

CRUISE REPORT
HUDSON 93019
LABRADOR SEA
WOCE LINE AR7/W
JUNE 17 - 28, 1993

A. CRUISE NARRATIVE

1. Highlights

Cruise Designation: 18HU93019/1
Ship: C.S.S. Hudson
Agency: Bedford Institute of Oceanography
Box 1006
Dartmouth N.S. B2Y 4A2, Canada
Chief Scientist: John R.N. Lazier
Ports of call: Sydney N.S. to Dartmouth N.S.
Dates: June 17 - 28, 1993

2. Cruise Summary

Cruise Track:

The CTD/rosette station positions are shown in Fig. 1. Heavy ice over the Greenland continental shelf prevented completion of three proposed stations at the eastern end of the line.

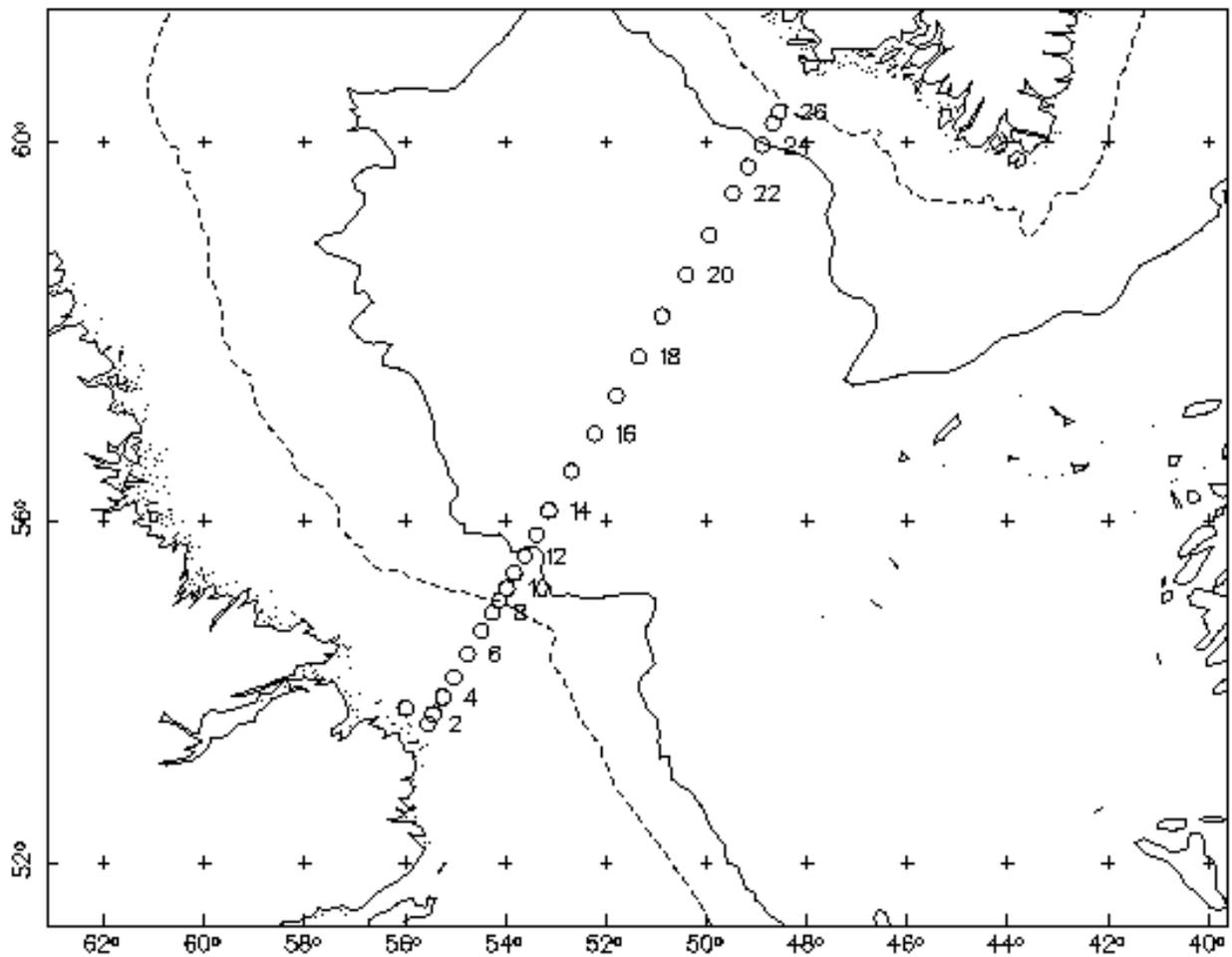


Figure 1. Stations along WOCE line AR7/W occupied during June 1993.

Sampling Accomplished:

The Seabird CTD acquired temperature, salinity and oxygen profiles. Rosette water samples were obtained for analyses of salinity, oxygen, nutrients, CFC-12, CFC-113, total carbonate, alkalinity, halocarbons, tritium and helium.

3. Principal Investigators

Name	Responsibility	Affiliation
John Lazier	CTD, salinity	BIO
Bob Gershey	CFC, O ₂ , alkalinity, CO ₂ , nutrients	BDR
Katarina Abrahamsson	Halocarbons	U of G
Lina Kohandoust	Tritium, Helium	LDEO (Peter Schlosser)

Institute Abbreviations and Addresses

BIO	Bedford Institute of Oceanography
	Box 1006
	Dartmouth, N.S. B2Y 4A2, Canada
BDR	BDR Research Ltd.
	Box 652, Sta. 'M'
	Halifax, N.S. B3J-2T3, Canada
U of G	University of Göteborg
	Göteborg, Sweden
LDEO	Lamont-Doherty Earth Observatory of Columbia University
	Palisades, NY, 10964, USA

Electronic Addresses

J. Lazier	j_lazier@bionet.bio.dfo.ca
R. Gershey	rgershey@fox.nstn.ns.ca
K. Abrahamsson	katarina@amc.chalmers.se
L. Kohandoust	lina@lamont.ldeo.columbia.edu

4. Scientific Program

One of the primary aims of the annual occupation of the AR7/W line is to monitor the properties of the Labrador Sea Water (LSW) which is renewed in severe winters by deep convection. Our 1993 observations indicate that convection was very active during the 1992-93 winter and that the LSW is now colder and denser than ever previously recorded.

To illustrate, the distribution of sigma 1.5 across the section is given in Fig. 2 and some curves of potential temperature vs sigma 1.5 for the central Labrador Sea are compared in Fig. 3 with other years. In the section the LSW is identified by the layer of very low vertical gradient in the central region (stations 14 to 22) between $\sigma_{1.5} = 34.68$ and 34.70 . Over the continental slopes (stations 10-13 and 23-26) the gradient between these two density surfaces is about five times greater than in the central region. This results in a large along isopycnal gradient in potential vorticity which restricts along isopycnal exchange. The result is that the central low gradient region tends to be isolated from the water of similar density over the continental slopes.

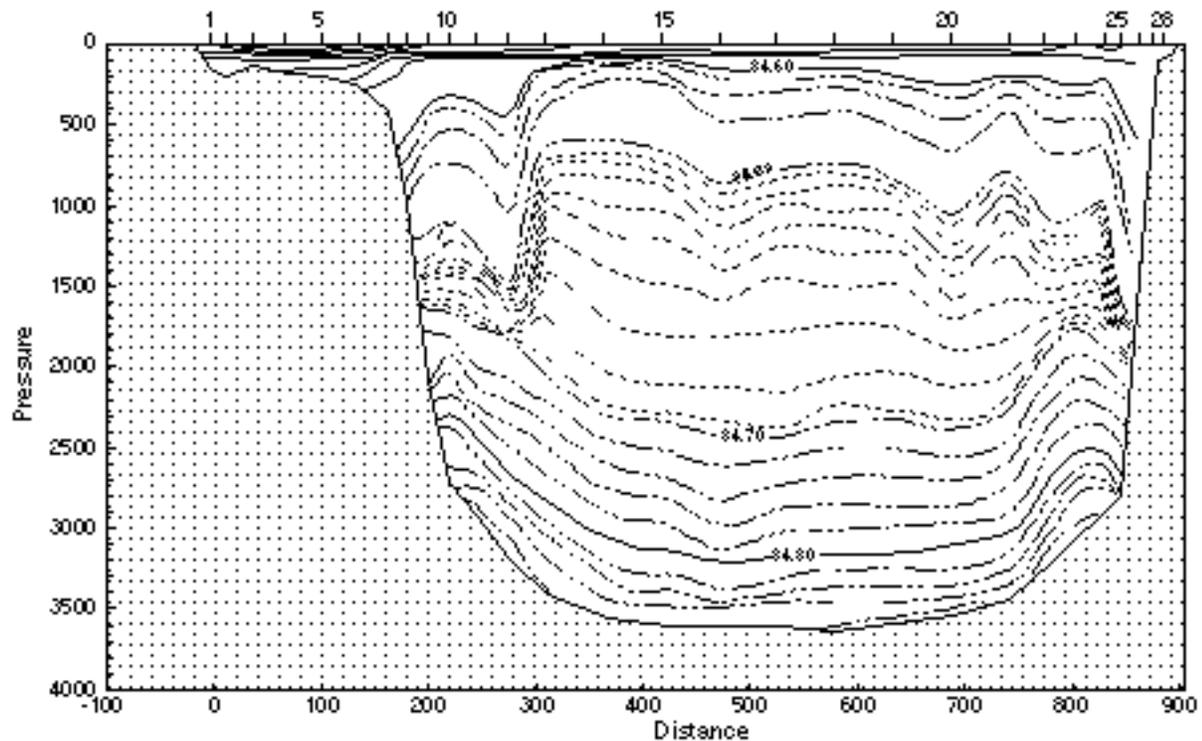


Figure 2. Section of potential density anomaly referenced to 1500 dbar (1.5) along the WOCE AR7/W line in June 1993.

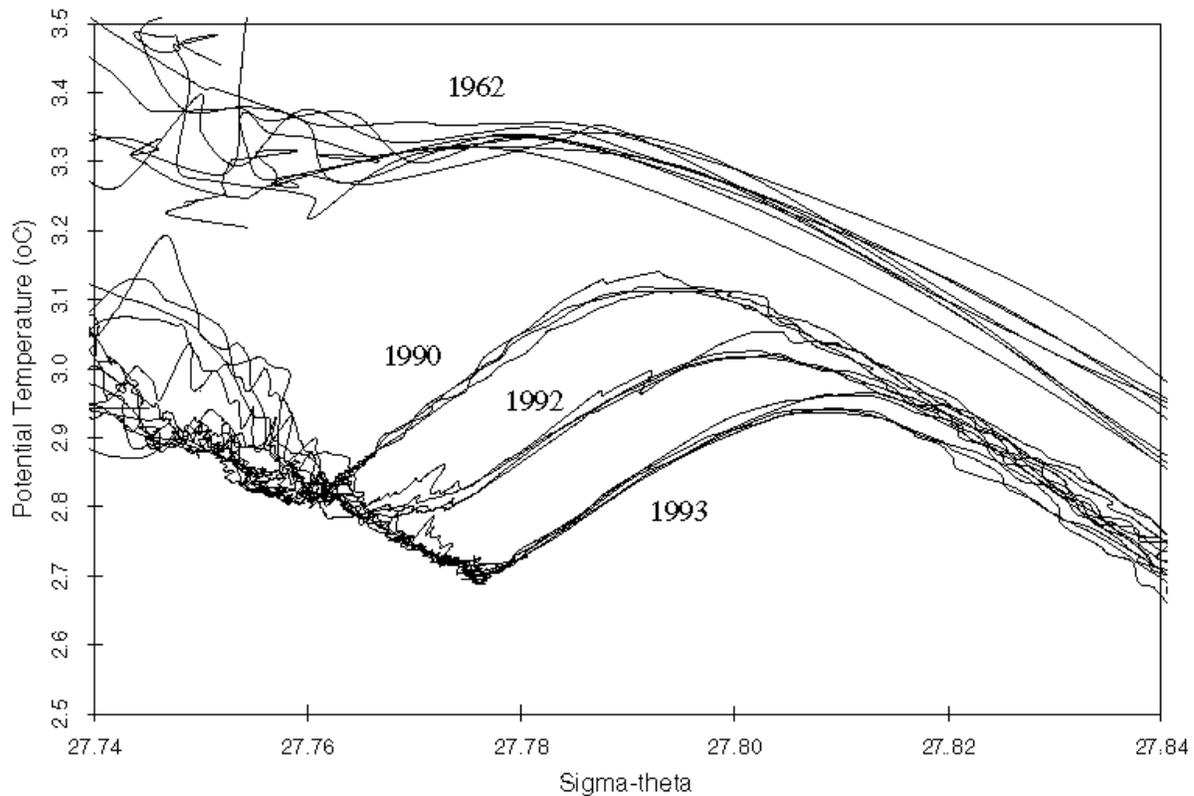


Figure 3. Potential temperature vs. sigma-theta at a selection of stations in the central Labrador Sea during 4 cruises; Erika Dan, March 1962; Hudson, June 1990, June 1992 and June 1993.

Also, recent current meter observations have shown the existence of a strong (0.2 m s^{-1}) barotropic current over the Labrador slope but almost no current ($<0.01 \text{ m s}^{-1}$) in the central region. Vorticity strongly confines the barotropic flow to stay over the slope which further tends to isolate the central region.

It appears that these features which limit mixing and advection between the central region and the boundary flows help to preserve the properties of the LSW through periods of weak convection in winter.

Some of the variation in the LSW properties over the years is shown in the sigma 1.5 vs potential temperature curves in Fig. 3. The LSW in 1993 is distinguished by the minimum temperature of $2.7 \text{ }^{\circ}\text{C}$ at $\text{st} = 27.775 \text{ kg m}^{-3}$. In 1990 this temperature minimum was at $2.8 \text{ }^{\circ}\text{C}$ at 27.760 kg m^{-3} and in 1992 it was somewhere between these two. The variation over these years indicates a continual cooling and increase in density of the convected water

mass. In the curves for 1992 (Erika Dan cruise) the minimum is not so clear as in the more recent data because the data were collected by widely spaced bottles rather than continuous recording CTDs. But a minimum is apparent at about 3.3 °C at $\sigma_t \approx 27.765 \text{ kg m}^{-3}$. Thus it appears that the density has stayed roughly constant while the temperature of the water has decreased by 0.6 °C. This decrease is attributable to the lower salinity water that now inhabits the Labrador Sea as a result of the large influx of fresh water from the Arctic in the late 1960s. Maintaining the nearly constant density of the fresher convected water has required a lower temperature. Similar observations from other years show however that there are slight variations in the density of the LSW and that the density in 1993 is the greatest yet observed.

5. Underway Measurements

At all times during the sampling program the position of the ship as determined by the Global Positioning System was recorded. The depth sounder was kept running between all CTD stations when ice and wave conditions permitted. A hull mounted Acoustic Doppler Current Profiler (ADCP) was also operated during the sampling program.

6. Major Problems and Goals not Achieved

Heavy ice over the Greenland shelf prevented occupation of the 3 easternmost stations over the Greenland continental slope and shelf.

Collision between the ship and the rosette resulted in damage to the rosette and sampling bottles at the end of the first cast on Station 13. This event also made the salinity and oxygen channels on the CTD noisier, however, this was repaired by carefully retying the water circulation tubes and electronic cables.

7. Other Incidents of Note

An Acoustic Doppler Current Profiler was deployed over the Labrador Shelf as part of the Bedford Institute's program to study the movement and stresses of the drifting pack ice. This study is under the direction of Dr. Simon Prinsenberg. The following report is by M. Scotney and A. Hartling of BIO.

Mooring No. 1133: A RD Instruments Self-Contained Acoustic Doppler Current Profiler housed within a Trawl Resistant Package was moored on June 19, 1993 at position 53 50.697 N and

56 03.145 W. The data from this instrument will enable the ice movement above to be monitored for the winter of 93/94 as part of the Labrador Ice Flux Study.

The package was moored in 86 meters of water using the new deployment frame. The system was free fallen to the bottom without difficulty. Hand tension was kept on the lowering rope during descent. The package dropped at a rate of approximately 35 meters per minute. Since the acoustic release on the lowering frame was fitted with a 6 degree tilt switch, it was confirmed acoustically that the package was not tilted more than 6 degrees prior to release.

The ADCP is set to start recording at 0100 hours on Nov.1, 1993. This will allow sufficient battery capacity for data to be recorded until recovery next year.

8. Cruise Participants

Name	Responsibility	Affiliation
Abrahamsson, Katarina	Halocarbons	U of G
Bellefontaine, Larry	CTD watchkeeper	BIO
Carson, Bruce	CTD tech/watchkeeper/salts	BIO
Clement, Pierre	Nutrients	BIO
Ekdahl, Anja	Halocarbons	U of G
Gershey, Robert	CFC, Alk., Carb.	BDR
Gohlin, Karin	Halocarbons	U of G
Griffies, Stephen	CTD watchkeeper	GFDL
Hartling, Bert	Mooring/ CTD watchkeeper	BIO
Hingston, Michael	CFC, Alk., Carb.	BDR
Hufford, Gwyneth	CTD watchkeeper	DEAPS
Kohandoust, Lena	Tritium/Helium	LDEO
Lazier, John	Chief Scientist	BIO
Moffatt, John	Oxygens	BIO
O'Neill, John	Computers/software	BIO
Rhines, Peter	Advisor/CTD watchkeeper	U of W
Ross, Charlie	Co-chief scientist	BIO
Scotney, Murray	Mooring/CTD watchkeeper	BIO
Swim, David	CTD watchkeeper	BIO
Zemlyak, Frank	CFC, Alk., Carb.	BIO

Institute Abbreviations and Addresses

BIO	Bedford Institute of Oceanography Box 1006, Dartmouth, N.S. B2Y 4A2, Canada BDR Research Ltd.
BDR	Box 652, Sta. 'M' Halifax, N.S. B3J 2T3, Canada
U of G	University of Göteborg, Göteborg, Sweden School of Oceanography, WB-10
U of W	University of Washington Seattle, WA, 98195, USA Lamont-Doherty Earth Observatory
LDEO	of Columbia University, Palisades, NY, 10964, USA Geophysical Fluid Dynamics Laboratory
GFDL	Princeton University Princeton, NJ, USA
DEAPS	Dept. of Earth, Atmos. and Planetary Sciences Massachusetts Institute of Technology, Cambridge USA

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B. DESCRIPTION OF MEASUREMENT TECHNIQUES AND CALIBRATIONS

1. CTD Operation (B.D. Carson/BIO)

The Seabird CTD (OC #1) was used on this cruise and once again performed well from a maintenance standpoint. It seems as though the data are a little more noisy this time and we had a little trouble with the pump. After the unit received a bump during recovery on station 13 a few of the 8 litre sampler bottles were damaged and the tube which connects the top of the TC duct to the pump, via the O2 sensor was jarred loose. The tube was replaced and made a little more secure after station 14 and was fine for the rest of the trip. The pump stopped working a little later and was replaced by a new one and the O2 sensor was also replaced at this time although it has not been determined if that was necessary. The old pump is intermittent and will be checked more closely in the lab at BIO.

2. Bottle Salinity (C.K. Ross/BIO)

The Guildline AUTOSAL 8400 salinometer (Autosal #3) worked well and was very stable once the lab temperature was stabilized. All salinity water samples were analyzed within 1-2 days of sampling. Duplicate samples were drawn from one or two rosette bottles on each station. Statistics of the absolute difference between duplicates are below:

Number of Points = 38

Median = 0.0004

Mean = 0.0011

Minimum = 0

Maximum = 0.0063

Standard Deviation = 0.0014

Throughout the mission, IAPSO standard batch number P117 seawater was used as the reference seawater.

An attempt at identifying suspicious bottle salinity values was made using the statistics of the differences between CTD salinity and bottle salinity. By identifying the 25 and 75 percentile differences (denoted by Q1 and Q3), we identified all differences outside of the following limits:

$\text{difference} < Q1 - 1.5*(Q3 - Q1)$

$\text{difference} > Q3 + 1.5*(Q3 - Q1)$

All bottles associated with these samples were flagged as 'leaking'. All associated salinity samples were flagged as 'questionable' or 'bad'. The 'bad' flag was subjectively assigned depending on the number of times a particular bottle was identified in this manner.

3. CTD Data Quality

(C.K. Ross and Anthony W. Isenor/BIO)

The Sea-Bird CTD model SBE 9plus (S/N 9P5676-0248) was paired with a 22 bottle rosette to allow calibration of the sensors as well as collection of water samples for other chemical determinations. The data were logged using SEASOFT software using the calibration data for the sensors when the instrument was delivered in February, 1992. The sensors have been calibrated since then but the figures presented are referenced to the original calibrations.

The pressure sensor (S/N 48361) was not compared at depth. The data were logged before the instrument entered the water to allow the determination of the pressure offset at 0 dbars. These have not yet been examined.

The temperature sensor (S/N 031247) was compared to a suite of six electronic digital reversing thermometers. Initially, thermometer calibration data from February 1991 were used to correct the thermometer readings. However, subsequent examination of the corrected temperatures using post-cruise calibration data from March 1994 showed improved differences (thermometer - CTD) statistics, namely a more peaked distribution and smaller difference from CTD.

The thermometer data were corrected using the March 1994 thermometer calibration data. The difference (thermometer - CTD) was then computed and the values sorted and plotted. The resulting curve showed that thermometer T352 gave consistently large differences as compared to the CTD. This thermometer was removed from the analysis and the resulting difference curve replotted. The curve showed a low slope region below the zero difference, indicating a high CTD temperature compared to the thermometers. After removing the outliers beyond the limit of median 1.5*IQR (interquartile range), the median value of the resulting set of differences was determined to be -0.002 C. The -0.002 value was used as the CTD temperature calibration.

The salinity determined from the CTD conductivity sensor (S/N 040954) was compared to the salinity of the water sample. For the 38 occurrences of CTD-bottle greater than 0.01, 13 were due to bottle BO11, 7 due to bottle OC7, 5 due to bottle OC6, 3 due to bottle OC1, 2 due to bottle OC3 and the other bottles having 1 or fewer. For the 12 occurrences of CTD-bottle less than -0.02, there were 2 each for bottles BO11, OC17, OC1 and BO17. It seems apparent that some bottles (in particular bottle BO11) were misfiring or leaking. More attention will have to be paid to this possibility.

The differences of CTD and bottle salinities were accepted if within the range -.01 to .002. This reduced the number of comparisons from 363 to 297. The variance of these data was .00000437. There appeared to be a possibility of a temperature dependence. A linear regression was fit:

$$DS(se=.0020) = -0.00036(se=7.22E-5)*T-0.00425$$

$$r^2=0.077$$

One could also fit the differences to salinity:

$$DS(se=0.0021) = -0.00058(se=.000185)S+0.0148$$

$$r^2=0.0318$$

If one removes the linear regression in temperature there is no apparent dependence of the salinity difference on pressure or time.

These data indicate that the CTD is reading low by 0.004 compared to the most recent laboratory calibration of 0.003 low. The standard deviation of differences is slightly greater than 0.002.

The equations used to convert CTD signals to engineering units were as follows:

Conductivity Sensor 040954 (all stations)

$$\text{Conductivity} = (afm + bf^2 + c + dt) / [10(19.57(108)p)]$$

where f is the frequency

t is the temperature

p is the pressure in dbars

$$a = 1.01513041E5$$

$$b = 5.69078601E1$$

$$c = 4.20143902$$

$$d = 2.42081062E4$$

$$m = 4.4$$

Temperature Sensor 031247 (All stations)

$$\text{Temperature} = 1 / \{a + b[\ln(fo/f)] + c[\ln^2(fo/f)] + d[\ln^3(fo/f)]\} + 273.15$$

where ln indicates a natural logarithm

f is the frequency

$$a = 3.68701496E3$$

$$b = 6.01256466E4$$

$$c = 1.53681774E5$$

$$d = 2.54555248E6$$

$$fo = 6590.790$$

Pressure Sensor 48361 (All stations)

$$\text{pressure} = c \left(1 - \frac{T_0}{T_2}\right) \left(1 - d \left[1 - \frac{T_0}{T_2}\right]\right)$$

where T is the pressure period

$$c = c_1 + c_2 U + c_3 U^2$$

$$d = d_1 + d_2 U$$

$$T_0 = T_1 + T_2 U + T_3 U^2 + T_4 U^3 + T_5 U^4$$

U is the temperature

$$c_1 = 2.651490E+4$$

$$c_2 = 1.537220E1$$

$$c_3 = 8.182160E3$$

$$d_1 = 3.319500E2$$

$$d_2 = 0.0$$

$$T_1 = 3.057779E+1$$

$$T_2 = 2.025480E4$$

$$T_3 = 4.254880E6$$

$$T_4 = 1.790020E9$$

$$T_5 = 0$$

Oxygen Sensor 130284 (Stations 1 to 19)

oxygen = A B C

where $A = \{Soc [oc + Tau d(oc)/dt] + Boc\}$

oc is the current from the oxygen sensor

d(oc)/dt is the time derivative of oc

Soc = 2.5328

Tau = 2.0

Boc = 0.0322

B = OXYSAT(t,s)

t is temperature

s is salinity

$C = e\{tcor [T + wt (ToT)] + pcor p\}$

e is natural log base

tcor = 3.3E2

pcor = 1.5E4

p is the pressure

wt = 0.670

To oxygen sensor internal temperature

T is the water temperature, where $T = kv + c$

k = 8.9625

c = 6.9161

v is the oxygen temperature sensor voltage signal

Oxygen Sensor 130287 (Stations 20 to 26)

oxygen = A B C

where $A = \{Soc [oc + Tau d(oc)/dt] + Boc\}$

oc is the current from the oxygen sensor

d(oc)/dt is the time derivative of oc

Soc = 1.9222

Tau = 2.0

Boc = 0.0106

B = OXYSAT(t,s)

t is temperature

s is salinity

$C = e\{tcor [T + wt (ToT)] + pcor p\}$

e is natural log base

tcor = 3.3E2

pcor = 1.5E4

p is the pressure

wt = 0.670

To oxygen sensor internal temperature

T is the water temperature, where $T = kv + c$

k = 8.9655

c = 6.9100

v is the oxygen temperature sensor voltage signal

The final CTD temperature calibration was:

$$T = T - 0.002$$

where T is the temperature.

The final CTD salinity calibration was:

$$S = S + 0.0052$$

where S is the salinity.

The final CTD oxygen calibration is discussed in detail in Appendix A.

4. Oxygens

(J. Moffatt/BIO and C.K. Ross/BIO)

a. Description of Equipment and Technique

The automated procedure to follow is based on the method developed by the Physical and Chemical Services Branch (PCS) of the Bedford Institute of Oceanography (BIO) (Levy et al. 1977).

The PCS procedure is a modified Winkler titration from Carritt and Carpenter (1966), using a whole bottle titration. In this method there is no starch indicator and a wetting agent (Wetting Agent A, BDH) is introduced to reduce bubble formation. The full description of the system and method can be found in Jones, et al. (1992).

In summary the automated titration system consists of an IBM PC linked to a Brinkmann PC800 colorimeter and a Metrohm 655 Multi-Dosimat Automatic Titrator. The PC talks to the peripherals through a Data Translation, DT2806 and three Data Translation DTX350s.

b. Sampling Procedure and Data Processing Technique

The sampling bottles are 125ml Iodine flasks with custom ground stoppers (Levy et al. 1977). The flask volumes are determined gravimetrically. The matched flasks and stoppers are etched with identification numbers and entered into the oxygen program database.

For this cruise 8 litre Niskin bottles were used to obtain the original sample. Then, the oxygen subsamples are drawn through the bottles spigot with a latex or silicone tube attached so as to introduce the water to the bottom of the flask. Once the flow is started the flask is inverted to ensure that there is no air trapped in the tube, then the tube partially pinched to reduce the flow rate and the flask reoriented and filled to overflowing. The flow is allowed to continue until at least two to three volumes have run through then the flask slowly retracted with continuous low flow to ensure that no air gets trapped in the flask. The flask is then brought to the reagent station and one ml of the Alkaline Iodide and Manganous Chloride Reagents are added and the stoppers carefully inserted, again ensuring that no air gets into the flasks. The flasks are shaken then carried to the lab for analysis.

c. Replicate analysis

A total of 428 seawater samples were analyzed for dissolved. Included in these samples were a total of 45 duplicate samples. Approximately 1-2 replicates were taken at each station to monitor precision which can be affected by flaws in sampling or titration.

A duplicate oxygen sample is drawn from one of the rosette bottles on every cast. Statistics related to the difference in duplicate values was determined using the absolute value of the difference. In total, 45 duplicate samples were drawn. Of these samples five (sample numbers 126062, 126149 [triplicate], 126219 and 126303) did not have a duplicate because one or both values were missing or bad.

Number of valid duplicates = 41

Median of [(absolute difference/sample mean concentration) * 100%] = 0.31 %		
Statistic	Value (ml/l)	Value (moles/kg)
Minimum	0	0
Maximum	1.274	55.4
Mean	0.081	3.5
Median	0.022	1.0
Standard Deviation	0.221	9.6
Cumulative Frequency	Oxygen Difference (ml/l)	Oxygen Difference (moles/kg)
50 %	0.022	1.0
68 %	0.030	1.3
95 %	0.504	21.9

5. Computer (J. O'Neill/BIO)

The PC-486 Seabird CTD computer and software ran with minor modifications. All 25 stations were processed in about 48% of real time which included conversion to archive ODF-ASCII format and (new to the PC system) generation of IGOSS significant points summary file.

The shipboard-resident MicroVax II was used to log continuous NMEA_NAV format from the Trimble GPS navigation receiver. These data were processed in real-time to distribute current positional information throughout the ship.

A considerable amount of available CPU on the MicroVax was used to generate post-acquisition graphics products, including sections derived from the CTD casts and bottle sampled data. In addition an evaluation of the oxygen sensor data was carried out using graphics and statistical modules of the OCEANS/PIPE system.

Backup of CTD and NMEA data were completed in triplicate to Exabyte streamer tapes (044374-044376).

6. Nutrients

(P. Clement/BIO and C.K. Ross/BIO)

Samples were analyzed for silicate, phosphate, and total nitrate (nitrate plus nitrite) using an AutoAnalyzer-II using a modified version of Technicon's original chemistries. Washwater was 33 ppt (w/v) NaCl and no salt correction was made.

Samples were collected in duplicate from the rosette bottles into 30 ml acid washed high density polyethylene screw-capped bottles. These were refrigerated until analysis, typically within 12 hours of collection. The water samples were transferred to 7 ml cups for analysis with the AutoAnalyzer.

Five mixed standards were run at the beginning and end of each run, with "check standards" interspersed every sixteen sample cups. Each batch of mixed standards are tested against Sagami CSK standards for nitrate and silicate before use.

Precision is a measure of the variability of individual measurements and in the following analysis two categories of precision are determined; field and analytical precision. Analytical precision is based on the pooled estimate of the standard deviation of the check standards over the course of a complete autoanalyzer run and is a measure of the greatest precision possible for a particular analysis. Field precision is based on the analysis of two or more water samples taken from a single Niskin sampling bottle and has an added component of variance due to subsampling, storage and natural sample variability.

Both categories of precision are determined by computing the variance, s^2 , of each replicate set, where i is the index of the replicate set. In the case of analytical (field) precision, a replicate set consists of all the check standards (duplicate samples). Given p replicate sets and n samples within any replicate set, the mean standard deviation, \bar{s} , is determined from

The precision expressed in percent is based on the mean concentration, M , of the check standards (analytical precision) or water samples (field precision) and is given by

The following table indicates the analytical and field precision obtained for this cruise.

	Silicate	Phosphate	NO₂+NO₃
Number of Samples	762	762	760
Number of Duplicates	381	381	381
Mean concentration (moles/kg)	9.27	0.94	13.21
Field Precision (moles/kg)	0.08	0.02	0.10
Field Precision (%)	0.9 %	2.1 %	0.8 %
Analytical Precision (moles/kg)	0.298	0.018	0.171
Analytical Precision (%)	0.88 %	1.38 %	1.02 %
Detection Limit (moles/kg)	0.187	0.056	0.101

The laboratory temperature during all analyses was between 21 and 23 °C.

The conversion to mass units for the analytical precision and detection limits used a standard density corresponding to 33 ppt and 15C.

Duplicate samples were drawn from each rosette bottle for the determination of silicate, phosphate and nitrate concentrations. The cumulative frequencies of differences (expressed as a percent of measured concentration) for each of the nutrients is:

cum freq	silicate	phosphate	nitrate
50%:	0.76%	0.94%	0.52%
67%:	1.13%	1.58%	0.76%
95%:	3.26%	7.03%	1.98%

The nutrient detection limits noted in the above table were applied to the dataset. All values at or below the detection limits were set to zero.

7. Halocarbons

(R.M. Gershey/BDR, F. Zemlyak/BIO and M.P. Hingston/BDR)

Objective:

1) To gather halocarbon concentration profiles using a purge-and-trap gas chromatographic method. Analytes included are CFC-11, CFC-12, CFC-113, CCl₄ (carbon tetrachloride) and CH₃Cl₃ (methyl chloroform).

Instrumentation for these measurements has been developed at the marine chemistry division of the Bedford Institute of Oceanography under a PERD funded program managed by E.P. Jones. The main objective of this program is to collect data to be used in modelling the rate of large scale convective transport of carbon dioxide gas from the atmosphere to the deep ocean. The flux of atmospheric CO₂ to the ocean can be estimated using measurements of alkalinity, total CO₂ and various transient tracers.

To increase throughput, two halocarbon analysis systems were put to use during this cruise. As a result our sampling density increased by a factor of two over previous years and allowed us to analyze samples from all but four stations. In addition, our colleagues from the University of Goteborg led by K. Abrahamsson were performing parallel analyses using similar instrumentation. This will allow us to both compare our results and fill in gaps in our data set.

Halocarbon data have been collected during four visits to WOCE line AR7/W and surrounding areas in the Labrador Sea during 1986, 1990, 1991 and 1992. The three main water masses in this area (NADW North Atlantic Deep Water, LSW Labrador Sea Water and DSOW Denmark Strait Overflow Water) have easily distinguished halocarbon concentrations. A halocarbon minimum characterizes NADW identifying it as being the least recently ventilated water mass in the area.

CFC-113 profiles have been successfully determined during this and the previous cruise. The results show that this short time scale tracer (< 10 years) is useful for identifying recently ventilated surface waters (LSW and DSOW) due the rapidly increasing source function for this compound.

It has long been believed that LSW is regularly subject to deep convection to depths of 1500 to 2400 meters. Tracer data collected last year (1992) showed a dramatic increase over the previous year's data, being a strong indication that deep convection occurred to about 2100-2400 m. Contrary to the expectation that the halocarbon levels we would measure during this cruise would be equivalent to or higher than those collected in 1992, preliminary analysis of the present data shows an apparent reduction of halocarbon concentrations to 1991 levels. Excluding analytical difficulties as an explanation for the disappearance of the tracers, horizontal advection of water having a low tracer content is suggested. This also implies that the extent of the ventilation event seen in 1992 may not have extended very far

to the north or south of the line. Unfortunately, there are at the present time virtually no data with which to confirm this suspicion.

The following are the values of blank samples. All values are in pico moles/kg.	
CFC 11	0.007 p moles/kg
CFC 12	- 0.006 p moles/kg
CFC 113	0.003 p moles/kg
carbon tetrachloride	0.013 p moles/kg
methyl chloroform	0.005 p moles/kg
The following precisions apply to these data:	
Freon 12	3.9%
Freon 11	4.3%
Freon 113	2.9%
Carbon Tetrachloride	3.1%
methyl chloroform	1.2%

Analytical accuracy relative to custom made gravimetric gas phase standards (Brookhaven National Labs, N.Y.) is of the same order as the precision of the analysis.

The following are the duplicate measurements used to compute the mean values given in the SEA file.

Summary: Halocarbon tracers (CFC-11, CFC-12, CFC113, CCl₄), methyl chloroform and total inorganic carbon were measured at 21 stations on WOCE line AR7/W. Comparison of halocarbon data collected during the last three years provides evidence for ventilation of the upper 2500 m of the Labrador Sea.

8. Total Inorganic Carbon

(R.M. Gershey/BDR, F. Zemlyak/BIO and M.P. Hingston/BDR)

Objective:

1) To perform high-precision analyses for the measurement of total inorganic carbon using a coulometric method.

Instrumentation for these measurements has been developed at the marine chemistry division of the Bedford Institute of Oceanography under a PERD funded program managed by E.P. Jones. The main objective of this program is to collect data to be used in modelling the rate of large scale convective transport of carbon dioxide gas from the atmosphere to the deep ocean. The flux of atmospheric CO₂ to the ocean can be estimated using measurements of alkalinity, total CO₂ and various transient tracers.

Determination of total inorganic carbon (CT) was accomplished using a SOMMA analyzer (developed at the University of Rhode Island) with coulometric detection. Samples were processed from 20 of the 26 stations sampled. Based on duplicate samples and analysis of carbon dioxide gas samples, a precision of 1-1.5 parts per thousand was consistently achieved. A seawater reference material obtained from the Scripps Institution was used to verify the accuracy of the method. The analyses were performed using the standard operating procedures specified by Dickson and Goyet (1991).

Summary: Measurements of Total Inorganic Carbon were made to the WOCE-suggested precision of plus or minus 1 part per thousand.

9. Biogenic Halocarbons

(K. Abrahamsson, A. Anja and K. Golin/U of G)

Analyses of biogenic halocarbons were performed at 22 stations. Due to the relatively long analysis time, emphasis was put on determinations of compounds in the surface waters. The water was collected in 100 ml glass syringes, and stored in coolers on deck. The compounds were degassed and concentrated with a purge and trap technique, and thereafter analysed by gas chromatography with electron capture detection. The purge and trap system has been developed in co-operation with Dr. E.P. Jones, Marine Chemistry Division of the Bedford Institute of Oceanography. The technique enables us to determine 19 individual fluorinated, chlorinated, brominated and iodated compounds. Blanks were run continuously throughout the cruise and standards were run every other day. Liquid standards were used for all compounds except for the CFC's (Freon-12, Freon-11 and Freon-113) and carbontetrachloride (CCl₄).

This has been the first sea-going test for our newly developed system. The automated sample handling and the increased extraction efficiency have improved both precision and limits of quantification. The technique also gives

us the possibility to study the volatile methylhalides, which could not be done with our former analytical method. An intercalibration was performed between our system and those of the BIO for the CFC's and CCl₄. It will be possible to compare results from approximately 150 water samples. The instruments were calibrated with the same gas standard.

We had hoped to collect micro-organisms in the upper 10 m of the water column with a plankton net at near-shore stations, in order to study the formation of halocarbons. However, the combination of bad weather, ice conditions, along with the work load, precluded us from using the net more than once. The sample showed increased concentrations of iodated compounds, due to micro-organism activity.

10. Vessel Mounted Acoustic Doppler Current Profiler (M. Scotney/BIO)

The VMADCP was set to profile at the beginning of the WOCE CTD line on June 19,1993 and continued to log data until June 26,1993. Logging was halted once we entered the Straits of Belle Isle on our return trip to B.I.O.

The instrument was configured to measure 4 metre depth cells to a water depth of 400 meters. Recorded data was averaged over 3 minute intervals with GPS navigation available for reference when bottom tracking was out of range.

During the trip some problems were encountered when the Trimble GPS receiver on the bridge failed to output the serial data feeding the ADCP. Consequently some blocks of data recorded on June 23 and 24 will not contain navigation data. Since we were in water depths greater than 400 meters, bottom tracking was not possible and this data can not be reduced to actual water velocities.

11. Alkalinity (R. Gershey/BDR)

This cruise saw the first use of a newly developed alkalinity titration cell based on the previous titration system. The titration cell differed in both size and automated sample handling. It was hoped that the increase in cell size and the automated sample handling technique would enhance both the precision and ease of operation. New software was developed to

accommodate these changes. Preliminary results show that the expected enhanced precision has not been realized. Thus, despite some problems with the new hardware and software, samples from 22 of the 26 stations were taken. In all, just about 300 samples were analyzed for alkalinity.

12. Thermometer Temperatures

(C.K. Ross and Anthony W. Isenor/BIO)

Three electronic digital reversing thermometers (T345, T350 & T352) were placed on bottle 1 and another three electronic digital reversing thermometers (T347, T348 & T354) on bottle 3.

Initially, thermometer calibration data from February 1991 were used to correct the thermometer readings. However, subsequent examination of the corrected temperatures using post-cruise calibration data from March 1994 showed improved difference (thermometer - CTD) statistics, namely a more peaked distribution and smaller difference from CTD.

The thermometer data were corrected using the March 1994 thermometer calibration data. The difference (thermometer - CTD) was then computed and the values sorted and plotted. The resulting curve showed that thermometer T352 gave consistently large differences as compared to the CTD. This thermometer was then removed from the analysis.

The values presented in the SEA file represent the mean thermometer temperature, on the ITS 90 scale, computed from all thermometers excluding T352.

The following statistics are on the differences between the readings of the digital thermometers on the same rosette bottles:

Thermometer Pairs	Mean Difference	Standard Deviation
T345-T350	-0.017	0.007
T345-T352	-0.035	0.002
T350-T352	-0.017	0.006
T347-T348	0.003	0.003
T347-T354	-0.003	0.032
T348-T354	-0.006	0.030

The following are the duplicate temperature measurements obtained from the reversing thermometers for the indicated sample ID numbers. The temperature values are in degrees celsius and are on the ITS90 scale. Thermometer T352 has been included in the list below although is not included in the calculation for the CTD temperature calibration nor is it included in the average value reported in the WOCE SEA file.

Appendix A:

93019 CTD Oxygen Calibrations

There were 26 stations occupied during cruise 93019. Based on cruise records there were two oxygen sensors used corresponding to the following station ranges: 1 to 19 and 20 to 26.

To create the data file to be used in the CTD oxygen calibration process, two merges were performed. First, a temporary file was created by merging the up trace CTD data, obtained from the CTD at the time of bottle closing, with the down trace CTD data. The two data sets were merged using pressure. Each record in the up CTD data file having a sample id number was combined with the down cast 2 dbar CTD data that had the closest pressure. If no down cast CTD data record was found, then no merged record was output for this sample id number. The final Merged file was created by merging the temporary file with the water sample oxygen file which contained the means of the water sample oxygen duplicates for each sample id number.

Information from the Merged file was taken for each of the two station ranges. Table 1 below lists the number of records for each station range that will be used in the CTD oxygen calibration process.

Table 1.

Station Range	Number of Unique Sample ID Numbers	Number of IDs having no water oxygen value(s)	Number of IDs not having a down CTD oxygen value and/or not being present in the Merged CTD file	Number of IDs having both a mean water sample oxygen value and a down CTD oxygen value that were contained in the Merged CTD file
1 - 19	257	4	1	252
20 - 26	132	2	0	130
TOTAL	389	6	1	382

For reference, the mean of all the water sample oxygens collected during this cruise was 7.016 ml/l. Using the WOCE accuracy guideline for CTD oxygen measurements of 1-1? %, we compute a deviation of 0.07 - 0.11 ml/l. This can be used in comparison with after calibration standard deviations.

Summary of Variables Used in Calibration Process

The following describes the notation used in the calibration.

j : station

i : observation taken on station j

n_j : is the number of observations taken for station j

p_{ij} : pressure for the i th observation of station j

b_{ij} : water sample oxygen for the i th observation of station j

c_{ij} : down CTD oxygen for the i th observation of station j

$d_{ij} = b_{ij} - c_{ij}$: i th oxygen difference for station j

$d.j =$: mean of the oxygen differences for station j

$e_{ij} = d_{ij} - d.j$: the i th oxygen difference expressed as a deviation from the mean oxygen difference for station j

e_{ij} : predicted value of e_{ij} from the regression analysis

$r_{ij} = e_{ij} - e_{ij}$: i th residual for station j from the regression analysis

k_{ij} : calibrated CTD oxygen

since $r_{ij} = e_{ij} - e_{ij} = b_{ij} - k_{ij}$

$d_{ij} - d.j - e_{ij} = b_{ij} - k_{ij}$

$b_{ij} - c_{ij} - d.j - e_{ij} = b_{ij} - k_{ij}$

therefore the calibration is:

Eqn 1. $k_{ij} = c_{ij} + d.j + e_{ij}$

Calibration of Stations 1 to 19

Station 1 data will not be used in the calibration process because it was a test station and all bottles were fired at the same shallow depth of 54 dbars. Using the data for stations 2 to 19 (233 data points), a plot of the difference between the water sample oxygen and the down CTD oxygen (d_{ij}) against pressure (p_{ij}) was produced (see Figure A-1). The data point (outlier) having sample id number 126224 (indicated in Figure A-1) was removed from the dataset leaving 232 points to be used in further analysis.

It was observed from Figure A-1 that a simple offset would be appropriate as an initial calibration step. Also, the near-surface region is avoided by omitting all data in the layer 0 to 250 dbars from the calibration process. The 250 dbar limit was determined subjectively from Figure A-1. Omitting data in this layer results in 150 data points to be used in the calibration. Stations 2 to 7 had no data below the 250 dbar cut-off so they were omitted at this point; how they were handled is discussed below.

For stations 8 to 19 the mean of the oxygen differences was calculated for each station and this value, the station offset ($d.j$), was subtracted from the individual down CTD oxygen values. The station offsets are listed in Table 2. Figure A-2 is a plot of e_{ij} against p_{ij} . The standard deviation for the e_{ij} 's was 0.09 ml/l.

Figure A-3 is a plot of d_{ij} versus pressure for stations 2 to 7. The station offsets were calculated for stations 2 to 7. The surface points, $p \leq 10$ dbars, which had the large oxygen differences were removed prior to calculating the station offsets. The station offsets and standard deviations are given in Table 2. Figure A-4 shows e_{ij} against pressure for stations 2 to 7. The standard deviation for the e_{ij} 's was 0.18 ml/l.

Calibration of Stations 20 to 26

The same steps were used for these stations as were used for stations 2 to 19, so only a brief explanation will be given. A plot of all d_{ij} against pressure is shown in Figure A-5. All points having a pressure ≤ 200 dbars were omitted leaving 103 data points for further analysis. The calculated station offsets and standard deviations are given in Table 2. Removing the station offsets results in Figure A-6, where e_{ij} is plotted against p_{ij} . A linear regression analysis was performed on all the stations in the group, using e_{ij} as the dependent variable and p_{ij} as the independent variable. Before the regression analysis was carried out two outliers were removed, sample id numbers 126284 and 126303; these are indicated in Figure A-6. The regression curve is also shown in Figure A-6. There was 101 observations used in the regression analysis.

The computed regression equation is:

$$\text{Eqn. 1 } e_{ij} = 0.1742 + 1.0513E04 \cdot p_{ij}$$

A plot of the residuals (r_{ij}) versus pressure is shown in Figure A-7. The residuals have a standard deviation 0.09 ml/l.

Station Offsets Removed in Calibration Process

The means of the oxygen differences, d_{ij} , and standard deviations for all stations analysed are given in Table 2 below.

Table 2. Station offsets (d.j).

Station	Mean of Oxygen Differences (ml/l)	Standard Deviation
2	2.849	0.59
3	2.212	0.17
4	2.251	0.14
5	2.294	0.05
6	1.005	0.19
7	1.123	0.16
8	1.456	0.26
9	1.204	0.17
10	1.154	0.04
11	1.140	0.04
12	1.136	0.06
13	1.074	0.06
14	1.165	0.12
15	1.145	0.12
16	1.197	0.07
17	1.168	0.07
18	1.208	0.08
19	1.187	0.10
20	-1.741	0.19
21	-1.655	0.19
22	-1.703	0.17
23	-1.667	0.11
24	-1.663	0.12
25	-1.647	0.15
26	-1.624	0.09

CTD Oxygen Calibration Procedure

We calibrated the CTD oxygen data for all stations according to the following expression:

$$\text{Eqn. 2 } k_{ij} = c_{ij} + d.j + e_{ij}$$

where k_{ij} is the calibrated CTD oxygen data

c_{ij} is the raw CTD oxygen data,

$d.j$ is given in Table 2 for all stations, and

$e_{ij} = 0$ for stations 2 to 19 and e_{ij} is given by Eqn. 1 for stations 20 to 26.

All CTD oxygen data for the listed stations, regardless of pressure, will be calibrated using this expression.

Station 1 will be left uncalibrated since all of its bottle data was taken at the same near surface depth.

93019: Stations 1 to 19

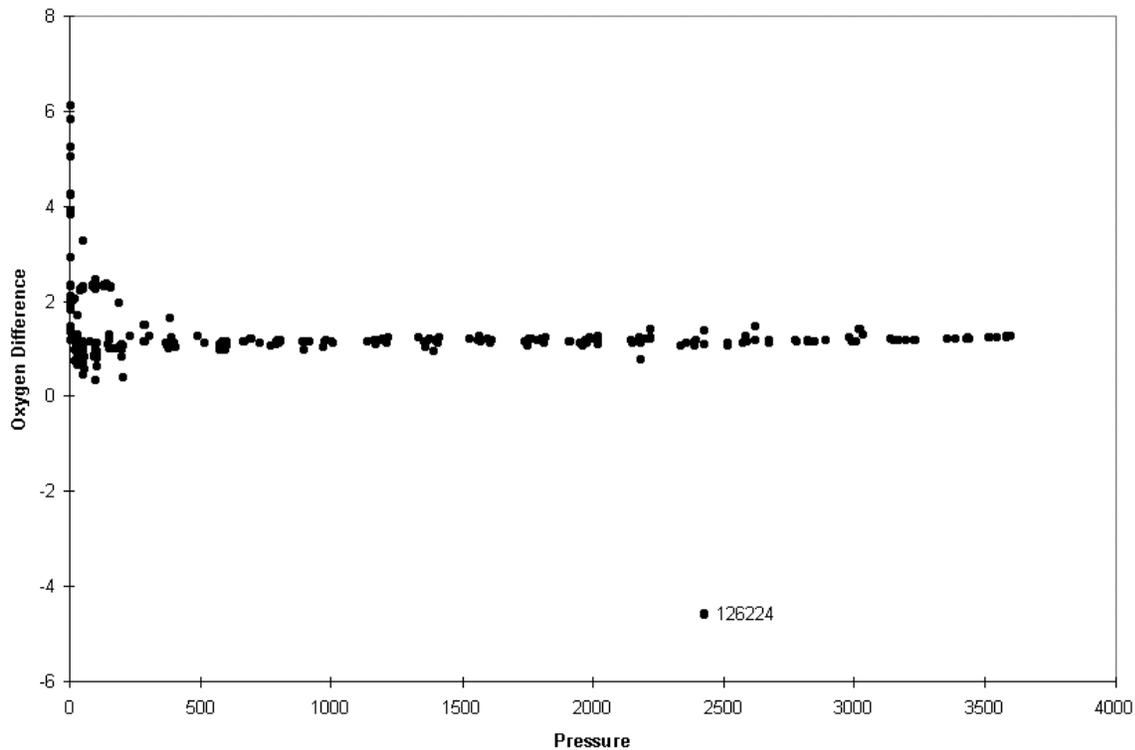


Figure A-1. Water sample oxygen minus CTD down cast oxygen, or dij, plotted against pressure.

93019: Stations 8 - 19

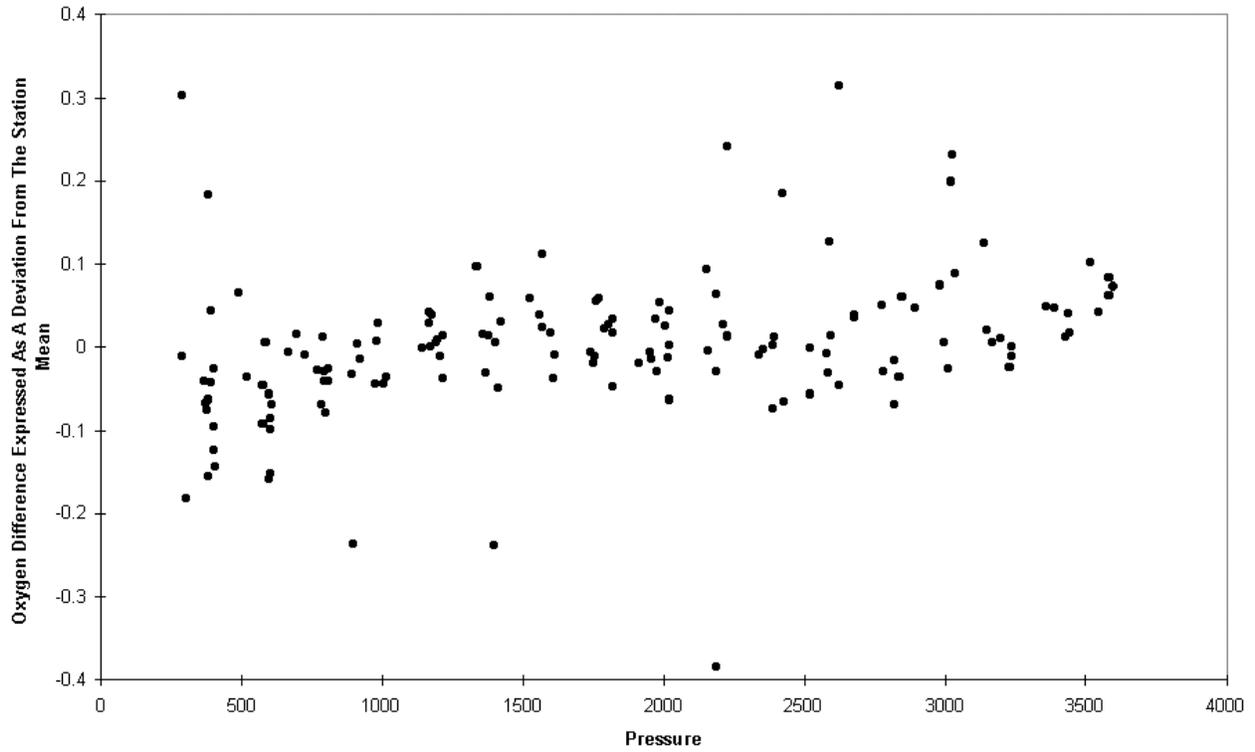


Figure A-2. Plot of e_{ij} values against pressure for data below 250 dbars.

93019: Stations 2 To 7

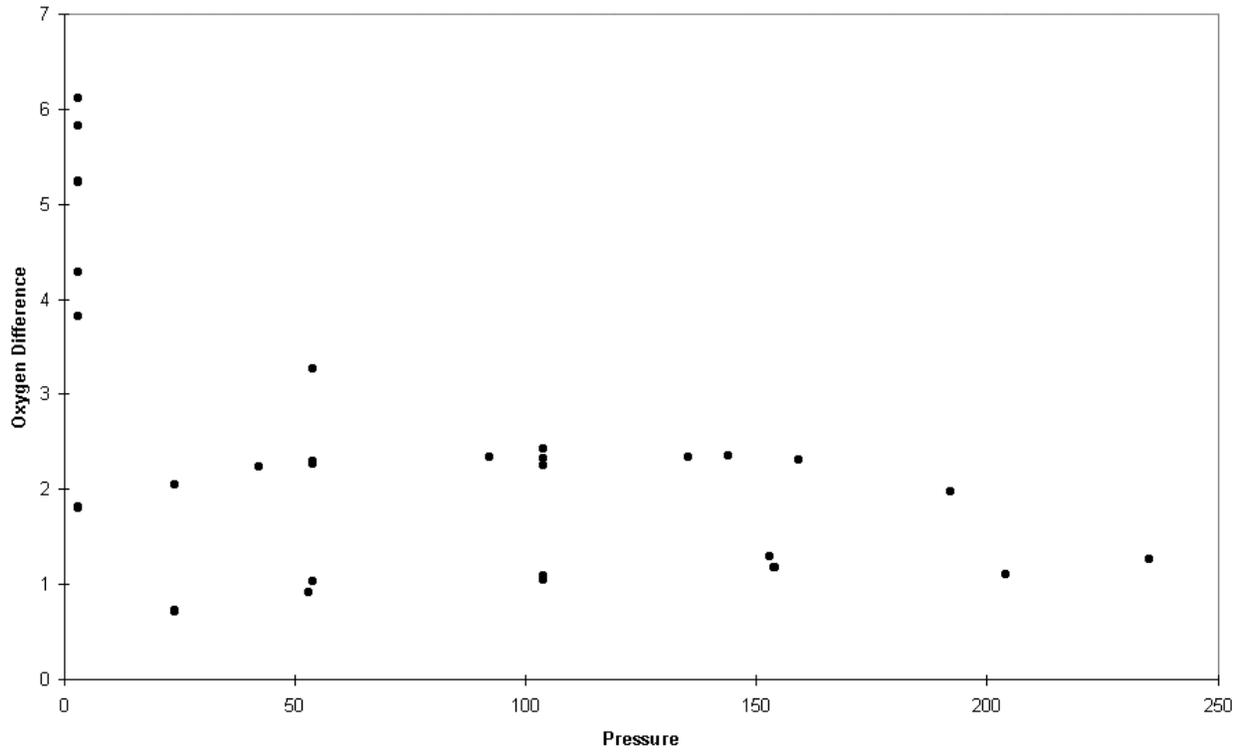


Figure A-3. Water sample oxygen minus CTD down cast oxygen, or dij, plotted against pressure.

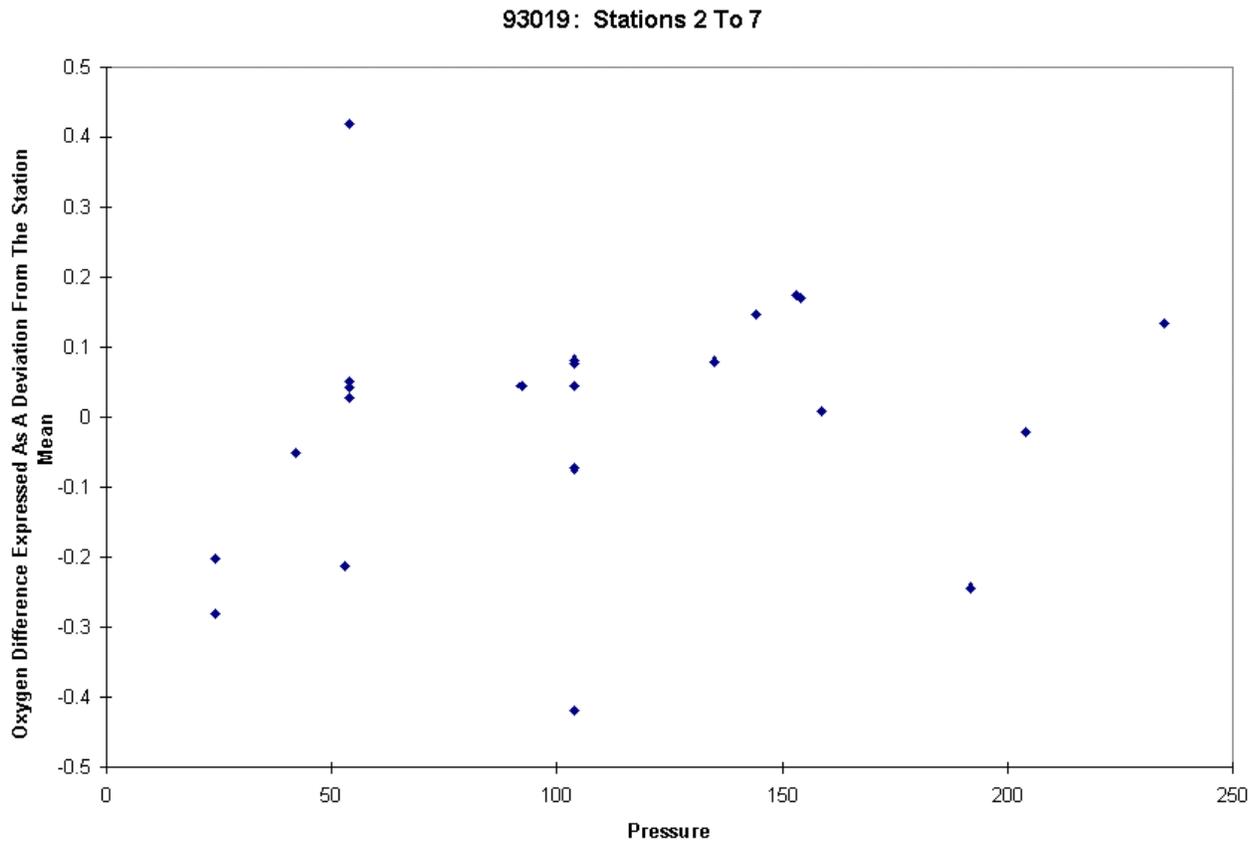


Figure A-4. Plot of e_{ij} values against pressure.

93019: Stations 20 To 26

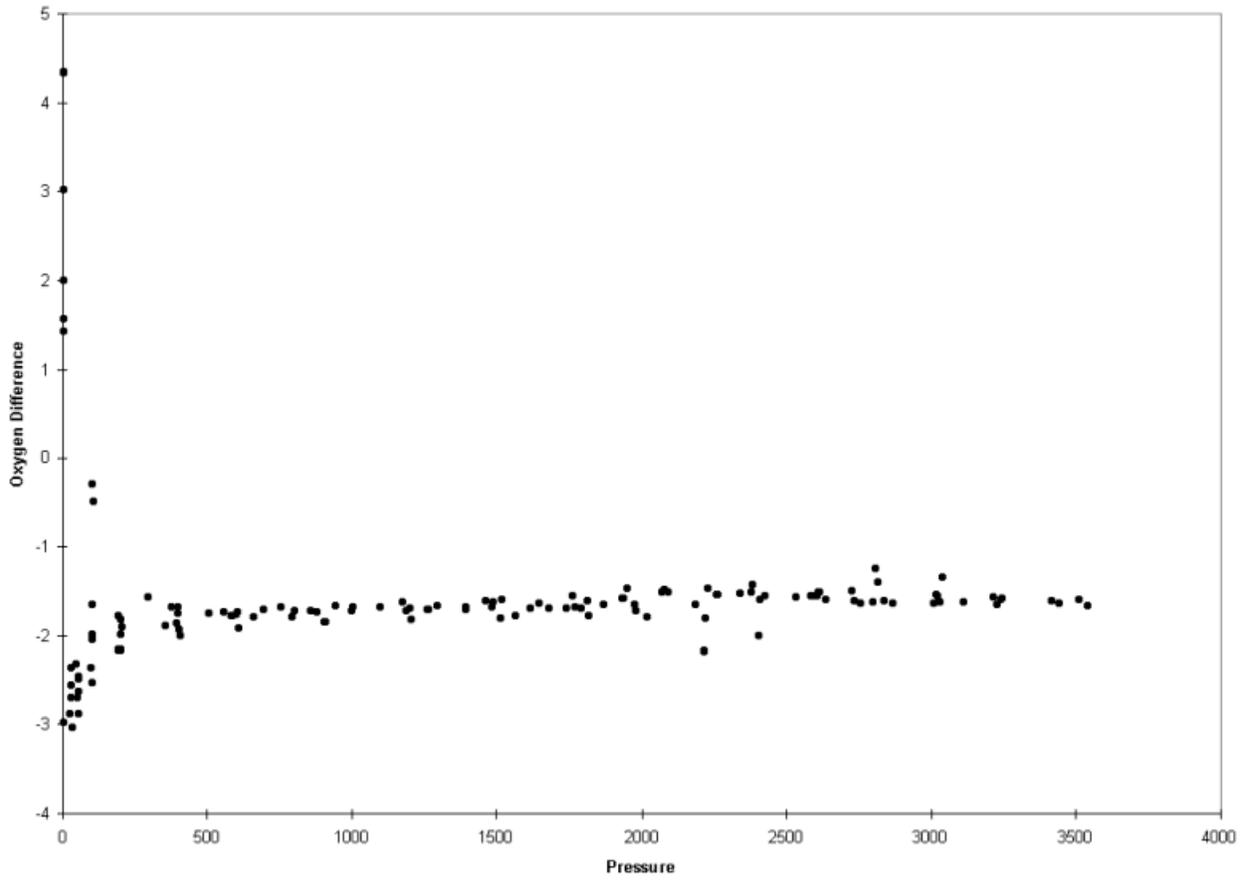


Figure A-5. Plot of water sample oxygen minus CTD down cast oxygen, or dij, against pressure.

93019: Stations 20 To 26

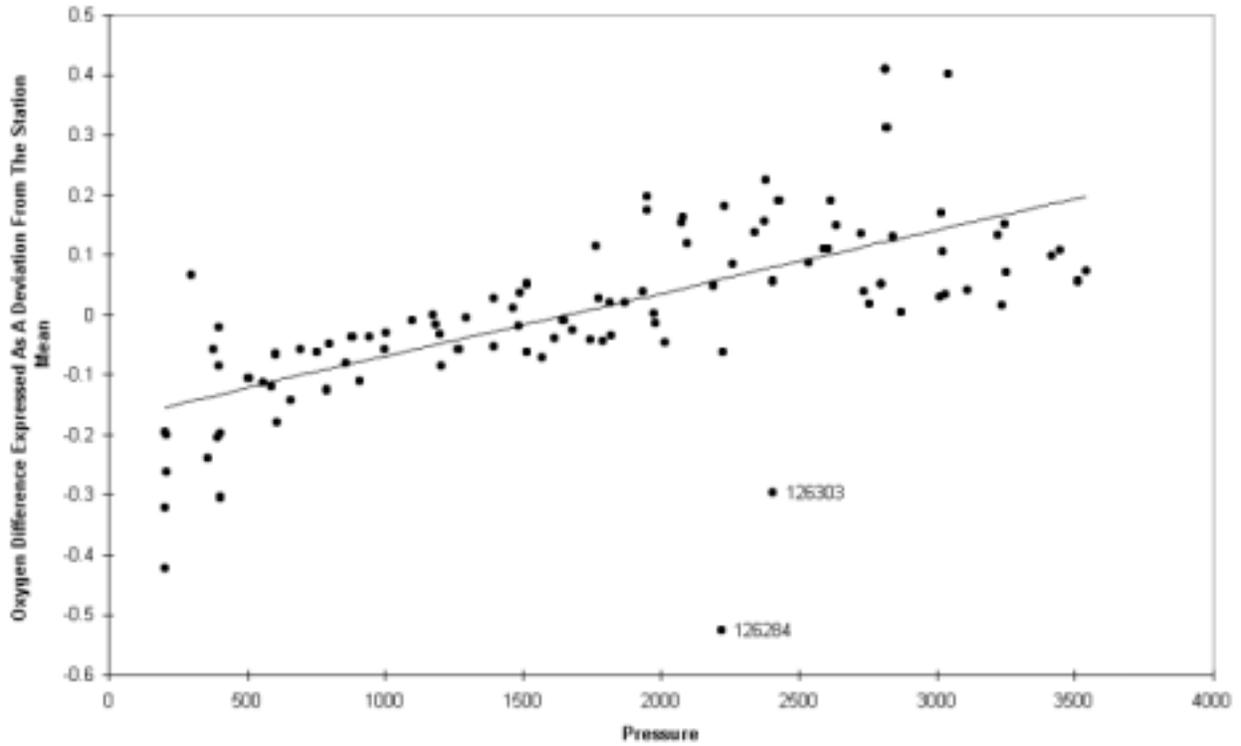


Figure A-6. Plot of e_{ij} values against pressure for data below 200 dbars. The regression line is also shown.

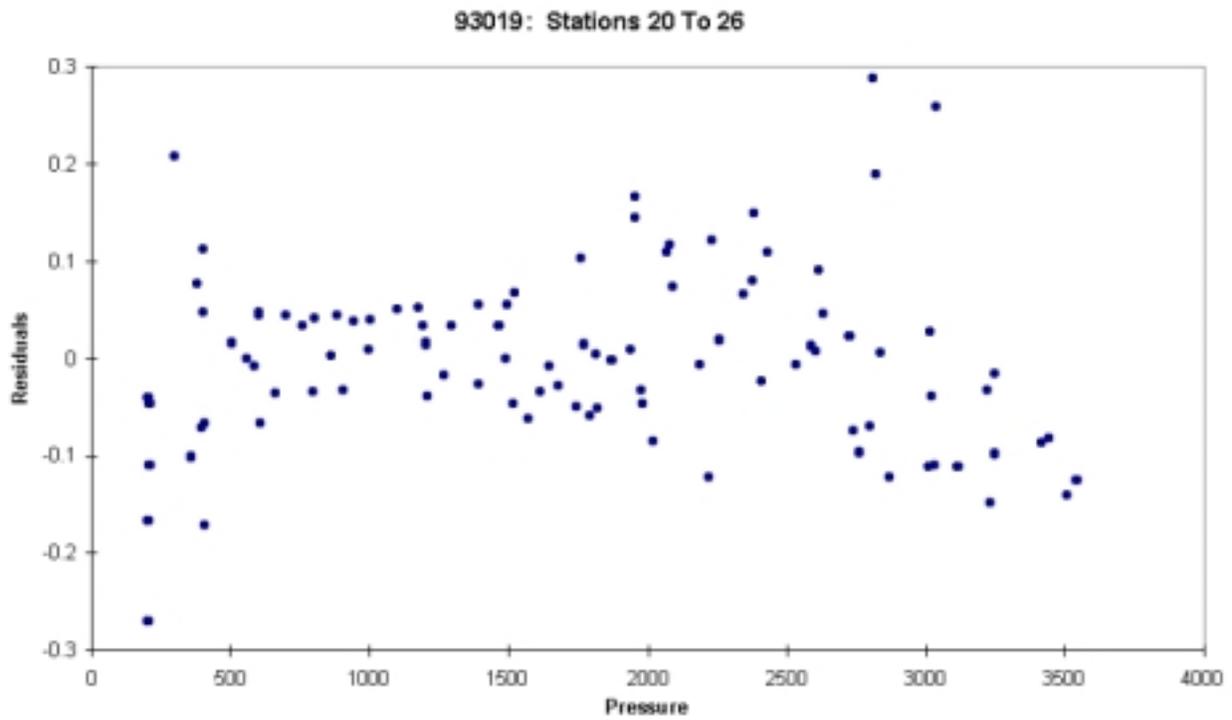


Figure A-7. Residuals (r_{ij}) remaining after the station and regression offsets have been removed.