CRUISE REPORT

HUDSON 2005016

LABRADOR SEA

WOCE LINE AR7W

May 26 – June 7, 2005

A. CRUISE NARRATIVE

1. Highlights

a. WOCE Designation:	WOCE Line AR7W Atlantic Circulation Experiment
b. Expedition Designation:	Hudson 2005016
c. Chief Scientist:	Glen Harrison Ecosystem Research Division Department of Fisheries and Oceans Bedford Institute of Oceanography PO Box 1006 Dartmouth, NS, Canada B2Y 2A4 Internet harrisong@mar.dfo-mpo.gc.ca
d. Ship:	CCGS Hudson
e. Ports of Call:	May 26 St. John's, NL, Canada June 7 BIO, Dartmouth, NS, Canada
f. Cruise Dates:	May 26 to June 7, 2005

2. Cruise Summary Information

a. Cruise Track

A cruise track is shown in Figure A.2.1. The ship's position at 0000Z on each day of the cruise is indicated with a date label.

The WOCE cruise station summary file (SUM) outlines the science operations conducted during the cruise.

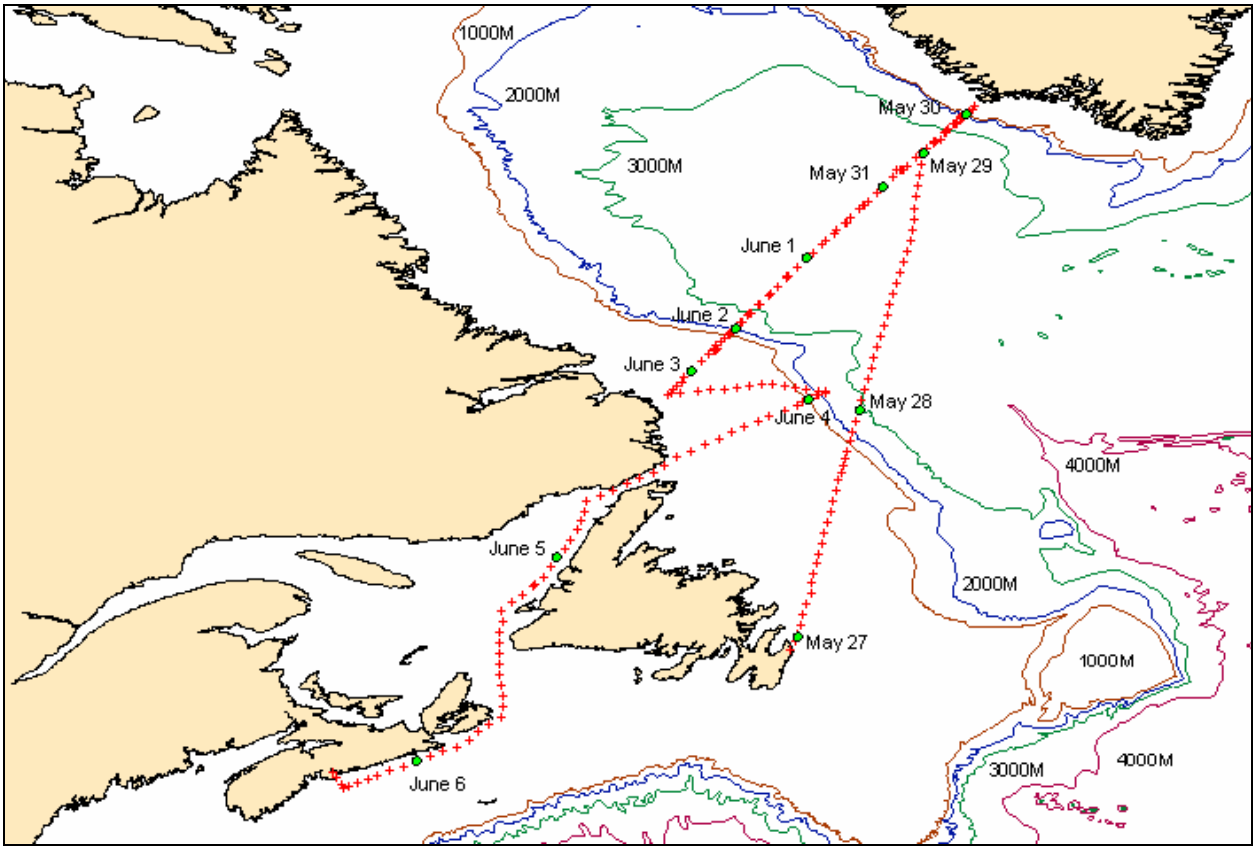

Figure A.2.1 Cruise track for 18HU2005016/1. The date labels indicate the ship's position at 0000Z.

b. Total Number of Stations Occupied

The CTD and ROS station positions are shown in Figure A.2.2. The WHP stations are all contained in the box defined by 44-61°N and 54-64°W. Table A.2.1 lists the science operations for 18HU2005016.

Cast Type	Number of Operations	Detailed Division	Operation Numbers
Rosette & CTD	31	28 regular AR7W Sites (L3 line) plus Sites 8.5, 25.3 and 25.7	see Table A.2.2
	1	Halifax Line Site 2	178
	4	Biology Casts not included in other tables	12, 46, 80, 113
	5	L4N Line (3, 4a, 4b, 5 and 6)	171 - 175
Moorings	2 1	1 recovery, 1 deployment Release test	148, 150 149
Floats	2	PROVOR floats deployed	52, 115
Biology	87	59, 200 μm net tows	1, 3, 5, 7, 9, 11, 14, 15, 17, 18, 22, 24, 26, 28, 33, 35, 43, 45, 53, 55, 61, 63, 69, 71, 77, 79, 87, 89, 95, 97, 104, 106, 110, 112, 118, 120, 123, 125, 128, 130, 132, 134, 136, 138, 140, 142, 144, 146, 151, 153, 155, 157, 159, 161, 163, 165, 167, 169, 176
		28, 76 μm net tows	2, 6, 10, 23, 27, 34, 44, 54, 62, 70, 78, 88, 96, 105, 111, 119, 124, 129, 133, 137, 141, 145, 152, 156, 160, 164, 168, 177
Chemistry	14	^{129}I surface	25, 29, 36, 56, 64, 81, 90, 107, 114, 131, 143, 147, 162, 166
	5	^{129}I profile	8, 47, 72, 98, 121
Other		257.9 hrs Ship Board ADCP	No number assigned
	45	XBT Deployments	30 - 32, 37 - 42, 48 – 51, 57 – 60, 65 – 68, 73 – 76, 82 – 86, 91 – 94, 99 – 103, 108, 109, 116, 117, 122, 127

Table A.2.1 Science operations conducted on 18HU2005016/1.

AR7W Site Number	2005016 Deep Cast Operation Number
1	170
2	166
3	162
4	158
5	154
6	147
7	143
8	139
8.5	135
9	131
10	126
11	121
12	114
13	107
14	98
15	90
16	81
17	72
18	64
19	56
20	47
21	4
22	36
23	8
24	29
25	13
25.3	20
25.7	21
26	25
27	19
28	16

Table A.2.2. AR7W (L3) sites and rosette and CTD operation numbers for 18HU2005016/1.

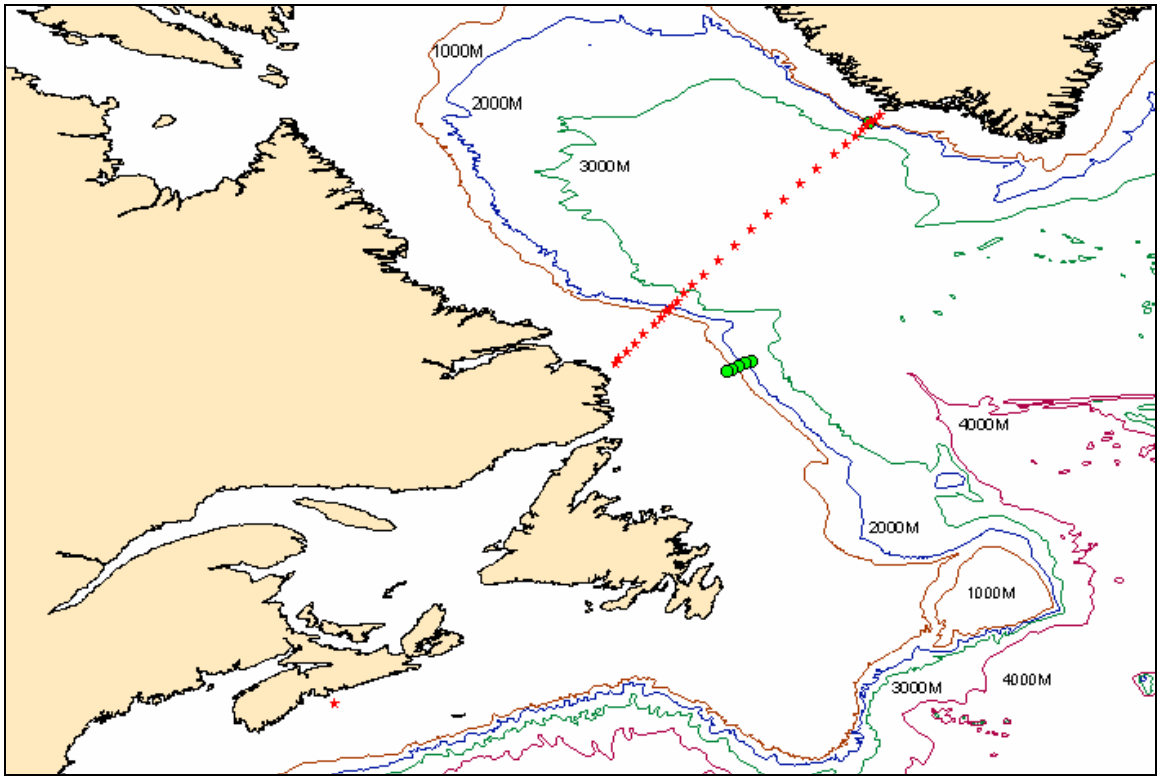

Figure A.2.2 This map shows the station positions for CTD only operations (green filled circles) and rosette/CTD operations (red filled star) for Hudson 18HU2005016/1.

Along AR7W, the stations were full-depth WHP small volume rosette casts with up to 24 rosette bottles. Water samples were analyzed for CFCs, carbon tetrachloride, total carbonate, alkalinity, oxygen, salinity, nutrients (nitrate, phosphate and silicate), total organic carbon (TOC), and bacteria abundance. Chlorophyll was analyzed at depths less than 200 m at all stations as well. On some casts, samples were collected for ^{129}I (iodine-129), nitrogen and oxygen stable isotopes.

c. Floats and Drifters deployed

Two Metocean PROVOR floats were deployed along the AR7W line. PROVOR MT-158 was deployed near station L3-19 at 58º 39.3041N and 050º 24.1092W in approximately 3440 meters of water. PROVOR MT-166 was deployed near station L3-12 at 55º 50.7535N and 053º 23.8087W in approximately 3080 meters of water. Both floats appeared to have started properly. Each sent Argos transmissions, gave 10 audible clicks from the solenoid valve and floated at the surface when deployed. Listed in table A.2.3 are the two PROVOR floats that were deployed.

PROVOR Float #	WMO #	Event Number	Launch Position		Start Date / Time	Launch Date / Time
			Latitude	Longitude		
MT-158	4900529	52	58º 39.3041N	050º 24.1092W	21:48 30 May 05	22:57 30 May 05
MT-166	4900537	115	55º 50.7535N	053º 23.8087W	14:20 1 June 05	14:42 1 June 05

Table A.2.3 PROVOR float deployments on Hudson 2005016

d. Moorings deployed or recovered

The Aanderaa current meter mooring near station L3-8 on the AR7W line was once again serviced on June 2nd. Mooring #1514 was recovered successfully under good sea conditions. The RCM8 appeared to have worked properly and all mooring tackle was in good condition. The replacement mooring #1555 was deployed successfully.

Deployment:

M 1555	55 07.1772 N 54 05.3113 W	Standard mooring consisting of one current meter positioned 20m below surface along AR7W on the Labrador Slope (12-month deployment) at the 1010 metres.

Recovery:

M 1514	55 07.0731 N 54 05.2760 W	Standard mooring consisting of one current meter positioned 20m below surface along AR7W on the Labrador Slope (12-month deployment) at the 1035 metres.

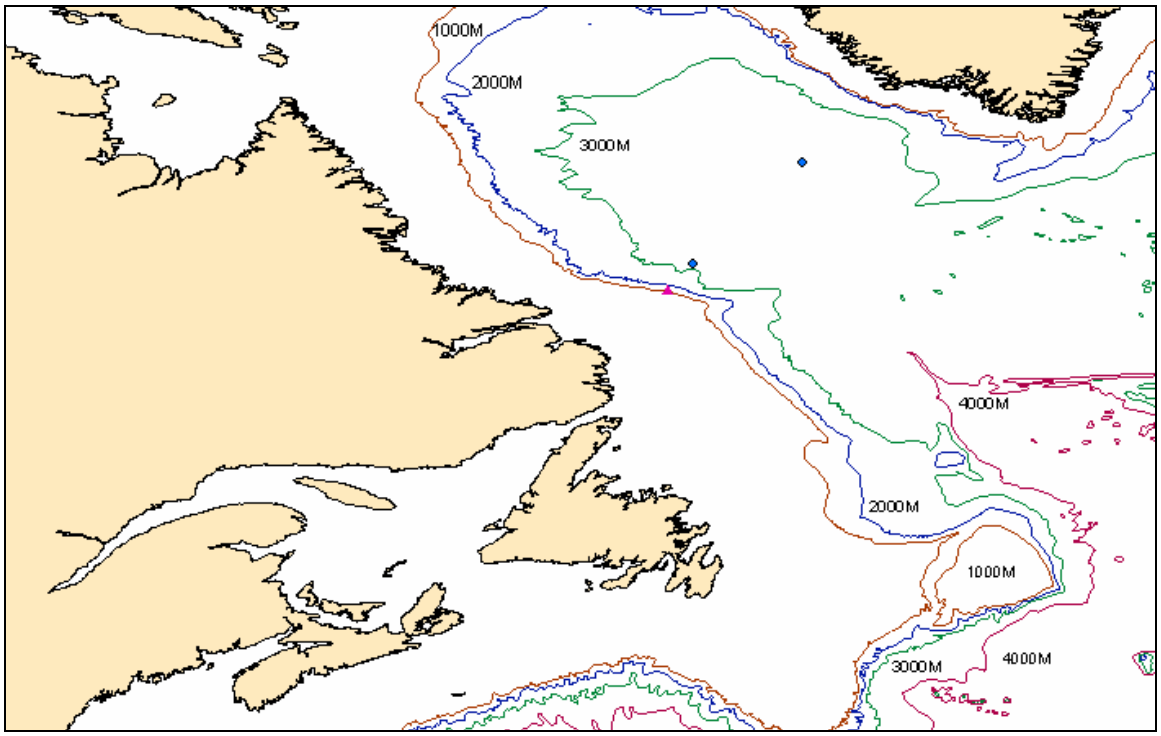

Figure A.2.3 Mooring operations (pink filled triangle - a mooring was recovered and a new one deployed in the same location) and float deployment locations (blue filled diamonds) for Hudson 18HU2005016/1.

3. List of Principal Investigators

Name	Affiliation	Responsibility
Allyn Clarke	BIO clarkea@mar.dfo-mpo.gc.ca	Senior scientist Overall co-ordination
Bob Gershey	BDR Research rgershey@fox.nstn.ns.ca	Alkalinity, carbonate, CFCs
Glen Harrison	BIO harrisong@mar.dfo-mpo.gc.ca	Coordinator biological program; carbon, nitrate and ammonium utilization by phytoplankton, sediment traps Labrador Sea.
Erica Head	BIO heade@mar.dfo-mpo.gc.ca	Macrozooplankton distribution, abundance and metabolism
Paul Kepkay	BIO kepkayp@mar.dfo-mpo.gc.ca	Dissolved organic carbon, colloid chemistry and plankton respiration
Peter Jones	BIO jonesp@mar.dfo-mpo.gc.ca	Alkalinity, carbonate, CFC's
John Lazier	BIO lazierj@mar.dfo-mpo.gc.ca	CTD data, moored instrument data
Bill Li	BIO lib@mar.dfo-mpo.gc.ca	Pico-plankton distribution and abundance, bacterial abundance and productivity
Robert Pickart	WHOI pickart@rsp.whoi.edu	Lowered ADCP
John Smith	BIO smithjn@mar.dfo-mpo.gc.ca	Chemistry isotopes
Igor Yashayaev	BIO YashayaevI@mar.dfo-mpo.gc.ca	Hydrography and XBTs

Table A.3.1. List of Principal Investigators. See Section 7 for addresses.

4.1 Physical - Chemical Program

a. Narrative

This expedition was conducting operations in support of four ongoing scientific initiatives.

The first initiative is in support of the North Atlantic Oscillation and the Atlantic Thermohaline Circulation Principal Research Areas of the Climate Variability and Predictability (CLIVAR) project of the World Climate Research Programme (WCRP). The occupation of the Labrador Sea section and the recovery of the one Labrador Sea mooring provide a measure of the winter cooling and water mass transformations over the winters of 2004/2005. The resetting of the mooring on the 1000 metre isobath on the Labrador slope continues a 20+ year observation program of the Labrador Current.

The second initiative is the continuation of the Labrador Sea project concerned with the natural and anthropogenic carbon cycles. The biological program is designed to characterize the late spring biological processes in the Labrador Sea and its shelf regions and is discussed in a later section of this document. The physical/chemical oceanographic program observes nutrients, total carbonate, alkalinity and CFCs over the entire water column in order to document the vertical transport of carbon via winter convection in the Labrador Sea as well as the changes in carbon storage in the deep waters of the North Atlantic.

The third initiative is to observe the physical and chemical parameters at the Halifax Section Station 2 fixed-station monitoring site in support of DFO's Atlantic Zonal Monitoring Program (AZMP).

The fourth initiative was to deploy profiling floats (PROVOR) as a Canadian contribution to the International GODAE/Argo program. Two floats were deployed in the Labrador Sea.

b. Radioisotope Sampling Program **John Smith**

Water samples were collected for ^{129}I from a near surface rosette bottle at 14 stations on the L3 (AR7W) line. Full depth sampling for ^{129}I was carried out at 5 stations on the same section. See table A.2.1 for the list of operations during which ^{129}I was sampled.

4.2 Biological Program

a. Narrative

The biological program conducted as part of cruise 2005016, with some modifications, was a continuation of studies began in 1994 to describe the large-scale (spatial and temporal) variability in plankton biomass, productivity and biogenic carbon inventories in the Labrador Sea.

The program has consisted of essentially five elements:

1) a phytoplankton biomass/primary productivity program conducted by Jeff Anning with assistance from Tim Perry (for Glen Harrison),
2) a microbial program conducted by Jeff Anning and Tim Perry,
3) a mesozooplankton program conducted by Les Harris (for Erica Head),
4) a dissolved organic carbon/community respiration program conducted by Jay Bugden (for Paul Kepkay), and
5) an additional program, investigating the stable isotope (nitrogen) content of mesozooplankton (collected from net tows) related to Right Whale diets, was also conducted by Tucker Williamson, University of New England.

The ultimate aim of these studies is twofold:

1) to provide a description of the inventories in and export of biogenic carbon from the Labrador Sea, their turnover rates and variability in space and time as part of Ecosystem Research Division's (ERD) continuing climate-studies and
2) to provide a description of plankton life-cycles and productivity in the Labrador Sea and its influence or contribution to ecosystems downstream in support of ERD's fisheries-related research.

In addition to the Labrador Sea study, phytoplankton, mesozooplankton and nutrient samples were collected at the Halifax line Station 2 in support of ERD/OSD's obligations to the Atlantic Zone Monitoring Program (AZMP).

b. Zooplankton Sampling **L. Harris / E. Head**

The zooplankton sampling is part of an ongoing program, the aim of which is to investigate the distribution, abundance and life history of the major zooplankton groups found in the Labrador Sea and its associated shelf systems. Particular emphasis is placed on the copepod species of the *Calanus* genus, which dominate the zooplankton in this region.

Vertical net tows were taken at 30 stations (1 on the Halifax Line and 29 on the L3 line). At all stations, tows were made from 100 meters to the surface using a 76 μmeter and a 200 μmeter ring net. At 27 of these stations an additional tow was made using a 200 μmeter ring net. See Figure A.4.2.1 below for station locations where nets were used.

c. Measurements Of Copepod Reproduction Rates **L. Harris / E. Head**

Egg production rates of *Calanus finmarchicus*, the dominant copepod species, were measured at 9 stations in the Labrador Sea and 3 stations on the Labrador Shelf.

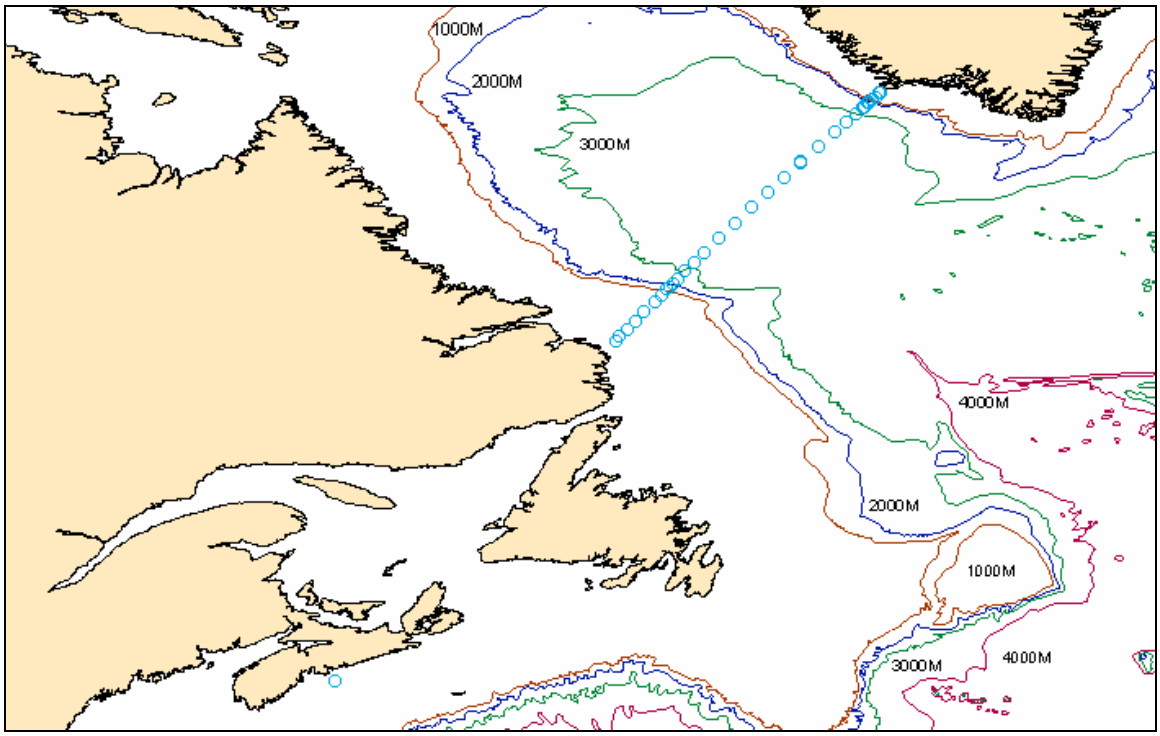

Figure A.4.2.1 Net tow (blue open circle) locations for 18HU2005016/1.

d. Total Organic Carbon (TOC) and Microbial Community Respiration

Jay Bugden / Paul Kepkay

In order to better understand the cycling of carbon and the mechanisms controlling it in the Labrador Sea, it is necessary to examine the pool of total organic carbon (TOC), and look at the activity of the microbial community in the water column. By examining the rate of respiration and size fractionating the TOC, information on the fate of carbon in this marine environment may be elucidated.

During CCGS Hudson cruise 2005-016 five (5) stations were sampled at the surface and at the chlorophyll maximum (usually between 10 and 50m depth) for gross microbial community respiration, and for the same stations only the surface was sampled for size fractionation of TOC (ultrafiltration). The stations sampled are listed below. TOC depth profiles were also collected from the stations indicated in the table below.

Station	Respiration	Ultrafiltration	TOC Profile
AR7W site 1			X
AR7W site 2			X
AR7W site 3			X
AR7W site 4			X
AR7W site 5			X
AR7W site 6	X	X	X
AR7W site 7			X
AR7W site 8			X

AR7W site 8.5			
AR7W site 9			X
AR7W site 10			X
AR7W site 11			X
AR7W site 12	X	X	X
AR7W site 13			X
AR7W site 14			X
AR7W site 15			X
AR7W site 16	X	X	X
AR7W site 17			X
AR7W site 18			X
AR7W site 19			X
AR7W site 20	X	X	X
AR7W site 21			X
AR7W site 22			X
AR7W site 23			X
AR7W site 24			X
AR7W site 25	X	X	X
AR7W site 26			X
AR7W site 27			X
AR7W site 28			X

Table A.4.2.2 Ultrafiltration, respiration and TOC sampling on CCGS Hudson cruise 2005016.

e. Primary Production Measurements — Jeff Anning

Water samples for primary production experiments were collected from the rosette at 10 stations. For each incubation experiment, 33 aliquots were inoculated with 14C of sodium bicarbonate and then incubated at in situ temperatures at 30 light levels (+ 3 dark bottles) for approximately 3 hours. At the end of the incubation period the cells were harvested onto GF/F glass fibre filters for later counting in a scintillation counter. Duplicate chlorophyll, duplicate particulate organic carbon, one HPLC, and one Absorption Spectra sample were collected for each incubation experiment.

Photosynthesis/Irradiance incubations were conducted at the following stations:

Station	Event	Lat. (deg)	Lat. (min)	Long. (deg)	Long. (min)	Date	Time GMT	Depth	ID
L3-25	12	60	17.673	48	33.669	29-Jun-05	1218	2.0	285562
L3-25	12	60	17.673	48	33.669	29-Jun-05	1218	30.0	285557
L3-27	19	60	27.134	48	22.23	29-Jun-05	1829	2.0	285609
L3-27	19	60	27.134	48	22.23	29-Jun-05	1829	30.0	285605
L3-20	46	59	3.964	49	57.43	30-May-05	1717	2.0	285690
L3-20	46	59	3.964	49	57.43	30-May-05	1717	20.0	285686
L3-16	80	57	22.727	51	47.293	31-May-05	1550	2.0	285803

L3-16	80	57	22.727	51	47.293	31-May-05	1550	30.0	285798
L3-12	113	55	50.712	53	23.708	01-Jun-05	1206	2.0	285916
L3-12	113	55	50.712	53	23.708	01-Jun-05	1206	20.0	285911
L3-6	147	54	45.027	54	27.937	02-Jun-05	1100	2.0	286069
L3-6	147	54	45.027	54	27.937	02-Jun-05	1100	10.0	286066

Table A.4.2.3. Photosynthesis/Irradiance incubations were conducted at the above stations.

f. Bacterial Abundance and Production of Microbial Plankton — Jeff Anning / Tim Perry

At every depth a sample was collected for bacterial counting by flow cytometer. Duplicate chlorophyll samples were collected in the surface waters (100m to surface) and a single sample for both HPLC and Absorption spectrum analysis were collected from the surface.

Water samples were collected from various depths at 4 stations (25, 16, 12, 3) and incubated for between 3 – 24 hours after inoculation with 3H labeled leucine. The cells were collected by centrifugation and prepared for scintillation counting back on shore.

g. Isotope analysis of copepods — Tucker Williamson

This project involved the collection of *Calanus finmarchicus* for natural isotope (nitrogen) concentration analysis. These copepods were collected at each of the AR7W stations, by performing a plankton tow. This collection was done as part of Prof. Steve Zeeman's NASA grant research project on whales. He is trying to map their distribution and one way to do this is by using isotope analysis. Since *C. finmarchicus* are extremely abundant in the sampled water, it stands to reason that it would be a major component in the diet of certain baleen whales. Thus, by knowing the range of *C. finmarchicus* and how much of its isotope signature is present in a whale; it is possible to gain an understanding about the population distribution of these whales.

5. Major Problems and Goals Not Achieved

No major problems; all goals achieved. Despite fewer sea days available for this mission then requested, due to late return of HUDSON to BIO after refit, (a) favourable weather and coastal ice conditions (b) operation of the ship on 3-engines during extended transits and (c) trouble-free equipment operation, resulted in all L3 line station work being successfully completed. Four additional unscheduled CTD stations were occupied off the northern Newfoundland slope as well as Halifax Line Station 2 on the transit back to BIO. The program was completed with time to spare allowing the ship to return to BIO a day earlier than scheduled.

6. Other Incidents of Note

The scientific seawater source in the ship's forward lab, used for the Continuous Flow Multisensor Package (CFMP), was inaccessible on this mission due to the external access valve being improperly installed during refit (see B3 below).

7. List of Cruise Participants

Name	Responsibility	Affiliation
Jeff Anning	Primary Production	BIO
Carol Anstey	Nutrients	BIO
Kumiko Azetsu-Scott	Scientist, CO_2, CFCs, Alkalinity	BIO
Jay Bugden	TOC Levels, respiration rates	BIO
Rick Boyce	Salts, moorings	BIO
Pierre Clement	Chemistry assistance	BIO
Bob Gershey	Contract, CO_2, CFCs, Alkalinity	BDR
Les Harris	Zooplankton, Net Tows	BIO
Glen Harrison	Senior Scientist	BIO
Ross Hendry	Scientist, O_2, Computer Room	BIO
Jeff Jackson	Data management, Computer Room	BIO
Kassiem Jacobs	CTD/rosette assistance	DAL
Andy Lin	CTD/rosette assistance	DAL
Tim Perry	Bacterial activity	BIO
Bob Ryan	Moorings, instrumentation	BIO
Tucker Williamson	Student, vertical net tows	UNE
Igor Yashayaev	Scientist, Computer Room	BIO
Frank Zemlyak	Technician, CO_2, O_2, CFCs, Alkalinity	BIO

BIO Bedford Institute of Oceanography
PO Box 1006
Dartmouth, NS, B2Y 2A4
Canada

BDR	BDR Research Ltd. Box 652, Station 'M' Halifax, NS, B3J 2T3 Canada
DAL	Dalhousie University Halifax, NS, B3H 4R2 Canada
UNE	University of New England Westbrook College Campus 716 Stevens Avenue Portland, Maine 04103

B. UNDERWAY MEASUREMENTS

1. Navigation and Bathymetry — Jeff Jackson

The navigation system onboard CCGS Hudson consists of a differential GPS receiver and AGCNAV. The receiver is one of many NMEA feeds into a multiplexer that provides all the NMEA strings to a PC on the bridge. The PC, which is running AGCNAV software, then rebroadcasts the NMEA strings to distribution units in the computer room, which provide 16 output lines for the working labs. The resulting broadcast navigation strings are at about 1 Hz. The navigation data are then logged at specified intervals on a PC. For this cruise the navigation was logged at 1 second, 10 seconds and 1 minute intervals during the cruise due to operator oversight. It was logged at a 30 second interval throughout the cruise.

AGCNAV is a PC based display and waypoint setting software package, developed at the Atlantic Geoscience Centre at BIO. This software graphically displays ship position, waypoints, course, speed, etc. to the various science working areas.

The echo sounder system used for collecting bathymetric data at station locations consisted of a Raytheon Line Scan Recorder, Model LSR 1811-1 (serial number A101) connected to a 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. One transducer is positioned on a Ram that can be lowered or raised depending on conditions. When the ram is up, the waterline to transducer offset is 6 m. When the ram is down, the offset is 8 m.

2. Vessel Mounted Acoustic Doppler Current Profiler — Murray Scotney

The Hudson was equipped with a hull mounted RDI Acoustic Doppler Current Profiler (ADCP). The transducer (serial number 177) had VM ADCP electronics (serial number 172). Logging, using Transect software on a 486 PC, was started on May 26 at 1925 Z leaving the St. John's Harbour.

The configuration used for logging resulted in 5-minute averages in 4 meter bins. The averaged data are stored to disk and backed up every few days. ADCP logging was stopped on June 6 at 13:20 Z in Halifax Harbour.

3. Continuous Flow Multisensor Package (CFMP) — Jeff Anning

Because of inaccessibility of scientific seawater system (external access value improperly installed during ship's refit), the CFMP was not operational on this mission.

4. XBT and XCTD

Igor Yashayaev

Expendable Bathythermographs were routinely deployed along the AR7W line on the way from Greenland to Labrador. See figure B.4.1 for a map with the XBT drops indicated. The XBTs were model T7 from Sparton of Canada. These types of probes are capable of measuring to maximum depths of 800 m (T7) at the full cruising speed 15 knots. The vertical resolution of the measurements was about 0.6-0.8 m. There were 45 XBTs launched during the cruise (Table A.2.1 lists the operation numbers when these were deployed).

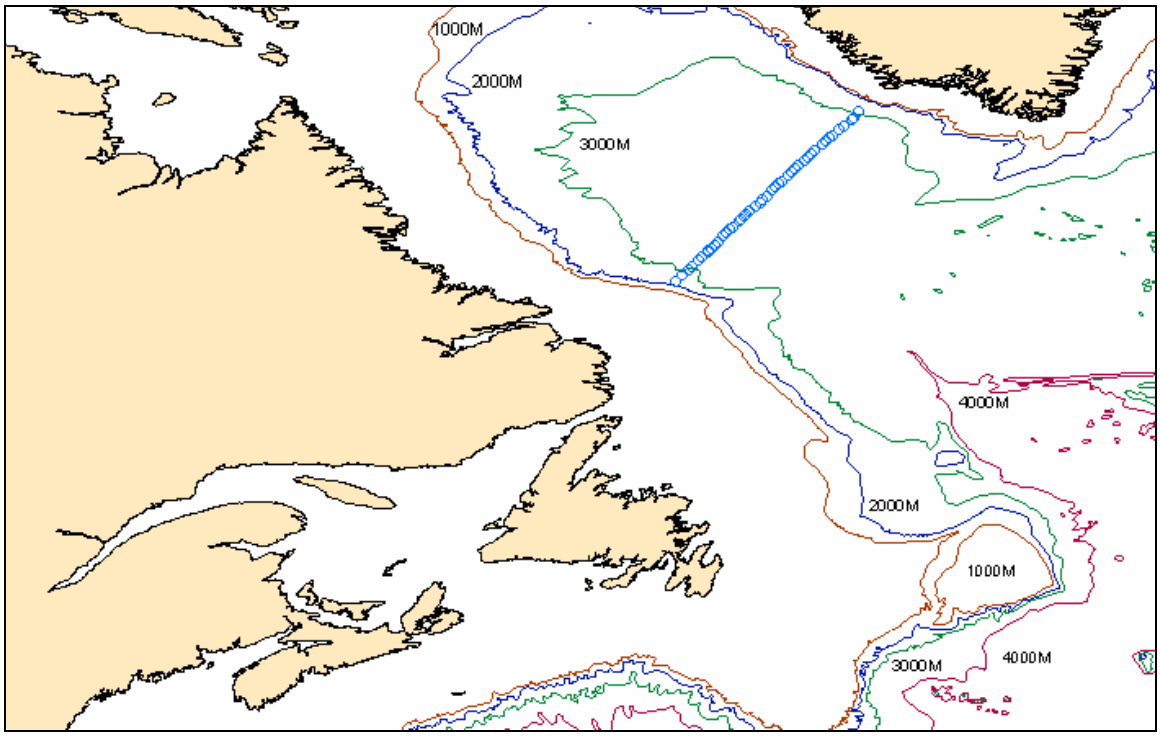

Figure B.4.1 XBT drop sites along the AR7W section (indicated by blue hollow circles).

5. Meteorological observations

The ship's crew logged routine reporting of meteorological variables.

6. Atmospheric Chemistry

There was no atmospheric chemistry program.

C. HYDROGRAPHIC MEASUREMENTS - DESCRIPTIONS, TECHNIQUES AND CALIBRATIONS

1. Salinity — Rick Boyce

a. Description of Equipment and Technique

Salinity samples were analyzed using a Guildline Autosal 8400B salinometer, serial number 61083. Samples were drawn into 200 ml bottles. Once the sample bottle was rinsed three times and filled to the shoulder, the neck and threads of the bottle were dried using paper towel and a new dry cap was installed. Once the bottles reached room temperature, the caps were retightened. The drying of the neck of the bottle and installing a dry cap has been a technique used since the HUD2000009 cruise.

The salinometer cell was filled and rinsed numerous times with sample water before readings were recorded. When three consecutive readings of conductivity agree to within 0.00001, this value was recorded for the sample. This value was then entered into the water sample database as the conductivity ratio for the water sample.

b. Data Processing Technique

Conductivities were entered into the ODIN database. Conductivities were used to compute salinities using the water sample conductivity ratio and the standard IAPSO formula applied in an ODIN module. Any changes in the salinometer readings between successive standardizations were assumed to have occurred as a linear drift of the instrument. Thus, the program applied a correction to the ratios, which varied linearly with the samples analyzed. An offset was also applied if the initial standardization was different from the quoted value given on the ampoule label. The computed salinity data was then placed in the water sample database.

c. Laboratory and Sample Temperatures

Full cases of samples were taken from the winch room to the GP lab where they were left for a period of at least 10 hours to equilibrate to room temperature before being analyzed. The temperature range in the GP lab of 21º to 25 ºC was common throughout the mission. The bath temperature was maintained at 24º for all samples.

d. Standards Used

The salinometer was standardized during the mission using IAPSO standard water, Batch P141 dated June 12, 2002 having a K15 value of 0.99993 and a salinity of 34.997. Typically, standardization checks were performed at the beginning of a run and then after 25 samples were analyzed. A sub-standard was sometimes used to check the performance of the instrument at some time during a run.

e. Performance of the Autosal salinometer

Overall the salinometer worked well during the mission. The lab temperature was stable during all runs which is an important factor when trying to optimize the performance of the instrument.

2. Oxygen — Rick Boyce / Ross Hendry

a. General

Samples for the determination of dissolved oxygen were drawn from approximately 66% of the rosette water sampling bottles (516 of 785 bottles). Essentially complete coverage was obtained for the primary AR7W line: for those stations, 86% (459 of 536) of all rosette bottles including all bottles for stations in water depths greater than 2000 m were sub-sampled and analyzed for oxygen. No water samples were taken at Event 63 (Site L3_8.5) or at Event 203 (a CTD station taken between Sites L3_18 and L3_19 to better resolve an eddy). Replicate samples were drawn and analyzed for 30 bottles, or about 6% of the bottles analyzed.

The samples were analyzed using the Winkler titration technique with a computer-driven automated system developed at the Scripps Institute of Oceanography.

There were major problems with the standardization of the oxygen titration system. These problems will have to be resolved before useful bottle oxygen values can be produced

b. Sampling Procedures

For this cruise 10 L bottles attached to a 24-bottle Rosette Sampler were used for water sampling. Oxygen sub-samples were drawn after chlorofluorocarbon (CFC) and total organic carbon (TOC) sub-samples. The oxygen sampling bottles are 125 mL 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.

All members of the CTD watches participated in the drawing of oxygen samples. Each oxygen sub-sample was drawn through a silicone rubber tube attached to the bottle spigot of the Rosette bottle. The flask was thoroughly rinsed and filled to overflowing; the flow was then allowed to continue until two to three flask volumes overflowed. The sampling tube was slowly retracted with continuous low flow to ensure that no air was trapped in the flask. The flask stopper was also rinsed.

Immediately thereafter, one mL each of alkaline iodide and manganous chloride was added from a dispenser in the winch room. The flask stopper was carefully inserted to avoid introducing air. The flask was then thoroughly shaken.

The oxygen samples were removed from the winch room to the General Purpose (GP) laboratory. The flasks were shaken a second time in the GP laboratory. The tops of the stoppers were sealed with distilled water while the precipitate settled prior to analysis.

c. Analysis Equipment and Technique

The oxygen samples were analyzed using an automated procedure developed by the Ocean Data Facility of the Scripps Institute of Oceanography (OSD/SIO, 2000). This procedure is a modified Winkler titration from Carritt and Carpenter (1966). The samples are acidified by the addition of 1.5 mL of sulphuric acid. Dissolved oxygen content is determined by an automated whole bottle titration using sodium thiosulphate and a UV end-point detection. A potassium iodate (KIO3) solution was used as the working standard. The temperatures of the KIO3 and thiosulphate are logged to allow for temperature-related corrections.

Experienced personnel prepared the standard solutions and set up of the titration apparatus. Two operators shared the oxygen titrations in addition to their general watch-standing duties. One of the operators was completely new to the procedure and had to be trained on the job.

Most of the samples were titrated between four and sixteen hours after the drawing of samples. The exceptions were twelve samples including two replicates from Events 36 and 40 (shallow Sites L3_03 and L3_04) that were analyzed approximately two hours after the second shaking.

d. Replicate Analysis

Replicate samples were drawn and analyzed from 30 rosette bottles, about 6% of the total number. Absolute differences in oxygen concentration for the replicate pairs are plotted as a function of titration time in Figure 1 below. Excluding two outliers with absolute differences greater than 0.1 mL/L, the maximum absolute difference was 0.018 mL/L and the root-mean-square difference of replicates was 0.008 mL/L. If the replicates were independent, this would imply a sampling and analysis precision of $0.008/\sqrt{2} = 0.006$ mL/L (standard deviation). The replicate statistics for samples run by the two operators were identical.

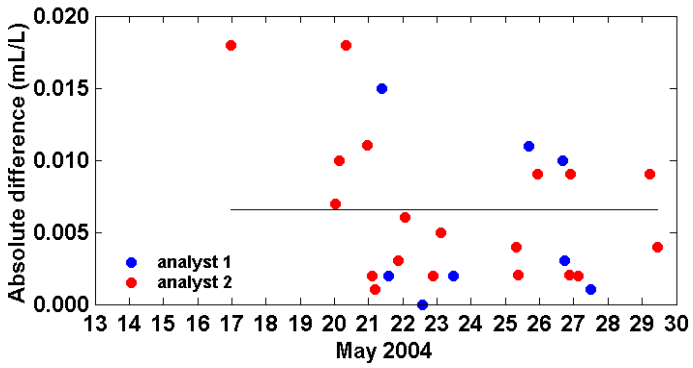

Figure 1 Absolute differences of oxygen replicates as a function of titration time. The solid line marks the mean value of 0.006 mL/L excluding two outliers that are not shown.

e. Standards and blanks

A total of approximately 60 standards and blanks divided into 15 sets were run at intervals during the cruise. Standards are determined by the titration of a precisely known volume (~10 mL) of KIO3 solution. The procedure followed was to obtain at least three self-consistent standards and blanks before each batch of samples was run. The oxygen analysis software allows the operator to subjectively flag a suspect individual titration as invalid. The average values of valid standards and blanks for each such set of titrations are used by the analysis program to compute oxygen concentration after each titration. The individual titration volumes and auxiliary information are stored for possible re-processing. Each of the 15 sets of standard and blank determinations involved between 3 and 14 individual titrations. The root-mean-square (rms) of the sample standard deviations for the 15 sets was approximately 0.002 mL for standards and 0.001 mL for blanks. The mean standard and blank values and the associated standard errors of the mean for the 15 runs are plotted as a function of titration time in Figures 2 and 3 below.

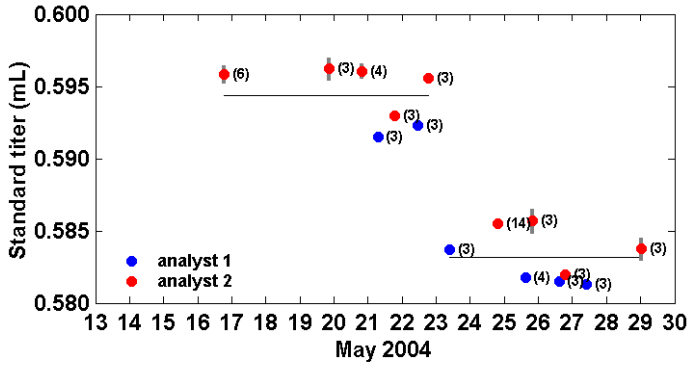

Figure 2 Set-mean standard titer as a function of titration time. The standard error of the mean and the number of individual titrations for each set are indicated. The solid lines mark the mean value of the set means before and after the shift in standard titers.

In principal, these values should not change appreciably during a cruise period. However, Figure 2 shows an abrupt shift in the standard from approximately 0.594 mL to 0.583 mL between early evening May 22 and mid-morning the following day. This 2% decrease in standard gives an increase in calculated oxygen concentration of 2%, or 0.12 mL/L for a nominal concentration of 6 mL/L. The standard values before and after the shift are self-consistent. The standard deviations for the run-average standards shown in Figure 2 before and after the shift are identical at 0.002 mL. The group includes seven values before the shift and eight values after the shift.

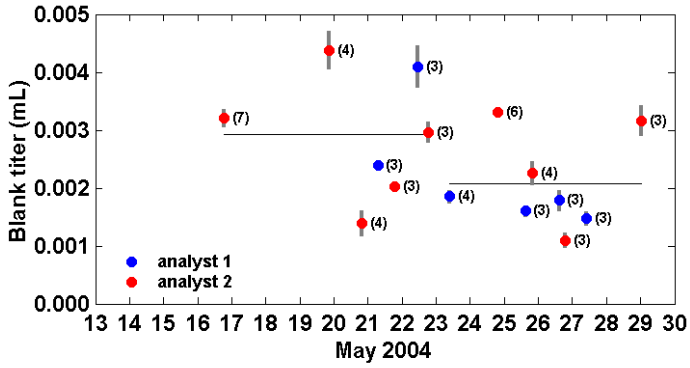

Figure 3 Set-mean blank titer as a function of titration time. The standard error of the mean and the number of individual titrations for each set are indicated. The solid lines mark the mean value of the set means before and after the shift in standard titers.

A post-cruise comparison of the Hudson 2004-016 bottle oxygen values reported by the oxygen analysis program for the AR7W sites with bottle oxygen values from the 2003 AR7W occupation on Hudson 2003-038 suggests that neither the of the internally-consistent groups of standards from the 2004 survey gives accurate results. The pre-shift 2004 oxygen concentrations are systematically 0.2 mL/L lower than the 2003 results and

post-shift 2004 oxygen concentrations systematically 0.1 mL/L lower than the 2003 results.

The standardization issues will need to be resolved to realize any useful bottle oxygen results. This problem is under investigation.

The 15 blank values in Figure 3 have an overall average of 0.0025 mL and overall standard deviation of 0.001 mL. The averages before and after the shift in standards are 0.0029 and 0.0021 mL respectively. The difference between the mean blank before and after the shift in standards is not statistically different from zero at the 95% confidence level.

f. Comments

The number of replicate samples was somewhat less than the 10% minimum recommended by the WOCE Hydrographic Program (WHP) Operations and Methods Manual for dissolved oxygen (Culberson, 1991). The WHP manual suggests as a minimum requirement that two times the root-mean-square (rms) difference in replicates should be less than 0.5% of the highest oxygen concentrations encountered. For the present cruise, this gives 0.044 mL/L for a maximum observed oxygen concentration of 8.9 mL/L. The two-times-rms statistic for the 28 replicates was 0.016 mL/L. This suggests a reasonable standard of sample drawing and analysis was achieved on the cruise.

In several instances, oxygen flasks presented for titration were found to have the wrong stoppers. Since each pair is individually calibrated, the sample volumes for the mismatched flask/stopper combinations must be recalibrated before these results can be used. All such instances were noted in the oxygen system log. However, it may not be obvious when switch was made.

Procedures for drawing and handling oxygen samples were not specifically reviewed with winch room personnel at the start of the cruise. In principle, it would be useful to do so.

The clamp that holds the oxygen flask for titration is awkward to manipulate. Although the operation improves with practice, a better design would make it easier on the operator and might improve the titration results.

The thiosulphate Dosimat failed to stop dispensing several times when the flushing function was invoked. The Dosimat had to be turned off and on and the PC titration system restarted when this happened.

For best results, the oxygen analyses should be done by a trained operator. The system is simple enough to use that inexperienced operators can achieve reasonable results under good conditions. Untrained personnel are less able to recognize and diagnose problems

when they occur. Thanks are owing to Frank Zemlyak for setting up the oxygen titration system and for his help with maintaining it on the cruise even though his other responsibilities left him with little time.

3. Nutrients — Carol Anstey

a. Description of Equipment and Technique

Samples were analyzed for silicate, phosphate, and total nitrate (nitrate plus nitrite) 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. (Strain and Clement, 1996).

b. Sampling Procedure and Data Processing Technique

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

A sample run includes six Calibration 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 (Sigma, ACS Reagent) as is the wash water. The standards are checked against reference standards: WAKO CSK Standards (Sagami Chemical Center, Japan) and NRC Intercalibration Reference Standard MOOS-1.

Analog data is converted to digital, processed and has statistics calculated on them by an in-house Pascal 7.0 program (AAII) on a PC. Chart recordings, hard copy and disk copies of the data are kept for reference.

c. Replicate Analysis

Samples were collected in duplicate from every bottle on the rosette into 30 ml acid washed HDPE screw-capped bottles. Total number of duplicate samples analyzed: 1398. These were refrigerated until analysis, typically within 12 hours of collection. The water samples were transferred to acid washed 7 ml cups for analysis with the AutoAnalyzer.

There were two technical problems encountered during analysis of the samples. Two days into the cruise, the PC hard drive used in acquisition of the data “crashed” and had to be replaced. This was done in a timely fashion thanks to the ship’s technician so as not to leave samples refrigerated for too long ~ 6 hours. Three days later, rough weather

shook the data acquisition board loose in the computer. That day's samples were frozen until the problem could be fixed. The affected samples were: 277237 – 277261 and 277278 – 277325. These samples were thawed at room temperature and run the following shift.

The data quality parameters, determined with check standards, CSK Reference Standards and RMS offset from the calibration curve, came well within accepted values. Frequent flushing of the system with 1N NaOH followed by Alpha-Q water helped to prevent sample flow problems and build-up of molybdate coating of the flow cells.

The laboratory temperature during all analyses was between 18 and 25 °C.

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

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

	Silicate	Phosphate	NO2+NO3
Detection Limit (μ moles/kg)	0.653	0.048	0.084

4. Total Inorganic Carbon in Seawater — Bob Gershey / Peter Jones

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 using a coulometric titration technique. This involves the reaction of carbon dioxide gas with a dimethysulfoxide solution of ethanolamine 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 ethanolamine 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 a 10% solution of carbon dioxide-free phosphoric acid. The solution in 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.

b. Sampling Procedure and Data Processing Technique

Samples for total inorganic carbon were drawn from all bottles tripped at standard hydrographic depths on whole-number sites on the AR7/W line.

Samples are drawn from the rosette immediately following the drawing of the oxygen samples in order to minimize exchange of carbon dioxide gas with the head space in the sampler. This exchange 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 analyzed within four to five hours, the sample is poisoned with 100 µl/250 ml of 50% saturated mercuric chloride solution. The bottle is tightly sealed and stored preferably at the temperature of collection in the dark.

Theoretically, the coulometer should give a direct measurement of the amount of carbon titrated based on calculations using the Nernst equation. In practice, the coulometer's calibration is checked using Certified Reference Materials obtained from the Scripps Institute of Oceanography, LaJolla, California. These samples are treated in the same manner as a seawater sample. Values are reported in units of µmol/kg. The overall precision of the analysis should be at least 1.5 µmol/kg for samples with concentrations in the range of 1800-2300 µmol/kg.

5. Alkalinity — Bob Gershey / Peter Jones

a. Description of Equipment and Technique

The total alkalinity of seawater is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with dissociation constants of less than $K=10^{-4.5}$) over proton donors (acids with $K>10^{-4.5}$) in a one kilogram sample. An automated potentiometric titration system is used to determine this quantity. During the course of the titration the pH is measured using a Ross combination electrode standardized using a Hansson seawater buffer. A known volume (~25ml) of sample is measured in a calibrated, thermostated pipette and dispensed in to an open cup. The alkalinity of the sample is estimated from its salinity and acid equivalent to 0.7 of this amount is added and the pH measured. A further three aliquots of acids are added to bring the titration to 90% completion. The Gran Function F3 (Stumm and Morgan) is then applied to these points to obtain a more refined estimate of the alkalinity. Five additional aliquots are then added to complete the titration.

b. Sampling Procedure and Data Processing Technique

Samples for alkalinity were drawn from all bottles tripped at standard hydrographic depths on whole-number sites on the AR7/W line. Samples are collected using the same procedure as for Dissolved Inorganic Carbon (see Section 5b).

The pH values for the last five points of the titration are used to evaluate the Gran Function F1 from which the final estimate of the equivalence point is obtained. Hydrochloric acid used in the titrations is calibrated is two ways: against a standard solution of sodium borate using an acid base titration and against potassium iodate using an iodometric titration with sodium thiosulphate. In addition, the calibration is checked using Certified Reference Materials obtained from the Scripps Institute of Oceanography, LaJolla, California. Values are reported in units of μmol/kg. The overall precision of the analysis is 1.5 μmol/kg for samples with concentrations in the range of 1900-2400 μmol/kg.

6. Halocarbons — Bob Gershey / Peter Jones

a. Description of Equipment and Technique

The suite of halocarbon compounds analyzed include the chlorofluorocarbons: CFC-12, CFC-11, CFC-113 and the halocarbons carbon tetrachloride and methyl chloroform. 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 used to collect the samples. A minimum of two volumes of water are used to rinse the sample pipette. The samples are purged for four minutes with ultra high purity nitrogen at a flow rate of 80 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 170°C. The contents of the trap are then passed through a 75m DB-624 megabore column. The resolved components exiting the column are quantified using electron capture detection.

b. Sampling Procedure and Data Processing Technique

Samples for halocarbons were drawn from all bottles tripped at standard hydrographic depths on whole-number sites on the AR7/W line, with the exception of location 14, which was not sampled.

Samples are collected directly from the rosette using 100 ml syringes to avoid contact of the sample with the atmosphere. 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 bottles. The samples are then stored in a water bath of continuously flowing surface sea water until analysis. Air samples are taken in the winch room at the start of the cruise to ensure that it is not contaminated. The analysis of the samples is always completed within

24 hours after they have been drawn. Duplicates are taken at each station, with some of these being run on each system to ensure that the results are comparable.

Chromatograms are analyzed using a commercial software package. Concentrations of the various components are evaluated from baseline-corrected peak areas. Calibration is carried out using working gas standards made up at Brookhaven National Laboratories. These standards have been calibrated in turn against a standard air sample ALM-64975 provided by CMDL/NOAA, Boulder Colorado. 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.

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