

CRUISE REPORT

HUDSON 94008

LABRADOR SEA

WOCE LINE AR7W

MAY 24 - JUNE 12, 1994

A. CRUISE NARRATIVE

1. Highlights

WOCE Designation: AR7W - Atlantic Repeat Hydrographic Section 7 West, Labrador to Greenland

JGOFS Labrador Sea biological program.

Cruise Designation: 94008

Ship: C.S.S. Hudson

Agency: Bedford Institute of Oceanography
Box 1006
Dartmouth N.S. B2Y-4A2
Canada

Chief Scientist: John R. N. Lazier

Fax 902 426 7827
Omnet Bedford.inst
Internet j_lazier@bionet.bio.dfo.ca

Ports of Call: Dartmouth to Sydney N.S.

Dates: May 24 to June 12 1994

2. Cruise Summary Information

2.1 Station Positions

The positions of the observations, ie. CTD stations, CTD plus rosette water samples stations, biological stations, XBT releases and a mooring are shown in Fig. 1. The WOCE AR7W line (see Fig. 2) runs between South Wolf Island Labrador and Cape Desolation Greenland, however, heavy ice prevented us from completing the stations over the Labrador shelf. A second CTD line was run off the North East Newfoundland shelf to capture some of the inflows and outflows of the Labrador Sea but heavy weather stopped work before completion of the 4 easternmost stations. The biological sampling took place along these sections and at various positions enroute with a concentration of sampling over the upper Labrador continental slope in the vicinity of Hamilton Bank.

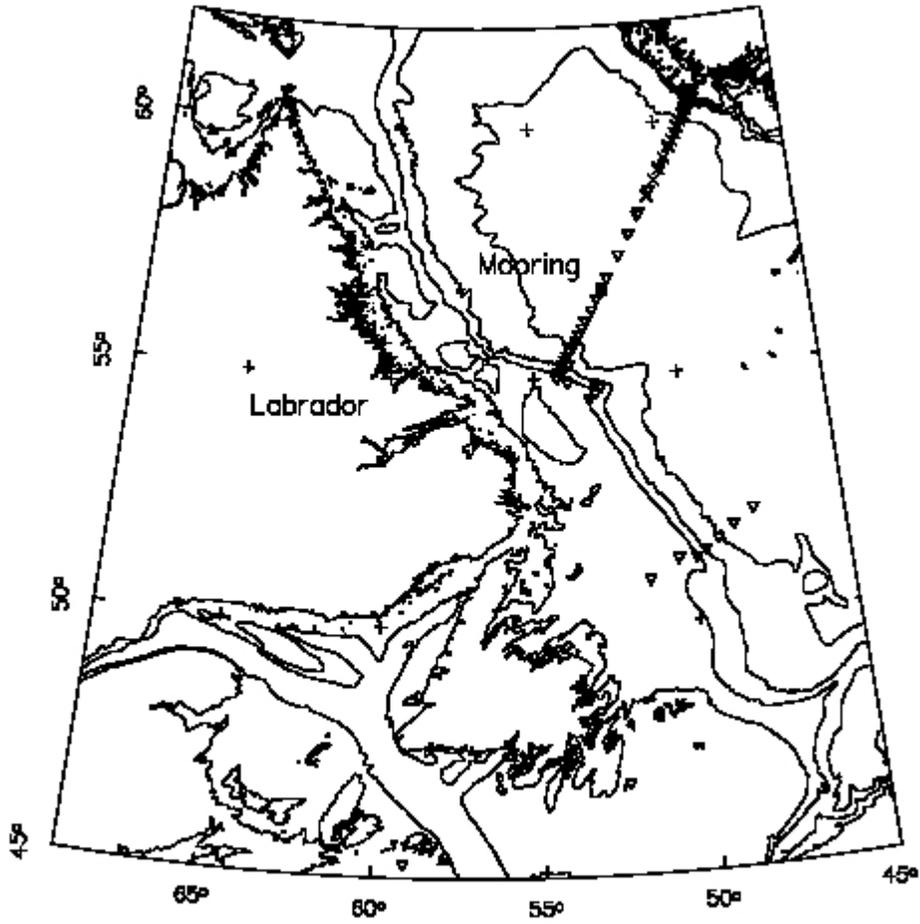


Figure 1. Study area, showing eastern coast of Canada, Labrador Sea and all stations. X - XBT, ∇ - CTD, ◆ - Mooring.

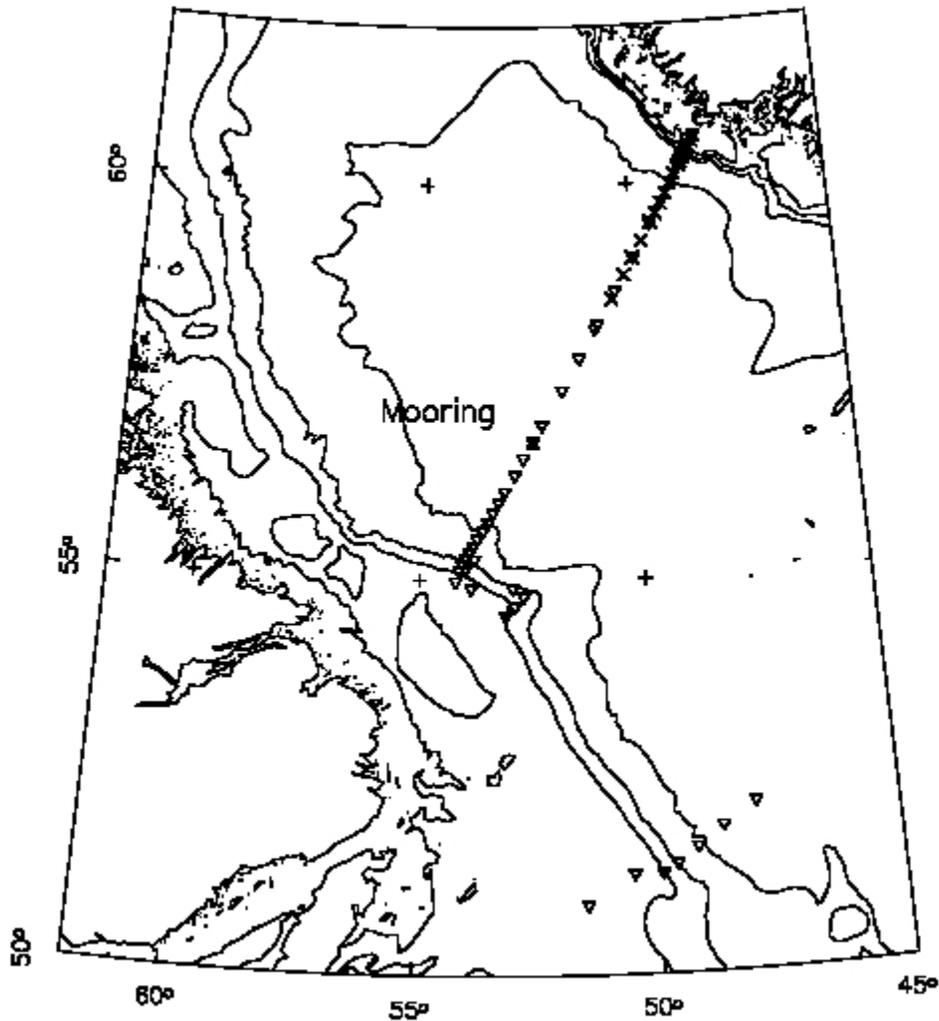


Figure 2. Instrument occupation along AR7W. X - XBT, ∇ - CTD, \blacklozenge - Mooring.

2.2 Sampling Accomplished

At the 35 CTD stations a Seabird CTD was used to obtain temperature, salinity and dissolved oxygen profiles for the full depth of the water column and at 28 of these positions a water sampling rosette acquired up to twenty 8 litre samples for analyses of salinity, dissolved oxygen, nutrients, CFC-11, CFC-12, CFC-113, carbon tetrachloride, total carbonate, alkalinity, halocarbons, tritium and helium. For the order of sample drawing, see Appendix 1.

At the 18 biological stations, samples were obtained with vertical net tows to 100 metres, submersible pumps to 100 m depth, rosette water bottles for analyses of chlorophyll, phytoplankton, zooplankton, phytoplankton pigments and growth rates.

A mooring was placed in 3500 m of water at 56 45.2' N 52 27.3' W. It suspends 6 Seacat temperature/conductivity recorders, 6 Aanderaa current meters, 1 Acoustic Doppler Current Profiler (ADCP), 1 WOTAN and 1 CTD with a device for measuring the total partial pressure of dissolved gas in the water. The mooring will be recovered in 1995. No floats or drifters were released during the cruise however 19 XBTs were launched in the West Greenland Current.

3. List of Principal Investigators for All Measurements

Name	Responsibility	Affiliation
David Farmer	WOTAN & dissolved gas	IOS
Bob Gershey	CFC, O ₂ , alkalinity, CO ₂ , nutrients	BDR
Erica Head	Zooplankton	BIO
Owen Hertzman	Delta PCO ₂	Dal. U.
Ed Horne	Biological Probe	BIO
John Lazier	CTD, salinity, mooring	BIO
Vivian Lutz	Phytoplankton pigments	BIO
Bob Moore	Natural Halocarbons	Dal. U
Peter Rhines	Mooring	U. W.
Peter Schlosser	Tritium, Helium	LDEO
Martin Visbeck	ADCP	MIT
Steve Calvert	Nutrient Uptake	UBC

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

LDEO Lamont-Doherty Earth Observatory
of Columbia University,
Palisades, NY, 10964, USA

U.W. University of Washington
Seattle, WA, USA

Dal.U. Dalhousie University
Halifax N.S. Canada

MIT Massachusetts Institute of Technology

Cambridge, MA, USA

IOS Institute of Ocean Sciences
 Sidney BC

UBC University of British Columbia

Electronic Addresses

S. Calvert	calvert@unixg.ubc.ca
D. Farmer	dfm@ios.bc.ca
R. Gershey	rgershey@fox.nstn.ns.ca
E. Head	erica@sfnet.dfo.ca
O. Hertzman	hertzman@open.dal.ca
E. Horne	e_horne@bionet.bio.dfo.ca
J. Lazier	j_lazier@bionet.bio.dfo.ca
V. Lutz	vlutz@ac.dal.ca
B. Moore	rmoore@ac.dal.ca
P. Rhines	rhines@killer.ocean.washington.edu
P. Schlosser	peters@ldeo.columbia.edu
M. Visbeck	visbeck@plume.mit.edu

4. Scientific Program and Methods

4.1 Physical-Chemical Program

One of the important objectives of the annual occupation of the WOCE AR7W line is to monitor the properties of the water masses in the region, especially the Labrador Sea Water, which is renewed by deep convection in winter to as much as 2300 m. The data along the AR7W line from 1993 showed the convected water to be colder, denser and deeper than previously observed which led us to believe convection had been unusually vigorous during the winter of 1992/1993. The salinity of the convected water was higher in 1993 than in 1992 and this too seems to have been an indication of vigorous convection penetrating into deeper layers of higher salinity water. The extreme convection appears to have been caused by a series of abnormally cold winters culminating in the very severe winter of 1992/93.

Salinity, temperature, and σ_{θ} profiles from 1994 (Figs. 3, 4, 5 and 6) indicate that the layer of convected water is colder but fresher than in 1993. The density (σ_{θ}) however appears to have remained about the same as in 1993. In Fig. 3, the convected water is indicated by the region of nearly homogeneous water between 500 and 2300 m. The solid curves from 1993 stations 19-22 show the salinity to be nearly constant through this interval but the dotted curves from this year's stations 32-35, obtained at the same positions, show the water to be slightly fresher at most positions. Also, the profiles appear to have more structure than in 1993. The temperature profiles in Fig. 4 also show the nearly homogeneous layer between 500 and 2300 m and the temperature is slightly but noticeably less in 1994. We conclude that convection took place during the winter of 1993-94 but that it was not as vigorous as during the previous winter. The difference is

probably due to the fact that the recent winter was not as cold as the 1992-93 winter. Such a difference is suggested in the winter monthly air temperatures over southern Baffin Island at Iqaluit. They were abnormally cold, by up to 10 °C, from October 1992 to March 1993 and from November to December 1993 but they were near normal from January to March 1994.

The σ_t -S curves in Fig. 6 again illustrate the changes between 1993 and 1994 and highlight the differences in the Labrador Sea Water in the range 2.65-2.80 °C and 34.82-34.84. The 1.5 curves in Fig. 5 contrast with the temperature and salinity curves by showing very little difference between the two years. This difference between the changes in density profiles and the other properties results from either the convection process itself or the restratification following convection. However we do not yet understand these processes well enough to explain how the changes in the distributions occur. We do not know, for example, if the deep convection is a predominantly isopycnal process or a diapycnal one. However, the data from this cruise and the previous ones are providing important clues and we anticipate that the data from the mooring and the future cruises will provide a much fuller understanding of the ventilation of the intermediate waters of the North Atlantic.

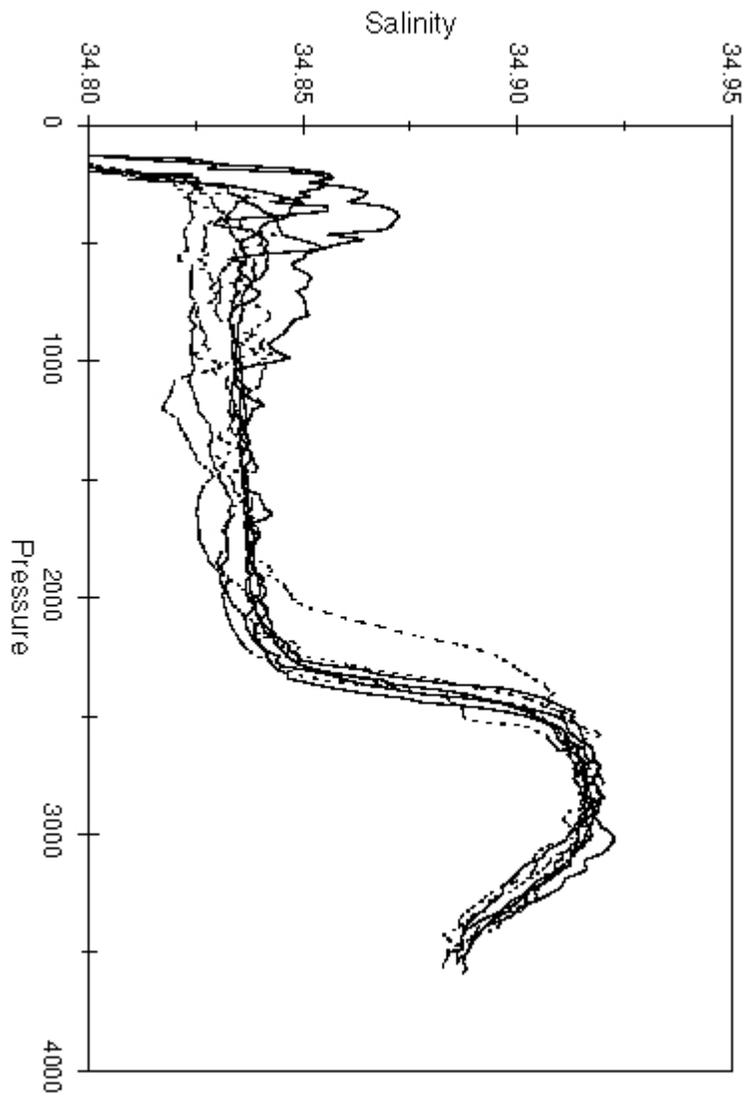


Figure 3. CTD salinity vs. pressure. Solid lines are from 1993, broken lines are from 1994.

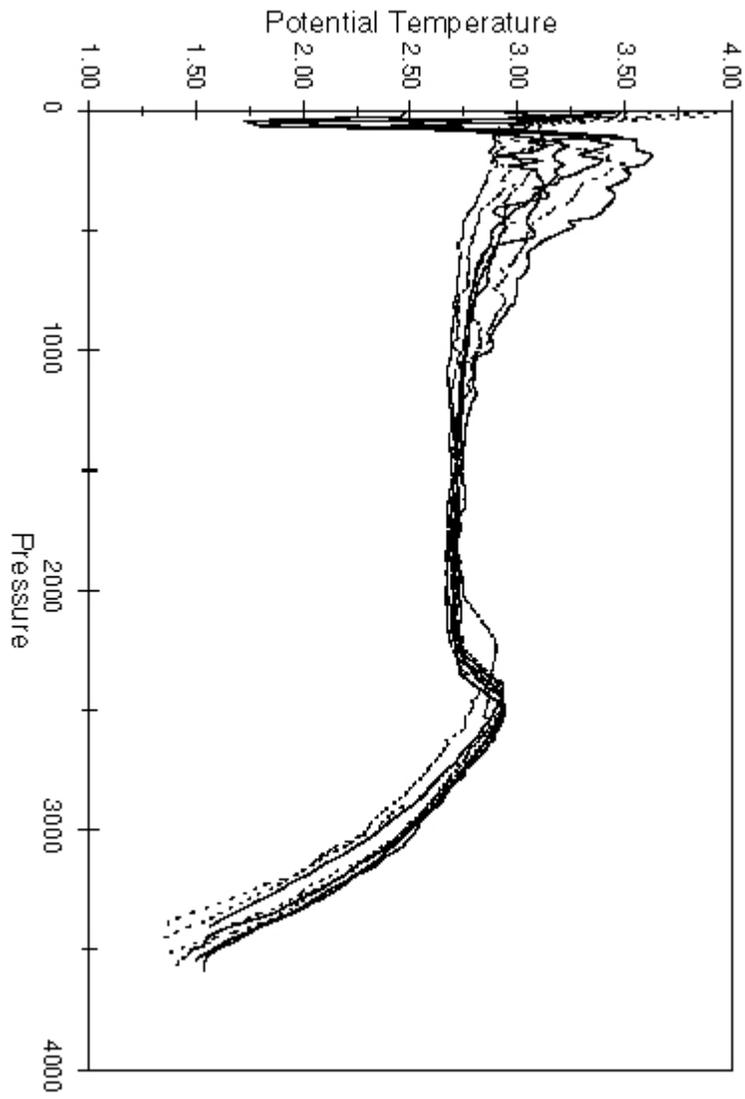


Figure 4. CTD Potential temperature vs. pressure. Solid lines are from 1993, broken lines are from 1994.

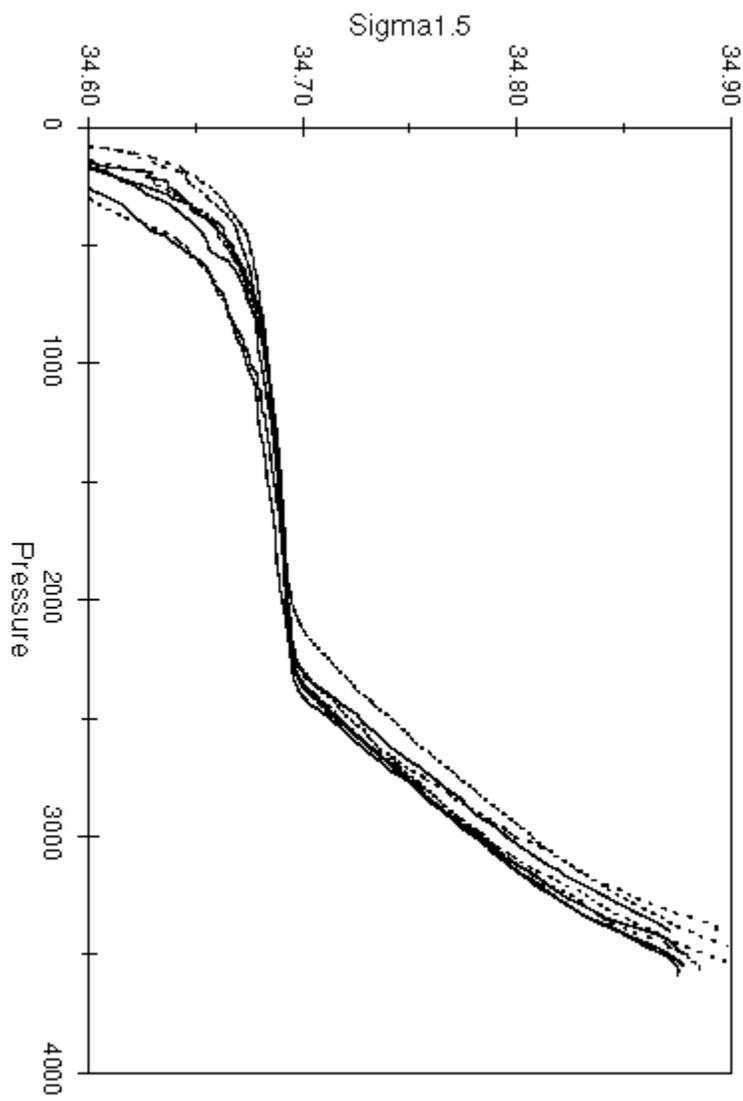


Figure 5. CTD density vs. pressure. Solid lines are from 1993, broken lines are from 1994.

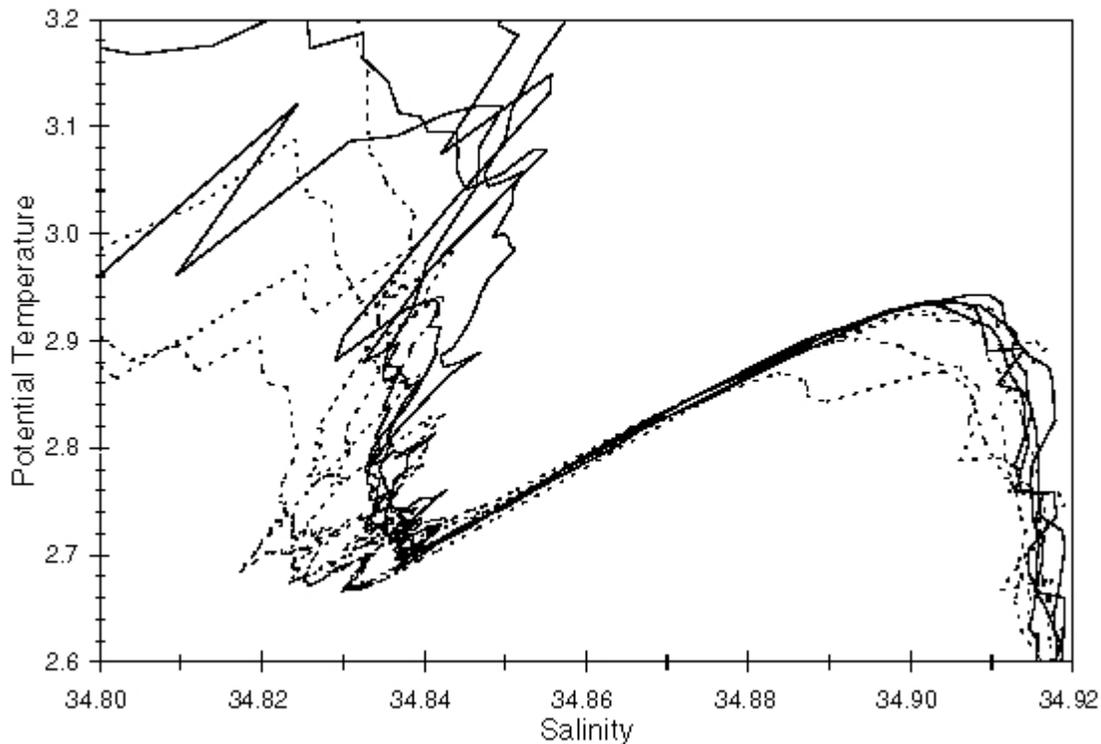


Figure 6. CTD temperature vs. salinity. Solid lines are from 1993, broken lines are from 1994.

4.2 Biological - Primary Production Programme

Water samples for primary production estimates were collected using the Biological Pump or from the surface using a bucket. A total of 13 profiles was completed.

The new Seabird CTD package was used on the Pump for the first time. This package included a Seatech fluorometer and a quantum sensor. All sensors worked well. An unexpected problem quickly became apparent when the "D" cells powering the CTD expired after less than 2 hours. The manufacturer of the CTD had claimed that the batteries would last more than 4 hours at 0 degrees. This resulted in many more battery changes than anticipated.

There were some mechanical problems with the HIAB crane used to deploy the Pump. At the first station the drive shaft for the hydraulic pump snapped when the Pump was still in the water. The pump had to be recovered by hand. This problem was overcome by moving a 20 HP pumping unit from the quarterdeck and hooking it up to the HIAB. At the end of the cruise the Hiab was used to deploy the Zodiac from the top of the container. The oil seal in the bending arm ruptured.

A total of 52 PI experiments were completed. Biomass ranged from less than 1mg to greater than 12mg chlorophyll per cubic metre. First estimates of assimilation numbers showed low values-range 1 to 2. Samples for inorganic nutrient estimates were collected at all sampled depths. These will be analyzed at BIO.

Surface temperature, salinity and chlorophyll were monitored continuously in the forward lab. Data from this indicated that there were large geographical areas on the banks and NE Newfoundland shelf where surface chlorophyll values were greater than 10 mg per cubic metre.

4.2.1 Optics

The Optics and turbulence programme was dealt a severe blow on this voyage when the BUD probe used to collect this data was lost on its second deployment. When the accident occurred the winch was holding the instrument at the rail of the ship. When the winch operator moved the winch control to lift the instrument a few inches the instrument began to freefall. By the time the winch began to take up line there were several metres of slack wire and when it fetched up the wire broke. The wire was new but was not supposed to ever experience this kind of snap load. The instrument had two safety mechanisms but both failed. This was probably due to the instrument hitting the side of the ship when it fell and breaking one of the glass lenses for the spectrometers. Then when the ballast weights were dropped the instrument would not have enough buoyancy to reach the surface.

4.2.2 Bacterial Production

Tritiated thymidine and leucine were used to determine the rate of bacterial production at 12 locations along the cruise track (see table). Samples were taken from the shallow (Biological) CTD cast at each location from the surface down to the 1% of surface light level, usually 7-8 depths. The light intensity profile for the water column was obtained from the Seabird CTD mounted on the pump. A rough simulation of the light intensity of each of the selected depths was made using various mesh sizes of nickle screen covering clear plexiglass incubation tubes in a surface seawater cooled bath, open to natural sunlight but with a blue transparent plexiglass bonnet over the tubes. The light intensity inside each tube had been measured previously using a 4 pi light meter. Some applications from 1 depth were incubated at 3 light intensities to check for the effect of light on the experiment. The effect of temperature had already been tested. Water samples were preserved with formalin and will be stained with Dapi dye for microscopic enumeration of bacteria. Samples were also preserved with 10% paraformaldehyde and flash frozen in liquid nitrogen for flow cytometric counts.

As part of the tritium experiments, one "isotope dilution" experiment was performed on June 1 to test the effects of spiking the seawater with thymidine or leucine. Eight different concentrations of the untritiated compound was added to replicates of the same seawater to see how uptake of the normal amount of the tritiated chemical was affected.

A final aspect of the tritium procedure concerning grazing in the sample vessels during incubation was tested using a "seawater dilution" experiment. This compared the uptake of thymidine or leucine over a 24 hour period between raw seawater and seawater diluted to 1 in 10

with 0.2 micron filtered seawater (the filtered seawater from the same sample). This experiment was done on water obtained from the pump on June 5/94.

Table 1

Date	CTD#	Lat	Lon	Experiment
May 26	2	46 48.18'N	52 29.85'W	Depth Profile Expt
May 27	3	50 51.63'N	51 27.80'W	"
May 29	6	58 09.90'N	50 56.05'W	"
May 30	27	60 21.62'N	48 29.76'W	Bill's Flow Cytometer Sample only
May 30	27/2	60 23.80'N	48 36.36'W	Depth Profile Expt
May 31	33/1	59 03.33'N	49 55.41'W	"
Jun 1/94	15:05	57 23.54'N	51 45.39'W	Isotope Pump Dilution Expt
Jun 1	37/1	57 23.54'N	51 45.39'W	Depth Profile Expt
Jun 2	41/1	56 19.52'N	52 52.34'W	"
Jun 3	46/1	55 36.57'N	53 36.22'W	"
Jun 4	48/1	55 24.98'N	53 47.47'W	Flow Cytometer Samples
Jun 4	48/2	55 24.65'N	53 47.98'W	Depth Profile Expt
Jun 5	54/1	54 52.86'N	53 51.57'W	"
Jun 5	14:15	54 52.86'N	53 51.57'W	Seawater Pump Dilution Expt
Jun 6	60/1	54 53.15'N	52 56.60'W	Depth Profile Expt
Jun 8	65/1	51 49.45'N	48 38.30'W	"

4.3 Biological - Zooplankton Program

Erica Head, Leslie Harris, Jesus Cabal

4.3.1 Determination of Zooplankton Biomass

Vertical tows were made between 100 m and the surface using both 200 mm and 100 mm mesh plankton nets. Biomass sampling stations were as follows:-

Date dd.mm.yy	Latitude	Longitude
25.05.94	45 15' N	59 05' W
26.05.94	46 48' N	52 29' W
27.05.94	50 52' N	51 27' W
29.05.94	58 09' N	50 56' W
30.05.94	60 24' N	48 36' W
31.05.94	59 03' N	49 56' W
01.06.94	57 23' N	51 47' W
02.06.94	56 19' N	52 54' W

03.06.94	55 37' N	53 38' W
04.06.94	55 26' N	53 47' W
05.06.94	54 52' N	53 52' W
06.06.94	54 53' N	52 57' W
08.06.94	51 48' N	48 35' W

4.3.2 Feeding Experiments with Copepods Grazing on Phytoplankton

Two types of feeding experiments were carried out: one in which the kinetics of digestion of chlorophyll a (from ingested phytoplankton) by copepods was followed over a 7 h period and one in which the effect of food concentration and changes in food concentration on chlorophyll a digestion by copepods were examined over 4 consecutive 12h feeding periods. Six of the first type and three of the second type were carried out.

Experiments were also carried out to see if the digestive products of chlorophyll a (phaeopigments) found in copepod guts were further degraded during egestion of faecal pellets (3 experiments) or lost from egested faecal pellets by leakage (1 experiment).

4.3.3 Egg Production by Copepods

Egg production rates were measured in 8 experiments, in which female *Calanus finmarchicus* were fed with seawater from the depth of the chlorophyll maximum for periods of three days. As the concentration of chlorophyll (phytoplankton) varied from day-to-day, these experiments should demonstrate the effect of food concentration on egg production rate. Four experiments were also carried out to see if experimentally determined egg production rates are affected by cannibalism (i.e. females eating their own eggs). In situ egg production rates will also be assessed by comparing the number of eggs in the water column with the number of female copepods and egg hatching rates (which were determined experimentally on several occasions). The estimates of abundances of eggs and females will be obtained from the 100 and 200 mm mesh biomass tows. On two occasions 100 l water samples were taken from 8 depths using the biological pump and the eggs screened off (100 mm mesh) to examine the distribution of eggs with depth in the 0-100 m range.

4.3.4 Additional Experiments (not part of the main zooplankton program)

a) Genetic population structure of *Calanus finmarchicus*

Samples were collected at all but the last station, which will be sent to Ann Bucklin at the University of New Hampshire, for the analysis of mitochondrial DNA. These will show if *Calanus finmarchicus* is genetically homogeneous throughout the sampling area, or if (for example) there are different populations associated with the Greenland and Labrador Currents.

b) Isotopic fractionation of nitrogen (^{14}N and ^{15}N) by copepods

Three experiments were run in which copepods were allowed to excrete metabolised nitrogen (ammonia) and defecate unmetabolised nitrogen (faecal pellets). These experiments were carried out in conjunction with Dr. N. Wasser and M. Soon, who will analyse the material collected to see if copepods excrete N^{15} depleted ammonia nitrogen and defecate N^{15} enriched particulate material (as is assumed in current geochemical thinking).

4.4 Biological - Stable Isotopes of Nitrogen and Carbon N. Waser and M. Soon

This work is part of a broader study of carbon and nitrogen recycling and export zone in the North Atlantic and North Pacific oceans, in the context of the Canadian Joint Global Ocean Flux Study (JGOFS). The objectives of this cruise are, (1) to study the variations of the natural isotope ratios of carbon and nitrogen in the dissolved inorganic nitrogen and particulate organic matter and, (2) to study nitrate, ammonium and carbon dioxide uptake rates using labelled nitrogen and carbon substrates.

4.4.1 Natural $^{15}N/^{14}N$ ratios of particulate organic matter

Large water samples were collected daily from the biological pump and filtered on board for the determination of natural $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios of suspended particulate organic matter. Plankton samples were collected from 20 mm and 200 mm mesh-size nets. Material from both tows was preserved for species identification. The rest of the material was kept frozen for isotopic analyses. All the isotopic analyses will be done by mass spectrometry in the laboratory at the University of British Columbia (Prof. Steve Calvert).

4.4.2 Natural $^{15}N/^{14}N$ ratios of nitrate

Water samples were collected daily from the shallow CTD cast (0-300m) and occasionally from a deep cast (0-bottom) for the determination of natural $^{15}N/^{14}N$ ratios in NO_3 . Some of the samples were processed on board by a vacuum-stripping method. Nitrate present in the sample was reduced to NH_4 by an alloy of Al, Cu and Zn. The ammonium evolved was stripped with N_2 , under vacuum, and adsorbed onto an ion exchange resin (zeolite). The $^{15}N/^{14}N$ ratios of the NH_4 extracted on zeolite will be determined in the laboratory.

4.4.3 Ammonium excretion by zooplankton

Experiments were pursued with E. Head and L. Harris to determine $^{15}N/^{14}N$ ratios of NH_4 excreted by a natural population of zooplankton. Plankton was collected from a 200 mm mesh-size net and incubated in filtered surface seawater (0.2 mm) for 3 and 24 hrs. The faecal pellets and zooplankton were kept for the determination of $^{15}N/^{14}N$ ratios. NH_4 were measured on board at time 0, 3 and 24 hrs by the manual colorimetric method. Water samples were taken after 3 and 24 hrs for the determination of $^{15}N/^{14}N$ ratios of the NH_4 excreted by zooplankton

during the incubations. Ammonium was extracted on zeolite on board. The isotopic analyses will be done in the laboratory.

4.4.4 Nitrate, ammonium and CO₂ uptake rates

Water samples for nutrients and Chl a measurements were collected from the shallow CTD cast daily. NH₄ was measured on board by the manual colorimetric method. NO₃ were determined by P. Clement on board on the autoanalyser. Chl a were measured on board by A. MacDonald. H¹³CO₂, ¹⁵NO₃ and ¹⁵NH₄ tracers were added to water samples collected at 5 depths from the shallow CTD. The samples were incubated in the afternoon for about 4 hours on deck. The samples will be analyzed for POC, PON and ¹⁵N and ¹³C labelled PON and POC by emission mass spectrometry by G. Harrison. The carbon and nitrogen utilization rates will be calculated.

4.3 Distribution of CTDs and Bottle Positions

Fig. 7 shows a cross section of the AR7W line with the CTDs as vertical lines and the bottle positions as circles. The 7 CTDs without rosette samples were added to increase the horizontal resolution in the boundary current over the Labrador shelf and slope. The sample identity numbers minus 140000 for the deep CTD/rosette stations on the two sections are given in Figs. 8 and 9. Note that the bottles with samples numbered 291 and 292 were tripped together at the depth indicated by the dot between numbers 290 and 293. Also, no samples were drawn from the bottle with sample ID 140544.

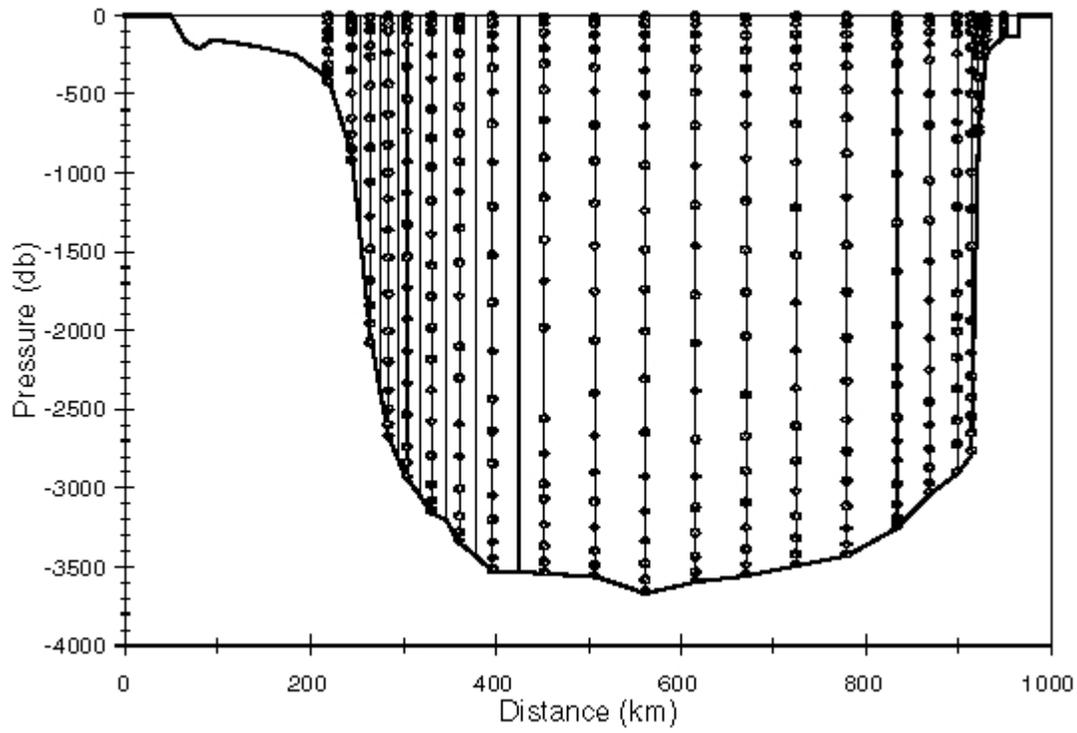


Figure 7. 1994 Bottle and CTD Positions. CTD profiles without bottles are indicated by vertical lines only. Bottle trips are indicated by solid dots.

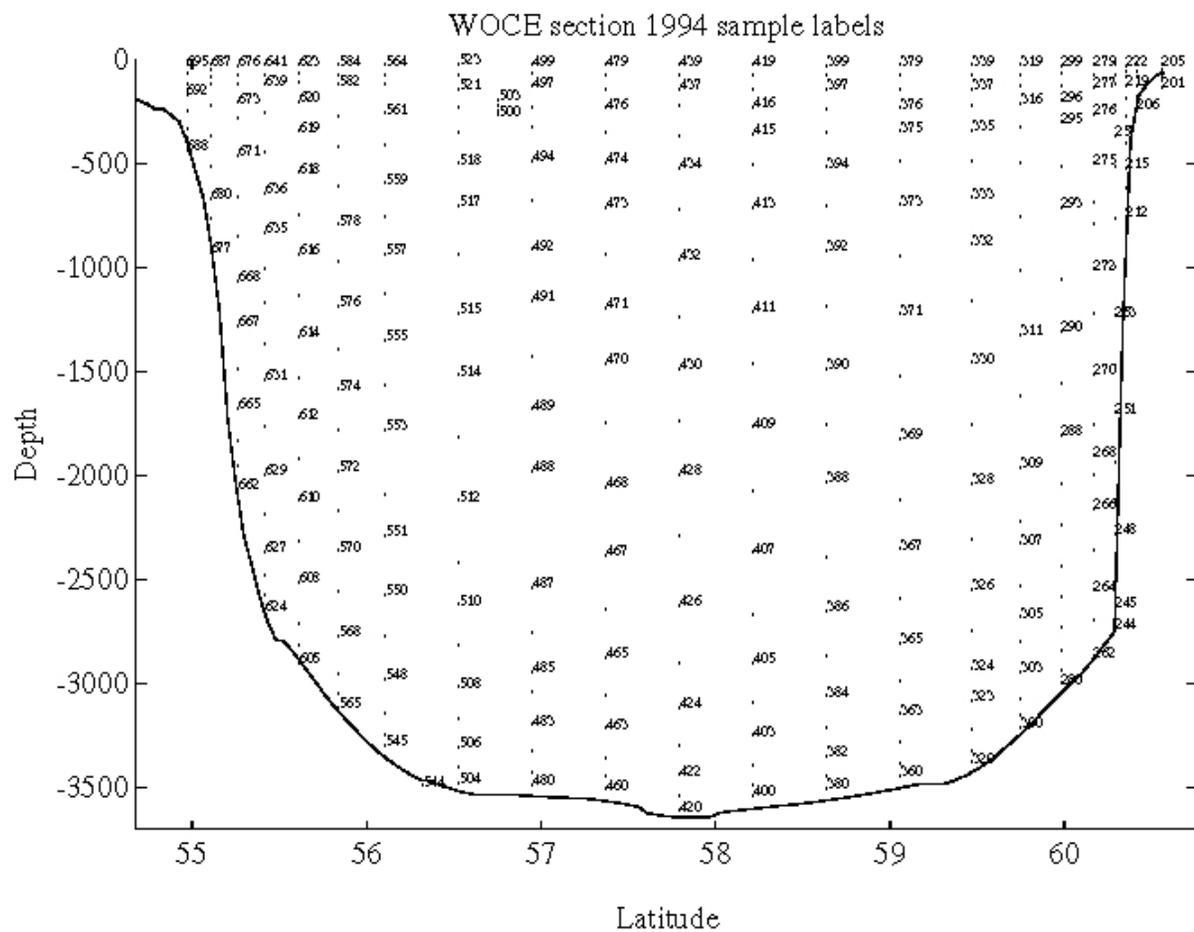
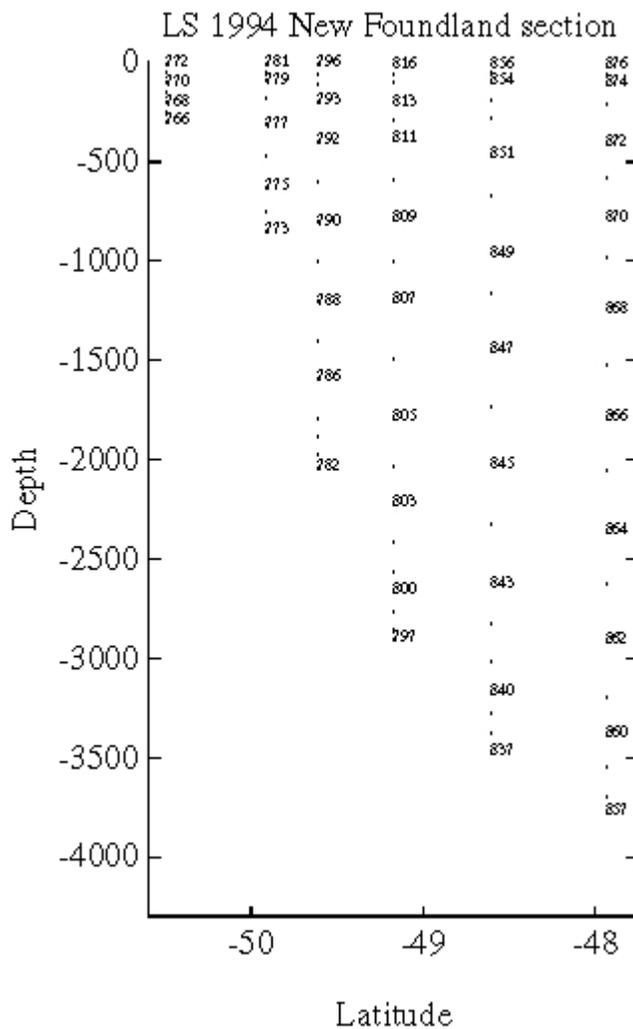


Figure 8. 1994 AR7W Bottle trip positions with the last 3 digits of the sample ID number.



6. Other Incidents of Note

A major component of the biological program is a new instrument under development which is capable of measuring to 500 m the vertical structure of temperature and conductivity to 1 cm scales; florescence to 10 cm scales and light spectra both up and down to 1 m scales. This is the "BUD Probe" for Biological-Up-Down-Probe and obtains data while falling freely at the end of a loose conducting-cable/tether. Sadly, however, the instrument was lost on recovery due to a malfunction in the recovery winch.

7. List of Cruise Participants

<u>Name</u>	<u>Responsibility</u>	<u>Affiliation</u>
Anning, Jeff	Productivity	BSB/BIO
Breger, Dee	Tritium/Helium	LDEO
Cabal, Jesus	Zooplankton	BSB/BIO
Carson, Bruce	CTD tech/watchkeeper/salts	PCS/BIO
Clement, Pierre	Nutrients/Oxygens	PCS/BIO
Dickie, Paul	Bacteria	BSB/BIO
Dunphy, Paul	Computers/software/watchkeeper	PCS/BIO
Gershay, Bob	CFC/Alkalinity/Carbonate	BDR Res.
Fraser, Brian	Electronics tech (BUD probe)	BSB/BIO
Harris, Leslie	Zooplankton	BSB/BIO
Head, Erica	Zooplankton	BSB/BIO
Horne, Edward	Co-chief scientist	BSB/BIO
Hingston, Michael	CFC/Alkalinity/Carbonate	BDR Res.
Hu, Zhongyao	Natural Halocarbons	Dal. U.
Irwin, Brian	Productivity	BSB/BIO
Isenor, Anthony	Data quality/watchkeeper	PCS/BIO
Lazier, John	Chief Scientist	PCS/BIO
Lutz, Vivian	Phytoplankton Pigments	PCS/BIO
MacDonald, Al	Productivity	PCS/BIO
Moore, Bob	Natural Halocarbons	Dal. U.
Parsons, Tom	Electronics tech (BUD probe)	Contract
Poliquin, Manon	Delta PCO ₂	Dal. U.
Rhines, Peter	Advisor/watchkeeper/mooring	U. W.
Scotney, Murray	Mooring/watchkeeper	PCS/BIO
Soon, Maureen	Nutrient Uptake	UBC
Visbeck, Martin	Advisor/ADCP/watchkeeper	MIT
Waser, Nathalie	Nutrient Uptake	UBC
Zemlyak, Frank	CFC/Alkalinity/Carbonate	PCS/BIO

5. Underway Measurements

During the cruise the following variables were recorded while the ship was underway and stopped on station;

- ship's position using a Global Positioning System (GPS),
- water velocity profile using a hull mounted Acoustic Doppler Current Profiler (ADCP),
- temperature, salinity and chlorophyll of the surface waters using a pump plus CTD and fluorometer, and
- CO₂ of the air and surface water.

Along the CTD lines bathymetry was recorded between stations every 5 minutes when conditions permitted.

Nineteen XBTs at 18 stations were launched in the West Greenland Current.

B. UNDERWAY MEASUREMENTS

1. Navigation and Bathymetry

Anthony W. Isenor

The navigation system onboard CSS Hudson consists of a Trimble Navigation Loran-GPS 10X decoder and AGCNAV. The decoder receives the satellite fixes and decodes the signals to obtain latitude, longitude and time. The decoder signals are about 1 Hz. All navigation data are logged directly to a micro VAX II (see Appendix 2). AGCNAV is a PC based display, and way-point setting software package developed at the Atlantic Geoscience Centre at BIO. The software runs on a PC and graphically indicates ship position, way-points, course, speed, etc.

The echo sounder system used for collecting bathymetric data consisted of a Universal Graphic Recorder model UGR-196C-11 connected to a hull mounted 12kHz transducer. The transducer beam width is 15 degrees. The sweep rate of the record was adjusted throughout the course of data collection to aid in identifying the bottom signal. The recorder was also linked to a clock, and thus could indicate 5 minute intervals on the sounder paper. The system was used to collect 5 minute bathymetric soundings during the occupation of AR7W while steaming from Greenland to Labrador.

2. Acoustic Doppler Current Profiler

Murray Scotney

The Hudson was equipped with a hull mounted RDI acoustic doppler current profiler. The transducer (serial number 177) had SC ADCP electronics (serial number 271) converted for ship board use. Logging, using Transect software, was started on May 25, 1994 at 2326Z near Cape Race, Newfoundland. The configuration of the equipment results in a bin length of 4 metres and a total of 100 bins. The raw data are stored to disk and backed up every two days. Two days of logging creates about 30 Mbytes of data. The data are also averaged in real-time over 1 minute intervals. ADCP logging was stopped on Jun 12, 1994 at 1035Z.

3. Thermosalinograph

John R. N. Lazier

A CTD and fluorometer were used to monitor the temperature, salinity and fluorescence (chlorophyll) of the near surface water at all times.

4. XBT and XCTDs

Murray Scotney and Anthony W. Isenor

An XBT system was used to obtain temperature-depth profiles across the West Greenland Current, along AR7W. The system consisted of a Sippican Ocean Systems Inc. MK9 deck unit (serial number 834003) logging data to a HP85B (serial number 2328A08033) computer. A hand held model LM3 launcher was used to launch T-7 XBTs. All launches occurred during steaming, with ship speeds less than 13 knots. Data were plotted on the HP85B in real-time. Later, the data were transferred to PC using the HP RS232 interface card.

A problem with the XBT launcher resulted in a slight inconvenience during the launch procedure. The problem was an electronic failure in a board in the XBT deck unit. The HP85B would not recognize loading of the XBT in the launcher. However, XBTs could be launched by manually grounding pin C on the launcher. Personnel would then proceed out of the lab area and launch the XBT. This procedure resulted in many XBT profiles that were vertically offset towards deeper values.

A total of 19 XBTs were dropped during the cruise. These casts are indicated in the Station Summary file. Of the 19 profiles, only 10 profiles produced usable data. Upon returning to BIO, these 10 profiles were quality controlled. A vertical adjustment was applied to those profiles suffering from the launching problem noted above. This adjustment brought the temperature data upwards toward the surface. The adjustment amounted to a removal of nonapplicable data records from the beginning of the profile and a recalculation of the depth based on the number of applicable data records and the fact that records are 0.1 seconds apart. The number of records removed at each station is indicated below.

<u>Station</u>	<u>Number of Removed Records</u>
9	1
14	57
16	181
17	27
22	135
24	53

No XCTD data was collected during this cruise.

5. Meteorological observations

John R. N. Lazier

Routine reporting of meteorological variables was carried out by the ship's crew.

6. Delta PCO₂

Manon Poliquin

The Dalhousie University PCO₂ system continuously measures PCO₂ between continuously pumped seawater and air. The system consists of an LI-COR 6262 differential non-dispersive infrared analyser, an equilibration tank in which air is brought into CO₂ equilibrium with seawater and a valving and pumping system to supply atmospheric air, equilibrated air, and standard gases to the analyser. The measurements on board the Hudson were done continuously from May 27, 1994 to June 10, 1994. These data will not be submitted to the WOCE DAC but will be delivered to the JGOFS data centre.

C. HYDROGRAPHIC MEASUREMENTS
- DESCRIPTIONS, TECHNIQUES AND CALIBRATIONS

1. CTD Measurements

John R. N. Lazier and Anthony W. Isenor

a. Description of the Equipment and technique

The CTD measurements are made with a standard SEABIRD model 9Plus CTD (serial number 09P7356-0289) that is equipped with model 3-02/F temperature sensor, model 4-02/0 conductivity sensor, a paroscientific digiquartz model 410K-105 pressure sensor and model 13-02 dissolved oxygen sensor. All but the pressure sensor are mounted in a duct through which a pump pulls sea water. Hence the water flow past the actual sensors is independent of the lowering rate; this simplifies the data processing considerably.

The Seabird CTD is mounted vertically within the BIO designed and built CTD/Rosette platform. This platform consists of a central 10 inch diameter aluminum tube which contains at its upper end a space to contain the sea unit for a General Oceanics Model 1015-24 bottle rosette (BIO Rosette #3, serial number 1348) unit and at its bottom end a smaller well that contains a General Oceanics model 6000 12 Khz pinger unit. The space between the central 6 inch diameter pinger well and the 10 inch outer tube is filled with lead and the bottom end of the tube is covered with a fibreglass nose cone that is acoustically transparent.

The CTD sea unit is held in a 6 inch diameter aluminum tube that is welded to the central tube. The CTD sensors are held in a heavy aluminum cage of approximately 6 inches in diameter which is welded to the opposite side. Around the mid point and the top of the central column are attached aluminum rings on which 20, 8 litre sampling bottles are attached. The number of bottles was set by the maximum diameter that we felt comfortable handling through the doors of our enclosed winch room on Hudson. The bottles are somewhat protected from damage by a metal band with a diameter a bit larger than the outer diameter of the bottles when they are mounted. This band is situated just below the bottom of the bottles.

The rosette bottles are of a BIO design that are now being made and manufactured by Brooke Ocean Technology, a local ocean engineering company. They differ from standard rosette bottles in that their tops and bottoms rotate about a horizontal axis to close. The energy to close the bottles is provided by stretching rubber tubing between the outside edges of the two lids along the outside surface of the bottle. This design has two advantages. First, the tubing is not inside the bottle either before or after the water sample has been captured. Second, the tubing is applied after the bottle is cocked in the rosette tripping mechanism and hence one doesn't have to fight the pull of the tubing when cocking the rosette.

b. Sampling Procedure and data processing techniques

The CTD was deployed and recovered at a rate of 60 metres/min. The CTD data is recorded onto disk by a 486 computer using SEABIRD SEASOFT Version 4.201 software (see Appendix 2). A screen display of temperature, oxygen and salinity profiles vs pressure are shown as a visual realtime verification of the proper functioning of the unit. The bottles are tripped using the enable and fire buttons on the SEABIRD deck unit. The SEASAVE software marks 72 scans at each bottle trip to identify these scans as occurring at the time the bottle was tripped.

At the end of the station, the SEASAVE software is used to create 1 and 2 dbar processed data files, an IGOSS TESAC message and a processed rosette trip file. All the raw and processed data files associated with the station are then transferred via ethernet to the ship's MicroVax computer for archive and subsequent access and distribution to various users on the vessel.

The data processing takes the following steps:

DATCNV	Converts the raw data to physical parameters.
SPLIT	Splits the data into DOWN and UP cast.
WILDEDIT	For every block of 12 scans, flags all scans whose pressure, temperature, conductivity and oxygen values differ from the mean by more than 2 standard deviations. Recomputes mean and standard deviation from unflagged data then marks as bad all scans exceeding 4 standard deviations from these new values.
FILTER	Low pass filter pressure and conductivity channels to time match parameters for salinity computation. Time constant used for conductivity is 0.045 seconds, for pressure 0.150 seconds.
LOOPEDIT	Marks as bad, all cycles on the down trace for which the vertical velocity of the CTD unit is less than 0.1 metres/sec.
ALIGNCTD	Aligns the temperature, conductivity and oxygen values relative to the pressure values accounting for the time delays in the system. Time offsets of 0.010 secs for conductivity, 0.000 secs for temperature and 3.000 secs for oxygen are used.
CELLTM	A recursive filter used to remove the thermal mass effects from the conductivity data. Thermal anomaly amplitude and time constants of 0.0300 and 9.0000 were used.
DERIVE	Computes oxygen values.

BINAVG	Averages the down cast into 1 or 2 dbar pressure bins. (Note: The procedure to produce the 2 dbar averages takes about 5% of the total processing time).
DERIVE	Computes salinity, potential temperature and σ_{θ} .

The above data processing steps use various specific magnitude or time offset coefficients. These coefficients were examined in detail using the data from Station 2 of this dataset. The analyses concentrated on the time offset relating the temperature and conductivity signals and the magnitude of the Lueck (1990) filter coefficient. The examination concluded that the time offset was appropriate for this dataset. The magnitude of the Lueck filter coefficient could not be properly verified due to excessive TS variability introduced by the frequent upcast stopping of the CTD for bottle trips.

c. Calibration Data

The CTD calibrations used during this cruise were supplied by Seabird Electronics are as follows:

Conductivity Sensor 041076 (all stations)

$$\text{Conductivity} = (af^m + bf^2 + c + dt)/[10(1-9.57(10^{-8})p)]$$

where

- f is the frequency
- m = 4.1
- p is pressure in dbars
- t is the temperature
- a = 2.21442246e-5
- b = 5.67193159e-1
- c = -4.19781901
- d = -1.23661793e-4

Temperature Sensor 031376 (All stations)

$$T = 1/\{a + b[\ln(f_0/f)] + c[\ln^2[f_0/f] + d[\ln^3(f_0/f)]]\} - 273.15$$

where

- ln indicates a natural logarithm
- f is the frequency
- a = 3.68093833e-3
- b = 6.00726775e-4
- c = 1.51819564e-5
- d = 2.19535579e-6
- f₀ = 6482.31

Pressure Sensor 51403 (All stations)

$$\text{pressure} = c (1 - T_o^2/T^2) (1 - d[1 - T_o^2/T^2])$$

where

T is the pressure period

$$c = c_1 + c_2 U + c_3 U^2$$
$$d = d_1 + d_2 U$$
$$T_o = T_1 + T_2 U + T_3 U^2 + T_4 U^3 + T_5 U^4$$

U is the temperature

$$c_1 = -38625.88 \text{ psia}$$
$$c_2 = 2.78422e-1 \text{ psia/deg C}$$
$$c_3 = 1.40578e-2 \text{ psia/deg C}^2$$
$$d_1 = 0.038824$$
$$d_2 = 0.0$$
$$T_1 = 30.62824 \text{ micro sec}$$
$$T_2 = -1.7328e-4 \text{ micro sec/deg C}$$
$$T_3 = 4.72380e-6 \text{ micro sec/deg C}^2$$
$$T_4 = 3.33300e-9 \text{ micro sec/deg C}^3$$
$$T_5 = 0$$

Oxygen Sensor 130265 (Stations 1 to 6)

$$\text{oxygen} = A B C$$

where

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

oc is the current from the oxygen sensor

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

$$Soc = 2.4323$$
$$\text{Tau} = 2.0$$
$$Boc = -0.0397$$

$$oc = Mv + b$$
$$m = 2.4608e-7$$
$$b = -4.9216e-10$$

$$B = \text{OXYSAT}(t,s)$$

t is temperature

s is salinity

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

e is natural log base

$$tcor = -0.033$$
$$pcor = 1.5e-4$$

p is the pressure

$$wt = 0.670$$

To oxygen sensor internal temperature

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

$$k = 8.9939$$

$$c = -6.8210$$

v is the oxygen temperature sensor voltage signal

Oxygen Sensor 130284 (Stations 7 to end)

$$\text{oxygen} = A B C$$

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

oc is the current from the oxygen sensor

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

$$Soc = 2.5328$$

$$\text{Tau} = 2.0$$

$$Boc = -0.0322$$

$$oc = Mv + b$$

$$m = 2.4528e-7$$

$$b = -3.9245e-9$$

$$B = \text{OXYSAT}(t,s)$$

t is temperature

s is salinity

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

e is natural log base

$$tcor = -0.033$$

$$pcor = 1.5e-4$$

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

The pre-cruise calibration undertaken at the BIO calibration facility showed the temperature sensor to be reading low by 0.0013 C and the salinity values to be low by 0.005. Neither of these calibrations have been applied to the data.

During the cruise the CTD salinity was monitored by comparing its average reading, on the uptrace, at the locations of the rosette samples with the values from the rosette samples. A plot of the 415 comparisons, Fig. 10, shows the CTD salinities have a pressure dependent offset

relative to the rosette bottle salinities. Similar comparisons from the 1992 and 1993 cruises during which Seabird CTDs were used did not show such an offset but in each year a different conductivity cell was used. We have begun communications with the company to find the source of the offset but in the meantime the error has been removed by adding a correction determined by fitting a 3rd order polynomial (thanks to Martin Visbeck) to the differences shown in Fig. 10. The fitted equation is;

$$\text{Offset} = -0.004712 - 4.014 \times 10^{-6} * P + 3.216 \times 10^{-9} * P^2 - 4.324 \times 10^{-13} * P^3$$

where P is the pressure in decibars.

After this correction was applied the distribution of ctd minus bottle salinities was re-evaluated. No pressure dependence could be found and the mean difference was 0. The 1st and 3rd quartile occur at differences of -0.0012 and +0.0012 respectively giving an interquartile range (IQR) of 0.0024. Following last years example we flag the samples which lie beyond $1.5 * \text{IQR} = 0.0036$ from the mean difference. About 14% of the samples fall in this category.

The post cruise temperature calibration consisted of an offset of -0.00536 C applied to the CTD temperatures. This offset is based on a comparison of 105 temperatures collected from digital thermometers and corresponding CTD temperatures. The stated offset is the median of the 105 differences between the CTD and thermometer temperatures. Thus, the CTD temperature calibration is:

$$T = T - 0.00536$$

where T is the CTD temperature in degrees celsius.

The CTD oxygen was also calibrated for stations 25 to 66 using a combination of upcast water sample data and downcast CTD profile data. The details of the calibration procedure and results are given in Appendix 3. Note that the WOCE SEA file column CTDOXY contains the down cast CTD oxygen data used in the calibration as opposed to the discrete CTD oxygen data obtained at the time of bottle trip.

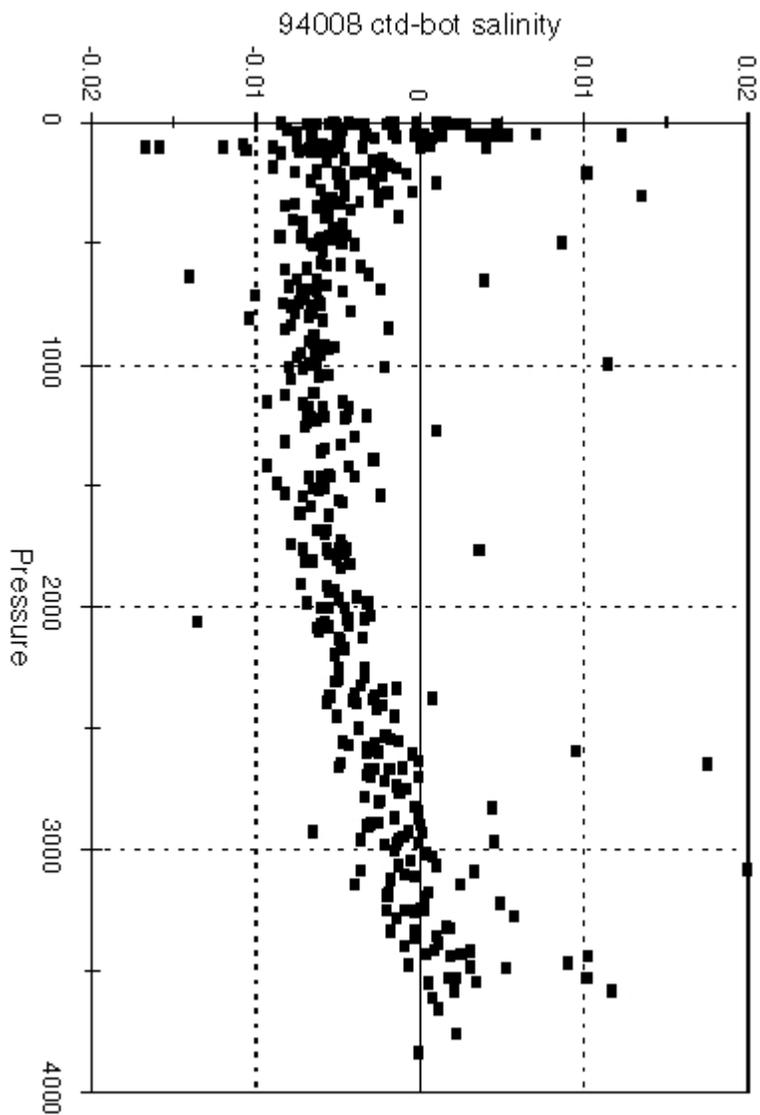


Figure 10. CTD salinity - water sample salinity vs. pressure.

2. Salinity

Bruce Carson

a. Description of Equipment and Technique

Salinity samples are analyzed on one of two Guildline Autosal model 8400 salinometers. Samples are drawn in 150 ml medicine bottles. New caps, equipped with plastic liners, are placed on the sample bottles for each use.

The salinometer cell is filled and rinsed three times with sample water before readings are recorded. Two readings of the salinometer are recorded for every sample and standardization. If the values are fluctuating, more readings are taken.

b. Sampling Procedure and Data Processing Technique

Salinity samples are drawn into 150 ml medicine bottles after three rinses. The bottles are filled up to the shoulders and then capped with new caps with plastic liners.

Files for each separate run are prepared. These files consist of various metadata (date, cruise, lab temperature, geographic location, operator, etc.) and sample specific data such as the bath temperature, sample ID number, and average conductivity ratio. A PC based program computes the salinity using average conductivity ratio of the runs and the standard IAPSO formula. Any changes in the salinometer readings between successive standardizations is assumed to have occurred as a linear drift of the instrument. Thus, the program applies a correction to the ratios, which varies linearly with the samples analyzed. The salinity data is then placed in the water sample database.

c. Laboratory and Sample Temperatures

Full cases of samples are taken from the winch room to the GP lab where they are left for a period of at least 10 hours to equilibrate to laboratory temperature before being analyzed.

The baths in these two salinometers were kept at 24°C and 27°C. The salinometer which was just above the current laboratory temperature would be the one that was used for any given run of samples.

d. Replicate Analysis

Only two duplicate salinity samples were drawn from the rosette bottles this year due partly to a shortage of water and partly to a lack of urgency as the duplicates always show excellent agreement. Duplicate salinity values are given in Table C.1.

Table C.1. Salinity Duplicate Measurements

Sample ID Number	Salinity
140691	34.5761
140691	34.5763
140321	34.8801
140321	34.8807

e. Standards Used

The salinometer was standardized using IAPSO standard water, Batch P123, prepared on June 10, 1993. Standardization with a new ampoule was carried out at the beginning, middle and end of every 32 bottle case and at intermediate points during a case if instrument drift was suspected.

3. Oxygen

Pierre Clement

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, BDR) 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.

In most cases 8 litre Niskin bottles are 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.

4. Nutrients

Pierre Clement

a. Description of Equipment and Technique

Nutrient concentrations are determined using a Technicon Autoanalyser II. The chemistries are standard Technicon (Silicate 186-72W, Phosphate 155-71W, Nitrate/Nitrite 158-71W) except for Phosphate which is modified by separating the Ascorbic Acid (4.0 gms/L) from the Mixed Reagent. This alteration is achieved by introducing the modified Mixed Reagent instead of water at the start of the sample stream at 0.23 ml/min. and the Ascorbic Acid is pumped into the stream between the two mixing coils at 0.32 ml/min..

b. Sampling Procedure and Data Processing Technique

Duplicate nutrient subsamples are drawn into 30 ml HDPE (Nalge) wide mouth sample bottles from 8 L Niskins. The bottles are 10% HCl washed, rinsed once with tap water, three times with Super-Q and oven dried at >100 Degrees F.

A sample run includes six Working Standards run at the beginning and end. Duplicate Check Standards are run every 16 samples followed by blanks as a Baseline Check. These Standards are made up in 33 ppt NaCl (VWR, Analar grade) as is the wash water. The Standards are tested against CSK Solution Standards (Sagami Chemical Center, Japan).

Analog data is converted to digital, processed and statistics calculated by a Pascal 6.0 in house program (Logger) on a PC. Chart recordings, hard copy and disk copies of the data are kept for reference.

c. Replicate Analysis

The following nutrient detection limits were applied (all detection limits are in micro moles/litre). All values at or below the detection limits were set to zero.

Silicate	0.134 micro moles/litre
Phosphate	0.065 micro moles/litre
NO ₂ +NO ₃	0.265 micro moles/litre

Duplicate nutrient subsamples were drawn for all deep casts along the AR7W line. The values for all duplicate subsamples are given in Table C.2.

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140101				140133			
140102				140134			
140103				140135			
140104				140136			
140105				140137			
140106				140138			
140107				140139			
140108				140140			
140109				140141	11.81	1.12	14.79
				140141	11.81	1.12	14.79
140110				140142			
140111				140143	9.80	1.07	11.28
140112				140144			
140113				140145	9.54	1.09	10.31
140114				140146	8.88	1.05	9.60
140115				140147			
140116				140148	8.58	.98	8.71
140117				140149			
140118				140150			
140119				140151			
140120				140152			
140121				140153	.79	.52	0.00
140122				140154			
140123				140155	.74	.41	0.00
140124				140156	.68	.42	0.00
140125				140157			
140126				140158	.64	.39	0.00
140127				140159	.68	.35	0.00
140128				140160			
140129				140161	10.86	1.17	15.04
140130				140161	10.86	1.17	15.30
140131				140162	10.84	1.18	15.28
				140162	10.97	1.16	15.30
140132				140163	10.85	1.17	15.26

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140163	10.85	1.17	15.07	140187	8.66	1.04	13.44
140164				140187	8.72	1.04	13.29
140165				140188	8.62	.99	12.61
140166	10.00	1.17	14.76	140188	8.65	1.01	12.52
140166	10.01	1.15	14.76	140189			
140167	10.77	1.17	15.38	140190	8.41	.94	11.47
140167	10.93	1.17	15.23	140190	8.49	.95	11.43
140168	10.93	1.16	15.72	140191	8.34	.92	11.40
140168	10.95	1.17	15.57	140191	8.52	.93	11.35
140169	11.12	1.16	15.50	140192	7.73	.74	8.35
140169	11.12	1.18	15.76	140192	7.74	.74	8.56
140170	11.02	1.17	15.65	140193			
140170	11.04	1.17	15.68	140194	7.68	.72	8.10
140171	10.52	1.14	16.07	140194	7.70	.72	7.99
140171	10.55	1.15	16.25	140195	7.66	.70	8.02
140172	10.99	1.17	16.19	140195	7.71	.72	7.89
140172	11.05	1.17	16.34	140196			
140173	10.90	1.17	16.11	140196			
140173	10.93	1.16	16.76	140197	7.72	.77	7.95
140174	11.13	1.15	16.12	140197	7.85	.77	7.96
140174	11.14	1.17	16.00	140198	7.50	.69	7.57
140175	11.11	1.19	16.28	140198	7.73	.70	7.78
140175	11.15	1.16	15.97	140199	7.76	.69	7.73
140176	11.12	1.19	16.14	140199	7.81	.70	7.66
140176	11.17	1.16	15.88	140200			
140177	11.10	1.17	15.99	140201			
140177	11.11	1.18	16.18	140202			
140178	11.08	1.15	15.95	140203			
140178	11.14	1.16	16.03	140204			
140179	11.08	1.16	15.71	140205			
140179	11.19	1.14	15.65	140206	7.24	.94	11.49
140180	11.08	1.16	15.65	140206	7.24	.93	11.53
140180	11.13	1.16	15.70	140207	6.64	.88	10.38
140181	9.46	1.17	15.71	140207	6.68	.88	10.23
140181	9.48	1.15	15.60	140208	6.31	.92	9.55
140182				140208	6.32	.84	9.51
140183	9.43	1.16	15.78	140209	5.76	.78	8.16
140183	9.56	1.16	15.66	140209	5.85	.78	8.21
140184				140210	5.26	.68	6.85
140185				140210	5.32	.70	6.86
140186	8.96	1.12	14.66				
140186	8.99	1.11	14.56				

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140211	3.71	.50	3.44	140235			
140211	3.83	.54	3.33	140235			
140212	9.36	1.13	15.73	140236			
140212	9.77	1.14	15.32	140236			
140213	9.41	1.18	15.40	140237	6.29	.84	8.92
140213	9.43	1.14	15.63	140237	6.35	.84	8.86
140214	8.35	1.08	14.59	140238			
140214	8.43	1.08	14.63				
140215	7.85	1.02	13.99	140239	6.05	.80	8.34
140215	7.95	1.04	14.01	140239	6.12	.81	8.22
140216	7.83	1.03	13.84	140240	6.07	.81	8.11
140216	7.86	1.03	13.84	140240	6.10	.77	8.10
140217	7.27	.95	11.57	140241			
140217	7.31	.96	12.13	140241			
140218	7.23	.93	11.81	140242			
140218	7.27	.94	11.59	140243	5.87	.76	7.78
140219	7.05	.93	11.49	140243	5.93	.76	7.73
140219	7.14	.92	11.48	140244	10.45	1.10	13.76
140220	6.92	.90	11.22	140244	10.45	1.12	13.82
140220	7.02	.91	11.21	140245	10.39	1.11	13.82
140221	6.89	.91	11.00	140245	10.47	1.11	13.89
140221	7.13	.93	10.95	140246	10.52	1.14	13.82
140222	6.49	.90	9.89	140246	10.53	1.15	13.86
140222	6.53	.86	9.96	140247	9.96	1.18	14.62
140223				140247	10.11	1.14	15.08
140224				140248	10.81	1.16	14.75
140224				140248	10.97	1.15	15.11
140225				140249	10.77	1.17	15.29
140226				140249	10.87	1.16	15.56
140227				140250	10.33	1.16	15.75
140227				140250	10.80	1.17	15.76
140228	6.92	.92	10.68	140251	9.97	1.22	15.89
140228	6.96	.91	10.66	140251	10.04	1.20	16.14
140229				140252	9.99	1.19	15.72
140230	6.88	.91	10.51	140252	10.08	1.17	15.77
140230	6.91	.92	10.58	140253	9.65	1.19	15.76
140231	6.87	.91	10.45	140253	9.67	1.19	15.72
140231	6.92	.93	10.51	140254	9.55	1.18	15.58
140232				140254	9.60	1.19	15.67
140233	6.82	.92	10.33	140255	9.34	1.16	15.63
140233	6.82	.91	10.31	140255	9.63	1.16	15.78
140234	6.70	.90	10.31	140256	8.92	1.14	15.39
140234	6.70	.90	10.25	140256	8.98	1.13	15.48
				140257	8.53	1.24	15.43

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140257	8.56	1.12	15.19	140279	7.90	1.01	12.26
140258	8.30	1.09	14.87	140279	7.96	1.02	12.17
140258	8.36	1.09	15.08	140280	10.71	1.13	14.00
140259	7.60	.98	12.21	140280	10.75	1.16	13.85
140259	7.76	.97	12.26	140281	10.70	1.11	13.75
140260	7.55	.92	11.28	140281	10.73	1.11	13.86
140260	7.63	.95	11.00	140282	12.11	1.14	14.30
140261	7.31	.87	10.10	140282	12.36	1.15	14.36
140261	7.34	.85	9.91	140283	12.09	1.15	14.69
140262	11.18	1.09	14.66	140283	12.12	1.15	14.74
140262	11.26	1.11	14.60	140284	12.05	1.17	14.63
140263	11.42	1.11	14.70	140284	12.06	1.16	14.94
140263	11.45	1.12	14.75	140285	12.30	1.16	15.23
140264	10.33	1.12	14.39	140285	12.41	1.16	15.12
140264	10.40	1.12	14.20	140286	12.01	1.18	15.42
140265	10.60	1.13	14.50	140286	12.02	1.16	15.76
140265	10.65	1.13	14.30	140287	11.60	1.19	15.97
140266	10.90	1.13	14.56	140287	11.68	1.19	15.92
140266	10.91	1.12	14.51	140288	10.78	1.17	15.77
140267	10.73	1.13	14.31	140288	10.85	1.20	15.90
140267	10.73	1.12	14.37	140289	9.88	1.17	15.98
140268	10.46	1.13	14.12	140289	9.95	1.17	15.92
140268	10.57	1.12	14.02	140290	9.98	1.20	16.31
140269	10.55	1.11	14.18	140290	10.02	1.19	16.46
140269	10.57	1.13	14.42	140291	9.80	1.19	16.52
140270	11.18	1.18	14.90	140291	10.04	1.21	16.48
140270	11.23	1.16	14.94	140292	9.71	1.21	16.45
140271	10.32	1.14	14.94	140292	9.80	1.18	16.33
140271	10.48	1.13	14.78	140293	9.78	1.18	16.05
140272	9.85	1.17	15.17	140293	9.78	1.18	16.19
140272	9.87	1.17	15.25	140294	9.65	1.18	16.31
140273	9.56	1.15	15.46	140294	9.68	1.17	16.11
140273	9.74	1.15	15.55	140295	8.84	1.14	15.44
140274	9.25	1.13	15.26	140295	8.93	1.15	15.27
140274	9.48	1.16	15.27	140296	8.66	1.12	14.75
140275	8.84	1.08	14.46	140296	8.67	1.12	14.70
140275	8.84	1.10	14.58	140297	8.37	1.05	13.44
140276	8.34	1.08	13.49	140297	8.45	1.05	13.22
140276	8.43	1.11	13.58	140298	7.88	.97	11.96
140277	8.04	1.05	12.60	140298	7.94	.98	11.99
140277	8.06	1.03	12.87	140299	7.36	.91	10.58
140278	7.97	1.03	12.41	140299	7.39	.89	10.66
140278	7.99	1.03	12.51	140300	10.41	1.08	14.97
				140300	10.41	1.11	15.08

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140301	10.62	1.09	15.02	140323	12.57	1.19	15.47
140301	10.64	1.07	15.10	140323	12.62	1.20	15.49
140302	11.10	1.11	15.15	140324	12.42	1.21	15.11
140302	11.20	1.13	15.31	140324	12.46	1.16	15.17
140303	11.34	1.15	15.51	140325	11.70	1.20	15.32
140303	11.42	1.14	15.51	140325	11.78	1.18	15.18
140304	11.71	1.15	15.42	140326	11.15	1.21	15.45
140304	11.73	1.14	15.32	140326	11.30	1.21	15.75
140305	12.59	1.19	15.53	140327	9.96	1.21	15.80
140305	12.63	1.19	15.51	140327	10.01	1.22	15.81
140306	11.95	1.16	15.54	140328	9.62	1.24	15.43
140306	12.08	1.17	15.59	140328	9.64	1.23	15.80
140307	11.42	1.19	15.59	140329	9.46	1.23	15.52
140307	11.42	1.19	15.23	140329	9.65	1.23	15.95
140308	11.68	1.20	15.57	140330	9.52	1.24	16.09
140308	11.75	1.21	15.75	140330	9.58	1.22	16.30
140309	11.14	1.21	15.58	140331	9.46	1.24	15.41
140309	11.18	1.21	15.66	140331	9.52	1.22	15.74
140310				140332	9.31	1.08	15.48
				140332	9.36	1.13	15.46
140311	9.78	1.21	15.59	140333	9.34	1.15	15.40
140311	9.79	1.22	15.54	140333	9.37	1.17	15.30
140312	9.64	1.23	15.79	140334	9.17	1.16	15.09
140312	9.65	1.21	15.43	140334	9.26	1.16	15.27
140313	9.73	1.22	15.88	140335	8.91	1.14	14.89
140313	9.75	1.23	16.02	140335	8.92	1.15	15.00
140314	9.44	1.22	15.36	140336	8.44	1.11	14.77
140314	9.48	1.21	15.56	140336	8.64	1.12	14.77
140315	9.08	1.20	15.03	140337	8.29	1.09	14.10
140315	9.11	1.19	15.11	140337	8.40	1.11	13.89
140316	8.69	1.16	14.44	140338	7.42	.85	9.50
140316	8.70	1.15	14.53	140338	7.46	.87	9.57
140317	8.23	1.09	13.29	140339	7.28	.81	9.02
140317	8.28	1.10	13.51	140339	7.37	.82	9.19
140318	7.40	1.00	11.17	140340			
140318	7.52	1.00	11.24				
140319	5.09	.62	5.52	140341			
140319	5.12	.61	5.57	140342			
140320	10.14	1.15	13.97	140343	9.02	1.11	13.59
140320	10.22	1.11	14.06	140343	9.08	1.09	13.81
140321	10.23	1.12	14.20	140344	8.64	1.01	12.19
140321	10.39	1.11	14.70	140344	8.69	1.02	12.30
140322	11.61	1.14	15.13	140345	8.35	.96	11.33
140322	11.66	1.15	15.23				

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140345	8.37	.97	11.71	140370	9.41	1.12	15.60
140346	8.34	.96	11.46	140370	9.43	1.15	15.72
140346	8.43	.98	11.77	140371	9.53	1.13	15.86
140347	8.24	.94	11.37	140371	9.55	1.14	15.81
140347	8.31	.95	11.47	140372	9.46	1.12	15.83
140348				140372	9.61	1.15	15.97
140349				140373	9.48	1.14	15.70
140350	8.00	.90	10.31	140373	9.49	1.15	15.98
140350	8.02	.90	10.39	140374	9.32	1.12	15.70
140351				140374	9.38	1.13	15.93
140352	7.83	.85	9.73	140375	9.33	1.11	15.66
140352	7.88	.87	9.86	140375	9.41	1.13	15.50
140353				140376	9.11	1.04	15.39
140354				140376	9.12	1.08	15.55
140355	7.89	.83	9.78	140377	8.71	1.04	14.15
140355	7.91	.84	9.79	140377	8.81	1.05	14.27
140356				140378	7.92	.84	10.32
140357				140378	8.06	.85	10.38
140358	7.83	.85	9.71	140379	7.75	.76	9.15
140358	7.95	.83	9.80	140379	7.76	.76	9.23
140359				140380	10.43	1.01	13.87
140360	10.23	1.01	13.25	140380	10.45	1.03	13.88
140360	10.28	1.04	13.35	140381	10.38	1.02	13.74
140361	10.76	1.04	13.37	140381	10.47	1.03	13.86
140361	10.86	1.04	13.33	140382	11.45	1.04	14.11
140362	11.56	1.07	13.66	140382	11.53	1.05	14.07
140362	11.59	1.07	13.66	140383	13.33	1.09	15.14
140363	12.69	1.10	14.34	140383	13.92	1.11	15.06
140363	12.70	1.11	14.26	140384	12.61	1.03	15.15
140364	13.21	1.14	14.83	140384	12.78	1.08	15.45
140364	13.42	1.15	14.72	140385	12.30	1.10	15.79
140365	12.51	1.14	14.67	140385	12.39	1.10	15.99
140365	12.60	1.14	14.70	140386	11.77	1.11	16.01
140366	11.65	1.15	14.64	140386	11.77	1.11	15.82
140366	11.66	1.15	14.58	140387	10.77	1.10	16.74
140367	10.88	1.14	14.77	140387	10.86	1.12	16.33
140367	11.00	1.16	15.51	140388	9.66	1.10	16.65
140368	10.06	1.09	15.23	140388	9.72	1.11	16.27
140368	10.12	1.14	15.33	140389	9.66	1.10	16.33
140369	9.51	1.13	15.35	140389	9.68	1.11	16.30
140369	9.55	1.13	15.49	140390	9.67	1.08	16.22
				140390	9.68	1.10	16.48
				140391	9.71	1.10	16.19

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140391	9.72	1.13	16.27	140413	9.86	1.11	17.10
				140413	9.87	1.12	16.98
140392	9.64	1.04	15.84				
140392	9.73	1.09	16.15	140414	9.80	1.10	16.98
				140414	9.80	1.11	17.00
140393	9.76	1.11	16.02				
140393	9.82	1.12	15.92	140415	9.80	1.10	16.36
				140415	9.86	1.12	16.82
140394	9.83	1.10	16.07				
140394	9.87	1.13	16.03	140416	9.53	1.05	15.96
				140416	9.67	1.11	16.59
140395	9.49	1.10	15.91				
140395	9.50	1.11	15.99	140417	9.49	1.10	15.81
				140417	9.53	1.11	15.52
140396	9.48	1.12	15.72				
140396	9.53	1.12	15.81	140418	8.82	.96	12.80
				140418	8.84	.98	12.84
140397	9.08	1.05	14.17				
140397	9.16	1.05	14.22	140419	7.70	.72	8.39
				140419	7.77	.73	8.52
140398	8.13	.86	10.57				
140398	8.29	.88	10.65	140420	11.48	1.00	14.30
				140420	11.51	1.01	14.28
140399	7.64	.72	8.26				
140399	7.69	.74	8.32	140421	11.45	1.01	14.08
				140421	11.52	1.02	14.28
140400	11.02	.98	13.95				
140400	11.15	1.03	13.74	140422	11.45	1.02	14.28
				140422	11.51	1.03	14.31
140401	11.38	1.02	13.46				
140401	11.45	1.02	13.58	140423	11.91	1.08	15.15
				140423	12.09	1.09	14.91
140402	11.50	1.02	13.62				
140402	11.55	1.03	13.70	140424	12.59	1.03	15.34
				140424	12.60	1.07	15.40
140403	11.83	1.08	14.55				
140403	11.86	1.08	14.31	140425	12.29	1.08	15.42
				140425	12.33	1.08	15.59
140404	12.50	1.08	15.02				
140404	12.59	1.09	15.34	140426	11.75	1.09	15.64
				140426	11.90	1.15	15.65
140405	12.31	1.09	15.83				
140405	12.40	1.11	15.73	140427	10.31	1.08	15.72
				140427	10.33	1.12	16.06
140406	11.85	1.10	15.95				
140406	11.90	1.12	16.18	140428	9.64	1.07	16.22
				140428	9.79	1.12	16.46
140407	11.26	1.11	16.63				
140407	11.36	1.12	16.57	140429	9.72	1.08	16.49
				140429	9.73	1.09	16.24
140408	9.88	1.03	16.48				
140408	9.94	1.07	16.64	140430	9.69	1.10	16.52
				140430	9.87	1.12	16.65
140409	9.81	1.07	16.61				
140409	9.88	1.08	16.56	140431	9.53	1.09	16.25
				140431	9.66	1.11	16.41
140410	9.75	1.09	16.48				
140410	9.76	1.09	16.45	140432	9.51	1.03	15.41
				140432	9.58	1.09	15.85
140411	9.76	1.11	16.50				
140411	9.85	1.11	16.85	140433	9.55	1.09	15.65
				140433	9.67	1.11	16.07
140412	9.87	1.09	16.94				
140412	9.88	1.11	16.88	140434	9.66	1.04	16.31
				140434	9.68	1.04	16.31

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140435	9.34	1.02	15.67	140460	10.93	1.10	13.52
140435	9.46	1.03	15.89	140461	11.62	1.07	13.49
				140461	11.68	1.09	14.32
140436	8.97	1.01	15.30	140462	12.90	1.15	14.13
140436	9.01	1.01	15.35	140462	12.93	1.13	13.86
140437	8.90	.97	13.89	140463	12.74	1.17	14.20
140437	8.94	.97	13.86	140463	12.77	1.15	14.34
140438	7.40	.63	7.86	140464	12.10	1.16	14.03
140438	7.41	.64	7.92	140464	12.12	1.16	14.03
140439	7.51	.68	7.75	140465	11.55	1.16	14.05
140439	7.52	.69	7.70	140465	11.69	1.17	14.19
140440				140466	10.54	1.19	14.41
140441				140466	10.54	1.19	14.15
140442				140467	9.62	1.16	14.60
				140467	9.64	1.17	14.76
140443				140468	9.51	1.15	15.02
140444	8.48	1.04	14.63	140468	9.53	1.16	15.33
140444	8.51	1.08	14.65	140469	9.45	1.15	15.09
140445	8.36	1.01	13.78	140469	9.54	1.16	15.11
140445	8.39	1.02	14.01	140470	9.42	1.15	15.13
140446				140470	9.48	1.13	15.11
140447	7.57	.79	9.95	140471	9.52	1.15	14.87
140447	7.77	.81	10.09	140471	9.54	1.15	14.94
140448	7.58	.78	10.04	140472	9.42	1.14	15.24
140448	7.64	.79	10.00	140472	9.49	1.14	15.10
140449				140473	9.43	1.13	15.32
				140473	9.52	1.13	15.34
140450	7.16	.66	8.59	140474	9.42	1.13	15.15
140450	7.21	.71	8.69	140474	9.67	1.14	15.29
140451				140475	9.23	1.14	15.44
140452	7.17	.69	8.59	140475	9.39	1.13	15.34
140452	7.32	.69	8.56	140476	8.82	1.10	14.76
140453				140476	9.00	1.08	14.69
140454				140477	8.57	1.07	14.30
				140477	8.59	1.07	14.36
140455	7.14	.69	8.48	140478	7.27	.75	8.97
140455	7.32	.70	8.69	140478	7.29	.78	9.08
140456				140479	7.14	.74	8.52
140457	7.13	.68	8.53	140479	7.17	.75	8.69
140457	7.23	.70	8.59	140480	10.91	1.05	13.91
140458				140480	10.99	1.05	13.64
140459				140481	11.25	1.05	14.03
				140481	11.31	1.05	13.91
140460	10.91	1.08	13.51				

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140482	12.39	1.08	14.38				
140482	13.02	1.09	14.41	140506	11.99	1.13	13.84
				140506	12.18	1.10	13.79
140483	12.65	1.12	14.94				
140483	12.71	1.12	14.94	140507	12.06	1.11	14.22
				140507	12.09	1.11	14.33
140484	12.95	1.10	15.07				
140484	13.51	1.10	14.98	140508	13.26	1.12	14.49
				140508	13.43	1.15	14.33
140485	9.81	1.11	15.25				
140485	9.83	1.12	15.15	140509	12.23	1.13	14.31
				140509	12.24	1.15	14.28
140486	12.00	1.13	14.84				
140486	12.10	1.13	14.52	140510	11.65	1.15	14.20
				140510	11.67	1.17	14.25
140487	11.26	1.15	14.62				
140487	12.60	1.29	15.94	140511	11.24	1.17	14.77
				140511	11.41	1.17	14.43
140488	9.63	1.14	14.84				
140488	9.65	1.14	14.91	140512	9.69	1.17	14.92
				140512	9.70	1.16	14.83
140489	9.49	1.15	14.72				
140489	9.56	1.14	14.80	140513	9.53	1.17	15.52
				140513	9.54	1.13	15.35
140490	9.50	1.14	14.89				
140490	10.11	1.16	14.82	140514	9.66	1.19	15.81
				140514	9.74	1.19	15.62
140491	9.53	1.14	14.85				
140491	9.69	1.12	14.88	140515	9.68	1.19	16.04
				140515	9.68	1.18	15.64
140492	9.47	1.15	14.61				
140492	9.53	1.14	14.74	140516			
140493	9.50	1.13	14.78				
140493	9.54	1.13	14.76	140517	9.89	1.20	15.73
				140517	10.48	1.20	15.78
140494	9.31	1.15	14.65				
140494	9.32	1.13	14.75	140518	9.65	1.19	15.99
				140518	9.66	1.19	15.63
140495	9.25	1.14	14.78				
140495	9.32	1.15	14.90	140519	9.67	1.20	15.72
				140519	9.75	1.21	15.71
140496	9.20	1.14	14.51				
140496	9.21	1.15	14.54	140520	9.72	1.21	15.82
				140520	9.75	1.20	15.79
140497	8.67	1.10	13.96				
140497	8.69	1.11	13.96	140521	9.44	1.20	15.31
				140521	9.48	1.17	15.40
140498	7.23	.76	7.41				
140498	7.28	.75	7.21	140522	6.31	.85	9.58
				140522	6.37	.87	9.72
140499	6.76	.67	6.58				
140499	7.25	.67	6.62	140523	5.08	.76	8.37
				140523	5.10	.76	8.40
140500				140524			
140501				140525			
140502							
				140526	9.18	1.13	14.44
				140526	9.28	1.14	14.49
140503							
				140527	8.87	1.09	13.67
140504				140527	8.90	1.10	13.31
140505				140528	8.66	1.05	12.70

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140528	10.28	1.05	12.57	140553	9.70	1.19	15.80
140529				140553	9.73	1.19	15.52
140530				140554	9.73	1.19	15.63
140531	8.69	1.06	12.83	140554	9.78	1.21	15.84
140531	8.72	1.06	12.88	140555	9.71	1.20	15.67
140532				140555	9.71	1.20	15.68
140533	8.56	1.04	12.34	140556	9.74	1.21	15.70
140533	8.68	1.04	12.44	140556	9.77	1.21	15.63
140534				140557	9.54	1.22	14.03
140535	8.48	1.00	11.78	140557	9.80	1.16	14.70
140535	8.51	1.01	11.68	140558	9.16	1.23	13.82
140536				140558	9.46	1.23	13.68
140537	7.79	.93	10.31	140559	9.43	1.25	14.22
140537	7.79	.93	10.32	140559	9.46	1.26	14.00
140538				140560	9.43	1.24	14.44
140539	6.09	.76	7.64	140560	9.44	1.25	14.54
140539	6.18	.77	7.61	140561	9.20	1.23	14.55
140540				140561	9.28	1.26	14.50
140541	6.05	.75	7.76	140562	8.76	1.19	14.12
140541	6.11	.74	7.80	140562	8.79	1.18	14.04
140542				140563	8.30	1.04	11.42
140543	6.06	.76	7.95	140563	8.42	1.04	11.28
140543	6.09	.74	7.91	140564	5.63	.80	8.04
140544				140564	5.68	.82	8.13
140545	11.36	1.06	14.19	140565			
140545	11.40	1.07	14.11	140566			
140546	11.41	1.12	14.12	140567	11.35	1.09	13.58
140546	11.45	1.09	13.89	140567	11.50	1.16	14.08
140547	11.60	1.12	14.36	140568	11.83	1.21	14.71
140547	11.73	1.09	14.25	140568	11.86	1.24	14.75
140548	12.19	1.14	14.86	140569	12.04	1.24	14.70
140548	12.26	1.16	14.85	140569	12.12	1.23	14.74
140549	12.40	1.17	15.46	140570	10.02	1.25	14.41
140549	12.47	1.16	15.09	140570	10.26	1.25	14.62
140550	11.73	1.19	15.44	140571	10.96	1.25	14.40
140550	11.83	1.19	15.29	140571	11.04	1.24	14.50
140551	10.72	1.20	15.98	140572	10.10	1.26	14.99
140551	10.78	1.18	15.69	140572	10.11	1.27	14.89
140552	9.76	1.18	15.43	140573	9.48	1.24	14.70
140552	9.83	1.20	15.58	140573	10.43	1.25	14.89
				140574	9.42	1.26	14.84
				140574	9.52	1.26	14.81
				140575	9.44	1.22	15.27

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140575	9.48	1.17	15.13	140600			
140576	9.63	1.25	15.31	140601	6.46	.77	8.82
140576	9.68	1.24	15.35	140601	6.47	.77	8.84
140577	9.59	1.26	15.70	140602	6.44	.76	8.59
140577	9.64	1.25	15.75	140602	6.46	.74	8.50
140578	10.02	1.28	15.51	140603			
140578	10.53	1.28	15.39				
140579	9.66	1.26	15.43	140604	6.42	.76	8.71
140579	9.70	1.26	15.34	140604	6.64	.77	8.74
140580	9.60	1.27	15.49	140605	11.25	1.13	13.99
140580	9.76	1.28	15.47	140605	11.30	1.15	14.16
140581	8.92	1.24	15.02	140606	11.16	1.15	14.10
140581	8.96	1.24	15.00	140606	11.21	1.14	14.14
140582				140607	11.76	1.17	14.56
				140607	11.77	1.15	14.73
140583	7.38	1.07	12.32	140608	12.07	1.28	14.84
140583	7.40	1.08	11.94	140608	12.12	1.18	14.85
140584	6.17	.81	8.37	140609	11.70	1.21	14.94
140584	6.32	.83	8.26	140609	11.72	1.19	15.04
140585				140610	11.19	1.23	15.19
				140610	11.23	1.21	15.37
140586							
140587				140611	10.65	1.22	15.46
				140611	10.82	1.22	15.82
140588	8.36	1.05	14.11	140612	10.69	1.22	15.69
140588	8.40	1.10	14.26	140612	10.69	1.22	15.66
140589	8.10	1.09	13.82	140613	9.70	1.20	15.71
140589	8.15	1.09	13.75	140613	9.78	1.19	15.99
140590	7.95	1.08	13.65	140614	9.64	1.21	15.82
140590	7.98	1.08	13.44	140614	9.69	1.21	15.97
140591	7.59	1.04	12.95	140615	9.48	1.21	15.75
140591	7.62	1.03	12.79	140615	9.52	1.21	15.96
140592				140616	9.71	1.20	16.01
				140616	9.72	1.20	16.10
140593							
140594	7.48	1.04	12.70	140617	9.68	1.22	15.91
140594	7.59	1.02	12.62	140617	9.74	1.23	16.07
140595	7.02	.95	11.32	140618	9.60	1.22	15.79
140595	7.11	.95	11.34	140618	9.65	1.22	15.84
140596				140619	9.32	1.22	15.65
				140619	9.32	1.21	15.62
140597				140620	8.97	1.20	15.20
				140620	10.23	1.19	15.06
140598							
140599	6.49	.78	8.88	140621	8.79	1.18	14.73
140599	6.51	.79	8.85	140621	8.83	1.17	14.78
				140622	7.54	1.07	13.00

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140622	7.54	1.09	12.93	140645			
140623	6.02	.71	7.40	140646	7.88	1.16	13.45
140623	6.08	.70	7.47	140646	7.93	1.15	13.54
140624	11.21	1.18	13.58	140647	7.67	1.10	12.99
140624	11.36	1.17	13.82	140647	7.72	1.11	12.94
140625	11.31	1.17	13.68	140648			
140625	11.36	1.16	13.93	140649	7.06	1.02	11.72
140626	11.44	1.20	13.86	140649	7.12	1.01	11.80
140626	11.51	1.19	13.90	140650			
140627	11.69	1.14	16.18	140651	6.93	1.04	11.43
140627	11.71	1.13	16.31	140651	6.98	1.01	11.49
140628	12.01	1.15	16.49	140652	6.95	1.03	11.47
140628	12.06	1.14	16.58	140652	7.00	1.03	11.62
140629	11.60	1.16	16.51	140653			
140629	11.63	1.14	16.58	140654	6.93	1.03	11.38
140630	10.92	1.17	16.86	140654	7.40	1.02	11.45
140630	11.01	1.17	16.71	140655			
140631	10.18	1.18	17.10	140656	5.92	.78	7.68
140631	10.30	1.17	17.24	140656	5.95	.78	7.78
140632	9.54	1.17	17.09	140657	5.87	.71	6.42
140632	9.72	1.17	17.24	140657	5.90	.72	6.48
140633	10.05	1.17	17.34	140658			
140633	10.06	1.19	17.36	140659	5.89	.72	6.32
140634	9.93	1.19	17.40	140659	5.95	.73	6.37
140634	9.97	1.18	17.24	140660			
140635	9.80	1.17	17.50	140661	5.96	.72	6.32
140635	9.95	1.15	17.50	140661	5.97	.72	6.45
140636	9.73	1.16	17.44	140662	11.90	1.18	16.03
140636	9.79	1.15	17.34	140662	11.98	1.17	16.14
140637	9.39	1.14	17.18	140663	11.65	1.17	16.40
140637	9.55	1.15	17.17	140663	11.81	1.15	16.54
140638	8.82	1.14	16.62	140664	11.43	1.18	16.94
140638	8.82	1.13	16.65	140664	11.45	1.17	16.87
140639	8.28	1.10	15.86	140665	11.07	1.18	16.92
140639	8.77	1.11	15.77	140665	11.14	1.18	17.00
140640	7.28	1.02	14.12	140666	10.32	1.18	17.05
140640	7.29	1.05	14.07	140666	10.47	1.22	16.99
140641	7.53	.77	6.79	140667	10.07	1.21	17.10
140641	7.56	.75	6.91	140667	10.09	1.21	16.85
140642				140668	9.84	1.21	17.21
140643				140668	9.95	1.20	17.35
140644							

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140669				140691	9.62	1.18	14.58
				140691	9.80	1.18	14.64
140670	9.96	1.20	17.37				
140670	10.00	1.20	17.45	140692	10.37	1.17	13.29
				140692	10.40	1.17	13.60
140671	9.48	1.20	17.05				
140671	9.51	1.21	17.06	140693	9.42	1.12	11.66
				140693	9.49	1.12	11.58
140672	8.92	1.16	16.64				
140672	9.02	1.17	16.67	140694	10.21	1.11	9.65
				140694	10.35	1.13	9.71
140673	8.75	1.15	16.42				
140673	8.77	1.15	16.56	140695	4.77	.74	2.10
				140695	4.80	.79	1.99
140674	8.48	1.12	15.98				
140674	8.53	1.13	15.96	140696			
140675	8.06	1.08	14.69	140697			
140675	8.07	1.09	14.60	140698			
140676	5.21	.59	6.97	140699			
140676	5.26	.61	7.02				
140677	10.13	1.19	16.85	140700			
140677	10.18	1.19	17.01	140701			
140678	10.27	1.19	17.06				
140678	10.29	1.18	17.00	140702	10.17	1.00	10.85
				140702	10.34	1.01	11.00
140679	10.06	1.20	16.88				
140679	10.12	1.21	17.07	140703			
140680	9.78	1.19	16.79	140704	11.37	1.06	9.90
140680	9.87	1.18	17.09	140704	11.52	1.08	9.89
140681	9.18	1.16	16.72	140705	12.05	1.13	9.62
140681	9.31	1.16	16.66	140705	12.07	1.13	9.58
140682	8.53	1.13	15.85	140706	12.12	1.11	9.15
140682	8.62	1.11	15.82	140706	12.20	1.13	9.26
140683	9.12	1.11	15.01	140707	12.17	1.11	9.11
140683	9.14	1.10	15.21	140707	12.18	1.11	9.00
140684	8.57	1.03	12.80	140708			
140684	8.63	1.00	12.91				
140685	7.85	.98	11.04	140709	10.40	1.02	7.11
140685	7.91	.94	11.14	140709	10.43	1.09	7.07
140686	8.82	.94	9.20	140710	8.89	.95	5.47
140686	8.83	.96	9.14	140710	8.91	.95	5.48
				140711			
140687	10.07	.94	5.79				
140687	10.14	.93	5.70	140712	7.65	.94	4.72
				140712	7.72	.96	5.02
140688	9.14	1.19	15.05				
140688	9.24	1.19	15.21	140713	2.82	.64	1.01
				140713	2.87	.67	.84
140689	9.12	1.20	15.39				
140689	9.12	1.19	15.34	140714	.89	.50	.26
				140714	.91	.51	.26
140690	9.09	1.20	15.29				
140690	9.22	1.18	15.19	140715			

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
140716				140749			
140717				140750	9.36	1.11	14.24
140718				140750	9.46	1.11	14.28
140719				140751	9.87	1.14	14.01
140720				140751	9.96	1.13	13.89
140721				140752	9.18	1.11	13.20
140722				140752	9.23	1.09	13.07
140723				140753	9.14	1.10	12.89
140724				140753	9.18	1.22	12.93
140725				140754	8.32	1.06	11.67
140726				140754	8.41	1.06	11.98
140727				140755	7.77	.99	10.36
140728				140755	7.79	.97	10.52
140729				140756			
140730				140756			
140731				140757			
140732				140757			
140733				140758	7.15	.89	8.79
140734				140758	7.16	.90	8.77
140735				140759	6.30	.84	7.64
140736				140759	6.31	.86	7.42
140737				140760			
140738				140760			
140739				140761	1.24	.44	0.00
140740				140761	1.25	.41	0.00
140741				140762			
140742				140762			
140743				140763	1.21	.39	0.00
140744				140763	1.22	.37	0.00
140745				140764			
140746				140764			
140747				140765	1.20	.37	0.00
140748				140765	1.21	.39	0.00
140749				140766	10.85	1.25	16.03
140750				140766	10.86	1.20	16.21
140751				140767	10.39	1.21	15.71
140752				140767	10.44	1.18	15.86
140753				140768	9.70	1.13	14.83
140754				140768	9.77	1.14	14.99
140755				140769	9.43	1.12	14.07
140756				140769	9.51	1.13	14.02
140757				140770	8.83	1.07	12.89
140758				140770	8.90	1.07	12.73

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140771	8.93	1.06	11.68	140792	9.47	1.18	17.16
140771	9.14	1.08	11.75	140793	9.15	1.18	16.68
140772	.72	.32	0.00	140793	9.19	1.18	16.88
140772	.76	.38	0.00	140794	8.76	1.15	16.20
140773	9.97	1.20	17.04	140794	8.79	1.17	15.98
140773	10.14	1.23	16.93	140795	7.09	1.01	13.45
140774	9.77	1.27	16.67	140795	7.21	1.01	13.43
140774	9.84	1.19	16.70	140796	1.01	.49	1.40
140775	9.71	1.21	16.63	140796	1.08	.39	1.70
140775	9.75	1.20	16.47	140797	11.36	1.10	15.39
140776	9.74	1.21	16.49	140797	11.55	1.09	15.63
140776	9.78	1.21	16.60	140798	11.37	1.13	15.38
140777	9.75	1.23	16.42	140798	11.54	1.09	15.43
140777	9.86	1.22	16.60	140799	11.49	1.11	15.44
140778	8.99	1.19	15.93	140799	11.58	1.09	15.39
140778	9.03	1.18	15.95	140800	12.03	1.11	15.75
140779	8.44	1.09	14.99	140800	12.08	1.12	15.72
140779	8.45	1.11	15.07	140801	12.23	1.14	16.11
140780	8.39	1.06	13.94	140801	12.36	1.14	16.04
140780	8.46	1.05	13.76	140802	12.53	1.16	16.30
140781	.82	.35	.24	140802	12.66	1.16	16.18
140781	1.88	.55	.92	140803	12.65	1.32	16.57
140782	11.66	1.22	16.63	140803	12.77	1.16	16.40
140782	11.82	1.19	16.63	140804	12.23	1.18	16.69
140783	11.65	1.19	16.77	140804	12.33	1.18	16.68
140783	11.66	1.19	16.86	140805	11.50	1.16	16.89
140784	11.45	1.17	16.52	140805	11.74	1.20	16.90
140784	11.51	1.19	16.63	140806	10.88	1.24	17.11
140785	11.41	1.19	16.80	140806	10.92	1.17	16.80
140785	11.43	1.21	17.01	140807	10.10	1.20	16.82
140786	10.87	1.20	16.58	140807	10.10	1.20	16.81
140786	10.92	1.23	16.52	140808	10.02	1.18	16.95
140787	10.13	1.18	16.59	140808	10.06	1.18	16.90
140787	10.13	1.20	16.59	140809	9.95	1.19	16.85
140788	10.03	1.19	16.78	140809	9.96	1.19	16.95
140788	10.10	1.20	16.99	140810	9.83	1.18	16.91
140789	9.95	1.20	16.70	140810	9.93	1.20	17.05
140789	10.03	1.20	16.67	140811	9.74	1.19	16.98
140790	9.64	1.21	17.06	140811	9.78	1.19	16.97
140790	9.68	1.24	16.85	140812	9.57	1.17	16.71
140791	9.58	1.20	17.04	140812	9.63	1.17	16.80
140791	9.60	1.19	16.85	140813	9.25	1.14	16.26
140792	9.46	1.18	16.84	140813	9.26	1.16	16.13

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
--							
140814	8.10	1.09	14.02				
140814	8.28	1.07	14.05	140836	3.65	.70	8.94
				140836	3.71	.70	9.02
140815	1.32	.52	3.62				
140815	1.35	.52	3.81	140837	12.60	1.12	15.91
				140837	12.66	1.10	15.71
140816	1.06	.44	2.83				
140816	1.08	.42	2.88	140838	12.69	1.17	15.46
				140838	12.88	1.13	15.48
140817	8.92	1.13	15.85				
140817	8.96	1.15	15.49	140839	13.88	1.16	16.01
				140839	13.92	1.15	16.09
140818	8.63	1.12	15.11				
140818	8.66	1.10	14.89	140840	15.14	1.17	16.09
				140840	15.27	1.18	16.22
140819	8.39	1.08	14.00				
140819	8.44	1.07	13.80	140841	15.60	1.22	16.70
				140841	15.62	1.17	16.38
140820	7.93	1.03	12.96				
140820	7.93	1.02	12.75	140842	14.64	1.19	16.48
				140842	14.65	1.19	16.44
140821							
140821				140843	14.44	1.21	16.74
				140843	14.50	1.21	16.74
140822	5.47	.88	10.69				
140822	5.47	.85	10.56	140844	13.17	1.21	16.81
				140844	13.37	1.22	16.96
140823	3.02	.70	8.68				
140823	3.04	.74	8.64	140845	12.27	1.25	16.99
				140845	12.36	1.23	17.10
140824							
140824				140846	10.93	1.26	16.90
				140846	10.94	1.23	16.95
140825	3.06	.68	8.71				
140825	3.12	.70	8.73	140847	10.51	1.22	17.06
				140847	10.53	1.23	17.12
140826							
140826				140848	10.48	1.24	17.21
				140848	10.51	1.24	17.14
140827	3.33	.71	8.71				
140827	3.34	.71	8.77	140849	10.23	1.24	17.35
				140849	10.36	1.24	17.36
140828	3.09	.68	8.75				
140828	3.10	.68	8.70	140850	10.37	1.24	17.25
				140850	10.39	1.24	17.35
140829							
140829				140851	10.29	1.26	17.69
				140851	10.47	1.23	17.21
140830							
140830				140852	9.87	1.25	16.97
				140852	9.99	1.24	17.08
140831							
140831				140853	8.89	1.18	15.23
				140853	8.93	1.17	15.30
140832	3.45	.70	8.79				
140832	3.52	.68	8.76	140854	8.60	1.12	14.71
				140854	8.68	1.07	14.81
140833							
140833				140855	4.99	.76	9.11
				140855	5.02	.75	9.18
140834	3.77	.69	8.88				
140834	3.83	.72	8.98	140856	4.94	.75	9.02
				140856	4.97	.74	9.05
140835							
140835				140857	11.70	1.11	15.32

Table C.2 Nutrient Duplicate Measurements

Sample ID NO2+NO3	Silicate	Phosphate	NO2+NO3	Sample ID	Silicate	Phosphate	
140857	11.71	1.10	15.42	140867	9.89	1.21	16.43
140858	11.83	1.11	15.46	140867	10.00	1.20	16.47
140858	12.03	1.14	15.44	140868	9.57	1.20	16.06
140859	11.84	1.11	15.44	140868	9.72	1.20	16.35
140859	12.00	1.12	15.16	140869	10.24	1.25	16.76
140860	12.68	1.16	15.66	140869	10.34	1.23	16.98
140860	12.70	1.15	15.68	140870	10.11	1.27	16.80
140861	14.55	1.19	16.20	140870	10.25	1.23	17.04
140861	14.58	1.20	16.23	140871	9.85	1.21	16.63
140862	13.92	1.21	16.54	140871	9.94	1.20	16.74
140862	13.92	1.23	16.33	140872	10.26	1.26	17.13
140863	11.95	1.19	16.09	140872	10.37	1.25	17.15
140863	11.98	1.18	16.33	140873	9.31	1.19	15.85
140864	11.29	1.21	16.58	140873	9.41	1.21	15.94
140864	11.35	1.19	16.38	140874	7.72	1.05	13.73
140865	10.50	1.21	16.61	140874	7.81	1.07	13.83
140865	10.56	1.19	16.72	140875	2.88	.71	7.97
140866	10.14	1.20	16.46	140875	3.00	.72	7.98
140866	10.21	1.21	16.69	140876	1.88	.51	5.44
				140876	1.92	.51	5.40

5. Dissolved Inorganic Carbon in Seawater

Bob Gershey

a. Description of Equipment and Technique

The total dissolved inorganic carbon content of seawater is defined as the total concentration of carbonate ion, bicarbonate ion and unionized species of carbon dioxide. Before analysis, the sample is treated with acid to convert all ionized species to the unionized form, which is then separated from the liquid phase and subsequently measured coulometric titration technique. This involves the reaction of carbon dioxide gas with a dimethylsulfoxide solution of ethanoline to produce hydroxyethylcarbamic acid. The acidic solution is titrated with hydroxide ion formed by the electrolytic decomposition of water. The progress of the titration is followed through colorimetric measurement of the absorbance of a Ph indicator dye (thymolphthalein) in the ethanoline solution.

A known volume of seawater is dispensed into a stripping chamber from a pipet of known volume and temperature controlled to within 0.4 °C. It is then acidified with ten percent its volume of an 8% solution of carbon dioxide-free phosphoric acid. The solution is stripped of carbon dioxide gas by bubbling with a stream of nitrogen gas directed through a glass frit. The carrier gas exiting the stripper passes through a magnesium perchlorate trap to remove water vapour and acidic water droplets.

The gas stream is then directed into the coulometric titrator where the total amount of carbon dioxide gas is quantified. The coulometer is calibrated in two ways. Calibration using gas loops is accomplished by filling stainless steel sample loops (1.5, 2.5 ml) with 99.995% carbon dioxide gas and injecting these into the coulometer. The temperature and pressure of the gas within the loops must be known to within 0.05 °C and 20 Pa respectively. Standard solutions of sodium carbonate are also used to calibrate the system. These samples are treated in the same manner as a seawater sample.

Values are reported in units of $\mu\text{mol}/\text{kg}^{-1}$. The overall precision of the analysis should be at least $1.5 \mu\text{mol}/\text{kg}^{-1}$ for samples with concentrations in the range of 1800-2300 $\mu\text{mol}/\text{kg}^{-1}$.

b. Sampling Procedure and Data Processing Technique

Water samples are initially collected using a Niskin bottle or similar sampler. Samples for analysis of total inorganic carbon must be taken as soon as possible after recovery of the samples to minimize exchange of carbon dioxide gas with the head space in the sampler which will typically result in a loss of carbon dioxide. It is desirable that the samples be drawn before half the sampler is emptied and within ten minutes of recovery. Clean borosilicate glass bottles are rinsed twice with 30 - 50 ml of the sample. The bottle is then filled from the bottom using a length of vinyl tubing attached to the spigot of the sampler. The sample is overflowed by at least a half of the volume of the bottle (typically 250 ml). A head space of 1% is left to allow for expansion without leakage. If samples are not to be analysed within four to five hours, the sample are poisoned with 100 $\mu\text{l}/250 \text{ ml}$ of 50% saturated mercuric chloride solution. The bottle is tightly sealed and stored preferably at the temperature of collection.

c. Replicate Analyses

The following carbonate detection limit was applied. All values at or below the detection limit were set to zero.

Carbonate 0.6 micro moles/Kg

One duplicate sample is typically drawn for each deep CTD cast. Table C.3 lists the duplicate measurements.

Table C.3 Carbonate Duplicate Measurements

Sample ID Number	Total Carbonate
140208	2113.5
140208	2114.4
140214	2154.1
140214	2155.1
140217	2136.5
140217	2136.8
140245	2158.0
140245	2158.2
140249	2157.6
140249	2157.9
140265	2155.4
140265	2164.5
140505	2149.2
140505	2149.5
140548	2152.2
140548	2152.6
140566	2152.8
140566	2153.7
140609	2134.7
140609	2135.6
140627	2150.9
140627	2153.0
140666	2151.8
140666	2152.3
140681	2150.3
140681	2150.5
140768	2135.1
140768	2135.6
140774	2150.8
140774	2151.4
140785	2153.5
140785	2154.2
140839	2157.4
140839	2157.5
140841	2099.4
140841	2157.0

d. Blank Value

The blank value of 4.2 micro moles/Kg was subtracted from all data.

e. Error Estimates

The data presented here has an accuracy of 1.0 micro moles/Kg and a precision of 1.1 micro moles/Kg.

6. Alkalinity

Frank Zemlyak

a. Description of Equipment and Technique

Total alkalinity is determined using the Marine Chemistry automated titration system. Total alkalinity is determined using a potentiometric titration of the sea water sample using hydrochloric acid. Once the sample is connected to the system, the operation proceeds automatically, from the glass reaction vessel being rinsed and filled with the sea water sample, to the final calculations at the conclusion of the titration.

When the reaction vessel is filled, the semi-micro combination Ross electrode senses when the sample has come to equilibrium, the initial relative mvolt reading is then logged, at the same time, the cell temperature is also recorded. At this point, a rather large quantity of 0.2N hydrochloric acid, is added to the cell via a Metrohm E-655 Dosimat. The increase in volume is accommodated by the withdrawal, by a stepper motor via an Acme lead screw, of an internal glass piston. This large quantity of acid added titrates the sample beyond the carbonate endpoint, at this point, smaller aliquots (0.040mL) of acid are added until the sample has been titrated to and beyond the second inflection point. With each addition of acid the sample is allowed to come to equilibrium, the mvolt reading is logged. Thus, with these relative changes in the voltage in the cell, the endpoint is calculated by using a modified Gran function. Corrections to the final total alkalinity result are made by using the sample salinity, sample temperature and the nutrients, silicate and phosphate.

b. Sampling Procedure and Data Processing Technique

The 500 mlitre samples used for alkalinity analysis are collected from 8 L Niskin bottles in much the same fashion as oxygen samples. The samples were stored in a cold water bath whilst awaiting analysis.

7. CFC's

Mike Hingston

a. Description of Equipment and Technique

The analyses are carried out on two purge and trap systems developed at the Bedford Institute of Oceanography. The water samples are injected into the systems directly from the syringes. To ensure proper rinsing, at least two volumes of water is passed through the sample pipette before the actual sample volume. The samples are purged for 4 minutes with ultra high purity nitrogen at a flow rate of 60 ml/min. The components are trapped in Porapak-N trap which is cooled to a temperature of less than 10 C. They are then desorbed by heating the trap up to at least 170 C. The contents of the trap are then passed through a 75m DB-624 megabore column.

b. Sampling Procedure and Data Processing Technique

All samples are collected directly from the Niskin bottles using 100 MI syringes. The syringes are rinsed three times before they are filled. To prevent contamination, the CFC samples are the first samples which are collected from the Niskin bottles. The samples are then stored in a water bath of continuously flowing surface sea water until analysis. Air samples from the winch room are taken periodically to ensure that it has not become contaminated. The analysis of the samples is always completed within 24 hours after they have been drawn.

c. Replicate analysis

The following CFC detection limits were applied. All values at or below the detection limit were set to zero.

CFC-11	0.022 pico moles/Kg
CFC-12	0.017 pico moles/Kg
CFC-113	0.010 pico moles/Kg
Carbon Tetrachloride	0.040 pico moles/Kg
Methyl Chloroform	0.017 pico moles/Kg

Duplicates are taken at each station, with some of these being run on each system to ensure that the results are comparable. Table C.4 lists the duplicate measurements.

Table C.4 CFC Duplicate Measurements

Sample ID Number	CFC 12	CFC 11	CFC 113	Methyl Chl.	Carbon Tet.
140205	2.724	5.191	.941	16.804	9.954
140205	3.223	5.880	1.151	20.909	12.227
140206	2.097	3.970	.678	10.091	7.428
140206	2.606	4.721	.811	16.654	9.752
140215	2.385	3.911	.659	10.634	6.934
140215	2.449	4.358	.809	15.775	8.961
140251	1.778	2.899	.300	9.113	5.786
140251	1.843	3.283	.473	13.909	7.129
140255	2.086	3.684	.504	14.468	7.737

140255	2.318	3.798	.548	14.609	7.849
140266	1.139	2.208	.183	15.115	4.689
140266	1.285	2.336	.168	10.939	4.588
140272	1.522	3.060	.384	9.132	5.843
140272	2.103	3.581	.428	13.636	7.513
140283	.904	1.982	.228	.608	3.703
140283	1.390	2.259	.320	8.934	5.000
140290	1.672	3.030	.281	9.014	5.376
140290	1.975	3.549	.489	35.129	7.555
140311	1.564	3.245	.391	6.027	5.747
140311	2.038	3.667	.435	17.596	7.837
140327	1.815	3.240	.295	11.921	6.945
140327	1.895	2.944	.228	4.029	5.419
140365	.966	1.414	.107	3.328	2.913
140365	1.299	1.537	.051	6.023	3.963
140370	3.290	3.811	.486	14.412	7.956
140370	5.029	3.413	.238	10.182	6.713
140383	.670	1.603	.122	2.867	2.656
140383	.997	1.803	.110	7.316	4.379
140391	2.263	3.740	.378	14.467	7.865
140391	3.045	3.584	.231	15.428	7.406
140419	2.503	4.510	.495	13.692	8.567
140419	2.814	4.539	.502	12.340	8.156
140424	.953	1.912	.128	7.406	4.463
140424	.974	1.888	.118	7.250	4.435
140434	1.869	3.433	.371	9.329	5.128
140434	1.929	3.794	.498	14.510	7.938
140466	1.369	2.316	.225	6.486	4.377
140466	1.481	2.249	.182	5.496	4.081
140476	1.975	3.596	.597	9.352	4.470
140476	2.109	4.280	.580	16.286	8.842
140481	1.397	2.579	.266	10.704	5.594
140481	2.978	4.849	1.078	14.888	8.096
140488	1.795	3.279	.486	9.606	5.651
140488	1.949	3.640	.458	14.476	7.669
140498	2.670	4.927	.745	18.753	10.531
140498	2.802	4.907	.665	17.772	10.457
140550	.858	1.745	.087	6.745	4.221
140550	1.041	1.706	.069	4.357	3.611
140560	1.788	3.564	.289	14.110	7.576
140560	2.802	3.642	.383	15.158	7.849
140567	1.110	2.215	.199	9.308	5.153
140567	1.267	2.235	.182	1.527	3.902
140612	1.382	2.928	.786	13.092	6.557
140612	1.693	2.996	.255	12.010	6.482
140622	2.275	4.737	.528	9.246	9.024
140622	2.450	4.845	.617	18.508	10.116
140628	.714	1.556	.079	1.481	2.965
140628	.977	1.855	.098	7.210	4.439
140638	1.745	3.542	.407	6.988	6.238
140638	2.356	3.736	.363	8.522	6.488
140664	1.111	2.004	.116	6.869	4.592
140664	1.117	2.037	.121	7.343	4.755
140674	2.237	3.697	.553	4.387	6.061
140674	2.334	4.271	.514	16.245	8.490
140681	1.674	3.422	.539	3.456	4.914
140681	2.184	3.905	.428	14.592	7.562
140695	2.909	5.163	.999	4.035	7.267
140695	3.007	5.883	.935	22.883	12.072
140767	2.170	3.995	.642	15.347	7.877

140767	2.595	3.451	.585	11.244	6.256
140770	2.295	4.040	.733	13.128	6.342
140770	3.159	4.288	.782	12.608	7.891
140777	2.052	3.144	.517	28.808	5.831
140777	2.282	3.099	.469	13.181	5.798
140778	2.101	3.798	.631	14.307	7.417
140778	2.332	3.209	.568	10.906	4.881
140787	1.461	2.559	.368	8.701	3.926
140787	1.648	3.025	.398	11.837	6.434
140809	1.179	2.532	.298	19.237	5.475
140809	1.648	3.240	.429	13.166	6.838
140839	.890	1.579	.178	3.153	2.862
140839	1.050	1.778	.192	6.820	4.230
140860	.943	1.734	.188	1.614	2.348
140860	1.099	1.885	.242	7.742	4.302
140870	1.417	2.711	.342	10.537	5.791
140870	1.648	2.728	.346	10.281	5.690

d. Standards Used

Standardization is carried out using gas standards made up at Brookhaven National Laboratories. Standard volumes are corrected for lab temperature and pressure. Results are reported in units of pmol/kg of sea water. Clean air samples are also analyzed with each station, as a check on the standardization.

e. Blanks

The following CFC blank values were subtracted from all data.

CFC-11	0.007 pico moles/Kg
CFC-12	0.006 pico moles/Kg
CFC-113	0.003 pico moles/Kg
Carbon Tetrachloride	0.013 pico moles/Kg
Methyl Chloroform	0.005 pico moles/Kg

f. Error Estimates

The data presented here has precisions as indicated below. Precisions are expressed as a percent of the data value, in pico moles/Kg.

CFC-11	4.3%
CFC-12	3.9%
CFC-113	2.9%
Carbon Tetrachloride	3.1%
Methyl Chloroform	1.2%

8. Reversing Thermometers

Anthony W. Isenor

a. Description of Equipment and Technique

Sensoren-Instrumente-Systeme digital reversing thermometers model RTM 4002 were used to verify CTD thermistor readings on most deep stations. The thermometers have a depth range of up to 10000 m. The pressure housing is made of a glass tube closed at the ends by metal stoppers. One end contains the platinum sensor and the other end is the battery compartment. The thermometers were placed on bottles 1 and 3 on the rosette, thus sampling temperature at the deepest and third deepest bottle trips.

The thermometers are placed in standard reversing thermometer racks on the Niskin bottles. Before deployment, a magnet is passed over the thermometers to clear the display and place the thermometer in sample mode. A new temperature will then be recorded upon reversal of the thermometer.

On three stations, unprotected mercury in glass thermometers were attached to the bottle tripped at the bottom. Only one station resulted in good measurements for pressure calculations.

b. Sampling Procedure and Data Processing Technique

The thermometers indicate the temperature reading via a digital display. The temperature is read and noted on log sheets. The readings are later digitized and calibrations applied using the water sample database system.

c. Calibration Data

The digital reversing thermometers were calibrated at BIO in March 1994. These calibrations were considerable different than the most recent previous calibration, performed in 1991. During the cruise, thermometer readings were calibrated using both the 1991 and 1994 calibrations. The resulting temperatures were carefully monitored. A clear improvement in the inter-thermometer comparison was noted when using the 1994 calibrations. All results and CTD calibrations were therefore based on the March 1994 calibrations.

The unprotected mercury in glass thermometers were last calibrated in 1989.

d. Replicate Analyses

Table C.5 lists the duplicate temperatures measurements from the thermometers. Table C.6 lists pressure measurements based on mercury thermometers.

Table C.5 Reversing Thermometer Temperature Duplicate Measurements

Sample ID Number	Rev. Thm. Temp.	Sample ID Number	Rev. Thm. Temp.
140101	.248	140400	1.690
140101	.251	140402	1.907
140101	.254	140402	1.909
140103	.193	140420	1.673
140103	.205	140420	1.677
140103	.206	140422	1.851
140161	3.102	140422	1.852
140161	3.104	140462	2.326
140163	3.097	140462	2.328
140163	3.110	140482	2.122
140201	-.214	140482	2.122
140201	-.209	140502	2.122
140203	-.219	140502	2.122
140203	-.216	140506	1.961
140206	3.047	140506	1.964
140206	3.050	140526	2.884
140208	1.908	140526	2.885
140208	1.910	140547	1.940
140212	3.309	140547	1.942
140212	3.311	140565	1.656
140214	3.994	140565	1.659
140214	4.002	140567	1.972
140224	3.113	140567	1.974
140224	3.114	140585	1.656
140226	2.756	140585	1.659
140226	2.757	140587	1.972
140244	2.330	140587	1.974
140244	2.333	140605	1.635
140246	2.450	140605	1.638
140246	2.456	140607	2.053
140262	1.911	140607	2.056
140262	1.914	140624	1.793
140264	2.165	140624	1.797
140264	2.187	140626	1.934
140280	1.860	140626	1.936
140280	1.864	140662	2.486
140282	2.074	140662	2.490
140282	2.074	140664	2.845
140300	1.561	140664	2.845
140300	1.565	140677	3.350
140302	1.925	140677	3.354
140302	1.926	140679	3.465
140320	1.630	140679	3.466
140320	1.634		
140322	2.005		
140322	2.007		
140340	3.000		
140340	3.002		
140342	2.945		
140342	2.948		
140360	1.580		
140360	1.583		
140362	1.935		
140362	1.937		
140380	2.078		
140380	2.083		
140382	2.060		
140382	2.076		
140400	1.687		

Table C.6 Reversing Thermometer Pressure Duplicate Measurements

Sample ID Number	Reversing Therm. Press.
140460	129.1
140460	130.1
140460	130.2
140480	
140480	3447.4
140480	3479.0
140544	3476.2
140544	3477.8

9. Helium/Tritium

Dee Breger

Approximately 250 each of He and Tr samples were collected by Dee Breger for Peter Schlosser of Lamont-Doherty Earth Observatory, Columbia University. Stations sampled were: (station/cast) 5/1, 25/1, 26/1, 27/1, 28/1, 29/1, 30/1, 31/1, 33/2, 35/1, 37/2, 40/1, 42/1, 44/1, 46/2, 48/1, 52/1, 53/1, 61/1, 62/1, 63/1, 64/1, 65/2 and 66/1.

a. Description of Equipment and Technique

He samples were collected through tygon tubing into copper tubes (40 g capacity) bolted into metal channels for support and protection. Tr samples were collected into one-litre brown glass bottles, via tygon tube up to station 42 and directly from the Niskin spigot thereafter.

b. Sampling Procedure and Data Processing Technique

He samples were drawn after CFCs. Delivery was through tygon tubing which was monitored for air bubbles. Better detection of bubbles was effected by directing the light from a headlamp onto the line, and frequently wiping the tygon with laboratory tissue; all detected bubbles were worked out of the line, after which the metal channel holding the copper sample tube was struck several times on both sides with a ratchet in a pattern from the intake end towards the outflow end of the copper tube in order to pass any air bubbles out of the sample tube. Flushing of the copper tube took place during both parts of the bubble-removing procedure. When air removal and flushing were complete, both ends of the copper tube were sealed by tightening the two bolts at each end with a ratchet wrench. GMT time of sampling was routinely noted for each sample. These samples will be shipped to Lamont for analysis.

Tritium samples were collected into argon-filled bottles without rinsing or flushing, after all other samples were collected from the rosette. At first a tygon tube was used for delivery but starting at station 42 the tygon tube was eliminated so that the sample was drawn directly into the bottle. The bottle caps were secured with electrical tape at the completion of each station. These samples will be shipped to Lamont for analysis.

Replacement watches were handed out to all persons in the scientific party and the winch drivers who normally wore luminous-dial watches, and a sign was posted at each rosette room door to avoid wearing luminous-dial watches inside the room. Due to the doubling up of two scientific programs on this cruise, the replacement watches ran out before one of the winch drivers received one. He routinely removed his own watch before his stations except for the first few times.

The possibility of tritium contamination of the rosette room and Niskin spigots arose with the presence on board of a bacterial productivity program that uses tritium in its procedures. Paul Dickie from BIO ran the program, sampling at the rosette during biology stations and processing them in a container on the helicopter deck, near the hangar where the He and Tr sample boxes were stored. Approximately 10 people routinely went back and forth between this container and the rosette room during the cruise and a new sign requesting that these people thoroughly wash their hands on exiting the container was mounted on its door to reinforce the signs already posted. At the beginning of the cruise, swabs were taken and analyzed of random spigots, Breger's and Dickie's hands, to establish a baseline. Swabs were taken of random Niskin spigots on nearly all stations sampled for He and Tr, either before or after the sampling, especially after a biology cast. Several blank swabs were interspersed during the cruise. One swab was taken on the wrist of the winch driver who habitually wore a luminous dial watch and forgot to take it off before driving the winch several times early in the program. Breger did not enter or touch the container housing the bacteriology lab during the cruise. Dickie agreed to drain his Tr only during steaming and not during any stations. At station 42 a surface sample was taken by bucket (from a deck on the opposite side of the ship from the bacteriology container) and left in the rosette room for a day. A Tr sample was taken from this bucket, as was one from the bucket filled with leftover Niskin water that had been stored in the rosette room and used to cure the sampling delivery tubes. Tube-curing water, taken from the surface by bucket, was thereafter stored outside the rosette room and fresh tubes were subsequently routinely used for drawing He after they had cured.

10. Methyl Halides

R.M. Moore and Z. Hu

Objectives:

- To refine estimates of the magnitude of methyl halide fluxes from the ocean to the atmosphere.
- To provide information on the production mechanisms of these compounds.

Results:

Water samples, mainly from the upper 300 m of the water column, were collected at ca. 15 stations and analyzed on board for dissolved methyl halides. In addition to these vertical profiles, surface water samples and atmospheric samples were taken. The analytical equipment, being used in the field for the first time, performed satisfactorily and sample collection was accomplished very efficiently.

A preliminary interpretation of the results indicates that surface waters in the area studied are not substantially supersaturated in methyl chloride or bromide. This would suggest that current estimates of global ocean-atmosphere fluxes of both compounds based on saturation levels and gas exchange coefficients are likely to be too high. There was no obvious indication of a relationship between chlorophyll levels and the concentrations of methyl chloride and bromide. However, atmospheric methyl chloride and bromide levels in the marine boundary layer were found to be unexpectedly variable, and in the case of methyl bromide, with some values very much higher than the accepted mean tropospheric concentration. In view of the relative invariance of surface water concentrations, these results suggest that both compounds might be produced in the boundary layer rather than being primarily of biogenic origin.

This study needs to be followed up with further field measurements using the most highly selective and sensitive procedures offered by gas-chromatography with mass selective detection.

D. REFERENCES

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E. APPENDICES

- Appendix 1: Order of Sampling and Estimated Water Volumes
- Appendix 2: Computer Report, Hudson 94008
- Appendix 3: 94008 CTD Oxygen Calibrations

Appendix 1: Order of Sampling and Estimated Water Volumes

The order of samples drawn from the Niskin bottles for all Physical-Chemical casts is indicated below. The approximate volume of water required to draw each sample is also indicated. These values are averages of several measurements. A large spread in some of the measurements was noted. Note that we were using 8 litre Niskin bottles that contain 7.6 litre of usable water.

Parameter	Required Water (ml)
1. Freons	450
2. Helium	1000
3. Oxygen	750
4. Halocarbons	250
5. Carbonate	500
6. Alkalinity	800
7. Nutrients	150
8. Salinity	250
9. Tritium	1000

We logged CTD data on a 33 MHz 80486 based micro computer equipped with 4 Mb of RAM and a 210 Mb fixed disk. The operating system was MS-DOS 6.20. We used version 4.201 of SeaBird's SEASOFT logging and processing software. This was a major upgrade from previous years. In addition, we were using a CTD deck unit retrofitted with a NMEA 183 interface. The upgraded software and the automated acquisition of the NMEA navigation resulted in some changes in the format of the data. We made some significant changes to our custom (BIO) software to adapt to this. We also enhanced the processing batch job to create 2 dbar data sets in keeping with WOCE requirements. In previous years, we observed our processing took somewhere between 26% and 30% of real time, depending on the file size. This year we reduced this to about 20% to 22% in spite of the addition of the 2 dbar WOCE data set generation. We attribute this to three things: increased efficiency of the SEASOFT software, upgrading to MS-DOS 6.20 and the enabling of disk caching using DOS's SMARTDRV.

Data sets were backed up to the Hudson MicroVAX II using NCSA's FTP software as part of the processing job. This was done immediately after each cast to reduce the risk of data loss. Once daily these data sets were further backed up to Exabyte tape from the VAX's disk system.

NMEA 183 navigation data was logged continuously during the voyage on the Hudson MicroVAX II. We used our standard LOGGER program to acquire this data and our PIPE processing software to display it in several labs. This data was also backed up daily to Exabyte tape. In addition, the MS-DOS based program AGCNAV was used to display, but not log, navigation data at various locations throughout the ship.

All systems worked well during the entire cruise and there were no significant problems. We did uncover one bug in the SEASOFT program ROSSUM. It occasionally generated erroneous times for the rosette bottle trips. We have informed SeaBird of this.

Appendix 3: 94008 CTD Oxygen Calibrations

There were 66 stations occupied during cruise 94008. Based on cruise records there were two oxygen sensors used corresponding to the following station ranges: 1 to 6 and 25 to 66 (stations 7 to 24 were XBT drops).

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. Note that the WOCE SEA file column CTDOXY contains the down cast CTD oxygen data used in the calibration as opposed to the discrete CTD oxygen data obtained at the time of bottle trip.

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 - 6	100	80	0	20
25 - 66	676	216	1	460*
TOTAL	776	296	1	479

For reference, the mean of all the water sample oxygens collected during this cruise was 7.012 ml/l. Using the WOCE accuracy guideline for CTD oxygen measurements of 1-1½ %, we compute a deviation of 0.07 - 0.11 ml/l. This can be used in comparison with after calibration standard deviations.

* : The one record noted in column 4 (“Number of IDs not having a down CTD oxygen value and/or not being present in the Merged CTD file”) for the station range 25-66 is included in the 216 records in column 2. Thus, the record subtraction is 676 - 216 = 460

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

$d_{.j} = \frac{\sum_{i=1}^{n_j} d_{ij}}{n_j}$ **Error! Switch argument not specified.** : 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

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

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

k_{ij} : calibrated CTD oxygen

since $r_{ij} = e_{ij} - \epsilon_{ij} = b_{ij} - k_{ij}$
 $d_{ij} - d_{.j} - \epsilon_{ij} = b_{ij} - k_{ij}$
 $b_{ij} - c_{ij} - d_{.j} - \epsilon_{ij} = b_{ij} - k_{ij}$

therefore the calibration is:

Eqn. 1 $k_{ij} = c_{ij} + d_{.j} + \epsilon_{ij}$

No Calibration For Stations 1 to 6

Only station 5 had water sample data taken for these stations. The 20 bottles that were fired for station 5 were all fired around 2400 dbars. Therefore no oxygen calibration will be calculated for these stations.

Calibration of Stations 25 to 66

A plot of the difference between the water sample oxygen and the down CTD oxygen (d_{ij}) against pressure (p_{ij}) was produced for these stations (see Figure 1).

It was observed from Figure 1 that a simple offset would be appropriate as an initial calibration step. The near-surface region was 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 1. Omitting data in this layer resulted in Figure 2. Stations 25 and 26 were omitted at this point because these stations had no data below the pressure of 250 dbars. There were 341 data points remaining to be used in the calibration process for $p > 250$ dbars.

For each station the mean of the oxygen differences was calculated and this value, the station offset ($d_{.j}$), was subtracted from the individual down CTD oxygen values resulting in e_{ij} 's. The station offsets and standard deviations are listed in Table 2. Four points were omitted before calculating the $d_{.j}$'s; the sample id numbers were 140364, 140413, 140569 and 140872. These points are identified in Figure 2.

A plot of e_{ij} against p_{ij} is shown in Figure 3. The plot indicates a negative correlation with pressure. Therefore, a linear regression analysis was performed on the data, using e_{ij} as the dependent variable and p_{ij} as the independent variable, to obtain a linear equation that could be used to remove this pressure dependence. The resulting regression equation is given below as Eqn. 1. The regression line is drawn in Figure 3.

The computed regression equation is:

$$\text{Eqn. 1} \quad \epsilon_{ij} = 0.0995 - 5.445E-05 \times p_{ij}$$

A plot of the residuals (r_{ij}) versus pressure is shown in Figure 4. The residuals have a standard deviation 0.08 ml/l.

Station Offsets Removed in Calibration Process

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

Table 2. Station offsets.

Station	Mean of Oxygen Differences \pm Standard Deviation (ml/l)
25	3.334 \pm 0.27
26	3.062 \pm 0.21
27	2.201 \pm 0.13
28	1.723 \pm 0.10
29	1.628 \pm 0.06
30	1.548 \pm 0.10
31	1.466 \pm 0.10
32	1.475 \pm 0.11
33	1.502 \pm 0.15
34	1.432 \pm 0.13
35	1.423 \pm 0.10
36	1.444 \pm 0.08
37	1.460 \pm 0.12
38	1.407 \pm 0.09
39	1.636 \pm *
40	1.390 \pm 0.09
41	1.388 **
42	1.386 \pm 0.09
43	1.376 **
44	1.366 \pm 0.10
45	1.323 **

46	1.280 ± 0.06
47	1.310 **
48	1.339 ± 0.11
49	1.288 **
50	1.238 ± 0.10
51	1.254 **
52	1.270 ± 0.08
53	1.249 ± 0.07
54 - 60	1.339 **
61	1.429 ± 0.03
62	1.307 ± 0.14
63	1.312 ± 0.08
64	1.206 ± 0.06
65	1.340 ± 0.09
66	1.283 ± 0.06

* This station only had one oxygen difference so no standard deviation could be computed.

** Stations 41, 43, 45, 47, 49, 51 and 54 to 60 did not have any oxygen water samples drawn, so the mean offset for these stations is given as the mean between the two adjacent stations.

CTD Oxygen Calibration Procedure

We calibrated the CTD oxygen data for stations 25 to 66 according to the following expression:

$$\text{Eqn. 1} \quad k_{ij} = c_{ij} + d_{\cdot j} + \varepsilon_{ij}$$

where k_{ij} is the calibrated CTD oxygen data

c_{ij} is the raw CTD oxygen data,

$d_{\cdot j}$ is given in Table 2 for all stations, and

$\varepsilon_{ij} = 0$ for stations 25 and 26 and ε_{ij} is given by Eqn. 1 for stations 27 to 66.

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

Stations 1 to 6 will not be calibrated.

94008: Stations 25 To 66

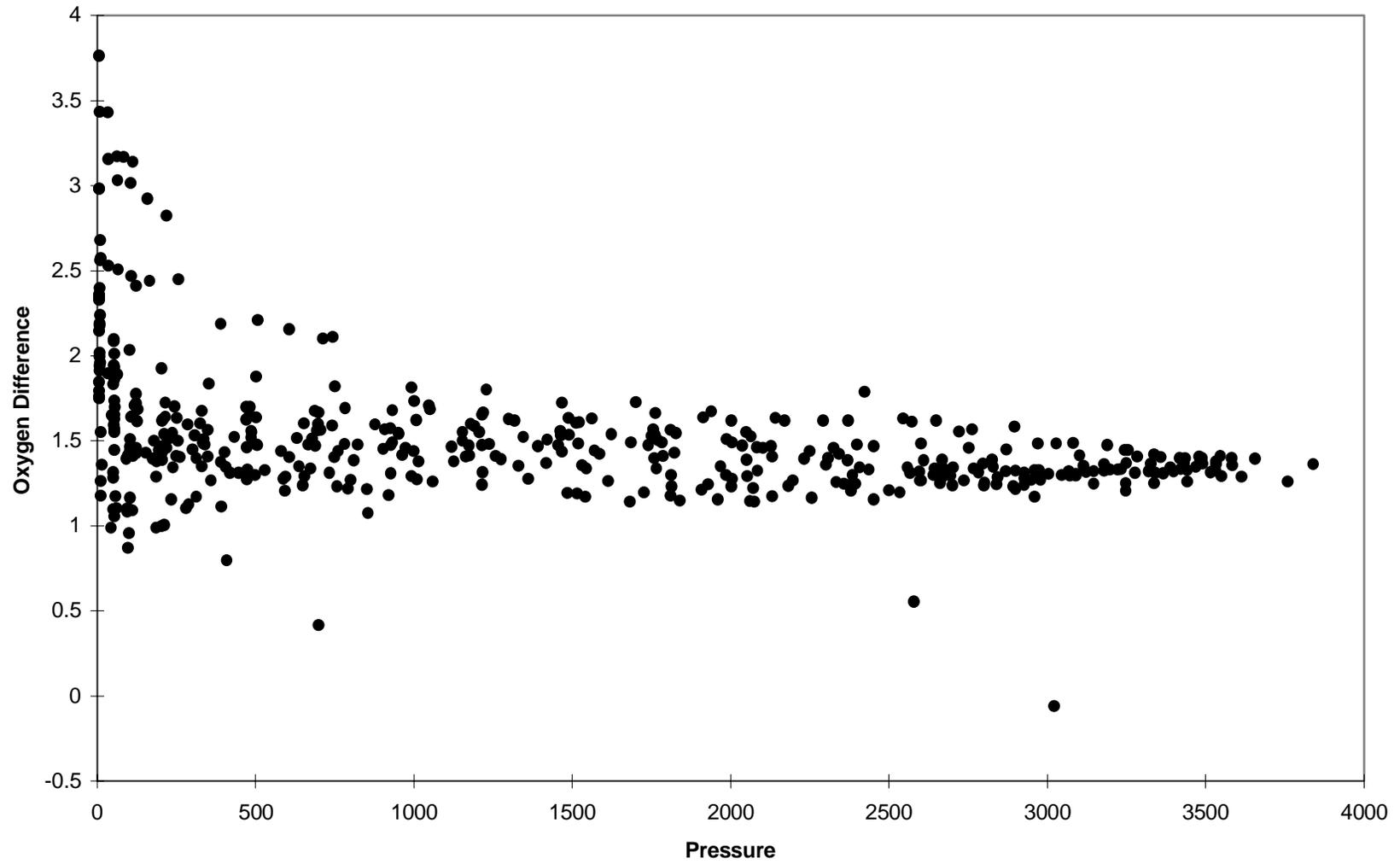


Figure 1. Water sample oxygen data minus the down cast CTD data, d_{ij} , plotted against pressure.

94008: Stations 25 To 66

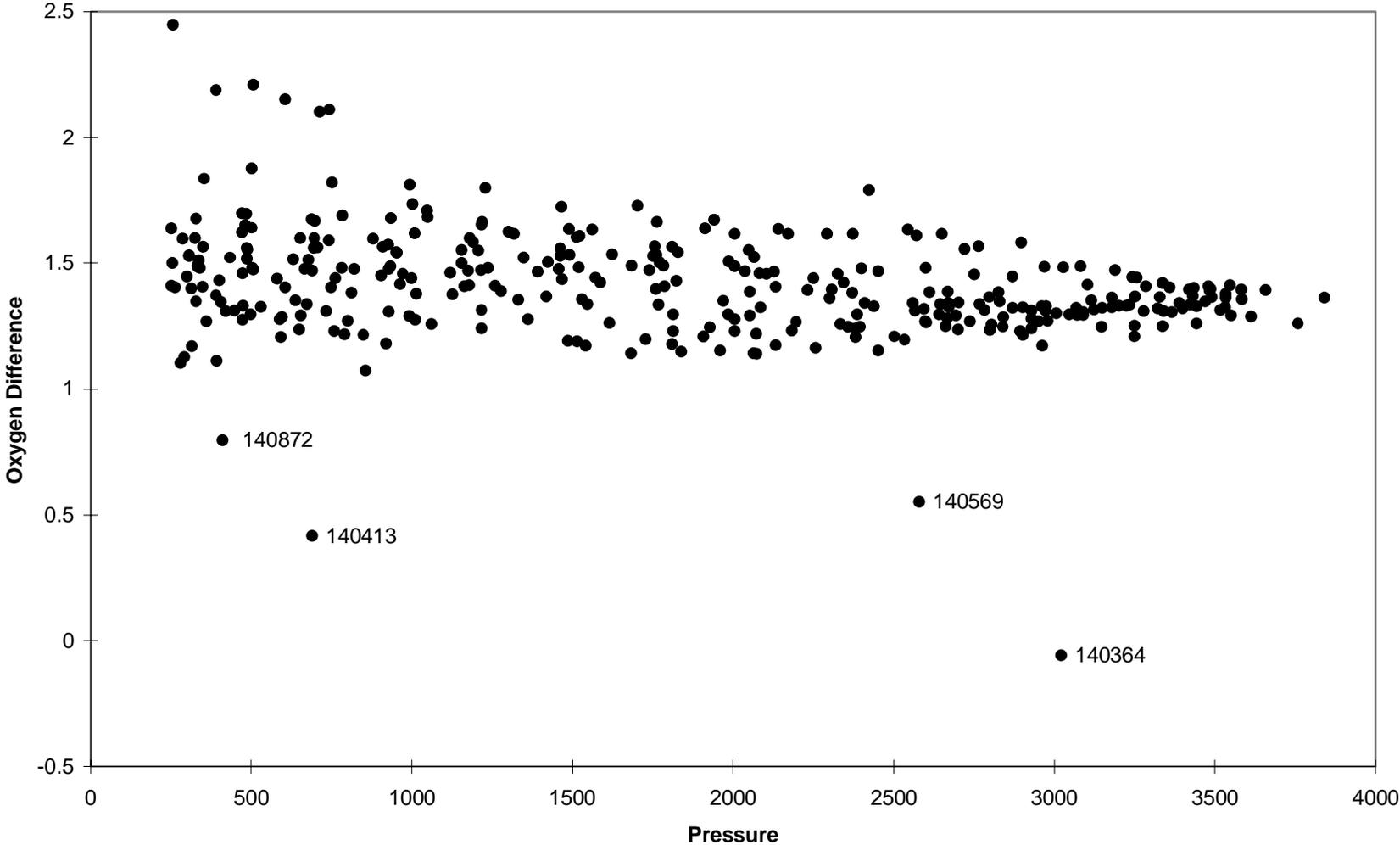


Figure 2. Oxygen differences, d_{ij} , plotted against pressure for data points having a pressure below 250 dbars.

94008: Station 25 To 66

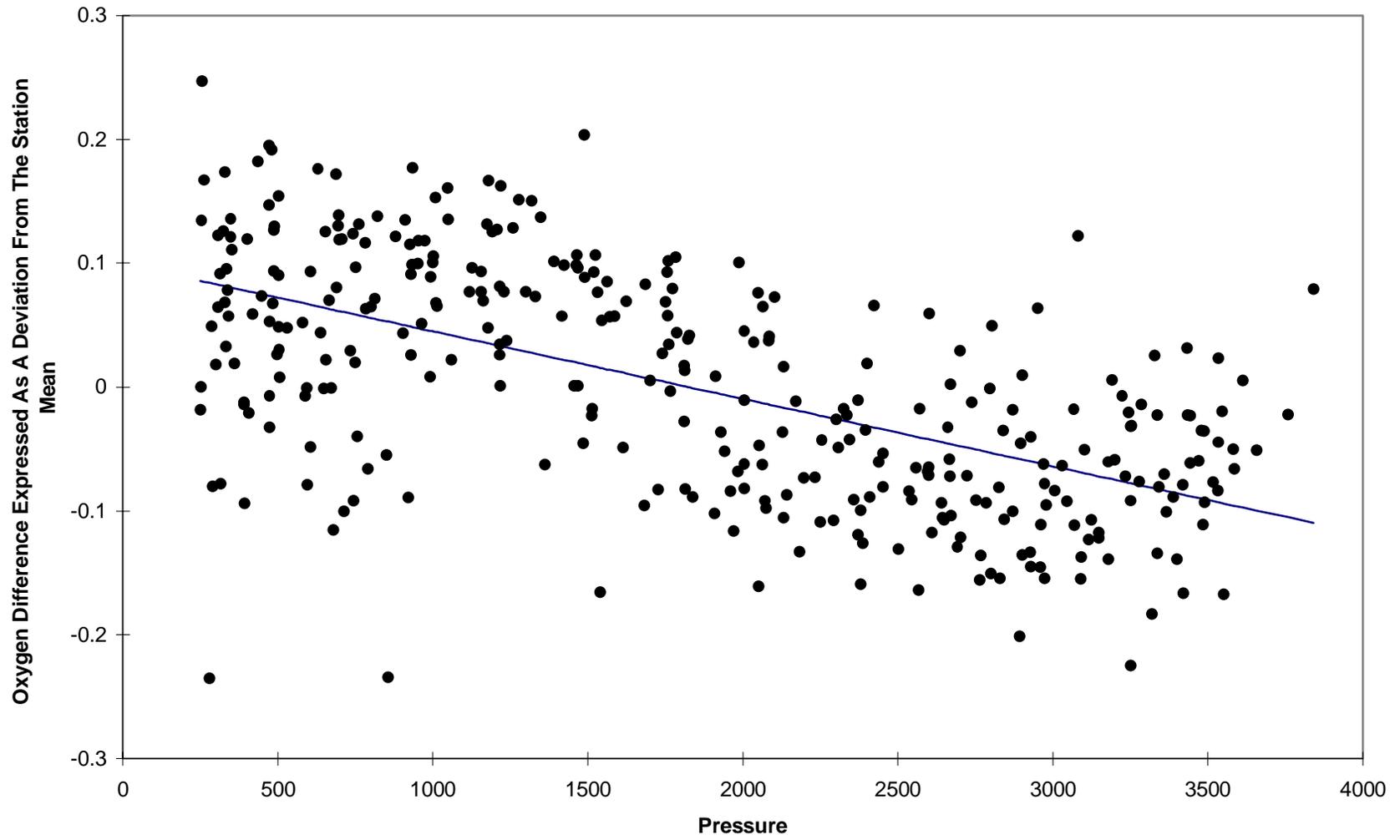


Figure 3. e_{ij} plotted against pressure with the associated regression line.

94008: Stations 27 To 66

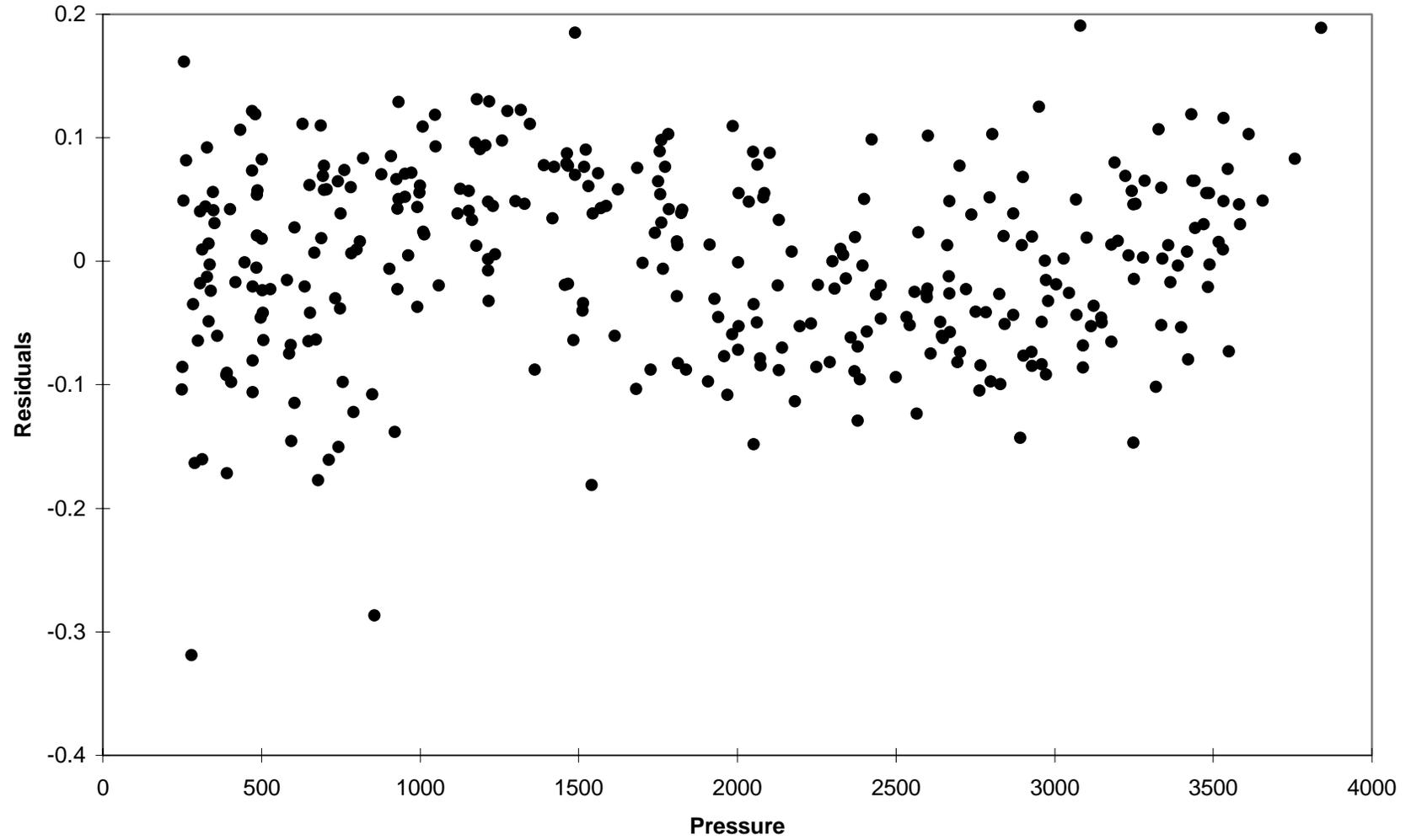


Figure 4. Residuals remaining after the calibration has been applied to the down cast CTD oxygen data.