CRUISE REPORT

HUDSON 2014007

LABRADOR SEA,
WOCE LINE AR07W
Extended Halifax Line

May 2 – May 24, 2014

A. CRUISE NARRATIVE

1. Highlights

a. WOCE Designation:	WOCE Line AR07W & Extended Halifax Line
b. Expedition Designation:	HUD2014007 or 18HU14007 (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 Igor.Yashayaev@dfo-mpo.gc.ca
d. Ship:	CCGS HUDSON
e. Ports of Call:	May 02, 2014, BIO, Dartmouth, NS, Canada May 24, 2014, BIO, Dartmouth, NS, Canada
f. Cruise Dates:	May 02 to May 24, 2014

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.

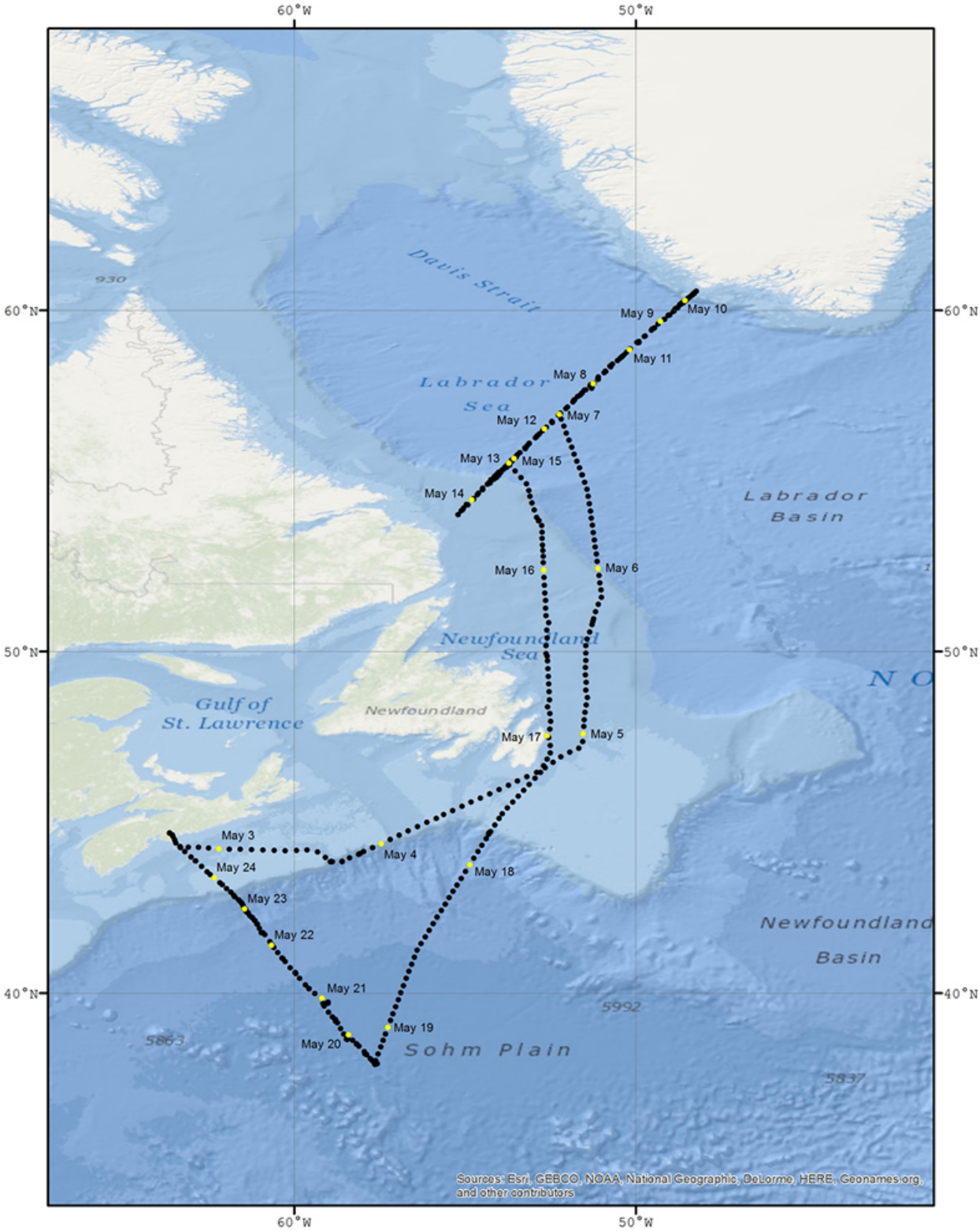

Figure A.2.1 Cruise track for HUD2014007. The yellow dots indicate the ship's position for each hour of the voyage. The red dots and date labels indicate the ship's position at 0000 UTC for that particular date.

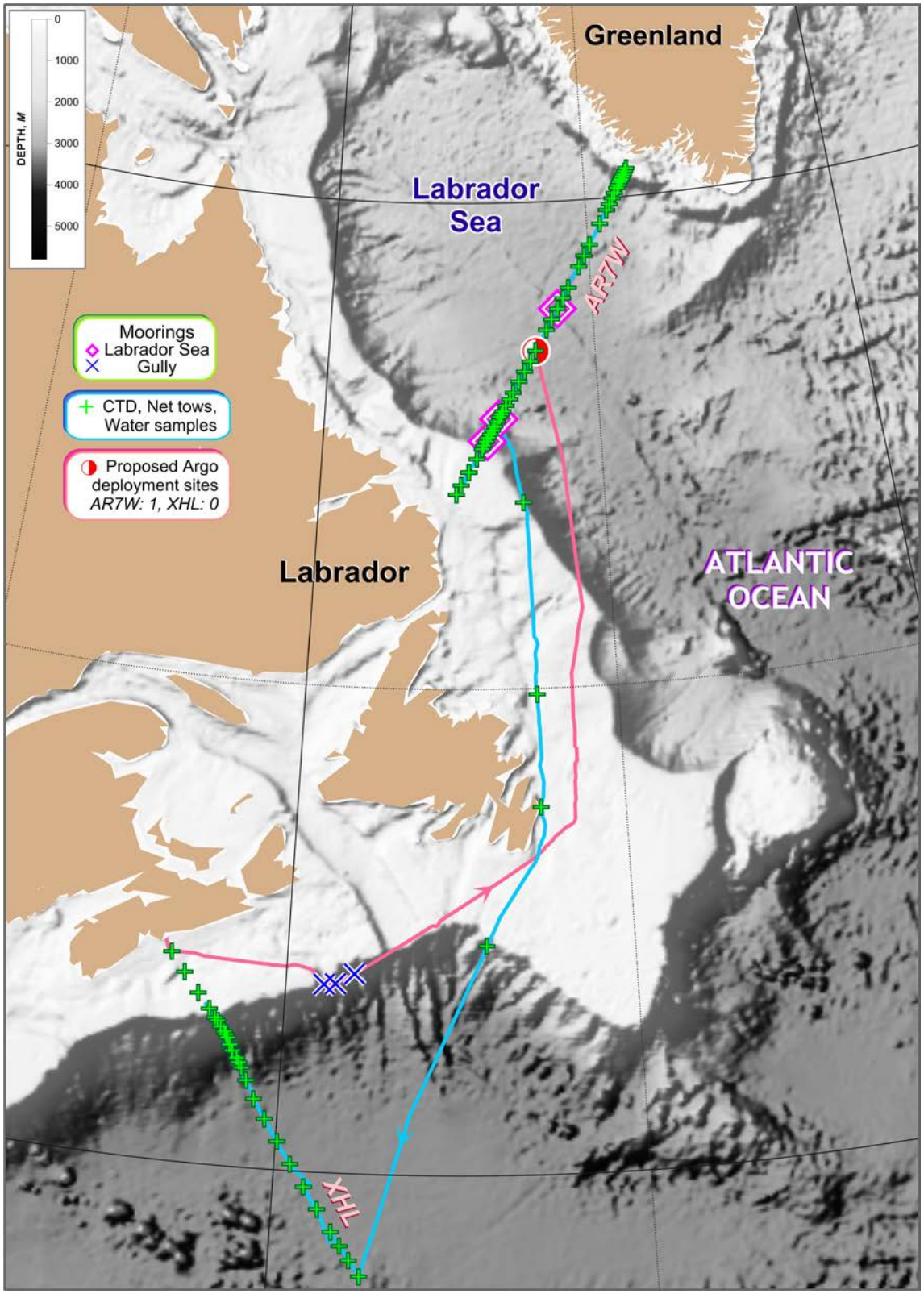

Figure A.2.2 Cruise track for HUD2014007 with CTD stations, mooring locations and Argo float deployment site. The pink line indicates the outbound track and the light-blue line indicates the inbound track.

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 HUD2014007.

Along AR07W, the stations were full-depth WHP small volume rosette casts with up to 24 rosette bottles. Water samples were analyzed for CFC-12, SF6, total inorganic carbon (TIC), total alkalinity, oxygen, salinity, nutrients (nitrate, phosphate, and silicate), pH, and bacterial abundance. Chlorophyll was analyzed at depths less than 200m at most stations. Samples were collected for ^{129}I (iodine-129) and O-18 (Oxygen-18) on selected casts.

Cast Type	Number of Operations	Operation Details	Operation Numbers
Rosette & CTD	44	26 of the 28 regular AR07W sites (L3 line) were occupied. Sites 1 and 2 could not be occupied because of ice cover. Extra occupations included: 7.5, 8.5, 9.5, 10.5, 11.5, 11.51, 12.5, 13.5, 14.5, 16.5, 17.5, 19.5, 22.5, 23.5, 24.5, 25.5, 26.5, 27.5	see Table A.2.2
	1	Bedford Basin Test Station	1
	26	Halifax Line sites:	4, 172, 173, 174, 176, 178, 180, 182, 184, 186, 188, 190, 192, 193, 199, 200, 201, 202, 203, 205, 207, 208, 211, 214, 217, 220
	2	Other Casts	16, 160
	9	Biology Casts	9, 17, 33, 47, 86, 120, 150, 157, 165
	7	Aborted Casts	28, 76, 167, 169, 170, 171, 196
MVP	5	Moving Vessel Profiler Tows	13, 149, 154, 161, 166
Moorings	2 5 3	Recovery Deployment Release Tests	135, 140 6, 10, 12, 36, 136 5, 11, 35
COPS	11		19, 20, 34, 49, 50, 69, 87, 88, 139, 153, 162
Oblique Profiler	9		18, 48, 68, 89, 97, 121, 138, 151, 152
Biology	42	200 micron net tows	See Table A.4.2.1. for occupation locations
	30	76 micron net tows	See Table A.4.2.1. for occupation locations
	9	Egg Production rates	See Table A.4.2.1. for occupation locations
	14	Multinet	See Table A.4.2.1. for occupation locations
	1	Oblique Ring Net tow	92

Table A.2.1 Science operations conducted on HUD2014007.

AR0W Site Number	2014007 Deep Cast Operation Number
1	-
2	-
3	129
4	125
5	122
6	117
7	113
7.5	130
8	110
8.5	131
9	134
9.5	137
10	109
10.5	147
11	108
11.5	144
11.51	107
12	106
12.5	105
13	104
13.5	103
14	102
14.5	101
15	25
16	29
16.5	96
17	37
17.5	93
18	40
19	43
19.5	91
20	51
21	54
22	90
22.5	55
23	58
23.5	82
24	81
24.5	78
25	77
25.5	59
26	73
26.5	70
27	62
27.5	67
28	65

Table A.2.2. AR07W (L3) sites with rosette / CTD operation numbers for HUD2014007.

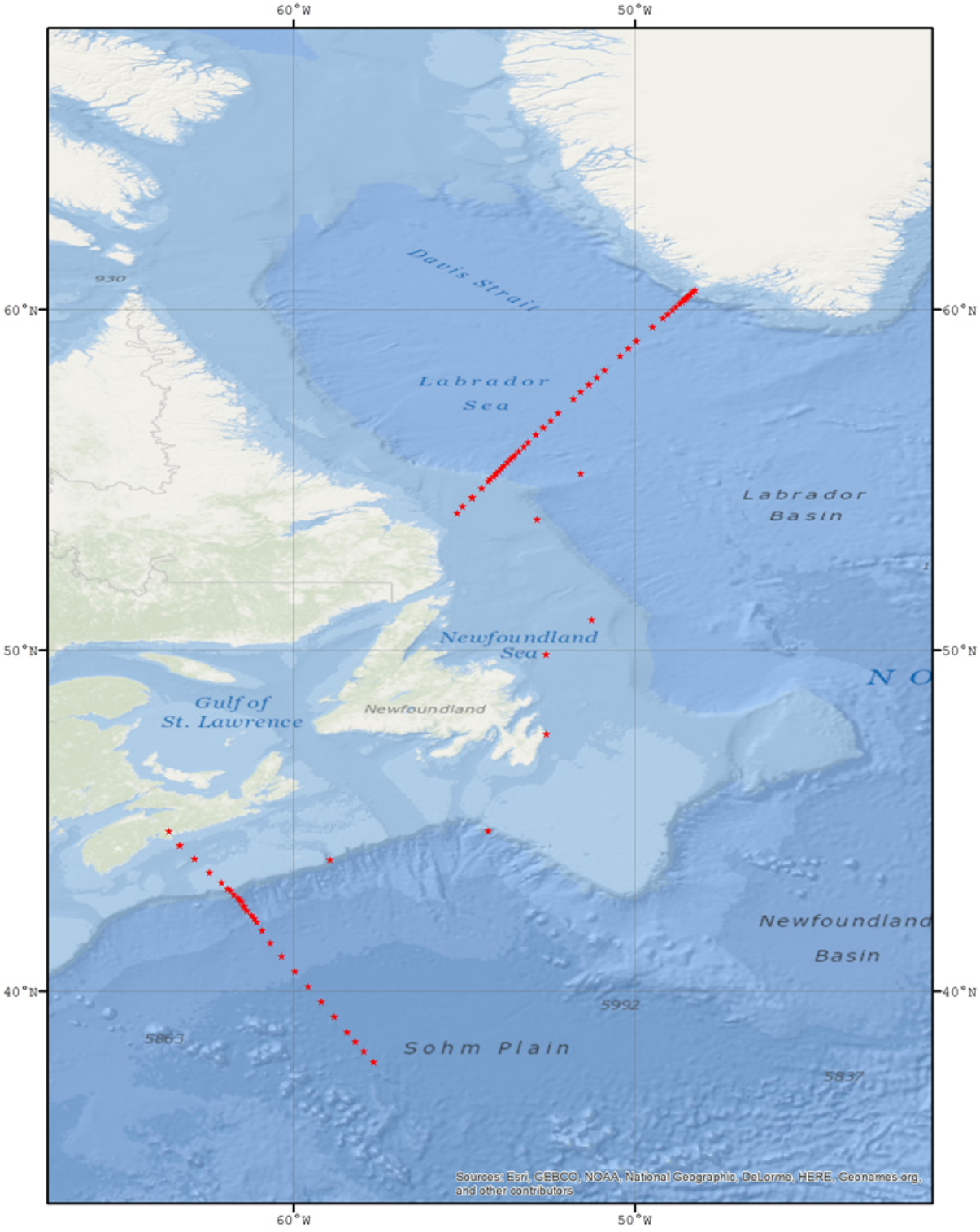

Figure A.2.2 HUD2014007 locations (red-filled stars) for operations involving one or more of the following data collection methods: Rosette, CTD and LADCP.

Stations along the AR07W Labrador Sea section and station HL_02 of the Halifax Section (HL) were occupied during the mission.

c. Floats and Drifters deployed

No floats or drifters were deployed.

d. Moorings deployed or recovered

The Aanderaa current meter mooring near station L3_08 on the AR7W line was once again recovered on May XX, 2014. Mooring #1824 was recovered successfully under good sea conditions. A new mooring was deployed in the central deep channel of the Labrador Sea – the North Atlantic Mid-Ocean Channel (NAMOC) at location XXX, depth XXX, date XXX. The replacement mooring #1844 was deployed successfully on May XX, 2014. These moorings were both in the water for X days for comparison. (Did we do the same overlap in 2014?) Two other mooring – one at 2900 m on the Labrador side – was recovered successfully. That deep Labrador Slope mooring was not replaced.

Three Amar acoustic moorings for Hilary Moors-Murphy were deployed near the Gully area to monitor whale activity. (please update this)

Recoveries:

M 1823	55º 33.4968' N 53º 41.1712' 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 2756 metres.
M 1824	55º 07.1844' N 54º 05.5209' 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 1034 metres.

Deployments:

		NAMOC mooring
M 1844	55º 06.8651' N 54º 05.2361' W	Standard mooring consisting of one current meter and two Microcats. It was positioned in the Labrador Sea on the Labrador Slope for a 12-month deployment at about 1000 metres.
M1849	43º 51.7349' N 58º 54.5984' W	Amar mooring MidGul at 1580 meters (Middle of Gully).
M 1850	43º 51.8254' N 58º 35.2911' W	Amar mooring GulSho at 1583 meters (halfway between the Gully and Shortland canyons).
M 1851	44º 05.8633' N 58º 03.3814' W	Amar mooring ShoHald at 1545 meters (halfway between Shortland and Haldimand canyons).

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.

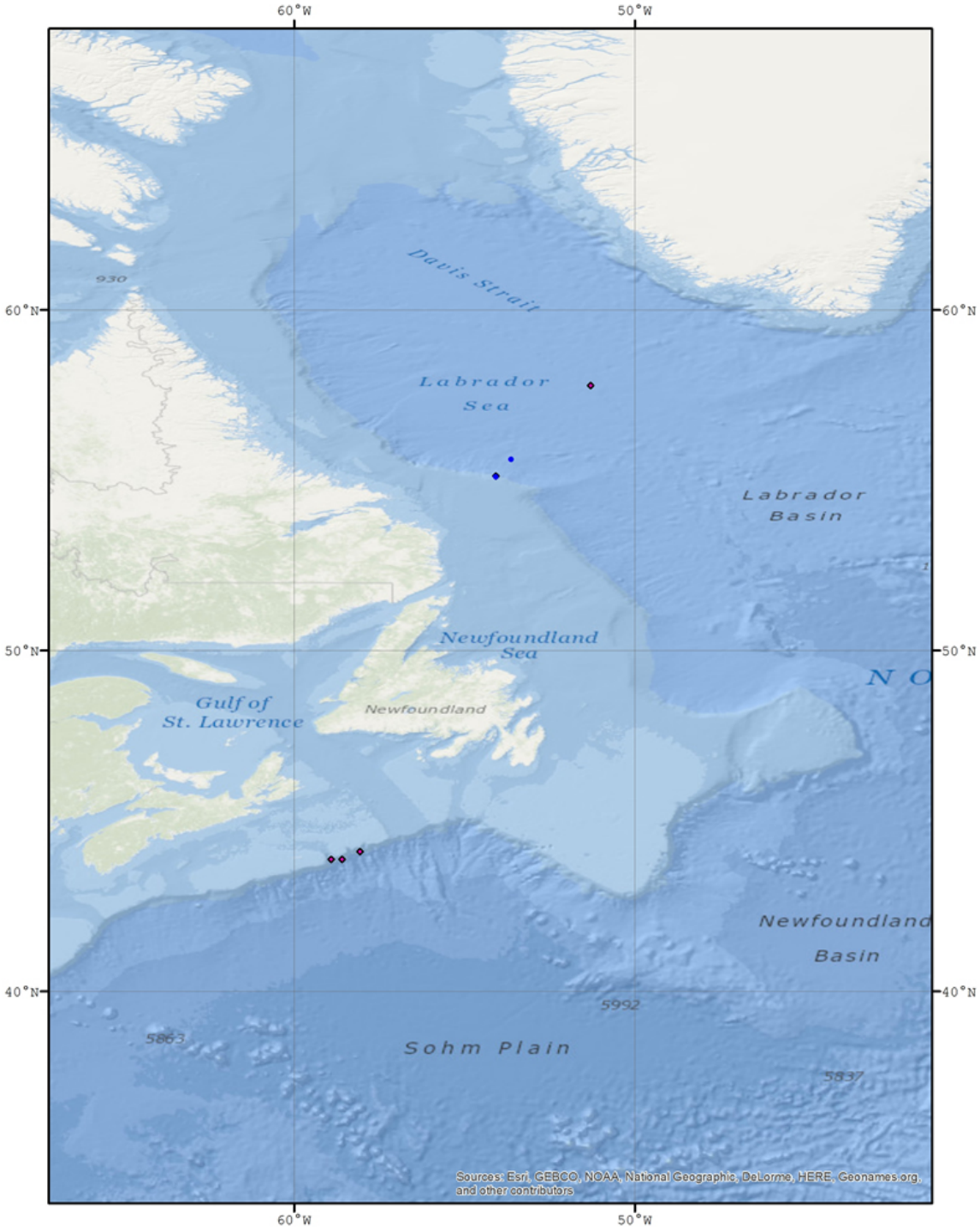

Figure A.2.3 HUD2014007 mooring deployment locations (pink-filled diamonds) and mooring recovery locations (blue-filled circles).

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^{18}, SF6, and pH.
Erica Head	BIO HeadE@mar.dfo-mpo.gc.ca	Biological program coordination, 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, Argo and mooring program coordination

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 2014007 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 inter-annual 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 (when feasible) 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. In the 2014 mission we occupied the longest ever version of this line (CTD, water sampling at all stations and multinet tows at all deep stations and shallow net tows over the shelf). As a result we crossed the same Gulf Stream meander three times and sampled Antarctic Bottom Water providing a good reference for transient tracer measurements.

We recovered two moorings over the continental slopes off Labrador (at about 1000 m and 2900 m isobaths) and redeployed the shallower on the Labrador Slope and one in the central trench (NAMOC – see below).

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 2014007 program elements included:

1. CTD profile measurements of pressure, temperature, salinity, dissolved oxygen, pH, fluorescence, and light intensity at a fixed set of stations (AR07W/L3 line) spanning the Labrador Sea from Hamilton Bank on the Labrador Shelf to Cape Desolation Island on the West Greenland Shelf;
2. XHL – please insert from 2013 report
3. Measurements of salinity, dissolved oxygen, nutrients (nitrate/nitrite, phosphate, silicate), CFC-12, SF6, dissolved inorganic carbon, alkalinity 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 one current meter moorings at 2900 m isobath on the western and eastern ends of AR07W;
6. Deployment of a mooring in the NAMOC.
7. Current measurements at CTD stations from a Lowered Acoustic Doppler Current Profiler (LADCP) and Electromagnetic (EM) current meter;
8. Temperature profile measurements from eXpendable BathyThermographs (XBTs) at selected points between CTD stations (not done in the 2014007, but we mention this to reflect XBT as a part of the program);
9. Autonomous float deployments as part of the Canadian Argo Program and the international Argo Project;
10. MVP
11. Physical and chemical measurements on station HL2 of the Halifax Line on the Scotian Shelf in support of the Atlantic Zone Monitoring Program (AZMP);
12. A phytoplankton biomass/primary productivity program conducted;
13. A microbial program;
14. A mesozooplankton program.

The Labrador Sea and Extended Halifax Line (XHL) station work went well except for problems with CTD cable termination on the Extended Halifax Line. Eight additional stations were conducted on the Labrador Sea (western) side and ten on the Greenland (eastern) side of AR07W. Due to ice conditions the two inshore stations on the Labrador Shelf were not occupied during this mission.

MVP was towed in transit to the AR7W line and between AR7W and XHL but shortly after passing the continental slope on the way to XHL, the cable got separated from the drum of the MVP winch and lost with the sensor package due to instrumental failure.

b. Chemical Oceanography

The chemistry program conducted in the GP Lab during HUD2014007 included analysing water samples for total dissolved inorganic carbon (TIC), 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}I from a near surface rosette bottle at 12 stations on the L3 (AR07W) line. Fuller depth sampling for ^{129}I was carried out on four L3 stations. See table A.2.1 for the list of corresponding operation numbers.

4.2 Biological Program

a. Biological Oceanographic Sampling Program

Jeff Anning and Tim Perry

Nearly all stations occupied were sampled for a number of biological parameters. 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 all stations duplicate phytoplankton samples, integrated over the upper 50 m., were preserved with Lugol's and formalin.

b. Zooplankton Sampling

Marc Ringuette / Erica 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.

We occupied a total of 51 stations where we performed a grand total of 108 net hauls. Vertical tows were taken on the way out of Halifax harbour at HL_02, at 3 stations in transit to the AR7W line, at 26 stations on the AR7W line, at 3 stations in transit to the to the Halifax Extended Line (HXL) line including Station 27 off St-John's and at 18 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 and station 27 where tows were from 1000 m or bottom. Additional tows were made using a using a 30 cm 76 µm mesh ring net at 42 stations. See Table A.4.2.1 for details.

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

Marc Ringuette / Erica Head

EPr was measured at 12 different stations with the primary goal being to measure the secondary production of the predominant copepod species of the Labrador Sea. The number of eggs laid during the 24 hours following capture allows estimation of the egg production females would have had *in-situ* on a daily basis.

Ongoing work on summarizing egg production rates of *Calanus finmarchicus* throughout the entire North Atlantic Ocean led us to believe that a part of the generally observed high variability may be due to methodological discrepancies. We therefore evaluated the rates with set-ups regularly used by other laboratories: all methods sharing attempts to try to avoid cannibalism as much as possible. Three different treatments were used. For two Large Petri dishes (LP), 90mm in diameter were used and for one Large Volume chambers LV (>300ml volume) with funnels and mesh inserts at the bottom were used. For each treatment 20 females were put into individual vessels. For one of the LP treatments and the LV treatment females were incubated for 24 hours. For the second LP treatment, eggs were removed and counted every 6 hours and eggs spawned during the first 6 hour interval were kept aside (LP*6hrs) and recounted at the end of the 24 hour incubations. Comparisons of the 3 methods were done at 9 stations in the Labrador Sea. See Table A.4.2.2 for details.

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

Marc Ringuette / Erica Head

The vertical depth distribution of *Calanus finmarchicus* in the Slope Water off the Scotian Shelf was investigated at 14 stations, from HL_20, in the Gulf Stream, to HL_06 at the Scotian Shelf shelf break. 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 200µm mesh nets. See Table A.4.2.1 below.

e. Euphausiid EtOH samples

Marc Ringuette / Erica Head

A 1 m diameter ring net fitted with a 500 µm mesh was lowered to ~100 m at Station L3_18A and then hauled in at a rate of ~ 1 m s^{-1} as the ship proceeded at a speed of 1.5 knots, giving an oblique tow. This procedure was designed to catch euphausiids, which are less abundant and more mobile than most zooplankton forms. At another station (L3_10.5), euphausiids were observed to be quite abundant in one of the routine vertical 200 µm mesh net tows. An extra tow was done at this station for the specific purpose of collecting euphausiids. These 2 samples were preserved in EtOH 95% for genetic analysis, to be carried out by colleagues at the University of Connecticutt.

			Ring Net		
Station	Date	Multi-net	200µm	76µm	EPr/Livebugs
HL2	2 May			X	X
MIDGULLY	3 May			X	
NFLD Shelf	5 May			X	
Transit SWLS	6 May			X	
L3_15				X	X
L3_16	7 May			X	X
L3_17				X	X
L3_18				X	X
L3_19	8 May			X	X
L3_20				X	X
L3_21				X	X
L3_23	9 May			X	X
L3_27				X	X
L3_28				X	X
L3_27.5					
L3_26				X	X
L3_25				X	X
L3_24	10 May			X	X
L3_22				X	X
L3_18A	11 May		X		
L3_16.5				X	X
L3_14.5				X	X
L3_07	13 May			X	X
L3_06				X	X
L3_05				X	X
L3_04				X	X
L3_03				X	X
L3_09	14 May			X	X
L3_11.51				X	X
L3_10.5	15 May			X	X
NFLShelf BIO/02	16 May			X	
STN27				X	X
Off Grand Banks	17 May			X	
HL_20	19 May	X			
HL_18	20 May	X			
HL_17		X			
HL_16		X			
HL_15	21 May	X			
HL_14		X			

HL_13		X			
HL_12		X			
HL_11	22 May	X			
HL_02	2 May			X	X
MIDGULLY	3 May			X	
NFLD Shelf	5 May			X	
Transit SWLS	6 May			X	
L3_15				X	X
L3_16	7 May			X	X
HL_10	22 May	X			
HL_09		X			
HL_07		X	X		
HL_08		X			
HL_06	23 May	X	X		
HL_05			X	X	
HL_04			X	X	
HL_03	24 May		X	X	
HL_02			X	X	

Table A.4.2.1. List of net tows carried out on Labrador Sea monitoring mission HUD2014007.

Station	LP*6hrs	LP*24hrs	LV*24
MIDGully	X	X	X
NFLD Shelf	X	X	X
Transit SWLS	X	X	X
L3-17		X	
L3-20	X	X	X
L3-27.5		X	
L3-22	X	X	X
L3-14.5	X	X	X
L3-06	X	X	X
L3-11.51	X	X	X
NFLShelf BIO-02	X	X	X
Off Grand Banks		X	

Table A.4.2.2. Egg production rates experiments during HUD2014007 cruise in the Labrador Sea.

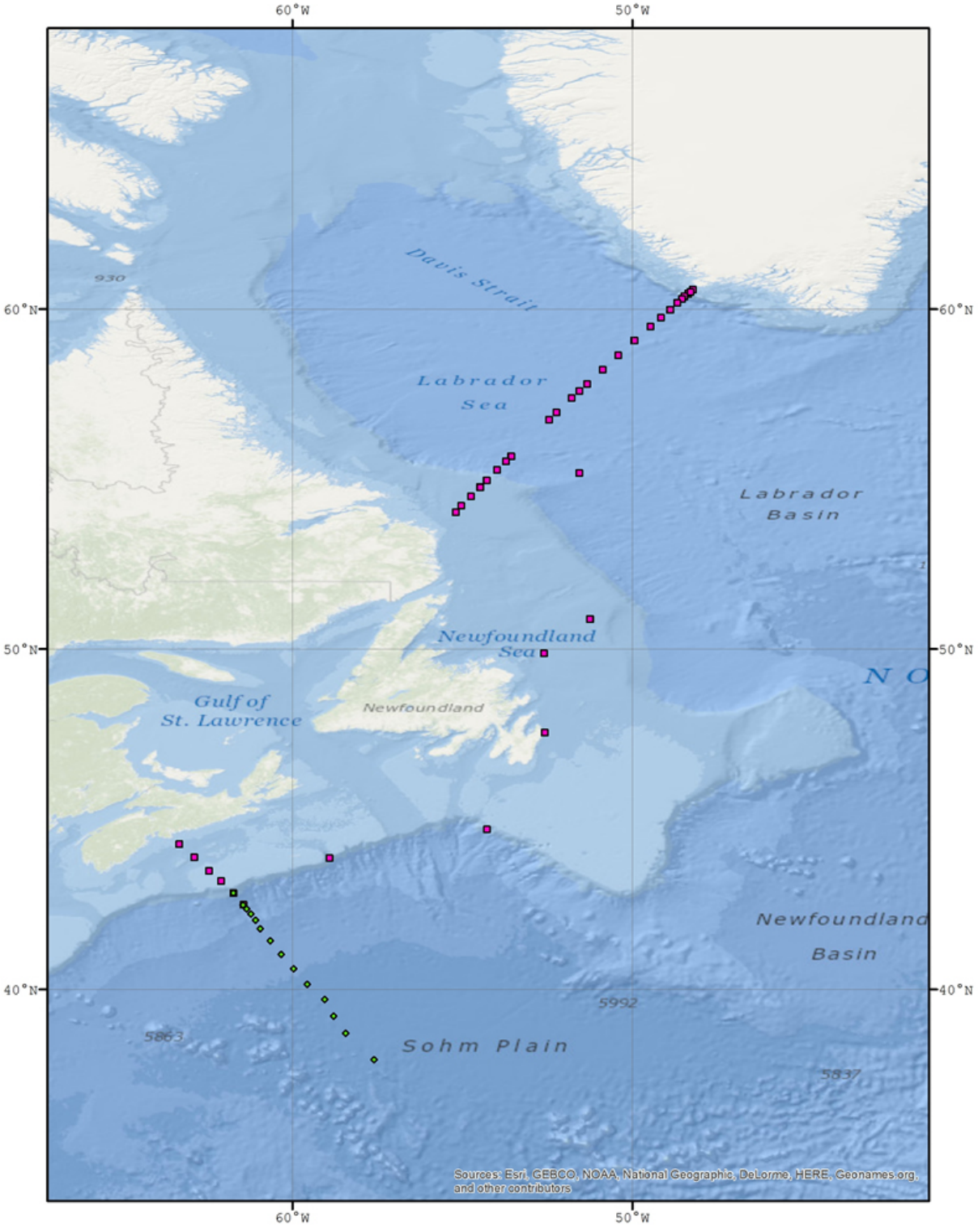

Figure A.4.2.1 HUD2014007 Ring net tows (pink-filled squares) and multi-net tows (green-filled diamonds) locations.

e. Primary Production Measurements

Jeff Anning

Water samples for photosynthesis-irradiance (P-I) experiments were collected from the rosette at the surface and 30m at 7 stations. For each incubation experiment, 33 aliquots were inoculated with ^{14}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. Samples for chlorophyll, particulate organic carbon, pigment composition by HPLC, and absorption spectra were collected for each incubation experiment.

Station	Event	Lat.	Long	Date	Time	Depth	ID
L3-17	33	57.7957	-51.3347	"May 07 2014"	"14:57:26"	1.7	400146
L3-17	33	57.7957	-51.3347	"May 07 2014"	"14:55:46"	29.0	400137
L3-20	47	59.0698	-49.9388	"May 08 2014"	"14:09:43"	1.1	400242
L3-20	47	59.0698	-49.9388	"May 08 2014"	"14:07:57"	29.5	400233
L3-27.5	67	60.5077	-48.2927	"May 09 2014"	"14:56:20"	1.9	400363
L3-27.5	67	60.5077	-48.2927	"May 09 2014"	"14:53:25"	30.4	400353
L3-22	86	59.7465	-49.1602	"May 10 2014"	"13:42:37"	2.2	400465
L3-22	86	59.7465	-49.1602	"May 10 2014"	"13:40:42"	30.3	400456
L3-16.5	96	57.5865	-51.5723	"May 11 2014"	"13:07:56"	3.0	400561
L3-16.5	96	57.5865	-51.5723	"May 11 2014"	"13:04:09"	31.2	400552
L3-05	120	54.487	-54.7505	"May 13 2014"	"14:44:07"	2.9	400802
L3-05	120	54.487	-54.7505	"May 13 2014"	"14:41:18"	29.7	400793
L3-9.5	137	55.3428	-53.9015	"May 14 2014"	"17:38:21"	2.3	400887
L3-9.5	137	55.3428	-53.9015	"May 14 2014"	"17:36:06"	29.7	400878

Table A.4.2.3. P-I experiments conducted during the HUD2014007 mission in the Labrador Sea.

4. Major Problems and Goals Not Achieved

Not all AR07W sites could be occupied due to ice cover and weather.

5. Other Incidents of Note

There were none to report.

6. List of Cruise Participants (please update from Form B)

Name	Responsibility	Affiliation
Anning, Jeffrey	Biological	OESD, BIO
Clement, Pierre	Salts	OESD, BIO
Courchesne, Isabelle	VITALS, Winch Room Sampling	ULAV
Duerkson, Steve	pH, O^{18}	DAL
Duffy, Steve	Bird Observer	EC
Fung, Raymond	Technical Operations	PCSD, BIO
Gagnon, Jonathan	VITALS, Winch Room Sampling	ULAV
Geshelin, Yuri	Oxygens	OESD, BIO
Head, Erica	Biological Lead	OESD, BIO
Hsieh, Pei-Yuan	Winch Room Sampling	UCAL
Jackson, Jeffrey	Data management, Computer Room	PCSD, BIO
Jørgensbye, Helle	Biological, DNA	Denmark
LaBrie, Richard	VITALS, Winch Room Sampling	UM
Laliberté, Julien	VITALS, Winch Room Sampling	UQAR
King, Randy	Technical Operations Head, MVP	PCSD, BIO
Nelson, Richard	Carbonate, Alkalinity	OESD, BIO
Perry, Timothy	Biological, Net Tows	OESD, BIO
Punshon, Stephen	Chemistry Lead, CFC-12, SF6	OESD, BIO
Raimondi, Lorenza	Carbonate, Alkalinity	DAL
Ringuette, Marc	Biological, Net Tows	OESD, BIO
Ryan, Robert	CTD Tech., Winch Room, Floats	PCSD, BIO
Sauve, Daniel	Chemistry	UO
Thamer, Peter	Nutrients	OESD, BIO
Wang, Zeliang	Computer Room	DAL
Wood, Dan	Electronics Tech, Winch Room	PCSD, BIO
Yashayaev, Igor	Chief Scientist	OESD, BIO

BIO	Bedford Institute of Oceanography Dartmouth, Nova Scotia, Canada
DAL	Dalhousie University Halifax, Nova Scotia, Canada
EC	Environment Canada
OESD	Ocean Ecosystem Science Division
PCSD	Program Coordination and Support Division
UCAL	University of California Berkeley, California, United States
UM	University of Montreal Montreal, Quebec, Canada
UO	University of Ottawa Ottawa, Ontario, Canada, K1N 6N5

UQAR	University of Quebec at Rimouski Rimouski, Quebec, Canada
UVAL	University of Laval Québec City, Québec, Canada

B. UNDERWAY MEASUREMENTS

1. Navigation and Bathymetry

The differential GPS navigation system was provided onboard by the CCGS HUDSON. Navigation information was broadcast on the ships network for access in all lab areas.

Mooring locations, station locations and navigation were monitored using the Aldebaran II electronic charting software from CNS Systems.

All navigation data was logged using the Geological Survey of Canada's (GSC) Survey Suite navigational software. A time and date stamp is added to each navigation string acquired.

The echo sounder system included a Raytheon PTR echo sounder, a Raytheon Line Scan Recorder and an Edo 12kHz transducer. The Edo 12 kHz transducer was mounted on the ram located in the well on the forward deck and remained flush with the hull during the mission.

A Benthos 7000 transducer was also mounted on the ram for use during mooring operations and mooring position and depth calibration.

2. CTD Motion Study

An attitude and heading reference sensor (Xsens MTi) was mounted on the CTD package. Data from the motion sensor was monitored in real-time to provide information on the dynamics of the package during a CTD cast. The Motion Data acquisition software combined each motion sensor sample with CTD and Instrumented Block System data. This information will hopefully aid in the prevention of motion induced failures in the mechanical wire termination on the CTD package. Motion data was logged at 10Hz for almost all CTD casts during this mission.

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 Thermosalinograpgh 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. Unfortunately the thermosalinograph system became unstable during the cruise so very little reliable data was collected.

4. Meteorological observations

The officer of the watch manually logged meteorological variables at regular intervals.

5. Atmospheric Chemistry

There was no atmospheric chemistry program.

C. HYDROGRAPHIC MEASUREMENTS - DESCRIPTIONS, TECHNIQUES AND CALIBRATIONS

1. Salinity

Pierre Clement

Salinity samples were taken from rosette bottles and collected in hard glass bottles for analysis. The bottles were rinsed three times, the tops wiped dry and closed with new Polyseal caps tightened snugly. Samples were stored in trays and analysed using an Autosal 8400 salinometer. The system was set to run at 24°C.

The instrument was setup Drawing Room of the Hudson. The pump was turned on and the system run for ~20-30 minutes to condition the instrument in advance of analysis.

Calibration

The Autosal was calibrated before and after analysis runs using OSIL standard seawater (SSW). The SSW bottle was immersed in a 22°C water bath to the neck to temperature condition, then shaken and blotted dry before opening. The analysis cell was emptied, the 'sipping' straw wiped dry and two rinses done before attempting to read the conductivity. Two separate reads were done and if the measures were consistent to 0.000001, the system adjusted to read the standard value. A second standard was processed following the same procedure to confirm the setting. The reference number was recorded and for any give machine that number tends to be stable from day to day assuming the room temperature is relatively constant and bath temperature set the same. If there is a deviation in the Ref number the analyst should be cautious about continuing.

Sample Processing

Sample analysis consisted of keeping sample trays in the 22°C water bath and the sample bottles were shaken by inversion, three times, left to settle for at least 30 seconds. The Autosal sipping straw wiped dry and the sample introduced with two complete washes before attempting to read. The third fill was read followed by a refill and read done to confirm the measure. If the read was within 0.000001 the value accepted, if not a third and subsequent reads done until there was a set of acceptable measurements.

Once the sample run was completed a new calibration standard was run, following the above mentioned protocol and, if reasonable, the measure recorded and any change assumed to be system drift. The analyst has to assess whether there has been sufficient change in the Ref number and general conditions to accept any change in the SSW read value. A drift is not uncommon but the system can be very stable over long periods of time.

All information was recorded on Bedford Institute of Oceanography Salinity Log Sheets. All fields were filled in and the data transcribed to an Excel 2010 spreadsheet. To aid in quality control sample times were recorded at intervals, with particular emphasis in the start and end of a run and any breaks in operation within the run. These data were added to the spreadsheet and gaps filled in assuming 1.25 - 2.5 minutes between samples to match the recorded intervals.

OPERATIONAL STORY

The sample analyses were problematic the first couple days. The Autosal seemed to be working well but on May 12th there was significant drift between the start and end SSW and the Ref number did not seem stable. A decision was made to cut short the morning run, investigate the system more carefully and start the backup in case it was needed. The water chamber in the backup salinometer was empty and while filling it was noticed that the main Autosal chamber was not completely filled. Another 3-5 liters was added and once the system returned to 24 C a set of replicates were run to test its operation. Replicates were reserved to compare the two systems on May 13th.

The replicates were run in the AM after warming the system up by running 20 - 30 minutes of mock samples. From the replicate analysis the system seemed stable, so after lunch on May 13th sample analysis of regular samples continued. The backup system was not tested and left idle for the time being.

Date	Run Number	ID Start/Finish	Number Samples (Inc Std)
May 6, 2014	1	400014-079	20
May 7, 2014	2	400080-121	45
May 8,2014	3	400152-215	70
May 9, 2014	4	400216-261	23
May 10, 2014	5	400267-379	77
May 10, 2014	6	400380-433	45
May 11, 2014	7	400434-521	66
May 12, 2014	8	400522-575	34
May 13, 2014	9	400576-665	104
May 14, 2014	10	400666-833	102
May 15, 2014	11	400834-926	101
May 17, 2014	12	400957-975	16
May 20, 2014	13	400981-1095	77
May 21, 2014	14	401096-191	91
May 22, 2014	15	401197-1278 (with 50 reps)	165
May 23, 2014	16	401284-1405	101
May 24, 2014	17	401411-1474	31
Totals	**17**		**1164**

Replicates

As part of the regular sampling the Chief Scientist included the collection of replicate samples which were to be run as 'aged samples' to look at changes in conductivity over time in un-opened sample bottles. This concept was expanded to include several sets of replicates to also look at Autosal/analyst performance over time. There is a concern that there is a temporal effect both in sample quality the longer samples were in bottles and a systematic instrumentation drift through the period of an analytical run.

After the problems on the 13th and the system stabilized, which resulted in the use of several OSIL standards, it was suggested that replicates might serve as a means to assess whether there had been drift in the run.

These statistics will be discussed further.

DATA PROCESSING

Conductivity measurements were written on Bedford Institute of Oceanography Salinity Log Sheets and transcribed to an Excel 2010 workbook. The QAT files from CTD operations were also copied to the workbook allowing for analysis of differences between manual (AutoSal) and instrumental determinations.

The AZOMP Matlab scripts (***compute_run_sal.m*** and ***compute_sal.m***) were used to calculate salinities from the measured conductivities and with respect the standardization values with drift corrections.

Excel Workbook

SalinityCompareMMMDD.xlsx

1. **QAT** – all the QAT file data
2. **CTDSalts** – Subset of the QAT files including, ID, Date, Time of bottle closure at depth, Instrument Salinity for each of the two CTD conductivity cells, Event number and rosette bottle number
3. Salinity – transcription of the conductivity data from the Log Sheets. Includes function to calculate salinity from conductivity and bath temperature as well as date and time of Autosal analysis for each of the runs.
4. **Uncorrected Salts** – Subset of the Salinity worksheet with Run number, date/time. ID and salinity. No drift corrections were applied.
5. **Delta Salts** – A lookup version of each the manual salinities from Salinity and CTD salinities from QAT and the difference between the Manual salinity -CTD 1 (Delta1) and Manual salinity -CTD 2 (Delta2). Includes time of autosal analyses ID, Run number and Event number.
6. **2014007Cond** – Export from Salinity with fields for Jeff J Compute_sal.m
    a. Crun = Run Number
    b. ID = Identifier
    c. Crep = Replicate number within the run
    d. Ctime = DateTime of analysis

    e. Cond = measured Conductivity
    f. Bath_Temp = Temperature of Autosal bath
7. **2014007StdSw**- Export from Salinity
    a. Srun = Run Number
    b. Svalue = Standard Conductivity, set at start of run and read within or at end of run
    c. Stype = ????
    d. Stime = DateTime of analysis
8. **Replicates** – subset of Delta Salts for all manual sample that were run as replicates. Includes all the fields in Delta Salts.

Matlab

A few simple Matlab scripts (***compute_run_sal.m***, ***Salt_ana_AllEvents_test1.m***, ***ReplicateStats.m***) were written as part of the assessment of error in the manual Salinity processing. These scripts were written to:

1. plot out the Delta (Autosal – CTD1 salinities) for each of the runs on a scale of ±0.005 salinity units with a breakout by the Event number. The images of generated from the plots for each run will be used to help understand the source of error.
2. Display all the Differences over time by Event
3. Look at the replicate stats

RESULTS

Manual salinities are used primarily on the Labrador Sea missions to calibrate the Seabird Salinity Conductivity Temperature and Depth (CTD) instrumentation estimates. Historically the Seabird CTD has proved very reliable and stable after proper sensor calibration and the manual or Autosal measurements have only been used as a check (pers. Comm., Igor Yashayaev). The chief scientist has expressed concern that there seems to be some systematic error in the Autosal salinities (salts) and has asked that this be looked at. For the purposes of this work, the Autosal Salts will be considered with respect to the CTD estimates as the difference between Autosal-CTD in Salinity units.

The Seabird CTD has two conductivity sensors in order to provide redundancy. When the differences between the sensors (Figures C.1.1 & C.1.2) were plotted it was evident that there was a problem with 9 of the CTD1 estimates. These values show up as a tail just under 35 PSU in a plot of the two sensors (Figure C.1.3). The slope and R^2 of the linear fit suggest that there is a -0.0432 offset between the two sensors. The chief scientist suggested he had more confidence in the Primary or CTD1 sensor, so for the purposes of investigating error in the sample salinities the CTD1 sensor will be considered, except for the 9 odd values where CTD2 will be used.

A comparison of CTD1 and the drift corrected Autosal estimates (Figure C.1.4) using a regression analysis shows a large number of outliers, with an R^2=0.89, n=1169, a slope of 0.94 and an intercept of 1.996. As a rough check, removing n = 95 outliers that are identified as differing by ±0.01 PSU the regression changes dramatically with the Autosal over estimating the CTD by 0.0327 (Figure C.1.5) with an R^2 = 1, thus looks like a reasonable offset correction.

A plot of the Autosal-CTD1 salinities broken out by run number shows no obvious trend by run (Figure C.1.6). There are a series of 7 points that seem to line up in a secondary line above the main line but they are not replicates or can the offset be explained.

Finally a little experiment was run to look at whether salinity quality was affected by sampling order. Traditionally the 'Mission sampling order' takes precedence over any Research sampling done by groups that join the mission for their own purposes and are outside of the Mission mandate. In general the 'normal' order includes priority to volatile substances like gasses (DO, Freons, etc.) whose concentrations may be altered as the sample bottle warms up in the winchroom after recovery. On HUD2014007 a group from Laval Uni. collected Nitrous Oxide (NO) and Methane (CH_4) gaseous sub-samples, but being Research priority these samples were taken all Mission samples including Salinity and nutrients. Given concern for loss of volatiles by waiting and alternatively worry that the salinities could be contaminated, a little experiment was run where duplicate Salts were subsampled in normal position and a second set taken after the Research gasses were collected. This Before and After experiment is presented below.

Manual Salinity Error

The source of the error in estimating salinity manually is a product of three main factors. Error can be introduced at sampling, through storage and at the analytical stage. There can also be data entry errors but these are readily identified and have been corrected for this dataset.

For this assessment the assumption is that the CTD1, and the 9 CTD2, estimates are accurate although they may be shifted through a calibration. The outliers of the difference between AutoSal and CTD1 are then products of one of the three sources of error.

Sampling and Analytical Error

Estimating the error attributable to mishandling of the samples at collection and analysis is difficult to separate and assess. The suggestion here is to look at trends in runs and over the whole set of runs to allow for comment on any analytical drift. The spread of the difference over time may also identify some analytical systematic error. To elucidate the contribution of sampling error it is suggested that the amount and spread of the differences by event should show whether there was some aspect in sample handling that could be attributed to the event and thus related to some practice at the time of sample collection.

To assess any analytical error it would be expected that the ideal set of AutoSal - CTD1 (Delta) differences would straddle Delta = 0 noting that there is probably a positive offset, so in the best case the values should tend to be above the line. The chief scientist suggested that error should be evaluated with the ±0.005 bounds.

Looking at Delta against date and time of analysis, there seems to be a trend in analytical error from runs 1 through 17 in a negative direction (Figures C.1.7 & C.1.8). The same trend is evident when looking at Delta against Identification number, which can serve as a surrogate for time but spreads the numbers out (Figure 9). Looking more carefully at each run the tendency is

the same with 9 runs above (2,3,5,6,7,8,9,12,17), 3 neutral or bounding 0 difference (4,10,11) and 5 below (1,13,14,15,16) (Figures C.1.9 – C.1.11).

To look at the sample handling the AutoSal - CTD1 difference (Delta) was plotted for each analytical run and color coding the differences by Event number (Figures C.1.10 – C.1.12). The expectation is that if there was a sampling handling problem then there could be a broader spread in Delta or some other standout anomaly when looking at the data from the event point of view.

Storage or Bottle Effect

There is a general consensus that manual salinities need to be done relatively soon after collection and that the longer the sample remained in a hard glass bottle the sample would degrade. Also analysis at sea is considered an issue because of poor temperature control in the lab which can affect the operation of the instrument. A practice of conditioning the samples by putting the trays in a water bath prior to analysis has sped the procedure up and added more confidence to the analysis. There is a discussion that maybe the analyses should be done post mission, on shore, so assessing the bottle effect will help in that decision.

To look at this bottle effect, several sample replicates were taken and run at different intervals after the original sampling. The date and time of analysis was recorded as well as when the rosette bottle was closed at depth collecting the sample. The difference between collection and analysis date was determined as 'Days since Collection' and plotted against the AutoSal - CTD1 or Delta (Figure C.1.13).

There were only 17/356 Delta values greater than ±0.005 and these occur at various times between 0.05 and 8.9 days after collection. The plot shows that the error does not display a trend of analysis from time of collection, if anything the error looks stable. The mean Delta is 0.0131 (stdv = 0.17144, N = 356) removing three outliers (-1.0 < Delta > 1.0) yields a mean of -0.00094 (stdv = 0.06545, N = 353).

The 356 replicate samples are plotted against the number of replicates taken for each sample (Figure C.1.14). The expectation is that the more replicates the lower the mean difference (Delta) and a reduced standard deviation. The plot shows that trend suggesting again that there is no bottle effect. The few outliers were duplicates or triplicates and ranged from 0.5 days to 8 days from when the samples were collected.

Before and After Experiment

This experiment was quickly proposed to look at whether sampling salinities was affected by sub-sampling before Research gases or after. Fourteen sets of duplicates were collected in the normal priority and a second set collected 'After' the Research gases.

All samples were analysed in the same Run with the Mission Salts analysed in the normal analytical run order while the After Salts in a group.

One set of samples was rejected because there was only a singlet for the After or Research duplicate. The analysis of the 13 sets of duplicates was to look at the average Delta for each duplicate set and the Average and standard deviation of the groups.

The data show that there is no significant difference between the Deltas using a T-Test ($P_{0.05}$ = 0.384 or > 0.01). The means difference is actually lower for the After or Research sub-samples but not significantly so.

ID	Mission	Research
401199	-0.0028	-0.00199
401207	-0.0029	-0.00015
401213	-0.0030	-0.00104
401216	-0.0011	-0.00203
401229	-0.00065	-0.00184
401232	-0.00131	-0.00092
401237	-0.00134	-0.00124
401241	-0.0012	-0.00173
401245	-0.00593	-0.00574
401259	-0.00128	-0.00099
401263	-0.00191	-0.00102
401267	-0.00169	-0.00129
401274	0.008004	0.007315
MeanDiff	-0.0013	-0.0010
StdevDiff	0.003118	0.002824

Table C.1.1 Statistics from the Beginning and End Test. The values represent the average difference between AutoSal - CTD1 for each set of duplicates taken before (Mission) and after the Research Gases (Research).

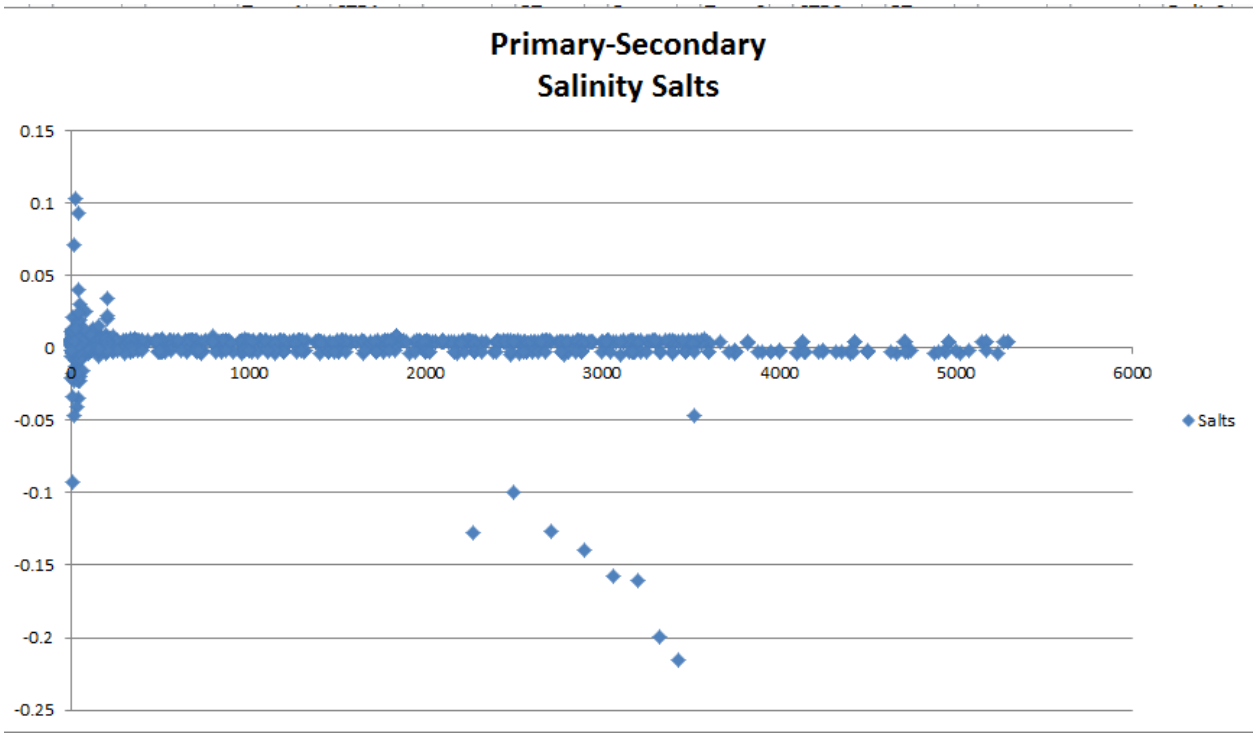

Figure C.1.1 Difference between the Primary and secondary Salinity estimates plotted against Pressure.

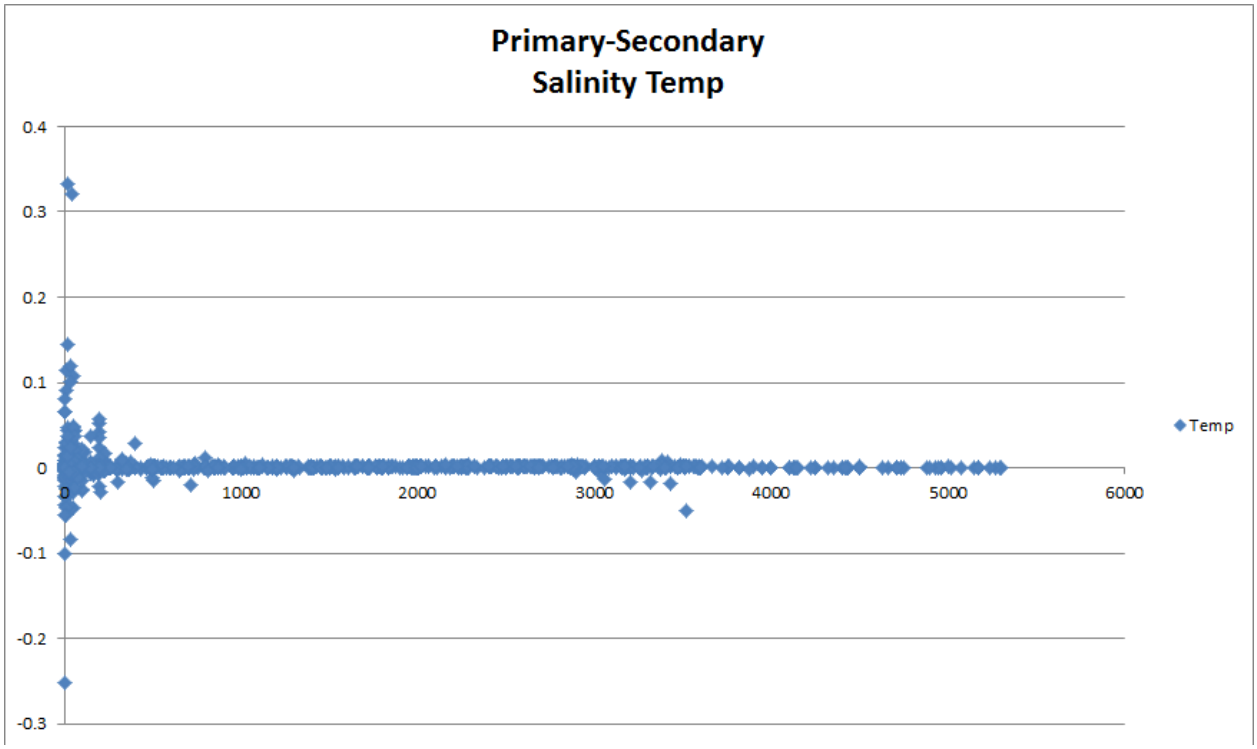

Figure C.1.2 Difference between Primary and Secondary Temperature sensors plotted against Pressure.

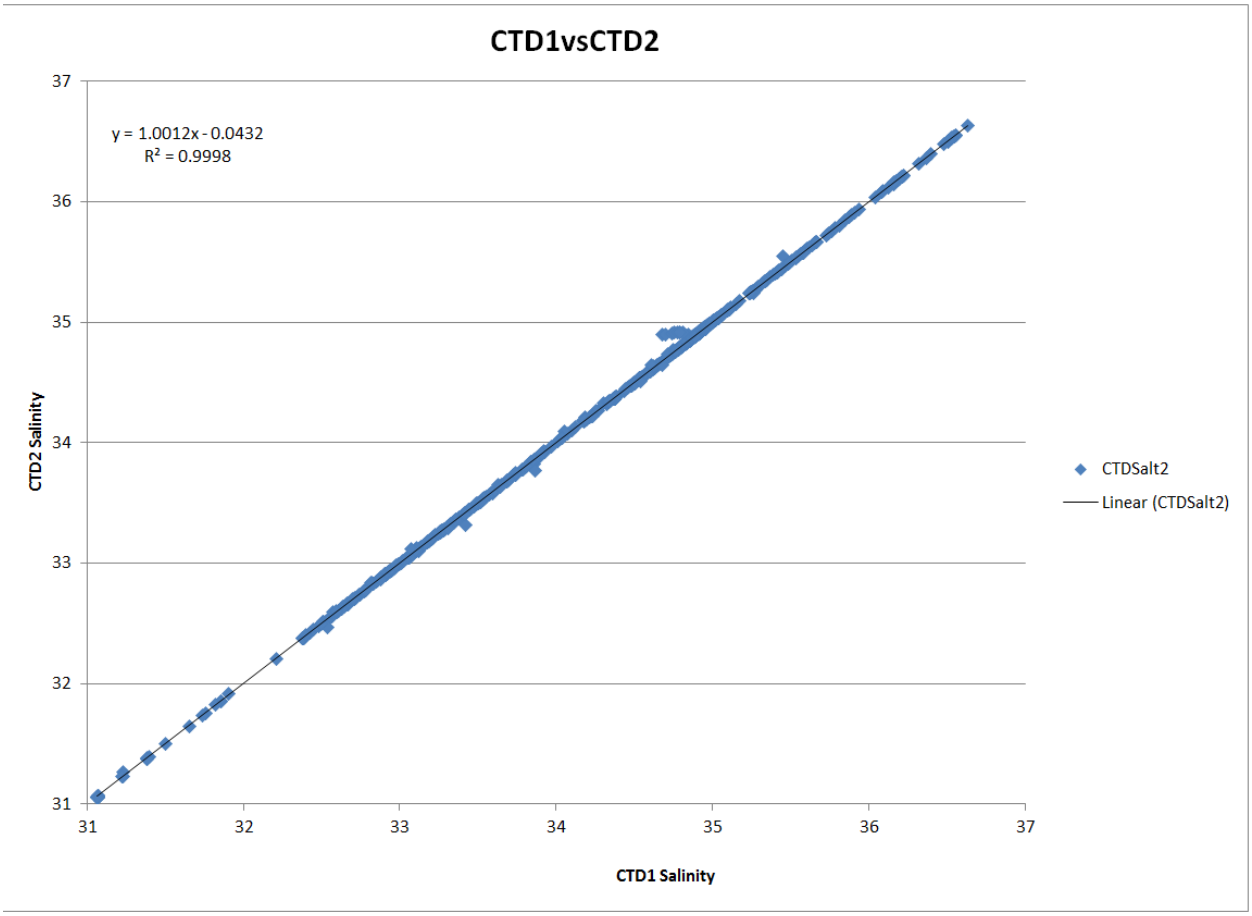

Figure C.1.3 Primary (CTD1) vs Secondary (CTD2) salinity estimates. Notice offset just under 35PSU caused by some irregularity in CTD1 estimate; resulting in CTD2 being used in subsequent analyses.

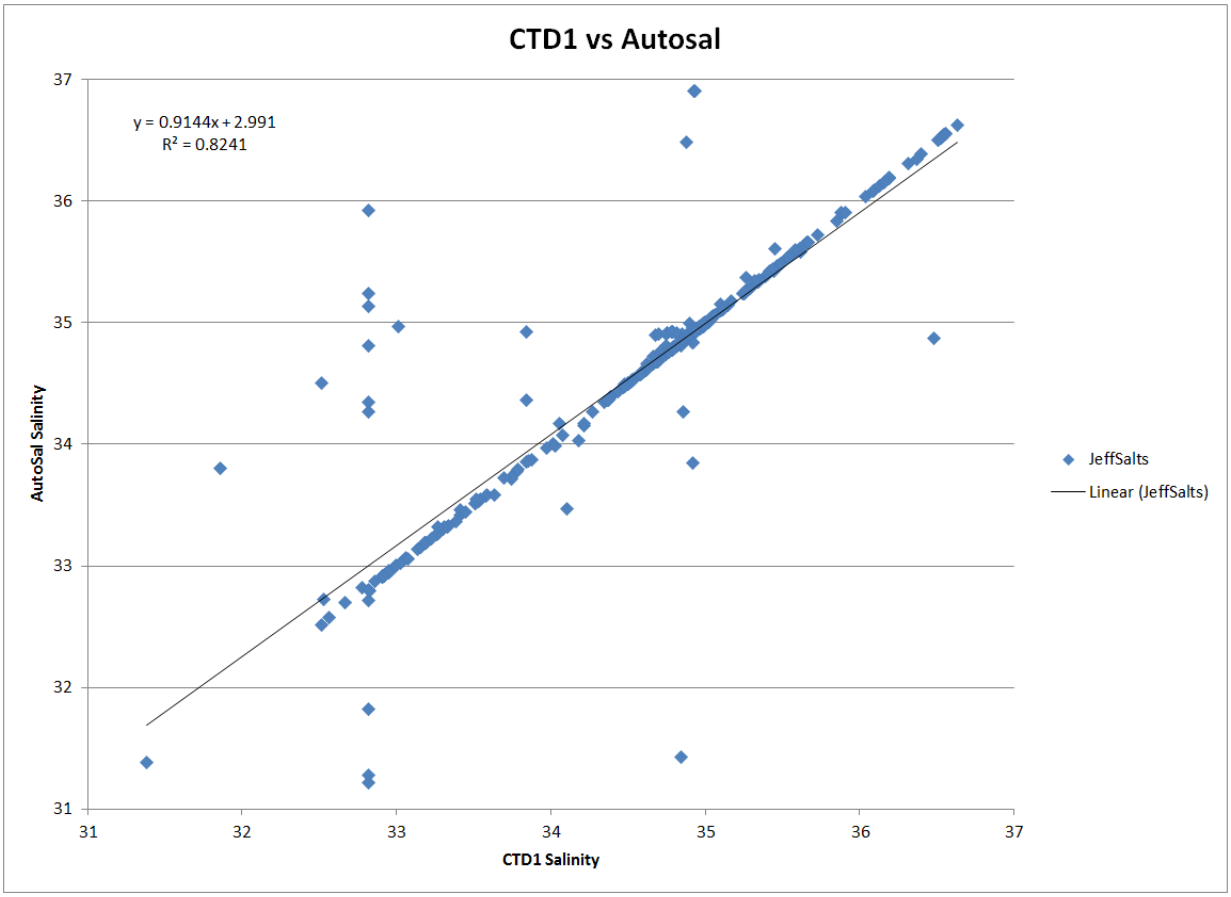

Figure C.1.4 Primary salinity estimate versus the Autosal estimate; includes all outlier data.

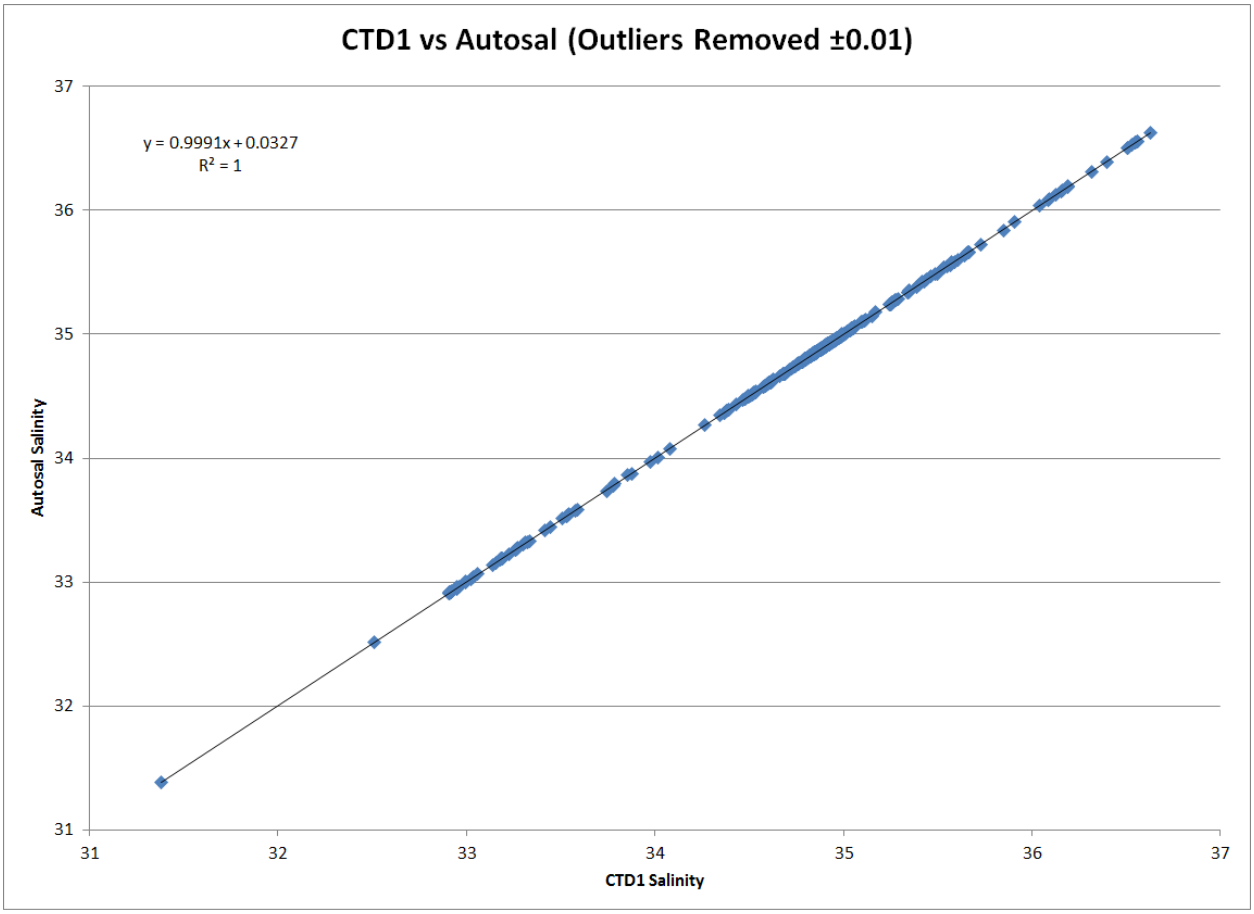

Figure C.1.5 CTD1 versus AutoSal estimates with outliers removed and anomalous CTD1 estimates replaced by CTD2 estimates.

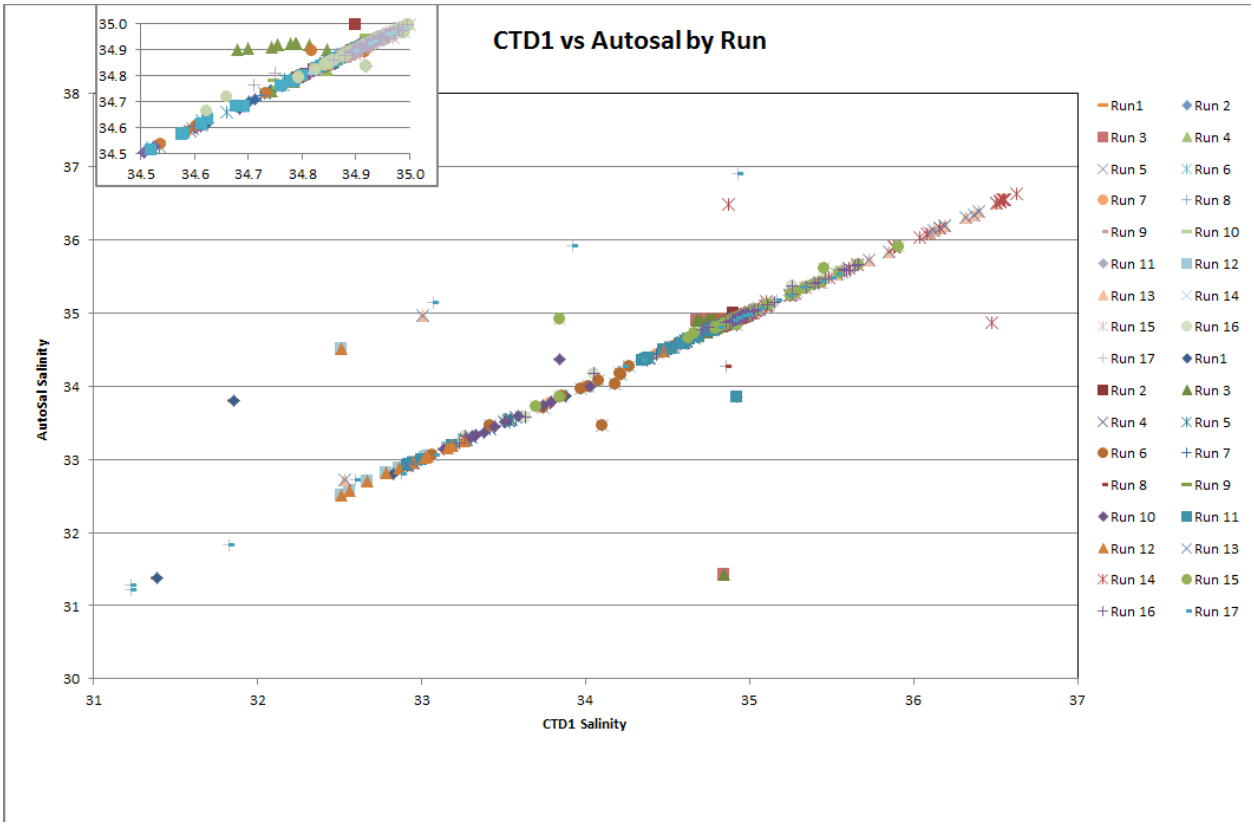

Figure C.1.6 CTD1 versus Autosal broken out by Analytical Run. Note inset showing the CTD1 anomalous data. These points were replaced using CTD2 for the subsequent analysis of error.

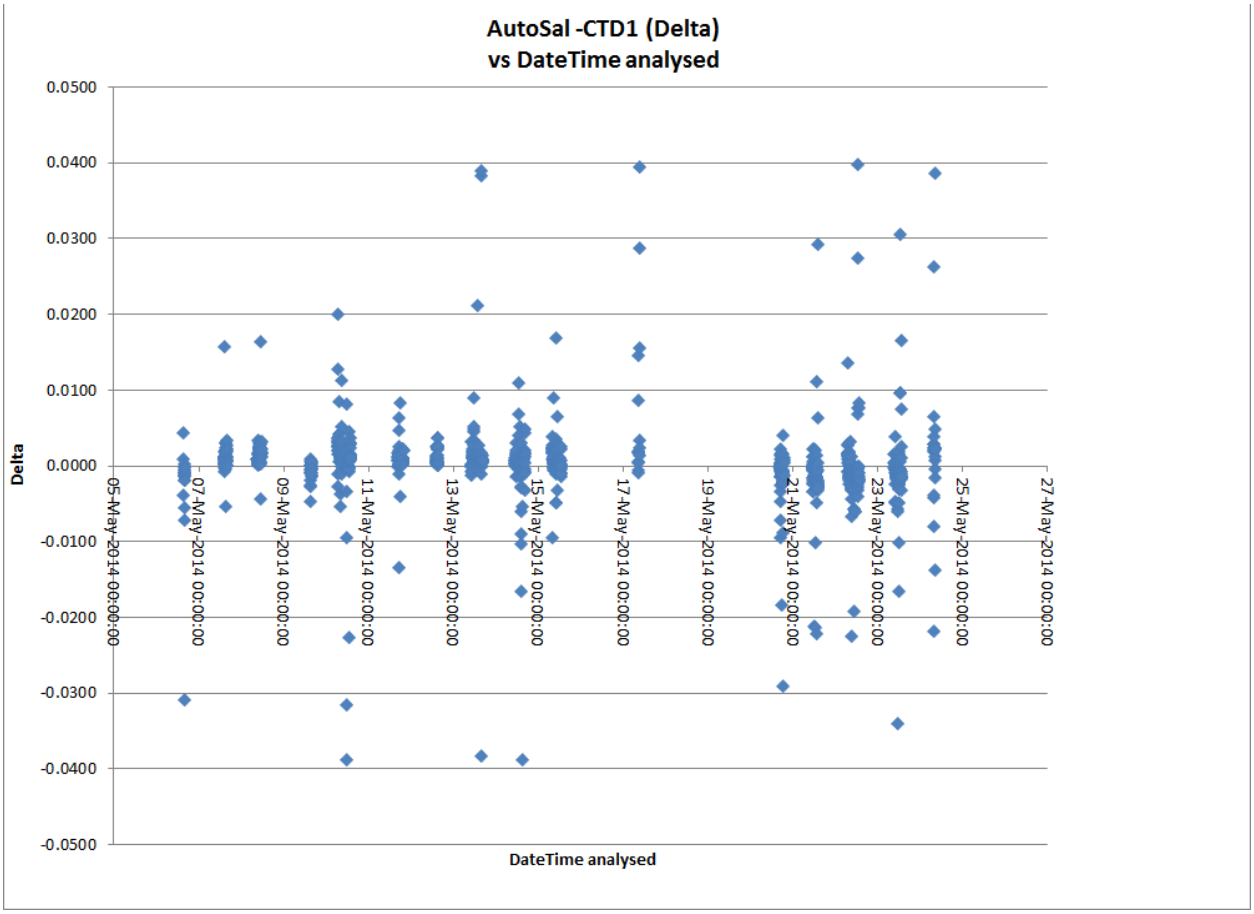

Figure C.1.7 Delta plotted against date and time analysed.

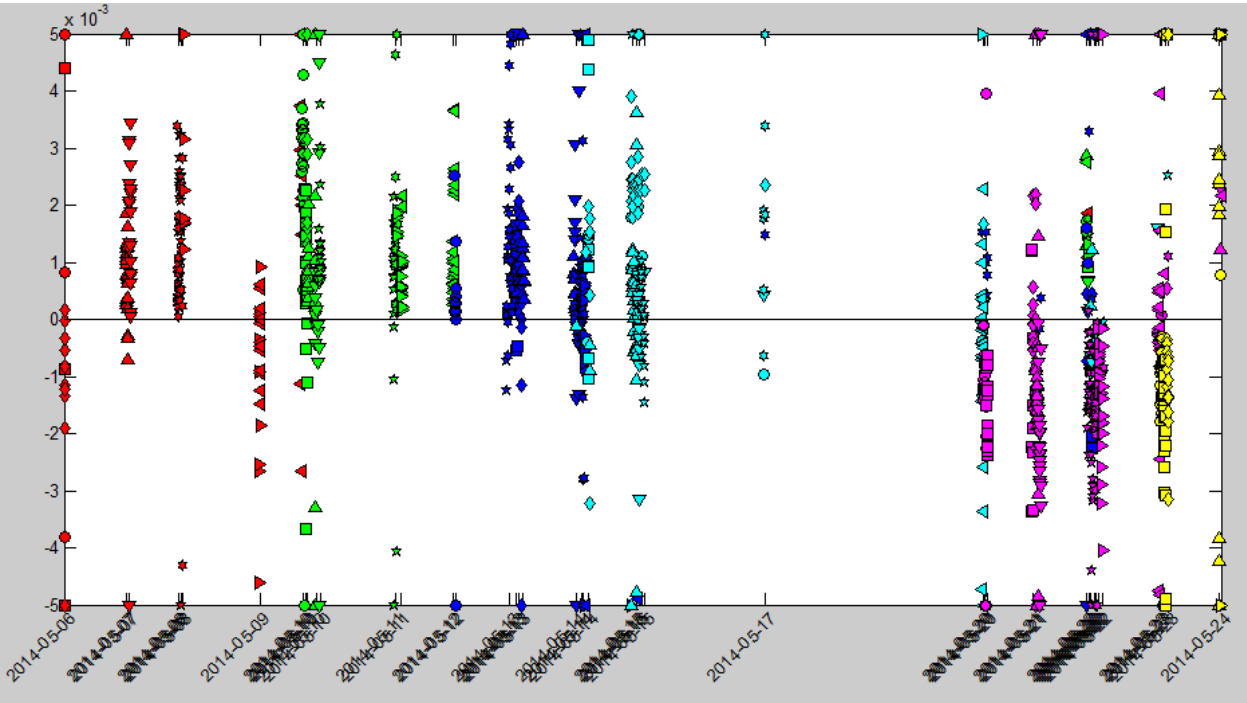

Figure C.1.8 All Delta by Time of analysis, broken out by Event. This plot still needs a legend and work on the color scheme to get a better discrimination between Events.

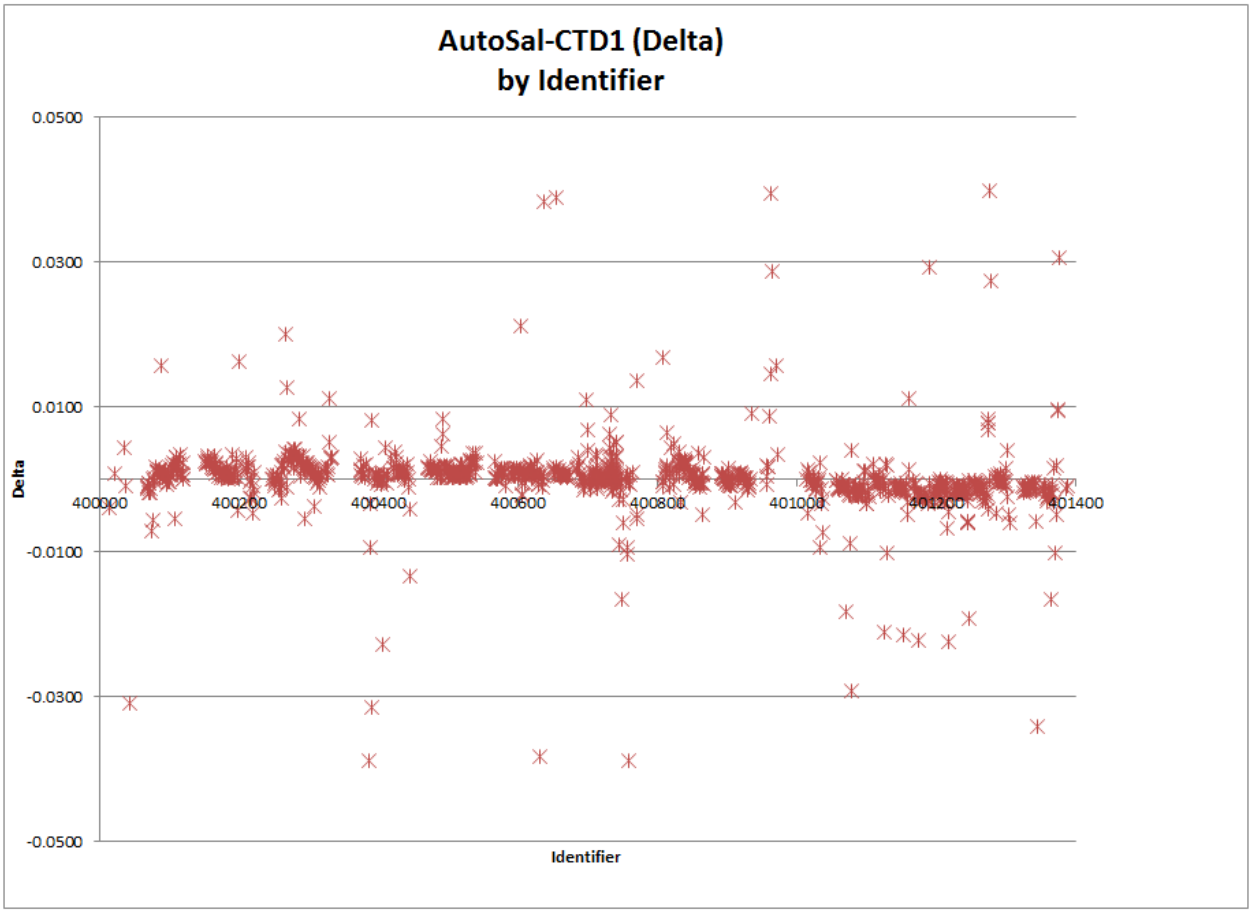

Figure C.1.9 Delta against the sample Identifier. This can be interpreted as a surrogate of time but is not very accurate. It does display the trend from a minor positive to negative error over the course of the mission.

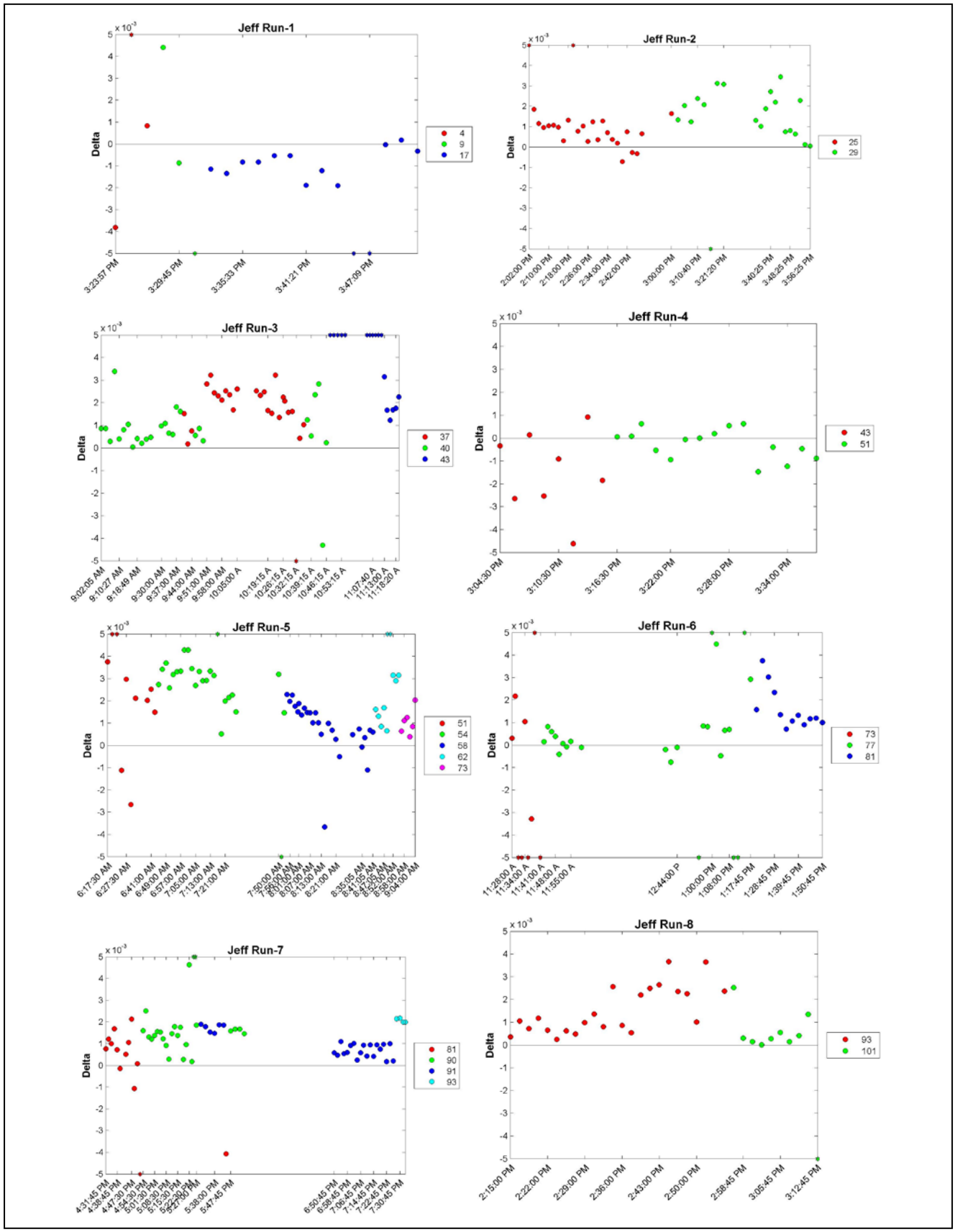

Figure C.1.10 Delta for each Run broken out by the Event when they were collected (Runs 1 – 8).

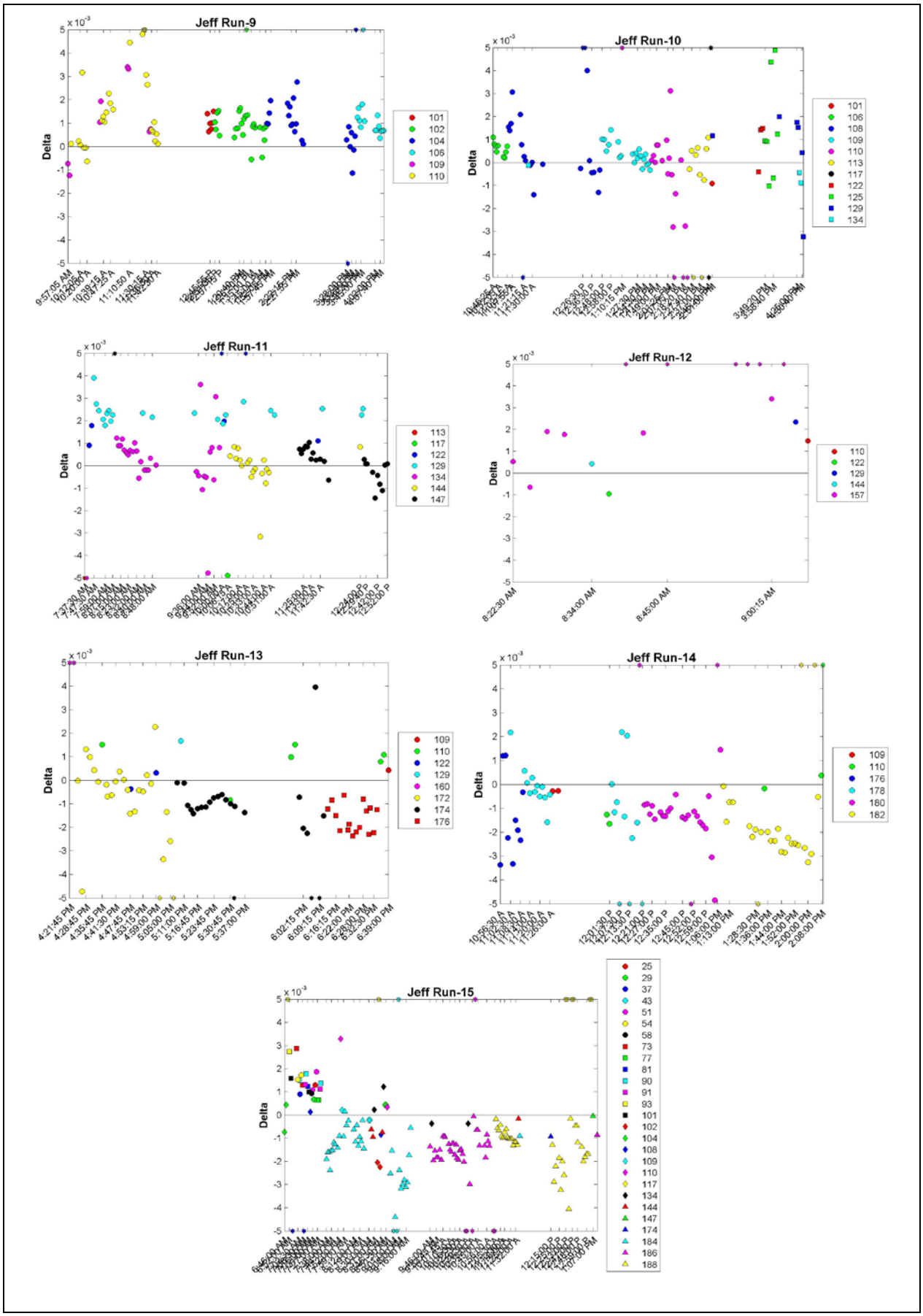

Figure C.1.11 Delta for each Run broken out by Event number (Runs 9-15).

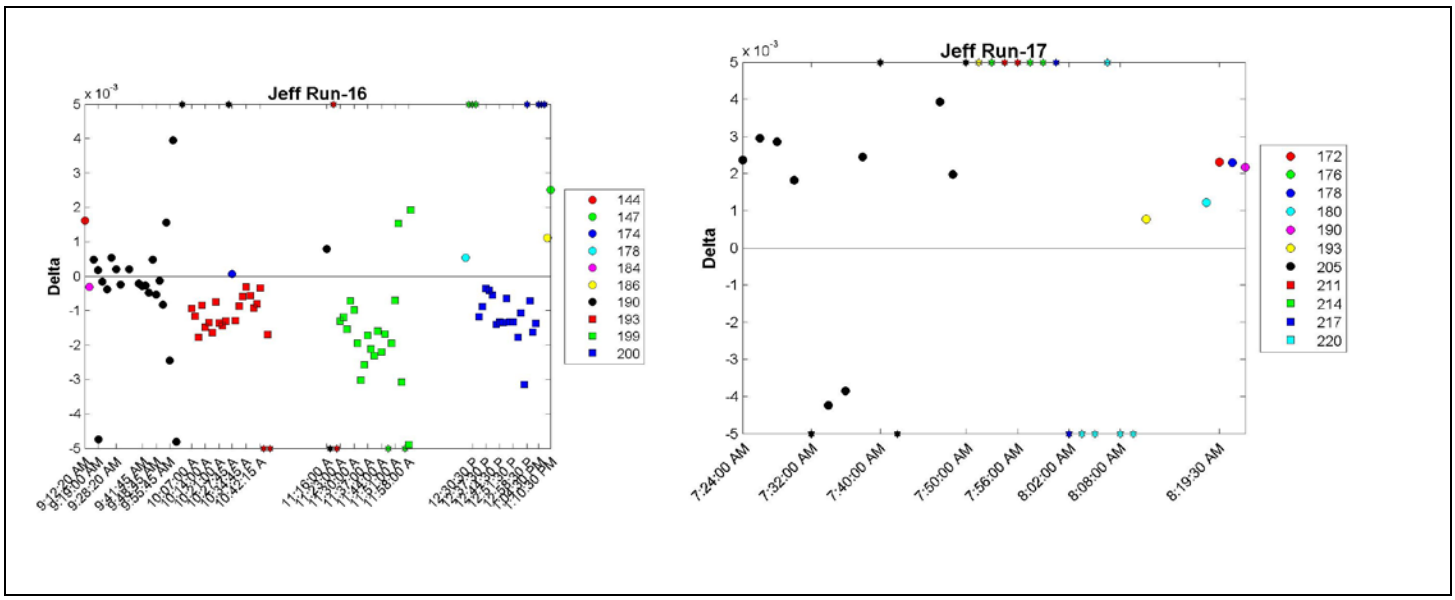

Figure C.1.12 Delta for each Run broken out by Event number (Runs 16-17).

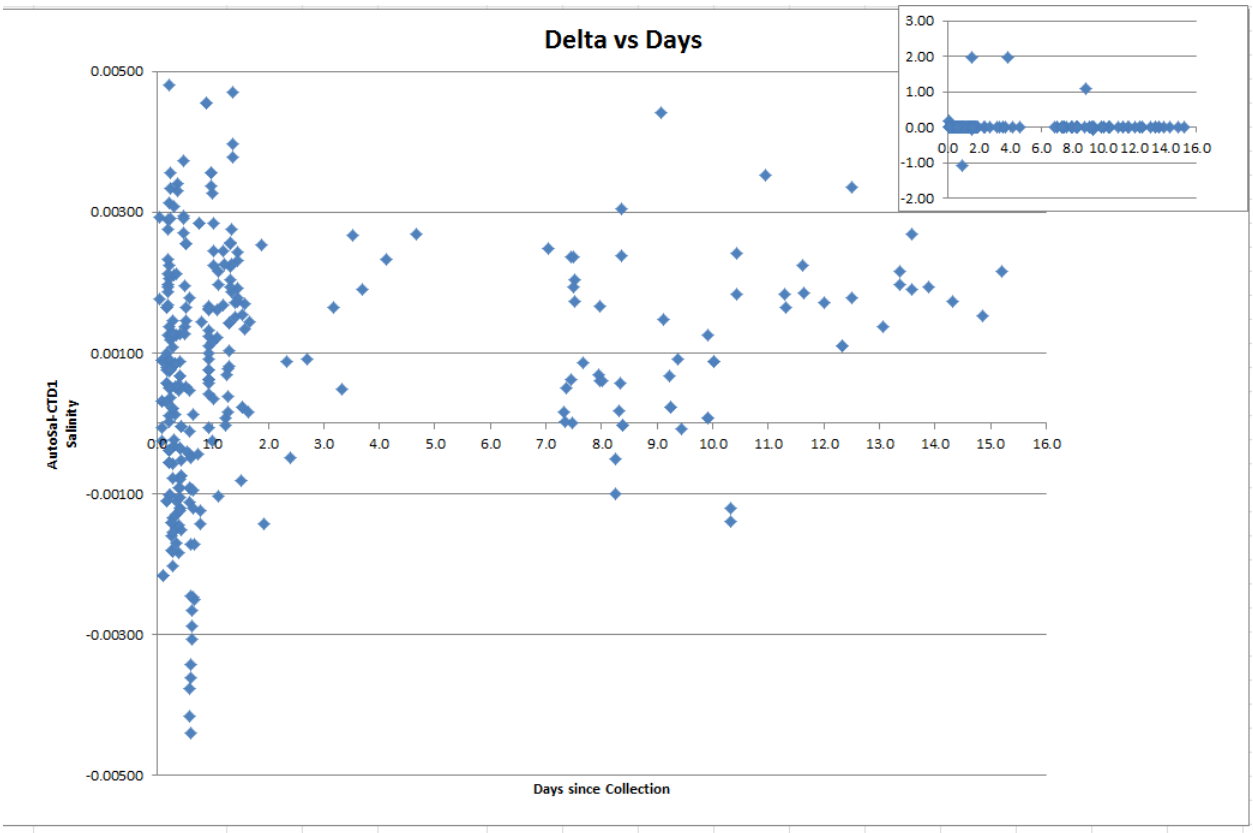

Figure C.1.13 Replicate Delta against day since sample was collected. Inset shows that there are 5 values that are outliers ranging between 0.5 and 8 days since collection.

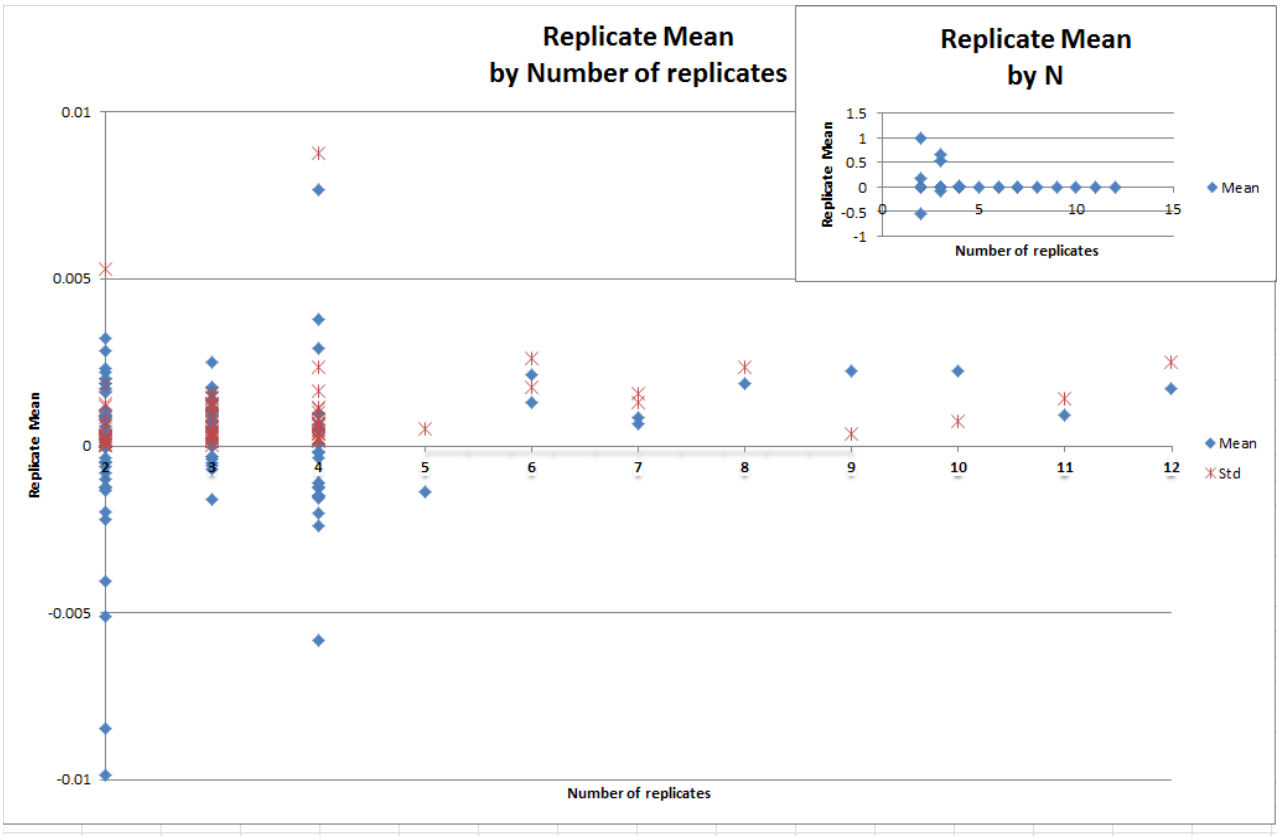

Figure C.1.14 Replicate Mean and Standard Deviations ordered by the number of replicate samples collected. Inset shows that 5 sets of replicates were outside the ±0.01 window (Outliers and all out of less than three replicates.

2. Measuring Dissolved Oxygen Concentration and calibration of Sea-Bird oxygen sensors on the HUDSON 2014-007 mission.

Yuri Geshelin
11-FEB-2015

1. Introduction

In May of 2014, the CCGS Hudson carried out the annual field mission of the Atlantic Zone Off-shelf Monitoring Program (AZOMP): cruise 2014-007, which included the spring occupations of the ARW7 (WOCE) transect across the Labrador Sea and of the Extended Halifax line across the Scotian Shelf, Slope and Rise. At various depths samples and standard measurements of dissolved oxygen (DO) were taken in accordance with the standard cruise program. This was accomplished with the use of titration methods and by means of Sea-Bird DO primary and secondary sensors. Preliminary attempts to calibrate both sensors were made during the cruise, taking into account the experience gained on previous cruises in 2010-2013. We employed the Winkler method of titration in our analysis.

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. The results are compared with those obtained on some previous cruises.

2. Methods and procedures

Oxygen sub-samples were drawn from 10-L bottles attached to the operational 24-bottle Rosette Sampler. Air contamination of the samples was reduced to a minimum as much as possible. This was accomplished by drawing samples almost immediately after the Rosette Sampler was drawn on board. The only property that was in some cases sampled prior to DO was chlorofluorocarbon, as chlorofluorocarbon samples are more sensitive to atmospheric oxygen than DO. As usual, an attempt was made to draw at least one DO sample from every closed bottle. At CTD casts, when this was impossible due to operational constraints, some bottles (levels) were skipped. At some levels, more than one sample was drawn from the same Rosette bottle to ensure that the whole procedure is accurate. The analysis of these duplicates is presented in the current report.

The oxygen sampling bottles were Iodine flasks with matched custom ground stoppers. The approximate volume of each flask is 125 mL. Precise volumes of flasks with the corresponding stoppers were determined gravimetrically prior to the cruise, and volume data were saved to titration programs. The flasks and matched stoppers are etched with identification numbers, and care is taken to ensure that flasks always correspond to their stoppers counterparts.

A silicone tube was attached to the spigot of each Niskin sample bottle mounted on the CTD rosette. The other end of the tube was then attached to a flask, and each DO sample was drawn

in succession through the tubing in accordance with the procedure described in *L. Codispoti, 1988*. First, the flask and stopper were thoroughly rinsed, and the tube was inserted in the flask all the way to its bottom. Next, the grip on the tube was slowly released to avoid introducing bubbles, and the flow was allowed to continue until at least three flask volumes were overflowed. The sampling tube was then rotated inside the flask and thus rubbed against the neck to prevent bubbles from forming on it. Next, the 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. Two reagents were then immediately added to oxidize the sample: 1.0 mL each Alkaline Iodide and Manganous Chloride. During this procedure, the tip of the spout was submerged under the surface of the sample. After that, the stopper was inserted carefully to avoid introducing air. The flask was then turned upside down several times but not vigorously shaken. This completed the collection of samples proper. Immediately upon the collection the samples were stored before the titration for at least 1 hour in a semi-dark place at room temperature.

The employed method of titration was implemented with the use of a colorimeter and the "BOB" software developed by Caroline Lafleur at the Maurice Lamontagne Institute, Quebec.

3. Analysis of duplicates

As mentioned in the introduction, different numbers of duplicates were taken at different casts. These numbers are summarized in Table C.2.1.

Number of duplicates taken from a Rosette bottle	Total number of instances	Number of successful titrations
2	90	87
3	15	15

Table C.2.1. Number of duplicates (triplicates) taken at different casts.

We have analysed the differences between any two values of DO concentration derived by means of the Winkler method. More specifically, in our analysis, we took into account all possible combinations of paired values. For example, when three duplicates were taken, we computed the absolute values of the differences between the first and the second, the second and the third, the first and the third samples. In total, this approach allowed us to obtain 132 paired values, for which the titrations were successful. The histogram of absolute values of differences between these paired values is presented in Figure C.2.1.

As seen from the figure, most of the differences fall in the 0 – 0.01 mL/L interval. This suggests that on average, the titrations were performed fairly accurately. By way of comparison, the similar histograms in percentage occurrence for the cruises in 2010 and 2011 are presented in Figure C.2.2. These field missions were carried out in the same area and same time of the year. We estimate 56% below 0.01 ml/L in 2014, compared to 58% and 41% in 2010 and 2011.

4. Problems

There occurred only three freezes (lock-ups) of the computer designated for running BOB software. As in the past, they were dealt with by way of rebooting the PC, colorimeter and DOSIMAT. To prevent these freezes, when the colorimeter was left idle for a prolonged time (an hour or more), the same strategy was used as on the previous cruises (Geshelin, 2012). Namely, a faked titration of blank solution was started, and if it did not cause any freeze, it was immediately terminated. The comment "This was a test" was entered to instruct the processing software to discard such titration.

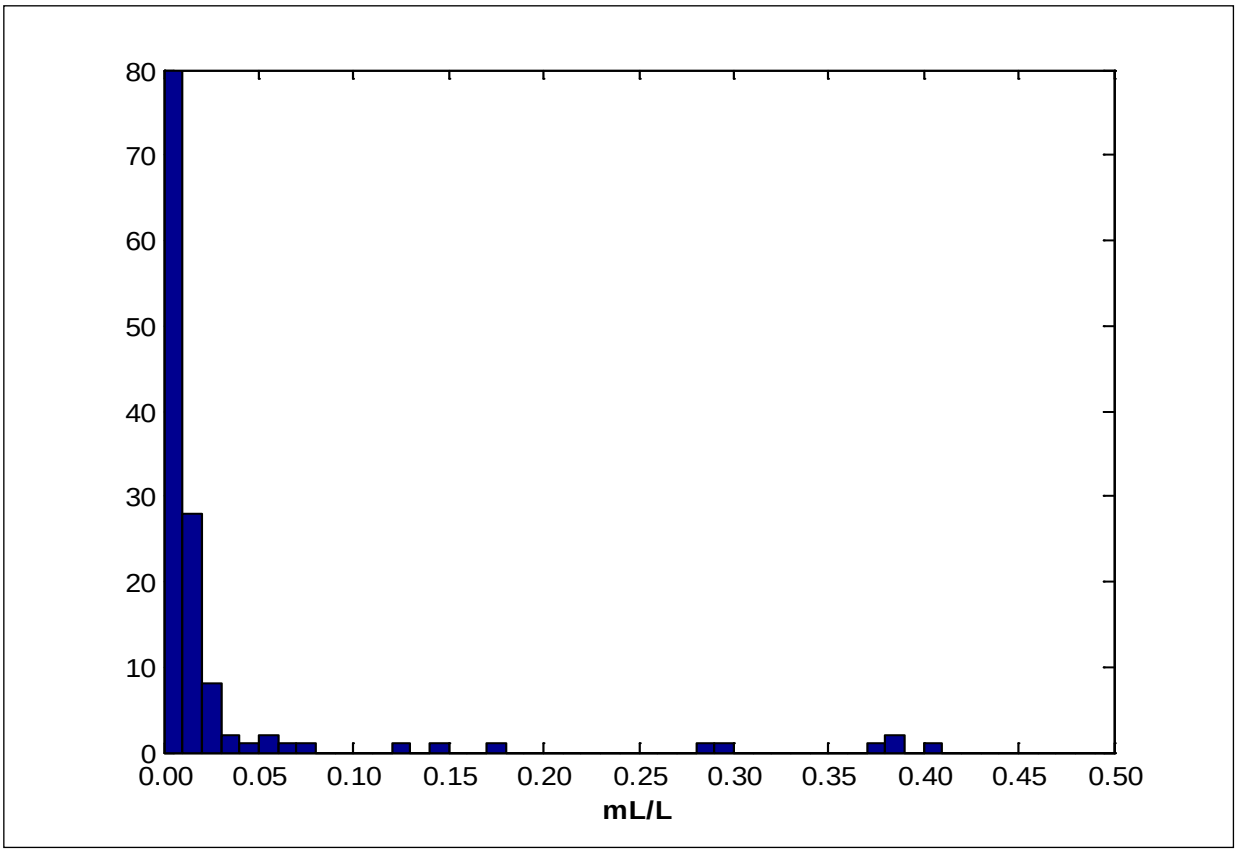

Figure C.2.1. The histogram of differences (absolute values) between the DO concentrations obtained from the same Rosette bottle by means of the Winkler method.

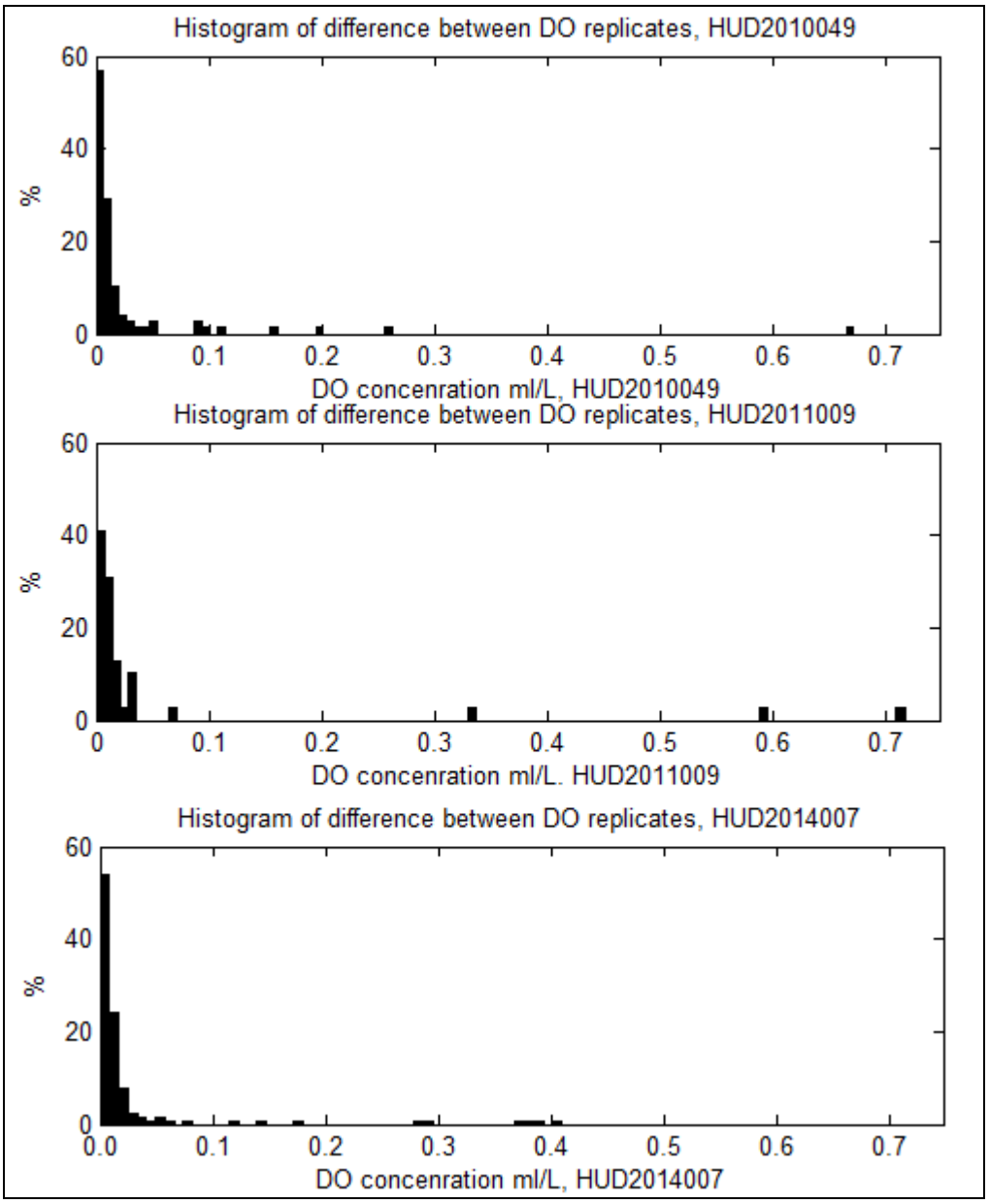

Figure C.2.2. The histogram of differences (absolute values, in percentage occurrence) between the DO concentrations obtained from the same Rosette bottle (Winkler method) on three cruises in 2010 – 2014 (Geshelin, 2011, and this report).

5. Sea-Bird – Winkler comparisons

As in the past, the ultimate goal of the intercomparisons between Sea-Bird and Winkler methods was to perform the calibration of the Sea-Bird sensors, as the chemical method is supposed to provide more accurate values. The comparisons were carried out for both primary and secondary sensors. The number of data points employed in the analysis is 1138 both for the primary and secondary sensors[4].

Figure C.2.3 presents the results of comparisons in the form of Sea-Bird vs Winkler DO scatter plots for the raw (unedited) data. The left panels present the scatter plot of the two concentrations. Plotted on the right panels is the relationship between pressure and the difference between the two concentrations. As in the past, this measure was taken to check whether the differences are dependent on pressure. As expected, the unedited data contain many outliers, most of which are accounted for. For example, the obvious blue clusters in the lower and right parts of the panels are due to the malfunction of the titration equipment. Namely, during the titration, air bubbles were accidentally drawn into the silicon tubes, because the level of a reagent in a bottle became too low. This glitch and other similar situations were verified with the ship log, and the total of 59 outliers was removed. The Sea-Bird vs Winkler comparisons of the refined data set are presented in Figure C.2.4. As seen from the figure, the elimination of the outliers resulted in noticeably reduced scatter and higher SeaBird – Winkler correlation coefficients. For the primary sensor, the correlation coefficient increases from 0.96 to 1.00 and from 0.98 to 0.99 for secondary.

[4] This includes the duplicates (see Section 3) and outliers.

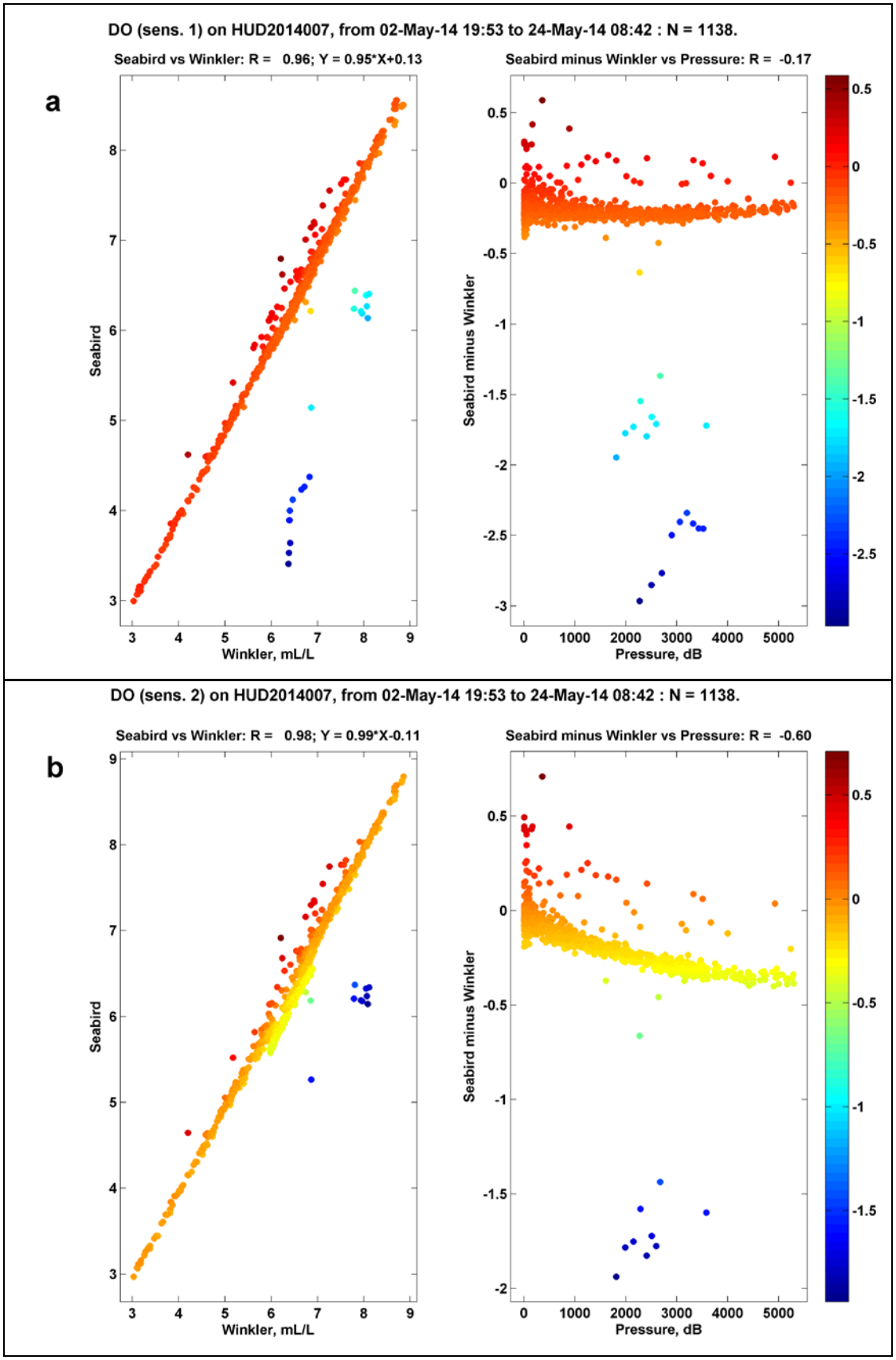

Figure C.2.3. Scatter plot of Sea-Bird vs Winkler DO concentrations (left panels) and Sea-Bird – Winkler difference vs pressure (right panels). (a) – primary; (b) - secondary Sea-Bird sensor. Outliers were not removed.

Closer inspection of Figure C.2.4b reveals that there is still a group of outliers (blue points in the middle of the panel). The absence of a similar group in Figure 4a suggests that this may be a problem with the secondary DO sensor. This issue is in need of further investigation.

Based on the refined data set, the correlation coefficients between Sea-Bird – Winkler differences and pressure are –0.19 and –0.93 for the primary and secondary sensors respectively. This suggests that in the case of the secondary sensor the calibration process is significantly dependent on pressure. Such undesirable dependence took place on some earlier Hudson cruises (Geshelin, 2011, 2012, 2014), but in the current data set the effect is most prominent (see Figure C.2.4b). It also suggests that the issue of the pressure term in the Sea-Bird calibration equation raised in the previous technical reports still needs to be addressed. It is seen from Figure C.2.4, that for both sensors the scatter is larger at shallower depths.

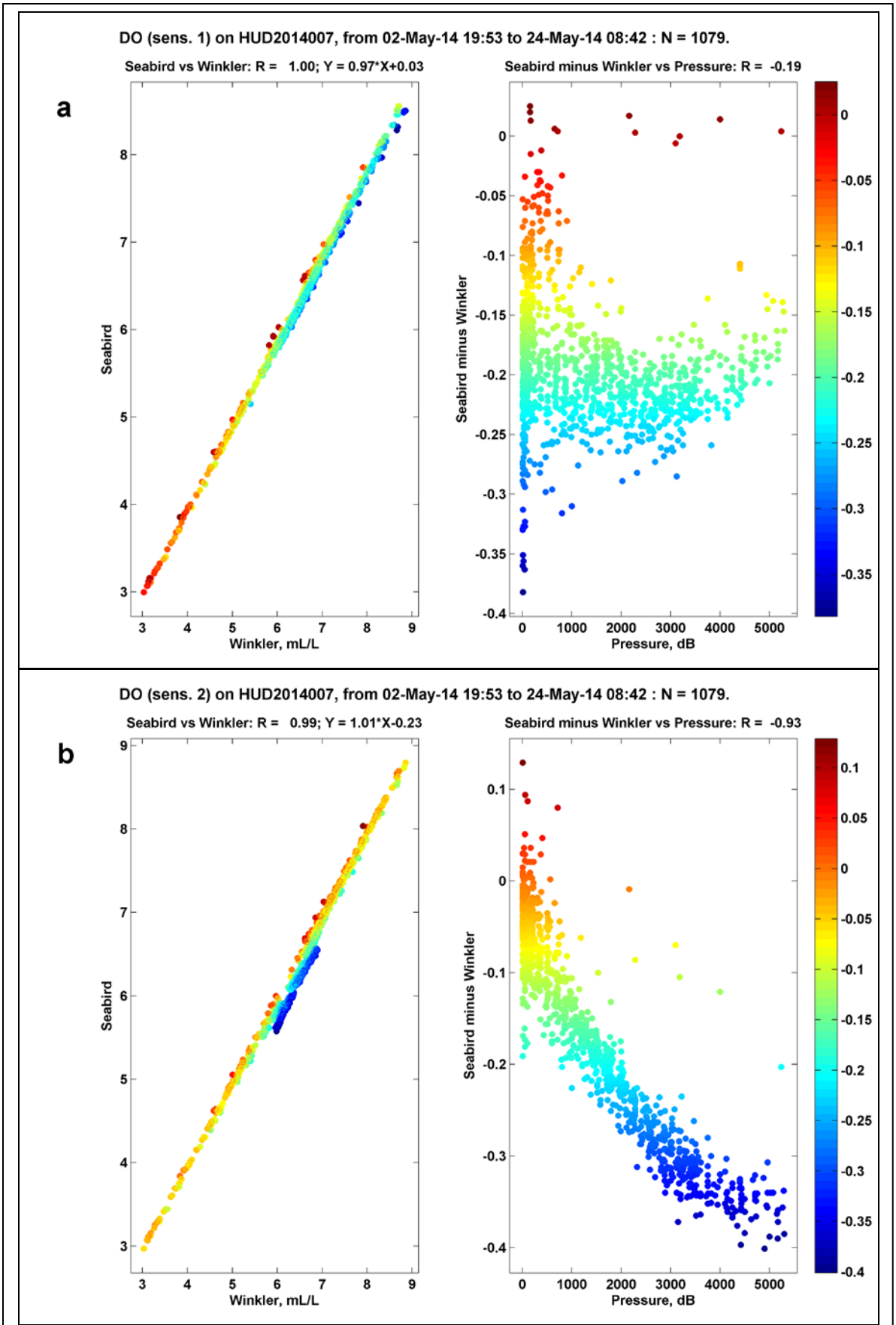

Figure C.2.4 Scatter plot of Sea-Bird vs Winkler DO concentrations (left panels) and Sea-Bird – Winkler difference vs pressure (right panels). (a) – primary; (b) - secondary Sea-Bird sensor. Outliers have been removed.

6. Conclusions

We have summarized the procedures for and results of sampling, measuring and calibrating the DO concentrations on the Hudson cruise in the spring of 2014. The two sets of results are presented: prior and after the elimination of outliers whose reasons are understood and accounted for. The reasons for the remaining outliers are yet to be investigated, but on the whole, they do not reduce the overall correlation. In fact, the highest level of our sampling and titration techniques was achieved on the cruise covered by this report. This is seen from Table C.2.2, which summarizes the Sea-Bird – Winkler correlation coefficients derived on 8 cruises.

Cruise	Ship	Primary Sea-Bird sensor	Secondary Sea-Bird sensor
2010-014	Hudson	0.46	N/A
2010-049	Hudson	0.97	0.87
2011-009	Hudson	0.93	0.94
2011-043	Hudson	0.99	0.99
2012-001	Martha L. Black	0.90	0.93
2012-042	Hudson	0.94	0.95
2013-008	Hudson	0.92	0.92
2014-007	Hudson	1.00	0.99

Table C.2.2 Correlation coefficients between Winkler- and Sea-Bird-derived values of DO concentration.

The main results are:

- The issue of pressure-dependent Sea-Bird values still needs to be addressed (see Section 5).
- The histogram of differences between the DO concentrations obtained from the same Rosette bottle by means of the Winkler method suggests that most measurements were taken fairly accurate: 56% of all differences are below 0.01 ml/L. However, for the 2010 cruise (2010-049) this percentage was higher: 58%.
- The removal of outliers considerably reduces the scatter and improves the correlation. However, some outliers are not yet accounted for. Most likely, they are due to the problems with secondary DO sensor.
- The database of all quality-controlled DO values obtained by Seabird and the Winkler method in 2010-2014 has been created. It will be useful in the future research.

References

1. Lou Codispoti, 1988. One Man's Advice on the Determination of Dissolved Oxygen in Seawater. Technical note.
2.Y.Geshelin, 2011. Measuring Dissolved Oxygen Concentration and calibration of Sea-Bird oxygen sensors on the Hudson 2011-043 cruise. Technical report.
3. Y.Geshelin, 2012. Measuring Dissolved Oxygen Concentration and calibration of Sea-Bird oxygen sensors on the Hudson 2012-042 cruise. Technical report.
4. Y.Geshelin, 2014. Measuring Dissolved Oxygen Concentration and calibration of Sea-Bird oxygen sensors on the Hudson 2013-008 cruise. Technical report.

3. Nutrients

Peter Thamer

a. Description of Equipment and Technique

Samples were analyzed for silicate, phosphate, nitrate (nitrate plus nitrite), nitrite and ammonia using a SEAL Autoanalyzer III. The analytical methods were the same used historically with the Technicon Autoanalyzer II: *Technicon for Seawater Analysis (Silicate 186-72W, Phosphate 155-71W, Nitrate/Nitrite 158-71W),* .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 duplicate Calibration Standards at the beginning plus duplicates of the second most concentrated Calibration Standard for drift followed by a blank for detection limit and a baseline check run every 8 sample duplicates. The standards, wash water and blanks for phosphate, silicate and nitrate/nitrite were made up in 33 ppt NaCl (Sigma, ACS Reagent); for ammonia and nitrite, NANOPure water only. The quality of analysis was checked by analyzing an Intercalibration Reference Material MOOS-3 for nutrients produced by NRC, Ottawa. There is no existing ammonia Reference Material.

The data was collected and concentrations calculated by the SEAL AA-3 analytical software program provided with the new instrument. The data was reported as collected and stored on the hard drive (backed up on memory stick).

c. Shipboard Analysis

Total number of duplicate samples analyzed for **AR7W Labrador Sea Mission HUD2014-007: 1205** (including the Halifax Line). Any samples collected off watch were kept refrigerated (4^{o}C) and analyzed within twelve hours of collection. Samples collected at Halifax Line Station 2 through the year have always been frozen. To duplicate sample treatment, samples collected at that station were frozen and processed on the fourth day of shipboard analysis. This station was sampled a second time (our last station), and will be analyzed back at BIO.

All 5 nutrients were analyzed at sea: nitrate/nitrite, silicate, phosphate, ammonia and nitrite. The Barnstead NANOPure system was brought on board along with 340 litres of lab produced NANOPure water in acid washed 20 litre carboys. This water was purified again with the Barnstead system just before making up all reagents, including the 33‰ NaCl wash water.

The Autoanalyzer III was assembled in the Geo-Chem lab this year to minimize temperature fluctuations and for the added stability of being lower in the ship. Phosphate and ammonia levels began to rise in wash water if left exposed in the lab for too long. To minimize changes in detection limits due to the increasing phosphate and ammonia levels over time, wash water was changed every half hour. The heaters used in phosphate and ammonia analysis were off for samples 400308 to 400381 resulting in questionable data for phosphate and unfortunately no data for ammonia. Some issues occurred with phosphate the night of May 10th as random drift cups (second highest standard) throughout the run were showing values equal to or greater than the highest standard. Flushing the line with strong acid seemed to solve the problem. The auto analyzer pump required maintenance on the 15th of May as there were some issues with peak shape (SiO) and baseline drift (NO3) from the previous night. Despite a different peak shape the samples looked consistent throughout the run. When plotted by Igor, there were noticeable differences between the surrounding stations.

An Intercalibration Reference Material MOOS-3 produced by NRC, Ottawa was used as a check for data quality (except for Ammonia). Unfortunately, the supply of MOOS-3 is now limited and therefore was not run daily. May 14th nitrate results were high, due to the gradual degradation of the cadmium column over the course of the run. Nitrate values also seem to be consistently a little high due to the drift correction (over correcting).

QC\QA MOOS-2	NO_3+NO_2 NITRATE µM	NO_2 NITRITE µM	PHOSPHATE µM	SILICATE µM
Accepted Values	24.9+/-1.0	3.31+/-0.18	1.58 +/-0.10	28.8+/-1.0
06-May-14	26.85	3.60	1.783	28.27
	26.94	3.70	1.760	28.47
07-May-14	26.71	3.40	1.769	28.69
	26.80	3.25	1.760	28.66
13-May-14	26.87	3.45	1.728	28.97
	26.74	3.40	1.708	28.72
14-May-14	**26.64**	3.50	1.580	**29.85**
Corrected	**26.61**	3.60	1.578	**29.74**
18-May-14	27.12	3.45	1.607	29.19
	27.23	3.40	1.625	28.98
19-May-14	26.89	3.45	1.619	28.70
	26.90	3.65	1.624	28.48

Det. Limits	NITRATE	NITRITE	PHOSPHATE	SILICATE	AMMONIA
<DL	µM	µM	µM	µM	µM
06-May-14	0.18	0.04	0.012	0.10	0.525
07-May-14	0.43	0.06	0.055	0.07	0.103
08-May-14	0.40	0.02	0.025	0.35	0.096
09-May-14	1.26	0.04	0.119	0.12	0.375
10-May-14	0.67	0.01	0.014	0.08	0.173
11-May-14	0.90	0.03	0.076	0.08	0.325
12-May-14	0.63	0.08	0.120	0.05	0.173
13-May-14	0.18	0.03	0.045	0.14	0.338
14-May-14	0.68	0.05	0.058	0.08	0.345
15-May-14	0.05	0.04	0.020	0.06	0.326
16-May-14	0.23	0.03	0.028	0.08	0.209
18-May-14	0.16	0.03	0.009	0.11	0.220
19-May-14	0.06	0.04	0.015	0.26	0.248
20-May-14	0.19	0.03	0.169	0.77	0.200
21-May-14	0.06	0.04	0.018	0.04	0.167
22-May-14	0.07	0.03	0.006	0.18	0.101
23-May-14	0.11	0.03	0.012	0.37	0.240

4. Ocean Chemistry Group

Stephen Punshon (June 20, 2014)

Transient Tracers SF_6 and CFC-12

Seawater samples from the rosette were drawn directly into 250 mL glass syringes which were then stored at ~ 4 °C in a low-temperature incubator for up to 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_6 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 in a dewar containing liquid nitrogen. 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_6 and CFC-12 were separated on a 1 m pre-column packed with Porasil B and a 3 m main column packed with Molecular Sieve 5A held isothermally at 95 °C. Total run-time was 11 minutes and 50 seconds for a water sample. 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 around ± 2 % for SF6 and ± 0.7 % for CFC-12.

Eighteen seawater samples for SF_6 and CFC-12 were typically collected from every deep CTD cast, this number being determined by the total stock of glass syringes (36 syringes in 6 racks) and available time between stations. On the Extended Halifax Line, the sampling density was increased to 24 depths at the deep stations. A total of 449 water samples were analysed for

dissolved SF6 and CFC-12 on the AR7W line (Stations 3-28 plus extra intermediate stations) and 315 on the Extended Halifax Line (Stations 2-19). Air samples were collected from the upwind side of the ship during the outward transit to the AR7W line to measure the atmospheric mole fractions of SF_6 and CFC-12 in order to calculate seawater saturation states. Twenty six air samples were analysed, giving mean atmospheric mixing ratios of 8.44 ± 0.10 parts per trillion for SF6 and 527.6 ± 10.9 parts per trillion for CFC-12.

pH

Samples for pH analysis were collected from every depth at Stations 3 – 28 on the AR7W line, and from every depth at stations 2-19 on the XHL. In addition, samples were collected from selected depths at shallow biological stations on the AR7W and Extended Halifax Lines where the SeaBird pH sensor was deployed. Seawater was analysed for pH according to the spectrophotometric method described in "Guide to best practises for ocean CO_2 measurements" SOP 6B, edited by Andrew Dickson. Water was collected from the rosette in 60 mL borosilicate glass tubes, allowing each sample to overflow by at least one volume. Racks of tubes were then placed in a water bath held at 25 °C and allowed to thermally equilibrate for 30 minutes. Each sample was then introduced into a water-jacketed 10 cm quartz cell and 30 µL of the indicator dye *m*-cresol purple added before mixing well. The absorbance of light at the wavelengths 434 and 578 nm was measured with an Agilent photodiode array spectrophotometer and the resulting extinction coefficients at these wavelengths were used to determine the pH of the sample. Measurements were conducted during both night and day shifts and samples were stored in a low temperature incubator at 4 °C until immediately prior to analysis. The maximum time between sampling and analysis was about 4 hours. The sample absorption spectra were not referenced to a Certified Reference Material as in the past due to the current unavailability of these CRMs. A total of 623 pH samples were analysed from the AR7W line and 342 from the Extended Halifax Line.

Total Inorganic Carbon (TIC) and Total Alkalinity (TA)

A total of 780 seawater samples from whole number stations 3-28 on the AR7W and 2-19 on the XHL were collected in 500 mL borosilicate glass bottles and preserved with mercuric chloride following the method described in "Guide to best practises for ocean CO_2 measurements". The samples were subsequently transported back to the Bedford Institute of Oceanography for analysis. TIC was later 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 full curve Gran Point determination using a Titrando dosimat with Tiamo software in conjunction with a sample delivery system built in-house. Bottles of Batch 134 Certified Reference Material (CRM) (supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, San Diego, USA) were analyzed in duplicate at intervals to evaluate accuracy.

Discrete pCO_2

Water samples for pCO_2 measurements were drawn from the rosette (following dissolved oxygen) into 160 mL volume crimp seal vials, allowing each sample vial to overflow by about

2 volumes before immediately preserving with 50 μL of saturated mercuric chloride solution and crimp sealing with butyl rubber septa. The samples were stored at 4 ºC until the return to BIO. Surface samples were collected from every station throughout the cruise and full depth profiles were collected from Stations 17 and 18 on the AR7W line. pCO_2 was later determined by headspace equilibrium gas chromatography.

Underway pCO2

A Pro-Oceanus pCO_2 sensor was plumbed into the underway seawater de-bubbler and distribution manifold located above the sink in the forward lab. Data from this was acquired almost continuously throughout the cruise on a PC running Docklight RS232 terminal software.

Sampling Stations

Stations 3 to 28 were sampled on the AR7W line, stations 1 and 2 were inaccessible due to sea ice. Additional stations 19.5, 17.5, 14.5, 11.5 and 10.5 were sampled for transient tracers in order to provide extra resolution in the upper 1800 m of the water column. On the Extended Halifax Line, whole number stations 2 to 19 were all sampled.

Sample identification numbers ranged from 400001 to 400939 on the AR7W line and 401015 to 401474 on the Extended Halifax Line.

Additional sample collection

Full profiles of samples for δ18-O were collected in 60 mL Boston Round bottles from every whole-number station on the AR7W line on behalf of Dalhousie University. Additionally, 5 profiles of samples for δ13-C TIC were collected from the AR7W Line in ~300 mL BOD bottles, also for Dalhousie University.

Sampling and Analytical Problems

The non-original spigot taps fitted to the Niskin bottles continue to present a contamination problem for transient tracer measurements, particularly in the deep abyssal water of the Extended Halifax Line, where concentrations of SF6 are extremely low. A number of Niskin bottles persistently leaked during the first few days of sampling but this problem was eventually rectified.

No analytical problems were encountered.

5. **VITALS Biology Team**

PI's:
Simon Bélanger (UQAR),
Roxane Maranger (Université de Montréal)
Jean-Éric Tremblay (Université Laval)

Cruise Participants:
Jonathan Gagnon & Isabelle Courchesne (Université Laval)
Julien Laliberté (UQAR)
Richard LaBrie (Université de Montréal)

1. General objectives.

The main objectives of the VITALS biology team were to:

1) understand how physical properties and nutrient availability in different water masses affect the structure of microbial communities and the rates of new and regenerated primary production, bacterial production, respiration and key nitrogen cycling steps along the AR7W line in the Labrador Sea, and
2) obtain *in situ* optical measurements that will serve to refine remote-sensing algorithms.

2. Methods

2.1. Water sampling, incubations and biogeochemical measurements

The list of stations and variables measured is provided at the end of this document (Table 1).

- In addition to the core nutrient samples taken by BIO, samples for inorganic nutrients were taken in the bottles from which we took water for our incubations (Biology cast). Samples for nitrite, nitrate, orthophosphate, silicate and urea were frozen for subsequent analysis at Laval University using a Seal Analytical AutoAnalyzer 3. Ammonium and urea samples were processed immediately after collection using the fluorometric method of Holmes et al. (1999) and the colorimetric method of Goeyens et al. (1998), respectively.

- Deck incubations with trace additions of ^{15}N-labeled nitrogen sources (nitrate, ammonium, urea) were performed to estimate daily rates of nitrogen assimilation, nitrification and microbial ammonification at 6 different depths (0, 10, 20, 30, 40, and 60 m). Incubations were terminated by filtration onto GF/F filters. Filters were dried and stored for subsequent analysis of the amount and isotopic enrichment of particulate organic N by Isotope-Ratio-Mass-Spectrometry at Laval University. Filtrates were killed and stored refrigerated. The dissolved ammonium contained in filtrates will be extracted by the diffusion technique of Raimbault and Garcia (2008) to obtain microbial ammonification rates. Nitrification rates will be obtained by converting nitrate to N_2O using the bacterial denitrification method (e.g. Christman et al. 2011).

- Parallel incubations with ^{14}C-bicarbonate were made to estimate daily net primary production. We assessed the amounts of ^{14}C retained in the particulate organic pool (POC), passing into dissolved organic carbon pool (DOC) and accreted in the particulate inorganic pool (PIC, providing an estimate of calcification) (Gosselin et al. 1997, Paasche and Brubak 1994). Bacterial production was estimated from short-term 3H-leucine incorporation and bacterial respiration was assessed by Winkler titration after 3 hours of incubation.

- Water from the upper mixed layer was pump continuously using the ship's water intake and analyzed for core properties (nutrients, temperature, chlorophyll) by BIO collaborators and net community production (NCP) by us using the O_2/Ar method with equilibrator inlet mass spectrometry (EIMS) (Cassar et al. 2009). This measurement integrates biological processes over the time scale of a week. The data will also be used to provide spatial context for the discrete sampling and to ground truth satelitte-based estimates of PP. Discrete determinations of O_2/Ar will be used to post-calibrate the EIMS (Hamme, gases team).

- Additional samples were taken at the surface and in the subsurface chlorophyll maximum (or 30 m) to determine pigments (HPLC), the elemental C, N, P, Si composition of particulate organic matter, the concentration of cocolithophores and the taxonomic composition of the phytoplankton community. Samples were also taken for the determination of bacterial abundance by epifluorescence microscopy (DAPI staining) and flow cytometry. DNA was preserved on 3-µm and 0,8-µm filters for subsequent molecular analysis of bacterial diversity.

2.2. Optical deployments

The list of deployment sites is provided at the end of this document (Table 2).

- The C-OPS (Biospherical Instruments) was deployed from the foredeck with partial success due to problems of pitch and roll during the instrument's free fall. This sensor measures apparent optical properties (spectral downwelling irradiance and upwelling radiance at 19 wavelengths across the ultraviolet-visible-near infrared domains). Another sensor package measuring inherent optical properties (spectral absorption and backscattering coefficients) along with fluorescent dissolved organic matter, temperature and salinity was successfully deployed.

References

Cassar et al. 2009. Continuous high-frequency dissolved O2/Ar measurements by Equilibrator Inlet Mass Spectrometry (EIMS). Analytical Chemistry. 81:1855-1864.

Christman et al. (2011) Abundance, Diversity, and Activity of Ammonia-Oxidizing Prokaryotes in the Coastal Arctic Ocean in Summer and Winter. Appl. Environ. Microbiol. 77 :2026-2034.

Goeyens et al. 1998 Estuarine, Coastal and Shelf Science (1998) 47, 415–418

Gosselin et al. (1997) New measurement of phytoplankton and ice algal production in the arctic ocean.

Holmes et al. (1999) Can J Fish Aquat Sci 56:1801–1808

Paasche and Brubak (1994) Enhanced calcification in the cocolithophorid *Emiliania Huxleyi* (Haptophyceae) under phosphorus limitation. Phycologia 33: 3324-330.

Raimbault P, Garcia N. (2008). Evidence for efficient regenerated production and dinitrogen fixation in nitrogen-deficient waters of the South Pacific Ocean: impact on new and export production estimates. Biogeosciences 5: 323–338

Table 1. List of sampling stations and measurements made on water obtained from the Biology Rosette cast

Date	Station	Frozen nutrients	Fresh NH4	Fresh Urea	Nitrogen uptake & POC/PON	Primary production	15N/18O of nitrate	Pigments HPLC	POP	BioSi	Cocolitophores	Taxonomy	CDOM	DOC/TDN/TDAA	Bacterial production	Bacterial respiration	Bacterial abundance	DNA	O-N-Ar gases
05/05/2014	NFL-SHELF	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
05/07/2014	L3_17	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
05/08/2014	L3_20	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/09/2014	L3_27,5	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/10/2014	L3_22	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/11/2014	L3_16,5	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/13/2014	L3_05	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/14/2014	L3_9,5	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/15/2014	NFL_SHELF1	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
05/16/2014	NFL_SHELF2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
05/20/2014	HL-17	X	X	X	X	X	X	X	X	X	X	X							
05/21/2014	HL-14	X	X	X	X	X	X	X	X	X	X	X							
05/21/2014	HL-13	X	X	X	X	X	X	X	X	X	X	X							
05/22/2014	HL-10	X	X	X	X	X	X	X	X	X	X	X							
05/22/2014	HL-9,5	X	X	X	X	X	X	X	X	X	X	X							

Table 2. List of deployments for apparent optical properties

Stations	Repeat casts	UTC Time
Test_Station	1	14:22:29
	2	14:25:09
L3_20	1	14:48:37
	2	14:51:25
	3	14:55:49
	4	14:58:35
	5	15:00:51
L3_27,5	1	15:32:17
	2	15:34:30
	3	15:36:18
L3_22	1	14:02:56
	2	14:05:13
	3	14:07:18
	4	14:11:12
	5	14:11:32
	6	14:12:07
	7	14:13:35
	8	14:14:24
L3_9,5	1	18:15:57
	2	18:18:18
	3	18:21:26
	4	18:23:25
NFL_SHELF1	1	15:56:12
	2	15:58:57
	3	16:01:02
	4	16:04:08
	5	16:10:19
HL-17	1	17:25:06
	2	17:28:44
	3	17:31:11
	4	17:33:07
	5	17:34:28
	6	17:37:38