# CHALLENGER 108C/93

LOIS RACS 1

11-23 December 1993

CRUISE REPORT

G.E. MILLWARD

Department of Environmental Sciences
University of Plymouth
PLYMOUTH PLA 8AA

# **HUMBER-TWEED COASTAL ZONE**

## **CRUISE REPORT**

**VESSEL:** 

RRS CHALLENGER

**PERIOD:** 

11 - 23 December 1993.

**PERSONNEL:** 

G.E. Millward (University of Plymouth) Principal Scientist

M.R. Williams (University of Plymouth)

T. Sands (University of Plymouth)

D. Purdie (University of Southampton)

R. Williams (University of Southampton)

E.P. Achterberg (University of Liverpool)

S. Jones (University of Liverpool)

W.D. Hiorns (University of Liverpool)

R.S. Bellerby (Plymouth Marine Laboratory)

A. Machin (Proudman Oceanographic Laboratory)

G. Ballard (Proudman Oceanographic Laboratory)

A. Harrison (Proudman Oceanographic Laboratory)

R. Powell (Research Vessel Services)

A. Taylor (Research Vessel Services)

## **OBJECTIVES:**

- i) To quantify hydrodynamical transports and the processes affecting transformations, interactions and fates of particles, biogeochemically important elements and representative contaminants from land sources to the coastal zone;
- ii) To provide the first integrated environmental data base for a UK coastal region covering seasonal cycles and inter-annual variability and incorporating measurements of fluxes of materials and rates of biological productivity;
- iii) To generate a new quantitative understanding of estuarine and coastal zone processes controlling the fluxes and reactivities of both natural and anthropogenic materials;
- iv) To provide integratable models of these processes as building blocks for comprehensive coastal zone system models which will realistically predict the affects of future environmental change.

# **CRUISE TRACKS AND ITINERARY:**

## Cruise Tracks:

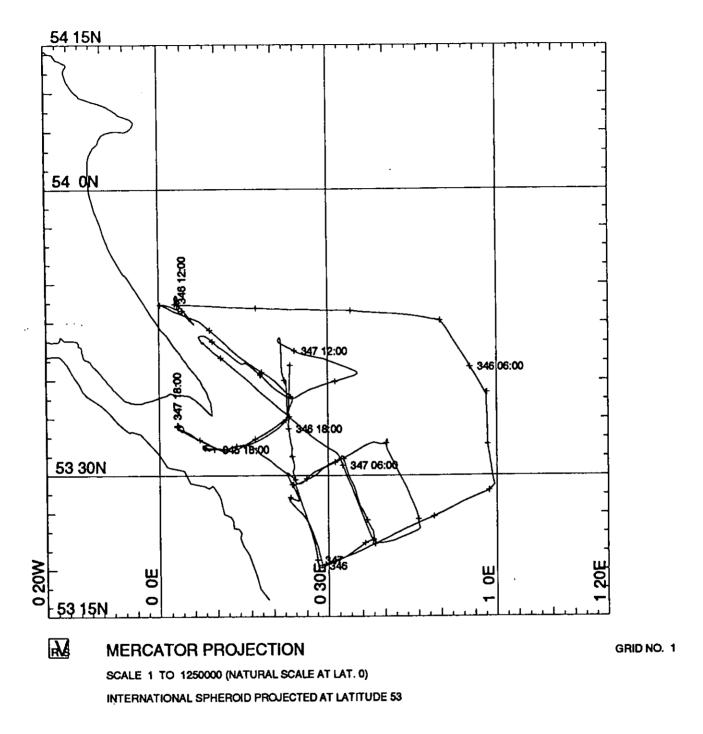
The cruise tracks in the Humber Plume region are shown in Figure 1. The Humber-Tweed track is shown in Figure 2 and the Humber-Wash track in Figure 3.

## Itinerary:

Friday 10th December: Members of the scientific party for Leg C of CH108 arrived at the ship in Hull prior to the disembarkation CH108B/93 scientists. Information was exchanged on outstanding issues to be completed during Leg C. Equipment was loaded onto the vessel.

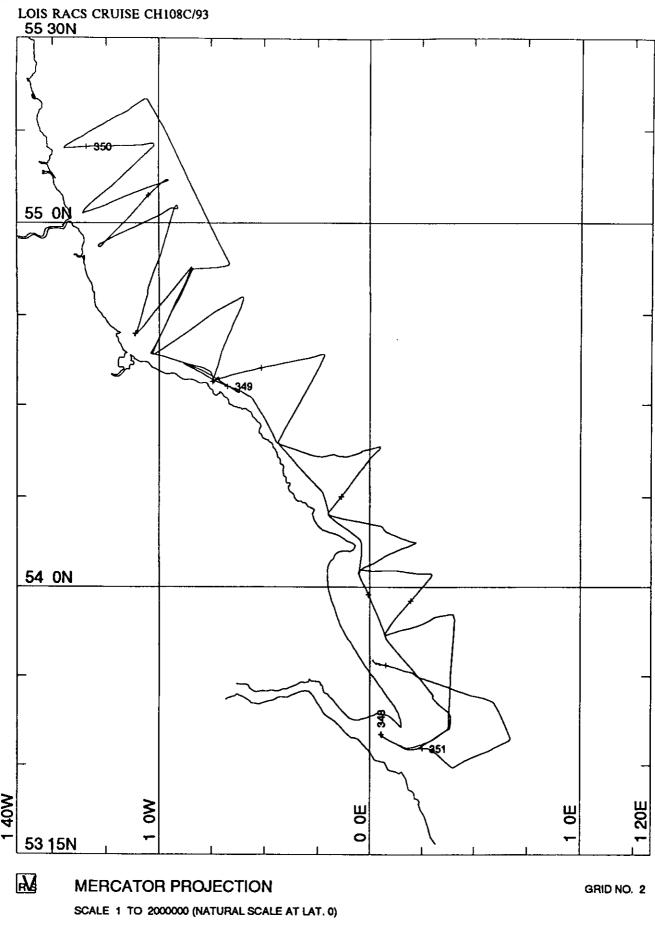
Saturday 11th December: Equipment was set up in the Main Laboratory (Harrison & Ballard), the Wet Laboratory (Achterberg, Hiorns, Jones, Purdie and Williams, R.) and the clean container (Sands and Williams, M.). The ship left her berth at 15.10 and steamed to first CTD station (see Figure 4) and arrived at CTD001, at the mouth of the Humber Estuary, at 17.50. The CTD was successfully deployed. Attempts were made to deploy the PES fish, with LUDO pumped supply attached, but this failed due to a winch malfunction. Time was lost attempting to solve the problem. Subsequently, the CTD was deployed at CTD002 and CTD003 (see Figure 4). The weather deteriorated and CTD operations were abandoned for the remainder of the night. The ship steamed slowly on the cruise track in the general heading of the mooring sites (see Figure 1).

Sunday 12th December: At 05.00 the wind abated and CTD operations resumed and samples were collected at CTD004 and CTD005. The ship moved to mooring site B and deployed the BM/CM/Trans/WLR mooring by 10.00 (see Figure 5 for mooring sites). The PMP mooring at Site 2, an operation left over from CH108B/93, was successfully recovered at 10.45. The remaining mooring operations were then suspended because of a strong easterly wind and no CTDs were possible. The ship moved to the grid at the mouth of the Estuary following a tight pattern. The weather improved later in the day and CTD operations resumed at 20.50 and samples were collected at CTD006; 007; 008 during the rest of the day.



Humber-Wash Survey, Challenger 108C

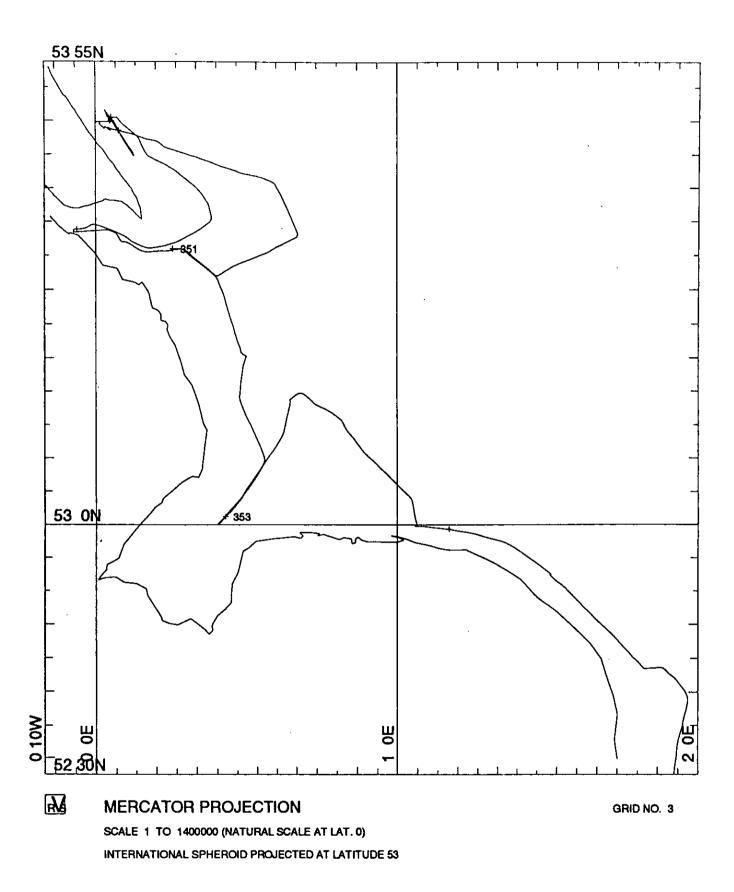
Figure 1: The survey track for the Humber Plume and mooring the sites.



INTERNATIONAL SPHEROID PROJECTED AT LATITUDE 54

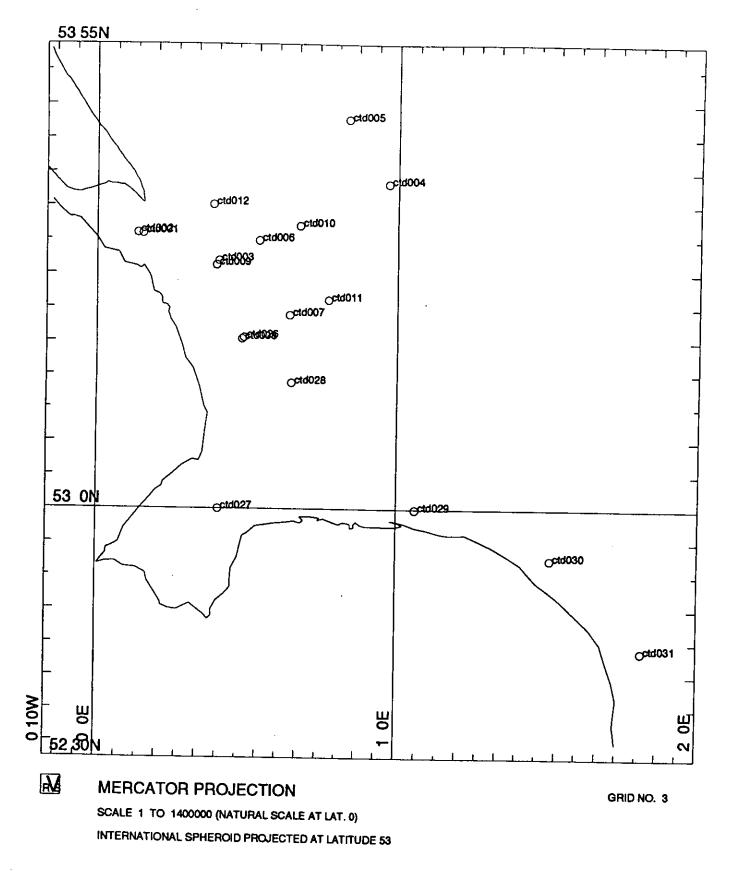
RRS Challenger Cruise 108C - Humber/Tweed Survey

Figure 2: The survey track for the Humber-Tweed coastal zone.



RRS Challenger Cruise 108C - 2nd Humber/Wash Survey

Figure 3: The survey track for the Humber-Wash region.



RRS Challenger Cruise 108C - HW CTD Stations

Figure 4: The Humber-Wash CTD stations.

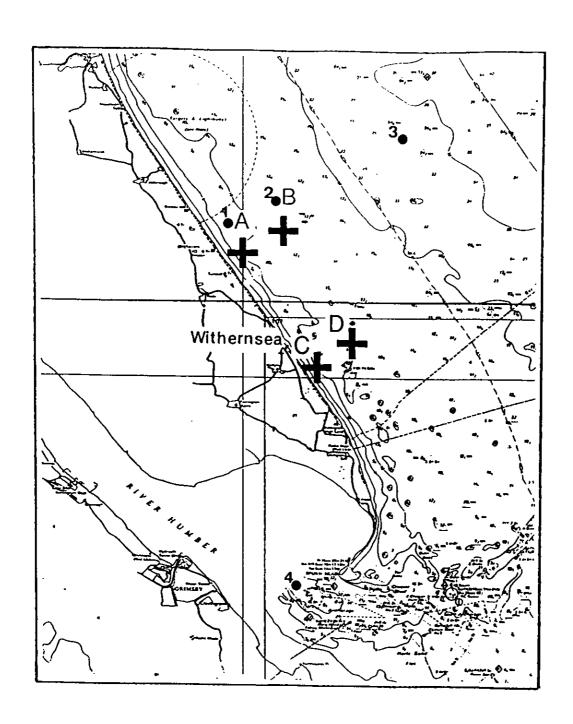


Figure 5: Locations of the POL moorings. The original sites were numbers 1-4 but were changed to A-D for CH108A/93.

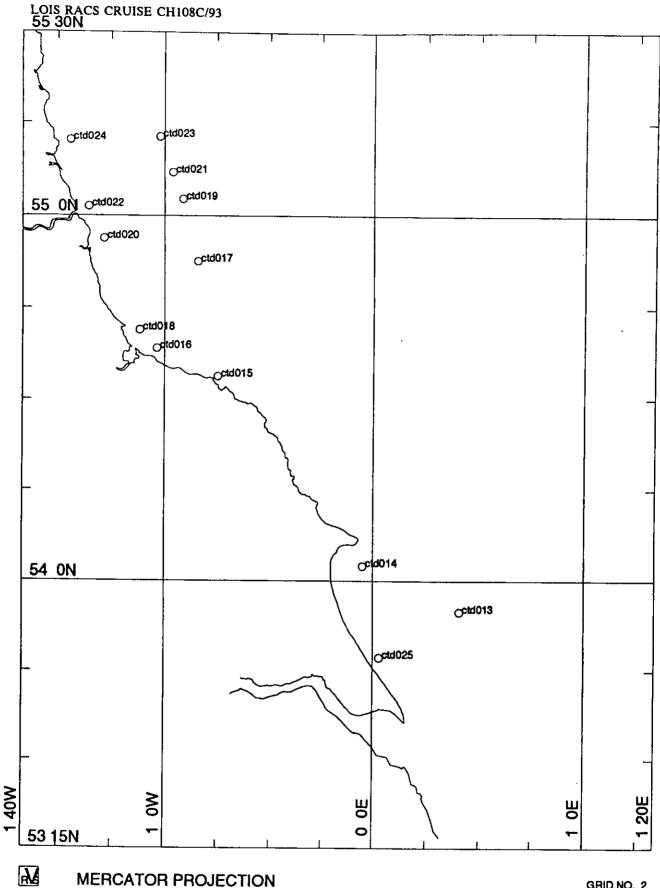
Monday 13th December: CTD operations continued through the night, with sampling at CTDs 009; 010; 011; 012, while the ship headed in the direction of the moorings. At 08.45 a PMP mooring was deployed at Site D but more bad weather at midday prevented any deployments at the inshore sites A and C (see Figure 5). The ship returned to the track at reduced speed to enable deployment of the PES fish but further problems developed with intermittent water supply. The ship moved to a safe anchorage at the mouth of the Estuary to enable Harrison and Ballard to disembark to the Pilot Boat at 15.25. The ship remained at anchor overnight and the difficulties with the pumped supply resolved.

Tuesday 14th December: Anchor aweigh at 06.00. The vessel proceeded to the start of the Humber-Tweed track and arrived 09.00. The PES fish was deployed for underway sampling. The vessel steamed on Humber-Tweed track, with sampling at CTD013 at 09.40 and CTD014 at 14.00 (see Figure 6). Adverse weather conditions developed and the ship started to roll badly and CTD operations suspended at 17.35. The vessel steamed slowly, close to coast (Figure 2 shows the track south of the Tees Estuary) to avoid heavy weather and the science was suspended due to severe south westerly winds.

Wednesday 15th December: The vessel restarted on the Humber-Tweed track and CTD operations resumed at 06.00 and samples collected at from CTD015 to CTD023 during the day. Underway sampling for trace metals continued successfully. The Humber-Tweed track not fully completed due to the requirement to pick up Alan Harrison at Spurn Head.

Thursday 16th December: The vessel continued on outside line of the Humber-Tweed track and returned to zig-zag pattern to pick up points missed during the uptrack. Sampling at CTD024. Problems developed with the pumped supply and the vessel heaved to at 20.00 for recovery of PES fish. She then steamed to Spurn Point to collect Alan Harrison, Pilot Boat arrives at 23.30 and Harrison came aboard.

Friday 17th December: It was very windy during the night and the ship steamed slowly on the track, with the objectives of returning to the moorings at first light. The CTD was deployed at 07.10 at CTD025 during a lull in the bad weather. The PMP mooring at Site 1, remaining from CH108B/93, was successfully recovered at 08.25. However, during the



SCALE 1 TO 2000000 (NATURAL SCALE AT LAT. 0)

GRID NO. 2

INTERNATIONAL SPHEROID PROJECTED AT LATITUDE 54

RRS Challenger Cruise 108C - HT CTD Stations

Figure 6: The CTD stations in the Humber-Tweed coastal zone.

attempt to recover the BM/CM/TRANS/WLR mooring on Site B, at about 08.50, the mooring line became caught in the ship's propeller and was cut off. Ship then moved to mooring D and successfully recovered the PMP at 10.45. The ship returned to the vicinity of mooring B and a grapnel was used to drag for the ground line. Eventually the mooring was recovered undamaged at 13.45. It was estimated that 25-35 metres of steel cable was around the propeller thus making passage difficult, the Master decided to make a port call at Grimsby to rectify the problem. The ship docked in Grimsby at 17.30.

Saturday 18th December: The divers arrived at 08.00 and the job was completed by 09.30. However, tidal conditions did not allow the ship to depart before 17.30, leaving little time to complete the Humber-Wash track. Eventually, the ship rejoined the Humber-Wash track in a configuration designed to complete as much as possible. The CTD was deployed at CTD026 at 21.15. PES fish deployed at 21.30 and underway sampling for trace metals was resumed.

Sunday 19th December: The CTD operations continued through the night at stations CTD027 to CTD031. The weather deteriorated and waves influenced the vessels movement. The final CTD of the cruise was completed at 09.30 and the vessel headed out of the survey area.

Monday 20th December: Passage to Barry. At 12.00 the vessels heaved to and a search commenced with acoustic hydrophone of a SUDO instrument. This was located at 12.42 and the position noted. The passage was restarted.

Tuesday 21th December: Passage to Barry.

Wednesday 22nd December: Passage to Barry. PES fish recovered at 10.30. Ship arrives in Barry at 12.00.

### INDIVIDUAL CRUISE REPORTS:

### Nutrients and Phytoplankton Productivity:

**Duncan Purdie and Richard Williams** 

On-Deck Incubation Experiments: A series of 6 experiments were conducted using water samples collected before dawn (when possible) to determine uptake rates of <sup>14</sup>CO<sub>2</sub> and <sup>15</sup>N-nitrate and <sup>15</sup>N-ammonia (see Table 1). Water was collected rom sub-surface (water was well-

Table 1: Positions, dates and times of <sup>14</sup>C and <sup>15</sup>N incubation experiments.

Incubation Number	Date	CTD Number	Sample Time	Incubation Start	Position
1	12.12.93	5	06.44	07.30	53.76 N; 0.835 E
2	13.12.93	12	07.00	07.45	53.36 N; 0.229 E
3	14.12.93	13	09.45	10.20	53.91 N; 0.405 E
4	15.12.93	17	09.41	10.20	54.87 N; 0.842 E
5	17.12.93	25	07.08	07.30	53.78 N; 0.029 E
6	19.12.93	30	07.38	08.20	52.89 N; 1.512 E

mixed at all stations) using the CTD rosette Niskin samplers. For <sup>14</sup>C experiments, 21, 60 ml polycarbonate bottles were filled directly from a Niskin. The <sup>14</sup>CO<sub>2</sub> was added and 3 bottles placed at each of 6 different light levels and 3 in the dark. Incubators were situated on the boat deck and supplied with surface seawater. The <sup>15</sup>N-nitrate spike solution was added to a total of 12 x 2 litre polycarbonate bottles and similarly for the <sup>15</sup>N-ammonia spike. Two bottles containing ammonia and two containing the nitrate spike were incubated at each of 6 light levels in on-deck incubators supplied with surface seawater. At dusk all bottles were placed in the dark then the following morning filtered through either 0.2 µm Nuclepore filters (for <sup>14</sup>C) or pre-combusted GF/C filters (for <sup>15</sup>N). The <sup>14</sup>C filters were stored over a desiccant and will be assayed at PML. The <sup>15</sup>N filters were placed in petri dishes and placed in a deep-freeze to be analysed later. Due to an error, not all <sup>15</sup>N filters were washed with filtered seawater; all samples from incubations 1-4 will need to be washed with filtered seawater prior to drying. Discrete chlorophyll samples (GF/F filtered) were additionally collected from each incubation sample for separate analysis.

Continuous Dissolved Oxygen Measurements: Continuous underway measurement of sea surface dissolved oxygen was monitored using a pulsed dissolved oxygen electrode system. The electrodes were supplied with seawater from the non-toxic supply at a flow rate of ca. 2 litres per minute. Measurements were logged every five minutes from 10 december on leaving Hull until Lands End on 21 December (with a break of one day in Grimsby). The data was logged to a personal computer and subsequently transferred to the ship-board mainframe computer. Approximately 2500 measurements of sea surface dissolved were made using this system. To calibrate the output from the pulsed oxygen electrodes, approximately every six hours water samples (in triplicate) were collected from the non-toxic seawater supply and fixed using the standard Winkler method. These samples were analysed at sea using a photometric end-point titration system. Forty one calibration points were used to adjust the probe data to produce absolute dissolved oxygen concentrations. All dissolved oxygen data, once calibrated can be obtained from BODC.

Phosphate Samples: Samples for the analysis of organic, inorganic and particulate phosphates were collected from the non-toxic water supply, periodically water samples were drawn from CTD Niskin bottles, to be used to determine possible contamination from the non-toxic supply. The samples were collected on the Humber-Wash (30 samples) and Humber-Tweed (36 samples) survey grids. All the samples taken for phosphate analysis were filtered through ashed and preweighed GF/F filters in all glass filtration equipment and the filtrate and filter were stored in a freezer. Samples will be analysed at Southampton University following the cruise.

Chlorophyll, Suspended Solids and Phytoplankton Sampling: Water samples were taken from surface CTD Niskin bottles for chlorphyll, suspended solids (determined gravimetrically) and phytoplankton lugols and formalin-preserved bottles. At sample sites where the CTD was not deployed, the samples were taken from the non-toxic supply. Chlorophyll samples were filtered using 0.2 µm Nuclepore filters and then frozen. The lugols and formalin samples were taken directly from the Niskin bottle or the non-toxic supply and then stored unfrozen. Samples for suspended solids were collected by filtering water through pre-combusted, preweighed GF/C filters and storing the filters unfrozen (the filter being washed with Milli-Q water prior to storage, to remove traces of salt). For chlorophyll and suspended solids there were 27 samples on the Humber-Wash grid and 22 on the Humber-Tweed. For Phytoplankton there were 9 samples from the Humber-wash grid and 7 samples from the Humber-Tweed. Phytoplankton samples were also collected from all incubation experiments. In addition, the suspended solids data will be used to calibrate the transmissometer signal and

the discrete chlorophyll measurements to calibrate the fluorometers in the non-toxic supply and on the CTD.

Problems Encountered: (a) insufficient lugols/formalin bottles supplied by PML; (b) non functioning of CTD downwelling irradiance sensor (noticed by D. Purdie and repaired by R. Powell on 15 December), probably the sensor was not functioning on the earlier two legs of CH108; (c) scientific fridge in the wet laboratory did not function; (d) ammonia analyses were not available for the <sup>15</sup>N experiments, thus ammonia analysis of discrete water samples was attempted. Excepting incubation number 1 samples preserved in phenol and returned to Southampton for analysis.

### Continuous, Underway Nutrient Analyses:

### Rebecca Bellerby

During CH108C/93 continuous underway monitoring of phosphate, nitrate and nitrite was carried out over the Humber-Tweed grid as far as CTD024 and the Humber-Wash inshore grid points. Bad weather made it impossible to complete the track in its entirety. The nutrient data was edited and plotted during the cruise. A small number (5) of discrete samples were analysed for initial nutrient concentrations on water used for productivity and <sup>15</sup>N measurements. Very few problems were encountered. However, the problems experienced with the new Ismatec peristaltic pump, during the previous leg, continued in spite of replacement parts being delivered at the changeover in Hull. Minor flaking of the plastic pump-tube cartridges rendered them useless, and without a spare pump one channel would have been shut down. The copper/cadmium reduction coil also proved a problem due to its premature break-up. This caused minute particles of the metals to invade the nitrate optical system, altering the absorbance readings. It is suggested that a filter or glass wool plug be used in conjunction with the coil to eliminate this problem.

## Continuous, Underway Dissolved Trace Metal Analyses:

### Eric Achterberg and Simon Jones

During the cruise water samples have been taken for trace metal studies. In order to obtain uncontaminated samples, a clean sampling system was used consisting of a 50 m hose, coupled to a large peristaltic pump. Water was pumped from about 4-5 m depth, with the end of the hose immersed in the water by attaching it to the PES fish, which was deployed by means of a winch. Whenever, the fish was deployed seawater was pumped continuously and this was used in two ways: - (a) quantities of up to 50 litres of seawater were concentrated down to about 400 ml, using a tangential flow system to obtain a particle slurry. The slurry

will be used for adsorption-desorption laboratory experiments in Liverpool. About 20 concentrated samples were collected from the region near the Humber Estuary; (b) testing and implementation of an automated voltammetric metal monitor was carried out during the cruise. This comprised of two components (i) to determine total Cr and (ii) to determine total Cu, Cd and Ni. Sub-samples were taken from the clean seawater supply by means of peristaltic pumps and the flow was passed through in-line UV digestion units, in order to destroy metal complexing organic material. Reagents for the cathodic stripping voltammetry were added in-line to the sample flow.

The metal monitoring was very successful. Using the automated system determinations of Cu, Cd and Ni were obtained every 20 minutes and every 35 minutes for Cr. This way 220 determinations of Cu, Cd and Ni were achieved and 120 determinations of Cr. Furthermore, on the return journey, from the Humber Estuary to Barry, the metal monitors were used continuously, resulting in an extensive data set along the east coast of England, the English Channel, the Straits of Dover and the Bristol Channel.

# Trace Metal Sampling and Radiotracer Studies:

Mark Williams, Tonia Sands and Geoff Millward

Sampling for Suspended Particulate Matter (SPM): The principle objective was to examine the distribution, transport and behaviour of trace metals in SPM (mainly Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) within the LOIS coastal zone. Near-surface SPM samples were collected along the Humber-Wash and Humber-Tweed tracks. Sampling stations were pre-selected and coincided with those sampled on CH108A/93. Samples were obtained using 10 litre pre-treated Go-Flo sampling bottles deployed on the CTD rosette and pre-set to open at a depth of approximately 10 m. On retrieval the Go-Flos were transferred from the rosette and mounted on the exterior of the clean container, which was located on the after deck of "Challenger". The water samples were filtered, under nitrogen gas pressure, through 142 mm PTFE filter presses fitted with acid-washed, pre-weighed, 0.4 μm poresize Nuclepore polycarbonate filters. Water volumes in the range 2 to 20 litres were filtered, depending on the approximate turbidity gauged from the transmissometer reading, to give approximately 100 mg of particulate material. The SPM was washed with about 20 ml of Milli-Q water to remove excess sea salt and then stored at -18°C. A total of 31 SPM samples were obtained.

Radiotracer Experiments: The radiotracer experiments were carried out to establish partition coefficients ( $K_d$ s) for selected particle populations and for a cocktail of  $\gamma$ -emitting radiotracers  $^{51}$ Cr,  $^{137}$ Cs,  $^{54}$ Mn,  $^{65}$ Zn and for  $\beta$ -emitting  $^{63}$ Ni. The fact that Ni is a  $\beta$ -emitter means that separate experiments had to be carried out, in addition to those with the cocktail

of  $\gamma$ -emitters. Water samples for the radiotracer experiments were collected immediately prior to the vessel's departure from Hull from several locations, including Spurn Head, Trent Falls and an Ni/Zn-rich effluent. These samples were retrieved manually and were collected in 10 litre acid-washed carboys. Additional seawater samples were obtained either from CTD deployments or from the non-toxic supply on the ship.

Radiotracer incubations were carried out on board in the clean container, with due regard for the normal safety protocols. The experiments were of three types (i) a salinity gradient was made up twice using the water samples from Trent Falls and Spurn Head to yield water of approximate salinities 0, 5, 10, 15 and 34.5 psu. One salinity gradient was doped with the radiotracer Cr, Cs, Mn, and Zn cocktail and one with the radiotracer Ni. The samples were incubated at seawater temperature, with a pH about 7.8, for a period of 5 days; (ii) a turbidity gradient was made up consisting of Humber Estuary water (of approximate salinity 12 psu) and the metal-rich effluent. This was incubated under similar conditions to (i); a mixing experiment designed to simulate the mixing of SPM coming from the Holderness coastline and the Humber Estuary was undertaken. Holderness water was mixed with estuarine in the proportions from 100% Holderness to 100% Humber in 20% intervals. The experimental conditions were similar to those indicated in (i).

# Sampling for Ammonia-Oxidising Bacteria:

Will Hiorns

Samples were collected from the LOIS coastal zone in two ways. Firstly, tangential flow filtration (or cross flow filtration) was used to concentrate solids of greater than  $0.1~\mu m$  diameter. Material from 100 litres of water was finally suspended in one litre and fixed with formaldehyde. Secondly, membrane filtration of seawater was also performed using a range of pore sizes (2.7, 0.45, 0.2 and 0.1  $\mu m$ ). A combination of these methods was also used; a ten-fold concentration of seawater particles was filtered onto 0.1  $\mu m$  poresize membranes. This approach allowed solids from ten litres of seawater to be conveniently applied to a single 47 mm diameter filter, circumventing the need for centrifugal recovery of biomass, known to be inefficient for marine bacteria. Throughout the cruise 3 fixed suspensions of particles were collected (2 in the Humber-Wash and one in the Humber-Tweed) and 13 membrane filtered particles (3 in the Humber-Wash, 7 in the Humber-Tweed and 3 on the return track).

Nucleic acids will be purified from these samples and subjected to molecular biological analysis. Polymerase chain reaction amplification and oligonucleotide probing will allow a basic characterisation of the ammonia-oxidiser populations sampled (e.g. the distribution of

bacteria from terrestrial and sewage habitats, the occurrence of beta- and gamma-Proteobacterial marine nitrifiers). Nucleic acids will also be cloned for detailed sequencing and comparison with laboratory type strains. Additionally, workers have found a linear relationship between growth rate and rRNA content in some bacteria, and the possibility of rRNA quantification as an indicator of ammonia-oxidising activity is being investigated.

### **Mooring Operations:**

#### Alan Harrison

The original mooring sites were numbered 1-4 and are shown in Figure 5. However, during CH108B/93 it was decided that there would be some relocation of sites and these are labelled A to D in Figure 5. During the Hull port call on 10th December data was down loaded from the instruments and the batteries were changed. Unfortunately bad weather during CH108B/93 had precluded the retrieval of the PMP moorings at Site 1 and Site 2. However, as explained previously all moorings were finally retrieved and the data down loaded and Table 2 gives a summary of the performance of all the instruments across all cruises.

### Data Recording and Processing:

#### A. Machin

The aims of the BODC data recording and processing activities were (i) to maintain and keep a full and accurate record of scientific events on the cruise and (ii) to participate in general watchkeeping duties as necessary. The rough log was successfully kept up to data, enabling the accurate time of all activities to be registered. The BESTNAV navigation file will be used to extract an accurate position for each event. Accurate timing also is vital for later comparisons with continuously logged parameters (chlorophyll fluorescence, transmittance, temperature, salinity, light and nutrients). The rough log was also kept in separate spreadsheets for each of the sampling methods (CTD, non-toxic pumped water supply, clean pumped water supply) which allows sampling by different methods to overlap. While the imposition of an independent station numbering system (Humber-Wash grid way points 1-31, Humber-Tweed way points 1-32 (not shown in this report) was confusing, it was felt to be necessary as it allows for several visits to one station to be distinguished. Notes have been kept in the rough log which will allow the station number to be determined from the grid way point number.

Finally, a plea to all scientists to submit their data to BODC promptly. In return, we will process and calibrate all automatically logged data (CTD and underway) which will then be freely available.

<u>Table 2</u>; Summary of instrumental performance on POL moorings.

SITE								
Site 1								
S4 CM	Data.	Data.	Memory full.					
WLR	Data.	Data.	Data.					
EMP 2000	Data. No data. Incorrect Programming.							
Transmissometer	Data.	Data.	Data.					
ADCP	Data.	Data.	Memory full.					
Site 2								
S4 CM	Data.	Poor Quality.	Memory full.					
WLR	Data.	Data.	Data.					
EMP 2000	Data.	Not fitted for CH108B/93 & CH108C/93.						
Transmissometer	Data.	Data.	Data.					
ADCP	Incomplete record.	Data.	Memory full.					
Acoustic Backscatter	Not fitted.	Data.	Data.					
Site 3								
S4 CM	Data.	Data.	Site not occupied.					
WLR	No data. Water leak.	Data.						
Transmissometer	Data.	Data.						
ADCP	Data.	Data.						
Site 4								
S4 CM	Data.	Data.	`					
WLR	Data.	Not fitted.	]					
EMP 2000	Data off range.	No data. Programming	Site not occupied.					
	•	егтог.						
Transmissometer	Data.	Data.	<b>i</b>					
ADCP	Data.	Not fitted.	]					
Site B								
S4 CM			Data.					
WLR	Site not occupied.	Site not occupied.	Data.					
Transmissometer			Data					
Site D								
S4 CM	1	Site not occupied.	Data.					
WLR			Data.					
EMP 2000	Site not occupied.		Data.					
Transmissometer			Data.					
ADCP			Data.					

# PRELIMINARY RESULTS:

# Temperature, Salinity, Transmission and Dissolved Oxygen

Temperature: The temperature is best described in terms of its evolution over the six weeks of investigation. Plate 1 shows the temperature distribution during CH108A/93 where large areas of the survey region have temperatures in the range 9-10°C. The lowest temperatures were observed in the Humber-Wash region, where a significant amount of cooler, fresher water is draining from catchment areas which probably have lost a significant quantity of their heat. There is little evidence of inputs of cooler water from the Tees, Tyne and Tweed. Plate 2 shows the temperature distribution for CH108B/93, where the water temperature has dropped, over about two weeks, to under 9°C. Again the lowest temperatures were observed in the Humber-Wash region where they were 7°C or less. Two weeks later, during CH108C/93, the temperature had fallen even further (see Plate 3), with large areas of the coastal zone having temperatures <8°C. Thus, a significant amount of heat loss is occurring over relatively short time frames.

Salinity: The salinity distributions show the extent of offshore penetration of regions of freshwater influence. Plate 4 shows only weak estuarine plumes for the Tees, Tyne and Tweed during CH108A/93, whereas the Humber Plume has pushed offshore and into the Wash. As time progresses the estuarine plumes become more evident and during CH108B/93 freshwater signals are seen emerging from the Tyne and Tweed but not for the Tees. The Humber Plume remains confined to the coastline, possibly driven inshore by strong easterly winds at that time. A similar observation is shown in Plate 6 the Humber Plume does not cover as an extensive an area as CH108A/93, presumably because of the effects of easterly winds. In addition, the regions of freshwater influence for the Tyne and the Tees are more in evidence than in the previous two surveys.

Transmission: The transmittance plot is shown in Plate 7. This shows that there is a region of high turbidity close to the coast, which begins in the vicinity of the Tees Estuary. The turbidity plume extends further offshore south of Flamborough Head and is evident through to the Wash.

Dissolved Oxygen: Preliminary results indicate that the water was slightly undersaturated with dissolved oxygen in the high turbidity coastal regions (see Plate 7) and was approximately 96% saturated. This suggests a substantial oxygen demand caused by bacterial

oxygen removal, even at the winter water temperature of 6-7°C.

### **Nutrients**

Nitrate and Nitrite: The distribution of dissolved nitrate and nitrite during CH108C/93 are shown in Plates 8 and 9, respectively. The highest concentrations of nitrate were observed in the Humber-Wash region, with evidence of relatively small inputs in the vicinity of the Tees and Tyne estuaries. Additionally, a pool of relatively high nitrate is observable north of Flamborough Head, possibly associated with sediment resuspension. In contrast, the concentrations of nitrite is relatively low in the Humber-Wash but high nitrite is observable at the mouth of the Tees Estuary, which appears to drift south along the coastline.

Phosphate: Phosphate concentrations, during CH108C/93, were highest in the Humber-Wash region but there is evidence of inputs from the Tees and Tyne Estuaries, see Plate 10. The distribution bears some similarity to that of salinity, as shown in Plate 6. It is also of interest to compare the distribution of phosphate during CH108A/93. Plate 11 shows that high phosphate concentrations were obtained in the Humber-Wash region but there were elevated concentrations in the vicinity of Flamborough Head. Here tidal and/or wind activity could be remobilising sediments and inducing porewater infusions of phosphate. Also there is a significant plume of phosphate apparently associated with the Tweed Estuary. This is a surprising observation because the salinity plot (see Plate 4) shows no evidence of any freshwater plume. Clearly, this phosphate plume needs further investigation.

## Data from the Moorings

Figure 7 shows the results of the transmissometer and temperature at Mooring D over a 4-day period. The transmissometer profile reveals a significant resuspension event at the beginning of the period coupled with evidence of periodic bursts of resuspension, possibly associated with diurnal tidal effects. Furthermore, Figure 8 shows a regular temperature cycle which is in phase with pressure and pH and in Figure 9 temperature and conductivity are highly coherent. Furthermore Figure 9 shows that even though the temperature and conductivity were oscillating throughout the survey their general tendency was to decrease. This suggests an invasion of water, into the region, which had lower salinity, temperature and pH but the source of this water is hard to identify although the salinity distribution in Plate 6 shows some evidence of lower salinity water edging along the Holderness coastline from the south. Thus the observation may be a combination of wind and tide.

Additional measurements were also made by ADCP (see Figure 10) and S4 current meters (see Figure 11) at Mooring D. The latter shows the effects of the storm conditions at the beginning of the time frame and the tidal component becomes recognizable after the effects of the storm have been damped out. Similar effects are also observed by the S4 current meter. Figure 12 shows the data from the S4 current meter at Site 1 (see Figure 5 for locations) and this is a relatively long record from 26th November to 8th December. The data from Site B is shown in Figure 13. The data from the S4 current meters (Figures 11, 12 and 13) all show a consistently higher current velocity for the northerly component of the current than for the easterly, although some easterly increase could be occurring when high winds are blowing.

## **Trace Metal Chemistry**

Automated Continuous Metal Monitoring: This procedure was carried out for most of the cruise. Measurements of dissolved trace metals were made in the Humber-Wash region, part of the Humber-Tweed track and on the voyage to Barry. The trace metals were determined by automated voltammetry and every sample was calibrated using standard metal addition. The ranges of the results were:-

Chromium 170 determinations, with values in the range 1.30 to 6.71 nM;

Copper 380 determinations, with values in the range 3.99 to 151 nM;

Nickel 380 determinations, with values in the range 1.99 to 49.5 nM;

Cadmium 250 determinations, with values in the range from below detection (0.1 nM) to 9.85 nM.

Dissolved and Particulate Trace Metals: Thirty one particulate samples were collected during the deployment of the CTD and these were returned to the laboratory and are awaiting analysis. These samples were complemented by suspended particulate samples collected along the Holderness coastline, which were filtered in the same way as those from offshore. Aliquots of Humber Estuary and Holderness waters were retained for the particle-water interaction studies described below. During the filtration of some of the samples the filtrate was retained for analyses of dissolved metals. This was achieved by pre-concentrating the trace metals using a organic complexation-Freon solvent extraction technique, followed by

determination with graphite furnace atomic absorption spectrometry. The results for Ni are shown in Figure 14 and the values (given in  $\mu$ g/l on the figure) are in the range from 3.2 to 80.1 nM, which are similar to those above found by the LUDO group, using an electrochemical detection method.

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Radiochemistry: A particle-water interaction experiment was carried out using  $^{63}$ Ni (a  $\beta$ -emitter) and various mixtures of Humber Estuary and Holderness coastal water. The aim of the experiment was to simulate particle mixing processes using particles from these two source regions and to examine whether the removal of dissolved trace metals occurs in an additive or non-additive way. The results of this experiment are shown in Figure 15 which shows the partition coefficient ( $K_d$ ) as a function of the amount of Humber particles in the sample. The Humber Estuary particles have a higher  $K_d$  (Ni) possibly because they have surfaces coated with iron and manganese oxides. On the other hand the  $K_d$  for the Holderness material is about an order of magnitude less because these natural particles are, potentially, less surface active. As the particles from these two source regions mix the scavenging potential of the mixtures behaves linearly, in concert with Zn and Fe but in contrast to Cd and Mn. Other particle-water interaction studies were carried out but the data is still being synthesised.

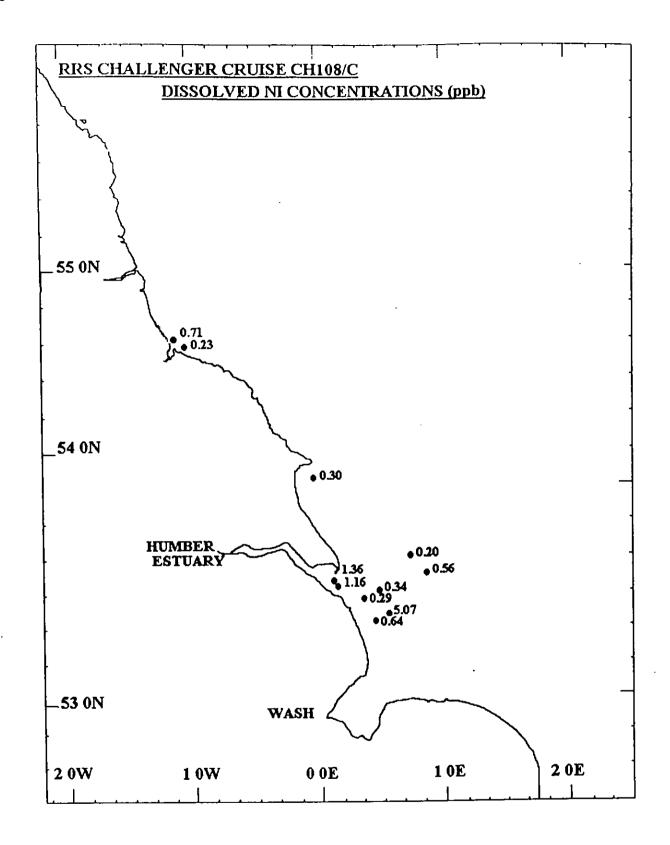


Figure 14: Dissolved nickel in the Humber-Wash coastal zone during CH108C/93.

# Plot of percentage Humber water verses Kd

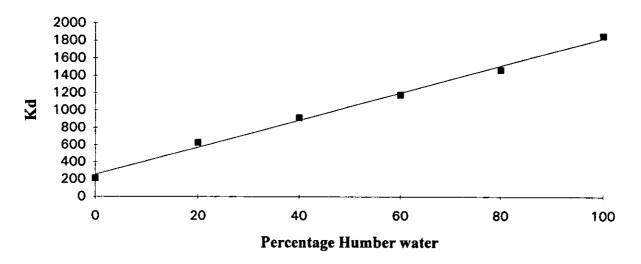


Figure 15: Particle-water interaction study involving <sup>63</sup>Ni.

The K<sub>d</sub> (Ni) is given as a function of the relative amount of Humber particles in the sample compared to the amount of Holderness particles.

