



**National  
Oceanography Centre**

NATURAL ENVIRONMENT RESEARCH COUNCIL

## **National Oceanography Centre**

### **Cruise Report No. 20**

### **RRS *Discovery* Cruise 368**

15 JUL – 04 AUG 2011

Hydrographic measurements on  
WOCE line A16N

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2012

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## DOCUMENT DATA SHEET

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<i>ABSTRACT</i> <p>RRS <i>Discovery</i> Cruise 368 was a repeat occupation of part of the Atlantic hydrographic section designated by the World Ocean Circulation Experiment (WOCE) as A16N. A total of 29 CTDO (conductivity-temperature-depth-oxygen) stations were occupied. This included one test station, 27 stations between 49N and 23N on the WOCE A16N '20W' line, and one final station near the ESTOC site close to Tenerife. Continuous profile measurements were CTDO and Lowered Acoustic Doppler Current Profiler (LADCP). Discrete bottle measurements from a 24-place rosette included salinity and dissolved oxygen analysed on board, and dissolved inorganic nutrients, Dissolved Inorganic Carbon and Total Alkalinity for analysis ashore. Underway measurements included Vessel-Mounted ADCP, surface ocean measurements and surface meteorology. The cruise was a UK contribution to the GO-SHIP sustained hydrography program. It was a partial repeat of the line designated in WOCE as A16N, which was previously occupied as a comprehensive cruise in 2003. In addition, a microbial program was carried out as an opportunistic activity by scientists who would remain on board for the following cruise.</p> <p>This report describes the methods used to acquire and process the data on board the ship during RRS <i>Discovery</i> Cruise 368.</p>	
<i>KEYWORDS</i> ADCP, Atlantic Ocean, carbon, circulation, cruise D368 2011, CTD, Discovery, Lowered ADCP, nutrients, oxygen, shipboard ADCP	
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## **Background and Objectives**

RRS *Discovery* Cruise 368 was a repeat occupation of part of the Atlantic hydrographic section designated by the World Ocean Circulation Experiment (WOCE) as A16N. The cruise was assembled at short notice, when a gap became available in the *Discovery* cruise program, with some time available on a leg between the UK and Tenerife. This partial re-occupation of the A16N line was proposed and accepted as a way to make good use of the time. The cruise was led by a PI from NOC, and staffed mainly with a collection of undergraduate and postgraduate students from the UK. In response to an international invitation, a group from Instituto Canario de Ciencias Marinas agreed to fill a gap by undertaking the nutrient measurements. A microbial program that led into the following cruise was added opportunistically, since equipment would already be on board, and personnel were available to undertake this short leg in addition to their primary work on Cruise 369.

Objectives:

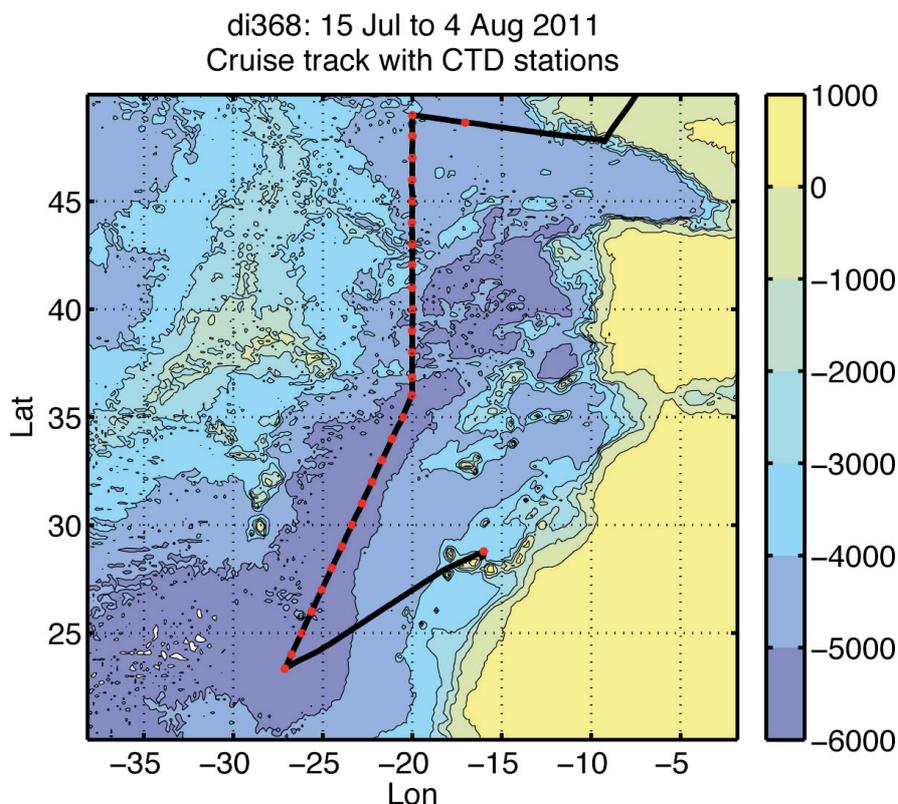
- 1) To make GO-SHIP measurements on the A16N from 50°N to 24°N.
- 2) To undertake an opportunistic microbial program.
- 3) To close the A16N section with an east-west sections towards the European continent at a latitude near 50°N.

Objectives 1 and 2 were completed. Objective 3 was thwarted by the weather. The work area was early in the cruise, the weather was unfavourable and we could not afford to get behind the required itinerary so early in the cruise for a secondary objective.

## **Summary**

A total of 29 CTDO (conductivity-temperature-depth-oxygen) stations were occupied. This included one test station, 27 stations between 49°N and 23°N on the WOCE A16N '20W' line, and one final station near the ESTOC site close to Tenerife. Continuous profile measurements were CTDO and Lowered Acoustic Doppler Current Profiler (LADCP). Discrete bottle measurements from a 24-place rosette included salinity and dissolved oxygen analysed on board, and dissolved inorganic nutrients, Dissolved Inorganic Carbon and Total Alkalinity for analysis ashore. Underway measurements included Vessel-Mounted ADCP, surface ocean measurements and surface meteorology. The cruise was a UK contribution to the GO-SHIP sustained hydrography program. It was a partial repeat of the line designated in WOCE as A16N, which was previously occupied as a comprehensive cruise in 2003. In addition, a microbial program was carried out as an opportunistic activity by scientists who would remain on board for the following cruise.

## Itinerary and Cruise Track



Cruise track: Station positions for RRS *Discovery* Cruise 368. 15 July to 4 August 2011.

### Diary

All times UTC

#### 15 July 2011 Friday Day 196

RRS *Discovery* Cruise 368 sailed from Liverpool on 15 July 2011, casting off at 0630 and passing through the lock at 0730. An emergency muster was arranged for 1515, and a science briefing for the following day. The initial course was towards the continental slope off the south-west of the UK. A test station was planned for 47°45.9'N, 9°15.0'W.

#### 18 July 2011 Monday Day 199

On arrival in the first planned work area, the weather was unworkable, and was clearly going to remain so for at least 24 hours. When there was no sign of improvement, and since this work was not the primary objective, a course was set instead towards 49°N, 20°W, to start the '20W' section. The steaming distance to the new waypoint was 440 miles.

#### 19 July 2011 Tuesday Day 200

Station 1 was conducted en route to the 20W line as a test station, ending at 1515.

#### 20 July 2011 Wednesday Day 201

After a further 120 miles steaming, Station 2 marked the start of the 20W line. The line would now be occupied at a latitude spacing of 1 degree latitude.

**25 July 2011 Monday Day 206**

Station 15 at latitude 36°N marked the corner in the 20W line. South of this latitude the line has a westwards kink, so the section remains in the deepest part of the basin.

**31 July 2011 Sunday Day 212**

Station 27 (24°N) was the last of the stations at 1 degree spacing. In order to ensure we had sufficient time to steam towards Tenerife and occupy the ESTOC station, Station 28 was moved to 23°20'N, thereby saving a round-distance steam of 40 miles. After completing Station 28, a course was set towards the ESTOC station. The critical objective of crossing the latitude of the WOCE A5 hydrographic section had been achieved.

**4 August 2011 Thursday Day 216**

Station 29 was completed at 0238 on this day, at 28°46.9'N, 16°00.1W. This position was a compromise between the exact position of the ESTOC station, and practical considerations of time and steaming distance. Cruise 368 ended when *Discovery* arrived on a berth in Tenerife at 0744.

## 1. CTD Systems Operation

### 1.1. CTD and Sensors

1) One CTD system was prepared; the first water sampling arrangement was a NOC 24-way stainless steel frame system, (s/n SBE CTD4 (1415)), and the initial sensor configuration was as follows:

Sea-Bird 9plus underwater unit, s/n 09P-46253-0869

Sea-Bird 3P temperature sensor, s/n 03P-4116, Frequency 0 (primary)

Sea-Bird 4C conductivity sensor, s/n 04C-2580, Frequency 1 (primary)

Digiquartz temperature compensated pressure sensor, s/n 100898, Frequency 2

Sea-Bird 3P temperature sensor, s/n 03P-4782, Frequency 3 (secondary, vane mounted)

Sea-Bird 4C conductivity sensor, s/n 04C-2841, Frequency 4 (secondary, vane mounted)

Sea-Bird 5T submersible pump, s/n 05T-2279, (primary)

Sea-Bird 5T submersible pump, s/n 05T-3002, (secondary, vane mounted)

Sea-Bird 32 Carousel 24 position pylon, s/n 32-31240-0423

Sea-Bird 11plus deck unit, s/n 11P-34173-0676

2) The auxiliary input initial sensor configuration was as follows:

Sea-Bird 43 dissolved oxygen sensor, s/n 43-1940 (V0)

Tritech PA200 altimeter, s/n 6196.118171 (V2)

Chelsea MKIII Aquatracka fluorometer, s/n 88-2050-095 (V3)

Chelsea MKII 25cm path Alphatracka transmissometer, s/n 07-6075-001 (V6)

WETLabs light scattering sensor, red LED, 650nm, s/n BBRTD-169 (V7)

3) Additional instruments:

Ocean Test Equipment 10L water samplers, s/n's 1-24

Sonardyne HF Deep Marker beacon, s/n 245116-001

NOC 10 kHz acoustic bottom finding pinger, s/n B6

TRDI WorkHorse 300kHz LADCP, s/n 13329(downward-looking)

NOC WorkHorse LADCP battery pack, s/n WH001

Sea-Bird *9plus* configuration file D368\_st\_NMEA.xmlcon was used for all CTD casts, with D368\_st\_no\_NMEA.xmlcon used for the back-up, simultaneous logging desktop computer. The LADCP command file used for all casts was WHMD368.txt

### 1.2. Other instruments

*Autosal salinometer*---One salinometer was configured for salinity analysis, and the instrument details are as below:

Guildline Autosal 8400B, s/n 68958 installed in Constant Temperature Laboratory as the primary instrument, Autosal set point 24C. The rear lamp was noticed to not be flashing and the check heater light was illuminated for long periods. The bulb in the unit was replaced.

*Valeport MIDAS SVP* (NOCL)

A self logging sound velocity probe was mounted on the frame for all casts in order to run in the instrument prior to its use by NOCL. The instrument was run in profile mode from casts 1 – 25. In profile mode the instrument samples at 8Hz and records data at 1dbar intervals.

Casts 26 – 28 the instrument was placed in continuous 1Hz Mode.

The time in the SVP was synced to the ships NTP Server at the beginning of the cruise.

### ***1.3 CTD Appendix A: Technical detail report***

#### **S/S CTD**

Cast D368001 – It was suggested by management at NMFSS to deploy the first CTD without the vane. For this cast only the secondary sensors set were frame mounted on the CTD. They were returned to the vane for all subsequent casts.

During the up cast it was noted that the Dissolved Oxygen Sensors (43-1940) data had become very noisy. This appears to be due to a torn membrane. The instrument was serviced recently and this is its first deployment since that service.

The unit was replaced by 43-1642.

Cast D368002 – Prior to the cast the CTD vane was reattached and the CTD Secondary sensors and Pumps reattached to the vane. During the reassembly the T Duct Tubing was not properly secured and consequently came disconnected between the temperature sensor and the conductivity cell. This caused the Temperature sensor to measure a different water mass as the water was not being drawn past it by the pump as normal. This was rectified on the following cast and there are no signs of any other problems with the instrument.

Cast D368003 Bottle 17 failed to close. The bottle fire was initiated however the latch on the carousel was stuck. The latch could not be manually released on deck and so the carousel latch assembly was removed. The latch assembly was washed in Freshwater and a test conducted by turning the carousel latch assembly upside down to see if the latch would free fall on release. It would not and so the latches were disassembled. The latch in question was loosened  $\frac{1}{4}$  of a turn. It was then reassembled and successfully fell on release.

Cast D368005. During this cast the CTD Deck unit was reset by persons leaning on the units reset button. 2 Files exist for this cast 368005.hex and 368005b.hex.

Cast D368014. Following several casts where Bottle 1 (Bottom Water) had a higher temperature reading than Bottle 2 (Bottom -50meters) the Carousel Latch Assembly was replaced with a spare from another Carousel. The Carousel was now made up of the Magnet and electronics section of 32-0423 and Latch assembly of 32-0369. The problems were no longer reported after the assembly was exchanged.

Cast D368018. It was noted at 400m of this cast that the oxygen sensor was not performing correctly. This was due to the pump having been disconnected between casts, had not had its power cable reattached. The data in D368018 for the primary sensors is unpumped. The CTD was recalled and the cast restarted under file D368018\_1.

Total number of cast's S/S frame: 29

Deepest cast's m S/S frame: 5496

### **CTD Wire**

During the port call prior to the cruise the Steel CTD Wire was replaced.

Following CTD's 1 (no vane) and 2 (vane attached) the CTD came out of the water with a large twist located 1 – 1.5m above the termination. This was due to the torque in the cable being released during the cast. No loss of data occurred however the wire had to be reterminated both times.

Prior to cast 3 a Weight and Swivel were deployed to alleviate any remaining torque within the wire.

During cast 1 and 2 the LADCP indicates that the CTD span in a clockwise direction approximately 175 times and 13 times respectively.

During several casts at the early stages of the cruise the scrolling was adjusted due to the changing profile of the new wire. The new wire appears to stretch during the CTD Deployment. With the wire out often being 10M or so less than the CTD Depth by the time the CTD reaches the bottom. The value's never match perfectly however they do start out within 1 – 2m and increase as the depth increases.

### **LADCPs**

One LADCP was installed in the downward looking position. No problems encountered.

The ADCP was very useful in determining the wire related issues due to induced torque in the cable.

Some communications issues developed with the LADCP as well as charging issue's. This was due to loss of continuity in the star cable. This was due to excessive force being placed on the connector stretching the conductors. The cable was replaced and the ADCP functioned correctly.

During D368009 the ADCP began writing a file to the secondary disk due to lack of space on the primary. This is not an issue however the files were downloaded as 2 separate files and then remerged using WinADCP. This also occurred on cast 023.

The LADCP was configured with the following script for casts D368001 to D368017.

```
PS0
CR1
CF11101
EA00000
EB00000
ED00000
ES35
EX11111
EZ0011101
WM15
```

LW1  
LD111100000  
LF0500  
LN016  
LP00001  
LS1000  
LV250  
SM1  
SA001  
SW05000  
TE00:00:01.00  
TP00:00.00  
CK  
CS

Prior to cast 018 the LADCP configuration was changed to use Beam Coordinates instead of Earth Coordinates :

PS0  
CR1  
CF11101  
EA00000  
EB00000  
ED00000  
ES35  
EX00000  
EZ0011101  
WM15  
LW1  
LD111100000  
LF0500  
LN016  
LP00001  
LS1000  
LV250  
SM1  
SA001  
SW05000  
TE00:00:01.00  
TP00:00.00  
CK  
CS

C. Barnard, P. Duncan

## 2. CTD Data Processing and Calibration

### 2.1. Data Processing

The processing of the CTD data followed much the same method as many previous cruises, especially the methods of the di346 cruise. The initial SeaBird data conversion, alignment and cell thermal mass corrections were performed using the SBE Data Processing, Version 7.21a software. The final corrected output files were then copied to nosea2 using the UNIX exec *ctd linkscript* command and symbolic links were made to each CTD station file. The ASCII files created by this process are in the format of *ctd\_di368\_nnn\_ctm.cnv* and *ctd\_di368\_nnn.bl*.

Correction for oxygen sensor upcast/downcast hysteresis is now performed as part of the Mstar CTD processing suite in step *mctd\_2b*. The Mstar software suite runs in Matlab and uses NetCDF files to store the data. These are either stored as SAM, CTD, DCS or FIR files, depending on the data they hold about the CTD casts. Before the processing suite can be performed the m-file *m\_setup* must be run to load the Mstar tools. The following m-files were then run in the order given: *msam\_01*, *mctd\_01*, *mctd\_2a*, *mctd\_2b*, *mctd\_condcal\_di368* (for both sensors 1 and 2, as both sensors were giving continually good results with the exception of stations 5 and 2), *mctd\_oxycal*, *mctd\_03*, *mdcs\_01*, *mdcs\_02* (after which the bottom pressure was noted), *mdcs\_03*, *mctd\_04*, *mplotxy\_ctdck* (this creates figures which allow for comparison with previous stations to ensure instruments are not drifting and that there are no large spikes in the data which could indicate fouling), *mdcs\_04*, *mfir\_01*, *mfir\_02*, *mfir\_03*, *mfir\_04*, *mwin\_01*, *mwin\_03* and *mwin\_04*.

The only changes made to the m-files were associated with *mctd\_condcal\_di368* and *mctd\_oxycal* which are stated in Sections 2.2 (salinity calibration) and 2.3 (oxygen calibration) respectively and *mctd\_sensor\_choice*, which is called upon by *mctd\_03*, in this m-file the sensor choice must be given. The default is for sensor 1 and was only changed for station 5 for which sensor 2 was used for conductivity, as sensor 1 was giving some unusual results. First choice sensor data are then stored in the variables temp and cond.

If the Mstar suite had been run without the *mctd\_condcal\_di368* or the *mctd\_oxycal* stages (i.e. for the earlier stations when the calibration had yet been set) then the m-file *smallscript* was used, which ran the steps *mctd\_02b*, *mctd\_condcal* or *mctd\_oxycal*, *mctd\_03*, *mctd\_04*, *mfir\_03* and *mfir\_04*, as these are all the files which make use of conductivity/oxygen values.

Once all bottle sample data has been integrated into the SAM files the files were appended to create a file named *sam\_di368\_all.nc*, which, along with the 2db CTD files, was used by *run\_mgridp\_ctd\_di368.m* to produce gridded and interpolated section data in NetCDF format. This gridded file was then loaded using *mload* which was then plotted for salinity, potemp and oxygen with the *mcontr* command. The final plots for which can be seen in Figures 2.1 to 2.3. This allowed the progress of the cruise to be monitored throughout and ensured all stages of the data processing had been performed correctly and any erroneous points had been flagged.

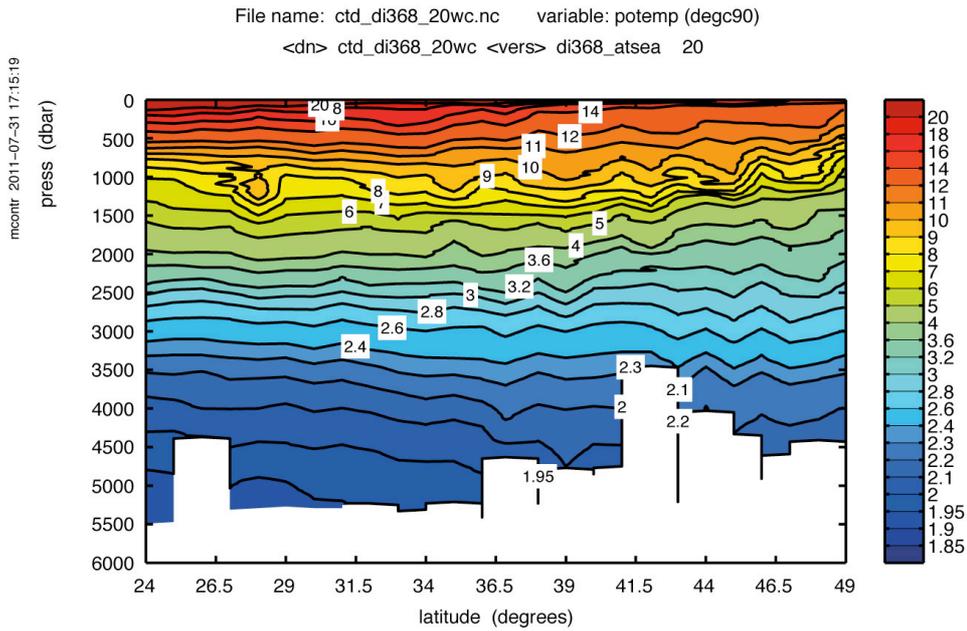


Figure 2.1 Potential Temperature for the A16N section of the survey (stations 2 to 28), recorded at 1° latitude spacing and binned in 20 dbar, white areas indicate where data were not collected.

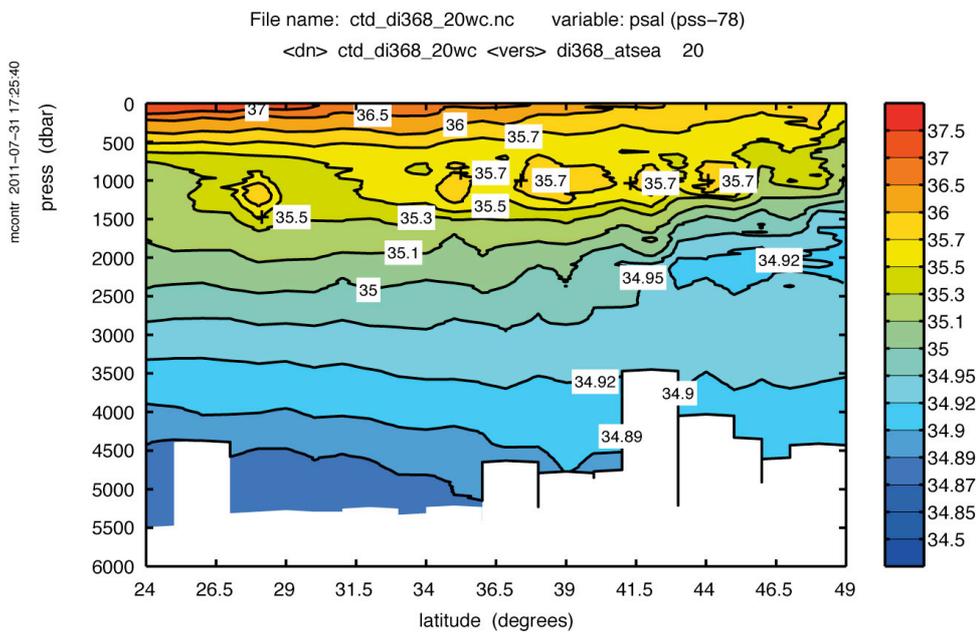


Figure 2.2 As Figure 2.1 but Practical Salinity.

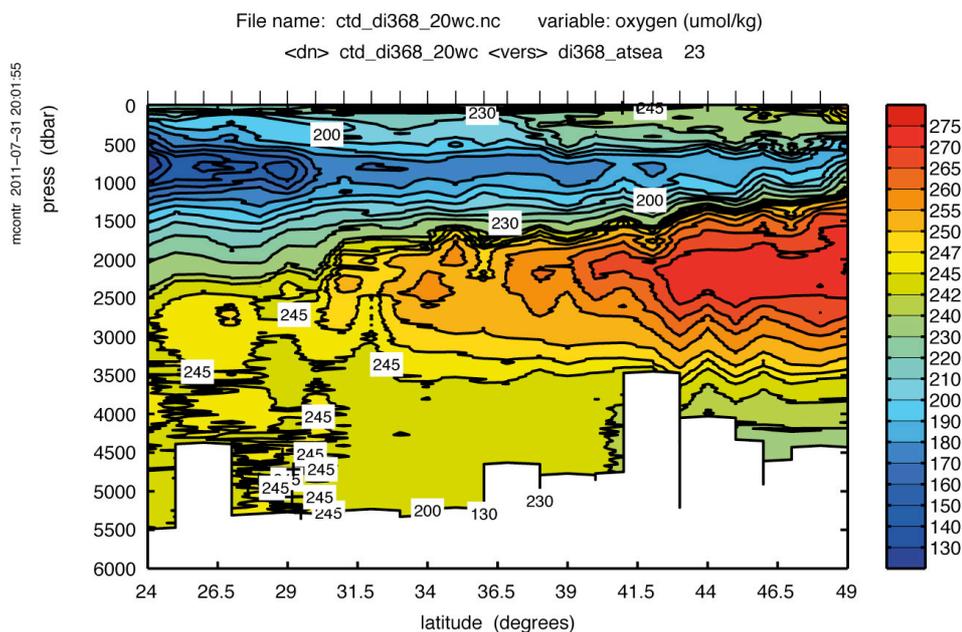


Figure 2.3 As Figure 2.1 but Dissolved Oxygen ( $\mu\text{mol/kg}$ ).

## 2.2 CTD Conductivity Calibration

CTD conductivities are calibrated by comparison with bottle conductivities obtained during the CTD upcast. The CTD upcast is calibrated and the same calibration applied to the downcast.

Once *msal\_01* and *msal\_02* had been applied and the CTD data had been processed up to *mctd\_2b* an m-file called *mctd\_condcal\_di368* was applied. This m-file calls upon the function *cond\_apply\_cal* and requires the user to input the sensor number ('senscal') required for calibration, both sensors 1 and 2 were calibrated for all stations. *Cond\_apply\_cal* inputs the variables of sensor number, station number, pressure, temperature and conductivity.

In order to calculate the calibration required all stations were appended into *sam\_di368\_all.nc*, which was then loaded firstly for sensor 1 and then for sensor 2.

The first step of the calibration is a multiplication factor ('fac'), which is derived from 1 minus the mean of the ratio of conductivity from the bottle samples to the conductivity from the CTD upcast for deep-water values (below 2500m). When applied this gives the dataset an average of zero.

The second step is to apply an additive correction ('condadj') to correct for the pressure dependence. A lookup table was created from the residuals for both sensors

1 and 2, seen in tables 2.1 and 2.2. This table is then linearly interpolated to cover all depths and added to the conductivity CTD value.

Pressure (dB)	Residual offset
-10	0.0008
0	0.0008
2000	0.0018
4500	0
10000	0

*Table 2.1 Lookup table for residual offsets to be applied to sensor 1*

Pressure (dB)	Residual offset
-10	0.001
0	0.001
3500	0.001
5500	-0.0005
10000	-0.0005

*Table 2.2 Lookup table for residual offsets to be applied to sensor 2*

In the case of sensor 2 a discernable drift in the differences towards more positive residuals was noticed. This was corrected for, using the *polyfit* and *polyval* functions which applied a first order polynomial with an intercept of -0.0018 and a gradient of  $5.81 \times 10^{-5}$  with respect to the station number. Although sensor 1 had a drift it was not deemed significant enough to apply a correction for.

The post-calibration residuals can be seen for both sensors 1 and 2 in Figures 2.4 and 2.5 respectively.

**The following anomalies were noted**

For station 5, sensor 1 was apparently fouled at the beginning of its ascent, therefore sensor 2 is used as the sensor of choice for this station. Even after selecting the secondary sensor the bottle data for this station did not agree well with the CTD data for reasons unknown.

The secondary sensor gave erroneous data for station 2, so for this station sensor 1 should be used only.

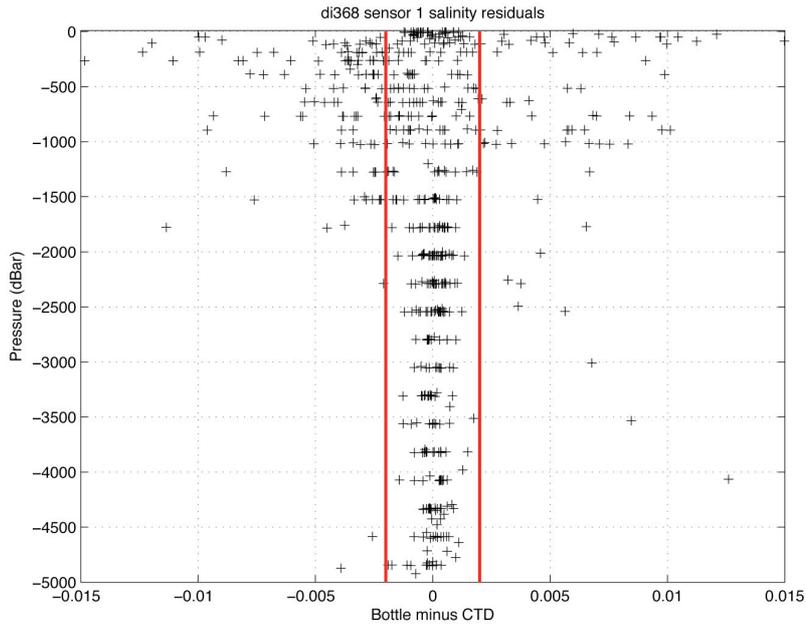


Figure 2.4 Salinity residuals of bottle minus CTD values once calibration has been applied for sensor 1

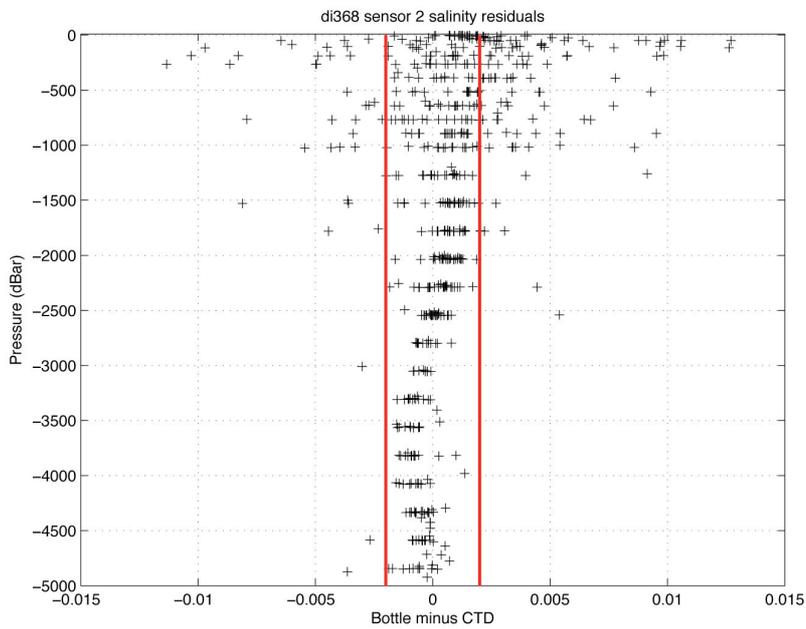


Figure 2.5 As Figure 2.4, but sensor 2

## 2.3 CTD Oxygen Calibration

The oxygen sensor was attached to the conductivity-temperature sensor on the CTD frame. Following initial sensor poor performance on station 1, the first oxygen sensor was swapped for an alternative for the remainder of the stations. This oxygen sensor performed well and showed a stable drift compared to the bottle oxygen measurements for the rest of the cruise. Initial conversion of the oxygen sensor data from the raw Sea-Bird programs was run as a batch job by the CTD technicians.

Downcast-upcast sensor hysteresis is corrected during mstar processing by *mctd\_02b*. This applies an algorithm provided by Sea-Bird for oxygen concentration values measured by the SBE 43 sensor.

The algorithm has the form:

$$Oxnew_{conc} = \left\{ \left( Oxygen_{conc}(i) + (Oxnew_{conc}(i-1) \times C \times D) \right) - (Oxygen_{conc}(i-1) \times C) \right\} / D$$

Where:

$$D = 1 + H1 \times \left( \text{exponential}(P(i)/H2) - 1 \right)$$

$$C = \text{exponential} \left( -1 \times (Time(i) - Time(i-1)) / H3 \right)$$

i=indexing variable, P=pressure (dbar), Time=time (seconds), H1=amplitude of hysteresis correction function (default -0.033), H2=function constant or curvature function for hysteresis (default 5000), H3=time constant for hysteresis (seconds, default 1450). The default Sea-Bird hysteresis factors were used for all the cruise resulting in a downcast-upcast hysteresis of typically a few  $\mu\text{mol/kg}$  following this procedure.

Bottle oxygen data was uploaded to the discfs server by the analyst. The *oxy\_linkscript* batch job copied the files to the main processing directory, and set up symbolic links. Using *moxy\_01* and *moxy\_02*, the bottle oxygen sample data was uploaded to the master sample file. Following the hysteresis correction, upcast sensor oxygen concentrations were calibrated against oxygen concentrations derived from bottle samples. Final calibrations were applied using the *oxy\_apply\_cal.m* function called by *mctd\_oxycal.m* and applied to the 24 Hz file oxygen data before cascading through to 1 Hz, psal, 2 db and SAM files.

After replacing the oxygen sensor after station 1, bottle oxygen and CTD oxygen showed a clear linear relationship on a station-by-station basis. The sensor oxygen was firstly calibrated for station dependence using the relationship:

$$OC = [1 + \gamma(S - 3)]Os$$

Os is the original sensor oxygen,  $\gamma$  is the coefficient for the gradient of the relationship between sensor oxygen/bottle oxygen (Os/Ob) versus station number and OC is the calibrated CTD sensor oxygen. This removes station dependence, converting all sensor oxygen based on the values in station 3. Station 3 is regarded as a reliable station after changing the oxygen sensor prior to station 2.  $\gamma$  is determined to be  $8.251e-4$ . To remove the actual offset of the sensor oxygen from the bottle oxygen. A plot of all station dependence adjusted sensor oxygen, and bottle oxygen gives a gradient,  $\alpha$  and a y-intercept  $\beta$ . The sensor oxygen is scaled using the gradient,  $\alpha = 1.0533$ , and offset using the y-intercept,  $\beta = -5.22$ . Coefficients are calculated for stations 3-25, and applied to stations 2-28. An additional  $1\mu\text{mol/kg}$

offset was added to station 2. The poor performance of the station 1 oxygen sensor data was beyond successful calibration.

After application of this correction, bottle-sensor oxygen residuals retained clear structure against pressure. Above 1000dbar residuals were generally positive whilst below is generally negative. To remove this pressure dependence, a pressure lookup table is constructed to account for the pressure offset. Adjustments are chosen at boundary positions and offsets in-between are linearly interpolated. The pressure lookup table is shown below:

Pressure	Offset applied ( $\mu\text{mol kg}^{-1}$ )
-10	-1.0
1000	0.5
1500	-0.5
2500	0.9
4000	1.0
5500	-0.5
10000	-0.5

Table 2.3: Pressure lookup table showing the boundary offsets, with linear interpolation applied in-between.

Following this procedure, bottle-CTD residuals were reduced to  $\pm 2 \mu\text{mol/kg}$  for the oxygen sensor.

Final offsets for all CTD-bottle pairs are showing in Figure 2.6, with a single outlying datapoint excluded.

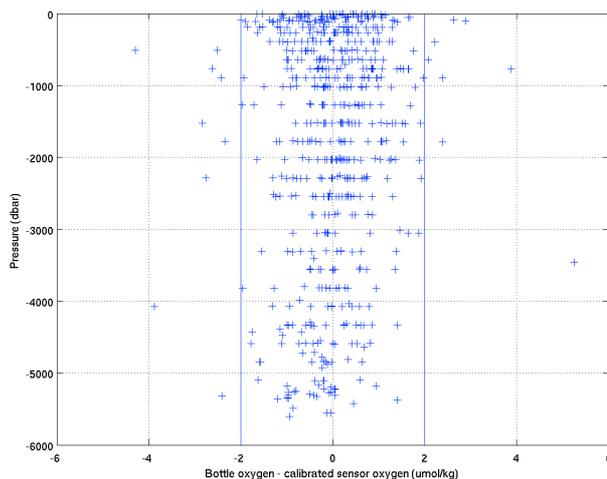


Figure 2.6: Offsets from the bottle oxygen minus calibrated CTD sensor oxygen. Vertical blue lines indicate a  $\pm 2 \mu\text{mol/kg}$  offset range.

Amelia Astley (CTD and Salinity)  
Gavin Evans (Oxygen)

### **3. Water Sample Salinity Analysis**

#### ***3.1 Equipment***

Salinity sample analysis was performed on the UKORS Guildline 8400B Salinometer, Serial No. 68958, in the Constant Temperature (CT) laboratory. The salinometer water bath temperature was set to 24°C and the laboratory temperature maintained between 21.5°C and 22.5°C.

#### ***3.2 Sample Collection and analysis***

For each CTD cast, one water sample was drawn per Niskin bottle for salinity analysis, from bottles that had fired successfully, were not leaking and were not required for microbial analysis. Samples were taken in 200ml glass sample bottles, which were rinsed three times including the screw on cap and sealed with a disposable plastic stopper and cap, after drying the neck of the bottle and inside of the cap. Samples were stored in the CT laboratory for a minimum of 24 hours before analysis to allow equilibration to the laboratory temperature, except for the last station and TSG crate where the delay between sampling and analysis was reduced to 4 hours due to time constraints.

Amelia Astley, Ben Edwards, Gavin Evans and Edwin Lizarazo carried out all the analysis following standard procedure. A sample of IAPSO Standard Seawater was run before and after each 24 samples for salinometer calibration. One Standard Seawater batch used was P153, dated 8<sup>th</sup> March 2014, with a K15 value of 0.99979 giving a 2xk15 value of 1.99958. The standardisation dial was set to 496 after the first test station and was not changed during the cruise. Once set to 496 all values given by the standards were in the range of 1.99955 to 1.99965. The standby (SBY) and zero numbers varied little from 6067 to 6068 and zero to -0.00002 respectively.

For station 13 the suppression dial was not used for sample numbers 10 to 17. After a small experiment involving standard water and using the suppression dial, it was found that the software still recorded the correct value with an offset of 0.1. As the samples were at the limit of the suppression the relationship between the salinity and conductivity value may not have been linear, so these samples should still be used with caution.

#### ***3.3 Sample recording and merging with CTD data***

Bottle sample data (conductivity and salinity) are recorded by the data-logging program *autosal\_2009 V8.5* into an excel file to which sample numbers are manually entered in the format *Stn{num}*, giving a 4 digit number. A hard copy is also kept of bottle number, the three conductivity ratios and the average ratio, which proved useful in the case of station 26 when the program failed to record 2 of the conductivity ratios. Any missed out Niskin bottles are added with the corresponding sample bottle number and sample number with the time, date, conductivity and salinity given the value of -99999. Standards are given the sample number value of 999{num}, where {num} is a chronological standard number starting with 01. This file is then saved as a comma-separated csv file, with the name *sal\_di368\_{num}.csv*, which was then copied across to the UNIX system and saved in the BOTTLE\_SALTS directory. Two m-files are then run *msal\_01* and *msal\_02*, which read in the bottle samples and copies them into a sam file respectively, giving the output file the name *sam\_di368\_{num}.nc*.

Bottles were flagged using the m-file *msam\_setflags*, which was set to automatically flag as -4 any missing bottles where either the Niskin misfired and no sample was given, or the bottle was not available for use for salinity sampling e.g. when the entire Niskin was required for microbial analysis.

Residuals of CTD salinity were plotted using the m-file *msam\_display\_psal\_residuals*. The m-file *bottle\_inspection* was used to make a comparison of oxygen and salinity bottle data to CTD, the m-file also highlights those bottles already flagged, so can be used to identify cases where other samples may not be as reliable due to bottle misfiring/leaking etc.

### ***3.4 Offsets Applied to Autosol Ratios***

An offset was applied to all bottle samples to correct for the difference between the displayed reading and 2 x K15. This was a constant value of -0.00002, with the exception of stations 4,5,6,8,9 which were given an offset of -0.00001, and station 1 and tsg-01 which were given an offset of -0.0002 due to the resetting of the standardization dial after these two crates were processed. These values are listed in Table 3.1.

Station	Offset
1	-0.00020
2,3	-0.00002
4,5,8,9	-0.00001
6,7,10 to 28	-0.00002
TSG-01	-0.00020
TSG-02 and 03	-0.00002

Table 3.1 Offsets applied to each station's conductivity ratio, calculated from the difference between the 2 x K15 value and the average reading from the standards run before/after the station's bottles. Note: TSG-01 and station 1 have a much greater offset due to the resetting of the Rs dial after these crates were run

Amelia Astley

## **4. Inorganic Nutrient Analysis**

ICCM was invited to participate in RRS *Discovery* Cruise 368 with the aim to carry out the nutrient sampling (DIN, DIP and DISi). After end of A16N line, the seasonal ESTOC sampling was carried out. ESTOC (European Station for Time-Series in the Ocean Canary Islands) was initialized as a cooperative project established by four research institutions: Institut für Meereskunde, Kiel (IFMK) and the Fachbereich Geowissenschaften der Universität Bremen (UBG) in Germany, and in Spain the Instituto Español de Oceanografía (IEO) and the Instituto Canario de Ciencias Marinas (ICCM). Observations started in 1994 (Llinás et al., 1994) and the objectives are maintained until nowadays. Many cruises have taken place to the north and east of the Canary Islands; among them it is worth mentioning those made within the European project CANIGO, ANIMATE and MERSEA. ESTOC is currently a Spanish open ocean observatory and internationally is belonging to the current European network “EuroSITES”.

### ***4.1. Narrative of the sampling with technical details***

The sampling started on July 20th 2010 after some days steaming from Liverpool port. The sampling was run in profiles from surface to bottom. The equipment was a Seabird 911 plus CTD and a 24 bottles water sampler. Temperature, Conductivity, dissolved oxygen and chlorophyll were measured by the CTD, whereas samples of dissolved oxygen, Dissolved Inorganic Carbon (DIC), nutrients (Nitrate, phosphate and silicate), salinity and pigments were taken to analyze on board (O<sub>2</sub> and salinity) and ashore (DIC, DIN, DIP, DISi and pigments). Samples were collected immediately after the bottles were on board from each depth.

The nutrients were taken in polypropylene tubes which were previously cleaned and washed with HCl acid and were completely dry. Samples were duplicated and were immediately frozen at -20°C, to analyze them as soon as possible ashore. The nutrient determination ashore will be performed with a segmented continuous-flow autoanalyser, a Skalar® San Plus System in the ICCM laboratory. Freezing the samples is a common practice; it does not or only in a non-significant way affect the nitrate+nitrite and the phosphate values (by a slight decrease) and is not noticeable in the silicate values (Kremling and Wenck, 1986; McDonald and McLunghlin, 1982). Nitrate+Nitrite: The automated procedure for the determination of nitrate and nitrite is based on the cadmium reduction method; the sample is passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite (Wood et al., 1967), using ammonium chloride as pH controller and complexer of the cadmium cations formed (Strickland and Parsons, 1972). The optimal column preparation conditions are described by several authors (Nydahl, 1976; Garside, 1993).

Phosphate: Orthophosphate concentration is understood as the concentration of reactive phosphate (Riley and Skirpow, 1975) and according to Koroleff (1983a) is a synonym of “dissolved inorganic phosphate”. The automated procedure for the determination of phosphate is based on the following reaction: ammonium molybdate and potassium antimony tartrate react in an acidic medium with diluted solution of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex, ascorbic acid. The complex is

measured at 880nm. The basic methodology for this anion determination is given by Murphy and Riley (1962); the used methodology is the one adapted by Strickland and Parsons (1972).

Silicate: The determination of the soluble silicon compounds in natural waters is based on the formation of the yellow coloured silicomolybdic acid; the sample is acidified and mixed with an ammonium molybdate solution forming molybdosilicic acid. This acid is reduced with ascorbic acid to a blue dye, which is measured at 810nm. Oxalic acid is added to avoid phosphate interference. The used method is described in Koroleff (1983b).

Chlorophyll "a" is sampled from 200 m to the surface using one-liter polypropylene bottles. Phytoplankton pigments are collected by filtration of 500ml of the water sample using Whatman GF/F 47mm glass microfibre filters applying a filtration pressure recommended by the JGOFS protocols (1994); each filter is saved in 10ml glass tubes and frozen subsequently at -20°C. One at the ICCM laboratory, 10ml of acetone (90%) will be added to each filter to extract the pigments; the filters are left in the refrigerator for 24 hours and then chlorophyll "a" is measured using fluorometric analysis following methodology described by WELSCHMEYER (1994). The determination is achieved using a fluorometer TURNER 10-AU-000.

## 5. Dissolved Oxygen

All stations occupied during D368 were sampled for dissolved oxygen (DO) which were the first samples to be drawn from the Niskin bottles. Only those Niskin bottles that were identified as having leaked, and the occasional bottle reserved for biological analysis were not sampled. Seawater was collected directly into pre-calibrated glass bottles using a Tygon® tube. Before the sample was drawn, the bottles were flushed with seawater for several seconds (for about 3 times the volume of the bottle) and the temperature of the water was recorded simultaneously using a handheld thermometer. The fixing reagents (i.e., manganese chloride and sodium hydroxide/sodium iodide solutions) were then added. Care was taken to avoid bubbles inside the sampling tube and sampling bottle, and a water seal was used after the sample was fixed. Samples were thoroughly mixed following the addition of the fixing reagents and were then kept in a dark plastic crate for 30-40 min to allow the precipitate to settle to <50% the volume of the bottle. Once the precipitate had settled all samples were thoroughly mixed for a second time in order to maximize the efficiency of the reaction.

### 5.1. Methods

DO determinations were made using a Winkler  $\Omega$ -Metrohm titration unit (794 DMS Titrimo) with an amperometric system to determine the end point of the titration (*Culberson and Huang, 1987*). Chemical reagents were previously prepared at NOCS following the procedures described by *Dickson (1994)*. Recommendations given by *Dickson (1994)*, and by *Holley and Hydes (1994)* were adopted. In general, thiosulphate calibrations were carried out twice a week using a 1.667mmol L<sup>-1</sup> certified OSIL iodate standard, with the aid of a  $\Omega$ -Metrohm 776 Dosimat unit. Calibration values are summarised in Table 5.1 and shown in Figure 5.1. The thiosulphate solution was prepared at the beginning of the cruise by dissolving 50g of sodium thiosulphate in 1L of Milli-Q water. This solution was left to stabilise for 24 hours before the initial calibration, with a subsequent calibration 12 hours later to ensure the thiosulphate had stabilised. Calculation of oxygen concentrations were facilitated by the use of an Excel spreadsheet provided by Dr. Richard Sanders (NOCS). This spreadsheet has been modified/corrected to include pipettes" calibrated dispensing volumes (i.e., reagents and iodate standard additions have been calibrated). Figure 5.2 shows a time series of replicates.

### 5.2. Observations

- 1 Despite appearing to have stabilised, a calibration of the thiosulphate 5 days after the initial calibrations showed significant drift in the thiosulphate molarity. Subsequent calibrations were consistent with the latter calibration. For the period of possible drift, the latter calibration was used but it was noted that a possible drift in the calculated oxygen values could have occurred.
- 2 The use of the 776 Dosimat as a dispensing unit for calibration allowed for very precise calibrations with relative standard deviations ranging from 0.09 % - 0.12 %.
- 3 In general, replicate measurements of selected samples were carried out in order to test for reproducibility. At least one Niskin bottle was always sampled in duplicate, typically the deepest Niskin bottle. Any misfires were used to duplicate further Niskin bottles. The mean difference between replicates was  $0.4 \pm 0.3 \mu\text{mol O}_2 \text{ L}^{-1}$ , results are shown in Figure 5.2.

- 4 Between stations 13 and 16, the average replicate difference was 1.0  $\mu\text{mol O}_2 \text{ L}^{-1}$ , significantly higher than the previous stations. The cause of this discrepancy could not be ascertained as the only change in the set up was the sulphuric acid, which should not have caused such an effect. The sulphuric acid was replaced and the thiosulphate thoroughly cycled by the titration unit. At station 17, six replicates were collected from a deep Niskin bottle. Of the six samples, five were within 0.4  $\mu\text{mol O}_2 \text{ L}^{-1}$  of each other, suggesting that any systematic problem with the operating procedures had been solved. However, the sixth sample was significantly lower. This was a result of having to pause the analysis and flush the system again to remove bubbles prior to the analysis of this sample. It was therefore observed that the use of dummy seawater samples at the beginning of each run, as outlined in D346, should be extended so that after any large pause a dummy sample should be used to counter the system's tendency to produce erroneous measurements. A batch of dummy samples was prepared for this purpose and used throughout the remainder of the cruise.

Table 5.1: D368  $\text{O}_2$  calibrations; thiosulphate calibration number (\*new reagents used), date of calibration, mean blank titre volume (BLK), standard titre volume (STD), STD minus BLK, molarity of thiosulphate solution and the stations from which each calibration was used.

Calibration number	Date	BLK (mL)	STD (ml)	STD – BLK (ml)	Thiosulphate Molarity	Used from CTD No.
1	17/07/2011	0.0034	0.4998	0.4964	0.2015	
2	22/07/2011	0.0011	0.5173	0.5162	0.1938	1
3*	22/07/2011	0.0001	0.5164	0.5163	0.1937	7
4	25/07/2011	0.0001	0.5159	0.5158	0.1939	13
5*	28/07/2011	0.0000	0.5163	0.5163	0.1937	20

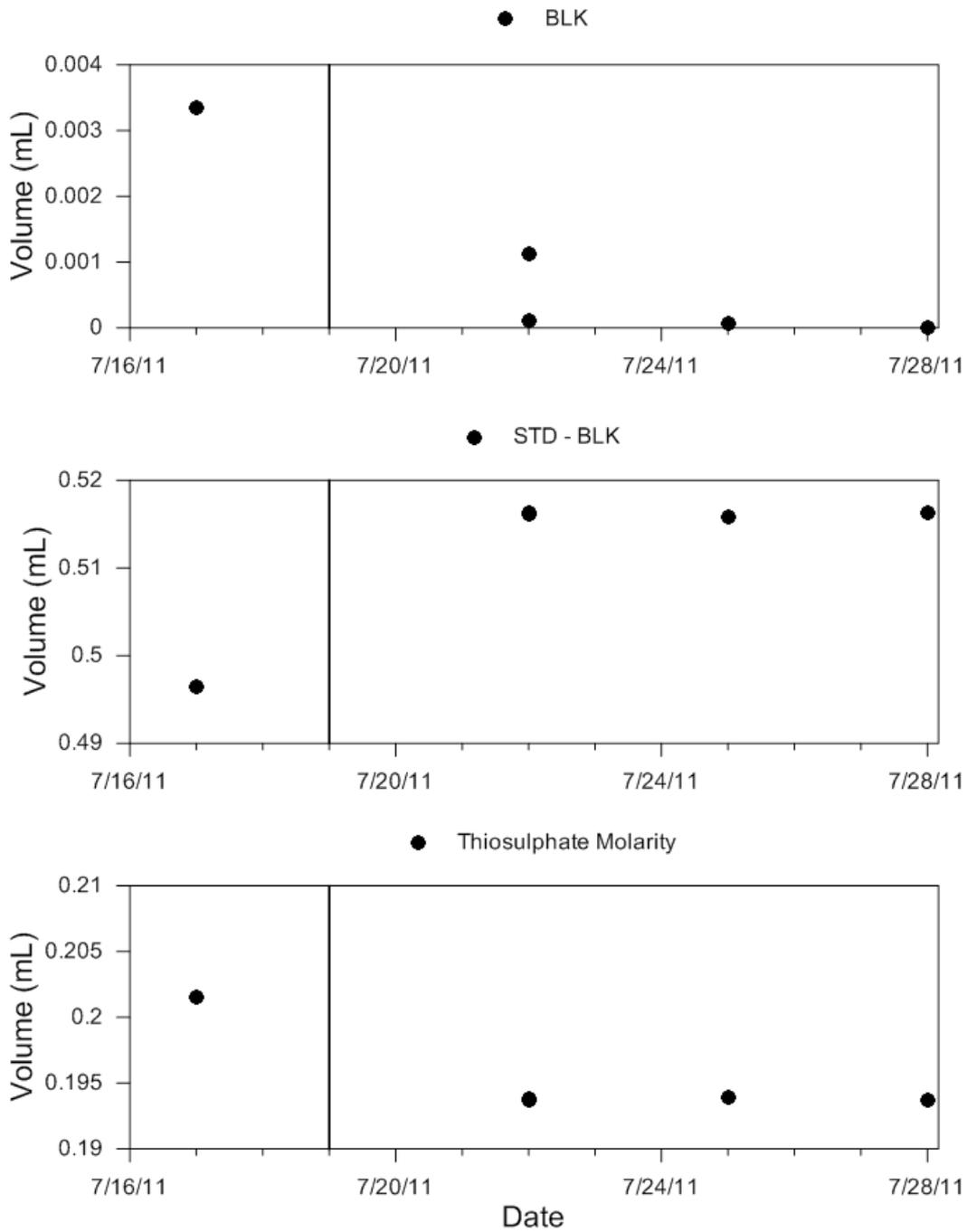


Figure 5.1: Calibrations for dissolved oxygen analysis. Blank volume titre, standard minus blank and thiosulphate molarity. The blank line indicates the date of the first sample collection. Values plotted here are shown in Table 5.1.

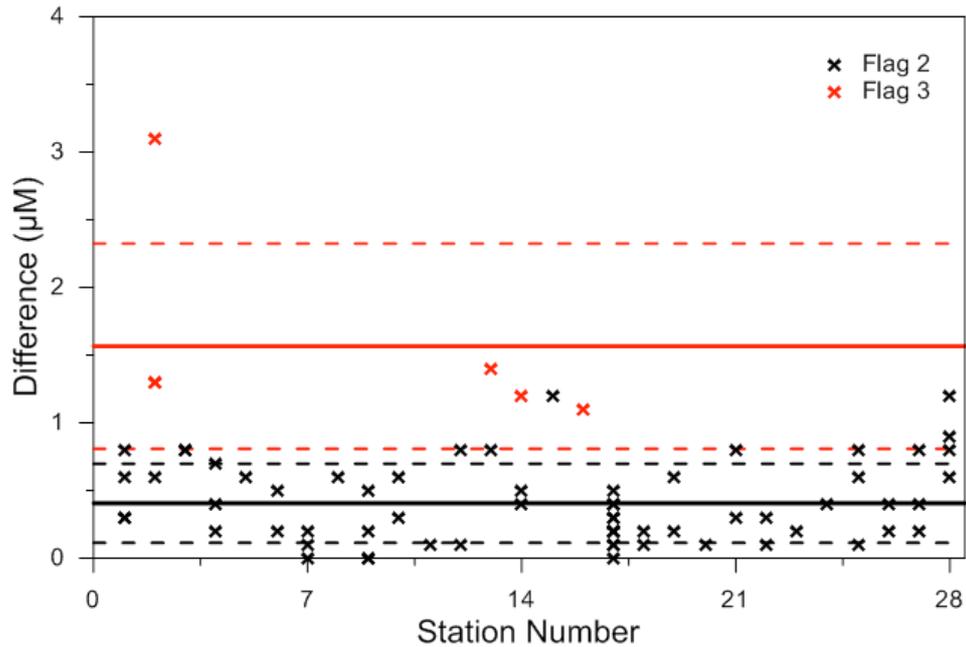


Figure 5.2: The absolute replicate difference for oxygen bottles in each CTD cast. The mean ( $0.4 \mu\text{mol L}^{-1}$ ) and standard deviation are specified with solid and dashed lines respectively. Black symbols indicate values flagged as good (Flag 2) and red symbols are those values flagged as dubious (Flag 3).

## References

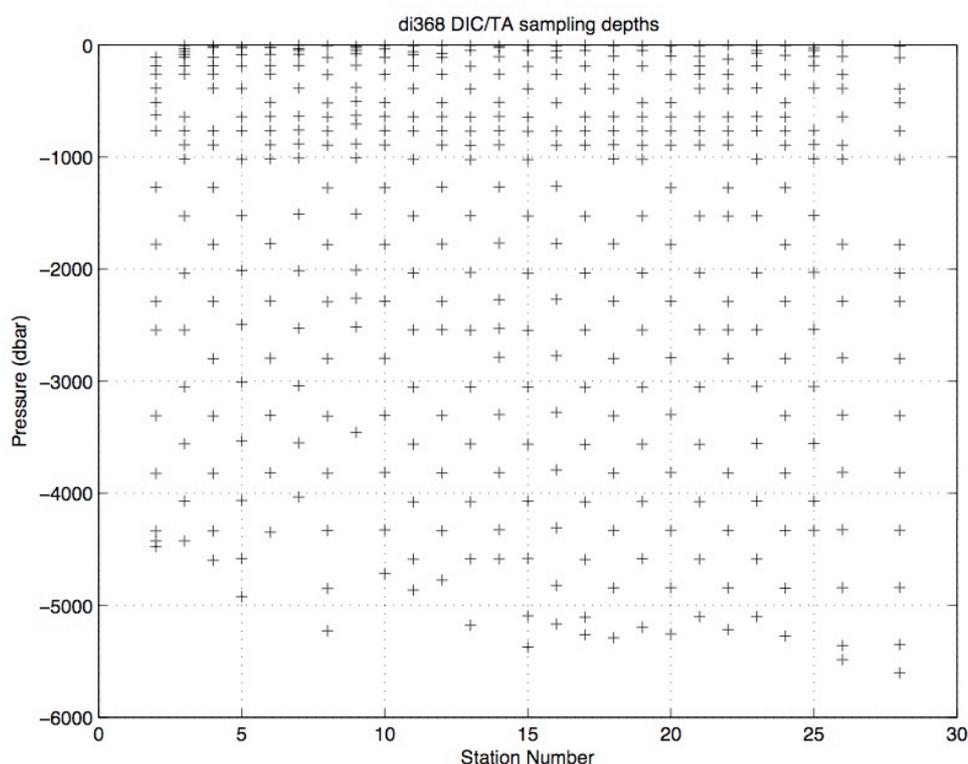
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**Chris J. Daniels**

## 6. Inorganic Carbon from water column samples

### 6.1. Sample Collection

Four hundred and sixty discrete water samples were collected in total for determination of DIC (Dissolved Inorganic Carbon) and TA (Total Alkalinity) using a standard CTD rosette system. Full water-depth carbon samples were taken from 49° 00'N 20° 00'W (CTD station 002) to 23° 21'N, 27° 08'W (CTD station 028) and at the ESTOC station (CTD station 29), Figure 6.1. At station 001, four test samples were drawn and Mercuric Chloride  $HgCl_2$  was added to prevent biological activity. These samples were then discarded in a tightly sealed waste container to allow the bottles to be reused. From stations 002 to 028 sixteen depth samples were drawn from a selection of 33 bottle depths and one replicate was taken at each station, at ~ 3000m, with the exception of station 27 which was not sampled due to lack of bottles. This carbon sub-sampling strategy was based on a selection of depths that alternated between odd and even stations, so that 33 depths could be sampled from 24 Niskin bottles. Two extra depth samples were taken at station 002, and at station 028 seven replicates were taken in total from the deepest Niskin bottle depth. At the ESTOC station 10 discrete water samples were taken at a range of depths throughout the water column for the determination of DIC and TA and to allow me to compare the data with that of previous measurements to assess the reliability of my data.



**Figure 6.1.** Dissolved Inorganic Carbon and Total Alkalinity sampling depths taken from stations 002 to 029 on the cruise Di368.

All the samples were collected in 250ml borosilicate glass bottles and a headspace of 2.5ml was created to allow for the expansion of water on heating. Saturated Mercuric

Chloride (7%) of 0.02% (50  $\mu$ L) by volume of the sample volume was then added to the sample to prevent biological activity, which was tightly sealed with a greased ground glass stopper held in place with strong electrical tape. Samples were then inverted several times to ensure the sample was thoroughly mixed and stored in dark sealed boxes for analysis ashore. Sample collection procedures followed that described by Dickson *et al.* (2007).

## **6.2. Analysis**

Samples are to be analysed ashore at the National Oceanography Centre, Southampton, using a Vindta 3C system to determine DIC, TA, pH and pCO<sub>2</sub>.

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## 7. Computing

### 7.1. Data logging and backups

As on previous recent cruises, the majority of data were logged and backed up on the TECHSAS system. CTD, LADCP and VMADCP data were archived on the discofs file server in binary files generated by the data acquisition software of those instruments.

The NOC physics group brought a linux workstation (nosea2), which was the primary platform for data analysis during the cruise. Directories from TECHSAS and discofs were mounted on nosea2, so data could be copied to nosea2 for processing.

A complete dump of cruise data and software was copied daily using rsync from nosea2 to one of two Freecom portable hard drives, alternate days being copied to alternate drives. These drives were used to carry data back to NOC at the end of the cruise.

### 7.2. TECHSAS data streams

The following TECHSAS streams were processed on nosea2 during the cruise. Most were processed in 24-hour segments, with cleaning and appending as required. Winch data were processed by CTD station.

GPPAT-GPPAT.GPPAT	Ashtech ADU attitude
s9200G2s-FUGRO.GPS	Fugro GPS
position-4000.gps	Trimble GPS4000
gyro-GYRO.gyr	Synchro Gyrocompass
PES-Simrad_PT1.PES	Echo sounder
CLAM-CLAM.CLAM	Winch data
EMLog-LOGCHF.EMLog	Chernikeef EM log
MET-SURFMET.SURFMETv2	Surfmet package met parameters stream
Light-SURFMET.SURFMETv2	Surfmet package radiometers stream
Surf-SURFMET.SURFMETv2	Surfmet package thermosalinograph stream
SBE45-SBE45.TSG	SBE Thermosalinograph

### 7.3. mexec software

The mexec suite of programs was installed and used throughout the cruise, running under Matlab v2007b. A set of the mstar software used during the cruise was archived with the cruise dataset.

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

### 8.1 Instrument setup and performance

Five RDI 300kHz Workhorse LADCP units were available for use on the Di368 cruise: three aluminium cased units and two titanium-cased units. The LADCP configuration was the standard 16 x 10m bins and was also configured to ping in water track mode. For stations 1-17 data was collected in beam co-ordinates and rotated internally to earth co-ordinates. For stations 18-28 data were collected in beam co-ordinates and rotated to earth co-ordinates in the processing. The instruments were mounted in a downward looking orientation on the Rosette frame.

Prior to deployment at each station the LADCP was connected to a laptop in the main lab for pre-deployment tests and programming (via a serial port – USB adapter). Following the retrieval of the Rosette the LADCP was reconnected to the laptop for the retrieval of the data. In between stations the battery pack was charged to prevent the LADCP losing power during casts.

Despite having five LADCP units on board only one, the aluminium unit 133299, was ever used.

### 8.2. Data Processing

The data collected by each cast was downloading following retrieval of the rosette and stored in the directory `/cruise/data/ladcp/uh/raw/di1107/ladcp` as binary files with file names of the form `D368NNNm.000`.

The data for each station was then processed using two different software packages. The first software package was developed by the University of Hawaii (UH) and uses the shear of the water column to calculate absolute current velocities. A secondary function of this software is that it also provides information regarding heading and tilt of the CTD package. The second piece of software used was developed by the Lamont-Doherty Earth Observatory (LDEO). Using an inverse method it calculates velocities. The LDEO software can also be used to obtaining bottom tracking profiles and is often used to monitor the beams of the instrument.

Data were collected in beam coordinates, as this is the recommended method of collection. The UH software handled this format with no modifications. The LDEO software required an updated version of their `loadrdi.m` program.

As previously stated the data was collected in earth co-ordinates for stations 1-17 and beam co-ordinates for stations 18-28. Despite the change in co-ordinates halfway through the cruise the software packages were still able to run.

All the processing for the LADCP was carried out on the `NOSEA2` Linux terminal.

The sequence of the routine processing for the LADCP data was almost identical to the d346 cruise although there were some small modifications.

#### 8.2.1. UH Processing

The UH processing was identical to that used in the d346 cruise although an addition command, `shearcheck(NNN)`, was added, where `NNN` is the station number. This command can be run in the `data/ladcp/uh/pro/di1107/ladcp/proc` directory at any

time after the station of interest has been processed. It makes no changes to the data files, but is used to make a first assessment of the data quality (see section N.4.).

### **8.2.2. LDEO Processing**

The LDEO processing was identical to that used in the d346 cruise except that the LDEO processing always occurred after the CTD data had been processed to the 1Hz file.

Useful bottom velocities are also extracted by the LDEO processing. these velocities are used as a method of verifying the reality of the near bottom velocities calculated by the LDEO inverse calculation.

### **8.3. Mstar Formatting**

The data from both processing routes were read into M\* files. Two M\* files were created for each station: one for the UH profile and one for the LDEO profile

### **8.4. Data Quality**

In areas with low numbers of scatterers, it is possible to receive data from a LADCP which is of very dubious quality. This may appear in the initial *uh* or *ldeo* processing as X-profiles, especially if the *echo amplitude* is low (*ldeo*), or the *shear standard deviation* is high (*uh*). *shearcheck(NNN)* was written to provide a simple sanity check and initial assessment of data quality, by comparing the upcast and downcast for each station. However, it is important to keep in mind that since a cast takes several hours to complete, during this time internal waves may shift water layers vertically, and the ship will undoubtedly move horizontally during a station. Thus differences between the upcast and downcast could represent real ocean variability.

*shearcheck(NNN)* takes the upcast and downcast velocity profiles of the requested station, as produced by the *uh* processing, and calculates the shear of each independently (i.e., not taking the mean of the upcast and downcast). The shears are then smoothed by applying a running mean over 300 m. The first figure produced shows the smoothed upcast and downcast shears, and the difference between them, for both u and v. If the difference is of greater magnitude than the upcast and downcast shears, this suggests the data quality may be poor. The second figure produced shows the upcast and downcast velocities, each with a barotropic component added such that the median value between 200 m and 600 m is zero, on the assumption that there were likely more scatterers in the upper ocean. The difference between the upcast and downcast is also shown. When these velocities deviate markedly at depth, this again suggests the data quality may be poor at these depths. This should not be taken to mean the data is definitely of good quality at shallower depths.

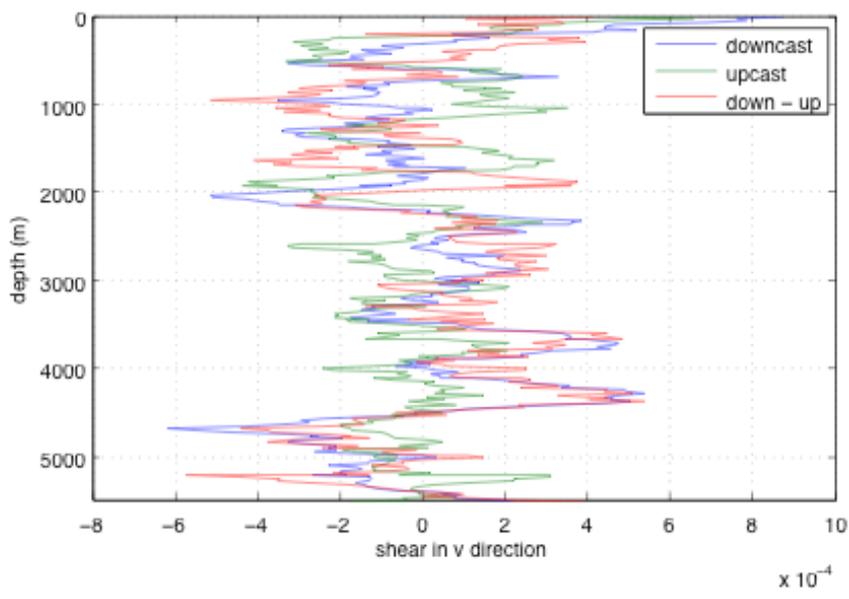
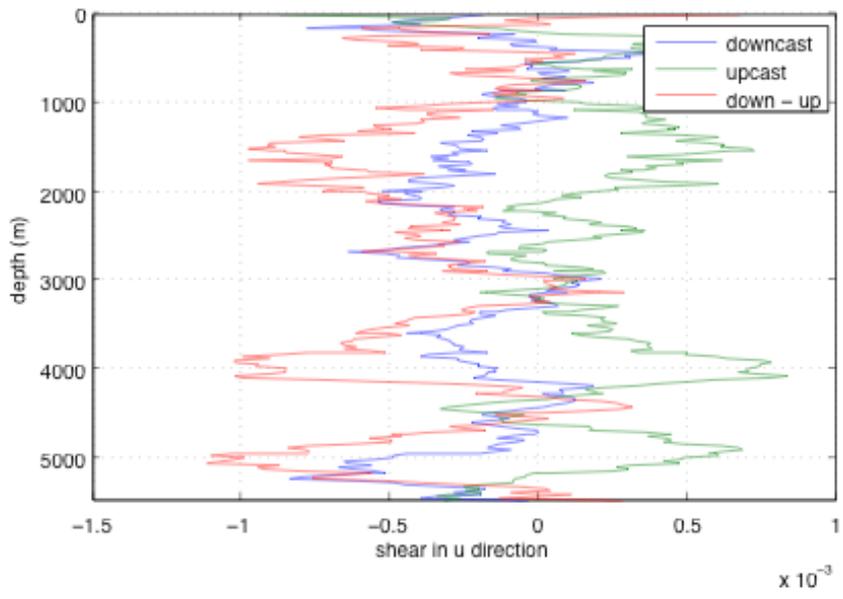


Figure 8.1: example output from *shearcheck*, for station 28. The *u* shear is obviously suspect.

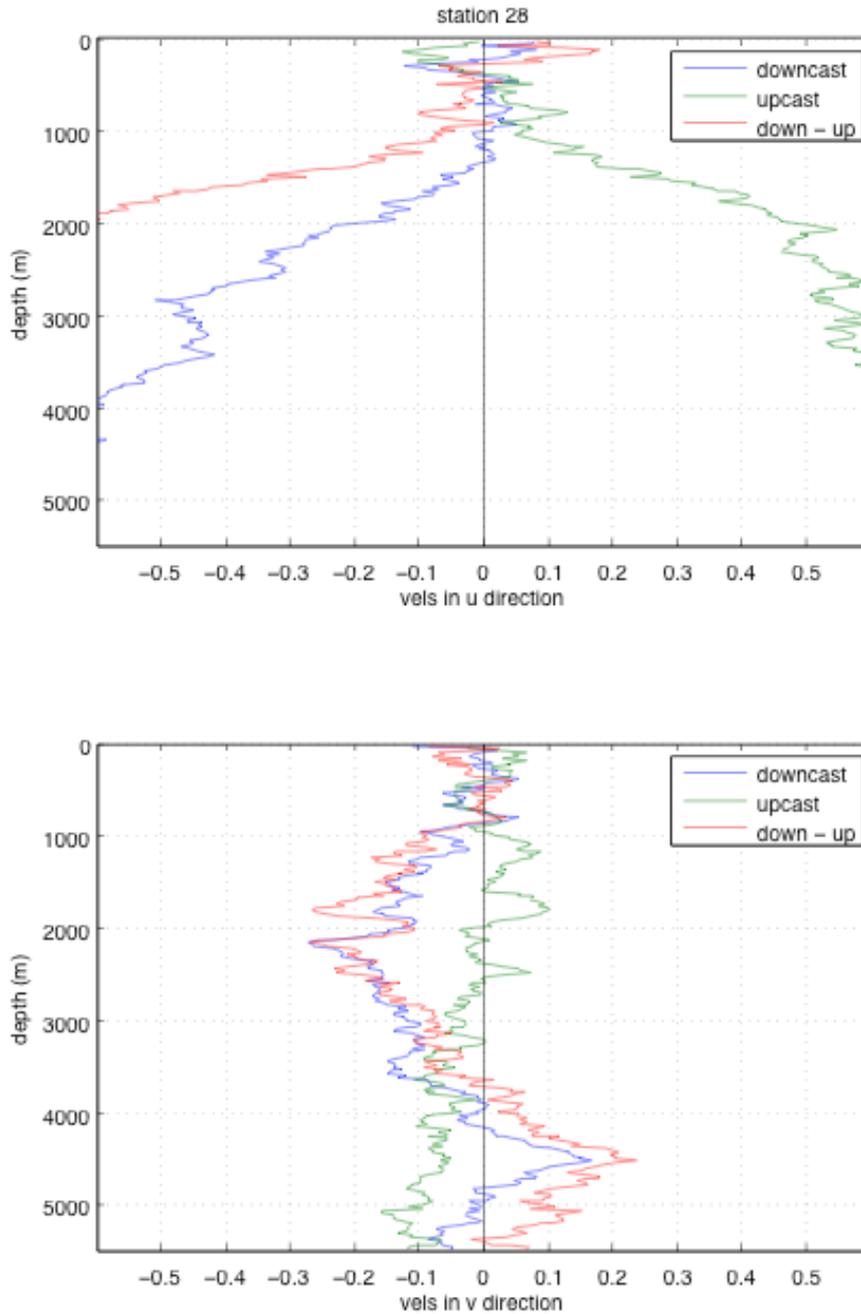


Figure 8.2: example output from *shearcheck*, for station 28. The upcast and downcast  $u$  velocities diverge markedly below 1000m. The behaviour of the  $v$  velocities is less obviously bad, but the divergence below 1000 m is still indicative of poor quality data, even though they converge at greater depth.

**Ben Edwards**  
**Gillian M. Damerell**

## 9. Underway Temperature, Salinity, Fluorescence & Transmittance

Only temperature and salinity were processed out of the surface pumped seawater data stream. Other data were acquired and archived as raw data.

### 9.1. Underway Salinity Sample Collection and Analysis

Underway salinity samples were collected recorded and analysed following similar procedures to the Niskin samples detailed above, the only differences being: The use of the same crate of bottles over 4 days (as samples collected every 4 hours and crates hold 24 bottles). The time was recorded to the nearest minute (to allow the bottle to be matched up to the corresponding underway measurement), these times were then manually added to an extra column in the excel file in the format of day, hour, minutes, seconds (ddhhmmss) where seconds were given the value '00'. And the m-file used to load in the csv files used was given the name *mtsg\_01\_di368*, which gave an output file in the format *ctd/tsg\_di368\_{num}.nc* (where {num} is the chronological crate number) and *tsg\_di368\_all.nc* (the file containing all existing tsg bottle data appended which is automatically created each time the m-file is run).

Samples were run on the Autosal, and adjusted with the offsets listed in Table 3.1.

### 9.2. Underway Conductivity Calibration

A single correction was applied to all underway samples for the offset between the instrument and bottle samples. Firstly all TSG files were read in and appended with the m-file *tsg\_01\_di368*, to create the file *tsg\_di368\_all* this was then merged with the appended underway conductivity file to create the file *tsg\_00\_botmerge*. From this file the ratio of conductivity of the bottle samples to the underway samples minus 1 was calculated. Outliers less than -0.0004 and more than 0.0002 were rejected. The dataset was cropped using the m-file *mplxved* to remove initial readings before the pump was turned on and from day 199, 17:10, until day 201, 04:30, when the de-bubbler failed.

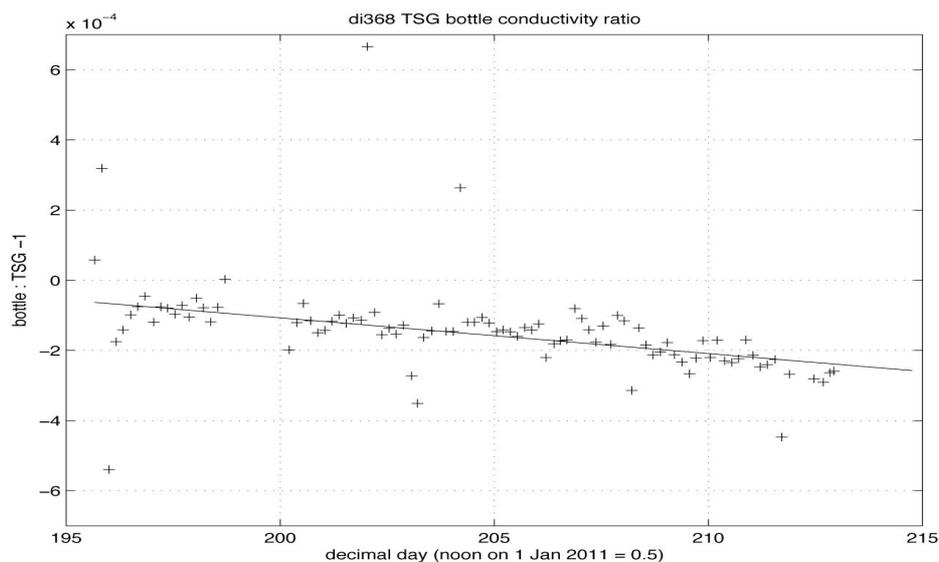
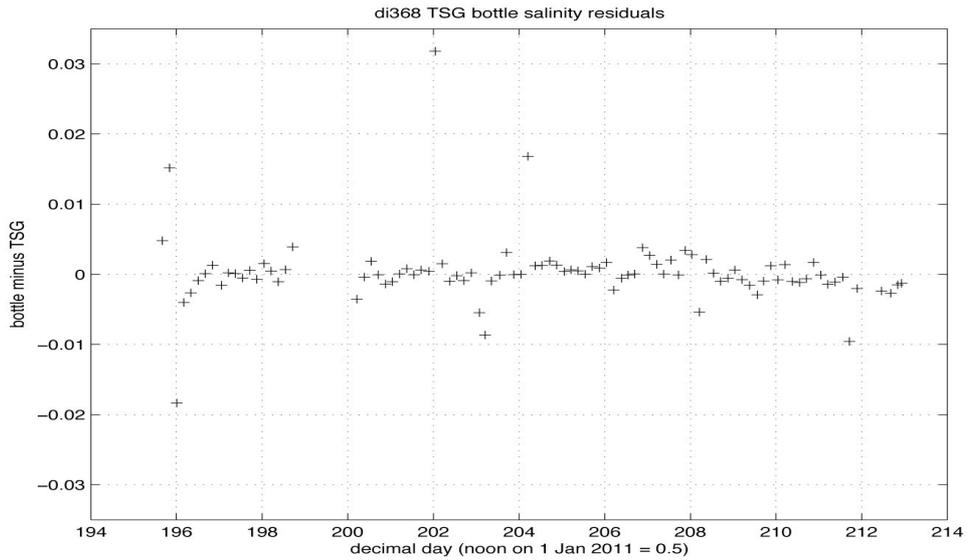


Figure 9.1 Conductivity ratio of bottle to TSG values before calibration has been applied. The best-fit line used to calibrate the sensor drift is plotted as a solid line.

Conductivity ratio was fitted with a first order line of regression, which is then applied to offset all underway measurements. The best-fit line had an intercept of  $-0.5954 \times 10^{-4}$  and gradient of  $-0.0944 \times 10^{-4}$  when the time was started on decimal day 195, seen in Fig. 9.1.

The calibration is applied using the m-file *met\_tsg\_calcsalt*, this performs the correction to the underway conductivity after which it is converted to salinity, creating files called *met\_tsg\_di368\_cal* and *met\_tsg\_di368\_psal* respectively. The final corrected underway salinity can be seen in Fig. 9.2.



*Figure 9.2. Salinity residuals of bottle to TSG values after calibration has been applied*

Amelia Astley

## **10. Daily processing of TECHSAS streams**

### ***10.1. Surface Meteorological Sampling System (SURFMET)***

#### ***10.1.1. Instrumentation***

RRS *Discovery* was equipped with a variety of meteorological sensors to measure air temperature and humidity, atmospheric pressure, total irradiance, photosynthetically active radiation, wind speed and wind direction throughout the cruise.

The radiation and pressure variables were logged in the data/met/surflight directory. The remaining data was logged in /met/surfmet.

#### ***10.1.2. Routine Processing***

Files were transferred from the onboard logging system (TECHSAS) to the UNIX system on a daily basis, using the script *mday\_00\_get\_all.m*. The raw data files have extensions of the form *\_di368\_d\*\*\*\_raw.nc*, where \*\*\* represents the day number. The data were plotted using the script *mday\_plot\_surfmet\_di368.m* and *mday\_plot\_01\_di368.m*.

Once the meteorology and navigation data had been processed, the true (Earth relative) wind speed and direction was computed from the cleaned, ship relative wind data using the script *mtruew\_01.m* and saved in the file *met\_di368\_trueav.nc*.

### ***10.2. Bathymetry***

Data were logged and cleaned following procedures established on *Discovery* Cruise 346.

Files were transferred from the onboard logging system (TECHSAS) to the UNIX system on a daily basis using the Matlab function *mday\_00\_get\_all(day)*. The raw data files have extensions of the form *\_di368\_d\*\*\*.nc* where \*\*\* is the number of the Julian day.

During the cruise, the echosounder often failed to detect the bottom and reported either zeros or spuriously large depths. The script *msim\_01.m* was run to remove data outside a tolerated range and apply a 5-minute median despiking, outputting the file *sim\_di368\_d\*\*\*\_smooth.nc*. The script *msim\_plot.m* copied the smoothed data to the file *sim\_di368\_d\*\*\*\_edited.nc* and called the function *mplxeyed* to allow a manual removal of the remaining spikes.

### ***10.3. Navigation***

The list of navigation streams processed from TECHSAS was given in Section 7.2.

Navigation processing followed the templates from *Discovery* Cruise 346, without significant modification..

**Edwin Lizarazo**

## 11. Vessel Mounted ADCP Instruments

### 11.1. Introduction

A vessel-mounted Acoustic Doppler Current Profiler (ADCP) onboard *RRS Discovery* was used throughout the cruise to measure the horizontal velocity field (cross-track and along-track). The 150kHz Ocean Surveyor (OS) instrument was supplied by Teledyne RD Instruments. (The 75kHz instrument normally mounted in addition to the 150kHz instrument had been found to be unserviceable during previous maintenance, so had been removed for repair.) Unlike *RRS James Cook*, *RRS Discovery* does not have retractable keels so VMADCPs are fitted to the hull of the ship. The depth of the transducer is 5.3m. The transducer is phased-array, which means that it is made up of many elements each transmitting in different phase. This is advantageous, because it means that the accuracy of the velocities, derived from the Doppler shifted return signals, is not affected by speed of sound changes throughout the water column. However, the range and accuracy of the instruments has been observed in this cruise, as it has previously, to be affected by exposure to bubbles.

The 150kHz instrument has small depth bins and consequently high vertical resolution, but the signal is rapidly attenuated and typically only penetrates to approximately 400-500m.

### 11.2. Real Time Data Acquisition

The data from the instrument was acquired using the RD Instruments VmDas software package version 1.42. This software is installed on a PC in the main laboratory. The software allows data acquisition in a number of configurable formats and performs preliminary screening and transformation of the data from beam to Earth coordinates.

In order to collect data in VmDas:

- Open VmDas from the Start Menu and click on “Collect Data” in the File Menu.
- Under Options, click “Edit Data Options” and then set the configurable parameters to the values outlined in the JC029 cruise report (Section 9.3.2).
- Recording commences by clicking the blue record button in the top left of the screen.
- Collection stops by pressing the blue stop recording button in the top left of the screen. Data collection was typically stopped and restarted with a new file segment number every evening during the cruise. Leaving it on the same file for too long allows the files to become too large and post-processing in CODAS becomes slow.

#### 11.2.1. Files Produced by VmDas

The files produced have names of the form *D368 os<inst><nnn>\_<filename>. <ext>*, where *<inst>* is the instrument name (150), *<nnn>* is the file segment number, *<filename>* is the number of the sequential file within the segment and *<ext>* is the extension. We set a new *<filename>* to occur every time a file size of 100Mb was reached, but in fact none of the files reached this size since we stopped and restarted every day, so all the filenames are 000000. Thus all the filenames are

of the form D368os150<nnn>\_000000.<ext>. VmDas automatically increments the file segment number every time data collection is stopped and restarted.

The list of files produced is given below:

- .ENR files are the binary raw data files.
- .ENS files are binary ADCP data after being screened for RSSI and correlation and with navigation data included.
- .ENX files are ADCP single ping data and navigation data after having been bin-mapped, transformed to Earth coordinates and screened for error velocity and false targets.
- .STA files are binary files of short-term average ADCP data (**120 s**, user-specified in VmDas).
- .LTA files are binary files of long-term average ADCP data (**600 s**, user-specified in VmDas).
- .N1R files are ASCII text files of raw NMEA navigation data from the NMEA1 stream.
- .N2R files are ASCII text files of raw NMEA navigation data from the NMEA2 stream.
- .NMS files are binary files of navigation data after screening.
- .VMO files are ASCII text files specifying the option settings used for the data collection.
- .LOG files are ASCII text files logging all output and error messages.

These files were stored in the following directory:

C:\RDI\DATA\D368

These were copied over to */DISCOFS/OS150Khz/raw\_data* – the *Discovery* file store (from which we copied the files over to the *NOSEA2* terminal used for processing the data). At first the copy to */DISCOFS/OS150Khz/raw\_data* was performed rather irregularly, and at intervals of as much as 10 hours, but this was changed to every 2 hours so that the data were backed up regularly.

### ***11.2.2. Real Time Data Monitoring***

The ‘R’, ‘S’ and ‘L’ tabs on the VmDas menu bar allow you to swap between graphical output from the .ENR, .STA and .LTA files. When in ‘R’ mode, the default upper left hand display in VmDas is the raw velocity parallel to each beam, but this can be difficult to interpret as it is shown in beam coordinates. A more useful plot can be made in either the ‘S’ or the ‘L’ mode, displaying the current at a specified depth level as a stick plot in Earth coordinates. To produce these plots, ensure ‘Ship Track 1’ and/or ‘Ship Track 2’ is ticked in the Chart menu. The bins used in the stick plot are specified within “Options”, “Edit Display Options”.

Several other things were also regularly checked whilst the ADCPs were recording:

- We made sure the ensemble number in the real time display of VmDas was increasing during the 4 hourly watchkeeping log, and that the “NAV good” light in the bottom right hand corner of the display was green.

- We ensured that records of the files created are kept up-to-date.

### **11.2.3. Alignment**

As the alignment is close to zero, we used the EA00900 command setting to enable real time monitoring of the currents and for internal VmDas processing.

### **11.2.4. General Settings**

During D368, we ran the instrument in narrowband single-ping mode. Where depth permitted, for the first few days of the cruise, we ran the instrument in bottom track mode to obtain the most accurate phase and amplitude calibrations. Once we left the Celtic Shelf, the instrument was switched to water tracking mode. A table of the bottom track phase and amplitude calibrations is given in Section 11.3.4.

The OS150 was set up to have 60 bins at a size of 8m. A blanking distance of 4m was used in order to avoid ringing from the transmit pulse. Using the VmDas options the instruments were switched between bottom track and water track mode on decimal day 198 when the sea floor was out of range of bottom tracking.

### **11.2.6. Sound Speed Considerations**

Measurements of  $x$  and  $y$  velocities are independent of the speed of sound for phased array ADCP instruments such as those used on D368. If the speed of sound changes in the vertical water column or in front of the transducer, the angle of the beam will consequently change. This change in beam angle change occurs in the same ratio as the Doppler shift equation, meaning that a change in the Doppler frequency shift of a particle moving parallel to the face is compensated entirely by the corresponding beam angle shift, cancelling out the change in the speed of sound. For a more in-depth account of speed of sound considerations when using ADCP units please refer to JC032 cruise report (*King et al., 2010*).

## **11.3. Post-Processing**

The final processing of the data was done using the CODAS (Common Ocean Data Access System) suite of software provided by the University of Hawaii. This suite of Unix and Matlab programs allows manual inspection and editing of bad profiles and provides best estimates of the required rotation of the data, either from water profiling or bottom tracking.

### **11.3.1. Transferring the Data**

CODAS was run on the *NOSEA2* terminal, so the raw data files had to be copied over from *discofs*. The raw data were moved into the */vmadcp/di368\_os150/rawdata* directory. This was performed every morning for the files of the previous evening. Navigation data was processed every night, so was available when processing the VMADCP data the following morning.

### **11.3.2. Setting Up the Directories and Using quick\_adcp**

Once loaded into the *rawdata* directory, the following steps were followed:

1. *vmadcp\_movescript* was typed in the Unix command window. This creates a new directory called *rawdata<nnn>* (*nnn* denoting the file sequence) and moves the relevant data to this new location.

2. Problems with missing navigation data (see below, Section 11.4.3) were fixed in Matlab by typing *m\_setup* and *codaspaths*, then running the script *fixnav\_di368('150','nnn',0)* in the */vmadcp/di368\_os150* directory. This created a directory called *rawdata<nnn>\_fixnav* containing the *enx* file with corrected navigation data.

3. The command *adcpree.py di368<nnn>nbenx --datatype enx* was typed at the command window. This command sets up a directory tree for the CODAS dataset and an extensive collection of configuration files, text files and m files.

4. The directory was then changed to *di368<nnn>nbenx* using the *cd* command, and the control files *q\_py.cnt*, *q\_pyedit.cnt*, *q\_pytvrot.cnt* and *q\_pyrot.cnt* were copied into that directory. *q\_py.cnt* was edited to refer to the relevant segment *<nnn>*, and the *rawdata<nnn>\_fixnav* directory. We then used the command: '*quick\_adcp.py --cntfile q\_py.cnt*', which loads the data into the directory tree, performs routine editing and processing and makes estimates of both water track and (if available) bottom track calibrations. The raw ping files are also averaged into 5-minute periods. The calibration values are stored in the *adcpal.out* and *btcaluv.out* files found in the *cal/watertrk* and *cal/botmtrk* directory respectively and are appended each time *quick\_adcp.py* is run.

### **11.3.3. Applying the Heading Correction**

Applying this rotation to the data required several different steps. Initially a heading correction file was created in Matlab by typing *m\_setup* and running the script *make\_g\_minus\_a(150,<nnn>,'enx')* in the *di368<nnn>nbenx* directory in order to subtract the Ashtech heading from that of the shipboard gyro.

Back in Unix, the processing continued in the *di368<nnn>nbenx/cal/rotate* directory where the *rotate.tmp* file was edited using *emacs* in order to provide the appropriate time angle file for data which was created in the previous processing step, *../edit/di368<nnn>nxx.rot*. To apply the rotation to the database the following command was typed; *rotate rotate.tmp*.

Using *quick\_adcp.py --cntfile q\_pytvrot.cnt* the time dependent heading correction was then run.

### **11.3.4. Calibration**

The *quick\_adcp.py* script estimates amplitude and phase corrections for each set of data. It is only by specifying a calibrated rotation in the *q\_pyrot.cnt* file that accurate velocities could be obtained.

The best calibration estimates are obtained when the velocity data is collected using the seabed as a reference. However, bottom track calibration estimates are only

obtainable when the water depth is within the ADCP profiling range. Bottom tracking was performed at the beginning of the section on the Celtic Shelf from day 196-198. A table of the bottom tracking calibrations was created to calculate mean phase and amplitude of the instruments, which were then used as the rotation values in the *q\_pyrot.cnt* control file. As can be seen from Table 11.1 the final calibration check (highlighted in yellow) shows very little difference from the original rotations applied to the data and is well within acceptable limits (i.e. a tenth of a degree). The calibrations given were as follows: OS150 rotation angle = 0.636, amplitude = 1.0069.

Table 11.1: Bottom track calibration data for the OS150 instrument. The ‘after tvrot’ line is after applying the time-varying gyro minus ashtech correction. The ‘final’ line are data from the end of the cruise (last good segment before heading into strengthened wind and current, which produced large biases) after applying the accepted adjustment of 0.636 for phase and 1.0069 for amplitude.

File		Amplitude (median)	Amplitude (mean)	Amplitude (STD)	Phase (median)	Phase (mean)	Phase (STD)
di368000nbenx	Raw	1.0065	1.0065	0.0011	1.0672	1.3713	0.7236
79 points	After tvrot	1.0065	1.0066	0.0012	0.6293	0.6270	0.0796
di368001nbenx	Raw	1.0062	1.0064	0.0011	2.1784	1.8958	0.4823
52 points	After tvrot	1.0061	1.0063	0.0011	0.6876	0.6774	0.1157
di368002nbenx	Raw	1.0071	1.0069	0.0023	1.5653	1.5745	0.2876
172 points	After tvrot	1.0072	1.0070	0.0023	0.6505	0.6528	0.1409
di368003nbenx	Raw	1.0086	1.0089	0.0032	2.1923	2.1850	0.2029
87 points	After tvrot	1.0087	1.0089	0.0032	0.5230	0.5076	0.2148
di368019nbenx	Final	1.0045	1.0015	0.0097	0.0265	0.0685	0.1250

Comparison with the water track rotations (Table 11.2) shows close similarity with the bottom track calibrations. The mean phase and amplitude calculated from the water track data were as follows: phase = 0.583, amplitude = 1.013. The numbers are not identical to those found using bottom tracking, but this was not expected.

Table 11.2: Water track calibration data for the OS150 instrument

File	No. points	Amplitude (median)	Amplitude (mean)	Amplitude (STD)	Phase (median)	Phase (mean)	Phase (STD)
di368004nbenx	none	-	-	-	-	-	-
di368005nbenx	2	1.0205	1.0205	0.0163	0.6110	0.6110	0.0679
di368006nbenx	none	-	-	-	-	-	-

di368007nbenx	2	1.0245	1.0245	0.0205	0.7000	0.7000	0.2022
di368008nbenx	3	1.0160	1.0263	0.0179	0.7140	0.2787	0.7775
di368009nbenx	5	1.0060	1.0070	0.0063	0.4440	0.5278	0.7132
di368010nbenx	5	1.0170	1.0146	0.0078	0.7990	0.7696	0.2989
di368011nbenx	5	1.0110	1.0108	0.0029	0.4200	0.3816	0.3800
di368012nbenx	5	1.0110	1.0086	0.0073	0.2860	0.6270	0.6312
di368013nbenx	5	1.0100	1.0100	0.0041	0.7420	0.6506	0.3614
di368014nbenx	2	1.0115	1.0115	0.0049	0.6270	0.6270	0.1739
di368015nbenx	none	-	-	-	-	-	-
di368016nbenx	4	1.0155	1.0128	0.0104	0.4365	0.3783	0.3007
di368017nbenx	5	1.0130	1.0106	0.0055	0.5590	0.6222	0.3331
di368018nbenx	4	1.0065	1.0085	0.0059	0.5895	0.5443	0.1490
di368019nbenx	4	1.0115	1.0082	0.0094	0.6675	0.7075	0.1243
di368020nbenx	4	1.0110	1.0103	0.0034	0.5715	0.5383	0.0751

The final calibrations were applied to each file sequence using *quick\_adcp.py --cntfile q\_pyrot.cnt* in the *di368<nnn>nbenx* directory in the Unix terminal window. This rotates the data by the phase and amplitude specified by the user in the control file *q\_pyrot.cnt*. A recalculated calibration (after taking the first calibration into account) is printed to the *\*.out* file(s). The data were then checked in Gautoedit to ensure that any vertical striping associated with on/off station differences had been removed by application of the calibration. Any alterations that needed to be made to the files, for example due to bad profiles or bad bins, were made using Gautoedit.

### 11.3.5. Gautoedit

The Gautoedit package within CODAS allows the user to review closely the data collected by VmDas and flag any data that is deemed to be bad. These flags can then be passed forward and, using the *q\_pyedit.cnt* control file, the data removed. Typically, the data were reviewed as follows:

1. Matlab was opened in the *di368<nnn>nbenx/edit* directory. In the command window, typing:  
*m\_setup; codaspaths; gautoedit*

An editing GUI, shown in Figure 11.1. The editing was done from here.

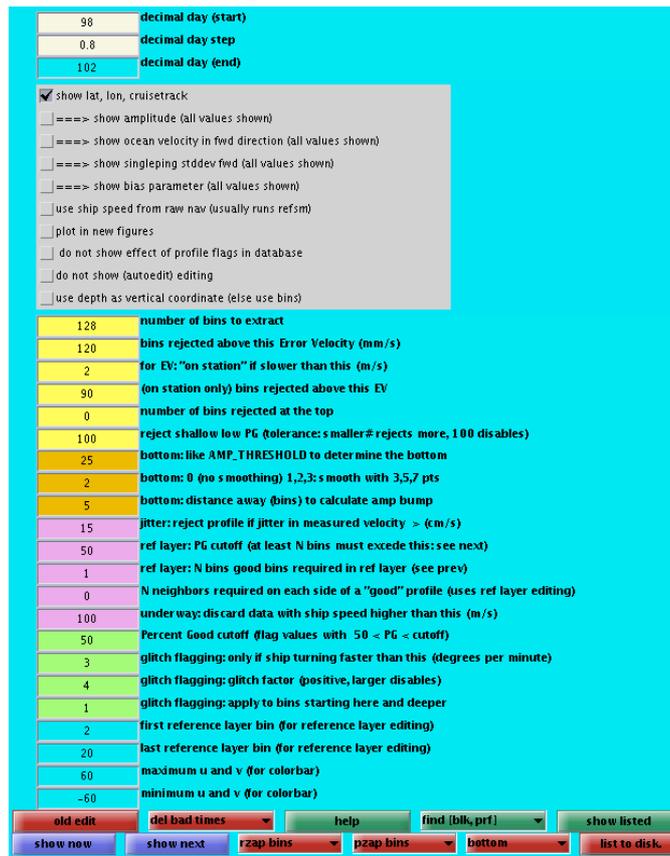


Figure 11.2: The Gautoedit window within the CODAS suite of programs in Matlab

2. Gautoedit was initially used after the first *quick\_adcp.py* step to observe whether the ENX files had processed correctly. The start time of the ENX file was entered in the *decimal day (start)* box and the length of the dataset (in days) was entered in the *decimal day step* box. Upon pressing *Show Now*, two plots are displayed according to the default plot selections. One contains four subplots: the first displays the absolute east-west (U) velocity component, the second shows the absolute north-south (V) component, the third shows the percentage good parameter and the fourth shows the ship speed (in m/s) and an editing parameter called jitter. The second figure contains subplots of the ships' track and mean absolute velocity vectors at the reference layer. However, it was noted that throughout the duration of the cruise there was a bug within this part of the software, as when *show now* was clicked, Gautoedit crashed during the plotting of the ships' track and velocity vectors. This did not present a problem to the processing because simply pressing *show now* once more succeeded in plotting the vectors. An error command will appear if there are no data in the selected time range. This initial review of the data allows the user to confirm the direction of steaming, identify the position of on-station and off-station parts of the file and spot any areas with low percentage good. It is also useful to identify the maximum and minimum values of *u* and *v* to allow a suitable colour bar to be used when examining the data more closely (by default -60 to +60 is used). To change this, use the *maximum u* and *v* and *minimum u* and *v* boxes.

3. To inspect the data more closely and to start applying edits, the data must be inspected in shorter time sections. Typically, we worked from the start of the data in 0.1 day portions as this allowed us to see the individual 5-minute bins. Once the edits were finished on one portion, the *List to Disk* option was selected to save the flags before using *Show Next* to advance onto the next 0.1 day section.

Routine editing for each section included:

- looking for bad profiles (i.e. those in which the  $u$  and/or  $v$  had a systematic offset over all depth levels). These were flagged using the *del bad times* command and choosing the select time range option.
- looking at the jitter parameter in the bottom subplot. A high level of jitter either indicates noise in the navigation and/or rapidly changing velocities. Generally, the default jitter threshold (set in the *Jitter: reject profile if jitter in measured velocity*) of 15cm/s seemed to be a reasonable value for flagging potentially bad profiles and did not need to be changed.

4. In particular, the presence of either enhanced scattering layers in the profiles or bubbles directly beneath the ship are known to bias the underway velocities in the affected layers in the direction of steaming. These biases are discussed further in Section 11.4.

5. Once satisfied with the changes made, the *List to Disk* option is selected which creates and updates  $a^*.asc$  files in the  $di368<nnn>nbenx/edit$  directory.

### ***11.3.6. Applying the Edits***

Once the  $a^*.asc$  files have been created, the edits are applied using the following command at the Unix terminal prompt from within the  $di368<nnn>nbenx$  directory:

```
quick_adcp.py -cntfile q_pyedit.cnt
```

The  $q\_pyedit.cnt$  file has to have the correct *instname* command line (i.e. OS150).

### ***11.3.7. Creating the Output Files***

Once the editing and rotations were completed, the final velocities were collated into Mstar files (\*.nc) using the following commands in the  $di368<nnn>nbenx$  directory of a Matlab command window:

```
m_setup  
mcod_01  
mcod_02
```

(type the file number and instrument number when prompted to specify the input file).

The first command sets up the Mstar suite of programs and the relevant paths. The other two commands load in the final data for the file sequence and save it as two

Mstar files. The first command produces a file of the form *os150\_di368<nnn>nnx.nc* that includes the following variables:

- time - (in seconds since [2010 1 1 0 0 0])
- lon - (0 to 360)
- lat - (-90 to 90)
- depth - (of bin)
- uabs - (absolute *u* velocity in cm/s)
- vabs - (absolute *v* velocity in cm/s)
- uship - (*u* velocity of ship over ground)
- vship - (*v* velocity of ship over ground)
- decday - (decimal day of year)

The second file is of the form *os150\_di368<nnn>nnx.nc* and includes, (in addition to the above variables):

- speed - (scalar water speed in cm/s)
- shipspd - (scalar ship speed over ground in cm/s).

The individual *os150\_di368<nnn>nnx.nc* files are then appended together into a single output file for the cruise using a script called *mcod\_mapend*. This command relies on an input file containing the paths of all the individual files to be merged. This was created in the */di368\_os150* directory and was named *os150list*. The final output file was *os150\_di368\_all.nc* which contain appended on-station and underway data.

## ***11.4. Data Quality Issues***

Whilst carrying out *Gautoedit* editing, several quality control issues were identified that warrant discussion.

### ***11.4.1. Bubble Contamination and Bias***

Two potential issues arise from the presence of bubbles immediately below the transducer face. Bubbles can prevent penetration of the transmit pulse and lead to truncated or bad quality profiles. This was not widely observed on cruise D368. It is also known that the high amplitude return from bubbles can cause anomalous velocities in the direction of ship steaming. It is commonly identified by a relatively low percentage good in the top few bins, and a red surface stripe in the along-track bias parameter. This was not a significant problem for much of the cruise, except when we turned to head north-east after station 28, to go to the Canary Islands. The weather had deteriorated significantly over the previous 24 hours, and we were then heading into the wind, waves and current. *Fischer et al, (2003)* relate an increase in bubble formation with increased inclement weather conditions, however this does depend on the location of the transducer on the ships' hull, as some areas may be more prone to bubble formation than others. After the end of station 28, (15:45 on day 212), the velocities have a large, obvious bias in the direction of travel. This

affects the last few hours of segment 20, and the whole of segments 21 and 22. We have not removed these data, as it may be possible to extract some information if treated with great care.

#### ***11.4.2. Anomalous Scattering Bias***

Previous subtropical cruises, e.g., cruises 324 and 346 on *RRS Discovery* and cruise 032 on *RRS James Cook*, have noticed the presence of anomalous scattering layers (due to scatterers such as zooplankton) leading to along-track velocity bias. Cruise D346, for example, found (with the 75kHz instrument) a large anomalous scattering layer between 460-660 metres across much of the section. We did not observe any such large, consistent bias on D386, but this may be simply because we only had a 150kHz instrument, which could not penetrate as far into the ocean as a 75kHz instrument.

### 11.5. Start and End Times of Data Segments

Table 11.3: The sequence log of the OS150 instrument.

Sequence Number	Start Date	Start Time	End Ensemble	End Date	End Time	BT/WT	Notes
0	196			196	19:31	BT	
1	196	19:31		197	00:38	BT	
2	197	00:38	15755	197	17:34	BT	1
3	197	17:35	11404	198	06:15	BT	
4	198	06:15	4947	198	11:27	BT	1,2
5	198	11:28	10715	198	21:08	WT	
6	198	21:09	25685	199	20:20	WT	
7	199	20:21	26076	200	19:53	WT	
8	200	19:54	27043	201	20:19	WT	
9	201	20:19	29130	202	22:37	WT	
10	202	22:38	25899	203	22:01	WT	
11	203	22:01	24071	204	19:45	WT	
12	204	19:46	26490	205	19:41	WT	
13	205	19:41	27723	206	20:43	WT	
14	206	20:43	13971	207	09:21	WT	3
15	207	09:21	11292	207	19:33	WT	3
16	207	19:33	27005	208	19:56	WT	4
17	208	19:57	697	209	20:00	WT	5
18	209	20:00	26383	210	19:49	WT	
19	210	19:50	26453	211	19:43	WT	
20	211	19:43	26113	212	19:18	WT	
21	212	19:18	27882	213	20:28	WT	
22	213	20:28	24568	214	18:39	WT	
23	214	18:40	36729	216	03:49	WT	6

#### Notes

1. Data collection stopped at unusual time of day when watchkeepers discovered “NAV good” showing a red light. On restart, “NAV good” showed green.

2. Although the instrument was still in bottom tracking mode for this segment, the bottom was out of range.
3. Data collection stopped at unusual time of day when watchkeepers discovered “NAV good” showing a red light (014). On restart, “NAV good” was still red. On resetting the splitter which distributes to a variety of instruments the NAV data to the PC running VmDas, “NAV good” showed green (015).
4. A new splitter was used from the start of this segment. The change of splitters was made during the first half-hour of this segment, hence there was some missing NAV data during this period.
5. The end ensemble number shown in VmDas was 697 – extremely low for the end of a day’s data collection. While this caused some concern at the time, the file size was appropriate, and the data processing completed in a satisfactory manner. No data appears to have been lost.
6. This last segment was collected, but not processed during the cruise. We noticed that although the “NAV good” light remained green, in fact NAV data were missing for the first few hours of this segment.

### ***References***

Fischer, J., P. Brandt, M. Dengler, M. Müller, and D. Symonds, (2003), Surveying the Upper Ocean with the Ocean Surveyor: A New Phased Array Doppler Current Profiler. *J. Atmos. Oceanic Technol.*, **20**, pp. 742–751.

**Gillian M. Damerell**

## 12. Carbonate chemistry from underway samples

### 12.1. Objectives

The main objective was to obtain high spatial resolution surface carbonate chemistry measurements from the underway non-toxic water supply along the A16N transect. Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA) and pH measurements were made at intervals of 3, 30 and 6 minutes respectively. All measurements were made on the ship immediately after sample collection.

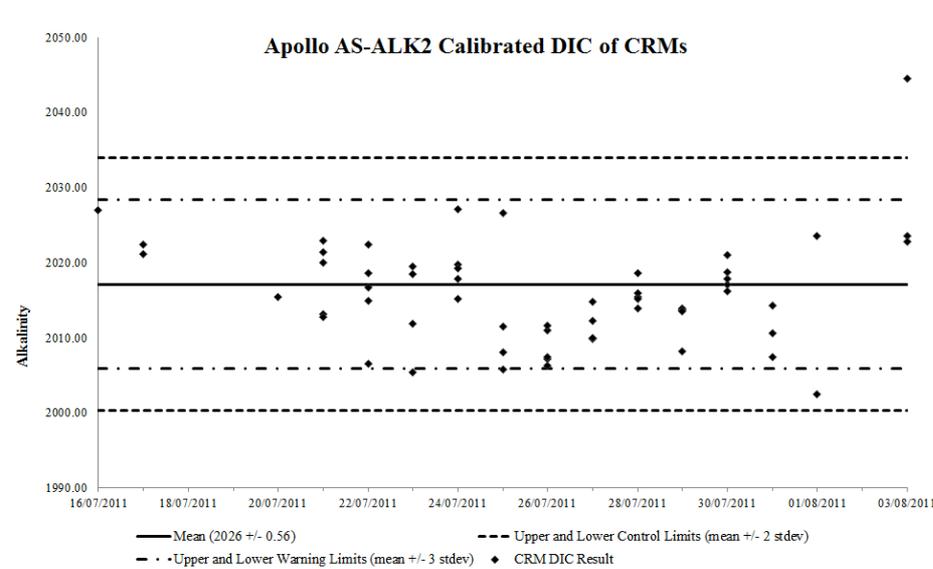
### 12.2. Sampling Protocol and Analysis

#### *Dissolved Inorganic Carbon*

The DIC instrument was connected via a piece of silicon tubing to a direct pipe to the underway non-toxic water supply. An air-tight seal was maintained between the tubing and the analyser inlet. The instrument was the Apollo AS-C3 (Apollo SciTech, USA), which uses a LI-COR (7000) CO<sub>2</sub> infrared analyser for detection, a mass flow controller to control the carrier gas (N<sub>2</sub>) flow, and a digital pump to measure and transport accurate volumes of the sample and reagent. Excess 10% phosphoric acid was added to each 0.75ml sample to convert all carbonic acid species to CO<sub>2</sub>.

The system was calibrated every other day using Certified Reference Material (batch 109) from A.G. Dickson (Scripps Institution of Oceanography). Unused CRM after each calibration was siphoned into a medical blood-bag to minimise air contact and then re-measured throughout the cruise at intervals of 80 runs (c. 4 hours) to check for any drift in the measured seawater values.

DIC measurements commenced on 16/7/11 after the underway water supply had been turned on and the system flushed through. The system was then run continuously throughout the cruise, only being stopped to allow for calibration



A problem arose when an internal tube transferring N<sub>2</sub> gas from the LI-COR to the Apollo unit in the Apollo DIC Analyser became detached. This was resolved by

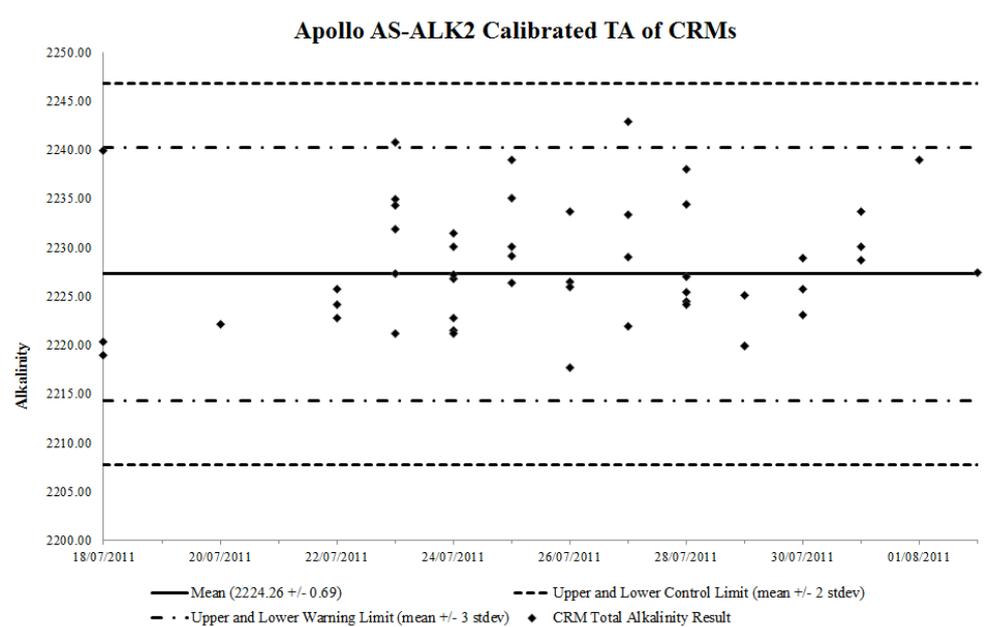
reducing the N<sub>2</sub> gas cylinder pressure to 35 psi, after which the system was flushed with Milli-Q and re-started.

### Total Alkalinity

Samples were collected from the underway water supply tap in 40ml EPA vials and TA was measured within at most an hour, so poisoning was not required. Sampling for TA commenced on 18/7/11, as the sea was too rough before this to use the water bath necessary to maintain a constant temperature required for the analysis. Samples for TA were collected every 30 minutes whilst in transit between CTD stations and every hour whilst on station. Once the A16N transect had been completed, samples were taken every hour until the final station was reached.

The instrument used for the determination of Total Alkalinity was the Apollo AS-ALK2 (Apollo SciTech, USA). This system used a combination pH electrode (8102BNUWP, Thermo Scientific, USA) and a temperature probe in order to measure the temperature (Star ATC probe, Thermo Scientific, USA). These were both connected to a pH meter (Orion 3 Star benchtop pH meter, Thermo Scientific, USA). Samples were analysed by coulometric titration with hydrochloric acid 0.1M using an open-cell titration (Dickson et al. 2007). The temperature during TA analysis was regulated at 25°C (±0.1 °C) with a water-bath (GD129, Grant, UK). Small increments of acid are added to the sample and the electromotive force is monitored for each step until the carbonic acid equivalence point is reached (protonation of carbonate and bicarbonate ions). This is reached through the system conducting an automated Gran Titration.

Certified Reference Material (batch 109) from A.G. Dickson (Scripps Institution of Oceanography) was used as standards to calibrate the system every other day during analysis as well as to standardise the acid. CRM was analysed every 4-6 hours throughout the cruise to check for any drift in the machine's results.



*pH Measurements* (modified from D366 report by Victoire Rerolle, School of Ocean and Earth Science, NOCS)

### *Introduction*

The carbonate system is a key component of the chemical perspective of oceanography as it plays an important role in the oceans' capacity to take up atmospheric CO<sub>2</sub>. Dissolved inorganic carbon (DIC) is present in seawater in three forms (CO<sub>2(aq)</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) which are in equilibrium on timescale longer than a few minutes. In oceanography, the carbonate system can be determined by four parameters: DIC, pCO<sub>2</sub>, alkalinity and pH.

This project aims to measure seawater pH. This cruise was an opportunity to test the spectrophotometric pH sensor developed by Victoire Rerolle for her PhD. An automated sensor running continuously on the non-toxic water supply was used.

### *Method*

*pH sensor-* pH is measured by adding a colored indicator to the seawater sample and measuring the color of the mix. The indicator used is Thymol Blue. The pH sensor has been developed at the NOCS (Sensor group).

*Underway measurements-* The automated pH system was running continuously on the non-toxic water supply from the 06/06/2011 to the 07/07/2011. Measurements were only interrupted for system performance checking and maintenance.

The consistency of the data will be checked thanks to continuous pCO<sub>2</sub> measurements (see Ian Brown and Dorothee Bakker), DIC/Alkalinity sampled on the underway supply every two hours (see Dorothee Bakker) and trends in other parameters such as chlorophyll, temperature, salinity and nutrients.

### *References*

Dickson, A.G., Sabine, C.L., Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO<sub>2</sub> measurements. PICES Special Publication 3, IOCCP report No. 8, 191 pp.

**Rebecca J. Hampshire and Matthew P. Humphreys**

### 13. Metabolic activities and phylogenetic composition of eukaryotic and prokaryotic populations

#### Aims:

- Assess metabolic activities of prokaryotic organisms in the deep Mediterranean water.
- To quantify prokaryotic and eukaryotic groups along the water column down to the seafloor bottom.
- In the North Atlantic Gyre, to measure the concentration of inorganic phosphorous (Pin) and its uptake by the dominant prokaryotic groups. To evaluate the influence of light in Pin uptake.
- To taxonomically identify and quantify the dominant and active prokaryotic and eukaryotic groups in order to link community composition and function.
- To determine the diversity of the active pico-phytoplankton, including prokaryotes (*Synechococcus* and *Prochlorococcus*) and eukaryotes.

#### Objectives:

- To estimate turnover rates of dissolved organic nutrients and phosphorus using methionine, adenosine tri-phosphate and phosphate tracers.
- To collect seawater samples for molecular analysis in order to phylogenetically identify the composition of microbial groups sorted by flow-cytometry. Prokaryotic and eukaryotic groups will be identified by 16S- and 18S-rRNA pyro-sequencing respectively, and quantified by fluorescence *in situ* hybridisation (FISH) or quantitative PCR.

#### 13.1 Microbial activity

Ambient concentrations as well as uptake rates of the amino acids methionine, inorganic and organic phosphate by total microbial plankton were measured using isotopic dilution time-series incubations (Zubkov et al 2004, Zubkov et al 2007). The uptake of methionine and organic phosphate was evaluated in the Mediterranean deep water and in the oxygen minimum zone. Microbial inorganic phosphorus dynamics were determined in the phosphate-depleted North Atlantic gyre to estimate ambient concentrations and turnover rates of the bioavailable fraction. Phosphorus microbial uptake was evaluated in surface waters and in the deep chlorophyll maximum. Moreover, the effect of light on the microbial phosphorous uptake was evaluated. The relative contributions of the dominant prokaryotic groups to the amino acid and phosphate cycle were determined using flow cytometric cell sorting.

##### 13.1.1 Sample collection

Samples were collected into acid-washed 1L thermo flask using acid soaked silicone tubing. Thermo flasks were washed three times with seawater sample before collection. Sample was processed within 1 hour after collection.

**Table 13.1:** stations sampled for microbial activity, including CTD no., dates, and depth.

Station	Depth (m)	Latitude	Longitude	Julian Day	Time (GMT)	Date
CTD001	605	48 39.68 'N	017 01.80' W	200	10:00	19/07/2011

CTD 002	500	49 00.03' N	019 59.89' W	201	05:30	19/07/2007
CTD 002	625	49 00.03' N	019 59.89' W	201	05:30	19/07/2007
CTD 004	1000	47 00.04' N	020 00.00' W	202	07:05	20/07/2007
CTD 004	750	47 00.04' N	020 00.00' W	202	07:05	20/07/2007
CTD 007	375	44 00.28' N	020 00.06' W	203	11:25	21/07/2007
CTD 007	1000	44 00.28' N	020 00.06' W	203	11:25	21/07/2007
CTD 009	1250	42 03.0' N	019 59.96' W	204	05:55	22/07/2007
CTD 009	750	42 03.0' N	019 59.96' W	204	05:55	22/07/2007
CTD 009	5	42 03.0' N	019 59.96' W	204	05:55	22/07/2007
CTD10	50	40 59.9' N	020 00.08' W	204	14:50	22/07/2007
CTD12	65	39 00.00 ' N	020 00.00' W	205	09:25	23/07/2007
CTD12	5	39 00.00 ' N	020 00.00' W	205	09:25	23/07/2007
CTD14	50	36 50.00 ' N	020 00.00' W	206	06:30	24/07/2007
CTD16	50	36 00.00 ' N	020 33.00' W	207	02:35	25/07/2007
CTD19	25	32 00.00 ' N	22' 05.05 W	208	10:40	26/07/2007
CTD21	101	30 00 00' N	023 22.57 ' W	209	07:15	27/07/2007
CTD21	50	30 00 00' N	023 22.57 ' W	209	07:15	27/07/2007
CTD25	25	25 59.97' N	025 37.45 ' W	211	06:05	29/07/2007
CTD25	100	25 59.97' N	025 37.45 ' W	211	06:05	29/07/2007
CTD27	50	23 59.91' N	026 45.00' W	212	02:15	30/07/2007
CTD27	100	23 59.91' N	026 45.00' W	212	02:15	30/07/2007

### 13.1.2. Ambient concentrations and turnover rate of amino acid and organic phosphate

Ambient concentrations as well as uptake rates of the amino acid methionine and of organic and inorganic phosphate by total microbial plankton were measured using isotopic dilution time-series incubations, bioassays, at tracer concentrations (Zubkov et al 2004, Zubkov et al 2007). L-[<sup>35</sup>S] methionine (specific activity 1000 Ci mmol<sup>-1</sup>) was added in a range of concentrations between 0.02 and 0.2 nM. [ $\alpha$  <sup>32</sup>P]- ATP (specific activity 3000 Ci mmol<sup>-1</sup>) was added at a concentration of 0.02 nM or 0.2 nM. Samples were fixed after 30, 60, 90 and 120 minutes with 1% (w/v) paraformaldehyde final concentration. Experiments were performed in 1.6 mL crystal clear vials in duplicated. Samples were filtered onto 0.2  $\mu$ M pore size polycarbonate filters and washed twice with 4 ml of MQ water. Duplicated samples were pooled in one filter. Radioactivity retained on the filters was measured as counts per minute using a liquid scintillation counter. Experiments were counted twice, for 2 minutes each. Results were obtained within approximately 10 hrs of sampling and used to evaluate the dilution series to be used in the following experiment.

For determination of phosphate ambient concentration and uptake rates, [<sup>33</sup>P]orthophosphate (3000 Ci mmol<sup>-1</sup>) was added at a concentration of 0.05 nM and diluted with non-labelled Na<sub>2</sub>HPO<sub>4</sub> using a dilution series in a range between 0.04 nM and 4 nM. Samples were fixed after 10, 20, 30 and 40 min with 1% (w/v) paraformaldehyde final concentration. Samples were filtered and counted as detailed above.

For flow cytometric sorting of isotopically labelled cells, 8 mL to 20 mL of samples was incubated in pyrex glass bottles. Methionine, ATP and phosphate were added at a final concentration of 0.1 nM. Samples were incubated between 2 and 8 hrs in the light and dark, or only in the dark for deep samples, at *in situ* temperature. Subsamples were taken every two hours to check that the uptake was linear. 600  $\mu$ L of sample was harvested onto 0.2  $\mu$ M pore size polycarbonate filters and radioactivity retained in the filters measured in scintillation counter. For samples below 500 m, the total experiment volume was concentrated in the presence of 0.01% pluronic solution. The concentrated sample was used for cell sorting. Cells were stained with SYBR Green I DNA stain prior of analysis by flow cytometry. Different number of HNA, *Prochlorococcus*, LNA and total bacterioplankton cells were sorted, using the single-cell sort mode. Sorted cells were collected onto 0.2  $\mu$ M polycarbonate filters and the radioactive retained on the filters counted in scintillation counter. Four proportional numbers of cells were sorted, and the mean cellular tracer uptake was determined as the slope of the linear regression of radioactivity against the number of sorted cells.

### **13.1.3. Preliminary observations.**

#### *Methodological considerations*

Due to the low metabolism of microorganism in deep waters and the low concentration of organic molecules, measuring its activity using substrates at ambient concentrations is a challenge. We measured the uptake rates of amino acids in the salinity maximum and in the oxygen minimum zone by the total prokaryotic community. However it was not possible to measure the uptake rates of single cells, separated by flow cytometer cell sorting, due to the low uptake of the cells and their low abundance. Samples were concentrated, in order to increase the number of cells, however measurements were still below the detection limit of the scintillation counter.

Scintillation counts were carried out on board the ship (Packard Tri-Carb 3100). Bioassayed concentrations of methionine ranged between 0.005 and 0.04 nM with a slow turnover rate between 66 and 2000 hrs. Organic phosphorus concentration was 0.003 and 0.017 in the oxygen minimum zone, however it was not possible to measure it in the salinity maximum (1000 m).

In samples above 100 m, concentration of inorganic phosphorus (Pin) was between 1.6 and 3.6 nM and the turnover time of the Pin pool was between 43 and 300 hrs. In general, the concentrations of Pin were higher in the DCM than in surface samples while its uptake rate (nM Pin day<sup>-1</sup>) was slower in the DCM.

After the cruise, the collected tracer samples of flow sorted cells we be analysed in detail on low background counters due to the sensitivity limitations of the scintillation counters on board.

### **13.2. Microbial diversity**

Bacterioplankton and picophytoplankton are essential components of the Ocean. Bacterioplankton play key roles in many biogeochemical processes. Understanding which bacterioplankton communities dominate and what they respond to remains a fundamental ecological question. An important first step towards understanding the roles of various prokaryotes in the ocean is determining the numbers and relative

abundances of different bacterioplankton groups. In this study, we intend to better characterize the phylogenetic and functional relevance of cytometrically defined groups along the water column through a transect 49 – 24 °N. Moreover, picophytoplankton has been shown to contribute significantly to the primary production in the ocean. This group comprises prokaryotes (*Synechococcus* and *Prochlorococcus*) as well as eukaryotes. The diversity of these groups has extensively been studied over the last decade. However, new taxa are frequently discovered, even in well-studied regions of the Ocean, thanks to new high-throughput technologies. Also, the ecology of these groups has essentially been assessed through the study of their rDNA. We here set up a new protocol to allow coupling sorting of pigmented cells by flow cytometry technology and analysis of their composition through their rRNA. This new approach allows us to target specifically photosynthetic active microbes.

### 13.2.1 Sample collection

Water samples have been collected at different depth (Tab. 13.2), depending of the water masses encountered. Vertical profiles have been collected at regular frequency. Briefly, water samples of 2-5L were prefiltered through 30 or 5µm pore-size membranes, to remove large plankton and particles, and then cells were collected either using concentration devices or on 0.2µm pore-size membranes, respectively. Each sample was preserved with and without buffer to preserve the rRNA. All samples were frozen immediately after processing and stored at -80°C. Samples of 50-100ml were also collected onto 0.2µm pore-size membranes and preserved with PFA (1% final conc.) at -80°C. Samples were also collected at the different depth for each CTD sampled to determine the microbial community structure by flow cytometry analysis.

Table 13.2: stations sampled for microbial diversity, including CTD no., dates, and depth.

Station	Depth (m)	Latitude	Longitude	Julian Day	Time (GMT)	Date
CTD001	4720, 605	48 39.63 'N	017 01.85' W	200	10:00	19/7/11
CTD 002	625, 500	49 00.03' N	019 58.82' W	201	5:37	20/7/11
CTD 004	2257, 1256, 1000, 750, 250, 100, surf.	46 59.89' N	019 59.74' W	202	07:11	21/7/11
CTD 007	1000, 375	44 00.39' N	020 00.15' W	203	11:30	22/7/11
CTD 009	1250, 1000, 700	42 03.04' N	019 59.89' W	204	5:59	23/7/07
CTD12	65, 5	39 00.00' N	020 00.00' W	205	9:25	24/7/07
CTD13	5100	38 00.00' N	020 00.00' W	205		24/7/11
CTD14	50	36 50.00' N	020 00.14' W	206	06:40	25/7/07
CTD16	50	34 59.96' N	020 33.64' W	207	2:35	26/7/07
CTD18	5241, 4259, 3260, 2008, 1007, 387, 101, 53, 8	33 00.11' N	021 41.29' W	208	23:52	27/7/11
CTD19	DCM, 25	31 59.99' N	21' 14.94 W	208	10:41	27/7/07
CTD21	5206, 5008, 101, 50	30 00 00' N	023 22.57 ' W	209	7:15	28/7/07
CTD25	4311, 4260, 3006, 2007, 1008, 757, 382, 103, 27	26 00.02' N	025 37.41 ' W	211	6:07	30/7/07
CTD27	5445, 114, 52	23 59.91' N	026 45.00' W	212	2:15	31/7/07

### **13.2.2 Results**

Molecular analyses will be performed back to the laboratory at University Blaise Pascal (Clermont-Ferrand, France) and University Paris-Sud (Paris, France). No preliminary results are available at this time.

**Paola Gomez-Pereira, Ludwig Jadillier and Isabelle Mary**

## 14 Float Deployments

Three PROVOR floats were supplied by IFREMER as part of the Argo program. These were equipped with dissolved oxygen sensors. Floats were deployed as the ship departed from CTD stations. Calibrated CTDO data for the deployment stations are available at CCHDO.

Each float was activated, checked according to the checklist supplied by IFREMER, (CTD pump, valve activations and Argos transmission) and deployed by manual lowering gently into the water.

The following table gives deployment information

Serial number	Deployment date/time (UTC)	Lat	Lon	CTD station number	Water depth (m)
OIN-10-S3-DO-01	21 July 2011 Day 202 20:46	45°58.97' N	20° 00.79'W	005	4839
OIN-10-S3-DO-02	23 July 2011 Day 204 08:59	42° 02.45'N	20° 00.95'W	009	3336
OIN-10-S3-DO-04	24 July 2011 Day 205 23:30	38° 01.65'N	19° 59.82'W	013	5028

*Table 14.1: Details of float deployments.*

B. King

## Appendix: RRS *Discovery* Cruise 368 Station List

Stn	Date YY/MM/DD	Time HHMM	Lat Deg N	Lat dec min	Lon Deg W	Lon Dec min	Water Dep Corr (m)	Max CTD Dep (m)	Min Ht off Bot (m)	Max Wire Out (m)	Max CTD Pres (dbar)	Num depths sampled	Num salin samples	Num oxygen samples
	11/07/19	1009												
1	11/07/19	1224	48	38.99	17	01.54	4771	4752	12	4720	4847	3	6	4
	11/07/19	1515												
	11/07/20	0539												
2	11/07/20	0750	49	00.33	19	59.73	4410	4396	11	4388	4481	22	20	19
	11/07/20	1038												
	11/07/20	2049												
3	11/07/20	2212	48	01.52	19	59.65	4355	4344	10	4346	4426	24	21	22
	11/07/21	0108												
	11/07/21	0713												
4	11/07/21	0839	47	00.02	19	59.27	4525	4513	10	4505	4600	22	21	21
	11/07/21	1059												
	11/07/21	1648												
5	11/07/21	1822	45	59.38	20	00.08	4842	4829	11	4826	4925	24	24	24
	11/07/21	2039												
	11/07/22	0225												
6	11/07/22	0345	45	00.14	20	00.40	4285	4270	12	4267	4349	23	22	22
	11/07/22	0550												
	11/07/22	1130												
7	11/07/22	1245	44	00.55	20	00.93	3986	3964	99	3970	4034	23	21	21
	11/07/22	1436												
	11/07/22	2030												
8	11/07/22	2209	43	00.18	19	59.47	5137	5125	10	5116	5229	24	24	24
	11/07/23	0030												
	11/07/23	0600												
9	11/07/23	0706	42	02.85	20	00.05	3415	3404	9	3410	3459	22	19	19
	11/07/23	0854												
	11/07/23	1455												
10	11/07/23	1625	41	00.05	20	00.51	4691	4679	9	4674	4769	24	22	22
	11/07/23	1830												
	11/07/24	0020												
11	11/07/24	0151	39	59.66	19	58.99	4788	4774	12	4770	4865	24	24	24
	11/07/24	0355												
	11/07/24	0932												
12	11/07/24	1108	38	59.88	20	00.42	4716	4688	63	4680	4776	23	22	22
	11/07/24	1316												
	11/07/24	1902												
13	11/07/24	2042	38	00.70	20	00.14	5139	5129	9	5126	5231	23	22	22
	11/07/24	2324												
	11/07/25	0641												
14	11/07/25	0809	36	50.62	20	00.09	4565	4556	7	4560	4640	24	21	19
	11/07/25	1031												

	11/07/25	1600												
15	11/07/25	1738	36	00.55	20	00.64	5329	5317	10	5323	5424	24	23	23
	11/07/25	1955												
	11/07/26	0236												
16	11/07/26	0412	35	00.18	20	32.73	5140	5124	14	5132	5224	23	23	22
	11/07/26	0628												
	11/07/26	1304												
17	11/07/26	1445	33	59.95	21	07.58	5227	5214	11	5203	5316	24	23	23
	11/07/26	1707												
	11/07/26	2356												
18	11/07/27	0136	33	00.60	21	41.52	5253	5242	9	5235	5345	24	22	22
	11/07/27	0413												
	11/07/27	1042												
19	11/07/27	1219	31	59.83	22	14.95	5163	5149	12	5145	5248	24	22	22
	11/07/27	1427												
	11/07/27	2045												
20	11/07/27	2218	31	00.47	22	48.06	5220	5207	10	5201	5309	24	24	24
	11/07/28	0056												
	11/07/28	0717												
21	11/07/28	0900	30	00.24	23	22.65	5241	5207	31	5200	5308	23	22	22
	11/07/28	1118												
	11/07/28	1742												
22	11/07/28	1919	28	59.87	23	55.87	5185	5172	11	5164	5271	24	21	20
	11/07/28	2142												
	11/07/29	0836												
23	11/07/29	1015	28	01.08	24	30.42	5218	5204	12	5195	5303	24	24	24
	11/07/29	1240												
	11/07/29	1918												
24	11/07/29	2102	26	59.98	25	03.67	5238	5228	8	5216	5328	24	24	24
	11/07/29	2331												
	11/07/30	0608												
25	11/07/30	0735	26	00.09	25	37.42	4322	4311	13	4304	4384	22	21	20
	11/07/30	0933												
	11/07/30	1608												
26	11/07/30	1747	24	59.67	26	11.48	5397	5384	11	5373	5488	24	22	22
	11/07/30	2001												
	11/07/31	0222												
27	11/07/31	0403	24	00.05	26	45.56	5456	5446	9	5440	5551	23	21	21
	11/07/31	0620												
	11/07/31	1051												
28	11/07/31	1236	23	20.54	27	08.15	5508	5498	9	5500	5605	24	20	20
	11/07/31	1541												
	11/08/03	2339												
29	11/08/04	0045	28	46.92	16	00.09	3473	3460	11	3455	3512	24	12	23
	11/08/04	0238												