

# **DY033 Cruise Report**

## **RRS Discovery**

**11<sup>th</sup> July – 3<sup>rd</sup> August 2015**

**PS: Prof. Mark Moore (University of Southampton)**

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# 1. General cruise information

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From left: Malcolm Woodward, Alex Poulton, Richard Sims, Mathew Fishwick, Simon Ussher, Nick Stephens, Glen Tarren, Elena Garcia Martin, Stephen Woodward, Jo Hopkins, Carol Robinson, Anthony Burchill, Lucie Munns, Chris Daniels, Sharon McNeil, Andy Rees, Julie Wood, Dougal Mountfield, Sari Giering, Emlyn Jones, Dagmara Rusiecka, Nick Rundel, Tom Roberts, Mark Maltby, Seona Wells, Andrew Leadbeater, Clare Davis, Ian Murphy, Mark Moore, Isabel (Chata) Seguro

## **Scientific background**

Cruise DY033 was the summer pelagic cruise of the NERC/Defra-funded Shelf Sea Biogeochemistry (SSB) research programme. Both pelagic (Workpackage 1, WP1) and benthic (Workpackage 2, WP2) work is associated with the research programme, the fieldwork components of which comprise a series of cruises through 2014 and 2015. The overall goals of the pelagic (WP1) component of the programme are to determine the magnitude of carbon that the NW European shelf exports to the deep ocean, alongside establishing how the biogeochemical system on the shelf sustains this export. A further component to the overall programme (Workpackage 3, WP3) involves investigation of the role of the shelf system in supplying the micronutrient iron to the open ocean. DY033 was the third and final pelagic cruise of the SSB programme serving WP1 and the pelagic components of WP3.

The main objectives of the cruise were:

1. To continue the times-series of process measurements at the Central Celtic Sea (CCS) site, the shelf edge site (CS2) and benthic workpackage (WP2) sampling site 'A' to examine the functioning of the shelf sea biogeochemical system in the post spring bloom stratified period;
2. To make a number of observations at other sites across the Celtic Sea in order to put the main process sites into a wider context;
3. To continue the mooring record at the CCS site through the recovery of an ADCP chain, temperature chain and bedframe;
4. Deploy, and where appropriate recover, a series of gliders (including long-term and short-term deployments of Ocean Microstructure Gliders (OMGs), a Slocum glider with nitrate sensor and a further Slocum glider;
5. Deploy and recover two Wirewalker moorings at CCS;
6. Collect samples for the measurement of iron and other trace metals/isotopes along two transects at the shelf edge (WP3 of the SSB programme).

Despite losing some time to weather and other issues (see below), overall the cruise was very successful, sampling transects across the shelf edge and through the central Celtic Sea up towards the Irish Sea during the post bloom highly stratified summer period. A total of three process stations were performed at the Central Celtic Sea (CCS) site, with a further process station undertaken at the shelf edge site (CS2). Work during these process stations comprised of CTDs for water sample collection and autotrophic and bacterial rate measurements; use of Marine Snow Catchers (MSC) and Stand-Alone-Pumps (SAPS) for collection of suspended and sinking particles; and zooplankton net hauls for biomass, species composition and a variety of experimental work including measurements of grazing, respiration and excretion rates. A near surface gas profiling buoy was also deployed at these process stations and elsewhere. Two CTD transects were also sampled for standing stock of state variables including dissolved and particulate nutrients and carbon, one between the shelf edge station (CS2) and the central

Celtic Sea (CCS) site (O-transect) and one between the Celtic Deep (Site A) and the CCS (J-transect) see Figure 1.1. Additionally two cross-slope transects, each consisting of 7 stations between water depths of 2500 m and 200 m, were carried out to measure iron chemistry. Ongoing measurements by the mooring array at CCS were also facilitated through the deployment of two Wirewalker moorings at the beginning of the cruise followed by the successful recovery of one of the Wirewalkers alongside the planned three additional longer term moorings at the end of the cruise. Unfortunately one of the Wirewalker moorings was lost. A total of 8 gliders were deployed/recovered, including two Micro-Structure gliders (one at CCS, one at CS2), a Glider equipped with a nitrate sensor, and a long term glider deployment at the shelf edge.

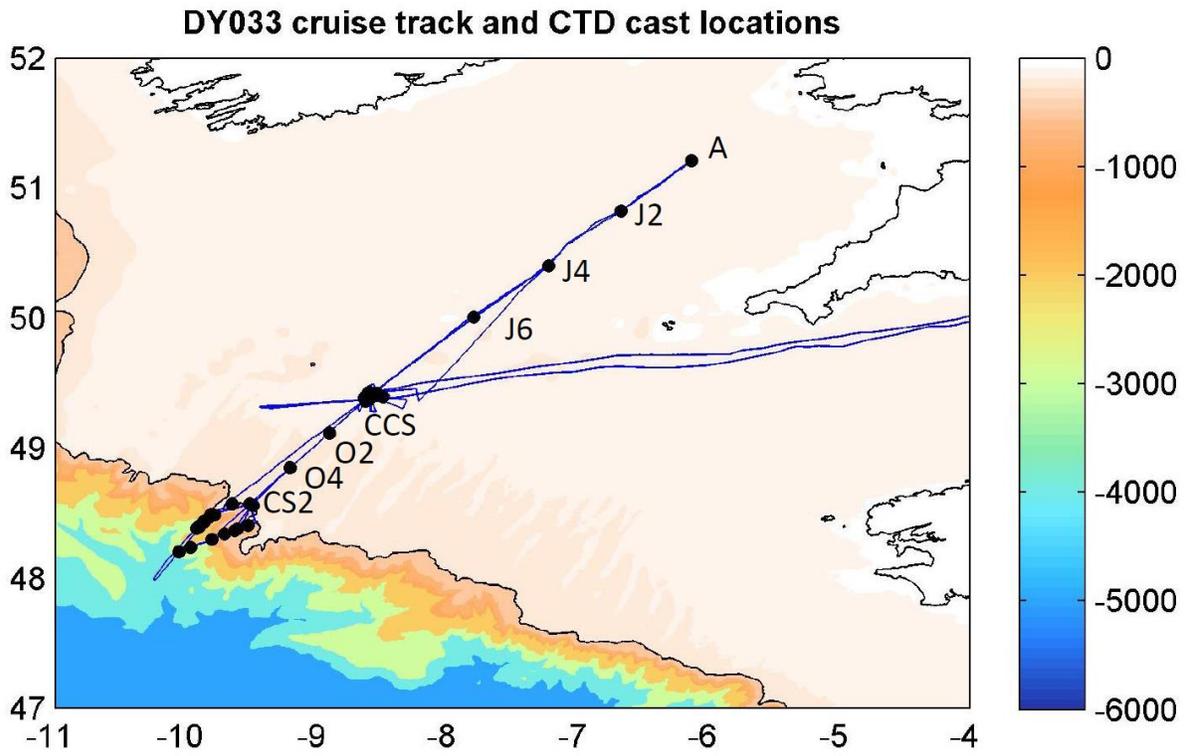


Figure 1.1: Cruise track (blue line) and CTD sampling stations (Black Dots) overlaid onto bathymetric map of the Celtic Sea. Key Sampling sites labelled.

## **DY033 Day summary**

<b>Date</b>	<b>Location</b>	<b>Activities</b>
11/07	Transit	Sail from Southampton (1800)
12/07	Transit	On transit to CCS, initial TMS FISH deployment,
13/07	CCS	Arrive CCS, Deploy glider, CTDs, Wirewalker deployments, Nets, PML buoy test, MSC tests
14/07	CCS	CCS Process station 1, Day 1: CTDs, Nets, PML buoy, Deploy OMG Glider
15/07	CCS and 'Boat'	CCS Process station 1, Day 2: CTDs, Nets, SAPS, Snowcatcher, investigation and recovery of drifting boat.
16/07	Fe transect II	Glider deployments, Fe II transect start, CTDs, Nets
17/07	Fe transect II	CTDs, steam to deep water to investigate ADCP
18/07	Fe transect II	CTDs, glider recovery, underway sampling
19/07	CS2	CS2 Process station, Day 1: CTDs, Nets, PML buoy
20/07	CS2	CS2 Process station, Day 2: CTDs, Nets, SAPS, Snowcather, PML buoy
21/07	Fe transect I	Fe I transect starts, CTD termination/cable problems, CTDs, PML buoy
22/07	Fe transect I	Fe I transect and additional sampling at CS2
23/07	Fe transect I	Fe I transect and stations 'O2' and 'O4' on route to CCS
24/07	CCS	CCS Process station 2, Day 1: CTDs, SAPS, downtime due to weather
25/07	CCS	CCS Process station 2, Day 2 and mooring recoveries: CTDs, Nets, PML buoy, moorings
26/07	Transit A, transect A-J2	CTDs at A and J2, slow steaming through poor weather/sea state
27/07	Transect J2 - CCS	Slow steaming through poor weather. CTD cast at CCS, injury to crewman and medevac
28/07	Transect	medevac, stations J4 and J6
29/07	CCS	CCS Process station 3, Day 1: CTDs, Nets, PML buoy, wirewalker recovery
30/07	CCS	CCS Process station 3, Day 2: CTDs, Nets, PML buoy, Glider recovery, MSC

31/07	CCS	Tidal cycle, bedframe and glider recoveries
01/08	CCS – Transit	Tidal cycle ends, end over side sampling, depart Southampton
02/08	Transit	Transit, Arrive Southampton

## DY033 Cruise narrative

Date	Time (GMT)	Time (ships)	Activity/event	Site/Location
11/07	0900 1200 1400 1700 1815	1000 1300 1500 1800 1915	Shore leave ends Lifeboat drill Science meeting Sailed Southampton on route CCS Pilot offloaded  Mobilisation completed efficiently (amazing how fast it goes when people are well practised!). Departure delayed by ~8hrs.	50° 45.88'N 1° 20.76'W
	1830 1930	1930 2030	Potential propulsion problems... Transit continues, propulsion OK	
12/07	0800 0950  ~1500  1500	0900 1050  ~1600  1600	Sunday meeting senior staff <b>Event 001:</b> TMS FISH deployed  Ship slow pushing into tide and wind, shakedown casts postponed until Monday am  Security briefing video for science staff (with some great acting and nasal hair)  Weather overcast/raining in morning/early afternoon, improved a bit later in the day	49° 51.4'N 5° 02.3'W
13/07	0528  0637  0748 0837  1004  1117  1226  1318 1459  1620	0628  0737  0848 0937  1104  1217  1326  1418 1559  1720	<b>Event 002:</b> Glider deployment (Sensors on Gliders, SN 534) <b>Event 003:</b> Post glider CTD (CTD001), sampled for glider calibration. CTD start delayed due to problems with winch monitor camera system. DCM located at temperature of 11.6°C. Well mixed surface and bottom layer, thermocline around 20m thick, bottom temp 10.34°C. <b>Event 004:</b> Wirewalker ballast test <b>Event 005:</b> Wirewalker (WW1) deployment, to North of CCS mooring array <b>Event 006:</b> Titanium CTD (CTD002). Post glider deployment calibration cast and soak for bottles. All bottles fired 85m. <b>Event 007:</b> Wirewalker (WW1) deployment, to North of CCS mooring array <b>Event 008:</b> Midday CTD cast (CTD003). DCM at 12.0°C, bottom temp 10.45°C. <b>Events 009-013:</b> Zooplankton nets <b>Events 014-016:</b> Marine snow catcher deployments (tests), deployed at 70, 90, 110m, temperature measured following recovery and time of messenger descent measured (~3 m/s). <b>Event 017:</b> PML Gas profiler buoy deployed.	CCS



	1956	2056	<p><b>Events 049-051:</b> Marine Snow Catchers (MSC)s deployed to 10m.</p> <p><b>Event 052:</b> TMS FISH deployed</p> <p><b>Events 053-055:</b> Marine Snow Catchers (MSC)s deployed to 80m (90m wire out).</p>	CCS
	2302	2402	Off station CCS steaming towards Fe14	
16/07	0645	0745	On station Fe14	Fe14
	0649 0717	0749 0817	<p><b>Event 056:</b> Glider deployment (OMG Glider 424).</p> <p><b>Event 057:</b> Glider deployment (Deep glider 533).</p> <p>Note, repositioned while on 'Fe14' to be clear of gliders for CTD deployment</p>	
	0828	0928	<b>Event 058:</b> Stainless CTD (CTD 013). Post glider CTD at Fe14 (approx.). Initial problem with wrong CTD system connected, CTD recovered and redeployed. Broad DCM (profile typical of shelf edge). Very spikey fluorescence and transmittance through DCM.	
	0905	1005	<b>Events 059- 063:</b> Zooplankton nets (N25-N29).	
	0949	1049	Off station Fe14 steaming towards Fe08	
	1105	1205	On station Fe08	Fe08
	1136	1236	<b>Event 064:</b> Titanium CTD cast (CTD014). Full depth profile Fe08. Package touched bottom at 2375m with 2595m water depth reported by echo sounder. Sensor issues apparent suggesting considerable sediment disturbed. Package recovered to check all OK. Potential offset in primary conductivity cell remains.	
	1409	1509	<b>Event 065:</b> Titanium CTD cast (CTD015). Full depth profile Fe08. Repeat cast. Poor echosounder trace and no bottom trace with altimeter. Profile OK. Full set of bottles.	
	1705	1805	<b>Event 066:</b> Stainless CTD (CTD016). Full depth profile Fe08.	
	2134	2234	Off station Fe08 steaming at 3kts to Fe09	
	2200	2300	On station Fe09	Fe09
	2236	2336	<b>Event 067:</b> Titanium CTD cast (CTD017). Full depth profile Fe09.	
17/07	0119	0219	<b>Event 068:</b> Stainless CTD cast (CTD018). Full depth profile Fe09.	Fe09
	0336	0436	<b>Events 069-070:</b> Zooplankton nets (N30-N31)	

			Slight delay due to requirement for grey water discharge.	
	0650	0750	Off station Fe09	
	0713	0813	On Station Fe10	Fe10
	0740	0840	<b>Event 071:</b> Titanium CTD cast (CTD019). Full depth profile Fe10.  Decision made to delay glider recovery to 18/07. Some hydraulic problems before stainless CTD cast.  Iridium beacon for wirewalker (WW1, 'North') no longer working	
	1126	1226	<b>Event 072:</b> Stainless CTD cast (CTD020). Full depth Fe10.  Fe transect sampling suspended to allow trace metal team to rest following end of sampling of CTD020.	
	1320	1420	Off station Fe10	
	2159	2259	On station Fe11	Fe11
	2220	2320	<b>Event 073:</b> Titanium CTD cast (CTD021). Full depth profile Fe11. Wrong bottles fired (bottles placed in different place on rosette to those fired, second cast required).	
18/07	0002	0102	<b>Event 074:</b> Titanium CTD cast (CTD022). Full depth profile Fe11. Second titanium case at Fe11.	Fe11
	0050	0150	<b>Event 075:</b> Stainless CTD cast (CTD023). Full depth profile Fe11.	
	0230	0330	Off station Fe11	
	0300	0400	On station Fe12	Fe12
	0321	0421	<b>Event 076:</b> Titanium CTD cast (CTD024). Full depth profile Fe12. No stainless cast this station.	
	0444	0544	Off station Fe12	
	0500	0600	On station Fe13	Fe13
	0511	0611	<b>Event 077:</b> Stainless CTD cast (CTD025). Full depth profile Fe13.	
	0727	0827	<b>Event 078:</b> Titanium CTD cast (CTD026). Full depth profile Fe14.	
	0840	0940	Off station Fe13	
	0936	1036	On Station Fe14	Fe14

	0938 1129  1247 1446  1622  2250	1038 1229  1347 1546  1722  2350	<p><b>Event 079:</b> Stainless CTD cast (CTD027). Full depth profile Fe14.</p> <p><b>Event 080:</b> Titanium CTD cast (CTD028). Full depth profile Fe14</p> <p>Moved off station to find glider.</p> <p><b>Event 081:</b> Stainless CTD cast (CTD029). Cast at glider (408) recovery location.</p> <p><b>Event 082:</b> Glider 408 recovery</p> <p>Steamed off to transit line Fe14 - Fe07 then through CS2 and to O4 before return to CS2. Cross shelf edge transect. Fe14 – Fe07 – CS2 – O4 – CS2.</p> <p>Transect ends at CS2 for process station</p>	<p>48 28.168 N, 09 49.074 W</p> <p>48 28.827 N, 09 49.954 W</p> <p>CS2</p>
19/07	0108 1057  1211  1319 1542  2118	0208 1157  1311  1219 1642  2218	<p>Process station commences at CS2. Second process station overall</p> <p><b>Event 083:</b> Pre-dawn CTD (CTD030), stainless cast</p> <p><b>Event 084:</b> Midday CTD (CTD031), stainless cast. Note large amount of variability in upper water column structure between first two casts at CS2.</p> <p><b>Events 085-090:</b> Zooplankton nets (N32-37). Interesting phytoplankton in net sample, including some pheaocystis and a big diatom with visible cytoplasmic streaming.</p> <p><b>Event 091:</b> PML Gas profiler buoy deployed (2hrs)</p> <p><b>Event 092:</b> CTD cast for zooplankton experiments (CTD032)</p> <p><b>Events 093-101:</b> Zooplankton nets (N93-N101)</p>	
20/07	0205 0322  0502  0622 1056 1211 1316 1518  1545  1733  1925	0305 0422  0602  0722 1156 1311 1416 1618  1645  1833  2025	<p>CS2 process station day 2</p> <p><b>Event 102:</b> Pre-dawn CTD (CTD033), stainless cast</p> <p><b>Event 103:</b> Titanium CTD cast (CTD034), profile at CS2.</p> <p><b>Event 104:</b> Stainless CTD cast (CTD035), to choose SAPS depths, no bottles</p> <p><b>Event 105:</b> SAPS deployed pumping for 1 hour</p> <p><b>Event 106:</b> Midday CTD (CTD036), stainless cast.</p> <p><b>Events 107-112:</b> Zooplankton nets (N47-N52)</p> <p><b>Event 113:</b> PML Gas profiler buoy deployed.</p> <p><b>Event 114:</b> Stainless CTD cast (CTD037), to choose MSC depths, no bottles</p> <p><b>Events 115-117:</b> Marine Snow Catchers (MSC)s deployed to 10m and 80m for pictures. Note misfire on first deployment (Event 115), no samples collected.</p> <p><b>Events 118-120:</b> Marine Snow Catchers (MSC)s deployed to 10m.</p> <p><b>Events 121-123:</b> Marine Snow Catchers (MSC)s deployed to 80m.</p>	

	2208	2308	<b>Events 124-129:</b> Zooplankton nets (N53-N58)	
	2320	0020	Off station CS2, repositioned to Fe07, steaming line Fe07-Fe01 for TM Fish sampling.	
21/07	0403	0503	On station Fe01	Fe01
	0421	0521	<b>Event 130:</b> Titanium CTD cast (CTD038). Intended full depth profile Fe01. Cast aborted at 0450, depth 1142m due to loss of communications. CTD recovered to deck.  Inspection on initial recovery revealed potential loose connector, redeployed to check.	
	0533	0633	<b>Event 131:</b> Titanium CTD cast (CTD039). Aborted, communication failure at ~100m.  Further investigation of wire and termination indicated failure in tail of termination. Insulation of cores in wire also poor, decision made to remove ~400m of wire up to point of known hole in outer wire housing. New termination of wire performed, load testing all OK, CTD prepared for redeployment. Loss of ~6 hours.	
	1308	1408	<b>Event 132:</b> PML Gas profiler buoy deployed (while waiting for CTD repair).	
	1508	1608	<b>Event 133:</b> Stainless CTD cast (CTD040), full depth profile Fe01.	
	1852	1952	<b>Event 134:</b> Titanium CTD cast (CTD041), successful full depth profile Fe01 following re-termination. Some issues with altimeter.	
	2117	2217	Off station Fe01	
	2210	2310	On station Fe02	
	2229	2329	<b>Event 135:</b> Stainless CTD cast (CTD042), full depth profile Fe02.	Fe02
22/07	0120	0220	<b>Event 136:</b> Titanium CTD cast (CTD043), full depth profile Fe02.	
	0340	0440	Off station Fe02	
	0445	0545	On station Fe15	Fe15
	0450	0550	<b>Event 137:</b> Stainless CTD cast (CTD044), full depth profile Fe15.	
	0718	0818	<b>Event 138:</b> Titanium CTD cast (CTD045), full depth profile Fe15.	
	0926	1026	Off station Fe15, reposition to CS2 for extra sampling, dilution/respiration expts.	
	1206	1306	On station CS2	CS2

	1208 1301 1553  1749  2010   2319	1308 1401 1653  1849  2110   0019	<p><b>Events 139-140:</b> Zooplankton nets (N59-N60)</p> <p><b>Event 141:</b> PML Gas profiler buoy deployed.</p> <p><b>Events 142-144:</b> Marine Snow Catchers (MSC)s deployed to 10m.</p> <p><b>Events 145-147:</b> Marine Snow Catchers (MSC)s deployed to 90m.</p> <p><b>Events 148-151:</b> Zooplankton nets (N61-N64)</p> <p>Off station CS2</p> <p>On station Fe03</p> <p><b>Event 152:</b> Titanium CTD cast (CTD046), full depth profile Fe03.</p>	Fe03
23/07	0108  0202  0400 0616  0732  0836  0838  1202  1100 1154  1202  1308 1439  1441 1531	0208  0302  0500 0717  0832  0936  0938  1302  1200 1254  1302  1408 1539  1541 1631	<p>Off station Fe03</p> <p>On station Fe04</p> <p><b>Event 153:</b> Titanium CTD cast (CTD047), full depth profile Fe04.</p> <p><b>Event 154:</b> Stainless CTD cast (CTD048), full depth profile Fe04.</p> <p>Off station Fe04</p> <p>On station Fe06</p> <p><b>Event 155:</b> Stainless CTD cast (CTD049), full depth profile Fe06. (Note stations run out of order to save time as no stainless required at Fe05).</p> <p><b>Event 156:</b> Titanium CTD cast (CTD050), full depth profile Fe06.</p> <p>Off station Fe06</p> <p>On station Fe05</p> <p><b>Event 157:</b> Titanium CTD cast (CTD051), full depth profile Fe05.</p> <p>Off station to glider position</p> <p>On glider location</p> <p><b>Event 158:</b> Stainless CTD cast (CTD052) for glider calibration</p> <p><b>Event 159:</b> Glider 424 recovery. Note glider recovered early due to poor medium range weather forecast.</p> <p>Repositioned to station O4</p>	<p>Fe04</p> <p>Fe06</p> <p>Fe05</p> <p>48 33.47 N, 09 29.37 W</p> <p>O4</p>

	1827	1927	<b>Event 160:</b> Stainless CTD cast (CTD053), full depth profile, station O4	O2
	1915	2015	Off station O4	
	2135	2235	On station O2	
	2138	2238	<b>Event 161:</b> Stainless CTD cast (CTD054), full depth profile, station O2	
	2220	2320	Off station O2, proceed CCS	
24/07	0040	0140	On station CCS for start of 2 <sup>nd</sup> CCS process station	CCS
	0100	0200	<b>Event 162:</b> Pre-dawn CTD (CTD055), stainless cast	
	0630	0730	<b>Event 163:</b> SAPS deployed, pumping for 1.5 hrs	
	1113	1213	<b>Event 164:</b> Midday CTD (CTD056), stainless cast.	
			Sampling suspended due to deteriorating weather, no nets or gas profiler deployment possible afternoon/evening of 24 <sup>th</sup>	
25/07			2 <sup>nd</sup> day of 2 <sup>nd</sup> CCS process station	CCS
	0215	0315	<b>Event 165:</b> Pre-dawn CTD (CTD057), stainless cast, aborted. Wire jumped sheave and was damaged. Re-termination required. Re-termination took the majority of day on 25 <sup>th</sup> , titanium CTD used as replacement to collect water required for pre-dawn samples/experiments.	
	0317	0417	<b>Event 166:</b> Titanium CTD (CTD058), Fe samples and sampling for cancelled pre-dawn cast.	
	0535	0635	<b>Event 167:</b> Titanium CTD (CTD059), sampling for missed fired bottles and zooplankton experiment.	
	0732	0832	<b>Event 168:</b> Zooplankton net (N65)	
	0808	0908	Reposition to moorings	
	0842	0942	<b>Event 169:</b> Titanium CTD (CTD060), calibration CTD for thermistor chain mooring recovery	
	0957	1057	<b>Event 170:</b> Thermistor chain mooring recovery at CCS. Mooring and all sensors recovered, biofouling on many instruments.	
	1052	1152	<b>Event 171:</b> Sub-surface ADCP mooring recovery at CCS. Mooring and all sensors recovered, heavy biofouling on some instruments.	
	1220	1320	<b>Events 172-179:</b> Zooplankton nets (N66-N73)	
	1409	1509	<b>Event 180:</b> PML Gas profiler buoy deployed.	
	1716	1816	<b>Events 181-183:</b> Marine Snow Catchers (MSC)s deployed to 15m.	
	1930	2030	Load tests on new stainless CTD termination <b>Events 184-186:</b> Marine Snow Catchers (MSC)s deployed to 75m.	
	2015	2115	<b>Events 187-188:</b> Zooplankton nets (N74-N75).	
	2134	2234	<b>Events 189-190:</b> Marine Snow Catchers (MSC)s deployed to 15m (x1) and 75m (x1).	
	2221	2321	<b>Event 191:</b> Stainless CTD cast for zooplankton experiments (CTD061). First cast following re-termination of cable.	

	2340	0040	All sampling complete by end of 2248. Samples collected from final MSC deployment by midnight, departed for station A. Overnight winds force 8 for 3-4hours on route to A.	
26/07	1500	1600	Proceeding underway towards 'A'. Timing of bad weather prevents pre-dawn being undertaken at 'A' On station 'A'	A
	1509 1622	1609 1722	<b>Event 192:</b> Stainless CTD cast (CTD062), station 'A' <b>Event 193:</b> Titanium CTD cast (CTD063), station 'A'	
	1720	1820	Off station 'A' for station J2	
	2329	0029	<b>Event 194:</b> Stainless CTD cast (CTD064), station J2  Titanium CTD cast not possible at station J2 due to increasing wind speeds and deteriorating sea state. Proceed off station J2 towards J4.	J2
27/07	0000	0100	Sea state and wind continues to be poor/unworkable, proceeding down line 'J' towards CCS. Not possible to hold position on J4 or J6 during passage, continue to CCS.	
	2055	2155	On station CCS. Wind and sea state dropped significantly.	
	2119	2219	<b>Event 195:</b> Stainless CTD cast (CTD065), station CCS, long duration nitrate sensor cast.	CCS
	2314	0014	CTD recovered, science suspended due to crewman injury. Following CTD recovery package was re-lifted off deck instead of slack wire being paid out. Package swung toward starboard bulwark crushing crewman Raoul Lafferty hard against gates in bulwark. First aid applied to Raoul while maintaining him immobile on back on deck. Medevac arranged by helicopter from RAF Culdrose to Treliske hospital in Cornwall. Subsequently confirmed the following morning (28/07) that Raoul sustained no serious injuries beyond major bruising. Nasty accident which could potentially have been much worse. Much of the impact of the CTD was taken directly against the side rail rather than onto Raoul. Procedures reviewed and revised following identification of cause to emphasise that no one should stand between CTD package and bulwark during paying out of cable. The PSO commends all the crew and scientists involved for the calm professional manner in dealing with incident.	
28/07	0300	0400	Set heading for station J4	

	1132 1246 1325 1715 1732 1843 1918	1232 1346 1425 1815 1832 1943 2018	<p><b>Event 196:</b> Stainless CTD cast (CTD066), station J4  <b>Event 197:</b> TMS Fish deployed  <b>Event 198:</b> Titanium CTD cast (CTD067), station J4</p> <p>Off station J4  On station J6</p> <p><b>Event 199:</b> Stainless CTD cast (CTD068), station J6  <b>Event 200:</b> Titanium CTD cast (CTD069), station J6</p> <p>Off station towards CCS</p>	J4    J6
29/07	0033  0044 0126 0248 0403  0650  0820 0918  1208 1340 1604  1803 2135	0133  0144 0226 0348 0503  0950  0920 1018  1308 1440 1704  1903 2235	<p>On station CCS for 3<sup>rd</sup> process station at site (4<sup>th</sup> overall)</p> <p><b>Events 201-202:</b> Zooplankton nets (N76-N77).  <b>Event 203:</b> Stainless CTD cast (CTD070), pre-dawn  <b>Event 204:</b> Titanium CTD cast (CTD071)  <b>Event 205:</b> Stainless CTD cast (CTD072), nitrate sensor cast, 3 stops.</p> <p>Repositioned to wirewalker location. On arrival at WW2 ('South') it was noted that the other wirewalker (WW1, 'North') was not visible at surface in expected location. WW1 was wirewalker with failed Iridium beacon</p> <p><b>Event 206:</b> Stainless CTD cast (CTD073), calibration cast for wirewalker recovery  <b>Event 207:</b> Wirewalker (WW2, 'South') recovery. Mooring recovered fine. Evidence of considerable wear to sections of rope above region where it would have been dragging on the seabed. Most damaged sections look close to potential failure.</p> <p><b>Events 208-214:</b> Zooplankton nets (N78-N84)  <b>Event 215:</b> PML Gas profiler buoy deployed.  <b>Event 216:</b> Stainless cast (CTD074), zooplankton experiments  <b>Event 217:</b> Stainless cast (CTD075), nitrate sensor cast, 4 stops  <b>Events 218-226:</b> Zooplankton nets (N85-N93)</p> <p>Overnight off station searching for missing wirewalker, 2.5hrs</p>	CCS
30/07	0215 0328 0508 1000  1129 1211 1350	0315 0428 0608 1100  1229 1311 1450	<p>Process station at CCS continues</p> <p><b>Event 227:</b> Stainless cast (CTD076), pre-dawn  <b>Event 228:</b> Titanium cast (CTD077)  <b>Event 229:</b> SAPS deployed, pumping for 1.5 hrs  <b>Event 230:</b> Stainless cast (CTD078), sensors on glider recovery calibrations and 'midday' cast. O2 sensor failed.</p> <p><b>Event 231:</b> 'SOG' glider recovery (glider 534)  <b>Events 232-239:</b> Zooplankton nets (N94-N101)  <b>Event 240:</b> PML Gas profiler buoy deployed.</p>	CCS



	1200	1300	Underway sampling system shut down Pilot Docked	
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## **Station positions**

Note: positions are nominal. Please refer to logs of individual events.

Station ID	Latitude N	Longitude W	Depth	Comments
CCS	49° 24'	8° 36'	150 m	Main process / mooring site
CS2	48° 34.26'	9° 30.58'	203 m	Shelf edge process station
O1	49° 16.0'	8° 45.0'	Not sampled	Transect between CCS and CS2
O2	49° 07.0'	8° 54.3'	157 m	"
O3	49° 00.0'	9° 02.7'	Not sampled	"
O4	48° 51.2'	9° 12.0'	166 m	"
O5	48° 43.1'	9° 21.1'	Not sampled	"
Site A	51° 12.8'	6° 7.8'	111 m	Benthic work package site A
J1	51° 01.5'	6° 23.75'	Not sampled	Transect between site A and CCS
J2	50° 49.7'	6° 40.0'	103 m	"
J3	50° 37.5'	6° 56.5'	Not sampled	"
J4	50° 24.438'	7° 13.306'	100 m	Moved to avoid cable
J5	50° 12.7'	7° 30.0'	Not sampled	"
J6	50° 00.556'	7° 47.945'	118 m	Moved to avoid cable
J7	49° 48.5'	8° 03.0'	Not sampled	"
J8	49° 36.3'	8° 19.8'	Not sampled	"
Fe01	48° 12.35'	10° 3.24'	2422 m	Iron transect 1

Fe02	48° 14.37'	9° 57.92'	2001 m	"
Fe03	48° 20.45'	9° 42.25'	1480 m	"
Fe15	48° 18.0'	9° 48.0'	1480 m	(extra station along transect)
Fe04	48° 22.21'	9° 37.71'	934 m	"
Fe05	48° 22.69'	9° 36.49'	727 m	"
Fe06	48° 24.53'	9° 31.56'	469 m	"
Fe07	48° 25.71'	9° 28.03'	Not sampled	"
Fe08	48° 23.11'	9° 55.06'	2597 m	Iron transect 2
Fe09	48° 23.97'	9° 54.06'	1954 m	"
Fe10	48° 24.61'	9° 53.37'	1555 m	"
Fe11	48° 25.33'	9° 52.72'	922 m	"
Fe12	48° 25.77'	9° 52.26'	705 m	"
Fe13	48° 26.24'	9° 51.78'	485 m	"
Fe14	48° 29.49'	9° 48.51'	250 m	"
Fe16	48° 25.246'	9° 56.491'	Not sampled	Iron transect 3
Fe17	48° 32.0'	9° 56.0'	Not sampled	"
Fe18	48° 34.671'	9° 55.36'	Not sampled	"
Fe19	48° 37.0'	9° 50.0'	Not sampled	"
Fe20	48° 37.516'	9° 47.62'	Not sampled	"
Fe21	48° 37.595'	9° 46.98'	Not sampled	"
Fe22	48° 40.0'	9° 42.0'	Not sampled	"

## 2. Gas profiler deployments, DIC and Alkalinity

*Richard Sims (Plymouth Marine Laboratory)*

### Near Surface Ocean Profiler Measurements and PhD related work

#### **Aims and objectives**

- Take near surface trace gas profiles of CO<sub>2</sub> in the top 7m of the ocean at different sites across the Celtic Sea.
- Take sea surface skin measurements using ship based radiometers.
- Collect discrete seawater samples for analysis for TA/DIC whilst profiling

#### **Method**

The method used was similar to that used for DY026, DY017 and DY033. Measurements of near surface gradients were collected using the Near Surface Ocean Profiler (NSOP). The profiler was positioned around 7-8m from the side of the ship and was positioned using 3 tethers (on the rear crane arm on the deck of the ship and the aft crane). An instrument cage containing a Seabird microCTD (logging every 10secs) was raised and lowered in the top 7m of the ocean by a remotely operated winch; this gave temperature, salinity, depth measurements. Water was pumped back to the ship at around 2-3.5L/min through tubing attached to the instrument cage at the same depth as the depth sensor.

Onboard the ship the pumped seawater was passed through a membrane equilibrator where it was rapidly equilibrated with a counter nitrogen flow at 100ml/min. The air flow was then dried using a nafion dryer and passed into a Licor 7000 for analysis for CO<sub>2</sub> content. The Licor measured a number of variables including the partial pressure and xCO<sub>2</sub>, the pressure, temperature, and water vapour content. Temperature and flow rate of the seawater inflow were also logged going into the equilibrator. 3 CO<sub>2</sub> Standards were also run pre and post deployment on average 3 hours apart, the times that these standards were run was noted in the lab book. The water inflow from the peristaltic pump was 'T'd' before entering the equilibrator so that unaltered seawater at 500ml/min could be used to fill up bottles for TA/DIC.

A temperature calibration was carried out during the cruise with a post cruise temperature calibration planned. The calibration of the flow sensor was done on-board the ship using a measuring cylinder and a stopwatch.

Sea surface skin measurements were taken using Campbell IR-120 sensors positioned on the bow of the ship, sea surface temperature can be computed from the raw voltage and resistance using calibration coefficients and the oceans emissivity. A 2 axis accelerometer was also collocated with the IR-sensor to give the angle of the IR-sensor.

#### **Issues**

There were some issues with ruptured tubing on the peristaltic pump which were rectified by resitting the tubing. There were also a few occasions where logging of measurements stopped, namely the flow rate and temperature sensors. Weather conditions prevented deployments on

several days. Intermittent problems related to outages with the IR-sensor and random outages from the voltage of the second upward facing IR-sensor.

### **Measurements taken**

The measurements for this cruise consist of the microCTD, Licor (CO<sub>2</sub>), PT100 and flow rate sensor data for the 9 NSOP deployments 13<sup>th</sup>, 14<sup>th</sup>, 19<sup>th</sup>, 20<sup>th</sup>, 21<sup>st</sup>, 22<sup>nd</sup>, 25<sup>th</sup>, 29<sup>th</sup>, 30<sup>th</sup> July. The pCO<sub>2</sub> system was also setup to sample underway data for two hours on 1 day to make a direct comparison with the ships underway system. In an effort to prevent turbulence by the ships props the ship was allowed to drift during the deployment, the locations of these samples can be inferred from the ships cruise track.

TA/DIC samples were collected on every NSOP deployment profile, 6 bottles were collected per profiles (9x6= 54 bottles in total). 2 bottles were filled at the surface and then at the first, second, fourth and sixth depths of the respective profiles. The times when these bottles were filled was recorded so depth could be determined.

IR sensor data (voltages and resistances) and accelerometer data (voltages) were collected every second for the entirety of the cruise except where there were data outages.

### **CTD sampling and underway measurements**

TA/DIC measurements were taken following the SOP's for the shelf seas biogeochemistry programme. For TA/DIC analysis data please contact Matthew Humphreys (m.p.humphreys@soton.ac.uk).

### **CTD measurements**

TA/DIC was collected on the following CTD's 6 depths for 003, 8 x CTD 005, 8 x CTD009, 5 x CTD015, 8x CTD 017 , 8 x CTD 023, 10 x CTD030 , 8x CTD 033, 12 x CTD 041 , 12 x CTD 043 , 10 x CTD 045 , 8 x CTD 046, 9 X CTD047, 6 x CTD 050, 10 x CTD 051, 10 x CTD053, 10 x CTD054, 8x CTD 055, 7 x CTD 058 , 6 x CTD 062, 6 x CTD 064, 7 x CTD066, 7 x CTD068, 10 x CTD 070, 10 x CTD 076 = TOTAL 209

### **Underway measurements**

Underway measurements of TA/DIC were collected on the 12<sup>th</sup>, 13<sup>th</sup>, 14<sup>th</sup>, 15<sup>th</sup>, 16<sup>th</sup>, 17<sup>th</sup>, 21<sup>st</sup>, 23<sup>rd</sup>, 24<sup>th</sup>, 25<sup>th</sup>, 26<sup>th</sup>, 27<sup>th</sup>, 30<sup>th</sup>, 31<sup>st</sup> July . These measurements coincided with an underway nutrients sample (contact Malcolm Woodward) = TOTAL 14

The underway pCO<sub>2</sub> system was fully functioning during the whole cruise (contact Vas Kitidis).

### 3. Underway navigation, sea surface hydrography and meteorology

*Jo Hopkins (National Oceanography Centre, Liverpool)*

#### Instrument description

##### **Navigation**

The following navigational sensors were used for processing positions, ship heading and sea floor depth (Table 3.1). The POS MV GPS unit was one of the primary GPS sources for science. It was capable of differential GPS (DGPS), accurate to 0.5 m and not prone to drop outs. The POS MV system also comprised an Inertial Measurement Unit (IMU) which was accurate to  $0.010^\circ$  with a 4 m baseline. The gyro heading was filtered and was preferred to the ship gyro which may be prone to oscillations. The Kongsberg Simrad EM122 swath bathymetry sensor was located on the port drop keel approximately 6.5 m below seawater (when retracted). The central beam was the preferred source of sea floor depth because it was corrected for local sound velocity during the cruise using sound velocity probes (SVP) mounted on the stainless steel CTD frame and was not prone to heavy noise.

##### **Meteorology**

The suite of ship-fitted meteorological sensors formed part of the ship's scientific *surfmet* system. The sensors were mounted on the meteorology platform which was located on the ship's foremast at the bow of the ship. According to the ship's plans, the foremast was approximately 17.4 m above typical sea level (16.2 m above the maximum loading mark - 7 m draft mark) and approximately 38 m in front of the nearest ship superstructure. Table 3.2 describes the current suite of sensors. Figure 3.1 shows the orientation of sensors on the platform. The met platform had two sonic anemometers. The starboard-side was used for science while the port-side anemometer was used by the MET office. The scientific anemometer orientation was  $0^\circ$  on the bow.

##### **Sea surface hydrography**

The suite of ship-fitted sea surface hydrography sensors formed part of the ship's scientific *surfmet* system (Table 3.2). The sea surface hydrography suite of sensors were plumbed, in-line, to the clean seawater pumped system. The Sea-Bird SBE 38 temperature sensor (SST) was located close to the seawater intake towards the hull of the ship where it was less likely to suffer from any interior heating effects. The remaining sensors were located in the clean seawater laboratory on the main deck, directly above the intake pipe (estimated to be ~ 5 m). The depth of the seawater intake was estimated to be approximately 5.5 m below sea level. In the clean laboratory, the flow of seawater through the system was initially down-regulated to 16-18 L/min using a flow meter and de-bubbled using an Instrument Laboratory, Vortex VDB-1H de-bubbler. The flow was then further regulated to approximately 1500 ml/min using a floating ball flow meter prior to the first sensor, the fluorometer. This was followed in-line by the transmissometer and finally the thermosalinograph (TSG) before the water was wasted to the drain.

## **Data processing**

Output from the *surfmet* sensors were initially logged by a designated PC. Some of the sensor's firmware, connection modules and PC software manipulated the output (Figure 3.2). All the sensors used (including the *surfmet* sensors) were then registered by the TECHSAS logging system and broadcast to NetCDF, pseudo-TECHSAS ascii and UKORS format in the *raw\_data* area of the level-C logging system. With the exception of the wind, data used here was extracted from the daily TECHSAS ascii files.

## **Navigation**

Daily pseudo-TECHSAS ascii files were copied to the local PC where they were reformatted and appended using the following matlab scripts:

***uw\_nav*** – reformatted daily 1 Hz POS MV positional files (*#Applanix\_GPS\_DY1.aplnx*) to ascii (*DY033\_NAV\_#\_raw.txt*).

***uw\_swath*** - reformatted daily 1 Hz swath files (*#EM120\_DY1.EM1\_1*) to ascii (*DY033\_SWATH\_#\_raw.txt*).

***uw\_gyro*** - reformatted daily 1 Hz POS MV gyro files (*#GYRO1\_DY1.GYRO1*) to ascii (*DY033\_GYRO1\_#\_raw.txt*).

***uw\_append*** – appended daily 1 Hz ascii files to master ascii files (*DY033\_NAV\_master\_raw.txt*, *DY033\_SWATH\_master\_raw.txt* and *DY033\_GYRO1\_master\_raw.txt*)

The swath bathymetry was filtered of noise and averaged as follows:

***uw\_swclean*** – filtered the swath bathymetry (*DY033\_SWATH\_master\_raw.txt*). Output: *DY033\_SWATH\_master\_filt.txt*.

***uw\_swavg*** – averaged the filtered 1 Hz data (*DY033\_SWATH\_master\_filt.txt*) over 30 second (*DY033\_SWATH\_master\_30secav.txt*) and 150 second (*DY033\_SWATH\_master\_150secav.txt*) intervals.

The swath bathymetry was filtered of noise twice by applying a moving average window of 60 seconds and removing all data outside 2 standard deviations of that average.

## **Sea surface temperature and TSG**

Sea surface temperature (*temp\_r*, from the SBE38 at the water inlet) and the water temperature (*temp\_h*) and salinity (*salin*) from the SBE45 housing were duplicated in both the *sbe45* and *surfmet* streams, however, the *sbe45* stream was considered the best source for this data as it is unlikely to be delayed in time. Therefore, daily pseudo-TECHSAS ascii files were copied to the local PC where they were reformatted, appended and cleaned using the following matlab scripts:

**uw\_tsg** - reformatted daily 1 Hz TSG files (*#SBE45\_DY1.SBE45*) to ascii (*DY033\_TSG\_#\_raw.txt*).

**uw\_append** – appended daily 1 Hz ascii files to a master ascii file (*DY033\_TSG\_master\_raw.txt*)

**uw\_tsgclean** – applied moving average filters to the TSG data (*temp*, *temp*, *con* and *salin*). Output: *DY033\_TSG\_master\_filt.txt*

All channels (*temp*, *temp*, *salin*, *con*) were filtered of noise once by applying a moving average window of 60 seconds and removing all data outside 2 standard deviations of that average.

## **Meteorology**

Aside from the relative and absolute winds all the meteorological data was taken from the daily pseudo-TECHSAS ascii files. To limit file sizes and ease memory issues on the laptop being used for processing variables were split into two groups and processed separately.

### **Air temperature, humidity, pressure**

The TECHSAS ascii files were copied to the local PC where they were reformatted, appended and cleaned as follows:

**uw\_met**–reformatted daily 1 Hz SURFM files (*#SM\_DY1.SURFM*) to ascii (*DY033\_MET\_#\_raw.txt*)

**uw\_append** – appended daily 1 Hz ascii files to a master ascii file (*DY033\_MET\_master\_raw.txt*)

**uw\_metclean** – Flagged suspect data. Applied moving average filters to air temperature, humidity and pressure (*DY033\_MET\_master\_filt.txt*)

Air temperature was filtered of noise once by applying a moving average window of 120 seconds and removing all data outside 2 standard deviation of that average. A 60 second window and a standard deviation threshold of 2 was applied to the humidity and pressure.

### **PIR and TIR**

The TECHSAS ascii files were copied to the local PC where they were reformatted, appended and cleaned as follows:

**uw\_pirtir** –reformatted daily 1 Hz SURFM files (*#SM\_DY1.SURFM*) to ascii (*DY033\_PIRTIR\_#\_raw.txt*)

**uw\_pirtircal** – applied manufacturers calibrations (*DY033\_PIRTIR\_#\_raw\_mcal.txt*)

**uw\_append** – appended daily 1 Hz ascii files to a master ascii file (*DY033\_PIRTIR\_master\_raw.txt*)

The raw light channels (*ppar*, *spar*, *ptir*, *stir*) were initially converted to volts and calibrated as follows:

$$[\text{voltage}] = \text{raw} \times 10^{-5}$$

$$[\text{W/m}^2] = (\text{voltage} \times 10^6)/x$$

where *raw* is the raw light channel, *voltage* is the output in volts and *x* is the calibration scale factor. Scale factors were as follows for each sensor:

$$\text{spar} = 10.36 \mu\text{V/W m}^{-2} \text{ (s/n 28556, starboard, 04/07/2013)}$$

$$\text{ppar} = 10.05 \mu\text{V/W m}^{-2} \text{ (s/n 28561, port, 01/05/2015)}$$

$$\text{stir} = 10.14 \mu\text{V/W m}^{-2} \text{ (s/n 962276, starboard, 13/11/2014)}$$

$$\text{ptir} = 10.97 \mu\text{V/W m}^{-2} \text{ (s/n 973134, port, 19/03/2015)}$$

### **Winds**

The relative and absolute winds were taken from the level-C logging system after processing through *bestnav*, *prodep* and *prowind*.

***uw\_prowind*** – reformatted daily 1 Hz files from *prowind* to ascii (*DY033\_PRO\_#\_raw.txt*)

***uw\_append*** – appended daily 1 Hz ascii files to a master ascii file (*DY033\_PRO\_master\_raw.txt*)

***uw\_proclean*** – Flagged suspect data. Applied moving average filters to relative and absolute wind speed and direction. Removal of directions > 360 degrees. Conversion of absolute wind speed from knots to m/s (*DY033\_PRO\_master\_filt.txt*).

Speed and direction (relative and absolute) were filtered of noise once by applying a moving average window of 120 seconds and removing all data outside 2 standard deviation of that average.

### **Fluorescence and transmittance**

The TECHSAS ascii files were copied to the local PC where they were reformatted, calibrated, appended and cleaned as follows:

***uw\_opt\_fl*** – reformatted daily 1 Hz SURFM files (*#SM\_DY1.SURFM*) to ascii (*DY033\_OPTF\_#\_raw.txt*)

***uw\_opt\_tr*** – reformatted daily 1 Hz SURFM files (*#SM\_DY1.SURFM*) to ascii (*DY033\_OPTT\_#\_raw.txt*)

***uw\_optcal\_fl*** – applied manufacturers calibrations to obtain chlorophyll-a  
(*DY033\_OPTF\_#\_raw\_mcal.txt*)

***uw\_optcal\_tr*** – applied manufacturers calibrations to obtain beam transmission and  
attenuation (*DY033\_OPTT\_#\_raw\_mcal.txt*)

***uw\_append*** – appended daily 1 Hz ascii files to a master ascii file  
(*DY033\_OPTF\_master\_raw.txt* and *DY033\_OPTT\_master\_raw.txt*)

***uw\_optclean\_fl / uw\_optclean\_tr*** – Removed suspect data. Applied moving average  
filters to chlorophyll-a, beam transmission and attenuation (*DY033\_OPTF\_master\_filt.txt*  
and *DY033\_OPTT\_master\_filt.txt*)

Chlorophyll-a, beam transmission and attenuation were filtered of noise once by applying a  
moving average window of 120 seconds and removing all data outside 1.5 standard deviations  
of that average.

The fluorescence voltage channel (*fluo*) was converted to *chl a* using the following calibration:

$$Chl\ a\ [\mu g/L] = SF (fluo - CWO)$$

where SF = 5.5  $\mu g/L/V$  and CWO = 0.068 V.

The transmissometer voltage channel (*trans*) was converted to beam transmission (*beamtrans*)  
and beam attenuation (*atten*) as follows:

$$trans\ [V] = trans \geq V_{dark}$$

$$beamtrans\ [\%] = \left( \frac{[trans - V_{dark}]}{[V_{ref} - V_{dark}]} \right) 100$$

$$atten\ [per\ m] = \left( -\frac{1}{pathlength} \right) \ln\left( \frac{beamtrans}{100} \right)$$

where  $V_{dark} = 0.058\ V$ ,  $V_{ref} = 4.623\ V$  and  $pathlength = 0.25\ m$ .

## **Calibration**

Salinity and SST will be calibrated against underway discrete salinity samples and CTD  
temperature after the cruise.

*Dates and times of salinity samples taken from the underway non-toxic supply*

<b>Date</b>	<b>Time</b>	<b>Depth (m)</b>	<b>Crate #</b>	<b>Bottle #</b>
12/07/2015	07:05		TSG01	32
12/07/2015	10:48		TGS01	31
12/07/2015	12:59		TSG01	30
12/07/2015	18:08		TSG01	29
13/07/2015	06:23		TGS01	28
13/07/2015	10:49	146	TSG01	27
13/07/2015	16:08		TSG01	26
13/07/2015	19:43		TGS01	25
14/07/2015	06:04	146	TSG01	33
14/07/2015	10:50		TSG01	34
14/07/2015	12:55		TGS01	35
15/07/2015	13:08	149.5	TSG01	36
15/07/2015	13:59		TSG01	37
15/07/2015	16:24		TGS01	38
15/07/2015	18:58	150	TSG01	39
15/07/2015	23:15	143	TGS01	40
16/07/2015	07:10	205	TSG01	41
16/07/2015	10:50	2095	TSG01	42
16/07/2015	17:07	2387	TSG01	43
17/07/2015	01:13	1862	TSG01	44
17/07/2015	06:57	2127	TSG01	45
17/07/2015	16:04	3823	TSG01	46
17/07/2015	17:17	3635	TSG01	47
17/07/2015	20:23	2513	TSG01	48
18/07/2015	06:53	476	TSG02	49
18/07/2015	10:58	249	TSG02	50
18/07/2015	11:03	249	TSG02	51
18/07/2015	16:16	280	TSG02	52
19/07/2015	06:35	204	TSG02	53
19/07/2015	11:01	202	TSG02	54
19/07/2015	15:56	203	TSG02	55
19/07/2015	19:47	203	TSG02	56
19/07/2015	22:25	228	TSG02	57
20/07/2015	07:44	206	TSG02	58
20/07/2015	11:07	202	TSG02	59
20/07/2015	16:17	203	TSG02	60
20/07/2015	20:41	205	TSG02	61

21/07/2015	06:31	2501	TSG02	62
21/07/2015	15:28		TSG02	63
21/07/2015	22:03	2005	TSG02	64
22/07/2015	06:54	1573	TSG02	65
22/07/2015	09:54	1751	TSG02	66
22/07/2015	17:04	203	TSG02	67
22/07/2015	20:25	204	TSG02	68
23/07/2015	08:05	480	TSG02	69
23/07/2015	11:00	467	TSG02	70
23/07/2015	16:58	169	TSG02	71
23/07/2015	19:23	161	TSG02	72
24/07/2015	07:58	146	TSG01	25
24/07/2015	11:38	146	TSG01	26
24/07/2015	17:00	144	TSG01	27
24/07/2015	19:34	145	TSG01	28
25/07/2015	06:21	144	TSG01	29
25/07/2015	11:18	147	TSG01	30
25/07/2015	17:14	146	TGS01	31
26/07/2015	00:33	143	TSG01	32
26/07/2015	07:12	107	TGS01	33
26/07/2015	11:07	103	TGS01	34
26/07/2015	17:01	105	TSG01	35
27/07/2015	06:32	105	TGS01	36
27/07/2015	11:13	113	TSG01	37
27/07/2015	17:05	112	TSG01	38
28/07/2015	07:46	121	TSG01	39
28/07/2015	12:18	118	TSG01	40
28/07/2015	17:00	117	TGS01	41
29/07/2015	06:50	146	TSG01	42
30/07/2015	10:17	143	TSG01	43
30/07/2015	14:08	148	TGS01	44
30/07/2015	17:19	148	TSG01	45
30/07/2015	22:25	145	TSG01	46
31/07/2015	13:14	146	TSG01	47
31/07/2015	14:39	148	TSG01	48

## Data quality notes

Bubbles - The transmissometer was affected by trapped bubbles in the detector chamber throughout the cruise. This severely degraded the data.

The flow rate needed frequent adjustment. Data that was compromised during these periods was removed.

The SKE510 Par sensor on the starboard side (S/N 28556) requires a post cruise calibration.

## Log of significant events

11/07/2015 20:30 – Underway started

12/07/2015 06:52:56 Mark readjusted the pressure – it had been very low overnight

12/07/2015 08:01:55 Shutdown for mods (?) to waste to stabilize flow

12/07/2015 08:07:18 Restarted and flow more stable

12/07/2015 08:24 Bubbles in system and transmissometer compromised

14/07/2015 12:55 Shutdown due to non-tox system cleaning

15/07/2015 13:05 Underway restarted

20/07/2015 18:36 to 20/07/2015 18:53 – System turned off for cleaning. After restart, bubbles ruined transmission. Period of instability in TSG until 21/07/2015 21:36:00. Salinity very noisy.

22/07/2015 Overnight – large drop outs – no flow. Longest period was 22/07/2015 01:28 to 06:39

26/07/2015 15:00 – Transmission very noisy – bubbles in the system

29/07/2015 08:24:10 Shutdown for cleaning. Startup at 08:57:30.

02/08/2015 12:00 Underway switched off

Table 3.1. Navigation sensors used for processing

<b>Manufacturer</b>	<b>Model</b>	<b>Function/Data types</b>	<b>Comments</b>
Applanix	POS MV 320 V5	DGPS and IMU 7	General use gyro. Secondary <i>bestnav</i> positional source.
Kongsberg	EM122	Deep Water Multi-Beam echo sounder	Port drop keel

Table 3.2. Surfmet sensors used for processing

<b>Manufacturer</b>	<b>Sensor</b>	<b>Serial No.</b>	<b>Comments (e.g. port)</b>	<b>Calibration applied?</b>	<b>Last calibration (DD/MM/YYYY)</b>
Skye	PAR SKE510	28556	Starboard	No	04/07/2013 (2yr)
Skye	PAR SKE510	28561	Port	No	01/05/2015 (2yr)
Kipp & Zonen	TIR CM6B	962276	Starboard	No	13/11/2014 (2yr)
Kipp & Zonen	TIR CM6B	973134	Port	No	19/03/2015 (2yr)
Gill	Windsonic Option 3	071121	Starboard Inv:250004845	No	N/A (tested 25/02/2015)
Vaisala	HMP155 Temp./Hum.	K0950058		No	16/01/2015
Vaisala	PTB110 Air Pres.	L0650612		No	06/02/2015
Wet Labs	WS3S Fluorimeter	WS3S-248	Inv:240002939	No	14/10/14
Wet Labs	CST Transmissometer	CST-112R	Inv:240002369	No	26/06/2014 (2yr)
Sea-Bird	SBE38 Temperature	3854115- 0491		No	25/06/2015
Sea-Bird	SBE45 TSG	4548881- 0230		No	23/09/2014 (1yr)

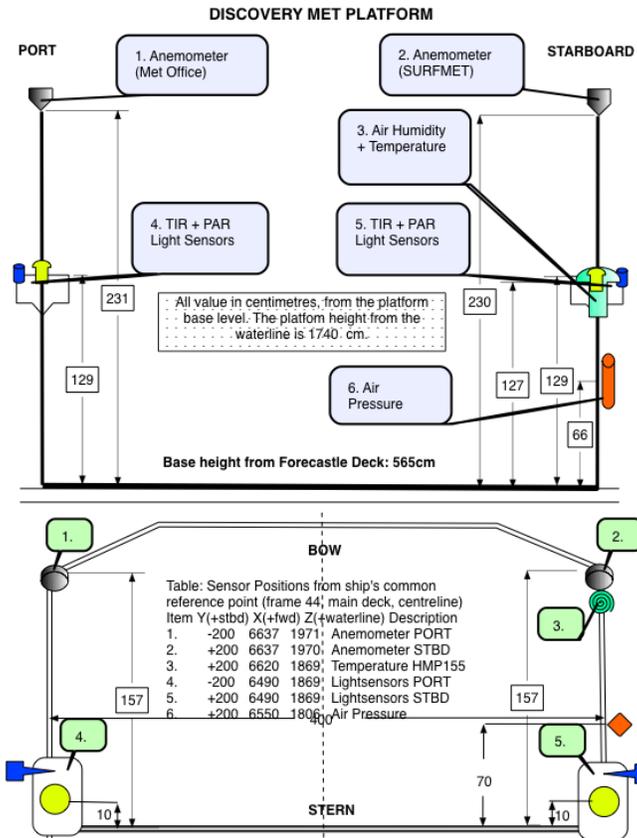


Figure 3.1. Schematic of Discovery met platform layout

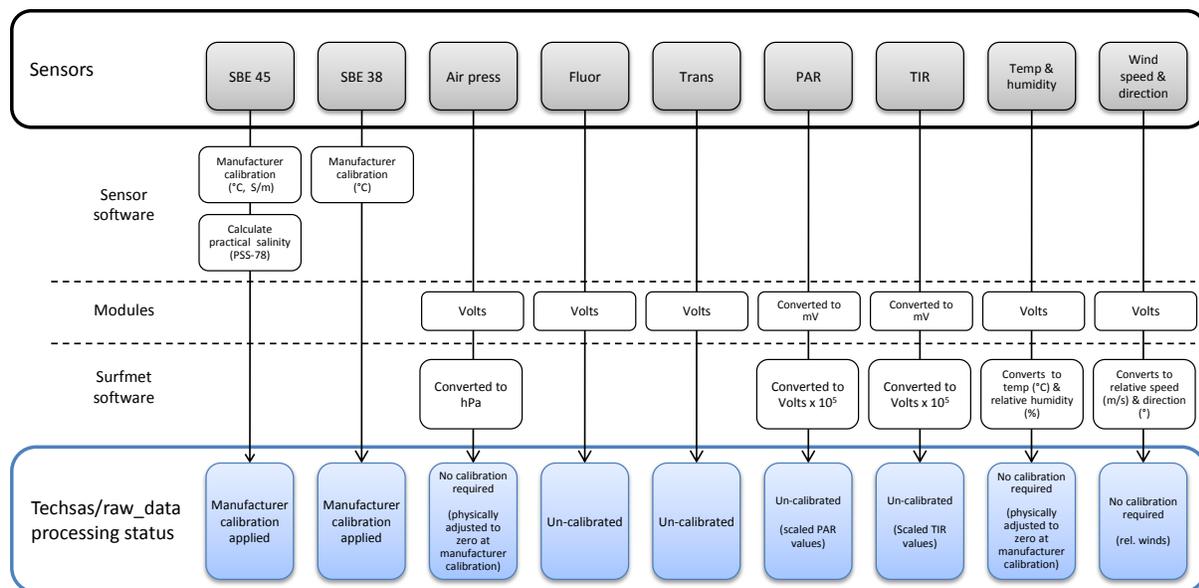
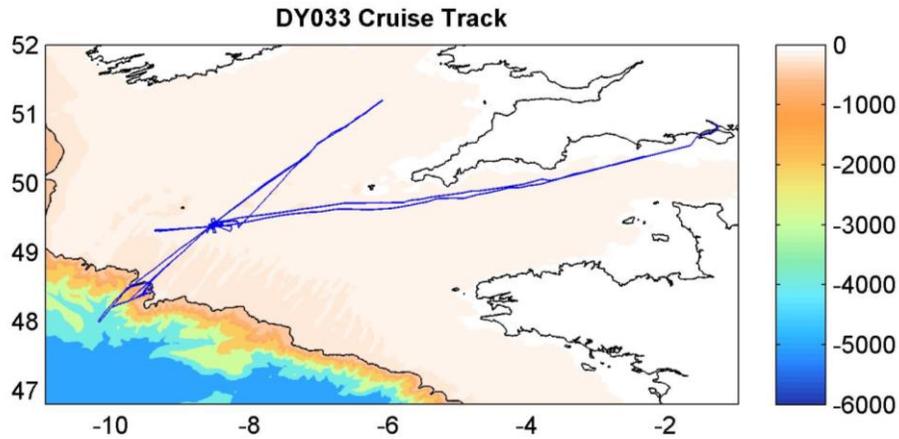
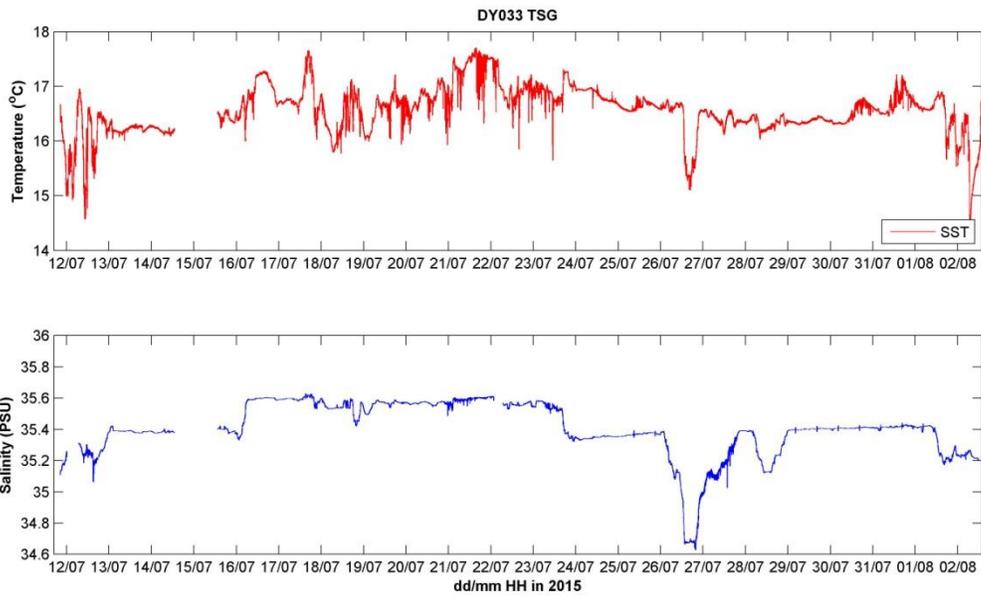


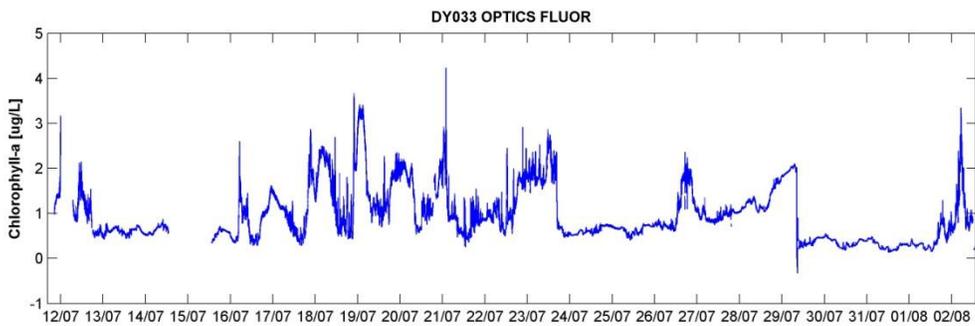
Figure 3.2. Surfmet data processing. Diagrams shows the processing route from sensor to raw\_data in the level-C logging system.



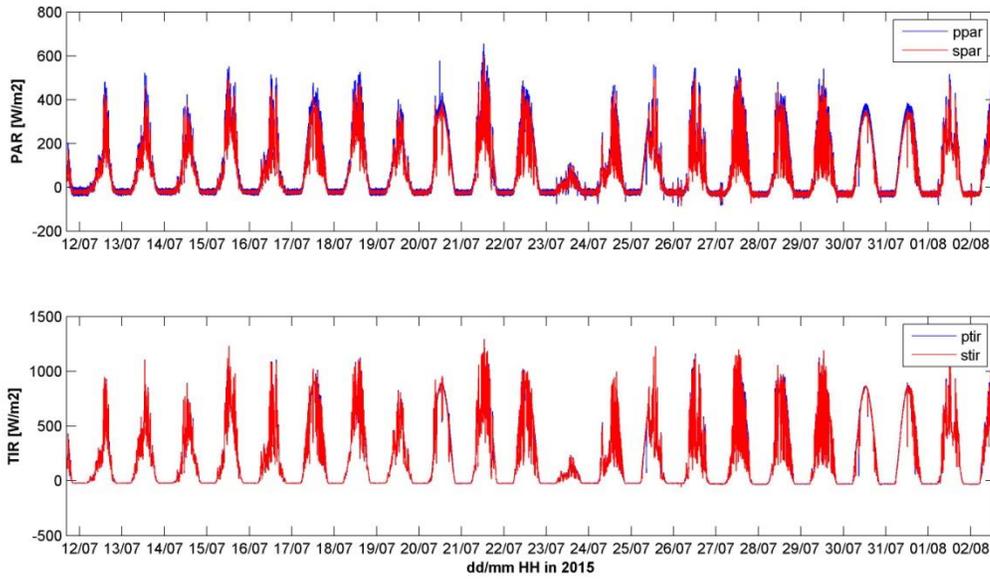
DY033 cruise track



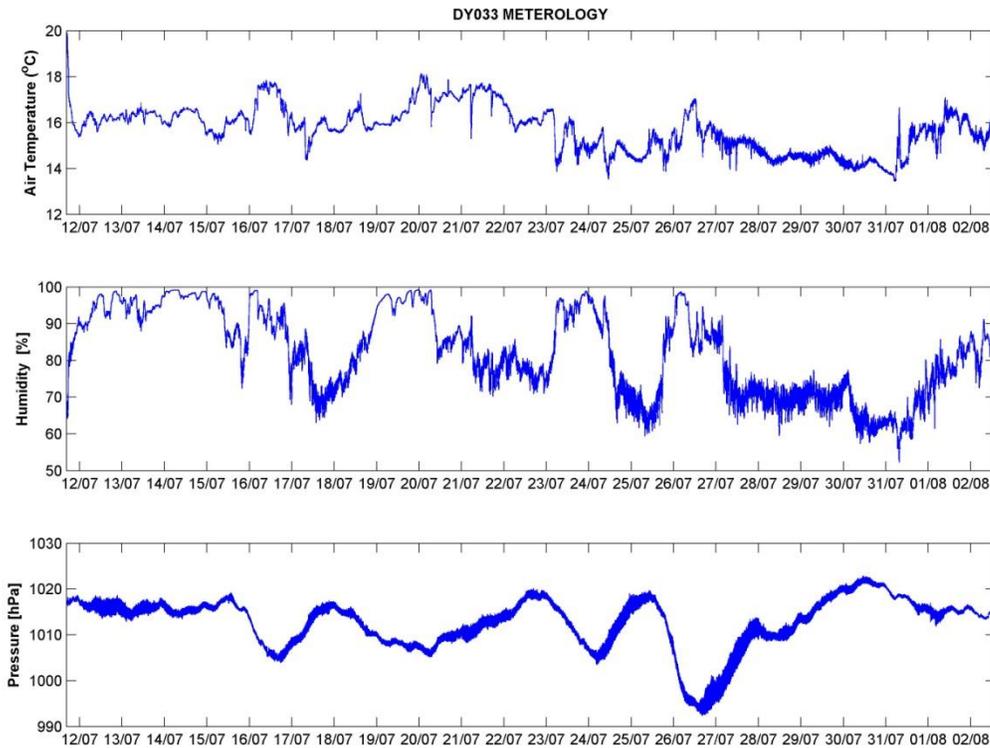
DY033 SST (top) and salinity (bottom)



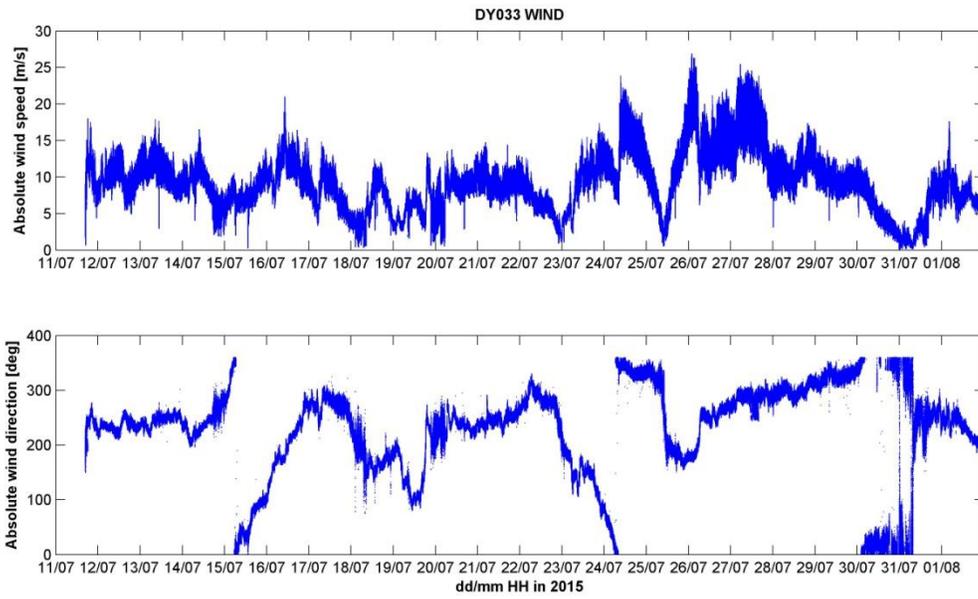
DY033 chlorophyll – note that jump on 29/07/2015 corresponds to a system clean



DY033 PAR (top) and TIR (bottom)



DY033 air temperature (top), humidity (middle) and pressure (bottom)



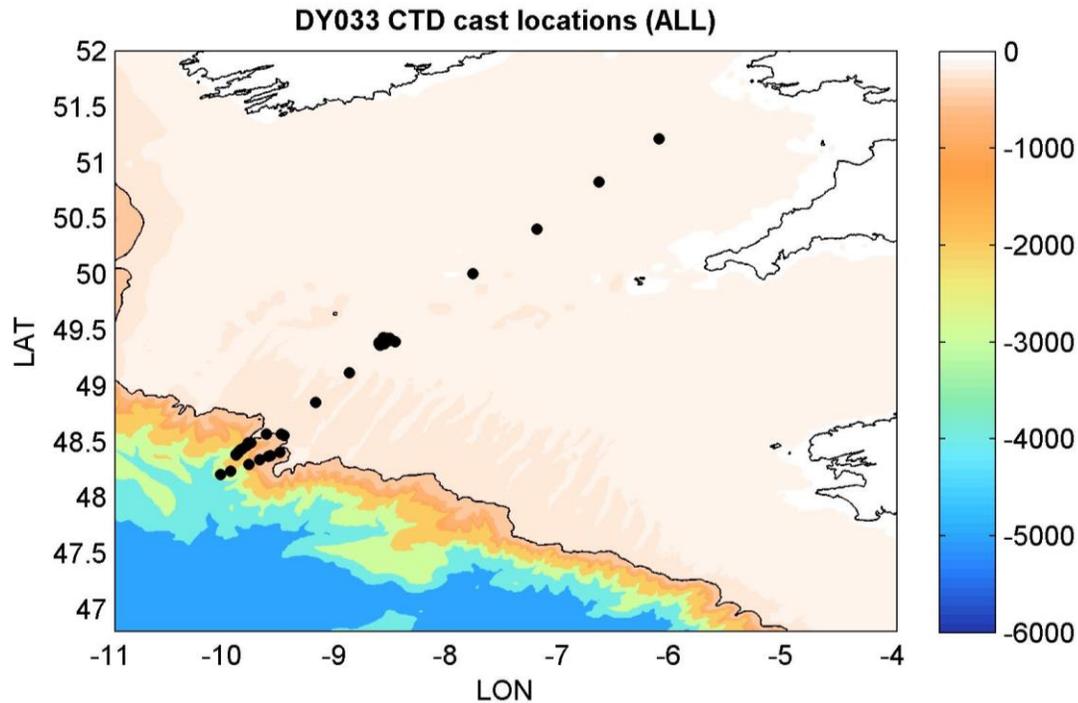
DY033 wind speed (m/s) and direction (deg)

## 4. CTD processing

*Jo Hopkins (National Oceanography Centre, Liverpool)*

A total of 47 useable casts with the stainless steel frame and 41 useable casts with the titanium CTD frame were completed. See technical reports for sensor serial numbers and channels.

### Map of CTD cast locations



### Raw data files

The following raw data files were generated:

DY033\_001.bl (a record of bottle firing locations)

DY033\_001.hdr (header file)

DY033\_001.hex (raw data file)

DY033\_001.con (configuration file)

Where \_001 is the cast number (not STNNBR)

Files generated by the titanium CTD frame have a suffix 'T', e.g DY033\_007T.bl etc

## **SBEDataProcessing steps**

The following processing routines were run in the SBEDataProcessing software (Seasave Version 7.23.2):

1. **DatCnv:** A conversion routine to read in the raw CTD data file (.hex) containing data in engineering units output by the CTD hardware. Calibrations as appropriate though the instrument configuration file (.CON) are applied.

Data Setup options were set to the following:

Process scans to end of file: yes

Scans to skip: 0

Output format: ascii

Convert data from: upcast & downcast

Create file types: both bottle and data

Source of scan range data: bottle log .BL file

Scan range offset: -2.5 seconds for stainless, -1 second for titanium

Scan range duration: 5 seconds for stainless, 1 second for titanium

Merge separate header file: No

Apply oxygen hysteresis correction: yes (2 second window)

Apply oxygen Tau correction: yes

Selected output variables:

- Time [seconds]
- Pressure [db]
- Temperature [ITS-90, °C] and Temperature 2 [ITS-90, °C], referring to primary and secondary sensors)
- Conductivity and Conductivity 2 [S/m]
- Salinity and salinity 2 [PSU, PSS-78]
- Oxygen raw, SBE 43 [V]
- Oxygen, SBE 43 [µmol/l]

- Beam attenuation [1/m]
- Fluorescence [ $\mu\text{g/l}$ ]
- PAR/irradiance, downwelling [ $\text{W m}^2$ ]
- Turbidity [ $\text{m}^{-1} \text{sr}^{-1}$ ]
- Altimeter [m]
- Voltage channel 2: Light scattering Wetlabs BBRTD [*Stainless*]; Upwelling Irradiance sensor (UWIRR) [*Titanium*]
- Voltage channel 3: Altimeter [*Stainless*]; Downwelling Irradiance sensor (DWIRR) [*Titanium*]
- Voltage channel 4: Fluorometer [*Stainless*]; Altimeter [*Titanium*]
- Voltage channel 5: Transmissometer [*Stainless*]; Light scattering Wetlabs BBRTD [*Titanium*]
- Voltage channel 6: Downwelling Irradiance sensor (DWIRR) [*Stainless*]; Transmissometer [*Titanium*]
- Voltage channel 7: Upwelling Irradiance sensor (UWIRR) [*Stainless*]; Fluorometer [*Titanium*]

2. **Bottle Summary** was run to create a .BTL file containing the average, standard deviation, min and max values at bottle firings. .ROS files were placed in the same directory as the .bl files during this routine to ensure that bottle rosette position was captured in the .btl file.

Output saved to DY033\_001.btl (DY033\_007T.btl)

3. **Wild Edit:** Removal of pressure spikes

Standard deviations for pass 1: 2

Standard deviations for pass 2: 20

Scans per black: 100

Keep data within this distance of the mean: 0

Exclude scans marked as bad: yes

4. **Filter:** Run on the pressure channel to smooth out high frequency data

Low pass filter time B: 0.15 seconds

5. **AlignCTD:** Based on examination of different casts a 3 second advance was chosen for alignment of the oxygen sensor on the stainless steel CTD and 3 seconds for the titanium casts. This alignment is a function of the temperature and the state of the oxygen sensor membrane. The colder (deeper) the water the greater the advance needed. The above alignments were chosen as a compromise between results in deep (cold) and shallow (warmer) waters.
6. **CellTM:** Removes the effect of thermal inertia on the conductivity cells.  $\text{Alpha} = 0.03$  (thermal anomaly amplitude) and  $1/\text{beta} = 7$  (thermal anomaly time constant) for both cells.

Output of steps 1-6 above saved in DY033\_001.cnv (24 Hz resolution) (DY033\_007T.cnv)

7. **Derive:** Variables selected are

Salinity and Salinty 2 [PSU, PSS-78]

Oxygen SBE43 [ $\mu\text{mol/l}$ ]

Oxygen Tau correction: yes (2 second window)

Output saved to DY033\_001\_derive.cnv (24 Hz resolution) (DY033\_007T\_derive.cnv)

8. **BinAverage:** Average into 2Hz (0.5 seconds),

Exclude bad scans: yes

Scans to skip over: 0

Casts to process: Up and down

9. **Strip:** Remove salinity and oxygen channels from the 2 Hz file that were originally created by DatCnv, but then later regenerated by Derive.

Output saved to DY033\_001\_derive\_2Hz.cnv (DY033\_007T\_derive\_2Hz.cnv)

## **Matlab processing steps**

The following processing steps were performed in MATLAB:

- (1) Create a .mat file of meta data extracted from the cruise Event Log with the following variables:

CRUISECODE e.g. DY033

STNNBR (as per BODC data management guidance for the Shelf Sea Biogeochemistry programme)

DATE and TIME of the cast at the bottom of the profile (when known)

LAT and LON when the CTD was at the bottom of the profile (when known)

DEPTH (nominal water depth in metres from echo sounder)

CAST (CTD cast number, e.g. 001)

File created: DY033\_metadata.mat

- (2) Extract data from 2Hz averaged files (e.g. DY033\_001\_derive\_2Hz.cnv), merge with metadata and save into a matlab structure for each cast. Each file (DY033\_001\_derive\_2Hz.mat) contains the following un-calibrated channels.

CTD001 =

CRUISE: 'DY033'

CAST: 1.00

STNNBR: 3.00

DATE: '13/07/2015'

TIME: '06:47'

LAT: 49.43

LON: -8.59

DEPTH: 144.00 [m]

CTDtime: [4276x1 double] [seconds]

CTDpres: [4276x1 double] [db]

CTDtemp1: [4276x1 double] [°C]  
 CTDtemp2: [4276x1 double] [°C]  
 CTDcond1: [4276x1 double] [S/m]  
 CTDcond2: [4276x1 double] [S/m]  
 CTDoxy\_raw: [4276x1 double] [V]  
     CTDatt: [4276x1 double] [1/m]  
 CTDfluor: [4276x1 double] [µg/l]  
     CTDpar: [4276x1 double] [Wm<sup>2</sup>]  
 CTDturb: [4276x1 double] [m<sup>-1</sup> sr<sup>-1</sup>]  
     CTDalt: [4276x1 double] [m]  
 CTDturb\_raw: [4276x1 double] [V]  
     CTDalt\_raw: [4276x1 double] [V]  
 CTDfluor\_raw: [4276x1 double] [V]  
     CTDatt\_raw: [4276x1 double] [V]  
 CTDpar\_dn\_raw: [4276x1 double] [V]  
 CTDpar\_up\_raw: [4276x1 double] [V]  
     CTDsal1: [4276x1 double] [PSU]  
     CTDsal2: [4276x1 double] [PSU]  
 CTDoxy\_umoll: [4276x1 double] [µmol/l]  
     CTDflag: [4276x1 double]

(3) Extract data from 24Hz files (e.g. DY033\_001\_derive.cnv), merge with metadata and save into a matlab structure for each cast. Each file (DY008\_001\_derive.mat) contains the following un-calibrated channels.

CTD001 =

```

CRUISE: 'DY033'
CAST: 1.00
STNNBR: 3.00
DATE: '13/07/2015'
  
```

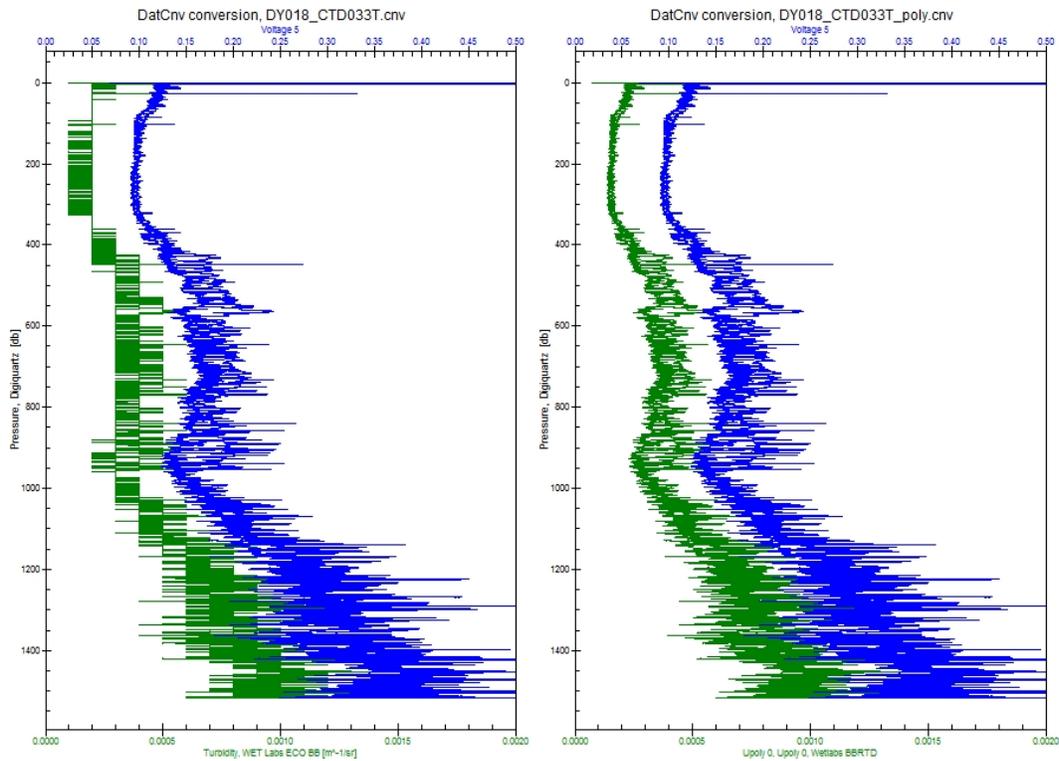
TIME: '06:47'  
 LAT: 49.43  
 LON: -8.59  
 DEPTH: 144.00 [m]  
 CTDtime: [51306x1 double] [seconds]  
 CTDpres: [51306x1 double] [db]  
 CTDtemp1: [51306x1 double] [°C]  
 CTDtemp2: [51306x1 double] [°C]  
 CTDcond1: [51306x1 double] [S/m]  
 CTDcond2: [51306x1 double] [S/m]  
 CTDsal1\_1: [51306x1 double] [PSU]  
 CTDsal2\_1: [51306x1 double] [PSU]  
 CTDoxy\_raw: [51306x1 double] [V]  
 CTD\_oxy\_umoll\_1: [51306x1 double] [µmol/l]  
 CTDatt: [51306x1 double] [1/m]  
 CTDfluor: [51306x1 double] [µg/l]  
 CTDpar: [51306x1 double] [Wm<sup>2</sup>]  
 CTDturb: [51306x1 double] [m<sup>-1</sup> sr<sup>-1</sup>]  
 CTDalt: [51306x1 double] [m]  
 CTDturb\_raw: [51306x1 double] [V]  
 CTDalt\_raw: [51306x1 double] [V]  
 CTDfluor\_raw: [51306x1 double][V]  
 CTDatt\_raw: [51306x1 double] [V]  
 CTDpar\_dn\_raw: [51306x1 double] [V]  
 CTDpar\_up\_raw: [51306x1 double] [V]  
 CTDsal1: [51306x1 double] [PSU]  
 CTDsal2: [51306x1 double] [PSU]  
 CTDoxy\_umoll: [51306x1 double] [µmol/l]  
 CTDflag: [51306x1 double]

Note that ‘\_1’ for the first instances of salinity and oxygen in this file are variables before re-derivation in the SeaBird Processing routines.

Inspection of the turbidity channel (CTDturb) and comparison to the original raw voltage (CTDturb\_raw) reveals a bug in the SeaBird DatCnv conversion module whereby the converted ECO-BB output is reported to a fixed precision. This has been confirmed by SeaBird (see email chain at the end of cruise DY018). It is demonstrated below (left) where the raw voltage channel (blue) is compared to the SeaBird DatCnv output (green). Direct conversion using the scale factor (SF) and dark counts (DC) supplied in the manufacturer’s calibration appears to rectify this problem (right plot). We therefore replace the original turbidity channel in the .cnv files with a corrected version using:

$$\text{CTDturb} = \text{CTDturb\_raw} .* \text{SF} - (\text{SF} \times \text{DC});$$

This appears to reinstate the original resolution.



- (4) Manual identification of the surface soak (while waiting for pumps to turn on) and the end of the downcast using the 2Hz files. Times to crop were saved to DY033\_stainless\_castcrop\_times.mat and DY033\_titanium\_castcrop\_times.mat

CAST: [48x6 char]

STNNBR: [48x1 double]

CTDstart: [48x1 double] [seconds]

CTDstop: [48x1 double] [seconds]

This was then used to crop both the 2Hz and 24Hz files and output (i.e. just the downcast recordings) saved to DY033\_CTD001\_derive\_2Hz\_cropped.mat and DY033\_CTD001\_derive\_cropped.mat respectively.

- (5) De-spiking of downcast 24 Hz data. The salinity, conductivity, temperature, oxygen, attenuation, turbidity and fluorescence channels were all de-spiked. The worst spikes were identified using an automated routine (similar to WildEdit) where the data was scanned twice and points falling outside a threshold of  $nstd \times$  standard deviations from the mean within a set window size were removed (turned into NaNs).

Window size (#scans) and number of standard deviations from the mean (nstd) used for each channel.

Channel	Pass 1 window	Pass 1 nstd	Pass 2 window	Pass 2 nstd
Temperature, conductivity, fluorescence	100	3	200	3
Salinity, turbidity	200	2	200	3
Oxygen	100	2	200	3

Auto-despiking saved to DY033\_CTD001\_derived\_cropped\_autospike.mat

Large 'spikes' were often observed in the CT sensors lasting a few seconds, predominantly in the thermocline. This is a persistent problem in shallow water with strong property gradients (e.g. see for example D352, D376); particularly where a large CTD package carrying large volume bottles is used. The spikes coincide with a decrease in the decent rate of the CTD package and are therefore likely associated with inefficient flushing of water around the sensors. It is caused by the pitch and roll of the boat, so is accentuated in rough weather. As the decent rate of the CTD package slows on the downcast 'old' water (from above and therefore typically warmer) is pushed back passed the sensors. As the decent rate increases again 'new' water is flushed past the sensors. A similar problem can occur if the veer rate on the CTD winch varies (as was the case on CD173).

The largest and most significant warm anomalies identified in the primary and secondary CT sensors were removed. This was at times up to 5 m of the profile. The impact of smaller scale anomalies that were not removed is mostly minimised during the averaging processes, but care should be taken when interpreting smaller scale features, particularly through the thermocline. The casts are more than good enough for looking at large scale trends and anomalies but should probably not be used for Thorpe scale analysis and interpretation of fine scale structures. To achieve this in a shelf sea environment free fall profiling techniques are more suitable.

Although 'old' water would also have been flushed back past the auxiliary sensors (turbidity, oxygen, chlorophyll, attenuation) the coincident measurements in these channels were (a) not always anomalous and/or (b) any associated anomaly did not always exactly coincide (or could even be confidently identified, especially for oxygen). As such removal of data from auxiliary channels using scans flagged as bad in the primary/secondary CT channels was not always appropriate or did not improve data quality. The worst individual spikes within these channels however were manually identified and removed (NaN'd).

Output saved to DY033\_CTD001\_derived\_cropped\_autospike\_manualspike.mat

Additional channels added into this file:

Vectors of 0's and 1's indicating data that has been NaN'd (=1). Outputs depend on channels loaded and viewed so each column may have variable meaning and is saved for processing archive purposes only.

Pindex: [18900x3 double]

Sindex: [18900x3 double]

Aindex: [18900x4 double]

- (6) Average 24Hz (cropped and de-spiked data) into 1 db. Linear interpolation used when no data available for averaging.

Files for each cast were created: DY033\_CTD001\_1db\_dn.mat

All the 1 db profiles (except PAR and fluor) are then further smoothed with a 5 m running median window. To help preserve fine scale structure through the SCM a 3 m window was used for the fluorescence. Note that all non-smoothed (24 Hz) data is available on request.

File output: DY033\_CTD001\_1db\_dn\_smth.mat

- (7) Application of calibrations to salinity, chlorophyll and oxygen in 1db smoothed downcasts. Calibrated files saved to DY033\_001\_1db\_dn\_smth\_calib.mat.

Sigma theta ( $\sigma_\theta$ ) (relative to 0 pressure) is also calculated at this stage using the matlab function sw\_pden-1000 from the SEAWATER toolkit.

CTD001 =

CRUISE: 'DY033'

CAST: 1.00

STNNBR: 3.00

DATE: '13/07/2015'

TIME: '06:47'

LAT: 49.43

LON: -8.59

DEPTH: 144

pres: [140x1 double] [db]

time: [140x1 double] [seconds]

temp1: [140x1 double] [°C]

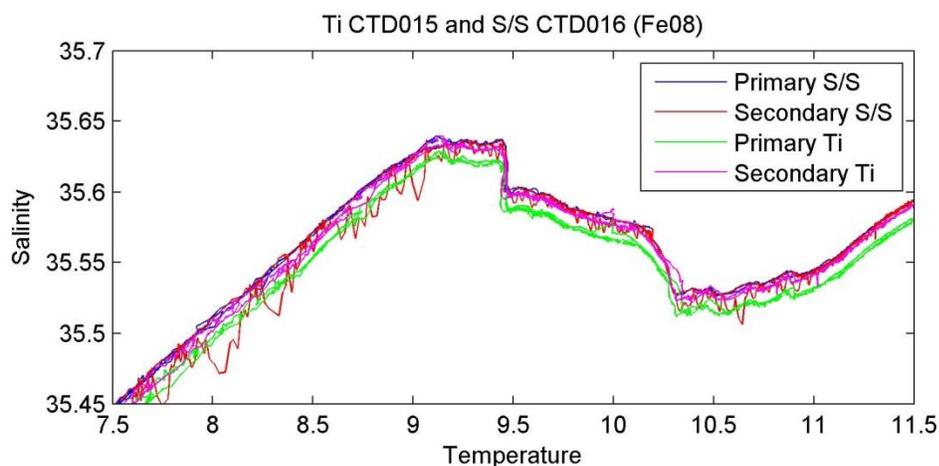
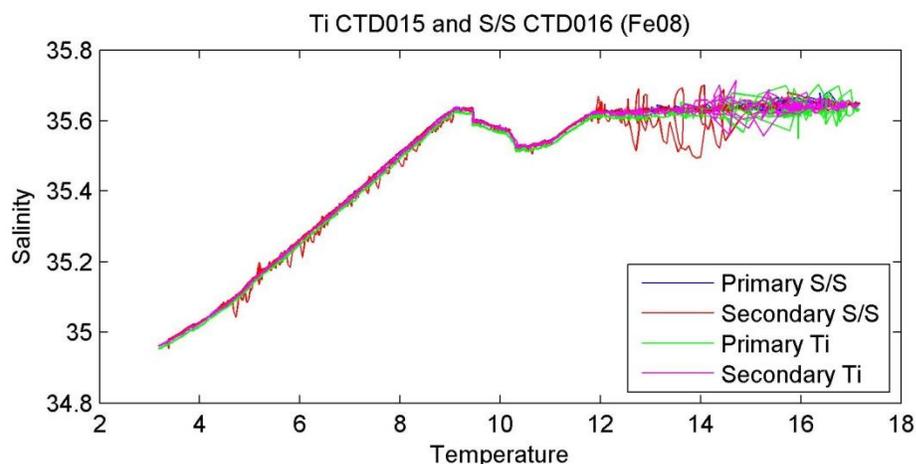
temp2: [140x1 double] [°C]  
sal1: [140x1 double] [PSU] - calibrated  
sal2: [140x1 double] [PSU] - calibrated  
cond1: [140x1 double] [S/m] – not calibrated  
cond2: [140x1 double] [S/m] – not calibrated  
oxy\_umoll: [140x1 double] [µmol/l] – calibrated  
fluor: [140x1 double] [µg/l] – calibrated  
par: [140x1 double] [Wm<sup>2</sup>]  
turb: [140x1 double] [m<sup>-1</sup> sr<sup>-1</sup>]  
att: [140x1 double] [1/m]  
sigma\_theta: [140x1 double]

The calibrations were also applied to the 24 Hz data (cropped and de-spiked) and output to .mat files DY033\_001\_derive\_cropped\_autospike\_manualspike\_calib.mat containing the same variables as above.

- (8) Application of salinity, chlorophyll and oxygen calibrations to bottle firing data. A new file, DY033\_stainless\_btl\_calib.mat/ DY033\_titanium\_btl\_calib.mat, with variables CTDsal1\_cal, CTDsal2\_cal, CTDoxy\_umoll\_cal and CTDFluor\_cal was created.

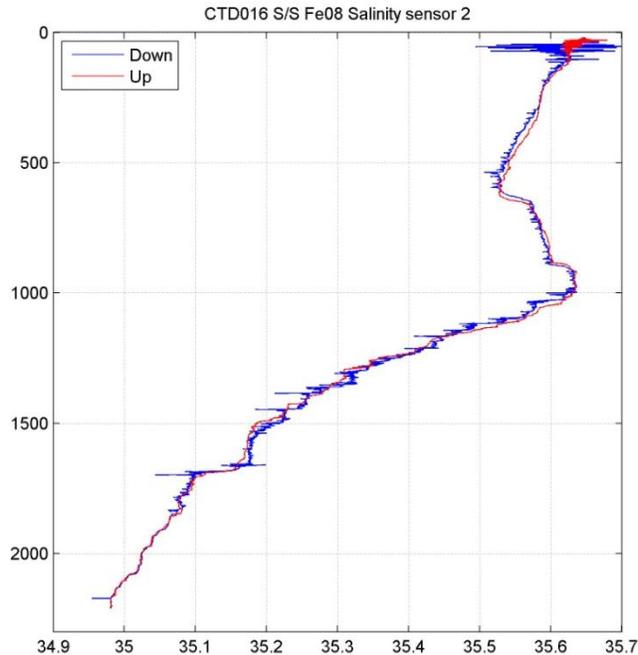
## Notes

- (a) CTD014T hit the bottom (approx. 2500m). The primary titanium conductivity cell was subsequently offset and salinities too low. The primary to secondary salinity offset increased from 0.001 to 0.01 PSU. The primary conductivity sensor was changed after cast CTD019T (SN 04-4138 to SN 04-2571). CTD021T is the first cast with the new sensor. Separate calibrations will be required.



T-S plots of CTD015T (Ti) and CTD016 (S/S) demonstrating the salinity offset in the primary titanium sensor after collision with the seabed.

- (b) The secondary conductivity on the downcast of CTD016 (S/S) is very noisy. There was probably something stuck in the cell. It cleared for the upcast.



#### Up and downcast salinity from CTD016 (S/S)

- (c) Stainless casts 1- 44 were recorded with incorrect calibration coefficients entered for the SBE43 oxygen sensor. A new master configuration file was therefore created (DY033\_ss\_oxy\_final\_cal\_NMEA.XMLCON) and all casts up to CTD075 were processed in the SeaBird software using this new file (as opposed to the individual ones generated for each cast).
- (d) The PAR sensor was taken off the titanium CTD from cast 14 onwards (only rated to 500 m). The stainless PAR sensors were deep rated and cosine response rather than hemispherical. The PAR sensor was reattached on cast CTD58T. The PAR channel in the final calibrated files has been NaNd when no sensor was attached.
- (e) Casts 38T and 39T were aborted due to termination failure. Usable data was collected from CTD038T but not from CTD039T.
- (f) On CTD057 (S/S) the wire was caught in the sheave and damaged (new termination required). No data is available for this cast.
- (g) The BBRTD cable on the stainless frame developed a leak and the connector slowly dissolved. There are drop outs in preceding casts but large sections of the turbidity in casts 40-44 is entirely un-usable. These sections have been removed but the remainder of the profile should still be treated with caution. The connection was changed after cast 44.
- (h) On CTD074 the stainless oxygen sensor started reading unrealistically low values (~160  $\mu\text{mol/kg}$ ). This problem persisted in cast CTD075. The SBE43 SN0709 was subsequently replaced with SBE43 SN0619 (casts CTD076 onwards). A new config. file

was created (DY033\_SS\_new\_oxy\_0619.xmlcon) and used for casts CTD076 onwards. Oxygen from casts 74 and 75 has been removed from the final files.

- (i) The new S/S oxygen sensor (SN 0691) looked to be faulty on cast CTD078 – potential cable problem? Oxygen samples were taken to allow a profile to be constructed from discrete data points. Oxygen from casts 78 and 90 has been removed from the final files.
- (j) On cast CTD021T there was some confusion around bottle firing order and position. For clarification, the following bottles (ROSPOS) were on the frame and closed: 1, 2, 3, 4, 5, 6, 7 (depth 895-400 m) and then 13, 14 (30 and 20 m depth). Positions 8-12 were fired but no samples collected because these positions did not have bottles mounted.

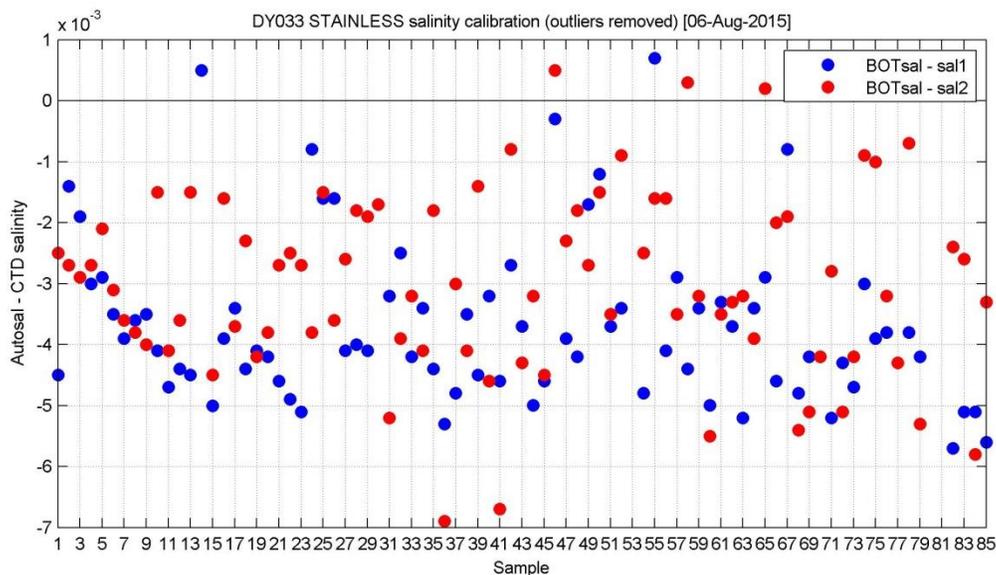
## **Calibrations**

### **Salinity**

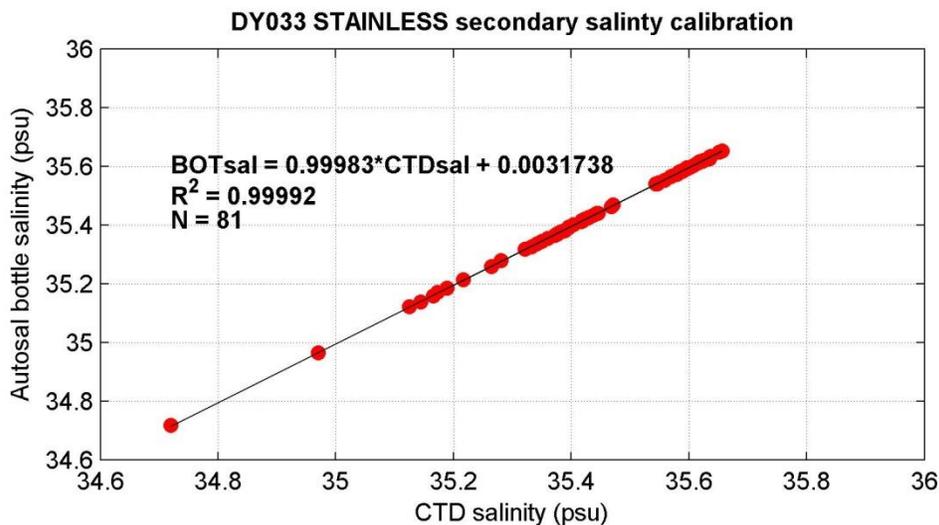
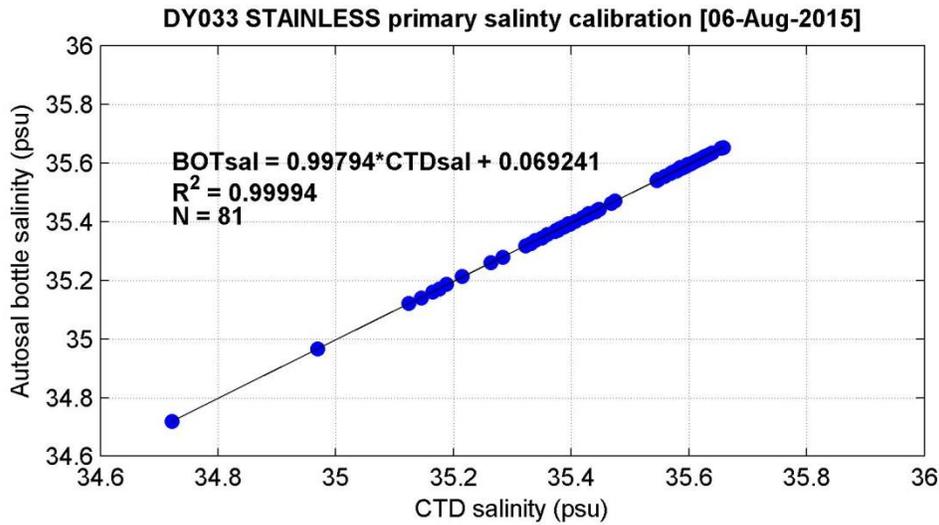
139 salinity samples (93 stainless, 46 titanium) were taken for analysis on a Guildline 8400B (s/n 71185). 8 samples from the stainless bottles and 4 samples from the titanium however could not be matched against a cast and bottle position from the logs so are not useable.

#### ***Stainless***

Using all samples the mean and standard deviation of residuals from the primary and secondary sensors were  $0.0012859 \pm 0.047523$  and  $0.0018212 \pm 0.047426$  respectively. After removal of outliers where the difference between Autosol and CTD values was greater than 1 standard deviation and/or  $> 0.002$ , the mean  $\pm$  standard deviations for the primary and secondary sensors was reduced to  $-0.0036901 \pm 0.0013353$  and  $-0.0030173 \pm 0.001501$  respectively.



The following regressions were applied to the profiles:



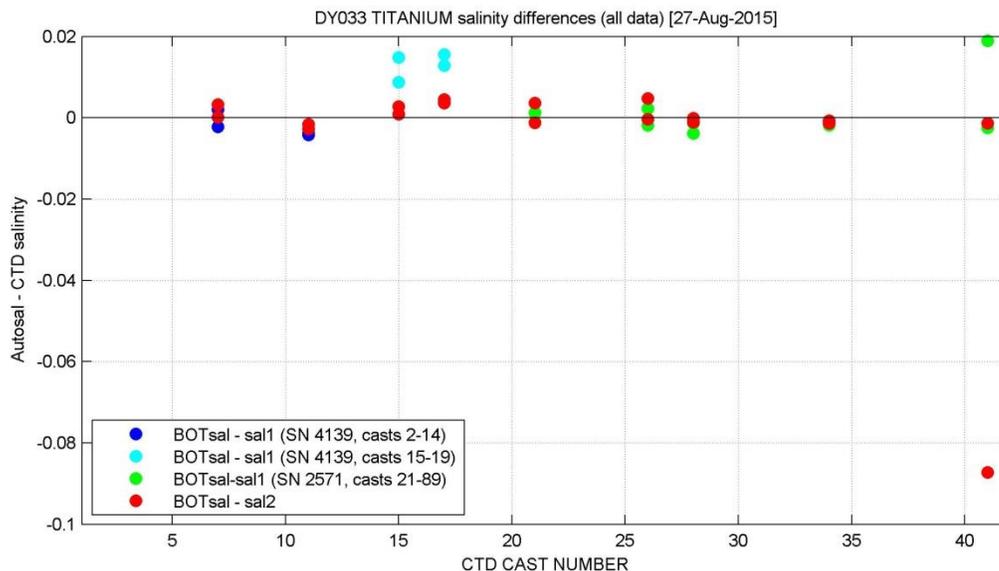
### ***Titanium***

After the CTD frame hit the bottom on CTD014T, a much larger offset was introduced to the primary conductivity sensor (for casts 15, 17 and 19). See notes above. The primary titanium conductivity sensor was replaced from cast CTD021T onwards. Three separate calibrations are therefore necessary for the primary sensor:

SN 04-4138 Casts 2-14 (STNNBRs 6-64)

SN 04-4138 Casts 15-19 (STNNBRs 65-71)

SN 04-2571 Casts 21-89 (STNNBRs 73-280)



Autosal – CTD salinity for all samples (titanium)

Using all samples the mean and standard deviation of residuals from the primary and secondary sensors were:

Primary casts 2-14 (SN 4138):  $-0.002075 \pm 0.0028558$  (mean  $\pm$  std)

Primary casts 15-19 (SN 4138):  $0.012975 \pm 0.0030837$

Primary casts 21-89 (SN 2571):  $0.0017941 \pm 0.0042938$

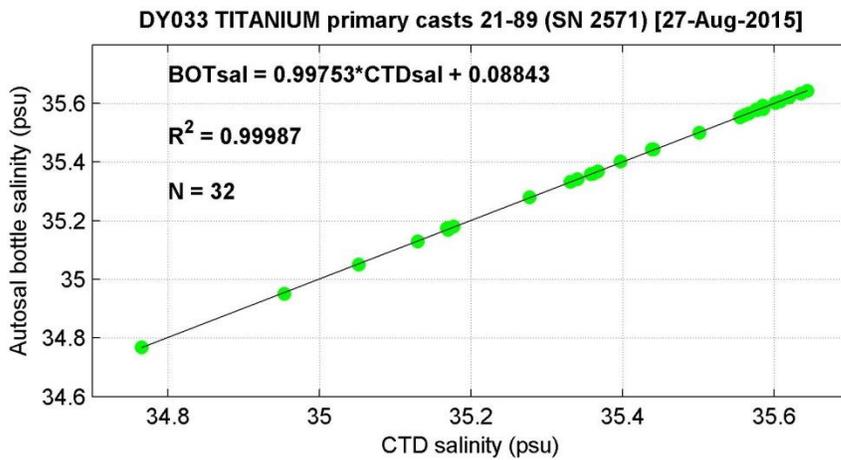
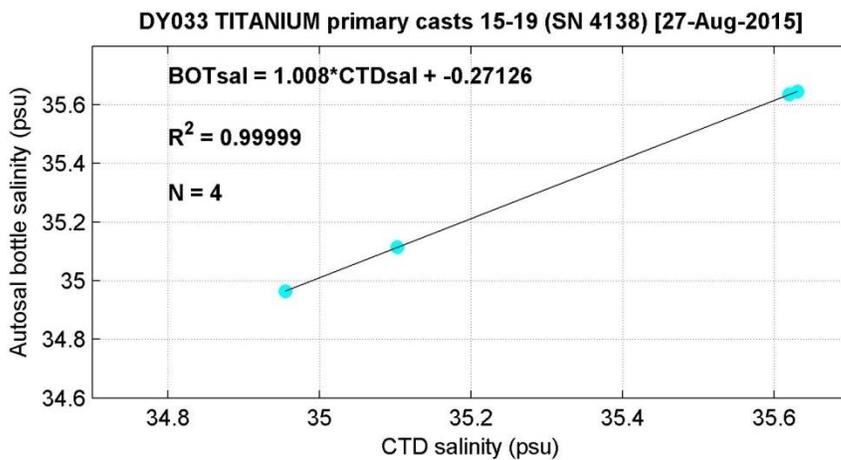
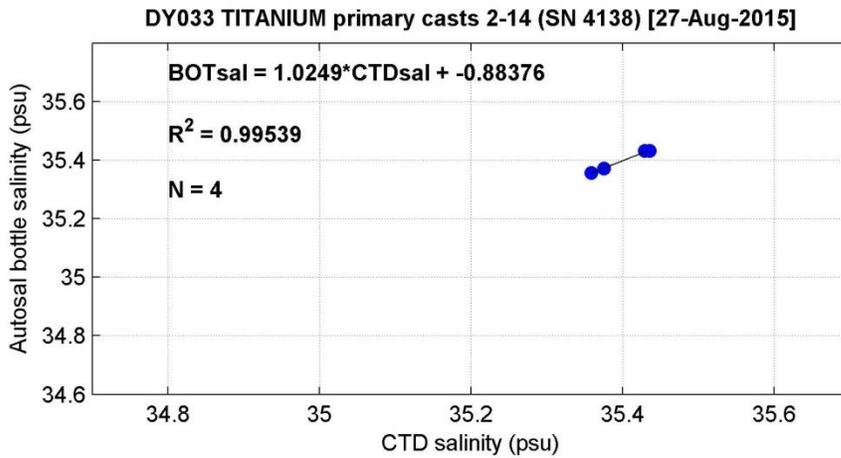
Secondary:  $-0.00090476 \pm 0.013903$

After removal of outliers in the replacement primary sensor (SN2571) and in the secondary sensor where the difference between Autosal and CTD values was greater than 1.5 standard deviations the mean  $\pm$  standard deviations reduced to:

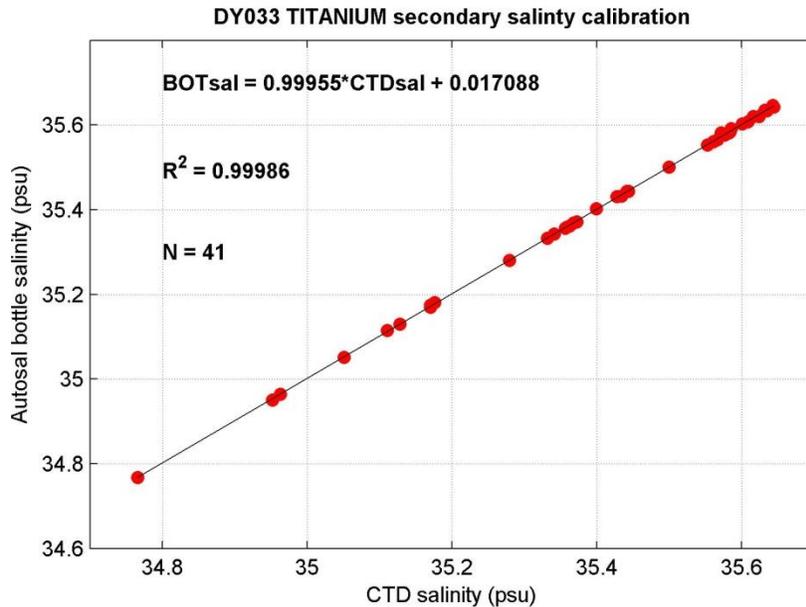
Primary casts 21-89 (SN 2571):  $0.00096562 \pm 0.0025739$

Secondary:  $0.0012024 \pm 0.0026419$

The following regressions were applied:



Linear regressions applied to the primary titanium salinity.



Linear regression applied to the secondary titanium salinity.

After calibration the means and standard deviations are reduced to the following:

Primary casts 2-14 (SN 4138):  $0 \pm 0.0026895$

Primary casts 15-19 (SN 4138):  $7.1054e-15 \pm 0.0012602$

Primary casts 21-89 (SN 2571):  $-4.6629e-15 \pm 0.0025135$

Secondary:  $0 \pm 0.00264$

## Oxygen

### ***Stainless***

The oxygen sensor on the stainless frame was clearly giving suspect readings on casts 74 and 75 and subsequently changed from cast 76 onwards. Casts 1-70 are therefore used to calibrate the original sensor (SN0709). As the performance of the sensor deteriorated there is firstly a significant ( $p$ -value < 0.05) linear temporal drift that requires correction based on the daynumber of the CTD cast.

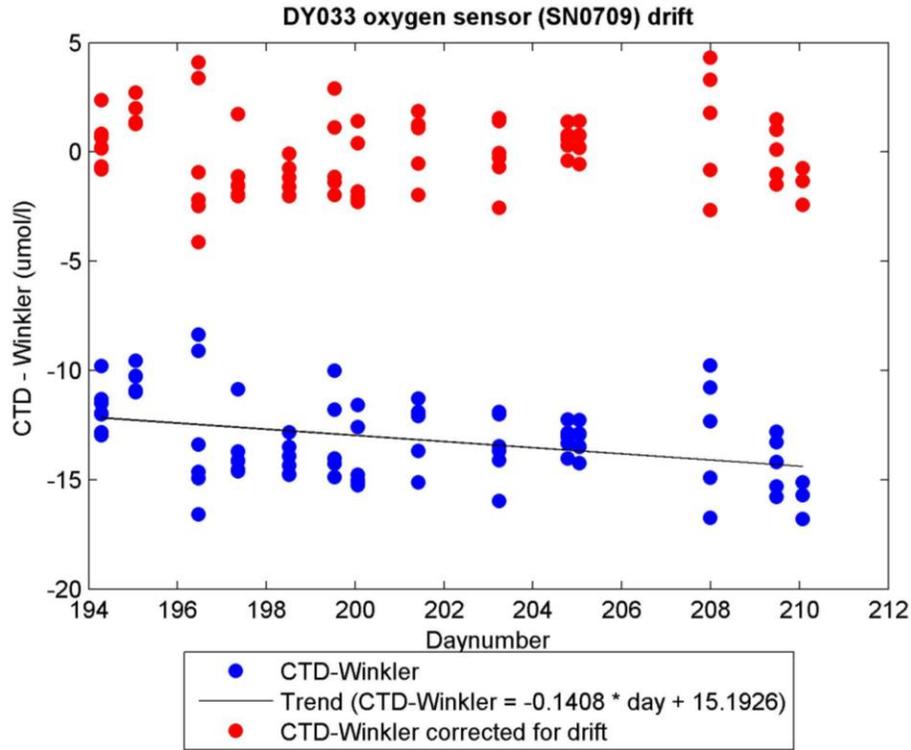
CTD profiles are therefore first corrected according to the following:

$$\text{CTDoxyt} = \text{CTDoxys} - ([\text{slope} * \text{daynumber}] + \text{intercept}),$$

where

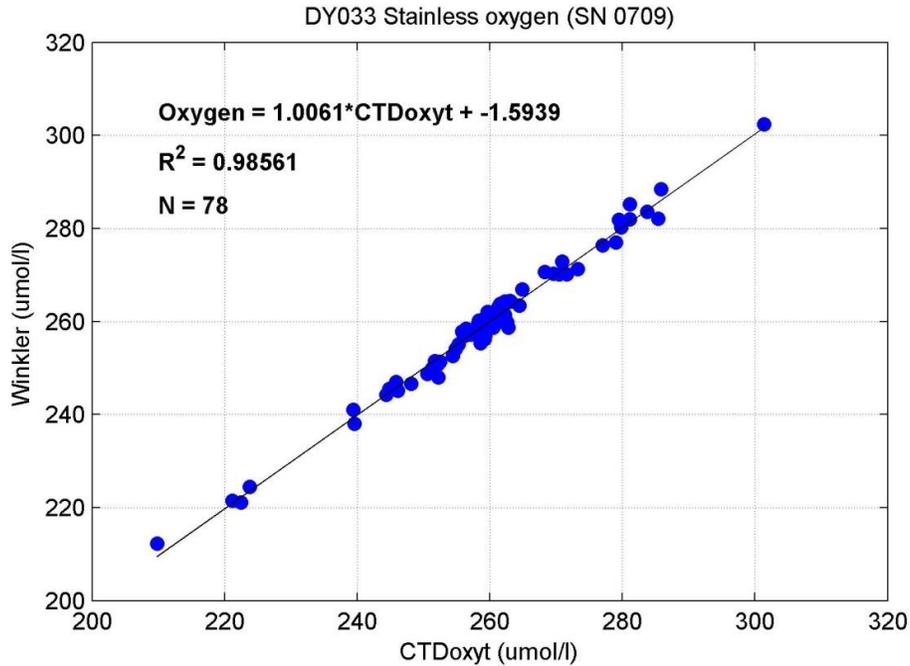
slope = -0.1408

intercept = 15.1926

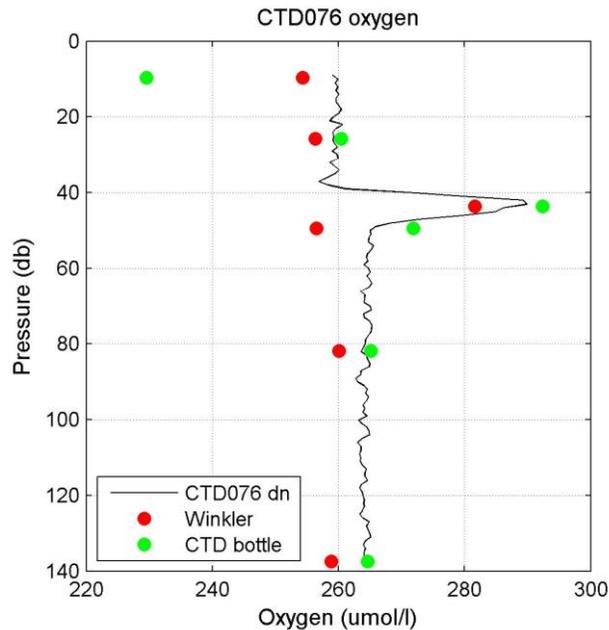


Linear regression against day number for stainless oxygen (casts 1-70). CTD readings that differed from the winkler analysis by more than 17 umol/l were removed.

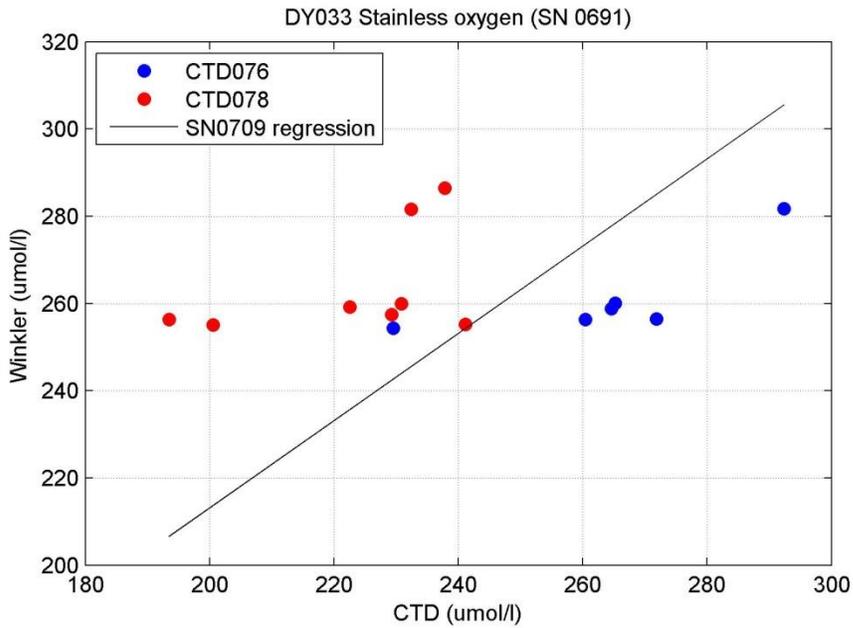
The following regression (winkler vs CTDoxyt) was then applied up to and including cast 70:



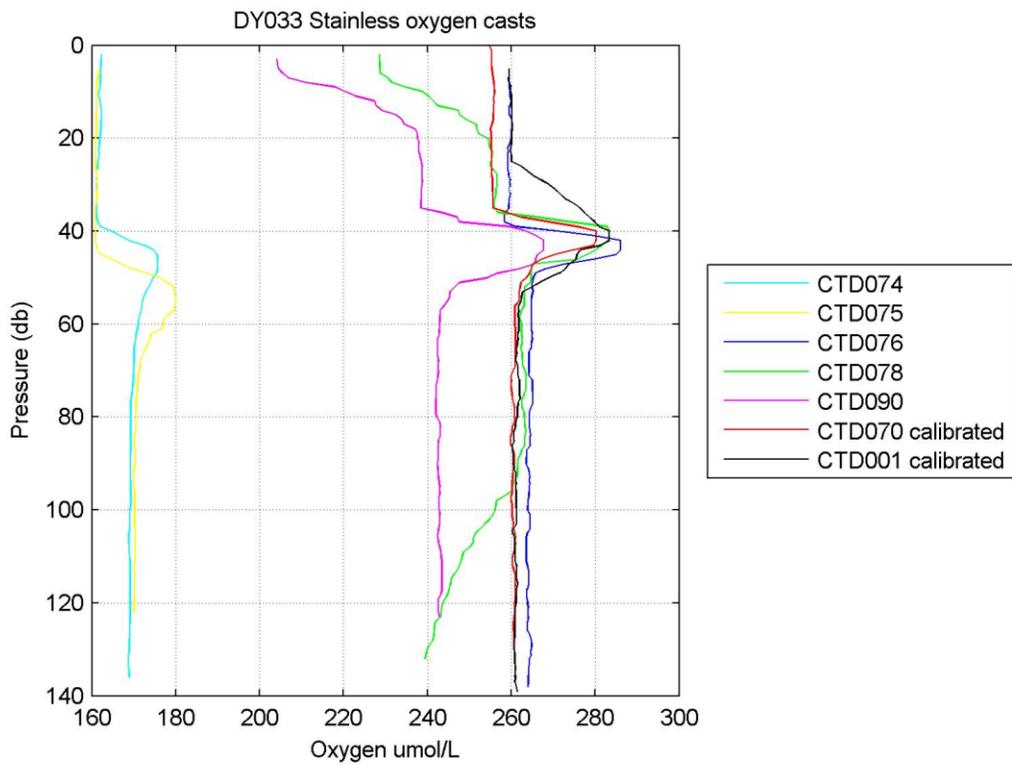
One potentially useable cast with the replacement oxygen sensor (SN0691) was completed (CTD076). Six samples were taken for calibration, although the CTD measurement at the time of firing the surface bottle is clearly far too low. With only 5 samples remaining that do not generate a robust regression no calibration is applied. Winkler samples were also taken from CTD078 but CTD readings below 90 m and above 30 m reinforce a problem with this new sensor.



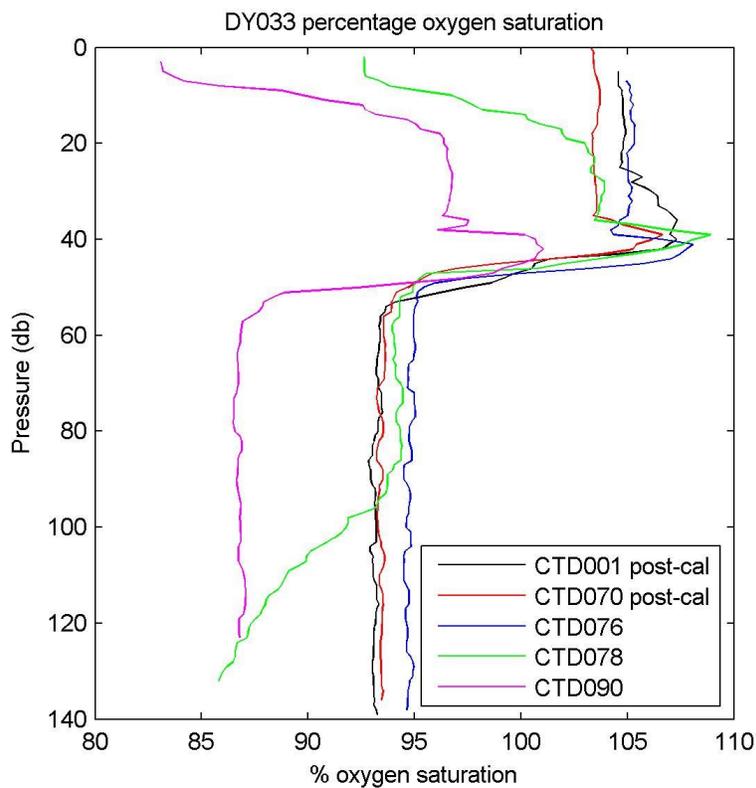
Downcast profile from CTD076 together with the winkler and CTD bottle values from the upcast.



CTD vs winkler oxygen for casts CTD076 and CTD078. No sensible regression for sensor SN 0691 is possible.



Oxygen profiles from all casts with SN 0691 (CTD076-CTD090). Calibrated profiles from CTD001 and CTD070. Profiles CTD074 and CTD075 with SN 0709 indicated sensor failure.



Percentage saturation for casts CTD001 and CTD070 (SN 0709) and casts CTD076, CTD078 and CTD090 (SN 0691)

In summary:

Oxygen on casts CTD001-CTD070 has been calibrated.

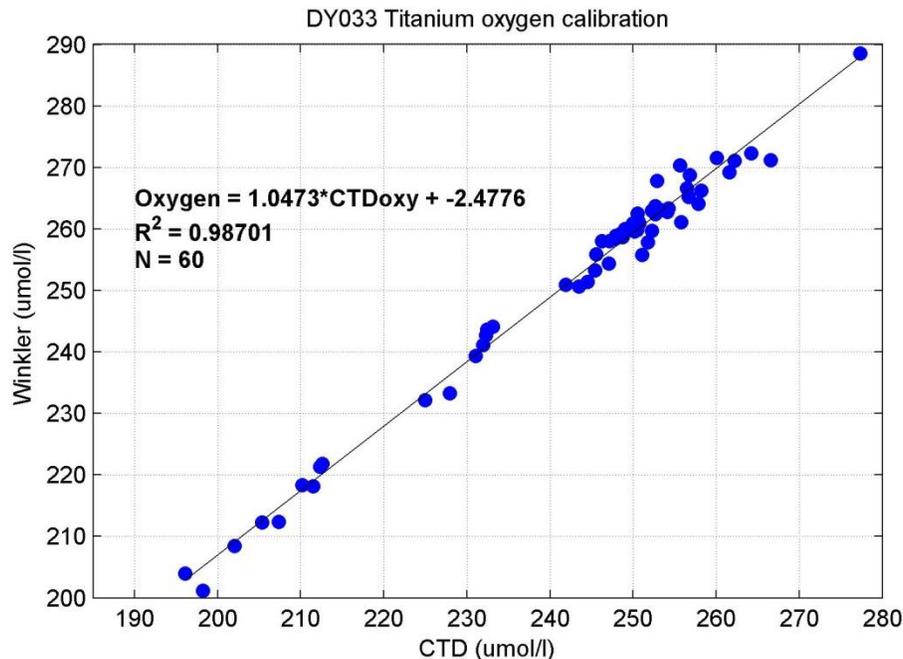
Oxygen from CTD074 and CTD075 has been removed

Oxygen on CTD076 is retained but is uncalibrated and should be treated as unreliable

Oxygen from casts CTD078 and CTD090 has been removed

## Titanium

CTD readings that differed from the winkler analysis by more than 17  $\mu\text{mol/l}$  were removed. There is not a significant temporal drift that needs correction therefore the following regression is applied.



## Chlorophyll

A total of 362 samples were taken for calibration of the CTD chlorophyll fluorescence (stainless+titanium). Samples taken during daylight hours at depths shallower than 30 m were removed. Outliers from sampling and/or recording errors were also discarded.

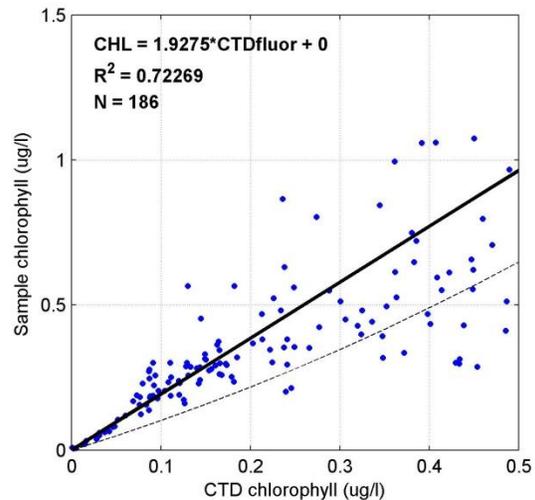
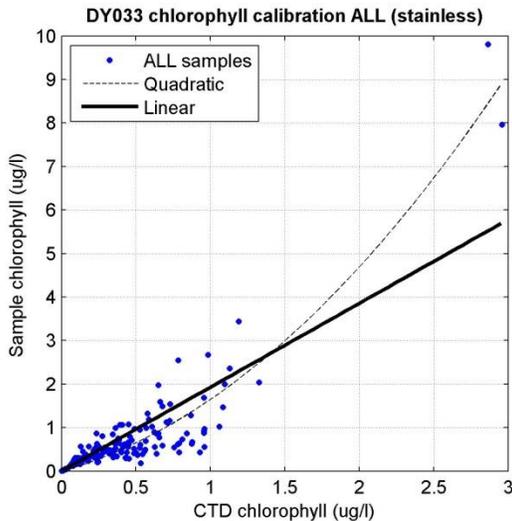
For both the stainless and titanium sensor a linear trend was fitted using ALL the samples. This however is a simplification of the more complicated relationship between the extracted chlorophyll and that reported by the CTD. There are clear regional differences (e.g. on-shelf vs off-shelf) and separate calibrations could be applied to regional subsets. Examples are provided below. Defining these regions however is subjective and in reality there are likely to be gradients between them. There are also probably vertical and horizontal gradients in physiology (e.g. taxonomy, light, other environmental factors...) that account for some of the remaining scatter. To maintain consistency across all SSB cruises a linear trend was fitted to all the data.

## Stainless

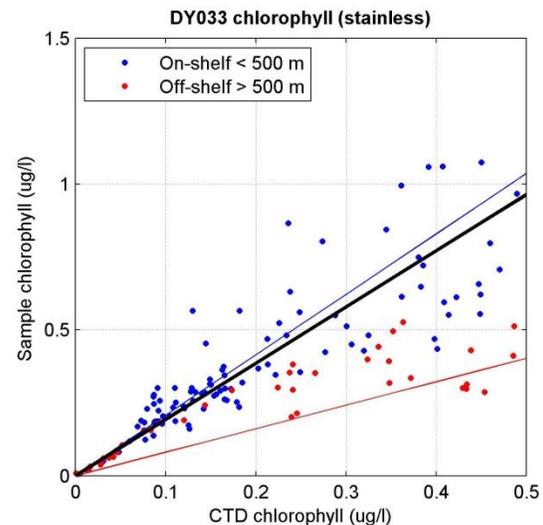
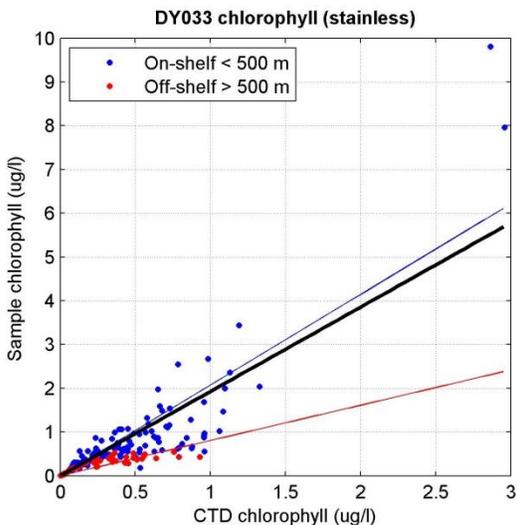
The following regression was applied (forced through origin):

$$\text{CHL} = 1.9275 * \text{CTDfluor} + 0 \text{ [ug/l]}$$

For low chlorophyll concentrations this regression is reasonable but is less suitable at higher concentrations. Peak values will be under-reported. A quadratic regression (see below) would calibrate the chlorophyll peaks much more satisfactorily but (a) performs poorly at lower concentrations (CTD < 0.5  $\mu\text{g/l}$ ) and (b) is not justified by any mechanistic reason.



Linear chlorophyll calibration (thick black line) applied to ALL stainless CTDs.



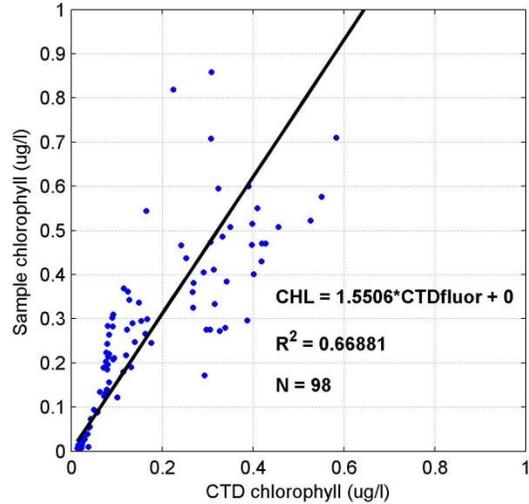
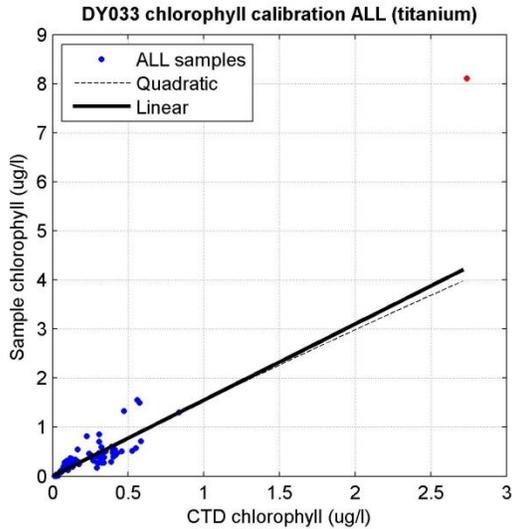
Example of regional differences in CTD vs extracted chlorophyll relationship (stainless). On-shelf is nominally defined as depths < 500 so includes the slope. Off-shelf is defined as depths > 500 m. A 3<sup>rd</sup> shelf-edge /slope region could be defined if desired. Thick black line is the regression applied here.

### Titanium

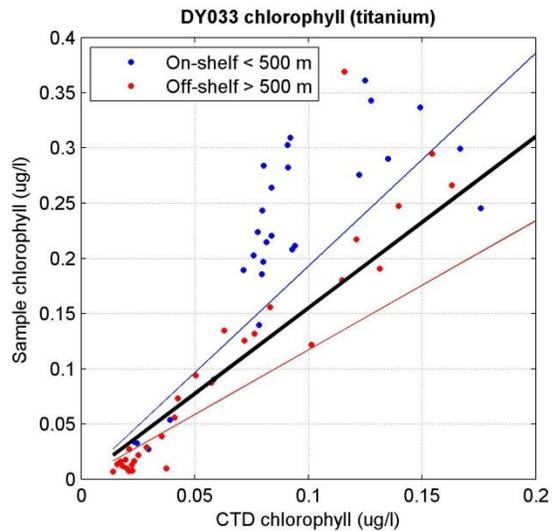
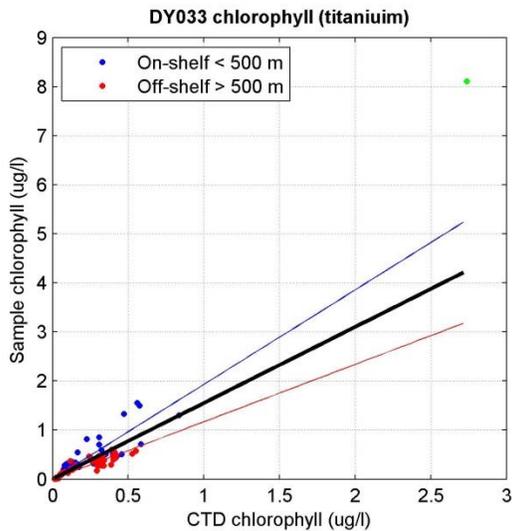
The following regression was applied (forced through origin):

$$\text{CHL} = 1.5506 * \text{CTDfluor} + 0 \text{ [ug/l]}$$

As for the stainless sensor, for low chlorophyll concentrations this regression is reasonable but is less suitable at higher concentrations. Peak values will be under-reported.



Linear chlorophyll calibration (thick black line) applied to ALL titanium CTDs. Note that the high concentration sample (red dot) was removed to improve the fit at lower concentrations (CTD < 1 ug/l)



Example of regional differences in CTD vs extracted chlorophyll relationship (titanium). On-shelf is nominally defined as depths < 500 so includes the slope. Off-shelf is defined as depths > 500 m. A 3<sup>rd</sup> shelf-edge /slope region could be defined if desired. Thick black line is the regression applied here.

## 5. Vessel-mounted ADCP (VMADCP)

*Jo Hopkins (National Oceanography Centre, Liverpool)*

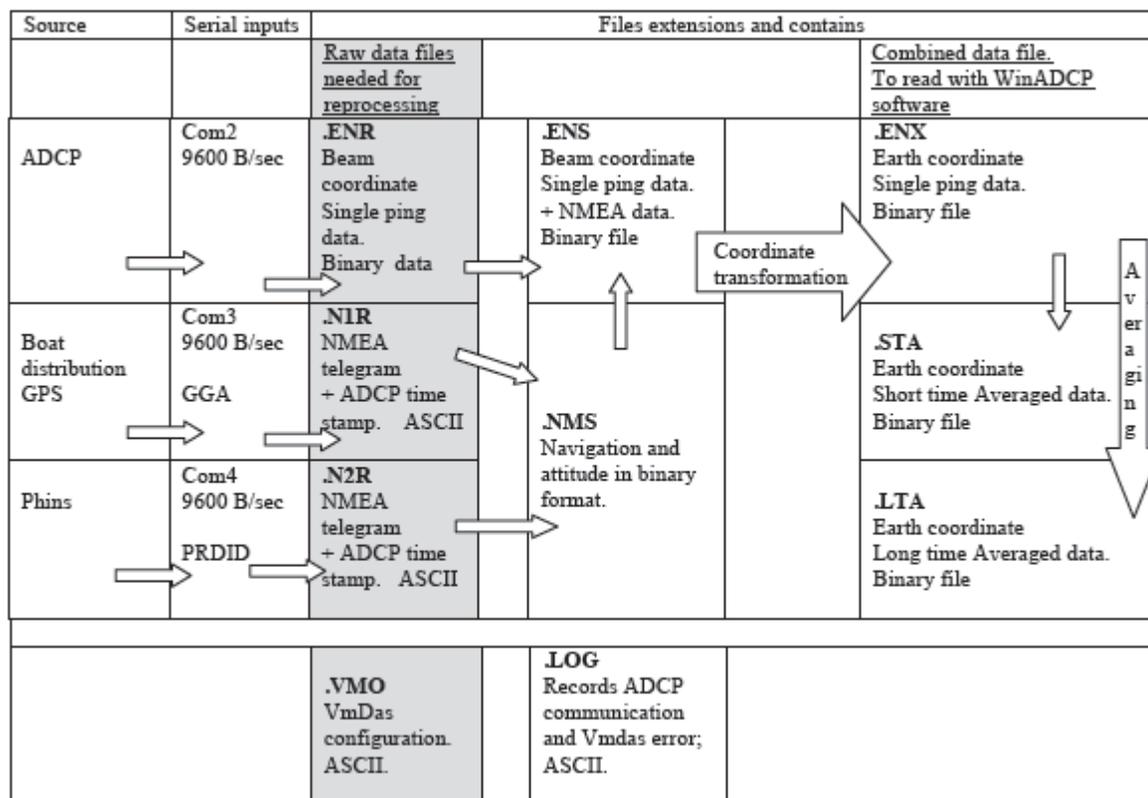
### Instrument description

The RRS Discovery is fitted with RD Instruments 75 kHz and 150 kHz Ocean Surveyor ADCPs. The following table, taken from the Dock Side and Sea Acceptance Test report (June 3-5, 2013), details the serial numbers, computer operating systems and software versions installed. Note however that the chassis for the OS75 has been changed to SN 1813.

<b>SYSTEM / SHIP INFORMATION</b>		
Vessel Length	99.70 m	
Vessel Weight		
System Frequency	<b>150 KHz</b>	<b>75 kHz</b>
XDCR Serial Number	SN 648108	SN 640594
Chassis Serial Number	SN 28550	SN 1813
Cable Length	20+30 m	20+30 m
ADCP Electronics Rack or Table mounted	Rack	Rack
Transducer Mounting Angle (Bow, 45 starboard ...)	-45	-45°
Transducer Mounting Type (Acoustic Window, Flush, Keel, Gondola ...)	Hull + windows	Hull + windows
PC System type		
Operating System	Windows 7 64 bits	Windows 7 64 bits
Computer Ram	6 GB	6 GB
Comports available on Computer	COM2, COM 3, COM 4, COM5	COM2, COM 3, COM 4, COM5
Network Card	Yes	Yes
Hard Drive Space		230 GB
RDI Programs Installed	VMDAS 1.46, BBTalk 3.08, WinADCP 1.14	VMDAS 1.46, BBTalk 3.08, WinADCP 1.14

The instruments are mounted 6.6 m below the ships waterline and beam 3 (Y-axis) is rotated -45° (anti-clockwise) relative to the ships centreline. A nominal rotation of -45° (misalignment angle) is therefore necessary to remove the ships velocity from the data. Fine tuning of this misalignment is performed in the Matlab post-processing routines.

The VmDas computer setup and file structure recorded by each OS ADCP was as shown in the schematic below.



There are two navigation (NAV) feeds into the VMDas software. NMEA1 stream is from the Kongsberg Seapath (\$IN) and Applainix PosMV GPS (\$GP) and contains navigation (heading) information. This is written to the .N1R files. NMEA2 stream is from the IXSEA PHINS and contains both navigation (heading) and attitude (pitch and roll) information.

N1R contents (from Seapath and PosMV)

\$INZDA : Date and time information

\$INGGA : Time, position and fix related to the GPS receiver

\$INVTG : Track made good and Ground speed (relative to the ground)

\$INRMC : Date, time, position speed and tracks made good, magnetic variation

\$GPGST : GPS pseudorange noise statistics

\$PADCP : Time stamp from the VmDas software every time the ADCP pings

N2R contents (from PHINS)

\$PRDID : Ships heading, pitch and roll from PHINS

\$PADCP : Time stamp from the VmDas software every time the ADCP pings

The Matlab post processing uses the \$PRDID string in the .N2R files and the binary .ENX file from VMDAS that contains single ping, bin mapped, earth coordinate data (transformed within the software using the heading and tilt sources specified).

### **DY033 OS150 setup**

A number of OS150 command files and user options were used during DY033. All were files for use with k-sync.

- (1) DY033 OS150 Narrowband and Bottom track with sync.txt  
96 x 4 m bins  
Used for misalignment angle calculation
- (2) DY033 OS150 Narrowband and NO Bottom track with sync.txt  
96 x 4 m bins  
Used on-shelf (< 200 m)
- (3) DY033 OS150 Narrowband and NO Bottom track with sync 8m.txt  
48 x 8 m bins  
Used off-shelf (> 200 m), including time spent at CS2

The following setup was the same across all configuration files:

Blanking distance: 4 m  
Transducer depth: 6.6 m  
Processing mode: low resolution (long range, narrow band)  
Bottom track: on (range 800 m)  
Ensemble time: 2 seconds (1 second between bottom and water pings when BT on).  
This must match the active period in k-sync  
Output velocity, correlation, echo intensity and percent good  
Output beam data

Max file size: 10 mb  
NMEA Ship Position (GGA) Source: NMEA1  
NMEA Ship Speed (VTG) Source: NMEA1

Transform: Heading/tilt source: PRDID; NMEA2  
Custom NMEA from C:\\RDI\\VmDas  
ADCP misalignment correction: -45 degrees  
All data screening unchecked  
Do NOT set a backup location

### **DY033 OS75 setup**

A number of OS75 command files and user options were used during DY033. All were files for use with k-sync.

- (1) DY033 OS75 Narrowband bottom track with sync.txt  
100 x 8 m bins  
Misalignment angle calculation when on-shelf
- (2) DY033 OS75 Narrowband NO bottom track sync.txt  
100 x 8 m bins

- On-shelf (< 200m)  
(3) DY033 OS75 Narrowband NO bottom track sync 16m.txt  
45 x 16m bins  
Off-shelf (>200m)

The following setup was the same across all configuration files:

Blanking distance: 8 m  
Transducer depth: 6.6 m  
Processing mode: low resolution (long range, narrow band)  
Bottom track: on (range 1200 m)  
Ensemble time: 3 seconds (1.5 second between bottom and water pings when BT on).  
This must match the active period in k-sync  
Output velocity, correlation, echo intensity and percent good  
Output beam data

Max file size: 10 mb  
NMEA Ship Position (GGA) Source: NMEA1  
NMEA Ship Speed (VTG) Source: NMEA1

Transform: Heading/tilt source: PRDID; NMEA2  
Custom NMEA from C:\\RDI\\VmDas  
ADCP misalignment correction: -45 degrees  
All data screening unchecked  
Do NOT set a backup location

### **Post-processing in Matlab**

A suite of Matlab routines was used to perform data screening and transformation into absolute velocities in Earth coordinates. The routines were first obtained from IfM Kiel by Mark Inall and adapted for use on the RRS James Clark Ross by Deb Shoosmith in 2005. Since then numerous bug fixes and refinements have been added by various users, the most recent by Sam Jones on DY017. In short the following processing takes place:

1. RDI binary file with extension ENX (single-ping ADCP ship referenced data from VMDAS) and extension N2R (ascii NMEA output from PHINS saved by VMDAS) read into MATLAB environment. NB: The N2R file consists of ADCP single ping time stamps (\$PADCP string) and pitch, roll and heading information (\$PRDID string).
2. Ensembles with no ADCP data removed
3. Ensembles with bad or missing PHINS heading data identified and adjusted GYRO heading substituted
4. Attitude information time-merged with single ping data
5. Heading data used to rotate single ping ADCP velocities from vessel centreline reference to True North reference

6. Transducer mis-alignment error corrected for (derived from the mis-alignment determination)
7. Ship velocity derived from PHINS positional information
8. Further data screening performed:
  - Max heading change between pings (10 degrees per ping)
  - Max ship velocity change between pings ( $>2\text{ms}^{-1}\text{pingrate}^{-1}$ )
  - Error velocity greater than twice Stdev of error velocities of single ping profile
9. All data averaged into 300-second super-ensembles
10. Determine absolute water velocities from either bottom track derived ship velocity or PHINS GPS derived ship velocity, dependent on depth.

Further scripts are then run to:

- (a) strip any velocity readings from below the seabed (using 2.5 minute averaged and cleaned data from the EM122 swath)
- (b) adjust the 'days' time stamp such that day 1.5 relates to 12:00 1<sup>st</sup> January

The final post processing output is saved to **OS150\_DY03300x\_000000\_zz\_abs.mat** where "zz" is the number of the last file in the concatenation. Two structures are saved in this .mat file.

Data to be banked by BODC are contained within the structure OS75\_abs (n.b. both 150 kHz and 75 kHz data are saved in structures called 'OS75' but it does contain the correct information). Underlined variables are those to be banked.

OS75\_abs =

ref: [1x1 struct]

vel: [96x2x3094 double] : Absolute velocity in m/s (zonal, meridional)

nav: [1x1 struct]

depth: [96x3094 double] : bin depths (m) of velocity profiles

OS75\_abs.nav =

txy1: [3x3094 double] : array of time (daynumber), longitude and latitude

txy2: [3x3094 double]

## **Output**

Files 1-7 for the OS150 and files 1-6 for the OS75 were used to calculate the misalignment angle on the transit out to the main process site CCS.

OS150

Misalignment angle = 0.2091°

Scaling factor = 0.999079

OS75

Misalignment angle = 0.6062°

Scaling factor = 1.007777

It was not possible to create one long concatenated file for the entire cruise due to changes in configurations, data drop outs and file sizes. The following 5 min average data files have therefore been created.

### **OS150**

PART 1 - files: 1, 2, 3, 4, 7, 8 [4 m bins]

Dates: 11/07/15 18:56 to 16/07/2015 15:16

Saved to OS150\_DY03300x\_000000\_8\_abs.mat

PART 2a – files: 9 [8 m bins]

Dates 16/07/2015 15:19 to 16/07/2015 18:02

Saved to OS150\_DY03300x\_000000\_9\_abs.mat

PART 2b – files: 10, 11, 12, 13, 14, 15, 18 , 19, 20, 21, 22 [8 m bins]

Dates: 16/07/2015 18:03 to 23/07/2015 16:14

Saved to OS150\_DY03300x\_000000\_22\_abs.mat

PART 3 – files: 23, 24, 25, 26, 27, 28, 29 [4 m bins]

Dates: 23/07/2015 16:17 to 02/08/2015 09:20

Saved to OS150\_DY03300x\_000000\_29\_abs.mat

### **OS75**

PART 1 - files: 1-7 [8 m bins]

Dates: 11/07/2015 18:56 to 16/07/2015 13:54

Saved to OS75\_DY03300x\_000000\_7\_abs.mat

PART 2a - files: 31 [16 m bins]

Dates: 16/07/2015 16:15 to 16/07/2015 19:01

Saved to OS75\_DY03300x\_000000\_31\_abs.mat

PART 2b - files: 29, 32, 34-38, 42, 46-47 [16 m bins]

Dates: 16/07/2015 14:57 to 23/07/2015 16:20

Saved to OS75\_DY03300x\_000000\_47\_abs.mat

PART 3 - files: 50, 51, 52, 53, 54, 55, 56 [8 m bins]

Dates: 23/07/2015 16:24 to 02/08/2015 9:20

Saved to OS75\_DY03300x\_000000\_56\_abs.mat

## Log of files opened and closed during the cruise

### OS150

DATE	TIME (GMT)	FILENAME	O/C	COMMENTS
11/07/2015	18:56	OS150_DY033001	O	In western channel  Narrowband and bottom track with sync.txt  4 m
12/07/2015	18:32		C	
12/07/2015	18:33	OS150_DY033002	O	Steaming to CCS
13/07/2015	04:39		C	
13/07/2015	04:39	OS150_DY033003	O	At CCS – just before first glider deployment
14/07/2015	06:11		C	
14/07/2015	06:11	OS150_DY033004	O	At CCS – process station
15/07/2015	06:48		C	
15/07/2015	06:51	OS150_DY033007	O	At CCS – last day at process station  Files 5 and 6 had error when starting
16/07/2015	07:39		C	
16/07/2015	07:40	OS150_DY033008	O	At Fe014  Narrowband and NO bottom tack with sync.txt  4 m bins
16/07/2015	15:16		C	
16/07/2015	15:19	OS150_DY033009	O	Narrowband and bottom track with sync 8 m.txt  8 m bins
16/07/2015	18:02		C	

16/07/2015	18:03	OS150_DY033010	O	Narrowband and NO bottom track with sync 8 m .txt
17/07/2015	06:41		C	
17/07/2015	06:42	OS150_DY033011	O	Narrowband and NO bottom track with sync 8 m .txt
17/07/2015	13:17		C	
17/07/2015	13:17	OS150_DY033012	O	Narrowband and NO bottom track with sync 8 m .txt
				Steaming into deep water away from shelf edge to check acoustic range
				Heave to at 16:20 in deep water (3790 m)
18/07/2015	07:22		C	At Fe013
18/07/2015	07:22	OS150_DY033013	O	Narrowband and NO bottom track with sync 8 m .txt
19/07/2015	07:07		C	
19/07/2015	07:08	OS150_DY033014	O	At CS2 for process station
20/07/2015	07:10		C	At CS2
20/07/2015	07:10	OS150_DY033015	O	Narrowband and NO bottom track with sync 8 m .txt
				At CS2
21/07/2015	07:13		C	At Fe01
21/07/2015	07:16	OS150_DY033018	O	Files 16-17 had problems starting – ADCP not initialized
				Narrowband and NO bottom track with sync 8 m .txt
21/07/2015	19:08		C	Dougal testing altimeter on CTD
21/07/2015	20:10	OS150_DY033019	O	Back on after CTD being recovered
21/07/2015	20:18		C	
21/07/2015	20:21	OS150_DY033020	O	

22/07/2015	01:25		C	Fe02 CTD altimeter problems
22/07/2015	02:06	OS150_DY033021	O	
22/07/2015	20:04		C	
22/07/2015	20:04	OS150_DY033022	O	
23/07/2015	16:14		C	En-route to CCS from CS2
23/07/2015	16:17	OS150_DY033023	O	Narrowband and NO bottom track with sync.txt  4 min bins
25/07/2015	14:02		C	
25/07/2015	14:03	OS150_DY033024	O	At CCS and transit to site A
27/07/2015	08:04		C	
27/07/2015	08:04	OS150_DY033025	O	Running back from A towards CCS
28/07/2015	12:03		C	
28/07/2015	12:03	OS150_DY033026	O	
30/07/2015	12:15		C	At CCS
30/07/2015	12:15	OS150_DY033027	O	
31/07/2015	14:50		C	At CCS
31/07/2015	14:50	OS150_DY033028	O	
01/07/2015	18:18		C	En route to Southampton
01/07/2015	18:21	OS150_DY033029	O	
02/07/2015	09:20		C	

**OS75**

DATE	TIME (GMT)	FILENAME	O/C	COMMENTS
11/07/2015	18:56	OS75_DY033001	O	In western channel Narrowband and bottom track with sync.txt 8 m bins
12/07/2015	18:35		C	
12/07/2015	18:35	OS75_DY033002	O	Steaming to CCS Narrowband and bottom track with sync.txt 8 m bins
13/07/2015	04:40		C	
13/07/2015	04:41	OS75_DY033003	O	At CCS just before first glider deployment
14/07/2015	06:09		C	
14/07/2015	06:09	OS75_DY033004	O	At CCS process station
15/07/2015	06:52		C	
15/07/2015	06:53	OS75_DY033005	O	At CCS – last day of process station
16/07/2015	07:42		C	At Fe014
16/07/2015	07:43	OS75_DY033006	O	Narrowband and NO bottom track with sync.txt 8 m bins
16/07/2015	13:37		C	Closed to check data range
16/07/2015	13:38	OS75_DY033007	O	
16/07/2015	13:54		C	Closed to try to resolve ranging issue. Only getting velocity data to approx. 200 m  Series of short test files run: changing to BB, changing to 16 m bins, BT on and off, Sybc on and off

16/07/2015	14:57	OS75_DY033029	O	Narrowband and NO bottom track with sync 16m.txt 16 m bins
16/07/2015	16:01		C	
16/07/2015	16:03	OS75_DY033030	O	Narrowband Bottom Track NO sync 8 m bins
16/07/2015	?		C	
16/07/2015	16:15	OS75_DY033031	O	Narrowband Bottom Track No sync 16 m bins
16/07/2015	19:01		C	
16/07/2015	19:02	OS75_DY033032	O	Narrowband NO bottom track with sync 16 m .txt 16 m bins Separate trigger in k-sync to the 150 kHz
17/07/2015	06:44		C	
17/07/2015	06:44	OS75_DY033034	O	Narrowband NO bottom track with sync 16 m .txt (file 33 had a starting error) 07:31 – central azi turned off 07:43 – central azi back on (jet thrusters were having to work harder)
17/07/2015	13:14		C	
17/07/2015	13:16	OS75_DY033035	O	Ship moving out into deep and clear water
18/07/2015	07:24		C	At Fe013
18/07/2015	07:25	OS75_DY033036	O	
19/07/2015	07:10		C	
19/07/2015	07:10	OS75_DY033037	O	At CS2 for process station

20/11/2015	07:11		C	
20/07/2015	07:12	OS75_DY033038	O	Narrowband NO bottom track with sync 16 m .txt At CS2
21/07/2015	07:18		C	At Fe01
21/07/2015	07:24	OS75_DY033042	O	Narrowband NO bottom track with sync 16 m .txt At Fe01 Files 39-41 had problems initializing
21/07/2015	14:04		C	
21/07/2015	14:16	OS75_DY033046	O	Files 43-45 were tests of changing correlation threshold and false target threshold
22/07/2015	20:05		C	
22/07/2015	20:06	OS75_DY033047	O	
23/07/2015	16:20		C	En-route to CCS from CS2
23/07/2015	16:24	OS75_DY033050	O	Narrowband and NO bottom track with sync.txt 8 m bins Files 48 and 49 had command file errors on startup
25/07/2015	14:04		C	At CCS still
25/07/2015	14:04	OS75_DY033051	O	
27/07/2015	08:06		C	
27/07/2015	08:07	OS75_DY033052	O	Back down from site A towards CCS
28/07/2015	12:01		C	
28/07/2015	12:02	OS75_DY033053	O	
30/07/2015	12:13		C	At CCS

30/07/2015	12:14	OS75_DY033054	O	
31/07/2015	14:51		C	
31/07/2015	14:51	OS75_DY033055	O	At CCS
01/08/2015	18:19		C	En route to Southampton
01/08/2015	18:20	OS75_DY033056	O	
02/08/2015	09:20		C	

## 6. Mooring deployments and servicing

*Emlyn Jones and Jo Hopkins (National Oceanography Centre, Liverpool)*

### Long term mooring objectives

WP1 of the Shelf Sea Biogeochemistry programme has maintained a series of long-term moorings in the central Celtic Sea (CCS) since early 2014. They have provided an unprecedented record of both physical and biogeochemical measurements across a full seasonal cycle providing the research community with (a) a long term record of the physical parameters that help control biogeochemical cycling rates and pathways, (b) a background against which to set process studies and (c) essential data for model validation and development. On DY033 three of these moorings were recovered for the final time.

### Recoveries

Three long term moorings deployed on DY029 (April 2015) at the Central Celtic Sea (CCS) site were recovered: (1) temperature chain, (2) ADCP-string and (3) ADCP bedframe.

### Temperature Chain

Recovered: 25/07/2015 09:57 GMT  
49° 24.1129'N, 8° 36.2489'W

The following 23 self-logging instruments sampling every 300 seconds were successfully recovered.

Nominal depth (m)	Instrument	Serial number	Parameter
10	SBE 16+	4597	Conductivity, temperature, pressure
15	RBR Solo	76797	Temperature
20	Star Oddi Starmon	3578	Temperature
25	RBR Solo	76806	Temperature
30	SBE 37	4998	Conductivity, temperature, pressure
35	Star Oddi Starmon	3584	Temperature
37	RBR Solo	76807	Temperature
40	Star Oddi Starmon	3580	Temperature
42	RBR Solo	76798	Temperature
45	SBE 16+	5309	Conductivity, temperature, pressure
47	Star Oddi Starmon	2836	Temperature
49	SBE 37	7459	Conductivity, temperature, pressure
54	Star Oddi Starmon	3890	Temperature
59	Star Oddi Starmon	3581	Temperature
64	Star Oddi Starmon	3891	Temperature
69	SBE 37	2010	Conductivity, temperature, pressure
74	RBR Solo	76799	Temperature

79	Star Oddi Starmon	3582	Temperature
89	Star Oddi Starmon	3583	Temperature
99	SBE 37	5434	Conductivity, temperature, pressure
109	RBR Solo	76800	Temperature
120	RBR Solo	76801	Temperature
129	SBE 16+	4738	Conductivity, temperature, pressure

### ADCP-string

Data set PI : Tom Rippeth (University of Bangor)

Recovered: 25/07/2015 10:52

49° 24.0414'N, 8° 36.0783'W

Three RDI 600 kHz Workhorse ADCPS were recovered (see mooring diagram):

SN 7301 (Top)

SN 3725 (Middle)

SN 4015 (Bottom)

Instrument	Break command sent (stopped logging) in GMT	ts? (Instrument clock)	GMT	ADCP drift
S/N 7301	28/07/2015 08:27	28/07/2015 08:29:55	28/07/2015 08:28:30	ADCP 1 min 25 seconds ahead
S/N 3725	26/07/2015 18:10	26/07/2015 18:13:48	26/07/2015 18:11:30	ADCP 2 min 18 seconds ahead
S/N 4015	28/07/2015 09:26	28/07/2015 09:30:10	28/07/2015 09:27:06	ADCP 3 min 4 seconds ahead

Data collected by these ADCPS will be used to estimate the dissipation rate of turbulent kinetic energy using the structure function method.

The following setup commands were sent pre-deployment in April 2015:

CR1  
CB411  
CF11101  
EA0  
EB0  
ED500  
ES35  
EX00000  
EZ1111101  
WA50  
WB0

WD111100000  
WF88  
WM5  
WN40  
WP1  
WS10  
WZ10  
TB00:20:00.00  
TC300  
TE00:00:01.00  
TP00:01.00



Bio-fouling on ADCP S/N  
3725 was particularly bad

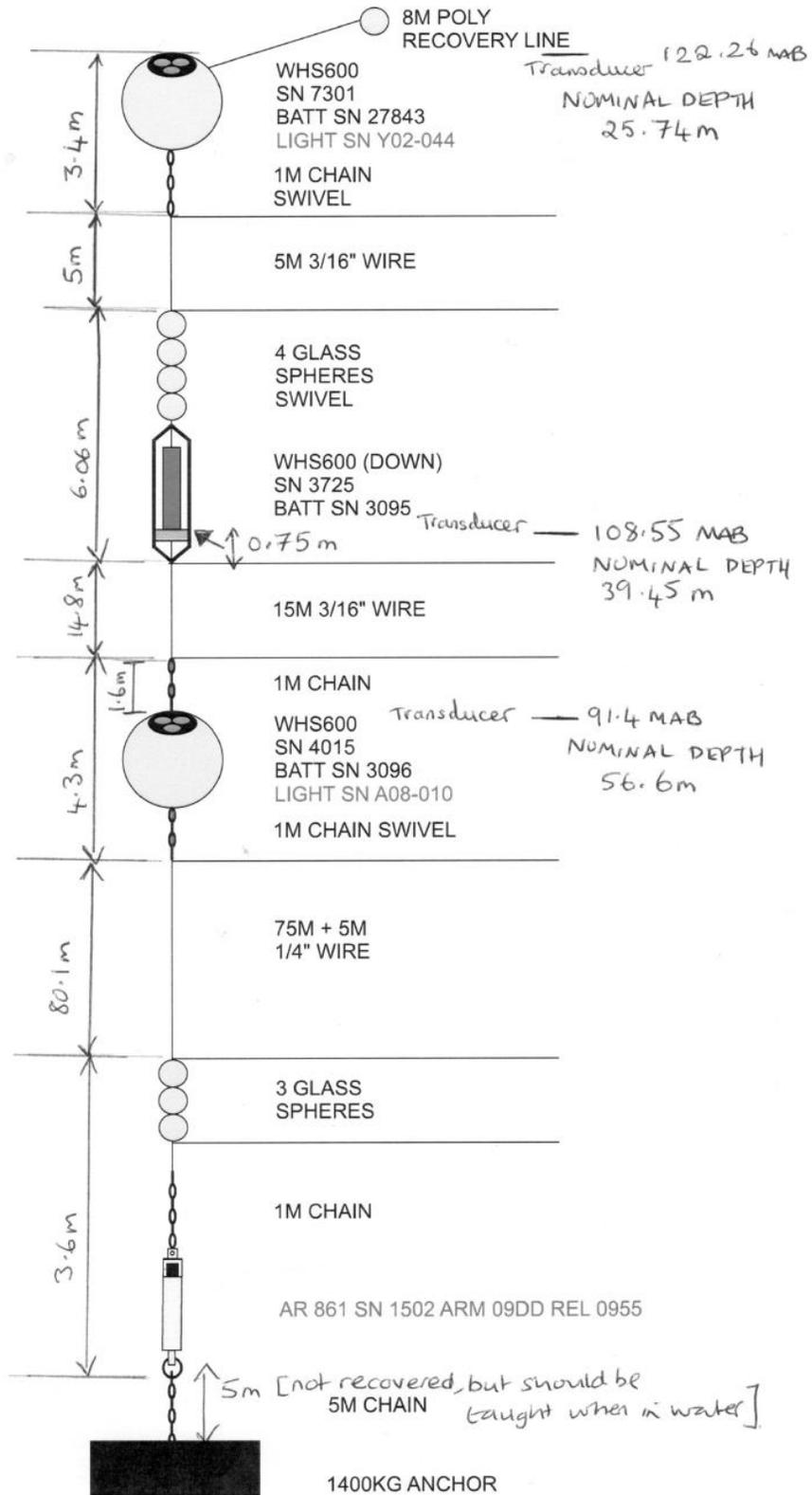
The instruments were deployed as per the mooring diagram below. Exact measurements of the layout were taken following recovery to help clarify uncertainty over the exact deployment depths of each of the transducers.

SSBG WHS1  
AS DEPLOYED  
APRIL 2015

49 24.0940N  
008 36.0414W

148M DEPTH  
ON RECOVERY  
25/07/15

Measurements probably  
accurate to within  
~ 1m +/-



WATER DEPTH  
145M

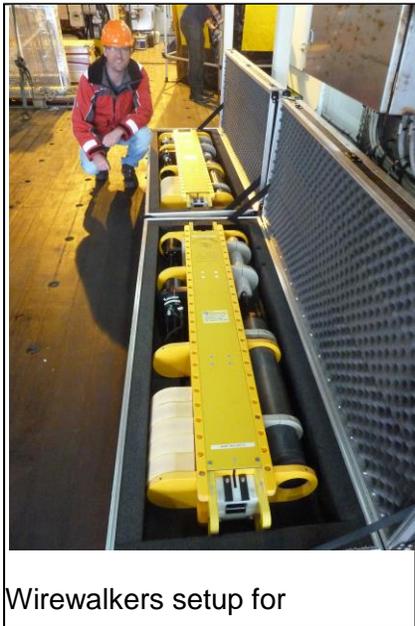
## Bedframe

Recovered: 31/07/2015 17:14  
49° 23.919'N, 8° 34.994'W

The following instrumentation was mounted on the recovered frame:

150 kHz Flowquest ADCP (S/N 011043) [2.5 min ensembles, 2 m bins]  
600 kHz RDI workhorse (S/N 5807) [setup in turbulence mode]  
SBE 16 + CTD (S/N 4596) sampling every 300 seconds

## Wirewalkers (short term deployment)



Wirewalkers setup for

again.

The Wirewalker is a wave-powered autonomous profiler. It uses the surface wave field to power continual vertical profiling. Internally powered and recording instrumentation attached to the Wirewalker collects a two-dimensional depth-time record. Briefly, the mooring itself includes a surface buoy, a wire suspended from the buoy, a weight at the end of the wire, and the profiler attached to the wire via a cam mechanism. A mooring diagram is included below. The wire and weight follow the surface motion of the buoy. The wave-induced motion of the water is reduced with increasing depth, and the relative motion between the wire and the water is used to propel the profiler. The cam engages the wire as it descends and releases it as it ascends, pulling the profiler downwards. At the bottom of the wire, the wirewalker hits a mechanical stop that causes the cam to remain open and the profiler free floats to the surface. At the top of the wire, the cam is reset and the wirewalker is ratcheted downwards

Two independent wirewalkers were setup and deployed at the main CCS site for the duration of the cruise, each on 110m of wire. They will be used to study the evolution of the water column structure and chlorophyll peaks in much finer detail than is possible with traditional CTD casts.

### **Wirewalker 1:**

Deployed: 13/07/2015 09:03 at 49° 24.3238'N, 8° 36.2466'W (just north of the main array)

Recovered: NOT recovered – mooring most likely broke loose

Instrumentation:

- RBR Concerto Fast SN 060047 sampling at 6 Hz (Temperature, Conductivity and Pressure)
- Wetlabs Triplet SN 2560 sampling at 4 Hz (Chlorophyll-a, Phycoerythrin and CDOM fluorescence)
- DH-4 Logger SN 096

**Wirewalker 2:**

Deployed: 13/07/2015 11:41 at 49° 23.617'N, 8° 36.142'W (just south of the main array)

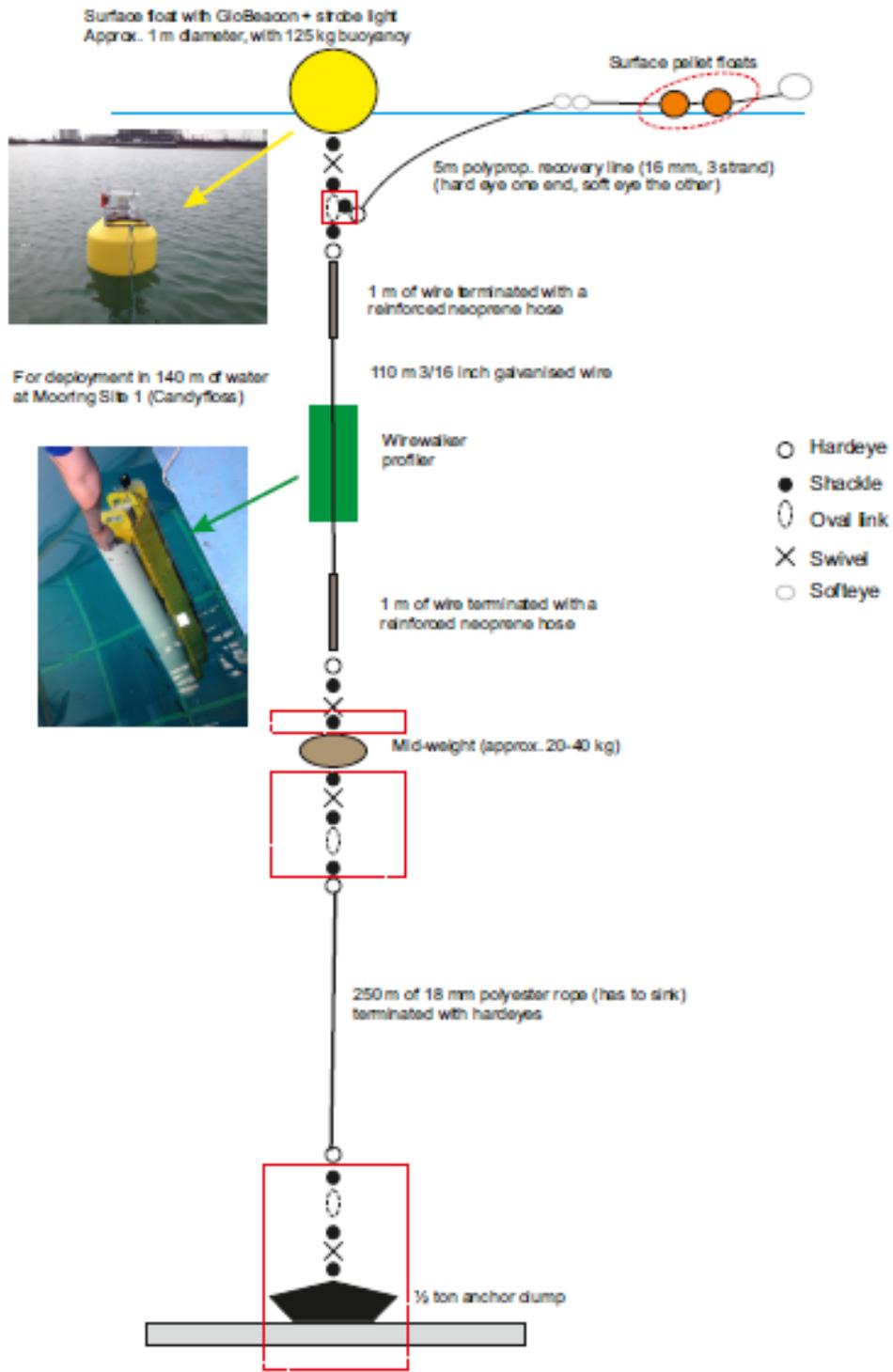
Recovered: 29/07/2015 09:18 at 49° 23.554, 8° 36.119'W.

Instrumentation:

- RBR Concerto Fast SN 060048 sampling at 6 Hz (Temperature, Conductivity and Pressure)
- Wetlabs Triplet SN FL2-800 sampling at 4 Hz (Chlorophyll-a, CDOM and Turbidity)
- DH-4 Logger SN 119

RBR Concerto Fast SN 060048 was calibrated by attaching it to the stainless steel rosette frame on cast CTD090. Its sensors were 86 cm above those of the CTD. The triplet (SN FL2-800) will be calibrated against the post deployment and pre-recovery CTDs (CTD003 and CTD073).

# Mooring diagram



## 7. Glider operations cruise report

*Stephen Woodward (MARS Gliders, NMF-SS, NOCS)*

### **Objectives**

Glider operations on DY033 consisted of supporting three elements of the Shelf Seas Biogeochemistry (SSB) and Sensors on Gliders (SoG) projects.

1. A continuous glider presence in the study area has been maintained over the duration of the SSB project. The final glider turnaround involved replacing Slocum glider 408 (Growler) with Seaglider 533 (Canopus) at the CS2 study site, to continue the shelf break monitoring pattern occupied over the entire project. This was an unscheduled turnaround, with higher than expected battery consumption on 408 necessitating its replacement.
2. The deployment of two Ocean Microstructure Gliders (OMGs) at the CCS and CS2 study sites for two week deployments to cover a full tidal cycle.
3. Deployment of Seaglider 534 (Denebola) at CCS for a two week deployment as part of the SoG project. This glider was equipped with a 'Lab on a Chip' (LoC) Nitrate sensor.

All glider deployments were carried out from the starboard deck crane, using rigid rope rigs. Recoveries were carried out using the starboard P-frame gantry winch. Slocum gliders were recovered by jettisoning the nose recovery device (the buoyant nose is detached using a burn wire, and drifts away from the vehicle whilst attached by a buoyant line which can be grappled from the deck). The Seaglider was recovered using a telescopic carbon fire hoop, lassoing the rudder for recovery.

Calibration CTD casts were performed at deployment and recovery of each glider, with gliders in the water and diving to a depth of >60m (with the exception of SG534, which had poor comms on the morning of recovery and so the decision was taken not to make the glider dive again after a technical fault delayed the CTD. The CTD cast began 20 minutes after the glider surfaced for the last time).

### **Deployments/Recoveries**

#### **Shelf break turnaround**

Slocum glider SN\_408 ('Growler'). Recovered 18/07/2015 (49°29.263 N, 8°33.653 W).

Seaglider SN\_533 ('Canopus'). Deployed 16/07/2015 (48°29.606 N, 9°47.535 W).

#### **OMG tidal cycle observations**

Slocum glider SN\_423 ('OMG2'). Deployed 16/07/2015 (48°29.931 N, 9°48.402 W). Recovered 31/07/2015 (49°23.002 N, 8°35.714 W)

Slocum glider SN\_424 ('OMG3'). Deployed 15/07/2015 (49°23.024 N, 8°38.499 W). Recovered 23/07/2015 (48°33.204 N, 8°38.249 W)

## LoC Nitrate sensor deployment

Seaglider SN\_534 ('Denebola'). Deployed 13/07/2015 (49°26.125 N, 8°35.954 W). Recovered 30/07/2015 (49°23.002 N, 8°35.714 W)

### Sensor Packages

<b>Slocum glider SN_408:</b>	Seabird CT sensor S/N 9109	
	Aanderaa Oxygen optode S/N 243	
	WetLabs Fluorometer S/N 3324	
<b>Seaglider SN_533:</b>	Seabird CT sensor S/N 0209	
	Aanderaa Oxygen optode S/N 288	
	WetLabs Fluorometer S/N 789	
	Biospherical PAR sensor S/N 50181	
<b>Slocum glider SN_423:</b>	Seabird CT sensor S/N 207	
	Aanderaa Oxygen optode S/N 252	
	Rockland Microrider S/N 106:	Shear probe 1 – S/N M1077
		Shear probe 2 – S/N M1075
		Thermistor 1 – S/N T838
		Thermistor 2 – S/N T698
<b>Slocum glider SN_424:</b>	Seabird CT sensor S/N 0221	
	Aanderaa Oxygen optode S/N 268	
	Rockland Microrider S/N 105:	Shear probe 1 – S/N M1073
		Shear probe 2 – S/N M1074
		Thermistor 1 – S/N T838
		Thermistor 2 – S/N T699
<b>Seaglider SN_534:</b>	Seabird CT sensor S/N 0230	
	WetLabs Fluorometer S/N 791	
	LoC Nitrate sensor	

## **Problems encountered**

Slocum 424 was scheduled for a two week deployment at CS2. However, a severe weather forecast on 23/07 prompted a decision to recover the glider early.

On recovery, Slocum 424's nose release became detached from the recovery line. The cause of this is unknown, but is probably due to either a material failure of the cable tie holding the recovery line to the nose or a mistake made during assembly. The glider was recovered safely by grappling the loose line to the bulwark after several attempts, but the nose could not be recovered so no inspection was possible.

Slocum 408 was found to still be powered on several days after normal post-mission checks were concluded and with a non-shorting plug in place. The glider was opened, and batteries disconnected from the mainboard. This points to a fault in the wiring of the battery cables or a short within an internal cable. Further investigation is required, but this may prove to be the root cause of 408's abnormally high battery consumption.

The configuration file for Microrider s/n 106 contains an incorrect coefficient (coef0) for the pressure sensor. This will need to be accounted for in post-processing.

## 8. Marine snow catchers

*E. Elena Garcia-Martin (University of East Anglia)*

### **Background**

Marine Snow Catchers (MSCs) are designed to capture 3 different fractions of particles: suspended, slow and fast sinking particles. The measurement of organic matter associated to these different fractions and the carbon and nitrogen remineralisation provide essential data to understand the biological carbon pump and the relationship between the benthos and overlaying water column.

Three small MSC (100 L, Fig. 8.1) were deployed in this cruise at three different locations (see Table 8.1 for specific details). After 1 hour 20 minutes the suspended and slow sinking fractions were sampled from the top and bottom tap. The fast sinking particles were collected from the tray at the bottom of the tower once that it was drained.

The characterization of the organic matter, aerobic respiration, bacterial production and nitrogen assimilation were determined from the three fractions (see individual reports from C. Davis, E.E García-Martin and Robinson, S. McNeill and A. Rees for specific details).



Figure 8.1. Marine Snow Catchers

Table 8.1. Station details for Marine Snow Catcher deployment. OM: Organic matter characterization; CR-BR: community/bacterial respiration; BP: bacterial production; N assimilation: nitrogen assimilation.

Date	Time (GMT)	Event Number	Latitude	Longitude	Depth (m)	Sampler	Variable
13/07/2015	14:59	4	49 23.14 N	8 37.56 W	70		Test
	15:17	15	49 23.15 N	8 37.53 W	90		Test
	15:34	16	49 23.14 N	8 37.52 W	110		Test
15/07/2015	19:56	49	49 22.77 N	8 36.58 W	10	A. Rees	N asimilation
	20:07	50	49 22.77 N	8 36.59 W	10	E.E. García-Martín	CR - BR/ BP
	20:16	51	49 22.78 N	8 36.59 W	10	C. Davis	OM
	22:12	53	49 22.77 N	8 36.58 W	80	E.E. García-Martín	CR - BR/ BP
	22:27	54	49 22.78 N	8 36.61 W	80	C. Davis	OM
	22:46	55	49 22.79 N	8 36.69 W	80	A. Rees	N asimilation
20/07/2015	15:45	115	48 34.26 N	9 30.55 W	10	C. Seguro	Misfire
	15:58	116	48 34.26 N	9 30.55 W	10	C. Seguro	Photographs
	16:10	117	48 34.26 N	9 30.55 W	80	C. Seguro	Photographs
	17:33	118	48 34.27 N	9 30.52 W	10	A. Rees	N asimilation
	17:51	119	48 34.27 N	9 30.52 W	10	C. Davis	OM
	18:05	120	48 34.26 N	9 30.45 W	10	E.E. García-Martín	CR - BR/ BP
	19:20	121	48 34.26 N	9 30.56 W	80	A. Rees	N asimilation
	19:39	122	48 34.24 N	9 30.48 W	80	E.E. García-Martín	CR - BR/ BP
	20:53	123	48 34.27 N	9 30.57 W	80	C. Davis	OM
22/07/2015	15:53	142	48 34.21 N	9 30.55 W	10	E.E. García-Martín	CR - BR/ BP
	16:04	143	48 34.21 N	9 30.55 W	10	E.E. García-Martín	Misfire
	16:18	144	48 34.21 N	9 30.62 W	10	E.E. García-Martín	CR - BR/ BP
	17:49	145	48 34.25 N	9 30.56 W	90	E.E. García-Martín	CR - BR/ BP
	18:04	146	48 34.25 N	9 30.56 W	90	E.E. García-Martín	CR - BR/ BP
	18:19	147	48 34.25 N	9 30.56 W	90	E.E. García-Martín	CR - BR/ BP
25/07/2015	17:16	181	49 24.84 N	8 36.11 W	15	A. Rees	N asimilation
	17:28	182	49 24.84 N	8 36.11 W	15	C. Davis	OM
	17:38	183	49 24.84 N	8 36.11 W	15	E.E. García-Martín	CR - BR/ BP
	19:30	184	49 24.84 N	8 36.11 W	75	A. Rees	N asimilation
	09:43	185	49 24.84 N	8 36.11 W	75	C. Davis	OM
	19:56	186	49 24.84 N	8 36.11 W	75	E.E. García-Martín	CR - BR/ BP
	21:34	189	49 24.95 N	8 35.81 W	15	C. Seguro	Photographs
	21:46	190	49 24.95 N	8 35.81 W	75	C. Seguro	Photographs

Table 8.1 (continuation)

30/07/2015	15:52	241	49 24.85 N	8 33.85 W	75	C. Seguro	Photographs
	16:15	242	49 24.85 N	8 33.85 W	10		Misfire
	16:27	243	49 24.85 N	8 33.85 W	10		Misfire
	16:37	244	49 24.85 N	8 33.85 W	10	C. Seguro	Photographs
	18:11	245	49 24.85 N	8 33.85 W	10	E.E. García-Martín	CR - BR/ BP
	18:33	246	49 24.85 N	8 33.85 W	10	A. Rees	N asimilation
	18:44	247	49 24.85 N	8 33.85 W	10	C. Davis	OM
	20:33	248	49 24.85 N	8 33.86 W	70	A. Rees	N asimilation
	20:49	249	49 24.85 N	8 33.90 W	70	C. Davis	OM
	21:05	250	49 24.83 N	8 33.89 W	70		Misfire
	21:16	251	49 24.83 N	8 33.90 W	70		Misfire
	21:30	252	49 24.83 N	8 33.90 W	70		Misfire

### **Acknowledgements**

We would like to acknowledge all the crew of the RSS Discovery 033 and the NMF staff (Steve, Willie, Mark, Craig and Phil) for their help and patience in the deployment of the Marine Snow Catcher. Particular thanks to Chata Seguro, Andy Rees, Carol Robinson, Clare Davis, Emlyn Jones, Sharon McNeill, Nick Stephens and Steve Woodward for help with the deployments. Equally importantly, the chief scientist Mark Moore and our other scientific colleagues on board who generously assisted and supported our work throughout DY033.

## 9. Dissolved inorganic nutrients

*Malcolm Woodward (Plymouth Marine Laboratory)*

### **Objectives**

To investigate the spatial and temporal variations of the micromolar nutrient species: Nitrate, Nitrite, Silicate, Ammonium and Phosphate during the DY033 research voyage in the Celtic Sea, Shelf Edge, and Off Shelf sea areas off the West of the UK. Including specific 'Iron' transects (WP3) for a series of stations in from 2500m deep in the Atlantic up onto the Shelf.

We also used a nanomolar nutrient analytical system for phosphate using liquid waveguide technology for detection.

To carry out nutrient analysis from zooplankton and benthic experiments where required as part of the SSB programme (Giering and Wells), plus other samples for snow-catcher depth confirmations (Rees, Seguro), DOM experiments (McNeil), and ground truthing the NOC Nitrate sensor deployed on a glider (Moore, Lohan), and from Underway daily sampling as part of the SSB Shelf-wide sampling programme.

Please see individual cruise reports for these colleagues as to their individual sampling protocols.

### **Sampling and analytical methodology**

#### **Sample preparation and procedure**

There was absolutely minimal storage of the CTD water column samples except for the time waiting to be analysed in the laboratory. These samples were always run at lab temperature and were not filtered. 60ml HDPE Nalgene bottles were used for all the nutrient sampling, these were aged, acid washed and cleaned initially, and stored with a 10% acid solution between sampling. Samples were taken from the Sea-Bird CTD systems on-board the RRS Discovery, both Stainless Steel and Titanium units. The sample bottle was washed 3 times before taking final sample, and capping tightly. This was then taken immediately to the analyzer in the lab, and analysis conducted as soon as possible after sampling. Nutrient free gloves (Duratouch/Semperguard) were used and other clean handling protocols were adopted as close to those according to the GO-SHIP protocols, (2010) as possible.

Water samples were taken from the 24 x 10 litre Stainless Steel CTD/Rosette system (SeaBird). Clean handling techniques were employed to avoid any contamination of the samples, particularly for the ammonium samples. Gloves used were Dura-Touch to minimise nutrient contamination. Samples were kept tightly closed until just before analysis for the ammonium, this to avoid any contamination from external sources.

#### **Sample Analysis**

The micro-molar segmented flow auto-analyser used was the PML 5 channel (nitrate, nitrite, phosphate, silicate and ammonium) Bran and Luebbe AAIII system, using classical proven colorimetric analytical techniques.

The instrument was calibrated with home produced nutrient standards and then compared regularly against Nutrient Reference Materials, from KANSO Technos, Japan. The results from this also being part of a global nutrient programme (the INSS, International Nutrient Scale System) and International SCOR group (COMPONUT), both aimed to improve nutrient analysis data quality world-wide.

The analytical chemical methodologies used were according to Brewer and Riley (1965) for nitrate, Grasshoff (1976) for nitrite, Kirkwood (1989) for phosphate and silicate, and Mantoura and Woodward (1983) for ammonium.

For the nanomolar phosphate the method was as that described by Zhang and Chi, 2002.

## References

Brewer P.G. and Riley J.P., 1965. The automatic determination of nitrate in seawater. Deep Sea Research, 12, 765-72.

Grasshoff K., 1976. Methods of seawater analysis. Verlag Chemie, Weinheim and New York, 317pp.

Kirkwood D., 1989. Simultaneous determination of selected nutrients in seawater. ICES CM 1989/C:29.

Mantoura, R.F.C and Woodward E.M.S, 1983. Estuarine, Coastal and Shelf Science, 17, 219-224.

Zhang, J-Z and Chi, J, Environ.Sci.Technol, 2002, 36, 1048-1053.

## CTD Samples Analysed by AAll Micromolar analysis

Date	CTD	Event	Position	CTD bottle analysed
12/07/15	CTD_001	003	49°25.064'N 8°35.547'W	Bottles 1,3,5,7,9,11,13,15,17,19,21(depths: 137,100,80,60,50,45,41,35,20,12,5,m)
13/07/15	CTD_003	008	49°23.583'N 8°36.325'W	Bottles 1,3,5,7,9,11,13,15,17,19,23(depths: 137,100,80,60,50,45,40,30,20,10,5m)
14/07/15	CTD_005	025	49°23.216'N 8°37.849'W	Bottles 2,3,7,9,11,14,16,18,19,24 Depths: 140,110,80,60,53,50,40,26,15,8m
14/07/15	CTD_006	026	49°25.544'N 8°32.552'W	Bottles 2,6,10 (depths: 90,45,15m)

14/07/15	CTD_007	027	49°23.316'N 8°38.062'W	Bottles 21,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17(depths:133,133,133,133,123,123,123,123,80,60,60,53,53,53,53,30,20m
14/07/15	CTD_008	029	49°23.450'N 8°37.848'W	Bottles 1,3,5,7,8,10,12,14,16,17,18,20,22(depths 133,100,80,65,60,55,48,45,40,3,20,10,4,m
15/07/15	CTD_009	044	49°22.71'N 8°36.627'W	Bottles 2,4,7,9,10,12,14,16,18,20,22,24 (depths:136,110,80,5,52,49,45,38,30,25,15,9 m
15/07/15	CTD_011	045	49°22.711'N 8°36.627'W	Bottles 1,2,3,4,5,6,7,8,9,10 (depths: 137,137,127,127,80,55,45,45,30,20m
16/07/15	CTD_015	065	48°23.124'N 9°55.05'W	Bottles 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,18,19,20,21,23,24(depths:2360,2300,2150,2000,1850,1650,1500,1250,1000,900,850,800,750,650,500,400,250,200,150,100,35,20m
16/07/15	CTD_016	066	48°23.120'N 9°55.046'W	Bottles 1,2,3,4,5,6,7,9,10,11,13,14,15,16,17,18,19,20,21,22,23,24 (depths:2170,2170,1500,1000,650,500,250,1000,100,80,60,60,55,45,40,40,35,25,10,10,5,5m
16/07/15	CTD_017	067	48°23.970'N 9°54.043'W	Bottles 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24(depths:1810,1810,1750,1650,1400,1250,1000,800,700,600,500,400,300,200,100,80,60,53,53,53,40,20,20,20m
17/07/15	CTD_018	068	48°23.96'N 9°54.04'W	Bottles 1,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,21,22,23(depths:1810,1750,1650,1400,1250,1000,800,700,600,500,400,300,200,100,80,60,45,40,35,20,10m
17/07/15	CTD_019	071	48°24.61'N 09°53.35'W	Bottles 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24(depths:1410,1350,1250,1100,950,850,750,625,500,450,400,350,300,250,200,150,100,90,70,70,60,40,20,20m
17/07/15	CTD_020	072	48°24.608'N 09°53.350'W	Bottles 1,3,4,6,7,10,12,13,14,15,16,17,18,19,20,22,23,24(depths:1420,1100,950,750,500,300,200,150,100,90,70,65,55,50,40,20,10,5m

17/07/15	CTD_021	073	48°25.337'N 09°52.702' W	Bottles1,2,3,4,5,6,7,18,19(depths:895,885,800,700,600,500,400,30,20m
18/07/15	CTD_022	074	48°25.331'N 09°52.701' W	Bottles15,16,17,18,19(depths:300,200,150,80,55m
18/07/15	CTD_023	075	48°25.331'N 09°52.701' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24(depths:895,895,850,800,750,700,600,500,450,400,300,250,200,100,80,60,40,40,30,20,10,5,5m
18/07/15	CTD_024	076	48°25.761'N 09°52.269' W	Bottles1,2,3,4,5,6,7,13,14,15,16,17,18,19(dept hs:655,655,550,450,400,300,200,150,100,80,60,40,20,20m
18/07/15	CTD_025	077	48°26.231'N 09°51.787' W	Bottles1,3,5,6,7,9,10,11,13,14,15,17,18,19,21,23(depths:470,400,350,250,200,150,100,70,60,50,30,20,10,5m
18/07/15	CTD_026	078	48°26.188'N 9°51.775'W	Bottles1,2,4,5,6,13,14,15,16,17,18(depths:470,450,400,350,300,200,150,100,80,50,20m
18/07/15	CTD_027	079	48°29.50'N 9°48.51'W	Bottles1,3,4,6,8,9,10,12,14,15,18,20,22(depths:240,200,150,100,80,70,60,50,40,30,20,10,5m
18/07/15	CTD_028	080	48°29.500'N 9°48.518'W	Bottles5,6,7,8,19,20,21,22(depths:240,210,150,100,90,60,35,22m
19/07/15	CTD_030	083	48°34.25'N 9°30.59'W	Bottles2,3,4,7,9,12,14,16,18,19,24(depths:190,140,90,50,235,20,18,15,10,8,5m
19/07/15	CTD_031	084	48°34.268'N 9°30.591'W	Bottles2,3,4,5,7,8,11,12,13,15,17,20,22,23(depths:197,150,120,100,80,60,50,45,40,35,32,20,10,5m

20/07/15	CTD_033	102	48°34.25'N 9°30.58'W	Bottles 2,4,6,8,10,12,14,16,18,20,22,24 (depths:190,150,110,70,50,32,25,20,16,14,10, 5m
20/07/15	CTD_034	103	48°34.25'N 9°30.58'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15 (depths: 190,190,190,170,170,170,135,80,60,50,40,20, 20,20,20m
20/07/15	CTD_036	106	48°34.265'N 9°30.557'W	Bottles 2,3,4,5,7,8,9,11,12,14,16,18,20,22,23 (depths:190,150,120,100,80,60,50,45,40,30,2 5,20,15,10,5m
21/07/15	CTD_040	133	48°12.359'N 10°03.16'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 19,20,21,22,23,24(depths:2466,2466,2000,20 00,1500,1500,1200,1200,900,900,700,500,25 0,250,100,70,30,30,20,10,5,5m
21/07/15	CTD_041	134	48°12.353'N 10°03.157' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24(depths:2460,2460,23 00,2100,1964,1724,1500,1204,1000,852,753, 656,655,502,353,200,410,90,70,51,35,23,20,2 0m
21/07/15	CTD_042	135	48°14.375'N 09°57.902' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24(depths:1963,1963,18 00,1600,1400,1200,1000,900,900,800,600,40 0,200,100,80,60,50,40,35,35,30,20,10,5m
22/07/15	CTD_043	136	48°14.375'N 09°57.902' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24(depths:1960,1960,19 00,1800,1650,1550,1300,1100,950,750,750,6 50,550,400,300,200,150,100,90,75,35,35,20,2 0m
22/07/15	CTD_044	137	48°18.00'N 09°48.00'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,20,21,22,23,24(depths:1502,1502,1400, 1200,1050,1050,950,850,750,650,500,400,30 0,200,100,80,60,40,30,20,10,5,5m
22/07/15	CTD_045	138	48°17.79'N 09°47.98'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20(depths:1500,1400,1390,1250,115 0,1050,950,850,750,660,600,480,300,200,150 ,90,70,55,30,20m

23/07/15	CTD_046	152	48°20.458'N 09°42.238' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20(depths:1465,1465,1350,1350,125 0,1250,1200,1100,1000,900,700,500,400,300, 200,100,70,50,20,20m
23/07/15	CTD_047	153	48°27.20'N 09°37.22'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15(dep ths:952,900,800,700,600,500,400,250,150,90, 70,55,40,20,20m
23/07/15	CTD_048	154	48°22.202'N 09°37.722' W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24(depths:956,956,800, 700,650,600,500,500,400,300,200,100,100,80 ,60,40,30,30,20,15,10,5,5,5m
23/07/15	CTD_049	155	48°24.53'N 09°31.56'W	Bottles1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 18,19,20,21,22,24(depths:467,467,400,400,35 0,350,300,200,150,100,100,60,60,40,40,30,20 ,20,10,10,5m
23/07/15	CTD_050	156	48°24.53'N 09°31.57'W	Bottles1,2,3,4,5,6,13,14,15,16,17,18(depths:4 67,450,400,350,300,250,200,150,100,80,40,2 0m
23/07/15	CTD_051	156	48°22.712'N 09°36.467' W	Bottles7,8,9,10,11,12,19,20,21,22,23,24(depth s:714,600,500,400,300,200,100,75,55,40,28,2 0m
23/07/15	CTD_053	160	48°51.18'N 09°12.09'W	Bottles1,3,5,7,9,11,13,15,19(depths:152,120,8 0,60,50,42,30,20,10,3m
23/07/15	CTD_054	161	49°07.170'N 08°54.321' W	Bottles1,2,4,6,8,10,12,14,16,18(depths:140,10 0,60,50,42,38,30,20,10,5m
24/07/15	CTD_055	162	49°22.10'N 08°37.63'W	Bottles2,4,7,10,12,14,16,18,20,24(depths:135, 100,75,55,42,32,20,16,10,5m
24/07/15	CTD_056	164	49°22.100'N 08°37.582' W	Bottles2,3,4,5,6,7,9,10,12,15,16,17,18,19,21,2 2,23(depths:130,130,100,100,75,75,60,55,50, 47,47,40,35,20,15,8m

25/07/15	CTD_058	166	49°22.025'N 08°37.509' W	Bottles1,5,7,9,11,12,13,15,16,18,19,21,22,24( depths:132,100,100,80,80,80,58,58,47,47,38, 38,20,20m
25/07/15	CTD_059	137	49°22.01'N 08°37.58'W	Bottles2,3,4,5,6,10,14(depths:132,132,20,20,2 0,20m
26/07/15	CTD_062	192	51°12.787'N 06°07.680' W	Bottles1,2,4,5,7,8,10,11,13,14,16,17,19,22(de pths:92,92,80,80,50,50,35,35,27,27,25,25,5m
26/07/15	CTD_062	192	51°12.787'N 06°07.680' W	Bottles1,2,4,5,7,8,10,11,13,14,16,17,19,22(de pths:92,92,80,80,50,50,35,35,27,27,25,25,5m
26/07/15	CTD_063	193	51°12.785'N 06°07.680' W	Bottles1,2,3,4,6,7,14,15,16,17,18,19(depths:9 7,97,97,93,80,50,50,50,30,20,20,20m
26/07/15	CTD_064	194	50°49.685'N 06°39.895' W	Bottles1,2,4,6,7,8,10,11,13,16,19,20,22(depth s:90,90,70,70,50,50,45,40,40,35,30,20,20,8m
28/07/15	CTD_066	196	50°24.28'N 07°13.29'W	Bottles2,5,7,9,10,11,12,13,15,16,17,19,21,22( depths:105,85,75,65,50,50,45,45,43,43,35,20, 5,5m
28/07/15	CTD_067	198	50°24.27'N 07°13.30'W	Bottles2,3,4,5,6,7,13,14,15,16,17,18(depths:1 04,104,104,95,60,48,44,44,44,31,16,16,16m
28/07/15	CTD_068	199	50°00.540'N 07°47.830' W	Bottles1,2,3,5,7,8,10,12,13,14,16,17,18,19,20, 22,23(depths:100,100,90,75,75,55,50,46,45,4 5,44,44,35,35,20,4,4m
28/07/15	CTD_069	200	50°00.540'N 07°47.830' W	Bottles2,3,4,5,6,7,13,14,15,16,17,18(depths:1 02,102,102,80,80,80,60,47,38,20,20,20m

29/07/15	CTD_070	203	49°25.28'N 08°34.55'W	Bottles1,2,3,4,5,6,9,10,11,12,14,15,16,17,18,19,20,23,24(depths:134,134,100,100,70,70,46,46,42,42,38,32,32,24,24,14,14,8,8m
29/07/15	CTD_071	204	49°25.48'N 08°34.55'W	Bottles2,3,4,5,6,7,8,14,(depths:137,110,90,60,60,50,50,20,20m
29/07/15	CTD_072	205	49°25.48'N 08°34.55'W	Bottles6,5,4,3,2,1(depths:10,10,50,50,90,90,m
29/07/15	CTD_075	217	49°25.514'N 08°34.207'W	Bottles8,7,6,5,4,3,2,1(depths:20,20,45,45,50,50,90,90,m
30/07/15	CTD_076	218	49°24.578'N 08°34.407'W	Bottles1,3,5,7,8,10,12,15,17,18,20,22,23(depths:135,110,80,65,51,48,45,42,40,32,24,14,8m
30/07/15	CTD_077	219	49°24.57'N 08°34.40'W	Bottles2,3,4,5,6,7,8,9,10,11,12,13,14,15(depths:135,135,135,135,120,80,80,80,80,80,49,40,20,20m
30/07/15	CTD_078	230	49°24.372'N 08°32.085'W	Bottles1,3,5,7,9,12,14,16,18(depths:130,90,60,47,44,40,25,10,5m
31/07/15	CTD_079	262	49°24.737'N 08°34.459'W	Bottles2,3,4,5,6,7,8(depths:140,135,125,105,60,55,20m
31/07/15	CTD_080	263	49°24.90'N 08°33.910'W	Bottles10,12,13,14,15,16,18(depths:138,133,123,102,52,39,20m
31/07/15	CTD_081	266	49°23.750'N 08°35.857'W	Bottles2,3,4,6,7,8,9,16(depths:138,138,133,103,75,55,49,20m
31/07/15	CTD_083	269	49°23.726'N	Bottles3,4,5,6,7,8(depths:135,126,105,56,48,20m

			08°35.891' W	
31/07/15	CTD_084	270	49°23.72'N 08°35.891' W	Bottles2(depths:141m
31/07/15	CTD_085	275	49°23.814'N 08°35.478' W	Bottles3,4,5,6,7,8,9(depths141,136,126,106,55,47,20m
1/08/15	CTD_086	276	49°23.872'N 08°35.429' W	Bottles2,3,4,5,6,7,14(depths:138,133,123,103,57,45,20m
1/08/15	CTD_087	278	49°23.72'N 08°35.50'W	Bottles2,3,4,5,6,7,8,9(depths:138,138,133,123,103,55,48,20m
1/08/15	CTD_088	279	49°23.81'N 08°35.08'W	Bottles2,3,4,5,6,7,8,9(depths:138,138,133,123,103,50,45,20m
1/08/15	CTD_089	280	49°23.82'N 08°35.26'W	Bottles3,4,5,6,7,9(depths:140,135,125,105,50,44,20m

### Nanomolar Phosphate Analysis

Date	CTD	Event	Position	CTD bottle analysed
13/07/15	CTD_003	008	49°23.583'N 8°36.325'W	Bottles13,15,17,19,23(depths: 40,30,20,10,5m)
14/07/15	CTD_005	025	49°23.216'N 8°37.849'W	Bottles14,16,18,19,24Depths:50,40,26,15,8m
15/07/15	CTD_009	044	49°22.71'N 8°36.627'W	Bottles14,16,18,20,22,24(depths:45,38,30,25, 15,9m
16/07/15	CTD_016	066	48°23.120'N 9°55.046'W	Bottles18,19,20,21,22,23,24(depths:40,35,25, 10,10,5,5m
17/07/15	CTD_018	068	48°23.96'N 9°54.04'W	Bottles19,21,22,23(depths:40,35,20,10m
17/07/15	CTD_020	072	48°24.608'N 09°53.350' W	Bottles20,22,23,24(depths:40,20,10,5m
18/07/15	CTD_023	075	48°25.331'N 09°52.701' W	Bottles19,20,21,22,24(depths:40,30,20,10,5m
18/07/15	CTD_025	077	48°26.231'N 09°51.787' W	Bottles18,19,21,23(depths:30,20,10,5m
18/07/15	CTD_027	079	48°29.50'N 9°48.51'W	Bottles16,18,20,22(depths:30,20,10,5m
19/07/15	CTD_030	083	48°34.25'N 9°30.59'W	Bottles9,12,16,18,19,24(depths:35.20.15.10.8. 5m
20/07/15	CTD_033	102	48°34.25'N 9°30.58'W	Bottles12,14,16,18,20,22,24(depths:32,25,20, 16,14,10,5m

21/07/15	CTD_040	133	48°12.359'N 10°03.16'W	Bottles20,21,22,24(depths:30,20,10,5m
21/07/15	CTD_042	135	48°14.375'N 09°57.902' W	Bottles18,20,21,22,23,24(depths:40,35,30,20, 10,5m
22/07/15	CTD_044	137	48°18.00'N 09°48.00'W	Bottles18.20.21.22.24(depths:40,30,20,10,5m
28/07/15	CTD_066	196	50°24.28'N 07°13.29'W	Bottles16,17,19,21,22(depths:43,35,20,5,5m
28/07/15	CTD_068	199	50°00.540'N 07°47.830' W	Bottles16,17,18,19,20,22,23(depths:44,44,35, 35,20,4,4m
29/07/15	CTD_070	203	49°25.28'N 08°34.55'W	Bottles12,14,16,18,19,20,23,24(depths:42,42, 38,32,24,14,14,8,8m

### **Underway samples**

14 separate daily samples were taken at approximately midday during the cruise.

12<sup>th</sup>, 13<sup>th</sup>, 14<sup>th</sup>, 15<sup>th</sup>, 16<sup>th</sup>, 17, 21<sup>st</sup>, 23<sup>rd</sup>, 24<sup>th</sup>, 25<sup>th</sup>, 26<sup>th</sup>, 27<sup>th</sup>, 30, 31<sup>st</sup> July

### **Sharon McNeil DOM remineralisation**

15<sup>th</sup> July: 6 samples

17<sup>th</sup> July: 6 samples

20<sup>th</sup> July: 12 samples

21<sup>st</sup> July: 6 samples

26<sup>th</sup> July: 12 samples

28<sup>th</sup> July: 12 samples

30<sup>th</sup> July: 18 samples

### **Sari Geiring and Seona Wells Zooplankton experiments**

14<sup>th</sup> July: 48 samples

16<sup>th</sup> July: 48 samples

20<sup>th</sup> July: 48 samples

23<sup>rd</sup> July: 48 samples

26<sup>th</sup> July: 48 samples

30<sup>th</sup> July: 48 samples

### **Iron/Nutrient/Zooplankton excretion experiments**

26<sup>th</sup> July: 24 samples

30<sup>th</sup> July: 24 samples

31<sup>st</sup> July: 24 samples

### **Preliminary Results**

All data was worked up to a preliminary stage at sea which helped a number of groups with planning follow up experiments. Data quality and output looked good with reference materials showing good results from the analyser throughout.

### **Cruise Summary**

#### **Science**

The 5-channel autoanalyser worked very well throughout the cruise.

KANSO nutrient reference materials (Batch BU) were run regularly to check analyser integrity and analytical continuity from one day to the next. Very good continuity in sensitivity for all 5 channels was found, demonstrating excellent analytical performance.

#### **Thanks**

To the officers and engineers of RRS Discovery, the NMF technicians and crew who made things work for us and kept them working, and of course Mark and Amy for excellent food.

## 10. Dissolved and particulate organic matter

Clare Davis (University of Liverpool) and Lucie Munns (University of Southampton)

### Sampling protocols

#### Dissolved nutrients

**Total dissolved phosphorus (TDP):** Samples were collected from between 6 and 12 depths from the CTD and were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) and stored in acid-cleaned 175 mL HDPE bottles at  $-20^{\circ}\text{C}$  for later laboratory analysis to determine total dissolved phosphorus concentration.

**Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN):** Samples were collected from between 6 and 12 depths from the CTD and were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) and stored in 20 mL muffled glass vials with 20  $\mu\text{L}$  50% hydrochloric acid and stored at  $4^{\circ}\text{C}$  for later laboratory analysis.

**Dissolved free and total hydrolysable amino acids (DFAA, THAA):** Samples were collected from between 6 and 12 depths from the CTD and were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) and stored in 20 mL muffled glass vials at  $-20^{\circ}\text{C}$  for later laboratory analysis.

**Coloured Dissolved Organic Matter (CDOM):** Samples were collected from between 6 and 12 depths from the CTD and underway system. Samples were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) and then through 0.2  $\mu\text{m}$  Durapore filters. Samples were kept in the dark and analysed on board using a Shimadzu UV-1650PC spectrophotometer and a Horiba Fluoromax-4 spectrofluorometer. Data will later be processed using PARAFAC by Nealy Carr (PhD student, University of Liverpool) to determine the source and composition of CDOM.

**Stable isotopes of dissolved nitrate ( $\delta^{15}\text{N}$ ):** Samples were collected from 6 to 9 depths from the predawn CTDs. Samples for the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) and stored in 60 mL HDPE bottles (HCl acid washed) at  $-20^{\circ}\text{C}$  for later analysis.

**Stable oxygen isotopes of dissolved phosphate ( $\delta^{18}\text{O}_\text{p}$ ) (10 samples):** Samples were collected from the bottom mixed layer. 10L was filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) on a glass filter rig, 200 mL of 1M NaOH solution was added. The resulting precipitate was left to settle for 3-6 hours before the supernatant was removed under low vacuum pressure. The precipitate was transferred to HDPE bottles and stored at  $-20^{\circ}\text{C}$  for later analysis.

#### Particulate nutrients

**Particulate organic carbon (POC), particulate organic nitrogen (PON) and particulate phosphorus (POP):** Samples were collected from 8 depths from the predawn CTDs and marine snow catcher deployments. For particulate carbon and nitrogen (POC/PON), 2L was filtered onto 25 mm GF/F (combusted, Whatman, nominal pore size 0.7  $\mu\text{m}$ ) on a plastic filter rig

under <12 kPa vacuum pressure. For particulate phosphorus (POP), 1L was filtered onto 25 mm GF/F (combusted and HCl acid washed, Whatman, nominal pore size 0.7µm) on a plastic filter rig under <12 kPa vacuum pressure. All filters were stored at -20°C for later laboratory analysis.

**Particulate lipids, pigments and particulate amino acids:** Samples were collected from 8 depths from the predawn CTDs and marine snow catcher (lipids only). For separate lipid, pigment and amino acid samples, 2L was filtered onto 47 mm GF/F (combusted, Whatman, nominal pore size 0.7µm) on a 3-port glass filter rig under <12 kPa vacuum pressure. Filters were stored at -80°C for later laboratory analysis.

**δ<sup>15</sup>N of particulate nitrogen (δ<sup>15</sup>PN):** Samples were collected from the predawn CTDs. Samples for δ<sup>15</sup>N-particulate nitrogen were collected by filtering 2L onto 25 mm GF/F (combusted, Whatman, nominal pore size 0.7 µm) and stored at -20°C for later analysis. Samples for the δ<sup>15</sup>N and δ<sup>18</sup>O of nitrate were collected on transects, filtered (47 mm GF/F combusted, Whatman, nominal pore size 0.7 µm) and stored in 60 mL HDPE bottles (HCl acid washed) at -20 °C for later analysis.

**Stand Alone Pump System (SAPS):** Three depths were sampled during each SAPS deployment to collect samples for POC, PON, POP, particulate lipids, particulate amino acids and pigments from two fractions: particles >53 µm and particles between 0.7 – 53 µm. The surface mixed layer SAPS was deployed at ~10-15 m, the mid depth SAPS was deployed at the depth of the chlorophyll maximum, and the deep SAPS was deployed at ~20 m below the base of the thermocline. The SAPs was programmed to pump for 1 hour once at that depth. Upon recovery, the 53 µm mesh fraction was washed onto a 47 mm GF/F (combusted, Whatman, nominal pore size 0.7µm) which was stored at -80°C for later analysis. Below the mesh were two 27.3 cm diameter GF/Fs (combusted, Whatman, nominal pore size 0.7 µm) one was the sample GF/F and the second was stored as the blank GF/F, both were stored at -80 °C for later analysis.

**Zooplankton sloppy feeding/grazing experiment:** With Sari Giering and Seona Wells experiments were conducted to investigate the change in the DOM (TDP, DOC, TDN, AA) and POM (POC, PON, POP, lipid) pools resulting from zooplankton excretion and sloppy feeding, separately. All experiments were conducted in triplicate with controls and repeated during the day and night.

## **Sample inventory**

### **Dissolved nutrient (DOC, TDN, TDP, DFAA, THAA, δ<sup>15</sup>N) sampling from the stainless steel CTD (total 94):**

EV3 ROS1, ROS5, ROS9, ROS11, ROS13, ROS15, ROS17, ROS19

EV8 ROS2, ROS23

EV25 ROS1, ROS6, ROS8, ROS10, ROS13, ROS15, ROS17, ROS23

EV29 ROS1, ROS22

EV48 ROS2, ROS5, ROS10, ROS13, ROS15, ROS18, ROS20, ROS23

EV83 ROS1, ROS3, ROS4, ROS6, ROS8, ROS11, ROS15, ROS23

EV160 ROS1, ROS4, ROS7, ROS11, ROS15, ROS17

EV161 ROS1, ROS2, ROS6, ROS11, ROS12, ROS17

EV162 ROS1, ROS6, ROS9, ROS11, ROS13, ROS15, ROS17, ROS19, ROS23

EV192 ROS3, ROS6, ROS9, ROS12, ROS18, ROS21

EV194 ROS1, ROS5, ROS7, ROS11, ROS16, ROS20

EV196 ROS2, ROS3, ROS7, ROS11, ROS13, ROS15, ROS17, ROS19, ROS22

EV199 ROS1, ROS5, ROS8, ROS10, ROS14, ROS18, ROS20, ROS23

EV203 ROS1, ROS5, ROS9, ROS11, ROS15, ROS17, ROS19, ROS23

**Dissolved nutrient (DOC, TDN, TDP, DFAA, THAA,  $\delta^{15}\text{N}$ ) sampling from the titanium CTD (total 125):**

EV64 ROS1, ROS5, ROS7, ROS9, ROS13, ROS15, ROS19, ROS21, ROS23, ROS24

EV67 ROS1, ROS4, ROS6, ROS8, ROS10, ROS12, ROS15, ROS18, ROS21, ROS22

EV71 ROS1, ROS4, ROS8, ROS12, ROS15, ROS17, ROS19, ROS21, ROS23

EV73 ROS1, ROS3, ROS5, ROS7, ROS14, ROS16, ROS17, ROS18, ROS19

EV76 ROS2, ROS3, ROS5, ROS7, ROS13, ROS16, ROS18

EV78 ROS1, ROS5, ROS13, ROS15, ROS17, ROS18

EV80 ROS5, ROS7, ROS8, ROS19, ROS20, ROS21, ROS22

EV134 ROS1, ROS3, ROS5, ROS7, ROS9, ROS13, ROS15, ROS17, ROS19, ROS21, ROS22, ROS23

EV136 ROS2, ROS4, ROS6, ROS9, ROS11, ROS14, ROS16, ROS19, ROS21, ROS23

EV138 ROS1, ROS4, ROS7, ROS11, ROS13, ROS15, ROS17, ROS18, ROS20

EV152 ROS2, ROS4, ROS6, ROS10, ROS12, ROS15, ROS17, ROS18, ROS20

EV153 ROS2, ROS4, ROS6, ROS8, ROS10, ROS11, ROS13, ROS14

EV156 ROS1, ROS6, ROS13, ROS16, ROS17, ROS18

EV157 ROS7, ROS9, ROS11, ROS199, ROS21, ROS23

EV166 ROS2, ROS7, ROS11, ROS15, ROS18, ROS21, ROS24

**$\delta^{18}\text{O}_P$  sampling from stainless steel CTD (10 total):**

EV8 ROS4

EV104 ROS1

EV135 ROS2, ROS9, ROS13

EV160 ROS4

EV161 ROS2

EV194 ROS5

EV196 ROS3

EV199 ROS5

**CDOM samples (total 236):**

EV3 ROS1, ROS5, ROS11, ROS13, ROS15, ROS19

EV25 ROS6, ROS8, ROS10, ROS13, ROS15, ROS17

DOM REMIN DOM1 DAY 0, DEP1, DEP2, DEP3

EV58 ROS1, ROS3, ROS5, ROS7, ROS9, ROS11

EV65 ROS1, ROS7, ROS9, ROS15, ROS19, ROS21, ROS23, ROS24

EV67 ROS1, ROS4, ROS6, ROS8, ROS10, ROS12, ROS15, ROS18, ROS21, ROS22

EV71 ROS1, ROS4, ROS8, ROS12, ROS15, ROS17, ROS19, ROS21, ROS23

EV73 ROS1, ROS3, ROS5, ROS7, ROS14, ROS16, ROS17, ROS18, ROS19

EV76 ROS2, ROS3, ROS5, ROS7, ROS13, ROS16, ROS18

EV78 ROS1, ROS5, ROS13, ROS15, ROS17, ROS18

EV80 ROS5, ROS7, ROS8, ROS19, ROS20, ROS21, ROS22

EV81 ROS1, ROS3, ROS5, ROS7

DOM REMIN DOM1 DAY 4 DEP1, DEP2, DEP3

EV83 ROS1, ROS3, ROS4, ROS6, ROS8, ROS11, ROS15, ROS23

DOM REMIN DOM2 DAY 0 DEP1, DEP2, DEP3

DOM REMIN DOM1 DAY 6 DEP1, DEP2, DEP3

EV134 ROS1, ROS3, ROS5, ROS7, ROS9, ROS13, ROS15, ROS17, ROS19, ROS21, ROS22, ROS23

EV136 ROS2, ROS4, ROS6, ROS9, ROS11, ROS14, ROS16, ROS19, ROS21, ROS23

EV138 ROS1, ROS4, ROS7, ROS11, ROS13, ROS15, ROS17, ROS18, ROS20

EV152 ROS2, ROS4, ROS6, ROS10, ROS12, ROS15, ROS17, ROS18, ROS20

EV153 ROS2, ROS6, ROS8, ROS10, ROS11, ROS13, ROS14

EV156 ROS1, ROS4, ROS6, ROS13, ROS16, ROS17, ROS18

EV157 ROS7, ROS9, ROS11, ROS19, ROS21, ROS23

REMIN DOM2 DAY 3 DEP1, DEP2, DEP3

EV160 ROS1, ROS4, ROS8, ROS12, ROS16, ROS18

EV161 ROS1, ROS2, ROS6, ROS11, ROS12, ROS17

REMIN DOM1 DAY10 DEP1, DEP2, DEP3

EV166 ROS7, ROS11, ROS15, ROS18, ROS21, ROS24

EV167 ROS2

REMIN DOM2 DAY6 DEP1, DEP2, DEP3

EV192 ROS3, ROS6, ROS9, ROS12, ROS18, ROS21

EV194 ROS1, ROS5, ROS7, ROS11, ROS16, ROS20

REMIN DOM3 DAY0 DEP1, DEP2, DEP3

REMIN DOM2 DAY9 DEP1, DEP2, DEP3

REMIN DOM 3 DAY2 DEP1, DEP2, DEP3

EV196 ROS2, ROS7, ROS11, ROS13, ROS17, ROS19

EV199 ROS1, ROS5, ROS8, ROS14, ROS18, ROS20

EV203 ROS1, ROS5, ROS9, ROS11, ROS15, ROS17, ROS19, ROS23

REMIN DOM1 DAY15 DEP1, DEP2, DEP3

REMIN DOM2 DAY11 DEP1, DEP2, DEP3

REMIN DOM3 DAY4 DEP1, DEP2, DEP3

**Particulate nutrient (POC, PON, POP, LIPIDS, PIGMENTS, AMINO ACIDS,  $\delta^{15}\text{PN}$ )  
samples collected from the stainless steel CTD:**

EV25 ROS1, ROS6, ROS8, ROS10, ROS13, ROS15, ROS17, ROS23

EV83 ROS1, ROS3, ROS4, ROS6, ROS8, ROS11, ROS15, ROS23

EV162 ROS1, ROS6, ROS9, ROS11, ROS13, ROS15, ROS17, ROS19, ROS23

EV166 ROS1, ROS6, ROS10, ROS14, ROS17, ROS20, ROS23

EV192 ROS3, ROS6, ROS9, ROS12, ROS18, ROS21

EV203 ROS1, ROS5, ROS9, ROS11, ROS15, ROS17, ROS19, ROS23

**Tidal cycle on titanium CTD (TDP, DOC, TDN, POC, PON, POP):**

EV262 ROS2, ROS3, ROS4, ROS5, ROS6, ROS8

EV263 ROS10, ROS12, ROS13, ROS14, ROS15, ROS18

EV266 ROS2, ROS4, ROS6, ROS8, ROS9, ROS17

EV269 ROS2, ROS3, ROS4, ROS5, ROS6, ROS8

EV275 ROS3, ROS4, ROS5, ROS6, ROS7, ROS9

EV276 ROS2, ROS3, ROS4, ROS5, ROS6, ROS14

EV278 ROS3, ROS4, ROS5, ROS6, ROS8, ROS9

EV279 ROS3, ROS4, ROS5, ROS6, ROS7, ROS9

**Marine Snow Catcher samples (POC, PON, POP, LIPIDS):**

EV51 10M; EV54 80M

EV119 10M; EV123 80M

EV182 15M; EV185 75M

EV247 10M; EV249 70M

**SAPS deployments (POC, PON, POP, LIPIDS, PIGMENTS, AMINO ACIDS; total 12):**

EV46 15M, 45M, 80M

EV105 15M, 50M, 80M

EV163 15M, 45M, 75M

EV229 15M, 45M, 70M

**Zooplankton sloppy feeding/excretion experiments (DOC, TDN, TDP, AA, POC, PON, POP, LIPIDS; total samples 28):**

EV142-147

EV272, 273, 277

**Acknowledgments**

Team organic would like to thank Dougal, Nick, Julie, Tom, Andy and Steve for their help with CTDs and SAPS and general brilliance. We'd like to thank the crew for all their hard work, particularly the patient snow catcher watch. We'd like to thank team Fe for sampling their super clean Niskin bottles for us during iron transects and the tidal cycle. We'd also like to thank everyone for pre-dawn banter and keeping morale up and Malcolm for providing the soundtrack to SSB. Thanks Mark for running a remarkably smooth cruise in the face of numerous adjustments to the schedule.

## **11. Chlorophyll-a and particulate silicate**

*Ian Murphy (Marine Institute) and Alex Poulton (National Oceanography Centre, Southampton)*

Once the CTD was brought back on board seawater from various depths in the water column were sampled by scientists from the rosette of Niskin bottles, attached to the CTD frame. Water samples were collected in Nalgene plastic containers to avoid any reaction between water and plastic. Seawater was used for a variety of experiments.

### **Chlorophyll-a**

Six to eight depths for most CTD casts. Measurements of total chl-a were collected by filtering 200 ml sea water samples through 25 mm diameter Whatman GFF filters (effective pore size 0.7  $\mu\text{m}$ ). The filter paper is then placed inside small glass jars and 6ml of Acetone is added. The samples are then refrigerated for later analysis in the lab.

### **Size-fractionated Chlorophyll**

Size-fractionated chl-a were only collected from the six depths on the pre-dawn CTD casts . Samples for size-fractionated chl-a were collected by sequentially filtering 200 ml of seawater through 47 mm diameter 20  $\mu\text{m}$ , 2  $\mu\text{m}$  and 0.2  $\mu\text{m}$  filters. Filters are then collected placed in glass jars, 6ml of Acetone is added and the samples are refrigerated for later lab analysis.

Filters for both total chlorophyll samples and size-fractionated chlorophyll were extracted in 6 mL of 90% acetone for 18-24 h and the resulting chl-a fluorescence was measured on a Turner Trilogy fluorometer calibrated against a solid standard and a chl-a extract (Sigma).

### **Particulate Silicate**

500ml of seawater is filtered through 0.8 micron polycarbonate filters. Filters are rinsed with pH adjusted milli-Q (De-ionised water) and folded and placed inside 50ml falcon tubes. Samples are then placed inside an oven at low heat for 18-20 hours.

### **Cellulose nitrate**

1L of seawater is filtered through cellulose nitrate filters. Filters are rinsed with pH adjusted milli-Q (De-ionised water) and place in a petri dish. Filters are then placed in a low heat oven for 18-20 hours before being turned into permanent microscope slides.

## **12. SEM, HPLC and phytoplankton isolations**

*Lucie Munns (National Oceanography Centre, Southampton)*

### **CTD Sampling**

For selected stainless steel CTD casts 2-3 of litres water from each of 6-8 depths, with high resolution in the upper ~60 meters was drawn into blacked out carboys.

### **HPLC**

In most cases 1 L was filtered onto Whatman GFF filters for HPLC analysis in NOC Southampton and sometimes 1 L onto Whatman GFF filters for HPLC analysis at University of Essex (James Fox). After filtration, samples were quickly transferred to cryovial tubes and stored in the -80°C freezer.

### **SEM**

Between 300 – 1000 ml (depending on the amount of phytoplankton in the water) was filtered onto 0.8µm polycarbonate filters (with a 5.0µm backing filter), rinsed with pH adjusted MilliQ (>8.0) to remove salts and dried in the oven (40°C) for at least 4 hours. Samples were then stored in petri slides at room temperature. SEM images of these filters will be taken in Southampton to look at the abundance and community composition of coccolithophores and diatoms.

### **Phytoplankton isolations**

At chosen depths at some stations, plankton was concentrated using 0.8µm polycarbonate filters to filter 300-500 ml of water until ~20 ml remained. This concentrated sample was transferred by pipette into a 50 ml centrifuge tube and 10-20 ml of K/20 culture media with soil extract was added. Samples were then incubated in the temperature controlled container (16°C) at 20% light level in a 16:8 hour light:dark cycle. Isolation of any coccolithophore strains growing in these samples will be attempted at NOC Southampton.

Event	008	029	048	066	072	077	079	084	106	133	135	137	154	155	160	161	192	194	196	199
CTD	003	008	012	016	020	025	027	031	036	040	042	044	048	049	053	054	062	064	066	068
Site	CCS	CCS	CCS	Fe08	Fe10	Fe13	Fe14	CS2	CS2	Fe01	Fe02	Fe15	Fe04	Fe06	O4	O2	A	J2	J4	J6
Niskin																				
1		+							+											
2			+					+												
3																				
4								XO												
5	XO																			
6							XO									XO				
7	XO	XO+						XO+	+						XO		+		+	
8		XO	+					+								XO	XO	XO		XO
9	XO						XO		i						XO					
10		XO															+	XO	XO+i	XO
11	XO	XO		XO		XO		XO							XO+	XO	XO			
12							XO	XO	+							XO			XO+i	XO
13	XO				XO	XO									XO	XO+	+	XO		XO
14		XO+		XO+	XO	XO	XO						XO				XO			
15	XO			XO		XO		XO	i	XO	XO		XO	XO	XO	XO				
16		XO+		XO	XO		XO			XO+		XO	XO				+	XO	XO+	XO
17	XO		+	XO+	XO	XO		+			XO	XO <i>i</i>	XO			XO	XO		XO	
18		XO+	+			XO	XO		i		XO	XO		XO	XO+					XO
19	XO			XO	XO	XO		XO		XO+	XO		XO	XO	XO+			XO	XO <i>i</i>	
20		XO		XO	XO		XO	XO	+	XO	XO	XO <i>i</i>	XO				XO			
21					XO	XO			i	XO+		XO	XO	XO					XO	
22		+	+	XO+			XO	XO+	+	XO	XO	XO <i>i</i>	XO				+	XO	+	XO
23			+		XO	XO		+	+	+	XO	XO					XO			
24				+							XO			XO						

Symbols: x = HPLC (NOCS)      + = HPLC (Essex)      o = SEM      i = isolation

## 13. Autotrophic rate processes and standing stocks

*Alex Poulton & Chris Daniels (National Oceanography Centre, Southampton), and Ian Murray (Marine Institute)*

### **Rationale**

As part of the pelagic component of the Shelf Sea Biogeochemistry (SSB) research programme we made biogeochemical rate measurements from seven CTD profiles (see Table 13.1) at six light depths (see Table 13.2) at the two major process sites (Central Celtic Sea, Shelf Edge) sampled during DY033. Rate measurements included short term (6 h) measurements of carbon fixation and phosphorus uptake, and the production of dissolved organic carbon (DOC) and phosphorus (DOP), as well as long term (24 h) measurements of calcite production, and size-fractionated (0.2-2  $\mu\text{m}$ , 20-20  $\mu\text{m}$ , >20  $\mu\text{m}$ ) primary production. Chlorophyll (total and size-fractionated) concentrations were also measured and samples were collected for determination of coccolithophore abundance and particulate opal concentrations. During DY033 we also ran several iron uptake experiments at offshore sites and across the shelf in order to determine biological iron uptake and iron partitioning between particulates, dissolved and colloidal fractions. Each of these iron uptake experiments were ran in parallel with measurements of carbon and phosphorus uptake.

Combined these measurements will allow us to examine biogeochemical interactions between carbon (C), phosphorus (P) and iron (Fe) uptake (and recycling) by summer phytoplankton communities in the Celtic Sea, as well as examine growth dynamics of coccolithophores and diatoms in shelf sea environments. An identical suite of samples and measurements has now been collected on DY018 (November 2014) and DY029 (April 2015) allowing seasonal changes in these processes to be fully examined. The underlying goal of this work is to address the hypothesis that 'autotroph community structure and resource (nutrients, light) availability influence the stoichiometry of organic matter through increasing C:N:P:Si:Fe ratios under resource limited conditions'.

### **Methods**

#### **General water sampling**

Water samples were collected from pre-dawn (2-3 am) CTD casts from six light depths (60%, 40%, 20%, 10%, 5% and 1% of surface irradiance) in the water column. Light depths were determined based on the assumption that the chlorophyll maximum was situated at the 5% light level. Water samples for chlorophyll-*a* analysis, coccolithophore enumeration (cellulose nitrate filters), particulate opal and all rate measurements (see section 4) were collected in dark brown opaque bottles.

#### **Chlorophyll-*a* and biogenic silica ( $\text{bSiO}_2$ )**

Water samples for total chlorophyll-*a* (chl-*a*) analysis were collected from six to eight depths for most CTD casts while samples for size-fractionated chl-*a* were only collected from the six depths on the pre-dawn CTD casts. Measurements of total chl-*a* were collected by filtering 200 ml sea water samples through 25 mm diameter Whatman GFF filters (effective pore size 0.7

µm). Samples for size-fractionated chl-a were collected by sequentially filtering 200 ml of seawater through 47 mm diameter 20 µm, 2 µm and 0.2 µm filters. Filters were extracted in 6 mL of 90% acetone for 18-24 h and the resulting chl-a fluorescence was measured on a Turner Trilogy fluorometer calibrated against a solid standard and a chl-a extract (Sigma).

Water samples for analysis of particulate silica concentrations were only collected from pre-dawn CTD casts. Particulate silica samples were collected by filtering 500 mL seawater samples through 25 mm 0.8 µm pore size Nucleopore filters, oven drying (50-60°C, 10-12 h) and stored in 15 mL centrifuge tubes for later analysis following Poulton et al. (2006).

### **Coccolithophore enumeration**

Samples for the determination of coccolithophore abundance and community composition were collected in parallel to rate measurements of calcite production (daily calcification). 0.5 to 1 L water samples were filtered through 25 mm 0.8 µm pore size Whatman cellulose nitrate filters under gentle pressure. Cellulose nitrate filters were then oven dried (50-60°C, 10-12 h) and stored in Millipore petri-slides until they are converted into permanent glass slides using Norland Adhesive no. 74 following Poulton et al. (2010). Slides prepared from cellulose nitrate filters will be examined under cross-polarised light to enumerate coccolithophore cells and detached coccoliths.

### **Rate measurements**

Biogeochemical rate measurements were made at seven process sites (Table 13.1) during DY033 using radioactive isotopes (<sup>14</sup>C, <sup>33</sup>P, <sup>55</sup>Fe) following methodology adapted from several references (see Table 13.3). To summarise, carbon fixation (CFIX) and phosphorus uptake (PUP) were made on short term incubations (6 h), and the production of dissolved organic carbon (pDOC) and dissolved organic phosphorus (pDOP) were measured on filtrates from these incubations. Over 24 h, calcite production (CAL), and size-fractionated primary production (SF-PP). Iron uptake (FeUp) was measured over 12 hour incubations with sampling from sacrificial bottles at six time points (30 min, 60 min, 90 min, 3 hrs, 6 hrs, 12 hrs).

**Table 13.1. Station details for biogeochemical rate measurements.** CCS indicates the Central Celtic Sea site, CS2 indicates the Shelf Edge site. Rate measurement abbreviations are: CAL, daily calcite production; CFIX, short term (6 h) carbon-fixation; *p*DOC, production of dissolved organic carbon; PUP, short term (6 h) uptake of phosphorus; *p*DOP, production of dissolved organic phosphorus; SFPP, size-fractionated (>20  $\mu$ m, 20-2  $\mu$ m, 2-0.2  $\mu$ m) primary production; FeUp. All measurements apart from FeUp were made at 6 light depths in the water column. ND indicates not determined.

Date	Site	Event number	CFIX	<i>p</i> DOC	PUP	<i>p</i> DOP	CAL	SF-PP	FeUp
14 July	CCS	025	X	X	X	X	X	X	ND
15 July	CCS	044	X	ND	X	ND	X	X	ND
15 July	CCS	047	X	ND	X	ND	ND	ND	X
17 July	Fe09	067	X	ND	X	ND	ND	ND	X
19 July	CS2	083	X	X	X	X	X	X	ND
20 July	CS2	102	X	X	X	X	X	X	ND
20 July	CS2	103	X	ND	X	ND	ND	ND	X
22 July	Fe02	136	X	ND	X	ND	ND	ND	X
24 July	CCS	162	X	X	X	X	X	X	ND

**Table 13.2. Niskin bottles sampled from each CTD cast.**

Event number	NMF CTD ID	Niskin bottles
025	005ss	24, 20, 18, 16, 14, 11
044	009ss	24, 22, 20, 16, 12, 10
047	010tt	23
067	017tt	iDs 76-78, 72-74
083	030ss	24, 19, 18, 16, 14, 12
102	033ss	24, 23, 21, 19, 17, 14
103	034tt	162-165
136	043tt	212-213, 210-211
162	055ss	24, 20, 18, 14, 12, 10

**Table 13.3. Methodological details of the rate measurements made on DY033.**

Rate measurement	Incubation length	Methodological reference(s)	Synopsis
Carbon fixation (CFIX)	6 h (dawn + 6 h)	(1, 2)	<sup>14</sup> C-labelled sodium bicarbonate addition; three light and one dark bottle.
DOC production (ρDOC)	6 h (dawn + 6 h)	(3)	0.2 μm filtrate from CFIX light and dark bottles; 3 depths (60%, 5% and 1%) only; acidified to remove <sup>14</sup> C-DIC as <sup>14</sup> C-CO <sub>2</sub> .
Phosphate uptake (PUP)	6 h (dawn + 6 h)	(4)	<sup>33</sup> P-labelled orthophosphoric acid addition; three light and one dark bottle; P addition <5% of ambient concentrations.
DOP production (ρDOP)	6 h (dawn + 6 h)	(4, 5)	0.2 μm filtrate from PUP light and dark bottles; three depths (60, 20 and 1%) only; 1 M NaOH addition to precipitate DIP and centrifuged.
Calcite production (CAL)	24 h (dawn-dawn)	(1)	<sup>14</sup> C-labelled sodium bicarbonate addition; uses Micro-Diffusion Technique (Balch et al. 2000) to separate inorganic and organic particulate production; three light and one formalin-killed blank; measures coccolithophore calcite production (daily calcification) and community primary production.
Size-fractionated primary production (SF-PP)	24 h (dawn to dawn)	(2)	<sup>14</sup> C-labelled sodium bicarbonate addition; sequential filtering through 20 μm, 2 μm and 0.2 μm filters.
Iron uptake (FeUp)	12 h (dawn + 12 h)		<sup>55</sup> Fe spiked in trace concentrations; filtered through 0.02 μm, 0.2 μm and 2 μm; one set of 0.2 mm washed with Ti-EDTA. (Note CFIX and PUP measured in parallel and filtered through 0.2 μm and 2 μm filters).

Methodological references: (1) Poulton et al. (2014); (2) Poulton et al. (2006a); (3) Lopez-Sandoval et al. (2011); (4) Reynolds et al. (2014); (5) Karl and Tien (1992); (6) Poulton et al. (2006b).

Differences in temperature at different light depths resulted in incubations being carried out in three different incubators: upper water column depths (60, 40, 20%) were incubated in a adapted refrigeration container, lower water column depths (10, 5 and 1%) were incubated in two laboratory culture cupboards (LMS, Fytoscope). The light levels in the refrigeration container (see Richier et al. 2014) were replicated through the use of LED light panels, grey light (neutral density) filters of varying optical density. The light in the LMS and Fytoscope were also modified to reflect in situ light availability using neutral density filters. All incubators had the same light:dark cycle and a day length of 16 hours. The light levels (60%, 40%, 20%, 10%, 5% and 1% of incidental irradiance) had absolute light intensities which had been chosen to reflect the average light available at that percentage irradiance depth during November (pre-determined from 5 yrs of satellite PAR data). The absolute instantaneous light intensity for each

light depth was checked using a  $4\pi$  light sensor (Biospherical Instruments). These absolute irradiance levels for DY033 were: 25.3 mol photons  $m^{-2} d^{-1}$  (60% of average July-August incidental irradiance), 15 mol photons  $m^{-2} d^{-1}$  (40%), 5.8 mol photons  $m^{-2} d^{-1}$  (20%), 4.2 mol photons  $m^{-2} d^{-1}$  (10%), 1.4 mol photons  $m^{-2} d^{-1}$  (5%) and 0.5 mol photons  $m^{-2} d^{-1}$  (1%).

## **References**

Karl and Tien (1992), MAGIC: A sensitive and precise method for measuring dissolved phosphorus in aquatic environments. *Limnology and Oceanography* 37, 105-116.

Lopez-Sandoval et al. (2011), Dissolved and particulate primary production along a longitudinal gradient in the Mediterranean Sea. *Biogeosciences* 8, 815-825.

Poulton et al. (2006a), Phytoplankton carbon fixation, chlorophyll-biomass and diagnostic pigments in the Atlantic Ocean. *Deep Sea Research II* 53, 1593-1610.

Poulton et al. (2006b), Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean. *Global Biogeochemical Cycles* 20, GB4002.

Poulton et al. (2010), Coccolithophore dynamics in non-bloom conditions during late summer in the central Iceland Basin (July-August 2007). *Limnology and Oceanography* 55, 1601-1613.

Poulton et al. (2014), Coccolithophores on the North-West European shelf: calcification rates and environmental controls. *Biogeosciences* 11, 3919-3940.

Reynolds et al. (2014), Evidence for production and lateral transport of dissolved organic phosphorus in the eastern subtropical North Atlantic. *Global Biogeochemical Cycles* 28, 805-824.

Richier et al. (2014), Phytoplankton responses within highly-replicated shipboard carbonate manipulation experiments around the Northwest European continental shelf. *Biogeosciences* 11(17), 4733-4752.

## 14. Gross and net production estimates from triple O isotopes

(Chata) Isabel Seguro (University of East Anglia)

Full title: Shelf-sea gross and net production estimates from triple oxygen isotopes and oxygen-argon ratios in relation with phytoplankton physiology

### Objectives

1. Infer spatial variations of net ( $N$ ) and gross ( $G$ )  $O_2$  production rates from  $O_2/Ar$  [ $N(O_2/Ar)$ ] and triple oxygen isotopes [ $G(^{17}O)$ ] in the Celtic Sea (spring bloom).
2. Derive 24 h in-situ production rates from diurnal changes at one process station.
3. Calculate seasonally integrated production estimates from cruise-to-cruise changes.
4. Compare  $G(^{17}O)$  with FRRF-based physiological turnover and  $CO_2$  fixation rates.
5. Use statistical tools to relate  $N$  and  $G$  to production estimates based on  $^{15}N$ - and  $^{14}C$ -uptake, respiration rates, light availability, nutrient supply, community structure and other SSB consortium data products.

### Introduction

In order to increase the resolution of dynamic waters such as shelf seas, continuous underway measurement systems have been demonstrated a good choice.

Membrane inlet mass spectrometry is a technique invented by Hoch and Kok in 1963. This technique permits the sampling of dissolved gases from a liquid phase. The principle is a semipermeable membrane that allows dissolved gases pass through but not the liquid into the mass spectrometer flying tube. The advantages of the MIMS are several with the exception of the precision. These can be mounted onboard which permit the analysis of several dissolved gases of seawater in situ and continuously. Phytoplankton photosynthesis and respiration understandings can be achieve from the analysis of stable isotopes distribution of certain gases or to obtaining chemical exchange rates (Beckmann et al., 2009). This is also a very simple way to analyze volatile gases, do not require exhaustive preparation of material for sampling nor the use of chemicals, and data is recorded directly in the computer without the need of post analysis in the laboratory.

The dissolved  $O_2$  in seawater gives an estimation of the NCP. Physical process such us variation in temperature and pressure, transport fluxes, diffusion and bubble injection also changes the amount of dissolved  $O_2$  in seawater. Now is clear that we need a tracer that separates oxygen produced biologically from the one added or removed from physical processes. Argon does not react during photosynthesis or respiration and have similar solubility and diffusivity than  $O_2$ . Variation in  $O_2$  concentration due to biological production can be separated from physical forces using the  $\Delta O_2/Ar$  ratio.

Craig and Hayward (1987) were the first ones describing a technique for using  $\Delta O_2$  and Ar differences to determinate NCP. The equation that is now used is  $\Delta O_2/Ar$  ratio, and is defined as follow in Eq. (1).

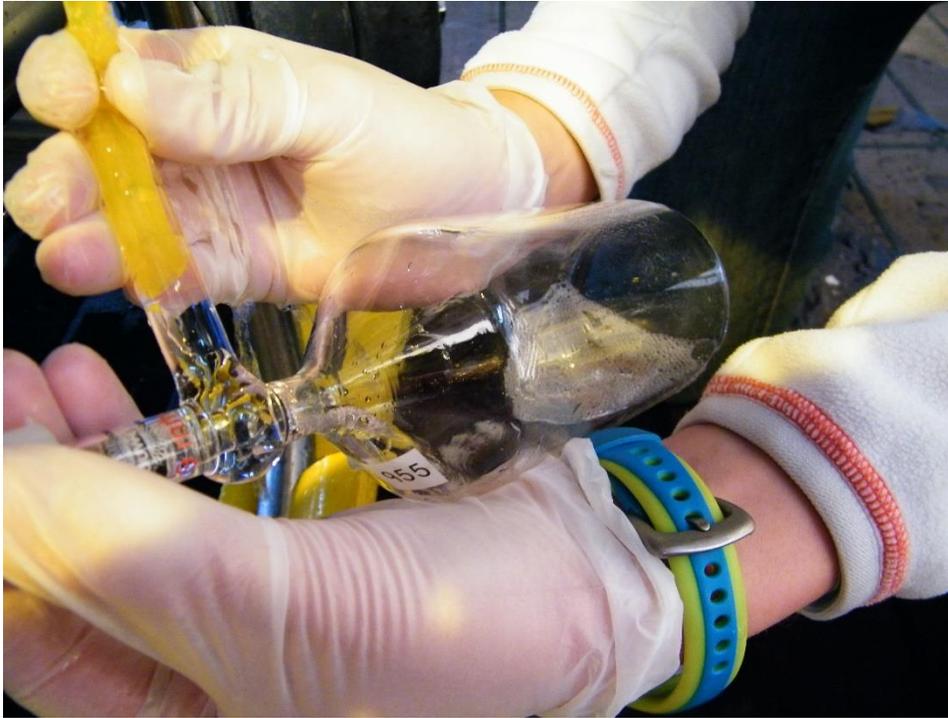
$$\Delta O_2/Ar = [c(O_2)/c(Ar)]/[c_{sat}(O_2)/c_{sat}(Ar)]-1 \quad (1)$$

Where  $c$  is the dissolved gas concentration ( $\text{mol m}^{-3}$ ) and  $c_{sat}$  is the saturation concentration at known temperature, pressure and salinity (Kaiser, 2005).

This technique was considered very sensitive (Hoch and Kok, 1963) but nowadays, even if modern MIMS have high sensitivity (Beckmann et al., 2009) these instruments lack the ultra-high precision of IRMS. Thus, in addition to the underway measurements, discrete samples were taken for calibration purposes and to measure the  $^{17}O/^{16}O$  and  $^{18}O/^{16}O$  isotope ratio analysis of dissolved oxygen. Triple oxygen isotope measurements combined with  $O_2/Ar$  data can be used to estimate the ratio of net community production to gross production and the ratio of gas exchange to gross production. Again, in combination with suitable wind-speed gas-exchange parameterizations this can be used to estimate gross production over large regional scales at timescales of weeks to months.

## **Methodology**

Continuous measurements of dissolved  $N_2$ ,  $O_2$ , and Ar were made by MIMS on board RRS Discovery. The ship's underway sampling system was used to pump water through a tubular Teflon AF membrane (*Random Technologies*). The membrane was connected to the vacuum of a quadrupole mass spectrometer (*Pfeiffer Vacuum Prisma*). The intake of the underway sampling system is located at the bow at a nominal depth of 5-6 m. The water from the underway sampling system passed through an open bottle at several litres per minute to remove macroscopic bubbles and to avoid pressure bursts. A flow of about 45 ml/min was continuously pumped from the bucket through the membrane, using a gear pump (*Micropump*). In order to reduce  $O_2/Ar$  variations due to temperature effects and water vapour pressure variations, the exchange chamber with the membrane was held at a constant temperature of 13°C (3 to 5°C below the sea surface temperature, to avoid temperature-induced supersaturation and subsequent bubble formation) The flight tube was in a thermally insulated box maintained at 50°C.



#### *Sampling for isotope mass spectrometry*

In addition to the continuous underway measurements, I also analysed CTD samples with the MIMS in order to characterize the depth profile of the  $O_2/Ar$  ratio in regions of the Celtic Sea.

The  $O_2/Ar$  ratio measurements will be calibrated with discrete water samples taken from the same seawater outlet as used for the MIMS measurements. 200 cm<sup>3</sup> samples were drawn into pre-evacuated glass flasks poisoned with 7 mg  $HgCl_2$  [Quay *et al.*, 1993]. These samples will be later analysed with an isotope ratio mass spectrometer (IRMS, *Thermo Finnigan*) for their dissolved  $O_2/Ar$  ratios and the oxygen triple isotope composition relative to air [Hendricks *et al.*, 2004]. Raw  $O_2/Ar$  ion current ratio measurements were made every 10 to 20 s and had a short-term stability of 0.05%.

$O_2$  concentrations were also measured continuously with an optode (*Aanderaa* model 3830, serial no. 241), readings at 10 s resolution. The measurements were taken from the open bottle connected to the underway sampling system used to measure the  $O_2/Ar$  ratios as well. This optode attached to the underway system and both the stain steel and titanium CTDs optode were calibrated by automatic Winkler titration of discrete water samples with potentiometric endpoint detection. Calibration of the underway water was made four times, which were taken in triplicate. The highest error was assumed to be due to the wrong calibration of some of the volume of the bottles. Comparisons between Winkler samples from Niskin bottles fired at the surface and Winkler samples taken from the non-toxic supply at the same time of the surface firing agreed well (standard deviation of 0.045, error of 0.0008). That means that the non-toxic underway sea water supply is working in good conditions and the Winkler method is measuring consistently during the cruise.



*From left to right: Winkler station, Marine snow catcher camera, MIMS and FRRf.*

### **Others**

The CTD profile has shown a stratified water column during all the cruise sampling. The mixed layer was between 30 – 80 meters deep. Peaks of chlorophyll maximum or oxygen were found within the mixed layer, been both peaks at the same depth of slightly shallower for the oxygen.

Discrete oxygen samples were taken from 6 Niskin bottles to calibrate the oxygen sensor (Polarographic membrane) of the stain steel and titanium CTDs every day. Samples were drawn carefully into borosilicate glass bottles and later analyzed by whole-bottle Winkler titration to a potentiometric endpoint. Oxygen concentration was calculated according to Culberson (1991) and blank according to Holley and Hydes (1993). The data from the Winkler measurements was given to Jo Hopkins, please read her cruise report for more information about CTD oxygen corrections.

Continuous and discrete samples were run in two FRRf systems (Fast Ocean) in parallel with O<sub>2</sub>/Ar and oxygen triple isotope. This will allow future research comparing G (<sup>17</sup>O) with FRRF-based physiological. The data will be given to James Fox (Essex PhD student).

Discrete samples for TEPs analysis (1L.) were taken and fixed with 100 ml of formaldehyde (37%). Samples will be given to Gianfranco Anastasi (UEA PhD student).

Discrete samples for zooplankton genetic determination were taken from the Marine Snow Catcher trays and fixed with buffered borax formaldehyde (4%) by Alex Poulton. Before sampling of the fast sinking particles, the tray was photographed using an imaging rig build by Stephanie Wilson. Approximately 35 pictures were taken of each tray and will be processed at a later date using Image J. Using these pictures, the size of the particles and their particulate organic carbon content can be estimated. The pictures are further scanned for any fecal pellets

to compare their proportion to other particle aggregates. Samples and photos will be given to Stephanie Erin Wilson (Bangor University).

The following discrete samples were collected:

Event	CTD	O <sub>2</sub> /Ar	<sup>16,17,18</sup> O	CTD O <sub>2</sub> sensor	FRRF	TEPS
3	1	✓		✓		
8	3	✓	✓			
25	5			✓		
27	7			✓		
29	8	✓	✓		✓	✓
47	11			✓		
48	12	✓	✓	✓	✓	
58	13			✓		
65	15			✓		
66	16	✓	✓		✓	
72	20			✓		
73	21			✓		
80	28			✓		
81	29			✓		
83	30			✓		
84	31	✓	✓		✓	
103	34			✓		
106	36	✓	✓	✓	✓	✓
130	40	✓	✓	✓	✓	
134	41			✓		
137	44			✓		
138	45			✓		
157	51			✓		

160	53	✓	✓	✓	✓	
161	54	✓	✓			
162	55			✓		
164	56	✓	✓			
192	62	✓	✓		✓	✓
193	63			✓		
194	64	✓	✓	✓		
196	66	✓	✓	✓	✓	
198	67			✓		
199	68	✓	✓		✓	
203	70			✓	✓	
204	71			✓		
218	76	✓	✓	✓		
219	77			✓		
221	78	✓	✓	✓	✓	
262	79		✓			
263	80		✓			
266	80		✓	✓		
269	83		✓			
275	85		✓			
276	86		✓			
278	87		✓			
279	88		✓			
280	89		✓			

## **Acknowledgements**

I would like to thank scientists, crew, officers and engineers of RRS Discovery Cruise DY033 for the help and good environment during the entire cruise, especially for demonstrating been high qualified professionals in difficult situations. To the iron team to allow me to join the party. And a big thank to Mark Moore for helping me to run the FRRf and for managing this cruise very well (regardless of not been able to control the weather ;-)) but giving us dolphins and even whales!



## **References**

Beckmann, K., Messinger, J., Badger, M. R., Wydrzynski, T. and Hillier, W. (2009). On-line mass spectrometry: membrane inlet sampling. *Photosynth Res*, 102, 511-22.

Culberson, C. H. (1991). WHP Operations and Methods. Dissolved Oxygen. College of Marine Studies. University of Delaware. Newark, U.S.A.

Hoch, G. and Kok, B. (1963). A mass spectrometer inlet system for sampling gases dissolved in liquid phases. *Archives of Biochemistry and Biophysics*, 101, 160-170.

Holley S. E. and Hydes D. J. (1993). Procedures for the determination of dissolved oxygen in seawater. James Rennell Centre for Ocean Circulation, 33.

Kaiser, J. (2005). Marine productivity estimates from continuous O<sub>2</sub>/Ar ratio measurements by membrane inlet mass spectrometry. *Geophysical Research Letters*, 32.

Quay, P. D., S. Emerson, D. O. Wilbur, and C. Stump (1993), The  $\delta^{18}\text{O}$  of dissolved oxygen in the surface waters of the subarctic Pacific: A tracer of biological productivity, *J. Geophys. Res.*, 98, 8447-8458.

## 15. Bacterial production measurements

Sharon McNeill (Scottish Association for Marine Science)

### Introduction

Radiolabelled leucine methods were used to determine bacterial production in the Celtic Sea. Water column and marine snowcatcher samples were chosen to correspond to respiration studies. A full list of bacterial production samples taken and analysed on board are shown in Table 15.1.

### Method

Water samples were collected from the CTD in acid washed polycarbonate bottles then incubated for bacterial production. Aliquots of 10ul leucine working solution (4 KBq ml<sup>-1</sup>) were pipetted into each 2ml sterile centrifuge tube then additions of 1.6ml sample added. For each depth two samples in duplicate were run for T0, T1, T2 and T3, then incubated either in a coolbox in the CT container at above thermocline or in an incubator set to temperature below thermocline in the RN container. Samples were fixed with 80ul of 20% paraformaldehyde (giving a final concentration of 1%). Samples were filtered with 25mm GFF and 0.2um polycarbonate filters pre-soaked in 1mM non labelled leucine in separate petri dishes, placed on the 25mm filter rig with the GFF as a backing filter. The sample pipetted into each filter holder and then deionised water used to rinse any remaining sample from each vial. Both samples at each time point were combined and filtered as one. The 0.2um polycarbonate filter was placed into a scintillation vial and dried overnight in the fume hood, 4ml Optiphase Hi-Safe II scintillant added and samples read in the scintillation counter after 24 hours. Marine snowcatcher samples were analysed on 3 fractions, suspended, slow and fast sinking using the method describe above. Marine snowcatcher fast fractions samples were taken from the respiration studies tray approximately 30ml and diluted with suspended at a 1:1 concentration.

### Calibration experiment- Leucine

Three replicate water column samples A, B and C were prepared into a 1litre polycarbonate bottle, 900ml of each filtered through a 0.2um filter vacuum cap with 100ml unfiltered making up the volume. Each replicate was sampled at T0, T6, T12, T18 and T24 for leucine, bacterial abundance counts for flow cytometer and dapi slide prep. Samples were incubated in a CT container with 20% light, and then processed as water column methods for leucine.

Table 15.1: Leucine sampling

Date	CTD	Event No.	Depth (m)	Niskin	Comments	Coordinates
14/07/2015	005-SS	25	8	24	Predawn	Lat:49 23.21N
			26	18		Long:8 37.84 W
			40	16		
			50	14		
			53	11		
			80	7		

15/07/2015	012-SS	48	20	21	Calibration exp	Lat:49 22.71 N Long:8 36.61 W
15/07/2015	MSC (Tom)	50	10		Suspended Slow Fast	Lat:49 22.77N Long:8 36.59W
15/07/2015	MSC (Tom)	53	90		Suspended Slow Dilution 1:1 (Fast:Sus)	Lat:49 22.77N Long:8 36.58W
19/07/2015	030-SS	83	5	24	Predawn	Lat:48 34.25N Long:9 30.59W
			10	18		
			15	16		
			20	12		
			35	9		
			50	7		
20/07/2015	MSC (Tom)	120	10		Suspended Slow Dilution 1:1 (Fast:Sus)	Lat:48 34.26N Long:9 30.45W
20/07/2015	MSC (Tom)	122	80		Suspended Slow Dilution 1:1 (Fast:Sus)	Lat:48 34.24N Long:9 30.48W
22/07/2015	MSC (Tom & Jerry)	142 & 144	10		Dilution exp	Lat:48 34.21N Long:9 30.55W
22/07/2015	MSC (Tom, Jerry & Hardy)	145,146 & 147	90		Dilution exp	Lat:48 34.25N Long:9 30.56W
24/07/2015	055-SS	162	5	24	Predawn	Lat:49 22.10N Long:8 37.63W
			16	18		
			32	14		
			42	12		
			55	10		
			75	7		
25/07/2015	MSC (Tom)	183	15		Suspended Slow Dilution 1:1 (Fast:Sus)	Lat:49 24.84N Long:8 36.11W
	MSC(Jerry)	190	75*		Suspended Slow Dilution 1:1 (Fast:Sus) *misfire at shallower depth	Lat:49 24.95N Long:8 35.81W
29/07/2015	070-SS	203	8	24	Predawn	Lat:49 25.48N Long:8 34.55W
			24	18		

			32	16		
			42	12		
			45	10		
			70	6		
30/07/2015	MSC (Tom)	245	10		Suspended	Lat:49 24.85N
					Slow	Long:8 33.85W
					Dilution 1:1 (Fast:Sus)	

## 16. DOM degradation experiments

Sharon McNeill (Scottish Association for Marine Science)

### Introduction

Dissolved organic matter degradation experiments were carried out to determine remineralization rates in the Celtic Sea. Water was collected at 3 stations throughout the cruise, for comparison of changes due to seasonal mixing see Table 16.1.

### Method

Water samples were filtered through pre-combusted (450 degree C for 6hrs) GF/F filters (pore size ~ 0.7µm) and transferred to 150ml amber bottles. A microbial culture was added by filtering water from the same depth through a GF/C filter (pore size ~1.2µm) and inoculated at 5% of the total volume. The degradation experiments were set up in duplicate for each depth, surface mixed layer, thermocline and ~100M (i.e. below thermocline). Bottles were then incubated in the dark either in the CT room or cold room at temperatures as similar to in situ as possible for a period of 80 days. During the incubation period 7 samples were collected (days 0,3,6,10,15,25 and 80) from amber bottles using an acid washed glass syringe with a 25mm pre-combusted GF/F filter. The filter first rinsed with deionised water 3 times before collecting samples for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), total dissolved phosphorous (TDP), inorganic nutrients, bacterial abundance, FISH, DOM fluorescence and amino acids. Inorganic nutrient and flow cytometry samples were analysed on the ship, DOM fluorescence and amino acids by C Davis (Liverpool) and the rest of analysis to be completed at SAMS.

Table 16.1: DOM degradation experiments

Date	CTD	Event No.	Depth (m)	Niskin	Comments	Coordinates
14/07/2015	008-SS	29	10	20	Surface mixed layer	Lat:49 23.44N
			45	15	Thermocline	Long:8 37.85W
			100	4	Below thermocline	
19/07/2015	031-SS	84	10	21	Surface mixed layer	Lat:48 34.26N
			20	20	Thermocline	Long:9 30.59W
			100	6	Below thermocline	
26/07/2015	062-SS	192	15	20	Surface mixed layer	Lat:51.12.78N
			35	11	Thermocline	Long:6 7.60W
			80	5	Below thermocline	

## 17. Community and bacterial respiration

*E. Elena García-Martín and Carol Robinson (University of East Anglia)*

Contact: E.E García-Martín (Enma.Garcia-Martin@uea.ac.uk)

Full title: Measurements of community and bacterial respiration by changes in O<sub>2</sub> concentration after 24 hours incubation, in vivo INT reduction capacity method and continuous oxygen decrease using oxygen optodes

### **Background**

Dissolved oxygen (O<sub>2</sub>) in seawater is produced by photosynthesis and consumed by respiration and photochemical reactions in the surface waters. Community respiration (CR) represents the magnitude of biologically fixed carbon that is available for export to the deep ocean or for transference to upper levels of the marine food-web. Bacteria play an important role in this balance, although their contribution to community respiration has been difficult to characterize due to methodological difficulties to separate them from the rest of the plankton community. The possible biases that the separation could cause in the bacterial respiration rates could be minimised with the applicability of the in vivo INT reduction method (ivINT). This method allows size fraction without distorting the natural community as the size fraction is performed after the incubation. Moreover, the short incubation time needed (<1-2 h) reduces the likelihood of community structure changes and corresponds with the incubation times for bacterial production determinations. This method has been successfully applied to samples from the water column and in this cruise a modification of the method was applied to the marine snow samples.

### **Aims**

1. To determine the daily plankton community respiration with Winkler technique (CR<sub>O<sub>2</sub></sub>) and oxygen optode throughout the water column from CTD samples.
2. To determinate plankton community (CR<sub>INT</sub>) and bacterial respiration (BR<sub>INT</sub>) with the ivINT method at short incubation times from CTD samples.
3. To quantify community and bacterial respiration of the three fractions of the Marine Snow Catcher (MSC), i) suspended, ii) slow sinking and iii) fast sinking, above and below the thermocline with Winkler technique and ivINT method.
4. To log and quantify continuously the respiration of fast and suspended particles with oxygen optodes.

### **Sampling and analytical methodology of CTD samples**

Water samples (5-6 L) were collected from predawn CTD casts at each station from 4-5 depths in the euphotic zone and 1 depth in the aphotic zone (see Table 1 for specific details of the depths and stations) in 10-20 L carboys. The depth of the aphotic sampling was coincident with the depth of the deep deployment of the MSC, around 10-30 m below the thermocline.

Each carboy was subsampled for community respiration by in vitro changes of dissolved oxygen concentration, community and bacterial respiration by the size-fractionated in vivo INT reduction capacity method and oxygen optodes (see below).

### **Community respiration by in vitro changes of dissolved oxygen concentration**

CR<sub>O2</sub> was measured by monitoring changes in oxygen concentrations after 24h dark bottle incubations. Dissolved oxygen concentration was measured by automated precision Winkler titration performed with a Metrohm 765 Titrino titrator, using a photometric end point (Carritt & Carpenter, 1966).

Ten gravimetrically calibrated 60 mL glass Winkler bottles were carefully filled with water from each depth. Water was allowed to overflow during the filling, and special care was taken to prevent air bubble formation in the silicone tube. Five bottles were fixed at the start of the incubation (“zero”) with manganese sulphate and a solution of sodium iodide/sodium hydroxide. The other five bottles were placed underwater in temperature controlled incubators inside the constant temperature room for 24 hours. The incubation temperatures were  $\pm 1$  °C of the in situ temperature. Bottles were removed from the incubators after 24 hours and fixed as above. All bottles were analysed within 24 hours. Community respiration was calculated from the difference in oxygen concentration between the means of the “zero” measurements and the replicate dark incubated samples.

The sodium thiosulphate titrant was calibrated every day before the analysis of the samples and the coefficient of variation of the calibration was <0.1%.

### ***In vivo* community and bacterial respiration (CR<sub>INT</sub> and BR<sub>INT</sub>) by INT reduction method.**

Five 200 mL dark glass bottles were filled with seawater from each 10 litre carboy from the CTD. Two replicates were immediately fixed by adding formaldehyde (2% w/v final concentration) and used as killed controls. Twenty minutes later all five replicates were inoculated with a sterile solution of 7.9 mM 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyl tetrazolium salt (INT) to give a final concentration of 0.8 mM. The solution was freshly prepared for each experiment using Milli-Q water. Samples were incubated in the same temperature controlled water bath as the dissolved oxygen bottles for ca. 0.5- 1 hour and then fixed by adding formaldehyde, as for the killed controls. After 20 minutes, samples were sequentially filtered through 0.8 and onto 0.2  $\mu$ m pore size polycarbonate filters, air-dried, and stored frozen in 1.5 mL cryovials at  $-20^{\circ}\text{C}$  until further processing (at UEA). The CR<sub>INT</sub> (i.e. the sum of respiration of the >0.8  $\mu$ m and 0.2-0.8  $\mu$ m fractions) and BR<sub>INT</sub> (considered as the respiration of the 0.2-0.8  $\mu$ m fraction) will be measured following Martínez-García et al. (2009).

A time-course experiment was carried out in order to know the optimal incubation time for these samples.

### ***Optimal incubation time test***

14 samples of 100 mL of surface water CTD were collected and dispensed to glass bottles. Incubations were undertaken in the dark for 0, 0.5, 1, 1.5, 3 and 6 hours at in situ temperature. Optimal incubation time was considered as the time period, prior to saturation of the formazan concentration, during which the relationship between concentration versus time remained linear.

### **Continuous monitoring of in vitro oxygen evolution**

Changes in oxygen concentration were measured continuously with three optode systems (YSI ProODO) and two Neofox O<sub>2</sub> optodes. Prior to each experiment, all sensors were air-calibrated simultaneously. Two different depths were measured: one with the YSI optodes and the other with Neofox (see Table 17.1 for further details)

Two glass YSI optode chambers of 100 mL were filled from water samples collected from one depth sampled. Water (120-150 mL) from the same depth was collected and filtered through 0.2 µm pore size polycarbonate filters. A third chamber of 100 mL was filled with this filtered sea water (FSW) and monitored continuously with the third YSI optode sensor. The filtered water was used as a background for abiotic changes in oxygen concentration due to any temperature changes during the incubation. Samples for bacterial abundance were collected from the FSW sample (see Glen Tarran report for the bacterial abundance protocols).

Chambers containing samples were gently stirred. Incubation was performed at the in situ temperature conditions  $\pm 0.5$  °C inside a dark water bath (Figure 17.1). After half an hour of acclimation, oxygen concentration was recorded every three minutes for 21-24 hours .

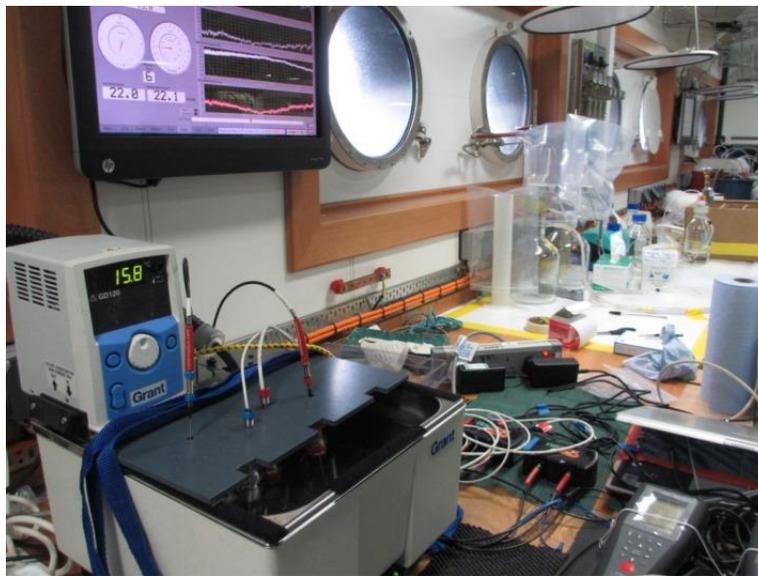


Figure 17.1. YSI ProODO and Neofox optodes and the water bath used.

### **Sampling and analytical methodology of MSC samples**

Small (100 L) marine snow catchers were used during this cruise (Figure 17.2). Two depths were sampled at each station: 10 m and 70 m. The sampling was done early evening for the shallower deployment (ca. 18.00 h) and at sunset for the deep one (ca. 20.00-21.00 h), avoiding any external light during the collection of the particles.

Following deployment and after 1 hour 20 minutes period of settling, water samples from the suspended, slow and fast sinking fractions were collected (see Table 2 for sampling data). Suspended water was collected siphoning the water required from the top tap of the MSC and the slow sinking water was collected from the lower tap (see Garcia-Martin and Lozano DY029 cruise report for a schematic draw).



Figure 17.2. Small Marine Snow Catchers ready for deployment and the recovery manoeuvre (pictures by Carol Robinson)

Water samples (2 - 6 L) of suspended material and slow sinking particles were collected in 2-10 L carboys and transported in darkness to the Controlled Temperature room of the RRS Discovery for subsequent subsampling and analysis of community and bacterial respiration, as outlined below. Special care was taken to prevent the exposure of the samples to light, the room was completely in darkness and two red lights were used while handling the samples. Water with suspended material was used to rinse all the Winkler and ivINT bottles before collecting the water samples. The fast sinking material was collected from the tray at the bottom of the MSC (Figure 17.2 and 17.3). The tray was transported to the controlled temperature room and the whole sample was used for

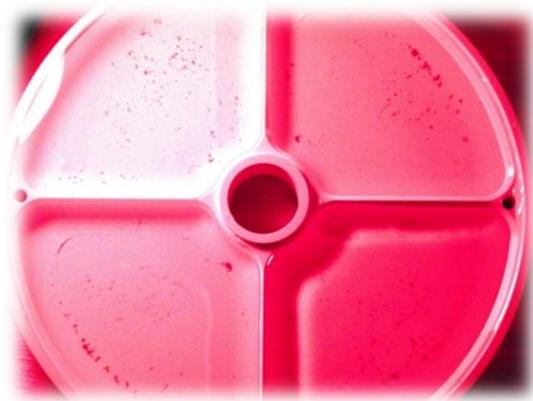


Figure 17.3. Marine snow catcher tray with fast sinking particles

respiration measurements. Particles were collected with a turkey baster and put into a 500 mL plastic beaker from where it was subsampled for the different methodologies. As the water volume was not enough for the three techniques, 1:1 dilutions (suspended: fast) were applied.

### **Community respiration by in vitro changes of dissolved oxygen concentration**

CR was measured by monitoring changes in oxygen concentrations after 24h dark bottle incubations as outlined above (section 1.1). Ten gravimetrically calibrated 60 mL glass Winkler bottles were carefully filled with water from the suspended material sample and the other ten with the slow sinking fraction. The sampling methodology differed for the fast sinking fraction. 15 mL sample of fast sinking particles were collected with a 10 mL precise pipette and put into 10 gravimetrically calibrated 30 mL glass Winkler bottles. These were then topped up with suspended material sample water (15 mL). If there was sufficient sample, one or two bottles were filled only with fast sinking particles. Five replicate bottles of each fraction were fixed at the start of the incubation (“zero”) and the other five bottles were placed underwater in temperature controlled incubators inside the CT room for 24 hours. Experiments were undertaken to check any differences between diluted and non diluted fast sinking particle incubations. After 24 hours, the incubated samples were fixed as above. Respiration was estimated from changes in oxygen concentration as described above (see section 1.1 for further details).

### ***In vivo* community and bacterial respiration (CR<sub>INT</sub> and BR<sub>INT</sub>) by INT reduction assay**

Community and bacterial respiration were measured by the ivINT reduction method as outlined in section 1.2. For the Marine Snow Catcher samples, five 80-100 mL dark glass bottles were filled with suspended and slow sinking seawater samples. Five 50 mL dark glass bottles were filled with 15-20 mL of fast sinking sample and 15-20 mL of suspended material sample, maintaining the same dilution ratio as the Winkler technique. See section 1.2 for further details of the analysis.

#### ***Dilution test***

A dilution test was applied in the CS2 station in order to test if the dilution applied to the fast sinking particles affected the respiration rates measured with the Winkler and ivINT technique. Ten gravimetrically calibrated 60 mL glass Winkler bottles were carefully filled with suspended water, ten 30 mL with fast sinking water and another ten 30 mL with 15 mL of suspended water and 15 mL of fast sinking particles (dilution 1:1). Five replicate bottles of each treatment were fixed at the start of the incubation (“zero”). The other five replicates bottles of each treatment were placed underwater in temperature controlled incubators inside the CT room for 24 hours. After 24 hours, all incubated replicates were fixed in the same manner as the “zero” ones.

### **Continuous monitoring of in vitro oxygen evolution.**

Oxygen concentration was recorded continuously from the suspended and fast sinking particles. The third YSI oxygen sensor measured any oxygen change in 0.2 µm filtered suspended material water. Further information on the methodology can be found in section 1.3.

The two Neofox optodes measured oxygen change in the fast sinking particles and FSW.

## **Preliminary results**

4 vertical profiles of six depths were sampled for community and bacterial respiration rates (Winkler and ivINT method).

3 incubations for continuous oxygen consumption (ProODO YSI optodes and NEofox optodes) were run with water samples from the CTD.

7 MSC were sampled to calculate the carbon remineralization rates of the different fractions above and below the thermocline.

1 time-course experiment for the ivINT reduction capacity method was completed with a sample taken from the CTD.

1 dilution test was performed in order to check if the dilution of the fast sinking particles with suspended water from the same depth affected the remineralization rates (Winkler and ivINT method).

Respiration analyses with Winkler technique were all performed on board, but data will be processed on return.

## **Problems encountered**

The depth of the MSC sample may be in error as the only way to measure the depth was by measuring the metres of wire out. Sometimes the wire was not completely vertical and so the sampling depth would be shallower than required. Attaching salinity or pressure loggers to the MSC would confirm the depth of sampling. Nutrient measurements were taken from all the MSC casts to verify the depths sampled, however these were not available in real time. Several misfires occurred during this cruise and the MSC did not fire at 75 m for the deep sample for the dilution test (22/07/2015), or for the 25<sup>th</sup> and 30<sup>th</sup> July 2015 experiments.

## **Acknowledgements**

We would like to acknowledge all the crew of the RSS Discovery 033 and the NMF staff for their help and patience in the deployment of the Marine Snow Catcher. Particular thanks to Chata Seguro, Emlyn Jones, Sharon McNeill, Nick Stephens and Steve Woodward for help with the deployments. Equally importantly, the chief scientist Mark Moore and our other scientific colleagues on board who generously assisted and supported our work throughout DY033.

## **References**

Carritt, D.E. and Carpenter, J.H., 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater; a NASCO Report. *Journal of Marine Research*, 24: 286-319.

Martínez-García, S., Fernández, E., Aranguren-Gassis, M., Teira, E., 2009. *In vivo* electron transport system activity: a method to estimate respiration in natural marine microbial planktonic communities. *Limnology and Oceanography Methods* 7, 459-469.

Table 17.1. Station and CTD cast details for respiration measurements.

Date	CTD ID	Event		Longitude	Nisking bottle	Depth (m)	Variable
		Number	Latitude				
14/07/2015	5	25	49 23.21 N	8 37.84 W	24	8	Winkler, ivINT, YSI optode
					18	26	Winkler, ivINT, Neofox optode
					16	40	Winkler, ivINT
					14	50	Winkler, ivINT
					11	53	Winkler, ivINT
					7	80	Winkler, ivINT
19/07/2015	30	83	48 34.25 N	9 38.59 W	24	5	Winkler, ivINT, YSI optode
					18	10	Winkler, ivINT, Neofox optode
					16	15	Winkler, ivINT
					12	20	Winkler, ivINT
					9	35	Winkler, ivINT
					7	50	Winkler, ivINT
24/07/2015	55	161	49 22.10 N	8 37.63 W	24	5	Winkler, ivINT, YSI optode
					18	16	Winkler, ivINT, Neofox optode
					14	32	Winkler, ivINT
					12	42	Winkler, ivINT
					10	55	Winkler, ivINT
					7	75	Winkler, ivINT
29/07/2015	70	203	49 25.28 N	8 34.55 W	24	8	Winkler, ivINT
					18	24	Winkler, ivINT
					16	32	Winkler, ivINT
					12	42	Winkler, ivINT
					10	45	Winkler, ivINT
					6	70	Winkler, ivINT

Table 17.2. List of collected water samples for respiration measurements from the small Marine Snow Catcher (SMSC).

Date	Event Number	Latitude	Longitude	Depth (m)	Fraction	Variable
15/07/2015	50	49 22.77 N	8 36.59 W	10	suspended slow fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT Winkler, ivINT, O <sub>2</sub> sensors
15/07/2015	53	49 22.77 N	8 36.58 W	80	suspended slow fast	
20/07/2015	120	48 34.26 N	9 30.45 W	10	suspended slow fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT Winkler, ivINT, O <sub>2</sub> sensors
20/07/2015	122	48 34.24 N	9 30.48 W	80	suspended slow fast	
22/07/2015	142	48 34.21 N	9 30.55 W	10	suspended fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT, O <sub>2</sub> sensors
	143	48 34.21 N	9 30.55 W	10	fast	
	144	48 34.21 N	9 30.62 W	10	fast	
22/07/2015	145	48 34.25 N	9 30.56 W	90	suspended fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT, O <sub>2</sub> sensors
	146	48 34.25 N	9 30.56 W	90	fast	
	147	48 34.25 N	9 30.56 W	90	fast	
25/07/2015	183	49 24.84 N	8 36.11 W	15	suspended slow fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT Winkler, ivINT, O <sub>2</sub> sensors
25/07/2015	186	49 24.84 N	8 36.11 W	75	Misfire	
25/07/2015	190	49 24.959	8 35.81 W	75	suspended slow fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT Winkler, ivINT, O <sub>2</sub> sensors
30/07/2015	245	49 24.85	8 33.85 W	10	suspended slow fast	Winkler, ivINT, O <sub>2</sub> sensors Winkler, ivINT Winkler, ivINT, O <sub>2</sub> sensors
30/07/2015	250	49 24.83	8 33.89 W	Misfire		
30/07/2015	251	49 24.83	8 33.90 W	Misfire		
30/07/2015	252	49 24.83	8 33.90 W	Misfire		

## 18. Pelagic nitrogen regeneration, fixation and assimilation

*Andy Rees (Plymouth Marine Laboratory)*

### **Overview**

Bacterial degradation of particulate and dissolved organic matter (P/DOM) simultaneously regenerates inorganic nutrients and renders the residual material of lower nutritional quality. Given sufficient time, the exposure of POM and DOM to a sufficiently broad range of microbes with their associated biochemical machinery renders organic material recalcitrant. This material represents a quantitatively significant form of carbon storage. The preferential regeneration and retention of nutrients such as nitrogen and phosphorous during this process, generically termed the microbial carbon pump, sustains productivity of the shelf sea region.

During this program of research, the nutrient recycling processes of  $\text{NH}_4^+$  regeneration and nitrification were examined. The former is primarily associated with bacterial degradation of organic molecules and excretion processes associated with microplankton. The latter is the two stage oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , facilitated by specific clades of bacteria and archaea. In combination,  $\text{NH}_4^+$  regeneration and nitrification have the capacity to significantly influence the concentration and composition of the dissolved inorganic nitrogen (DIN) pool, which sustains autotrophic primary production.

The processes of inorganic nitrogen assimilation were also investigated. Primarily these are autotrophic processes although bacteria may also make a contribution to observed rates. Three forms of inorganic nitrogen were used for this study;  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ . During this cruise incubations were also performed using additions of  $^{15}\text{N}-\text{N}_2$  to assess the potential for and rates of nitrogen fixation.

All rates were derived using stable isotope techniques during both observational CTD casts and Marine Snow Catcher (MSC) deployments. The aim of this research was to understand variability in N-cycle processes by investigating how rates related to water column structure and particle loading.

### **Experiments**

#### **Marine Snow Catcher**

Marine Snow Catcher (MSC, 100 L volume) experiments: The regeneration of N associated with 3 particle fractions (suspended, slow and fast sinking) was determined during MSC deployments at depths within the photic zone (approximately 10 meters) and at a depth in the lower mixed layer (approximately 70 meters). The rates of  $\text{NH}_4^+$  regeneration,  $\text{NH}_4^+$  oxidation and  $\text{NO}_2^-$  oxidation were measured on each fraction. Method details are provided below.

#### **Observational casts**

At observational stations water was collected at three depths (approximately 5, 30 and 70 meters). The regeneration and assimilation of each form of dissolved inorganic nitrogen (DIN;  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) was measured at each depth. Rates of nitrogen

fixation were assessed routinely at surface only but on separate occasions rate incubations were performed on 1) water collected from the depth of the deep chlorophyll maximum and 2) on picked colonies of filamentous *Trichodesmium*.

## **Methods**

The regeneration of inorganic nitrogen was investigated using  $^{15}\text{N}$  dilution methods (Clark et al 2006, 2007). The MSC was used to collect seawater from a specific depth. N-regeneration rates were determined in three particulate fractions (suspended particle (SP); slow sinking particle (SSP); fast sinking particle (FSP)). Following deployment and a 2 hour period of settling, 15L of SP seawater was collected from the MSC. 1.5L of this water was added to each of 3 2.2 L bottles containing either  $^{15}\text{NO}_3^-$ ,  $^{15}\text{NO}_2^-$  or  $^{15}\text{NH}_4^+$ . The  $^{15}\text{N}$  addition was estimated to provide a 20% enrichment of the DIN pool, based on recently determined nutrient concentration profiles. A further 4.0L of water containing SSP was collected from the MSC directly into bottles containing  $^{15}\text{N}$ . FSP were recovered in a tray from the MSC, and in a constant temperature room under low intensity red light the particle tray was screened for magnetic particles. FSP were then transferred to 2.2L bottles containing  $^{15}\text{N}$ . One third of the total FSP load (equating to the FSP content of approximately 100 L of seawater) was added to each of 3 bottles (each representing one process). SP water was used to dilute the FSP to a total volume of 1.5L. The 9 x 2.2 L bottles (3 processes, 3 particles fractions) were placed in a temperature controlled room for 30 minutes to ensure that the isotope was homogeneously distributed. Following this period, bottles were used to fill 1.0L incubation bottles and placed in an incubator simulating appropriate light and temperature for a period of 24 hours. The remaining  $^{15}\text{N}$  amended seawater was filtered using 47mm GF/F. The filter was retained to enable a measure of particulate carbon and nitrogen content. The filtrate was used to derive the pre-incubation DIN concentration and isotopic enrichment by synthesising indophenol from ammonium and sudan-1 from nitrite (nitrate is quantitatively reduced to nitrite prior to further analysis). Following the incubation period, samples were filtered using GF/F. The filter was retained to enable an estimation of the particulate carbon and nitrogen content of the incubated sample. The filtrate was used to generate post-incubation samples for DIN concentration and isotopic enrichment.

Indophenol was synthesised in samples by adding the first reagent (4.7 g phenol and 0.32 g sodium nitroprusside in 200 mL Milli Q water) in the proportion of 1 mL per 100 mL of sample volume, mixing the sample and leaving for 5 minutes. The second reagent (1.2 g sodium dichloro-isocyanurate and 2.8 g sodium hydroxide in 200 mL Milli Q) was then added in the proportion of 1 mL per 100 mL sample volume, mixed and left for 5 hours at room temperature for indophenol development. Indophenol was collected by solid-phase extraction (SPE) as described below. Sudan-1 was synthesised by adding the first reagent (0.8 g of aniline sulphate in 200 mL 3M HCl) to samples in the proportion 0.5 mL per 100 mL sample volume. Samples were mixed and left for 5 minutes to homogenise after which sample pH was verified to be < 2.0. Reagent 2 (24 g NaOH and 0.416 g 2-naphthol in 200 mL Milli Q) was added in the proportion 0.5 mL per 100 mL sample volume. Samples were again mixed, left for 5 minutes before sample pH was verified to be approximately 8.0. Sudan-1, the development of which was complete after 30 minutes of incubation at room temperature, was collected by SPE as described below.

Deuterated internal standards were added to samples immediately prior to SPE collection. Deuterated indophenol and deuterated sudan-1 were synthesised according to methods described previously (Clark et al. 2006; 2007). Standard solutions in methanol were prepared ( $100 \text{ ng} \cdot \mu\text{L}^{-1}$ ) and the concentration verified against analytical standard solutions (Sigma-Aldrich). Appropriate volumes of deuterated internal standards (i.e. comparable to sample size) were added to samples following acidification by citric acid and prior to SPE collection.

Indophenol and sudan-1 were collected by SPE using 6 mL/500 mg C18 cartridges (Biotage, UK) which were prepared for sample collection by first rinsing with 5 mL methanol, followed by 5 mL Milli Q water and 5 mL 0.22  $\mu\text{m}$  filtered seawater. Prior to sample collection seawater samples were acidified with 1 M citric acid to a pH of 5.5, before collection by SPE under low vacuum (120 mmHg) at a flow rate of approximately 1 mL per minute without drying. Samples were then rinsed with 5 mL 0.22  $\mu\text{m}$  filtered seawater and 5 mL Milli Q water before being air dried under high vacuum (360 mmHg). Samples were stored frozen until further processing at the land based laboratory.

The assimilation of inorganic nitrogen was investigated using methods described in Clark et al 2011; 2014. Briefly, seawater collected from a specific depth was separately amended with separate  $^{15}\text{N}$  solutions of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  to a final concentration equivalent to <10% of ambient. Volumes were incubated for 3-4 hours under appropriate temperature and light conditions before collection by filtration using 25mm GF/F. The concentration of particulate nitrogen and its natural abundance of  $^{15}\text{N}$  was derived from material collected by filtration from additional volumes of un-amended seawater. The concentration of particulate nitrogen and its enrichment with  $^{15}\text{N}$  was determined by isotope ratio mass spectrometry from which the rates of nitrogen assimilation were derived.

### **Sampling events table**

<b>Event</b>	<b>Date</b>	<b>GEAR</b>	<b>Depth (m)</b>	<b>CTD bottle</b>	<b>Process</b>
025	14/07/2015	CTD05	8,50,80	21,12,5	$\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{NH}_4^+$ assimilation $\text{NH}_4^+$ Regen, $\text{NH}_4^+$ oxdn, $\text{NO}_2^-$
oxdn			8	22	$\text{N}_2$ Fixation
049	15/07/2015	MSC	10		$\text{NH}_4^+$ Regen, $\text{NH}_4^+$ oxdn, $\text{NO}_2^-$
oxdn					
055	15/07/2015	MSC	80		$\text{NH}_4^+$ Regen, $\text{NH}_4^+$ oxdn, $\text{NO}_2^-$
oxdn					
083	19/07/2015	CTD30	2, 20, 50	22, 10, 5	$\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{NH}_4^+$ assimilation $\text{NH}_4^+$ Regen, $\text{NH}_4^+$ oxdn, $\text{NO}_2^-$
oxdn			2	21	$\text{N}_2$ Fixation
118	20/07/2015	MSC	10		$\text{NH}_4^+$ Regen, $\text{NH}_4^+$ oxdn, $\text{NO}_2^-$
oxdn					

121	20/07/2015	MSC	80		NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
153	23/07/2015	CTD48	2	24	N <sub>2</sub> Fixation
162	24/07/2015	CTD55	5, 55, 75	21, 8, 5	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> assimilation NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
181	25/07/2015	MSC	10		NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
184	25/07/2015	MSC	75		NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
	26/7/2015	CTD62	surf	24	N <sub>2</sub> Fixation
196	28/7/2015	CTD66	surf		N <sub>2</sub> Fixation
203	29/07/2015	CTD70	8, 46, 70	21, 8, 7	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> assimilation NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
			8	22	N <sub>2</sub> Fixation
246	30/07/2015	MSC	10		NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
248	30/07/2015	MSC	70		NH <sub>4</sub> <sup>+</sup> Regen, NH <sub>4</sub> <sup>+</sup> oxdn, NO <sub>2</sub> <sup>-</sup> oxdn
218	30/7/2015	CTD76	45	13	N <sub>2</sub> Fixation

### **Status of samples and data availability**

No data is available during the cruise. The samples are stored at -20°C in the form of solid-phase extraction cartridges and GF/F filters to be analysed at the land-based laboratory. The former will be used for isotope dilution studies and the later for quantifying the carbon and nitrogen content of incubated samples and for assimilation rate determinations. Analysis will take approximately 3 months, after which a high quality data set is expected to be delivered.

### **References**

Clark, D. R., T. W. Fileman, and I. Joint (2006), Determination of ammonium regeneration rates in the oligotrophic ocean by gas chromatography/mass spectrometry. *Mar. Chem.* 98: 121-130.

Clark, D. R., A. P. Rees, and I. Joint (2007), A method for the determination of nitrification rates in oligotrophic marine seawater by gas chromatography/mass spectrometry. *Mar. Chem.* 103: 84-96.

Clark, D. R., Miller, P., Woodward, M and Rees, A. (2011). Inorganic nitrogen assimilation and regeneration in the coastal upwelling region of the Iberian Peninsula. *Limnol. Oceanogr.*, 56(5), 2011, 1689–1702

## 19. Nitrous oxide and methane

*Nick Stephens and Andy Rees (Plymouth Marine Laboratory)*

Nitrous oxide and methane are biogenically produced trace gases whose atmospheric concentrations are increasing at a rate in the order of 0.7 ppbv y<sup>-1</sup>. Both gases are radiatively active, contributing approximately 6% and 15% of “greenhouse effect” respectively, whilst N<sub>2</sub>O contributes to stratospheric ozone depletion and CH<sub>4</sub> limits tropospheric oxidation capacity.

The oceans are generally considered to be close to equilibrium relative to the atmosphere for both gases. However, oceanic source/sink distributions are largely influenced by oxygen and nutrient status and regulatory processes are complicated and are currently not well understood. Shelf seas and ocean areas overlying sub-oxic waters and upwelling areas dominate the ocean source and saturations of up to 300% have been reported.

### Aim

To perform vertical profiles of N<sub>2</sub>O and CH<sub>4</sub> concentration in order to assess variability in the source-sink strength and exchange of both gases across benthic-pelagic, pycnocline and ocean-atmosphere boundaries within the Celtic Sea.

### Methods

Samples were collected from CTD bottles at stations identified below. 1 litre seawater samples were equilibrated with compressed air and headspace analysis performed onboard using flame ionisation detection-gas chromatography (FID-GC) and electron capture detection-gas chromatography (ECD-GC) for CH<sub>4</sub> and N<sub>2</sub>O respectively<sup>1</sup>. Atmospheric concentrations were determined by the same methods using samples collected from the ships bow into a sealed Tedlar bag.

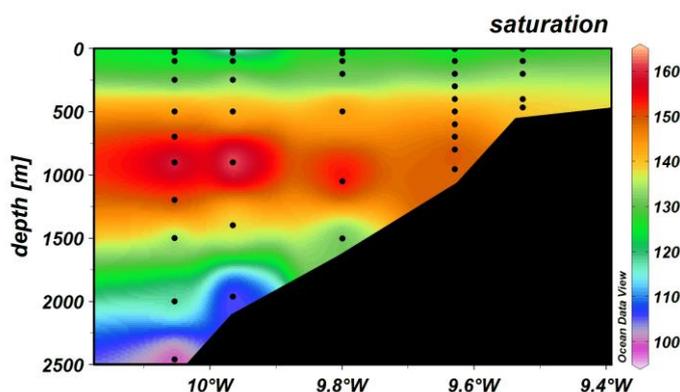


Figure 19.1. Example of preliminary N<sub>2</sub>O saturation calculated from the data obtained during the shelf edge Fe transects (Days 12-14)

<sup>1</sup> *Upstill-Goddard R.C., A.P. Rees & N.J.P. Owens (1996) Simultaneous high-precision measurements of methane and nitrous oxide in water and seawater by single phase equilibration gas chromatography Deep-Sea Research I. Vol. 43, No. 10, PP. 1669-1682*

## **N<sub>2</sub>O, CH<sub>4</sub> sampling date and position**

Day	Station	CTD	Lat (°N)	Lon (°W)	Niskin	Depths Sampled
13	CCS	3	49.4893	8.5891	1,5,11,15,19,21	137,80,45,35,12,surf
14	CCS	5	49.3870	8.6308	2,3,7,9,11,14,16,18,19,24	140,110,80,60,53,50,40,26,15,8
14	CCS	8	49.3908	8.5951	1,3,8,16,17,22	133,100,60,40,30,4
15	CCS	12	49.3783	8.6102	2,4,5,9,11,13,15,17,20,23	133,100,80,60,49,45,43,40,20,4
16	Fe	16	48.3853	9.9173	1,4,5,6,7,9,13,21,23	2170,1000,650,500,250,100,60,10,4
17	Fe9	18	48.3993	9.9007	2,5,7,11,14,15,21,23	1810,1400,1000,500,200,100,35,10
17	Fe10	20	48.4102	9.8892	1,3,4,7,10,13,16,19,20,22,24	1420,1100,950,500,300,150,70,50,40,20,surf
18	Fe11	23	48.4222	9.8784	1,4,8,10,12,14,16,18,21,24	895,800,500,400,300,200,80,40,20,4
18	Fe13	25	48.4372	9.8632	1,3,7,11,15,19,23,	470,400,250,100,50,20,2
18	Fe14	27	48.4917	9.8085	1,4,6,12,18,22	240,150,100,50,20,surf
19	CS2	30	48.5703	9.6599	2,3,4,7,9,12,18,24	190,140,90,50,35,20,10,4
19	CS2	31	48.5711	9.5049	2,4,5,8,15,23	191,120,100,60,35,4,
20	CS2	33	48.5708	9.5097	2,4,6,8,10,12,14,16,22,24	190,150,110,70,50,32,25,20,10,5
20	CS2	36	48.5711	9.5093	2,3,5,9,18,23	190,150,100,50,20,4
21	Fe1	40	48.2060	10.0527	1,3,5,7,9,11,12,13,15,19,23	2460,2000,1500,1200,900,700,500,250,100,30,4
21	Fe2	42	48.2396	9.9650	1,5,8,12,13,14,19,24	1963,1400,900,500,250,100,35,4
22	Fe15	44	48.2992	9.7990	2,6,11,14,15,19,23	1502,1050,500,200,100,40,surf
23	Fe4	48	48.3700	9.6287	1,3,4,6,7,9,10,11,12,22	956,800,700,600,500,400,300,200,100,4
23	Fe6	49	48.4088	9.5260	1,3,7,9,11,24	467,400,300,200,100,4
24	CCS	55	49.3683	8.6272	2,6,9,11,15,17,19,23	135,75,55,42,28,16,10,5
24	CCS	56	49.3683	8.6263	2,4,6,10,15,20,21,23	130,100,75,55,47,30,20,8
25	CCS	58	49.3669	8.6264	1,5,9,13,16,19,22	132,100,80,58,47,38,20
26	A	62	51.2130	6.1280	1,4,7,10,16,22	97,80,50,35,25,7
26	J2	64	50.8272	6.6647	2,4,6,10,19,22	90,70,50,40,20,8
28	J4	66	50.4047	7.2215	1,5,7,12,19,21	105,85,75,45,20,surf
28	J6	69	50.0090	7.7972	3,6,13,14,15,17	120,80,60,47,38,20
29	CCS	70	48.4213	6.5758	1,4,6,10,12,18,24,	134,100,70,46,42,24,surf
30	CCS	76	49.4095	8.5733	1,3,5,8,10,12,15,18,20,23	135,110,80,51,48,45,42,32,24,8
31	CSS	79	49.4117	8.5743	2,5,7,8	140,105,55,20
31	CCS	80	49.4150	8.9318	11,14,16,18	138,103,39,20
31	CCS	81	49.3958	8.5976	2,6,9,16	138,103,49,20
31	CCS	83	49.3954	8.5982	5,7,8	105,48,20
31	CCS	84	49.3954	8.5982	2	141
31	CCS	85	49.3969	8.5913	3,6,8,9	140,105,45,20
31	CCS	86	49.3979	8.5905	2,5,7,14	138,93,45,20
1-08	CCS	87	49.3955	8.5918	2,6,8,9	138,103,48,20
1-08	CCS	88	49.3967	8.5848	3,5,8,9	138,123,45,20
1-08	CCS	89	49.3972	8.5877	3,6,8,9	140,105,44,20

## 20. Plankton community abundance and composition

Glen Tarran (Plymouth Marine Laboratory)

### Objectives

To determine the distribution, abundance and community structure of nano- and picophytoplankton, and heterotrophic bacteria by flow cytometry and microplankton and mesophytoplankton by microscopy from CTD casts

### **Pico- and nanoplankton community structure and abundance by flow cytometry**

Seawater samples were collected in clean 250 mL polycarbonate bottles from a Seabird CTD system containing either a 24 bottle rosette of 20 L Niskin bottles on a stainless steel frame or a rosette of up to 24 10 L Niskin bottles on a titanium frame from CTD casts. Samples for enumeration of phytoplankton were stored in a refrigerator and all samples analysed within 1.5 hours of collection on high flow rate (Approx.  $170 \mu\text{L min}^{-1}$ ) for 4 minutes. Samples for bacteria enumeration were fixed immediately after collection with glutaraldehyde solution (0.5 %final concentration) and left to fix in a fridge for 30 mins. Samples were then stained with the DNA stain SYBR Green I (Sigma) for 1 hour in the dark at room temperature before analysis by flow cytometry, either at medium or low flow rate (approx.  $54$  or  $13.5 \mu\text{L min}^{-1}$  respectively) for 1 or 2 minutes, depending on the event rate  $\text{s}^{-1}$ . All samples were generally analysed within 3 hours of surfacing. Samples were measured using a Becton Dickinson FACSort flow cytometer which characterised and enumerated *Prochlorococcus* sp. and *Synechococcus* sp. (cyanobacteria), and pico- and eukaryote phytoplankton and heterotrophic bacteria, based on their light scattering and autofluorescence properties. Data were saved in listmode format and analysed onboard. Table 20.1 summarises the CTD casts sampled and analysed during the cruise.

During iron transects, the nearest sample to the surface was at 20 m, so, in order to increase near-surface resolution, samples were collected from the clean seawater supply in the clean seawater laboratory. These samples are identified in Table 20.1 as samples at 6 m where the titanium frame was used.

### **Microplankton and mesophytoplankton community structure and abundance by microscopy**

Seawater samples were collected in 250 mL amber glass jars containing 5 mL Lugol's iodine solution as a preservative. Samples were generally collected from predawn CTDs at 6 nominal light depths: 60, 40, 20, 10, 5, and 1% of surface light. Samples will be returned to the laboratory for microscopic analysis after the cruise. Table 20.1 summarises the CTD casts sampled during the cruise (items in bold).

*Table 20.1:* CTD casts sampled for phytoplankton and heterotrophic bacteria and heterotrophic flagellate community structure & abundance. Casts and depths in bold were also sampled for microplankton and mesophytoplankton community structure & abundance

DATE	EVENT	STATION	CTD	TIME on deck (GMT)	LAT N	LONG E	NOMINAL DEPTHS SAMPLED NISKIN BOTTLES SAMPLED
13-Jul	8	CCS	C003SS	13:01	49.39	-8.61	3 6 10 20 30 40 45 50 60 80 100 137 24 22 19 17 15 13 11 9 7 5 3 2
14-Jul	25	CCS	C005SS	01:35	49.39	-8.63	8 15 26 40 50 53 60 80 110 140 24 19 18 16 14 11 9 7 3 2
14-Jul	29	CCS	C008SS	13:07	49.39	-8.63	3 10 20 30 40 45 48 55 60 65 80 100 133 23 20 18 17 16 14 12 10 8 7 5 3 1
15-Jul	44	CCS	C009SS	01:36	49.38	-8.61	9 15 25 30 38 45 49 52 65 80 110 136 24 22 20 18 16 14 12 10 9 7 4 2
15-Jul	48	CCS	C012SS	11:53	49.38	-8.61	2 10 20 35 40 43 45 49 55 60 65 80 100 133 23 22 20 18 17 15 13 11 10 9 8 5 4 2
16-Jul	65	Fe08	C015T	16:35	48.39	-9.92	6 20 35 100 150 200 250 500 1000 1500 24 23 21 20 19 17 15 9 7
17-Jul	68	Fe09	C018SS	03:06	48.40	-9.90	10 20 35 40 45 60 80 100 200 300 400 500 1000 1400 23 22 21 19 18 17 16 15 14 13 12 11 7 5
17-Jul	71	Fe10	C019T	09:39	48.41	-9.89	6 20 40 60 70 90 100 200 300 350 400 500 1000 23 22 21 19 18 17 15 13 12 11 9 5
17-Jul	73	Fe11	C021T	23:48	48.42	-9.88	6 20 30 400 500 600 800 885 19 18 7 6 5 3 1
18-Jul	74	Fe11	C022T	00:32	48.42	-9.88	55 80 150 200 300 17 16 15 14 13
18-Jul	76	Fe12	C024T	04:23	48.43	-9.87	20 40 60 80 100 150 200 300 400 450 550 655 18 17 16 15 14 13 7 6 5 4 3 2
18-Jul	78	Fe13	C026T	08:20	48.44	-9.86	6 20 50 80 100 150 200 300 350 400 450 470 18 17 16 15 14 13 6 5 4 3 1
18-Jul	80	Fe14	C028T	12:03	48.49	-9.81	6 22 35 60 90 100 150 210 240 22 21 20 19 8 7 6 5
19-Jul	83	CS2	C030SS	01:35	48.57	-9.51	4 8 10 15 18 20 35 50 90 140 190 24 19 18 16 14 12 9 7 4 3 2
19-Jul	84	CS2	C031SS	11:37	48.57	-9.51	4 10 20 32 35 40 45 50 60 80 100 120 150 191 23 22 20 17 15 13 12 11 8 7 5 4 3 2
20-Jul	102	CS2	C033SS	02:42	48.57	-9.51	5 10 14 16 20 25 32 50 70 110 150 190 23 21 19 17 15 14 11 9 7 5 3 1
20-Jul	106	CS2	C036SS	11:34	48.57	-9.51	4 10 15 20 25 30 40 50 60 80 100 120 150 190 23 21 19 17 15 14 12 11 9 8 7 5 4 3 2

21-Jul	134	Fe01	C041T	21:17	48.21	-10.05	6 20 23 35 51 70 90 110 200 353 502 655 23 22 21 20 19 18 17 16 15 14 13
22-Jul	136	Fe02	C043T	03:29	48.24	-9.97	6 20 35 75 90 100 150 200 300 400 550 950 1530 23 21 20 19 18 17 16 15 14 13 9 6
22-Jul	138	Fe15	C045T	09:27	48.30	-9.80	6 20 30 55 70 90 150 200 480 600 1050 1250 1500 20 19 18 17 16 15 14 12 11 6 4 1
22-Jul	152	Fe03	C046T	00:58	48.34	-9.70	6 20 50 70 100 200 300 400 500 1000 1465 20 18 17 16 15 14 13 12 9 2
23-Jul	153	Fe04	C047T	05:54	48.37	-9.63	6 20 40 55 70 90 150 250 400 500 900 14 13 12 11 10 9 8 7 6 2
23-Jul	156	Fe06	C050T	10:54	48.41	-9.53	6 20 40 80 100 150 200 250 300 350 467 18 17 16 15 14 13 6 5 4 1
23-Jul	157	Fe05	C051T	13:04	48.38	-9.61	6 20 28 40 55 75 100 200 300 500 714 24 23 22 21 20 19 12 11 9 7
24-Jul	162	CCS	C055SS	01:33	49.37	-8.63	5 10 16 28 32 42 55 75 100 135 24 20 18 16 14 12 7 4 2
24-Jul	164	CCS	C056SS	11:49	49.37	-8.63	8 15 20 30 40 44 47 50 55 60 75 100 130 23 22 21 19 18 17 15 13 11 9 7 5 1
25-Jul	166	CCS	C058T	03:50	49.37	-8.63	6 20 35 45 58 80 100 132 22 19 16 13 9 6 1
26-Jul	192	A	C062SS	15:52	51.21	-6.13	7 15 25 27 35 50 80 92 22 19 16 13 10 7 4 1
26-Jul	194	J2	C064SS	23:58	50.83	-6.66	2 20 35 43 45 50 65 75 85 105 21 19 17 15 12 10 8 7 3 1
28-Jul	196	J4	C066SS	12:00	50.40	-7.22	2 20 35 43 45 50 65 75 85 105 21 19 17 15 12 10 8 7 3 1
28-Jul	199	J6	C068SS	18:18	50.01	-7.80	5 20 35 44 45 46 50 55 75 90 100 22 20 18 16 13 12 10 8 5 3 1
29-Jul	203	CCS	C070SS	01:59	49.42	-8.58	8 14 24 32 38 42 45 70 100 133 24 20 18 16 14 12 10 6 4 2
30-Jul	227	CCS	C076SS	02:51	49.41	-8.57	8 14 24 32 40 42 45 48 51 65 80 110 135 24 22 21 19 17 15 12 11 9 7 6 4 2
30-Jul	230	CCS	C078SS	10:31	49.41	-8.53	3 10 25 40 44 47 60 90 130 18 16 14 12 9 7 5 3 1

## **Collaborative sample analysis by flow cytometry**

### **Dilution grazing experiments**

4 dilution experiments were conducted during the cruise by Sari Giering and Seona Wells (see their cruise report for details). In addition to standard fluorometric analysis of samples, 2 and 4 mL samples were preserved with glutaraldehyde solution (0.5% final concentration) and left to fix in a fridge for a minimum of 1 hour. Samples were then analysed by flow cytometry as described above to quantify phytoplankton. 100% undiluted seawater samples were analysed for 5 minutes. 70% for 8 minutes, 40% for 12 minutes and 20% for 16.5 minutes. All samples were analysed on high flow rate (Approx.  $170 \mu\text{L min}^{-1}$ ).

### **Dissolved organic material incubation experiments.**

Samples were analysed to quantify the growth of bacteria in 3 experiments set up by Sharon McNeil at various time points throughout the cruise (see her cruise report for details).

## 21. Zooplankton biomass and metabolic rates

Sari Giering (*National Oceanography Centre, Southampton*) and Seona Wells (*University of Aberdeen*)

### **Scientific motivation**

Zooplankton play a significant role in the biogeochemical cycle of the sea as they ingest particulate organic matter and transform it into (1) CO<sub>2</sub> via respiration, (2) N-rich dissolved matter via excretion, and (3) particulate matter via the production of biomass, eggs and C-rich faecal pellets. The N-rich excretion products are likely to remain in the dissolved phase, whereas the C-rich faecal pellets may sink to depth at rates of up to 2700 m per day (review by Turner 2002). This differential recycling, with N staying in the upper ocean and C being exported to depth, has been postulated to enhance decoupling of C and N in shelf regions.

During DY033, we collected mesozooplankton (here zooplankton larger than 63 µm) to assess their abundance, elemental composition and to carry out experiments measuring excretion and grazing for mixed zooplankton communities in different size fractions (63-200 µm, 200-500 µm, >500 µm). We further measured excretion and grazing of pteropods.

### **Material & Methods**

#### **Abundance estimates**

Samples for zooplankton biomass and elemental composition were sampled using WP2 nets of two different mesh sizes (63 µm and 200 µm). At each process station, WP2 nets fitted with non-filtering cod-ends and a closing mechanism were deployed 6 times during daytime and 6 times during night-time sampling the deep chlorophyll maximum (DCM), and above and below the thermocline. Zooplankton of the size between 63-200 µm were collected using a 63-µm WP2 net hauled at 0.2 m/s. Zooplankton larger than 200 µm were collected using a 200-µm WP2 net hauled at 0.5 m/s. Collected zooplankton was size-fractionated into 63-200 µm, 200-500 µm, and >500 µm. Each size fraction was split: half was preserve in borax-buffered formaldehyde for identification and counts and half was frozen at -80°C for POC/N/P analyses. Net samples for distribution and abundance will be complemented by vessel-mounted ADCP backscatter data. Samples for microzooplankton abundance and distribution (preserved with Lugol's iodine) were taken from 6 depth from each pre-dawn CTD by Glen Tarran.

#### **Rate-series experiments**

Vital rates experiments were aimed to measure excretion and grazing of the same 'mixed community'. To do so, we transferred groups of zooplankton of one size class (63-200 µm, 200-500 µm and >500 µm) in triplicates through sequential experiments determining rates. Zooplankton was first acclimated in unfiltered sea water from the DCM for 2-3 hours. Animals were placed into filtered water and excretion of ammonium and nutrients was measured over a period of 3 hours. Animals were then transferred into 2.3-L bottles filled with unfiltered water from the DCM and incubated for 24 hours to measure ingestion of microplankton. The order is chosen to combine acclimation phases with actual rate measurements. A similar experiment was carried out with

gelatinous zooplankton. 10-30 pteropods were incubated in filtered water and excretion of ammonium and nutrients was measured over a period of 5 h. The pteropods were then transferred into 2.3-L bottles with unfiltered water and incubated for 24 hours on a plankton wheel. Size-fractionated chlorophyll (0.2-2, 2-20, and >20  $\mu\text{m}$ ) was measured before and after the incubation to estimate grazing on phytoplankton. All equipment was acid-washed, bottles and carboys were rinsed three times with incubation water prior to filling, and gloves and hair nets were worn at all times.

### **Microzooplankton grazing**

We carried out four dilution experiments to measure microzooplankton grazing (Landry & Hassett 1982). Water was collected from two depth (20 m depth and DCM) using Niskin bottles mounted on a CTD rosette. Water was either gently pre-screened with 63- $\mu\text{m}$  mesh and transferred into carboys or filtered through an in-line filter cartridge (0.2  $\mu\text{m}$ ). Dilutions were made up in separate carboys as 100%, 70%, 40% and 20% unfiltered water with the remainder being filtered water. 1.2-L glass bottles were filled in triplicates and incubated for 24 hours at in situ temperature and at the local photoperiod. Samples were taken for total Chlorophyll a (GF/F filters), pico- and nanoplankton community structure and abundance (flow cytometry), coccolithophore abundance, and microplankton (preserved using Lugol's iodine). All equipment was acid-washed, bottles and carboys were rinsed three times with incubation water prior to filling, and gloves and hair nets were worn at all times. The experiments were set up in darkness and exposure to light was minimized at all times.

### **Iron excretion by mesozooplankton**

We carried out six iron excretion experiments and one control to measure the release of Fe(II), Fe(III), total dissolvable iron (TDFe), dissolved organic carbon (DOC), and nutrients by mesozooplankton. Ambient seawater was collected from the surface (20 m) using a titanium CTD rosette and filtered (0.2- $\mu\text{m}$ ) through a cartridge to remove any particulates. Mesozooplankton were collected using a 200- $\mu\text{m}$  WP2 net fitted with a closing mechanism and a non-filtering cod-end. Depth intervals were chosen to represent excretion in the DCM and in the surface during both day and night. Upon recovery of the net, the cod-end was bagged and transported into the clean container. There, mesozooplankton were carefully screened through a submerged mesh dish (2000- $\mu\text{m}$ ) to remove larger zooplankton and briefly washed in filtered seawater. Mesozooplankton were then transferred into 9 L of filtered seawater and incubated for 5 h in darkness at the ambient sea surface temperature ( $\sim 17^\circ\text{C}$ ). Samples for Fe(II), Fe(III), total dissolvable iron (TDFe), dissolved organic carbon (DOC), and nutrients were collected before the introduction of experimental mesozooplankton ( $t_0$ ) and thereafter 11 times at intervals of increasing length (15–60 min). Samples were obtained using a peristaltic pump fitted with silicone tubing whose inlet was covered with mesh (50  $\mu\text{m}$ ). The water was stirred slowly throughout the experiments using a magnetic stirrer. At the end of the experiment, mesozooplankton were removed from the incubation water and preserved in 4% borax-buffered formaldehyde. Samples for particulate organic matter and HEME were collected from the remainder of the incubation water. All equipment was acid cleaned with 10% hydrochloric acid before use and experiments were conducted using trace metal clean protocols.

### **Sample summary**

113 nets were deployed in total (Table 21.1). Daytime/night-time distribution was sampled 6 times, resulting in a total of 105 samples for abundance and biomass and 105 samples for elemental composition. Four zooplankton vital rates experiments, two pteropod vital rates experiments and four dilution experiments were carried out. 57 biomass samples from zooplankton experiments were collected. A total of 352 ammonium and nutrient samples were collected, and analysed on board by Malcolm Woodward. From the grazing and dilution experiments, 380 samples for Chlorophyll a were taken and analysed on board using a Turner fluorometer. 128 samples for pico- and nanoplankton community structure and abundance were taken and analysed on board by Glen Tarran using flow cytometry. 188 samples for microplankton (preserved using Lugol's iodine) were taken from the zooplankton grazing experiments and dilution experiments. Lugol's-preserved samples will be analysed on shore.

### **References**

Landry MR & RP Hassett (1982) Estimating the grazing impact of marine micro-zooplankton. *Mar Biol* 67:283–288

Turner JT (2002) Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms, *Aquat Microb Ecol*, 27:57–102, doi:10.3354/ame027057

## 22. Zooplankton community respiration

*E. Elena García-Martín and Carol Robinson (University of East Anglia), Sari Giering (National Oceanography Centre, Southampton) and Seona Wells (University of Aberdeen)*

Contact: E.E García-Martín (Enma.Garcia-Martin@uea.ac.uk)

Full title: Measurements of zooplankton community respiration by changes in O<sub>2</sub> concentration and continuous oxygen decrease using oxygen optodes

### **Background**

Zooplankton contributes to the carbon biogeochemical cycle through their physiological processes (feeding and respiration rates) and represents the link between the microbial autotrophic and the nekton community.

During this cruise the turnover of organic matter (respiration rates) of zooplankton community divided in three different size fractions was examined.

### **Collection of the samples**

The zooplankton community was sampled at night at three locations (see Table 22.1 for dates and locations) using WP2 Nets of 200 and 63 µm mesh size. Collected zooplankton was size-fractioned into 63-200 µm, 200-500 µm, and >500 µm and stored in separate buckets filled with filtered sea water (FSW) until the start of the experiments the following morning.

Seawater from the continuous 5 m non-toxic supply was filtered through 0.8/0.2 µm (Pall AcroPack cartridge) and collected in a 25 L carboy at the time of the zooplankton collection and stored in the controlled temperature room (~14 °C) until the start of the experiments. The filtered sea water (FSW) was always less than one day old when used for the experiments.

### **Experimental procedure**

Three different size range animals were selected: 63 µm, 200-500 µm and > 500 µm.

The number of individuals selected was dependent on their body size and the volume of the bottles chosen. Thus, respiration of:

- 15 individuals > 500 µm were measured in 100 ml bottles,
- 30 organisms of 200-500 µm were measured in 100 ml bottles and,
- 60 individuals of 63 µm were placed into 35 ml Winkler bottles or 10-15 individuals in 4-5 ml bottles for the optical sensors.

The measurement of the respiration of the different size classes was done consecutively, starting with the >500 µm sample, then the 63 µm fraction, and finally the 200-500 µm zooplankton community. This was done in order to be able to measure concurrently the discrete Winkler O<sub>2</sub> samples and the continuous measurements with O<sub>2</sub> optical sensors. The experimental information can be found in Table 22.2.

## Respiration rates

### **Measurements of zooplankton respiration by in vitro changes of dissolved oxygen concentration.**

Dissolved O<sub>2</sub> was determined by automated Winkler titration using photometric end-point detection as described in Williams and Jenkinson (1981). Twenty gravimetrically calibrated 100 ml glass Winkler bottles, for the large and medium fraction, and 30 ml glass bottles for the smallest fraction were carefully filled with 0.8/0.2 µm FSW. Ten bottles were used to measure the respiration of the zooplankton community while the other 10 were used as a control of the oxygen decrease associated to any bacteria or microbes in the FSW. The animals were selected with the aid of a binocular microscope and placed into the ten correspondent bottles (see Fig. 21.1). The control bottles were subjected to a similar procedure as the zooplankton bottles: the tweezers were inserted in the water containing the zooplankton sample and subsequently into the Winkler bottles the same number of times as for the bottles containing zooplankton. Then, any microbes introduced into the zooplankton bottles by small drops of water or attached to the tweezers, were also added to the control bottles.



Figure 22.1. Selection of the zooplankton and the Winkler bottles used (picture by Carol Robinson).

All bottles were closed at the same time. Five bottles of each treatment (control and zooplankton) were fixed at the start of the incubation (“zero time”) with manganese sulphate and a solution of sodium iodide/sodium hydroxide. The other five bottles of each treatment were placed under water in temperature controlled incubators in the controlled temperature room for 2.5-4 hours. The incubation temperatures were  $\pm 0.5$  °C of the in situ temperature. Bottles were removed from the incubators after the incubation time and fixed as above. All bottles were analysed within the next 24 hours.

Zooplankton community respiration was calculated from the difference in oxygen concentration between the means of the “zero” measurements and the replicate dark incubated samples. The respiration measured in the FSW in the three different fractions were not statistically different from zero, except for the Event 201. Thus, the

respiration measured in the zooplankton bottles could be attributed primarily to zooplankton.

Two extra bottles were filled with zooplankton samples for particulate organic matter analysis (see Giering & Wells report for further information).

### **Measurements of zooplankton respiration by continuous O<sub>2</sub> optical sensors**

Two different sized chambers were used for the O<sub>2</sub> continuous recording:

- a) 100 ml for the two largest fractions and
- b) 5 ml for the smallest fraction.

Three YSI ProODO optical sensors and two Neofox probes were used simultaneously: one of each brand (YSI and Neofox) were inserted in the chamber containing zooplankton, one YSI probe was inserted in a chamber containing 0.8/0.2 µm FSW and the third YSI and second Neofox were used to measure the oxygen concentration of FSW sample filtered through 0.2 µm pore size polycarbonate filters. The 0.2 µm sample was considered to be free of any living organisms and was used as a control for abiotic changes in oxygen concentration associated to any temperature changes during the incubation. The three sensors were air-calibrated simultaneously, at the beginning of the experiment. Incubations were performed at the in situ temperature conditions  $\pm 0.5$  °C inside a dark water bath. After half an hour of acclimation, oxygen concentration was recorded every three minutes during 3 - 4 hours.

Oxygen consumption rates were determined as the slope of the oxygen concentration decrease as a function of time.

### **Particulate organic carbon content**

The two chambers used with the oxygen sensors (YSI and Neofox probes) and the two extra Winkler ones filled with zooplankton samples were filtered for particulate organic carbon analyses.

### **References**

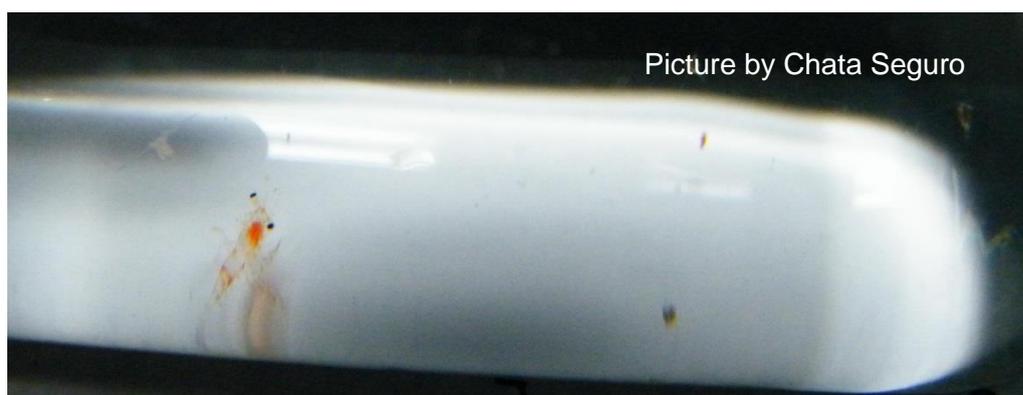
Carritt, D.E. and Carpenter, J.H., 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater; a NASCO Report. *Journal of Marine Research*, 24: 286-319.

Table 22.1. Nets casts sampled for zooplankton community respiration

Date	Net number	Event Number	Latitude	Longitude	Depth opened (m)	Depth closed (m)	Mesh size (µm)
17/07/2015	30	69	48 23.98 N	9 54.02 W	60	0	WP2 200 µm
	31	70	48 23.96 N	9 53.98 W	60	0	WP2 63 µm
22/07/2015	63	150	48 34.22 N	9 30.11 W	60	0	WP2 63 µm
	64	151	48 34.21 N	9 29.98 W	60	0	WP2 200 µm
29/07/2015	76	201	49 25.48 N	8 34.55 W	60	0	WP2 200 µm
	77	202	49 25.48 N	8 34.55 W	60	0	WP2 63 µm

Table 22.2. Summary of the characteristics of the different zooplankton respiration experiments performed.

Date	Size fraction (µm)	N organisms (discrete sample)	Bottle volume discrete O2 sample (ml)	N organisms (optical sample)	Bottle volume optical O2 sample (ml)	Incubation T discrete O2 (°C)	Incubation T optical O2 sample (°C)	Incubation time (h)
17/07/2015	>500	15	100	15	100	15.3	16.2	3.6
	200-500	30	100	30	100			3.9
	63	60	30	10	5			4.7
23/07/2015	>500	15	100	15	100	15.5 - 16	16.2	4.3
	200-500	30	100	30	100			4.1
	63	90	60	60	5			4.6
29/07/2015	>500	15	100	15	100	15 15.3	16.2	3.8
	200-500	30	100	30	100			3.86
	63	60	30	10	5			4.45



## 23. Trace metal sampling

*Antony Birchill, Matthew Fishwick and Simon Ussher (University of Plymouth), and Dagmara Rusiecka (National Oceanography Centre, Southampton and IfM GEOMAR, Kiel)*

Sample logs for all Ti-CTD casts and fish sampling are available in the Appendix. Samples were collected for trace metal analysis in both the dissolved and particulate fractions using the dedicated trace metal 10 L OTE bottles mounted on a Ti-frame rosette system.

The trace metal samples collected will be analysed at different institutes for differing parameters:

Total dissolvable, dissolved and soluble Iron – Antony Birchill and Matthew Fishwick at the University of Plymouth

Total dissolvable and dissolved Trace Metals (excluding iron) – Dagmara Rusiecka at NOCS and IfM GEOMAR.

Iron(II) – Ship-board analysis by Antony Birchill (University of Plymouth).

Ligands – Dagmara Rusiecka (NOCS and IfM GEOMAR).

Suspended Particulate Material (SPM) – Angela Milne (University of Plymouth).

A total of 1341 profile seawater samples were collected over the 34 trace metal casts. 881 of these were for iron analysis and 396 were for trace metal analysis and 64 samples for Fe binding ligand analysis. At each station, selected depths were sampled for Suspended Particulate Material resulting in 135 samples. At each deployment of the trace metal rosette, unfiltered samples were collected for macronutrients from all OTE bottles and at selected depths for salinity, oxygen and chlorophyll *a* for sensor calibration.

In addition, selected casts were sampled for flow cytometry (Glen Tarran, Plymouth Marine Laboratory), alkalinity (Mark Moore, NOC), dissolved organic matter (Claire Davis, University of Liverpool), Fe isotopes (Jessy Klar, NOC), Cr isotopes (Rachel James, NOC), N<sub>2</sub>O (Andy Rees, PML) and SPM. Separate to the water column profiles, seawater was also collected for a number of incubation experiments (including <sup>55</sup>Fe uptake and zooplankton grazing). These additional samples are detailed in the log sheets (contained in the appendix).

Underway surface samples were collected by pumping surface seawater into a trace metal clean sampling laboratory using a Teflon diaphragm pump (Almatec A-15, Germany) connected by an acid-washed braided PVC tubing to a towed fish positioned at approximately 2 - 3m depth alongside the ship. Both unfiltered and filtered (0.2 µm Sartobran P membrane filter capsule, Sartorius) seawater samples were collected over 4 transects; Fe1, Fe2, Fe3 and the J line. A total of 190 surface seawater samples were collected at 30 time points. This includes 76 for Fe analysis (30 total dissolvable, 30 dissolved and 25 soluble) and 58 for Trace Metal analysis (29 total dissolvable, 29 dissolved and 21 for ligands). Samples for nutrient analysis were collected at every time point.

### **Problems encountered**

Over the casts sampled for trace metals, several OTE bottles either did not fire or the bottles did not fully close and therefore these depths were not sampled. These are detailed in the

individual cast sample logs in the appendix. Bottle 5 seemed to be leaking more regularly towards the end.

An issue with the conducting cable on the 21<sup>st</sup> July 2015, during the Fe-1 transect, resulted in the cable needing to be cut and re-terminated.

Deployment and use of the clean tow-fish in the port side position worked well. The tubing could withstand rougher waters in part because it was cable tied and taped to the steel cable ~5 feet above the fish body. The tow-fish was deployed with cable ties on the tubing which comes out of the nose to avoid the hose slipping out of the fish and larger (1/2") braided hose was pushed through the body of the fish making a tighter fit. Sampling was avoided between 06:00 and 08:00 which was the daily pumping time for waste from the port side and the pump was turned off when on station. Regular contact was maintained with engineering/bridge during fish sampling periods.

With regards to the clean sampling laboratory, the improvements made to the facility (since last used on DY017, DY018 and DY033) have greatly improved its workability in terms of bottle racking, gassing and the ability to sample more efficiently. However, a couple of issues still remain and a couple of new ones have arisen.

- The opening/closing of the outer doors (the ones used to access the changing area) still remains as issue. Windows, or some other means of notification, need to be added so it is known when the inner laboratory door is open therefore maintaining a clean working environment in the sampling area. Visibility from the changing area through to the deck lab would also prevent opening the door when someone is passing by (this has nearly happened on a couple of occasions).
- The re-spacing of the bottles is good however this has unfortunately meant that the 2 outer bottles (1 and 24) are extremely close to a wall are therefore difficult to rack and, in bottle 24s case, very difficult to sample from (the tap points towards the wall).

## **Total dissolvable, dissolved and soluble iron**

*Antony Birchill, Matthew Fishwick and Simon Ussher (University of Plymouth)*

### **Objectives**

Iron (Fe) is an essential nutrient for primary productivity in the ocean. Due to its low solubility iron can be a limiting factor for the growth of phytoplankton in the open ocean as well as in coastal seas (de Baar et al., 1990; Hutchins and Bruland, 1998; Martin and Fitzwater, 1988). It has become evident that the atmosphere (Duce and Tindale, 1991), rivers (De Baar and de Jong, 2001), hydrothermal activity (Tagliabue et al., 2010 ; Klunder et al.,2011) and advection of shelf derived sediment to the open ocean (Bucciarelli et al., 2001; Lam and Bishop, 2008) are significant transport pathways for iron to the ocean. Fe fluxes from shelf seas to the open ocean are poorly constrained, although estimates indicate they could be 2-10 times higher than atmospheric inputs (Elrod et al. 2004) and thus potentially be a major contributor to the oceanic Fe cycle. Shelf edge biogeochemical processes that result in Fe export to the ocean are not well understood and key questions remain about the magnitude and significance of Fe fluxes from the shelf to the open ocean. We aim to investigate and quantify the supply and transport of iron in the shelf region off the North West of Scotland.

## Sampling protocol

On recovery, the 10 L OTE bottles were transferred into a clean sampling laboratory where they were immediately sampled for oxygen, nutrients, salinity and total dissolvable iron before being pressurised to approximately 7 psi with 0.2 µm filtered air using an oil free compressor. After the collection of particulate samples (see section on Particulate Trace Metals), a Sartobran 300 (Sartorius) filter capsule (0.2 µm) was used to collect filtered seawater samples into clean LDPE sample bottles. Bottles and caps were rinsed 3 times with the filtered sample before being filled. All samples, including underway samples, were acidified to 0.024 M (UpA HCl, Romil) and stored, double bagged, for shore based analysis.

## Samples collected

A total of 881 samples were collected for total dissolvable, dissolved and soluble iron as detailed in Table 23.1.

## Sample analysis

Samples for dissolved iron will be analysed at the University of Plymouth after 2 months acidification, whereas samples for total dissolvable iron will be left for at least 6 months prior to analyses. Flow Injection with chemiluminescence detection (FI-CL) (Obata et al. 1993; de Jong 1998; Klunder et al. 2011) will be used for all sample analyses using Toyopearl AF-650-M resin for pre-concentration.

## References

- Bucciarelli E., Blain, S., Treguer, P., 2001. Iron and manganese in the wake of the Kerguelen Islands (Southern Ocean). *Marine Chemistry*, 73, 21-36.
- de Baar, H.J.W., Buma, A.G.J., Nolting, R.F., Cadee, G.C., Jacques, G. and Treguer, P.J., 1990. On iron limitation of the Southern Ocean: experimental observation in the Weddell and Scotia Seas. *Mar. Ecol. Progr. Ser.*, 65(2): 105-122.
- De Baar, H.J.W., de Jong, J.T.M., 2001. Distributions, Sources and Sinks of Iron in Seawater. Chapter 5 in: Turner, D. and Hunter, K.A. (eds.) *Biogeochemistry of Iron in Seawater*, IUPAC Book Series on Analytical and Physical Chemistry of Environmental Systems, Volume 7, pp. 123-254.
- De Jong, J. T. M., Den Das, J., Bathmann, U., Stoll, M. H. C., Kattner, G., Nolting, R. F. & De Baar, H. J. W. 1998. Dissolved iron at subnanomolar levels in the Southern Ocean as determined by ship-board analysis. *Analytica Chimica Acta*, 377, 113-124.
- Duce, R.A. and Tindale, N.W., 1991. Atmospheric transport of iron and its deposition in the ocean. *Limnol. Oceanogr.*, 36: 1715-1726
- Elrod, V. A., Berelson, W. M., Coale, K. H. and Johnson, K. S. 2004. The flux of iron from continental shelf sediments: A missing source for global budgets. *Geophysical Research Letters*, 31
- Klunder, M. B., Laan, P., Middag, R., De Baar, H. J. W., and Van Ooijen, J. C. 2011. Dissolved iron in the Southern Ocean (Atlantic sector). *Deep-Sea Research Part II-Topical Studies in Oceanography*, 58, 2678-2694

Hutchins, D.A. and Bruland, K.W., 1998. Iron-limited diatom growth and Si : N uptake ratios in a coastal upwelling regime. *Nature*, 393(6685): 561-564.

Lam, P.J., and Bishop, K.B., 2008. The continental margin is a key source of iron to the HNLC North Pacific Ocean. *Geoph. Res. Lett.* 35, L07608.

Martin, J.H. and Fitzwater, S.E., 1988. Iron-deficiency limits phytoplankton growth in the northeast pacific subarctic. *Nature*, 331(6154): 341-343.

Obata, H., Karatani, H. & Nakayama, E. 1993. Automated-Determination of Iron in Seawater by Chelating Resin Concentration and Chemiluminescence Detection. *Analytical Chemistry*, 65, 1524-1528

## **Total dissolvable and dissolved trace metals**

*Dagmara Rusiecka (National Oceanography Centre, Southampton and IfM GEOMAR, Kiel)*

### **Objectives**

Iron is well established as a limiting element for phytoplankton growth, however the role and cycling of other trace elements are less understood and there is a lack of data on the concentration and distribution of these elements in the global ocean. While elements such as cadmium, zinc and cobalt have a biological role, reflected in their nutrient like profiles, other trace elements can be used as tracers of inputs to the ocean, e.g. aluminium (Al) is an indicator of aerosol deposition (Tria et al., 2007), and manganese (Mn) can indicate sedimentary or hydrothermal inputs (Johnson et al., 1992; Middag et al., 2011). As with Fe, there is a paucity of data concerning the input, and cycling, of trace metals from shelf regions. The questions surrounding the magnitude and export of Fe from the shelf to the open ocean also apply to a suite of trace metals. We aim to investigate and quantify the supply and transport of selected trace metals from the shelf off the North West of Scotland.

### **Sampling protocol**

Following recovery of the Ti-rosette, the OTE bottles were transferred into a clean sampling laboratory where they were immediately sampled for oxygen, nutrients, salinity and total dissolvable trace metals before being pressurised to approximately 7 psi with 0.2 µm filtered air using an oil free compressor. After the collection of particulate samples (see section on Particulate Trace Metals), a Sartobran 300 (Sartorius) filter capsule (0.2 µm) was used to collect filtered seawater samples into clean LDPE sample bottles. Bottles and caps were rinsed 3 times with the filtered sample before being filled. All samples, including those from the underway system, were acidified to 0.016 M (UpA HCl, Romil) and stored, double bagged, for shore based analysis.

### **Sample analysis**

Samples will be analysed for a range of trace metals e.g. Ag, Al, Mn, Cd, Zn, Cu, by inductively coupled mass spectrometry (ICP-MS) at IfM GEOMAR (Milne et al. 2010). For Al analysis, flow injection with fluorescence detection (Resing and Measures, 1994) will be used following the modified method of Brown and Bruland (2008). Dissolved samples will be analysed after 2 months acidification whereas dissolvable samples will be left for at least 6 months before analysis.

## References

- Brown, M. T. and Bruland, K. W. 2008. An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. *Limnology and Oceanography-Methods*, 6, 87-95
- Johnson, K. S., Berelson, W. M., Coale, K. H., Coley, T. L., Elrod, V. A., Fairey, W. R., Iams, H. D., Kilgore, T. E. & Nowicki, J. L. 1992. Manganese flux from continental margin sediments in a transect through the oxygen minimum. *Science* 257, 1242-1245.
- Middag, R., de Baar, H. J. W., Laan, P. & Klunder, M. B. 2011. Fluvial and hydrothermal input of manganese into the Arctic Ocean. *Geochimica et Cosmochimica Acta* 75, 2393-2408.
- Milne, A., Landing, W., Bizimus, M. and Morton, P. 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica Chimica Acta*, 665, 200-207
- Resing, J. A., and C. I. Measures (1994), Fluorometric determination of Al in seawater by flow injection analysis with in-line preconcentration, *Anal. Chem.*, 66(22), 4105-4111
- Tria, J., Butler, E. C. V., Haddad, P. R. & Bowie, A. R., 2007. Determination of aluminium in natural water samples. *Analytica Chimica Acta* 588, 153-165.

## Iron(II)

*Antony Birchill and Matthew Fishwick (University of Plymouth)*

### Objectives

In shelf sediments microbial oxidation of organic carbon delivered from primary productivity in the overlying shallow water column is the main driver of early diagenesis which produces dFe. For cohesive sediments (~40% of the North Sea floor), Fe(II) is principally generated by dissimilatory reduction of Fe(III), and is subsequently transferred to the water column via diffusion and sediment resuspension. Sedimentary supply of dFe(II) has been reported in low oxygen shelf waters (Lohan & Bruland, 2008) and in more oxic European shelf waters (Ussher et al. 2007). While the benthic cruise is determining Fe(II) in the sediments, our goal was to determine how much Fe(II) is in the bottom water overlying these sediments. In addition Fe(II) is produced in the upper water column from photochemical processes and from biological production. As Fe(II) is a transient species this was determined onboard ship.

### Sampling protocol

On recovery of the Ti-rosette, the OTE bottles were transferred into a clean sampling laboratory where they were immediately sampled for Fe(II) from 6 depths. Only 6 depths were chosen due to the transient nature of Fe(II) and the analysis time needed for completion of the measurements. Samples for Fe(II) were the first samples to be collected from the OTE bottles using a technique similar to oxygen sampling (initially filling the sampling bottle while it is upside down and overfilling the bottle in order to reduce oxygen from entering the sample).

## **Samples collected**

For the first time on the cruises Fe(II) was determined on the off-shelf transects and the on-shelf process stations. A total of 125 samples were collected and analysed for Fe(II), these are detailed in Table 23.1.

## **Sample analysis**

Samples were analysed using flow injection with chemiluminescence detection (Fe-CL) according to procedures outlined in Ussher et al. (2007). Briefly, a 1L sample of seawater was collected from the cast prior to Fe(II) analyses and stored in the dark. This aged seawater was adjusted to pH 5.5 with ammonium acetate and used to calibrate the Fe (II) system using the method of standard additions. Calibrations were done prior to sample collection (to ensure that the system was ready for immediate measurements) and again after the analyses of all samples. Samples were filtered in-line using 0.2 µm luer lock filter.

## **References**

Lohan, M.C. and Bruland, K.W. (2008). Elevated Fe(II) and dissolved Fe in hypoxic shelf waters off Washington and Oregon: An enhanced source of Fe to coastal upwelling regions. *Environ. Sci. Technol.*, 17, 6462-6468.

Ussher, S.U., Worsfold, P.W., Achterberg, E.P., Laes, A., Blain, S., Laan, P. & deBaar, H.J.W. (2007). Distribution and redox speciation of dissolved iron on the European continental margin. *Limnol. Oceanogr.* 52: 2530-2539.

## **Iron binding ligands**

*Dagmara Rusiecka (National Oceanography Centre, Southampton and IfM GEOMAR, Kiel)*

## **Objectives**

Understanding the biogeochemistry of Fe requires the ability to measure its oceanic chemical speciation. Fe is present in seawater as chelates with strong metal-binding organic ligands (Bruland & Lohan, 2004) which dramatically influences its chemical behaviour. These ligands have a stabilising influence, preventing inorganic precipitation (e.g. Liu and Millero, 2002) and increasing the availability of metals for biological uptake. They are therefore an important component in understanding the cycling and distribution of Fe in any system. Ligand samples will therefore be collected at selected stations along the cruise.

## **Sampling protocol**

On recovery of the Ti-rosette, the OTE bottles were transferred into a clean sampling laboratory where they were immediately sampled for oxygen, nutrients, salinity and total dissolvable elements before being pressurised to approximately 7 psi with 0.2 µm filtered air using an oil free compressor. After the collection of particulate samples (see section on Particulate Trace Metals), a Sartobran 300 (Sartorius) filter capsule (0.2 µm) was used to collect filtered seawater samples into clean LDPE sample bottles. Bottles and caps were rinsed 3 times with the filtered sample before being filled. All samples were double bagged and stored unacidified at -20°C until analysis.

## **Samples collected**

A total of 85 speciation samples were collected as detailed below.

## Sample analysis

The concentrations and conditional stability of Fe ligands, Fe<sup>3+</sup> (soluble inorganic Fe) and free aqueous Fe will be measured at NOCS/IfM GEOMAR by competitive ligand exchange cathodic stripping voltammetry (CLE-CSV) with the ligand TAC (Croot and Johansson, 2000).

## References

Bruland K. W. And M. C. Lohan, 2004. Controls on trace metals in seawater, In the Oceans and Marine Geochemistry Vol 6. Treatise on Geochemistry (eds. H. D. Holland and K. K. Turekian). Elsevier, London, pp. 23-49.

Croot, P. L. & Johansson, M., 2000. Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-thiazolylazo)-p-cresol (TAC). *Electroanalysis* 12, 565-576

Liu, X. W. & Millero, F. J. 2002. The solubility of iron in seawater. *Marine Chemistry*, 77, 43-54

## Particulate trace metals

*(Simon Ussher, University of Plymouth)*

### Objectives

Particulate trace metals may occur in several forms, including stable refractory phases or as coatings on surfaces that can be rapidly recycled. Particulate behaviour is metal specific with, for instance, the majority of particulate Fe occurring in refractory phases while Zn is primarily associated with more labile phases (Hurst & Bruland, 2005). Few studies have concurrently measured trace elements in both the dissolved and particulate phases. Furthermore, labile particulate trace metals which are biologically available could be considerably higher than the dissolved phase (Berger et al., 2008). Assessment of total biologically available trace elements may thus require the determination of both dissolved and labile particulate metal phases (Lam & Bishop, 2008). A step towards a quantitative description of the cycling of trace elements between the dissolved and particulate phases required for their realistic incorporation into biogeochemical ocean models is to measure the standing stock of the particulate fraction. To address this, particulate material will be filtered on selected water samples collected using the trace metal rosette.

### Sampling protocol

OTE bottles were transferred from the Ti-rosette into a clean sampling laboratory where they were immediately sampled for oxygen, nutrients, salinity and total dissolvable elements. The OTE bottles to be sampled for particulate material were inverted three times to gently mix the seawater and re-suspend particulates before being pressurised, to approximately 7 psi, with 0.2 µm filtered air using an oil free compressor. Clean filter holders (Swinnex, Millipore) containing acid washed 25 mm (0.2 µm) polyethersulfone filters (PES, Supor, Pall Gellman) were attached to the taps of the OTE bottles and up to a maximum of 7 L of seawater from selected depths was then passed over the filters. Following filtration, the filter holders were removed and placed in a laminar flow bench. Using an all polypropylene syringe attached to the top of the filter holder, residual seawater was forced through the filter using air from within the flow hood. The filter holders were gently opened and the PES filter folded in half using plastic tweezers, the filters were then placed in acid clean 2 mL LDPE

vial and frozen at -20°C until analysis. Filtration was completed in approximately three hours.

SPM (suspended particulate matter) was also determined using preweighed 25 mm GFF filters which were also used in Swinnex filter holders under 0.5 bar of pressure from an air compressor. Typically >5 L was filtered through the filter and then 40 mL of Milli-Q water and 40 mL of air were syringed over the filter to rinse of residual salt. These were returned to the lab for drying and gravimetric analysis.

SAP (Stand Alone Pumps) were also sampled on 3 occasions at 3 depths on PES filters and a 53 um nylon mesh for large particles and swimmers.

### **Samples collected**

A total of 135 particulate samples were collected as detailed in Table 23.1.

### **Sample analysis**

Samples will be analysed for both labile and refractory particulate Fe, Mn, Al, Co, Zn, Cd, Ba, Ni, Cu, Ti and potentially other trace elements using ICP-MS at the University of Plymouth. For labile particulate trace elements the filter is subjected to a weak acid leach (25% acetic acid at pH 2) with a mild reducing agent (0.02 M hydroxylamine hydrochloride) and a heating step (20 min 90-95°C). This approach is fully detailed in Berger et al. (2008). After the labile fraction has been determined the refractory trace elements will be determined following the method of Ohnemus and Lam (Deep Sea Research, in press). Briefly, the filters will be digested following a three step heating/dry-down process, firstly H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> are used to digest the filter, followed by HNO<sub>3</sub>, HCl and HF and finally HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> to digest the particulate material. The final solution is dried down and the residue brought back into solution with 2 % HNO<sub>3</sub> for analysis by ICP-MS. The samples are then spiked with an internal reference material such as In for drift correction.

### **References**

Berger, C. J. M., Lippiatt, S. M., Lawrence, M. G. and Bruland, K. W. 2008. Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington. *Journal of Geophysical Research-Oceans*, 113.

Hurst, M. P. and Bruland, K. W. 2007. An investigation into the exchange of iron and zinc between soluble, colloidal, and particulate size-fractions in shelf waters using low-abundance isotopes as tracers in shipboard incubation experiments. *Marine Chemistry*, 103, 211-226.

Lam, P. J. and Bishop, J. K. B. 2008. The continental margin is a key source of iron to the HNLC North Pacific Ocean. *Geophysical Research Letters*, 35.

Table 23.1. Record of trace metal cast samples on DY033

Station	Nuts	Fe (II)	Salin	O2	Alk	TdFe	TdTM	PES	dFe	dTM	sFe	Ligs	DOM	SPM	Synch	FC	Chla	Other
CCS_14	8	0	0	3	0	8	0	0	8	0	0	0	7	0	0	0	0	N2O sampled and O2 isotopes
CCS_13	8	0	0	3	0	8	0	0	8	0	0	0	7	0	0	0	0	N2O sampled and O2 isotopes
CCS_12	8	0	0	3	0	7	0	0	7	0	0	0	6	0	0	0	0	N2O sampled and O2 isotopes
CCS_11	8	0	0	3	0	8	0	0	8	0	0	0	7	0	0	0	0	N2O sampled and O2 isotopes. 20L for Anthony (carbony) and 60 L for Sari
CCS_10	7	0	0	3	0	7	0	0	7	0	0	0	6	0	0	0	0	N2O sampled and O2 isotopes
CCS_9b	4	0	0	0	0	2	0	0	2	0	0	0	2	0	0	0	0	N2O sampled and O2 isotopes
CCS_9	14	0	0	3	0	6	0	0	6	0	0	0	2	0	0	0	0	N2O sampled and O2 isotopes
CCS_8	10	0	0	3	0	10	0	0	10	0	0	0	6	0	0	0	0	N2O sampled and O2 isotopes plus 30L for Dagnara (nanoparticles)
CCS_7	9	0	0	3	0	7	0	0	7	0	0	0	6	0	0	0	0	N2O sampled and O2 isotopes (50L for Sari incubations)
CCS_6	7	0	0	3	0	7	0	0	7	0	0	0	6	0	0	0	0	N2O sampled and O2 isotopes
CCS_5	19	0	2	6	0	8	6	3	16	7	6	0	0	3	3	0	5	Geotraces duplicate dFe samples, Anthony sampled 50L for incubations, Chris Fe55
CCS_4	9	0	2	5	0	7	5	3	7	7	6	0	0	0	0	0	6	Anthony experiments and Chris Fe55 experiments
J4	12	6	2	6	2	6	3	3	6	6	6	0	0	3	3	0	0	N2O
J4	12	6	2	5	6	6	3	3	6	6	6	0	0	3	3	0	0	
SiteA	12	5	2	6	0	6	3	3	6	6	5	0	0	3	3	0	4	Extra bottles for flushing new filters
CCS_3b	6	0	2	0	0	1	0	1	2	1	1	1	1	0	0	0	0	Recast for Antony Experiments and Fe 55 incubations
CCS_3	16	6	2	0	7	7	3	3	7	7	5	2	7	3	0	7	6	POM, N2O
Fe6	12	6	2	0	6	12	6	3	12	12	8	3	6	0	0	10	6	0
Fe5	12	6	2	6	10	12	6	3	12	9	6	3	6	0	0	10	6	0
Fe4	15	7	2	0	8	14	7	3	19	10	6	3	8	0	0	10	6	2
Fe3	20	8	2	6	8	15	9	5	15	11	6	3	9	0	5	10	0	0
Fe15	20	7	2	6	11	20	10	6	20	14	6	4	9	0	0	12	6	0
Fe2	24	7	2	6	12	20	11	6	20	14	6	5	10	0	0	12	6	2
Fe1	24	7	2	6	12	22	10	6	22	15	6	5	12	0	0	12	6	double filter blanks conducted for sartorius cartridge foilter
CS2	15	6	2	6	6	8	4	2	8	8	6	3	0	3	4	0	6	Cr isotopes and Fe55
Fe14	8	0	2	6	0	8	4	3	8	8	6	3	8	0	0	8	5	0
Fe13	11	6	2	0	0	11	6	3	11	11	6	3	6	0	0	12	6	0
Fe12	14	6	2	0	0	12	7	3	12	10	6	3	6	0	0	12	6	3
Fe11	14	7	2	4	2	12	12	3	14	12	6	2	9	0	0	10	5	12
Fe10	24	7	2	0	5	22	12	6	23	16	6	6	9	0	0	12	0	0
Fe9	24	7	2	0	8	19	10	6	19	13	6	6	10	0	0	0	6	7
Fe8	24	9	2	6	5	24	13	6	36	30	6	5	12	0	0	12	6	0
CCS_2	10	0	2	6	0	7	0	3	7	0	5	0	0	0	0	0	6	0
CCS_1	17	6	2	6	0	8	5	3	8	8	6	4	0	3	4	0	0	0
Cast Count	34	34	34	34	34	34	34	34	34	34	34	34	34	34	34	34	34	
<b>Total</b>	<b>457</b>	<b>125</b>	<b>48</b>	<b>119</b>	<b>108</b>	<b>357</b>	<b>155</b>	<b>89</b>	<b>386</b>	<b>241</b>	<b>138</b>	<b>64</b>	<b>181</b>	<b>21</b>	<b>25</b>	<b>149</b>	<b>109</b>	
Fe Analysis						881												
TM Analysis						396												
Ligands						64												1341 Total profile samples
Fish	31					31												
Fe Analysis						31												
TM Analysis						31												
Ligands						29												91 Total surface samples

## 24. NMF-SS Sensors & Moorings

*Dougal Mountifield & Julie Wood (NMF Sea Systems)*

### CTD, LADCP, FRRF, SAPs and Salinometry Operations

#### **Supplied Equipment**

Two CTD packages were deployed on the cruise, a Stainless Steel frame with 20l Niskins and a Titanium frame with 10l Trace Metal Free Niskins.

A CTG Fastracka mkI FRRF was used for a few casts on the Stainless Steel Frame, but unfortunately poor battery condition resulted in poor performance and some lost FRRF profiles.

Three CTG FastOcean (mkIII) FRRF systems were supplied for bench-top and underway flow-through use. The FastAct base units were user-supplied.

The user-supplied OTEG nitrate sensor v3 was opportunistically deployed on the CTD frame in place of Niskin #24 for a few casts.

#### **CTD Systems Cast Summary**

Total number of casts: 90

Titanium frame casts: 43

Stainless steel frame: 47

Casts deeper than 2000m:

Titanium frame – 2

Stainless steel frame – 2

Deepest casts:

Titanium frame - 2460m (041T)

Stainless steel frame – 2466m (040)

#### ***Titanium Frame***

The first water sampling arrangement was a 24-way titanium frame system (s/n SBE CTD TITA1), and the initial sensor configuration was as follows:

Sea-Bird 9*plus* underwater unit, s/n 09P-77801-1182 (Ti)

Sea-Bird 3P temperature sensor, s/n 3P-5700 (Ti), Frequency 0 (primary)

Sea-Bird 4C conductivity sensor, s/n 4C-4138 (Ti), Frequency 1 (primary)

Digiquartz temperature compensated pressure sensor, s/n 129735, Frequency 2

Sea-Bird 3P temperature sensor, s/n 3P-5785 (Ti), Frequency 3 (secondary)

Sea-Bird 4C conductivity sensor, s/n 4C-4143 (Ti), Frequency 4 (secondary)

Sea-Bird 5T submersible pump, s/n 5T-3085, (primary)

Sea-Bird 5T submersible pump, s/n 05T-6916, (secondary)

Sea-Bird 32 Carousel 24 position pylon, s/n 32-60380-0805 (Ti)

Sea-Bird 11*plus* deck unit, s/n 11P-34173-0676 (main)

Sea-Bird 11*plus* deck unit, s/n 11P-24680-0589 (spare)

The auxiliary input initial sensor configuration was as follows:

Sea-Bird 43 dissolved oxygen sensor, s/n 43-2055 (V0)

CTG 2Pi-PAR Irradiance Sensor (DWIRR), s/n 02 (Ti) (V2)

CTG 2Pi-PAR Irradiance Sensor (UWIRR), s/n 04 (Ti) (V3)

Benthos 916T altimeter, s/n 62679 (V4)

WETLabs light scattering sensor, s/n BBRTD-758R (V5)

WETLabs CStar transmissometer, s/n 1718TR (V6)

Chelsea Aquatracka MKIII fluorometer, s/n 088244 (V7)

Also fitted to the titanium frame system were:

TRDI/WHM300kHz Downward looking LADCP, s/n 13399 (T)

NOCS LADCP battery pressure case, s/n WH006T

Sea-Bird 9*plus* configuration file DY033\_tita\_NMEA.xmlcon was used for the initial titanium frame CTD casts.

OTE Trace metal free 10L water samplers (s/n 1T-24T) were attached to the frame.

#### *Changes to instrument suite*

The primary conductivity sensor (s/n 4C-4138) was changed following cast 019T. The replacement conductivity sensor (s/n 4C-2571) was used from cast 021T onwards.

Following the change of conductivity sensors, Sea-Bird 9*plus* configuration file DY033\_tita\_4C\_2571\_NMEA was used for casts 021T onwards.

As usual PAR sensors were removed for casts deeper than 500m, and kept off until dawn at the earliest.

### ***Stainless steel frame***

The second water sampling arrangement was the 24-way stainless steel frame system (s/n SBE CTD1), and the initial sensor configuration was as follows:

Sea-Bird 9*plus* underwater unit s/n 09P-39607-0803 (Ti)

Sea-Bird 3P temperature sensor, s/n 3P-4782, Frequency 0 (primary)

Sea-Bird 4C conductivity sensor, s/n 4C-2450 (Ti), Frequency 1 (primary)

Digiquartz temperature compensated pressure sensor, s/n 93896, Frequency 2

Sea-Bird 3P temperature sensor, s/n 3P-6320 (Ti), Frequency 3 (secondary)

Sea-Bird 4C conductivity sensor, s/n 4C-2231 (Ti), Frequency 4 (secondary)

Sea-Bird 5T submersible pump, s/n 5T-5247, (primary)

Sea-Bird 5T submersible pump, s/n 5T-6320, (secondary)

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

Sea-Bird 11*plus* deck unit, s/n 11P-34173-0676 (main)

Sea-Bird 11*plus* deck unit, s/n 11P-24680-0589 (spare)

The auxiliary input initial sensor configuration was as follows:

Sea-Bird 43 dissolved oxygen sensor, s/n 43-0709 (V0)

WETLabs light scattering sensor, s/n BBRTD-1055 (V2)

Benthos 916T altimeter, s/n 59493 (V3)

Chelsea Aquatracka MKIII fluorometer, s/n 88-2615-124 (V4)

Chelsea Alphatracka MKII transmissometer, s/n 161-2642-002 (V5)

Biospherical QCP Cosine PAR irradiance sensor (UWIRR), s/n 70510 (V6)

Biospherical QCP Cosine PAR irradiance sensor (DWIRR), s/n 70520 (V7)

Also fitted to the stainless steel frame system were:

TRDI/WHM300kHz Downward looking LADCP, s/n 22797

NOCS LADCP battery pressure case, s/n WH009T

Sea-Bird *9plus* configuration file DY033\_ss\_NMEA.xmlcon was used for the initial stainless steel CTD casts.

OTE 20L water samplers were also attached to the frame (1A-24A).

### *Changes to instrument suite*

Low dissolved oxygen readings were noted on casts 074 & 075. The dissolved oxygen sensor (s/n 43-0709) was replaced with dissolved oxygen sensor (s/n 43-0709) after CTD075. The replacement oxygen sensor was again identified as faulty during cast 078.

OTE water sampler bottle 17 was found to be cracked after cast 065. This was replaced with a spare bottle.

The Mkl CTG FRRF was first fitted on cast 062. The instrument was found not to be flashing on retrieval after cast 068. The battery was in poor condition and unfortunately so was the spare battery unit. Both battery packs require replacement post-cruise.

There were a few problems identified with incorrectly entered oxygen calibration coefficients. Hence there are additional con files as these were identified and corrected:

DY033\_ss\_oxy\_correction\_NMEA.xmlcon DY033\_ss\_oxy\_final\_cal\_NMEA.xmlcon

Replacement of the failed dissolved oxygen sensor resulted in an additional configuration file: DY033\_ss\_new\_oxy\_0619\_NMEA.xmlcon.

### ***Titanium CTD***

The PAR sensors on the titanium frame were removed after cast 011T as they are only rated to a depth of 500m. They were reattached prior to cast 058T after deep work was completed.

On cast 014T, the CTD hit the bottom due to very poor soundings caused by the steep bottom topography. Wire out was 2380m water depth reading was 2595m. The Echogram was very difficult to read and there was only brief altimeter contact. The cast was aborted and the CTD returned to deck. No physical damage was observed during subsequent visual inspection.

On the next cast, there was an offset between the two conductivity sensors. Repeated flushing and cleaning did not rectify the problem, hence the primary conductivity sensor was replaced prior to cast 021T.

During cast 038T telemetry was lost with the Titanium CTD. Telemetry was re-established when recovered to deck. Test cast CTD039T confirmed failure again once was the package was submersed.

The synthetic CTD cable was found to have water ingress due to punctures in the jacket. It is possible that this damage was incurred during the bottom contact during cast 014T. The cable was cut back past the damaged section and re-terminated.

041T was the first titanium cast with the new termination.

## ***Stainless Steel CTD***

The OTE Nitrate sampler was deployed on the Stainless CTD frame for casts 001-004, and 008 for normal CTD operations. On cast 065 and 072, the Nitrate sensor was deployed and 3 off 30 minute long bottle stops were completed for sensor characterisation. This was extended on cast 075 where 4 off 30 minute stops were completed.

Pronounced spiking in backscatter from the BBrtD was seen on cast 040. The analogue Y-cable had suffered water ingress at the junction with the BBrtD cable resulting in the power pins dissolving completely. Both cables were replaced.

Dissolved oxygen reading low on cast 074.

On cast 057 the wire jumped a sheave resulting in damage to the CTD wire. The CTD wire was cut back past the damaged section and re-terminated.

## **NOC OTEG v3 Nitrate Sensor**

This sensor is a self-contained, wet-chemistry type, with low-volume microfluidic pumps. It incorporates an internal data-logger with real-time clock, and completes a measurement cycle every 15 minutes.

The control system and pumps are installed in a pressure-balanced, oil-filled housing that is mounted to an Ocean Test Equipment Niskin bottle mount. This allows simple and secure fitment and removal.

The liquid standards, blanks and reagents are stored in small blood bags external to the pressure balanced housing, and are protected within a free-flushing guard at one end of the housing.

The instrument has a battery unit with a pressure-switch to power the system once submerged to approximately 10m. The pressure-switch powers the system down prior to recovery to prevent air being ingested into the pump system.

The nitrate sensor was occasionally left on the CTD frame for normal profiling and bottle stops, but dedicated casts were also completed for acquiring nutrient inter-calibration data. For the dedicated casts bottle stops were extended to ~30 minutes with the intention of acquiring 2 nitrate sensor measurement cycles with the CTD package stationary.

## **Lowered Acoustic Doppler Current Profilers (LADCPs)**

The Teledyne RDI 300kHz LADCPs on both CTD frames were configured in a downward looking configuration. During deployment, the BBtalk session was logged to a file of the form DY033\_xxxm.txt, where xxx was the cast number. For titanium casts a T suffix was used for the cast number. Prior to deployment the baud rate was changed to 9600 (CB411), the clock checked (TS?) and the recorder space checked (RS?). The pre-deployment tests (PA, PT200 and PC2) were run. The following command file was sent:

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

Upon recovery, the instrument was stopped pinging by sending a break, the baud rate was then changed to 115,200 (CB811), the number of deployments checked (RA?), then the data was downloaded using Recover Recorder in BBtalk. The RDI file was then re-named in a similar form to the log file (DY033\_XXX.000), where XXX was the cast number, with an additional T if the titanium frame was used. The data was backed up to the network and each data file was checked using WinADCP to identify deterioration in the beams.

The LADCPs worked well during the cruise. The LADCP mounted on the titanium frame was running an old firmware version (v50.38). This was identified following cast 007T, when it was impossible to communicate with the LADCP prior to deployment. The firmware was updated to v50.40 before the next titanium cast (010T). There were not further issues with the LADCPs.

There are no LADCP files for some of the casts. These are listed here:

007T – communication problems. Firmware on ADCP needed updating.

020 - communication problems of unknown cause. Worked next deployment.

022T – recast of 021T as bottles were incorrectly fired (gap in bottles on the rosette).

035 – only 2 bottles fired, no LADCP done.

037T – profile only with no bottles fired.

057 – Wire damage, hence no profile

060T – calibration dip, no bottles fired.

072 – nitrate sampler fitted on CTD.

073 – calibration dip only.

082T – calibration dip only.

084T – recast of 083T due to a bottle at a critical depth leaking.

### **Winch and Handling Systems**

The Stainless Steel CTD was deployed using the midships P-frame over the starboard side. A Rochester 11.43mm double-armoured GEIPS wire was used. The CTD wire provides power and telemetry with a single PTFE insulated copper core. The CTD wire was handled using the vessel CTD winch suite.

The Titanium CTD was deployed using the bull-horn over the starboard side. A Cortland 15.25mm PU coated Vectran strength member synthetic cable was used. The MF cable provides power and telemetry with 4 18AWG conductors that were bonded in two pairs to reduce line impedance and also for redundancy. The MF cable was used with the Rolls-Royce containerised portable MF winch.

### **Salinometry**

A Guidline 8400B, s/n 71185, was installed in the Salinometer Room as the main instrument for salinity analysis. A second Guildline 8400B, s/n 71126, was also installed in the Salinometer Room as a spare instrument.

The ambient temperature control in the dedicated Salinometer room ranged between 21 – 22°C throughout the analysis. The Autosal bath temperature was set to 24°C.

The machine was standardised at the beginning of the cruise and the Rs Pot set, yielding a standby value of 5975. The standby value varied between 5974 and 5976 throughout analysis. At the start of each day of analysis, the standardisation procedure was run to obtain machine offset from standard, but the pot was not adjusted throughout the cruise. A standard was run as a sample before and after each crate of 24 samples. All standards were described as STD with a bottle number of 999. As the Autosal was well trimmed and stable, the variation in measured standard value due to bath temperature fluctuation was always more significant than the machine offset from standard.

IAPSO 35 PSU standard seawater batch P155 was used throughout analysis. The label K15 ratio was 0.99981, yielding a double conductivity ratio of 1.99962. The salinity of the standard was 34.993.

Standards were always flushed 5 times prior to measurement, samples were flushed 4-5 times depending on the volume of sample available in the bottle. After flushing, 10-15 seconds was allowed for the bath to stabilize before switching the machine from standby to read. The software subsequently waits 5 seconds before taking a 10 second average for each of the three discrete measurements which are averaged themselves for the final double conductivity measurement. The software was configured with a standard deviation limit of 0.00002 in double conductivity ratio. This limit yields 0.4 mPSU for one, 0.8 mPSU for two and 1.2 mPSU for three standard deviations. This is acceptable for a stable machine operating in a stable environment.

7 crates of 24 bottles of CTD samples and 3 crates for TSG samples were analysed using the Autosol. Dr Jo Hopkins, Emelyn Jones (Liverpool) and Steve Woodward (NOC – MARS) operated the Autosol.

### **Stand Alone Pumps (SAPS)**

Six Challenger Stand Alone Pumps were used on the cruise. Prior to deployment, filters were installed and all final checks made before starting timers. The SAPs were then transferred from the Main Lab to the Deck Lab where the units were primed with Milli-Q. Once primed, the pumps were then moved to the deployment location via the hanger.

The SAPs were deployed from starboard mid-ships using two 96 kg plastic coated lead SAP ballast weights. Nominal separation from the lower SAP and the ballast was approximately 15m. Delay times were sent to 1 hour 30 minutes and pump times were 1 hour.

Following each deployment, the flowmeters were recorded prior to filter housing removal. Subsequently the SAPs were rinsed with freshwater and dried before moving back to the Main Lab. The batteries were boost charged at 20V at the packs (20.7V at the charger), trickle charged at 18.3V at the packs (19V at the charger) and floated at 17.3V at the packs (18V at the charger). When the SAPs were not in use, they were left continuously on float charge.

The SAPs operated well. For the first three deployments, all six SAPs were deployed. On the final deployment, only three SAPs were deployed (s/n 03-04, 03-06 and 03-07) giving four deployments in total.

On recovery of the first deployment, 02-002 was still pumping which may have contaminated the sample.

Before the second deployment, when the filter housings were being filled with milliQ water, both 03-06 and 03-07 were leaking from the pump housing. This was due to the o-ring being incorrectly located within the pump housing and was fixed before the next deployment. There was no apparent problem with the samples collected from these SAPs.

At the end of the cruise the batteries were fully charged and isolated prior to sealing pressure housings for packing. The filter housings were soaked in freshwater for 2 hours and rinsed with milliQ water. They were left to dry before packing away.

## Seabird SBE39 Temperature & Pressure Recorders

Sea-Bird 39 temperature and pressure were mounted to each SAP frame to provide a record for each SAP in-situ throughout the deployment. These were configured to sample every five seconds. Following retrieval of the SAPs, a stop command was sent to each 39 and the data was recovered.

SAP s/n	Purpose	Nominal depth	Sea-Bird 39 s/n
02-002	Trace metal	75-80m	6755
03-01	Trace metal	40-45m	6754
03-03	Trace metal	15m	6753
03-04	Biological	15m	6752
03-06	Biological	40-45m	6751
03-07	Biological	75-80m	6750

SAP serial numbers with the serial number of the Sea-Bird 39 temperature and pressure unit attached.

## Appendix A: Configuration files

### Titanium CTD frame

*Date: 07/17/2015*

*Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\DY033\DY033\_tita\_4C\_2571\_NMEA.xmlcon*

*Configuration report for SBE 911plus/917plus CTD*

-----  
*Frequency channels suppressed : 0*

*Voltage words suppressed : 0*

*Computer interface : RS-232C*

*Deck unit : SBE11plus Firmware Version >= 5.0*

*Scans to average : 1*

*NMEA position data added : Yes*

*NMEA depth data added : No*

*NMEA time added : Yes*

*NMEA device connected to : PC*

*Surface PAR voltage added : No*

Scan time added : Yes

1) Frequency 0, Temperature

Serial number : 03P-5700

Calibrated on : 23 January 2015

G : 4.34171397e-003

H : 6.28714187e-004

I : 1.88566108e-005

J : 1.18971078e-006

F0 : 1000.000

Slope : 1.00000000

Offset : 0.0000

2) Frequency 1, Conductivity

Serial number : 04C-2571

Calibrated on : 12 June 2015

G : -9.93530237e+000

H : 1.54150392e+000

I : 6.37686708e-005

J : 9.47604748e-005

CTcor : 3.2500e-006

CPcor : -9.57000000e-008

Slope : 1.00000000

Offset : 0.00000

3) Frequency 2, Pressure, Digiquartz with TC

Serial number : 129735

Calibrated on : 12 March 2014

C1 : -6.064446e+004

C2 : 6.966022e-001

C3 : 1.971200e-002  
D1 : 2.882500e-002  
D2 : 0.000000e+000  
T1 : 3.029590e+001  
T2 : -6.713679e-005  
T3 : 4.165400e-006  
T4 : 0.000000e+000  
T5 : 0.000000e+000  
Slope : 1.00000000  
Offset : 0.00000  
AD590M : 1.279181e-002  
AD590B : -8.821250e+000

4) Frequency 3, Temperature, 2

Serial number : 03P-5785  
Calibrated on : 23 January 2015  
G : 4.33680677e-003  
H : 6.28133080e-004  
I : 1.97124698e-005  
J : 1.48509243e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

5) Frequency 4, Conductivity, 2

Serial number : 04C-4143  
Calibrated on : 22 January 2015  
G : -9.81324031e+000  
H : 1.32701833e+000  
I : -1.39063899e-003

*J* : 1.66413237e-004  
*CTcor* : 3.2500e-006  
*CPcor* : -9.57000000e-008  
*Slope* : 1.00000000  
*Offset* : 0.00000

6) *A/D voltage 0, Oxygen, SBE 43*

*Serial number* : 43-2055  
*Calibrated on* : 19 December 2014  
*Equation* : Sea-Bird  
*Soc* : 3.63700e-001  
*Offset* : -7.11000e-001  
*A* : -3.01680e-003  
*B* : 1.57020e-004  
*C* : -2.76270e-006  
*E* : 3.60000e-002  
*Tau20* : 1.99000e+000  
*D1* : 1.92634e-004  
*D2* : -4.64803e-002  
*H1* : -3.30000e-002  
*H2* : 5.00000e+003  
*H3* : 1.45000e+003

7) *A/D voltage 1, Free*

8) *A/D voltage 2, PAR/Irradiance, Biospherical/Licor*

*Serial number* : PAR 02  
*Calibrated on* : 7 May 2013  
*M* : 0.47913900  
*B* : 1.05925300

*Calibration constant : 100000000000.00000000*

*Multiplier : 0.99960000*

*Offset : 0.00000000*

*9) A/D voltage 3, PAR/Irradiance, Biospherical/Licor, 2*

*Serial number : PAR 04*

*Calibrated on : 21 November 2013*

*M : 0.43427300*

*B : 1.61542400*

*Calibration constant : 100000000000.00000000*

*Multiplier : 0.99950000*

*Offset : 0.00000000*

*10) A/D voltage 4, Altimeter*

*Serial number : 62679*

*Calibrated on : 27 March 2014*

*Scale factor : 15.000*

*Offset : 0.000*

*11) A/D voltage 5, Turbidity Meter, WET Labs, ECO-BB*

*Serial number : BBRTD-758R*

*Calibrated on : 3 June 2013*

*ScaleFactor : 0.002903*

*Dark output : 0.043100*

*12) A/D voltage 6, Transmissometer, Chelsea/Seatech*

*Serial number : 1718TR*

*Calibrated on : 15 April 2015*

*M : 21.1867*

*B : -0.1059*

*Path length : 0.250*

*13) A/D voltage 7, Fluorometer, Chelsea Aqua 3*

*Serial number : 088244*

*Calibrated on : 6 August 2014*

*VB : 0.236800*

*V1 : 2.151000*

*Vacetone : 0.305900*

*Scale factor : 1.000000*

*Slope : 1.000000*

*Offset : 0.000000*

*Scan length : 45*

**Stainless steel CTD frame**

*Date: 07/29/2015*

*Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\DY033\DY033\_ss\_new\_oxy\_0619\_NMEA.xmlcon*

*Configuration report for SBE 911plus/917plus CTD*

-----  
*Frequency channels suppressed : 0*

*Voltage words suppressed : 0*

*Computer interface : RS-232C*

*Deck unit : SBE11plus Firmware Version >= 5.0*

*Scans to average : 1*

*NMEA position data added : Yes*

*NMEA depth data added : No*

*NMEA time added : Yes*

*NMEA device connected to : PC*

*Surface PAR voltage added : No*

Scan time added : Yes

1) Frequency 0, Temperature

Serial number : 03P-4782

Calibrated on : 23 January 2015

G : 4.34985490e-003

H : 6.36317437e-004

I : 2.07562308e-005

J : 1.73187181e-006

F0 : 1000.000

Slope : 1.00000000

Offset : 0.0000

2) Frequency 1, Conductivity

Serial number : 04C-2450

Calibrated on : 7 October 2014

G : -1.04318594e+001

H : 1.66122258e+000

I : -1.36779205e-003

J : 2.45209441e-004

CTcor : 3.2500e-006

CPcor : -9.57000000e-008

Slope : 1.00000000

Offset : 0.00000

3) Frequency 2, Pressure, Digiquartz with TC

Serial number : 93896

Calibrated on : 9 July 2014

C1 : -8.331332e+004

C2 : -3.281962e-001

C3 : 2.216060e-002  
D1 : 2.906000e-002  
D2 : 0.000000e+000  
T1 : 3.005232e+001  
T2 : -3.843669e-004  
T3 : 4.436390e-006  
T4 : 0.000000e+000  
T5 : 0.000000e+000  
Slope : 1.00001000  
Offset : -1.35810  
AD590M : 1.289250e-002  
AD590B : -8.106440e+000

4) Frequency 3, Temperature, 2

Serial number : 03P-5495  
Calibrated on : 23 January 2015  
G : 4.38192095e-003  
H : 6.30409856e-004  
I : 1.98978713e-005  
J : 1.49777155e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

5) Frequency 4, Conductivity, 2

Serial number : 04C-2231  
Calibrated on : 22 January 2015  
G : -1.07880202e+001  
H : 1.70078204e+000  
I : -4.18412701e-003

*J* : 4.28242497e-004  
*CTcor* : 3.2500e-006  
*CPcor* : -9.57000000e-008  
*Slope* : 1.00000000  
*Offset* : 0.00000

6) *A/D voltage 0, Oxygen, SBE 43*

*Serial number* : 43-0619  
*Calibrated on* : 5 September 2014  
*Equation* : Sea-Bird  
*Soc* : 5.40200e-001  
*Offset* : -5.02000e-001  
*A* : -3.80340e-003  
*B* : 1.93390e-004  
*C* : -3.24880e-006  
*E* : 3.60000e-002  
*Tau20* : 1.24000e+000  
*D1* : 1.92634e-004  
*D2* : -4.64803e-002  
*H1* : -3.30000e-002  
*H2* : 5.00000e+003  
*H3* : 1.45000e+003

7) *A/D voltage 1, Free*

8) *A/D voltage 2, Turbidity Meter, WET Labs, ECO-BB*

*Serial number* : BBRTD-1055  
*Calibrated on* : 13 March 2013  
*ScaleFactor* : 0.002365  
*Dark output* : 0.061000

9) A/D voltage 3, Altimeter

Serial number : 59493

Calibrated on : 25 March 2013

Scale factor : 15.000

Offset : 0.000

10) A/D voltage 4, Fluorometer, Chelsea Aqua 3

Serial number : 88-2615-124

Calibrated on : 21 January 2015

VB : 0.463400

V1 : 2.044300

Vacetone : 0.474400

Scale factor : 1.000000

Slope : 1.000000

Offset : 0.000000

11) A/D voltage 5, Transmissometer, Chelsea/Seatech

Serial number : 161-2642-002

Calibrated on : 3 September 2014

M : 23.5891

B : -0.5661

Path length : 0.250

12) A/D voltage 6, PAR/Irradiance, Biospherical/Licor

Serial number : 70510

Calibrated on : 6 January 2015

M : 1.00000000

B : 0.00000000

Calibration constant : 2020000000.00000000

*Multiplier* : 1.00000000

*Offset* : -0.05051050

13) *A/D voltage 7, PAR/Irradiance, Biospherical/Licor, 2*

*Serial number* : 70520

*Calibrated on* : 6 January 2015

*M* : 1.00000000

*B* : 0.00000000

*Calibration constant* : 19500000000.00000000

*Multiplier* : 1.00000000

*Offset* : -0.05251338

*Scan length* : 45