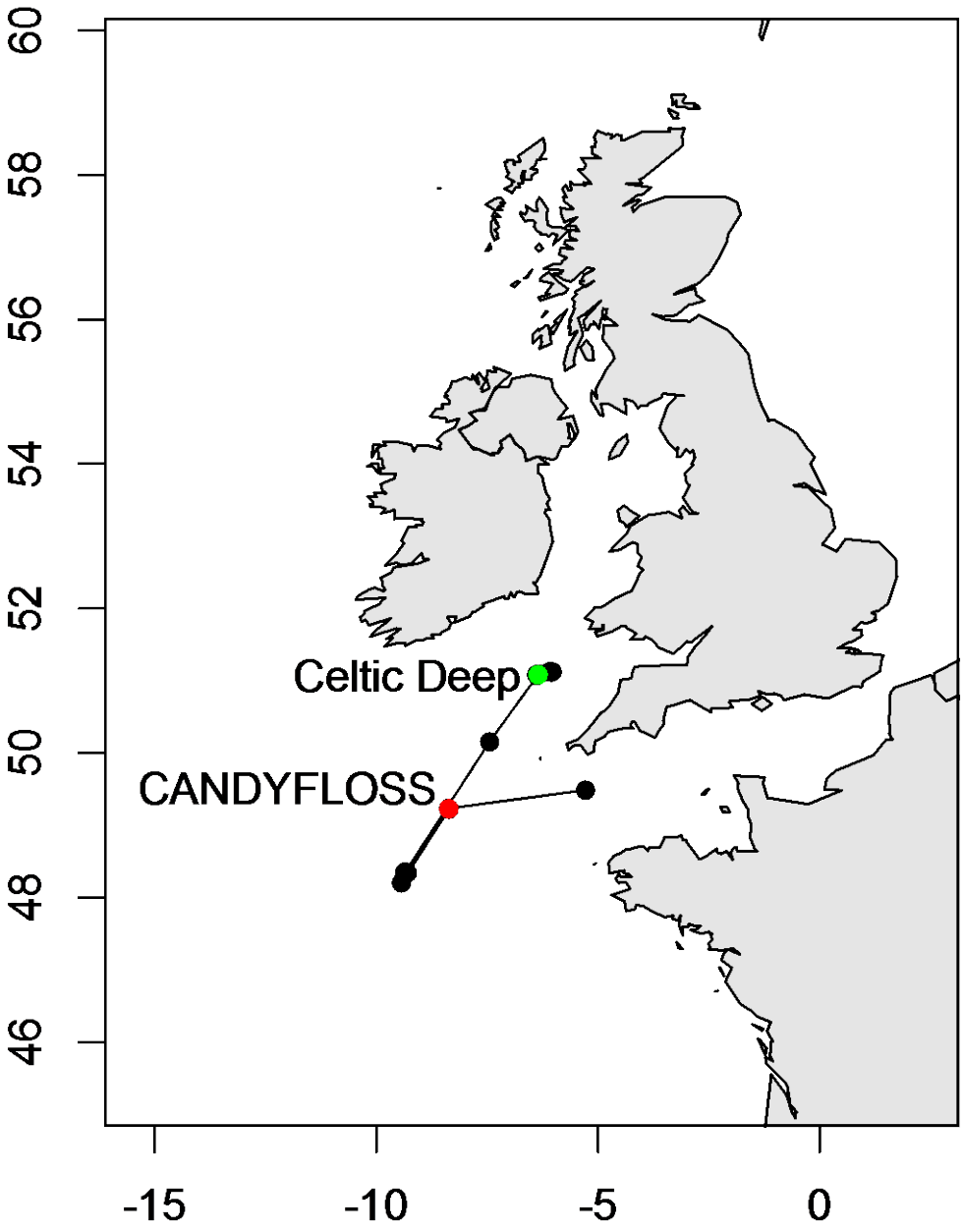
DY026 Shelf Seas Biogeochemistry cruise to the Celtic Sea

3rd August – 14th August 2014



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DY026 Overview and Objectives

DY26a formed part of the NERC shelf sea biogeochemistry programme. It had four principal objectives:

1. To continue the seasonal time series sampling at the three key sites (Shelf break, Candyfloss, Celtic Deep).
2. To provide sampling opportunities for the Shelf sea biogeochemistry students
3. To obtain samples of sinking particulate organic matter at differing stages of the tidal cycle to examine the role of tidal resuspension on elemental cycling beneath the thermocline.
4. To trial autonomous nitrate sensors CTDs and gliders as part of the Sensors on Gliders programme

Objective 1 We conducted CTD casts at each key site, sampling for DIC and nitrate concentrations to evaluate the differential uptake and remineralisation of these tracers which is key to the operation of the shelf sea pump. In addition we made at each site many of the rate measurements the programme needs to make to understand the differential elemental cycling.

Objective 2 Each SSB student (Matthew Bone, sediment coring, Richie Sims, near surface ocean profiler, Isabel Seguro, O2/ Ar ratios, Kieran Curran, phytoplankton processes) got a good range of sampling opportunities at various sites in varying weather conditions).

Objective 3 Following the standard SSB observations outlined in objective 1 we undertook a highly temporally resolved timeseries of observations at the Celtic Deep. This comprised hourly CTDs with very high resolution sampling near the bed coupled to hourly snowcatcher deployments and near bottom respiration, bacterial production and nitrification measurements. Following this we revisited the same site over a tidal cycle and collected near bed suspended material for similar biological rate measurements.

Objective 4 The Sensors on gliders programme has integrated a nitrate sensor into a glider. This combination was trialed at the shelf break and on one further occasion during the cruise. Both deployments produced useful data. In addition the nitrate sensor itself was deployed on the CTD in standalone mode on two occasions with extended bottle stops to allow reliable measurements to be made.

Sensors On Gliders Cruise Report

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Objectives

For the Sensors On Gliders project, DY026 was a technology-proving cruise to practice deploying the NOC's Lab-On-Chip (LOC) nitrate sensors on a glider at sea.
The primary objectives were:

- to prove that the glider could be operated successfully with the 3.5Kg sensor-pair payload
- to prove that the base station, glider and sensor could communicate successfully at sea
- to develop optimal sampling patterns for operating the sensors on the glider

A secondary objective was to deploy the sensor on the CTD frame at every opportunity to gather more field data for this relatively new technology.
There were no science objectives for the Sensors On Gliders project on this cruise.

Equipment

2 x NOC LOC Nitrate sensors in a single housing with external oil bladder and no battery
1 x NOC LOC Nitrate sensor housed with internal battery and oil bladder, and a CTD bottle clamp
1 x NOC LOC Nitrate sensor (spare)
2 x Kongsberg Seagliders (SG534 + SG533 spare)

Sensor

The NOCS Lab-On-Chip nitrate sensor is one of a suite for sensors developed by the OTE Group at NOCS for different chemistries using microfluidic technology. The nitrate sensor allows in-situ measurement of nitrate+nitrite (or nitrite only) with a limit of detection of 0.025µM (nitrate) and 0.02µM (nitrite) and uses very small quantities of reagent (Beaton,2012).

Inputs of sea water sample, artificial sea water blank or 10 µM potassium nitrate standard are sequentially combined with Imidazole buffer and passed through a cadmium column to convert nitrate to nitrite, then combined with Griess reagent to develop a colour which is measured by absorption of light from a 525nm LED. The results from the sample, standard and blank are combined to give the nitrate+nitrite result. The chemical processing is done in-situ, so for example when deployed on the CTD frame, the chemistry is complete and raw results are available when the frame is lifted from the water.
The mixing cells, reaction cells and measurement channels are all contained in a microfluidic chip, so called because the central layer superficially resembles an electronic printed circuit. The picture shows a disassembled sensor with the chip at the base and the electronics, valves and syringe pumps fixed directly to it. The chemicals are stored externally in blood bags and connected to the opposite face of the chip. The external housing varies to suit the platform on which the sensor is deployed.
The total pumping and reaction time with the current technology is around 6.5 minutes for each input giving about 20 minutes for a blank-sample-standard pattern. In some contexts, for example long-term monitoring of a river, this is not a problem, but holding up a CTD cast with long stops at depth is inconvenient, and holding the Seaglider at depth (loitering) is tricky. The sensor is programmable, so we tried five different sampling patterns on this cruise, all designed to reduce the sampling interval. They were as follows:

PATTERN 1	PATTERN 2	PATTERN 3	PATTERN 4	PATTERN 5
wait until in water	wait until in water	start immediately	start immediately	start immediately
BLANK	BLANK	BLANK	BLANK	BLANK
SAMPLE	SAMPLE	STANDARD	STANDARD	STANDARD
STANDARD	STANDARD	BLANK	BLANK	BLANK
repeat whole pattern for rest of cast	SAMPLE	STANDARD	STANDARD	STANDARD
	repeat whole pattern for rest cast	wait until below surface	wait until depth exceeds 10m	wait until depth exceeds 10m
		SAMPLE	STANDARD	SAMPLE
		repeat sample to end of dive	repeat sample to end of dive	SAMPLE
		BLANK	BLANK	BLANK
		STANDARD	STANDARD	repeat SSB to end of deployment
		BLANK	BLANK	
		STANDARD	STANDARD	
		wait for ascent	wait for ascent	
		SAMPLE	SAMPLE	
		repeat sample to just below surface	repeat sample to just below surface	
		BLANK	BLANK	
		STANDARD	STANDARD	
		BLANK	BLANK	
		STANDARD	STANDARD	

PATTERN 1 gives the best nitrate results but each iteration takes 3x6.4 minutes which means on a CTD cast (where the sensor is running continuously) you need to hold the CTD at each required depth for 4x6.4 minutes to guarantee a complete set of blank-sample-standard. The wait at the start is to avoid drawing in air on the deck. We used this pattern in Deployment 2.

PATTERN 2 is an attempt to reduce the time between obtaining samples to try to get results from a CTD cast moving at normal speed. Each sample has a neighbouring blank but is not bracketed by blank and standard. We used this in Deployment 3 (with no stops) and Deployment 4 (with 10 minute stops).

PATTERNS 3 & 4 were designed to run as a pair on two sensors on the Seaglider. One sensor is doing samples for the whole deployment except for a blank+standard at the start and end of the descent and ascent. The other sensor is doing standards the whole time. This pattern requires enough time at the top and bottom of the dive to complete the bracketing blank+standard and at 0.1m/s dive speed that means at least 42m at the top and bottom, so it's only practical if there's sufficient depth of water. It also fails if the Seaglider doesn't reach its target depth. Hence this pattern was only used on Deployment 1 in 1500m of water.

PATTERN 5 was designed on the cruise to solve two problems. Firstly we were to remain at the shallow benthic sites (<100m) for the remainder of the cruise and secondly we only had one functioning sensor for the Seaglider. The results from Deployment 2 suggest that there is no depth-dependence on the results of standards measurements with this sensor, so it needs to be done at the start of deployment only, allowing us to reduce the time between sampling. We used this pattern in

Deployment 5 and would have tried it (without the depth check) on a further CTD deployment but unfortunately the sensor failed before we were able to try it.

Glider

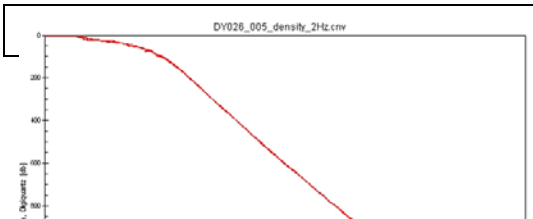
The Kongsberg Seaglider is an autonomous underwater vehicle that has no direct propulsion but instead rely on the forward motion generated by small wings as they descend or ascend in the water. This saving in power allows them to be deployed for extended periods.

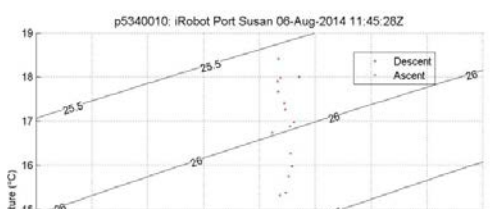
They control their buoyancy by pumping oil in and out of an external bladder and they pitch and roll by moving their battery around to alter their trim. They are capable of navigating from one waypoint to another in a series of dive profiles, and they return data and gather new instructions each time they surface by communicating via Iridium to a base station. These instructions can set new mission parameters and sensor settings as well altering the trim of the Seaglider based on the telemetry from the previous dive. Piloting the Seaglider (sending these instructions) was done from NOC as a reliable Internet connection is needed to upload the command files.

The Seaglider has a large free-flooding payload bay which is sufficient to house the sensor on a custom mounting. Connection to the Seaglider is via IE55 serial cables which carry power and RS232 serial communications. For this cruise we configured the Seaglider to send its GPS time (to allow us to correlate the sensor data with the Seaglider's own sensor data) at the start of the deployment and depth+direction (i.e. ascent and descent) every five seconds to allow the sensor to make depth-dependent decisions in its processing (see PATTERNS 4 & 5 above). It is also possible to include three arbitrary sensor parameters in the command file sent to the Seaglider and we used those to set the cut-off depths used in the sampling logic by the sensor.

Installation of dual Lab-on-Chip (LOC) Nitrate sensors onto a Seaglider requires a more extensive reballasting procedure than is normal before a deployment due to both their size and weight (2548cm^3 and 3635g for the combined sensor housing, plus bags and cables). Using an Ogive fairing with increased payload capacity in the aft fairing was essential. To compensate for the negative buoyancy of the sensor, TG-42 syntactic foam pieces were added (384.3g in strips around the circumference of the battery hull and 600g in machined blocks bolted to the aft fairing top hatch cover).
Aiming for a target density (rho) of 1026.8kg/m^3 at 1000m depth, ballasting was checked by weighing the Seaglider (SG534) – first dry, then suspended in a freshwater tank with its buoyancy device (VBD) pumped to maximum and minimum volume. Additionally, the Seaglider was deployed tethered from the marina at NOCS. Erring on the side of caution, 728g of brass nose weight and 150.5g of lead ballast were added to give a calculated thrust of 50-100cm^3 at rho. Pitch, VBD and roll centres were measured during the dock tests.

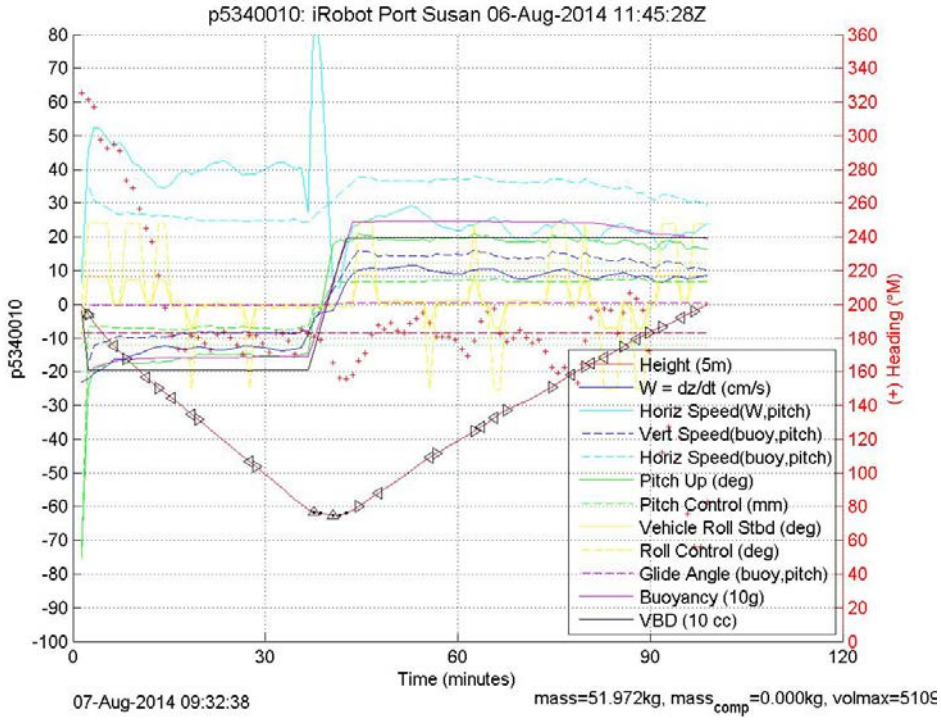
The density profile from CTD002 (Central Celtic Sea processing station, 04/08/2014) showed a surface density of 1025.3kg/m^3, rising to 1027.6kg/m^3 at 100m. In anticipation of the SG534 therefore being too buoyant and unable to dive to >100m, 136.2g of lead ballast was added to the aft fairing, giving a calculated 150cm^3 of thrust at a new rho of 1027.8kg/m^3.
SG534 was not as buoyant as predicted, probably due to inaccuracy of the Seaglider CT sensor (SBE s/n 0156). Between dives 6 and 10, the centre point of the VBD ($C_VBD) had to be adjusted from 3498 t0 2798 A/D counts, a change of 170cm^3.





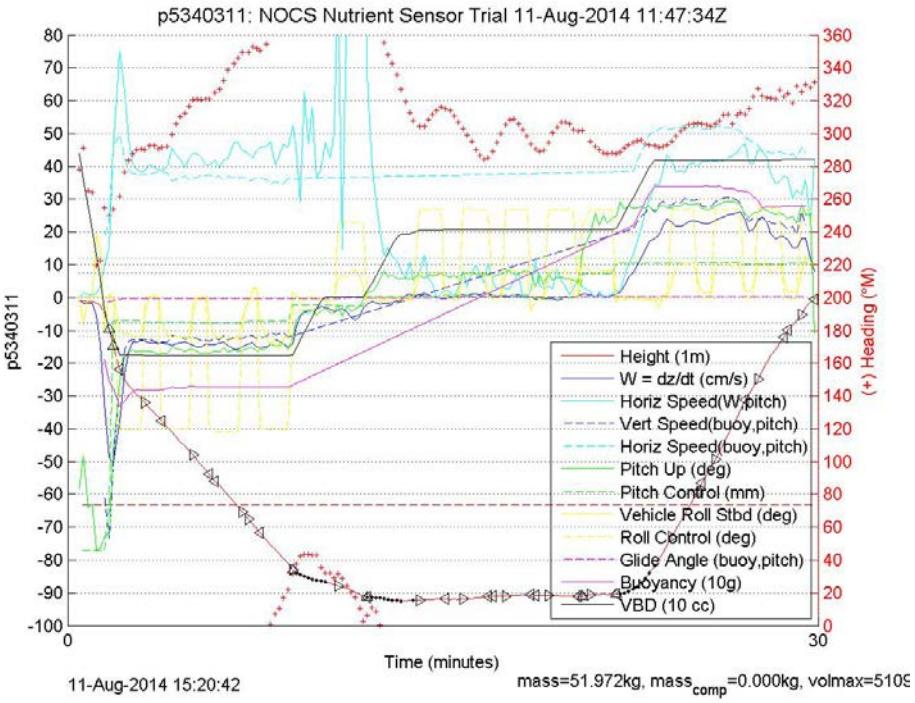
Deployed CTD005 and SG534 dive 10 density profiles. Seaglider density at apogee (~300m) = 1027.2kg/m^3. Deployed CTD density at 300m = 1028.6kg/m^3.

The main dive plot for dive 10 shows a roughly symmetrical profile. Vertical velocity is quite stable in both the dive phase (~12cm/s) and climb phase (~10cm/s). The apogee maneuver is reasonably smooth, with only a minor drop in horizontal speed. After the initial shallow dives, SG534 made steady progress towards its waypoint. Although some further adjustment is required, from this point there is no doubt that SG534 could be trimmed to perform well over a longer deployment in this area. It is therefore clear that the Ogive fairing Seaglider is a suitable platform for deployment of the LOC Nitrate sensor.



Main dive plot for SG534 dive 10

One function of the Seaglider platform which could be potentially useful for LOC sensor sampling strategies is the ability to loiter at depth. Using the $T_LOITER parameter, SG534 was held at 90m for 10 minutes on dive 311.



Main dive plot for SG534 dive 311

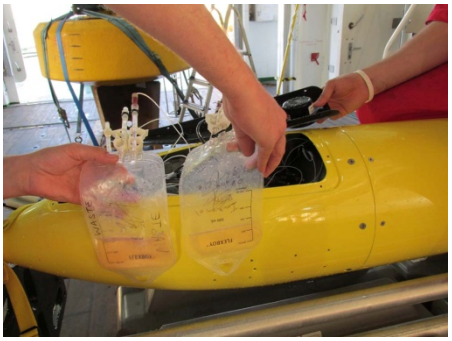
Deployment 1

6 August (J14218) 48˚20'N, 9˚43' W in 1500m water: Seaglider test dives to 50m, 300m and 500m
This was the first Seaglider deployment with the sensor. The sensor was loaded into the payload bay the night before, about an hour's work to get the sensors and all the bags organized and tied down. The sample inlet tubs were passed through the fairing with the filters on the outside.

Pre-flight system checks are carried out on deck and these took about 45 minutes on this deployment while the actual launch of the Seaglider took less than 10 minutes. The Seaglider remains with its communication antenna just out of the water until it receives its instruction to dive and we waited to see the Seaglider dive successfully before moving the ship back to the day's process station about 1 nautical mile way (to avoid any collisions).

The first test dives went well and the Seaglider flew better than expected with the heavy sensor installed.

Both sensors were enabled for the 300m and 500m dives, deployed as a pair using sampling PATTERNS 3 & 4 as described earlier.



Data for both dives was retrieved from the Seaglider when it was recovered, together with the summary data downloaded by the Seaglider itself from the sensors at the end of each dive. The communications with the sensor worked perfectly and both sensors operated correctly for the 300m dive and the first part of the 500m dive. The data has yet to be processed back at NOC. Sadly one of the sensors (the one running PATTERN 3) failed with a pump jam at about 300m. We attempted a repair using parts from the spare sensor but it did not appear to be returning good results when tested on the ship with a standard as input and so was not deployed again (although it went back out as a passenger in Deployment 5 so as not to alter the buoyancy of the Seaglider).

An incorrect setting (RECORDABOVE) in the command file for the 300m dive meant that the Seaglider told the sensors to stop at 100m and ceased sending it status messages. The sensors ignore

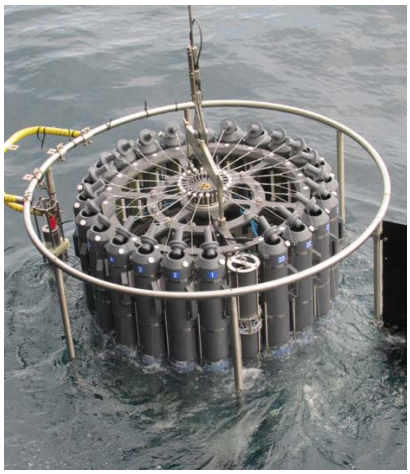
stop messages from the Seaglider so in fact they have data all the way down to 300m but the depth is not known and the bottom blank-standard sequence did not run, highlighting a significant flaw in PATTERN 3 which is addressed by PATTERN 5.
The 500m dive was aborted by the Seaglider shortly after beginning its ascent. Therefore this dive yielded data in the first part of the dive only. The Seaglider was running beta software so it was considered imprudent to deploy it again without an investigation by the manufacturer into what went wrong and whether or not it was safe to redeploy the Seaglider. Happily, we did in Deployment 5.

Deployment 1						
SG Dive #	Event	**Longitude N**	**Latitude W**	**Date**	**Time UTC**	**Depth**
	Deployed	4820.440	0943.190	060814	0658	
6	**Dive Start**	4820.407	0943.224	060814	0805	85
	Dive End	4820.421	0943.224	060814	0829	
7	**Dive Start**	4820.367	0943.041	060814	0841	90
	Dive End	4820.392	0943.123	060814	0906	
8	**Dive Start**	4820.354	0943.181	060814	0917	100
	Dive End	4820.263	0943.287	060814	0958	
9	**Dive Start**	4820.246	0943.352	060814	1004	225
	Dive End	4820.196	943.729	060814	1133	
10	**Dive Start**	4820.254	943.856	060814	1145	190
	Dive End	4819.596	943.674	060814	1345	
11	**Dive Start**	4819.742	-943.660	060814	1356	500
	Dive End	4819.246	-943.643	060814	1747	
	Recovery	4818.770	-942.790	060814	1830	

SG534 was deployed from the forward auxiliary winch on the P frame using the rigid rope deployment rig. Conditions were calm and a buoyancy test was undertaken. Once the deployment team were satisfied that SG534 was sitting in the correct position whilst in the water it was deployed and began its mission. The recovery went very smoothly due to the calm conditions and SG534 was recovered using the mid ships crane once the rudder was noosed using the carbon fiber recovery pole and aluminum hoop.

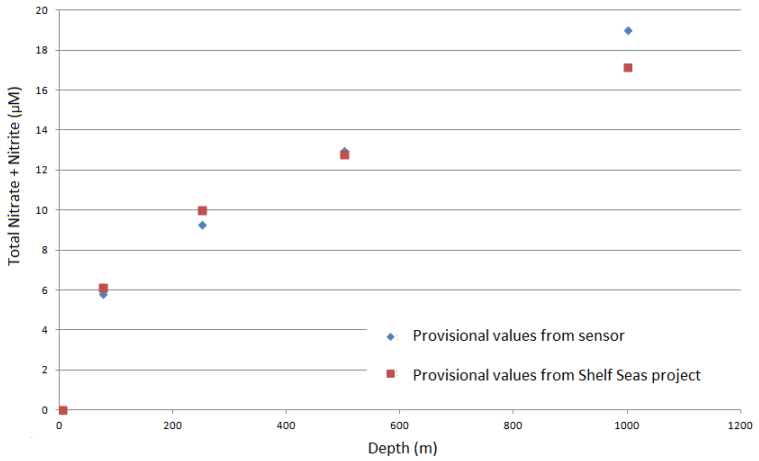
Deployment 2

6 August (J14218) 48˚20'N, 9˚43' W in 1500m water: CTD cast to 1500m (with 25 minute stops at 1000m, 500m, 250m, 75m and 5m but the sensor running continuously for the whole cast)



This was the first CTD deployment of the sensor on this cruise. One improvement to the sensor housing design over previous cruises was the addition of a bottle clamp allowing it to be easily swapped for a bottle on the CTD bottle carousel. This worked well although it was suggested that a handle on the front (as the bottles have) might make it slightly easier.
The top half of the sensor housing in the picture contains the blood bags and the bottom half contains the sensor, the pressure-compensating bladder and a battery.
With PATTERN 1 sampling, the sensor has to be started (by attaching a shorted IE55 terminator) shortly before it enters the water to ensure it doesn't draw in air. For this deployment we allowed half an hour; in subsequent deployments we allowed 10 minutes and in all cases the CTD was in the water within 2 minutes of starting the sensor, so the delay is unnecessary as the first blank cycle takes 6.4 minutes.

This was the most successful and informative deployment of the sensor on the cruise as it was our only opportunity to put it onto the CTD in deep water. The CTD cast went to 1500m and the sensor was logging continuously throughout. However we also halted the CTD at 5 locations long enough to complete 1 cycle of the CTD FAST sampling pattern. The provisional results (shown below) correlate quite well with the provisional lab-based nitrate values produced for the Shelf Seas project on the same cruise using water from the same CTD cast.



Two other interesting features from these results are an indication that the nitrate values obtained for the standard are not depth-dependent so it may be sufficient to process the standard a couple of times at the start of the dive, increasing the possible sampling rate. In addition, the nitrate values for the depths between the 25-minute stops appear to correlate well with those where we stopped, so sampling on the move looks feasible at least when nitrate values are changing relatively slowly and continuously with depth (the sensor is only actually drawing in sea water for about 2.5 minutes in the 20 minute cycle which may explain why the results were reasonable).
The electronic components in the sensor are pressure rated to 6000m and the sensor returned to the surface fully functional. Shortly after the deployment one electronic component (Dallas Semiconductor DS1374 real time clock) did report a failure and we swapped out the processor board out for a spare to be able re-deploy the sensor a couple of days later. In subsequent testing however the board seemed to be functioning correctly so possibly the fault was due to a faulty connection rather than the collapse of a component.

Deployment 3

8 August (J14220) 50˚15'N, 7˚44'W in 106m water: CTD cast to 100m (with no stops)
This was a first attempt to deploy on a CTD without stopping, but in 100m water, only one complete sample was achieved showing the limitations of sampling PATTERN 2 in shallow water. The result is yet to be processed. From the CTD results we'd expect a surge in nitrate (to about 8µM) at around 45m and deeper.

Deployment 4

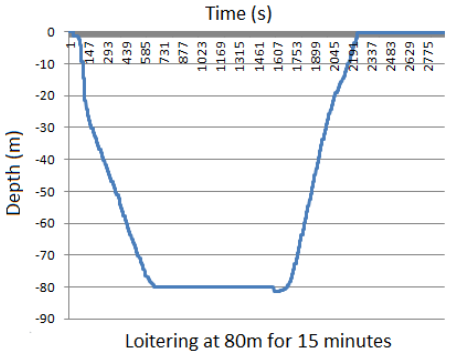
9 August (J14221) 51˚7'N, 6˚37'W in 103m water: CTD cast to 85m (with 10 minute stops at 85m,75m,65m,55m,45m,35m,25m,15m,10m,5m)
This deployment was made to see if a compromise of using PATTERN 2 (with at most 6.5 minutes between samples) and stopping for 10 minutes at selected depths would produce good results. They should also provide a good reference for the glider operations in the next deployment. Bottle samples were also processed for us by the Shelf Seas project giving provisional figures for the same depths.
We would have expected to see a significant drop in the nitrate levels at around 40m due to a spike in activity of phytoplankton during rough weather.
Unfortunately the results from the sensor indicate that something failed in the optical processing, either the LED failed or the optical cell became blocked, so no sensor results are available for this cast.

Deployment 5

11 August (J14223) 51˚7'N, 6˚37'W in 103m water: Seaglider "loitering" trials to 60m

This second deployment with the Seaglider aimed to test the Seaglider's "loitering" capability. The Seaglider is theoretically capable of holding a particular depth for a period of time during its normal dive profile. This suits the nitrate sensor because we can process a full sample at a specific depth, just as we do when the CTD is halted. For this deployment we designed a new sampling pattern where the standards were run at the start of the dive profile only, then two samples to each blank for the remainder. We retained the depth check at the start to avoid sucking in surface bubbles (although this may not be necessary) but the other two depth parameters were not used. Both sensors were deployed to avoid altering the Seaglider's buoyancy, but only one was enabled in the command file.

Communications with the piloting team at NOC were hampered by the Iridium phone getting a poor signal and several iterations of the pre-flight checks were required to establish that the Seaglider had the correct parameters. To be able to do this from the ship would make the task significantly easier, at least for trial deployments.



The Seaglider uses an altimeter to avoid colliding with the seabed and several dives were required to get this working properly (the altimeter gives false returns at a range of 5-8m until sensitivity is set correctly). However one dive was successfully completed with the Seaglider loitering at depth for just over fifteen minutes which is a good result (the plot is taken from the depths reported to the sensor by the glider).

In quite lively seas the Seaglider was located and recovered as quickly and smoothly as before.

As with Deployment 1, all communications between Seaglider and sensor worked correctly and a full set of files was retrieved from the Seaglider on completion of the dive. This showed the sensor had correctly executed the sampling pattern. Unfortunately the results from the chemistry are clearly not valid and an extended post-deployment test of the sensor has produced similar results. The cause is not yet identified.

Deployment 5						
SG Dive #	**Event**	**Longitude N**	**Latitude W**	**Date**	**Time UTC**	**Depth**
	Deployed	5112.679	608.471	11/08/14	0642	
304	**Dive Start**	5112.714	608.392	110814	0650	30
	Dive End	5113.269	608.093	110814	0727	
305	**Dive Start**	5113.439	607.966	110814	0739	30
	Dive End	5113.860	607.846	110814	0815	
306	**Dive Start**	5113.932	607.828	110814	0822	45
	Dive End	5114.182	607.929	110814	0854	
307	**Dive Start**	5114.215	607.926	110814	0900	70
	Dive End	5114.167	608.196	110814	0936	
308	**Dive Start**	5114.158	608.195	110814	0941	95
	Dive End	5114.007	608.764	110814	1013	
309	**Dive Start**	5113.957	608.763	110814	1021	70
	Dive End	5113.623	609.110	110814	1057	
310	**Dive Start**	5113.492	609.105	110814	1108	90
	Dive End	5113.318	609.421	110814	1138	
311	**Dive Start**	5113.180	609.399	110814	1147	90

	Dive End	5111.240	609.015	110814	1349	
312	**Dive Start**	5111.147	608.935	110814	1354	85
	Dive End	5110.811	608.330	110814	1445	
313	**Dive Start**	5110.662	608.150	110814	1455	85
	Dive End	5110.639	607.347	110814	1554	
314	**Dive Start**	5110.607	607.269	110814	1559	87
	Dive End	5110.975	606.509	110814	1658	
315	**Dive Start**	5110.997	606.443	110814	1703	82
	Dive End	5111.294	606.167	110814	1726	
	Recovery	5111.850	605.69	110814	1815	

The same methods for deployment and recovery of the Seaglider were used as in Deployment 1. Conditions were worse (sea state 4-5). The deployment team made the decision to proceed, having confidence in the ships station holding capabilities and its maneuverability in recovery operations. SG534 was recovered in sea state 5 - 6, the ship was impressive in positioning itself next to the Seaglider in a large swell. In a slight variation from the first recovery, The recovery line was tied to an eye on the bulwark and a boss hook was attached which enabled the Seaglider to be pulled out of the water at double the speed.

Successes

We have demonstrated that it is possible to run the LOC nitrate sensors on a Seaglider at sea. The Seaglider operated well and the communications between the Seaglider and the sensor worked perfectly.

The data we have gathered from the two Seaglider deployments should be sufficient to design optimal sampling strategies for operating the sensors on the Seaglider in both deep and shallow waters.

We have demonstrated that it is now very easy to deploy the sensor onto the CTD frame and by picking a strategy that does not require long stops at each depth, we can operate on that platform whenever there is a bottle slot spare with no significant impact on CTD operations.

The deployment on the deep CTD cast (to 1500m) has given us valuable experience of operating the sensor at significant depth and the correlation of the nitrate values obtained by the sensor and those obtained from the water samples gives us further confidence in this sensor technology. It has also shown that standards measurements do not vary with depth with this sensor, so it should be sufficient to take a couple of standards measurements at the start of a CTD cast or Seaglider profile and then iterate samples and blanks, achieving a higher sampling rate than was thought possible.

Room for improvement

The discrepancy between the provisional nitrate values obtained on the deep CTD deployment and those obtained by conventional processes from the water samples will need further investigation.

The cause of the failure of the sensor's real time clock and syringe pump presumably due to pressure will also need further explanation.
The requirement to fill the sensor housing with oil (to balance the sea pressure) makes the job of fixing the sensors at sea much harder than it would otherwise be, because the housing needs careful re-sealing and testing before it can be re-deployed.
The sensor fits in the Seaglider's payload bay with room to spare, especially to the sides of it and in the tail. The most time-consuming aspect of the installation was securing the blood bags. If these can be contained in some way (as they are in the CTD sensor housing) the process may be speeded up. Alternatively, if running with a single sensor is considered to be adequate, it might be possible to locate the bags behind the sensor in the tail space with no need to secure them.
Ways to reduce the processing time need to be explored further to reduce the sampling interval to operate the sensor more effectively on moving platforms like the CTD and the Seaglider. This will be achieved by a mixture of new technology (we're investigating new pump seals that should reduce flushing time) and alternative sampling strategies.
It should be possible to get sensor data back via the Seaglider and Iridium to the base station but this has yet to be proven. Whilst it would not be possible to recover all of the raw data from the sensor in this way, it certainly is possible to get a status report and some averaged results - on this cruise we demonstrated getting that data back as far as the Seaglider.

Acknowledgements

Thanks to Malcolm Woodward for providing the nitrate figures and processing an extra set of bottles for us in Deployment 3. Also to our colleagues in the MARS group back home for piloting the Seaglider at unsociable hours and our colleagues in the OTEG group for ongoing support and for processing the data. Finally, thanks to the technicians and scientists on the cruise for allowing us the opportunity to conduct these trials.

NUTRIENTS Cruise Report

Malcolm Woodward
PLYMOUTH MARINE LABORATORY, UK

OBJECTIVES:

To investigate the spatial and temporal variations of the micromolar nutrient species; Nitrate, Nitrite, Silicate, Ammonium and Phosphate during the DY026 research voyage in the Celtic Sea and Western Approaches off the West coast of the UK. Carry out nutrient analysis from zooplankton and benthic experiments where required as part of the SSB programme (Giering and Bone).
Please see individual cruise reports for these colleagues as to their individual sampling protocols.

SAMPLING and ANALYTICAL METHODOLOGY:

Sample preparation and procedure

There was minimal storage of the Underway non-toxic and 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. 60m ml 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 system on-board the RRS Discovery. 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) were used and other clean handling protocols were adopted as close to those according to the GO-SHIP protocols, (2010).

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 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) 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.

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.

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 minimize nutrient contamination. Samples were kept tightly closed until just before analysis for the ammonium, this to avoid any contamination from external sources.

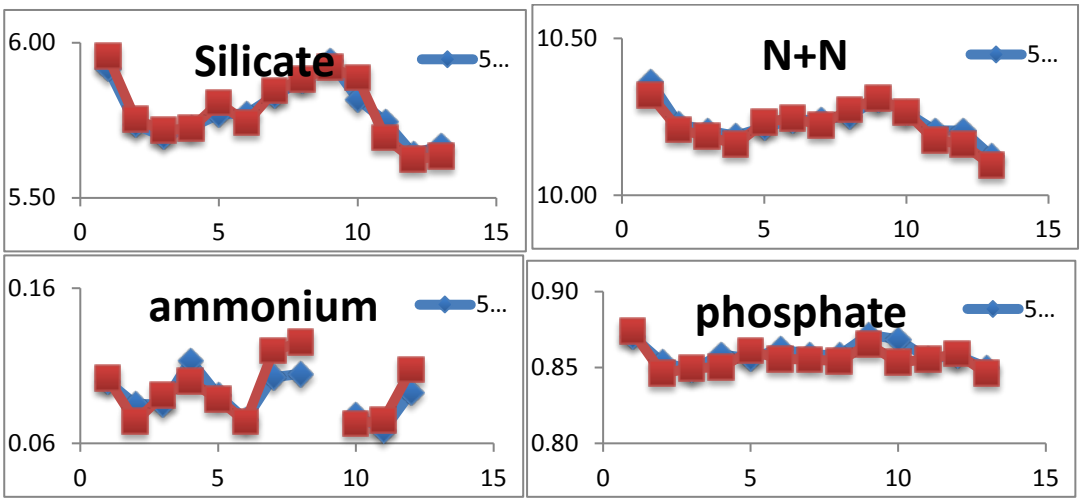
CTD Samples Analysed by AAIII Micromolar analysis:

Date	CTD	Station	Position	CTD bottle analysed
04/08/14	CTD_001	001	$49^0$48.80'N $5^0$28.66'W	Bottles 1,5,7,10,14,16,18,20 (depths: 80, 65, 50, 35, 25, 17, 17, 5m)
05/08/14	CTD_002	006	$49^0$23.194'N $8^0$37.129'W	Bottles 4,7, 10, 13, 16, 19, 24 (depths: 136, 100, 60, 45, 30, 20, 5m)
05/08/14	CTD_003	011	$49^0$23.012'N $8^0$36.70'W	Bottles 3, 5, 8, 12, 17, 21 (depths: 137, 100, 50, 34, 20, 5m)
05/08/14	CTD_004	021	$49^0$22.311'N $8^0$36.465'W	Bottles 1,4,6,9,10, 16, 19, 22 (depths: 136, 100, 60, 45, 40, 30, 20, 5m)
06/08/14	CTD_005	030	$48^0$20.30'N $9^0$43.62'W	Bottles 2,3, 4,5, 6, 7, 11, 16, 18, 19, 23 (depths: 1000, 500, 250, 125, 75, 50, 35, 26, 20, 10, 5m)
07/08/14	CTD_006	035	$48^0$34.193'N $9^0$30.616'W	Bottles 1, 4, 7, 11, 15, 19, 22 (depths: 197, 120, 50, 40, 35, 15, 5m)
07/08/14	CTD_007	044	$48^0$34.193'N $9^0$30.616'W	Bottles 1,3,6,9,11,15,17,21 (depths: 170, 120, 90, 55, 42, 30, 20, 5m)
07/08/14	CTD_008	047	$48^0$34.27'N $9^0$30.27'W	Bottles 2,4,7, 10, 13, 16, 19, 24 (depths: 195, 120,90,60,40,29,15,5m)
08/08/14	CTD_009	056	$50^0$15.48'N $7^0$44.61'W	Bottles 1,3,7,9,12,15,18,22 (depths: 93,60,45,36,34,32,20,5m)
09/08/14	CTD_010	061	$51^0$08.26'N $6^0$35.14'W	Bottles 1,4,7,11,15,18,19,22 (depths: 85,60,50,36,30,20,10,5m)
09/08/14	CTD_011	071	$51^0$07.748'N $6^0$37.33'W	Bottles 1,3,5,8,16,17,19,21,1 (depths: 92,70,50,36,34,28,15,5m)
09/08/14	CTD_012	076	$51^0$07.099'N $6^0$37.499'W	Bottles 1,2,3,4,5,6,7,8,9,10(depths: 85,75, 65,55,45,35,25,15,10,5m)
09/08/14	CTD_013	078	$51^0$07.099'N $6^0$37.499'W	Bottles 14,8,12,14,16,19,22(depths: 92,65,48,39,37,25,15,5m)
10/08/14	CTD_014	086	$51^0$09.42'N $6^0$34.27'W	Bottles 1,4,5,6,7,8(depths: 92,87,82,77,30.5,5m)
10/08/14	CTD_015	088	$51^0$09.415'N $6^0$34.252'W	Bottles 9,2,13,14,16,17(depths: 90, 85,80,75,28,5m)
10/08/14	CTD_016	090	$51^0$09.35'N $6^0$34.60'W	Bottles 1,4,5,6,8,9(depths: 91, 86 81,76,25,5m)
10/08/14	CTD_017	092	$51^0$09.12'N $6^0$35.49'W	Bottles 10,13,14,15,17,18(depths: 88,83,78,73,32,5m)
10/08/14	CTD_018	094	$51^0$08.98'N $6^0$35.83'W	Bottles 9,12,13,14,15,18,21(depths: 91,86,81,76,55,30,5m)
10/08/14	CTD_019	096	$51^0$08.869'N $6^0$36.153'W	Bottles 1,4,5,6,7,9(depths: 90,85,80,75,21,5m)
10/08/14	CTD_020	098	$51^0$08.8'N $6^0$36.31'W	Bottles 10,13,14,15,16,18(depths: 93,88,83,78,23,5m)
10/08/14	CTD_021	100	$51^0$08.75'N $6^0$36.39'W	Bottles 19,22,23,24,1,3(depths: 93,88,83,78,27,5m)
10/08/14	CTD_022	102	$51^0$08.74'N $6^0$36.39'W	Bottles 6,9,10,11,12,14(depths: 95,90,85,80,15,5m)
10/08/14	CTD_023	104	$51^0$08.74'N $6^0$36.29'W	Bottles 1,4,5,6,7,10(depths: 95,90,85,80,18,5m)

10/08/14	CTD_024	106	51^{0}08.74'N 6^{0}36.238'W	Bottles 1,4,5,6,7,8(depths: 96,91,86,81,22,5m)
10/08/14	CTD_025	108	51^{0}08.74'N 6^{0}36.24'W	Bottles 2,4,5,6.7,9(depths: 99,90,85,80,23,5m)
10/08/14	CTD_026	110	51^{0}08.7'N 6^{0}36.24'W	Bottles 1,4,5,6,7,9(depths: 94,89,84,79,23,5m)
11/08/14	CTD_027	113	51^{0}12.701'N 6^{0}08.489'W	Bottles 1,4,7,10,13,16,19,22(depths: 95,70,50,31,28,25,15,5m)
12/08/14	CTD_029	135	51^{0}08.91'N 6^{0}36.24'W	Bottles 1,6,7,10,13,16,19,24(depths: 95,70,50,15,20,15,10,5m)
12/08/14	CTD_030	142	51^{0}08.40'N 6^{0}37.29'W	Bottles 1,3,5,8,9,13,15(depths: 92,75,55,35,24,20,5m)
13/08/14	CTD_033	159	51^{0}12.574'N 6^{0}03.353'W	Bottles 1,3,5,79,11,13,17,19(depths: 90,70,48,48,40,37,35,20,5m)

Preliminary Results

On the 10th August we carried out hourly CTD's concentrating on the bottom 20 meters of the sediment, firing a bottle every 5 meters, plus taking the Chloro max and surface bottles.
The results below are for the concentrations of nutrients in the bottom waters, and show a tidal cycle with the water passing back and forth, but there was little or no evidence of sedimentary nutrient resuspension as had been postulated. Obviously this is only a single experiment but implies little nutrient resuspension occurs in the late summer in the Celtic Sea.



Cruise Summary

The 5-channel autoanalyser worked very well throughout the cruise.
KANSO nutrient reference materials (Batch BU) were run each day 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 the catering team for excellent food.

Malcolm Woodward 14th August 2014

Determination of oxygen concentrations

Claire Mahaffey
University of Liverpool, UK

Methods

125 ml optically-clear glass oxygen bottles triple-rinsed with Milli-Q and stored full of Milli-Q. Each bottle is pre-calibrated for volume and has unique identifying number on shoulder and on stopper. Oxygen samples were drawn first from Niskin as soon as rosette was secured on deck. Tygon tubing was used to fill bottles from Niskin and bottle was overflowed three times to ensure no bubbles. Temperature of each sample was taken immediately then sample was fixed with 1ml manganese sulphate (3M) and 1ml alkaline iodide and shaken vigorously for a 20 seconds. Samples were reshaken prior to storage approximately 15 minutes later.

Samples were stored upright under water in a dark 60L container until the precipitate had settled. Samples were analysed within 24 hours of collection. Prior to analysis 1ml sulphuric acid (10N) was added to each sample to dissolve the precipitate.

Samples were analysed for dissolved oxygen concentration onboard using the modified Winkler method (Carpenter, 1965) and a PC-controlled potentiometric titration system (Metrohm Titrando 888). Reagent blanks were run using 0.1N potassium iodate (1 aliquots) and sodium thiosulphate titrant (~ 0.18 N). Each of these was performed in triplicate (at minimum) prior to analysis of samples each day. Lab temperature was monitored throughout analysis. Calculation of dissolved oxygen concentration was according to HOT protocol (website given below) and Grasshoff (1983). Samples were analysed to produce a dissolved oxygen concentration in µmol l^{-1} and these values were forwarded to the oxygen sensor calibration team for conversion to µmol kg^{-1} and further processing.

Samples were taken from 12 CTDs (Table 1). The coefficient of variation was typically better than 0. 44% for triplicate analysis. Mean reagent blank was 0.0102 ± 0.005 mL over the course of the cruise and mean thiosulphate normality was 0.1732 ± 0.0008 N. Oxygen concentrations measured ranged from 200 µmol O_2 l^{-1} to 300 µmol O_2 l^{-1}. Data will be submitted to BODC for conversion to µmol kg^{-1} and calibration of the oxygen sensor on the CTD.

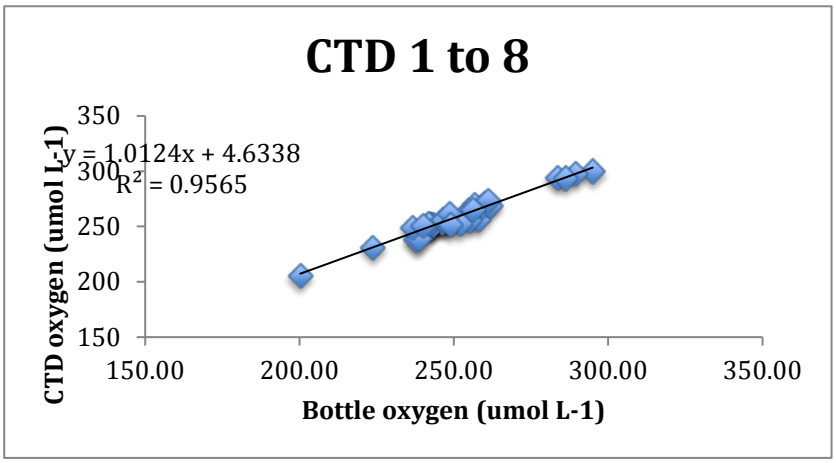
On CTD 13, it was noted that the oxygen sensor on the CTD giving highly variable readings. This is noted in the poor relationship the CTD oxygen and bottle oxygen from CTD9 to The oxygen sensor was cleaned just before CTD27, which improved the regression between the CTD oxygen and the bottle oxygen data although the slope (0.93, Figure 1c) was different to the slope estimated at the start of the cruise (1.02, Figure 1a).

Table 1. List of rosette casts which were sampled for dissolved oxygen.

Date	CTD no.	Lat	Long	Depths(m)
04/08/12	1	49° 48.8 N	5° 28.55 W	3 depths
05/08/14	6	49° 48.8 N	5° 28.66 W	7 depths
05/08/14	21	49° 22.3 N	8° 36.48 W	8 depths
06/08/14	30	48° 20.3 N	9° 43.63 W	9 depths
07/08/14	35	48° 34.2 N	9° 30.60 W	7 depths
08/08/14	56	50° 15.4 N	7° 44.62 W	8 depths
09/08/14	61	51° 08.3 N	6° 35.16 W	7 depths
09/08/14	78	51° 07.1 N	6° 37.52 W	8 depths

11/08/14	113	8 depths
12/08/14	142	6 depths
13/08/14	159	6 depths

(a)



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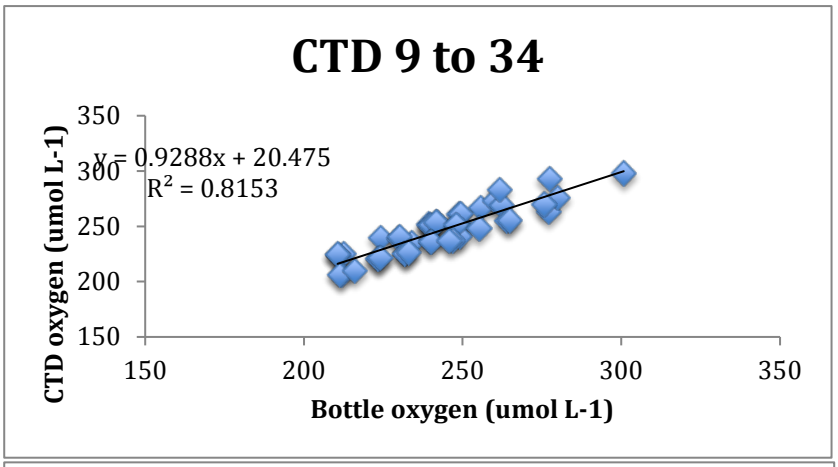

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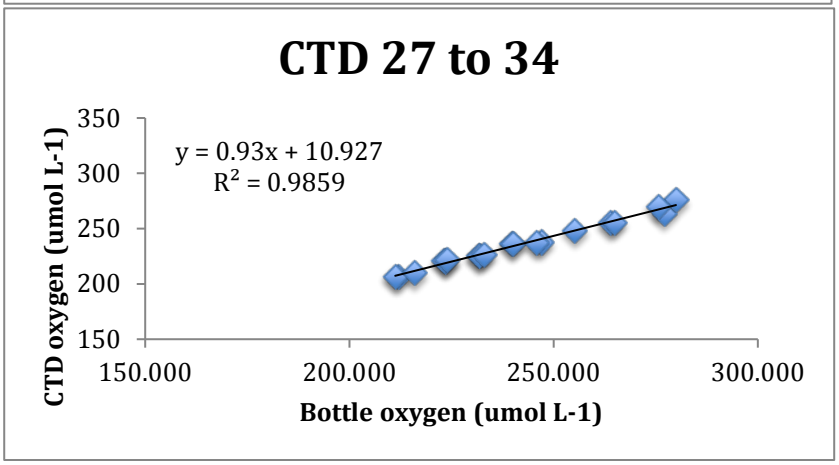

References

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Grasshoff, K. Ehrhardt, M, and K. Kremling (1983). Methods of Seawater Analysis. Grasshoff, Ehrhardt and Kremling, eds. Verlag Chemie GmbH. 419 pp.

http://hahana.soest.hawaii.edu/hot/protocols/chap5.html

Collection and processing of samples for determination of dissolved and particulate organic matter

Clare Davis and Claire Mahaffey
University of Liverpool

Dissolved organic nutrients: Samples were collected from between 6 and 10 depths from the CTD and were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7 µm) and stored in acid-cleaned 175 mL HDPE bottles at -20°C for later laboratory analysis to determine dissolved organic carbon (DOC), organic nitrogen (DON) and organic phosphorus (DOP) concentrations.

Dissolved free and total hydrolysable amino acids: Samples were collected from between 6 and 10 depths from the CTD and were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7 µm) and stored in 20 mL muffled glass vials at -20°C, and then moved to the -80°C freezer for later laboratory analysis.

Coloured Dissolved Organic Matter (CDOM): Samples were collected from between 6 and 10 depths from the CTD and underway system. Samples were filtered through 47 mm GF/F (combusted, Whatman, nominal pore size 0.7 µm) and then through 0.2 µm 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 (Sensors on Gliders student) to determine the source and composition of CDOM.

Particulate organic carbon, particulate organic nitrogen and particulate phosphorus: Samples were collected from between 6 and 10 depths from the CTD and marine snow catcher. For particulate carbon and nitrogen (PC/PN), 2L was filtered onto 25 mm GF/F (combusted, Whatman, nominal pore size 0.7µm) on a plastic filter rig under <12 kPa vacuum pressure. For particulate phosphorus (PP), 1L was filtered onto 25 mm GF/F (combusted and HCl acid washed, Whatman, nominal pore size 0.7µm) on a 3-port plastic filter rig under <12 kPa vacuum pressure. All filters were stored at -80°C for laboratory analysis.

Particulate lipids and particulate amino acids: Samples were collected from between 6 and 10 depths from the CTD and marine snow catcher. For both lipids and amino acids, 3L 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^{15}N of particulate nitrogen and nitrate: Samples were collected from between 6 and 10 depths from the CTD. Samples for the δ^{15}N and δ18O of nitrate were collected and stored in 60 mL HDPE bottles (HCl acid washed) and stored unfiltered at -20 °C for later analysis. Samples for δ^{15}N-particulate nitrogen were collected by filtering 3L onto 25 mm GF/F (combusted, Whatman, nominal pore size 0.7 µm) and stored at -80°C for later analysis.

Stand Alone Pump System (SAPS): The SAPS was deployed four times to collect samples for PC/PN, PP, particulate lipids and particulate amino acids from two fractions: particles >53 µm and particles between 0.7 – 53 µm. Each time the SAPs was deployed to 50 m depth, to match that of snow catcher deployments made at similar times. 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.

CTD Samples: Table 1 summarises the samples taken from the CTD for particulate carbon and nitrogen (PCPN), particulate phosphorus (PP), particulate lipids (LIPIDS), particulate amino acids (P-AA), dissolved and particulate δN^{15} (dN15), and dissolved organic nutrients including CDOM and amino acids (DOM).

Table 1: Summary of sample collection from the CTDs.

CTD #	Niskin #	PCPN	PP	LIPIDS	P-AA	dN15	DOM
2	3, 6, 9, 12, 18, 23	X	X	X	X		
3	2, 6, 7, 11, 16, 21 3, 5, 8, 12, 17, 20	X	X				 X
4	2, 5, 7, 8, 11, 17, 20, 23	X	X			X	
5	2, 3, 4, 5, 10, 16, 18, 19, 23	X	X				X
6	1, 5, 8, 12, 16, 20, 23	X	X	X	X		
7	2, 4, 7, 10, 12, 16, 18, 22 1, 3, 6, 9, 11, 15, 17, 21	X	X				 X
8	1, 5, 12, 15, 18, 21, 22	X	X			X	
9	1, 3, 7, 9, 12, 15, 18, 22						X
10	1, 4, 8, 12, 16, 20, 23	X	X	X	X		
11	2, 4, 6, 9, 16, 20, 24 1, 3, 5, 8, 15, 17, 19, 21	X	X				 X
13	2, 5, 7, 11, 13, 17, 20, 23	X	X			X	
14	1, 4, 5, 6, 7, 8	X	X				X
15	9, 12, 13, 14, 16, 17	X	X				
16	1, 4, 5, 6, 8, 9	X	X				X
17	10, 13, 14, 15, 17, 18	X	X				
18	9, 12, 13, 14, 18, 21	X					X
19	1, 4, 5, 6, 7, 9	X	X				
20	10, 13, 14, 15, 16, 18	X	X				X
21	1, 3, 19, 22, 23, 24	X	X				
22	6, 9, 10, 11, 12, 14	X	X				X
23	1, 4, 5, 6, 7, 10	X	X				
24	1, 4, 5, 6, 7, 8	X	X				X
25	2, 4, 5, 6, 7, 9	X	X				
26	1, 4, 5, 6, 7, 9	X	X				X
27	1, 4, 7, 10, 13, 16, 19, 22						X
29	2, 6, 8, 11, 14, 18, 20, 24					X	
30	1, 3, 5, 9, 13, 15						X

Marine snow catcher: For the snow catchers, the filtering protocols were as stated above with the exception that for the fast sinking fraction (F3) the total tray contents were filtered rather than a volumetric measure.

Table 2: Summary of sample collection from the marine snow catcher.

MSC #	Fraction	PCPN	PP	LIPIDS	P-AA
1	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X	X	X

2	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X	X	X
3	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X	X	X
9	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X	X	X
10	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
11	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
12	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X	X	X
13	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
14	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
15	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
16	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
17	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
18	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
19	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
20	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
21	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
22	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
23	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		
24	Susp (F1), Slow sinking (F2), Fast sinking (F3)	X	X		

SAPs Deployments

SAPs were deployed on 5th August (SAPs 1 and 2), 7th August (SAPs 3) and 9th August (SAPs 4).

Table 3: Summary of SAPS deployments and volume filtered.

SAPS	Depth	Deployment length (h)	Meter start	Meter End	Litres filtered
1	60 m	1	105457	105982	525
2	20 m	1	105982	106365	383
3	50m	1	106365	106962	597
4	50m	1	106962	107442	480

The determination of pelagic nitrogen regeneration rates.

Darren Clark.

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 P/DOM recalcitrant. This material represents a significant C-export flux. 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, pelagic nitrogen regeneration will be investigated. Specifically, the processes of NH_4^+ regeneration and nitrification will be examined. The former is primarily associated with the bacterially mediated degradation of organic molecules; if the C:N ratio of organic matter utilized by bacterial cells exceeds the cells C:N (i.e. cellular N-requirements) the excess is released as NH_4^+. The latter is the two stage oxidation of NH_4^+ to NO_2^- to NO_3^-, facilitated by specific clades of bacteria and Achaea. In combination, 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 aim of this research is to understand variability in N-regeneration processes, how rates relate to particle loading, and how tidal re-suspension of benthic particles may influence exchange processes with the base of the water column.

Experiments

Large Marine Snow Catcher (LMSC) experiments: The regeneration of N associated with 3 particle fractions (suspended, slow and fast sinking) was determined during LMSC deployments below the photic zone (50m). The rates of NH_4^+ regeneration, NH_4^+ oxidation and NO_2^- oxidation were measured on each fraction. Method details are provided below. The volume of LMSC was 300L. Each quarter of the fast sinking particle tray represented the particle load from 75L of seawater. For deployments at station 008 and 040, 25% of the particle tray was used for N-regeneration incubations. The remainder was used for respiration measurements (Elena) and particle characterization (Emma). For station 060, 75% of the tray was used with the remainder used for particle characterization.

Tidal study: The CTD was used to collect seawater samples from the base of the water column within close proximity to the seabed. Water was collected every 2 hours over a 12 hour period. An estimation of N-regeneration rates (NH_4^+ regeneration, NH_4^+ oxidation) in samples containing various degrees of tidally re-suspended material was undertaken.

Methods

The regeneration of DIN was investigated using ^{15}N dilution methods (Clark et al 2006, 2007). The LMSC was used to collected seawater from a specific depth. When the aphotic zone was sampled, the transparent viewing windows of the LMSC were covered to stop light intrusion. 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 LMSC. 1.5L of this water was added to each of 3 2.2 L bottles containing either $^{15}NO_3^-$, $^{15}NO_2^-$ or $^{15}NH_4^+$. The ^{15}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}N. FSP were recovered in a tray from the LMSC, 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}N. One quarter of the total FSP load (equating to the FSP

content of approximately 75L 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 incubator for 30 minutes to ensure that the isotope was homogenously distributed. Following this period, bottles were used to fill 1.0L incubations bottles and returned to the incubator for a period of 12-24 hours (experiments tested differing incubation times). The remaining ^{15}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 synthesizing 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 synthesized 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 synthesized 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 homogenize after which sample pH was verified to be < 2.0. Reagent 2 (24 g NaOH and 0.416 g 2-napthol 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 $ng \cdot \mu L^{-1}$) and the concentration verified against analytical standard solutions (Sigma-Aldrich). Appropriate volumes of deuterated internal standards (i.e. comparable to samples 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 µm 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 µm 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.

Sampling events table.

STNNBR	Date	Lat/Long	Gear	Depth	Process
008	5/8/14	49 23.18/8 37.13	LMSC	50m	NH_4^+ Reg
008	5/8/14	49 23.18/8 37.13	LMSC	50m	NH_4^+ Ox
008	5/8/14	49 23.18/8 37.13	LMSC	50m	NO_2^- Ox
040	7/8/14	48 34.57/9 31.0	LMSC	50m	NH_4^+ Reg
040	7/8/14	48 34.57/9 31.0	LMSC	50m	NH_4^+ Ox
040	7/8/14	48 34.57/9 31.0	LMSC	50m	NO_2^- Ox
060	9/8/14	51 08.26/6 35.16	LMSC	50m	NH_4^+ Reg
060	9/8/14	51 08.26/6 35.16	LMSC	50m	NH_4^+ Ox
060	9/8/14	51 08.26/6 35.16	LMSC	50m	NO_2^- Ox

088	10/8/14	51 09.38/6 34.52	CTD(Nisk 2)	92m	NH_4^+ Reg/Ox
092	10/8/14	51 09.38/6 34.52	CTD(Nisk 2)	92m	NH_4^+ Reg/Ox
096	10/8/14	51 09.38/6 34.52	CTD(Nisk 10)	92m	NH_4^+ Reg/Ox
100	10/8/14	51 09.38/6 34.52	CTD(Nisk 11)	92m	NH_4^+ Reg/Ox
104	10/8/14	51 09.38/6 34.52	CTD(Nisk 7)	92m	NH_4^+ Reg/Ox
108	10/8/14	51 09.38/6 34.52	CTD(Nisk 2)	92m	NH_4^+ Reg/Ox
110	10/8/14	51 09.38/6 34.52	CTD(Nisk 2)	92m	NH_4^+ Reg/Ox

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. Analysis will take approximately 6 weeks, after which a high quality data set is expected to be delivered.

Modifications to be made for the SSB cruise program.

- LMSC deployments for N-regeneration studies will be undertaken at night, removing the risk that samples are exposed to sunlight.
- 75% of the particle tray from LMSC deployments will be used for N-regeneration incubations. An incubation period of 24 hours will be used.
- The full programme will include N-assimilation rate determinations. This will include urea assimilation.

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

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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.
2. Derive 24 h-in situ production rates from diurnal changes at process stations
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 are 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. 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. 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 ΔO_2/Ar ratio.

Craig and Hayward (1987) were the first ones describing a technique for using ΔO_2 and Ar differences to determinate NCP. The equation that is now used is ΔO_2/Ar ratio, and is defined as follow in Eq. (1).

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

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

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 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 12ºC (5 to 10ºC below the sea surface temperature, to avoid temperature-induced supersaturations and subsequent bubble formation) The flight tube was in a thermally insulated box maintained at 50ºC.

In addition to the continuous underway MIMS measurements, I also analysed CTD samples 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^3 samples were drawn into pre-evacuated glass flasks poisoned with 7 mg $HgCl_2$ [*Quay et al.*, 1993]. These samples will be later analyzed 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), resolution of 10 second. The measurements were from the open bottle connected to the underway sampling system that I have used to measure the O_2/Ar ratios.

Discrete samples:

The CTD profile has shown a stratified water column during all the cruise sampling. The mixed layer was between 15 – 40 meters deep and the euphotic zone was always around 5 meters deeper. Peaks of chlorophyll maximum and oxygen were mostly found in the below the bottom of the mixed layer and in the euphotic zone. The following samples were collected:

CTD	Latitude N	Longitude W	Start date	Start time (GMT)	Niskin Bottle	Depth	500ml bottle	Ev. Bottle
1	49 48 80	005 28 66	04/08/2014	11:20:00	19	5	24	
					15	17	25	945
					11	25	27	991
					9	35	28	
					8	50	29	
					6	65	31	
					2	80	36	
2	49 23 194	08 37 127	05/08/2014	5:10:00	22	5	24	
					17	20	25	
					14	30	27	956
								997

								998
					11	45	28	964
								952
								961
					8	60	29	
					5	100	31	
4	49 22 311	08 36 465	05/08/2014	16:08:00	24	5	24	
					21	20	25	
					15	40	27	983
								946
								960
					9	45	28	963
								967
								104
					7	60	29	
5	48 20 30	009 43 62	06/08/2014	8:24:00	22	5	24	
					16	25	25	976
					12	35	27	947
					9	50	28	
					6	75	29	
					2	1000	31	
6	48 34 193	009 30 616	07/08/2014	6:05:00	24	5	24	
					21	15	25	
					18	35	27	957
								971
								958
					10	40	28	943
								972
								851
					9	50	29	
					6	120	31	
7	48 34 59	009 30 92	07/08/2014	11:09:00	24	5	24	
					19	20	25	
					14	42	27	970
								944
								968
					8	55	28	936
								980
								962
					6	90	29	
					5	120	31	
8	48 34 270	009 30 276	07/08/2014	15:00:00	23	5	24	
					20	15	25	166
					17	29	27	975
								949
								990
					14	40	28	950
					11	60	29	965
					9	90	31	
9	50 15.483	007 44.611	08/08/2014	11:04:00	20	5	24	
					19	20	25	175
								940
								996
					13	34	27	995
								984
								994
					8	45	28	959
					4	60	29	
					2	93	31	
10	51 08.265	06 35.149	09/08/2014	6:09:00	24	5	24	

					18	20	25	96
								124
								62
					17	30	27	
					13	35	28	101
								183
								77
					9	50	29	
					6	60	31	
					3	85	36	
					11	35	phyto	10L
11	51 7.248	6 37.283	09/08/2014	10:40:00	24	5	24	
					18	28	25	113
								79
								73
					15	34	27	109
								202
								12
					10	36	28	
					7	50	29	
					3	70	31	
12	51 7.097	6 37.498	09/08/2014	16:05:00	24	5	24	
					21	15	25	108
								5
								78
					18	25	27	103
								90
								82
					15	37	28	
					9	48	29	
					6	65	31	
15	51 9.41	6 34.252	10/08/2014	8:23:00	15	30	24	84
16	51 9.35	6 34.600	10/08/2014	9:16:00	7	31	24	74
17	51 9.17	6 3536	10/08/2014	10:13:00	16	36	24	106
18	51 8.989	6 35.833	10/08/2014	11:22:00	17	30	24	93
19	51 8.869	6 36.153	10/08/2014	12:18:00	8	17	24	105
20	51 8.80	6 36.31	10/08/2014	13:14:00	17	16.3	24	100
21	51 8.75	6 3639	10/08/2014	14:17:00	2	17	24	110
22	51 8 747	6 36.39	10/08/2014	15:25:00	13	9	24	88
23	51 08.742	6 36.29	10/08/2014	16:24:00	22	18	24	97
24								
25	51 8 74	6 36.24	10/08/2014	18:20:00	8	15	24	94
26	51 8 74	6 36.24	10/08/2014	19:24:00	8	15	24	992
27	51 12.701	6 8.489	11/08/2014	11:00:00	23	5	24	
					20	15	36	942
					17	25	25	
					14	28	27	941
					11	31	28	
					8	50	29	
					5	70	31	
29	51 8.91	6 36.24	12/08/2014	7:00:00	4	70	24	
							4	
					5	70	25	
					16	15	27	
							20	
					17	15	28	
					22	5	29	
							36	
					23	5	31	

31	51 8.218	6 37.771	12/08/2014	13:44:00	4 4 4 4 4 4	21 21 21 21 21 21	4 20 36 31 28 25	

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Phytoplankton community composition and marine snow catcher measurements focusing on the chlorophyll maximum

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Introduction

In seasonally stratified temperate coastal and shelf seas, a mid-water chlorophyll maximum, 'thin layer', is often detectable just below the thermocline, with associated increased abundances of phytoplankton cells. The relative importance of these summer subsurface chlorophyll maxima in relation to export production however has not been previously investigated. Therefore, the main aim for the cruise was to sample these chlorophyll maxima in order for later establishment of their potential for export of organic carbon.

Research Approach

Two sampling devices were used:-

1. A CTD mounted on a niskin rosette system
2. A small marine snow catcher

Samples from niskin bottles and from the marine snow catcher were processed as follows.

1. CTD niskin samples: Niskin bottles on the CTD rosette system were sampled when a chlorophyll maximum was present. Since phytoplankton community composition is a key factor that influences export production, lugol's and glutaraldehyde samples were collected for 4-7 depths (spanning depth to surface, and on many occasions spanning the chlorophyll maximum) for many of the cruise CTD casts, along with occasional size fractionated chlorophyll (total, >10µm and >50µm) and HPLC samples. Therefore, phytoplankton community composition of the chlorophyll maxima, bottom mixed layer and upper mixed layer could later be assessed.

2. Marine snow catcher samples: 3 small marine snow catcher deployments to just below the chlorophyll maximum and 3 paired small marine snow catcher deployments to just below he chlorophyll maximum and in the upper mixed layer were conducted over the cruise, with the suspended, slow sinking and fast settling fractions being analysed for all deployments. For the suspended and slow sinking fractions POC, HPLC and lugol's samples were collected. While the fast sinking fraction was photographed using an imaging rig to allow for later determination of the POC content of the fraction, and then particle setting experiments were conducted to allow for later determination of the sinking rate of the fast sinking fraction. Additionally, 18-20 randomly picked aggregates were placed on a GF/F filter to allow for later pigment analysis of the fast sinking fraction using the HPLC technique.

TECHNIQUES EMPLOYED

- Lugol's preservation - 1ml of lugol's iodine added to 50ml of sample
- Glutaraldehyde preservation - 50µl of 50% glutaraldehyde added to 10ml of sample
- Size fractionation - 50ml of sample filtered through appropriately sized mesh or track-etched membranes, before being filtered through a 25mm dia. GF/F filter (filtration performed using a syringe pump)
- HPLC sample collection - 1-2L of sample filtered through a 25mm dia. GF/F filter using a filtration rig
- POC sample collection - 1-2L of sample filtered through a pre-combusted 25mm dia. GF/F filter using a filtration rig
- Settling experiments - 2 sinking times recorded as individual particles passed two discrete points within a 2L measuring cylinder filled with suspended fraction seawater

MEASUREMENTS

Date	Station	Event	Depths (m)	Measurements
05/08	011	CTD cast 3	138.7	Lugol's and glutaraldehyde
			101.4	
			51.8	
			35.4	
			21.1	
			5.8	
05/08	021	CTD cast 4	136.4	Lugol's and glutaraldehyde
			100.8	
			45.8	
			40.4	
			30.8	
			5.7	
06/08	030	CTD cast 5	125.0	Lugol's, Glutaraldehyde and HPLC on all depth samples, with size fractionated chlorophyll measurements just on 26.6m and 25.4m
			50.0	
			26.6	
			25.4	
			5.8	
06/08	031	MSC 4	~35.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
07/08	035	CTD cast 6	120.4	Lugol's and glutaraldehyde
			51.2	
			40.4	
			35.4	
			15.8	
			5.6	
07/08	046	CTD cast 8	~120.0	Lugol's and glutaraldehyde
			~90.0	
			~60.0	
			~40.0	
			~29.0	
			~5.0	
08/08	056	CTD cast 9	61.2	Lugol's, Glutaraldehyde and HPLC on all depth samples, with size fractionated chlorophyll measurements just on 37.0m, 35.0m and 33.7m
			46.1	
			37.0	
			35.0	
			33.7	
			6.1	
08/08	057	MSC 8	~40.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
09/08	061	CTD cast 10	~85.0	

			61.6	Lugol's and glutaraldehyde on all depth samples, with HPLC on 35.6m
			51.9	
			35.6	
			~30.0	
			6.4	
09/08	071	CTD cast 11	~70.0	Lugol's, glutaraldehyde and HPLC on all depth samples, with size fractionated chlorophyll measurements just on 36m, 34m and 28.2m
			~50.0	
			36.0	
			34.0	
			28.2	
			6.0	
09/08	072	MSC 13	~40.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
09/08	078	CTD cast 13	~65.0	Lugol's, glutaraldehyde and HPLC
			39.0	
			37.4	
			25.4	
			~5.0	
11/08	112	CTD cast 27	50.7	Lugol's, glutaraldehyde and HPLC (+ chlorophyll to be analysed by Emma)
			31.8	
			29.0	
			25.8	
			~5.0	
11/08	116	CTD cast 28	60.8	Lugol's, glutaraldehyde and HPLC (+ chlorophyll to be analysed by Emma)
			34.6	
			33.5	
			32.1	
			5.5	
11/08	117	MSC 27	~40.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
11/08	118	MSC 28	~20.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
12/08	142	CTD cast 30	56.0	Lugol's and glutaraldehyde (+ chlorophyll to be analysed by Emma)
			25.6	
			21.5	
			6.7	
12/08	146	CTD cast 31	61.8	Lugol's, glutaraldehyde, HPLC, chlorophyll and nutrients
			21.4	
			17.7	
			18.2	
			6.7	

12/08	147	MSC 35	~30.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
12/08	148	MSC 36	~15.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
12/08	150	CTD cast 32	50.7	Lugol's, glutaraldehyde, HPLC, chlorophyll and nutrients (no HPLC on 14.0m)
			26.0	
			23.0	
			20.2	
			17.5	
			14.0	
			6.6	
12/08	151	MSC 37	~30.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken
12/08	152	MSC 38	~15.0	HPLC, POC and Lugol's samples taken for suspended and slow sinking fraction. Particle settling expt.s on fast sinking fraction, with HPLC aggregate sample also taken

Measurements of community and bacterial respiration by changes in O_2 concentration after 24 hours incubation, in vivo INT reduction capacity method and continuous oxygen decrease using oxygen optodes.

E. Elena Garcia-Martin (University of East Anglia) and Michelle Barnet (National Oceanographic Centre, Southampton).

The aims of this work were:

1. To determine the variability of the organic carbon remineralization (community and bacterial respiration, CR and BR) during a tidal period and study the effect of the material resuspended by tides on the respiration.
2. To settle the protocol to measure community and bacterial respiration with in vivo INT reduction capacity method (ivINT method), in order to be able to estimate accurate bacterial growth efficiencies of particle attached bacteria.
3. To quantify community and bacterial respiration of the three fractions of the Marine Snow Catcher (suspended, slow sinking and fast sinking) above and below the thermocline with Winkler technique and ivINT method (once established the protocol).
4. To log and quantify continuously the respiration of fast and suspended particles with an oxygen optode.

1.- Sampling and analytical methodology

Seawater was collected directly from Niskin bottles from three morning CTD casts (Table 1) from 3 depths in 10 L carboys. The sampling depths were: above and below the thermocline (matching the Marine Snow Catcher deployment) and the deep chlorophyll maximum. Each carboy was subsampled for measuring community respiration by in vitro changes of dissolved oxygen concentration, community and bacterial respiration by the size-fractionated in vivo INT reduction capacity method (see below).

Water samples from the suspended, slow and fast sinking fractions were collected from the Marine Snow Catcher at 4 stations (Table 2). Suspended material and slow sinking were collected in 2-5 L carboys and transported to a dark room for subsequent subsampling and analysis of community and bacterial respiration, as outlined below. The fast sinking material was taken from one of the quarters of the tray in dark conditions. Special care was taken at all moments to prevent the exposure of the samples to light, and a red light was used while handling the samples (Figure 1). The fast sinking particles were gently siphoned with a pipette into a bottle and it was subsampled from here to the different methodologies. As the water volume was not enough for the different techniques, dilutions of 10:1 and 1:1 (suspended: fast) were applied.

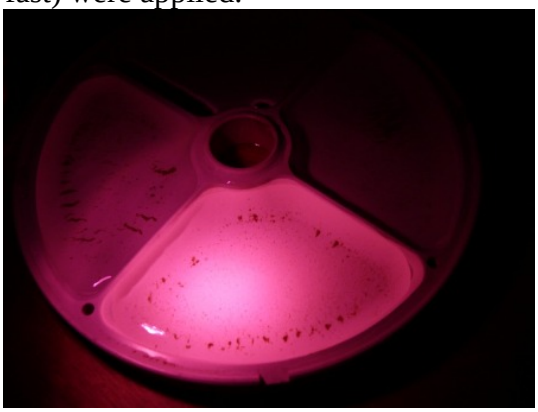


Figure 1. Tray of a large Marine Snow Catcher and the fast sinking particles.

2.- Community respiration by in vitro changes of dissolved oxygen concentration.

CR 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, utilising a photometric end point (Carritt & Carpenter, 1966).
Six 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. Three bottles were fixed at start of the incubation ("zero") with 0.5 ml of sulphate manganese and 0.5 ml of a solution of sodium iodine/sodium hydroxide. The other three bottles were placed in a water temperature controlled incubators inside the CT room for 24 hours. Bottles were removed from the incubators after the 24 hours and fixed as the "zero". All bottles were analysed within the next 24 hours. The concentrations of the thiosulphate used were 0.1 and 0.12 N. Thiosulphate was calibrated every day before the analysis of the samples.
Community respiration was calculated from the difference in oxygen concentration between the means at time zero and at 24 hours dark incubation.

3.- ***In vivo*** **community and bacterial respiration (CR_{INT} and BR_{INT}) by enzymatic assay.**

Four 50-200 ml ambar glass bottles were filled with seawater from each 10 litre carboy from the CTD and seawater from the different fractions from the Marine Snow Catcher. One replicate was immediately fixed by adding formaldehyde (2% w/v final concentration) and used as a killed control. Twenty minutes later all four replicates were inoculated with a sterile solution of 7.9 mM 2-(ρ-iodophenyl)-3-(ρ-nitrophenyl)-5phenyl 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 1-2 hours and then fixed by adding formaldehyde, as for the killed control. After 20 minutes, samples were put inside an ultrasound bath for one minute and then they were sequentially filtered through 0.8 and 0.2 µm pore size polycarbonate filters, air-dried, and stored frozen in 1.5 ml cryovials at –20°C until further processing (one or two days later). The CR_{INT} (i.e. the sum of respiration of the >0.8 µm and 0.2-0.8 µm fractions) and BR_{INT} (considered as the respiration of the 0.2-0.8 µm fraction) were measured following Martínez-García et al. (2009) with a Helios spectrophotometer.
This is the first time that this novel technique was applied to sinking particles and several tests were carried out in order to know the optimal sonication time to detach the bacteria from the particles and a time-course experiment in order to know the optimal incubation time that these samples should be incubated.

Optimal incubation time test.

17 samples of 50 ml from the fast sinking particles from the Marine Snow catcher and from the CTD were collected and dispensed to glass bottles. Incubations were undertaken in the dark for 0, 0.5, 1, 1.5, 2 and 4 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. The optimal incubation time was found to be <2 h and this was adopted as the maximum incubation time for the INT reduction assay.

Optimal sonication time test.

5 samples of 40 ml water (10:1, suspended: fast sinking particles) were collected in glass bottles and fixed with glutaraldehide. Bottles were put inside an ultrasound bath for 0, 5, 10, 30 and 60 seconds. After the sonication time, samples were taken for DAPI counts (see McNeill report).

Dilution test.

A dilution test was applied in order to test if the dilution applied to the fast sinking particles affected the respiration rates measured with the Winkler and ivINT technique. The dilution tested were 1:1, 10:1 (suspended:fast sinking) and non-diluted. Respiration was estimated with changes in oxygen concentration and in vivo INT reduction methods. The sampling procedure was the same as described above but the four quarters of the tray from the small Marine Snow Catchers were used.

There are no data from the fast particles from the Winkler technique as the fast sinking particles were full of sand that interfered with the photometric end point detector.

4.- Continuous monitoring of in vitro oxygen evolution.

Changes in oxygen concentration were measured continuously with three optode systems (YSI ProODO). Prior to each experiment, all the sensors were air calibrated simultaneously. 100 ml seawater sample from the suspended water was collected and filtered by 0.2 μm pore size polycarbonate filters. Samples from the suspended, fast sinking fraction and the filtered suspended water of the deep Marine Snow catcher were taken into 50 ml glass bottles and left inside the water bath system to acclimate during 0.5-1 hour. This was done as the samples experienced a temperature increase during the settle time on deck (2 hours, see Cavan et al. report for the deployment and procedure with the Marine Snow Catcher). Incubation was performed at the in situ temperature conditions ±0.5 °C inside a dark water bath (Figure 2). The filtered water was used as a background for abiotic changes in oxygen concentration associated to any temperature changes that the samples could have experienced during the incubation inside the water bath. After one hour of acclimation, 5-6 ml subsamples were taken and put inside the YSI ProODO glass chambers. The cambers were sealed to the probe with parafilm. Oxygen concentration was recorded every minute during c.a. 24 hours in a chart recorded. Oxygen consumption rates of the fast sinking and suspended material were determined as the slope of the oxygen concentration decrease as a function of time.

Figure 2. YSI PrODO optodes deployment and the water bath used.

Preliminary results.

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

4 incubations for continuous oxygen consumption (ProODO YSI optodes) were run with fast sinking particles from the Marine Snow catcher.

4 Marine Snow catchers were sampled to calculate the carbon remineralization rates of the different fractions above and below the thermocline.

1 tidal effect experiment was performed sampling every two hours at 5 m under the surface and 5 metres above the seabed for in vitro oxygen consumption and at 5 m above the seabed for in vivo INT reduction method.

2 time-course experiments for the in vivo INT reduction capacity method were done, one with samples from the CTD and the other with the slow sinking fraction of a Marine Snow Catcher samples.

1 sonication time-course experiment was performed in order to know the optimal sonication time to detach as many bacteria as possible without damaging the cells.

1 dilution test was performed in order to check if the dilution of the fast sinking particles with suspended water from the same depth affect the remineralization rates.

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

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 1. List of collected water samples for measurements of respiration from CTD.

Gear Code	St N	Date	Time	Site	Latitude	Longitude	Niskin	Depth (m)	Variable/Test
CTD	1	04/08/2014	10:21	Test south of Lizard	49 48.8 N	5 28.66 W	19	5	Optimum incubation time
CTD	6	05/08/2014	05:10	Candyfloss	49 23.18 N	8 37.13 W	17, 11, 8	20, 45, 60	
CTD	35	07/08/2014	06:04	Shelf break	48 34.2 N	9 30.6 W	21, 17, 9	15, 35, 50	
CTD	56	08/08/2014	11:05		50 15.48 N	7 44.62 W			Optode test
CTD	61	09/08/2014	06:08	Celtic Deep	51 08.26N	6 35.16 W	21, 13, 10	10, 35, 50	
CTD	86	10/08/2014	06:58	Celtic Deep	51 09.42N	6 34.28 W	8, 3	5, 92	
CTD	90	10/08/2014	08:59	Celtic Deep	51 09.34N	6 34.65 W	9, 3	5, 92	
CTD	94	10/08/2014	11:03	Celtic Deep	51 08.99 N	6 35.83 W	21, 11	5, 91	
CTD	98	10/08/2014	12:59	Celtic Deep	51 08.80 N	6 36.31 W	18, 12	5, 90	
CTD	102	10/08/2014	15:08	Celtic Deep	51 08.75 N	6 36.39 W	14, 8	5, 95	
CTD	106	10/08/2014	17:00	Celtic Deep	51 08.74 N	6 36.24 W	9, 3	5, 96	
CTD	110	10/08/2014	19:06	Celtic Deep	51 08.74 N	6 36.24 W	10, 3	5, 94	

Table 2. List of collected water samples for measurements of respiration from the Marine Snow Catchers.

Gear Code	St. N	Date	Time	Site	Latitude	Longitude	Depth (m)	Variable/Test	Notes
LMSC	4	04/08/2014	14:27	Test south of Lizard	49 48.71 N	5 28.69 W	40	Optimum incubation time	1 quarter of the fast sinking tray
LMSC	7	05/08/2014	06:05	Candyfloss	49 23.18 N	8 37.13 W	20		1 quarter of the fast sinking tray
LMSC	8	05/08/2014	07:25	Candyfloss	49 23.18 N	8 37.13 W	60		1 quarter of the fast sinking tray
LMSC	12	05/08/2014	12:04	Candyfloss	49 23 N	8 36.6 W	100		1 quarter of the fast sinking tray
LMSC	34	07/08/2014	05:48	Shelf break	48 34.2 N	9 30.6 W	50		1 quarter of the fast sinking tray
LMSC	40	07/08/2014	08:48	Shelf break	48 34.57 N	9 31.0 W	10		
LMSC	62	09/08/2014	06:42	Celtic Deep	51 08.26N	6 35.16 W	50		3 quarter of the fast sinking tray
LMSC	70	09/08/2014	10:22	Celtic Deep	51 07.29N	6 37.22 W	10		2 quarter of the fast sinking tray
SMSC	136	12/08/2014	07:42	Celtic Deep	51 08.91N	6 36.24W	100		whole tray fast sinking particles
SMSC	137	12/08/2014	08:02	Celtic Deep	51 08.91N	6 36.24W	100		whole tray fast sinking particles

Bacterial Production Measurements: RRS Discovery DY026

Sharon McNeill

1.1 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 1.

1.2 Method

Leucine

Water samples were collected from the CTD in acid washed polycarbonate bottles then incubated for bacterial production, samples were also taken for flow cytometer and dapi counts these were frozen at -80C to be analysed back at SAMS. For bacterial production aliquots of 10ul leucine working solution (0.01 MBq ml^{-1}) were pipetted into each 2ml sterile centrifuge tube then additions of 1.6ml sample added this was carried out in the radioisotope container. For each depth two samples in duplicate were run for T0, T1, T2 and T3, and incubated in a coolbox in the CT room at above and below thermocline temperatures. Samples were fixed with 80ul of 20% paraformaldehyde (giving a final concentration of 1%). Samples were then transferred to the radiochemistry container for processing, 25mm GFF and 0.2um polycarbonate filters presoaked in 1mM non labelled leucine in separate petri dishes, were placed on the 25mm filter rig with the GFF as a backing filter. Additions of 2ml of deionised water added onto the filter unit then the sample pipetted into each filter holder. Both samples at each timepoint were combined and filtered as one. To remove the remaining sample the tube was rinsed with deionised water. The 0.2um polycarbonate filter was placed into a scintillation vial and dried overnight in the fumehood, 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 and also on 5ml sample volumes at 1:10, 1:5 and 1:1 dilutions with fast and suspended fractions. Marine snowcatcher fast fractions samples were taken from a quarter tray approx 40 of the 200ml shared with Elena.

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 count for flow cytometer and dapi slide prep. Samples were incubated in a screened deck tank. Then processed as water column methods for leucine.

Sonication experiment- Dapi

A snowcatcher sample was taken from fast particulate material on the first day for a sonication trial. Samples were fixed in 1% glutaraldehyde and then sonicated in duplicate for 0,5,10,30 and 60 seconds. Samples were then stained with DAPI at 25µl per 5ml sample and left to stain for a maximum of 5 minutes. The sample was filtered onto a 0.2µm black polycarbonate filter with a 0.8µm cellulose nitrate as a backing filter. The filter was then placed on a microscope slide and frozen at -20C till ready to enumerate.

Table 1: Leucine sampling

Date	CTD	MSC	Depth	Bottle	Fraction	Comments
05/08/2014	2		20	17		
	2		45	11		
	2		60	8		
		1	20		Suspended, Slow and Fast (Giant Snowcatcher)	Above thermocline
		1	60		Suspended, Slow and Fast (Giant Snowcatcher)	Below thermocline
07/08/2014	6		15	21		
	6		35	17		
	6		50	9		
		5	50		Suspended, Slow and Fast (Giant Snowcatcher)	Below thermocline
		6	10		Suspended, Slow and Fast (Giant Snowcatcher)	Above thermocline
08/08/2014	9		20	19	T0,T6,T12,T18,T24	24hr calibration experiment
09/08/2014	10		50	10		
	10		38	13		
	10		10	21		
		10	50		Suspended, Slow and Fast (Giant Snowcatcher)	Below thermocline
		12	10		Suspended, Slow and Fast (Giant Snowcatcher)	Above thermocline
10/08/2014	14		92	3		Tidal sampling
	16		92	3		Tidal sampling
	18		91	11		Tidal sampling
	20		90	12		Tidal sampling
	22		95	8		Tidal sampling
	24		96	3		Tidal sampling
12/08/2014		31	100		Suspended, Slow and Fast (Small Snowcatcher)	Below thermocline dilution experiments
		32	100		Suspended, Slow and Fast (Small Snowcatcher)	Below thermocline dilution experiments

Marine snow catcher deployments and particle characterization

Emma Cavan

Giant MSC

Scientific motivation

The marine snow catchers (MSCs) are an integral part of the Shelf Seas Biogeochemistry program. They are used to collect sinking particles in 3 sinking rate fractions, suspended, slow and fast sinking. On these particles bacterial production, aerobic respiration, sinking rates, organic chemistry and total mass can be measured. This method of capture allows *in situ* rates and states to be measured and links the pelagic and benthos, particularly during tidal studies. The MSCs allow us to quantify how much organic material produced in the surface either reaches the sediment, consumed in the water column or advected off the shelf.

Methods

At the 3 process stations (Candyfloss, Shelf break and Celtic Deep) we deployed the MSC above and below the deep chlorophyll maximum and above the sea bed (~20, 40 and 90 m respectively). The MSC is deployed with both ends open and a messenger fired to close the plungers and brought immediately to deck to be left to settle. Ideally it should stand for 2 hours in custom-made deck frames. After 2 hours the suspended fraction can be sampled, then this is drained and the slow sinking fraction is sampled. After this the tray with the fast sinking particles can be removed.

Deployments

On board we had the entire NOCS 'fleet' of MSCs. This consists of 3 small MSCs from the original design and 2 giant MSCs. The small MSCs can hold 100 L of water and the giant MSCs 350 L. On this cruise we deployed 38 MSCs with a <90 % success rate in 8 days, a WORLD RECORD! During the 3 process station on this cruise the MSC was analyzed by all parties. During the tidal study the rate groups only analysed the CTD and so here organics, mass and microscope analysis were collected for. Additionally Michelle Barnett (NOCS) undertook opportunistic sampling using the small MSC.

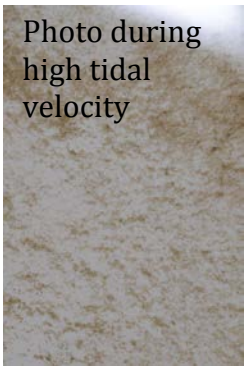


Photo during high tidal velocity

Limitations

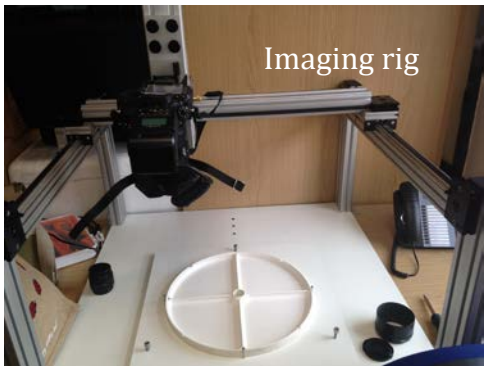
In terms of deployments there are a few issues that arose with the giants MSCs on this cruise. Firstly we did not have the deck frames which meant lashing against the bulwark and using a step ladder to release the wire from the top of them, at 2.5 m tall this presents serious health and safety concerns. Also deploying them in any high wind or sea state is risky due to their weight, ~1/3 of a ton. Additionally the clips used to secure the base to the top are not suitable for the size of the giant MSCs which resulted in using ratchet straps and as a result often leaking. All of the above led us to use the small MSCs when sampling in high resolution or high winds. This is a slight concern for future cruises as the small MSCs do not provide enough material for rate measurements. Even ¼ of the giant MSC tray in the summer may not have been enough for rate measurements.

All rate measurements on this cruise needed the samples to remain in the dark from capture to measurements. This presented some trouble as the base of the MSCs are clear plastic. We used bin liners and tape to block out light.

Broken base of small MSC

However when separating the top from the base the particles in the tray were exposed to light and therefore excitation and potential bleaching. Again we used a plastic bag to cover the base but some exposure is inevitable. Even using a clear tube for siphoning into a dark bottle exposes them to light. These things can and must be overcome by November cruise. The easiest solution is for particles to be collected at night when rate measurements are done.
We used 2/3 of the small MSCs and during one of the final deployments part of the base of a small MSC cracked. Although still useable this shall need to be fixed before it can be used regularly at sea again.

Stephanie Wilson, particle characterization


Imaging rig

To determine how representative the quarters of the tray of fast sinking particles are of the entire tray Stephanie Wilson built an imaging rig to photograph the trays before the samples were split and analysed by various groups. Depending on the size of the tray (small or giant) 30-100 photos were taken which can then be stitched together at a later date using Image J. When particles were collected for rate measurements these 1/4s had to be removed before flash photography could take place. Using the area of particles and conversion rates of Alldredge (1998) particulate organic carbon content can be estimated. This is the conventional method used to estimate POC for the MSC fast sinking fraction. However as POC was also chemically measured the two methods can be compared.
The other motivation for the photography is to work out the proportion of faecal pellets compared to other particles in the tray such as aggregates.
When possible ¼ of a tray was also fixed in formalin. This is to allow later analysis in the lab using a microscope and further characterization of the type of particles in the Shelf Seas. In the November cruise Stephanie will continue with these measurements and also collect particles for molecular analysis with a focus on the role of zooplankton on export.

Table of deployment information

cruise	station	date	lat	long	event	Time	MSC	Type	depth	photo	formalin				
								all	15	1	0	0	0	na	michelle

Near Surface Gradients

Richard Sims

Science Background-

Physical and biological mechanisms affect the sea surface concentration and flux of carbon dioxide (CO_2) between the ocean and atmosphere. Gradients in temperature and salinity between the bulk sub-surface water and the sea/air interface are likely. Variations in phytoplankton primary production also have the potential to create vertical gradients in pCO_2. This studentship seeks to improve understanding of these physical and chemical gradients in near surface (<10 m) shelf waters.

This work will help answer a critical question within the Shelf Sea Biogeochemistry (SSB) research programme:
What are the current annual exchanges of carbon between UK/European shelf seas, the atmosphere, and the open ocean?

Cruise Objectives-

- Test the deployment of the NSOP on board the ship to find a workable deployment strategy
- Obtain first data from the SSB cruises about near surface gradient
- Install IR-sensors on the front of the ship and get them continuously logging
- Familiarise myself with life at sea and with the Discovery so I can improve my setup for next time.
- Help with the shelf sampling by collecting TA/DIC samples from the midday CTD.
- Prepare and attach temperature sensors onto CEFAS smartbouy.

Day by Day account of events-

July28th- August 1st (Setup days) – Setup took much longer than expected mostly in part due to the installation required for the IR sensors on the bow of the ship. The IR sensors eventually started working once the 15core cable had been run up from the met lab up through to the met platform and into the logger box stored there. The accelerometer was not setup. Gas standards were stored in a rack in the hanger flowing into the deck lab where the remainder of my kit was stored. The PC, nafion dryer, temperature sensor electronics, membrane equilibrator and peristaltic pump were located at the far end of the lab close to the sink with the bench to the left for working. The remainder of my equipment was kept underneath the bench except for the reel of tubing and the buckets on nylon rope. Nitrogen and compressed air cylinders were put in the gas bottle store.

August 4th- First Deployment day

The lower IR sensor stopped working when we left Southampton and was patchy for the majority of the cruise, probably because of a loose connection. The NSOP winch was faulty and would not work. Despite the winch not working NSOP was still deployed. We trailed deploying off the aft of the ship on the crane, this proved to be unsuitable as the dp or movements by the bridge caused the buoy to rock, when there was a sharp movement by the ship the buoy almost flipped! It was eventually decided with some hesitance from some NMF staff to put it out of the CTD hanger on one of those winches with slack on the crane line it appeared to work well. It was noted that the CTD only logs at a maximum rate of once every 6s which is a minor issue. NSOP rope floats were ineffective at providing buoyancy.

August 5th- Repairs/Transit

Lots of effort went into fixing the winch and it was discovered that it was a wiring fault which was fixed with the help of Jon Short.

August 6th -First successful deployment/disaster

The IR sensor began working again which indicated that the problem was intermittent. NSOP was deployed from the CTD crane unsuccessfully as even with a slightly slack cable NSOP was forced

around considerably and eventually the strop was cut apart on the stainless steel plates. This was a blessing in disguise as the buoy happily drifted away from the ship and was positioned by the two slack lines. This deployment last 3 hours, the lifting bar/strop was hooked on to the crane using a pole during retrieval. An eyelet was welded onto the top of NSOP for the deployment the next day. The water column was being mixed heavily by the use of the aft thrusters, communication with the captain to discuss this was poor on this day. The large head for the pump reduced its efficiency substantially.

August 7th –

NSOP was successfully deployed again today. The buoy was deployed on the crane at the back and lowered into the water using a quick release to detach it from the crane. The captain agreed to turn off the DP after discussions with him. Slack lines were improved by making the bit near the buoy a chain so the nylon would not be damaged by the stainless plates. Pump flow rates are a problem as the water side flow kept dropping during the deployment. Helped turn on and activate the underway pco2 system on the discovery.

August 8th

Another successful deployment, the arm on the back of the ship extended the slack line point substantially and helped keep the buoy away. Bubbles were seen on the equilibrator outflow, indicative of non equilibration probably due to a flow rate drop form 2L to 1L. Winch spool problem as the rope was not spooled by hand, this resulted in the Kevlar being sliced and the cage falling free, meaning it was recovered separately. Go pro footage of the shark was taken on this day. Chata also got 1 discrete depth sample for her MIMS, this sample was not analysed. Liqui-cel equilibrator cleaning in the evening.

August 9th –

Another successful deployment using a cleaned liquid-cel and a new piece of marprene tubing. No apparent flow rate problems

August 10th-

Bad weather prevented deployments on this day. Instead I spent the day collecting CTD bottle water for Claire Mahaffy during the tidal cycle experiment using the snowcatchers.

August 11th-

Another successfully deployment. Very small changes in pump efficiency. Considerable bad weather meant that NSOP was shunted around a lot and the captain was apprehensive of deploying NSOP in similar conditions again.

August 12th

Temperature calibration in a waterbath conducted in the morning. The deployment was cut short as the battery enclosure lid was forced off by the surrounding stainless steel lifting it off. The enclosure then flooded with water and the circuit shorted and stopped working. NSOP was then redeployed and dried out. Refixed the underway pco2 system on the discovery after the water error.

August 13th

Final day of sampling and unfortunately the pumping efficiency dropped substantially in a very short amount of time. Less than 5 minutes to a flow less than 0.5L/min. At this point I decided to cancel the deployment and tried to fix the pump unsuccessfully.

Data Collected- `

- Sporadic underway co2 measurements to compare with the onboard system
- Primary Data- Vertical profiles of co2 (and ancillary information), temperature and salinity
- SST skin temperature and down welling irradiance
- 60 TA and DIC sample bottles for post analysis by NOC staff (not responsible for this)
- Underway Pco2 system (not responsible for this)

Outcomes-

- All of my objectives were achieved to some extent on this cruise.

- I had several successful deployments, I would have liked to have gotten more data as there were a lot of missed opportunities as a result of equipment not working in one form or another including winch failure, winch spool problems, pump problems and IR sensor wiring.
- NSOP is not completely seaworthy and needs a lot of additional work before she is fit to come out to sea without any faults.
- My relationship with the crew was good and this helped immensely during deployments.
- I have not had an opportunity to connect the accelerometers up which has meant I wasted a good opportunity to get data for that and test it.
- The TA and DIC sampling whilst not difficult did cause some clashes as it demanded 40minutes of my time at moments when I was about to deploy.
- Time was wasted on some of the CO_2 side of things, the gap between calibration and retrieval was also long at times.
- A lot of time was wasted trying to get the underway co2 system working on the discovery, this was not my responsibility but the data was needed for comparisons.
- I enjoyed my time at sea and am now accustomed to life at sea and the ship.

Success Rating- 7/10

Mesozooplankton biomass and metabolic rates

SLC Giering

1. 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_2 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/d. 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 DY026, zooplankton biomass and composition was sampled using WP2 nets. These samples will compliment the SSB zooplankton biomass data time series by providing data for autumn. I further used this opportunity to trial the methods that I proposed to do during the forthcoming SSB cruises. These experiments targeted measuring the process rates (excretion, sloppy feeding, and grazing) by mixed communities using incubation experiments.

2. Material & Methods

2.1. Abundance estimates

8 WP2 nets fitted with non-filtering cod-ends and a closing mechanism were deployed at each process station: 4 during daytime and 4 during night-time to sample below and above 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-fractioned 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 CN analysis.

2.2. Rate-series experiments

The rate-series experiments were aimed to measure different metabolic rates of the same ‘mixed community’. To do so, I transferred the same group from one size class of zooplankton (63-200 µm and 200-500 µm) through sequential experiments determining rates of (1) excretion of DOC, ammonium, and nutrients, (2) sloppy feeding release of DOC, ammonium, and nutrients, and (3) ingestion. The order is chosen to combine acclimation phases with actual rate measurements.

3. Sample summary

51 nets were deployed in total (Table 1) at five stations. Two rate-series experiments, which measured excretion and sloppy release of DOC, ammonium, and nutrients, were carried out. Ammonium and nutrient samples were analysed on board. DOC samples were frozen and stored at -20°C degrees for on-shore analysis. Two grazing experiments were carried out, from which one was conducted in conjunction with a rate-series experiment. From the grazing experiments, samples were taken for Chlorophyll and phytoplankton (preserved using Lugol's iodine).

Figure 1 Zooplankton abundance samples from 12th August. The colours indicate that the deep 63-µm net collected sediments whilst the shallow 63-µm net collected large phytoplankton from the chlorophyll maximum.

Date	Daytime	Stn Name	Stn #	Net	Position (N)	Position (W)	Time Opened (hh:mm)	Time Closed (hh:mm)	Depth (m)	Mesh size (µm)	Use
04/08/14	Day	Test Station	005	1							
05/08/14	Day	Candyfloss	013	2	44°22.31	8°36.46	13:10	13:35	120-30	63	Frozen (2x)
05/08/14	Day	Candyfloss	014	3	44°22.31	8°36.46	13:41	14:10	120-30	63	Formalin
05/08/14	Day	Candyfloss	015	4	44°22.31	8°36.46	14:12	14:27	30-0	63	Frozen (2x)
05/08/14	Day	Candyfloss	016	5	44°22.31	8°36.46	14:29	14:42	30-0	63	Formalin
05/08/14	Day	Candyfloss	017	6	44°22.31	8°36.46	14:45	14:55	120-30	200	Frozen (2x)
05/08/14	Day	Candyfloss	018	7	44°22.31	8°36.46	14:59	15:10	120-30	200	Formalin
05/08/14	Day	Candyfloss	019	8	44°22.31	8°36.46	15:12	15:21	30-0	200	Frozen (2x)
05/08/14	Day	Candyfloss	020	9	44°22.31	8°36.46	15:22	15:30	30-0	200	Formalin
05/08/14	Night	Candyfloss	024	10	49°22.33	8°36.46	21:29	21:42	120-30	63	Frozen / Formalin
05/08/14	Night	Candyfloss	025	11	49°22.33	8°36.46	21:45	22:00	30-0	63	Frozen / Formalin
05/08/14	Night	Candyfloss	026	12	49°22.33	8°36.46	22:10	22:15	120-30	200	Frozen / Formalin
05/08/14	Night	Candyfloss	027	13	49°22.33	8°36.46	22:21	22:26	30-0	200	Frozen / Formalin
05/08/14	Night	Candyfloss	028	14	49°22.33	8°36.46	22:27	22:30	30-0	200	Exp 1
07/08/14	Day	Shelf Break	036	15	48°34.21	9°30.64	07:08	07:16	120-50	63	Frozen / Formalin
07/08/14	Day	Shelf Break	037	16	48°34.21	9°30.64	07:27	07:37	50-0	63	Frozen / Formalin
07/08/14	Day	Shelf Break	038	17	48°34.21	9°30.64	07:54	07:58	120-50	200	Frozen / Formalin
07/08/14	Day	Shelf Break	039	18	48°34.21	9°30.64	08:09	08:14	50-0	200	Frozen / Formalin

07/08/14	Night	Shelf Break	050	19	48°34.74	9°35.3	20:50	21:01	120-50	63	Frozen / Formalin
07/08/14	Night	Shelf Break	051	20	48°34.74	9°35.3	21:13	21:18	50-0	63	Frozen / Formalin
07/08/14	Night	Shelf Break	052	21	48°34.74	9°35.3	21:29	21:34	120-50	200	Frozen / Formalin
07/08/14	Night	Shelf Break	053	22	48°34.74	9°35.3	21:41	21:45	50-0	200	Frozen / Formalin
09/08/14	Day	Celtic Deep	064	23	51°08.27	6°35.12	07:35	07:42	95-50	63	Frozen / Formalin
09/08/14	Day	Celtic Deep	065	24	51°08.27	6°35.12	07:50	07:55	50-0	63	Frozen / Formalin
09/08/14	Day	Celtic Deep	066	25	51°08.27	6°35.12	08:20	08:27	95-50	200	Frozen / Formalin
09/08/14	Day	Celtic Deep	067	26	51°08.27	6°35.12	08:32	08:40	50-0	200	Frozen / Formalin
09/08/14	Day	Celtic Deep	068	27	51°08.27	6°35.12	08:43	08:48	50-0	200	Exp 2
09/08/14	Night	Celtic Deep	080	28	51°08.84	6°38.49	20:38	20:42	25-0	200	Exp 3
09/08/14	Night	Celtic Deep	081	29	51°08.84	6°38.49	20:47	20:59	95-50	200	Frozen / Formalin
09/08/14	Night	Celtic Deep	082	30	51°08.84	6°38.49	21:06	21:09	50-0	200	misfired
09/08/14	Night	Celtic Deep	083	31	51°08.84	6°38.49	21:15	21:20	50-0	200	misfired
09/08/14	Night	Celtic Deep	084	32	51°08.84	6°38.49	21:22	21:29	50-0	200	misfired
09/08/14	Night	Celtic Deep	085	33	51°08.84	6°38.49	21:35	21:38	50-0	200	Frozen / Formalin
11/08/14	Day	Benthic A	116	34	51°12.7	6°08.49	12:34	12:51	40-0	63	Exp 4
11/08/14	Day	Benthic A	120	35	51°12.08	6°07.96	15:40	15:48	90-40	63	Discarded
11/08/14	Day	Benthic A	121	36	51°12.08	6°07.96	16:00	16:10	90-50	63	Frozen / Formalin

11/08/14	Day	Benthic A	122	37	51°12.08	6°07.96	16:16	16:22	50-0	63	Frozen / Formalin
11/08/14	Day	Benthic A	123	38	51°12.08	6°07.96	16:33	16:40	90-50	200	Frozen / Formalin
11/08/14	Day	Benthic A	124	39	51°12.08	6°07.96	16:47	16:51	50-0	200	Frozen / Formalin
11/08/14	Night	Benthic A	125	40	51°11.94	6°05.76	20:35	20:41	90-50	63	Frozen / Formalin
11/08/14	Night	Benthic A	126/7	41	51°11.94	6°05.76	20:54	21:02	50-0	63	Frozen / Formalin
11/08/14	Night	Benthic A	128	42	51°11.94	6°05.76	21:08	21:17	90-50	200	Frozen / Formalin
11/08/14	Night	Benthic A	129	43	51°11.94	6°05.76	21:26	21:30	50-0	200	Frozen / Formalin
12/08/14	Day	Celtic Deep	138	44	51°08.91	6°36.24	08:49	08:57	100-40	63	Frozen / Formalin
12/08/14	Day	Celtic Deep	139	45	51°08.91	6°36.24	09:07	09:14	40-0	63	Frozen / Formalin
12/08/14	Day	Celtic Deep	140	46	51°08.91	6°36.24	09:27	09:32	100-40	200	Frozen / Formalin
12/08/14	Day	Celtic Deep	141	47	51°08.91	6°36.24	09:43	09:48	40-0	200	Frozen / Formalin
12/08/14	Night	Celtic Deep	143	48	51°08.1	6°37.89	20:40	20:49	100-40	63	Frozen / Formalin
12/08/14	Night	Celtic Deep	144/a	49	51°08.1	6°37.89	20:58	21:04	40-0	63	Frozen / Formalin
12/08/14	Night	Celtic Deep	144/b	50	51°08.1	6°37.89	21:12	21:17	100-40	200	Frozen / Formalin
12/08/14	Night	Celtic Deep	145	51	51°08.1	6°37.89	21:25	21:30	40-0	200	Frozen / Formalin

Sediment Cores

Matthew Bone

Departed the National Oceanographic Center Southampton, 14:00 hours, 3rd August 2014.

Heading out of Southampton docks as the cumulus clouds rolled over the mask of the ship greeting the English Channel with a roar. Our first meeting was held soon after, giving the chance to meet all the scientists aboard and briefly explain what each member intends to carry out.

My contribution on this cruise would be to collect sediment form the designated sites via a NIOZ sediment core, and look at various parameters associated with the collected sample.

The main experiment aboard would examine the change in ammonium (NH_4^+) as a sheer and vertical stress is applied to the sediment core. This would be carried out by placing a sediment erosion device (FloWave) directly into the core. The experiment would run continuously for approximately two hours and the NH_4^+ analysed at a high time resolution (139 times per second) using a hacked High Performance Liquid Chromatograph (HPLC). This set up was installed and ensured in working order before the cruise set out. On the 3rd, a plan was agreed that would accommodate the experimental needs as well as the crew. A preliminary experimental protocol to undertake a multitude of experiments was also drawn up.

- Sub sampling the mud and freezing for microbiological work.
- Subsampling and incubating mud in the bottom water.
- Running the resuspension experiments and measuring NH_4^+.
- Sampling the resuspension experiments for $^{15}N/^{18}O$ isotopes.
- Setting up a way to continuously measure the concentration on NH_4^+ in the surface water using the underway system.

On the 4th August, several trials were planned to ensure the working of deployable equipment. In this time, there was no planned deployment of the sediment corer and time was spent creating a method to sample from the underway system. The first trail of this method was successfully carried out at a stationary site (49 48.80412N, 5 28.65816W) from 12:33 BST onwards.

A second continuous sampling was carried out during transit from the stationary location (49 47.24790N, 5 41. 556566W) to the Candyfloss site. The continuous sampling continued for 640minutes until the experiment stopped as the pressure exceeding the maximum limit. The pressure fluctuation caused problems during analysis; as the pressure varied by 10bars, the lumosity changed accordingly. The route of the problem is unknown; however, pressure limits can be applied to control the minimum and maximum limits. A disadvantage with setting limits is if they are exceeded, there is a failsafe shutdown of the machine.
During the evening of the 4th, continuous checking of the sampling was undertaken throughout the night to ensure an effective working method.

04.08.18
A new system was set up to continuously measure form the under way system using the HLPC. Two attempts were made and a calibration of the machine carried out (Lat 49 47.24790, Lon 5 41.556566).
A detailed fluorescent scan was undertaken on the surface sea water from the under way system to determine the most suited wavelength to measure ammonium using the HPLC set up.
05.08.14
Two cores were taken from the Shelf break (Lat 49 22.33440, Lon 8 36.46206), but due to the neoprene not stuck on effectively, both cores slumped and leaked water thus rendering them useless for resuspension analysis due to chemical change.
Four incubations were carried instead taking syringe cores from three depths and one throughout the depths sampled and spiked with a nitrification inhibitor. The experiments ran for the next six hours to determine any rapid change in ammonium.

06.05.14
A calibration was carried out on the HPLC to analyse nano-molar concentrations of ammonium.

07.08.14
Three cores were taken between 10am – 12pm from Benthic Site H (Lat 48 34.58532, Lon 9 30.96324). The first core slumped during transit on deck, with water and mud leaking out. The overlying water was syphoned off into brown bottles, and the sediment subsampled using syringes. The sediment was added to the bottles. The incubation experiments ran for 6hours. Due to software error, the data from these experiments were lost. The second core was used in a FloWave resuspension device experiment. A second high resolution scan was carried out from the overlying water on the NIOZ core before the FloWave experiment. Samples were taken for microbiological work – frozen at -80oc.
09.08.14
Three cores (Lat 51 7.09974, Lon 6 37.49844).
ATU experiments were undertaken form sediment collected at Benthic Site H, Core one.
Incubation experiments measuring ammonium were undertaken from sediment collected at Benthic Site H Core one.
Samples were taken for microbiological work – frozen at -80oc.
A FloWave resuspension experiment was ran on intact Core three measuring ammonium, Core one.
The HPLC was set to measure continuously from the underway. On several occasions it failed, but was up and running to measure the impact of increased turbulence and wind forcing upon ammonium concentrations in the ocean.

10.08.14
A FloWave experiment was undertaken from a Core taken at 11am at Benthic Site H.
Sampling continuously from the underway system.

11/08/2014
Three cores taken from Benthic site A (mud).
Samples were taken for microbiological work – frozen at -80oc.
Incubation experiments set up to measure nitrification of NH4+ within the sediment.

- Control
- Control + sediment
- Control + sediment + inhibitor

Underway measurements were made during the spring tide.

12/08/2014
A FloWave experiment was undertaken.

13/08/2014
A NIOZ sediment core was taken from Benthic Site A at 7:30am(Lat 51 12.56622, Lon 6 3.75258). A sediment resuspension experiment then ran for the next hour with measurements of oxygen, nutrients, DOC, 15N/18O and NH4+ being taken throughout.
Resuspension experiment on Core 9 taken from Bethic A.
Microbial samples taken from Core 6 and frozen at -80oc.
Calibrated machine.

Cruise narrative

3rd August 2014. The ship sailed at 14:00 hours having completed fuel maintenance procedures. Engine propulsion trials were carried out in the channel prior to dropping off an engineer via boat transfer at Weymouth at approx 22:30.

4th August 2014. The ship remained on passage, stopping just south of the Lizard to undertake trials of the PML Near Surface Ocean Profiler, the large marine snowcatcher and the nets

5 August 2014. The ship arrived on station at the Candyfloss site early in the morning and undertook a long day of station work similar to that which the main Candyfloss programme will aim to undertake at three key sites, Candyfloss itself, the shelf break and the Celtic Deep. This involved snowcatcher deployments throughout the water column, nets, productivity work, SAPS, coring.

6 August 2014. The ship moved off the shelf break station into deep water in order to trial the combination of gliderbased nitrate sensor and new glider bodyshape which the Sensors on Gliders programme has been working on. This was followed by station work and a deployment of the PML Near Surface Ocean prior to glider recovery. Following the recovery the ship undertook overnight winch trials.

7 August. We conducted a long process station at the shelf break starting at 05:15 and ending at 23:55. This involved corers, nets, the PML near surface ocean profiler, SAPS, snowcatchers and CTDs

8 August We undertook a long transit to the Celtic deep.

9 August We undertook a long process station at the Celtic deep similar to those conducted on 5 and 7 August.

10 August Having completed the basic suite of candyfloss sampling at each station we undertook a 12 hour station with very highly resolved temporal sampling using the CTD and snowcatchers both being deployed every hour.

11 August. The intense sampling on the previous two days resulted in a low activity day with just a noon CTD, PML bouy deployment, nets and snowcatchers being deployed.

12 August. This day was devoted to obtaining samples of deep near bed particulate material in the Celtic deep for biological rate measurements including respiration, bacterial production and organic phosphorus utilisation. We also deployed the PML near surface ocean profiler which flooded on deployment and undertook a detailed study of particle fluxes out of the deep chlorophyll maximum

13 August We undertook the regular noon CTD and obtained sediment cores for Matthew Bone. The PML Near Surface profiler was deployed but failed to function satisfactorily . Following the noon CTD we left for home.

14 August: On passage. The ship docked in Southampton at 19.30

Event Log

Stn	Gear	Site	Description	Date	Start time	Latitude	Long itude
001	CTD	Test south of Lizard	Test South Of lizard	04/08/ 2014	11:21	49 48.8	5 28.66
002	Buoy	Test south of Lizard	Test South Of lizard	04/08/ 2014	13:07	49 48.8	5 28.66
003	Buoy	Test south of Lizard	Test South Of lizard	04/08/ 2014	14:15	49 48.78	5 28.66
004	LMSC	Test south of Lizard	Test South Of lizard	04/08/ 2014	15:27	49 48.71	5 28.69
005	Net	Test south of Lizard	Test South Of lizard	04/08/ 2014	17:20	49 48.71	5 28.79
006	CTD	Candyfloss	Process Station	05/08/ 2014	05:10	49 23.18	8 37.13
007	LMSC	Candyfloss	Process Station	05/08/ 2014	06:05	49 23.18	8 37.13
008	LMSC	Candyfloss	Process Station	05/08/ 2014	07:25	49 23.18	8 37.13
009	SAPS	Candyfloss	Process Station	05/08/ 2014	08:00	49 23.18	8 37.13
010	SAPS	Candyfloss	Process Station	05/08/ 2014	09:45	49 23.10	8 37.13
011	CTD	Candyfloss	Process Station	05/08/ 2014	11:03	49 23.0	8 36.7
012	LMSC	Candyfloss	Process Station	05/08/ 2014	12:04	49 23.0	8 36.6
013	Net	Candyfloss	Process Station	05/08/ 2014	13:10	49 22.9	8 36.6
014	Net	Candyfloss	Process Station	05/08/ 2014	13:41	49 22.7	8 36.4

015	Net	Candyfloss	Process Station	05/08/ 2014	14:12	49 22.6	8 36.4
016	Net	Candyfloss	Process Station	05/08/ 2014	14:27	49 22.6	8 36.4
017	Net	Candyfloss	Process Station	05/08/ 2014	14:42	49 22.7	8 36.4
018	Net	Candyfloss	Process Station	05/08/ 2014	15:01	49 22.7	8 36.4
019	Net	Candyfloss	Process Station	05/08/ 2014	15:11	49 22.7	8 36.4
020	Net	Candyfloss	Process Station	05/08/ 2014	15:20	49 22.7	8 36.4
021	CTD	Candyfloss	Process Station	05/08/ 2014	16:10	49 22.3	8 36.48
022	Corer	Candyfloss	Process Station	05/08/ 2014	19:31	49 22.33	8 36.48
023	Corer	Candyfloss	Process Station	05/08/ 2014	19:57	49 22.33	8 36.48
024	Net	Candyfloss	Process Station	05/08/ 2014	21:10	49 22.33	8 36.44
025	Net	Candyfloss	Process Station	05/08/ 2014	21:53	49 22.33	8 36.44
026	Net	Candyfloss	Process Station	05/08/ 2014	22:02	49 22.33	8 36.44
027	Net	Candyfloss	Process Station	05/08/ 2014	22:21	49 22.33	8 36.39
028	Net	Candyfloss	Process Station	05/08/ 2014	22:28	49 22.33	8 36.12
029	Glider	Deep Glider Station	Deep Glider Station	06/08/ 2014	07:57	48 20.46	9 43.16
030	CTD	Deep Glider Station	Deep Glider Station	06/08/ 2014	08:23	48 20.3	9 43.63
031	SMSC	Deep Glider Station	Deep Glider Station	06/08/ 2014	12:58	48 20.31	9 43.63
032	Buoy	Deep Glider Station	Deep Glider Station	06/08/ 2014	13:30	48 20.32	9 43.62

033	LMSC	Shelf Break	Shelf Break	07/08/ 2014	05:15	48 34.2	9 30.6
034	LMSC	Shelf Break	Shelf Break	07/08/ 2014	05:48	48 34.2	9 30.6
035	CTD	Shelf Break	Shelf Break	07/08/ 2014	06:04	48 34.2	9 30.6
036	Net	Shelf Break	Shelf Break	07/08/ 2014	06:56	48 34.22	9 30.63
037	Net	Shelf Break	Shelf Break	07/08/ 2014	07:23	48 34.3	9 30.74
038	Net	Shelf Break	Shelf Break	07/08/ 2014	07:45	48 34.38	9 30.84
039	Net	Shelf Break	Shelf Break	07/08/ 2014	08:05	48 34.56	9 31.0
040	LMSC	Shelf Break	Shelf Break	07/08/ 2014	08:48	48 34.57	9 31.0
041	Corer	Shelf Break	Shelf Break	07/08/ 2014	09:25	48 34.57	9 30.97
042	Corer	Shelf Break	Shelf Break	07/08/ 2014	09:48	48 34.57	9 30.97
043	Corer	Shelf Break	Shelf Break	07/08/ 2014	10:10	48 34.57	9 30.97
044	CTD	Shelf Break	Shelf Break	07/08/ 2014	11:10	48 34.58	9 30.97
045	LMSC	Shelf Break	Shelf Break	07/08/ 2014	12:25	48 34.57	9 30.9
046	SAPS	Shelf Break	Shelf Break	07/08/ 2014	13:00	48 34.57	9 30.87
047	CTD	Shelf Break	Shelf Break	07/08/ 2014	15:00	48 34.3	9 30.3
048	Buoy	Shelf Break	Shelf Break	07/08/ 2014	16:12	48 34.27	9 30.27
049	Buoy	Shelf Break	Shelf Break	07/08/ 2014	18:54	48 34.16	9 33.33
050	Net	Shelf Break	Shelf Break	07/08/ 2014	20:40	48 34.66	9 35.17
051	Net	Shelf Break	Shelf Break	07/08/ 2014	21:09	48 34.85	9 35.48
052	Net	Shelf Break	Shelf Break	07/08/ 2014	21:24	48 34.9	9 35.52

053	Net	Shelf Break	Shelf Break	07/08/ 2014	21:41	48 35.15	9 35.47
054	Corer	Shelf Break	Shelf Break	07/08/ 2014	22:12	48 35.45	9 35.44
055	Corer	Shelf Break	Shelf Break	07/08/ 2014	22:37	48 35.38	9 35.26
056	CTD	Noon Station	Noon Station	08/08/ 2014	11:05	50 15.48	7 44.62
057	SMSC	Noon Station	Noon Station	08/08/ 2014	12:02	50 15.48	7 44.62
058	Buoy	Noon Station	Noon Station	08/08/ 2014	12:58	50 15.48	7 44.62
059	LMSC	Celtic Deep	Celtic Deep	09/08/ 2014	05:06	51 08.26	6 35.16
060	LMSC	Celtic Deep	Celtic Deep	09/08/ 2014	05:30	51 08.26	6 35.16
061	CTD	Celtic Deep	Celtic Deep	09/08/ 2014	06:08	51 08.26	6 35.16
062	LMSC	Celtic Deep	Celtic Deep	09/08/ 2014	06:42	51 08.26	6 35.16
063	SMSC	Celtic Deep	Celtic Deep	09/08/ 2014	07:06	52 08.26	6 35.16
064	Net	Celtic Deep	Celtic Deep	09/08/ 2014	07:32	53 08.26	6 35.37
065	Net	Celtic Deep	Celtic Deep	09/08/ 2014	07:56	51 08.20	6 35.59
066	Net	Celtic Deep	Celtic Deep	09/08/ 2014	08:13	51 08.09	6 35.91
067	Net	Celtic Deep	Celtic Deep	09/08/ 2014	08:28	51 08.00	6 36.07
068	Net	Celtic Deep	Celtic Deep	09/08/ 2014	08:39	51 07.93	6 36.11
069	SAPS	Celtic Deep	Celtic Deep	09/08/ 2014	09:05	51 07.84	6 36.33
070	LMSC	Celtic Deep	Celtic Deep	09/08/ 2014	10:22	51 07.29	6 37.22
071	CTD	Celtic Deep	Celtic Deep	09/08/ 2014	10:40	51 07.24	6 37.3
072	SMSC	Celtic Deep	Celtic Deep	09/08/ 2014	11:42	51 07:10	6 37.51

073	Corer	Celtic Deep	Celtic Deep	09/08/ 2014	12:00	51 07.10	6 37.52
074	Corer	Celtic Deep	Celtic Deep	09/08/ 2014	12:22	51 07.10	6 37.52
075	Corer	Celtic Deep	Celtic Deep	09/08/ 2014	12:40	51 07.10	6 37.52
076	CTD	Celtic Deep	Celtic Deep	09/08/ 2014	13:30	51 07.10	6 37.52
077	LMSC	Celtic Deep	Celtic Deep	09/08/ 2014	15:46	51 07.10	6 37.52
078	CTD	Celtic Deep	Celtic Deep	09/08/ 2014	16:04	51 07.10	6 37.52
079	Buoy	Celtic Deep	Celtic Deep	09/08/ 2014	17:37	51 07:09	6 37.51
080	Net	Celtic Deep	Celtic Deep	09/08/ 2014	17:37	51 08.94	6 38.49
081	Net	Celtic Deep	Celtic Deep	09/08/ 2014	20:38	51 08.86	6 38.56
082	Net	Celtic Deep	Celtic Deep	09/08/ 2014	20:45	51 08.64	6 38.73
083	Net	Celtic Deep	Celtic Deep	09/08/ 2014	21:04	51 08.61	6 38.77
084	Net	Celtic Deep	Celtic Deep	09/08/ 2014	21:13	51 08.53	6 38.87
085	Net	Celtic Deep	Celtic Deep	09/08/ 2014	21:22	51 08.44	6 38.98
086	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	06:58	51 09.42	6 34.28
087	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	07:37	51 09.42	6 34.27
088	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	08:00	51 09.38	6 34.52
089	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	08:39	51 09.38	6 34.52
090	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	08:59	51 09.34	6 34.65
091	Corer	Celtic Deep	Celtic Deep	10/08/ 2014	09:31	51 09.23	6 35.04
092	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	10:00	51 09.17	6 35.38

093	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	10:33	51 09.04	6 35.74
094	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	11:03	51 08.97	6 35.91
095	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	11:48	51 08.86	6 36.2
096	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	12:04	51 08.86	6 36.2
097	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	12:44	51 08.8	6 36.32
098	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	12:59	51 08.8	6 36.32
099	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	13:42	51 08.75	6 36.4
100	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	13:59	51 08.75	6 36.4
101	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	14:48	51 08.75	6 36.41
102	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	15:08	51 08.74	6 36.4
103	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	15:30	51 08.74	6 36.42
104	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	16:10	51 08.74	6 36.32
105	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	16:42	51 08.74	6 36.25
106	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	17:00	51 08.74	6 36.25
107	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	17:42	51 08.74	6 36.25
108	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	17:57	51 08.74	6 36.25
109	SMSC	Celtic Deep	Celtic Deep	10/08/ 2014	18:50	51 08.74	6 36.25
110	CTD	Celtic Deep	Celtic Deep	10/08/ 2014	19:06	51 08.74	6 36.25
111	Glider	Benthic A	Benthic A	11/08/ 2014	06:42	51 12.57	6 08.52
112	Buoy	Benthic A	Benthic A	11/08/ 2014	07:49	51 12.70	6 08.5

113	CTD	Benthic A	Benthic A	11/08/2014	10:58	51 12.70	6 08.5
114	SMSC	Benthic A	Benthic A	11/08/2014	11:47	51 12.70	6 08.5
115	SMSC	Benthic A	Benthic A	11/08/2014	11:59	51 12.70	6 08.5
116	Net	Benthic A	Benthic A	11/08/2014	12:31	51 12.70	6 08.5
117	CTD	Benthic A	Benthic A	11/08/2014	14:01	51 12.33	6 08.51
118	SMSC	Benthic A	Benthic A	11/08/2014	15:08	51 12.33	6 08.5
119	SMSC	Benthic A	Benthic A	11/08/2014	15:25	51 12.28	6 08.5
120	Net	Benthic A	Benthic A	11/08/2014	15:36	51 12.24	6 08.52
121	Net	Benthic A	Benthic A	11/08/2014	15:54	51 12.18	6 08.45
122	Net	Benthic A	Benthic A	11/08/2014	16:14	51 12.12	6 08.25
123	Net	Benthic A	Benthic A	11/08/2014	16:26	51 12.09	6 08.07
124	Net	Benthic A	Benthic A	11/08/2014	16:44	51 12.1	6 07.9
125	Net	Benthic A	Benthic A	11/08/2014	20:37	51 11.92	6 05.67
126	Net	Benthic A	Benthic A	11/08/2014	20:52	51 11.96	6 05.97
128	Net	Benthic A	Benthic A	11/08/2014	21:04	51 11.98	6 06.23
129	Net	Benthic A	Benthic A	11/08/2014	21:23	51 12.00	6 06.63
130	Corer	Benthic A	Benthic A	11/08/2014	21:51	51 12.02	6 07.04
131	Corer	Benthic A	Benthic A	11/08/2014	22:10	51 12.03	6 07.12
132	Corer	Benthic A	Benthic A	11/08/2014	22:36	51 12.02	6 07.21
133	SMSC	Celtic Deep	Celtic Deep	12/08/2014	05:00	51 08.91	6 36.25

134	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	05:24	51 08.91	6 36.25
135	CTD	Celtic Deep	Celtic Deep	12/08/ 2014	07:00	51 08.91	6 36.25
136	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	07:42	51 08.91	6 36.25
137	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	08:02	51 08.91	6 36.25
138	Net	Celtic Deep	Celtic Deep	12/08/ 2014	08:41	51 08.91	6 36.32
139	Net	Celtic Deep	Celtic Deep	12/08/ 2014	09:02	51 08.83	6 36.45
140	Net	Celtic Deep	Celtic Deep	12/08/ 2014	09:20	51 08.77	6 36.68
141	Net	Celtic Deep	Celtic Deep	12/08/ 2014	09:40	51 08.59	6 36.86
142	CTD	Celtic Deep	Celtic Deep	12/08/ 2014	11:00	51 08.39	6 37.32
143	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	11:50	51 08.33	6 37.58
144	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	12:05	51 08.3	6 37.62
145	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	12:18	51 08.25	6 37.7
146	CTD	Celtic Deep	Celtic Deep	12/08/ 2014	13:26	51 08.22	6 37.77
147	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	14:40	51 08.1	6 38.01
148	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	14:54	51 08.1	6 38.01
149	Buoy	Celtic Deep	Celtic Deep	12/08/ 2014	15:27	51 08.10	6 38.00
150	CTD	Celtic Deep	Celtic Deep	12/08/ 2014	18:00	51 08.10	6 38.00
151	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	18:40	51 08.10	6 37.9
152	SMSC	Celtic Deep	Celtic Deep	12/08/ 2014	19:05	51 08.10	6 37.9
153	Net	Celtic Deep	Celtic Deep	12/08/ 2014	20:35	51 08.10	6 37.96

154	Net	Celtic Deep	Celtic Deep	12/08/ 2014	20:52	51 07.97	6 38.11
155	Net	Celtic Deep	Celtic Deep	12/08/ 2014	21:09	51 07.95	6 38.24
156	Net	Celtic Deep	Celtic Deep	12/08/ 2014	21:24	51 07.88	6 38.29
157	Corer	Benthic A	Benthic A	13/08/ 2014	06:37	51 12.28	6 07.3
158	PML Buoy	Benthic A	Benthic A	13/08/ 2014	07:18	51 12.28	6 07.3
159	CTD	Benthic A	Benthic A	13/08/ 2014	11:00	51 12.57	6 03.36