

**CRUISE REPORT**

**HUDSON 2011009**

**LABRADOR SEA,  
WOCE LINE AR7W**

**SCOTIAN SHELF AND SLOPE,  
EXTENDED HALIFAX LINE**

**LAURENTIAN FAN**

**May 6 – May 28, 2010**

## **A. CRUISE NARRATIVE**

### **1. Highlights**

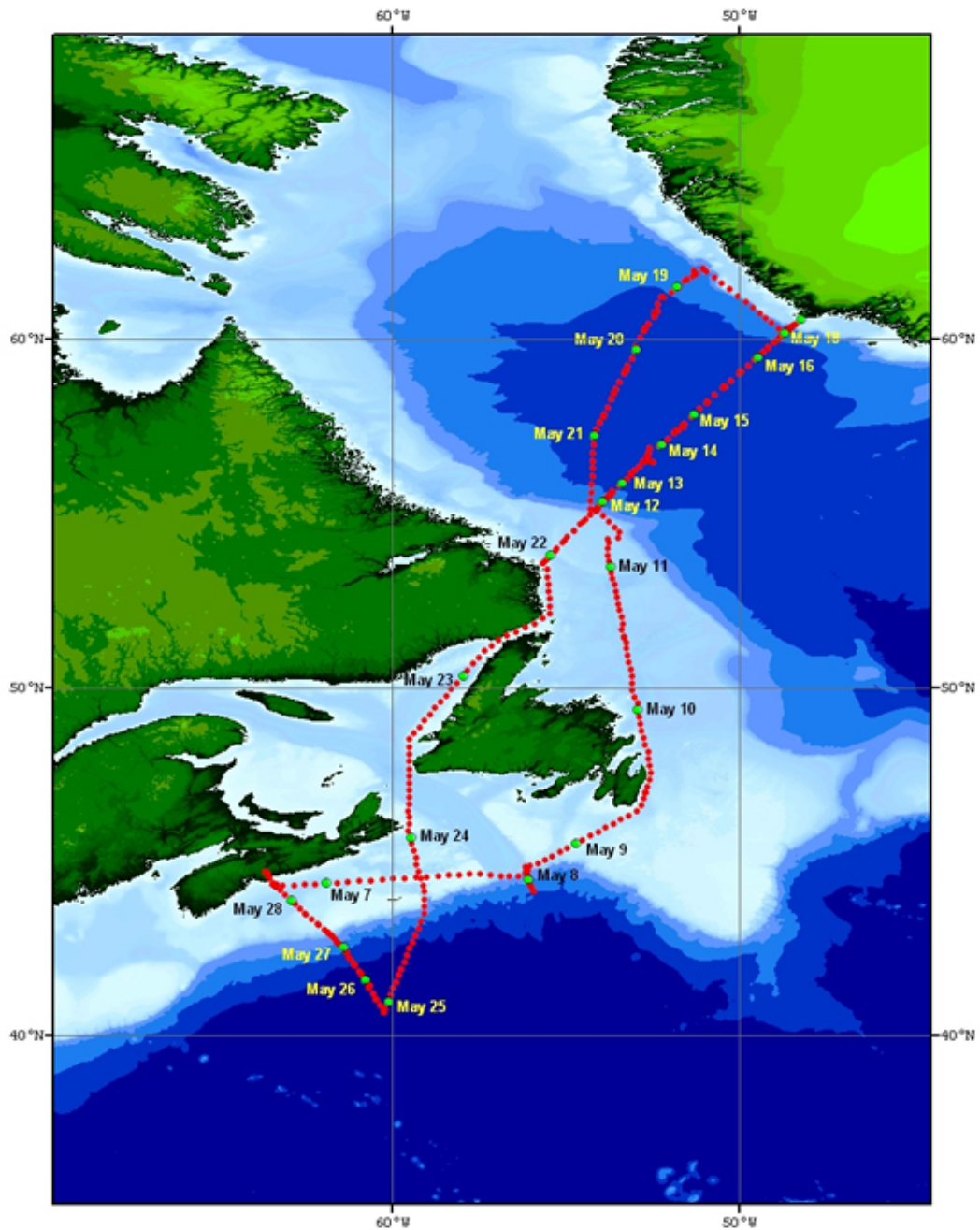
- a. WOCE Designation: WOCE Line AR7W
- b. Expedition Designation: HUD2011009 or 18HU11009 (ISDM format)
- c. Chief Scientist: Igor Yashayaev  
Ocean Sciences Division  
Department of Fisheries and Oceans  
Bedford Institute of Oceanography  
PO Box 1006  
Dartmouth, NS, Canada B2Y 2A4  
Internet Igor.Yashayaev@dfo-mpo.gc.ca
- d. Ship: CCGS Hudson
- e. Ports of Call: May 6, 2011 BIO, Dartmouth, NS, Canada  
May 28, 2011 BIO, Dartmouth, NS, Canada
- f. Cruise Dates: May 6 to May 28, 2011

### **2. Cruise Summary Information**

#### **a. Cruise Track**

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

The World Ocean Circulation Experiment (WOCE) - format cruise station summary file (SUM) outlines the science operations conducted during the cruise.



**Figure A.2.1** Cruise track for HUD2011009. The red dots indicate the ship's position for each hour of the voyage. The green dots and date labels indicate the ship's position at 0000 UTC for that particular date.

## b. Total Number of Stations Occupied

The CTD / ROS station positions are shown in Figure A.2.2. Table A.2.1 lists the science operations for HUD2011009.

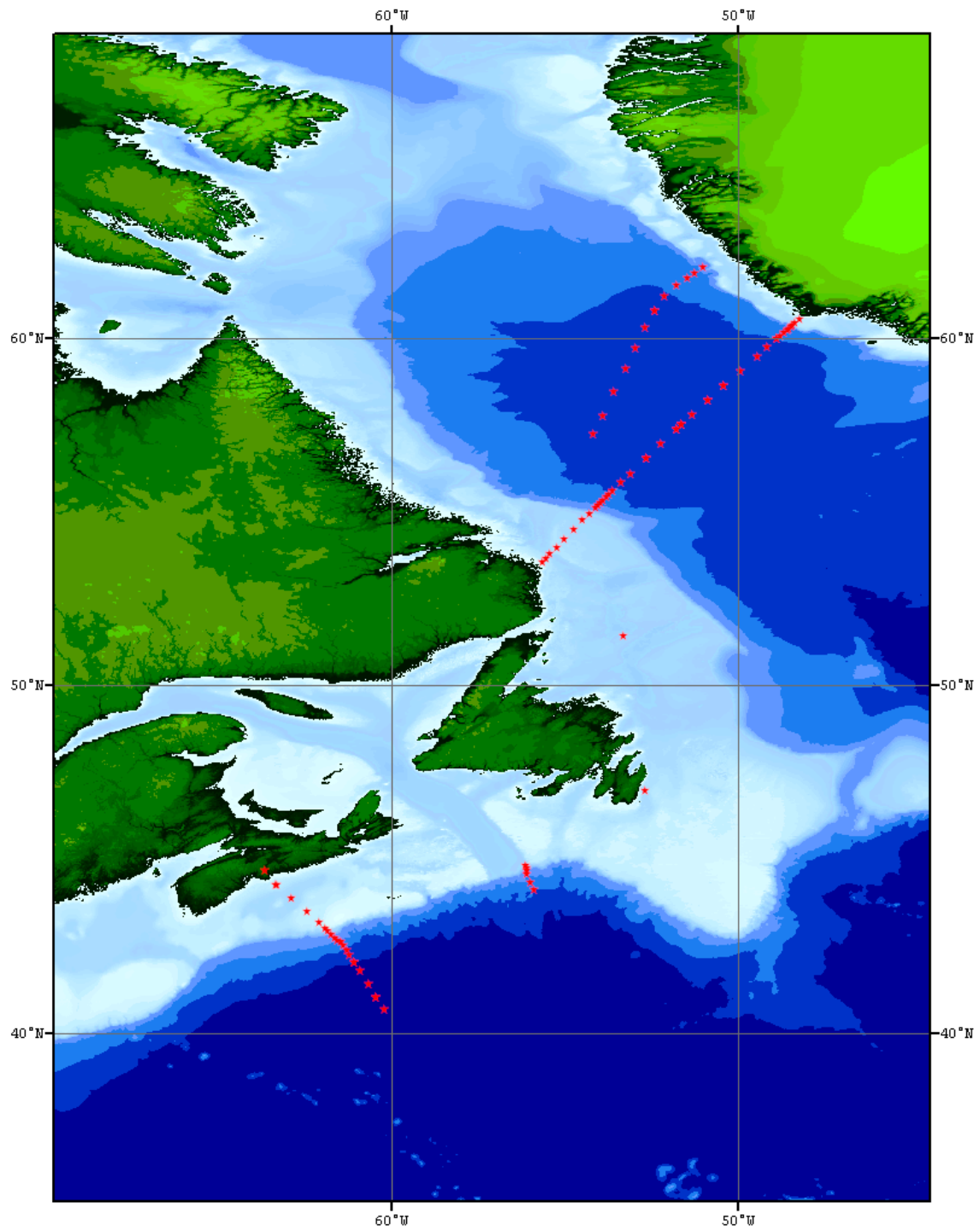
Along AR7W, the stations were full-depth WHP small volume rosette casts with up to 24 rosette bottles. Water samples were analyzed for CFC-12, SF<sub>6</sub>, total inorganic carbon (TIC), total alkalinity, oxygen, salinity, nutrients (nitrate, phosphate, and silicate), total organic carbon (TOC), pH, and bacterial abundance. Chlorophyll was analyzed at depths less than 200m at most stations. Samples were collected for <sup>129</sup>I (iodine-129), O-18 (Oxygen-18), and noble gases on selected casts.

Cast Type	Number of Operations	Operation Details	Operation Numbers
Rosette & CTD	36	The 28 regular AR7W sites (L3 line) plus some extra occupations: 0, 8.5, 9.5, 10.5, 16.3, 23.5, 24.5, and 25.5	see Table A.2.2
	19	Extended Halifax Line sites: 2 (twice), 3, 4, 5, 5.3, 5.5, 6, 6.3, 6.5, 6.7, and 7 - 14	4, 344, 346, 350, 352, 354, 357, 359, 361, 364, 366, 367, 369, 371, 372, 374, 376, 378, 381
	12	Sites all a line north of L3	216, 219, 222, 227, 234, 245, 252, 262, 271, 283, 293, 301
	6	Laurentian Fan sites: 3.5, 5, 6, 7, 8, and 9	7, 8, 9, 10, 12, 13
	8	Biology / Transit Casts	1, 16, 19, 69, 144, 183, 348, 356
	5	Unsuccessful CTD Operations	98, 102, 103, 129, 244
Moorings	3	Recovery	6, 11, 24
	4	Deployment	5, 25, 42, 189
Floats	15	APEX floats deployed	52, 72, 85, 97, 115, 131, 146, 168, 185, 235, 246, 253, 272, 284, 294
Biology	53	200 micron net tows	See Table A.4.2.1. for occupation locations
	43	76 micron net tows	See Table A.4.2.1. for occupation locations
	18	Egg Production rates	See Table A.4.2.1. for occupation locations
	6	Successful Multinet tows	345, 351, 353, 355, 358, 360
	2	Unsuccessful Multinet tows	347, 362
Chemistry	14	<sup>129</sup> I surface	23, 51, 84, 104, 130, 145, 158, 176, 193, 196, 215, 333, 340, 343,
	3	<sup>129</sup> I bottom	32, 204, 344
	12	<sup>129</sup> I profile	40, 60, 70, 114, 167, 184, 346, 350, 352, 354, 357, 359
Other		~ 525 Hrs Ship Board ADCP	No number assigned
	150	XBT Deployments	-
	1	Unused Operation Number	71

**Table A.2.1** Science operations conducted on HUD2011009.

<b>AR7W Site Number</b>	<b>2011009 Deep Cast Operation Number</b>
0	343
1	340
2	337
3	333
4	330
5	326
6	323
7	320
8	23
8.5	28
9	32
9.5	33
10	36
10.5	41
11	40
12	51
13	60
14	70
15	84
16	96
16.3	104
17	114
18	130
19	145
20	158
21	167
22	176
23	184
23.5	211
24	215
24.5	212
25	204
25.5	200
26	199
27	196
28	193

**Table A.2.2.** AR7W (L3) sites and rosette and CTD operation numbers for HUD2011009.



**Figure A.2.2** HUD2011009 locations (red-filled stars) for operations involving one or more of the following data collection methods: Rosette, CTD and LADCP.

The AR7W Labrador Sea section and the extended Halifax Section were occupied during the HUD2011009 mission. These survey lines combined with the Orphan Basin lines occupied within the same four week period on HUD2009011 provide a comprehensive assessment of the oceanographic conditions in the Canadian sector of the Atlantic Ocean.

**c. Floats and Drifters deployed**

Fifteen APEX profiling floats (Teledyne Webb Research, E. Falmouth, MA) equipped with SBE-41 temperature-conductivity sensors (Sea-Bird Electronics, Inc., Bellevue, WA) were deployed as a Canadian contribution to the international Argo project. This effort was jointly supported by Fisheries and Oceans Canada and the Canadian Ice Service of Environment Canada. Table A.2.3 gives details of the float deployments.

Apex Float		Event	Launch Position		Start Time	Launch Time
Type	SN		Latitude	Longitude	UTC	UTC
APEX-SBE	5660	52	55° 51.85' N	053° 21.28' W	12 May 2011 22:59	13 May 2011 00:13
APEX-SBE	5659	71	56° 34.05' N	052° 38.90' W	13 May 2011 16:00	13 May 2011 16:36
APEX-SBE	5664	85	56° 58.03' N	052° 13.26' W	13 May 2011 23:20	14 May 2011 00:38
APEX-SBE	5663	97	57° 22.76' N	051° 47.55' W	14 May 2011 05:00	14 May 2011 08:01
APEX-SBE	5652	115	57° 47.90' N	051° 19.99' W	14 May 2011 22:36	14 May 2011 23:45
APEX-SBE	5666	131	58° 13.38' N	050° 53.22' W	15 May 2011 05:35	15 May 2011 05:59
APEX-SBE	5665	146	58° 38.57' N	050° 23.44' W	15 May 2011 12:43	15 May 2011 13:09
APEX-SBE	5654	168	59° 29.57' N	049° 28.96' W	16 May 2011 01:32	16 May 2011 02:39
APEX-SBE	5653	185	59° 58.80' N	048° 54.07' W	16 May 2011 13:31	16 May 2011 14:15
APEX-SBE	5662	235	61° 11.99' N	052° 13.74' W	19 May 2011 06:58	19 May 2011 08:02
APEX-SBE	5661	246	60° 47.44' N	052° 20.28' W	19 May 2011 13:16	19 May 2011 14:12
APEX-SBE	5658	253	60° 19.21' N	052° 41.49' W	19 May 2011 18:56	19 May 2011 19:38
APEX-SBE	5657	272	59° 06.53' N	053° 13.91' W	20 May 2011 06:25	20 May 2011 07:30
APEX-SBE	5656	284	58° 26.26' N	053° 35.83' W	20 May 2011 13:45	20 May 2011 14:13
APEX-SBE	5655	294	57° 45.62' N	053° 55.31' W	20 May 2011 19:33	20 May 2011 20:17

**Table A.2.3** APEX float deployments on HUD2011009.

#### **d. Moorings deployed or recovered**

##### **Moorings deployed and recovered**

The Aanderaa current meter mooring near station L3\_08 on the AR7W line was once again serviced on May 11, 2011. Mooring #1771 was recovered successfully under good sea conditions. The replacement mooring #1800 was deployed successfully on the same day.



**Recoveries:**

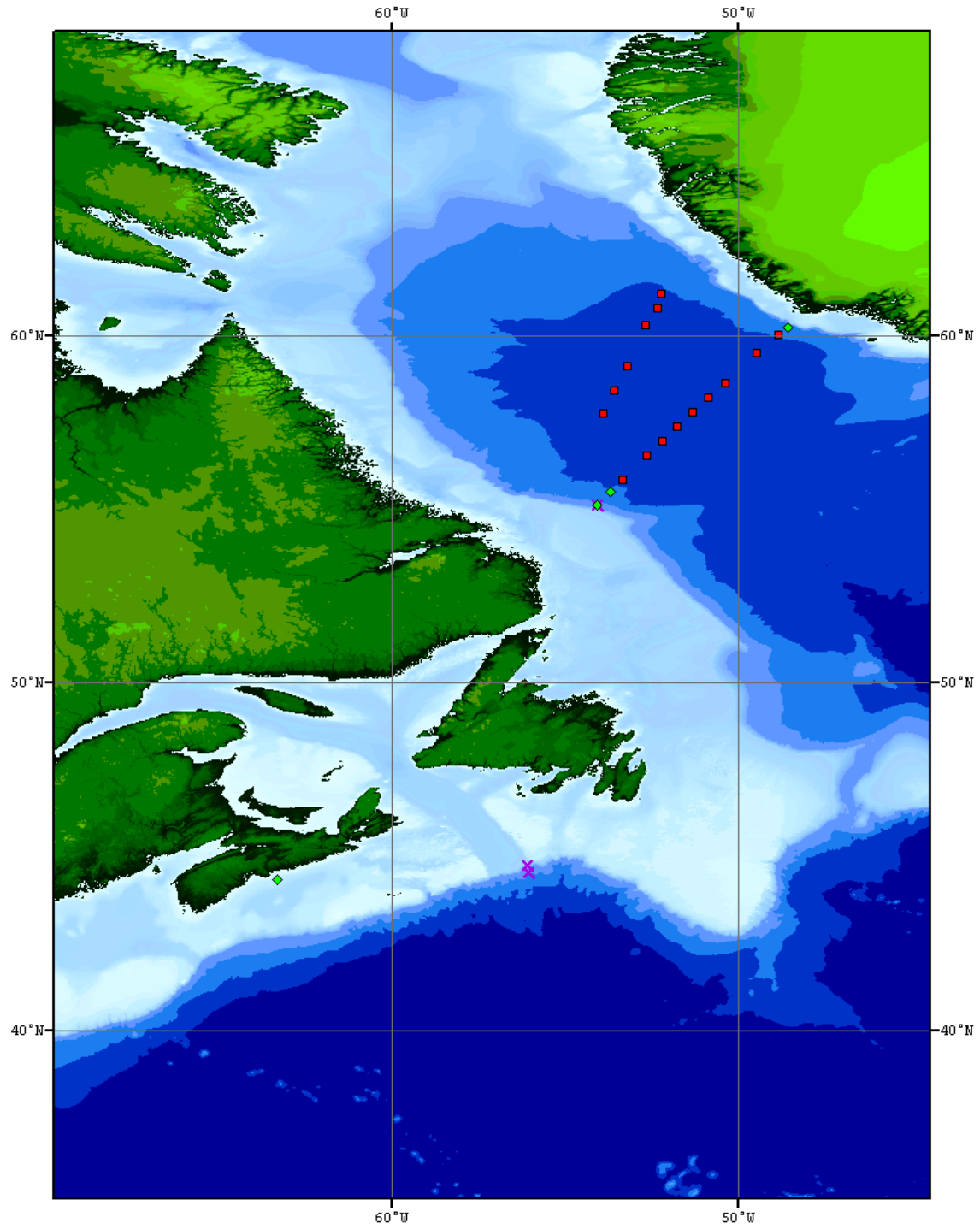
M 1771	55° 07.2120' N 54° 05.3901' W	Standard mooring consisting of one current meter positioned 20m above bottom along AR7W on the Labrador Slope (12-month deployment) at the 1000 metres.
M 1768	44° 33.3570' N 56° 03.9353' W	Standard mooring consisting of five current meters and one microcat. It was positioned within the Laurentian Fan area for a 12-month deployment at 2000 metres.
M 1769	44° 44.7909' N 56° 05.1443' W	Standard mooring consisting of four current meters and one microcat. It was positioned within the Laurentian Fan area for a 12-month deployment at 1100 metres.

**Deployments:**

M 1794	44° 20.8550' N 63° 18.3459' W	Standard mooring consisting of one ADCP. It was positioned near Halifax Line Station 2.
M 1798	60° 14.7114' N 48° 35.1256' W	Standard mooring consisting of one current meter and two microcats. It was positioned within the Labrador Sea on the Greenland Slope for a 12-month deployment at 2800 metres.
M 1799	55° 31.1353' N 53° 43.2353' W	Standard mooring consisting of one current meter and two microcats. It was positioned within the Labrador Sea on the Labrador Slope for a 12-month deployment at 2800 metres.
M 1800	55° 07.1682' N 54° 05.2179' W	Standard mooring consisting of one current meter and one microcat. It was positioned within the Labrador Sea on the Labrador Slope for a 12-month deployment at 1000 metres.

A software package called M-Cal (Mooring Calibrator) V 1.04 was used. M-Cal is a subset of a program called WorkBoat by James Illman of Software Engineering Associates. This enables the user to position the mooring once on the bottom. A computer is linked to the ship's navigation as well as, in this case, to the Benthos DS7000 deck unit. As the ship travels near the mooring, M-Cal transponds to the acoustic release and measures the time interval between the send and reply pulses. This information combined with the navigation data enables the program to calculate the position of the release. As more and more data is gathered, the position continually updates. M-Cal also calculates a depth for the release.

This software is of great use if a mooring is off location for some reason. M-Cal gives a position so that locating the mooring is much quicker. Transponding to a release only gives a slant range and not a direction. A ship has to randomly travel to minimize this slant range which could be time consuming.



**Figure A.2.3** HUD2011009 mooring deployment locations (purple X), mooring recovery locations (green-filled diamonds), and float deployment locations (red-filled squares).

### 3. List of Principal Investigators

Name	Affiliation	Responsibility
Kumiko Azetsu-Scott	BIO Azetsu-ScottK@mar.dfo-mpo.gc.ca	Chemistry program coordination, TA, TIC, CFC-12, O <sup>18</sup> , SF6, and pH.
Roberta Hamme	UVIC	Inert Gas Sampling
Glen Harrison	BIO HarrisonG@mar.dfo-mpo.gc.ca	Biological program coordination
Erica Head	BIO HeadE@mar.dfo-mpo.gc.ca	Macrozooplankton distribution, abundance, and metabolism
Bill Li	BIO LiB@mar.dfo-mpo.gc.ca	Pico-plankton distribution and abundance, bacterial abundance and productivity
John Smith	BIO SmithJN@mar.dfo-mpo.gc.ca	Radioisotope sampling program
Igor Yashayaev	BIO YashayaevI@mar.dfo-mpo.gc.ca	Senior Scientist, hydrography and mooring program coordination, XBTs

Table A.3.1. List of Principal Investigators (see Section 7 for addresses).

#### 4.1 Physical - Chemical Program

##### a. Narrative

The physical and chemical program on Hudson 2011009 continued an annual series of measurements in the Labrador Sea that began in 1990 as a contribution to the World Climate Research Programme and has evolved into a component of a multidisciplinary regional monitoring effort. The broad goals are to investigate interannual and long-term changes in the physical and chemical properties of the Labrador Sea and better understand the mechanisms that cause these changes. A particular focus is on changes in the intensity of winter overturning of surface and intermediate-depth waters and the resulting formation of Labrador Sea Water with varying temperature and salinity properties. This overturning is part of the thermohaline circulation that plays a role in the global climate system. Convection also transfers atmospheric gases such as oxygen and carbon dioxide from the surface layers to intermediate depths. The resulting oceanic storage of anthropogenic carbon reduces the rate of increase of carbon dioxide in the atmosphere but also increases the acidity of oceanic waters.

An occupation of the extended Halifax Line crossing the Scotian shelf, slope and in so-called Slope Water region complements the study of the Labrador Sea and is seen as an important part of the offshore monitoring program.

Finally, the mission was also aimed to recover two tall moorings and occupy a CTD section in the Laurentian Fan region.

The physical-chemical investigations are part of a larger multidisciplinary effort seeking a better understanding of interannual and long-term changes in regional ecosystems.

Hudson 2011009 program elements included:

1. CTD profile measurements of pressure, temperature, salinity, dissolved oxygen, pH, fluorescence, and light intensity at a fixed set of stations (AR7W/L3 line) spanning the Labrador Sea from Hamilton Bank on the Labrador Shelf to Cape Desolation Island on the West Greenland Shelf;
2. Same as 1 but on the Northern Labrador Sea line.
3. Measurements of salinity, dissolved oxygen, nutrients (nitrate/nitrite, phosphate, silicate), CFC-12, SF6, dissolved inorganic carbon, alkalinity, Noble gases and Iodine-129 from discrete water samples from a rosette sampler on the CTD package;
4. Recovery and redeployment of a current meter mooring providing near-bottom current and temperature measurements on the Labrador Slope in 1000 m water depth;
5. Recovery of two current meter moorings in the LF region;
6. Deployment of two new current meter moorings at 2800 m isobath on the western and eastern ends of AR7W;
7. Current measurements from a ship-mounted acoustic current profiler;
8. Current measurements at CTD stations from a lowered acoustic doppler current profiler (LADCP);
9. Temperature profile measurements from Expendable Bathythermographs (XBTs) at selected points between CTD stations;
10. Autonomous float deployments as part of the Canadian Argo Program and the international Argo Project;
11. Physical and chemical measurements on the Halifax Line on the Scotian Shelf in support of the Atlantic Zone Monitoring Program (AZMP);
12. Physical and chemical measurements on the Scotian Slope in support of an expanded offshore monitoring program and a joint study with the UK Proudman Oceanographic Laboratory;
13. Physical and chemical measurements in the LF region in support of PERD;
14. A phytoplankton biomass/primary productivity program conducted;
15. A microbial program;
16. A mesozooplankton program

The Labrador Sea station work went well except for problems with CTD cable termination, instrument cables, bird caging and tearing of CTD cable, and malfunctioning latching mechanisms on the water-sampler carousel. Two (or three we need to check) additional stations added on the Labrador Sea (western) side and two (or three) on the eastern side of AR7W. Favourable ice conditions on the eastern and western sides of the Labrador Sea at the time of our survey allowed the occupation of all planned stations on either end of the line (West Greenland and Labrador shelves).

The combined eXtended Halifax Line (XHL) was surveyed with 18 CTD casts, \$\$ Multinet hauls with 5 sampling levels down to 1000 m (HL\_6 – HL\_9), and 5 vertical ring net tows (HL\_3–HL\_5). The offshore survey stopped at HL\_9 because of time constraints. HL\_6.5

and all AZMP Halifax Line stations except Stations 1 and 2 were occupied. An Apex profiling float was deployed at HL\_9.

## **b. Chemical Oceanography**

The chemistry program conducted in the GP Lab during HUD2011009 included analysing water samples for dissolved inorganic carbon (DIC), total alkalinity (TA), transient tracers (CFC-12 and SF6), nutrients, and dissolved oxygen. Water samples for pH and oxygen isotope composition were also collected, preserved, and stored for later analysis.

## **c. Radioisotope Sampling Program**

Water samples were collected for  $^{129}\text{I}$  from a near surface rosette bottle at 14 stations on the L3 (AR7W) line. Samples for  $^{129}\text{I}$  were collected from near bottom rosette bottle at two L3 stations and one Halifax Line (HL) station. Fuller depth sampling for  $^{129}\text{I}$  was carried out at six L3 stations and six HL stations. See table A.2.1 for the list of corresponding operation numbers.

## **d. Inert Gas Sampling**

The samples collected on this cruise are part of a joint NSF funded project between Dr. Steven Emerson at the University of Washington (UW) in Seattle, WA and Dr. Roberta Hamme at the University of Victoria (UVic) in Victoria, BC.

*Sea-going Technician:* Karina Giesbrecht (UVic)

### **Objective:**

To characterize the inert gas content of the major water masses available in the Labrador Sea region, with particular emphasis on the water masses that form the deep water of the North Atlantic.

### **Sampling plan:**

Quadruplicate samples were taken at 40 depths spread out along the AR7W and Northern Lines to give a total of 160 samples. Analysis of these samples will be split between UVic and UW to determine the dissolved O<sub>2</sub>, N<sub>2</sub>, Ar, Ne, Kr and Xe concentrations using isotope-ratio mass spectrometry. These samples will also provide a means for inter-lab calibration between UVic and UW.

Specific stations and sampling depths were:

<b>Station</b>	<b>Depth</b>	<b>Station</b>	<b>Depth</b>	<b>Station</b>	<b>Depth</b>
L3_10	2650	L3_12	3100	L3_14	3160
	2150		2560		2440
	1210		2010		1730
			890		680

L3_15	3560	L3_17	1070	L3_18	3590
	2870		70		2900
	1290		2		2020
	140				1290

L3_19	2020	L3_22	3260	L3_23	2500
	1770		2460		380
	1070		1030		260
	510		480		

L3_24	340	A/B-9	1800	B/C-10	1500
	240		1200		2
			2		

## 4.2 Biological Program

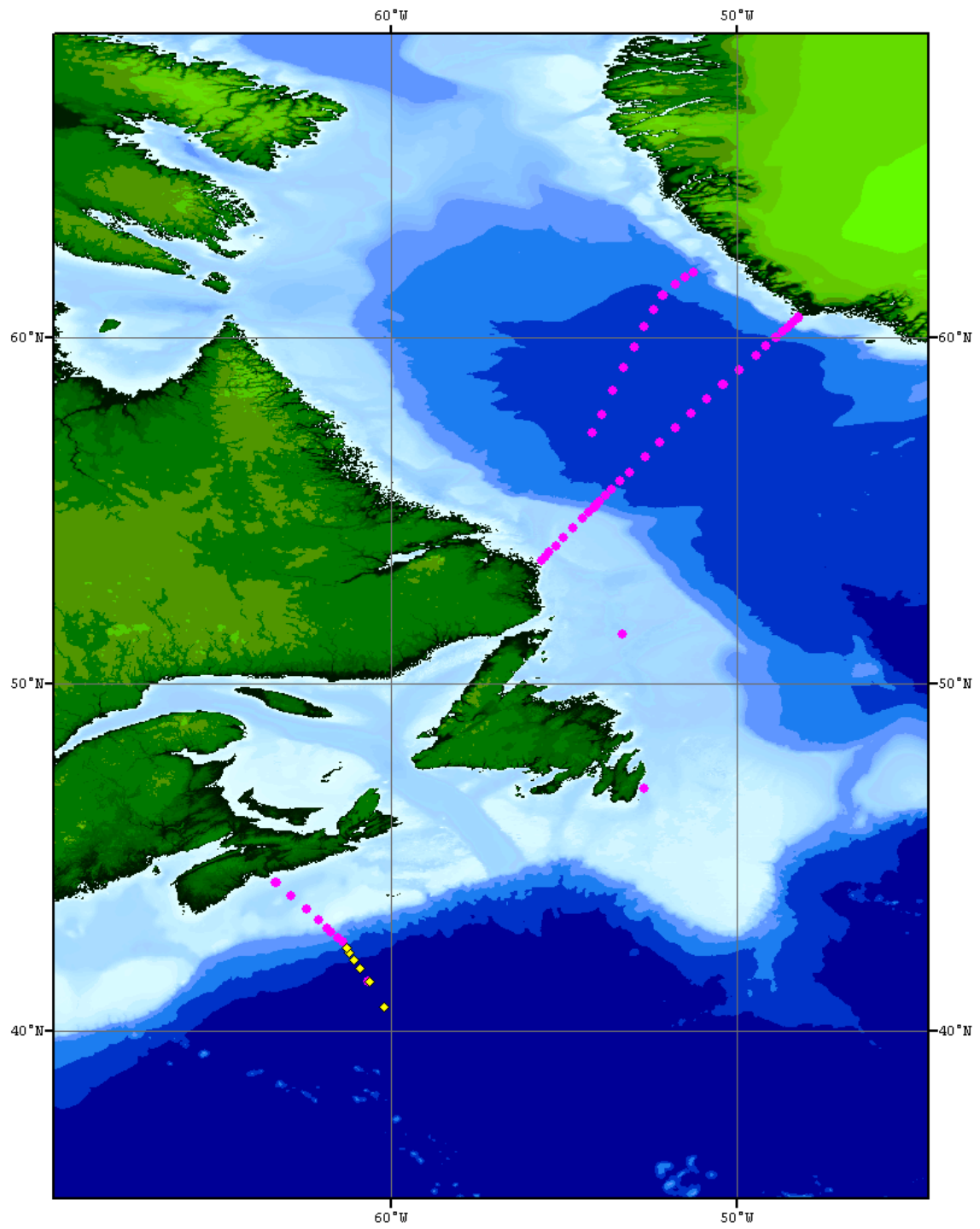
### a. Biological Oceanographic Sampling Program - *Jeff Anning, Tim Perry*

Nearly all stations occupied were sampled for a number of biological parameters. Samples were collected throughout the water column for bacterial identification and enumeration. In the upper 100 m samples were collected for chlorophyll analysis and at the surface samples were taken to measure particulate organic carbon, and determine pigment composition by HPLC and absorption spectra. At selected stations duplicate phytoplankton samples, integrated over the upper 50 m were preserved with Lugols and formalin.

### b. Zooplankton Sampling - *Marc Ringuette*

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.

We occupied a total of 58 stations, where we performed a grand total of 97 fishing activities. Vertical net tows were taken on the way out at HL2, at 2 stations in transit to the L3 line, at 30 stations on the L3 line, at 11 stations on the Northern Line and at 10 stations on the extended Halifax Line. At all stations, tows were made from 100 meters to the surface using a ring net of 75 cm in diameter and 200 µm mesh size, except on the Halifax Line where tows were from 1000 m or bottom. An additional tow was made using a using a 30 cm, 76 µm mesh ring net at 43 stations. See Table A.4.2.1 for details.



**Figure A.4.2.1** HUD2011009 ring net tow (pink-filled circles) and multi-net tow (yellow-filled diamonds) locations.

**c. Egg Production rates (EPr) of *Calanus finmarchicus* in the Labrador Sea - Marc Ringuette**

EPr was measured at 18 different stations the primary goal being to measure the secondary production of the predominant copepod species of the Labrador Sea. Egg production rate has been monitored for 24 hour to estimate the egg production they would have *in-situ* on a daily basis.

Hatching success measurements were done at stations L3\_02, L3\_04 and L3\_07. Water temperature was low (below 0°C) and the egg production was relatively high; therefore I thought it would be appropriate to make these measurements in order to more accurately adjust our estimate of the reproductive output.

**d. Depth Distribution of *Calanus finmarchicus* in the Slope Water off the Scotian Shelf - Marc Ringuette**

The vertical depth distribution of *Calanus finmarchicus* in the Slope Water off the Scotian Shelf was investigated. At six stations, HL -8 -9- 10 -11 -12 and -14, five depth strata (1000-800, 800-600, 600-400, 400-200, 200-0 meters) were sampled using a square 0.5 x 0.5 m multi-net fitted with five 200 µm mesh nets. See Table A.4.2.1 below. Battery pack died on us, so we weren't able to bring back any samples from the Multinet cast done at HL-13.

Also note that the wire on that winch will need to be replaced properly on the drum. The connection at the drum also needs to be redone because of corrosion that may cause problems at sea in upcoming cruises. The biggest problem we encountered was with the spooling device because it did not direct the cable in an appropriate manner. This resulted in cancelling the cast at station 7 and manually respooling the wire to retrieve the Multinet. This particular problem should be address before to let go this winch on another cruise.



Station	Date	Multi-net	Ring Net		EPr
			200µm	76µm	
HL2	6 May		X	X	
Biological cast #1	9 May		X		X
Biological cast #2	10 May		X		X
L3-8	11 May		X	X	X
L3-8.5			X	X	
L3-9			X	X	X
L3-10			X	X	
L3-11	12 May		X	X	X
L3-12			X	X	X
L3-13			X	X	
L3-14	13 May		X	X	
L3-15			X	X	X
L3-16			X	X	
L3-17	14 May		X	X	X
L3-18			X	X	
L3-19	15 May		X	X	X
L3-20			X	X	X
L3-21			X	X	
L3-22	16 May		X	X	
L3-23			X	X	X
L3-28			X	X	X
L3-27			X	X	
L3-26			X	X	
L3-25	17 May		X	X	X
L3-24			X	X	
A-4	18 May		X	X	
A-5			X	X	
A-6			X	X	
A/B-7	19 May		X	X	
B-8			X	X	X
B-9			X	X	
B/C-10			X	X	
C-11	20 May		X	X	
C-12			X	X	X
C-13			X	X	
C-14			X	X	
L3-07	21 May		X	X	X
L3-06			X	X	
L3-05			X	X	
L3-04			X	X	X
L3-03			X	X	
L3-02			X	X	X
L3-01			X	X	
L3-00	22 May		X	X	

**Table A.4.2.1.** Net tows performed and experiments on HUD2011-009.

Station	Date	Multi-net	Ring Net		EPr
			200µm	76µm	
HL-14	25 May	X			
HL-13				X	
HL-12	26 May	X			
HL-11		X			
HL-10		X			
HL-9		X			
HL-8		X			
HL-7	27 May		X		
HL-6.5			X		
HL-6			X		
HL-5			X		
HL-5.5			X		
HL-4			X		
HL-3			X		
HL-2			X	X	

**Table A.4.2.1 (continued):** Net tows and experiments performed on HUD2011009.

**e. Primary Production Measurements - Jeff Anning**

Water samples for photosynthesis-irradiance (P-I) experiments were collected from the rosette at 14 stations. For each incubation experiment, 33 aliquots were inoculated with <sup>14</sup>C labelled 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.

Station	Event	Lat.	Long.	Date	Time	Depth	ID
Bio-1/LF-3.5	13	44.825	-56.130	08/05/2011	"17:12:41"	29	378073
	13	44.825	-56.130	08/05/2011	"17:14:55"	3	378077
Bio-2	16	46.987	-52.691	09/05/2011	"12:00:26"	30	378086
	16	46.9867	-52.691	09/05/2011	"12:01:44"	10	378090
Bio-3	19	51.429	-53.307	10/05/2011	"12:35:53"	31	378101
	19	51.429	-53.307	10/05/2011	"12:37:50"	3	378106
Bio 4/L3-11.5	41	55.519	-53.724	12/05/2011	"13:05:23"	30	378208
	41	55.519	-53.724	12/05/2011	"13:07:24"	2	378211
L3-14	69	56.549	-52.662	13/05/2011	"10:57:26"	3	378270
L3-19	144	58.640	-50.417	15/05/2011	"06:30:22"	30	378399

	144	58.640	-50.417	15/05/2011	"06:32:42"	2	378402
L3-23	183	59.981	-48.901	16/05/2011	"07:43:17"	30	378506
	183	59.981	-48.901	16/05/2011	"07:46:01"	3	378509
L3-23.5	211	60.079	-48.787	17/05/2011	"14:56:23"	30	378611
	211	60.079	-48.787	17/05/2011	"15:00:18"	2	378617
A-3	216	62.040	-51.029	18/05/2011	"10:45:35"	30	378656
	216	62.040	-51.029	18/05/2011	"10:47:47"	5	378660
A/B-8	245	60.787	-52.431	19/05/2011	"10:58:58"	28	378753
	245	60.787	-52.431	19/05/2011	"11:01:01"	3	378756
C-12	283	58.450	-53.597	20/05/2011	"10:35:54"	3	378839
L3-7	320	54.960	-54.295	20/05/2011	"10:11:48"	30	378890
	320	54.960	-54.295	21/05/2011	"10:13:39"	2	378893
HL-13	348	41.044	-60.444	25/05/2011	"11:54:40"	31	379038
	348	41.044	-60.444	25/05/2011	"11:56:54"	3	379041
HL-10	356	42.040	-61.067	26/05/2011	"08:41:54"	30	379121
	356	42.040	-61.067	26/05/2011	"08:43:55"	2	379124

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

### 5. Major Problems and Goals Not Achieved

There were none to report.

### 6. Other Incidents of Note

There were none to report.

## 7. List of Cruise Participants

<b>Name</b>	<b>Responsibility</b>	<b>Affiliation</b>
Anning, Jeffrey	Biological	ERD, BIO
Anstey, Carol	Nutrients	ERD, BIO
Azetsu-Scott, Kumiko	Scientist, Carbonate, Alkalinity, O-18, pH	OSD, BIO
Boyce, Richard	Technical Operations Head, Salts, Moorings	OSD, BIO
Brittain, Derek	Winch Room, LADCP, VADCP	OSD, BIO
Brownell, Darlene	CFC-12, SF6, pH	OSD, BIO
Dimerov, Entcho	Computer Room, XBTs	MUN
Geshelin, Yuri	Oxygens	OSD, BIO
Giesbrecht, Karina	Inert Gas Sampling, Oxygens	UVIC
Greenan, Blair	Scientist , Computer Room	OSD, BIO
Jackson, Jeffrey	Data management, Computer Room	OSD, BIO
Kavanah, Mark	Computer Room, XBTs	MUN
Nelson, Richard	Carbonate, Alkalinity, pH	ERD, BIO
Perry, Timothy	Biological, Net Tows	ERD, BIO
Punshon, Stephen	CFC-12, SF6, pH	OSD, BIO
Ringuette, Marc	Biological, Net Tows	ERD, BIO
Ryan, Robert	CTD Tech., Winch Room	OSD, BIO
Yashayaev, Igor	Chief Scientist, Computer Room, XBTs	OSD, BIO

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

ERD Ecosystem Research Division

MUN Fisheries and Marine Institute of Memorial University of Newfoundland  
P.O. Box 4920 St. John's, NL Canada A1C 5R3

UVIC University of Victoria  
PO Box 1700 STN CSC  
Victoria BC V8W 2Y2, CANADA

OSD Ocean Sciences Division

## **B. UNDERWAY MEASUREMENTS**

### **1. Navigation and Bathymetry**

The navigation system onboard CCGS Hudson consists of one differential GPS receiver and navigation software. 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 running the navigation software, then rebroadcasts the NMEA strings to distribution units in the computer room, which provide many output lines for the working labs. The resulting broadcast navigation strings are ~ 1 Hz. The navigation data are then logged at specified intervals on a PC. For this cruise the navigation was logged approximately every second.

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. This has been the standard software package for years now. It was used on this mission to view the ship's position but it was not used to log the navigation data.

The navigation data was logged using the Geological Survey of Canada's (GSC) Survey Suite navigational software. This is a Microsoft Windows application package which grabs every NMEA string broadcast over the network. It adds a date/time stamp to every data record acquired. It is much easier to configure and operate than AGCNAV. The only negative observation is that it does not have a waypoint viewer.

The echo sounder system used for collecting bathymetric data at station locations consisted of a 12 KHz Raytheon PTR echo sounder that created an analog trace on a Raytheon Line Scan Recorder located in the forward laboratory. The transducer beam width is 15 degrees. The sweep rate of the recorder 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**

Ocean Surveyor II vessel mounted acoustic Doppler current profiler system consists of a 75 kHz phased array transducer assembly mounted in a well in the ship's hull. The deck unit and computer are located in the forward lab.

The transducer assembly is mounted on a ram penetrating the ships hull that can be lowered if necessary. Transducer remained in the retracted position for the duration of the cruise. It was determined during sea acceptance testing that lowering the transducer did not effect the operation of the system. The transducer is located approximately 6m below the waterline.

The system is capable of collecting bottom track data to 1000m and profile data to 650m. Setup includes 100-8m bins. The Ocean Surveyor was set to operate in the narrow band

single ping mode with 3 sec ensemble time. Position, heading, pitch and roll data is provided by the ADU5 attitude determination unit at a 1Hz rate. Ships gyro heading data is connected directly to the OSII deck unit. The Ocean Surveyor also includes a temperature sensor for sound speed calculations.

WinADCP software package used monitor profile data in real time. WinADCP is set to display times series of short-term averaged profile and attitude data. VmDas Software package used to deploy OSII and log raw data, VmDas option files, intermediate and processed files. Data back-up on external hard-drive. Data back-up includes only raw data and VmDas option files.

All NMEA strings are logged during data collection. The gyro heading is included in the raw data. Raw data is processed in real time for a short term average of 30sec and a long term average of 300sec.

Data will have to be reprocessed using gyro heading during periods with low quality or no attitude solution. Raw data can be reprocessed using VmDas.

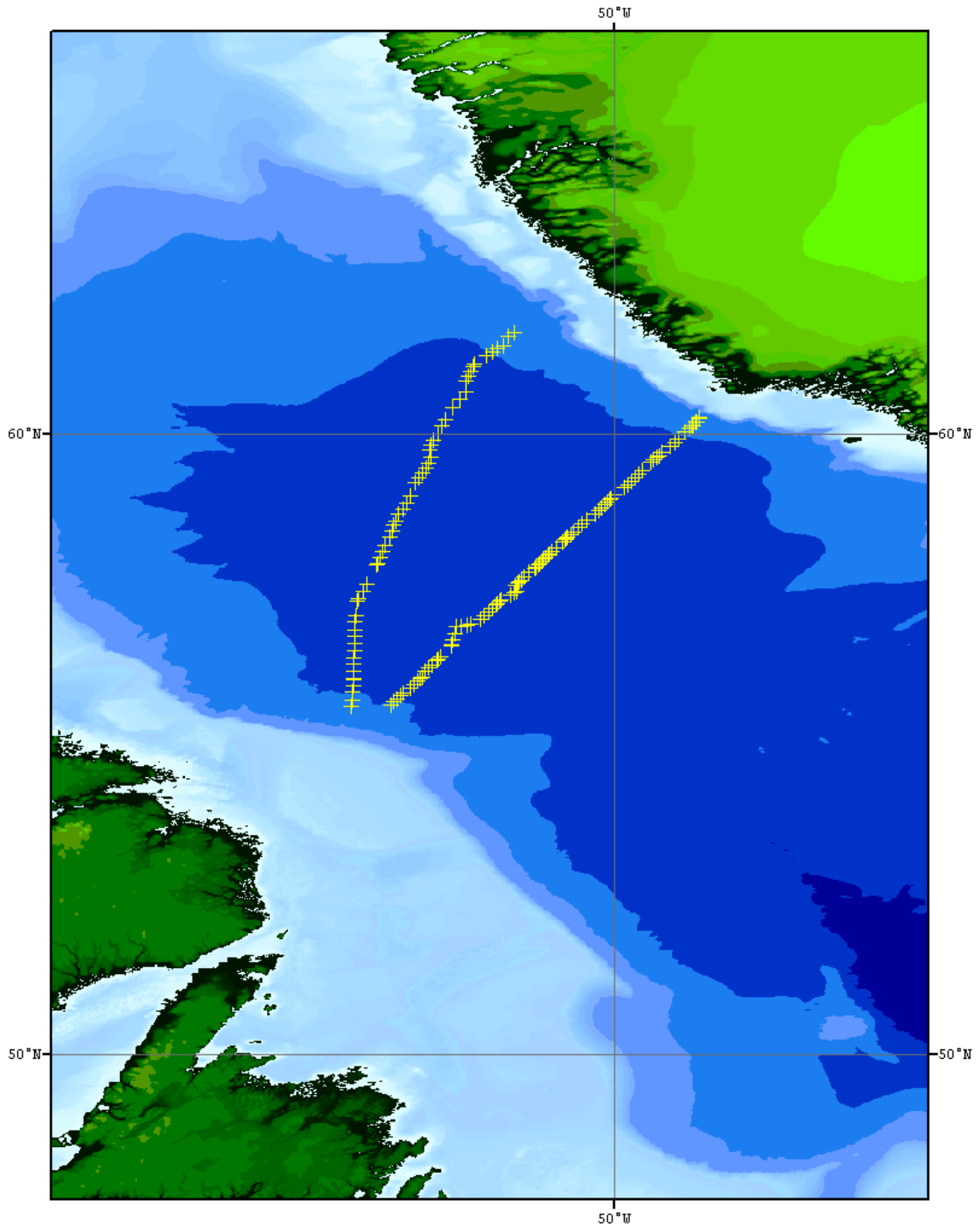
Significant increase in noise floor caused by bow thrusters while on station, during high sea states, or during travel at speeds in excess of 12 knots. Increase in noise floor results in significant decrease in data quality and reduction in profile range.

### **3. Continuous Flow Multisensor Package (CFMP)**

Water from approximately 4m was continuously pumped to the forward lab. The temperature, conductivity and fluorescence were measured and logged every 15 sec. The temperature and conductivity were measured with Sea-Bird Thermosalinograph and the fluorescence by a Wetlabs flow through fluorometer. Incident Photosynthetically Active Radiation was measured with a Li-Cor Spherical Quantum Sensor and this data was collected as hourly means. Exact time and positions were provided by the ships GPS and logged with the other data.

### **4. XBT measurements and high-resolution mapping of the thermal structure of the upper layer**

Expendable Bathythermographs were routinely deployed during the HUD2011009 mission. See Fig. B.4.1 for a map with the XBT drops indicated. We used three different models of XBTs: Sparton T5, Sippican T7 and Sippican T10. T5s are capable of measuring to maximum depths of 1900m at the cruising speed of 6 knots, T7s record temperature to 800m at the cruising speed 15 knots and T10s to 200m. The vertical resolution of the measurements was about 0.6-0.8m. There were 24 T5, 45 T7 and 27 T10 XBTs launched during the cruise (Table A.2.1 lists the operation numbers when these were deployed).



**Figure B.4.1** XBT sites (indicated by yellow crosses) during HUD2011009.

## **5. Ashtec ADU5 Attitude Determination Unit**

4-antenna receiver configuration uses differential carrier phase measurements to compute heading, roll, and pitch in real-time at a 5-Hz update rate.

Position and velocities are computed only for Antenna 1. The remaining antennas provide carrier phase data for attitude determination. Antenna 1 is a Beacon antenna providing differential position when in range of a base station. Beacon corrections were available for all but the most north – east portion of the cruise.

Antenna separations in a normal multipath environment determine the level of solution accuracy. Fore - aft antenna separation is 3m provides potential heading accuracy of 0.2 degrees. Port – starboard antenna separation of 1m provides potential pitch/roll accuracy of 0.6 degrees.

When the receiver is searching for the ambiguities, or when a valid solution has not been found code phase estimate of heading appears in the PASHR,AT2 string and pitch and roll are displayed as exactly 0.00. Heading may also be displayed as 0.00 if no estimate is available.

The PASHR, AT2 string contains a quality flag which indicated the quality of the solution.

When either of these situations exist, the attitude reset flag is set to 1 in the attitude output message (a 0 for the attitude reset flag indicates a good attitude solution).

If noisy or bad satellite measurement data was received by the ADU5 the Kalman filters sometimes get lost. This results in no valid solution. This often is the result of high multipath interference. BRMS and MRMS fields in the PASHR,AT2 string will exceed maximum noise levels, and the PDOP will become large. For a good solution PDOP should be less than 6.

Solution quality was monitored on a daily basis with the aid of the Teledyne RDI VMDAS and WinADCP software packages used to log and monitor the OSII ADCP current profile data.

## **6. Meteorological observations**

The officer of the watch manually logged meteorological variables at regular intervals. Negotiations are ongoing with the Meteorological Service of Canada to install an automated weather reporting system on Hudson.

## **7. Atmospheric Chemistry**

There was no atmospheric chemistry program.



## **C. HYDROGRAPHIC MEASUREMENTS - DESCRIPTIONS, TECHNIQUES AND CALIBRATIONS**

### **1. Salinity**

#### **Analyzed by Richard Boyce**

##### a. Description of Equipment and Technique

About 785 salinity samples were analyzed using a Guildline Autosol 8400B salinometer, serial number 69780. 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 should be retightened. The drying of the neck of the bottle and installing a dry cap has been a technique used since the HUD2000009 cruise and prevents salt crystals from forming under the cap if samples are left for a long period of time before analysis.

The samples are placed into a constant temperature water bath set to 23.5° C with the Autosol running at 24°C. The cell of the salinometer was filled and rinsed three times with sample water. A fourth sample was introduced into the cell and readings were averaged over a 10 to 15 second interval until the operator was satisfied that the correct value was attained. If there was any doubt in this value, subsequent refills were performed and readings averaged as above. Once satisfied, a sample ID number and Conductivity Ratio was recorded onto the Salinity Log Sheet. Periodically, the room temperature was recorded constantly.

##### b. Data Processing Technique

Conductivity ratios, sample ID's and standards were entered into the ODIN database. Conductivity ratios 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 Drawing Office. Cases of 24 salinity bottles were placed into water baths set at 23.5° C and allowed to equilibrate before analyzing. During this particular Mission, the room temperature in this area ranged remained quite stable hovering near 24 °C. The Autosal bath temperature was set to 23.5°C for all samples.

#### d. Standards Used

The salinometer was standardized during the mission using IAPSO standard water, Batch P151 dated May 20/12 having a K15 value of 0.99997, salinity of 34.999. Starting at ID# 378759, the standard changed to P152 dated May 5/13 having a K15 value of 0.99981, salinity of 34.993. Typically, standardization checks were performed at the beginning and end of a run.

#### e. Performance of the Autosal salinometer

Overall, the Autosal salinometer worked well during the mission. There was some drift in the standards over the cruise period. The introduction of water baths to bring the samples close to the temperature of the Autosal bath has made the analysis much better. The instrument spends very little time in bringing the sample to the temperature of the bath thus reducing bath fluctuations. The lab temperature was stable during all runs which is an important factor when trying to optimize the performance of the instrument. Historically the Autosal was setup in the General Purpose (GP) lab onboard Hudson. Air temperature was difficult to control in this area. For this mission the Autosal was installed in the Drawing Office where the operator could control the ambient air temperature much better than in the GP lab.

## **2. Measuring Dissolved Oxygen Concentration and calibration of Sea-Bird oxygen primary sensor on the Hudson 2011-009 mission**

**Analyzed by Yuri Geshelin**

### **1. Introduction**

In the spring of 2011, the CCGS Hudson carried out one field mission: 2011-009 (6-29 May 2010), which included the annual occupation of the AR7W / L3 line across the Labrador Sea. Samples and standard measurements of dissolved oxygen (DO) were taken at various depths as part of the cruise program with the use of titration methods and by means of Sea-Bird DO primary and secondary sensors. During the mission calibrations of both sensors were made taking into account the experience gained on previous missions (2010-009, 2010-014 and 2010-049). The original intention was to carry out the inter-comparisons between the two Winkler methods of titration: with the use of old (Scripps) system and the new one (colorimeter, developed at the Maurice Lamontagne Institute, Quebec, hereafter referred to as BOB). However, the lack of reagents prevented us from achieving this goal. Therefore, this report covers only the measurements taken with the use of BOB.

This note describes the methods of collecting samples, data acquisition and processing and presents some preliminary results of the expedition in the form of quantitative estimates.

### **2. Procedures and methods**

Oxygen sub-samples were drawn from 10L bottles attached to a 24-bottle Rosette Sampler. To reduce air contamination of the samples to a possible minimum, the sampling was done immediately after chlorofluorocarbon (CFC-12 / SF-6) sampling. On most oceanographic stations, replicate samples were collected at least at one depth. Normally, these depths were chosen to be at the minima and maxima of the DO vertical profile as determined from the CTD cast in the computer room. This strategy ensues from the calibration purpose: we strived for the maximum range of the calibration curve. Bottom (i.e. the deepest observation) is another characteristic point on the oxygen vertical profile, where, in most cases, duplicate samples were taken.

The oxygen sampling bottles were 125 mL Iodine flasks with matched custom ground stoppers. The volumes of flasks with the corresponding stoppers were predetermined gravimetrically, and volume data were saved to titration programs prior to the mission. The matched flasks and stoppers are etched with identification numbers.

Each oxygen sub-sample was drawn through a silicone tube attached to the spigot of the Rosette bottle. The flask and stopper were thoroughly rinsed. The flow was then allowed to continue until two to three flask volumes overflowed. The sampling tube was slowly

removed with continuous low flow to ensure that no air was trapped in the flask and the volume kept to the brim until the stopper was added.

Samples were immediately oxidized with the addition of 1.0 mL each Alkaline Iodide and Manganous Chloride. The tip of the spout was submerged under the surface of the sample during this procedure. The flask stopper was carefully inserted to avoid introducing air. The flask was then shaken and turned upside down several times.

The samples were stored immediately after collection for at least 1 hour in a dark place at room temperature.

### 3. Replicate analysis

As mentioned, replicate samples were collected at least at some depths. Normally, two samples (duplicates) were taken; on some occasions, more samples were taken. Figure C.3.1 below presents the histograms of the difference between the DO concentrations sampled at the same depth and determined by Winkler method. For the sake of comparison, the same histogram from the HUD2010049 mission is shown. As seen from the figure, on both missions, most of the differences fall within the 0 – 0.03 ml/L range. However, the figure suggests that the measurements taken on the HUD2010049 mission were more accurate (the higher peak at the 0 – 0.01 ml/L range).

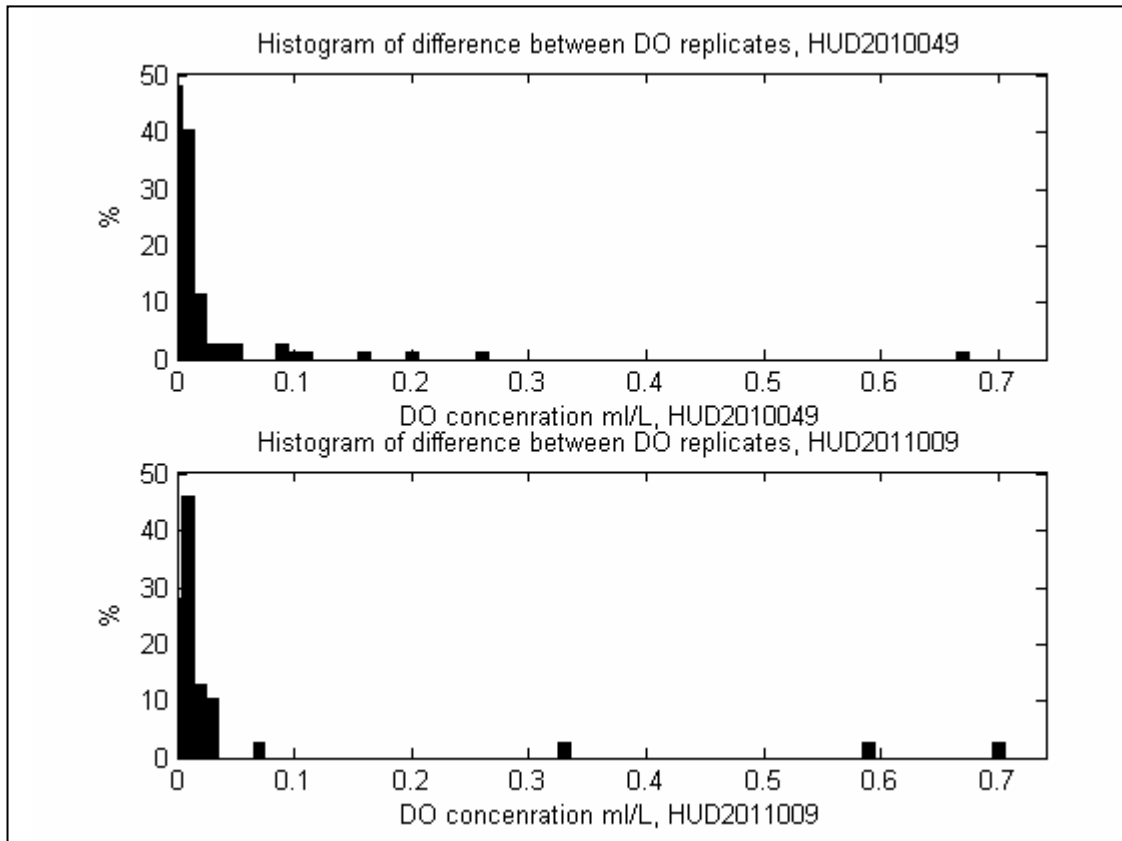
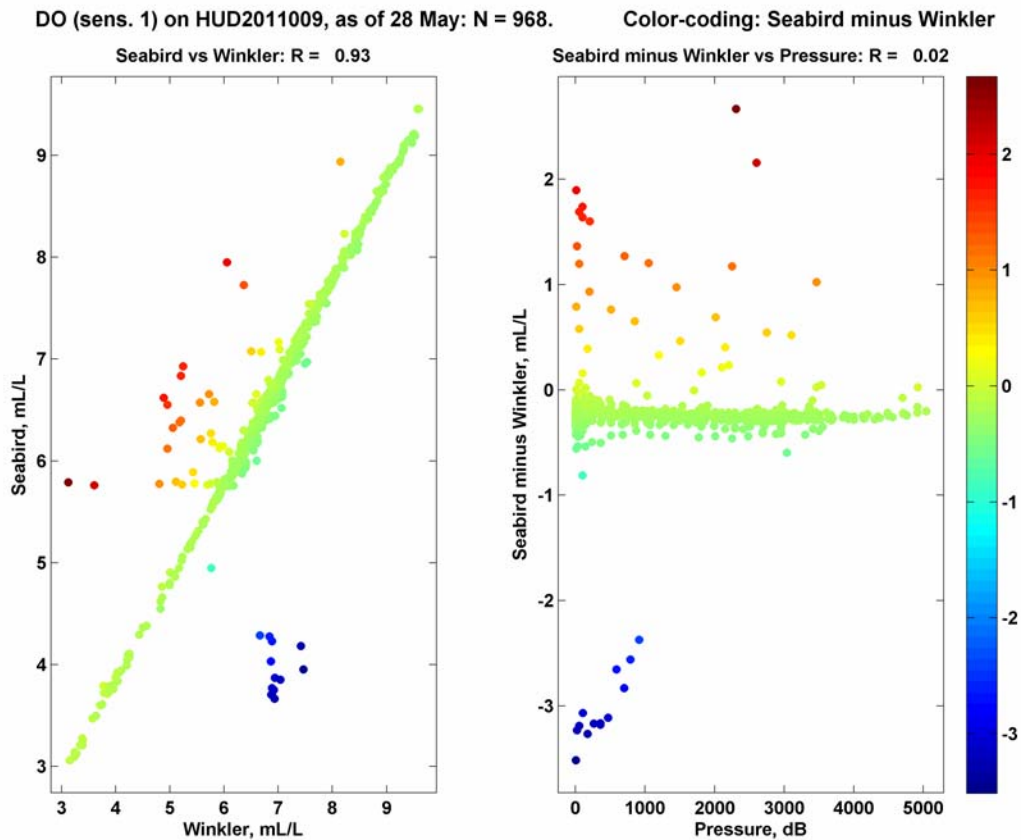


Figure C.3.1. Histograms of differences between the DO concentrations sampled at the same depth (Winkler titration).

#### 4. Sea-Bird – Winkler comparisons

The ultimate goal of the inter-comparisons between SeaBird and Winkler is to perform the calibration of SeaBird, because the chemical method should provide more accurate values. The comparisons were carried out for both primary and secondary sensors. The total of 968 data points are employed in the analysis, and the results of the comparisons are presented as scatter plots of Sea-Bird versus (vs) Winkler DO concentration in figures C.3.2 and C.3.3 below. On each of these figures, the left panel presents the scatter plot of the two concentrations. Plotted on the right panel is the relationship between the difference between the two concentrations and pressure. This was done to ensure that that difference is not dependent on pressure<sup>1</sup>.

While the correlation coefficients between SeaBird-Winkler differences and pressure are close to zero (which suggests the absence of the relation between these properties), careful investigation of Figure 3 reveals that there is still some correlation between them in the 0 – 3000 Db range (secondary sensor only).



<sup>1</sup> Such unwanted dependence took place on the 2010-014 and 2010-049 missions.

Figure C.3.2. Scatter plot of Primary SeaBird sensor vs Winkler DO concentrations (left panel) and SeaBird-Winkler difference vs pressure (right panel)..

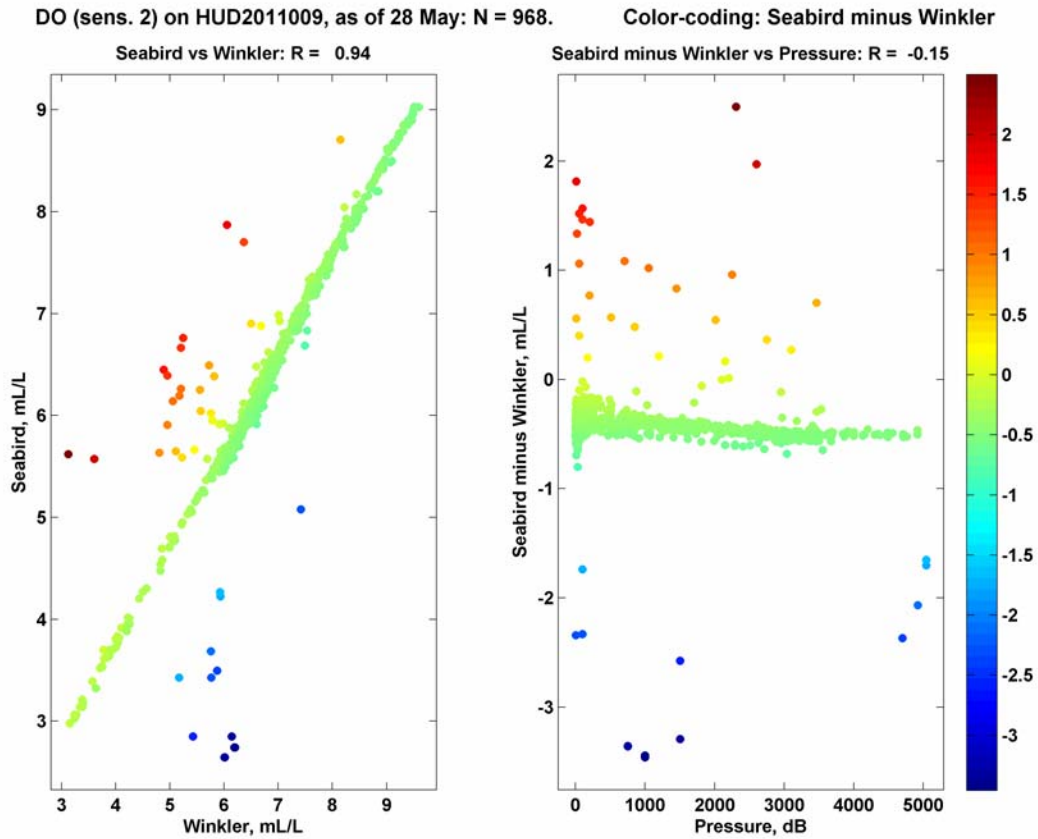


Figure C.3.3. Scatter plot of Secondary SeaBird sensor vs Winkler DO concentrations (left panel) and SeaBird-Winkler difference vs pressure (right panel).

Overall, despite some obvious spikes whose reason is yet to be found, the SeaBird - Winkler correlation is encouragingly high:  $R = 0.93$  and  $0.94$  for the primary and secondary sensors.

## 5. Conclusions

We have summarized the procedures for and results of sampling, measuring and calibrating the DO concentrations on the Hudson mission in the spring of 2011. Table C.3.1 summarizes the SeaBird - Winkler correlation coefficients derived on 3 missions and indicate some improvement in our sampling and titration techniques over the last year.

Mission	Primary SeaBird sensor	Secondary SeaBird sensor
2010-014	0.46	N/A
2010-049	0.97	0.87
2011-009	0.93	0.94

Table C.3.1. Correlation coefficients between Winkler and SeaBird derived values of DO concentration.

### 3. Nutrients

Analyzed by Carol Anstey

#### a. Description of Equipment and Technique

Samples were analyzed for silicate, phosphate, nitrate (nitrate plus nitrite), nitrite and ammonia using a Technicon Autoanalyzer II. The methods were standard Technicon for Seawater Analysis (Silicate 186-72W, Phosphate 155-71W, Nitrate/Nitrite 158-71W), except for ammonia. Ammonia was determined by a method developed by R. Kerouel and A. Aminot; *'Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis.'* Marine Chemistry 57 (1997) 265-275. The phosphate method has been modified by separating the Ascorbic Acid (4.0 gm/l) from the Mixed Reagent. The modified Mixed Reagent instead of sample water was introduced at the start of the sample stream (0.23 ml/min.) and the Ascorbic Acid was introduced separately between the two mixing coils (0.32 ml/min.) (Strain and Clement, 1996).

#### b. Sampling Procedure and Data Processing Technique

Duplicate nutrient samples were drawn into 30 ml HDPE (Nalgene) wide mouth sample bottles from the 10 L Rosette bottles. The sample bottles were pre-washed in 10% HCL, rinsed three times with NANOPure ultra-pure water and oven dried at >100 Degrees F.

A sample run included six Calibration Standards, analyzed in duplicate, at the beginning and end of each shift's analysis. The standards, wash water and blanks for phosphate, silicate and nitrate/nitrite were made up in 33 ppt NaCl (Sigma, ACS Reagent); for ammonia, NANOPure water only. The second most concentrated Calibration Standard was used as a Check Standard every 16 samples, followed by blanks as a baseline check. The quality of analysis was checked by analyzing an Intercalibration Reference Material MOOS-2 for nutrients produced by NRC, Ottawa. There was no existing ammonia Reference Material. Instead, a 2.0 µM Standard was prepared, stored refrigerated in 30 mL acid washed glass bottles and a fresh bottle was analyzed daily to get an indication of analysis performance.

The raw analog data was converted to digital data, processed and concentrations calculated using Michaelis-Menton Regression, including statistics, by an in-house Pascal 7.0 program (AII) on a PC. This year the relevant programs for editing and calculating

of raw nutrient data files could be uploaded to a common GP lab computer, provided mainly for producing QAT files. This solved the problem of calculating and editing data so it could be reported “real time” on board. However some data had to be brought back for a second editing and final calculations. Chart recordings, hard copy and disk copies of the data were archived.

### **c. Shipboard Analysis**

Total number of duplicate samples analyzed for AR7W Labrador Sea HUD2011-009: 2206. This total includes samples collected on the Orphan Basin which was not given a separate cruise number this year. Samples were analyzed as soon as possible after collection. Any samples collected off watch were kept refrigerated (4°C) and analyzed within eight hours of collection.

Again this year, all 5 nutrients were analyzed at sea: nitrate/nitrite, silicate, phosphate, ammonia and nitrite. A new water purification system had been purchased: Barnstead NANOPure, in hopes that it could be used at sea. Ship RO water was still not clean enough to purify for analysis use. Instead 440 litres of lab produced NANOPure water was brought on board in acid washed 20 litre carboys. This water was purified on board again just before making up all reagents, including the 33‰ NaCl wash water. The problems noted on earlier cruises with contamination of wash waters and reagents, severe drifts in baselines and high blanks, especially of phosphate and ammonia, likely caused by long term storage of Alpha-Q water, seemed very much improved. The new Barnstead system was easily used and maintained on board. Analyses were pretty much trouble free through out the cruise. On May 11<sup>th</sup> an I/O Board Error occurred where the data did not save to a voltage file. This day’s data was calculated from peak heights manually measured from the chart recordings; except nitrite was lost as no chart recordings were produced: the last Kipp&Zonen strip chart recorder broke down. Rough seas on May 12<sup>th</sup> did cause problems with air constantly being pulled into the phosphate flowcell. Extensive data editing on the voltage file had to be done before data could be reported and some phosphate data was lost.

The ammonia system air supply and reagent bottle were both fitted with a homemade gas trap consisting of a 10cc syringe filled with Sicacide® (sulphuric acid coated molecular sieve) to scrub ammonia from the air. The wash water and reagent was made up with freshly purified NANOPure water as in the lab. There was no increase in baseline or check standards throughout run and fluorometer settings for gain or sensitivity did not change from normal lab settings. This would indicate that neither the mixed reagent nor the wash water picked up ammonia contamination from shipboard air. A prepared “C” standard of 2.000 µM ammonia standard solution was stored at 4°C in acid washed 30 mL glass bottles. This was run each day as a “reference material”. Results remained stable throughout the cruise: 1.984±0.114. Data for sample runs were excellent: stable baselines and very good calibration RMS – ‘fit to curve’. A separate set of duplicate samples were taken from random stations to be analyzed in the lab for ammonia at a later date as a comparison between fresh and frozen samples.



A few problems with sample collection came up during the cruise: mislabelling, taking samples from the wrong Niskin and forgetting to fire the bottle. One severe case involved samples 378320 to 378342. Two sets of duplicates were taken for this station. One to be frozen and analyzed back at the lab for comparison and one analyzed fresh. Several of the fresh set samples were mislabelled with ID numbers that were not used according to the QAT file, unlabelled or double labelled with 4 samples having the same number. In this case both the fresh samples and the frozen (~4 hours in freezer) were analyzed and the data reported. The set of frozen samples appeared to be labelled correctly. These problems seemed to occur on the day shift when inexperienced students were running the CTD and sampling.

The lab temperatures remained cooler than previous years as CFCs were not analyzed (no excessive heat from the GC ovens). Plus nutrient analysis was run at night when the ambient temperatures were cooler in the GP Lab preventing degassing of molybdate reagents and build-up of precipitate in the nitrate colour reagent line.

An Intercalibration Reference Material MOOS-2, produced by NRC, Ottawa was used as a daily check for data quality, except for Ammonia where the in-house calibration standard was used. As seen in the summary of **QC/QA MOOS-2** data, results were much more within accepted values than last year probably due to the freshly purified water. Only a few Phosphate results were slightly out of range and Nitrate/Nitrite seemed to pick up a little contamination towards the second half of the cruise.

QC/QA	SILICATE	PHOSPHATE	NITRATE	NITRITE	AMMONIA
	$\mu\text{M}$	$\mu\text{M}$	$\mu\text{M}$	$\mu\text{M}$	$\mu\text{M}$
<b>Accepted Values</b>	28.8+/-1.0	1.58 +/-0.10	24.9+/-1.0	3.31+/-0.18	2.000
<b>May-09</b>	27.66	1.564	25.39	3.40	none
	27.69	1.564	24.78	3.32	
<b>May-10</b>	27.71	1.513	24.62	3.36	none
	27.66	1.511	24.84	3.30	
<b>May-11</b>	27.91	1.530	24.83	<b>lost data</b>	1.824
	27.84	1.532	24.84	<b>lost data</b>	1.941
<b>May-12</b>	28.07	<b>1.738</b>	24.48	3.36	1.745
	27.89	1.671	24.38	3.30	1.838
<b>May-13</b>	28.03	1.671	24.95	3.48	2.074
	28.41	<b>1.720</b>	24.94	3.46	2.016
<b>May-14</b>	<b>MOOS-2 no data</b>				1.760
					1.894
<b>May-15</b>	27.70	1.605	25.19	3.43	2.037
	27.67	1.613	25.29	3.40	2.142
<b>May-16</b>	27.70	<b>1.747</b>	25.97	3.57	1.829
	27.60	<b>1.746</b>	<b>26.11</b>	3.55	2.020
<b>May-17</b>	27.82	<b>1.736</b>	25.05	<b>3.81</b>	1.981
	27.96	1.578	25.04	<b>3.70</b>	2.029
<b>May-18</b>	27.90	1.622	24.82	3.49	2.078
	28.67	1.536	25.10	3.43	2.032
<b>May-19</b>	28.07	1.571	24.69	3.51	2.010
	27.77	1.582	24.81	<b>3.59</b>	1.941
<b>May-20</b>	27.79	1.562	24.83	<b>3.60</b>	1.992
	27.94	1.580	25.09	<b>3.56</b>	1.993

<b>May-21</b>	27.93	1.519	24.84	<b>3.72</b>	1.979
	28.08	1.519	25.35	<b>3.82</b>	2.097
<b>May-24</b>	27.52	1.458	<b>26.37</b>	<b>3.85</b>	2.285
	27.58	1.450	<b>26.05</b>	<b>3.83</b>	2.005
<b>May-25</b>	27.78	1.464	<b>25.98</b>	<b>3.81</b>	2.120
	28.06	1.458	<b>26.29</b>	<b>3.78</b>	2.057
<b>May-26</b>	28.03	1.519	<b>27.50</b>	<b>3.95</b>	1.934
	27.94	1.474	<b>27.21</b>	<b>3.95</b>	1.960
<b>May-27</b>	28.01	<b>1.704</b>	<b>28.39</b>	<b>3.96</b>	1.964
	27.72	1.569	<b>28.36</b>	<b>3.95</b>	1.944

RMS offset from the predicted calibration curve is a measure of how acceptable the calibration was for a specific analysis run. There is no firm cut-off for ‘good’ or ‘bad’ data. The data quality parameters, determined with check standards and RMS offset from the calibration curve, came well within accepted values. The following table lists acceptable limits for RMS fit determined by averaging 34 runs of data deemed to be acceptable by peak shape, stability of the baseline and precision between duplicates.

RMS Offset from Curve:

	SILICATE	PHOSPHATE	NITRATE	AMMONIA
Mean ( $\mu\text{M}$ ) (n=34)	0.115	0.042	0.089	0.080
Std. Deviation ( $\mu\text{M}$ )	0.115	0.020	0.043	0.032
Maximum ( $\mu\text{M}$ )	0.695	0.111	0.271	0.132
Cruise Average:				
HUD2011-009(n=21)	0.069	0.013	0.069	0.114
Std. Deviation ( $\mu\text{M}$ )	0.045	0.007	0.039	0.055

The nutrient detection limits are an average of all analytical runs from both the Orphan Basin and Labrador Sea legs of the cruise.

	Silicate	Phosphate	Nitrate	Ammonia	Nitrite
Number of Samples	1103	1103	1103	1103	1103
Number of Duplicates	2206	2206	2206	2206	2206
Detection Limit ( $\mu$ moles/L)	0.17 $\pm$ 0.12	0.025 $\pm$ 0.004	0.10 $\pm$ 0.08	0.095 $\pm$ 0.058	0.022 $\pm$ 0.013

### Analytical Precision: Standard Deviation of Check Standards

SILICATE	PHOSPHATE	NITRATE	NITRITE	AMMONIA
0.161	0.048	0.165	0.022	0.155
0.114	0.018	0.077	0.016	0.055
0.170	0.345	0.193	0.033	0.093
0.245	0.032	0.163	No data	0.141
0.473	0.047	0.394	0.027	0.333
0.285	0.077	0.631	0.024	0.195
0.251	No data	0.207	0.019	0.182
No data	No data	No data	0.027	0.113
0.212	0.025	0.234	0.033	0.150

0.240	0.041	0.225	0.022	0.110
0.270	0.012	0.082	0.028	0.159
0.243	0.019	0.163	0.022	0.166
0.032	0.017	0.023	0.040	0.104
0.193	0.043	0.181	0.062	0.225
0.259	0.025	0.205	0.221	0.476
0.243	0.030	0.232	0.039	0.115
0.241	0.038	0.160	0.040	0.095
0.571	0.041	0.549	0.034	0.081
0.257	0.196	0.494	0.034	0.117
0.112	0.030	0.317	0.030	0.140
0.265	0.023	0.450	0.029	0.163

#### **4. Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), and pH in Seawater**

**DIC/TA/pH analyzed by Kumiko Azetsu-Scott and Richard Nelson  
pH analyzed by Stephen Punshon and Darlene Brownell**

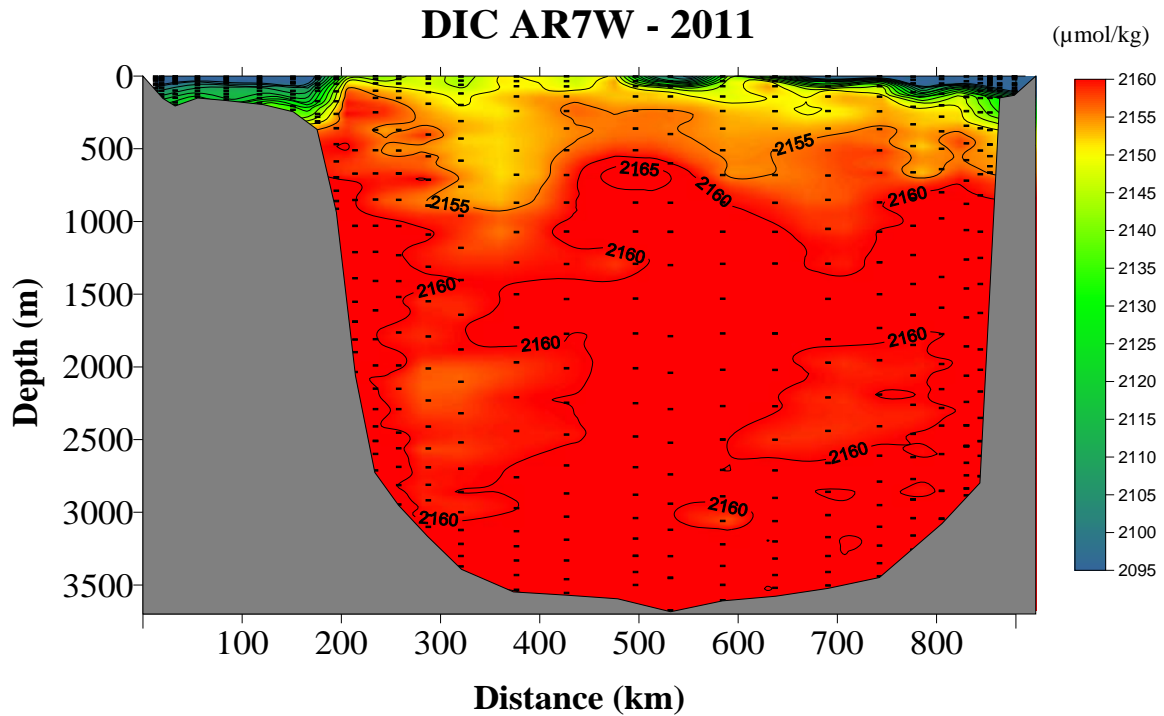
Samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected at standard hydrographic depths at the whole-number stations 0-28 on the AR7/W Line, A3 to C14 on the North line and stations 14 to 2 on the extended Halifax line.

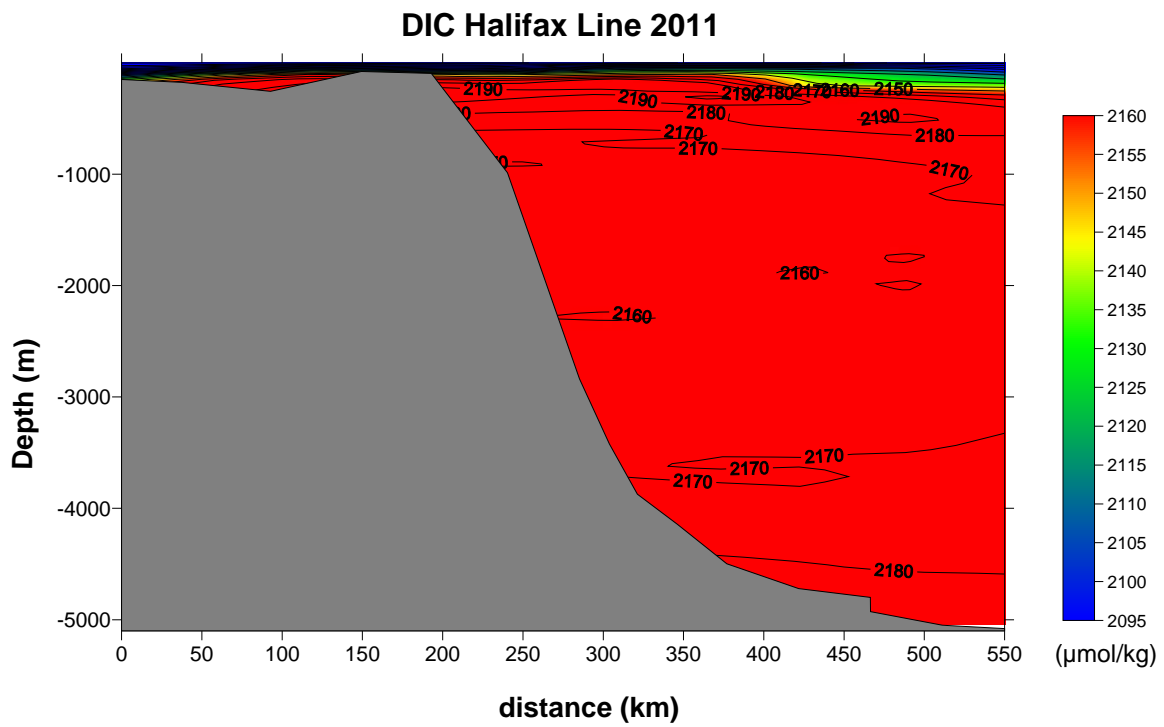
Seawater samples were collected in 500 mL borosilicate glass bottles and analyzed for DIC followed by TA typically within 12 hours of collection following the methods prescribed in “Guide to Best Practices for Ocean CO<sub>2</sub> Measurements” by Dickson *et al.* (2007). Water samples from stations 22 (event #176) on the AR7W were poisoned with 100µl of mercuric chloride to stop microbial activity and stored prior to analysis during the transit from the AR7W to Halifax line. This preservation procedure was necessary due to lack of analysis time between stations. A total of 486 samples for AR7W, 150 for the North line and 221 samples for the Halifax Line were analyzed.

DIC was determined using gas extraction and coulometric titration with photometric endpoint detection (Johnson, et al., 1985). Total alkalinity was measured by open-cell potentiometric titration with a five-point method (Haraldsson et al., 1997). Bottles of Batch 99 Certified Reference Material (CRM) (supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, San Diego, USA) were analyzed in duplicate every 20 samples to evaluate accuracy. Samples for pH measurements were collected at the same stations and depths as DIC/TA with additional samples taken at the biological stations (854 samples in total). pH samples were collected in 60 mL amber “Boston Round” glass bottles with poly-seal lined closures and poisoned by adding 20 µL of saturated mercuric chloride solution within one hour of collection. Samples from AR7W and the North line were analyzed during the transit from the North line to the extended Halifax line. Samples from the extended Halifax line were stored at room temperature for later analysis at the Bedford Institute of Oceanography. Prior to measurement, sample bottles were placed to a controlled temperature bath (25 °C). A 10 cm path-length, quartz-faced optical cell was filled with a sample and approximately 70 µL of 2.6 mM *m*-

CP (pH not adjusted by addition of HCl). The absorbance of three wavelengths, 434, 578, and 730 nm was measured by the spectrophotometer. CRM (supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, San Diego, USA) were run every 30-40 samples to assure the accuracy of measurements.

All instruments worked well. Minor problems included: (1) some old valves of SOMMA had to be replaced, (2) a stirrer for TA measurements tended to stick and malfunction, and (3) a computer for TA measurements froze once in a while.





**Figure C.5.1** Preliminary results for DIC from AR7W (top) and the extended Halifax line (bottom) are shown.

## 5. SF6/CFC-12

### Analyzed by Stephen Punshon and Darlene Brownell

The 2011 Labrador Sea Mission saw the introduction of a new gas chromatographic analytical system designed to measure sulphur hexafluoride (SF<sub>6</sub>) and CFC-12. SF<sub>6</sub> is an inert atmospheric trace gas arising almost entirely from anthropogenic sources. Its tropospheric mixing ratio, currently around 7 parts per trillion, has risen rapidly over the last two decades making it an extremely useful opportune tracer for recently ventilated water masses. However, the relatively low atmospheric abundance of SF<sub>6</sub> combined with very sparing solubility in water results in surface seawater concentrations that are three orders of magnitude lower than for CFC-12. Consequently, the analytical method requires a larger sample volume than previously used for CFC analysis in order to achieve the desired sensitivity. For this first sea-going trial, 12 depths were sampled at each deep station on the AR7W and Extended Halifax lines, with 6 depths being typically selected on the shallow shelf stations.

### Method

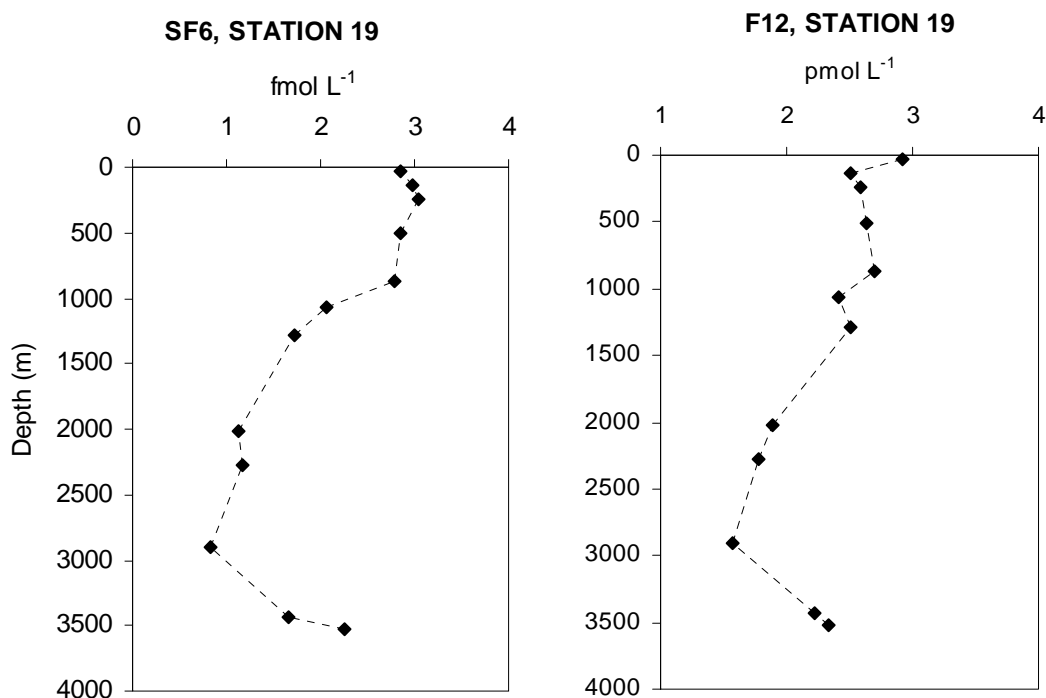
Seawater samples were drawn directly from Niskin bottles into 250 mL glass syringes which were then stored at 2 °C in a low-temperature incubator for no longer than 12 hours. Immediately before analysis, the samples were warmed to around 20 °C in a water bath then injected into the purge vessel of a custom made purge-and trap system where dissolved gases were stripped from the sample in a stream of ultra high purity nitrogen with a flow rate of 120 mL per minute. SF<sub>6</sub> and CFC-12 were quantitatively retained in a trap comprising 30 cm of 1/16" stainless steel tubing packed with 100-120 mesh Carboxen 1000 held at -70 °C. After each 7 minute purge cycle, the trap was heated to 180 °C with a low voltage electric current and the desorbed gases directed to a Varian gas chromatograph equipped with an electron-capture detector. SF<sub>6</sub> and CFC-12 were separated on a 1 m pre-column packed with Porasil B and a 2 m main column packed with Molecular Sieve 5A held at 80 °C. The sample run-time was 13.5 minutes which included ramping the oven temperature to 150 °C after the analyte peaks had eluted in order to clean the pre-column during back-flushing. The chromatographic sample peaks were quantified with Varian Galaxie software and the analytical system calibrated at least once each day using an air standard supplied by CMDL/NOAA, Boulder, Colorado. Analytical precision as determined by repeated standard injections was ± 5 % for SF<sub>6</sub> and ± 1 % for CFC-12.

### Results

A total of 388 water samples from the AR7W and Extended Halifax Line were analysed for SF<sub>6</sub> and F-12.

Figure C.6.1 below shows representative profiles of dissolved SF<sub>6</sub> and CFC-12 at Station 19 on the Labrador Sea AR7W line. The influence of recently ventilated Denmark Strait

Overflow Water is clearly seen in the deepest samples of both profiles. Note that the concentrations of CFC-12 samples are almost exactly 1000 times higher than SF6.



**Figure C.6.1.** Profiles of dissolved SF6 and CFC-12 at Station 19, AR7W line

### Analytical challenges and problems

A persistent problem encountered during the chromatographic runs was an intermittent “hump” in the baseline caused by an unknown slow-moving compound, possibly CFC-11. This was controlled by baking the columns for 10 minutes at 170 °C after every 3-4 sample injections. It will be highly desirable to eliminate this problem by adjusting factors such as back-flush timing, pre-column length, stationary phase, and oven temperature. The ultimate goal is to reduce the sample run time to 10 minutes or less so that more samples can be processed in the time available between stations, thus enabling higher resolution profiles. Other one-off problems encountered were:

- 1) The failure, early in the cruise, of an ageing mass-flow controller (mfc) delivering the purge gas at a rate of 120 mL/min. The spare mfc could only manage 100 mL/min, so although the purge time was increased, it will be necessary to re-evaluate the extraction efficiency of the less volatile CFC-12 under such conditions and apply a correction to the CFC-12 concentrations if necessary.
- 2) Samples were not collected from Station 23 on the AR7W line due to deteriorating peak shape and reduced sensitivity. The situation was rectified by thermal cleaning of the columns and detector.