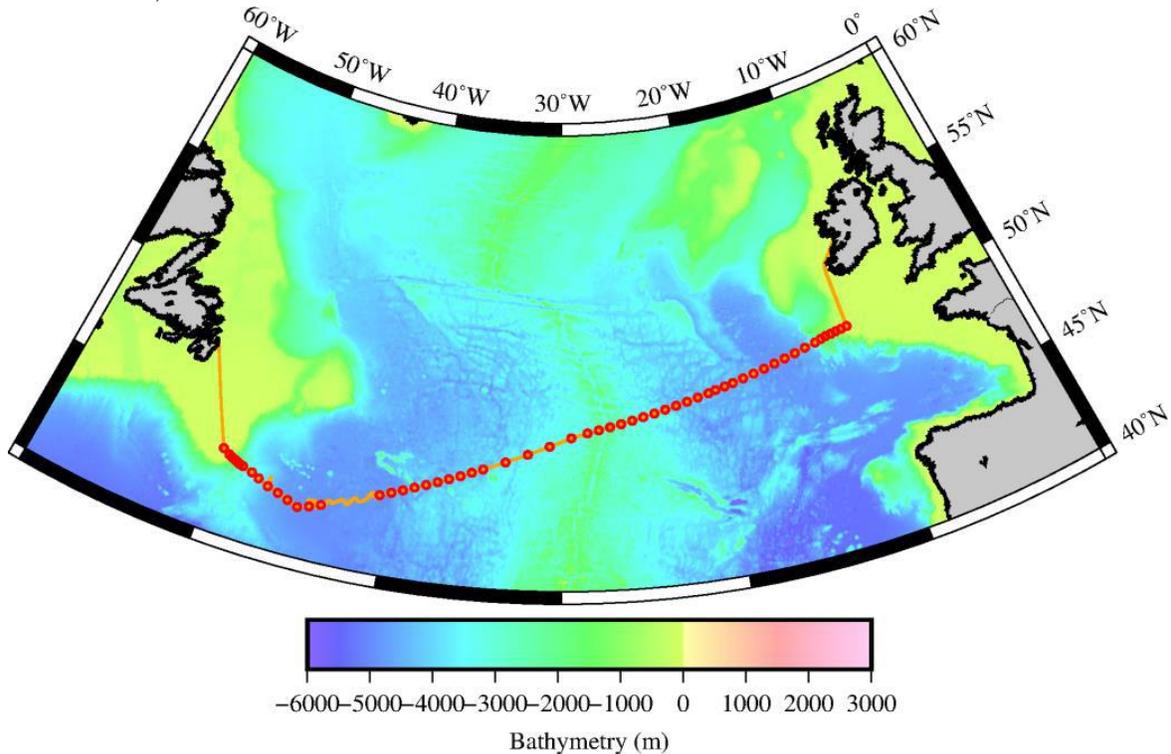


# CRUISE REPORT: A02

(Updated JUN 2021)



## Highlights

### Cruise Summary Information

Section Designation	A02
Expedition designation (ExpoCodes)	45CE20170427
Chief Scientists	Peter Croot / NUIG
Dates	27 April 2017 to 22 May 2017
Ship	RV Celtic Explorer
Ports of call	St. John's, Canada - Galway City, Ireland
Geographic Boundaries	49° 13' 55" N 50° 0' 18" W 10° 39' 0" W 42° 4' 12" N
Stations	58
Floats and drifters deployed	1 Argo float deployed
Moorings deployed or recovered	0

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Cruise Report of the 2017  
reoccupation of the GO-SHIP A02  
section by the RV Celtic Explorer,  
Ireland (CE17007)



NUI Galway  
OÉ Gaillimh

## Project Summary

Section Name	A02
Expocode	CE17007
Chief Scientist	Peter Croot
Principal Investigator	Evin McGovern
Dates	28 April 2017 to 22 May 2017
Ports of call:	St John's, Canada to Galway, Ireland
Stations occupied:	58 on A02 line
Equipment deployed:	1 Argo float

This is the cruise report of the GO-SHIP A02 repeat hydrography expedition carried out by the RV Celtic Explorer (CE17007) in April-May 2017. The opinions expressed in this report are only those of the authors.

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## 1. Summary

During CE17007, a combined chemical and physical oceanography research expedition reoccupied the existing A02 section in the North Atlantic as a contribution to the international GO-SHIP program. This expedition marked the first time that Ireland had organized and performed a major international hydrographic study. The work was performed in cooperation with international teams from Canada, Denmark, Germany, the United Kingdom and the United States of America.

The measurements made along the A02 repeat hydrography section included hydrographic measurements (CTD-rosette, Lowered and shipboard ADCP measurements) as well as freon, oxygen, nutrient and carbon system measurements. Bad weather encountered during the expedition resulted in us unfortunately having to omit 9 of the 67 planned CTD stations, however 58 full depth stations were occupied during the 2017 survey. All GO-SHIP level 1 parameter measurements were performed as planned and have contributed to a valuable data set for this important repeat hydrography section in the North Atlantic.

## 2. Research Program and Project Overview

Hydrographic measurements were made along the A02 section in April-May 2017 under the direction of the Global Ocean Ship-Based Hydrographic Investigation Program (GO-SHIP). This reoccupation of the A02 section was supported by the Irish Marine Institute and funded under the Marine Research Programme by the Irish Government. Individual teams were supported by the European Union's Horizon 2020 and the Canada Excellence Research Chair in Ocean Science and Technology (see section 9 for full details).

### 2.1. Information on the GO-SHIP repeat hydrography program

GO-SHIP ([www.goship.org](http://www.goship.org)) is an international program which addresses the ongoing requirement to monitor inventories and transports of CO<sub>2</sub>, nutrients, heat and freshwater in the ocean. In essence, the vital signs of the ocean system. The program provides measurements to assess the long-term changes and variability in marine biogeochemical and physical processes in response to natural and human-induced forcing. It does this by providing unique high-quality measurements of key oceanographic parameters at all ocean depths. These measurements have become the cornerstone of several major efforts to quantify long-term changes and decadal variability in ocean properties and are critical for calibrating and validating other observation and modelling programs. Earlier programs under the Joint Global Ocean Flux Study (JGOFS), World Ocean Circulation Experiment (WOCE), and Climate Variability and predictability (CLIVAR) programs provided an approximately decadal set of observations on hydrographic lines, including the A02 line that this GO-SHIP expedition builds upon. Examples of critical findings made possible by decadal measurements include ongoing ocean uptake and subsurface storage of anthropogenic CO<sub>2</sub> with consequent ocean acidification, ongoing warming and freshening of the deepest bottom waters, and accelerated overturning of intermediate depth water masses in the Southern Ocean. The Repeat Hydrography Program provides a robust observational framework to monitor these long-term trends.

Continuation of these programs under GO-SHIP involves reoccupying the same set of hydrographic transects spanning the global ocean with full water column measurements. These measurements are in support of:

- Model calibration and validation
- Studies of ocean circulation
- Carbon system studies
- Heat and freshwater storage and flux studies
- Changes in volumes and properties of water masses
- Quantification of turnover timescales
- Calibration of autonomous sensors and satellites

## 2.2. Atlantic Ocean cooperation – the Galway statement

### *Atlantic Ocean cooperation – the Galway statement*

Galway was the location where the European Union and the governments of Canada and the USA agreed a new alliance for Atlantic Ocean Research Alliance (AORA). The Galway Statement on Atlantic Cooperation signed in May 2013 by the 3 parties recognises that ocean observation is fundamental to understanding the ocean and forecasting its future and aims to align observation efforts to improve ocean health and promote sustainable management. In this manner the EU Horizon 2020 project AtlantOS supports and builds on the aims of the Galway Statement and other Atlantic basin initiatives, including Canada's recently-funded Ocean Frontier Institute. The international Atlantic-wide partnerships in AtlantOS are working to innovate, improve and enhance the existing integrated Atlantic Ocean Observing System. The GO-SHIP A02 transatlantic survey carried out over 27 days in April-May 2017, was accomplished through the cooperative approach envisaged in the Galway Statement.

Our GO-SHIP expedition is an international collaboration between Ireland, Canada, Germany, the U.S.A. and the U.K. and is a clear example of the ongoing spirit and commitment to the Galway agreement signed in May 2013 by the E.U., Canada and the

U.S.A in which all 3 parties recognised the mutual benefits of Atlantic Ocean Cooperation. This expedition also puts Ireland's marine research into focus on a global stage and demonstrates that Ireland has the capacity through the RV Celtic Explorer and its own marine scientists to undertake key works of international importance and not just of local interest to Ireland. This is an exciting time then for Marine Research in Ireland, with new marine geoscience work on marine acoustics, geophysics, biogeochemistry and remote sensing being conducted on the west coast of Ireland under the framework of the SFI funded research centre iCRAG (Irish Centre for Research in Applied Geoscience).

### 2.3. Previous occupations of the A02 section

The A02 section crosses both basins of the North Atlantic and it was originally called the "48°N"-section (WOCE/A2 and AR19) and runs from the edge of the Grand Banks (at a bottom depth of 65 m) to the Celtic shelf south of Ireland (at a bottom depth of 155 m) nominally along 48°N. The section was first occupied in 1957 and then again in 1982, subsequently during the WOCE and CLIVAR era there were several more occupations of the high-density, full-depth section carried out (see [Table](#) below). In recent years the western end of the A02 section has been sampled annually by German researchers examining changes in deep water formation via the measurement of CFC's. A full occupation of the A02 line for carbon system parameters had not been made since 2002. Work performed on the A02 line 20 years earlier was some of the first in the world to clearly show the uptake of anthropogenic carbon by the ocean.

**Table 2.1 Previous Occupations along the A02 line**

Cruise date (Year/month)	Research vessel	Cruise identifier	O <sub>2</sub>	Nuts	SADCP	LADCP	CFC	He	CO <sub>2</sub>	δ <sup>13</sup> C	<sup>14</sup> C	Comments
1957	<i>Discovery</i>		x	x								
1982/04-/05	<i>Hudson</i>	82-002	x	x								
1993/07-/08	<i>Gauss</i>	G226	x	x								
1994/10	<i>Hudson</i>	18HU94030	x	x			x		x			Only west of 42°W
1994/10-/11	<i>Meteor</i>	M30/2	x	x	x		x	x	x		x	
1995/04-/05	<i>Hudson</i>	18HU95003	x	x	x	x	x		x			Only west of 42°W
1996/05-/06	<i>Gauss</i>	G276	x	x								
1997/06	<i>Meteor</i>	M39/3	x	x	x	x	x		x			
1998/05	<i>Gauss</i>	G316/1	x	x								
1999/07-/08	<i>Meteor</i>	M45/3	x	x	x	x	x	x	x	x		Only west of 41°W
2000/05-/06	<i>Gauss</i>	G350/1	x	x	x	x			x			
2001/05	<i>Meteor</i>	M50/1	x	x	x	x	x		x			Only west of 30°W
2001/08	<i>Meteor</i>	M50/4	x	x	x	x	x	x	x			Only east of 28°W
2002/06	<i>Gauss</i>	G384/1	x	x	x	x			x			
2003/08	<i>Meteor</i>	M59/2	x	x	x	x	x		x <sup>a</sup>			
2003/09	<i>Meteor</i>	M59/3	x <sup>b</sup>		x	x	x					Only west of 30°W
2005/06	<i>Thalassa</i>	SUBPOLAR	x <sup>b</sup>		x	x	x					Only east of 31°W
2005/07-/08	<i>Thalassa</i>	WNA	x <sup>b</sup>		x	x	x					Only west of 30°W
2007/04	<i>Maria S. Merian</i>	MSM-05/1	x <sup>b</sup>		x	x	x					Only west of 33°W
2008/07-/08	<i>Maria S. Merian</i>	MSM-09/1			x	x	x					Only west of 30°W
2009/07-/08	<i>Maria S. Merian</i>	MSM-12/3	x <sup>c</sup>		x	x	x		x <sup>c</sup>	x <sup>c</sup>		Only west of 30°W
2010/08-/09	<i>Meteor</i>	M82/2	x <sup>b</sup>		x	x	x					

<b>Cruise date (Year/month)</b>	<b>Research vessel</b>	<b>Cruise identifier</b>	<b>O<sub>2</sub></b>	<b>Nuts</b>	<b>SADCP</b>	<b>LADCP</b>	<b>CFC</b>	<b>He</b>	<b>CO<sub>2</sub></b>	<b>δ<sup>13</sup>C</b>	<b><sup>14</sup>C</b>	<b>Comments</b>
2011/06-/08	<i>Meteor</i>	M85/1	x <sup>b</sup>		x	x	x			x <sup>d</sup>	x <sup>d</sup>	
2012/06-/07	<i>Maria S. Merian</i>	MSM-21/2			x	x	x					Only west of 30°W
2013/05-/06	<i>Maria S. Merian</i>	MSM-28	x <sup>b</sup>		x	x	x					
2014/05-/06	<i>Maria S. Merian</i>	MSM-38	x <sup>b</sup>		x	x	x			x <sup>e</sup>		Only west of 30°W
2015/05-/06	<i>Maria S. Merian</i>	MSM-43	x <sup>b</sup>		x	x	x	x <sup>f</sup>				Only west of 30°W
2016/03-/05	<i>Maria S. Merian</i>	MSM-53	x <sup>b</sup>		x	x	x					
2017/04-/05	<i>Celtic Explorer</i>	CE17007	x	x	x	x	x		x	x		GOSHIP A02
2017/05-/06	<i>Maria S. Merian</i>	MSM-64	x <sup>b</sup>		x	x	x			x <sup>g</sup>		

All expeditions made CTD and salinity measurements, though station spacing may be considerably different.

Meteor 45-3 includes pH measurements.

<sup>a</sup>Samples for δ<sup>13</sup>C DIC taken also. <sup>b</sup>No nutrient samples taken. <sup>c</sup>Samples for nutrients, DIC, alkalinity and δ<sup>13</sup>C taken for later analysis (no dataset found in Pangaea). <sup>d</sup>Cruise report indicates samples were taken for δ<sup>13</sup>C and Δ<sup>14</sup>C DIC as part of GEOTRACES-NL (S. van Heuven). <sup>e</sup> Samples for δ<sup>13</sup>C taken for later analysis (MARUM). <sup>f</sup>He samples were made during the expedition but not along the A02 line. <sup>g</sup> Samples for δ<sup>13</sup>C taken for later analysis (MARUM).

### 3. Narrative of the Cruise

The Celtic Explorer was ready to depart St John's in the evening of April 27<sup>th</sup> for CE17007 as planned, after a relatively smooth arrival of participants and vessel into Canada.

The majority of the laboratory containers to be used during CE17007 had been loaded on the Celtic Explorer prior to leaving Galway, this included the CFC container from GEOMAR, the CO<sub>2</sub> analysis van from the University of Exeter and the Nutrient lab from the Marine Institute (container on loan from NIOZ). The arrangement of the laboratory containers deployed on the working deck of the vessel had to be revised in St Johns from what was initially planned as when the Canadian container was loaded on in St Johns, it's intended location would have seen it block the external air vent of one of the other lab containers. A new optimal configuration of the container of the work deck was found and the laboratory containers were loaded and connected to water and electrical services well in time for the scheduled departure time. The flooring of the MI container was slightly damaged during mobilization, but was deemed still suitable for use.

There was also time to give a quick tour of the ship to Jim Kelly, Ireland's ambassador to Canada, and introduce him to the work that was to be done during this expedition. Canadian colleagues also took the opportunity to visit the vessel at this time, including Prof. Brad de Young from Memorial University in St John's and Prof. Doug Wallace from Dalhousie University whose research group was participating in this expedition.

Unfortunately, one of the scientific participants, part of GEOMAR's CFC team, had felt unwell while travelling to Canada and had been subsequently diagnosed by medical staff at a hospital in St John's on the day before the scheduled departure as suffering from acute Bronchitis. The medical opinion provided was that they were likely to improve with bed rest and medication, thus the decision was therefore taken to delay departure from St John's until the morning of the 28<sup>th</sup> of April and to reassess their condition, regarding, if they should sail with us or remain in St John's for further medical treatment. After a good night's sleep in the ship's hospital, the scientist in question was significantly improved in condition, that it was felt they could remain onboard and be given time to fully recover before starting work at sea. The rationale behind this was that we may miss some initial stations for CFCs while he was recovering but we would still be able to sample and measure CFCs at some point during the expedition. The ship then made final preparations to leave St John's at 9 am (St John's time) that morning.

The passage from St John's to the first station was slow at first due to dense fog and the necessity to be watchful for ice bergs near St John's, however after 29 hours we arrived at our initial station on the Grand Banks. During the steaming time to the first station, the internal springs on the new Niskin bottles, purchased especially for this expedition, had to be adapted as there was insufficient spring tension, this was accomplished by shortening the springs by doubling them back. Thanks to Marshall Swartz and Tom Gilmartin for their help with this.

The CTD deployment at the first station went well (April 29), with only a single bottle, number 15, failing to fire. Water sampling from the CTD at the first station went smoothly, with all of the groups having done a good deal of preparation before with regard to keeping to the assigned sampling order, preventing overcrowding around the CTD and maintaining safe

working practice throughout. The sampling of the first station involved all participating groups, apart from the CFC group (as indicated earlier).

During this expedition, the standard CTD procedures onboard the Celtic Explorer were followed, this includes when recovering the CTD to lower it onto a mat on the deck and then securing the CTD to the gunwales or other parts of the ship's superstructure via cables, extra care therefore had to be taken then for those sampling around the CTD and walking to and from the container labs at the aft due to the presence of the cables. It is suggested that for future work that an eye-hole be fitted in the deck so that the CTD can be directly secured to the deck and avoid this problem with the cables.

Work continued quickly across the shelf with 6 stations sampled on April 30 as everyone got quickly into their work and the outside temperature warmed up as we transited from the cold shelf waters to the Gulf stream. The SBE43 oxygen sensor (SN 3339, last calibrated 16 Feb 2017) was switched out of the CTD sensor package and replaced with an identical unit (SN 1416, last calibrated 18 Mar 2017) after station 3 as it was displaying erratic behaviour.

The CTD winch had been working well in continental shelf waters, however as the ship moved into deeper waters (> 2500 m), and the ship began to roll more, a problem developed with the heave compensator of the winch, by which the springs became overloaded (fully squeezed), would then suddenly release, making a dramatic noise but more importantly creating high tension in the CTD cable resulting in poor spooling on or off the drum. The crew were excellent in managing this issue as best as possible and were able to manually realign the spooling throughout the up cast when required. However overall this lengthened the time required for winch operations from that originally planned, and achieved on the shelf, as both down and up cast spooling rates had to be slowed appreciably. Even with these precautions in place, it was noticeable that in heavy swell conditions, that the CTD acquisition and LADCP data indicated appreciable vertical acceleration of up to  $1.5 \text{ m s}^{-2}$ . The presence of an inline tensiometer logging system would have helped here to provide the scientists and crew regarding the strain on the CTD wire and at what depths it had occurred. This issue with the heave compensator had apparently not arisen before during CTD operations, as previously the CTD wire had rarely been deployed deeper than 3000 m and not since 2014.

As the expedition made its way into the Gulf stream proper with subsequent higher current velocities, it was noticeable that when on station the vessel's dynamic positioning system was having trouble to maintain position and maintain a good wire angle. This was aggravated by the heavy swell encountered at this time making deployment and handling of the CTD difficult. The combination of these factors resulted in the ship drifting off station over the course of the occupation and there being a large difference between the wire out and the CTD depth. This resulted in much longer station times than planned and progress was much reduced from May 1-4.

At station 11 (May 3), there was a problem with the firing of the bottles due to a communication problem with the CTD at 1500 m on the up cast and the cast was repeated. During the subsequent deployment the bottle firing mechanism failed again, and a bird cage kink was found on the wire which required cutting off 300m of sea cable and retermination. The cable was checked onboard prior to redeployment and was found to be working fine.

Over the next 24 hours, 3 more stations were run without major incident (Stations 12-14) despite increasing wind and swell conditions.

On May 5, the weather conditions had unfortunately deteriorated further and the planned station 15 had to be abandoned when the CTD was at 1500 m due to increasing wind (Figure 3.1) and swell making operation of the equipment unsuitable. The high wind and sea state prevented reoccupation of this station again the following day and the ship was forced to heave to until the storm system had passed and the swell abated. On the morning of May 7, we attempted to occupy station 16 (UTC 07:00) however the weather conditions proved too rough to deploy the CTD, so the ship then progressed to station 17 (UTC 14:40) but again the sea state prevented occupation of the station. The safe operating window for station work was now clearly defined by the wind and sea state, with no operations permissible at Beaufort 7 or above (28-33 knots, swell > 4m). The decision was then made to bypass stations 18 and 19 and resume sampling at station 20 in the evening of May 8. As weather conditions improved 3 more stations (21-23) were completed on May 9.

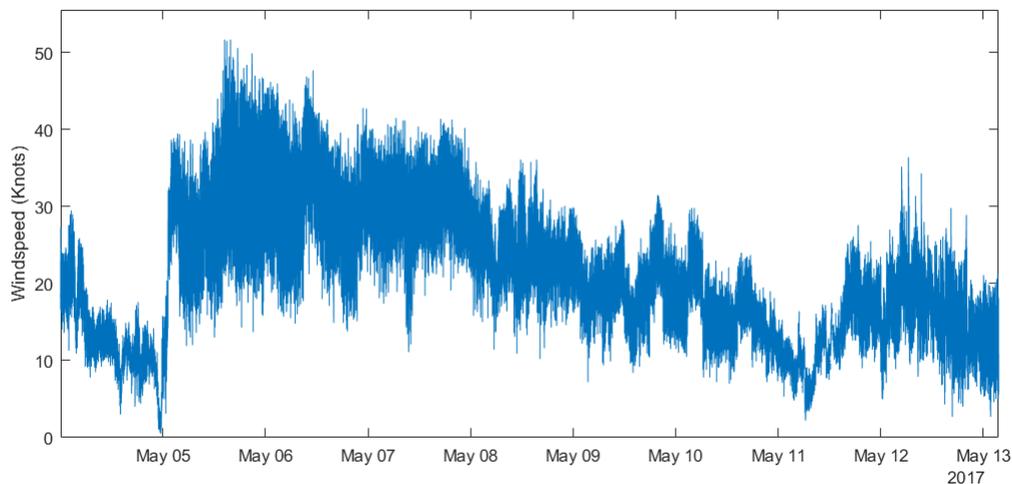


Figure 3.1 Wind speed observed by the ship's metrological sensors during the period May 4 – May 13, 2017.

At station 23 an incident occurred during the downcast, when at 1100 m, it was observed that the seabird software indicated bottle number 1 had closed on deck prior to deployment. The cast was retrieved in order to prevent implosion of the bottle, but on its return to the surface bottle number 1 was found to be still open. The cast was rerun without any further incident. However during the next station (24) there were further problems firing the bottles on the upcast, where bottles fired without being triggered, the CTD was returned to the surface and underwent a full check of the firing mechanism on deck where upon a small paint chip was found in the firing mechanism at this time and it is likely, though not definitely confirmed, that was this the cause of the problems. The cast was rerun without any further incident.

One bright note at this time was the introduction to the sampling team at station 23 of the GEOMAR team sampling for CFC's as they were now able to analyse samples after a team effort between scientists and crew to construct an improvised cooling system following a breakage of the GC-instruments cooling system.

At station 27 (May 11) a problem was encountered during the initial stages of the downcast with large differences observed between the primary and the secondary temperature and conductivity sensors, this resolved itself and was likely a partial blockage of the CTD pump in the primary channel. The system was checked prior to the next deployment. At the next station (28) temperature and salinity data indicated the presence of a cold core cyclonic eddy. Subsequent analysis of AVISO and shipboard ADCP data appeared to confirm this.

On May 12<sup>th</sup> with a further storm system forecast to follow us from the west and generate significant wind and swell, the decision was made to skip alternate stations to try and position ourselves further east of the storm system and allow us to optimise the amount of time with good working available to us to complete stations in the eastern basin. Stations 30, 32, 34, 36 and 38 were thus omitted from the sampling program due to time constraints.

Routine maintenance was carried out on the Niskin bottles after station 33 (May 13: 0200 UTC) in response to comments returned by the sampling group. The spigots were checked on all bottles (3 had been reported as difficult to open), the outer flange was removed, the valve body was taken out, the 2 inner o-rings were lifted and put back in, pushed inside, and then the reinstalled flange. No change of parts were made.

During the next week, good weather with light winds saw the sampling program get back into full swing and no significant further issues arose resulting in excellent progress as we made our way through the eastern basin. Shallow (0-150 m) plankton net tows were made at several stations in the central part of the section as part of a Marine Institute study into the dinoflagellate species *Azadinium*. Deep water samples were taken in the eastern basin at stations 58 and 60 for an international  $\delta^{13}\text{C}$  intercomparison organized by the group from Dalhousie. An ARGO float (S/N 7842: ARGO code 6901926) was successfully launched for the Marine Institute at station 60 (48° 53.394, 13° 43.506) on the morning of May 20. The final CTD station (67) was completed on the morning of May 21<sup>st</sup> and the vessel then proceeded north to the coast of Ireland.

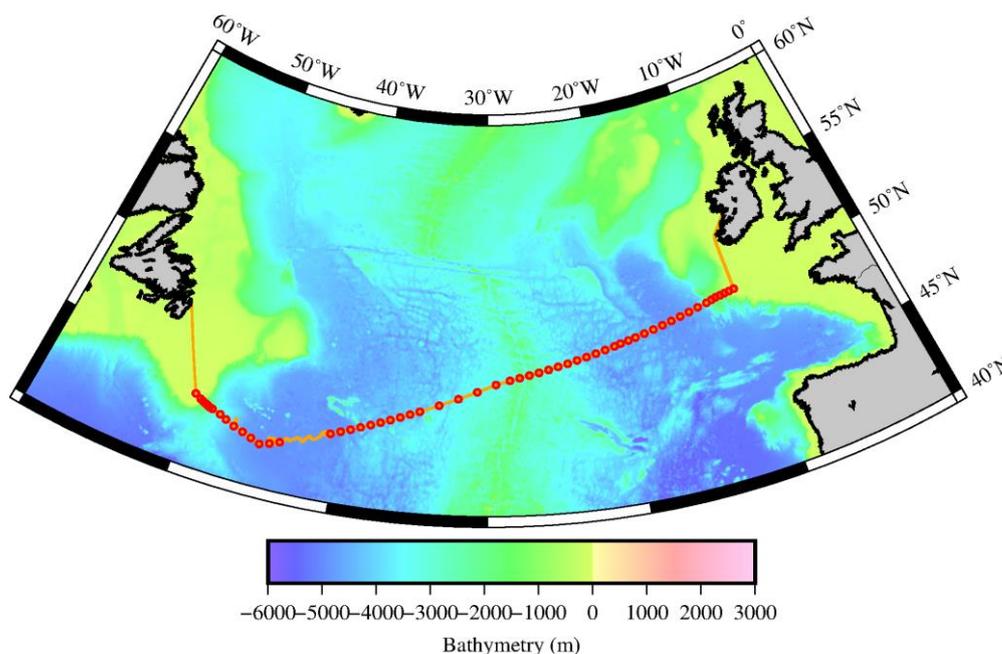


Figure 3.2 Cruise Track (orange) and location of completed stations (red circles) during CE17007.

On May 23<sup>rd</sup> the expedition sighted the Irish coast with good view of the Clare coast line and the cliffs of Moher and the Aran islands, and the Celtic Explorer entered Galway Bay and then as high tide approached the final progression was made into Galway Harbour under the watchful eye of a traditional Galway Hooker.

The Canadian ambassador to Ireland, Kevin Vickers, was also a welcome guest to the RV Celtic Explorer at the end of the Voyage and we were able to update him on what we had encountered and accomplished during the transit

Overall the main objectives of the expedition were achieved, as full water column sampling took place at 58 of the 67 planned stations; resulting in 85% coverage of the section for the hydrography, nutrients and LADCP. The entire section was completed in terms of the shipboard ADCP track.

## 4. Preliminary Results – Water Column Parameters

### 4.1. Conductivity Temperature Depth (CTD) Hydrography

(Peter Croot, Caroline Cusack and Marshall Swartz)

The main workhorse of CE17007 was the Seabird SBE911*plus* CTD connected to a SBE32 carousel. Power to the CTD and sensors was provided through the sea cable from an SBE11*plus* deck unit located in the dry lab in the ship. The sensor setup employed during CE17007 is located below in Table 4.1.

Table 4.1 Sensor setup on CTD for CE17007

Sensor Code	Parameter	Serial Number	Calibration/Service date
CTD SBE911 <i>plus</i> PSO513		09P19835-0513	M: 10 Nov 2014 POMs: 25 Jan 2015
SBE32	Bottle firing mechanism	unknown	unknown
SBE3	T1: Primary Temperature Sensor	4023	01 Sep 2016
SBE3	T2: Secondary Temperature Sensor	4927	28 Sep 2016
SBE35	Discrete depth bottle triggered Temperature sensor	0020	17 Oct 2016
SBE4	C1: Primary Conductivity Sensor	3480	20 Sep 2016
SBE4	C2: Primary Conductivity Sensor	2764	06 Oct 2016
SBE43	Oxygen Sensor <sup>1</sup>	3339	16 Feb 2017
SBE43	Oxygen Sensor <sup>1</sup>	1416	18 Mar 2017
VA500	Altimeter	46504	unknown
Wetlabs C-star	Transmissometer	CST-1101DR	08 Dec 2016
Wetlabs ECO-FLNTURTD	Fluorometer and Turbidity	1609	12 Oct 2009

<sup>1</sup>The original oxygen sensor (S/N 3339) was found to be performing poorly at station 3 and was swapped out for a replacement sensor (S/N 1416).

The CTD supplied a standard SBE-format data stream at a rate of 24 Hz. The CTD provided pressure plus dual temperature and conductivity data, with single sensors for oxygen, optical transmission, a combined fluorometry/turbidity sensor and an altimeter. The CTD system was equipped with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed into one pump circuit; and the secondary temperature and conductivity was on the other circuit. A Lowered Acoustic Doppler Profiler (LADCP) was also mounted on the rosette frame; it was powered separately and collected data internally. The original altimeter from this unit (Benthos) was swapped with a Valeport VA500 on loan from WHOI as the LADCP interferes with the Benthos device. Prior to every CTD deployment the transmissometer was checked and cleaned and a zero reading in air taken.

The primary temperature and conductivity sensors were used for reported CTD temperatures and salinities on all casts; the exception was station 27, where there was an initial problem with the primary signal, as evidenced by anomalously low O<sub>2</sub> readings and significant deviations from the values of secondary temperature and conductivity sensors, due to what is suspected was a transient pump blockage.

There were a number of issues that arose with the safe operation of the CTD winch system under heavy seas during this expedition and details on this can be found above in the narrative of the cruise. The rest of this section deals with issues that arose with the CTD system itself and not the operation and spooling on and off the winch.

At station 11 the pump stopped and started intermittently. Bottom connection warning alarm triggered a couple of times. Bottle firing communication error occurred. Water ingress on secondary pump connector, loose connections were tightened, the secondary pump was cleaned and the bottle firing mechanism was also cleaned.

Retermination of the cable: The cut off section was measured and found to have an intermittent low resistance (<50 ohms) core to ground and was likely a cause of the modulo errors. The sea cable was electrically evaluated with the ship's megohmmeter to test insulation integrity, and found to be >1000Megohms at 500VDC, passing the requirements. End to end continuity of the conductor was measured with a Fluke 112 in low resistance range, and found to be 32ohms steady, the value expected for this length of cable.

The Ship's Technician applied the normal re-usable mechanical termination to the new cable end, and then fabricated a new electrical termination using a ScotchCast 82F1 splice kit with 2131 Scotch resin, and reusing the 2m pigtail lead with MCIL2F connector and MCDLSF locking sleeve. After 3hr curing at 20° C, the splice kit shell was removed, inspected, found fully satisfactory and the termination was attached to the rosette. The system was tested again before the next station by running the SBE9/11/32 system with SeaSave to fire all mechanical release positions without attaching bottle lanyards. All systems operated as expected and system was then ready for next station.

Routine maintenance was carried out on the Niskin bottles after station 33 (May 13: 0200 UTC) in response to comments returned by the sampling group. The spigots were checked on all bottles (3 had been reported as difficult to open), the outer flange was removed, the valve body was taken out, the 2 inner o-rings were lifted and put back in, pushed inside, and then the reinstalled flange. No change of parts were made.

The CTD data and bottle trip files were acquired by SBE Seabird SeaSave V7 version 23.0.2 on the ship's Windows 7 workstation located in the dry lab. Pre-cruise calibration data were applied to CTD Pressure, Temperature and Conductivity sensor data acquired at full 24 Hz resolution. Bottles were close on the upcast through the software and were tripped 30 seconds after stopping at the required bottle depth to allow the rosette wake to dissipate and the bottles to flush. The upcast continued 30 seconds after closing a bottle to ensure that stable CTD and reference temperature data (SBE35) were associated with the bottle trip.

The performance of the sensors throughout the expedition was considered to be very good, as can be seen in [figures 4.1](#) and [4.2](#) below.

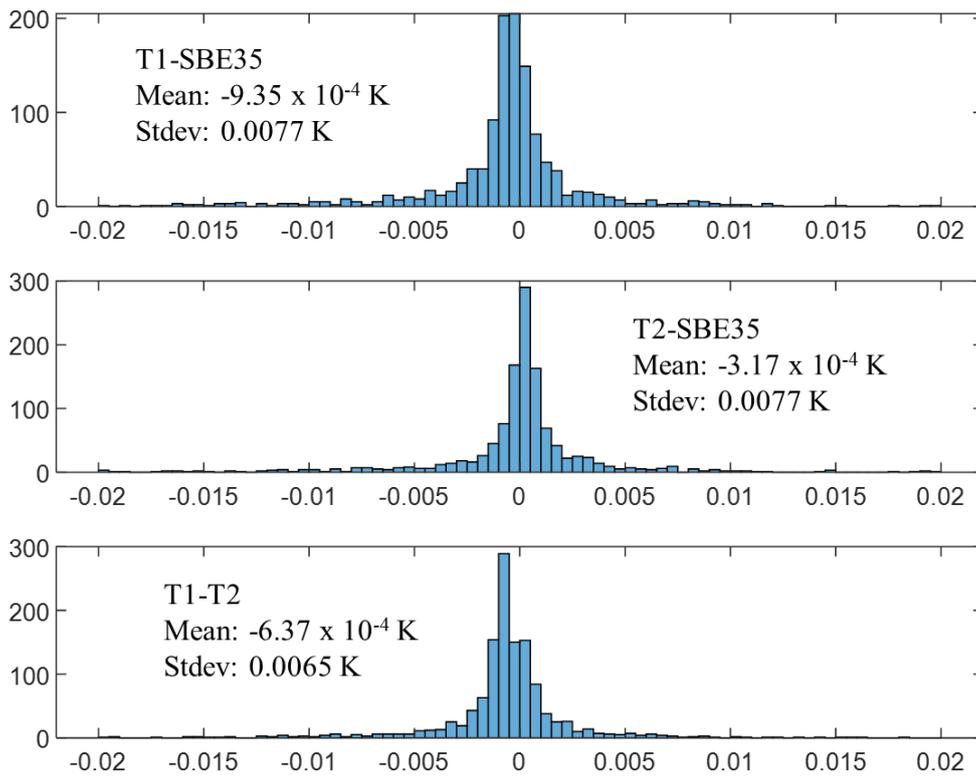


Figure 4.1 Histograms of the difference in temperature between the primary, secondary and SBE 35 temperature sensors during CE17007.

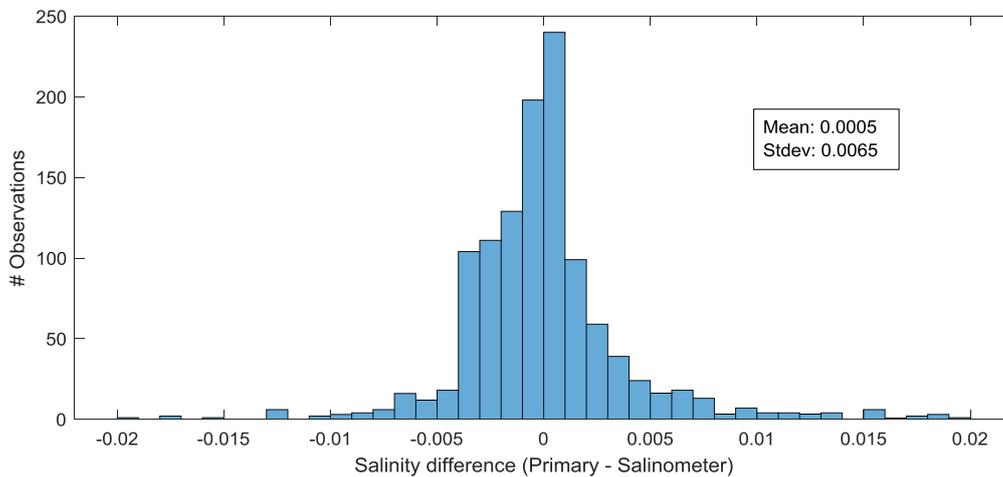


Figure 4.2: Histogram of the difference in salinity between the value calculated from the primary sensors and the measured salinometer salinity (n = 1195, 15 values discarded as clearly outliers using Grubb's test).

The comparison of the  $O_2$  data with the Winkler titration data is present later in this report. Data from the transmission sensor for the A02 sections is shown below. An anomaly at station 41 just beyond the ridge crest is apparent in the data and is likely the result of

something becoming lodged in the sensor at the time of deployment. Subsequent cleaning of the sensor prior to the next cast resulted in sensor performance returning to earlier pre station 41 values.

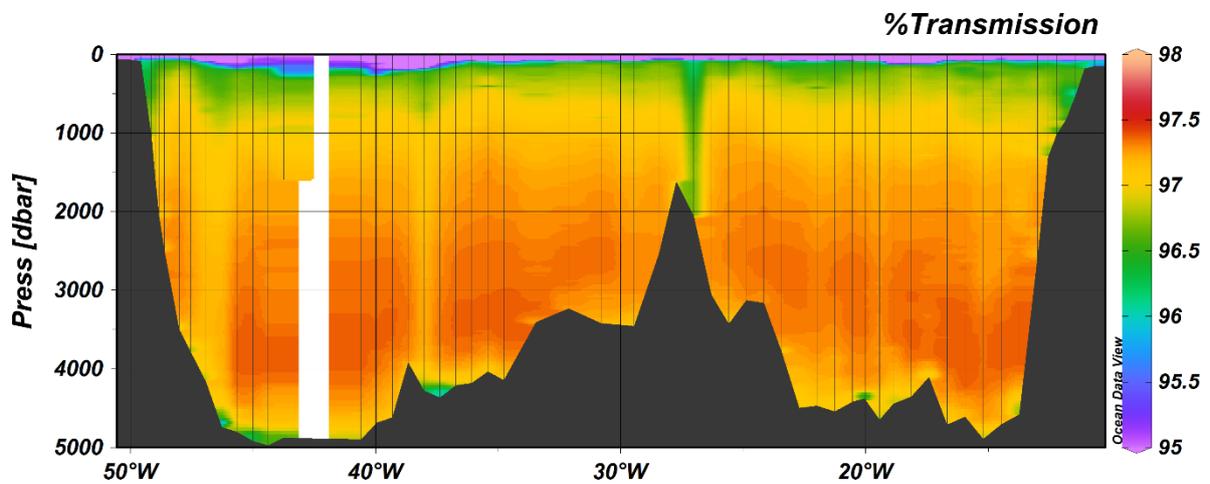


Figure 4.3 %Transmission along the A02 section

Of the derived variables commonly used in physical oceanography, potential vorticity is often employed as a tracer of water masses (Figure 4.3). In the figure below it can the anomalous station 27 (pump problem) is also clearly evident.

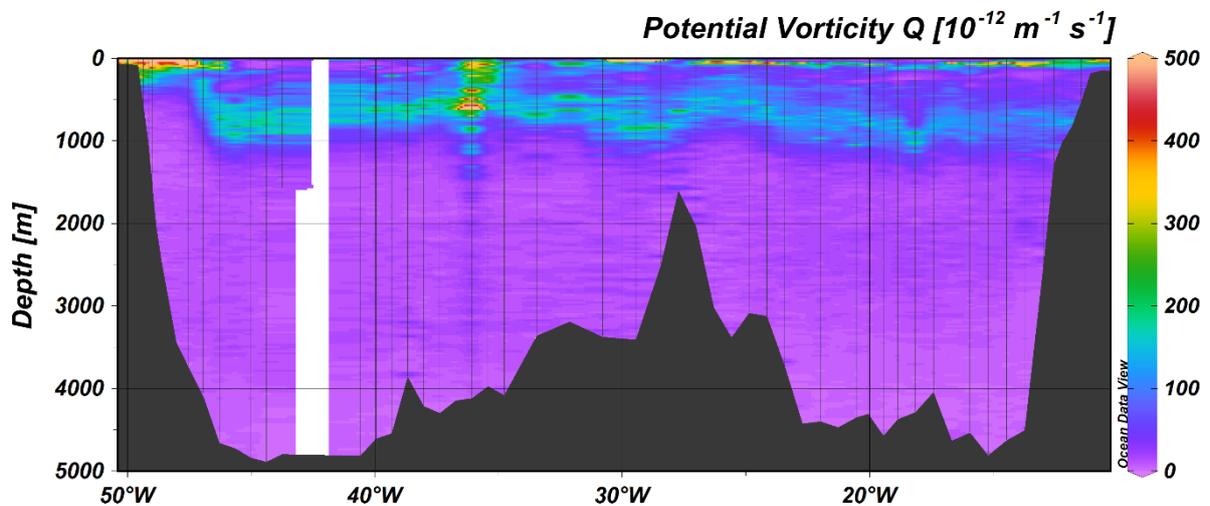


Figure 4.3 Potential vorticity along the A02 section.

The data from the NTU and fluorescence sensor were not corrected for during this expedition and no calibrations of these sensors were performed at sea.

## 4.2. Lowered Acoustic Doppler Current Profiler (LADCP)

(Daniel J. Torres – on land, Marshall Swartz - shipboard)

Voyage CE17007 of R/V Celtic Explorer was carried out from April 26 – May 22, 2017 in the North Atlantic Ocean. The cruise was a multi-national collaboration between 8 institutions as part of the GO-SHIP program covering the A02 section. The primary purpose of the cruise was to conduct a basin scale high resolution hydrographic/tracer/velocity survey of the North Atlantic Ocean from St. Johns, Newfoundland, Canada to Galway, Ireland. The WHOI contribution to the program was to collect lowered ADCP data at each CTD station while assisting personnel from the Marine Institute of Ireland develop their own LADCP measurement capability. All the objectives were successfully met.

### **Cruise Synopsis**

The cruise began in St. Johns, Newfoundland, Canada on April 26, 2017. The LADCP system consisted of a downward-facing Teledyne RD Instruments 150 kHz ADCP, an upward facing 300 kHz ADCP, an external 48 Volt rechargeable lead-acid battery pack, and a Linux based data acquisition computer. Both ADCPs and battery pack were mounted on a Seabird SBE32 24 10-liter bottle rosette. An extension stand for the frame was modified at WHOI to allow the mounting of the battery and downward facing ADCP. The SBE32 frame was modified at the Marine Institute in Ireland to allow mounting of the upward facing ADCP.

A total of 67 CTD stations were sampled (see [figure 1](#)). Due to time constraints, stations 16 – 19 and 30, 32, 34, 36, and 38 were not sampled with the LADCP. At station 8, the downward facing ADCP had a beam failure. Since only 3 beams are needed to achieve good velocity measurements and a backup 150 kHz ADCP was not available for this cruise, that instrument was left on the frame for the remainder of the cruise. Also at station 8, the upward facing 300 kHz ADCP was experiencing communication problems. So that instrument was swapped out for a spare. Those instruments successfully collected data for the remaining stations. A station log was kept noting specific details for each deployment. In order to post-process the LADCP data into absolute velocity profiles, CTD data were processed as a time series at 24 Hz for each station. Processed shipboard ADCP data were also made available (by another group) for LADCP post-processing. Raw LADCP data were provided to Andreas Thurnherr of LDEO for post-processing.

### CE177 LADCP Stations

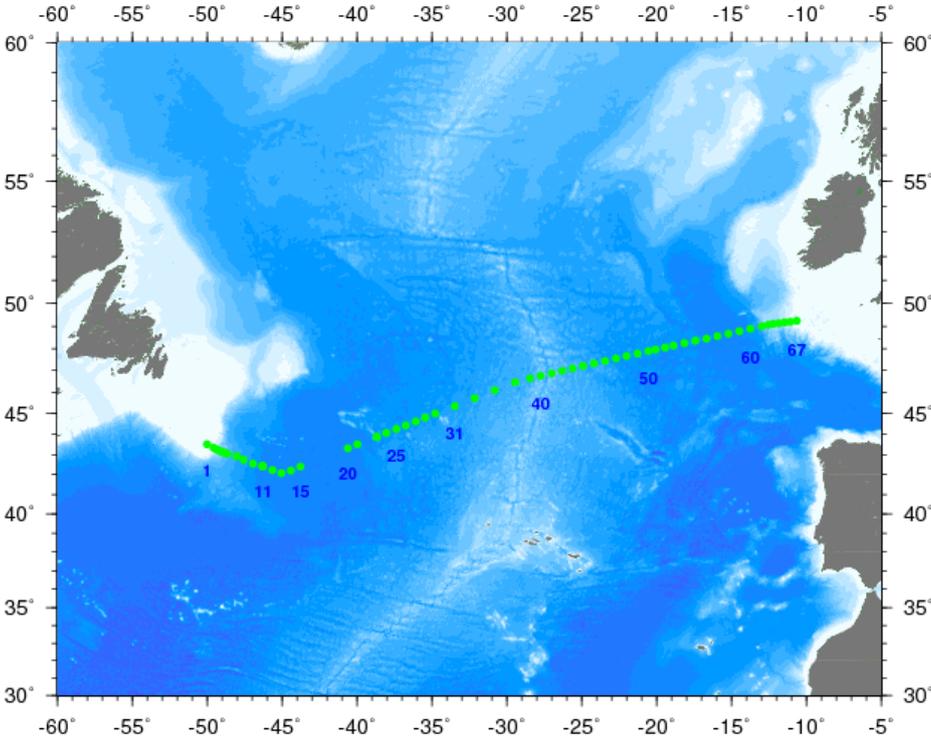


Figure 4.2.1. LADCP Station locations

### 4.3. Chlorofluorocarbons (CFCs)

#### 4.3.1. Measurements of CFC-12 and SF<sub>6</sub>

(B. Bogner, V. Merten, J. Bruckert, PI: T. Tanhua,)

During the cruise a GAS CHROMATOGRAPH / PURGE-AND-TRAP (GC/PT) systems was used for the measurements of the transient tracers CFC-12 and SF<sub>6</sub>. The systems “PT5” was a modified version of the set-up normally used for the analysis of CFCs (Bullister and Weiss, 1988). To cool the traps a system with refrigerated ethanol at -65°C was used.

The first 22 stations the instrument wasn't ready because of illness of the lab technician and because important parts of the trap-cooling equipment broke down. With dedicated help by the ship's crew and using the onboard -80°C freezer, we were able to start sampling every odd station from station 23 onward. Per station up to 18 depths were sampled, depending on freezer capacity, as it had trouble keeping the ethanol cold enough if measurement frequency was too high.

The trap was 100 cm of 1/16” tubing packed with 70cm Heysep D. The systems used a 1/8” packed main column consisting of 180 cm Carbograph 1AC (60-80 mesh) and a 50 cm Molsieve 5A, heated up to 60°C. The tracers were trapped at -60 to -68°C; desorption at 120°C. The pre-column was packed with 20 cm Porasil C and 20cm Molsieve 5A in a 1/8” stainless steel column. Detection was performed on an Electron Capture Detector (ECD). This set-up allowed efficient analysis of SF<sub>5</sub> and CFC-12.

Samples were collected in 250 ml ground glass syringes. An aliquot of about 200 ml of the samples was injected into the analytical system. Standardization was performed by injecting small volumes of gaseous standard containing SF<sub>6</sub> and CFC-12. This working standard was prepared by the company Dueste-Steiniger (Germany). The CFC-12 concentration in the standard has been calibrated vs. a reference standard obtained from R.F Weiss group at SIO, and the CFC-12 data are reported on the SIO98 scale. Another calibration of the working standard will take place in the lab after the cruise. Calibration curves were measured twice to characterize the non-linearity of the detector. Point calibrations were always performed between stations or every 15 samples to determine the short term drift in the detector. Replicate measurements were taken on a couple of stations depending on work load and freezer capacity. The determined values for precision and accuracy are listed in Table 4.3.1.

A total of 301 successful water samples, of which 32 were replicate samples, and 165 calibration measurements were performed during the cruise.

<b>Compound</b>	<b>Precision</b>
SF <sub>6</sub>	1.8%
CFC-12	0.038 fM
	0.59 %
	0.0092 pM

**Table 4.3.1:** Precision of tracer measurements determined from replicate measurements and approximate limit of detection.

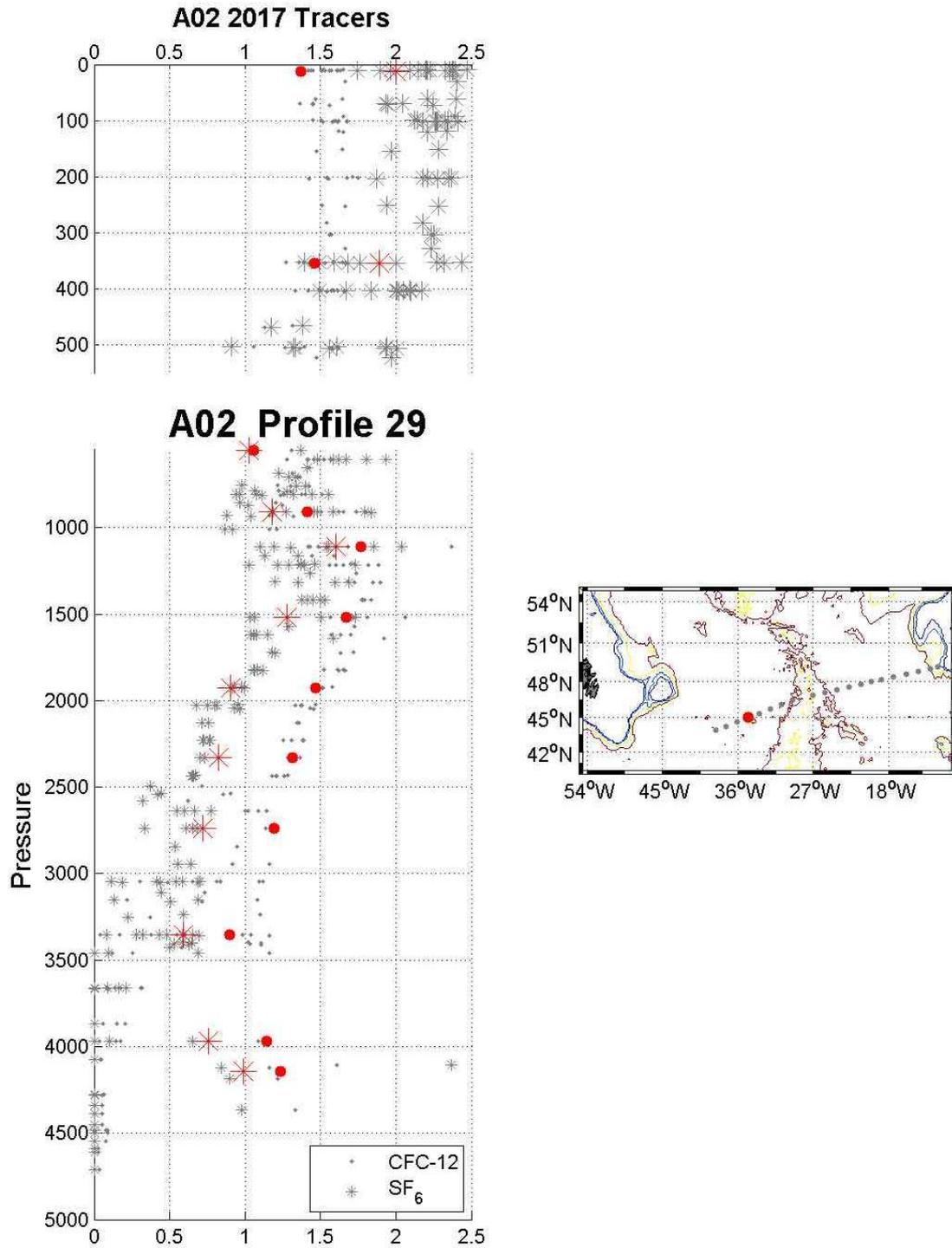


Figure 4.3.1. An example of a depth profile from the Western Basin. Note that this is preliminary data.

## 4.4. Dissolved Oxygen

(PI Evin McGovern MI, Fran Aparicio NUI Galway)

### 4.4.1 Methodology:

Water samples were collected at all sampling events for measurement of dissolved oxygen using the modified Winkler method. Samples were collected and tested at all 58 stations sampled in the GOSHIP A02 2017 section and dissolved oxygen concentration was determined in 1232 samples.

#### 4.4.1.1 Sampling

Water samples for dissolved oxygen (DO) testing were the first or second (after CFCs where CFCs were sampled) samples collected from Niskin bottles after it was returned to deck. Samples were taken following the GO-SHIP procedures described in Langdon (2010) and Dickson (1996). Water was collected in 100 mL pre-weighed glass flasks employing a Tygon® tube to avoid bubble formation. Samples were immediately fixed by adding 1 mL of manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  3M) and 1 mL of alkali-iodide solution (NaOH 8M + NaI 4M), then the stopper was inserted into the bottle and flasks were shaken vigorously. Temperature of the water at fixation was recorded in a separate glass bottle with a digital thermometer. The samples were allowed to sit and approximately 30 min later, samples were reagitated and the stoppered flask brims were filled with deionized water to ensure seal was maintained. Glass bottles were stored in darkness at room temperature typically for between 3-4 hours, before being analysed for dissolved oxygen. Two people performed the dissolved oxygen sampling to ensure rapid fixing once samples were collected from the Niskin bottles (Shift 1 Evin McGovern and Margot Cronin; shift 2 Fran Aparicio with Clynt Gregory, Liz Kerrigan or Véronique Merten).

#### 4.4.1.2 Analytical Method

Dissolved oxygen concentrations in the water samples were quantified using the modified Winkler method as described by Langdon (2010). Analyses was carried out with two automatic 5 mL burettes “848 Titrino plus” (Metrohm, Switzerland) and amperometric end-point detection. To dissolve the precipitate, 1 mL of sulphuric acid ( $\text{H}_2\text{SO}_4$  5M) was added to each sample and place on a magnetic stirrer. The sample was titrated with 0.2M thiosulphate.

Concentration of thiosulfate solution was periodically determined by standardization with potassium iodate solution (0.0023M). Reagent blanks were also measured periodically during the cruise. The final volume of dissolved oxygen contained in each sample was calculated with the equations presented in Langdon (2010).

#### 4.4.1.3 Volumetric Calibrations

Stoppered flask volumes were gravimetrically determined before the survey and analytical volumes dispensed were also gravimetrically calibrated pre-survey. Laboratory temperature was recorded throughout the survey.

### 4.4.2 QC:

107 replicates were collected typically, two on each cast. The mean difference between the duplicate samples was 0.38% with little difference between the titrinos used; duplicates

measured on titrino 1. 0.31% (n=27), titrino 2 0.46% (n = 19) and duplicates separately tested on each titrino 0.39% ( n = 61).

#### 4.4.3 Problems encountered

Overall, no major issues were encountered during the cruise.

#### 4.4.4 Preliminary Results

The preliminary modified Winkler dissolved oxygen profiles for the section are shown in Figure 4.4.1 below (results subject to full QC check to be completed). Highest values were measured in the colder surface waters at the Canadian shelf edge. Surface waters (<30m) were generally close to 100% saturation.(mean DO % Sat 105.1%, range 95.3– 116.8%, n =79).

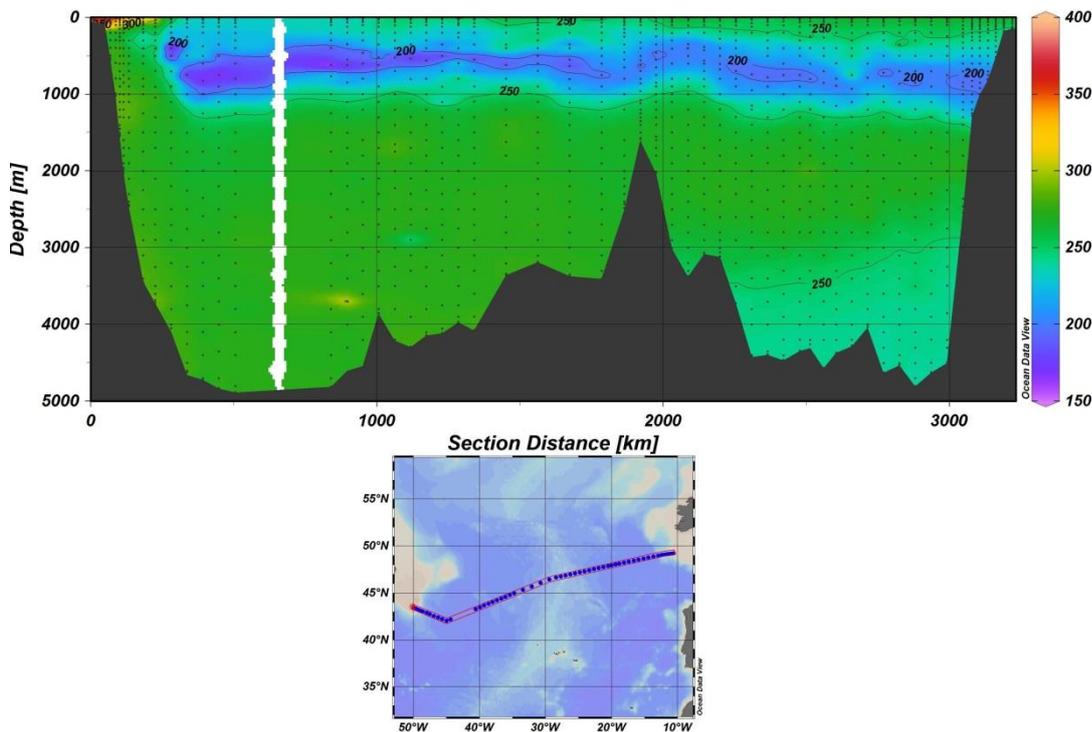


Figure 4.4.1; Dissolved oxygen ( $\mu\text{mol/kg}$ ) depth profiles as determined by modified winkler method (preliminary data not quality checked).

#### 4.4.5 Comparison with SBE 43 DO sensor:

An issue was identified with the SBE 43 sensor (SN 3339) for stations CE17007-01 to 03. The sensor was swapped out for station 4 and replaced with SBE 43 (SN 1416), Thereafter, the dissolved oxygen laboratory and sensor values correlated very well ( $r^2 = 0.97$  Figure 4.4.2) with the exception of station 27 where a problem with the CTD pump was noted. The winkler measured DO concentrations were on average  $12.4 \mu\text{mol/kg}$  higher than the SBE43. Although the correlation was good, a plot of the residuals between the SBE43 and laboratory measured dissolved oxygen (figure 4.4.3) indicates a greater deviation between sensor and laboratory measured for deep water samples. High and low outlier winkler concentrations at samples 100342 (st 21, 3698m) and 100439 (st 25, 2899m) not apparent in sensor profiles indicate likely sampling/titration error for these samples.

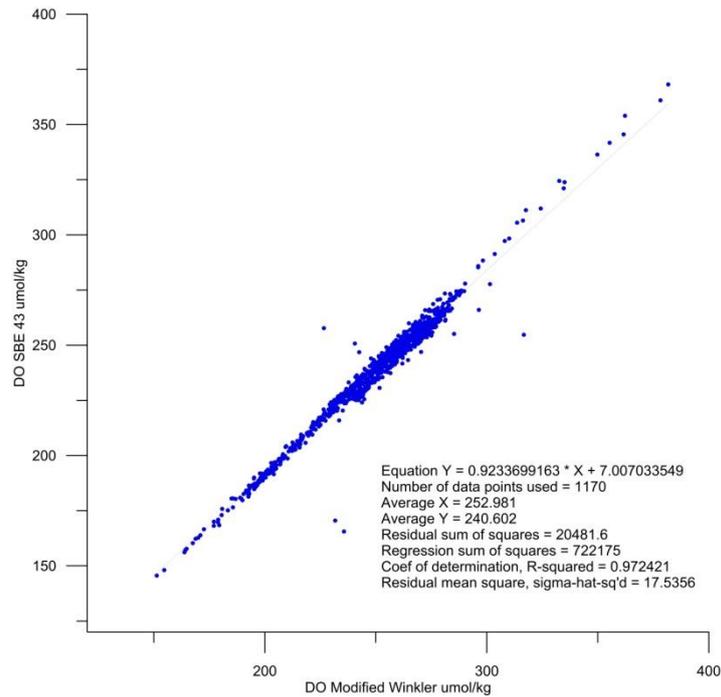


Figure 4.4.2: Laboratory measured DO vs SBE 43 in situ DO ( $\mu\text{mol/kg}$ ) for all data excluding stations 1-3 and 27 (Preliminary data) Inset zoom on central line

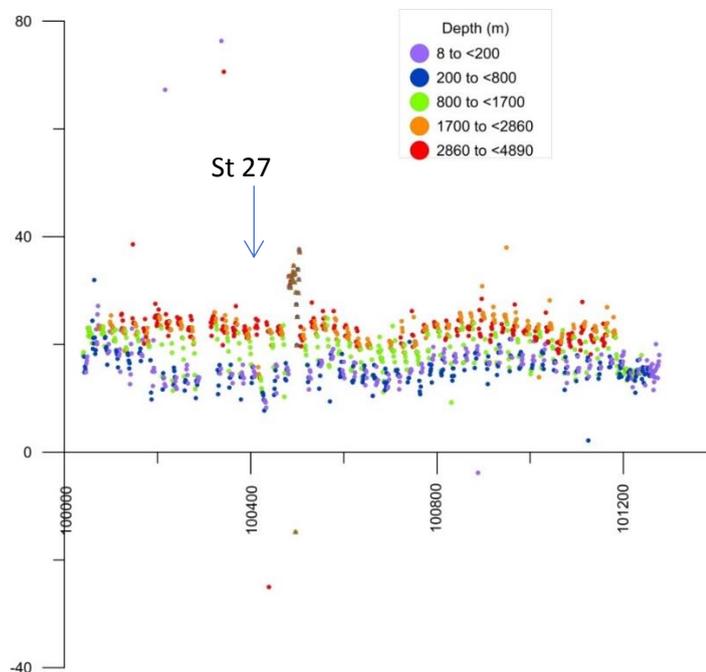


Figure 4.4.3 Class scatter plot of dissolved oxygen residuals (Winkler – SBE43  $\mu\text{mol/kg}$ ) against Bedford number (i.e. sample sequence over the course of the survey) shows depth dependency of the residuals. Triangles show station 27 where there was a problem with CTD pump. Stations 1-3 are omitted as there was a issue with the SBE 43 (subsequently swapped out)

#### 4.4.6 References

Langdon, C. 2010, Determination of Dissolved Oxygen in Seawater by Winkler Titration Using the Amperometric Technique in *The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines*. Hood, E.M., C.L. Sabine, and B.M. Sloyan, eds. IOCCP Report Number 14, ICPO Publication Series Number 134. Available online at: <http://www.go-ship.org/HydroMan.html>.

Dickson, A. D. 1996. *Determination of dissolved oxygen in sea water by Winkler titration*. WOCE Operations Manual, Part 3.1.3 Operations & Methods, WHP Office Report WHPO 91-

## 4.5. Nutrients (Nitrate, Nitrite, Phosphate and Silicate)

(Margot Cronin, Clynt Gregory, Claire Normandeau, Liz Kerrigan – shipboard, Doug Wallace – Land based, Triona McGrath – Land based (PI))

### 4.5.1. Objectives:

1. To repeat the sampling plan of GO-SHIP 1997
2. To carry out on-board analysis of samples from all stations and all depths
3. To carry out an on-board inter-comparison on similar nutrient analyser systems used by Marine Institute and Dalhousie University

### 4.5.2. Methodology:

The Marine Institute and Dalhousie University teams both independently sampled and tested inorganic nutrients on-board. The Marine Institute was the primary nutrients team, with the Dalhousie team additionally sampling from selected stations. Both teams used a Skalar SAN++ Continuous Flow Analyser for analysis. Sampling, sample preservation and analytical procedures on both systems followed methods outlined in the GO-SHIP guidelines for nutrient analysis at sea (Hydes et al., 2010), while both groups also incorporated their existing laboratory quality control (QC), which was specifically adapted to their individual instruments. Both teams operated similar sampling and analysis approaches with some minor differences. The Marine Institute methodological details are set out in [Table 4.5.1](#).

#### 4.5.2.1. Sampling Procedures

Both groups collected nutrient samples directly from the Niskin bottles into falcon tubes and as per GO-SHIP guidelines, the samples were not filtered. Samples were analysed on board typically within 12 hours of sampling.

Samples were taken in triplicate; “A” samples were analysed on board and replicates (“B” and “C”) samples were frozen at -20°C. As per GO-SHIP guidelines, samples were not filtered. Concentrations of nutrients ( $\text{PO}_4$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{Si}(\text{OH})_4$ ) were measured in 1277 samples from 58 stations.

#### 4.5.2.2. Analytical Methods

Analysis was carried out by Skalar SAN++ Continuous Flow Analyser, setup in containerised laboratories on deck. The nutrient system runs four channels of nutrients simultaneously; total-oxidised nitrogen, nitrite, silicate and phosphate. The instrument consisted of an auto-sampler, where a needle draws the sample into the analyser which is then split into the four channels. Each channel has its own set of reagents, where the stream of reagents and samples is pumped through the manifold to undergo treatment such as mixing and heating before entering a flow cell to be detected. The air-segmented flow promotes mixing of the sample and prevents contamination between samples. The reagents act to develop a colour, which is measured as an absorbance through a flow cell at a given wavelength. The Skalar Interface transmits all the data to the Skalar Flow Access software.

The reagents were made using high-purity chemicals, pre-weighed using a high-precision calibrated balance prior to the survey. They were stored in acid-washed polyethylene (PE) containers and mixed to final volume using Milli-Q water, see reagent compositions in [Table 1](#). Reagent storage time was in accordance with the Skalar methods, most can be stored for 1 week, the silicate ammonium heptamolybdate and oxalic acid reagents for 1 month, however fresh reagents were typically made every 2-3 days due to volume required on the survey.

Table 4.5.1. Details of sampling, instrument configurations (including sample and reagent tubing sizes) and reagent compositions for each nutrient from the Marine Institute, Ireland

<b>Sampling</b>	
Sample tubes	50ml falcon tubes
Primary sample	Within 12 hours of sampling
Replicate samples	Frozen immediately to -20°C
<b>Analysis</b>	
Auto-sampler size	300 cups
Auto-sampler cup	10ml
Baseline wash	Artificial Seawater
Analysis Lab	20°C
<b>Reagents (Chemicals g/L or ml/L)</b>	
Artificial Seawater	35g Sodium Chloride 0.5g Sodium hydrogen carbonate
<b>TOxN</b>	
Sample tubing size	1.02 ml/min
Colour Reagent	150ml Phosphoric Acid 10g Sulfanamide 0.5g N-(1-Naphthyl)ethylene diamine dihydrochloride (NEDD)
Reagent tubing	0.42 ml/min
Buffer Solution	80g Ammonium Chloride ~3ml Ammonia Solution 3ml Brij solution (surfactant)
Reagent tubing	0.8 ml/min
Cadmium column	Skalar 5358 activated Cd column
Copper Sulfate	
<b>Nitrite</b>	
Sample tubing size	0.42 ml/min
Colour Reagent	150ml Phosphoric Acid 10g Sulfanilamide 0.5g NEDD
Reagent tubing	0.23 ml/min
Wash Solution	3ml Brij solution
Reagent tubing	1.00 ml/min
<b>Silicate</b>	
Sample tubing size	1.40 ml/min
Sulfuric Acid	20ml Sulfuric Acid
Reagent tubing	0.23 ml/min
Ammonium	20g Ammonium heptamolybdate

Reagent tubing	0.42 ml/min
Oxalic Acid	44g Oxalic Acid
Reagent tubing	0.42 ml/min
L(+) Ascorbic Acid	40g Ascorbic Acid
Reagent tubing	0.32 ml/min
<b>Phosphate</b>	
Sample tubing	1.40 ml/min
Ammonium	0.23g Potassium antimony (III)
	70ml Sulfuric Acid
	6g Ammonium heptamolybdate
	2ml FFD6 (Skalar Surfactant)
Reagent tubing	0.42 ml/min
L(+) Ascorbic Acid	11g Ascorbic Acid
	60ml Acetone
	2ml FFD6
Reagent tubing	0.42 ml/min

*Determination of nitrite:* diazonium compound formed by diazotizing of sulfanilamide by nitrite in water under acidic conditions (due to phosphoric acid in the reagent) is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple colour, which is measured at 540 nm.

*Determination of silicate:* the sample is acidified with sulphuric acid and mixed with an ammonium heptamolybdate solution forming molybdosilicic acid. This acid is reduced with L(+)ascorbic acid to a blue dye, which is measured at 810 nm. Oxalic acid is added to avoid phosphate interference.

*Determination of phosphate:* ammonium heptamolybdate and potassium antimony(III) oxide tartrate react in an acidic medium (with sulphuric acid) with diluted solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex by L(+)ascorbic acid and is measured at 880 nm.

*Determination of total oxidised nitrogen (TOxN):* sample is buffered to pH 8.2, and passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple colour, which is measured at 540 nm.

The instrument was calibrated daily using a suite of calibration standards (see calibration range in [Table 4.5.2](#)). The primary standard for each nutrient was made up in the MI laboratory on shore just before the survey using a calibrated balance where the dry weight of each high purity chemical was diluted to 1L with Milli-Q water, as per Skalar methods. The primary stocks were stored in the fridge for the duration of the survey. Two batches of primary stocks were used to ensure no bias from an individual batch. Weekly secondary stocks were made from the primary stocks into 100ml PP flasks, which were stored in the fridge when not in use and could be used for one week. Daily standards were made from secondary stock into 100ml PP volumetric flasks.

Table 4.5.2. Concentrations of daily calibration standards in  $\mu\text{mol/l}$ . Standard 1 is the blank made of artificial seawater (sal 35). SSS are the system suitability standards that were analysed during a run as internal quality standards.

STD #	TOxN $\mu\text{mol/l}$	Silicate $\mu\text{mol/l}$	PO <sub>4</sub> $\mu\text{mol/l}$	NO <sub>2</sub> $\mu\text{mol/l}$
1	0	0	0	0
2	0.26	0.26	0.05	0.05
3	0.5	0.5	0.15	0.15
4	2.5	2.5	0.25	0.25
5	5	5	0.5	0.5
6	10	10	1	1
7	15	15	1.5	1.5
8	22.5	22.5	2.25	2.25
9	30	30		
10	40	40		
11	50	50		
12		60		
SSS	10	10	1	1
Drift	10	10	1	1

Secondary and daily calibration standards were made using calibrated fixed volume pipettes. The adjustable pipettes were tested prior to the start of the survey to ensure that the volumes delivered were accurate. The secondary stocks were made using Milli-Q water, while the daily standards were made using artificial seawater (ASW) with salinity of 35. Concentrations of daily standards for each system are in Table 2, where first order calibration was used and  $R^2 > 0.99$  was deemed acceptable, as per Skalar methods.

ASW was used as the baseline wash for all channels, at a similar salinity to the expected samples (salinity 35). Batches of sodium chloride used were tested prior to the survey to ensure no contamination with any of the nutrients. Calibration was not forced through zero, and baseline wash was run as the first standard.

#### 4.5.2.3. *Quality Control*

The Certified Reference Materials (CRMs) used on the survey were supplied from KANSO (Aoyama et al., 2016; Aoyama et al., 2007) and were analysed at the beginning and end of every run and monitored daily on quality control charts. Two batches were used (Batch CD and Batch BW) to cover the full range of nutrients expected on the survey, a CD and BW were analysed at the beginning of a run and another CD at the end of the run.

The silicate BW CRM (61.47  $\mu\text{mol/l}$ ) is higher than highest standard (60  $\mu\text{mol/l}$ ) used by both groups and is therefore only used as indicative QC for high levels of silicate.

#### 4.5.3. *Problems encountered.*

Persistent but untraced nitrite contamination resulted in CRM failures throughout the survey.

Ships vibrations were a particular problem for the MI containerised laboratory at its location on deck (not previously encountered including on transit leg). Communication problems between the interface and the laptop were encountered initially due to a faulty UPS. Later communication problems were considered to be a result of vibration from the engine at higher

revs or a build-up of nutrient data files in the flow access working folder. This did not compromise data quality since analysis ceased when there was a communication issue.

The above issues may have contributed to higher variability for TOxN and silicate was evident for the MI testing compared with routine shore-based method performance.

#### 4.5.4. Interim results

Interim summary results are shown below. Some minor data corrections will be expected following comprehensive QC checks.

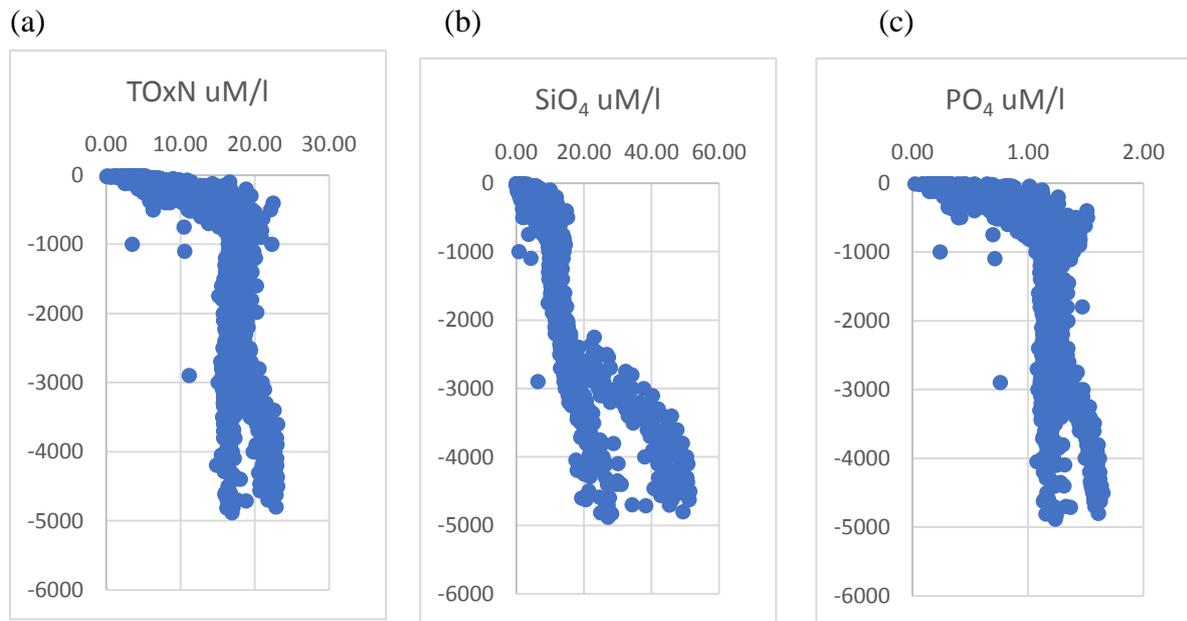


Figure 4.5.1. Vertical distribution of (a) TOxN, (b) SiO<sub>4</sub> and (c) PO<sub>4</sub> observed during CE17007 (preliminary shipboard data).

#### 4.5.5. Inter-comparison

A comprehensive analysis of the results of the inter-comparison has not been carried out. A brief initial comparison of results from 12 stations showed a good comparison in silicate and phosphate profiles (despite noise in phosphate data from the Dalhousie system), and while initially there appeared to be an offset TOxN data where the MI TOxN was lower in the deeper stations – after including the higher TOxN standards in the MI calibration (matching that of Canada), the results were comparable. The calibration standard concentrations for the MI system are given below [Table 5.4.3a](#), while the calibration standards for the Dalhousie system are given in [Table 5.4.3b](#). The MI uses an artificial seawater baseline matrix, while the Dalhousie system uses deionised water.

Samples from profiles of twelve stations were carried out by the team from Dalhousie University, Halifax (Dal) using similar but not identical methodology and a Skalar SAN++ CFA system,

Table 4.5.3. Calibration standard concentrations ( $\mu\text{M/l}$ ) for (a) the MI Skalar system and (b) the Dalhousie Skalar system.

<b>TOxN</b>	<b>NO<sub>2</sub></b>	<b>SiO<sub>4</sub></b>	<b>PO<sub>4</sub></b>	<b>TOxN</b>	<b>NO<sub>2</sub></b>	<b>SiO<sub>4</sub></b>	<b>PO<sub>4</sub></b>
0	0	0	0	0	0	0	0
0.26	0.05	0.26	0.05	10	1	10	1
0.5	0.15	0.5	0.15	20	2	20	2
2.5	0.25	2.5	0.25	30	3	30	3
5	0.5	5	0.5	40	4	40	4
10	1	10	1	50	5	50	5
15	1.5	15	1.5			60	
22.5	2.25	22.5	2.25				
30		30					
40		40					
50		50					
		60					

Slight differences between the two systems included

- Differences in some reagents
- Differences in some tubing sizes
- Differences in initial concentrations of some standards (Table 4.5.3).
- The MI uses an artificial seawater baseline matrix, while the Dalhousie system uses deionised water.

A comprehensive analysis of the results of the inter-comparison has not yet been completed. A brief preliminary comparison of results showed a good comparison in silicate and phosphate profiles, and while initially there appeared to be an offset in TOxN data where the MI TOxN was lower in the deeper stations – after including the higher TOxN standards in the MI calibration (matching that of Canada), the results were comparable.

It is intended to work up and publish the details and results of the inter-comparison.

#### 4.6. Carbon System Parameters

(Ellie Morris, Richard Sims, Lachlan Riehl and Riccardo Arruda – shipboard participants; Ute Schuster – Principal Investigator)

The carbon parameter analytical equipment was set up pre-cruise in a seagoing laboratory container belonging to the University of Exeter, Devon, UK. Discrete CTD samples were analysed for total inorganic carbon (DIC) and total alkalinity (TA).

##### *4.6.1. Sampling and Preparation for Analysis*

Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) measurements were performed on seawater samples collected from 10L Niskin bottles deployed on a 24 Niskin CTD rosette. 500ml glass bottles were used to sample the Niskin bottles triggered at the greatest and shallowest depths of each stations, in addition to two depths chosen at random, allowing for in bottle replicate measurements to be made. These are used during analysis to indicate the precision of the measurements made by the VINDTA machine at each station. All remaining Niskin bottles were sampled using 250ml glass bottles. Following Standard Operating Procedure (SOP) #01 (Dickson et al., 2007) the glass bottles were rinsed from the Niskin twice and then a Tygon sampling tube was inserted into the bottle, which was allowed to fill and then overflow for the same amount of time it took the bottle to fill. A glass stopper was then placed into the bottle and immediately after the samples were collected they were ‘fixed’ to prevent the growth of any organic matter. The samples were fixed by removing 250 $\mu$ L of seawater from each 250mL sample and adding 50 $\mu$ L of saturated mercuric chloride. Quantities were doubled for the 500mL samples. Once poisoned, samples were stored in foam-lined crates in the wet laboratory of the ship until analysis, at which point they were acclimatized to the 25°C air temperature of the laboratory container prior to resting in a 25°C water bath.

Due to inclement weather, the 24 Niskin CTD rosette could not be deployed at stations 15, 16, 17, 18 and 19 and thus no samples could be analysed. Stations 30, 32, 34, 36 and 38 were also missed in order to make up for lost time associated with weather and malfunctions with the CTD tether.

##### *4.6.2. Dissolved Inorganic Carbon Analysis*

All measurements were completed on two Versatile INstrument for the Determination of Titration Alkalinity (VINDTA, version 3C, SN#064 and #065, Marianda, Germany, Mintrop, 2004) each connected to a coulometer (SN135015020 and SN135015019 respectively). Water samples were first analysed for Dissolved Inorganic Carbon (DIC). An excess of phosphoric acid (1M, 8.5%) was added to a calibrated volume of seawater sample to convert all inorganic dissolved carbon to CO<sub>2</sub>. This CO<sub>2</sub> was then transported to the coulometer cell by oxygen-free-nitrogen gas (OfN), which was filtered through soda lime to remove any residual traces of CO<sub>2</sub> prior to coming in contact with the recently converted CO<sub>2</sub>. In the cell, all CO<sub>2</sub> is quantitatively absorbed to form an acid that is subsequently titrated via coulometry. See Dickson et al., (2007) SOP #02 for more detailed information.

The DIC pipette is surrounded by a water jacket to maintain the same temperature as the samples (25°C). Coulometer counts were calibrated against replicate analyses taken from the 500mL bottles and Certified Reference Material (CRM batch 163, certified at 2039.49  $\pm$  0.73 for DIC (Prof A Dickson, Scripps Institute of Oceanography, San Diego, USA)), which were run immediately before and after the coulometer cell was changed, in addition to

halfway between the first and last CRMs run on each cell. The coulometer cell was replaced every 24 hours with the cell and both lid IDs recorded for comparison purposes. The coulometer cells, anode and cathode solution used were purchased from Cobalt Scientific (Cobalt Scientific, Bensenville, Illinois, United States).

Initial DIC calibration was done during the cruise for each instrument by correcting all sample data by the difference between the mean of all CRMs. Post-cruise data quality control will include the calibration of the DIC readings for each coulometer cell used during CE17007, identification and removal of errors/outliers and accounting for instrument drift.

#### *4.6.3. Titration Alkalinity Analysis*

Total Alkalinity was measured by potentiometric titration using the same VINDTA machines as for DIC analysis. These systems use a highly precise Metrohm Titrino for acid addition, an ORION-Ross pH electrode, a Metrohm reference electrode and an auxiliary electrode. Similarly to the DIC analysis, the pipette and analysis cell were kept at the same temperature as the samples (25°C) by a water jacket. Hydrochloric acid (0.1M) made to the ionic strength of seawater was used as the alkalinity titrant as described in SOP#3B (Dickson et al., 2007). Alkalinity values were calibrated using replicate analyses taken from the 500mL bottles and CRM batch 163 (certified at  $2215.53 \text{ kg}^{-1} \pm 0.56$  for TA). See Dickson et al., (2007) SOP #03 for more detailed information. Post-cruise data corrections will include a recalculation of alkalinities using CTD temperature, salinity and nutrients, and also incorporate a recalibration of the alkalinity pipettes' volume and temperature sensors. Post-cruise Quality Control will identify and remove outliers and account for drift in the instruments' alkalinity measurements taken over the course of the cruise.

#### *4.6.4. Sample Analysis Strategy and Ship-board Instrument Maintenance.*

VINDTA #064 was connected to coulometer SN:135015020 and Metrohm Titrino SN:01270505. DIC pipette volume was 17.62ml\* and alkalinity pipette volume was 105.00ml as calibrated following SOP#12 (Dickson et al., 2007). On 4<sup>th</sup> May Metrohm electrode SN00562703 was swapped for new electrode SN00753480 as the glass tip was getting stuck regularly. On May 4<sup>th</sup>, analysis was changed from dual to single sample analysis, due to an irregularity between the two sample lines resulting in less precision between duplicates. From this point on, samples were analysed using only one sampling line, line 1.

VINDTA #065 was connected to coulometer SN:135015019 and Metrohm Titrino SN:17850010. DIC pipette volume was 111.05ml and alkalinity pipette volume was 17.96ml, as calibrated following SOP#12 (Dickson et al., 2007). The touch screen of coulometer SN:135015019 attached to VINDTA #065 was cracked on May 14<sup>th</sup> 2017 while analysing samples from station 31. It was kept functioning until the cell change on May 19<sup>th</sup> 2017 at approximately 03:00hrs, midway through station 52, after which the touch screen was no longer responsive and the cell could not be changed. With no spare coulometers or alternative control mechanisms to run the damaged coulometer, we were forced to shut down the VINDTA #064 machine on May 19<sup>th</sup> at approximately 11:00hrs. Limited time remaining on the vessel and only one machine remaining for analysis resulted in an adjusted sample analysis pattern for the remaining stations, as outlined below:

- Stations 1 – 52: All depths (24 per station) sampled and analysed.

- Stations 51, 53, 55, 57, 59, 61: 18 samples analysed per station to match depths taken by Chlorofluorocarbons (CFCs) and  $^{13}\text{C}$ . 6 remaining unanalysed samples stored and taken for analysis in laboratory at University of Exeter.
- Stations 52, 54, 56, 58, 60, 62, 64: sampled, fixed and stored for analysis in lab at University of Exeter.
- Station 63, 65 and 67: all depths sampled and analysed (shallow stations).

## References

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## 4.7. $\delta^{13}\text{C}$ Dissolved Inorganic Carbon (DIC)

(Lin Cheng, Claire Normadeau)

The Canadian team oversaw analysing the stable isotopes of carbon ( $\delta^{13}\text{C}$ ) on dissolved inorganic carbon (DIC) during this GO-SHIP scientific survey. To our knowledge, this is the first time that this measurement is being conducted at sea. Normally, the samples are collected and brought back to the laboratory for measurements on an isotope ratio mass spectrometer (IRMS). This time, an Apollo DIC analyzer coupled to a carbon dioxide Picarro cavity ring down spectrometer (CRDS) were taken on board the vessel, providing a more compact instrumentation that can be utilized at sea even in rough conditions. Overall the system behaved well and we were able to collect valuable data. The main objective of this project was to evaluate the system's precision and accuracy and to test this new instrument at sea.

### 4.7.1. *Sampling*

Samples were collected in 160 ml serum glass bottles and crimped with flat butyl/Teflon septa and aluminum seals. Media borosilicate glass bottles (250 ml) with plastic screw caps were also used. An isoversinic/viton tubing was connected to the Niskin bottles and the sample bottles were rinsed three times with the seawater samples. The bottles were filled gently from the bottom using the tube which extended from the Niskin drain to the bottom of the glass sample bottle. The bottles were overflowed by at least half their volume and they were crimped or screwed capped right away. After all samples were collected, they were brought back to the container where they were poisoned with 100  $\mu\text{l}$  of saturated mercury chloride solution (250  $\mu\text{l}$  of  $\text{HgCl}_2$  for the 250 ml bottles). To account for water expansion as samples warm up, 1.6 ml of water sample was taken out using a needle and syringe before adding the mercury chloride. A needle and syringe filled with sodium hydroxide on support was inserted through the septa while removing the water to prevent  $\text{CO}_2$  from entering the sample bottle. For the 250 ml screw cap bottles, they were simply opened, 2.5 ml sample was removed, mercury chloride was added and the bottle were re-capped. Samples were kept at least 30 min in a water bath set at  $21^\circ\text{C}$  before analysis.

Due to a rather long analysis time (30 min), only the odd station numbers were sampled (except for a few even station numbers at the beginning of the survey) and 14 depths were sampled per cast. Duplicate samples were taken at one depth on most casts.

### 4.7.2. *Instrumentation*

The analyses were conducted on an Apollo SciTech DIC- $\delta^{13}\text{C}$  Analyzer (model AS-D1) connected to a Picarro G2201i cavity ring down spectrometer for stable isotopes of carbon dioxide and methane. The Apollo analyzer consists of an acidification chamber cooled at  $4^\circ\text{C}$ , where 1 ml of 5% phosphoric acid is added to 3.8 ml of sample. The sample is then purged for approximately 10 min and the carbon dioxide is sent to the Picarro analyzer via an ultra-pure compressed air carrier gas flow of  $60\text{ ml}\cdot\text{min}^{-1}$ . For measurement with the serum and septa bottles, one needle connected to the Apollo analyzer with tygon tubing was inserted through the septum of the sample bottle. A carbon trap made of sodium hydroxide on support in a plastic syringe was also poked through the septum to prevent any  $\text{CO}_2$  from entering the bottle during the analysis. For measurement with screw cap bottles, the cap was removed and replaced with a similar cap in which an opening had been made for the sample tubing. Multiple measurements were made per sample bottle until a standard deviation of at least 0.12 was reached on dissolved inorganic carbon concentration.

#### *4.7.3. Preparation of standards and phosphoric acid*

The 5% phosphoric reagent acid was diluted from 85% o-phosphoric acid. Pre-combusted sodium chloride was added into the acid to obtain a 10% NaCl solution. This solution was dispensed in many 250 ml serum bottles, purged by ultra-pure helium gas for 30 mins, and then crimped.

All standards were prepared in 160 ml serum bottles. Three sets of standards for DIC concentration (1.8mM, 2.1mM, 2.4mM) were made by dissolving different quantities of pre-combusted sodium bicarbonate powder into helium purged MilliQ water. Three sets of  $\delta^{13}\text{C}$ -DIC standards were made by dissolving sodium carbonate and sodium bicarbonate powder with different  $\delta^{13}\text{C}$  values (pre-determined by an Elementar EA-IRMS) into pre-purged MilliQ water.

#### *4.7.4. Quality control*

Once a week, one calibration curve for d13C and DIC concentration were done and every day one CRM (batch 157) and one d13C standard was measured to check the stability of the measurements. Preliminary results show precisions of 0.06 permil on d13C and 6  $\mu\text{mol.kg}^{-1}$  on all CRMs run on the survey. Replicate injections of seawater samples had an average precision of 0.03 permil for d13C and an average standard deviation of 1.4  $\mu\text{M.kg}^{-1}$  on DIC.

Deep water samples from the West European Basin were taken and will be compared to previous studies providing cross-over analysis of the data.

The opportunity was taken to collect multiple samples from one same Niskin bottle at station 58 and 60 in the very deep waters located in the West European Basin. These samples will be used in an intercomparison round-robin activity that will hopefully take place in 2017. It will be a unique opportunity to have different laboratories measure and compare results on dissolved inorganic carbon concentrations as well as d13C.

#### *4.7.5. Problems*

The gas carrier air flow was set at 60  $\text{ml.min}^{-1}$  but had to be increased to 80  $\text{ml.min}^{-1}$  half way throughout the survey. For unknown reasons, the DIC peak shape changed and the desired precision could not be attained while using a 60  $\text{ml.min}^{-1}$  flow. All flows and valves were checked and were behaving perfectly, no leak was detected, so the source of the peak change was unknown. To be able to continue analysing samples, it was decided to increase the carrier flow to 80  $\text{ml.min}^{-1}$ . This improved peak shape and the desired precision was reached.

## 5. Preliminary Results – Underway measurements

### 5.1. Meteorological Data

Data from the shipboard system on the Celtic Explorer includes observations and measurements of meteorological (e.g. air temperature, atmospheric pressure, relative humidity, wind speed and direction) at 10m above sea level at a per minute rate. This data is available from the Marine Institute.

### 5.2. Thermosalinograph Data

Data from the shipboard system on the Celtic Explorer includes observations and measurements of oceanographic parameters (e.g. sea surface temperature/salinity) at approximately 3m below the surface. This data is available from the Marine Institute.

### 5.3. Shipboard ADCP

(Postprocessing of data: Christian Mohn)

(Shipboard ADCP group: Caroline Cusack, Peter Croot and Marshall Swartz)

#### 5.3.1. Introduction

Underway current and backscatter measurements were performed continuously along the cruise track using the ship's Acoustic Doppler Current Profiler (SADCP). The system used was a 75 kHz RDI Ocean Surveyor (OS75) mounted in the ship's hull. RDI's VMDas software was employed for SADCP setup and data collection. The overall recording period was from the 28-April-2017 (20:48) to 21-May-2017. The SADCP was run in broadband (BB) mode. The built-in transducer misalignment angle relative to the ship's keel was 45°. The number of depth bins was set to 60 with a bin size of 16 meters and a blanking distance of 8 meters. The transducer depth was 9 meters. Single ping bottom tracking was enabled during the whole cruise.

#### 5.3.2. Data Processing

Before data processing, single ping ENX velocity profiles were time-averaged to 5 min ensembles for reducing data noise, but retaining a sufficient horizontal along-track resolution. ENX files are single-ping data including navigation and are transformed into Earth coordinates and screened for error velocity and false targets. The Common Oceanographic Data Access System (CODAS) was used for data processing. CODAS is an SADCP data post-processing toolbox from the University of Hawaii (Firing et al. 1995; [http://currents.soest.hawaii.edu/docs/adcp\\_doc/index.html](http://currents.soest.hawaii.edu/docs/adcp_doc/index.html)). Post-processing was conducted following Go-ship recommendations (Firing and Hummon 2010). Water track calibration was conducted to obtain best estimates for the transducer amplitude scale factor and transducer orientation relative to the ship's heading. Bins 5–20 (93–333 m depth range) were taken as the oceanic reference layer, thus avoiding short-term variability caused by ship-induced turbulence and weather events. The correction factors for transducer orientation (phase angle) and amplitude from the water track calibration were 6.76° and 1.007, respectively. An additional bottom track calibration was conducted and largely confirmed the water track calibration values (phase angle 6.78°, amplitude 1.035). The next processing step included quality control of individual ensemble profiles and bins. The aim was to retain velocity profiles/bins not affected by ship-induced turbulence, object interference and bottom

reflection. Finally, the navigation calculation of the ship's position and speed was carried out to obtain best estimates for ship velocity and to calculate absolute current velocities.

### 5.3.3. Data set and results

The final dataset includes 5-minute ensemble averaged profiles of the 3D variables  $u$  (East-West velocity component in m/s),  $v$  (North-South velocity component in m/s, raw echo amplitude (raw counts) and percent good value (quality indicator in percent). Figure 1 shows the fully processed variables  $u$  (m/s),  $v$  (m/s) and echo amplitude (raw counts). Figure 2 (upper panel) shows vector plots of CE17007 measured SACDP currents in 56 m water depth (first available depth level). Only every 4th vector is shown. Velocity vectors are shown in light gray. The superimposed coloured contour plot shows the geostrophic surface current speed (in m/s) from the AVISO satellite altimetry (0.25 degree spatial resolution). Daily AVISO data were extracted for the cruise period (end of April to end of May 2017) and the time-average is presented here. The lower panel shows the AVISO geostrophic currents (m/s) as a vector plot. The blue line indicates the SADCPC cruise track. There is reasonable agreement between satellite data and SADCPC data in most areas.

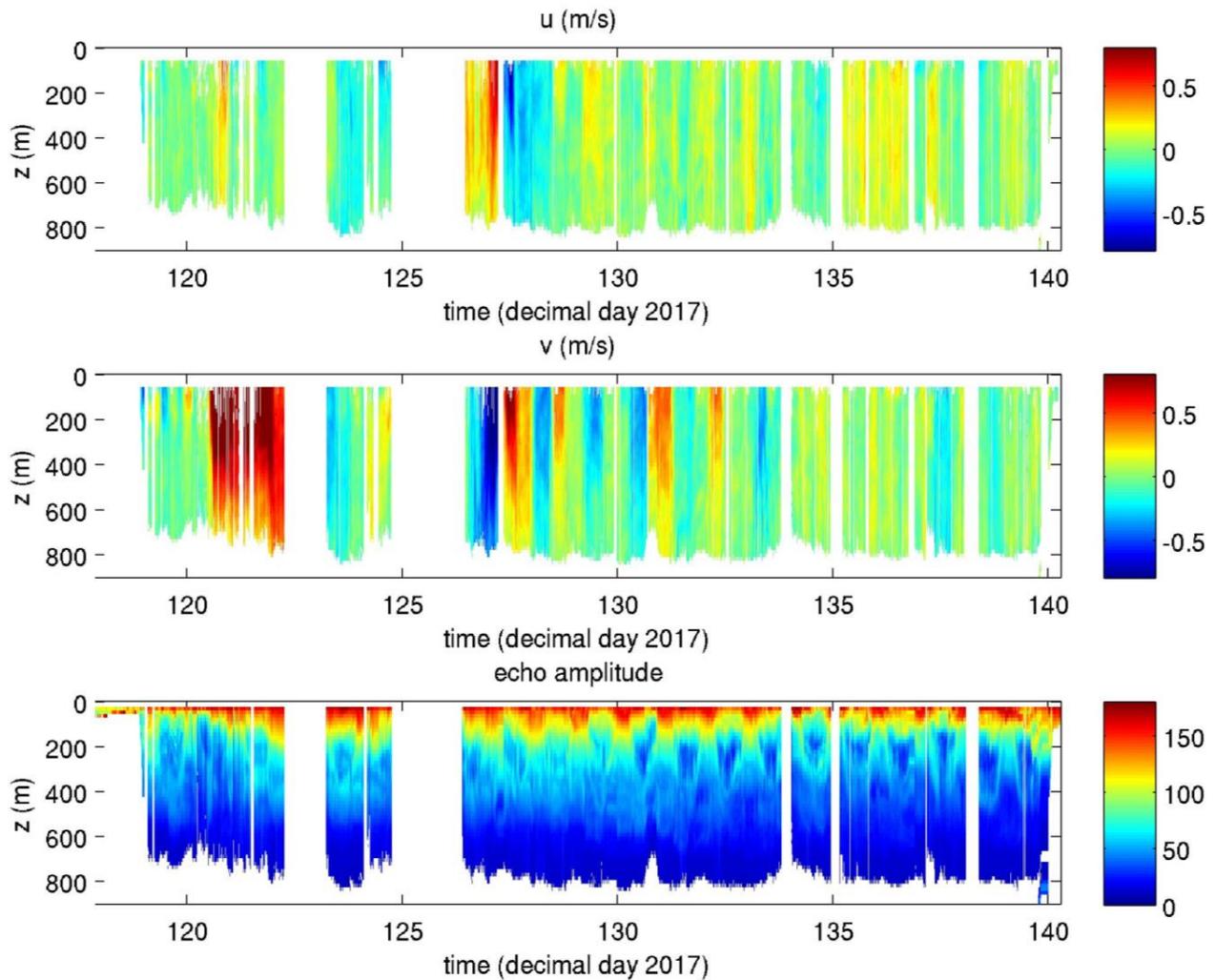


Figure 5.3.1. Velocity components  $u$  (upper panel),  $v$  (middle panel) and echo amplitude (raw counts) vs water depth (m) plotted along the cruise track. White areas indicated data gaps.

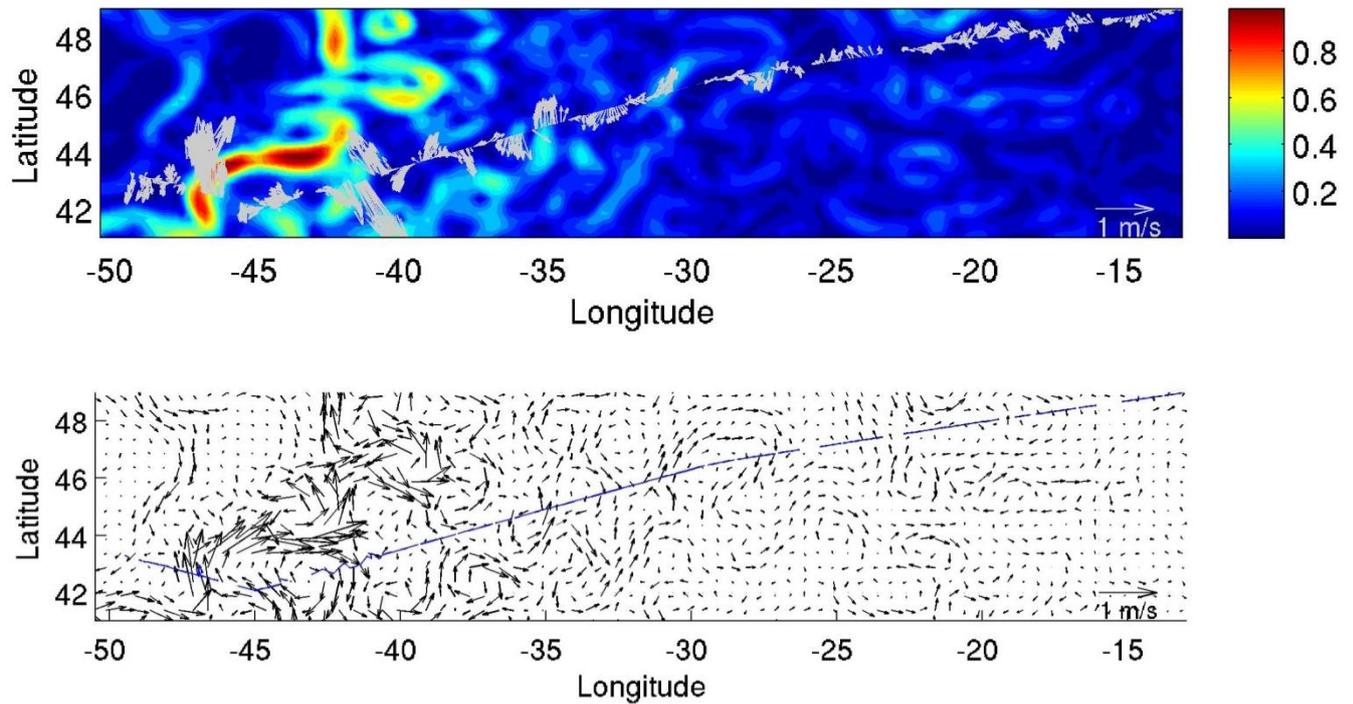


Figure 5.3.2. Upper panel: Vector plot of SADCP currents in 56 m water depth. Only every 4th vector is shown. Coloured contours show geostrophic surface current speed (in m/s) from the AVISO satellite altimetry (0.25 degree spatial resolution). Lower panel: Vector plot of AVISO geostrophic currents (blue line indicates SADCP cruise track).

#### References

- Firing E, Ranada J, Caldwell S (1995) Processing ADCP data with the CODAS Software System, Version 3.1. University of Hawaii, Honolulu, HI, USA.
- Firing, E., and J. M. Hummon (2010), Ship-mounted acoustic Doppler current profilers, in The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines, ICPO Publication Series Number 134, edited by E. M. Hood, C. L. Sabine, and B. M. Sloyan, International CLIVAR Project Office (ICPO), Southampton, U. K. (Available online at [http://www.go-ship.org/Manual/Firing\\_SADCP.pdf](http://www.go-ship.org/Manual/Firing_SADCP.pdf).)

## 5.4. Underway pCO<sub>2</sub> measurements (GO-8050)

(Margot Cronin, Anthony English)

### 5.4.1. Objectives

1. To carry out underway analysis of pCO<sub>2</sub> in surface (-6 m) seawater samples.
2. To carry out an on-board inter-comparison on different systems used by Marine Institute and Dalhousie University (see report from Ricardo Arruda)

### 5.4.2. Methodology

#### 5.4.2.1. Equipment

Underway measurements were carried out using a General Oceanics GO-8050 Automated Flowing pCO<sub>2</sub> measuring system (SN L12/21804/185). The pCO<sub>2</sub> system consists of a wet box (containing a shower-head equilibrator, pumps, chiller unit); a dry box, containing a LICOR™ non-dispersive infrared (IR) analyzer (LI-7000 SN IRF4-1263) through which the equilibrator headspace is circulated for measurement of xCO<sub>2</sub> and xH<sub>2</sub>O and a deck box (barometer and air intake).

Water intake was from a depth of 6m at the bow, a distance of approximately 45m from the instrument. Measurements of temperature and salinity at the intake were made by Seabird SBE 21, SN 3314 (to 4 May) and SN 3315 (4 May onwards).

Meteorological information was provided by Batos station. Air intake was positioned approximately 15m above sea level on a mast on the foredeck.

GPS information was supplied by the ship's GPS system.

#### 5.4.2.2. Instrument configuration

The GO-8050 was configured according to manufacturer's recommendations in (below):

Parameter	Range
<b>H<sub>2</sub>O flow</b>	2.7 – 3.0 l/min
<b>LICOR flow</b>	ATM 80 - 100 ml/min EQU 70 – 100 ml/min STD ~60ml/min
<b>CO<sub>2</sub> (μmol)</b>	ATM 300-450 μmol/min EQU 300 – 450 μmol/min STD within 1% of value
<b>Vent flow</b>	+/- 15ml/l
<b>H<sub>2</sub>O (mmol/m)</b>	<4 mmol/m
<b>EQU pump speed</b>	~ 85
<b>Condenser temperature</b>	5°C
<b>ATM &amp; EQU cond</b>	H <sub>2</sub> O > 9

Table 5.4.1 GO-8050 configuration for A02 survey (according to manufacturer's recommendation).

#### 5.4.2.3. System Overview (from General Oceanics manual)

Seawater is circulated through a closed chamber (the main equilibrator) at a flow rate of about 2 L/min and a pressure around 4 psi. The water enters the equilibrator via a spiral nozzle, creating a conical spray, which enhances the CO<sub>2</sub> gas exchanges between the water and the overlying air (headspace) in the equilibrator. The water is then gravity drained out of the system. An “inverted cup” system with a siphon break in the middle of the equilibrator effectively isolates the headspace gas from the outside air and greatly minimizes any gas loss due to air entrainment from the water flow. A smaller secondary equilibrator, where seawater flows at about 0.5 L/min and which is opened to the ambient air, is the replacement source for the minimal air loss that might still occur in the main equilibrator.

The headspace gas is circulated through the system and back to the equilibrator with a pump (headspace pump) at about 100 mL/min. It is first dried by going through a Peltier cooling block (the Condenser) operating at about 5 °C, then a Permapure Nafion tube. The dry gas is then sent to the Infrared LICOR analyzer (the LICOR) where its CO<sub>2</sub> and H<sub>2</sub>O mole fractions (xCO<sub>2</sub> and xH<sub>2</sub>O) are measured.

Atmospheric air is also being measured alternatively by the system. A dedicated pump (ATM pump) constantly draws outside air, a portion of which is dried in a second channel of the condenser and flushes the content of a small reservoir (the ballast), a short length of PVC pipe open to the ambient air. The dry ballast atmospheric air is circulated through the LICOR for analysis. In addition, the ballast air is also used for the countercurrent flow in the outer chamber of the Permapure Nafion® dryers and is pulled by a dedicated pump (the vacuum pump).

An 8-port 16-position VALCO multiposition valve (the VALCO valve) selects the gas being circulated through the LICOR. A set of CO<sub>2</sub> gas standards (supplied by the user) is measured regularly during normal operations in order to calibrate and correct for any drift of the LICOR.

#### 5.4.2.4. Samples:

Run sequence was as follow:

Step	Type	No. repetitions
0	zero	1
1	span	1
2	STD1	1
3	STD4	1
4	STD2	1
5	STD3	1
6	ATM	5
7	EQU	50
8	LOOP2	4
9	FILTER	1
10	STD1	1
11	STD4	1
12	STD2	1
13	STD3	1
14	END	1

Table 5.4.2 GO-8050 run sequence for A02 survey

Seawater samples from the ship's underway (non-toxic) system were passed through the shower-head equilibrator and analysed by LICOR 7000 NDIR approximately every 2.5 minutes.

5.4.2.5. Calibration Standards

Calibration standards were analysed for calibration at Mace Head Atmospheric Station using CRDS, Picarro G2301. Results as follows in Table 5.4.3.

CO2 (nominal)	200ppm	400ppm	600ppm	405ppm (408.83ppm certified)
CO2 (WMO-X2007)	198.29 ± 0.01	399.28 ± 0.01	606.52 ± 0.01	408.77 ± 0.01
CH4 (WMO-W2004A)	15.53 ± 0.02	25.29 ± 0.09	16.07 ± 0.09	1920.09 ± 0.04
port #	10	11	12	9
Analysis period	170216 1200 to 170217	170216 1200 to	170216 1200 to 170217	170216 1200 to 170217
Air Products serial #	<b>002047</b>	<b>089492</b>	<b>1108543</b>	
Luxfer serial #	2911A	DL1231	D048791	<b>CB12076</b>
Air Products PR code	349640	324946	349639	
Type/Manufacturer	Al Luxfer	Al Luxfer	Al Luxfer	N150 Al Luxfer
Size	50L	50L	50L	29.5L
Valve	BS3 brass	BS3 brass	BS3 brass	CGA590 brass
Fill date	09 Jan 2017	27 Dec 2016	09 Jan 2017	January 2017
Location	Worcester, UK	Keumiee, Belgium	Worcester, UK	

Table 5.4.3 Calibration results from CO<sub>2</sub> standards.

5.4.3.QA

Standards were run approximately eight times per day. Summary statistics are listed below.

	Actual value (ppm)	Mean measured value (uM)	Median measured value (uM)	SD	No. of measurements
Std1	0.00	-0.34	-0.12	0.58	176
Std2	198.29 +/- 0.01	199.38	199.58	0.78	172
Std3	399.28 +/- 0.01	398.83	399.17	0.97	172
Std4	606.52 +/- 0.01	606.04	606.41	1.11	174

Table 5.4.4 Summary statistics for calibration standards during A02 survey.

#### 5.4.4. Problems Encountered

1. On the transit journey to St John's, cold Labrador seawater ( $-0.7^{\circ}\text{C}$ ) and cold air ( $0^{\circ}\text{C}$ ) caused the chiller in the instrument to freeze, leading to damage of the fan. The instrument was shut down to allow installation of a replacement chiller, and not restarted again until beyond the colder Labrador waters on route to the survey line.
2. An intermittent electrical fault in a plug board caused sporadic shutdown over a period of several days leading to data gaps. Removal of the surge protector in the plug board resolved the fault.
3. The data feed from the SBE 21 crashed on four occasions. It was not possible to recover the data for some of the down time.
4. The FTP file upload process interrupted the writing of data on at least three occasions, leading to some data gaps.

#### 5.4.5. Interim results

xCO<sub>2</sub> results were pressure corrected and then temperature corrected (according to the formula derived by Takahashi et al, 1993 cited by Pierrot et al, 2009). Figure 5.4.1 below shows the pressure and sea surface temperature corrected pCO<sub>2</sub> sampled by date from the beginning of the survey.

Interim results for the cruise track are illustrated below. Following data reduction, the data from this instrument will be submitted to SOCAT.

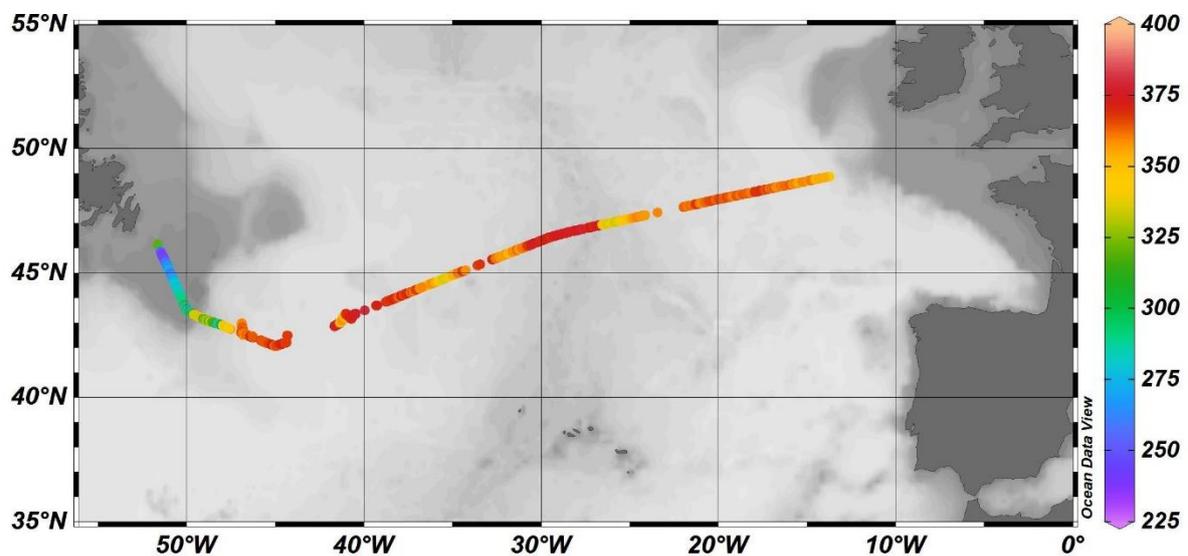


Figure 5.4.1. Preliminary (raw) surface pCO<sub>2</sub> (umol/mol) measured on A02 line, corrected for LICOR pressure and sea surface temperature.

#### References:

Pierrot, D., Neill, C., Sullivan, K., Castle, R., Wanninkhof, R., Lüger, H., Johannessen, T., Olsen, A., Feely R.A., Cosca, C.E., 2008. Recommendations for Autonomous Underway pCO<sub>2</sub> Measuring Systems and Data Reduction Routines. Deep-Sea Research Part II.

General Oceanics (2016) Instruction Manual, Model 8050, Automated Flowing pCO<sub>2</sub> Measuring System. xCO<sub>2</sub> results were pressure corrected and then temperature corrected (according to the formula derived by Takahashi et al, 1993 cited by Pierrot et al, 2009). [Figure 5.5.2](#) below shows the corrected pCO<sub>2</sub> SST sampled by date from the beginning of the survey.

## 5.5. Report of underway data (GO-SHIP Celtic Explorer – 2<sup>nd</sup> Leg) (Ricardo Monteiro da Silva)

### 5.5.1. Underway systems

In this Report of underway surface data in the Celtic Explorer we compare 3 underway systems (4 pCO<sub>2</sub> sensors). The systems are: SubCtech with sensors for pCO<sub>2</sub>, temperature and salinity; VOS (Aanderaa) with sensors for pCO<sub>2</sub> (Prooceanus), CO<sub>2</sub> optode, O<sub>2</sub> optode, temperature, conductivity and Chlorophyll; And General Oceanics (GO) with sensors for pCO<sub>2</sub> (air and water), temperature and salinity.

### 5.5.2. Temperature sensors

**Table 5.5.1: Underway temperature sensors**

Location	Model	Serial n
Intake	SBE38	Part n 90299.5, s/n: 3848425-0375
Before GO	SBE21	Part n 90399, s/n: 2148425-3315
SubCTech (outside)	SBE38	38.1110, s/n: 38-0799
SubCTech (inside)	SBE45	Part n ° 45.1, s/n: 45-0459
VOS	Aanderaa	??

### 5.5.3. Reference Gases

#### SubCtech

- Calibration with reference gases twice a day.
- (1) Praxair - 531 ppm
- (2) Praxair - 653 ppm
- Cross-referenced with NOAA - 447.38 ppm

#### General Oceanics

- Nitrogen Zero Reference
- STD2 - 198.29 ppm
- STD3 - 399.28 ppm
- STD4 - 606.52 ppm

#### Length from intake

From intake to Wetlab: 30.74m. (Pump flow: 6.3m<sup>3</sup> h<sup>-1</sup>).

#### 5.5.4. $pCO_2$

First comparison of  $pCO_2$  data, the gas pressure correction in Fig2 was made multiplying the raw data (in ppm) by the Licor gas pressure. Also, for SubCtech the pressure difference between the membrane and inside Licor needs to be added (Around 15 mbar).

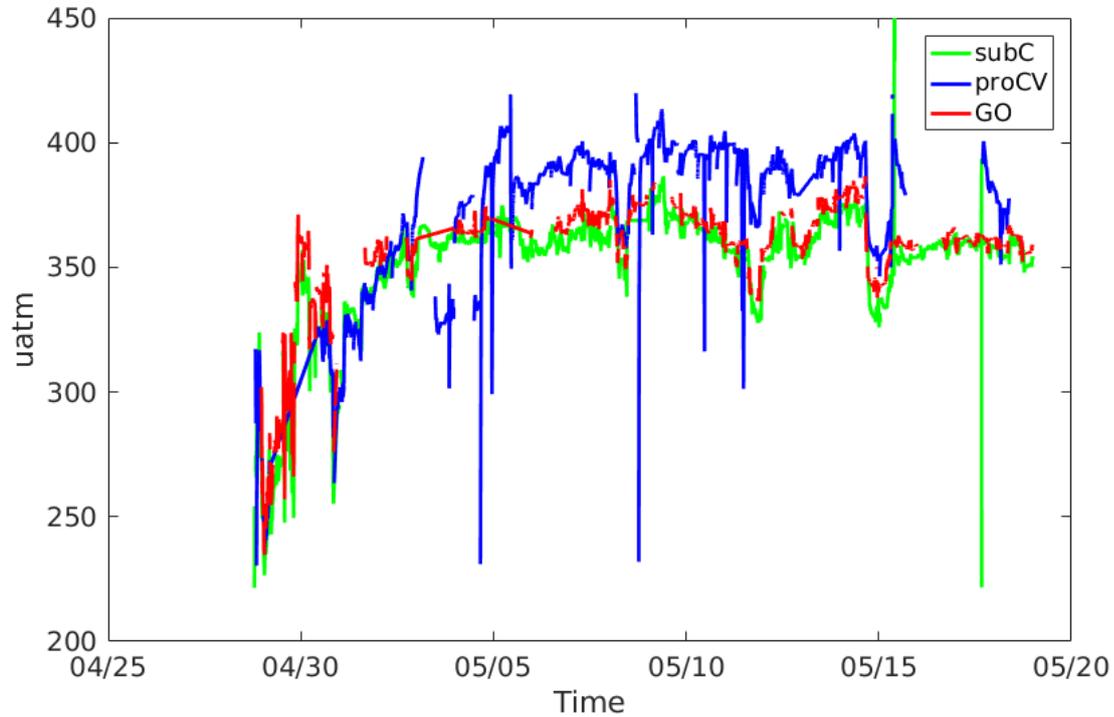


Figure 5.5.1 Comparison of  $pCO_2$  sensors showing raw data

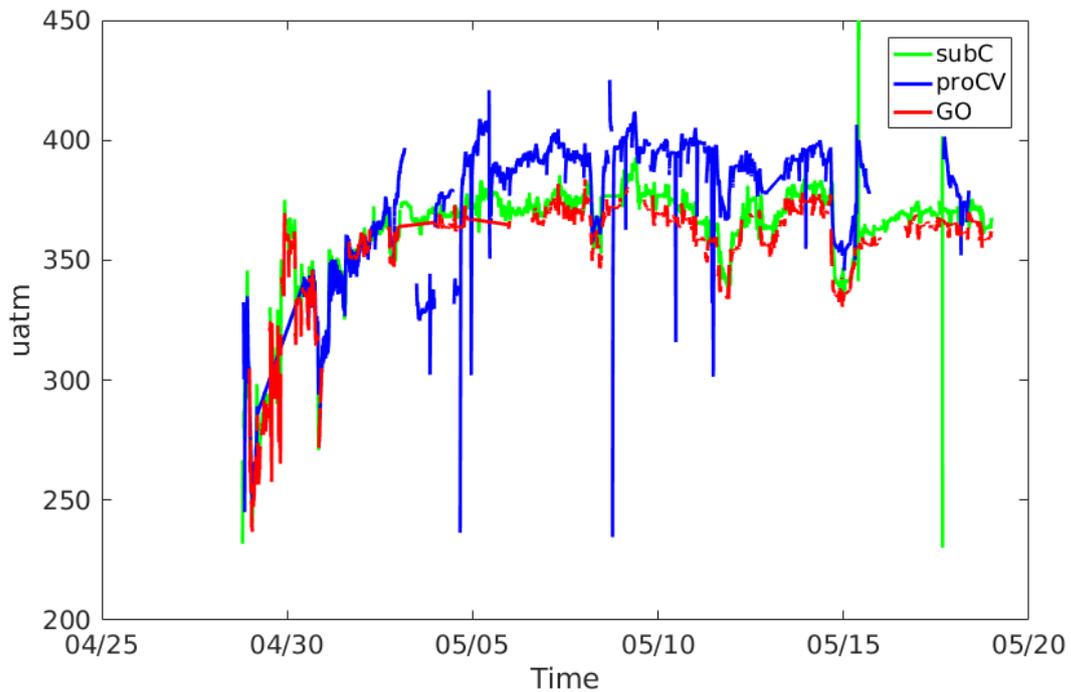


Figure 5.5.2 Comparison of  $pCO_2$  sensors corrected for gas pressure

### Gas pressure

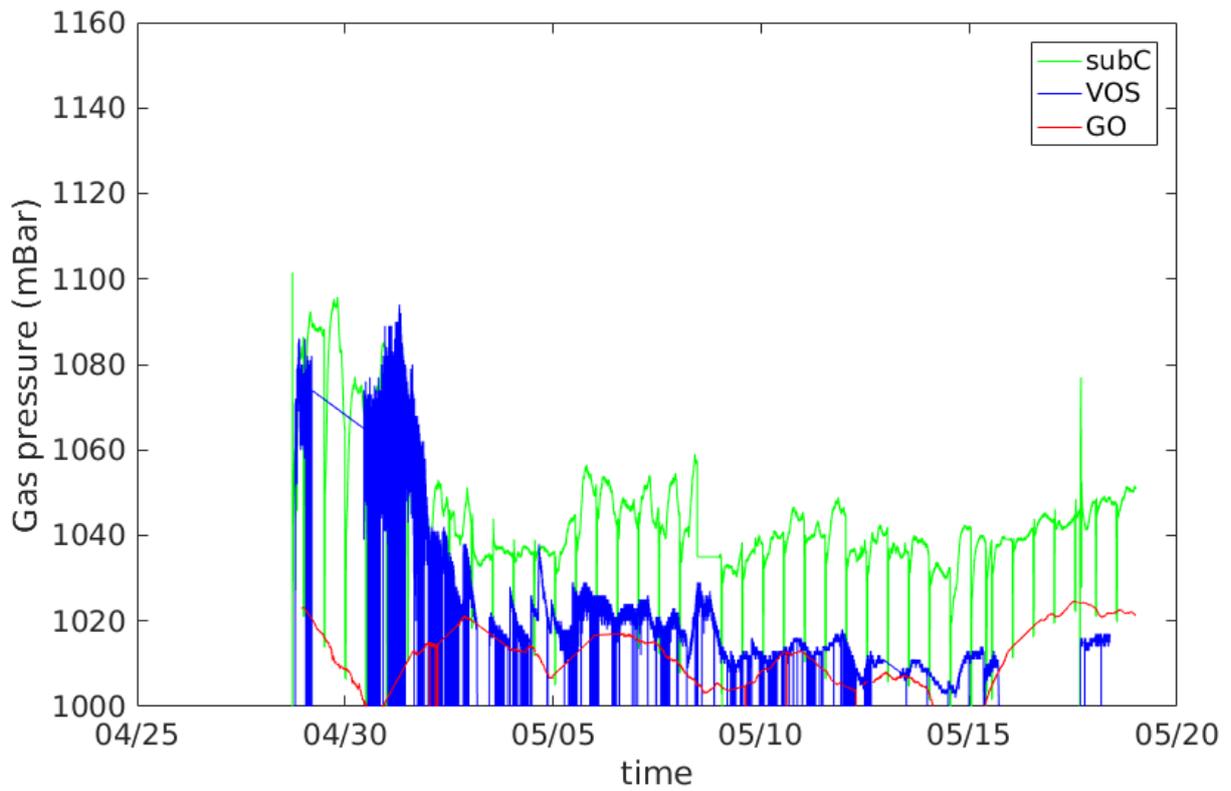


Figure 5.5.3 Comparison of Gas pressure at Licor from SubCtech, ProCV and GO.

### Temperature

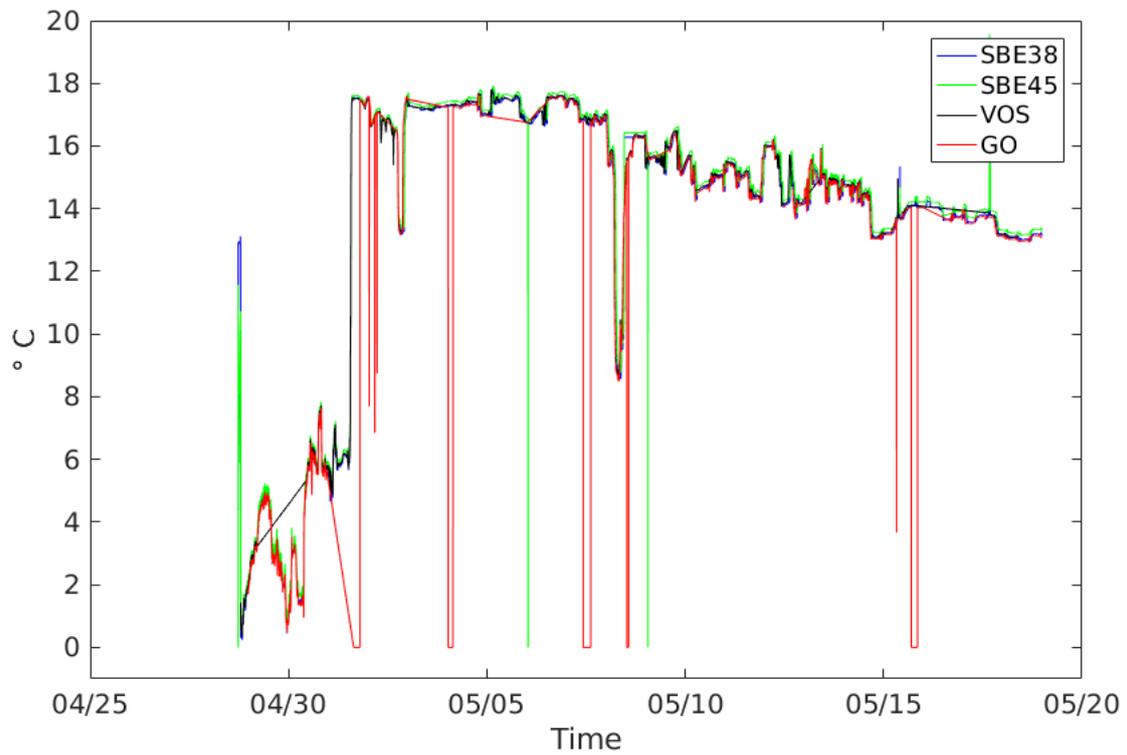


Figure 5.5.4 Temperature comparison from SubCtech (SBE38 and SBE45), VOS and GO

Other variables from VOS

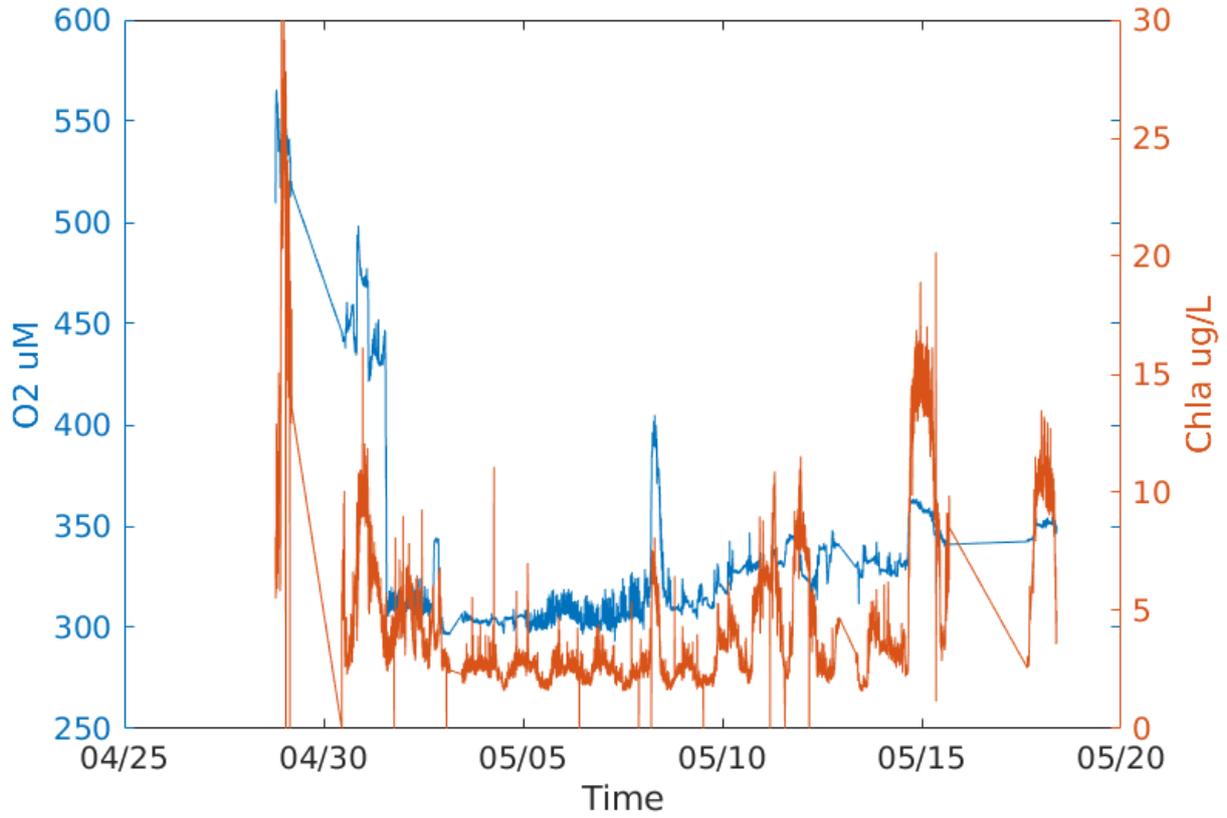


Figure 5.5.5 Surface Oxygen and Chlorophyll

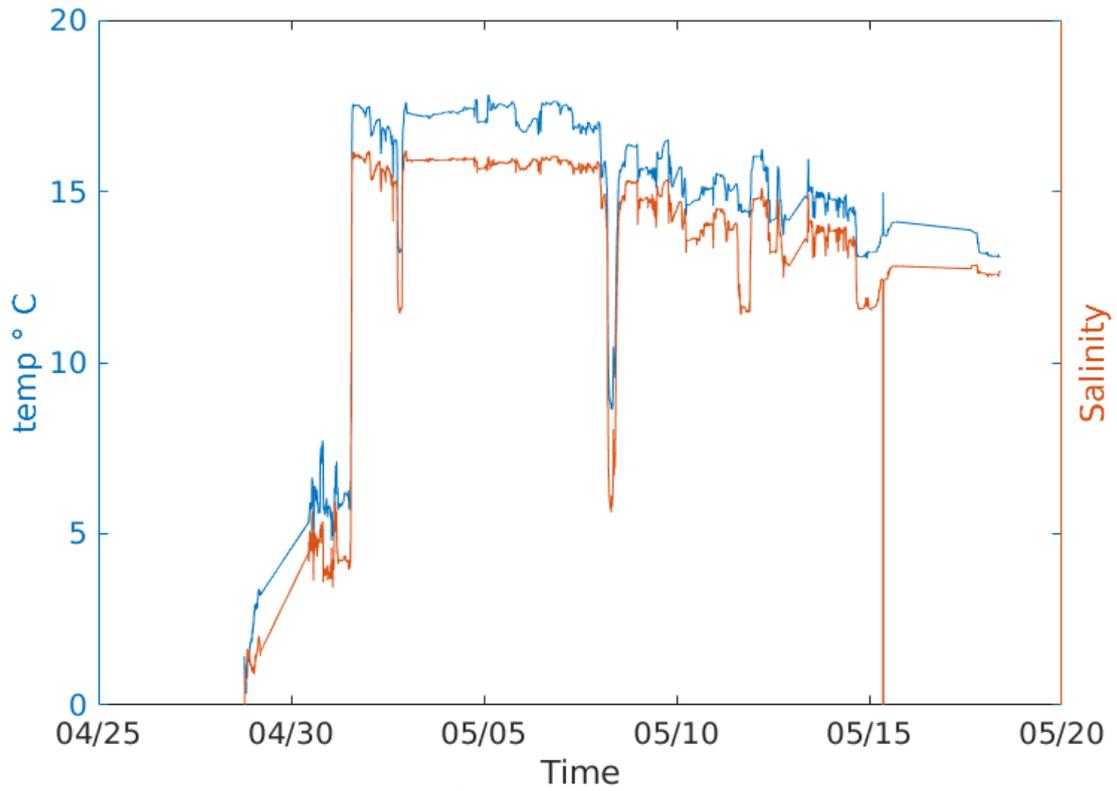


Figure 5.5.6 Temperature and salinity from VOS

## 6. Station Catalogue CE17007

Station #	Cast #	Cast Type	Date	Time (UTC)	Latitude °N	Longitude °W	Bottom Depth (m)	Nutrients O <sub>2</sub> , Salt	CFC	DIC & Alk	δ <sup>13</sup> C
1	1	CTD	29/4/2017	16:41	43.503	-50.0048	68	x		x	x
2	1	CTD	29/4/2017	21:15	43.335	-49.5818	86.8	x		x	
3	1	CTD	30/4/2017	00:21	43.2528	-49.3697	558.8	x		x	x
4	1	CTD	30/4/2017	04:27	43.1931	-49.1528	1045.5	x		x	
5	1	CTD	30/4/2017	08:32	43.1402	-48.9946	1573.3	x		x	x
6	1	CTD	30/4/2017	10:03	43.08817	-48.8475	2030	x		x	
7	1	CTD	30/4/2017	14:51	43.0503	-48.6269	2466	x		x	
8	1	CTD	30/4/2017	22:32	42.91733	-48.0277	3445	x		x	
9	1	CTD	1/5/2017	06:03	42.7605	-47.5552	3730	x		x	x
10	1	CTD	2/5/2017	16:14	42.56317	-46.9335	4100	x		x	
11	1	CTD	3/5/2017	00:56	42.41467	-46.2832	4662	x		x	x
11	3	CTD	3/5/2017	23:15	42.43417	-46.2912	4662	x		x	
12	1	CTD	4/5/2017	05:06	42.24233	-45.6465	4726	x		x	
13	1	CTD	4/5/2017	13:00	42.07033	-45.0178	4838	x		x	x
14	1	CTD	4/5/2017	20:38	42.21167	-44.391	4890	x		x	
15	1	CTD	5/5/2017	04:11	42.39633	-43.7607	4797	x		x	
20	1	CTD	8/5/2017	17:22	43.32083	-40.601	4816	x		x	x
21	1	CTD	9/5/2017	03:16	43.50417	-39.9557	4830	x		x	x
22	1	CTD	9/5/2017	12:02	43.68933	-39.3177	4609	x		x	x
23	1	CTD	9/5/2017	21:20	43.87267	-38.673	3862	x		x	x
23	2	CTD	9/5/2017	22:34	43.87283	-38.6728	3862	x	x	x	x
24	1	CTD	10/5/2017	06:27	44.0565	-38.028	4214	x		x	x
24	2	CTD	10/5/2017	11:47	44.05667	-38.0282	4214	x		x	x
25	1	CTD	10/5/2017	18:01	44.24233	-37.3783	4298	x	x	x	x
26	1	CTD	11/5/2017	01:18	44.42667	-36.732	4147	x		x	

27	1	CTD	11/5/2017	09:00	44.609	-36.081	4118	x	x	x	x
28	1	CTD	11/5/2017	16:43	44.79867	-35.4252	3974	x		x	
29	1	CTD	12/5/2017	00:05	44.9815	-34.7705	4082	x	x	x	x
31	1	CTD	12/5/2017	10:36	45.34983	-33.4555	3361	x	x	x	
33	1	CTD	12/5/2017	20:23	45.72067	-32.1278	3191	x	x	x	x
35	1	CTD	13/5/2017	05:11	46.09117	-30.7955	3375	x	x	x	
35	2	VPN	13/5/2017	09:26	46.09117	-30.7955	3375				
37	1	CTD	13/5/2107	15:36	46.45967	-29.4493	3410	x	x	x	x
37	2	VPN	13/5/2107	19:15	46.45967	-29.4493	3410				
39	1	CTD	13/5/2017	23:40	46.65417	-28.4375	2510	x		x	
39	2	VPN	13/5/2017	02:30	46.65417	-28.4375	2510				
40	1	CTD	14/5/2017	05:57	46.766	-27.7273	1606	x		x	
41	1	CTD	14/5/2017	11:08	46.879	-27.0163	2040	x	x	x	
41	2	VPN	14/5/2017	13:10	46.879	-27.0163	2040				
42	1	CTD	14/5/2017	17:23	46.99017	-26.3018	3018	x		x	
43	1	CTD	15/5/2017	00:28	47.10233	-25.5868	3382	x	x	x	
44	1	CTD	15/5/2017	07:44	47.2145	-24.873	3088	x		x	
45	1	CTD	15/5/2017	14:25	47.32733	-24.1527	3123	x	x	x	
46	1	CTD	15/5/2017	20:45	47.43933	-23.433	3730	x		x	
47	1	CTD	16/5/2017	03:34	47.55117	-22.712	4427	x	x	x	x
47	2	VPN	16/5/2017	08:25	47.55117	-22.712	4427				
48	1	CTD	16/5/2017	11:27	47.66183	-21.9903	4400	x		x	
48	2	VPN	16/5/2017	15:55	47.66183	-21.9903	4400				
49	1	CTD	16/5/2017	19:20	47.77467	-21.2677	4471	x	x	x	
50	1	CTD	17/5/2017	02:18	47.88667	-20.5408	4351	x		x	
51	1	CTD	17/5/2017	08:27	47.97	-20.055	4310	x	x	x	
52	1	CTD	17/5/2017	14:39	48.05767	-19.4355	4573	x		x	
53	1	CTD	17/5/2017	21:14	48.13567	-18.8678	4374	x	x	x	x
54	1	CTD	18/5/2017	04:07	48.24433	-18.149	4288	x		x	
55	1	CTD	18/5/2017	10:59	48.35183	-17.4163	4044	x	x	x	
56	1	CTD	18/5/2017	17:50	48.45867	-16.6808	4634	x		x	

<b>57</b>	1	CTD	19/5/2017	01:18	48.567	-15.9437	4535	x	x	x	
<b>58</b>	1	CTD	19/5/2017	08:54	48.67433	-15.2075	4810	x		x	
<b>59</b>	1	CTD	19/5/2017	16:22	48.781	-14.4673	4630	x	x	x	
<b>60</b>	1	CTD	19/5/2017	23:33	48.8895	-13.7233	4505	x		x	
<b>60</b>	2	ARGO	20/5/2017	03:39	48.8895	-13.7233	4505				
<b>61</b>	1	CTD	20/5/2017	06:47	48.98283	-12.9817	2553	x	x	x	
<b>62</b>	1	CTD	20/5/2017	12:08	49.05833	-12.5465	1290	x		x	
<b>63</b>	1	CTD	20/5/2017	15:58	49.11	-12.2023	1011	x	x	x	
<b>64</b>	1	CTD	20/5/2017	19:35	49.13967	-11.8222	827	x		x	
<b>65</b>	1	CTD	20/5/2017	23:29	49.16867	-11.4442	530	x		x	
<b>66</b>	1	CTD	21/5/2017	03:01	49.19967	-11.064	182	x		x	
<b>67</b>	1	CTD	21/5/2017	06:30	49.23183	-10.6497	149	x		x	

Notes:

CTD – CTD cast for Nutrients, O<sub>2</sub> and salinity from all depths, CFCs, DIC and alkalinity from a reduced number of depths at each station.

VPN - Vertical Plankton Net tow to 150 m to investigate if the dinoflagellate, *Azadinium* is present in oceanic waters. The 10µm mesh net was damaged during cast 47-2 and no sample was collected, the net was subsequently repaired by the crew and redeployed at station 48-2.

ARGO – deployment of an ARGO float (S/N 7842: Argo identifier 6901926).

## 7. Shipboard Participants

Name	Discipline	Institution
Croot, Peter. Prof.	Chief Scientist	NUIG
McGovern, Evin. Dr.	Principal Investigator, DO	MI
Aparicio, Francisco. Dr.	DO	NUIG
Szumski, Tom	Salinity	MI
Swartz, Marshall.	CTDO/LADCP/SADCP	WHOI
Cusack, Caroline. Dr.	CTDO/LADCP/SADCP	MI
Cronin, Margot. Dr.	Nutrients/Primary Underway pCO <sub>2</sub>	MI
Gregory, Clynt	Nutrients	NUIG
Normandeau, Claire	Nutrients, Carbon Parameters	DAL
Kerrigan, Liz	Nutrients	DAL
Bogner, Boie	CFCs	GEOMAR
Merten, Veronique	CFCs	GEOMAR
Bruckert, Julia	CFCs	GEOMAR
Morris, Ellie	Carbon Parameters	UE
Sims, Rich	Carbon Parameters	UE
Riehl, Lachlan	Carbon Parameters	DAL
Cheng, Lin	$\delta^{13}\text{C}$ DIC	DAL
Monteiro da Silva, Ricardo	Secondary Underway pCO <sub>2</sub>	DAL

### Participating Institutions:

NUIG	National University of Ireland Galway, Galway, Co. Galway, Ireland
MI	Marine Institute of Ireland, Rinvilla, Oranmore, Co. Galway, Ireland.
DAL	Dalhousie University, Canada
UE	University of Exeter, United Kingdom
GEO	GEOMAR, Kiel, Germany
WHOI	Woods Hole Oceanographic Institution, United States of America

<b>SHIP's CREW Celtic Explorer CE17007</b>	<b>RANK</b>
Kenny Downing	Master
Garvan Meehan	Chief Engineer
Basil Murphy	C/O & Security Off.
Barry Hooper	2/O & Safety Off.
Dave Stack	2 <sup>nd</sup> Eng
Michael Slyne	ETO
Frank Kenny	Bosun
Jimmy Moran	Cook
Shane Horan	Bosun's Mate
Tom Gilmartin	AB Deckhand
Martin Goggin	AB Deckhand
Anthony English	Technician
Cathal Murrin	AB Deckhand
Noel O'Driscoll	AB Deckhand
Maurice Murphy	Asst. Cook
Lukasz Pawlikowski	Technician

## 8. Data and Sample Storage and Availability

GO-SHIP data is stored in several repositories. Please go to <https://www.go-ship.org/DataDirect.html> for more information or contact the Marine Institute, Ireland.

## 9. Acknowledgments

This survey was carried out with the support of the Irish Marine Institute and funded under the Marine Research Programme by the Irish Government. The CFC and Carbon team activities are funded through the AtlantOS project under the European Union's Horizon 2020 research and innovation programme grant agreement No. 633211. Support for the Canadian Carbon and Nutrient teams was from the Canada Excellence Research Chair in Ocean Science and Technology and represents an initial activity of the newly formed Ocean Frontier Institute of which the Irish Marine Institute and GEOMAR are partners. The SDACP team activities have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 678760 (ATLAS). This output reflects only the authors' views and the European Union cannot be held responsible for any use that may be made of the information contained therein.

Special thanks to the Master, Kenny Dowling, and the crew and land support team of the RV *Celtic Explorer* and the GO-SHIP committee.



Lamont-Doherty Earth Observatory  
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## Data History

- **File Online Andrew Barna**

[45CE20170427\\_ctd.nc \(download\)](#) #418b1

**Date:** 2021-03-13

**Current Status:** dataset

**Notes**

CCHDO-1.0 CF netCDF files converted from ctd exchange file

- **File Online Jerry Kappa**

[74CE170007\\_JHS\\_hy1.csv \(download\)](#) #23634

**Date:** 2020-10-13

**Current Status:** unprocessed

- **File Submission Jim Swift**

[74CE170007\\_JHS\\_hy1.csv \(download\)](#) #23634

**Date:** 2020-10-07

**Current Status:** unprocessed

**Notes**

There were two fatal errors in the original 2019-12-13 submitted file for 74CE170007\_hy1.csv: The first line of the file had the values from column 2 written into column 1 (fixed here) and there was no CTDP RS column. Instead, the CTDP RS data were in the DEPTH (depth to bottom) column (fixed here). Another error was that the data were in reverse pressure order (fixed here). And there were no depth-to-bottom data (not fixed here). The file I submitted here is now readable as a WHP-Exchange file.

- **File Merge Carolina Berys**

[Cruise Report CE17007 A02 GO-SHIP Jan 2020 update .pdf \(download\)](#) #3322f

**Date:** 2020-01-24

**Current Status:** merged

- **File Merge Jerry Kappa**

[45CE20170427\\_do.txt \(download\)](#) #c1079

**Date:** 2020-01-24

**Current Status:** dataset

- **File Submission Jerry Kappa**

[45CE20170427\\_do.txt \(download\)](#) #c1079

**Date:** 2020-01-24

**Current Status:** dataset

**Notes**

The text version of A02\_2017's cruise report is ready for the CCHDO DataSet. It includes all of the PI-provided data reports and CCHDO Data Processing Notes.

- **File Online Carolina Berys**

[Cruise Report CE17007 A02 GO-SHIP Jan 2020 update .pdf \(download\)](#) #3322f

**Date:** 2020-01-22

**Current Status:** merged

- **File Submission Carolina for Caroline Cusack and Peter Croot**

[Cruise Report CE17007 A02 GO-SHIP Jan 2020 update .pdf \(download\)](#) #3322f

**Date:** 2020-01-22

**Current Status:** merged

**Notes**

Cruise Report received via email on 2020-01-22

- **File Merge Jerry Kappa**

[45CE20170427\\_do.pdf \(download\)](#) #ed4db

**Date:** 2020-01-14

**Current Status:** dataset

- **File Submission Jerry Kappa**

[45CE20170427\\_do.pdf \(download\)](#) #ed4db

**Date:** 2020-01-14

**Current Status:** dataset

**Notes**

The .pdf version of A02\_2017's cruise report is ready to be added to the DataSet. It includes all of the PI-provided data reports plus a CCHDO summary page and data processing notes.

- **File Online Carolina Berys**

[74CE170007\\_hy1.csv \(download\)](#) #78dc3

**Date:** 2019-12-13

**Current Status:** unprocessed

- **File Submission Carolina for ADam Leadbetter**

[74CE170007\\_hy1.csv \(download\)](#) #78dc3

**Date:** 2019-12-13

**Current Status:** unprocessed

**Notes**

Updated file submitted via email 2019-12-13. Note: TOxN is total oxidized nitrogen (see [https://www.researchgate.net/publication/331655704\\_A\\_rare\\_intercomparison\\_of\\_nutrient\\_analysis\\_at\\_sea\\_Lessons\\_learned\\_and\\_recommendations\\_to\\_enhance\\_comparability\\_of\\_open-ocean\\_nutrient\\_data](https://www.researchgate.net/publication/331655704_A_rare_intercomparison_of_nutrient_analysis_at_sea_Lessons_learned_and_recommendations_to_enhance_comparability_of_open-ocean_nutrient_data))

- **File Online Carolina Berys**

[74CE170007\\_hy1.csv \(download\)](#) #1fd0f

**Date:** 2019-12-12

**Current Status:** unprocessed

- **File Submission Adam Leadbetter**

[74CE170007\\_hy1.csv \(download\)](#) #1fd0f

**Date:** 2019-12-12

**Current Status:** unprocessed

- **File Merge CCHSIO**

[45CE\\_20170427\\_ct1.zip \(download\)](#) #e26d1

**Date:** 2019-01-16

**Current Status:** merged

• **Merged CTD data into Dataset CCHSIO**

**Date:** 2019-01-16

**Data Type:** CTD

**Action:** Merge

**Note:**

2017 45CE20170427 processing - CTD/merge - CTDPRS,CTDTMP,CTDSAL,CTDOXY

2019-01-16

CCHSIO

Submission

filename	submitted by	date	id
45CE_20170427_ct1.zip	Adam Leadbetter	2018-12-11	14251

Changes

45CE\_20170427\_ct1.zip

- added units comments
- added cruise information as commentes
- DEPTH is depth of the CTD. Therefore, removed bottom depth from header. Put it as a comment because this is not bottom depth, but it is the max depth of the CTD
- Changed EXPOCODE from 45CE\_20170427 to 45CE20170427
- Removed leading 0s from STNNBR
- Changed EXPOCODE from 45CE\_20170427 to 45CE20170427
- Renamed files to match EXCHANGE standard. Put original file name in file as a comment.

Conversion

file	converted from	software
45CE20170427_nc_ctd.zip	45CE20170427_ct1.zip	hydro 0.8.2-48-g594e1cb

Updated Files Manifest

file	stamp
45CE20170427_ct1.zip	20190116CCHSIO
45CE20170427_nc_ctd.zip	20190116CCHSIO

:Updated parameters: CTDPRS,CTDTMP,CTDSAL,CTDOXY

opened in JOA 5.2.1 with no apparent problems:

45CE20170427\_ct1.zip  
45CE20170427\_nc\_ctd.zip

opened in ODV with no apparent problems:

45CE20170427\_ct1.zip

- **File Online Carolina Berys**

[45CE\\_20170427\\_ct1.zip \(download\)](#) #e26d1

**Date:** 2018-12-18

**Current Status:** merged

- **File Submission Adam Leadbetter**

[45CE\\_20170427\\_ct1.zip \(download\)](#) #e26d1

**Date:** 2018-12-11

**Current Status:** merged

**Notes**

45CE20170427

Processed CTD cast data

- **File Online CCHDO System**

[45CE20170427\\_ct1.zip \(download\)](#) #19b03

**Date:** 2015-04-23

**Current Status:** dataset

**Notes**

Files migrated to new CCHDO backend, there is not enough information to know where this file should go in the timeline.

- **File Online CCHDO System**

[45CE20170427\\_nc\\_ctd.zip \(download\)](#) #7226c

**Date:** 2015-04-23

**Current Status:** dataset

**Notes**

Files migrated to new CCHDO backend, there is not enough information to know where this file should go in the timeline.