

University of Southampton  
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Southampton Oceanography  
Centre

Cruise Report: 95/33



**RRS Discovery Cruise 216**

**OMEX**

Ocean Margin EXchange Study  
26 August - 12 September 1995

*Dr Peter J. Statham*  
*Cruise Report 95/33, January 1996*

## Synopsis

*This RRS Discovery cruise forms part of an extensive sea time campaign on the Goban Spur and adjacent shelf break under the EU MAST funded project OMEX (Ocean Margin EXchange), and follows on from the RRS Charles Darwin Cruises 84 (Jan-Feb 1994) and 94 (June 1995); see cruise reports by Statham 1994, 1995, for details. The shelf break area has been chosen for study because of its importance in the flux of materials between the land and the open ocean. The main focus on this cruise was on biogeochemical processes, with additional work being undertaken which is relevant to the OMEX project. Weather conditions were generally very good apart from when a storm passed through the research area, and overall a large amount of sampling and data collection was done.*

*The cruise started at Barry, and this was the last departure of RRS Discovery from this port before relocating to Southampton as her base. The cruise track went west southwest directly to the main OMEX study site at the Goban Spur in the Celtic Sea. The primary sampling and data collection device was a CTD and rosette sampler fitted with 10L lever action and conventional Niskin bottles. Samples were collected for analysis of dissolved and particulate trace metals (particulate material collected by in situ pumping systems), oxygen, nutrients, dissolved and particulate organic carbon, pigments, and micro-zooplankton. Hydrographic data on temperature, salinity, oxygen, fluorescence, and transmission were obtained from the CTD in vertical profiles, and using the non-toxic pumped water supply on the ship for horizontal transects. A clean pumping system was used to collect underway data on nutrients and dissolved aluminium, as well as to test systems for the underway measurement of manganese, nickel and copper.*

*A series of cores from varying depths on the shelf were taken using a multi-corer device from the University of Bremen. Cores were sub-sampled to provide archive material and sediment samples for a variety of geochemical and sedimentological analyses including organic carbon, particle size and X-ray photography. Additional work relevant to the OMEX project work was undertaken and included recovery and re-deployment of a shallow current meter mooring, atmospheric sampling for particles for geochemical studies, and testing of equipment.*

*The cruise also provided an opportunity for sea going training and research for a series of students, because of the number of berths available on RRS Discovery.*

*All data generated from the cruise will be stored with the OMEX database, operated by the British Oceanographic Data Centre, The Observatory, Birkenhead, Merseyside, United Kingdom.*

## Acknowledgements

The success of a cruise is dependent on many factors, but high on this list is the attitude and input of the ship's complement. During the cruise there were several problems with weather and equipment, but it is a testament to the positive attitude and professional approach taken by the Officers and Crew that these problems were minimized as far as possible, and I am grateful to them, and the Master, Keith Avery, in particular, for their efforts. An especial word of thanks is due to the RVS technicians who had some significant difficulties to deal with, and who put in a sterling effort to try and overcome them. The scientists on board came with a wide range of backgrounds, experience and ages, but I was very impressed by the way in which this varied group meshed to become an effective working team, and how the cruise passed in a very affable and friendly atmosphere. I am grateful to them for their efforts and forbearance of my requests and directions!!

David Hydes and Dennis Burton provided helpful comments on an earlier version of this report.

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## 1. CRUISE PERSONNEL

### Officers:

Keith AVERY	Master
Peter NEWTON	Chief Officer
Richard WARNER	Second officer
Rob ATKINSON	Second officer
Brian DONALDSON	Radio officer
Sam MOSS	Chief engineer
Jim CROSBIE	Second engineer
Ray PERRIAM	Third engineer
Barry WALKER	Third engineer

### Crew:

Tiny POOK	Chief Petty Officer
Greg LEWIS	Petty Officer
Dave BUFFERY	Seaman
Stewart COOK	Seaman
Ian THOMSON	Seaman
Kevin HOGG	Seaman
Roy AVERY	Seaman
Eddy STAITE	Catering Manger
Paul DANE	Chef
Richard EDES	Steward/ messman
Andy DUNCAN	Steward
Pete ROBINSON	Steward
Alan BRIDGE	Motorman

### Scientists:

Peter STATHAM	Principal Scientist, SOC
David HYDES	SOC
Nick MORLEY	SOC
Anneke LUBBEN	SOC
Adrian MCDONALD	SOC
Ruth PARKER	SOC
Antonio SOARES	SOC
George NURSER	SOC
Jane READ	SOC
Paolo PEDRO	UA
Denise CUMMINGS	PML

Giancarlo BIANCHI	CAMES
Matt COOPER	CAMES
Marcel CURE	UCG
Garvan O'DONNELL	UCG
Miriam MOLLONEY	UCG
Lei CHOU	ULB
Eric ACHTERBERG	PU
Christian MAESS	UB
Holger DIERSSEN	UB
Isobella TINDALL	IH
Roy LOWRY	BODC

### RVS:

Howie ANDERSON	computing
Jeff JONES	mechanical
Richard PHIPPS	mechanical
Bernie WOODLEY	instruments
John WYNAR	instruments

A key to abbreviations used, and addresses of groups are given on the following page.

## *Participating Groups*

BODC  
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## 2. CRUISE OBJECTIVES

This RRS Discovery cruise forms part of an extensive sea time campaign at this area of shelf break under the EU funded project OMEX (Ocean Margin EXchange). The shelf break region has been chosen for study because of its potential importance in the flux of materials between the land and the open ocean. The general arguments and background are well summarised in Mantoura et al. (1991)<sup>1</sup>, and the detailed rationale and project description are given in the proposal to MAST. The OMEX Chief Scientist is Prof. R. Wollast, Université Libre de Bruxelles, Boulevard de Triomphe, 1050. Brussels, Belgium

This cruise focused on the work of the Biogeochemical Processes Sub-Task of OMEX, and provided an opportunity to study concentrations and distributions of materials of interest during a late summer/early autumn period at the shelf break. Other cruises (CD84 winter 1994, CD94 summer 1995, and cruises by other European colleagues) in combination with RRS Discovery 216 will provide a seasonal view of the distribution and concentrations of important chemical and micro-biological parameters in this dynamic environment. The general scientific objectives were:

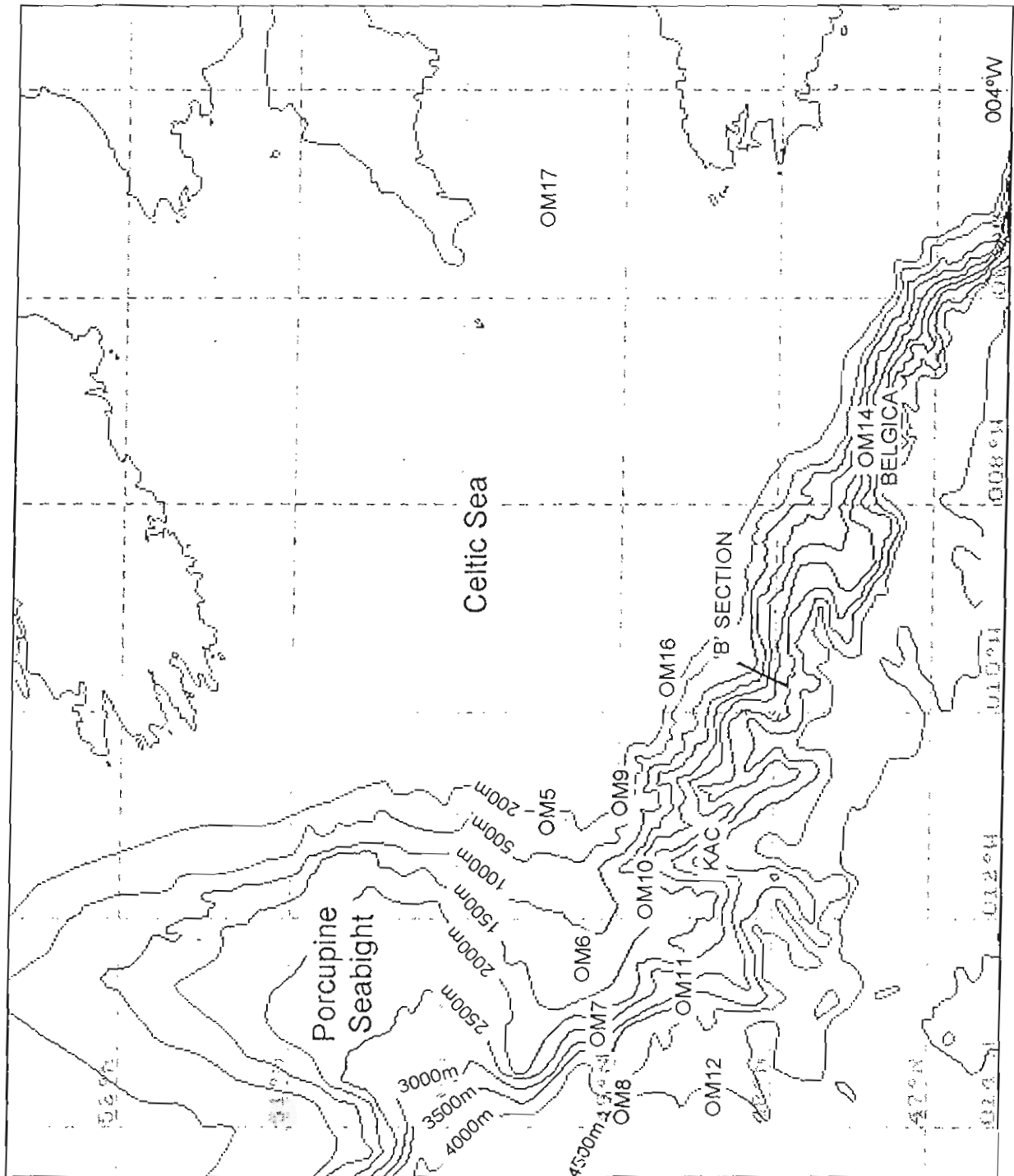
- 1) To study the role of biogeochemical and hydrographic processes in controlling the distributions of dissolved trace metals in the shelf break region and adjacent waters, with due regard to temporal variability.
- 2) To estimate fluxes across trace metal fronts in the shelf break region and evaluate the use of trace metals as tracers of advective exchanges of waters at the shelf break.
- 3) Based on these and other OMEX data, to further the development of models for frontal exchange of dissolved trace metals and the linking of these models to a shelf seawater quality model.
- 4) In addition to the trace metal work, to collect other information and samples relevant to the aims of the OMEX project.

The general strategy was to go from Barry in South Wales, initially to the main OMEX study zone at the Goban Spur. After shakedown stations for water column and sediment sampling, the ship was to move along the main sediment trap transect out to deeper water to the west. The intention was then to collect data and samples along a zigzag track over the shelf break, to the previously occupied BELGICA station at La Chapelle Bank, carry out a detailed water column sampling, and then return to Southampton Oceanography Centre. The sampling stations occupied during the cruise in the vicinity of the shelf break are shown in Figure 1a. The OM series of station numbers refer to locations either reoccupied, or in some cases occupied for the first time, on this cruise.

<sup>1</sup>Mantoura et al., eds (1991) "Ocean margin processes in global change" Wiley .



Figure 1a. Main CTD sampling stations for RRS Discovery Cruise 216.



### 3. CRUISE NARRATIVE

This was the last occasion that RRS Discovery left Barry in South Wales with the RVS centre there as her home base; her new home will be the new RVS facility at Southampton Oceanography Centre.

Loading and mobilization advanced reasonably well although with the larger number of personnel on board, and a wide range of activities to be catered for, more time would have been useful. There was a delay in sailing on Saturday the 26 August as the release mechanism on the port lifeboat was not operating correctly. An engineer was found for the Saturday, and the ship eventually set sail at 1700, with the lifeboat problem temporarily fixed. The route led directly to the main Goban Spur investigation site, with two dog legs introduced into the track to provide the opportunity to calibrate the ADCP. After tests of CTD and multi-corer systems in shallow water the main section off-shelf was started, which included stations to give a detailed section off-shelf with reoccupation of some sites, which is needed to gain insights into mixing and transport processes in this shelf break zone.

Unfortunately, a significant problem developed with the CTD cable which showed evidence of severe wear, to the extent that a substantial length of wire had to be removed (see later in the report). This and subsequent problems with the CTD cable led to the aborting of the A physical section and downgrading this to purely a section for the geochemical work. The multiple corer brought by the Bremen University group worked very well, and all stations requested bar one far out into the open Atlantic were sampled. After the two main transects of stations had been worked it was planned to recover a shallow current meter mooring which is vulnerable to fishing activity. Fortunately, the mooring was located and recovered successfully, and after removal of data and replacement of batteries, this was redeployed. The track now started a zigzag pattern across the shelf break. However, despite very conditions for the first few days, the weather deteriorated as an active depression (tropical storm Iris ) rapidly approached, and it was necessary to take evasive action. The ship moved nearly 200 miles to the NNW to keep clear of the force 10 and 11 winds at the core of the storm, and sheltered to the west of Ireland. Approximately 2.5 days of ship was lost due to the passing storm.

On re-entering the work area, a station was reoccupied to see the effect of any storm mixing on the water column structure, before a further physical transect (B) of CTD stations across shelf was done to provide data for estimates of water flow at this region of the shelf. In the limited remaining time, the Belgica station at La Chapelle Bank was re-occupied and also samples were taken at a station in the mouth of the Channel. Dr Chou transferred to the Belgica in the East Solent and the Cruise ended on the 12 September with RRS Discovery berthed near to the new Southampton Oceanography Centre. The full cruise track is given in Figure 1b.



## 4. REPORT ON SHIP BOARD INSTRUMENTS AND EQUIPMENT

Equipment onboard generally worked well, although there were some important problems as indicated below. As usual, the RVS personnel on the ship were extremely helpful, provided a friendly and professional service, and their presence was vital to the successful collection of data and samples which took place.

### 4.1. CTD wire

The CTD wire on the ship was in poor condition. On the first cast to over 1200m a dangerously frayed length of cable was noticed, and 1350 m of wire was cut from the drum. Later the same day there were further concerns over the cable and a further 150 m was cut off. When re-terminated there were problems with electrical connections to the deck unit which typically failed when strain was put on the cable. In total a further 500m of cable was removed before a usable length of wire was found and a good termination formed, thus limiting the depth capability of the CTD to circa 3900m. This was 600m less than the depths of deep-ocean stations on the OMEX transects to be sampled. A further 200m was later removed, reducing the depth capability even more. A major cause of the problems appears to be the cable haulers on the winch system, which gives the exterior layers of the wire a hard time.

The poor condition of the wire thus gave rise to two significant problems on the cruise 1) losing time on station during a critical section, which in the end had to be abandoned, and 2) losing the capability of sampling deep waters, where we had planned to study the Antarctic Bottom Water and its nutrient signature in this region.

There is an urgent and obvious need to make sure this problem does not arise again. Some suggested ways forward are:

1. test the cable before leaving the home port; a megger test would indicate if there was a breakdown of the insulation in the cable, and a length could be removed for laboratory testing for a full diagnosis (as is done on German ships)
2. make it routine for the cable to be inspected thoroughly before a cruise ends, so that any remedial action necessary can be taken before any subsequent cruise.
3. Carry a spare cable on the ship. Eventually this will be needed, and if it is there it can be used when needed, such as on this cruise. It could perhaps be located on the hydroline cable drum on Discovery if this is not heavily used

## **4.2. *Milli-Q high purity water system***

On this cruise, a source of high purity water was an essential item for nutrient analyses, work with trace metals and other general applications around the laboratory. The polishing unit on the system was set up and appeared to work satisfactorily, but unfortunately the reverse osmosis unit had problems from early on. After a series of tests, the main limiting factor appeared to be the pressure provided to the RO cartridge by the pump in the system; the rate of production of RO water was only circa 10L per 12 hours as opposed to 22L/h as the specification for the unit suggests. Ideally, this system should be tested prior to the departure of the ship from port, and a good range of spares should be carried at the base to cover the eventualities encountered here. By careful rationing major problems were averted. The careful assessment of the state of the system prior to departure of the ship is an important check to be made.

## **4.3 *Clean container for trace metal work***

I was extremely disappointed with the state of the "clean " container laboratory on arriving at the ship; I have never seen it in worse condition. There had been a problem with the emergency exit to the container, and new metal components had had to be installed. The metallic contaminants from these operations and previous work had left the container in a desperate state for trace metal work, with mms to cms of grime and rubbish on the main floor and surfaces of the container. It took the efforts of 1-2 people most of the time between arrival at the ship and the delayed departure to clean up the container sufficiently to allow the installation of a plastic cocoon inside by Nick Morley, for the handling of samples for the forthcoming cruise. There really is no point in having a container dedicated to trace metal work if it is allowed to deteriorate to a state worse than many of the other general labs and areas around the ship.

I recommend that this container is now retired and converted to a general purpose lab, and that one of the new containers obtained by RVS be upgraded to a trace metal container lab. The existing unit has provided excellent service over the past ten years in the Indian Ocean, North Sea and other environments, and has led to the publication of many papers in the literature. We have learnt much about the operation of such clean containers over the past decade and we can produce a first class facility that will see the marine chemistry community through well into the 21 st century.

## **4.4. *Winch for stand alone pumps***

As commented upon in the CD94 cruise report, the winch currently available makes deployment of the SAP pumping systems a laborious and long-winded affair. In addition to the elderly status of the cable, which had several

problems with reeving back on the drum, the meter wheel readout has problems and requires attention to ensure good operation.

## **5. HYDROGRAPHIC PARAMETERS**

Data on salinity, temperature, transmission and fluorescence were collected from both the CTD system, and the underway pumped system on the ship (other parameters from the CTD are considered below, as is the transmission data from the CTD in more detail). The CTD system worked well, and information for calibration of data by BODC were collected. In total there were 46 CTD casts. Although ship board checks on the thermosalinograph (TSG) indicated no obvious problems, unfortunately post cruise analysis of the data by BODC indicated that only 2 days worth of salinity data is usable. The problem seems to have been that the conductivity cell was not properly flushed, and that the expected amplitude of the signal was muted by about an order of magnitude.

## **6. STUDIES ON WATER FLOW AT THE SHELF BREAK**

The aim of this work is to gain understanding of the structure of the slope current. This current is believed to generally run northwestward along the continental slope, with its core at about 300-500m. Current meter moorings have shown northwestward long-term mean flow velocities reaching about 5-10cm/s, though the flow may reverse seasonally.

On this cruise the flows in the upper (~200 m) were measured directly with the Acoustic Doppler Current Profiler (ADCP), both while the ship was underway, and while the ship was on station. Temperature and salinity profiles from the CTD casts gave information on the vertical shear of the geostrophic flow, and the structure of the current.

Over the OMEX region, however, the tides (both barotropic and internal) are significant. The internal (depth-varying) tide is stimulated by the movement of the barotropic tide across the continental slope. These tides make it difficult to extract the mean flows from the ADCP. Moreover the internal tides may deform isopycnals, giving spurious geostrophic shears. Although models (e.g. the POL model) of the barotropic tide do exist, little is known of the baroclinic response of the tides (the internal tide). Rather than trying to remove the tidal velocities using a model, we therefore attempted to repeat stations at intervals of 6hrs 10 minutes, half the dominant (semi-diurnal) tidal period. Averaging over the two station occupations should then remove tidal velocities and variations in the depth of isopleths.

Two detailed hydrographic sections across the slope current were planned. Both involved repeat occupation of stations. The 'A' section was to run down the slope, along the main OMEX line over the Goban spur. It started at 49° 30' N 11° W (station A1) and finished at 48° 50' 13° 40' W (OMEX station OM8), and included also OMEX stations OM6 and OM7. Section 'B' ran down the slope further to the east, going roughly SSW from station B1, at 48° 11' N, 9° 32.5' W.

## The 'A' section

The continental slope is comparatively gradual over the Goban spur. In order to cover the slope, section 'A' needed to be fairly long, ~210km. There was not time to do repeat stations throughout the whole of such a long run, so that it was planned to repeat only the two stations A4 (OM6) [49° 13' N, 12° 36' W], and A5 [49° 8' N, 12° 48' W] which lay where the core of the slope current was believed to exist, at a water depth of 1000-1500m.

The shallow stations A1, A2 and A3 were successfully occupied. Unfortunately, while attempting casts at the key stations A4 and A5, the CTD cable repeatedly frayed resulting in considerable delays while it was cropped. Hence it was not possible to repeat stations A4 and A5 at intervals of 6hrs 10mins as planned. Moreover, the section could no longer be considered as synoptic. Station A4, however, was occupied on four separate occasions, at intervals of 10 and 12hrs, while station A5 was occupied twice, at intervals of 10hrs. Repeated casts were then made at the deep stations A6/OM7 and A7/OM8 (4 & 3 respectively) to enable bottle sampling over the whole of the water column. Repeat casts at intervals of ~6-7 hours were available at both stations, though they did not span the entire water column.

*Station positions and approx. running distances:*

	Lat	Lon	dist from A1 (km)	dist from prev. station (km)	water depth (m)
(OM5)A1	49° 30'	-11°	0	0	190
A2	49° 23'	-11° -30'	39.0350	39.0350	600
A3	49° 17'	-12°	76.9026	37.8676	1120
(OM6)A4	49° 13'	-12° -36'	121.0433	44.1408	1180
A5	49° 8'	-12° -48'	138.2701	17.2267	1600
(OM7)A6	49° 7'	-13° -12'	171.1172	21.3274	3680
(OM8)A7	48° 57'	-13° -40'	209.8975	38.7803	4500

## The 'B' series

Section B follows a ridge down the continental slope, at longitude ~ 9° 30' W, where the continental slope is steep. The section is therefore shorter than section 'A', with more closely spaced stations. Five stations lying at water depths of 200 to — B2 to B6 — were repeated at intervals of 6hrs 11m. The initial plan also involved a station on the shelf —B1— and three deep stations, B7, B8 and B9. However these stations had to be dropped owing to the loss of time caused by the passage of the storm 'Iris'.

CTD stations B2, B3 & B4 were visited twice, following the order B2-B3-B4-B2-B3-B4, and stations B5 & B6 visited in the order B5-B6-B5-B6.

Station positions and approx. running distances:

	Lat	Lon	dist from B2 (km)	dist from prev station (km)	water depth (m)
B2	48° 11' -9°	32.5	0	0	304
B3	48° 8' -9° 36'		7	7	696
B4	48° 4.4 -9°	38.5	14.3	7.3	1139
B5	48° 1.5 -9°	39.5	19.8	5.5	1500
B6	47° 57.5-9° -40'		27.2	7.4	2200
B7	47° 54.5-9° -40'		51.4	5.6	2700
B8	47° 47' -9° -40'		65.3	13.9	3500
B9	47° 35.5-9° -40'		86.6	21.3	4150

## 7. SATELLITE IMAGES

Two satellite images including data on the American Shelf and Bay of Biscay, were received on the ship (for 30 and 31 August). The images showed generally similar surface temperatures extending over the Celtic shelf and northern Bay of Biscay, with significantly higher temperatures evident to the south in the Bay of Biscay. This suggests the presence of a seasonal thermocline in the shelf waters which was not evident in the June (CD94) images for the area, where warm waters were found mainly off-shelf. One important and interesting feature was the presence of cooler waters running along the shelf side of the break. The origin of this water was not clear from the image, but may be cooler deeper waters which have been transported from depth by mixing processes at work at the shelf break. The data was useful during the cruise in refining the zigzag pattern taken across shelf, and in analysis of surface data post cruise.

## 8. NUTRIENT STUDIES

### 8.1. SOC Deacon Division nutrient analyzer

Samples taken for nutrient analysis were analysed for silicate, nitrate and nitrite, and phosphate, using the SOCDD "Chemlab" auto-analyser (AA-II type). Nutrient samples were collected, from all the rosette water bottles closed except those which were filtered in their entirety for determination of particle size spectrum. Samples were taken into new 30 ml plastic 'diluvial' containers that had been rinsed 3 times with the sample. All samples were analysed within 12 hours of collection. All measurements were made in the Deck Laboratory.



Silicate analysis followed the standard AAll molybdate-ascorbic acid method with the addition of a 37°C heating bath (Hydes, 1984). To obtain a linear response from the colorimeter over the concentration range up to 150 µM of silicate, it was fitted with a 15 mm flow cell and a 660 nm filter.

Nitrate analysis followed the standard AAll method using sulphanilamide and naphthylethylenediamine dihydrochloride. Since 1982 we have used a cadmium-copper alloy for the nitrate reduction column (Hydes and Hill 1984), but because of safety and contamination concerns we have discontinued its use, and used a Stainton (1974) cadmium wire reduction column for the first time on this cruise. Initial problems were experienced getting a stable active surface on the cadmium. With the high purity 99.998% wire supplied by Johnson Matthey the procedure recommended by Stainton produced a column which was over reactive and 90% reduction of nitrite occurred. The procedure adopted was to pump 1M HCl through the column for 15 minutes followed by a mixed solution (125g/l ammonium chloride 0.1g/l copper sulphate) for 15 minutes. This produced a wire with a uniform dark grey coating, and a reduction efficiency of 90 % for the conversion of nitrate to nitrite. Column efficiency was monitored on each run by including a nitrite standard in the set of standard solution at the start of the runs. The colorimeter was fitted with a 15 mm flow cell, and a sample volume of 0.2 ml/min used, to obtain a linear response up 0 to 40 µM of nitrate, .

Phosphate determinations used the standard AAll method (Hydes, 1984) which follows the method of Murphy and Riley (1962).

Primary calibration standards were prepared before the cruise from nutrient salt material dried at 110°C for 2 hours then cooled over silica gel in a dessicator before weighing (the precision of weighing was better than 1 part per thousand). 10 mmol/l stock solutions were :- silicate 0.960g of sodium silica fluoride; phosphate 0.681g of potassium dihydrogen phosphate (working phosphate standards were prepared from a secondary standard made by diluting 10.00 ml of primary standard to 100 ml in a glass volumetric flask, using a Finnpiquette digital 1-5 ml adjustable pipette); nitrate 0.345g of sodium nitrite. All primary stock standards were prepared in de ionised water and in 500 ml volumetric flasks for which the calibration had been checked.

A set of four mixed working standards were prepared daily or more frequently when necessary in 100 ml plastic volumetric flasks, using calibrated Eppendorf micro-litre pipettes. The same 40g/l sodium chloride artificial seawater solution used as the auto-analyser inter sample "wash" was used for these standards. A check on the calibration gradient in this matrix and standards prepared in surface sea water containing undetectable nutrient concentrations gave gradients of sodium chloride solution over sea water Si - 0.9898, NO<sub>3</sub> - 1.0016, PO<sub>4</sub> - 0.9959 (n=16). Once established for the appropriate concentration ranges at the start of the cruise the gain settings on the colorimeter were not changed (Si - 6.5, NO<sub>3</sub> - 6.1, PO<sub>4</sub> - 8.3). The gradients of the calibration lines were recorded along with the standard error of the least squares fit to the calibration data for each of the analytical runs

on which water column samples were analysed (31 Si & P; 28 for NO<sub>3</sub> with the copperised cadmium column). Si %RSD gradient 0.9, NO<sub>3</sub> %RSD gradient 4.3, PO<sub>4</sub> % RSD gradient 1.3. Std errors Si 0.22 ± 0.07, NO<sub>3</sub> 0.14 ± 0.05, PO<sub>4</sub> 0.011 ± 0.008.

An internal quality control sample was established at the first deep water station. A bulk sample was collected from the two deepest Niskin bottles then divided into 50 sample vials which were stored in the refrigerator at 4°C. One or more of these vials were then analysed on each analytical run (n=22). The precision of the data was Si mean 40.8µM %rsd 0.53 (n=68), NO<sub>3</sub> mean 21.58µM %rsd 1.23, PO<sub>4</sub> mean 1.41µM %rsd 1.01 (n=67).

Two ampoules of commercial phosphate standard prepared by the Sagami chemical company in Japan were analysed. These standards had passed their shelf life expiry date when delivered by Wako Chemical GMBH. The results were unsatisfactory. The certified value was 1.0µM P, we determined 0.86µM and 0.78µM.

A total of 437 water column samples were analysed with mean concentrations of all samples of Si 8.2µM, NO<sub>3</sub> 10.4 µM, PO<sub>4</sub> 0.66µM. In total 288 samples were determined in duplicate the mean differences between duplicates were Si 0.09±0.09µM, NO<sub>3</sub> 0.06±0.1µM, PO<sub>4</sub> 0.008±0.009µM.

A significant finding of the cruise was the consistency of the variation in the ratio of N:P with depth. The ratio of N:P and its change with depth appears to be a characteristic of particular water masses. We had available high quality data on the cruise, from three cruises of the American SAVE programme (South Atlantic Ventilation Experiment). Comparing the SAVE and OMEX data sets demonstrates that the N:P show characteristic values in North Atlantic Deep water which decrease as the water mixes with Antarctic Bottom Water

## References

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Murphy, J and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, 27, 31-66.

Stainton M.P. 1974. Simple efficient reduction column for use in automated determination of nitrate in water. *Anal. Chem.* 46, 1616.

## 8.2. UCG nutrient analyser

### *Objectives*

1. To measure nutrients NO<sub>3</sub> - N, and Si - Silicate aboard the ship.
2. To carry out an inter calibration of these nutrients with I.O.S.

### *Method*

An Alpkem Perstorp Auto Analyser was used to carry out the nutrient analysis. All analytical methods were based on the official Alpkem methods. Nitrate was determined by the standard diazotization procedure with sulphanilamide and subsequent coupling with N-1-naphthylethylene - diamine dihydrochloride using a cadmium reactor column to reduce nitrite to nitrate, and using EDTA to eliminate interference from iron, copper and other metals. Spectrophotometric detection was at 540 nm. Silicate was determined by (air) flow segmentation using ascorbic acid reduction of the  $\beta$ - molybdosilicic acid complex to molybdenum blue, using oxalic acid to suppress phosphate interference and the colored complex was detected spectrophotometrically at 660 nm. Both flow systems were washed thoroughly prior to use.

### *Sampling*

Samples were taken from CTD casts at various depths and from the surface (half hourly) along the ships course from the non toxic supply. At least 180 underway samples and samples from 31 CTD casts were analysed for both nitrate and silicate. Because the instrument had failed to work satisfactorily towards the end of the cruise the remaining 120 underway samples and samples from 11 CTD casts will be analysed back in Galway.

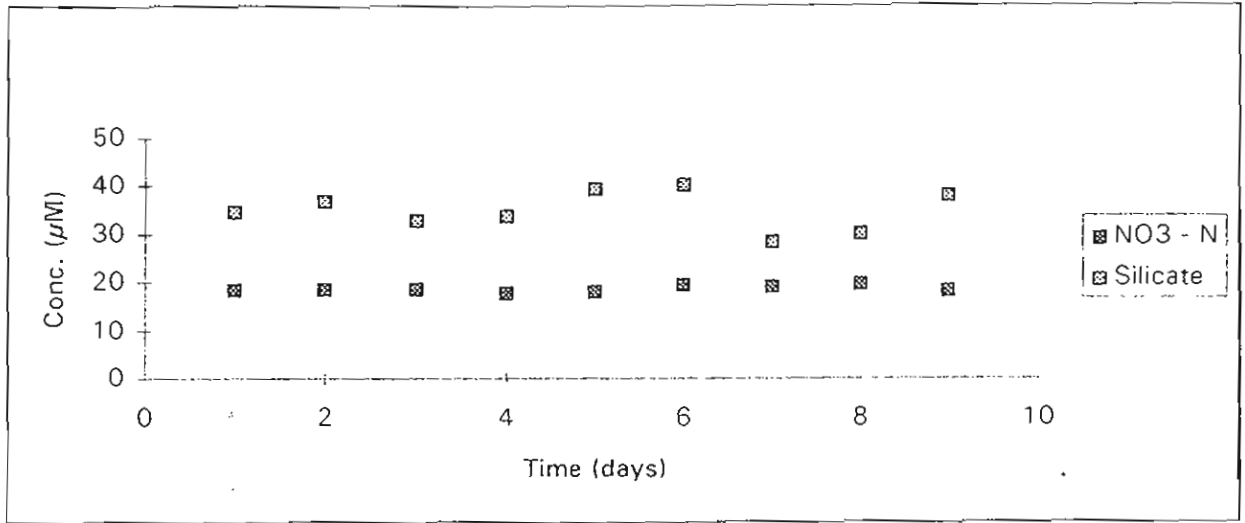
### *Precision and accuracy of results*

Detection limits obtained were :

NO <sub>3</sub> - N	0.05 $\mu$ M
Si - Silicate	0.035 $\mu$ M

Correlation coefficients for calibration graphs were greater than 0.980. A large seawater sample was taken early on in the cruise and was used as a QC check during analysis. The variation in concentration of this seawater with time is shown in Figure 2.

Figure 2. Analysis of quality control sea water sample during the cruise.



As can be seen from the above diagram, NO<sub>3</sub> - N shows little variation whereas Si - Silicate varies considerably. A statistical analysis of this data yielded the following % RSDs.

NO <sub>3</sub> - N	3.27 %
Si-Silicate	10.98 %

Figure 3. Comparison of IOS and UCG data for dissolved silicon at Station OM10

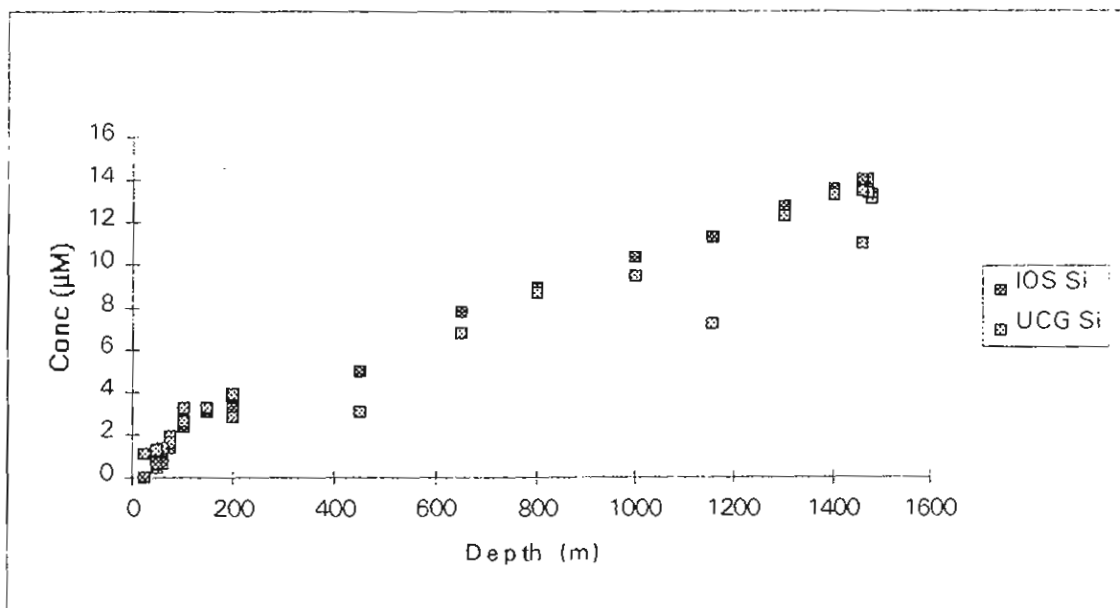
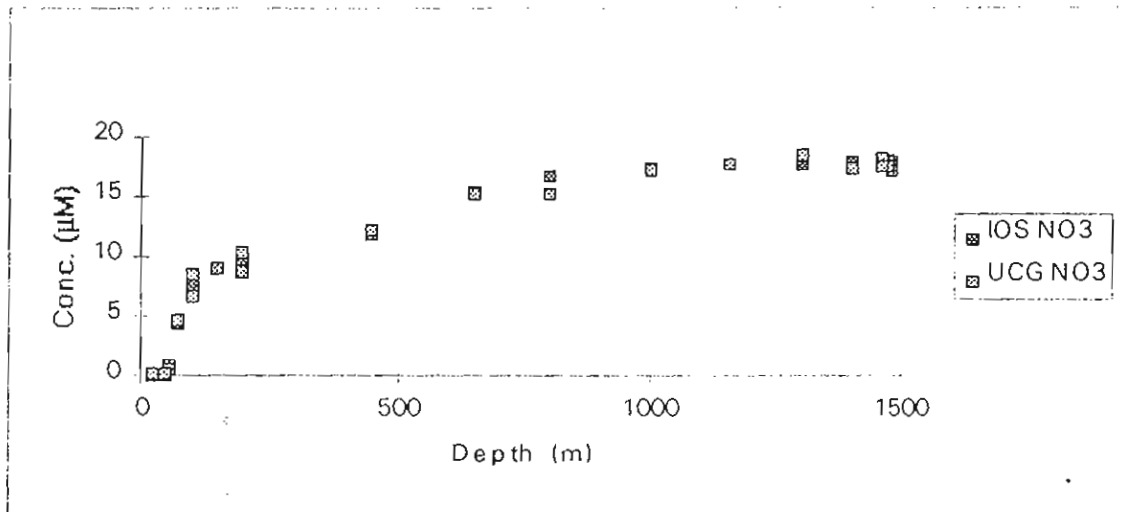


Figure 4 Comparison of IOS and UCG data for nitrate plus nitrite at station OM10



#### *Conclusion*

The objectives set out at the start were achieved. Samples were analysed on board within hours of being collected. The results obtained show expected trends. Typical profiles are shown in Figures 3 and 4. Both nitrate and silicate levels are low in surface waters and gradually increase with depth. In Mid- Atlantic water, one would expect to see a sharp increase in nutrients at approx. 1000 m. This is not apparent here due mainly to the intrusion of low nutrient Mediterranean water at this depth. Another feature of these profiles is the very good comparability of UCG and IOS data, with the exception of one or two points. This can be seen more clearly from a regression plot.

*Garvan O'Donnell*  
*Miriam Molloney*

### **8.3. Phosphorus measurements at low concentrations by ULB**

Surface water concentrations of dissolved reactive phosphorus were very low and below the conventional detection limit of the auto-analyser systems on the ship. Therefore a suite of surface samples from the non-toxic supply and from CTD casts were analysed manually for reactive phosphate using long path length cells to provide additional sensitivity. Using the 10 cm cells and an Hitachi U-2000 spectrometer, concentrations were typically just detectable using this method.

Lei Chou

## 9. DISSOLVED OXYGEN

As well as providing data on the oxygen concentration for the identification of the different water masses, work was carried out to compare two different methods of determining the end point of the Winkler titrations for determining dissolved oxygen in sea water. The two methods compared were the SUDO photometric method and the IOS amperometric method. Further work was carried out to study the precision of the IOS method and to try to improve the working procedures so that the precision required for work on the WOCE project (<0.1%) can be obtained regularly.

The SUDO method of end point determination is based on the decrease in the absorbance by the tri-iodide ion as its concentration decreases due to reduction by sodium thiosulphate. The end point is determined by manually observing when the transmittance attains its maximum value. The sodium thiosulphate is dispensed from a Dosimat unit with a 1ml capacity using a hand held switch to control additions.

The IOS method uses two bright platinum electrodes as the indicator electrodes. When a dc voltage of 200mV is applied to the electrodes the electrodes are depolarised by the iodine and iodide present in the solution giving rise to a current. As the sodium thiosulphate is added, reduction of the iodine occurs leading to a decrease in the current. This decrease is directly proportional to the iodine concentration. The sodium thiosulphate is dispensed and the titration controlled by an automatic Titrino unit with the results being logged to a PC.

Figure 5 shows the oxygen profile for station OM7 which is typical of the deep cast results. This shows a supersaturated sub surface oxygen maximum which is coincident with the fluorescence maximum which is due to photosynthetic oxygen production at this depth. At greater depths oxygen decreases due to the presence of low oxygen Mediterranean Water and also in part the degradation of organic matter. Below this there is an increase in concentration due to the presence of the oxygen rich Labrador Sea Water.

Oxygen proved to be a particularly useful identifier for the different water masses present in this study area. The two water masses, the Labrador Sea and Mediterranean, are easily distinguished due to their different oxygen concentrations.

For the inter-calibration exercise, duplicate samples were taken from each conventional Niskin bottle on the first 10 CTD casts of the cruise. The results obtained from the two methods are plotted against one another in Figure 6.

They show good agreement with the gradient of the regression line being 0.9947 with an  $r^2$  value of 0.9874. There is however a slight offset with the intercept of the regression line being negative (-0.88) which indicates the values for the IOS method are lower than those for the SUDO method.

Figure 5. Dissolved oxygen at Station OM7

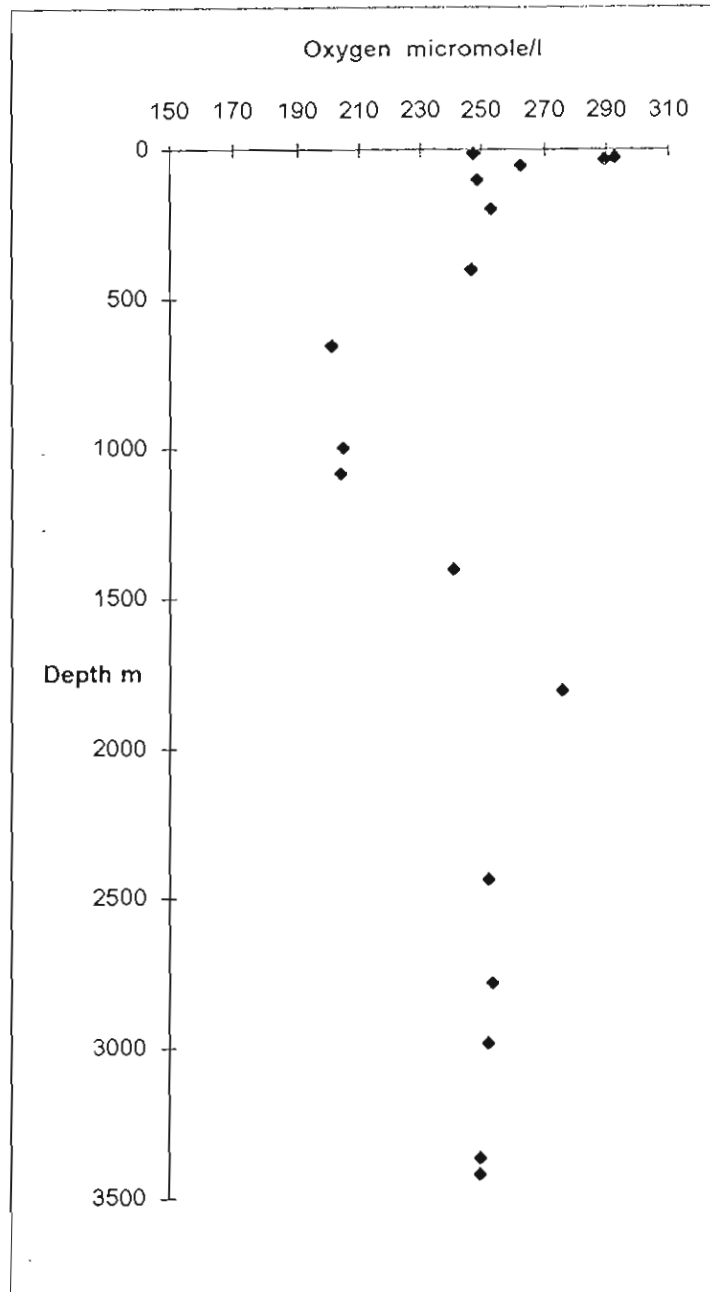
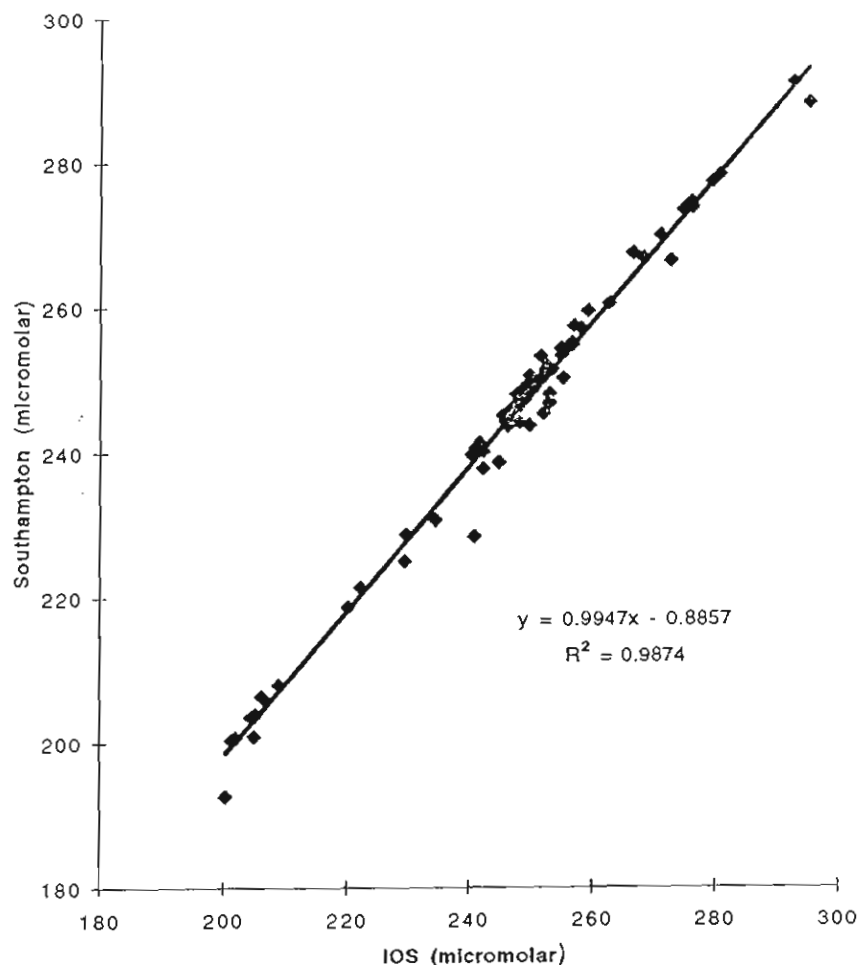


Figure 6. Comparison of oxygen data obtained by the IOS and SUDO techniques.



within the required range, however for the IOS method for the same period of time 46% of the samples fell within this range.

A further study was carried out on the three different sorts of oxygen bottles on board. These differed in shape of the stoppers base, tapered or flat, also there was a new batch of bottles with a long stopper. Seven duplicate samples of surface sea water were taken in each kind of bottle, these were then processed. The whole procedure was repeated by three different analysts, the results obtained were consistent for all three with the order of decreasing precision being flat stoppers, new bottles and tapered stoppers.

Matt Cooper  
Anneke Lubben



## 10. DISSOLVED ORGANIC CARBON

### Sampling

Water samples were taken from CTD casts throughout the cruise. Acid cleaned 300ml amber glass bottles were used to subsample the Niskin samplers. Fluorescence analysis was performed immediately on a Perkin Elmer LS-5 luminescence spectrophotometer using a 1cm cell. Instrumental parameters were set so as to optimise the fluorescence intensity, at the expense of spectral resolution (excitation slit width 10nm, emission slit width 20nm). Under these conditions, an acceptable signal to noise ratio was achieved despite the low levels of fluorescence encountered.

Fluorescence was measured at various wavelengths on filtered and unfiltered water from the surface zone, and unfiltered water from deeper samples, where possible interference from particulate matter such as phytoplankton should not be present.

### Preliminary results

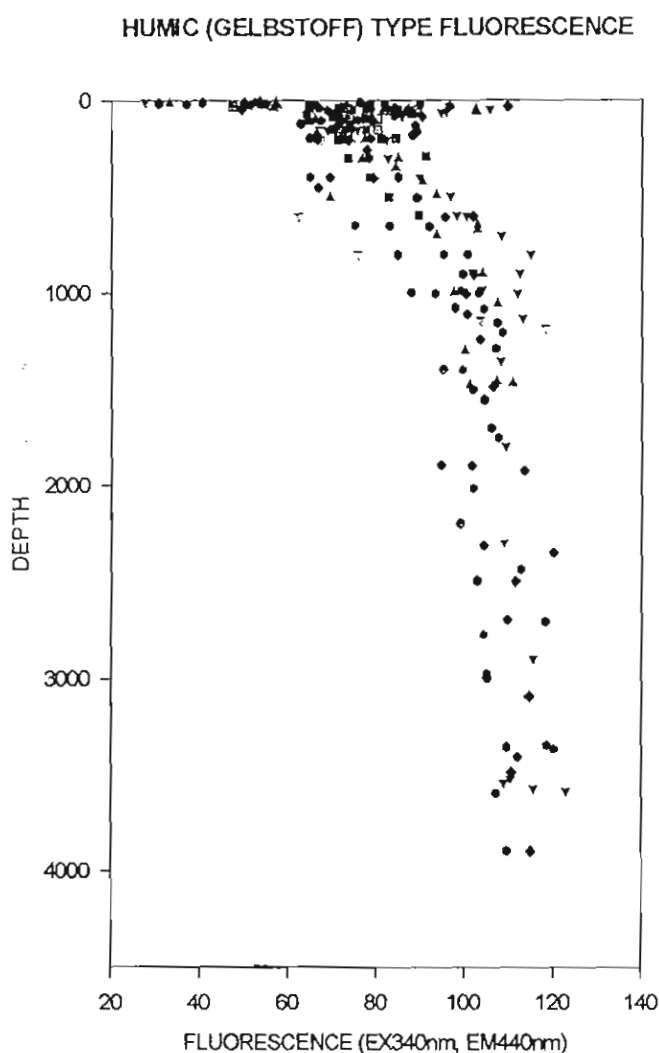
Results from depth profiles indicate low surface humic ("Gelbstoff") type fluorescence, caused by sunlight photobleaching. Fluorescence increases rapidly with depth in the thermocline zone and slowly increases in deep waters, with maximum values occurring in bottom waters. Fluorescence of this type shows good correlation with the nutrients nitrate and phosphate indicating similar regeneration processes, in combination with changes in organic composition, are occurring, although depth dependent deviations from the observed fluorescence:nutrient ratio are found. Small but distinct fluorescence peaks are evident on the depth profile in surface waters at depths roughly corresponding to the chlorophyll maximum. Such peaks have not been reported previously.

Ratios of "Gelbstoff" fluorescence measurements at different wavelengths showed considerable variation with depth, indicating the possibility of spectral modification, and by inference organic matter modification, by oceanic processes such as photobleaching or regeneration.

Depth profiles of fluorescence in the amino acid wavelength range show maxima in surface waters, with a sharp decrease at the thermocline and relatively constant, low deep water values. Particulate (unfiltered - filtered) fluorescence of this type showed maximum values in the chlorophyll maximum zone, but dissolved fluorescence showed a more homogenous distribution over the whole of the mixed layer with smaller increases in the chlorophyll maximum.

Depth profiles of "Gelbstoff" type fluorescence are shown below:

Figure 7. 'Humic' Fluorescence for samples collected at the main OMEX stations.



Adrian McDonald

## 11. PLANT PIGMENTS AND MICRO - ZOOPLANKTON

### 11.1 *Distribution Of Pigment Biomarkers In The Celtic Sea*

#### **INTRODUCTION**

Chlorophyll and carotenoid pigments have proved to be useful surrogate markers for quantifying phytoplankton biomass and determining the chemotaxonomic composition of the microalgal community. In addition the monitoring of phaeopigments has been used to indicate the processes involved in the transformation of chlorophyll through grazing and other

degradative activities. Within the framework of the European OMEX programme, pigment biomarkers have been utilised to investigate the seasonal fluxes in phytoplankton on the shelf break in the OMEX 'Box' at the Goban Spur and adjacent waters.

### ***SAMPLING AND METHODS***

Samples (1-2L) were drawn from shallow biogeochemistry CTD casts, filtered onto GF/F filters, and were snap frozen in liquid nitrogen. The pigments were then extracted in 90% acetone using ultrasonification and centrifugation. An aliquot was injected onto a C18 reverse phase column for high pressure liquid chromatographic separation and quantification of some 20 chlorophyll and carotenoid pigments using both absorbance (440nm) and fluorescence detection (Excitation 405nm; Emission 670nm). Underway samples were also taken to calibrate the on board fluorometer. All samples were analysed on board *Discovery*.

### ***PRELIMINARY RESULTS***

A number of pigments were detected in the Goban Spur region and these included chlorophylls a, b, c1c2, c3 and a variety of carotenoids. The following accessory biomarkers ; peridinin (per), 19'-butanoyloxyfucoxanthin (but), fucoxanthin (fuco), 19'-hexanoyloxyfucoxanthin (hex), zeaxanthin/lutein (zea/lut), and chlorophyll b indicated the presence of dinoflagellates, chrysophytes, diatoms, prymnesiophytes, cyanobacteria/green algae and green algae respectively. Diadinoxanthin(diadino) was also detected.

The depth distributions in Figures 8 and 9 show the variations in pigments at stations OM5 and King Arthurs Canyon respectively.

A chemotaxonomic interpretation of the accessory pigment data indicates that prymnesiophytes (hex) were the dominant algal group. The prominence of prymnesiophytes has important implications with respect to biogeochemical cycling in the Goban Spur area as these organisms are known to be one of the main producers of DMS and they also fix carbon dioxide and calcium carbonate when coccolithophores are present.

Denise G. Cummings

## ***11.2. Microzooplankton***

Samples taken in the upper 200m of the water column by water bottle casts, were preserved with lugols iodine. Microzooplankton analysis will be performed at the Plymouth Marine Laboratory (Elaine Edwards).

Figure 8. Pigments in the upper water column at Station OM5.

Station A1 (OM5) 28.8.95

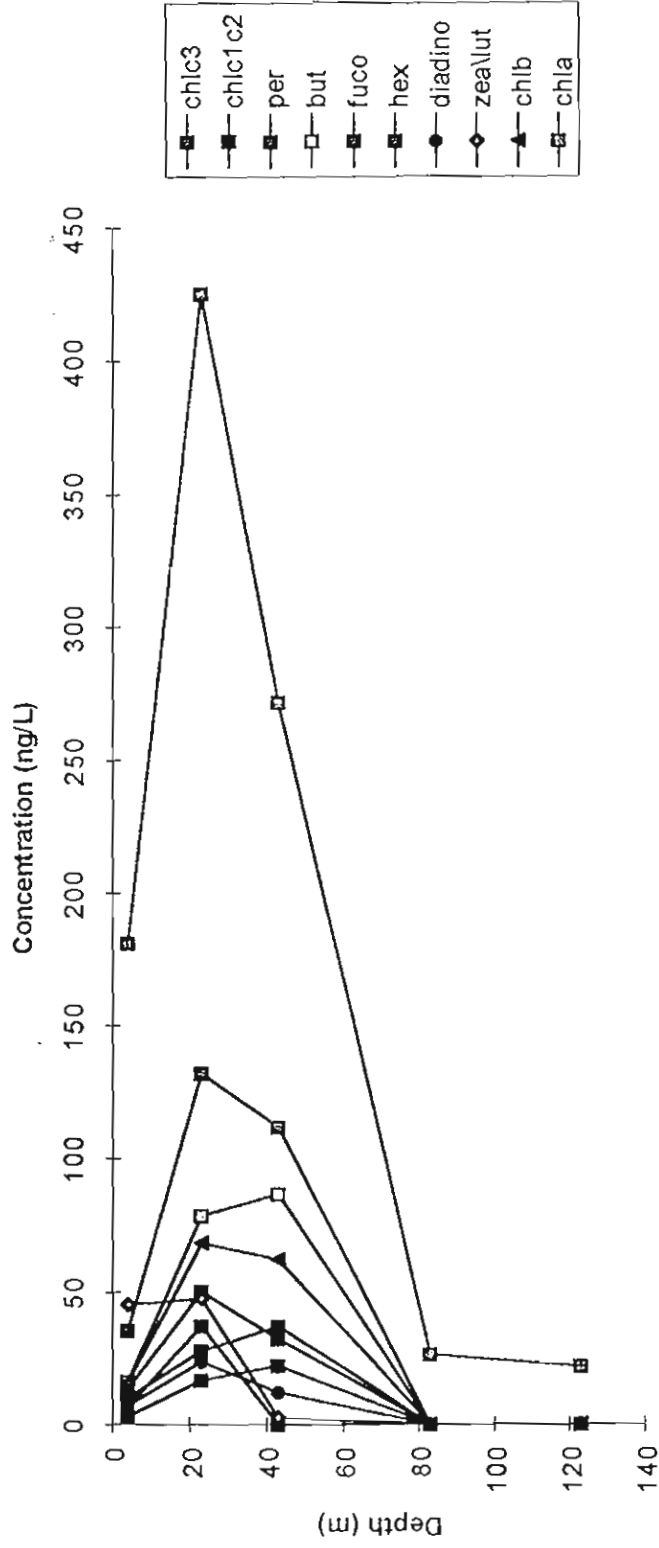


Figure 9. Pigments in the upper water column at Station KAC.

King Arthurs Canyon 4.9.95

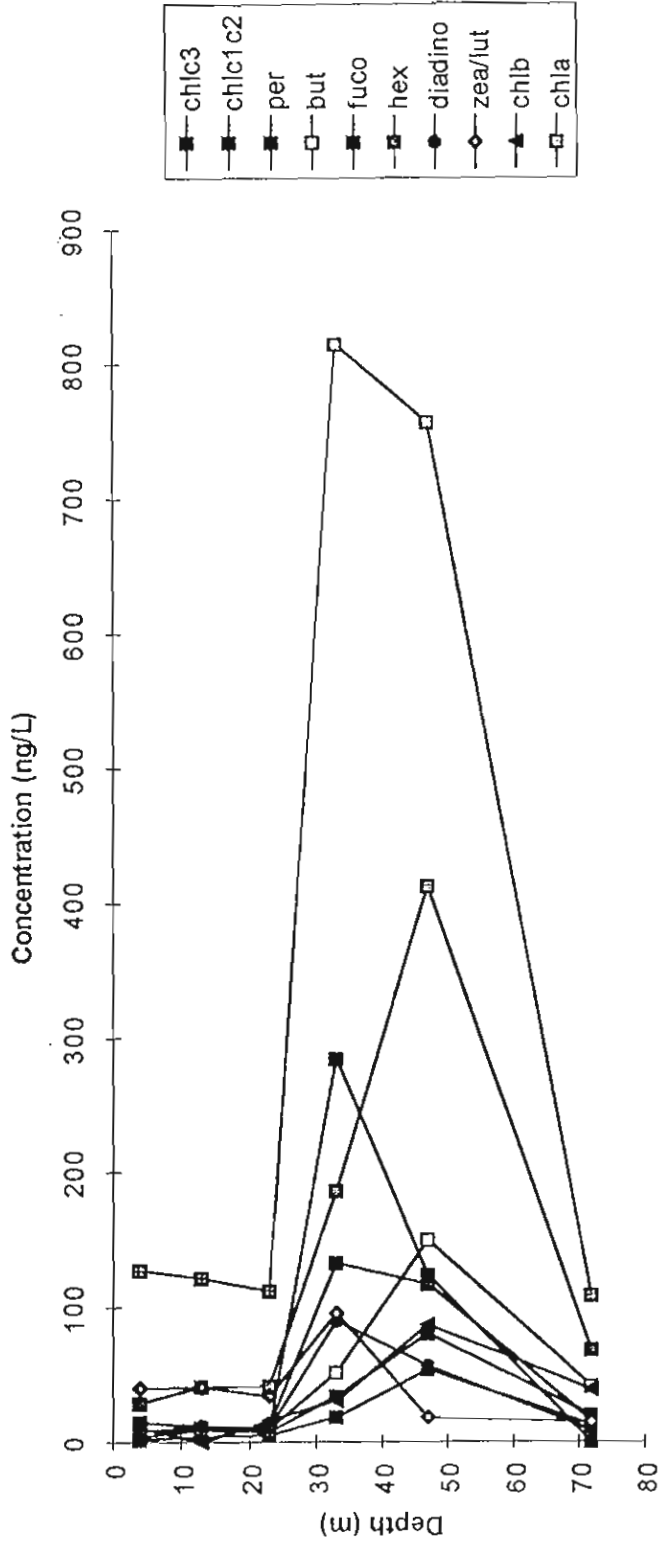


Table 1. Microzooplankton sampling

SAMPLES TAKEN FOR MICROZOOPLANKTON		
Date	Station	Depths (m)
8/28/95	A1(OM5)	23, 43, 83, 120, 183
8/28/95	A2	9, 29, 35, 54, 84, 103
9/28/95	A4(OM6)	15, 36, 64, 105
8/31/95	A5	14, 24, 34, 54, 103
9/1/95	A8(OM8)	6, 18, 48, 82
9/2/95	OM12	14, 33, 50, 103
9/2/95	OM11	9, 34, 49, 64, 103
9/2/95	OM10	23, 48, 58, 73, 102
9/3/95	OM9	13, 35, 47, 100
9/5/95	OM16	14, 24, 44, 58

Denise Cummings

## 12. DISSOLVED TRACE METALS

### 12.1. Trace Metal Sampling

New lever action Niskin (LN) bottles, which had been used for the first time on RRS Charles Darwin Cruise 94, were again used on RRS Discovery Cruise 216. Sampling for trace metals in the water column was done using these 10 litre LN bottles, which had been modified for trace metal work by replacing the conventional taps with ones made of Teflon. The choice of sampling depths was greatly facilitated by the use of an improved CTD data visualisation package developed by Simon Watts, which allows high resolution monitoring of water column features in real time, and effective sampling of fine structure features. All profiles were extended as close to the bottom as conditions and wire length permitted; using the newly fitted altimeter this was typically about 5 meters.

All handling of sea water samples for trace metal work was done inside the clean container laboratory, which had required extensive cleaning prior to use. Samples were pressure filtered (circa 0.8 bar) through acid washed 0.4  $\mu\text{m}$  Nuclepore membranes, using high purity filtered nitrogen gas.

Surface seawater samples were also collected from a modified 3.5KHz fish which was towed from the starboard side of the ship. A tube made of low density polyethylene of 12 mm internal diameter, led from the fish to a pneumatically operated all PTFE bellows pump, or peristaltic pump, on deck. As observed during CD94, fully wrapping the cable/tube assembly with PVC tape prior to deployment allowed continuous deployment at full passage speed without excessive noise. The clean surface seawater was used to feed continuous measurement systems for dissolved Ni and Cu (PU) and Mn (SOC).; see below.

Details of the work of individual groups represented on the ship are given below.

## ***12.2. Dissolved aluminium***

Dissolved and reactive particulate aluminium were determined by the lumogallion technique onboard, in filtered samples of seawater collected by the underway clean pumped system (see below), by the non-toxic supply and by lever action Niskin bottles. In general, concentrations were in the same range as has been noted previously in this region. A strong aluminium signal was evident in the Mediterranean outflow water, which was a clear feature in all CTD casts to greater than 1km.

Lei Chou  
Ruth Parker

## ***12.3. Dissolved metal samples for Southampton University***

The Southampton work, in parallel with particulate trace metal studies at ULB (see below), has the objective of measuring distributions of trace metals across the shelf break, and to assess this data for i) use of metals as tracers of cross shelf water movement ii) in improving our understanding of the biogeochemical cycling and fate of trace metals in the shelf break zone.

In addition to the samples collected for later analysis at Southampton, filtered samples were also taken for trace metal analysis at Institut de Biogéochimie Marine, Ecole Normal Superior Montrouge (similar range of metals to SUDO), and the Université de Lille (Cr and V).

Table 2. Samples collected for Southampton University Department of Oceanography, and other laboratories.

SITE	CASTS	DEPTH	SAMPLES	COMMENTS
OM 5	2	186	6	2 LANs misfired on first cast
OM 9	1	221	5	Sample lost on filtration
OM 6	2	1181	12	
OM 7	3	3640	18	SAPs deployed
OM 8	4	4500	23	Sample lost
OM 12	4	4355	24	
OM 11	3	3595	18	
CTD 33	1	1415	4	(SAPs depths only?)
OM 10	2	1500	12	
KAC	2	3320	12	Limited coverage
OM 13	4	4300	24	
CTD 46	1	180	4	Channel Station
OM 14	3	1925	18	BELGICA site, SAPs
OM 15	1	140	3	SAPs
OM 16	1	166	5	

Southampton samples will be acidified (1 ml of concentrated nitric acid per litre of seawater) to ensure no changes in concentration during storage. The metals Cd, Co, Cu, Mn, Ni, Pb and Zn will be determined in the shore laboratory by graphite furnace atomic absorption spectrometry (GFAAS) after pre-concentration and separation from the salt matrix by chelation and solvent extraction procedures, using the specialised facilities, including a dedicated clean laboratory, at the Southampton Oceanography Centre.

Nick Morley  
Peter Statham

#### **12.4 Underway trace metal measurements**

Underway measurements have been performed for Cu and Ni in the surface layer (2-4 m depth). Automated voltammetric instrumentation was used,



resulting in a sampling frequency of ca. 4 samples per hour. Each sample was calibrated (standard addition method) using a high precision syringe pump.

The seawater was sampled using the NERC 'fish', which was towed from the starboard side of the ship. Polyethylene tubing was used to carry the seawater from the fish to a peristaltic pump, which was placed near the instrumentation. The polyethylene tubing was attached to the winch cable with the use of cable ties, nylon cord and tape. We encountered many problems with this set-up during the cruise, resulting in the loss of large amounts of data. A reliable set-up for sampling of trace metal-clean seawater will be of great importance for future underway trace metal measurements. The recently purchased voltammetric instrumentation has worked very well, and despite the set-backs with the sampling system, well over 300 data points have been collected for Cu and Ni.

The trace metal measurements have been performed in unfiltered seawater using cathodic stripping voltammetry (CSV). A mixed ligand reagent consisting of 8-hydroxy-quinoline, dimethyl glyoxime and Hepes buffer was pumped into voltammetric cell prior to analysis. The seawater has not been subjected to on-line UV digestion. Therefore the determined concentrations are indicative for the 'electrochemically' labile trace metal fraction, i.e. the fraction which is complexed by the added CSV ligand. This fraction is subject to scavenging processes and is often assumed to be the biologically available fraction.

Two times per day a sample was taken from the trace metal-clean supply. The samples were stored in pre-cleaned HDPE bottles for analysis of total Ni and Cu levels in the laboratory in Plymouth (after UV-digestion, to destroy trace metal complexing organic material). Comparing the total Ni and Cu concentration with the ship-board underway results will show the fraction of organically complexed metal.

Filtered samples for trace metals have been taken from the lever action Niskin samplers. The samples have been taken at 6 stations in the OMEX region, at depths indicative for the different relevant water masses. A total of 71 samples have been taken in pre-cleaned HDPE bottles, and the samples will be analysed using automated CSV for Ni, Cu, Cr, V, Mo and U in Plymouth. In addition, 22 samples (3 stations) have been taken (filtered through 0.22  $\mu\text{m}$ ) for analysis of amino acids in the laboratory in Plymouth. The samples have been stored frozen. The purpose of the amino acid analysis is two-fold: firstly, to test the recently up-dated HPLC instrumentation and secondly to gain insight into trace metal complexing organic material.

Eric Achterberg

The opportunity of the cruise was also used to test an underway dissolved manganese analysis system based on a pre-concentration step followed by colorimetric analysis of the reactive manganese in the concentrate. Samples were collected in the same way as for the electrochemical procedures. Problems were experienced during the earlier part of the cruise, and only a restricted amount of time was available for detailed attention to the automated technique

because of pressures with the main sampling activities on the ship. However, the instrument provided good data towards the end of the cruise and a clear increase in concentration of reactive manganese was detected as the ship moved into Channel waters, thus demonstrating the potential for the technique.

Nick Morley

### 13. STUDIES ON PARTICULATE TRACE METALS

There exist very few data on the trace metal composition of particulate material in the oceanic water column. As with the earlier RRS Charles Darwin cruises, the objective of this study is to investigate the vertical and horizontal distribution of the trace metal content of suspended matter in the OMEX study area.

Particulate matter was collected by in-situ filtration of large volumes of seawater at various depths using the Stand Alone Pumps (SAPs) where a polypropylene filter holder is housed directly on top of the pump. Nuclepore filters of 293 mm diameter and 0.4  $\mu\text{m}$  porosity were used. Filter volumes varied from between ~50 and 300 litres of seawater. To allow the calculation of metal distribution

**Table 3. SAP sampling station data.**

OPERATION NO.	DATE	SAMPLING STATION	SAMPLING DEPTH (M)
SAP1	29/8/95	OM6	15 37 65
SAP2	30/8/95	OM6	105 155 204
SAP3	30/8/95	OM6	400 600 900 1150
SAP4	31/8/95	OM7	54 100 204 400
SAP5	1/9/95	OM7	14 34
SAP6	10/9/95	BELGICA	20 40 60 100 200 400

coefficients, sample depths were chosen to coincide with dissolved trace metal sampling campaign. At OM6, close to the sediment trap station OMEX II, samples were taken to allow a comparison of the suspended particles with those recovered from the traps. Wire time for the deeper traps was considerable due to the slowness of the SAPS winch (<~20 m/min).

Filters were rinsed thoroughly with Milli-Q water to remove sea salt and will be kept frozen until analysis. Suspended material will be detached from the filter ultrasonically. Solid materials will be dried. Particulate Mn, Zn, Fe, Cd, Co, Cu, Ni and Pb will be analysed by direct injection of solid samples suspended in an acidic medium using graphite furnace electrothermal atomic absorption spectrometry with Zeeman correction. Particulate aluminium will be determined as an indicator of terrestrial particles and used for normalisation.

Details of SAP stations are given in Table 3.

Lei Chou

## 14. RADIONUCLIDE SAMPLING

As part of a larger programme which is studying the dispersion of man-made radionuclides in shelf and nearshore waters, the opportunity provided by D216 was taken to collect samples from the western edge of the North West European Shelf. The programme is co-ordinated through Dr Pierre Guegueniat at the IPSM laboratory in Cherbourg. Concentrates for the later radiometric determination of Cs-137 and Sb-125 were separated from large volume seawater samples collected at the locations given in the following table:

Sample number	Day No / time (GMT)	Position		T (°C)	Salinity	Sample Volume (L)
		N	W			
R001	239/1027	50.3405	7.2596	19.722	35.29	115
R002	240/0550	49.5026	10.9957	18.837	35.32	120
R003	240/1803	49.2185	12.6021	18.729	35.33	120
R004	244/0840	48.9448	13.6600	19.415	35.93	120
R005	245/0616	48.3030	13.1789	19.245	35.84	120
R006	246/1339	49.0913	11.0824	18.758	35.79	120
R007	247/1522	48.3332	11.3465	19.844	35.82	120
R008	252/1214	48.1883	9.5429	17.101	35.84	120
R009	253/1642	47.4177	7.2658	16.906	35.86	120

**Table 5. Positions at which samples were taken for Radionuclide studies. Times and positions are mid-points of time and space ranges of sample collection.**

The precipitates with co-precipitated radio-nuclides will be sent to Cherbourg for the determination of radio-nuclides.

## 15. ATMOSPHERIC SAMPLING

The western English Channel has been defined as an area receiving an unknown atmospheric flux of trace metals (Al, Fe, Zn, Mn, Cu, Ni, Pb, Cd and Co). Equipment at a site on the south Devon coast has been used to collect atmospheric particulate and rain water samples, in an attempt to gain information on this flux of metals to the Channel. The aims of this study were to:

- assess the trace metal flux to the shelf boundary region of the Celtic Sea
- assess the trace metal content of pristine marine end-member aerosols
- compare land and sea based sampling, and
- assess the possible contamination caused by the passage of the wind over land prior to sampling.

In order to extend the airborne sampling to a truly marine environment, sampling of particles and rainwater was undertaken during RRS Charles Darwin Cruise 94 in June 1995 in the Celtic Sea area, and this activity was extended in the current cruise by Eric Achterberg acting on behalf of Chrisitna Hunt.

Atmospheric particulate samples were collected using an in-house built filter holder, connected via a length of flexi-hosing to a Secomak high volume pump. The filter heads were loaded with acid washed Whatman 41 filter papers, and suspended at the bow during periods of dry weather, for an accumulated 15-20 hours (approx.). Samples were collected over a number of consecutive days, provided the wind was from the same direction (Table 5). Further sample resolution was not considered to be beneficial due to the expected low concentration of trace metals in the sample. The sampling equipment was covered during wet periods, and also whilst stationary, to limit possible contamination from the stack.

Rain water samples were collected using a system comprising an acid washed funnel -filtration unit - bottle (containing 1ml 1:1 Aristar (BDH) HCl:Milli-Q water), whereby particulates were collected on acid washed cellulose acetate membrane filters by gravity filtration. The system, which was situated on the rail of the Bridge deck, was exposed during periods of wet weather, mostly drizzle, and covered with a large plastic bag during dry weather, again to minimise possible contamination from stack material.

Table 5: Samples collected during August-September 1995, OMEX, Celtic Sea (D 216).

Sample	Position		Wind direction	Exposure		Volume of rain water
	Latitude (N)	Longitude (W)		Particulate	Rain	
1	to 56 31.88	to 9 33.34	NW to SW	4.5 hours	Carried over	Carried over
2	56 27.17 to 51 10.23	8 57.19 to 12 30.02	W to NW	15 hours	17 hours	60ml (approx.)
3	49 57.35 to 49 30.36	12 23.78 to 13 28.55	N	10.5 hours	-	-
4*	48 34.87 to 48 54.05	13 20.09 to 11 49.66	N	54 hours	-	-
5	48 54.05 to 47 28.77	11 49.66 to 9 36.55	NE	29 hours	-	-
6	47 30.17 to 47 4.94	9 33.99 to 7 10.10	N to NW	16.5 hours	-	-
7	47 24.92 to 48 39.63	7 16.00 to 9 16.97	W to SW	-	14 hours	60ml (approx.)
8	48 49.92 to 49 15.13	7 0.96 to 8 30.25	W	6 hours	-	-
9	49 16.54 to 49 47.87	8 15.96 to 6 39.48	W	-	12 hours	

\* 'potentially polluted' sample.

All samples were stored frozen. At Plymouth, atmospheric and rain water particulate samples will undergo a hot HNO<sub>3</sub>/HF digest, with subsequent analysis by either FAAS/GFAAS or ICP-MS depending on the trace metal concentration. Rain water samples will be analysed by either adsorptive cathodic stripping voltammetry (ACSV) or ICP-MS, again depending on the trace metal concentration. Geometric means, enrichment factors and tentative fluxes will then be calculated. Weather information, obtained from the ship during the cruise, will be used to plot back trajectories for the air masses sampled.

Eric Achterberg

## 16. CORING OPERATIONS

### 16.1. 3.5kHz bottom record

The 3.5kHz was run in the approaches to most multicorer stations. It was also used as the primary surveying tool for the choice of the box core stations. Continuous records exist for the region between about 9° 30'-11°W and 48°-49°N. This area of the continental slope is characterised by

numerous turbidity channels and variable sedimentation patterns over short distances. A very strong surface reflector was recorded down to ~3,000m depth, suggesting a coarse (silt/sand) surface sediment texture.

Nonetheless, occasionally strong sub-bottoms were recorded down to 50m below the surface reflector.

As already noted in previous cruises (e.g.: CD88 and CD94) the 3.5kHz record deteriorates at speeds in excess of ~8 knots, therefore increasing survey times.

## 16.2. Multi-core samples

Because of very good weather conditions at the beginning of the cruise and the competence of the RVS technicians and the crew the coring was very successful. Samples were obtained at all seven stations. Only one tube was broken.

The standard sub-sampling procedure for the University of Bremen group was as follows:

Samples were taken of the overlying water for N<sub>2</sub>O, nutrient and trace metal analysis.

**Table 6. Multi core sampling data**

CORE	LAT N	LONG W	DEPTH (m)	TIME DATE
MC 3 (#433)	49.242305	-12.498078	1151	19.05 29/8/95
MC 4 (#430)	49.187493	-12.855547	1539	9.00 30/8/95
MC 5 (#428)	49.157555	-13.097567	2273	23.17 30/8/95
MC 6 (#427)	49.09956	-13.4172	3678	16.15 31/8/95
MC 7 (#426)	49.0009387	-13.757228	4556	16.05 1/9/95
MC 8 (#434)	49.400258	-11.52417	661	4.07 3/9/95
MC 9 (#435)	49.467547	- 11.21218632	236	6.40 3/9/95
MC 10	48.2537	-10.03248	1977	10.09 5/9/95

The barrels (inner diameter 9.5 cm) were sliced in the cool room at 6° C under inert gas (argon) in a box, then the samples were centrifuged and the overlying pore water extracted again in an oxygen free environment. The pore water was filtered (pore size 0.45 µm) and analysed on board for ammonia by

photometry. David Hydes kindly analysed very accurately phosphate, silicate and nitrate/nitrite (not from Station MC 9 and MC 10). Sediment samples were analysed by GC for N<sub>2</sub>O before pore water extraction. Sediment, acidified pore water and overlying water samples were stored and will be analysed for trace metal back at university.

At four stations cores were sampled under the same conditions by Paulo Pedro from Prof. Tomasz Boski's group at the Universidade do Algarve, Portugal, in order to analyse amino acids in the sediment (see below).

**Table 7. Sub-sampling of cores.**

CORE	Sub-samples
MC 3	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tube Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 1 tube sliced by Bremen for metals in sediment and pore water
MC 4	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tube Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 1 tube University Algarve for amino acids 1 tube sliced by Bremen for metals in sediment and pore water
MC 5	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tube Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 2 tubes sliced by Bremen for metals in sediment and pore water
MC 6	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tube Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 2 tubes sliced by Bremen for metals in sediment and pore water
MC 7	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tubes Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 1 tube University Algarve for amino acids 1 tube sliced by Bremen for metals in sediment and pore water

MC 8	2 tubes sliced by Cambridge, one stored in cool room, one frozen 2 tubes Southampton one for incubation using gel technique to extract dissolved trace metals in pore waters and another for extraction of dissolved trace metals using centrifugation 2 tubes sliced by Bremen for metals in sediment and pore water
MC 9	2 tube sliced by Cambridge, one stored in cool room, one frozen 1 tubes Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 1 tube University Algarve for amino acids 1 tube sliced by Bremen for metals in sediment and pore water
MC 10	2 tubes sliced by Cambridge, one stored in cool room, one frozen 1 tubes Southampton for incubation using gel technique to extract dissolved trace metals in pore waters 1 tube University Algarve for amino acids

### 16.3 Amino acid studies on core material

#### Objectives

The participation on Discovery 216 / OMEX cruise had as main objective the collection of cores for future amino acids determination and quantification in surface sediments and also the identification of clay materials by XRD.

#### Procedure

The 4 cores were taken from different stations (Table 8) using a multicorer device. This device can collect 6 cores with 9.5 cm diameter and 4 cores with 4.5 cm diameter. The cores tubes with 4.5 cm were not used on the coring operations.

Reference	MC4 (site 430)	MC7 (site 426)	MC9 (site 435)	MC10
Date	30/08/1995	01/09/1995	03/09/1995	05/09/1995
Latitude	49°11'25" N	49°00'56" N	49°28'05" N	48°15'22" N
Longitude	12°51'33" W	13°45'43" W	11°13'12" W	10°01'95" W
Depth	1539m	4556 m	236 m	1977 m
N/sub samples	27	30	24	27

Table 8 - Data on cores collected



The cores were maintained after collection at a constant temperature of 6° Celsius and cut into sub-samples within 24 hours after collection. The sub-sampling was done in a closed box with an argon atmosphere, and the cores were cut in 1 cm slices beginning from the top. The outer mm were excluded from the sub samples. The sub samples were then centrifuged at 5000 rpm for 4 minutes and the pore water obtained was excluded from the sub-sample with a syringe. The sub samples were then stored in sterilised vessels at a temperature of minus 20° Celsius. On land, analysis will be made for the determination and quantification of hydrolyzable amino acids with HPLC, XRD of clay materials, water content and grain size.

#### Acknowledgements:

To Christian Maess and Holger Dierssen (Bremen Group) for all the support and freedom to use their material (Multicorer, argon box, and centrifuge), and to all the scientists and crew who made Discovery 216 a very enjoyable cruise

### **16.4 Box core samples**

A 0.25m<sup>2</sup> Sandia Mark II box corer was used and entry speed was varied between 25 and 40m/min depending on the 3.5kHz record for the area.

The aim of the box coring operations was to collect sediments from around 1,000m depth, which should be close to the core of the north-west flowing eastern boundary current, in order to complement the core suite collected on previous cruises. However, the first test station was at 3,230m depth and the only attempts around 1,000m (19B(1) and 19B(2), ~880m) were fruitless, because of the coarse grained and hard nature of the bottom sediments. We therefore decided to try at greater depths. An appropriate site was spotted at ~2,000m. Unfortunately, because of the time constraint put upon us by the approaching of the sub-tropical storm 'Iris', we deployed the multicorer first, as it had greater chances to recover good sediment cores. After the successful recovery of 6 cores, we run out of time and no further attempts were made to obtain a box core from this site.

The standard sub-sampling (which partly also applied to the multicorer stations) included sub-cores, surface scrapes and bulk sediment samples from the top 5cm. When possible two samples of each were collected, one stored in a cool room (~2°C) and the other one frozen. Recent planktonic and benthonic foraminifera will be studied and analysis will be made of the total, organic and carbonate carbon content of the sediment. Short lived radioisotopes (<sup>210</sup>Pb and <sup>137</sup>Cs) will also be employed to determine biological mixing depths and rates.

Table 9. Data relating to the two box coring stations.

CORE	LAT. NORTH	LONG. WEST	DEPTH (m)	WIRE OUT (m)	TIME- DATE	LENGTH OF CORE (m)
18B	49.1199	13.1862	3230	3295(?)	10:30 31/8/95	0.24
19B(1)	48.7464	10.9462	881	882	03:58 4/9/95	WASHED OUT
19B(2)	48.7483	10.9517	869	865	05:04 4/9/95	WASHED OUT

Giancarlo Bianchi

## 17. SUSPENDED SEDIMENTS

Water samples were collected to determine the concentration of suspended particulate material gravimetrically, and to examine the composition of suspended particles using scanning electron microscopy. The samples will also provide the data necessary to calibrate the transmissometer readings.

The samples were obtained using 10L conventional Niskin bottles mounted on the CTD rosette. The suspended particles in samples were collected by filtration, under clean conditions, through individual pre-weighed (to  $10^{-6}$ g)  $0.4\mu\text{m}$ , polycarbonate (Cyclopore) membranes. The membranes were rinsed with 5x25ml sub-boiling distilled water to remove sea salt, air dried and stored in sealed polystyrene petri dishes awaiting laboratory analysis. All critical handling steps were performed within a Class-100 laminar flow hood.

Ideally sampling from layers of high optical turbidity and intervening clear waters should occur but unfortunately no pronounced nepheloid layers were observed. This will therefore only produce a narrow range of particle size concentrations, compromising the quality of the calibration curve for the transmissometer.

Two samples from the non-toxic water supply and another 11 from different depths at 5 stations were processed (see Table 10).

CTD CAST	STATION	FILTER NUMBER	DEPTH (m)	VOLUME FILTERED (l)
Surface	--	0111	5	6.04
Surface	--	0112	5	4.50
4	OM5	0113	505	4.60
10	OM6	0114	1186	10.55
10	OM6	0115	604	10.55
11	OM6	0116	903	10.55
11	OM6	0117	1153	10.55
11	OM6	0124	600	10.40
11	OM6	0125	160	10.45
11	OM6	0126	70	10.60
11	OM6	0127	20	2.55
12	OM7	0128	3411	10.50
22	OM11	0129	2600	10.45

**Table 10. Stations and depths at which samples for the determination of suspended particulate material were collected**

Giancarlo Bianchi

## 18. MOORING WORK

During CD94 a shallow mooring (#150) in 145m of water was deployed at 48° 00.96N 10° 27.06W. This was a replacement for an earlier mooring that had been destroyed, presumably by fishing action. In order to minimise possible data loss, this mooring was recovered on Sunday 3 September between 1015 and 1030h. After downloading data and replacing batteries, the mooring was then redeployed on the same day between 1622 and 1644 at the same location. Data will be sent to Dr Robin Pingree at the Plymouth Marine Laboratory, and also archived with the BODC data bank for OMEX.

John Wynar

## 19. AIR-SEA INTERACTION STUDIES

The Department of Oceanography at University College Galway (UCG) are coordinating a MAST programme to examine the influence of breaking

wave generated bubbles on the fluxes of gas (especially CO<sub>2</sub>) and particulates between the atmosphere and ocean. We have found remote sensing methods, i.e. use of high frequency sonar and video, to be the most effective in the difficult environment close to the ocean surface. We suspect that fluxes are dramatically enhanced during severe weather (see for instance Wallace and Wirick, 1992). In order to help with our modelling efforts the following measurements are sought - spectra of bubble sizes and the change following wave breaking, the depth of injection of bubbles by wave breaking, the frequency of wave breaking and the effect of 'trapping' of bubbles by sub-surface turbulence.

The chief difficulty has been to make measurements close to the sea surface under windy conditions and remote from the ships waves and wake. To accomplish this we are developing a sub-surface platform, U-KITE ( see Figures 10 and 11), towed from the ships bow and designed to fly ahead of the ship's waves and at an average depth of 4 m. For this experiment U-KITE had two instruments mounted on it - a vertically oriented 500 kHz Mills Cross configuration sonar with a beam width of 2 degs. and a pulse repetition frequency of 40 Hz, and a video system able to record the passage of bubbles with diameter greater than 0.25 mm through a 2x4 cm channel illuminated from the sides with parallel light. The sonar system with its very high frequency (sound wavelength 3 mm) has been designed to measure the development of the clouds of large and easily visible bubbles created by wave breaking.

**Figure 10. Photograph of the U-Kite (left) shown in its equilibrium attitude. The sonars can be seen just in front of the tail. The surface following float is to the right with the keel uppermost.**

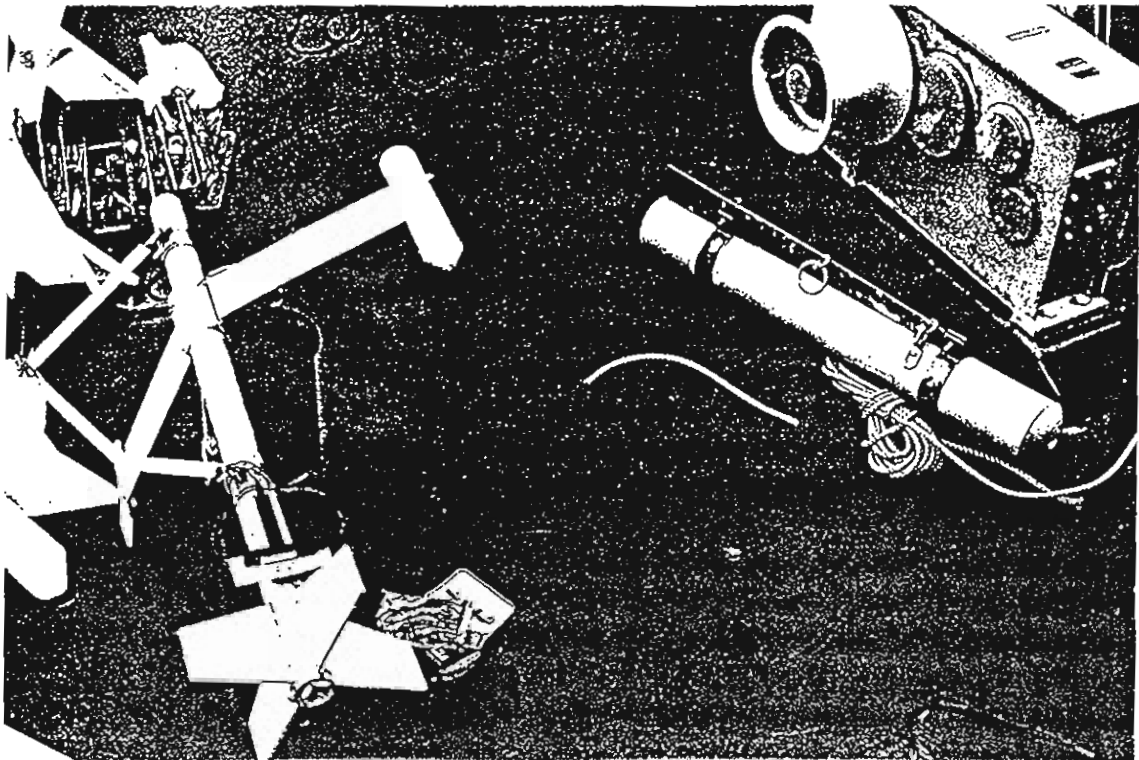
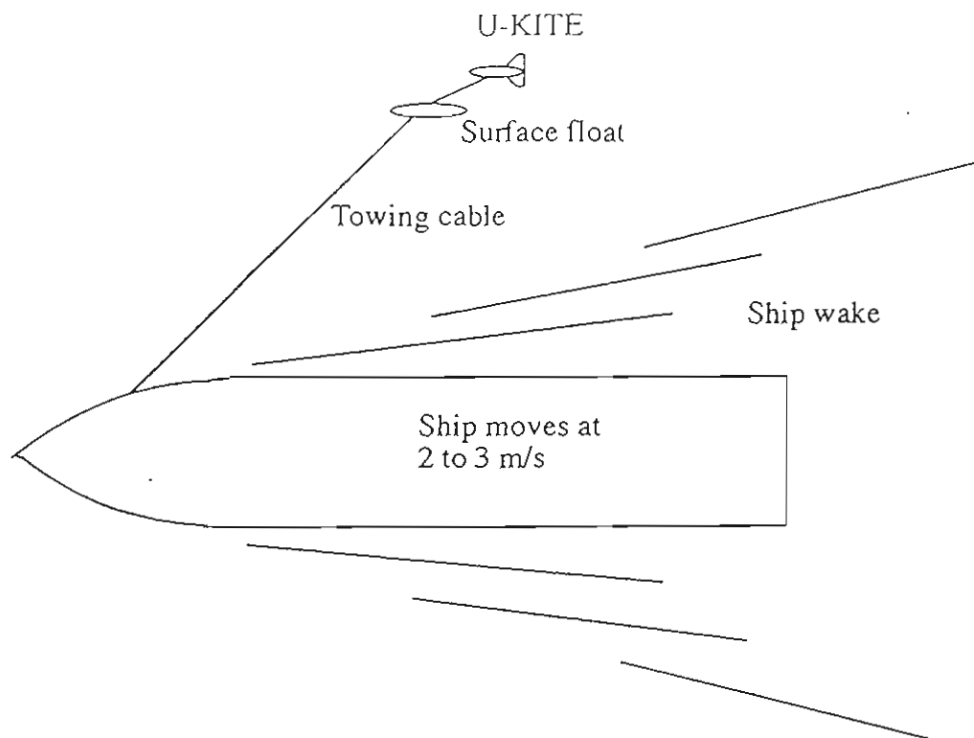


Figure 11. Diagram showing the position of the U-kite relative to the ship whilst measurements are being made.



This Discovery experiment is only the second time U-KITE has been deployed, and the first when the instruments were fitted. The intention was to make observations of the dynamic characteristics of U-KITE and to collect data under a variety of wind speeds, wave heights and tow directions relative to the wind. Four deployments were managed although some ship operational problems and the passage of a storm curtailed our more ambitious programme. Deployment and recovery were straightforward. At wind speeds below about 8 ms U-KITE behaved well although ocean waves occasionally reflected from the ship sides and interfered with the measurements. With larger breaking waves at wind speeds  $> 10$  ms there was a tendency for U-KITE to fly too close to the surface - although it was by no means unstable. This bears further investigation although it is suspected that a much longer tow line would help both problems. The sonar measurements clearly show wave breaking activity - the instrument mostly behaved satisfactorily. The video measurements look interesting with larger bubbles being clearly identifiable, although the smaller targets may be particles rather than bubbles. Unfortunately the sonar and video were mutual noise sources. On balance I am pleased with the performance of the instruments and U-KITE.

We intend to further develop U-KITE in the belief that the basic idea is sound. The instrument will be made more robust and a platform for other measurements such as vertical and horizontal acceleration, temperature and perhaps velocity microstructure. A much greater volume of data is needed, especially under windy conditions.

I am grateful to the PSO Peter Statham (SOC) and Nick Morley and to the crew of Discovery for the opportunity to participate in this cruise.

*Reference*

Wallace, D.W.R. and Wirick, C.D., 1992 'Large air-sea gas fluxes associated with breaking waves', *Nature* 356, 694-696.

**Table 11. Deployments of the U-KITE.**

Dep.	Date	Time (GMT)	Dur-ation (mins)	Wind to bow (degs)	Wind speed (ms)	Wave height (m)
1	29/8	1413	208	0,180	~6	~1
2	1/9	1824	93	var	~2	~0.5
3	3/9	1850	216	90	~5	~1.5
4	9/9	2203	58	0	~10	~2

**Marcel Curé**

**20. STANDARD SEAWATER COLLECTION**

A collection of 2000 litres of seawater was made for the Standard Seawater Service, using the shipboard non-toxic pump system. The collection took place at circa 48.953° N, 13.677° W. Approximate salinity and temperature, as provided by the shipboard thermosalinograph, were 35.916 and 19.43°C respectively.

**21. STUDENT TRAINING**

The relatively large number of berths on the RRS Discovery, and the absence of expected participation by French scientists, provided the opportunity for seven students to gain valuable training at sea in a variety of geochemical operations, and in most cases obtain samples and data directly relevant to their PhD studies. Four of the students hold NERC studentships.

**22. DATA MANAGEMENT AND QUALITY CONTROL**

The data management objectives for the cruise were:

- Quality control monitoring of the ship's automatically logged systems.

- Collation of all information required for post-cruise work up of these data at BODC.
- Compilation of a complete inventory of data sets collected during the cruise.
- Generation of spreadsheets documenting all data events.
- Acquisition of those sample data sets analysed during the cruise
- Quality control of the CTD and water bottle data through detailed inter-comparison.

From the data management perspective, participation in the cruise was an enjoyable and rewarding experience with all the desired objectives achieved. The post-cruise data management operation will be to a higher standard, more timely and less resource demanding as a result.

The quality control procedures revealed three main problems. First, the CTD pressure calibration was obviously in error, giving large negative values in air. Investigation revealed that a polynomial, rather than the usual linear expression, had been used. Reverting to a linear model resolved the problem.

Secondly, the air temperature data were consistently 4-5 C lower than the sea surface temperature in high pressure conditions during the entire first week of the cruise indicating a possible problem. This was confirmed by comparison with the bridge meteorological log. An empirical recalibration of the data against the bridge log data will be attempted during the post-cruise working up of the data.

Analysis of the water bottle and CTD data revealed that the CTD rosette was suffering from frequent misfires. The high quality bottle salinity and nutrient data available allowed the bottle firing depths to be corrected.

The data from Discovery 216 will be incorporated into the OMEX project database at BODC (Bidston Observatory, Birkenhead, Wirral, Merseyside L43 7RA). The underway and CTD data will undergo post-cruise calibration and despiking before being loaded into the system a few weeks after the cruise. Sample data sets will be merged into the database as they become available. Queries regarding the database and access to the data should be directed to Roy Lowry at BODC (e-mail [rkl@pol.ac.uk](mailto:rkl@pol.ac.uk)).

Roy Lowry  
Isabella Tindall

**APPENDIX 1 Station locations and operations carried out. (All times in GMT). Both conventional and lever action Niskin bottles were used for water column sampling.**

Date/ time	Lat. N	Long. W (degrees)	Activities (D= Discovery station)
26 August (d238) 1700			Depart Barry, departure delayed due to problem with releasing gear for lifeboat.
27 August (d239) 0330			Commenced ADCP calibration run
1352	49.9928	07.1190	MC1: test of Bremen multi corer in 115 m of water. Unsuccessful
1429	49.9910	07.1250	MC2: repeat test; 6 good cores collected.
28 August (d240) 0453	49.5345	11.0914	CTD 1 at Station OM5 (alternative designations A1 or Discovery 12793) test and cleaning of bottles
0552	49.5493	11.1329	CTD 2 OM5 test and cleaning of bottles
0705	49.5085	10.9878	CTD 3 OM5 profile samples
0936	49.8072	11.2290	CTD 4 A2 (Discovery 12794)
1402	49.282	12.601	CTD 5 A3 (Discovery 12795)
1811	49.2158	12.5910	CTD 6 OM6 / A4 (Discovery 12796)
2047	49.3512	12.5444	CTD 7 A5 (D12797),
29 August (d241)			major problem with CTD cable and >1.3 km cut off
0423	49.2147	12.6055	CTD 8 A4 (D12798)
0642	49.1327	12.8029	CTD 9 A5 (D12799)



Date/ time	Lat. N (degrees)	Long. W (degrees)	Activities (D= Discovery station)
0858			further 150 m of CTD cable cut
1846	49.2423	12.4981	MC3, Bremen site 433, D12800
2205	49.2167	12.6042	OM6/A4 Stand Alone pumps (SAPs), SAP1; D12801 #1
30 August (d242) 0210			OM6/A4 SAP2; D12801#2
0545	49.2168	12.6005	CTD 10 OM6 A4 ( D12801)
0829	49.1875	12.8556	MC4 (BREMEN #430) in 1539m
1128	49.215	12.605	CTD OM6/ A4 (D12803#1)
1500	49.2253	12.6053	SAP3; (D12803#2)
2137	49.1576	13.0976	MC5 (BREMEN #428)
31 August (d243) 0110	49.1158	13.2030	CTD 12 OM7 (D12805#1); after further 100m of wire cut off, to 3350m
0652	49.1239	13.1707	CTD 13 OM7 (D12805#2); to 2000m
0925	49.1200	13.1863	Box corer; at OM7 OM18B (D12805#3)
1235	49.1123	13.2041	CTD 14 to 200 m (D12805#4)
1456	49.0996	13.4172	MC6 (BREMEN #427) D12806
1904	49.1204	13.1814	CTD 15 OM7 (D12807#1) in 3303m
2145	as above		SAP4 (D12807#2) to 400m
1 Sept. (d244) 0148	49.1219	13.2045	SAP5 (D12807#3) to 34m

Date/time	Lat. N	Long. W (degrees)	Activities (D=Discovery station)
0505	48.9487	13.6576	CTD 16 (D12808#1), only to 3900 because of missing cable
0935	48.9481	13.6667	CTD 17 (D12808#2) to 2000m
1239	48.9494	13.6604	CTD 18 (D12808#3) to 200m
1428	49.0009	13.7572	MC7 (BREMEN #426), D12809
1815			U-KITE deployed between OM8 and OM12
2230	48.5860	13.3351	CTD 19 OM12 (D12810#1) only to 3900m
2 Sept. (d245) 0219	48.5744	13.3198	CTD 20 OM12 (D12810#2) to 2000m
0509	48.5822	13.3211	CTD 21 OM12 (D12810#2) to 200m
0825			CTD 22 (D12811#1) to 3500m; depth =3638m
1224	48.6650	12.9124	CTD 23 (D12811#2) to 2000m
1537	48.6711	12.9242	CTD 24 (D12811#3) to 200m
2123	48.9146	11.8345	CTD 25 (D12812#1) depth = 1485m
2350	48.9160	11.8004	CTD 26 (D12812#2) to 200m
3 Sept. (d246) 0350	49.4003	11.5242	MC8 (BREMEN #434); D12813
0558	49.4650	11.2103	MC9 (BREMEN #435); D12813
0630			Repeat of above
1015			Mooring recovery

Date/time	Lat. N (degrees)	Long. W (degrees)	Activities (D= Discovery station)
0647	48.0725	09.6443	CTD 35, B3 (D12824)
0830	48.0725	09.6443	CTD 36, B4 (D12825)
1120	48.1857	09.5419	CTD 37, B2 repeat (D12826)
1254	48.1316	09.6005	CTD 38, B3 repeat (D12827)
1602	48.0760	09.6442	CTD 39, B4 repeat (D12828)
1750	48.0233	09.6643	CTD 40, B5 (D12829)
1951	47.9570	09.6703	CTD 41, B6 (D12830)
2200			U-KITE deployment
2341	48.0255	09.6593	CTD 42, B5 repeat (D12831)
10 Sept. (d252) 0152	47.9584	09.6708	CTD 43, B6 repeat (D12832)
1300	47.4167	07.2700	CTD 44, OM14 (Belgica). Deep cast (D12833#1)
1520	47.4200	07.2633	CTD 45, OM14 (Belgica). Shallow cast to 200m (D12833#2)
1658	47.4192	07.2655	SAPS 6 (Belgica)
11 Sept. (d253) 1132	49° 30.0'	05° 00.0'	CTD 46, OM17, entrance to the English Channel
12 Sept. (d254) circa 0800			Arrive Southampton Port End of Cruise D216