Bureau of Weights and Standards employed with a Ruska model 4280-600 dead weight tester make up the Laboratory's pressure standard while "Wormley" water is the salinity standard. A precision temperature bridge interfaced to a platinum resistance thermometer (EG&G ATB-1250, and/or NBIS CT-2) is used as a transfer standard to calibrate the CTD instruments. This work is carried out in a large salt water bath whose temperature is shifted over the oceanographic range, and/or a set of 5 small freshwater baths held at fixed temperatures between 0 and 30 C. Full instrument immersion is achieved in the large bath; the lower endcap and sensor arm are immersed in the small baths. Stability of the transfer standards is checked regularly against the triple point and gallium cells; based on these data the transfer standard readings are believed accurate to +/- 1 mC. This uncertainty is probably doubled upon transfer to the CTD calibrations via the bath water.

The Ruska dead weight testor is stated by the manufacturer to be accurate to 0.01% (0.6 dbars at 6000 dbars). Our calibration procedure involves cycling the instrument between atmospheric pressure and 10,000 psi and back at 1000 psi intervals, followed by a set of measurements to 5000 psi maximum pressure and back. This is conducted at room temperature. The whole procedure is then repeated at the water ice point. From these data, coefficients in the polynomial regression between measured and true pressure (Millard et al., 1993) are determined.

Finally, a laboratory conductivity calibration is performed using a set of 5 salt water baths at room temperature spanning conductivities between 20 and 60 mmho. Water samples drawn and analyzed on a Guildline Autosal, in combination with conductivity transfer standard measurements with the 5 electrode probe of the EG&G Bridge provide reference information. These data verify CTD instrument functionality, and provide initial correction information for the CTD, which is updated with water sample salinity measurements in the field. In general, we use the laboratory information to determine the sensor bias (exploiting the much larger range of conductivity available in the laboratory tanks than in the open ocean) and use the field data to refine the sensor's range scaling.

CTD data quality flags were set by the chief scientist. Initially all values which were interpolated after removal of bad data were flagged as "6". Where the interpolation was over a pressure interval greater than 10 dbar, the interpolation was rechecked and the values subjectively flagged as either "6" if the interpolated profile fit smoothly with adjacent stations and the interpolation was not too much larger than 10 dbar, as "3" if the interpolation was longer and produced a questionable profile, and as "4" if the interpolation produced a clearly unacceptable profile. Interpolations over large pressure

intervals at station 255 were deleted entirely and the data replaced with -9. The number of scans listed in the CTD data files is "-9" if just one of the four measured values was interpolated, due to a shortcoming in the WHOI internal CTD data format. All CTD oxygen values between the sea surface and the heave compensator stop were flagged "3" based on experience with the P17C and P16S/P17C CTD data sets.

# C.1.a CTD TEMPERATURE

No electronic adjustments were made to the temperature sensor interface boards during laboratory calibrations in order to preserve the stability history of these sensors. Instead, corrections, determined by polynomial least-squares fits to laboratory calibration data, were applied to the data. Temperature calibrations consisted of quadratic fits to 8 temperature points ranging between 0 and 30 degrees C in reference to the platinum thermometer standard (Figure C.1.1). The following quadratic temperature correction algorithms were used in the reduction of CTD downcast and water sample rosette data collected on this cruise.

The June, August and October 1991 temperature calibration data were similar for CTD #10, and thus were combined in one polynomial fit for application to the CTD data. The shift in the temperature calibration was no more than 0.0015C, and the standard dviation of the combined fit was 0.00104C.

CTD #9 was calibrated in August and October 1991 (pre and post cruise). The temperature shifted no more than 0.001C. The post cruise information was used for CTD #9 temprerature, for which the standard of the fit was 0.612 x 10-4 C. CTD #10 (combination calibrations June, August, October 1991):

T= -.232143E-3 + .499794E-3 \* T(raw)+ .341585E-11 \* T(raw)\*T(raw)

CTD # 9 (post-cruise calibration, October, 1991):

where T(raw) is the raw counts of the temperature channel. A time lag correction of 0.250 seconds between C and T sensors was also applied.

# C.1.b CTD PRESSURE

Pre- and post- cruise pressure calibrations were completed using a dead weight tester in the laboratory; data were sampled at 1000 psi intervals with both increasing and decreasing pressure between 0 and 10000 psi. Data reduction employed a quadratic calibration algorithm determined from a least squares fit to these data (Figure C.1.2). Here, we ignore the average 1 dbar hysteresis characteristic of titanium strain gauge pressure sensors and combine increasing and decreasing laboratory pressure data in one quadratic fit to the data.

Following Millard et al (1993) the raw pressure data are scaled to calibrated values with the following polynomial:

2 Pi = A + B \* Praw + C \* Praw + S1 \* (Tp-T0) + S2 \* (Tp-T0) \* Praw

Here Praw are raw counts of the pressure channel. T0 is a reference temperature (21.8 degrees C which for convenience is the room temperature for one of the pressure calibration runs) and Tp is the (measured) temperature of the titanium strain gauge. Thus, S1 and S2 represent variation of the gauge bias and scale adjustments with temperature.

The pre and post cruise calibrations for CTD 10 shifted 1.5 dbar. The standard deviation of the fit for the post-cruise calibration was 0.333 dbar. The following post-cruise determined coefficients were applied to reduce the CTD #10 data:

 $\begin{array}{rcl} A &=& -1.85372 \\ B &=& 1.00331E\text{-}1 \\ C &=& -0.265076E\text{-}8 \\ S1 &=& 2.71E\text{-}6 \\ S2 &=& -0.054 \end{array}$ 

The pre and post cruise calibrations for CTD 9 shifted 1.5 dbar. The standard deviation of the fit for the post-cruise calibration was 0.523 dbar. The following post-cruise determined coefficients were applied to reduce the CTD #9 data:

 $\begin{array}{rcl} A &=& -1.73307 \\ B &=& 1.00489E\text{-}1 \\ C &=& 0.779511E\text{-}9 \\ S1 &=& 3.39E\text{-}6 \\ S2 &=& 0.015 \end{array}$ 

Due to a software error discovered after the cruise, the Tp data recorded at the times of water sample acquisition were corrupted. CTD pressure information in the water sample files was derived using external water temperature as a substitute for the gauge pressure Tp. This substitution incurs error only near the surface when the gauge temperature lags the external value. The effect in the derived pressure is small, comparable to the amplitude of typical ship roll or less. The down-cast data did not experience this error and were reduced using the observed internal gauge temperature.

# C.1.c CTD CONDUCTIVITY

## C.1.c.1 PRE-CRUISE CONDUCTIVITY ALGORITHM

Linear conductivity calibration algorithms, derived from pre-cruise laboratory data, were used for real time display during data acquisition at sea.

Figure C.1.3 shows plots of recent conductivity sensor laboratory calibrations for each CTD instrument. Notice that the post cruise (October, 1991) calibration for CTD 10 shows the markedly different characteristics of the newest conductivity cell which replaced a failed one at station 294.

The pre-cruise conductivity algorithms employed were: CTD # 10

C = -.734217E-02 + 0.100453E-02 \* C(raw) \* [1+A\*(T-T0)+B\*(P-P0)]

CTD # 9

C = -.944740E-02 + 0.977069E-03 \* C(raw) \* [1+A\*(T-T0)+B\*(P-P0)]

where:

C(raw)	is the raw counts of the conductivity channel
А	is the temperature correction coefficient (65E-5 degrees C)
В	is the coefficient of cell contraction with pressure
	(This term is generally 1.5E-8 db-1. However, a different value for
	this term was applied to each of the three conductivity cells employed
	on this cruise. An explanation follows in the discussion of final
	conductivity calibrations)
Т	is scaled temperature
Т0	is 2.8 degrees C
Р	is scaled pressure
P0	is 3000 db

# C.1.c.2 CONDUCTIVITY CALIBRATION PROBLEMS

The following were problems during this cruise which led to major difficulties in the final processing of the data:

The first four stations during P16C were very noisy in pressure, oxygen and salinity. The CTD was repaired by removal of the oxygen pump, replacing a chip in the CTD at station 225, and increasing the power to the CTD. CTD oxygen calibration for these data was impossible through station 226. Comparisons of CTD and rosette data in the rosette water sample file show large errors during these first stations; this is partially due to the erratic behavior of the CTD sensors as well as inconsistencies of rosette sampling procedures typical of watch standers at the start of a cruise.

One of the three conductors in the CTD conducting wire shorted to ground at station 234; the short was found to be at 5288 m wire out thus excluding the option of cutting the wire. The CTD/rosette package was reconfigured for use with 2 conductors and used that way for the remainder of the cruise. The CTD cable was reterminated twice during the cruise: prior to stations 259 and 303. Bottom contact by the CTD occurred at stations 242,245, and 288. CTD station 251 downtrace data exhibited excessive noise; thus, the uptrace data is the source of the final pressure averaged data. The CTD #10 conductivity sensor failed during station 294 at which point it was replaced with a new cell.

The rosette water sample salts are of relatively poor quality for the first part of this cruise. Of course, this is of major concern when the rosette water sample data make up the base of data used for deriving conductivity calibrations. [The variability of rosette data in the

deep water is greater than 0.005 psu.] Water sample quality improved through the cruise (Figures C.1.4a and C.1.4b).

The CTD touched bottom at station 245 and the conductivity calibration shifted prior to station 246. This was followed by a salinometer change between stations 246 and 247, which created difficulties with salvaging the calibration shift. A salinity shift of +0.004 psu occurred between stations 245 and 246 in the raw theta/salinity CTD profile; the replacement salinometer yielded higher salinity values (about 0.001-0.002 psu) after station 246. Final calibration work with the CTD salinity data has brought the overall shift, based on groups of stations prior to 245 and after 246, down to +0.001 to 0.002 psu which is within the standard deviation of the water sample data. A station dependent bias was applied to stations 228 through 245 in order to smooth out the unphysical shift between stations 245 and 246.

Both CTD/O2 instruments (#9 and #10) intermittently showed what we are calling "conductivity hysteresis". That is, the conductivity values retrieved during the downtrace and uptrace are significantly different (as large as .015 mmho/cm). This problem was at least partially explained by residual temperature sensitivity in the MKIII CTD conductivity interface (N.Brown, personal communication, 1992. An electronic fix has since been implemented with no recurrence of the problem.) After much thought, it was decided to modify our standard calibration scheme to derive conductivity scalings from the down-cast information. [Typically, CTD information from the up-cast at the times of water sample collection are used to derive scalings which are subsequently applied to the down- cast. Because of the conductivity hysteresis, this technique yielded down profiles that were not consistent with the water sample salinity data.]

The procedure adopted mimicked standard treatment of the CTD oxygen data. CTD downcast information was extracted at the depths where bottles were taken on the upcast. These data were then combined with the water sample salinity information to derive scalings for the down-cast conductivity data.

Two CTD/O2 instruments were used on the cruise, one of which employed two different conductivity cells. Strangely, of the three different conductivity cells used, none of them could successfully fit the rosette water sample salts in the deep water. After many false starts and much thought, we finally applied a negative conductivity pressure adjustment term ("B" in the algorithm in section C.1.c.1). to CTD #9 stations and a zero conductivity adjustment term to CTD #10 stations (both CO sensors). This is highly unorthodox since the term is then describing these conductivity cells as either expanding or remaining of constant dimension with increasing depth. Despite the ad hoc nature of this method, it significantly improves the consistency between CTD and bottle conductivities in the deep water. It has, on the other hand, induced an 0.002 difference between the two CTD instruments in the mid potential temperature range (2 - 7C) where there is minimal high quality rosette data, particularly for CTD #9.

Lastly, frequent problems with conductivity were encountered at the sea surface. Thus the first good conductivity listed for many stations is at 3 or 5 dbars rather than at 1 dbar. The

problem is likely due to contamination of the average conductivity by measurements in air prior to the package being fully submerged.

# C.1.c.3 FINAL CONDUCTIVITY CALIBRATION

Final conductivity calibrations were derived from a least-squares regression of CTD and water sample conductivity data to determine the slope and bias terms in the earlier mentioned algorithms (Millard and Galbraith, 1982). For both CTD/O2 instruments, the regression routine for estimating conductivity bias and slope adjustments was initially run over all water sample data using the nominal cell deformation terms in the conductivity scaling equation. Time series plots of water sample minus CTD conductivity differences were then constructed to identify station subgroups in which the CTD conductivity cell appeared to be stable (or drifted linearly) with time (Figure C.1.4a and C.1.4b). Expandedscale potential temperature/salinity plots were also used to confirm the groupings. Identified station groups with apparent homogeneous calibration characteristics were then rerun separately through least-squares regression fits of CTD and water sample conductivity data to obtain new conductivity bias and slope terms for each group over the entire water column. The slope term was then further refined by removing the conductivity bias term from the fit and refitting for conductivity slope only in the deep water (usually below 1500 db). Note that the laboratory conductivity bias term was used for CTD # 10, while the regression conductivity bias term was employed for CTD #9 whose laboratory conductivity calibration appeared to be in error (i.e. it did not describe the instrument behavior in the field).

Once station groups were identified it was necessary to apply station dependent conductivity slope adjustments to several station groupings whose time series plots showed a distinct drift with time. In addition, several stations required subjective conductivity slope adjustments to bring the odd station back in line with neighboring station theta/salinity profiles. Many of these adjustments were large (on the order of 0.006 psu in either direction) suggesting periodic instability of the CTD instruments being used.

Careful examination of the deep-water temperature/salinity information revealed a .001-.002 departure of the CTD trace from the water sample data in the deep water. This discrepancy was minimized by modifying the coefficient of cell deformation with pressure as noted above. Data groups were refit for conductivity calibration terms. Two recently analyzed data sets have had similar adjustments to the beta term in order to improve consistency between rosette and CTD salinity in the deep water (TPS-10, Epic Voyagers, 1991; Charles Darwin Cruise 29, Cook et al 1992).

The basic station groupings with derived conductivity bias and slope coefficient terms are listed below.

stations group	stations	bias	slope	
226 - 244	221-245	113775E-1	.10043116E-2	
252 - 286 even	246-250 all			
252 - 262 even		113775E-1	.10043321E-2	
264 - 284 even	264-284 even			
286 - 292 all	286-294 all	113775E	-1.10043156E-2	
CTD # 10 condu	ctivity sensor B:			
295 - 298	295-298	.122951E-2	.10071577E-2	
300 - 311	200 240	Station dependent slope		
300 - 311	299-310	Station depende	ent slope	
311 - 324	311-326	Station depende	ent slope .10070779E-2	
		.122951E-2		
311 - 324	311-326	.122951E-2		

CTD # 10 conductivity sensor A:

Further station by station adjustments to the conductivity slope terms of the above regression groupings are listed below.

station	<u>amt of adjust</u>	<u>new co slope term</u>
221	003	.10042366E-2
222	008	.10041116E-2
223	010	.10040616E-2
224	010	.10040616E-2
225	008	.10041116E-2
226	003	.10042366E-2
241	+.0015	.10043516E-2
251	+.016	.97536222E-3
253	+.006	.97600631E-3
259	001	.97585950E-3
261	002	.97585700E-3
263	001	.97585950E-3
256	+.002	.10043821E-2
258	+.002	.10043821E-2
293	+.003	.10043906E-2
294	+.004	.10044156E-2

Thus, the final conductivity bias and slope terms for all stations of the P16C CTD cruise, except for the station-dependent salinity correction applied after this calibration, follow:

STATION	BIAS	SLOPE	STATION	BIAS	SLOPE
221	<u>1137</u> 75E-1	.10042366E-2	273	039	.97586200E-3
222	113775E-1	.10041116E-2	274	113775E-1	.10043156E-2
223	113775E-1	.10040616E-2	275	039	.97616069E-3
224	113775E-1	.10040616E-2	276	113775E-1	.10043156E-2
225	113775E-1	.10041116E-2	277	039	.97612010E-3
226	113775E-1	.10042366E-2	278	113775E-1	.10043156E-2
227-240	113775E-1	.10043116E-2	279	039	.97607951E-3
241	113775E-1	.10043516E-2	280	113775E-1	.10043156E-2
242-245	113775E-1	.10043116E-2	281	039	.97603893E-3
246-250	113775E-1	.10043321E-2	282	113775E-1	.10043156E-2
251	039	.97536222E-3	283	039	.97599834E-3
252	113775E-1	.10043321E-2	284	113775E-1	.10043156E-2
253	039	.97600631E-3	285	039	.97595775E-3
254	113775E-1	.10043321E-2	286-292	113775E-1	.10043156E-2
255	039	.97586200E-3	293	113775E-1	.10043906E-2
256	113775E-1	.10043821E-2	294	113775E-1	.10044156E-2
257	039	.97586200E-3	295-298	.122951E-2	.10071577E-2
258	113775E-1	.10043821E-2	299	.122951E-2	.10072015E-2
259	039	.97585950E-3	300	.122951E-2	.10072043E-2
260	113775E-1	.10043321E-2	301	.122951E-2	.10071942E-2
261	039	.97585700E-3	302	.122951E-2	.10071841E-2
262	113775E-1	.10043321E-2	303	.122951E-2	.10071740E-2
263	039	.97585950E-3	304	.122951E-2	.10071639E-2
264	113775E-1	.10043156E-2	305	.122951E-2	.10071538E-2
265	039	.97586200E-3	306	.122951E-2	.10071437E-2
266	1137-1	.10043156E-2	307	.122951E-2	.10071336E-2
267	039	.97586200E-3	308	.122951E-2	.10071235E-2
268	113775E-1	.10043156E-2	309	.122951E-2	.10071134E-2
269	039	.97586200E-3	310	.122951E-2	.10071033E-2
270	113775E-1	.10043156E-2	311	.122951E-2	.10070932E-2
271	039	.97586200E-3	312-326	.122951E-2	.10070779E-2
272	113775E-1	.10043156E-2			

An upward jump in conductivity between stations 245 and 246, of 0.002 to 0.004 psu, was concluded to have resulted from bottom contact during station 245. Since there had been a slow shift in calibration prior to station 245, the shift was smoothed out by applying a station dependent salinity bias to stations 228 to 245. This correction was not performed on the conductivity data because it was done in 1995, long after the initial calibration.

Sta.	Salinity bias	Sta.	Salinity bias	Sta.	Salinity bias
	Correction		Correction		Correction
228	0.0000000e+000	234	-7.0588235e-004	240	-1.4117647e-003
229	-1.1764706e-004	235	-8.2352941e-004	241	-1.5294118e-003
230	-2.3529412e-004	236	-9.4117647e-004	242	-1.6470588e-003
231	-3.5294118e-004	237	-1.0588235e-003	243	-1.7647059e-003
232	-4.7058824e-004	238	-1.1764706e-003	244	-1.8823529e-003
233	-5.8823529e-004	239	-1.2941176e-003	245	-2.0000000e-003

Finally, manual editing of random data spikes (salt and temperature) was done, usually interpolating across the pressure bounds of the spikes (Table C.1.2).

Uncertainty in the final CTD salinity data may be measured by differences between CTD and water sample salinity data. Of course, absolute CTD salinity accuracy hinges on the accuracy of the water sample data. A time series plot of salinity differences as a function of station number shows the final data to be uniformly calibrated (Figure C.1.5). Plots of salinity and oxygen differences vs. depth show the consistency of the final calibrated CTD data to the rosette water sample data (Figure C.1.7). The histogram of salinity differences for the full data set (Figure C.1.8) is Gaussian with a mean indistinguishable from zero as would be expected from random measurement error. The standard deviation of the population is 0.0017 psu in the deep water (pressure greater than 2000 db). We consider this latter figure to be representative of the overall uncertainty in the salinity data.

## C.1.c.4 ADDITIONAL COMMENTS ON THE CONDUCTIVITY CALIBRATION

A. The average difference between the bottle and CTD salinities for potential temperatures less than 5.0C is 5.33E-04, with the CTD slightly lower than the bottles, based on the CTD and bottle salinities in the final bottle data file, dated October 27, 1993.

The first eight stations have somewhat lower CTD salinities: for potential temperature less than 5.0C, the average difference over stations 222 to 228 is 2.48E-03. The average difference over stations 229 to 326 is 3.72E-04.

B. As should be expected, there is a difference between CTD 9 and 10, as indicated by salinity and pressure on deep isotherms (Figures C.1.9, C.1.10 and table). The differences between the two CTD's are within the WHP guidelines for accuracy (0.002), and are close to the precision guidelines (0.001). CTD 9 salinity is fresher than CTD 10, and the differences between the two are particularly striking for CTD 9 stations 253 to 261 and for 277 to 285. The differences are less for the intermediate stations 263 to 275.

Average differences and standard deviations on isotherms: CTD10 (stations 250-286) - CTD9 (stations 251-285)

theta	del S	sig S	del P	sig P
2.000	0.0024	-0.4170E-03	-19.4	-1.8
1.900	0.0022	-0.8048E-03	-18.7	3.4
1.800	0.0019	-0.7370E-03	-20.5	-9.9
1.700	0.0020	-0.6350E-03	-22.2	4.7
1.600	0.0016	-0.1006E-02	-11.5	1.3
1.500	0.0011	-0.1394E-02	-0.2	3.6
1.400	0.0007	-0.1154E-02	-17.1	-13.3
1.300	0.0006	-0.1077E-02	-14.0	-2.5
1.200	0.0004	-0.8197E-03	-16.2	3.9
1.100	-0.0002	-0.9853E-03	-28.0	14.4

C. For these locations, for theta < 5C, bottle/CTD salinity differences are greater than 0.01:

sta	bot	pres	bottle-CTD salt	new flagging
223	15	1537.00	1.03989E-02	not flagged
224	15	798.900	1.56975E-02	not flagged
224	10	1638.40	1.12991E-02	not flagged
225	14	1618.80	1.02005E-02	not flagged
240	17	1635.00	-1.28021E-02	flag=3
253	б	1538.00	1.17989E-02	not flagged
300	21	928.100	1.42975E-02	flag=3
317	20	926.300	1.91994E-02	not flagged
321	21	720.200	1.95007E-02	not flagged

#### Sta. 223/1/15/1537 dbar:

This is merely the worst of a set of bottle-CTD salinities in which the bottles are higher than the CTD: the point just above is .008 different. The problem appears to be more in the CTD salinity processing than in the bottle salts, and so the bottle salts are not flagged.

#### Sta. 224/1/10,15/1638, 799 dbar:

Likewise, these are the two worst of a series of bottle salinities which are higher than the calibrated CTD salinity, and since the station is close to the start of the cruise when it appears that the calibration was settling in, none of the bottles have been flagged.

#### Sta. 225/2/14/1619 dbar:

Also in the group of starting stations, although the differences here are also negative in part. The two separate casts of 225 result in some inconsistencies in the differences between bottle and CTD salinities as well. This particular bottle is high relative to the cast 2 CTD, but appears to be quite low relative to the cast 5 CTD and other salinities.

#### Sta. 240/1/17/1635 dbar:

This bottle salinity is low, rather than high. It is one of many which are lower than the CTD on this station; the bottle just above it is almost as low. Because it creates a unsmoothness in the bottle salinity profile which is not present in the CTD profile, it has been flagged as 3.

#### Sta. 253/1/6/1538 dbar:

This is one of several bottles which is high on this station. The total number of bottles for calibration is quite small and the spacing in potential temperature is poor, so it is difficult to determine if this bottle should be flagged or not, so it was not flagged. This was a CTD 9 station which was particularly difficult to calibrate.

#### Sta. 300/3/21/928 dbar:

This bottle is pretty clearly the worst fitting of the bottles on this cast, although the one just above it is also slightly high. It has been flagged as questionable (3) in the .sea file.

#### Sta. 317/1/20/926 dbar:

This value is rather high, but the station shows interleaving and this bottle is at the top of a weak deep layer. Therefore, it could possibly be real, and is not flagged.

#### Sta. 321/1/21/720 dbar:

This is likewise a station with interleaving and the bottle in question is near 5C, so the salinity was not flagged.

## C.1.d CTD OXYGEN

As noted above, the first set of stations were very noisy. CTD oxygen calibration was not possible for stations 221 through 226. At station 251, on which the upcast was used, CTD oxygen was salvageable only for 191 to 2059 dbar. On station 255 there are no oxygens for pressures less than 193 dbar.

In processing the P17C and P16S/P17S data (SIO's Oceanographic Data Facility), which preceded P16C on the same ship with the same deck equipment, it was noted that the oxygen sensor usually drifted badly at the heave compensator stop near 20 dbar, so all oxygen values above that depth were considered to be questionable. Therefore all oxygens from the surface to the compensator stop were flagged "3" in this P16C data set; the pressure at the stop was clear from the number of scans listed unless there were bad values and the scans were listed as "-9". Also, the surface oxygen value (1.0 dbar) is bad on almost all stations and has been flagged 4. It should not be used under any circumstances.

Coefficients in the CTD oxygen sensor calibration algorithm were derived from in situ water sample oxygen data following Owens and Millard (1985).

The algorithm is:

Oxm = [A \* (Oc + B \* dOc/dt) + C] \* Oxsat(T,S)e\*\* D\*[T+E\*(T0-T)]+F\*P

Where

- Oc is the measured oxygen current
- T0 is the measured oxygen temperature
- Oxsat(T,S) is the oxygen saturation according to Weiss (1970)
- A is the oxygen current slope
- B is the oxygen sensor lag
- C is the oxygen current bias
- D, E, F are representative adjustments for the oxygen sensor's teflon membrane permeability sensitivity to temperature and pressure.

Initially, in the CTD oxygen calibration procedure, plots were made of differences between rosette and CTD oxygen data (using nominal calibrations to calculate CTD oxygens). Based upon these plots, CTD oxygen data were subdivided into station groups which appeared to have homogeneous calibration characteristics. A multiple regression technique was then employed to define the coefficients in the above equation. As

mentioned earlier, the regression is between downcast CTD oxygen sensor data and rosette water sample observations obtained on the upcast. This, is necessary because erroneous CTD oxygen data are obtained when the underwater package is stopped to close a rosette bottle. In addition, the oxygen sensor characteristically exhibits excessive up-down hysteresis.

During the P16C cruise, small station groups were typically used for regression analysis to account for frequent oscillations in oxygen sensor characteristics. No CTD oxygen data are available for stations 221-226 and 251 due to the poor quality of the CTD data and the inability of the above algorithm to describe the oxygen sensor characteristics. Erratic oxygen spiking occurred during the stations between 264 and 291 which were collected with CTD #10. These data were salvaged through extensive editing of data spikes in the 1500-3000 db range (Table C.1.2).

Despite the forementioned problems, the quality of the final CTD data oxygen set for P16C is very good. As with the salinity data, a measure of CTD derived oxygen data uncertainty is given by comparison with the water sample data (Figures C.1.6 and C.1.8 but the absolute accuracy depends directly on the water sample accuracy. The population of oxygen difference data has a standard deviation of 0.024 ml/l in the deep water (pressure greater than 2000 db), with a mean indistinguishable from zero.

The following details the station groupings used to generate the final data:

```
CTD 10:
station grouping 227-234 used for stations 227-233
                234
                        used for station 234 (alone)
station
station grouping 235-237 used for stations 235-237
station grouping 238-240 used for stations 238-240
station
                241
                    used for station 241 (alone)
station grouping 241-242 used for station 242
                                                  (alone)
station grouping 243-245 used for stations 243-280
station grouping 282-288 (even) used for stations 282-288 (even)
station grouping 289-293 used for stations 289-293
station grouping 294-295 used for stations 294-295
station grouping 296-299 used for stations 296-299
station grouping 300-304 used for stations 300-304
station grouping 305-310 used for stations 305-310
station grouping 311-316 used for stations 311-321
station grouping 322-326 used for stations 322-326
CTD 9:
station
                              used for station 253
                253 (alone)
                                                        (alone)
station
                257 (alone)
                              used for station 257
                                                        (alone)
station
               259 (alone)
                             used for station 259
                                                       (alone)
station grouping 261-271 (odd) used for stations 261-272 (odd)
station grouping 273-285 (odd) used for stations 273-285 (odd)
```
Thus, the final algorithm terms applied to all stations of the P16C CTD cruise are as follows:

CTD 10:

012	02DIF	BIAS	SLOPE	PCOR	TCOR	% OT	LAG
227	0.0671	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
228	0.0688	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
229	0.0975	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
230	0.0919	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
231	0.1064	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
232	0.1312	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
233	0.1410	0.3900E-01	0.8518	0.1483E-03	-0.2485E-01	0.8930	2.66
234	0.1722	-0.7900E-01	1.232	0.1572E-03	-0.3670E-01	0.7500	8.00
235	0.2070	0.3200E-01	0.8889	0.1524E-03	-0.2666E-01	0.7500	5.37
236	0.1826	0.3200E-01	0.8889		-0.2666E-01	0.7500	5.37
237	0.2129	0.3200E-01	0.8889	0.1524E-03	-0.2666E-01	0.7500	5.37
238	0.1998	0.3800E-01	0.8831	0.1516E-03	-0.2494E-01	0.9653	-0.99
239	0.2219	0.3800E-01	0.8831	0.1516E-03	-0.2494E-01	0.9653	-0.99
240	0.3021	0.3800E-01	0.8831		-0.2494E-01	0.9653	-0.99
241	0.3140	0.2800E-01	0.9375	0.1472E-03	-0.2684E-01	0.8602	8.00
242	0.3190	0.6400E-01	0.8087	0.1468E-03	-0.2326E-01	0.9935	4.07
	0.2293	-0.8000E-02	1.027	0.1524E-03			
	0.2372	-0.8000E-02	1.027	0.1524E-03			
	0.2304	-0.8000E-02	1.027	0.1524E-03			
	0.2153	-0.8000E-02	1.027	0.1524E-03			
	0.1988	-0.8000E-02	1.027	0.1524E-03			
	0.1954	-0.8000E-02	1.027	0.1524E-03			
	0.2009	-0.8000E-02	1.027	0.1524E-03			
	0.1982	-0.8000E-02	1.027	0.1524E-03			
	0.1991	-0.8000E-02	1.027	0.1524E-03			
	0.2056	-0.8000E-02	1.027	0.1524E-03			
	0.1922	-0.8000E-02	1.027	0.1524E-03			
	0.2020	-0.8000E-02	1.027	0.1524E-03			
	0.1954 0.1868	-0.8000E-02	1.027 1.027	0.1524E-03 0.1524E-03		0.8675	
	0.1694	-0.8000E-02	1.027	0.1524E-03 0.1524E-03			
	0.1593	-0.8000E-02	1.027	0.1524E-03 0.1524E-03			
	0.1558	-0.8000E-02	1.027	0.1524E-03			
	0.1575	-0.8000E-02	1.027	0.1524E-03			
	0.1421	-0.8000E-02	1.027	0.1524E-03			
	0.1180	-0.8000E-02	1.027	0.1524E-03			
	0.0874	-0.8000E-02	1.027	0.1524E-03			
	0.1408	-0.8000E-02	1.027	0.1524E-03	-0.2914E-01	0.8675	
	0.1568	-0.8000E-02	1.027	0.1524E-03		0.8675	
	0.1602	-0.1000E-02	0.9945			0.9059	
	0.1510	-0.1000E-02	0.9945			0.9059	
	0.1833	-0.1000E-02	0.9945			0.9059	
	0.1664	-0.1000E-02	0.9945			0.9059	
	0.1812	-0.1000E-02	0.9945			0.9059	
	0.2033	0.1000E-02	1.002	0.1484E-03		0.8269	
	0.1918	0.1000E-02	1.002	0.1484E-03		0.8269	
291	0.2024	0.1000E-02	1.002	0.1484E-03	-0.2844E-01	0.8269	7.60
292	0.1969	0.1000E-02	1.002	0.1484E-03	-0.2844E-01	0.8269	7.60

CTD	10:						
	O2DIF	BIAS	SLOPE	PCOR	TCOR	% OT	LAG
293	0.2057	0.1000E-02	1.002	0.1484E-03	-0.2844E-01	0.8269	7.60
294	0.1882	0.2000E-02	0.9787	0.1499E-03	-0.2683E-01	0.8371	6.25
295	0.1826	0.2000E-02	0.9787	0.1499E-03	-0.2683E-01	0.8371	6.25
296	0.1950	0.5000E-02	0.9738			0.8338	6.01
297	0.1904	0.5000E-02	0.9738	0.1504E-03	-0.2689E-01	0.8338	6.01
298	0.1836	0.5000E-02	0.9738			0.8338	6.01
299	0.1923	0.5000E-02	0.9738	0.1504E-03	-0.2689E-01	0.8338	6.01
300	0.2178	0.0000E+00	1.023	0.1463E-03	-0.2919E-01	0.7500	) 7.23
301	0.1875	0.0000E+00	1.023	0.1463E-03	-0.2919E-01	0.7500	7.23
302	0.2230	0.0000E+00	1.023	0.1463E-03	-0.2919E-01	0.7500	7.23
303	0.2234	0.0000E+00	1.023	0.1463E-03	-0.2919E-01	0.7500	7.23
304	0.2124	0.0000E+00	1.023	0.1463E-03	-0.2919E-01	0.7500	) 7.23
305	0.1805	0.2000E-02	0.9925		-0.2891E-01	0.7500	8.00
306	0.1907	0.2000E-02	0.9925	0.1473E-03	-0.2891E-01	0.7500	8.00
307	0.1928	0.2000E-02	0.9925	0.1473E-03	-0.2891E-01	0.7500	8.00
308	0.2231	0.2000E-02	0.9925	0.1473E-03	-0.2891E-01	0.7500	8.00
309	0.2151	0.2000E-02	0.9925		-0.2891E-01	0.7500	8.00
310	0.2072	0.2000E-02	0.9925	0.1473E-03	-0.2891E-01	0.7500	8.00
311	0.2163	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	8.00
	0.2027	0.0000E+00	1.022	0.1439E-03		0.7500	
313	0.1749	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	8.00
314	0.1886	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	8.00
	0.1775	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	
	0.1702	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	
	0.1726	0.0000E+00	1.022	0.1439E-03		0.7500	
	0.1825	0.0000E+00	1.022	0.1439E-03		0.7500	
	0.1834	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	
	0.1847	0.0000E+00	1.022	0.1439E-03	-0.2980E-01	0.7500	
	0.1345	0.0000E+00	1.022	0.1439E-03		0.7500	
	0.0624	0.0000E+00	1.032	0.1407E-03		0.8407	
	0.0396	0.0000E+00	1.032	0.1407E-03		0.8407	
-	0.0162	0.0000E+00	1.032	0.1407E-03		0.8407	
	-0.0231	0.0000E+00	1.032	0.1407E-03		0.8407	
326	0.1127	0.0000E+00	1.032	0.1407E-03	-0.3134E-01	0.8407	3.84

CTD 9:

O2DIF	BIAS	SLOPE I	PCOR 7	rcor	% OT	LAG
253-0.0794	-0.2800E-01	0.9616	0.1677E-03	-0.3043E-01	0.9670	8.00
255-0.2434	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
257-0.1835	-0.2300E-01	0.9127	0.1708E-03	-0.3175E-01	0.7500	8.00
259-0.2732	-0.2400E-01	0.8979	0.1658E-03	-0.3049E-01	0.7500	8.00
261-0.1926	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
263-0.2275	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
265-0.2261	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
267-0.2458	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
269-0.2618	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
271-0.2847	-0.1500E-01	0.8771	0.1717E-03	-0.2957E-01	0.7500	8.00
273-0.3036	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
275-0.3014	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
277-0.3078	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
279-0.3034	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
281-0.2866	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
283-0.2687	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06
285-0.2705	-0.4000E-02	0.8285	0.1658E-03	-0.2805E-01	0.8403	5.06

# TABLE C.1.2: MANUAL EDITING OF THE P16C CTD DATA

	- (11)	
STATION #	Pressure (db)	
221	1819 - 1823	interpolate TE,SA
	1 - 3639	ZERO all OX
222	1459 - 1463	interpolate TE,SA
	3147 - 3151	interpolate TE,SA
	3679 - 3685	interpolate TE,SA
	1 - 3007	ZERO all OX
223	3761 - 3769	interpolate TE,SA
	1 - 4119	ZERO all OX
224	1093 - 1097	interpolate TE,SA
	1251 - 1259	interpolate TE,SA
	1625 - 1629	interpolate TE,SA
	2665 - 2671	interpolate TE,SA
	1 - 3421	ZERO all OX
225	643 - 695	interpolate TE,SA
	991 - 997	interpolate TE,SA
	1105 - 1109	interpolate TE,SA
	1591 - 1595	interpolate TE,SA
	1 - 4381	ZERO all OX
226	1575 - 1579	interpolate TE,SA
	1961 - 1965	interpolate TE,SA
	2781 - 2785	interpolate TE,SA
	3701 - 3709	interpolate TE,SA
	3811 - 3827	interpolate TE
	4349 - 4371	interpolate TE
	3811 - 3825	interpolate SA
	4349 - 4365	interpolate SA
	1 - 4593	ZERO all OX
227	2965 - 2969	interpolate TE,SA
229	1	set surface $SA = 36.345$
235	301 - 321	interpolate OX
236	1	set surface $OX = 4.884$
	7	set OX VALUE = $4.827$
	41	set OX VALUE = $4.848$
	79	set OX VALUE = $4.762$
	121	set OX VALUE = $4.352$
	159	set OX VALUE = 3.968
	199	set OX VALUE = $3.685$
	3 - 7	interpolate OX
	7 - 41	interpolate OX
	41 - 79	interpolate OX
	79 - 121	interpolate OX
	121 - 159	interpolate OX
	159 - 199	interpolate OX
	199 - 209	interpolate OX
	325 - 355	interpolate OX
237	1	set surface SA = $35.942$
241	289 - 293	interpolate SA
249	1911 - 1919	interpolate SA
417		THEET POTAGE DA

STATION #	Pressure (db)	Type of edit
250	3-5	set TE and SA values to same as 7db values
	567 - 571	interpolate SA
	4843	set bottom SA = $34.700$
	4785 - 4843	interpolate SA
251	4	set surface SA to 6 db value
758 - 792		interpolate SA
	1008 - 1028	interpolate SA
	1732 - 1742	interpolate SA
	1746 - 1754	interpolate SA
	1756 - 1768	interpolate SA
	1770 - 1784	interpolate SA
	2014 - 2028	interpolate TE,SA,OX
	2058 - 2092	interpolate SA
	2454 - 2460	interpolate SA
	2014 - 2028	interpolate SA
	3054 - 3732	interpolate TE
	2087	set OXYGEN = 2.557
	3071	set OXYGEN = 3.247
	3545	set OXYGEN = 3.529
	4579	set OXYGEN = 4.240
	4794	set OXYGEN = 4.240
	768 - 786	interpolate OX
	2062 - 2087	interpolate OX
	2087 - 3071	interpolate OX
	3071 - 3545	interpolate OX
	3545 - 4579	interpolate OX
	4580 - 4794	interpolate OX
	1 - 191	ZERO all OX
	ALL DATA	interpolate 2db average even listings
		to 2db average odd listings
252	1-3	set TE and SA values to 5 db values
253	2855 - 2859	interpolate OX
	2865 - 2883	interpolate OX
	4627 - 4631	interpolate OX
	4647 - 4667	interpolate OX
255	5 - 11	interpolate TE
	45 - 207	ZERO TE
	255 - 267	interpolate TE
	1 - 221	ZERO SA
	227 - 237	interpolate SA
	251 - 267	interpolate SA
	1 - 191	ZERO all OX
	3111 - 3131	interpolate OX
	4307 - 4313	interpolate OX
256	1-3	set TE and SA values to 5 db values
257	2249 - 2317	interpolate OX
	2743 - 2767	interpolate OX
	3837 - 3857	interpolate OX
	4901	set bottom OX = $4.30$
	4805 - 4901	interpolate OX

STATION #	Pressure (db)	Type of edit
259	3515 - 3531	interpolate OX
	3759 -3763	interpolate OX
261	4137 - 4185	interpolate OX
264	1599 - 1605	interpolate OX
	1635 - 1643	interpolate OX
	1647 - 1651	interpolate OX
	1659 - 1667	interpolate OX
	1669 - 1677	interpolate OX
	1681 - 1687	interpolate OX
	1693 - 1697	interpolate OX
	1703 - 1711	interpolate OX
	1719 - 1727	interpolate OX
	1735 - 1739	interpolate OX
	1965 - 1871	interpolate OX
	2025 - 2029	interpolate OX
265	1029 - 1033	interpolate TE,SA
	1237 - 1241	interpolate TE,SA
	1245 - 1253	interpolate TE,SA
	1687 - 1695	interpolate TE,SA
	1745 - 1751	interpolate TE,SA
268	311 - 327	interpolate SA
	3067 - 4389	APPLY SA BIAS = .0028
	3067 - 3075	interpolate SA
	2313 - 2327	interpolate OX
	2401 - 2407	interpolate OX
	2433 - 2443	interpolate OX
	2557 - 2563	interpolate OX
	2605 - 2611	interpolate OX
070	2727 - 2735	interpolate OX
270	1641 - 1647	interpolate OX
274	1693 - 1699 1339 - 1345	interpolate OX
274	2665 - 2675	interpolate OX
	2693 - 2701	interpolate OX interpolate OX
	2725 - 2731	interpolate OX
	2745 - 2753	interpolate OX
278	1-3	set TE and SA values to 5 db values
143 - 151	TJ	interpolate SA
279	1-3	set SA value to same as 5 db value 280
595 - 601	1 5	interpolate SA
283	1	set SURFACE OX = $5.316$
285	- 125 - 163	interpolate SA
200	2273 - 2277	interpolate SA
286	643 - 647	interpolate SA
	653 - 657	interpolate SA
287	1 - 3	set TE and SA to same as 5 db value
294	2101	set SA value = 34.644
	2351	set SA value = 34.660
	2503	set SA value = 34.664
	2685	set SA value = 34.668
	2909	set SA value = $34.673$

STATION #	Pressure (db)	Type of edit
<u>STATION #</u>	Pressure (db) 3151 3403 3665 4001 4301 4635 5347 5475 1993 - 2101 2101 - 2351 2351 - 2503 2503 - 2685 2685 - 2909 2909 - 3151 3151 - 3403 3403 - 3665 3665 - 4001 4001 - 4301 4301 - 4635 4635 - 5347 5347 - 5475 91 - 99	Type of edit set SA value = 34.678 set SA value = 34.682 set SA value = 34.688 set SA value = 34.692 set SA value = 34.696 set SA value = 34.696 set end SA value = 34.696 interpolate SA interpolate SA
304	91 - 99 3	set SA to value of 5 db scan
306 322	3 - 5 5 - 5 5 - 561 571 - 605 931 - 945 571 - 605 769 - 773 875 - 883	<pre>set SA to value of 5 db scan set TE and SA to values of 7 db scan set surface SA = 34.648 set surface TE = 26.621 interpolate SA interpolate SA interpolate SA interpolate OX interpolate OX</pre>

## C.1.e CTD - INDIVIDUAL STATION COMMENTS

#### Stations 221-225:

noisy, with pressure, oxygen and salinity spikes. The CTD was cabled to only one center conductor, with the other two conductors being wired to the two rosette pylons for the 36 bottle rosette package. Redundant temp was not coming up the wire. Oxygen severely erratic. Prior to station 225, the OTM sensor (redundant temp) was temporarily disconnected to try to increase current to the CTD and oxygen pump. CTD failure at 1600m on the upcast, all AC went dead. Cast aborted at 1500m. The IC chip was replaced, station 225 cast 5 (2000m) still noisy. Increased voltage to the fish by switching to a different power supply.

## Station 226:

somewhat cleaner but somehow out of phase towards the end of cast. Removed SBE oxygen pump to reduce total power consumption of CTD package. Use of pump exceeded compliance voltage capability (150 VDC).

## Station 227:

Phase adjusted, and data were very clean, oxygen and pressure very smooth. No hysteresis (which was evident on prior stations).

Seabeam had problems (gyro?) between sta 227 and 228.

#### Stations 231-233:

O2 dropouts on the upcasts. CTD package hit side of ship upon retrieval of sta 233. Three bottles broken.

## Station 234:

O2 dropouts on upcast. Upon retrieval of sta 234, bottles 17-24 were not fired. Failure was due to short to seaground in center conductor of E/M wire (pylon # 1-24 position). Short 113 ohms from slipring and 180 ohms from fish termination. Rewired CTD pkg with one conductor dedicated to pylon # 1 plus CTD and second conductor to pylon # 2.

#### Stations 235 and 236:

O2 dropouts first 350 m on downcast. Sta 235 O2 dropouts and redundant temperature problems on upcast.

<u>Station 242:</u> bottom contact but no conductivity shift.

#### Station 245:

bottom contact; 0.004 psu salinity shift between 245 and 246. After nearly final calibration, potential temperature/salinity profiles for the groups of stations before and after this shift overlaid very well, within 0.002. There was a marked shift, of about 0.002 (coldest) to 0.004 (around 1.4C) at this point. Since this shift was judged to be due to the bottom contact of the CTD on station 245, and since the calibration was drifting slightly prior to this station, a station dependent bias correction was applied to stations 228 to 245.

#### Station 251:

First lowered acoustic doppler (LADCP) station, using CTD #9. Its battery was weak from sitting in sun on deck. Not enough current to fish. As a result, conductivity jumped near end of downcast when more voltage was applied. Station was processed by pressure sorting the upcast. This station was noisier than most other stations.

#### Stations 251, 253, 255 (CTD 9):

pressure hysteresis. Sensor settled down by stations 257 and 259. Hysteresis came back station 261 and seemed to remain a characteristic for the duration of casts with CTD 9.

## Station 253:

(CTD 9) salinity is lower than surrounding stations by about 0.005 - 0.007 for potential temperature about 1.3C and 5.8C (800-2800 dbar) (Fig. C.1.9). The offset is smaller although still marked below 2800 dbar. This station should be used only with extreme caution. All salinities are flagged as 3. An offset was not applied because the error is not of the same magnitude throughout the water column.

#### Station 259:

Retermination prior to station. Just before deploying 259, fatal failure with CTD 9. OTM board fried. As a result, redundant temperature had a serious departure from the platinum temperature for this station. For the rest of the CTD 9 stations, CTD 10's OTM was used. It was switched out every station.

#### Stations 264-291:

Erratic oxygen spiking CTD 10 stations only. Seemed pressure related- 1500-300db range only. Major editing done.

## Station 286:

to reduce oxygen spiking, tied off endcaps, lowered compliance voltage and debubbled receptacle. Spiking variable until stations 290-291 when spikes mysteriously disappeared.

Station 288: bottom contact. No apparent conductivity shift between 288 and 289.

<u>Station 292:</u> conductivity started drifting fresh.

Station 294:

conductivity cell died. Replaced sensor prior to station 295. Salinity was interpolated and is flagged 4 for 1993- 5471 dbar.

Station 302:

OTM flaky on upcast. New termination prior to station 303, as the sea cable from CTD to rosette got hung up on cart.

Station 306:

Pressure hysteresis in CTD 10.











Figure C.1.2a: Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory pressure calibration data



Figure C.1.2b: Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory pressure calibration data



Figure C.1.3a: Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory conductivity calibration data



Figure C.1.3b: Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory conductivity calibration data



Figure C.1.4a: CTD#10 conductivity sensors A and B. Pre-cruise nominally calibrated CTD conductivity data differenced from rosette water sample data.





Figure C.1.4b: CTD#9 conductivity sensors A and B. Pre-cruise nominally calibrated CTD conductivity data differenced from rosette water sample data.













Figure C.1.5: Salinity differences (rosette - CTD) of final calibrated CTD data. Full profile (bottom); Below 2000 db (top).



Figure C.1.6: Oxygen differences (rosette - CTD) of final calibrated CTD data. Full profile (bottom); Below 2000 db (top).









Figure C.1.8: Histogram plot of differences between final calibrated CTD and rosette water sample data.





Figure C.1.9: Salinity on potential temperature surfaces 1.1 to 2.0C, separated by 0.1C. The smoother overlying curve is CTD#10 only. The jagged curve includes both CTD#9 and 10.



Figure C.1.10: Average salinity vs. potential temperature for each isotherm 1.1 to 2.0C, separated by 0.1C. Error bars are one standard deviation. (a) CTD#9.(b) CTD#10. (c) The averages of both CTD#9 and 10 replotted from a and b.

## C.2 GERARD BOTTLES

Gerard pressures and temperatures were calculated from Deep- Sea Reversing Thermometer (DSRT) readings. Each DSRT rack normally held 2 protected (temperature) thermometers and 1 unprotected (pressure) thermometer. Thermometers were read by two people, each attempting to read a precision equal to one tenth of the thermometer etching interval. Thus, a thermometer etched at 0.05 degree intervals would be read to the nearest 0.005 degrees. Each temperature value is therefore calculated from the average of four readings provided both protected thermometers function normally.

The temperatures are based on the International Temperature Scale of 1990.

## C.3 SALINITY

(George Knapp - WHOI)

Analysis of bottle salinities were performed by two analysts from WHOI: George Knapp (stations 221-303) and Robert Stanley (stations 304-326). Methodology for both analyses are described WHOI Technical Report 90-35.

Guildline Autosal model 8400A salinometers were used during this cruise. They were standardized once a day with IAPSO Standard water, Batch P-114. During the cruise, Autosal #8 appeared to be giving erratic readings, due probably to sporadic shipboard radio interference. On September 9th, prior to station 247, use of this salinometer was discontinued and all further samples were run on Autosal #9. This salinometer appeared less sensitive to the radio interference. Also, salinometer operation was discontinued during regularly scheduled radio transmissions. Prior to station 304 the autosal was thoroughly cleaned. The following table contains salinity standardization data for the WOCE P16C cruise.

Bat	ch Sal#	0p	Tmp	Zero	Sby	Date	Time
STDZE	,P-114,8	3,GI	РК,24	,00002	,24+6736	,09-01-1991	15:07:47
STDZE	,P-114,8	B,RJ	JS,24	,00002	,24+6736	,09-01-1991	16:27:21
STDZE	,P-114,8	, RJ	JS,24	,00002	,24+6736	,09-02-1991	10:21:26
STDZE	,P-114,8	, RJ	JS,24	,00002	,24+6736	,09-03-1991	14:44:10
STDZE	,P-114,8	B,RC	JS,24	,00000	,24+6734	,09-04-1991	13:24:38
STDZE	,P-114,8	B,RC	JS,24	,00000	,24+6727	,09-05-1991	12:43:57
STDZE	,P-114,8	B,RC	JS,24	,00000	,24+6727	,09-06-1991	12:58:31
STDZE	,P-114,8	B,RC	JS,24	,00000	,24+6727	,09-07-1991	13:20:51
STDZE	,P-114,8	B,RJ	JS,24	,00000	,24+6726	,09-08-1991	13:02:33
STDZE	,P-114,8	, RJ	JS,24	,00000	,24+6728	,09-09-1991	16:17:39
STDZE	,P-114,9	, RJ	JS,24	,00000	,24+6099	,09-10-1991	14:04:17
STDZE	,P-114,9	, RJ	JS,24	,00002	,24+6099	,09-11-1991	13:50:40
STDZE	,P-114,9	, RJ	JS,24	,00002	,24+6098	,09-12-1991	13:29:16
STDZE	,P-114,9	, RJ	JS,24	,00002	,24+6097	,09-13-1991	15:47:29
STDZE	,P-114,9	, RJ	JS,24	,00002	,24+6098	,09-14-1991	08:56:13
STDZE	,P-114,9	, RJ	JS,24	,00002	,24+6095	,09-15-1991	14:03:03

Time Batch Sal# Op Tmp Zero Sby Date STDZE , P-114,9, RJS, 24, -.00001, 24+6092, 09-16-1991 15:15:07 STDZE ,P-114,9,RJS,24,-.00001,24+6089,09-17-1991 15:13:52 STDZE , P-114,9, RJS, 24, -.00001, 24+6086, 09-18-1991 18:33:48 STDZE , P-114,9, RJS, 24, -.00001, 24+6089, 09-19-1991 11:54:46 STDZE , P-114,9, RJS, 24, -.00001, 24+6089, 09-20-1991 14:22:33 STDZE , P-114,9, RJS, 24, -.00001, 24+6088, 09-21-1991 14:27:12 STDZE , P-114,9, RJS, 24, -.00001, 24+6088, 09-22-1991 13:32:34 STDZE , P-114,9, RJS, 24, -.00001, 24+6089, 09-23-1991 14:23:32 STDZE , P-114,9, GPK, 24, -.00001, 24+6087, 09-24-1991 14:36:32 STDZE , P-114,9,GPK,24,-.00001,24+6087,09-25-1991 14:25:44 STDZE , P-114,9, GPK, 24, -.00000, 24+6087, 09-26-1991 15:50:26 STDZE , P-114,9,GPK,24,-.00001,24+6089,09-27-1991 15:46:47 STDZE , P-114,9,GPK,24,-.00001,24+6089,09-28-1991 15:52:50 STDZE , P-114,9, GPK, 24, -.00001, 24+6087, 09-29-1991 16:56:11 STDZE , P-114,9,GPK,24,-.00001,24+6091,09-30-1991 17:26:43

## C.4. OXYGEN

(George Knapp - WHOI)

## C.4.a. DISSOLVED OXYGEN

Analysts: George Knapp (221-303) and Robert Stanley (304-326).

No unusual problems were noted.

#### C.4.b. NOTE ON CONVERSION TO GRAVIMETRIC UNITS

(L. Gordon, OSU)

The oxygens were converted to gravimetric units by Louis Gordon at Oregon State University. The WHPO 91-1 procedures were followed for the conversions. Oxygen was converted to micromoles per kg from the WHOI ml/l data using the densities of the samples computed at their potential temperatures and salinities. Where there were no bottle salinities the CTD salinities were used. The format for the oxygen concentration field in the original data file with ml/l was in the XX.XXX format. This was changed to to XXX.XX for the gravimetric units. This should keep the total number of columns in the table the same.

In order that the bottle and CTD oxygens in the bottle data file can be compared, the CTD oxygens were also converted to gravimetric units by Lou Gordon. The conversion from ml/l to micromoles/kg was done using 22.3914 I-STP/mole for the molar volume of oxygen and seawater density computed using the CTD salinity and potential temperature at the bottle depths indicated.

# C.4.c. This table, from George Knapp, contains all of the Dissolved Oxygen Standardization and Blank determinations made during WOCE cruise P-16C.

Mode	Cruise	Bur	ette Vols.	EndVolt	Thio	Date	Time
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.469	09-01-1991	16:06:55
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.491	09-01-1991	16:06:55
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.467	09-01-1991	16:06:55
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.460	09-01-1991	16:06:55
BLANK	P-16C	15.000	49.879 0.999	0.987	0.005	09-01-1991	16:18:03
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.462	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.466	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.499	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.496	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.478	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.471	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0210	4.482	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0140	4.473	09-02-1991	12:14:37
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.420	09-03-1991	12:46:59
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.418	09-03-1991	12:46:59
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.426	09-03-1991	12:46:59
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.415	09-03-1991	12:46:59
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.443	09-04-1991	12:22:28
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.437	09-04-1991	12:22:28
STDZE	P-16C	15.000	49.879 148.8	0.0150	4.444	09-04-1991	12:22:28
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.433	09-04-1991	12:22:28
STDZE	P-16C	15.000	49.879 148.8	0.0310	4.469	09-05-1991	13:01:40
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.466	09-05-1991	13:01:40
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.472	09-05-1991	13:01:40
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.465	09-05-1991	13:01:40
BLANK	P-16C	15.000	49.879 1.002	0.992	0.004	09-05-1991	13:13:05
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.493	09-06-1991	12:41:53
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.480	09-06-1991	12:41:53
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.492	09-06-1991	12:41:53
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.482	09-06-1991	12:41:53
STDZE	P-16C	15.000	49.879 148.8	0.0150	4.519	09-07-1991	01:40:05
STDZE	P-16C	15.000	49.879 148.8	0.0150	4.508	09-07-1991	01:40:05
STDZE	P-16C	15.000	49.879 148.8	0.0310	4.237	09-07-1991	14:10:07
STDZE	P-16C	15.000	49.879 148.8		4.255	09-07-1991	
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.262	09-07-1991	14:10:07
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.256	09-07-1991	14:10:07
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.273	09-08-1991	17:16:51
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.263	09-08-1991	17:16:51
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.274	09-09-1991	14:46:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.268	09-09-1991	14:46:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.272	09-09-1991	14:46:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.263	09-09-1991	14:46:39
BLANK	P-16C	15.000	49.879 1.002	0.992	0.002	09-09-1991	15:13:05
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.280	09 - 10 - 1991	13:06:13
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.277	09-10-1991 09-11-1991	13:06:13
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.473	09-11-1991	12:59:29

Mode	Cruise	Bur	ette Vols.	EndVolt	Thio	Date	Time
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.463	09-11-1991	12:59:29
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.480	09-11-1991	12:59:29
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.474	09-11-1991	12:59:29
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.483	09-12-1991	13:14:14
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.473	09-12-1991	13:14:14
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.482	09-13-1991	12:55:44
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.483	09-13-1991	12:55:44
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.491	09-13-1991	12:55:44
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.479	09-13-1991	12:55:44
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.510	09-14-1991	14:10:14
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.511	09-14-1991	14:10:14
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.454	09-14-1991	23:12:28
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.448	09-14-1991	23:12:28
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.461	09-14-1991	23:12:28
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.429	09-14-1991	23:12:28
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.498	09-15-1991	15:42:34
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.502	09-15-1991	15:42:34
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.548	09-15-1991	16:00:46
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.542	09-15-1991	16:00:46
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.526	09-15-1991	16:00:46
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.519	09-15-1991	16:00:46
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.555	09-16-1991	15:21:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.560	09-16-1991	15:21:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.557	09-16-1991	15:21:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.556	09-16-1991	15:21:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.555	09-17-1991	15:16:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.554	09-17-1991	15:16:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.562	09-17-1991	15:16:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.557	09-17-1991	15:16:12
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.430	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.447	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.441	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.435	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.471	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.467	09-18-1991	15:29:11
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.470	09-19-1991	15:55:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.475	09-19-1991	15:55:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.482	09-19-1991	15:55:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.480	09-19-1991	15:55:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.298	09-20-1991	22:34:37
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.303	09-20-1991	22:34:37
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.312	09-21-1991	15:54:19
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.304	09-21-1991	15:54:19
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.315	09-21-1991	15:54:19
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.304	09-21-1991	15:54:19
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.322	09-22-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.309	09-22-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.320	09-22-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.318	09-22-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.367	09-23-1991	16:12:58

Mode	Cruise	Bur	ette Vols.	EndVolt	Thio	Date	Time
STDZE	 P-16C	15.000	49.879 148.8	0.0160	4.354	 09-23-1991	 16:12:58
					4.354		
STDZE	P-16C	15.000	49.879 148.8	0.0160		09-23-1991	16:12:58
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.355	09-23-1991	16:12:58
BLANK	P-16C	15.000	49.879 1.002	0.992	0.002	09-23-1991	16:23:05
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.470	09-24-1991	15:35:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.475	09-24-1991	15:35:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.489	09-24-1991	15:35:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.481	09-24-1991	15:35:12
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.288	09-25-1991	22:34:37
STDZE	P-16C	15.000	49.879 148.8	0.0230	4.313	09-25-1991	22:34:37
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.302	09-26-1991	15:59:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.314	09-26-1991	15:59:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.305	09-26-1991	15:59:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.314	09-26-1991	15:59:39
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.322	09-27-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.309	09-27-1991	16:25:04
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.319	09-28-1991	17:21:34
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.325	09-28-1991	17:21:34
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.360	09-29-1991	16:10:00
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.364	09-29-1991	16:10:00
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.364	09-29-1991	16:10:00
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.365	09-29-1991	16:10:00
BLANK	P-16C	15.000	49.879 1.002	0.992	0.000	09-29-1991	16:21:22
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.367	09-30-1991	15:18:33
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.368	09-30-1991	15:18:33
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.364	09-30-1991	15:18:33
STDZE	P-16C	15.000	49.879 148.8	0.0160	4.375	09-30-1991	15:18:33

## C.5. NUTRIENTS

(Louis Gordon - Oregon State University) 22.APR.1992

## C.5.a. EQUIPMENT AND TECHNIQUES:

Nutrient analyses were performed by analysts from Oregon State University using a Technicon AutoAnalyzer II. The AutoAnalyzer used was provided by the Oceanographic Data Facility of Scripps Institution of Oceanography (ODF/SIO). A data acquisition system and the software used to process the nutrient data were developed and supplied by OSU. For this online document, all Greek letters have been replaced by similar English alphabet, e.g. umol, and superscripts put on the same line, e.g. kg-1.

The chemical methods used on Leg 3 (P16C) were essentially and deliberately the same as those used on the first two legs. All of the reagent and standard materials were provided by SIO/ODF. The methods are described in Atlas et al. (1972) and Gordon et. al. (in prep.), but with modifications in analytical protocols as employed by ODF. Calculation of nutrient concentrations from measured absorbances was done using OSU software on Leg 3 and SIO/ODF software on the first two legs.

Several changes in the pump tube sizes used in the AutoAnalyzer were made at the start of Leg 3. These were made to reduce the degree of non- linearity in the silicic acid and nitrate + nitrite (N+N) analyses. The plumbing of the cadmium reduction column used in the N+N analytical manifold was changed slightly to reduce dead volume.

## C.5.b. SAMPLING PROCEDURE:

Nutrient samples were drawn from all CTD/rosette casts except for the 11-bottle ADCP casts made between "regular" CTD casts in the equatorial region. A total of 89 stations were sampled. Additional samples were drawn from all Gerard barrels and their "piggyback" Niskin bottles. High density polyethylene (HDPE) centrifuge tubes of approximately 50 ml volume were used as sample containers, and positioned in the autosampler tray without further sample transfer. These sample tubes were routinely rinsed at least 4 times with one third to one half of their volume of sample seawater before filling.

Nutrient samples were drawn following those for trace gases, He, Tritium, dissolved oxygen and carbon dioxide. In some instances, the complete sampling procedure was not completed for almost 2 hours. At most stations, the AutoAnalyzer was started before sampling was completed to reduce the delay and minimize possible changes in nutrient concentration due to biological processes. Except for a series of deliberate sample storage experiments, all analyses were completed within a few hours of the end of the CTD/rosette casts.

## C.5.c. CALIBRATION AND STANDARDIZATION:

Volumetric labware and the pipettors used to prepare standards were gravimetrically calibrated in shore laboratories prior to the cruise. The Eppindorf Maxipettor adjustable pipettors used to prepare mixed standards typically have a standard deviation of less than 0.002 ml on repeated deliveries of 10 ml volumes. High concentration mixed standards containing nitrate, phosphate, and silicic acid were prepared at intervals of 4 to 7 days and kept refrigerated in HDPE bottles. At almost every station, a fresh "working standard" was prepared by adding 20 ml of the high concentration mixed standard to low nutrient seawater. A separate nitrite standard solution was also added to these working standards.

The pipet and volumetric flask calibrations were rechecked after the cruise in the OSU lab. Corrections to the preliminary data computed at sea, based upon the actual volumes of the flasks and pipettors, have been included in the final data. These are systematic, multiplicative corrections which ranged from 0.9987 to 1.003. Details of these corrections are included as Appendix 1.

The WOCE Operations Manual calls for nutrient concentrations to be reported in units of micromoles per kilogram (uM kg-1). Because the temperature and salinity information required to compute density is not usually available at the time of initial computation of the nutrient concentrations, our concentrations are always originally computed as micromoles per liter. The unit conversion has been made using the corrected salinity data for the individual seawater samples and the monitored, shipboard nutrient laboratory temperatures.

## C.5.d. ESTIMATION OF PRECISION:

## C.5.d.1. SHORT TERM PRECISION:

Throughout the cruise, replicate samples drawn in different sample tubes from the same Niskin bottle were run at almost every station. These replicate samples were analyzed both as adjacent samples (one after the other) and also at the beginning and end of sample runs to determine if there was deterioration in the samples or uncompensated instrumental drift. There was no statistically significant difference in the reproducibility of replicates separated by two hours and those run only minutes apart.

Our estimate of the precision obtained within a sample run during the P16C leg is presented as the average standard deviation of these replicate analyses are: Phosphate, 0.014; Nitrate + Nitrite, 0.13; Silicic acid, 0.2; Nitrite, 0.003. The units are uM, i.e. micromoles per liter.

## C.5.d.2. LONGER TERM PRECISION:

One of the factors in station-to-station variability of nutrient analyses is the precision of preparing working standards which have limited stable lifetimes. Refrigerated, they can be only be stored for less than six hours to keep deterioration to less than 0.1% for
phosphate, nitrate and silicic acid (see Appendix 2). A crude experiment designed to estimate an upper limit to this factor was performed during about 1/3 of the individual sample runs during the cruise. We compared a standard made for the previous station with the standard freshly prepared for that sample run.

"Leftover" standards were stored in the lab refrigerator until the following station, and then analyzed as if they were samples. The working standards are prepared in natural seawater and are not immune to biological degradation. Therefore one cannot separate the effects of precision of preparation from deterioration during refrigerated storage.

The mean differences between successive working standards, converted to concentration units (M): Phosphate, 0.011; Nitrate + Nitrite, 0.07; Silicic acid, 0.3; Nitrite, 0.011.

# C.5.e. CONVERSION TO GRAVIMETRIC UNITS.

The nutrients were converted from micromolar to micromoles/kg using densities computed from the sample salinities and the average nutrient lab temperature, 25.5C. The maximum range of lab temperatures was only +/-2.5C so the maximum error introduced by this scatter is < 0.1%. Nitrite concentrations have been subtracted from the nitrate + nitrite concentrations; the nitrate column heading is now correct and the micromoles/kg unit headings are now correct.

# C.5.f. APPENDIX 1: NUTRIENTS

I. Stations 221 - 234

Calibration "factors" for P16C WOCE cruise, R/V T. WASHINGTON, Sept 1 through Oct 1, 1991.

Preliminary concentrations reported during the cruise have been corrected by multiplying them by the appropriate calibration factors. These are based on gravimetric calibrations of volumetric flasks and pipets used during the cruise. Values which are calculated (as opposed to directly measured) are indicated by brackets []. Volumetric flasks are calibrated "to contain". Pipette tip delivery is defined as total volume delivered. All concentrations have units of umoles/liter.

```
SUMMARY:

Phosphate: reported concentration * 0.9987

Nitrate plus nitrite: reported concentration * 0.9988

Silicic acid: reported concentration * 0.9993

Nitrite: reported concentration * 1.003

Phosphate Nitrate Silicate Nitrite

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Formula weight 136.09 101.11 188.072 69

purity, % 100.00 100.00 100.00 100.00

grams weighed 0.3402 3.7912 0.4701 0.3451
```

["A" std conc.] Tip delivery "B" flask Vol.	999.50 2501.1 19.977 999.67 49.98 499.9 19.979 1.9975 2	19.977 999.67 749.68 499.9 19.979 29.961 30.00	499.9 19.979	10.007 1.003 1.00
Nitrate+Nitrite nominal N+N [calib. factor]	30.96 31 0.9988			
II. Stations 235 - (The pipet t		NO3 + PO4 wa	s changed.)	
Summary: Phosphate: Nitrate + Nitrite: Silicic acid: Nitrite:	reported co reported co	oncentration oncentration oncentration oncentration	* 0.9992 * 0.9993	
	Phosphate	Nitrate	Silicate	Nitrite
Formula weight purity, % grams weighed		100 3.7912	0.4701	100 0.3451
<pre>[ umoles ] "A" flask Vol. ["A" std conc.] Tip delivery "B" flask Vol. ["B" std conc.] Working Vol. Work. tip deliv. [ Working conc ] nominal conc. [calib. factor]</pre>	999.5 2501.1	999.5 37514.6	-	1000 5001.4 2.003 200 50.09 499.9 10.007 1.003 1.00
<pre>"A" flask Vol. ["A" std conc.] Tip delivery "B" flask Vol. ["B" std conc.] Working Vol. Work. tip deliv. [ Working conc ] nominal conc.</pre>	999.5 2501.1 19.985 999.67 50.00 499.9 19.979 1.9983 2	999.5 37514.6 19.985 999.67 749.98 499.9 19.979 29.973 30.00	- 999.67 2500.40 499.9 19.979 99.93 100.00	1000 5001.4 2.003 200 50.09 499.9 10.007 1.003 1.00
<pre>"A" flask Vol. ["A" std conc.] Tip delivery "B" flask Vol. ["B" std conc.] Working Vol. Work. tip deliv. [ Working conc ] nominal conc. [calib. factor] Nitrate+Nitrite nominal N+N [calib. factor] III. Stations 305</pre>	999.5 2501.1 19.985 999.67 50.00 499.9 19.979 1.9983 2 0.9991 30.98 31 0.9992 - 326 (end	999.5 37514.6 19.985 999.67 749.98 499.9 19.979 29.973 30.00 0.9991	- 999.67 2500.40 499.9 19.979 99.93 100.00 0.9993	1000 5001.4 2.003 200 50.09 499.9 10.007 1.003 1.00

Nitrate + Nitrite: Silicic acid: Nitrite:	reported co	ncentration	* 0.9997	
	—	Nitrate		
<pre>Formula weight    purity, % grams weighed    [ umoles ]    "A" flask Vol. ["A" std conc.]    Tip delivery    "B" flask Vol. ["B" std conc.]    Working Vol. Work. tip deliv. [ Working conc ]    nominal conc. [calib. factor]</pre>	136.09 100 0.3402 2499.8 999.50 2501.1 19.985 999.67 50.00 499.9 19.987 1.9991 2	101.11 100 3.7912 37495.8 999.5 37514.6 19.985 999.67 749.98 499.9 19.987 29.986 30.00	188.072 100 0.4701 2499.6 - - 999.67 2500.40 499.9 19.987 99.97 100.00	69 100 0.3451 5001.4 1000 5001.4 2.003 200 50.09 499.9 10.007 1.00 1.00
Nitrate+Nitrite nominal N+N [calib. factor]	31			

# C.5.g. APPENDIX 2: NUTRIENTS

#### NUTRIENT SAMPLE STORAGE EXPERIMENTS: P16C

During the latter half of the P16C leg, a series of sample storage experiments was carried out. The experiments were motivated by our observation of apparent instability of some freshly drawn samples from the first seven stations in the cruise, and by a desire to evaluate any loss of precision and/or accuracy caused by a delay in running nutrient samples. Alcohol (2-propanol), deionized water, and 10% HCl were used to prerinse the sample tubes prior to storage. Replicate sets of samples were stored in a refrigerator (2 - 5 C) and analyzed after storage for 6 to 24 hours. Most of the stored replicates were analyzed within 15 hours of the initial analysis, and all were analyzed in triplicate.

Twelve experiments consisting of 36 replicate samples each were done to compare the three different rinsing materials for treating the sample containers prior to storage. The seawater test samples were drawn from shallow, mid-depth, and deep Niskin or Gerard bottles. For each experiment, a series of replicate samples was taken at a normal CTD/rosette station. The first set of replicates was analyzed with the routine nutrient samples from the station at which they originated; the remaining replicates were stored in the lab refrigerator for the specified times and analyzed with the samples from subsequent stations. In all of the storage experiments, the sample containers used were the same type of 50ml polyethylene centrifuge tubes which were used for normal sampling on all three cruise legs according to the ODF protocol. As a control, in some of the experiments

a set of sample tubes was rinsed only with the sample seawater (SW), i.e. they received no other presampling rinse.

In half of the experiments nine sample tubes were rinsed with 10% HCI, nine with alcohol, nine with DIW, and nine with seawater only. Twelve of the replicate samples (three of each type of pretreatment) were analyzed initially, and the remaining replicates were stored in the lab refrigerator. The other half of the storage experiments focused on 10% HCI and alcohol as cleaning media. Table 1 summarizes the original stations and bottles from which storage experiment samples were taken and the precleaning media used in each experiment.

The following observations can be made:

- 1. There were no clear trends of monotonic increases or decreases in nutrient concentration versus time of storage or cleaning method.
- 2. For all of the precleaning methods used, many of the stored replicates had mean concentrations which differed from the initial concentration. These differences were often greater than our estimates of long and short term precision and were evident after as little as six hours of storage (Figures C.5.1-4).
- 3. Most of the stored replicates had mean concentrations which were within q0.03 M (phosphate), q0.40 M (N+N), q1.5 M (silicic acid), and q0.02 M (nitrite) of their original concentrations. These ranges are roughly q1 % of the maximum concentrations encountered in the water column, the desired and specified WOCE analytical precision. (Note that in many cases the variances of the stored samples comprise a significant fraction of, or exceed, this specification.)
- 4. In general, precleaning of sample tubes seems preferable to no treatment: the precision of triplicate determinations from precleaned sample tubes was better than for uncleaned tubes.
- 5. In this experiment virtually all of the stored sample sets exhibited considerably higher variance than the unstored samples. The stored variances were on order of twice or more than the variances of the original, unstored samples. Although this experiment applies only to the sample tubes and seawater samples used therein it is perhaps indicative of more general cases. Obviously, this experiment cannot resolve the effects of refrigerated storage times of less than six hours but it clearly indicates that storage times of this length or more can markedly degrade analytical precision.

Figures C.5.1-4 present the results of the storage experiments as departures from the means of measured concentrations of unstored samples, for each nutrient and for each precleaning method, as functions of storage times.

Table 1: Sequence of samples taken fr	rom Niskin bottles during P16C for storage
experiments.	

1         270         7         3+3+3         Alcohol           1         270         24         3+3+3         Alcohol           2         276         7         3+3+3         Alcohol           2         276         24         3+3+3         Alcohol           2         276         24         3+3+3         Alcohol           3         284         7         3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           4         291         33         3+3+3         DIW           4         291         33         3+3+3         DIW           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6	RUN	STN	BOTTLE	REPLICATES	WASH
1         270         33         3+3+3         Alcohol           2         276         7         3+3+3         Alcohol           2         276         24         3+3+3         Alcohol           3         284         7         3+3+3         Alcohol           3         284         7         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DlW           4         291         33         3+3+3         DlW           4         291         33         3+3+3         DlW           5         295         34         3+3+3         DlW           5         295         34         3+3+3         DlW           5         295         34         3+3+3         DlW           6         299         22         3+3+3         DlW           6         299         22         3+3+3         DlW           7			1		Alcohol
1       270       33       3+3+3       Alcohol         2       276       7       3+3+3       Alcohol         2       276       24       3+3+3       Alcohol         3       284       7       3+3+3+3       Alcohol         3       284       23       3+3+3+3       Alcohol         3       284       23       3+3+3+3       Alcohol         4       291       33       3+3+3       Mlcohol         4       291       33       3+3+3       Mlcohol         5       295       34       3+3+3       DlW         6       295       34       3+3+3       DlW         5       295       34       3+3+3       DlW         6       299       22       3+3+3       DlW         6       299       22       3+3+3       DlW         6       299       22       3+3+3       DlW         7       301       22	1	270	24	3+3+3	Alcohol
2         276         7         3+3+3         Alcohol           2         276         24         3+3+3         Alcohol           3         284         7         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         33         3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         I0% HCI           4         291         33         3+3+3         DIW           4         291         33         3+3+3         DW           5         295         34         3+3+3         DW           5         295         34         3+3+3         DW           5         295         34         3+3+3         DW           6         299         22         3+3+3         DW           6         299         22         3+3+3         DW           6         299         22         3+3+3         DW           7         301 <td>1</td> <td></td> <td>33</td> <td></td> <td></td>	1		33		
2         276         33         3+3+3         Alcohol           3         284         7         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         33         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301	2				
2         276         33         3+3+3         Alcohol           3         284         7         3+3+3+3         Alcohol           3         284         23         3+3+3+3         Alcohol           3         284         33         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301	2		24		
3         284         23         3+3+3+3         Alcohol           3         284         33         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           6         299         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301	2		33		Alcohol
3         284         23         3+3+3+3         Alcohol           3         284         33         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         DIW           5         295         34         3+3+3         DIW           6         299         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301	3		7		
3         284         33         3+3+3+3         Alcohol           4         291         33         3+3+3         Alcohol           4         291         33         3+3+3         DIW           4         291         33         3+3+3         DIW           4         291         33         3+3+3         SW           5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         DIW           5         295         34         3+3+3         SW           6         299         22         3+3+3         IO% HCI           6         299         22         3+3+3         IOW           6         299         22         3+3+3         IO% HCI           7         301         22         3+3+3         IO% HCI           7         301         22         3+3+3         IO% HCI           7         301 <td>3</td> <td>284</td> <td>23</td> <td>3+3+3+3</td> <td>Alcohol</td>	3	284	23	3+3+3+3	Alcohol
4       291       33       3+3+3       Alcohol         4       291       33       3+3+3       DIW         4       291       33       3+3+3       DIW         4       291       33       3+3+3       SW         5       295       34       3+3+3       Alcohol         5       295       34       3+3+3       DIW         5       295       34       3+3+3       DIW         5       295       34       3+3+3       SW         6       299       22       3+3+3       Alcohol         6       299       22       3+3+3       SW         6       299       22       3+3+3       DIW         6       299       22       3+3+3       SW         7       301       22       3+3+3       SW         7       301       22       3+3+3       IO% HCI         7       301       22       3+3+3       SW         8       304       23       3+3+3       IO% HCI         8       304       23       3+3+3       IO% HCI         8       304       23       3+3+3	3	284	33	3+3+3+3	Alcohol
429133 $3+3+3$ DIW429133 $3+3+3$ SW529534 $3+3+3$ Alcohol529534 $3+3+3$ DIW529534 $3+3+3$ DIW529534 $3+3+3$ SW629922 $3+3+3$ Alcohol629922 $3+3+3$ DIW629922 $3+3+3$ DIW629922 $3+3+3$ DIW629922 $3+3+3$ NW730122 $3+3+3$ Alcohol730122 $3+3+3$ DIW730122 $3+3+3$ DIW730122 $3+3+3$ DIW730122 $3+3+3$ DIW830423 $3+3+3$ Alcohol830423 $3+3+3$ DIW830423 $3+3+3$ DIW9308G93 $3+3+3$ DIW9308G93 $3+3+3$ DIW9308G93 $3+3+3$ DIW9308G93 $3+3+3$ 10% HCI103106 $3+3+3$ 10% HCI113147 $3+3+3+3$ 10% HCI1131432 $3+3+3+3$ 10% HCI123177 $3+3+3$ 10% HCI1231772 $3+3+3$ 10% HCI12317 <td< td=""><td>4</td><td>291</td><td>33</td><td>3+3+3</td><td>Alcohol</td></td<>	4	291	33	3+3+3	Alcohol
4         291         33         3+3+3         SW           5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         10% HCl           5         295         34         3+3+3         DIW           5         295         34         3+3+3         SW           6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Mcohol           7         301         22         3+3+3         Mcohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Mcohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         <		291	33	3+3+3	10% HCI
5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         10% HCl           5         295         34         3+3+3         DIW           5         295         34         3+3+3         SW           6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         Micohol           7         301         22         3+3+3         SW           7         301         22         3+3+3         Micohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Micohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Micohol           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DiW           8         304         23         3+3+3         DIW           9         308	4	291	33	3+3+3	DIW
5         295         34         3+3+3         Alcohol           5         295         34         3+3+3         10% HCl           5         295         34         3+3+3         DIW           5         295         34         3+3+3         SW           6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         Micohol           7         301         22         3+3+3         SW           7         301         22         3+3+3         Micohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Micohol           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Micohol           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DiW           8         304         23         3+3+3         DIW           9         308	4	291	33	3+3+3	SW
5         295         34         3+3+3         10% HCl           5         295         34         3+3+3         DIW           5         295         34         3+3+3         SW           6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Alcohol           7         301         22         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           9         308         G93 </td <td></td> <td>295</td> <td>34</td> <td></td> <td>Alcohol</td>		295	34		Alcohol
5       295       34       3+3+3       DIW         5       295       34       3+3+3       SW         6       299       22       3+3+3       Alcohol         6       299       22       3+3+3       DIW         6       299       22       3+3+3       DIW         6       299       22       3+3+3       SW         7       301       22       3+3+3       Alcohol         7       301       22       3+3+3       MChol         7       301       22       3+3+3       DIW         7       301       22       3+3+3       Mchol         7       301       22       3+3+3       DIW         7       301       22       3+3+3       Mchol         8       304       23       3+3+3       DIW         8       304       23       3+3+3       DIW         8       304       23       3+3+3       SW         9       308       G93       3+3+3       SW         9       308       G93       3+3+3       IO% HCl         9       308       G93       3+3+3       I	5	295	34	3+3+3	10% HCI
6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Alcohol           7         301         22         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93 <td>5</td> <td>295</td> <td>34</td> <td>3+3+3</td> <td>DIW</td>	5	295	34	3+3+3	DIW
6         299         22         3+3+3         Alcohol           6         299         22         3+3+3         DIW           6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Alcohol           7         301         22         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93 <td>5</td> <td>295</td> <td>34</td> <td>3+3+3</td> <td>SW</td>	5	295	34	3+3+3	SW
6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Alcohol           7         301         22         3+3+3         I0% HCl           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Mcohol           8         304         23         3+3+3         Alcohol           8         304         23         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         10% HCI           10         310	6	299	22	3+3+3	Alcohol
6         299         22         3+3+3         DIW           6         299         22         3+3+3         SW           7         301         22         3+3+3         Alcohol           7         301         22         3+3+3         I0% HCl           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         DIW           7         301         22         3+3+3         Mcohol           8         304         23         3+3+3         Alcohol           8         304         23         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         10% HCI           10         310		299	22	3+3+3	10% HCI
7       301       22       3+3+3       Alcohol         7       301       22       3+3+3       10% HCl         7       301       22       3+3+3       DIW         7       301       22       3+3+3       DIW         7       301       22       3+3+3       SW         8       304       23       3+3+3       Alcohol         8       304       23       3+3+3       DIW         8       304       23       3+3+3       SW         9       308       G93       3+3+3       Now HCl         9       308       G93       3+3+3       DIW         9       308       G93       3+3+3       SW         10       310       6       3+3+3       10% HCl         10       310       24       3+3+3       10% HCl         11       314       7       3+3+3+3       10% HCl         11       314       32       3+3+3+3	6	299	22	3+3+3	DIW
7       301       22       3+3+3       Alcohol         7       301       22       3+3+3       10% HCl         7       301       22       3+3+3       DIW         7       301       22       3+3+3       DIW         7       301       22       3+3+3       SW         8       304       23       3+3+3       Alcohol         8       304       23       3+3+3       DIW         8       304       23       3+3+3       SW         9       308       G93       3+3+3       Now HCl         9       308       G93       3+3+3       DIW         9       308       G93       3+3+3       SW         10       310       6       3+3+3       10% HCl         10       310       24       3+3+3       10% HCl         11       314       7       3+3+3+3       10% HCl         11       314       32       3+3+3+3	6	299	22	3+3+3	SW
7       301       22       3+3+3       DIW         7       301       22       3+3+3       SW         8       304       23       3+3+3       Alcohol         8       304       23       3+3+3       I0% HCl         8       304       23       3+3+3       DIW         8       304       23       3+3+3       DIW         8       304       23       3+3+3       SW         9       308       G93       3+3+3       Alcohol         9       308       G93       3+3+3       DIW         10       310       6       3+3+3       10% HCI         10       310       33       3+3+3       10% HCI         11       314       7       3+3+3+3       10% HCI         11       314       32       3+3+3+	7	301	22	3+3+3	Alcohol
7       301       22       3+3+3       SW         8       304       23       3+3+3       Alcohol         8       304       23       3+3+3       10% HCl         8       304       23       3+3+3       DIW         8       304       23       3+3+3       DIW         8       304       23       3+3+3       DIW         8       304       23       3+3+3       SW         9       308       G93       3+3+3       Alcohol         9       308       G93       3+3+3       DIW         9       308       G93       3+3+3       DIW         9       308       G93       3+3+3       DIW         9       308       G93       3+3+3       SW         10       310       6       3+3+3       SW         10       310       24       3+3+3       10% HCl         11       314       7       3+3+3+3       10% HCl         11       314       32       3+3+3+3       10% HCl         11       314       32       3+3+3       10% HCl         12       317       7       3+3+	7	301	22	3+3+3	10% HCI
8         304         23         3+3+3         Alcohol           8         304         23         3+3+3         10% HCl           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         SW           9         308         G93         3+3+3         Alcohol           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DW           10         310         24         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         32         3+3+3         10% HCI           12 <t< td=""><td></td><td>301</td><td>22</td><td>3+3+3</td><td>DIW</td></t<>		301	22	3+3+3	DIW
8         304         23         3+3+3         10% HCl           8         304         23         3+3+3         DIW           8         304         23         3+3+3         DIW           8         304         23         3+3+3         SW           9         308         G93         3+3+3         Alcohol           9         308         G93         3+3+3         10% HCl           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12		301	22	3+3+3	SW
8         304         23         3+3+3         DIW           8         304         23         3+3+3         SW           9         308         G93         3+3+3         Alcohol           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         22         3+3+3+3         10% HCI           11         314         32         3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12		304	23	3+3+3	Alcohol
8         304         23         3+3+3         SW           9         308         G93         3+3+3         Alcohol           9         308         G93         3+3+3         10% HCl           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI           12	8	304	23	3+3+3	10% HCI
9         308         G93         3+3+3         Alcohol           9         308         G93         3+3+3         10% HCl           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI <td< td=""><td>8</td><td>304</td><td>23</td><td>3+3+3</td><td>DIW</td></td<>	8	304	23	3+3+3	DIW
9         308         G93         3+3+3         10% HCl           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         SW           10         310         6         3+3+3         10% HCl           10         310         24         3+3+3         10% HCl           10         310         24         3+3+3         10% HCl           10         310         33         3+3+3         10% HCl           11         314         7         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl	8	304	23	3+3+3	
9         308         G93         3+3+3         DIW           9         308         G93         3+3+3         SW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         22         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12         317         22         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI		308	G93	3+3+3	Alcohol
9         308         G93         3+3+3         SW           10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         22         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12         317         22         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI </td <td></td> <td>308</td> <td>G93</td> <td>3+3+3</td> <td>10% HCI</td>		308	G93	3+3+3	10% HCI
10         310         6         3+3+3         10% HCI           10         310         24         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           10         310         33         3+3+3         10% HCI           11         314         7         3+3+3+3         10% HCI           11         314         22         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           11         314         32         3+3+3+3         10% HCI           12         317         7         3+3+3         10% HCI           12         317         22         3+3+3         10% HCI           12         317         32         3+3+3         10% HCI	9	308	G93	3+3+3	DIW
10         310         24         3+3+3         10% HCl           10         310         33         3+3+3         10% HCl           11         314         7         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl	9	308	G93	3+3+3	SW
10         310         33         3+3+3         10% HCl           11         314         7         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           Note:         G93 is Gerard bottle No. 93. All other bottle         501	10	310	6		10% HCI
11         314         7         3+3+3+3         10% HCl           11         314         22         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           Note:         G93 is Gerard bottle No. 93. All other bottle         State	10	310	24	3+3+3	10% HCI
11         314         22         3+3+3+3         10% HCl           11         314         32         3+3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         7         3+3+3         10% HCl           12         317         22         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           12         317         32         3+3+3         10% HCl           Note:         G93 is Gerard bottle No. 93. All other bottle         500 HCl	10	310	33	3+3+3	10% HCI
11       314       32       3+3+3+3       10% HCl         12       317       7       3+3+3       10% HCl         12       317       22       3+3+3       10% HCl         12       317       22       3+3+3       10% HCl         12       317       32       3+3+3       10% HCl         Note:       G93 is Gerard bottle No. 93. All other bottle       500 HCl		314		3+3+3+3	10% HCI
12       317       7       3+3+3       10% HCI         12       317       22       3+3+3       10% HCI         12       317       32       3+3+3       10% HCI         12       317       32       3+3+3       10% HCI         Note:       G93 is Gerard bottle No. 93. All other bottle       500 HCI		314		3+3+3+3	10% HCI
12       317       22       3+3+3       10% HCl         12       317       32       3+3+3       10% HCl         Note:         G93 is Gerard bottle No. 93. All other bottle	11	314	32	3+3+3+3	10% HCI
12         317         32         3+3+3         10% HCI           Note:         G93 is Gerard bottle No. 93. All other bottle	12	-	7	3+3+3	
Note: G93 is Gerard bottle No. 93. All other bottle				3+3+3	
	12	317	32	3+3+3	10% HCI
	Note:	G93 is	Gerard bott	e No. 93. All other	r bottle
number represent Niskin samples.					

## NUTRIENT QC NOTES: P16C Cruise

During the P16C cruise, the WHPO data editing program "Q1EDIT" was used to perform a first pass QC check on the nutrient data, primarily by comparing vertical profiles and nutrient/theta relationships. The version of Q1EDIT which was available on the cruise could only changes data quality flags from "2" (acceptable) to "3" (questionable). Following the cruise, all nutrient data were rechecked based on notes made while at sea and on plots produced in the laboratory. Some correctable errors were found and the appropriate corrections made. At this time, the data quality flags were edited to conform to the definitions in the WOCE Operations Manual (WOCE Report No. 67/91). Data quality flags were assigned as follows:

Quality byte	Definition
2	Acceptable measurement
3	Questionable measurement; no obvious problems found, but data somewhat out of trend.
4	Bad measurement; known analytical problems or data seriously out of trend.
9	Sample not drawn, usually due to Niskin bottle failure

At several stations, the bottle tripping order was deliberately (or accidentally) different from 1-36. At the end of the cruise, some of the data files did not include the correct bottle order which led to errors in some of the preliminary QC notes. The following notes apply to a list of QC comments prepared by the Chief Scientist (Lynne Talley) during the cruise. We have abbreviated phosphate as "P", nitrate + nitrite as "N+N".

#### STATION 236/01

Talley noted problems with P & N+N in bottles 2, 4, and 10; and that bottle 11 was a leaker. The actual bottle tripping sequence was 25 through 36 and then 1 through 24. The problems with P and N+N were actually in bottles 26 and 28 (vs 2 & 4), and the leaker was 35.

We think nutrients in bottle 34 (10 in Talley's notes) are OK and the quality bytes should be 2. On the other hand, bottle 33 (Talley's 9) did have P and N+N problems. (Note from Talley

the WHOI software did not permit the actual bottle numbers to be placed in the bottle data file, so positions 2 and 4 in that file are the ones with problems. There is now no flag on position 10; position 9 is flagged.)

#### STATION 260/01

The actual bottle tripping sequence was 25 through 36, then 1 through 24. The leaker was 2 and not 14. Therefore, the logbook is correct in saying that bottle 2 was a leaker. File 0260A001.nut had the bottle numbers in the wrong order at the end of the cruise. They have been corrected in our current 0260A001 file. (Note from Talley: again the WHOI software did not permit the actual bottle numbers to be placed in the bottle data file, so

position 14 in that file is the leaker. As Gordon notes, this was actually bottle 2, which is why there is a note to that effect in the data quality file - section D below.)

#### STATION 289/01

Bottle 19 vs. bottle 29. In file 0289A001.nut there are two bottles identified as 29. The first one corresponds to sequential number 19, thus we assume this was indeed bottle 19 and not 29. The second bottle 29 has a sequence Nr. of 29. Nutrient data for the first bottle 29 (actually 19) look OK for the corresponding depth.

### STATION 292/01

The actual bottle tripping sequence was 25-36 and 1-24. Bottle 32 rather than 8 was the leaker. (Note from Talley: here the bottle numbers are correct in the bottle file: so bottle 32 in position 8 was a leaker.)

#### STATION 319/01

Checked deep N+N; it seems to agree with adjacent stations. Talley had it flagged as "3". We think it should be assigned quality bytes of "2". (Note from Talley: this flag was changed back to 2.)

#### C.5.h. CHIEF SCIENTIST COMMENTS ON NUTRIENT MEASUREMENTS (Lynne D. Talley)

As noted in the cruise report portion of this text, there were problems with nitrate and phosphate on P16C. The following is an updated version of the text found in section A.5:

Difficulties were encountered with some nitrate and phosphate analyses on stations 226 to 244. Replicate samples using different sample tubes and water out of different Niskins indicated that the problem was with some of the sampling tubes used to collect water from the rosette sampler. All tubes were thoroughly cleaned with HCl before sta. 245, solving the problem, thus suggesting that biological fouling coupled with an absence of regular cleaning was the problem. Most of the nutrients from the affected stations are acceptable. With the exception of occasional random problems and problems with nitrate at stations 256 and 258, all data from stations 221-225 and 246-326 are acceptable. To compare with silica, which was excellent throughout the cruise: there were a total of 6 flagged questionable or bad silicas, 101 flagged phosphates, and 170 flagged nitrates, out of a total of 3273 water sample levels.

In an attempt to ensure that nutrient data from all three WOCE legs would be compatible despite the different lead analysis groups, the same equipment and standards were used on all three legs. Silica and phosphate values from legs 2 and 3 are consistent with each other. However, nitrate on leg 3 is systematically 1-2 mu moles/liter higher than on leg 2.



Figure C.5.1: Combined time series measurements of orthophosphate ( $\mu$ mol • I<sup>-1</sup>) using different washing methods for pre-cleaning the sampling tubes used during P16C to draw samples from the Niskin and Gerard bottles. The washing methods were: (A) Seawater, (B) Distilled water, (C) 80% isopropyl alcohol, and (D) 1.2 M HCl. The vertical lines on each sample represent the standard deviation of the mean (N=3). The horizontal broken line represents the root mean square deviation of all replicate samples for phosphate collected during P16C and analyzed within 2-3 hours after collection. This is an estimate of our short-term precision, which is close to the target precision level for WOCE nutrient measurements (WOCE Report No. 67/91). The solid line represents  $\pm$  1% of highest water phosphate column values. This is a target accuracy for WOCE



Figure C.5.2: Same as Fig. 1 but for nitrate + nitrite ( $\mu$ mol •  $I^{-1}$ ).



Figure C.5.3: Same as Fig. 1 but for nitrite ( $\mu$ mol • I<sup>-1</sup>)



Figure C.5.4: Same as Fig. 1 but for silicic acid ( $\mu$ mol • l<sup>-1</sup>).

### C.6. CARBON SYSTEMS

Abstracted from NDP-060

#### Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V Thomas Washington Cruise TUNES-3 in the Equatorial Pacific Ocean 1996

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(WOCE section P16C). ORNL/CDIAC-96, NDP-060. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

#### SUMMARY

This data documentation discusses the procedures and methods used to obtain total carbon dioxide (TCO2), total alkalinity (TALK), hydrographic, and chemical data during the Research Vessel Thomas Washington Expedition TUNES-3 in the Equatorial Pacific Ocean (Section P16C). Conducted as a part of the World Ocean Circulation Experiment (WOCE), the cruise began in Papeete, Tahiti, on August 31, 199 1, and finished in Honolulu, Hawaii, on October 1, 199 1. WOCE Meridional Section P16C along 150° W and between 18° S and 19° N was completed during the 31-day expedition. All 105 hydrographic and 8 large-volume stations were completed to the full water column depth. Station spacing was 30 nautical miles (nm), except between 3° N and 3° S where it was 10 nm. Twenty- five bio-optics stations were sampled for the Joint Global Ocean Flux Study, and at 21 stations carbon dioxide measurements were provided for the U.S. Department of Energy's CO2 program. Hydrographic and chemical measurements made along WOCE Section P16C included pressure, temperature, salinity, and oxygen measured by conductivity, temperature, and depth sensor; and bottle salinity, oxygen, phosphate, nitrate, nitrite, silicate, chlorofluorocarbon (CFC-11, CFC- 12, TC02, and TALK. In addition, potential temperatures were calculated from the measured variables.

The TC02 concentration in 652 seawater samples was determined by semi-automated coulometry using, an improved version of the instrument earlier described by Johnson et al., (1985, 1987). The precision of these measurements was estimated to be better than  $\pm 0.01\%$ . The desired accuracy was better than 4 µmol/kg. The TALK concentration in 539 seawater samples was determined by a potentiometric acid titration system that was designed and constructed at the Scripps Institution of Oceanography (SIO) by David Moss and Timothy Lueker (Guenther et al. 1994a).

Seventy-one replicate samples were also collected for later shore-based reference analyses of TC02 and TALK by vacuum extraction and manometry in the laboratory of C. D. Keeling of SIO.

The data set is available, free of charge, as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of two oceanographic data files, two FORTRAN 77 data-retrieval routine files, a documentation file, and this printed report, which describes the contents and format of all files and the procedures and methods used to obtain the data.

Keywords: carbon dioxide; total alkalinity; World Ocean Circulation Experiment (WOCE); Pacific Ocean; hydrographic measurements; carbon cycle

# C.6.1. BACKGROUND INFORMATION

The World Ocean plays a dynamic role in the Earth's climate: it captures heat from the sun, transports it, and releases it thousands of miles away. These oceanic- solar-atmospheric interactions affect winds, rainfall patterns, and temperatures on a global scale. The oceans also play a major role in global carbon-cycle processes. Carbon is unevenly distributed in the oceans because of complex circulation patterns and biogeochemical cycles, neither of which is completely understood, as well as the biological processes of photosynthesis and respiration. The oceans are estimated to hold 38,000 gigatons of carbon, 50 times more than that in the atmosphere and 20 times more than that held by plants, animals, and the soil. If only 2% of the carbon stored in the oceans were released, the level of atmospheric carbon dioxide (C02) would double. Every year, more than 15 times as much C02 is exchanged across the sea surface than the amount produced by burning of fossil fuels, deforestation, and other human activities (Williams 1990).

To better understand the ocean's role in climate and climatic changes, several large experiments have been conducted, and others are under way. The largest oceanographic experiment ever attempted is the World Ocean Circulation Experiment (WOCE). A major component of the World Climate Research Program, WOCE brings together the expertise of scientists and technicians from more than 30 nations. In the United States, WOCE is supported by the federal government under the Global Change Research Program. The multi-agency U.S. effort is led by the National Science Foundation and is supported by major contributions from the National Oceanic and Atmospheric Administration, the U.S. Department of Energy (DOE), the Office of Naval Research, and the National Aeronautics and Space Administration. Although total carbon dioxide (TCO2) is not an official WOCE measurement, a coordinated effort, supported in the United States by DOE, is being made on WOCE cruises (through 1998) to measure the global, spatial, and temporal distributions of TC02 and other carbon-related parameters. The goal of the C02 survey includes estimation of the meridional transport of inorganic carbon in the Pacific Ocean in a manner analogous to the oceanic heat transport (Bryden and Hall 1980; Brewer et al. 1989; Roemmich and Wunsch 1985), evaluation of the exchange of C02 between the atmosphere and the ocean, and preparation of a database suitable for carbon-cycle modeling and the subsequent assessment of the anthropogenic C02 increase in the oceans. The final data set is expected to cover -23,000 stations.

This report presents C02-related measurements obtained during, the 3 1 -day Leg 3 of the Research Vessel (RN) Thomas Washington TUNES Expedition (TUNES-3) along the WOCE zonal Section P16C, which is located in the equatorial part of the Pacific Ocean along the 150° W meridian, between 17.5° S and 19.0° N (Fig. 1).

The C02 investigation during the TUNES-3 Expedition was supported by a grant (No. DEFG02-90-ER60983) from DOE.

# C.6.2 TOTAL C02 MEASUREMENTS

During the TUNES-3 Expedition, 652 samples were analyzed for TC02 concentrations in seawater. The sampling frequency for measurements of the carbonate parameters was reduced to a complete depth profile (36 samples) ~ every fourth hydrographic station (Fig. 2). This reduction was implemented not according to any prearranged geophysical criterion but to accommodate the time constraints for two analysts on board to perform C02 sampling and measurements. In other words, the adopted C02 sampling strategy was to measure as many samples as was technically and humanly possible.

For TC02 measurements, the seawater samples were drawn into 500-mL borosilicate glass bottles equipped with Rodaviss joint closure systems, poisoned with 100 µL of a saturated solution of mercuric chloride (HgCl), and analyzed on board generally within 18 h. TC02 concentration was measured by semi-automated coulometry using an improved version of the instrument earlier described by Johnson et al. (1985, 1987) and calibrated using the procedure described in Goyet and Hacker (1992). This early "SOMMA-type" system did not have gas loops for calibration. Consequently, plans were to calibrate the system with standard solutions as described in Goyet and Hacker (1992); however, uncontrollable events (i.e., a hurricane occurred in Woods Hole a few days before the cruise) destroyed standard solutions that were prepared for the cruise. As a result, the certified reference materials (CRMs) were used as standards to calibrate the TC02 extraction/coulometer system. Precision of the measurements was estimated to be better than ±0.01%; the desired accuracy was better than 4 µmo/kg (Goyet et al. 1995). The automated coulometric system forced the sample into the pipet using a pressurized headspace gas. Pure nitrogen (N2) headspace gas was used for standard solution measurements, and C02 headspace gas (290 ppm in air) was used for seawater sample measurements. The volume of the pipet was calibrated with distilled water and seawater (volume was -30 mL, depending on the individual pipet used), and there was no significant difference in the delivery volume as a result of possible differences in surface tension at different salinities. The sample was drained from the pipet into a stripper containing 1.5 mL of 8.5% phosphoric acid.

This chamber and the added acid were purged of any CO2 with pure N2 carrier gas before the sample was added. In the stripper, the C02 gas was extracted from the acidified sample by a continuous flow of pure N2 gas through a frit at the bottom of the stripper. The gas (mainly C02, N2 and water vapor) was passed through a condenser thermostated with 4°C water and magnesium perchlorate [Mg(Cl04)] to remove water vapor. It was then passed through silica gel to remove residual aerosols and traces of

hydrogen sulfide (H2S) and phosphoric acid (H3PO4) before being bubbled into a commercially available coulometric solution containing ethanolamine [NH2(CH2)20H], dimethyl sulfoxide [(CH3)2SO], and thymolphthalein dye (made by UIC, Inc., Joliet, IL, USA). A coil made from glass tubing with thermostated water flowing through it was placed in the cell to maintain the solution at 24°C. The pH of the solution was monitored on an UIC, Inc., total C02 coulometer by monitoring the thymolphthalein-absorbance indicator at -610 nm. Hydroxide (-OH) ions were generated by the coulometer circuitry to maintain absorbance of the solution at a constant value. The analytical procedure was controlled by a microcomputer that also recorded the coulometric titration and computed the total CO2 extracted from the sample based on the amount of OH- generated to reach the end point.

Figure 3 summarizes the analytical results as a contour section plot of the TCO2, data from the WOCE Section P16C along -150° W.

# C.6.3 TOTAL ALKALINITY MEASUREMENTS

To determine the TALK concentration in seawater, 539 samples were titrated. Typically, 28 of the 36 samples from Niskin bottles collected on a station were analyzed during the cruise. The TALK was measured on aliquot of seawater taken from the same 500-mL bottle previously analyzed for TC02. Duplicate samples were collected on six stations and analyzed for TALK. The closed-cell potentiometric acid titration system was used to determine TALK concentration. The system was designed and constructed at SIO by David Moss with the developmental and experimental assistance of Timothy Lueker. A full description of TALK measurements is provided in Guenther et al. (1994a).

# C.6.4 SHORE-BASED REPLICATE MEASUREMENTS

The replicate samples from 100 Niskin bottles at 18 stations were collected for shorebased reference analyses at the laboratory of C. D. Keeling of SIO. The TC02 measurements were produced by vacuum extraction/manometric analysis and the TALK values by potentiometric titration. Both measurements were performed under controlled laboratory conditions using standards. The replicate sample standard deviation (s) for this large data set of 71 unflagged pairs is 1.0  $\mu$ mol/kg after omitting the three replicate pairs with deltas greater then 3s (a replicate sample standard deviation calculated from the set of analyses on duplicate samples) (Guenther et al. 1994b).

Substantial reduction in the calculated s of the ship-minus- shore comparison is made by omitting 24 comparisons of singlet replicate samples, plus 5 more that are greater than 3s for either the replicate pairs or the comparison difference. For the 66 remaining comparisons, the average ship-minus-shore difference is  $-2.1\pm2.4 \mu mol/kg$  (Guenther et al. 1994b). Figure 4 shows the ship-minus-shore differences for all available surface and deep data from the TUNES-3 Expedition. The plotted data indicate a bias for surface data relative to deep data; surface data show better agreement between shipboard and shore-based data than do deep data.

# C.6.5. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the NDP process at the Carbon Dioxide Information Analysis Center (CDIAC) involves the quality assurance (QA) review of data before distribution. Data received at CDIAC are rarely in a condition that permits immediate distribution, regardless of the source. To guarantee data of the highest possible quality, CDIAC conducts extensive QA reviews that involve examining the data for completeness, reasonableness, and accuracy. Although they have common objectives, these reviews are tailored to each data set and often require extensive programming efforts. In short, the QA process is a critical component \*in the value-added concept of supplying accurate, usable data for researchers.

The following information summarizes the data-processing and QA checks performed by CDIAC on the data obtained during the R/V Thomas Washington TUNES- 3 Expedition in the South Pacific Ocean (WOCE Section P16C).

- Carbon-related data and preliminary hydrographic measurements were provided to CDIAC by Catherine Goyet of WHOI and Peter Guenther and Dave Keeling of SIO. Hydrographic measurements and the station information files were provided by Lynne Talley of SIO and by the WOCE Hydrographic Program Office after quality evaluation. A FORTRAN 77 retrieval code was written and used to merge and reformat all data files.
- 2. The designation for missing values, given as "-9.0" in the original files, was changed to 11-999.9.11
- 3. To check for obvious outliers, all data were plotted with a PLOTNEST.C, program written by Stewart C. Sutherland (LDEO). The program plots a series of nested profiles, using the station number as an offset; the first station is defined at the beginning, and subsequent stations are offset by a fixed interval (Figs. 5 and 6). Several outliers were identified and removed after consultation with the principal investigators.
- 4. To identify "noisy" data and possible systematic, methodological errors, propertyproperty plots for all parameters were generated (Fig. 7), carefully examined, and compared with plots from previous expeditions in the South Pacific Ocean.
- All variables were checked for values exceeding physical limits, such as sampling depth values that are greater than the given bottom depths.
   Dates and times were checked for bogus values (e.g., values of MONTH < I or > 12, DAY < I or > 3 1, YEAR < or > 199 1, TIME < 0000 or > 2400).
- 6. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by Lynne Talley.

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Station Numbers



# Figure 2: Sampling depths at all hydrographic stations occupied during R/V Thomas Washington TUNES-3 Expedition.



Fig. 3: Distribution of the TCO2 in seawater along WOCE Section P16C.



Figure 4: Shipboard minus shore-based TCO<sub>2</sub> measurements vs date for surface and deep samples.Open circles represent near-surface samples; shaded triangles represent deep samples; vertical bracketed lines represent replicate pair deltas; and arrows indicate dates replicate samples were collected.

#### WOCE Section P16C



Profiles which exist in this Pressure (dbar) range are ordered on Station No. Plotted parameter ranges from 1900 to 2350

Figure 5: Nested profiles: Total carbon (µmol/kg) vs pressure (dbar).

#### WOCE Section P16C



Profiles which exist in this Pressure (dbar) range are ordered on Station No. Plotted parameter ranges from 2200 to 2450

Figure 6: Nested profiles: Total alkalinity (µtmol/kg) vs pressure (dbar).



Figure 7. Property-property plots for all stations occupied during R/V Thomas Washington TUNES-3 Expedition.

- C.7 CHLOROFLUOROCARBONS (John Bullister - NOAA/PMEL)
- C.8 TRITIUM (William Jenkins - WHOI)
- C.9 SHALLOW HELIUM-3 (William Jenkins - WHOI)
- C.10 DEEP HELIUM-3 (Harmon Craig - SIO)

# D. ACKNOWLEDGMENTS

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# F. BOTTLE DATA COMMENTS AND FLAGGING

(Lynne Talley - SIO)

For each discrete data point which has a flag other than "2", brief information is provided herein indexed by station number, bottle, sample, flag, CTD pressure, and CTD theta. Included also are sampling comments regarding potentially leaking bottles, even if the analyses appeared normal, in the event that a future analysis of a different chemical should show an irregularity.

Final revision: 7/25/95 LDT following comparison with CTD data.

bqflg refers to the WHP bottle quality flag. qflg refers to the WHP water sample quality flag.

# NOTES ON USE OF FLAGGED BOTTLE DATA:

- 1. Data with qflg .ne. 2 or with bqflg .ne. 2 should not be used. The flag 3 for data usually means there is a serious problem but the reason for the problem is unknown.
- 2. Nutrients were not collected on the odd numbered stations 251 283 inclusive.
- 3. Some nitrite flags may not be commented on: whenever both nitrate and phosphate are flagged, nitrite usually is also flagged. One of the indications of the pervasive nitrate, phosphate problem from stas. 226 to 244 was high nitrite deep in the water column. Deep nitrites greater than or equal to .02 were flagged. Negative nitrites (all .01 and most on station 258) were not flagged and are assumed to be 0.0.

221/01:	13 11			oxygen. sampling error. po4 (probably tube problem)
222/01:	1 2 26 29	bqflg=2 q bqflg=2 q	qflg=2 qflg=2	salinity - empty sample bottle leak (log sheet). no action leak (log sheet). no action possible O2 bubble. no action
223/01:	1 1 4 4 5 6	bqflg=2 q bqflg=2 q bqflg=2 q bqflg=2 q	aflg=3 aflg=4 aflg=3 aflg=4	<pre>leaking at bottom (log sheet). no action po4 sampling tube problem oxygen sampling error salinity .004 too high. no reason oxygen sampling error oxygen sampling error</pre>

	10	bqflg=2 qflg=	3 no3 sampling tube problem
	10	bafla=2 afla=	3 po4 sampling tube problem
	11		3 po4 sampling tube problem
			ssure sequencing resulted in pressure
			for bottle 1 and 4120 for bottle 2. The
			pressure in the CTD file is 4117. Bottle 2
			ually fired about 10 m above bottle 1. I don't
		know wh	y bottle 2 shows a higher pressure.
		No chan	ge to the pressure flags was made, but it
		might b	e at some later time.
224/01:	1	bafla=2 afla=	2 leaking at bottom. no action
	2		3 po4 sampling tube problem
	7		3 salinity problem - no reason
	8		3 salinity problem - no reason
	9	pdild=7 dild=	4 Salinity noise - no reason.
			no nutrients reported (no reason)
	11		3 salinity problem - no reason
	21		3 salinity problem - no reason
	22	bqflg=2 qflg=	3 salinity problem - no reason
	23	bqflg=2 qflg=	3 salinity problem - no reason
	24	bqflg=2 qflg=	3 salinity problem - no reason
	25	bqflq=2 qflq=	3 salinity problem - no reason
	26		3 salinity problem - no reason
225/02:	13	bafla=2 afla=	4 oxygen high .05 - no reason
220,02	14		2 salinity looks low relative to CTD
		Ddrið-7 drið-	cast 5, but no apparent reason to flag it.
			cast 5, but no apparent reason to rray it.
22E/0E ·	1	bafla-0 afla-	2 not compling tube problem
225/05:	1		3 po4 sampling tube problem
	4	pdiid=s diid=	4 salinity problem - no reason
006/01			A '
226/01:			4 nitrate, phosphate sampling tube problem
	20		2 leak. no action
	27		2 leak. no action
	29	bqflg=2 qflg=	2 leak. no action
227/01:	3	bqflg=2 qflg=	4 oxygen sampling error
	11	bqflg=2 qflg=	4 nitrate, phosphate sampling tube problem
228/01:	11	bqflg=2 qflg=	4 nitrate, phosphate sampling tube problem
229/01:	8	bqflg=4 qflg=	5 all. empty
,	11		4 nitrate, phosphate sampling tube problem
	13		4 nitrate, phosphate sampling tube problem
	18		2 nitrate, phosphate - checked and looks OK ldt
	25	pdild=7 dild=	4 salinity problem - no reason
220/01-	1 7	bafla 0 fl	E mitwate net wenested (analastical analastic
230/01:			5 nitrate not reported (analytical problem)
	10		3 phosphate sampling tube problem
	11		4 nitrate, phosphate sampling tube problem
	12		3 nitrate sampling tube problem
	13	bqflg=2 qflg=	4 nitrate,phosphate sampling tube problem
	18		2 nitrate, phosphate - checked and looks OK ldt
	24	bqflg=2 qflg=	2 nitrate, phosphate - checked and looks OK ldt

231/01:	1-33 10 11 12 13 15 18 24 25 26 32	bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl	<pre>=3 all nitrites - no reason =4 nitrate, phosphate problem =4 nitrate, phosphate problem =3 nitrate, phosphate problem =2 vent open. no action.</pre>	
232/01:	1 7 10 11 12 13 14 15 18 19	bqflg=2 qfl bqflg=2 qfl	<pre>=3 salinity problem - no reason =3 salinity problem - no reason =3 salinity problem - no reason =4 nitrate, phosphate problem =4 nitrate, phosphate problem =3 salinity problem - no reason =4 nitrate, phosphate problem =4 nitrate, phosphate, nitrite problem =4 nitrate, phosphate problem =4 nitrate, phosphate problem =4 nitrate, phosphate, nitrite problem =4 nitrate, phosphate, nitrite problem =3 nitrate, phosphate</pre>	
233/01:	2 7 10 11 12 13 14 15 18 19 21 22 25	bqflg=4 qfl bqflg=2 qfl	<pre>=3 salinity problem - no reason =9 empty (stopcock broken off) =4 nitrate, phosphate,nitrite problem =4 nitrate, phosphate,nitrite problem =4 nitrate, phosphate,nitrite problem =3 salinity problem - no reason =4 nitrate, phosphate,nitrite problem =3 nitrate, phosphate,nitrite problem =3 nitrate, phosphate,nitrite problem =4 nitrate, phosphate,nitrite problem =3,4 nitrate, phosphate,nitrite problem =4 all. Leaker, noted on log sheet.</pre>	
234/01:	10 12 13	bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=2 qfl bqflg=4 qfl bqflg=3 qfl bqflg=2 qfl	<pre>=4 all. Leaker, noted on log sheet. =4 salinity .01 too high - no reason. =4 phosphate problem. =4 phosphate problem. =4 phosphate problem. =5 all. empty =4 all. Leaker, not indicated on sample log. =2 leak (log sheet). no action =2 leak (log sheet). no action</pre>	
235/04:	12 27 32	bqflg=2 qfl	=4 nitrate, phosphate problem. =2 potential leaker (log sheet). no action =2 potential leaker (log sheet). no action	
236/01:	2 4 9 11	bqflg=2 qfl bqflg=2 qfl	=3 nitrate, phosphate problem. =3 nitrate, phosphate problem. =4 nitrate, phosphate problem. =4 all. Leaker, not noted on sample log sheet	

	The actual bottle tripping sequence was 25 through 36 and then 1 through 24, but the WHOI software did not permit the actual bottle numbers to be entered in the sea file.
237/01: 2	bqflg=3 qflg=4 all. Leaker, not noted on sample log.
10	bqflg=2 qflg=4 nitrate, phosphate problem.
11	bqflg=2 qflg=4 nitrate, phosphate problem.
12	bqflg=2 qflg=4 nitrate, phosphate problem.
15	bqflg=2 qflg=3 nitrate, phosphate problem.
238/01: 8	<pre>bqflg=2 qflg=4 salinity .01 too high - no reason</pre>
10	bqflg=2 qflg=4 nitrate, phosphate problem.
11	bqflg=2 qflg=4 nitrate, phosphate,nitrite problem.
12	bqflg=2 qflg=4 nitrate, phosphate problem.
13	bqflg=2 qflg=3 nitrate, phosphate problem.
15	bqflg=2 qflg=4 nitrate, phosphate problem.
20	bqflg=2 qflg=4 salinity .05 too high - no reason
21	bqflg=2 qflg=4 salinity .03 too high - no reason
239/01: 8	<pre>bqflg=2 qflg=2 nitrate, phosphate - checked and looks OK ldt</pre>
10	bqflg=2 qflg=4 nitrate, phosphate problem.
11	bqflg=2 qflg=4 nitrate, phosphate problem.
12	bqflg=2 qflg=4 nitrate, phosphate problem.
13	bqflg=2 qflg=3 nitrate, phosphate problem.
14	bqflg=2 qflg=3 nitrate, phosphate problem.
15	bqflg=2 qflg=3 nitrate, phosphate problem.
23	bqflg=2 qflg=4 oxygen problem - no reason?
240/01: 10	bqflg=2 qflg=4 nitrate, phosphate problem.
12	bqflg=2 qflg=4 nitrate, phosphate problem.
17	bqflg=2 qflg=3 salinity 0.01 low - no reason
27	bqflg=2 qflg=3 salinity 0.05 high - no reason
241/01: 1	bqflg=2 qflg=3 salinity problem- no reason
7	bqflg=2 qflg=3 salinity problem- no reason
8	bqflg=2 qflg=3 salinity problem- no reason
10	bqflg=2 qflg=3 salinity problem- no reason
11	bqflg=2 qflg=4 nitrite of .07 - tube problem
12	bqflg=2 qflg=4 nitrite, phosphate problem.
13	bqflg=2 qflg=4 nitrite - tube problem
15	bqflg=2 qflg=4 nitrite - tube problem
242/01: 1-36	bqflg=2 qflg=3,4 all nitrites bad.
1	bqflg=2 qflg=4 all. bottom sediment sample.
2	bqflg=4 qflg=5 all. empty
8-21	bqflg=2 qflg=3,4 nitrate, phosphate problem.
14	bqflg=2 qflg=2 Leaker (log sheet). no action
243/01: 1	<pre>bqflg=2 qflg=3 nitrate, phosphate.</pre>
1	bqflg=2 qflg=3 salinity might be .003 high
2	bqflg=3 qflg=4 all. Leaker, not noted on log.
3	bqflg=2 qflg=3 nitrate, phosphate problem.
4	bqflg=2 qflg=3,4 nitrate, phosphate, nitrite problem.
5	bqflg=2 qflg=3 salinity problem- no reason
6	bqflg=2 qflg=3 nitrate, phosphate.
8	bqflg=2 qflg=4 nitrate, phosphate problem.
9	bqflg=2 qflg=4 nitrate, phosphate problem.

10 bqflg=2 qflg=4 nitrate, phosphate problem. bqflg=2 qflg=4 nitrate, phosphate problem. 11 12 bqflg=2 qflg=4 nitrate, phosphate problem. bqflg=2 qflg=4 nitrite of .03 13 15 bqflg=2 qflg=4 nitrite of .03 17 bqflq=2 qflq=2 oxygen - checked and is ok 244/03:2bqflg=3 qflg=4 all. Leaker, not noted on log sheet bqflg=2 qflg=3 salinity .003-.005 high - no reason 5 8 bqflq=2 qflq=4 phosphate problem. 9 bqflg=2 qflg=3 salinity .01 high - no reason bqflg=2 qflg=4 phosphate problem. 10 bqflg=2 qflg=4 phosphate problem. 13 bqflg=2 qflg=2 silicate seems low, but fits other stations 14 bqflg=2 qflg=2 silicate seems low, but fits other stations 18 bqflg=2 qflg=3 nitrate, phosphate problem. 20 bqflg=2 qflg=2 stopcock leaking (log sheet). no action bqflg=2 qflg=2 nitrate checked against others and OK 23 24 bqflg=2 qflg=4 phosphate problem 29 bqflg=2 qflg=2 silica checked against others and OK bqflg=2 qflg=2 silica checked against others and OK 30 245/01: 1 bqflg=4 qflg=4 all. bottom sediment sample. bqflq=4 qflq=9 all. empty 2 3 bqflg=2 qflg=3 oxygen looks it was drawn from bottle 4 bqflg=2 qflg=2 vent open (log sheet). no action 4 14 bqflq=2 qflq=2 bottom leak (log sheet). no action bqflg=2 qflg=2 silica checked vs. other stations and OK 25 26 bqflg=2 qflg=2 silica checked vs. other stations and OK 246/02: 10 bqflg=3 qflg=4 all. Leaker, noted on log sheet. 14 bqflg=2 qflg=2 bottom not seated (log sheet). no action 33 bqflg=2 qflg=2 salinities at 33 and 34 might have been reversed 34 bqflq=2 qflq=2 247/01: 9 bqflg=4 qflg=9 all. empty bgflg=2 gflg=2 bottom leak (log sheet). no action 14 248/01: 31 bqflg=2 qflg=2 vent open (log sheet). no action 25 bqflg=2 qflg=2 ALL vs. theta - checked. no action. CTD 02 looks good. 249/02: 1 bqflg=2 qflg=3 nitrate, silicate small inversion - no reason bqflg=2 qflg=2 salinity about .01 high - no reason 10 20 bqflg=2 qflg=2 nitrate, phosphate checked and OK ldt 250/01: 14 bqflg=2 qflg=2 nitrate checked and OK ldt 251/01: 64 bqflg=4 qflg=5 all. empty, (6) record tag deleted I suspect this is "bottle" 6 68 bqflg=3 qflg=4 all. (2) Leaker, not noted on log sheet. I suspect this is "bottle" 2 252/01: 1-36 pylon off by one (36 tripped at deepest point and 35 at shallowest) - sorted out. no further action. no flags. 253/01: 68 bqflg=3 qflg=4 all. (3) Leaker, not noted on log sheet.

I suspect this is "bottle" 3

254/02:

255/01:	63 68 67	<pre>bqflg=4 qflg=9 all. empty, record tag deleted (8) (so no indication in .sea file of this trip) bqflg=3 qflg=9 all. Leaker, not noted on log sheet. bqflg=3 qflg=9 all. (4) Leaker, not noted on log.</pre>
256/01:	1-36 5 7 8 31	<pre>bqflg=2 qflg=3 all nitrates 0.5-1.0 too high bqflg=2 qflg=2 phosphate looks a little high, but no</pre>
257/01:	51	bqflg=4 qflg=9 all. empty I assume that 51 is "bottle" 11
258/01:	1-36	bqflg=2 qflg=3 nitrates 0.5-1.0 high.
259/01:		
260/01:	2 14 20	<pre>bqflg=2 qflg=2 leak (log sheet). no action. This was the actual bottle which leaked, and it was located in the position 14; since WHOI software did not permit actual bottle numbers to be entered, the leaker is at location 14 in the .sea file bqflg=3 qflg=4 all. Leaker, not noted on log sheet. bqflg=2 qflg=3 oxygen .3 ml/l high. no reason.</pre>
261/01:	51 62 63 ??	<pre>bqflg=4 qflg=9 all. empty, record tag deleted (11) bqflg=3 qflg=9 all. (9) Leaker, not noted on log. I assume this is "bottle" 9. bqflg=4 qflg=9 all. empty, record tag deleted (8) bqflg=2 qflg=9 I don't understand this one. There are no reported values for S or nuts but O2 is OK.</pre>
262/01:	4 19 20 35	bqflg=2 qflg=3 salinity .01 high - no reason bqflg=2 qflg=4 oxygen may be .051ml/l high - no reason bqflg=2 qflg=3 salinity .0102 high - no reason bqflg=2 qflg=2 vent open. No action.
263/01:	67 68 69	<pre>bqflg=4 qflg=9 all. empty (4)     I assume this is "bottle" 4 bqflg=3 qflg=4 all. (3) Leaker, not noted on log.     I assume this is "bottle" 3 bqflg=3 qflg=3: salinity flag     I assume this is "bottle" 2</pre>
264/01:	23 24	bqflg=2 qflg=3 salinity .05 low - no reason bqflg=2 qflg=3 salinity .05 low - no reason
265/01:	68 69	bqflg=3 qflg=4 all. (3) Leaker, not noted on log. bqflg=3 qflg=4 all. (2) Leaker, not noted on log. I don't know which is 68 or 69.

- 266/01: 3 bqflg=4 qflg=9 all. empty.
- 267/01: 51 bqflg=4 qflg=5 all. empty, record tag deleted (11) 68 bqflg=4 qflg=5 all. empty, record tag deleted (3) ONLY 8 TAGS
- 268/01: 31 bqflq=2 qflq=2 salinity thought .1 low but OK against CTD
- 269/01: 5 bqflg=3 qflg=9 all. Leaker, not noted on log sheet.
- 270/01: 2 bqflg=2 qflg=2 Leaker (log sheet). No action 25 bqflg=2 qflg=2 valve open (log sheet). No action.
- 271/01:
- 272/01: 11 bqflg=2 qflg=9 nutrients drawn from 10
  13 bqflg=4 qflg=9 all. empty
  35 bqflg=4 qflg=9 all. empty
- 273/01: all bottle mixup sorted out 65 bqflg=2 qflg=4 oxygen .8 ml/l high - no reason I assume this is "bottle" 4 68 bqflg=3 qflg=9 all. (3) Leaker, not noted on log. 2 others one other empty bottle, one other leaker
- 274/01: 1-36 bottle mixup sorted out
- 275/01: 61 bqflg=2 qflg=2 vent open (log sheet) (10). no action. 68 bqflg=2 qflg=2 vent open (log sheet) (3) no action.
- 276/01: 7 bqflg=2 qflg=3 salinity .01 low no reason 10 bqflg=2 qflg=4 oxygen problem - no reason
- 277/01: 62 bqflg=2 qflg=2 not closed tight (log sheet). (9) no action.
- 278/01: 1-36 bottle mixup, sorted out. no action.
- 279/01: 63 bqflg=3 qflg=9 all. (8) Leaker, not noted on log. I assume this is "bottle" 8
- 280/01: 1-24 bqflg=2 qflg=2 bottle mixup, sorted out. no action. 2 bqflg=2 qflg=2 bottle 2 replaced by 41 here. no action.
- 281/01:
- 282/01:
- 283/01: all bottle mixup sorted out. no further action 62 bqflg=2 qflg=2 hung up (log sheet) (9). no action. 65 bqflg=2 qflg=4 salinity .15 high - no reason (6) 67 bqflg=2 qflg=2 hung up (log sheet) (4). no action.
- 284/01: 14 bqflg=4 qflg=9 all. empty 18 bqflg=2 qflg=4 salinity .01 high - no reason 35 bqflg=2 qflg=2 vent open (log sheet). no action.
- 285/01: 63 bqflg=4 qflg=9 all. empty (8)

67 bqflg=4 qflg=9 all. empty (4)
286/01: 25-36 rosette off by one. sorted out.
2 bqflg=2 qflg=2 salinity .01 high - no reason
30 bqflg=2 qflg=4 oxygen 2 ml/l high - no reason

- 287/02: 25-36 bqflg=4 qflg=9 all. inner rosette not closed, empty
  3 bqflg=2 qflg=3 salinity no reason
  1 bqflg=2 qflg=3 salinity no reason
- 288/02: CTD touched bottom 1 bqflg=2 qflg=2 oxygen slightly high re CTD but may be fine
- 289/01: 1 bqflg=2 qflg=2 salinity slightly too high re CTD 2 bqflg=2 qflg=3 salinity 0.005 too high re CTD 3 bqflg=2 qflg=3 salinity 0.002 high - no reason 30 bqflg=2 qflg=3 oxygen - possible dupe draw
  - 36 bqflg=4 qflg=9 all. empty

Bottle 19 vs. bottle 29. In the nutrients file there are two bottles identified as 29. The first one corresponds to sequential number 19, thus we assume this was indeed bottle 19 and not 29. The second bottle 29 has a sequence Nr. of 29. Nutrient data for the first bottle 29 (actually 19) look ok for the corresponding depth.

- 290/01: 1 bqflg=2 qflg=2 oxygen slightly high re CTD 1 bqflg=2 qflg=3 salinity 0.005 high - no reason 3 bqflg=2 qflg=3 salinity 0.006 high - no reason 21 bqflg=2 qflg=2 oxygen checked against CTD and OK 31 bqflg=2 qflg=2 bottom cap leak (log sheet) no action
- 291/01:
- 292/01: 1-36 inner rosette fired first (25 to 36, then 1 to 24) 8 bqflg=3 qflg=4 all. Leaker, not noted on log. Bottle numbers are correct in the .sea file. Actual bottle 32 was the leaker, but in position 8.
- 293/01: 33 bqflg=4 qflg=9 all. empty
- 294/01: 3 bqflg=2 qflg=3 salinity .002 high no reason 27 bqflg=2 qflg=2 Leaker (log sheet). no action.
- 295/01: 8 bqflg=2 qflg=3 salinity .005 high no reason (CTD conductivity cell changed at this station)

296/01: 1 bqflg=2 qflg=4 oxygen may be .05 high - no reason salinity .002 high - no reason 5 bqflg=2 qflg=3 salinity .002 high - no reason 6 bqflg=2 qflg=3 salinity .002 high - no reason 11 bqflg=2 qflg=3 salinity .003 high - no reason

#### 297/01:

298/01: 1 bqflg=2 qflg=3 salinity 0.002 high - no reason

4 11 12 13 16 19 290-299 299/01:	bqflg=2 qflg=3 nitrate problem - no reason bqflg=2 qflg=4 salinity 0.005 high - no reason bqflg=2 qflg=4 nitrate problem - no reason bqflg=2 qflg=4 salinity 0.01 low - looks like out of 14 bqflg=2 qflg=4 oxygen 1.0 ml/1 high - no reason bqflg=2 qflg=2 oxygen looks funny but agrees with
300/03: 1 2 12 21 27 31	<pre>bqflg=2 qflg=4 salinity 0.007 high - no reason</pre>
301/01: 12	bqflg=3 qflg=4 all. Leaker, noted on log sheet.
302/01: 31 32	bqflg=4 qflg=9 all. empty bqflg=2 qflg=4 phosphate .6 low - looks like value from 33
303/01:	
304/01: 1 2 4 28	bqflg=2 qflg=2 oxygen might be .1 high, but reasonable bqflg=2 qflg=2 oxygen might be .1 high, but reasonable bqflg=2 qflg=2 Leaker (log sheet). no action. bqflg=4 qflg=9 misfire (log sheet). no action.
305/01:	
306/01:	
307/01: 1 10	bqflg=2 qflg=2 oxygen might be .1 high, but reasonable bqflg=2 qflg=2 silicate looks 2. high but reasonable.
308/01: 1 27 36	bqflg=2 qflg=2 oxygen might be .1 high, but reasonable bqflg=2 qflg=2 Leaker (log sheet). no action. bqflg=2 qflg=4 salinity 10.0 psu high (possibly a typo)
309/01: 32	bqflg=3 rosette struck ship, knocked valve off 32. salinity value OK. no O2 or nuts. watch for problems on bottles 25-36 - none found.
310/1: 1	bqflg=2 qflg=2 oxygen might be a little high but reasonable
311/1: 21	bqflg=2 qflg=3 silicate 5 low. Don't know why other nuts flagged.
312/1:	
313/1: 29 26	bqflg=2 qflg=4 salinity dupe draw of 28 bqflg=2 qflg=3 salinity may be dupe draw of 25
314/2:	

- 315/1: 10 bqflg=2 qflg=3 nitrate may be .2 high
  29 bqflg=2 qflg=2 vent open (log sheet). no action.
- 316/1: 10 bqflg=2 qflg=3 salinity .01 high no reason
- 317/2: 1-36 rosettes fired out of order. sorted out. 1 bqflg=2 qflg=3 oxygen .1 high - no reason
- 318/1: 1 bqflg=2 qflg=2 Leaker (log sheet). no action.
- 319/1: 12bqflg=2 qflg=2 silicate may be 2 high no reason12bqflg=2 qflg=3 salinity .002 high no reason
- 320/1: 1bqflg=2 qflg=2 oxygen looked high but fits 310-31911bqflg=2 qflg=3 salinity may be .002 low no reason
- 321/1: 1 bqflg=2 qflg=2 oxygen looked high but fits 310-320
- 322/1: 4 bqflg=2 qflg=3 oxygen might be .1 high no reason
- 323/1: 13 bqflg=2 qflg=9 no oxygen value
- 324/1:
- 325/1:
- 326/1:

#### FIGURES

- Figure A.2.1. Cruise track for WOCE P16C (31wttunes3), R/V T. Washington, 31 Aug 1991 - 1 Oct 1991. (a) Rosette/CTD station (circle). Large volume plus large rosette/CTD station (+). (b) Equatorial stations. Regular rosette stations with CTD10 (circles). LADCP rosette stations with CTD9 (+).
- Figure A.2.2. JGOFS bio-optical stations on P16C.
- Figure A.2.3. Small volume (10 liter) water samples on P16C.
- Figure A.2.4. Large volume (Gerard) water samples on P16C.
- Figure A.2.5. ALACE float (circles) and surface drifter (+) deployments on P16C.
- Figure A.2.6. (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate all vs. potential temperature, from Pl6S stations 216-220 (solid, R/V T. Washington, 8/91, 31wttunes2) and from Pl6C stations 221-225 (x's, R/V T. Washington, 9/91), near 18S.
- Figure A.2.7. (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate, all vs. potential temperature, from TEW stations 2-4 (solid) and P16C stations 228-232 (triangles), at 12S. The TEW stations were collected in June, 1987.
- Figure A.2.8. (a) Salinity, (b) oxygen, (c) silica, and (d) nitrate, all vs. potential temperature, from Moana Wave stations 128-131 (solid) and P16C stations 298-302 (triangles), at 10N. The Moana Wave stations were collected in April, 1989.
- Figure A.2.9. Phosphate vs. potential temperature, from (a) P16S
  stations 217-220 and P16C stations 221-224 near 18S,
   (b) TEW stations 2-4 and P16C stations 228-232 at
   12S, (c) Moana Wave stations 128-131 and P16C
   stations 298-302 at 10N.
- Figure C.1.1. Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory temperature calibration data
- Figure C.1.2. Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory pressure calibration data
- Figure C.1.3. Pre-cruise and post cruise quadratic fits to CTD #9 and CTD #10 laboratory conductivity calibration data
- Figure C.1.4a.CTD#10 conductivity sensors A and B. Pre-cruise nominally calibrated CTD conductivity data differenced from rosette water sample data.
- Figure C.1.4b.CTD#9 conductivity sensors A and B. Pre-cruise nominally calibrated CTD conductivity data

differenced from rosette water sample data.

- Figure C.1.5. Salinity differences (rosette CTD) of final calibrated CTD data. Full profile (bottom); Below 2000 db (top).
- Figure C.1.6. Oxygen differences (rosette CTD) of final calibrated CTD data. Full profile (bottom); Below 2000 db (top).
- Figure C.1.7. Final calibrated CTD salinity and oxygen data. Rosette minus CTD differences vs. pressure.
- Figure C.1.8. Histogram plot of differences between final calibrated CTD and rosette water sample data.
- Figure C.1.9. Salinity on potential temperature surfaces 1.1 to 2.0C, separated by 0.1C. The smoother overlying curve is CTD#10 only. The jagged curve includes both CTD#9 and 10.
- Figure C.1.10.Average salinity vs. potential temperature for each isotherm 1.1 to 2.0C, separated by 0.1C. Error bars are one standard deviation. (a) CTD#9. (b) CTD#10. (c) The averages of both CTD#9 and 10 replotted from a and b.
- Figure C.5.1. Combined time series measurements of orthphosphate (uM/l) using different washing methods for precleaning the sampling tubes used during P16C to draw samples from the Niskin and Gerard bottles. The washing methods were: (a) seawater, (b) distilled water, (c) 80% isopropyl alcohol, and (d) 1.2 M HCl. The vertical lines on each sample represent the standard deviation of the mean (N=3). The horizontal broken line represents the root mean square deviation of all replicate samples for PO3- 4 collected during P16C and analyze within 2-3 hours after collection. This is an estimate of our short-term precision. The solid line represents +-1% of highest water PO3- 4 column values. This is a target precision level for WOCE hydrographic measurements for dissolved inorganic nutrients.

Figure C.5.2. Same as Fig. C.5.1 but for NO3 (umo/l).

Figure C.5.3. Same as Fig. C.5.1 but for NO2 (umo/l).

Figure C.5.4. Same as Fig. C.5.1 but for silicic acid (umo/l).
# G. DATA QUALITY EVAULATION

#### G.1 DATA QUALITY EVALUATION of P16C HYDROGRAPHIC DATA (A. Mantyla) 28 June 1994

The data originators have done a very through job in evaluating and resolving the numerous data problems encountered on this cruise: I have made very few changes to their quality flags. I tended to be a little more accepting to a slight nutrient bumps and a little more critical on salinity errors.

In the cruise report, the PI's document differences between TUNES Leg II and III, as well as differences from other expeditions that crossed the TUNES III track. They point out the analytical problems encountered on the cruise and the surprising differences between the 2 TUNES legs where the cruises overlapped. There were unexpected problems in all analyses, considering the experience of the analytical groups on the cruise. For nutrient problems to persist for the first quarter of the cruise simply due to dirty sample tubes is astonishing! The salinity problems seen early in the cruise may not have been entirely analytical: the sample collection is also suspect. The CTD processing section of the cruise report noted that some salinity samples were not tightly sealed, which results in artificially higher results. There are also several stations, some listed below, where samples were evidently collected out of sequence. Deep oxygens showed unlikely station to station shifts. Some have been flagged questionable (usually higher), but at some point it became difficult to tell which were the unlikely ones, the higher one or the low one.

Many water samples are plainly not from discrete depths, but are "smeared" over some depth range, as revealed by large differences between the CTD and water sample salinity seen on many stations, particularly in depths of strong salinity gradients. The differences are usually in the direction of deeper salinity, indicating that the rosette bottles were either tripped on the fly, or too quickly to allow sufficient flushing of the rosette bottle at the target depth. The water samples are usable, but the essential salinity verification of correct trip and no leakage is lost in those cases. I would urge that the console operators slow down at the bottle stops and allow a little more time for the rosette bottle to collect a good sample at the desired depth before tripping the bottle. At present, wire casts do a better job of collecting discrete water samples, but there isn't any reason why rosettes can't do almost as well, given a little thought and care.

I'm not familiar with how CTD data is assigned to the bottle trips on this cruise, but it showed be the CTD data recorded for a few seconds before the bottle is tripped so as to be equivalent to the rosette bottle history just before the bottle closure. Station 221 had 5 trips at the same depth as indicated by the identical CTD P, T, and S data tabulated for the 5 trips, obviously not the actual CTD data at the time of each sequential trip. Since the CTD data were not taken at the time of each bottle trip, that may be part of the reason why CTD versus bottle comparisons are not as tight as seen on other cruises.

The following are some specific problems that may be able to be resolved by the PI's:

### 223 #1 and 2:

Odd pressure reversal in final pressures are not in raw pressures. From raw minus final pressure differences above, looks like # 1 should be at 4130 db instead of 4117 db. Suggest data originator make correction.

## 228 #'s 7,8, and 9:

I've flagged these 3 salinity questionable, but they would be OK if one assumed that they were actually collected from one depth deeper; the CTD salinity and adjacent station Theta-Salinity curves would support that assumption. Also, salinity samples 22 and 23 appear to have been reversed compared to the CTD salinity, but the errors are small for this depth, so I did not flag them.

# 232 #'s 7,8,and 9:

Flagged all salts questionable, thought would be ok if moved down one depth. Most likely a sample collection error.

# <u>249 #'s 7,8,9,10:</u>

Flagged all 4 salts uncertain, would be ok if from a depth or two deeper. O2's confirm not a rosette mis-trip, so most likely a sampling error.

### <u>308#36:</u>

Bottle salt 44.2580 must be a key entry error:34.--- would be ok. Suggest originator verify and correct, if so.

### <u>311#21:</u>

All water samples flagged as questionable. The profiles suggest that the data is from 50 to 100db shallower. Is there any way to verify the trip depth? It would be nice if this were just a typo and the data could be assigned to a more probably depth, and confirmed by the CTD salinity and oxygen.

# G.2 CTD DATA QUALITY EVALUATION (Neil White)

- 1. All temperatures are in t68. While WHOI may have made a decision to stick with t68 I had understood (e.g. from a memo from Peter Saunders, the chairman of the WHP subgroup on standards and calibration) that t90 should be adopted as soon as possible. Surely this data should have been converted to t90 before it was submitted to the WHP office?
- 2. All CTD station headers (in the stannn.wct files) have the 9th of September, 1991 as their date.
- 3. Many oxygen values which have been flagged as bad have silly values (e.g. -393.1) instead of -9. In addition where data has been flagged as bad the number ber of observations has been set to -9, even though there is still usable data in some channels.
- 4. Station 251 has 2 decibar averages centred on even integers. This is apparently due to the use of pressure-sorted upcast data in the absence of usable downcast data, but it is still a big alarming that no-one seems to know how this happened, or to care!
- 5. The documentation use ml/l for dissolved oxygen values. This is confusing when everything else is in molar units..

While a number of these poinsts are minor it all adds up to a data set whose presentation does not inspire confidence.

Another aspect of this data set which I found alarming was the extent to which the originators were prepared to interpolate over gasps in the data sometimes even interpolating between 'fudged' (their terminology) data points. If interpolated data is to be provided then it must, surely, be considered 'fit for purpose' in some sense. I find it very hard to think of any purpose for which same of the interpolated data provided would be fit. Station 225 is the most extreme example, with interpolation over substational depth ranges (100m) near the surface, completely ignoring the structure in this part of the water column. This is exacerbated by the fact that some of the values at the end points (flagged as 'good' data) are clearly wrong.

# WOCE AND NON-WOCE STATIONS

Stations are numbered from 221 to 326. Odd-numbered stations from 251 through 285 were not WOCE stations. I will restrict most of my comments to the WOCE stations.

# TEMPERATURE CALIBRATION

The temperature calibration procedure at WHOI is described, and a statement to the effect that the calibration is believed to be good to .002 C is made. Surely an error budget has been done for the calibration lab, in which case some confidence limits on the calibrations should be given.

# SALINITY AND DISSOLVED OXYGEN CALIBRATION

On the whole the data processors seem to have done a good job of calibration of the CTD salinity and dissolved oxygen channels. Lynne Talley has looked at deep Theta/salinity data. I have not repeated that analysis, but will look mainly at the actual goodness of fit between CTD and bottle data as requested. Inevitable some of the stations Lynne has hightlighted also get a mention here.

The willingness of the processors to take algorithms which are based on the physical properties of sensors and make them 'unphysical' worries me a bit. One example of this is the practice of changing the conductivity cell deformation coefficient to say that either it doesn't shrink with pressure, or that it expands with pressure. Another example is the negative lags accepted for the oxygen sensor for stations 238-240. While I can think of no better ideas and am award of many of the vagaries of oxygen sensors I find it worrying that what started as an attempt to model the behaviors of a sensor seems to have turned into an exercise purely in many-parameter fitting.

For salinity (figure 1) and oxygen (figure 2) 1 have plotted profiles of scaled offsets between bottles and downcast CTD ValLies. Deep offsets are plotted at a larger scale than shallow ones - the scale is shown by the two lines on the left hand side of each frame. At any depth the width of the wedge represents an offset (bottle - CTD) of .01 psu (figure 1) or 4 micro- moles (figure 2). Non-WOCE stations are Indicated by Stations numbers in brackets.

# Shallow (0 - 1000m) fits

The cruise report mentions sampling problems early in the cruise. Some of these seem to show up in the shallower samples. See figures 1 and 2 and figures 3a,b,c,...,I (plots of the stations mentioned).

While there is (understandably) an emphasis on minimizing the residuals in deep water I feel that , perhaps, a bit more attention should be paid to the quality of fit in shallower water. While we can't expect the fit in shallower water to be as good because of a variety of phenomena (oceaographic variability, internal waves, hight gradients, vertical distance between CTD sensors and sample bottle, long oxygen sensor time constant, etc) I feel that may of the problems mentioned below should have been picked up by the data processors. In places there are quite substantial misfits in both salinity and oxygen which are not explainable in terms of any of the above-mentioned phenomena, especially as, for some of them, the downcast and upcast CTD values agree quite closely, but the bottle values are substantially offset.

Note that only samples flagged as good data (quality byte=2) are considered here.

### STATION 224:

The salinity from about 200-400 metres are a very poor fit (out by up to .33 psu), and seem to e out by enough to wonder whether the bottle depths are incorrect.

# STATION 225:

Similar to 224 but the differences aren't as large. It is a pity that there is no oxygen profile data for these STATIONs as this might give some corroborating information on whether the bottle depths are correct or not

### STATION 229:

More problems in the thermocline, this time smaller differences, but in the opposite sense. The comments for the above-mentioned STATIONs apply here also. The oxygen profile doesn't really help to resolve the issue here

# STATION 230:

More of the same, and the fact that the oxygen samples are also offset suggests a sampling/bottle identification problem.

# STATION 234:

The samples at 260, 309 and 360 metres all look as if they have been misplaced or incorrectly sampled. Both salinity and oxygen samples are offset at all three depths

# STATION 237:

The samples at 209 and 260 metres are both offset. Both salinity and oxygen are offset at 260 metres

# STATION 241:

Salinity samples at 109 and 210 metres both look suspicious

# STATION 243:

Again, very poor salinity fits at 234, 258 and 284 metres, with fairly poor oxygen fits at 258 and 284

### STATION 245:

Again, poor fits in both salinity and oxygen at 205, 229 and 254 metres

### STATION 262:

While the fit is generally better that for some of these STATIONs, the CTD salinity profile seems to be consistently below the bottles in the 400-600 metres range and also at some other samples. In fact, the mean offset of the 17 samples from 0-1000 metres is .018 psu - surely too high

### STATION 289:

The oxygen sample at 252 metres is surely wrong.

# STATION 313:

There is a more-or-less consistent salinity offset from 69 to 365 metres. The mean offset of the 17 salinity samples from 0 - 1000 metres is .028psu.

# DEEP SALINITY FITS:

Overlaying theta/CTD salinity and theta/bottle salinity plots of stations 240-245 and 246-250. It shows that the CTD salinity for stations 240-245 are noticeably higher compared to the bottle salinity. One could also argue that the CTD salinity for stations 246-250 are a little low compared to the bottles. The mean offsets between 1000 and 5000 metres are:

Station	Mean offset
240	003
241	.001
242	002
243	.000
244	001
245	002
246	.002
247	.000
248	.000
249	.001
250	.000

I feel that this part of the cruise should be looked at again. The jump of .004 psu between stations 245 and 246 is presumably a function of the fact that this is a boundary between groups. It is a large jump in the context of the WOCE aims for accuracy.

Stations 253 and 263 should also be looked at again if WOCE accuracy is being southt for these (non-WOCE) stations.

Other stations where there seems to be a mean deep-water offset between the CTD profile and the bottles worth looking into are:

Stations	Mean offset (1000-5000m)
223	.003
224	.002
231	002
235	002
236	002
271	.002
276	002
282	002
284	002
288	002
291	002
305	002
319	002

None of these stations are at group boundaries and some of these offsets could well be due to the sampling problems early in the cruise. They could also be due to the tendency

of the CTD calibration process to smooth out the variability in the bottle data. However, I suggest that these stations be looked at again.

# **DEEP OXYGEN FITS**

The processors seem to have done a good job of calibrating the deep oxygen profiles. The only station which sticks out as one needing to be looked at again is station 319 with a mean offset of 2.0 micromoles (CTD higher than bottle) between 1000 and 5000 metres.

























Figure 3a



Figure 3b



Figure 3c







Figure 3e







Figure 3g



Figure 3h



Figure 3i





Figure 3k















Figure 4d



#### Using QC code 2 (good data) ONLY



### Using QC codes 2 & 6 (good + interpolated)



# Station 'before' (QC code 2 only)
#### Station 'after' (QC code 2 only)



# G.3. P16C TUNES-3 DQ Report for Large Volume Samples

(Robert M. Key)

# 1.0 General Information

WOCE section P16C was the third in a series of three cruise legs which have been collectively referred to as "TUNES". Most of the general information pertinent to this cruise have been reported by Lynne Talley who was chief scientist for this leg. This addendum to her report covers details of data collection and analysis for the large volume Gerard samples.

A total of 8 large volume (LV) stations was occupied on this leg. The cruise plan called for 2 Gerard casts of 9 barrels each at each LV station. The planned sampling density was 1 station every 5° of latitude (~300nmi). Each Gerard barrel was equipped with a piggyback 5 liter Niskin bottle which, in turn, had a full set of high precision reversing thermometers to determine sampling pressure as well as temperature. In the event of mistripped Gerard sampler(s), casts were repeated as time allowed in an attempt to collect the full suite of samples.

All LV casts for the TUNES cruises were done using the stern A-frame on the R/V Thomas Washington. As is generally the case, the combination of a small vessel with working off the stern led to an elevated failure rate for the LV work relative to working off the side of a larger vessel. This problem is a function of the accelerations on the trawl wire caused by ship motion and sea state. These problems were minimized by the exceptional effort and capability of the Washington's crew.

On the first cast at station 225, both Gerard and Niskin were sampled for salinity and silicate. On the remainder of the casts for this leg, salinity and the full complement of nutrients (silicate, phosphate, nitrite and nitrate) were run on each sample pair. These nutrient and salinity results have been used to help assure that the Gerard barrels tripped at the desired depth and to ascertain whether or not the Gerard barrel leaked during retrieval. For this leg,  $\Delta^{14}$ C was the only LV tracer measurement made on the Gerard samples. Table 1 summarizes the LV sampling.

# 2.0 Personnel

LV sampling for this cruise was under the direction of Paul Quay (U. Washington).

Station	Cast	Latitude	Longitude	No. Ger. Samples
225	1	15°31.4'S	150°39.4'W	5
	3			5
	4			3
235	1	10°30.5'S	150°58.5'W	8
	3			4
	4			5
244	2	6°0.0'S	151°0.0'W	9
	4			9
259	2	1°30.0'S	151°0.0'W	9
	3			9
288	1	4°0.0'N	151°0.0'W	9
	3			9
300	2	9°54.5'N	151°57.0'W	9
	4			9
308	1	13°51.5'N	152°41.5'W	9
	4			9
317	1	18°0.0'N	153°30.0'W	9
	4			9
Total	17			138

**TABLE 1. LV Sampling Summary** 

Quay and Robert Key (Princeton U.) are the principal investigators for this work. All LV <sup>14</sup>C extractions at sea were done by either Quay or Leonard Lopez (SIO-ODF). In addition to Quay and Lopez, deck work was done by the WHOI CTD group with assistance from many of the scientific party. Lopez was primarily responsible for reading thermometers. Salinities and nutrients were analyzed by the WHOI CTD group and the Oregon State Univ. group respectively. <sup>14</sup>C analyses were performed at Minze Stuiver's (Sta 225-259) and Göte Östlund's (Sta 288-317) laboratories. Key collected the data from the originators, merged the files, assigned quality control flags to all the data and submitted the data files to the WOCE office (12/13/94).

#### 3.0 Results

Prior to this, a preliminary subset of this data was submitted to the WOCE office. This data set and any changes or additions supersedes any prior submission.

In this data set Gerard samples can be differentiated from Niskin samples by the bottle number. Niskin bottle numbers are in the range 41-71 while Gerards are in the range 81-94.

#### 3.1 Pressure and Temperature

Pressure and temperature for the LV casts are determined by reversing thermometers mounted on the Niskin bottle. Each bottle was equipped with the standard set of 2 protected and 1 unprotected thermometer. All thermometers, calibrations and calculations were provided by SIO-ODF. Reported temperatures for samples in the thermocline are believed to be accurate to 0.01°C and for deep samples 0.005°C. Pressures were calculated using standard techniques combining wire out with unprotected thermometer data. In cases where the thermometers failed, pressures were estimated by thermometer data from adjacent bottles combined with wire out data. Because of the inherent error in pressure calculations and the finite flushing time required for the Gerard barrels, the assigned pressures have an uncertainty of approximately 10 dB. The pressures recorded in the data set for each Gerard-Niskin pair generally differ by approximately 0.5 dB with the Gerard pressure being the greater. This is because the Niskin is hung near the upper end of the Gerard. Maintaining this difference has a advantage for some computer software (particularly gridding and interpolation programs) which do not handle multiple data at exactly the same location.

#### 3.2 Salinity

Salinity samples were collected from each Gerard barrel and each piggyback Niskin bottle. Analyses were performed by the same personnel who ran the salt samples collected from the Rosette bottles so the analytical precision should be the same for LV salts and Rosette salt samples. When both Gerard and Niskin trip properly, the difference between the two salt measurements should be within the range 0.000 - 0.003 on the PSU scale. Somewhat larger differences can occur if the sea state is very calm and the cast is not "yoyo'ed" once the terminal wire out is reached. This difference is due to the flushing time required for the Gerard barrels and the degree of difference is a function of the salinity gradient where the sample was collected. In addition to providing primary hydrographic data for the LV casts, measured salinity values are used to calculate potential density values for these samples and to help confirm that the barrels closed at the desired depth. For the area covered by this leg, deep nutrient values (especially silicate) are more useful for trip confirmation than salt measurements due to the very low salt gradients.

#### 3.3 Nutrients

Nutrient samples were collected from Gerard and Niskin samples. On the first station, only silicate values were reported. LV nutrients were measured along with Rosette nutrients so the precision for these analyses should be the same. For some unknown reason, nutrients collected from LV casts are frequently subject to systematic offsets from samples taken from Rosette bottles. For this reason it is recommended that these data be viewed only as a means of checking sample integrity (*i.e.* trip confirmation). The Rosette-Gerard discrepancy is frequently less for silicate than for other nutrients. The raw nutrient data files provided by OSU were in units of  $\mu$ mol/liter. Conversion to  $\mu$ mol/kg was done using the measured sample salinity and a laboratory temperature of 25.5°C (Joe Jennings, personnel communication).

## 3.4 14C

The  $\Delta^{14}$ C values reported here have been distributed in various data reports produced by Östlund. Östlund's reports included preliminary hydrographic data and are superceded by this submission.

All Gerard samples deemed to be "OK" on initial inspection at sea were extracted for <sup>14</sup>C analysis using the technique described by Key (1991). The extracted <sup>14</sup>CO<sub>2</sub>/NaOH samples were returned to the Ocean Tracer Lab at Princeton and subsequently shipped to Östlund's lab. Östlund divided the sample set and shipped the samples for stations 225-259 to Stuiver. These two laboratories have been cooperating on sample analysis for approximately 20 years and are thoroughly intercalibrated. Östlund's lab reports a precision of 4‰ for each measurement based on a long term average of counting statistics. Stuiver's lab reports individual errors for each measurement which range from 2-4‰. Quality control of the resulting measurements showed no statistically significant difference between results from the two labs. Of the 138 Gerard samples summarized in Table 1, <sup>14</sup>C has been measured on 121 (88%). This exceeds the rate funded for this work (80%). Once the WOCE central Pacific data set is merged, some of the remaining samples may be analyzed if warranted.

Existing <sup>14</sup>C data for the area sampled on this cruise is limited to the GEOSECS measurements. Comparison of these two data sets indicates that they are in agreement to the precision of the measurements.

## 4.0 Data Summary

Figures 1-3 summarize the large volume <sup>14</sup>C data collected on this leg. All  $\Delta^{14}$ C measurements with a quality flag value of 2 are included in each figure. Figure 1. shows the  $\Delta^{14}$ C values plotted as a function of pressure. The error bars are not shown in this figure, but would be approximately 50% wider than the symbols used. The most noticeable characteristics are the strong minimum in the 2200-2600dB range for all stations and the fact that the measurements from Station 225 are significantly higher than for the other stations. Figures 2 and 3 show the  $\Delta^{14}$ C values plotted against measured Gerard barrel silicate values. Figure 2 covers the upper water column (shallowest sample at approximately 1000db) and Figure 3 the deep water column. In these two plots a few points which lie somewhat outside the envelop of data are marked (station-cast-bottle). No significance is implied by the linear regression on these plots other than to demonstrate the correlation.





P16C Large Volume Data 3000 <= Pressure (dB)



#### 5.0 Quality Control Flag Assignment

Quality flag values were assigned to all bottles and all measurements using the code defined in Tables 0.1 and 0.2 of WHP Office Report WHPO 91-1 Rev. 2 sections 4.5.1 and 4.5.2 respectively. In this report the only bottle flag values used were 2,3,4,6 and 9. For the measurement flags values of 2,3,4,5 or 9 were assigned. The interpretation of measurement flag values 5 and 9 is unambiguous, however the choice between values 2,3 or 4 is involves some interpretation. For this data set, the salt and nutrient values were checked by plotting them over the same parameters taken from the rosette at the same station. Points which were clearly outliers were flagged "4". Points which were somewhat outside the envelop of the other points were flagged "3". In cases where the entire cast seemed to be shifted to higher or lower concentrations (in nutrient values), but the values formed a smooth profile, the data was flagged as "2". Comments are given in the next section for flag values of 3 or 4 in almost all cases. Once the nutrient and salt data had been flagged, these results were considered in flagging the <sup>14</sup>C data. There is very little overlap between this data set and any existing <sup>14</sup>C data, so that type of comparison was impractical. In general the lack of other data for comparison led to a more lenient grading on the <sup>14</sup>C data.

When using this data set for scientific application, any <sup>14</sup>C datum which is flagged with a "3" should be carefully considered. My subjective opinion is that any datum flagged "4" should be disregarded. Comments on the <sup>14</sup>C data in the next section are significantly more detailed than the comments for the salt or nutrient data. When flagging <sup>14</sup>C data, the measurement error was taken into consideration. That is, approximately one-third of the <sup>14</sup>C measurements are expected to deviate from the true value by more than the measurement precision of ~4‰.

No measured values have been removed from this data set. When using this data set, it is advised that the nutrient data only be considered as a tool for judging the quality of the  ${}^{14}C$  data.

#### 6.0 Summary of Sample Collection and 14C Extraction Notes

The following list summarizes comments recorded on the sample collection, thermometer, and <sup>14</sup>C extraction log sheets. Any text in this listing shown in *italics* is a comment added after the fact to help the reader interpret the potential significance of the original comment. Comments from Talley's original LV report are repeated here.

• Station 225

Cast 1. Five barrels tripped. Silicate values are 3-5µmole/kg lower than Rosette values at comparable pressures. No nitrate or phosphate measurements were made on samples from this cast.

Gerard 89/Niskin - 45 N-G salt = -.005, data entry ok. Silicate value also indicated that 45 may have closed after cast started up.

Cast 3. Five barrels tripped. Messenger hang-up on bottle 89. Bottom 4 barrels sent back down as cast 4

Gerard 89 - low volume noted when sample transferred to  $^{14}$ C extraction drum.

Cast 4. Three barrels tripped.

Gerard 85/Niskin 71- did not trip. No messenger.

Gerard 90/Niskin 47 Niskin did not trip. No water or temperature. Gerard looks ok.

Gerard 93/Niskin 48 N-G salt =.004. Entry ok. Similar difference in nutrients, but does not indicate consistent leak in either.

• Station 235

Cast 1. Only 8 barrels hung. All tripped.

Gerard 89 lid slightly ajar. A Gerard lid can close and seal without latching.

Gerard 90 pinch clamp cracked during extraction in drum #8, may have leaked a little. *Possible decrease in extracted gas sample size, but generally not a significant problem.* 

Cast 3. Four barrels tripped. Messenger hang-up on bbl 87. Remaining 5 barrels sent back down as cast 4 (? <sup>14</sup>C extraction sheets record retry as cast 3; ODF records show retry as cast 4. Cast listed as #4 in these records).

Gerard 81 cork popped off for a few minutes near end of <sup>14</sup>C extraction. *Possible decrease in extracted gas sample size, but generally not a significant problem.* 

Gerard 84/Niskin 43 N-G salt = -.009. Nutrient data also indicates that Niskin 43 is a "bad" sample. Gerard looks ok.

Gerard 87/Niskin 45 N-G salt =.004 otherwise both samples look ok. Pinch clamp cracked on drum 13, leaked 1 minute during  $^{14}$ C extraction. *Possible decrease in extracted gas sample size, but generally not a significant problem.* 

Cast 4. Five barrels tripped.

Gerard 85/Niskin 49 Intended pressure was 2756dB. Therms and bottle data indicate trip depth of approximately 1812dB. Gerard data looks OK at this level and bottle flag set to 3. Niskin data still looks bad. Sample log: "Looks like barrel pretripped". Pinch clamp cracked on drum 17, leaked 1 minute. *Possible decrease in extracted gas sample size, but generally not a significant problem.* 

Gerard 90/Niskin 71 Intended pressure was 3053dB. Therms and bottle data indicate trip depth of approximately 1987dB. No water samples from Niskin. Consider all data highly suspect. <sup>14</sup>C data does not fit at this level.

Gerard - 93 leaks air on push(?) slight 0-ring damage. <sup>14</sup>C data looks OK.

• Station 244

Cast 2. Niskin  $PO_4$  values higher than Gerard values by 0.2. Gerard  $PO_4$  values look OK. Possible sample tube contamination.

Gerard 90/Niskin 71 Thermometers indicate Niskin tripped at approximately 4327dB rather than intended 5150dB. Water samples indicate that Gerard tripped at intended depth. Niskin samples marked "bad".

Cast 4.

Gerard 90/Niskin 71 Thermometer and Niskin samples indicate that Niskin tripped at approximately 1791dB. Gerard values indicate that it tripped closer to intended level of 2886dB, but salt, NO<sub>3</sub>, and PO<sub>4</sub> are save as level above (449/485 at 2632dB). Gerard silicate shows smooth trend. <sup>14</sup>C could be from shallower depth, but not as shallow as Niskin. <sup>14</sup>C flagged as questionable.

• Station 259

Cast 2.

Gerard 87/Niskin 43 N-G = -0.10. Nutrients also show very slightly anomalous differences.  $^{14}$ C looks ok.

Cast 3. Messenger hang-up on bbl 93. Remaining 3 barrels send back down. Both lowerings recorded as Cast 3. Six barrels tripped on first try, all three on second lowering.

Gerard 93/Niskin 50 Thermometer rack did not reverse. Pressure estimated from wire out and neighboring bottles. N-G salt = -.012. Silicate on Niskin also questionable. Niskin flagged as bad. Gerard looks OK

Gerard 83 Tygon tubing going to <sup>14</sup>C pre-stripper slipped off (extractor board #2) after 4 hours of extraction and was off for 20 minutes or less. *Decrease in extracted gas sample size, but probably not a significant problem this stage of the procedure.* 

• Station 288

Cast 1.

Gerard 84/Niskin 45 G-N differences indicate possible slight leak in Gerard. <sup>14</sup>C not reported for this Gerard

Cast 3.

Gerard 85/Niskin 49 N-G salt = 0.010, silicate 1.1 difference. <sup>14</sup>C looks OK.

Gerard 90/Niskin 48 N-G salt = -0.012, silicate 0.7 difference.  $^{14}$ C looks to be high by about 10‰ marked as questionable.

• Station 300

Cast 2.

Gerard 93/Niskin 71 N-G salt = -0.019. Nutrients also indicate problem with Niskin. All water values from Niskin marked as "bad". Gerard data looks OK including  $^{14}$ C.

Cast 4.

Gerard 85/Niskin 48 Gerard and therms look OK, no water in Niskin.

Gerard 90/Niskin 49 N-G = -0.010, silicate and  $^{14}$ C look OK.

• Station 308

Cast 1.

Gerard 90/Niskin 49 Tube slipped off on #8 extractor after <sup>14</sup>C extraction when transferring NaOH from extractor back into sample bottle. Solution loss estimated at 25 ml. *Decrease in sample size, but not a significant problem*.

Gerard 93/Niskin 71 N-G salt = 0.007, no silicate difference and some difference in NO<sub>3</sub> and PO<sub>4</sub>. <sup>14</sup>C looks to be low by approximately 10‰. Gerard values flagged as questionable.

• Station 317

Cast 1.

Gerard 84/Niskin 43 Both apparently mistripped at approximately 815dB rather than the planned level of 3483dB. Data from both looks OK at this level. <sup>14</sup>C not reported for this sample.

Gerard 87/Niskin 45 Sample log note implies mistrip with this pair, but hydro data all looks OK.

Cast 4.

Gerard 90/Niskin 71 Some serious confusion here. Temperature data sheet shows this pair at the deepest level while the Sample Log shows this pair to be next to the deepest for this cast. Temperature. data sheet has erasures and note: "change out" between 448/485 and 449/493. <sup>14</sup>C not reported for this sample.

Gerard 93/Niskin 49 See comments for 90/71 pair above. <sup>14</sup>C marked as questionable along with other data from Gerard.

# G.4. P16C TUNES-3 Final Report for AMS14C Samples

(Robert M. Key & Paul Quay) July 6, 1996

# 1.0 General Information

WOCE section P16C was the third in a series of three cruise legs referred to as "TUNES". Lynne Talley of SIO was chief scientist for this leg. This report covers details of data collection and analysis for the small volume radiocarbon samples. The reader is referred to "Documentation for WOCE Hydrographic Program section P16C" by Talley as the primary source for cruise information. Of 106 stations, 29 were sampled for radiocarbon. The AMS station locations are shown in Figure 1 and summarized in Table 1



**Figure 1:** <sup>14</sup>C station locations for WOCE P16C (TUNES-3). Stations indicated by a dot were sampled only in the thermocline using the AMS technique. Stations indicated by a + were sampled over the entire water column using AMS for the thermocline and large volume sampling for deep and bottom waters.

Station	Date 1991	Latitude	Longitude	Bottom Depth (m)
222	9/1	-16.994	-150.494	3770
226	9/3	-14.999	-150.835	4528
230	9/4	-12.993	-151.003	4595
235	9/6	-10.508	-150.988	4910
238	9/7	-9.000	-150.996	3840
242	9/8	-7.018	-151.003	5182
246	9/10	-5.013	-151.005	4985
250	9/11	-3.007	-151.013	4765
256	9/12	-1.998	-150.991	4749
262	9/14	-1.007	-150.997	4720
268	9/15	-0.005	-150.999	4340
274	9/16	0.993	-150.998	3803
280	9/17	1.996	-151.002	4409
286	9/18	2.978	-151.003	5087
290	9/20	4.996	-151.003	5060
294	9/21	6.959	-151.348	5384
298	9/22	8.943	-151.755	5056
302	9/23	10.907	-152.112	5345
306	9/25	12.865	-152.503	5561
310	9/26	14.839	-152.891	5815
314	9/28	16.802	-153.267	5185
319	9/29	18.400	-154.474	5162

Table 1: P16C <sup>14</sup>C Station Data

. <sup>14</sup>C samples were additionally collected for measurement by the large volume technique on 8 stations (225, 235, 244, 259, 288, 300, 308 and 317). AMS sampling was used for the upper thermocline and large volume sampling for the deep and bottom waters.

## 2.0 Personnel

<sup>14</sup>C sampling for this cruise was under the direction of the PI, Paul Quay (U. Washington). <sup>14</sup>C analyses were performed at the National Ocean Sciences AMS Facility (NOSAMS) at Woods Hole Oceanographic Institution, however, most of the sample extractions and accompanying <sup>13</sup>C measurements were made in Quay's lab. Salinities and nutrients were analyzed by the WHOI CTD group and the Oregon State Univ. group respectively. R. Key (Princeton) collected the data from the originators, merged the files, assigned quality control flags to the <sup>14</sup>C and submitted the data files to the WOCE office (7/96).

## 3.0 Results

This <sup>14</sup>C data set and any changes or additions supersedes any prior release.

## 3.1 Hydrography

Hydrography from this leg have been submitted to the WOCE office by the chief scientist and described in the previously mentioned report.

#### 3.2 14C

Most of the  $\Delta^{14}$ C values reported here have been distributed in a data report (NOSAMS, 1996). That report included preliminary hydrographic data and <sup>14</sup>C results which had not been through the WOCE quality control procedures. This report supersedes that data distributions.

At this time 346 of 384 samples have been measured and reported. Replicate measurements were made on 6 of the water samples. These replicate analyses are tabulated in Table 2. The table shows the mean and standard deviation for each set of replicates. For

	v				
Sta-Cast-Bottle	$\Delta^{14}C$	Err	Mean <sup>a</sup>	Standard Deviation <sup>b</sup>	
242-1-27	-87.5	2.7	97.0	0.6	
	-88.3	2.9	-87.9	0.6	
290-1-32	65.6	2.7	65.8	0.2	
	65.9	2.7	05.0	0.2	
302-1-30	-28.7	2.7	-34.9	8.7	
	-41.0	2.9	-34.9	0.7	
306-1-28	-117.1	3.6	-117.4	0.4	
	-117.7	2.8	-11/.4	0.4	
310-1-29	-87.1	2.8	-93.3	8.7	
	-99.4	3.9	-75.5	0.7	
319-1-28 <sup>c</sup>	-30.7	3.1			
	-32.8	3.4			
	-29.8	3.2	-33.6	4.2	
	-40.5	6.8			
	-34.3	4.1			

 Table 2: Summary of Replicate Analyses

a. Error weighted mean reported with data set

b. Error weighted standard deviation of the mean reported with data set.

c. 3 of 4 averaged for final data set

these few samples, the average standard deviation is 3.8‰. This precision estimate is

somewhat smaller than the mean for the time frame over which these samples were measured. For a summary of the improvement in precision with time at NOSAMS, see Key, *et al.* (1996). In the final data reported to the WOCE office, the error weighted mean and error weighted standard deviation of the mean are given for replicate analyses.

Because of the time and costs involved, direct comparisons were only infrequently made between the large volume and AMS methods for determining  $\Delta^{14}$ C. In general continuity between the methods was assured by slightly overlapping Gerard and Rosette sampling where both methods were used and by the fact that both analytic techniques use the same standards. On this leg, however, one entire station (235) was analyzed by both methods. Table 3 summarizes the results from that test. The last column in Table 3 is the difference

Cast	Bottla	Pressure	Colinity	sf	Large	Vol	ume	AM	S	Λ
Cast	Боше	riessuie	Samily	51	<sup>14</sup> C	σ	Flag	<sup>14</sup> C	σ	Δ
3	81	983.7	34.527	2	-167.7	3.3	2	-164.2	2.4	-3.5
3	83	1232.7	34.560	2	-189.6	3.0	2	-191.1	2.1	1.5
3	84	1481.9	34.600	2	-200.6	2.5	2	-206.1	2.4	5.5
3	87	1728.4	34.615	2	-211.1	2.4	2	-214.4	2.6	3.3
4	85	1812.5	NA	9	-215.1	2.2	2	-214.7	2.5	-0.4
4	90	1987.5	NA	9	-220.8	2.5	3 <sup>a</sup>	-220.0	3.5	-0.8
4	89	1992.9	34.640	2	-218.3	2.0	2	-223.7	2.2	5.4
4	93	2231.4	34.653	2	-219.4	2.2	2	-225.8	2.6	6.4
4	94	2484.4	34.666	2	-226.4	2.2	2	-227.7	2.2	1.3
1	81	3292.8	34.682	2	-214.9	2.0	2	-215.2	2.4	0.3
1	84	3542.6	34.684	2	-209.0	2.1	2	-221.2	3.4	12.2
1	87	3792.6	34.691	2	-202.6	2.7	2	-222.2	4.0	19.6
1	89	4043.9	34.693	2	-192.7	2.6	2	-209.6	3.6	16.9
1	93	4297.0	34.706	2	-188.3	3.7	2	-194.0	3.0	5.7
1	94	4551.9	34.703	2	-188.2	3.8	2	-186.7	2.8	-1.5
1	85	4807.1	34.704	2	-182.2	2.4	2	-187.8	3.0	5.6
1	90	5066.7	34.705	2	-178.8	4.1	2	-181.8	2.3	3.0

Table 3: Station 235 Accuracy Check

a. Since both analytical techniques used water from the same sampler, the fact that this result was flagged "questionable" has no bearing on the comparison made here.

(LV-AMS) in the results for the two techniques. For these samples the mean difference is +4.7‰. This value is remarkably close to the expected error in the difference for any two of the measurements based on simple propagation of errors. This mean value is not statistically different from zero, however the fact that most of the differences are of the same sign suggests the possibility of a small systematic error.

#### 4.0 Quality Control Flag Assignment

Quality flag values were assigned to all <sup>14</sup>C measurements using the code defined in Table 0.2 of WHP Office Report WHPO 91-1 Rev. 2 section 4.5.2. Measurement flags values of 2, 3, 4, 6 and 9 have been assigned to date. Approximately 40 samples remain to be measured. Currently, the unmeasured samples are incorrectly coded with a flag value of 9 (no sample collected) rather than 1 (sample collected) or 5 (no result reported). The choice between values 2 (good), 3 (questionable) or 4 (bad) is involves some interpretation. There is very little overlap between this data set and any existing <sup>14</sup>C data, so that type of comparison was difficult. In general the lack of other data for comparison led to a more lenient grading on the <sup>14</sup>C data.

When using this data set for scientific application, any <sup>14</sup>C datum which is flagged with a "3" should be carefully considered. My subjective opinion is that any datum flagged "4" should be disregarded. When flagging <sup>14</sup>C data, the measurement error was taken into consideration. That is, approximately one-third of the <sup>14</sup>C measurements are expected to deviate from the true value by more than the measurement precision. No measured values have been removed from this data set.

Table 4 summarizes the quality control flags assigned to this data set. For a detailed description of the flagging procedure see Key, *et al.* (1996). As more of the Pacific

Flag	Number
2	334
3	5
4	2
6	5

**Table 4: Summary of Assigned Quality Control Flags** 

data set becomes available, it is possible that some of these flag values may be modified. Any additional data received for this leg will be reported to the WOCE office as they become available.

## 5.0 Data Summary

Figures 2-4 summarize the AMS <sup>14</sup>C data collected on this leg. Only  $\Delta^{14}$ C measurements with a quality flag value of 2 or 6 are included in each figure. Figure 2 shows the  $\Delta^{14}$ C values with 2 $\sigma$  error bars plotted as a function of pressure for the upper 1.5 kilo-



meters of the water column. This figure clearly demonstrates the sampling strategy used

**Figure 2:** AMS  $\Delta^{14}$ C results for P16C stations shown with  $2\sigma$  error bars.Only those measurements having a quality control flag value of 2 are plotted.

during the TUNES legs. That is, AMS sampling was almost totally limited to the upper 1500 meters of the water column. Large volume sampling using Gerard barrels was used to cover the deep and bottom waters. This strategy was chosen primarily because the collection cost for AMS <sup>14</sup>C samples is significantly less than for the Gerard technique. At the time of this cruise, it was known that the AMS technique was less precise than the large volume technique, however Figure 2 demonstrates that AMS precision is easily sufficient to resolve the vertical gradients in  $\Delta^{14}$ C at least in the upper kilometer. The large spread in the data for the upper few hundred meters is due to the doming of the isopleths around the Equator. Most of the individual profiles have a subsurface maximum at approximately 200m.

Figure 3 shows the  $\Delta^{14}$ C values plotted against silicate for samples from the upper



2 kilometers of the water column. The straight line shown in the figure is the least squares

**Figure 3:**  $\Delta^{14}$ C as a function of silicate for P16C AMS samples. The straight line shows the relationship proposed by Broecker, *et al.*, 1995 ( $\Delta^{14}$ C = -70 - Si with radiocarbon in ‰ and silicate in µmol/kg).

regression relationship derived by Broecker *et al.* (1995) based on the GEOSECS global data set. According to their analysis, this line ( $\Delta^{14}C = -70$  - Si) represents the relationship between naturally occurring radiocarbon and silicate for most of the ocean. They interpret deviations in  $\Delta^{14}C$  above this line to be due to input of bomb-produced radiocarbon. Clearly, this relationship is not ideal for the P16C data set. The data points having silicate values greater than or equal to 60 µmol/kg almost certainly have no bomb-radiocarbon component and should therefore lie on, rather than below, the line as seen in Figure 3. For these data the slope of the line needs to be steeper or/and the intercept needs to be lower. A least squares fit of the data from samples between 1 and 2 km depth (n=27; R<sup>2</sup>=.88) gives an intercept of -74±9 which is easily within error of Broecker's -70, but the intercept value of -1.24±.09 is significantly steeper than the -1. calculated for the GEOSECS global data set.

Figure 4 is an objectively contoured section (LeTraon, 1990) of the  $\Delta^{14}$ C distribu-



tion for the upper kilometer of the water column. Obvious in Figure 4 is the doming of the

**Figure 4:**  $\Delta^{14}$ C concentration in the upper kilometer of TUNES leg 3; WOCE line P16C) along 155°W. Gridding done using the method of Letraon (1990); all samples measured using the AMS technique (Key, 1996a,b; Key, *et al.*, 1996). For most of the section the maximum concentration is found below the surface.

isopleths toward the Equator and the subsurface location of the maximum  $\Delta^{14}$ C concentration for most of the section. For this section the peak of the equatorial doming is shifted to the north by approximately 10 degrees.

# 6.0 References and Supporting Documentation

- Key, R.M., WOCE radiocarbon program reports progress, WOCE Notes, 8(1),12-17, 1996
- Key, R.M., WOCE Pacific Ocean radiocarbon program, Radiocarbon, submitted, 1996.
- Key, R.M., P.D. Quay and NOSAMS, WOCE AMS Radiocarbon I: Pacific Ocean results; P6, P16 & P17, *Radiocarbon, submitted*, 1996.
- LeTraon, P.Y., A method for optimal analysis of fields with spatially variable mean, J. *Geophys. Res.*, 95, 13543-13547, 1990.
- NOSAMS, National Ocean Sciences AMS Facility Data Report #96-019, Woods Hole Oceanographic Institution, Woods Hole, MA, 02543, 1996.
- Peng, T.-H., R. M. Key and H. G. Östlund, Temporal variations of bomb radiocarbon inventory in the Pacific Ocean, *Marine Chem., submitted*, 1996.

## G.5 FINAL CFC DATA QUALITY EVALUATION COMMENTS on P16C. (David Wisegarver) Dec 2000

During the initial DQE review of the CFC data, a small number of samples were given QUALT2 flags which differed from the initial QUALT1 flags assigned by the PI. After discussion, the PI concurred with the DQE assigned flags and updated the QUAL1 flags for these samples.

The CFC concentrations have been adjusted to the SIO98 calibration Scale (Prinn et al. 2000) so that all of the Pacific WOCE CFC data will be on a common calibration scale.

For further information, comments or questions, please, contact the CFC PI for this section

J. Bullister (johnb@pmel.noaa.gov) or David Wisegarver (wise@pmel.noaa.gov)

Additional information on WOCE CFC synthesis may be available at: http://www.pmel.noaa.gov/cfc.

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

# H RESPONSES TO DATA QUALITY EVALUATIONS

## H.1 Hydrography

Accepted all DQE suggestions concerning flags except: 331 #21 salts were not flagged questionable. Other changes: Station 221 silcate was changed from 3 to 2.

# H.2 RESPONSE TO CTD DQE

(Lynne D. Talley) October 10, 1995

The CTD data from P16C have been rechecked based on the useful and extensive comments from Neil White, which were conveyed to me on December 8, 1994.

In your letter you mention the following points, for which we have taken action:

- Identification of bad values in the CTD traces and the extensive interpolations, all of which were flagged only as "6" rather than some being flagged "3" or "4": We agree that flags other than "6" should have been used. We have now looked at all interpolations of more than 10 dbar in temperature, salinity and oxygen, and have made subjective changes to the flaggings. On one station (sta. 255) the poorly interpolated temperature and salinity values near the surface have been removed and replaced with - 9. (flag "5").
- 2. The temperatures are now being converted to T90 by Jane Baker, who provided the initial conversion of the WHOI CTD formatted data into WHPO format as a service to the WHOI CTD group.
- 3. The dates of the WHPO CTD stations have been reset to correct dates.
- 4. Conductivity calibrations for stations 228 to 245 have been shifted with a station dependent bias to smooth out the .002 to .004 shift in conductivity between stations 245 and 246.

Neil White's report mentions other points. Here is my response to points other than 1-4 above.

- 5. Missing oxygen values were reset to -9.
- 6. There is apparently no recourse to the flaggings of -9 where one channel was bad, since the WHOI internal data format did not store information for each channel at the time of this cruise.

- 7. The even decibars at sta. 251 were a way of flagging it as an upsast. We agree with Neil White that it is more practical to have the entire data set at either even or odd intervals. The data and number of scans have now been linearly interpolated to odd decibars.
- 8. Oxygen units in the documentation are now in umol/kg, except for comparisons with historical data. Because the CTD oxygen data were processed using units of mUI, calibration plots are still in ml/l.
- 9. Quantitative temperature and pressure calibration information is now supplied.
- 10. The shallow data could have received more attention. Especially bothersome were the bad values at and near the surface in both salinity and oxygen; if the bad salinity values are due to averaging of air and seawater conductivities, then it would have been easier if the software had been able to take this mto account. (The newest versions of WHOI CTD software do not have this problem.)
- 11. Station 224 shallow: agreed that there is probably a problem with the bottles, but I can't find any obvious reason. There were no problems noted with bottle firing, the problem did not occur where we went from one rosette to another, there were no apparent duplicate salinity values (suggesting a mistake in sampling), and the nutrients/oxygens are no help. Since there is a real offset, the flags have been changed for the bottle salinities at levels 21 through 26 to 3 (questionable).
- 12. Stations 225 229, 230, 237, 241, 243, 245: problem is smaller, and no flags have been changed.
- 13. Station 262: checked profiles and agree that bottle salinities look too high (0.01 to 0.03) in the range 413617 dbars; CTD data look OK compared with adjacent stations nothing suggestive of a problem with discrete samples in the log books. The down and up CTD casts have fairly similar shapes, so they were not sampling different water, which could have been another source of error. No change to flags.
- 14. Station 289: I agree with the assessment of bottle 30 at 252 meters and have changed the discrete oxygen flag to "3".
- 15. Station 313: It looks like sample 29 was a duplicate draw of bottle 28. The bottle flag for salinity has been changed to "4". Sample 26 could be a duplicate draw of bottle 25. The bottle flag for salinity has been changed to "3", since it is not as cleat a problem as the bottle 28-29 problem.
- 16. Station 245-246: we agree that the jump from 245 to 246 really is 0.002 to 0.004 and not 0.001. The calibration documentation indicating a smaller jump of 0.0015 was appropriate for a group of stations prior to 245 and after 246, rather than those two specific stations. The switch in Autosals between stations 246 and 247 complicated

the processing but there was no real shift in autosal salinities at that point (at most a decrease in the noise level). The jump m CTD conductivity starting at 246 was classic - looks like an exponential settling in to the new calibration. Therefore it would be pretty hard to remove. We have not done anything new with the calibration, just tried to clarify the documentation.

- 17. Station 253 calibration of this station was problematic, as noted in the documentation. The CTD salinities are flagged "3" throughout - perhaps they were not in the version which N. White was looking aL Station 263 - this seems to be a problem of bad bottle values rather than the CTD, although the latter seems a little low (and bottles ate high). There are no problems listed in the sample log sheets. The salinity at 4113 dbar (bottle 2) seems especially out of line since the CTD profiles indicate increasing salinity to the bottom, but this discrete value is higher than the salinity at the bottommost point just below it. Therefore I have changed the discrete salinity flag to "3".
- 18. Mean deep-water offset the problem here is that the conductivity adjustment which was made to improve the very deepest calibration threw off the intermediate depth calibration, as noted in the documentation. The calibration just simply is problematic and not quite to WHP standards for accuracy in the mid-depth range.
- 19. Oxygen at sta. 319: within the full envelope of CTD and bottle profiles, both the CTD and bottle data at this station look reasonable, and so no change has been made.

I also enclose a copy of the CTD editing comments provided by Maggie Cook, vis a vis the changes made to the CTD data set after it was DOEd.

#### H.2.a RESPONSE TO HYDROGRAPHY DQE

(Maggie Cook) October 10, 1995

#### 14 June 1995:

The following cast number corrections were made to the station headers per request of Kai Jancke. The station date in all \*.WCT files was corrected according to at sea station logs.

station	cast #
235	4
244	3
246	2
249	2
254	2
259	5
266	2
287	2
288	2
293	2
300	3
308	3
314	2
317	3

#### 24 Jul 1995:

All oxygen values that should have been 11-911 in the \*.WCT files have been corrected. They had been scrambled earlier during the conversion of units to ml/l. (stations 221,222,223,224,225,226, 251, and 255)

## 24 Jul 1995:

Station 251 has been interpolated to odd rather than even db intervals.

## 24 Jul 1995:

1 have edited the most recent \*.WCT WOCE format data files (which I received from Jane Dunworth) to CTD DQE specifications.

sta	250	
		set TE and SA values for 3 and 5 db to same as 7 db scan
		set TE and SA flags to 16' accordingly.
sta	251	set 4 db SA value to 35.415
		set SA flags to '6' accordingly.
sta	252	set TE and SA values for 1 and 3 db to same as 5 db scan
		set TE and SA flags to '6' accordingly.
sta	255	interpolate SA from 251 to 263 db and
		set SA flags to 7.
		set SA values to -9 from 3 to 181 db.
sta	256	set TE and SA values for 1 and 3 db to same as 5 db scan.
		set TE and SA flags to '6' accordingly.
sta	257	make note in final documents (p36) that this
		station does in fact go to 4901 rather than 4923 db.
sta	278	set TE and SA values for I and 3 db to same as 5 db scan.
		set TE and SA flags to 16' accordingly.
		interpolate SA from 143 to 151 db.
		set SA flags to 16, accordingly.

sta 279	set SA values for 1 and 3 db to same as 5 db scan.
	set SA flags to 16, accordingly.
sta 287	set TE and SA values for 1 and 3 db to same as 5 db scan.
	set TE and SA flags to '61 accordingly.
sta 304	interpolate SA from 91 to 99 db.
	set SA flags to 16' accordingly.
sta 306	set TE and SA values of 3 db scan to that of 5 db scan.
	set TE and SA flags to '6' accordingly. note in final documents
	(P37) that there is no 1db scan.
sta 322	set TE and SA values for 3 and 5 db values to same as 7db scan.
	set TE and SA flags to '6' accordingly.

#### 30 Aug 1995:

stations 228 - 245 had the following salinity bias adjustments made to them in order to minimize the salinity shift occurring at 245-246.

228	0.0000000e+000
229	-1.1764706e-004
230	-2.3529412e-004
231	-3.5294118e-004
232	-4.7058824e-004
233	-5.8823529e-004
234	-7.0588235e-004
235	-8.2352941e-004
236	-9.4117647e-004
237	-1.0588235e-003
238	-1.1764706e-003
239	-1.2941176e-003
240	-1.4117647e-003
241	-1.5294118e-003
242	-1.6470588e-003
243	-1.7647059e-003
244	-1.8823529e-003
245	-2.0000000e-003

#### 20 Jul 1995:

Within the P16C CTD data set there are a number of interpolations over more than 10 dbar. There is a question about how to flag them; shorter interpolations have all been flagged as 116". Here are the choices made (July, 1995 LDT).

Interpolation 225

Temperature:	643-695:	flag 1131,
Salinity :	643-695:	flag 1131,

Interpolations 226:

temperature:	3811-3827:	keep data,	flag	б
temperature:	4349-4371:	keep data,	flag	3
salinity:	3811-3825:	keep data,	flag	6
salinity:	4349-4365:	keep data,	flag	3

Interpolation 235

Oxygen: 301-321: keep data, flag 3

Interpolation flags 250: 4785-4843: keep data, flag 4 (interpolated to salinity: bottom) interpolations 251: temperature: 2017-2025: leave as is (6) temperature: 3057-3729: keep data, flag as 4 oxygen: 771-785: leave as is (flagged 6) 2017-4793: keep data, flag as 4oxygen: salinity: 761-789: leave data, flag as 1131, salinity: 1011-1025: leave data, leave flagged as "6" salinity: patches between 1735 and 1781: leave data, leave flag 116" salinity: 2017-2025: leave data, leave flag 116" salinity: 2061-2089: leave data, flag as 1141, salinity: 2457-2459: leave data, flag 6 salinity: 3047-4045: leave data, flag 4 Interpolation flags 253: 2865-2883: keep data, flag 3 Oxygen: Oxygen: 4647-4667: doesn't look like spike was actually removed. flag 4 Interpolations and changes: station 255 temperature: 45-207: delete and replace with -9., flag 5 Salinity: delete data (replace with -9. and 1-221: indicate flag 5). Salinity: 229-235: delete data and interpolate between 227 and 237, then flag as 6. Salinity: 257-261: delete and interpolate between 251 and 267 then flag 6. Oxygen: 3111-3131: keep data and flag 6 Interpolation: 257 Oxygen: 2249-2317: keep data flag 4 2743-2767: keep data flag 4(looks like big offset) Oyxgen: Oyxgen: 3837-3857: keep data flag 3 Oxygen: 4805-4901: keep data flag 4(bottom of cast) Interpolation: 259 oxygen: 3515-3531: keep data flag 3 Interpolation: 261 oxygen: 4137-4185: keep data flag 3 Interpolations 264: oxygen: various patches 1599-1739: looks ok, keep flag 6

Interpolation	n 268				
	salinity:	311-327:	keep data, flag 6		
Interpolation	n 285				
	Salinity:	125-163:	keep data flag 3		
interpolation	n 294				
	salinity:	1995-5475:	keep data, flag 4		
Interpolation 322					
	salinity: salinity: oxygen:	571-605: 931-945: 571-605:	keep data flag 4 keep data flag 3 keep data flag3		

# I. DATA PROCESSING NOTES

Date	Contact	Data Type	Data Status Summary
03/31/94	White	CTD	Agreed to do DQE
04/05/94	Mantyla	NUTs/S/O	Agreed to do DQE
04/07/94	Jenkins	He/Tr Shallow	Submitted for DQE

94 Jenkins He/Tr Shallow Submitted for DQE The next message (1000+ lines) contains the tritium-helium data for the TUNES 2 leg. Just to reiterate, this is the Thomas Washington cruise that took place in the summer of 1991, covering PI7c-PI6c along 135W and 150W respectively. The data are organized as one line per "sample", which may contain tritium, helium or both. -99 represents no data or sample for a variable. The columns are as follows:

Sta, Cast, Bottle, Pressure (db), tritium (TU), sigma-tritium (TU), delta-3He (permil), sigma-delta (permil), conc-Helium (nM/Kg), sigma-conc (nM/Kg), quall, qual2

The quality numbers for tritium (quall) are

- 1 = valid sample
- 2 = possible under-extraction
- 3 = possible contamination
- 7 = identity suspected
- 9 = no sample

In this data set, there were no quall values of 2,3 or 7

The quality numbers for helium (qual2) are

- 1 = valid sample
- 2 = possible under extraction
- 3 = possible (air) contamination
- 7 = identity suspected
- 9 = no sample

In this data set, there were no qual2 values of 7

Also, the obvious applies, if a sample value is null (-99) its error, which may not appear as null (-99) is meaningless.

Also, the tritium data has been corrected for a small (.0045 TU) blank due to cosmogenic production during storage.

Finally, I was hoping to finish up a paper that I am working on for this data: I don't mind you using it for demonstration purposes, but-I would hope that its distribution could be restricted over the next 4-5 months until I have had a chance to get it submitted and hopefully reviewed and accepted. Also, it will give me a chance to make one final pass at the data to ensure that there are no problems with it. I hope this is OK.

07/27/94	Mantyla	NUTs/S/O	DQE Report rcvd @ WHPO
08/25/94	Talley	NUTs/S/O	PI Responded to DQE Report
09/19/94	White	CTD	DQE Report rcvd @ WHPO
12/08/94	Joyce	CTD	DQE Report sent to PI
12/14/94	Key	DELC14	DQE Report rcvd @ WHPO
01/24/95	Key	DELC14	DQE Report sent to PI
01/27/95	Talley	CTD/BTL	Data Public
10/10/95	Talley	CTD	Final DQE Issues Resolved
12/14/98	Key	DELC14	Data are Public

04/29/99	Quay	DELC13	Data and/or Status info Requested by dmb
01/20/00	Key	DELC14 LV	Final Data Rcvd @ WHPO
02/04/00	Kozyr	ALKALI/TCARBN	Final Data Rcvd @ WHPO
04/13/00	of the sar	HELIUM/DELHE3 I files to your /INCOM i8nwoce.csv p13woce.csv p16cwoce.csv p19cwoce.csv me form as before, c le3 data flag, molal [H	omma delimited columns ofstation, cast, bottle, %delta
06/29/00	Anderson	LVS	Data Reformatted
	29 June 200 p16csu.txt p16clv.txt Left data as that is better	0 Reformatted .sum f Created .lvs file from reported.Did not fill o than reported.	16c.I also reformatted the .sum file. ile to conform with WHPO standard. m file sent by Bob Key. decimal places with zeros as that suggests a precision the format description for the .lvs files does not have
	nutrients.	line eren neegn	
	Assumed te	mperature was REVT	MP and pressure was REVPRS.
08/02/00	bottle file fo which cause	or P16C. A few lines ad the number of co ad problems for the	Website Updated: corrected formatting errors : I have corrected the formatting errors in the online had format overflows or incorrect NO_DATA values lumns to be inconsistent from one line to the next. It Exchange Format conversion tools and the NetCDF
09/26/00	Buck	LVS	Data added to website
11/21/00	should beco 2000.10.11 Files were f	nsidered WHP DOC t KJU ound in incoming dir eparated and placed	Submitted SUMMARIES and NOT sumfiles.Files listed below files. Documention is online. rectory under whp_reports. This directory was zipped, under proper cruise. All of them are sumfiles.Received
06/22/01	Uribe CTD and Bo	CTD/BTL ttle files in exchange	CSV File Added to Website format have been put online.
11/16/01	Bartolacci I have plac directory in a	CFCs ed the updated CF0 asubdirectory called 2001.07.09_P16C_	Updated CFC ata Ready to be Merged C data file sent by Wisegarver into theP16c original CFC_UPDT_WISEGARVER ocumentation and readme files. data are ready for
01/07/02	Uribe CTD has be	CTD en converted to excha	CSV File Added to Website ange using the new code and put online.
01/22/02	Hajrasuliha	CTD/BTL	Internal DQE completed

Note:created .ps files, check with gs viewer. Created *check.txt file
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04/04/02 Muus CFCs/He/DelHe3 Data Reformatted/OnLine Reformatted data online, New CSV file createdDeep Helium and DelHe3 from John Lupton and revised CFCs from Wisegarver merged and put on-line together with new exchange file.

Notes on P16C mergingApr 3, 2002D.Muus

1. Changed all quality flag "1"s to "9"s. Made QUALT2 same as QUALT1. Salinity, Oxygen & Nutrient DQE suggestions all shown in QUALT1.

2. Merged HELIUM, DELHE3, TRITUM and error values from:

/usr/export/html-public/data/onetime/pacific/p16/p16c/original/ 2000.04.13\_P16C\_LUPTON-EVANS\_He.Ne/p16cwoce.csv.txt into bottle file (20000802WHPOSIOSCD)

3. Merged CFCs from

/usr/export/html-public/data/onetime/pacific/p16/p16c/original/ 2001.07.09\_P16C\_CFC\_UPDT\_WISEGARVER/20010709.174359\_WIS EGARVER

\_P16C/20010709.174359\_WISEGARVER\_P16C\_p16c\_CFC\_DQE.dat into bottle file (20000802WHPOSIOSCD)

4. Made new exchange file for Bottle data.

5. Checked new bottle file with Java Ocean Atlas.

08/06/02 Kappa DOC PDF file compiled, TST file updated Both versions include: cruise report; DQE reports (CTD, BTL, CFCs,LVS and C14); chief scientest's responses to DQE reports, and WHPO data processing notes.PDF version also includes figures andlinks from relevant text passages to figures, tables, appendicies.