SOUTHAMPTON OCEANOGRAPHY CENTRE

CRUISE REPORT No. 24

RRS DISCOVERY **CRUISE 233**

23 APR - 01 JUN 1998

A Chemical and Hydrographic Atlantic Ocean Survey: CHAOS

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1999

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DOCUMENT DATA SHEET

ABSTRACT

RRS Discovery Cruise 233, CHAOS (Chemical and Hydrographic Atlantic Ocean Survey) combined a long meridional section notionally along 20°W from 20°N to Iceland with a detailed survey of the Rockall Trough. The meridional section was designed to i) establish the sources and sinks of halocarbons in subtropical and subpolar waters during spring bloom conditions; ii) to examine the decadal scale variability in the eastern Atlantic over the last 40 years by repeating the northern part of the WOCE A16 line first occupied in 1988 and again in 1993 (NATL 93), and parts of other sections occupied in 1957, 1973, 1983 and 1991; iii). to study the spreading mixing and ventilation rates of Labrador Sea Water, Mediterranean Water, and waters of Southern Ocean origin (Antarctic Intermediate Water and Antarctic Bottom Water) which extend into the northeast Atlantic. The detailed survey of the Rockall Trough comprised 4 zonal sections notionally at 57°N, 56°N, 54°N and 52°N in order to i) make a detailed study of the water masses in the Rockall Trough with particular emphasis on their circulation/recirculation patterns ii) to re-occupy stations along the Ellett line (57°N) to continue the time series dating from 1975. The sections were completed with CTD, LADCP, tracer chemistry (CFCs, nutrients, oxygen), alkalinity and pH measurements to full depth and a suite of halocarbon measurements together with sampling for plant pigments and biological species to 200m. Continuous measurements of atmospheric halocarbons,pCO2 meteorological measurements, VM -ADCP, depth, TSG, radiometer SST and navigation data were also made. All measurements were made to WOCE standards and the final data submitted to the WOCE programme.

KEYWORDS

ADCP, ALKALINITY, ATLNE, ATMOSPHERIC HALOCARBONS, BIOLOGY, CFC, CHAOS, C02, CRUISE 233 1998, DISCOVERY, HALOCARBONS. ICELAND WATERS, LADCP, METEOROLOGICAL DATA, METEOROLOGICAL MEASUREMENTS, NORTHEAST ATLANTIC, NUTRIENTS, OXYGEN, pH, PLANT PIGMENTS, ROCKALL TROUGH, SISTeR, TRACER CHEMISTRY, TRACERS, WOCE

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SCIENTIFIC PERSONNEL- Leg I

SCIENTIFIC PERSONNEL- Leg 2

SHIPS PERSONNEL

ACKNOWLEDGEMENTS

Firstly, I should like to thank the Master, Captain Keith Avery, for guiding me in my role as first-time Principal Scientist, his advise was much appreciated on many occasions. My sincere thanks also go to the officers and crew for their unending help throughout the cruise and, in particular, to the second officer, Alistair Mackay for his help with station timing/planning. Alistair's expertise in estimating, virtually to the half hour, where we would be in a week's time was unbelievable and without his help we would not have achieved so much.

I am most grateful to Melchor Gonzalez-Davila, University of Las Palmas and Aida Fernadez-Rios, University of Vigo for arranging equipment and scientific personnel for PC02, alkalinity and pH measurements. I am particularly thankful to Melchor for quickly arranging a replacement scientist when Stephen Boswell was unable to sail because of ill health. Without Melchor's quick response, the willingness of Maria Somoza-Rodriguez to join the ship in less than 12 hours, and the adaptability of Iris Soler-Aristegui to train Maria and thereby divide her time between pH and halocarbon analysis, the chemical results from the cruise would not have been so successful. I cannot over-express my gratitude to them.

I am also indebted to Sue Scowston, Andy Louch and Jackie Skelton of RVS operations and Rob Bonner for their handling of logistical arrangements; without Jacqui's help with travel many of us might never have reached Tenerife to join the ship.

My thanks are also given to the authorities of Mauritania, Algeria, Spain, Portugal, Ireland and Iceland for granting us permission to work in their territorial waters. So much more was achieved by having access to these waters.

Finally and, most importantly, I am extremely grateful to the entire scientific party for their dedication throughout a particularly long and arduous cruise. Without their assistance such a comprehensive data set would not have been collected; everyone of them made my first experience as Principal Scientist an enjoyable one.

The cruise was funded by the UK Natural Environment Research Council, Southampton Oceanography Centre as a final contribution to the WOCE Hydrographic Programme and in

support of the SASHES (Sources and Sinks of Halogenated Environmental Substances) commissioned project.

Denise Smythe-Wright

Figure 1.1 CHAOS cruise track showing CTD stations positions. Julian day (1998) is given in normal text, station number in italics.

1 CRUISE DESCRIPTION

1. 1 Details

1.2 Outline and Objectives

CHAOS (Chemical and Hydrographic Atlantic Ocean Survey) combined a long meridional section along 20°W from 20°N to Iceland with a detailed survey of the Rockall Trough. It was a joint effort between the George Deacon (GDD) and James Rennell (JRD) Divisions of Southampton Oceanography Centre (SOC). It formed a fundamental part of the GDD study of the Sources and Sinks of Halogenated Environmental Substances and the JRD core programme Observing and Modeling the Seasonal to Decadal Changes in Ocean Circulation. In addition, we were requested by the International WOCE community to complete the section to WOCE standards and submit the final data to the WOCE programme because the 20°W section was the only long meridional hydrographic section in the eastern North Atlantic during the late 1990s.

The objectives of the cruise were as follows

- to repeat a section, notionally along 20°W in the Northeast Atlantic, parts of which were occupied previously in 1957, 1973, 1983, 1988 and 1991, in order to examine the decadal scale variability in the eastern Atlantic over the last 40 years.
- to establish the sources and sinks of halocarbons in subtropical and subpolar waters during spring bloom conditions.
- to study the spreading, mixing and ventilation rates of Labrador Sea Water, Mediterranean Water, and waters of Southern Ocean origin (Antarctic Intermediate Water and Antarctic Bottom Water) which extend into the Northeast Atlantic.
- to make a detailed study of the water masses in the Rockall Trough with particular emphasis on their circulation/recirculation patterns.
- to contribute to the WOCE baseline survey of the North Atlantic.

1.3 Overview

The cruise commenced in Tenerife on 23 April with a 2.5 days passage leg to reach the start of the 20°W section at 20°N. During this time underway meteorological, atmospheric and hydrographic measurement were made and there was a test station at 26 $^{\circ}$ 13.1' N, 17 $^{\circ}$ 14.7' W in > 4000 m water when all bottles were fired at 3500 m.

We began the 20°W line in the early hours of Sunday 26 April with the first station (13415) at 20° 04.0' N, 20° 45.03' W. We then proceeded north-west to the 21° 20.0' W meridian working stations at 0.5 degree spacing (stations 13416- 13424). At 24°, 00.0' N we turned north and followed the 21° 20.0' W meridian to 35° 00.0' N (stations 13425-13466). From there, we made our way diagonally to 20' 00.0' W (stations 13466-13449) and continued due north from 36° 30.0' N. The reason for the dog leg was (a) to avoid Mauritanian territorial waters; despite having clearance to work, we were unable to accommodate a Mauritanian observer due to pressure on berth space (b) to avoid a number of sea mounts in the region 23-27°N (c) to cross the top edge of the Maderia Abyssal plain and hence the deep flow as obliquely as possible. Between 36° 30.0' N and 52° 00.0' N we completed stations 13467-13480 and then turned east to occupy 8 stations along 52°N to the 500 in contour of the Porcupine Bank (stations 13481-13488). We then made our way back to 20°W meridian and continued the 0.5 latitude spacing to 60° 00.0' N (stations 13489-13504). At this point it was necessary to make headway for Iceland to arrive in time for the ship's transfer next day. We completed the most northerly station of the section (station 13405) at 63° 19.3' N, 19° 59.3' W in the early hours of the morning of 22 May and steamed to the island of Vestmannaeyjar and then onto Thorlakshofh, Iceland to collect ships stores and exchange personnel. The second Icelandic port call was necessary because, due to fog, personnel leaving and joining the ship could not be transferred by air between Vestmannaeyjar and the mainland as originally planned.

Leg 2 began by making our way south to pick up the 20°W line at 63° 00.0' N and complete the section back to 60° 30.0' N (stations 13506-13511). At this point we crossed to Rockall (stations 13512-13520) to close off the flows to and from the north and during the last 9 days of the cruise completed three zonal sections across the Rockall Trough. The first along 57°N (stations 13521-13531) or thereabouts was a reoccupation of the Ellett line stations to continue the time series dating from 1975. The second and third, notionally along 56°N (stations 13532-13543) and 54°N (stations 13544-13553), along with the 52°N section completed earlier, where to make a detailed examination of the circulation/recirculation patterns of the water masses in the Trough.

A total of 139 full depth CTD stations were occupied during the cruise. At all stations we used the midships gantry to lower the CTD, LADCP and rosette sampler. Initially the 10 mm

CTD conducting cable was used (stations 13414-13417); however on the evening of 26 April a collapsed bearing developed in the winch and station 13418 was aborted. The wire was changed to the Deep Tow 17 min cable using a TOBI swivel and this was used until station 13436 by which time the 10 mm winch had been repaired and we changed back to this system for the remainder of the cruise.

Samples were collected at all stations for oxygen, nutrients and salts and at the majority of stations for CFC tracers/halocarbons, pigment and speciation analysis (although sometimes only from bottles corresponding to the top 200 in). In addition samples were collected at every other station for alkalinity and pH measurements and at selected stations for DON. A detailed listing of all station positions and samples collected is given in Appendix A. Continuous measurements through out the cruise included PC02 from the non toxic supply, low molecular weight atmospheric halocarbons from the foremast using a length of copper tubing and radiometric measurements of the sea surface temperature using the SISTeR instrument mounted on the foremast. Data was logged on the ship's computer system and processed using PSTAR. Navigation, meteorology, TSG VM-ADCP and ACCP was operational throughout the cruise.

2 CTD MEASUREMENTS

2.1 Equipment and operations

The equipment mounted on the CTD frame for this cruise was as follows.

- C71) Deep 04 WOCE Standard
- FSI 24 Bottle Rosette Pylon No 2.
- Chelsea Instruments Transmissometer SN 161/2642/003
- Chelsea Instruments Fluorometer SN 88/2360/108
- Simrad Altimeter 200 metre range
- RDA LADCP
- FSI 10 Litre Niskin Bottles
- SIS Digital Reversing Thermometers Nos T401,T714, T995
- SIS Digital Pressure Meters Nos P6393, P6075, P6394

During the previous cruise the FSI Rosette pylon No I had performed badly. It had failed to fire all positions whilst deployed, but would fire on deck. A replacement solenoid had been fitted in position 13 and the unit filled with silicon oil prior to the cruise. At this stage it can only be assumed that air remained inside the oil filled compartment containing the solenoids. It was decided to employ the second pylon for this cruise but this was also unsatisfactory. Whilst it would work on a short test lead, communications over the full CTD wire were poor.

The unit appeared to receive commands and fire the bottles but the return confirmation signals were corrupted. All efforts to tune the communications board failed to improve the situation. The communications board from pylon No 1 was removed, fitted in unit No 2 and tuned. The unit then performed without fault until the last 6 casts when position 7 failed to fire on a number of occasions although a confirmation signal was received.

In all 139 stations were occupied during the cruise. The 10 mm CTD cable was used with a swivel/slip ring assembly provided by RVS.

During the first test cast the oxygen sensor receptacle leaked oil continuously so this was replaced with one of a different design. This was incorrectly wired up, producing a voltage sufficiently high to affect the other DC analogue channels on the CTD. At this point power to the CTD was also lost. The fault was traced to the swivel/slip ring assembly. This was removed and the 10 mm CTD cable used without a swivel for further deployments. The wiring error was corrected but on station 13417 the sensor sensitivity was low. This was replaced and from station 13418 onwards worked satisfactorily.

Beginning with station 13419 the Deep Tow 17 mm cable was used with a TOBI swivel for the deeper stations. From station 13437 operations were resumed using the 10 min CTD cable.

SIS pressure meter SN P6075 failed on station 13440. The glass pressure housing had cracked and flooded the instrument with sea water. During heavy seas on station 13462 the frame containing SIS sensors T989 and P6132 was lost during the cast. On recovery of the package on station 13506 power and data connections to the CTD were lost. The CTD cable was short circuit at some point near the outboard end. Approximately 100 in of cable were cut off and the cable terminated.

The end caps from 3 bottles broke during the cruise and were replaced. Rob Bonner also replaced many of the taps as they became tight.

Apart from the initial problems with the FSI pylon and oxygen sensor, the rest of the equipment, both underwater and deck control units worked without fault throughout the cruise.

The cruise data were logged via the RVS level 'A' and SOC DAPS systems with few problems.

John Smithers

2.2 Data capture and processing

The CTD data were captured in dual streams: the SOC DAPS software and the RVS Level A. The main stream for processing was DAPS to PSTAR, with the RVS Level A used as backup.

DAPS

The Data Acquisition and Processing System (DAPS) utilises an Ultra-Sparc SUN workstation with an expansion box giving 16 extra serial ports, and is capable of real time acquisition/logging of data from a number of shipborne systems. The system has been developed at SOC, and is currently capable of logging CTD/SeaSoar/Bottles/GPS & Aquashuttle. On D233 it was used for logging CTD data.

For compatibility with the PEXEC suite of programs, DAPS data files are in ASCII format with time in decimal Julian day (with 1 millisecond resolution) in the first column. The variables that appear in other columns are configurable by the operator. Further compatibility with PEXEC is enabled with the use of 'dapsascin' which replaces 'pascin' and enables the user to specify a time range over which data are read in to PSTAR. Additionally, the utility 'dinfo' is a C-shell script that identifies data files logged by DAPS and displays the start and stop times of each file.

Unlike the RVS level A, B, C system where single data files for particular 'instruments' or 'data streams'remain in force for an entire cruise, DAPS allows the possibility for creating a new data file for each 'cast' or 'station' where applicable - e.g. CTD.

RVS Level A

Data are passed from the CTD deck unit the Level A. The level A averages the raw 16 Hz data to data at I Hz. Before averaging, the data are checked for pressure jumps and median despiked. The gradient of temperature over the I second sample of data is calculated. From the Level A, the data are passed to the Level B (logging) and then to Level C (archiving). Bottle firings are also logged using a separate Level A.

The Level A caused "serial overruns" when accepting and processing data from the CTD deck unit, but the clock input to the Level A was routinely removed to avoid data loss. The internal clock on the CTD Level A is sufficiently accurate over a cast if the Level A is allowed to communicate with the clock between stations.

Temperature

Temperature counts were first scaled by (2. 1) then calibrated using (2.2):

To correct the mismatch in the temperature and conductivity measurement temperature is "sped up" by (2.3):

$$
T = \begin{array}{ccc} & T +, & dT \\ & & \cdots \\ & & dt \end{array}
$$
 (2.3)

where the rate of change of temperature is determined over a one second interval and the time constant used was $r = 0.25$

Pressure

Raw pressure counts were scaled by (2.4) and then calibrated using (2.5):

Laboratory calibrations show the pressure sensor in DEEP04 shows little temperature dependence or pressure hysteresis, so no further corrections were made.

Conductivity

Raw conductivity was first scaled by (2.6) and then calibrated with (2.7).

The offset and slope were determined using bottle samples from al-I depths of the first seven casts. Over groups of stations small offsets derived from samples deeper than 2000 dbar were added to this correction, compensating for fluctuations in the CTD and in the bottle sampling. The corrections applied to the offset are listed in Table 2. 1. After the conductivity calibration, the salinity residuals (Bottle salinity - CTD salinity) revealed no pressure dependence. Table 2.2 gives salinity residuals statistics.

Oxygen

The oxygen model of Owens and Millard (1985) was used to calibrate the oxygen data (2.8)

02 -- x oxysat(S,T) x (Oc-) x exp { x $[$ f x TCTD+ $($ | -f) x Tlag]+ x P} (2.8)

where p is the slope, oxysat(S,T) is the oxygen saturation value after Weiss (1970), Oc is oxygen current, is the oxygen current bias, is the temperature correction, f is the weighting of TCM (the CTD temperature) and a lagged temperature Tlag and is the pressure correction. Five parameters, , (, , f, were fitted for each station. This approach minimises the residual bottle oxygen minus CTD oxygen differences but places complete reliance on the bottle oxygen being correct. Oxygen concentrations were calculated in μ mol I^{-1} . Stations 13415-13471 have no CTD oxygen data. Table 2.3 gives the parameters for each station and the postcalibration residual (bottle oxygen - CTD oxygen) statistics.

Transmittance, Fluorescence and Altimetry

Fluorescence was converted to voltages (2.9); this is a calibration of the voltage digitiser in the CTD. Transmittance was similarly converted to voltages with (2. 10) and further calibrated with (2.11). The altimeter had the calibration (2.12) applied.

Digital Reversing Temperature and Pressure Meters

Four digital reversing temperature meters were used, T401, T989, T995 and T714, and three reversing pressure meters P6075, P6394 and P6132. T401 and T714 became unfunctional after two casts (13415 and 13416), and T989 and P6132 were lost along with their frame on cast 13462. P6075 gave readings with a high offset and so was removed after cast 13439. T995 and P6394 were moved to position seven on the rosette after cast 13439 when the leaking Bottle 3 was replaced. The instruments had no calibrations applied. The arrangement of the reversing instruments is listed in Table 2.4.

Penny Holliday and Adrian New

| Station Numbers | Correction | | |
|------------------------|-------------------|--|--|
| 13414 - 13415 | 0.0000 | | |
| 13416 | 0.0014 | | |
| 13417 - 13420 | 0.0000 | | |
| 13421 - 13422 | -0.0010 | | |
| 13423 - 13424 | -0.0019 | | |
| 13425 - 13428 | -0.0027 | | |
| 13429 - 13436 | -0.0035 | | |
| 13437 - 13442 | -0.0044 | | |
| 13443 - 13456 | -0.0057 | | |
| 13457 - 13461 | -0.0043 | | |
| 13462 - 13474 | -0.0062 | | |
| 13475 - 13484 | -0.0067 | | |
| 13485 | -0.0020 | | |
| 13486 | 0.0000 | | |
| 13487 - 13488 | 0.0030 | | |
| 13489 - 13494 | 0.0000 | | |
| 13495 - 13500 | 0.0030 | | |
| 13501 - 13504 | 0.0013 | | |
| 13505 - 13516 | 0.0000 | | |
| 13517 - 13522 | -0.0038 | | |
| 13523 - 13546 | -0.0085 | | |
| 13547 - 13553 | -0.0070 | | |

Table 2.1 Corrections to the Conductivity Offset

Note: excludes residuals outside the range \pm 0.005 psu

Table 2.3a Oxygen Coefficients

| Station | ρ | α | β | f | χ |
|----------------|--------|--------------|---------|------------|--------|
| 13419 | 3.8932 | -0.0001856 | 0.03047 | -0.15471 | 0.0000 |
| 13420 | 4.3942 | -0.0001994 | 0.03201 | -0.16644 | 0.0000 |
| 13421 | 4.3549 | -0.0002106 | 0.03297 | -0.17140 | 0.0000 |
| 13422 | 4.5721 | -0.0002150 | 0.03372 | -0.17447 | 0.0000 |
| 13423 | 4.0884 | -0.0001978 | 0.02830 | -0.16046 | 0.0432 |
| 13424 | 4.3194 | -0.0001953 | 0.03061 | -0.16686 | 0.0000 |
| 13425 | 4.2225 | -0.0002006 | 0.02956 | -0.16762 | 0.0000 |
| 13426 | 3.9116 | -0.0002164 | 0.02510 | -0.16735 | 0.5695 |
| 13427 | 4.0425 | -0.0001972 | 0.02891 | -0.16268 | 0.0000 |
| 13428 | 4.0133 | -0.0002246 | 0.02568 | -0.17070 | 0.4714 |
| 13429 | 4.0249 | -0.0002044 | 0.02744 | -0.16450 | 0.0000 |
| 13430 | 4.0479 | -0.0001962 | 0.02787 | -0.16263 | 0.0000 |
| 13431 | 4.0061 | -0.0001899 | 0.02815 | -0.15898 | 0.0031 |
| 13432 | 4.0062 | -0.0002112 | 0.02650 | -0.16682 | 0.0586 |
| 13433 | 4.0769 | -0.0002072 | 0.02770 | -0.16608 | 0.0014 |
| 13434 | 4.2365 | -0.0002105 | 0.02909 | -0.17056 | 0.0092 |
| 13435 | 4.1219 | -0.0002040 | 0.02800 | -0.16572 | 0.0000 |
| 13436 | 4.0620 | -0.0001910 | 0.02888 | -0.16029 | 0.0014 |
| 13437 | 4.0909 | -0.0002143 | 0.02893 | -0.16921 | 0.0000 |
| 13438 | 4.1174 | -0.0001969 | 0.02898 | -0.16194 | 0.0000 |
| 13439 | 4.1636 | -0.0002015 | 0.02801 | -0.16528 | 0.0000 |
| 13440 | 4.1699 | -0.0002357 | 0.02719 | -0.17660 | 0.0000 |
| 13441 | 4.1699 | -0.0002357 | 0.02719 | -0.17660 | 0.0000 |
| 13442 | 4.0755 | -0.0001865 | 0.02907 | -0.15843 | 0.0000 |
| 13443 | 4.1102 | -0.0001937 | 0.02877 | -0.16176 | 0.0000 |
| 13444 | 3.8414 | -0.0001925 | 0.02518 | -0.15583 | 0.0000 |
| 13445 | 4.1128 | -0.0002541 | 0.02441 | -0.18169 | 0.0681 |
| 13446 | 4.1730 | -0.0002086 | 0.02736 | -0.16823 | 0.0000 |
| 13447 | 4.1933 | -0.0001994 | 0.02898 | -0.16504 | 0.0000 |
| 13448 | 4.1099 | -0.0002174 | 0.02683 | -0.17023 | 0.0000 |
| 13449 | 4.0538 | -0.0002404 | 0.02471 | -0.17661 | 0.1383 |
| 13450 | 4.1529 | -0.0001928 | 0.02915 | -0.16101 | 0.0000 |
| 13451 | 4.1935 | -0.0002424 | 0.02626 | -0.17906 | 0.0105 |
| 13452 | 4.1438 | -0.0001901 | 0.03086 | -0.16028 | 0.3694 |
| 13453 | 4.1168 | -0.0002160 | 0.02722 | -0.16866 | 0.2521 |
| 13454 | 3.9595 | -0.0002903 | 0.02077 | -0.18933 | 0.2276 |
| 13455 | 4.0358 | -0.0002717 | 0.02263 | -0.18464 | 0.2081 |
| 13456 | 4.0621 | -0.0001977 | 0.02685 | -0.16172 | 0.1287 |
| 13457 | 3.8924 | -0.0002914 | 0.01785 | -0.18809 | 0.0968 |
| 13458 | 4.0993 | -0.0001883 | 0.02878 | -0.15783 | 0.0000 |
| 13459 | 3.8292 | -0.0002274 | 0.02456 | -0.16368 | 0.6503 |
| 13460 | 4.0668 | -0.0001871 | 0.02939 | -0.15377 | 0.0000 |

| Station | 0 | α | 13 | | χ |
|----------------|--------|--------------|---------|------------|--------|
| 13548 | 3.8891 | -0.0001981 | 0.02359 | -0.15792 | 0.2760 |
| 13549 | 4.0338 | -0.0001188 | 0.03369 | -0.12926 | 0.0000 |
| 13550 | 3.7553 | -0.0002015 | 0.02193 | -0.15195 | 0.1625 |
| 13551 | 0.0114 | 0.0001507 | 0.05808 | 0.96337 | 0.6617 |
| 13552 | 3.2916 | -0.0001415 | 0.01993 | -0.11285 | 0.0000 |

Table 2.3b Calibrated oxygen residuals (bottle oxygen - CTD oxygen)

Note: excludes residuals outside the range \pm 15 µmol I^1

Table 2.4 Arrangement of Reversing Temperature and Pressure Meters

2.3 Post-cruise laboratory calibration

The calibration data used during D233 were from laboratory calibrations in July 1996. The post cruise calibrations carried out in October 1998 produced the following data:

The difference in pressure due to the linear term is only 2.6 dbar at full scale. The difference in temperature due to the offset is only 0.42 m°C and the linear terms differ by 1.65 m°C at full scale. It was concluded that these differences were sufficiently small that no additional calibrations need be applied.

S. Cunningham

2.4 References

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3 LOWERED ADCP MEASUREMENTS

The Lowered Acoustic Doppler Profiler (LADCP) is an RDI 150 kHz BroadBand ADCP (phase 111) with 30 degree beam angles. It is mounted vertically within the CTD frame with the bottom of the transducers protected by the base of the frame. The LADCP was installed on the CTD frame at the beginning of the cruise. It had been hoped to use a rechargeable power pack to avoid the regular removal and replacement of batteries. Unfortunately the enclosing pressure case for the rechargeable system could only be used down to 1000 db. Ten alkaline battery packs were on board at the start of the cruise including two part used ones. Two further packs were brought out by personnel joining the ship from Iceland for the last week of the cruise. To change the batteries, the pressure case was either removed from the frame and batteries removed in the lab, or in quiet sea states where no risk of spray was present, the case was left on the frame and the batteries removed. The latter method impeded sampling on one occasion because of the danger of wetting exposed cables. These slight difficulties will be avoided in future by use of the rechargeable system.

A few minutes before each cast, a command file was downloaded to the unit from a PC in the deck lab via a serial link. On this cruise the same command file was used throughout. A listing is given in Appendix C. It was decided at the beginning of the cruise to use bottom tracking throughout. This reduces the number of water track pings, but is justified because it allows a second independent estimate of the bottom current to be made. At regular intervals the instrument emits a bottom ping to test for range. Once the bottom was found the instrument recorded the velocity of the ground with respect to the package. It was hoped that this would provide a check of the quality of the absolute velocity data calculated by the more round about route described below.

The data were recorded internally and downloaded at the end of each cast by connecting a data link to the package from the PC. RDI utilities BBTALK and BBSC were used to interrogate the profiler and to download data to the PC. Power is supplied to the profiler via the serial cable in order to conserve the battery pack.

Data were transferred to the UNIX workstations via PC-NFS and then processed using a combination of PERL scripts and MATLAB m-files deve-loped by Eric Firing at the University of Hawaii. Processing was done in a number of steps which are briefly described:

- i. The binary data were first scanned to find useful information from the cast such as time at the surface, time at the bottom and number of ensembles.
- ii. The data were then read into a CODAS database. Magnetic variation and position were added to the database at this stage.
- iii. When CTD data were available, the pressure temperature and salinity data were added to the database in order to correct for the variation of sound speed with depth.
- iv. Absolute velocities were then found by calculating horizontal velocity shear to eliminate package motion, integrating with time to calculate the barotropic term and then merging with navigation data to remove the motion of the ship.

Bottom velocity data are not included in this processing path and had to be extracted manually from the binary file on the PC and processed separately from the water track data. Preliminary comparisons were made between the resulting velocities and the near bottom velocities extracted from the absolute water track data. No clear interpretation was achieved and more work is required here.

Comparisons with geostrophic profiles from the CTD data for the 20°W line are shown in Figure3.1. A horizontal line is drawn on each plot at 3210 m which is the level at which the

geostrophic velocity is assumed to be zero. If the water depth is shallower than 3210 m, a zero velocity is assumed at the bottom.

Steve Alderson, Lisa Redborn and Chris Wilson

4 VESSEL MOUNTED ADCP MEASUREMENTS

4.1 Description and Processing

The instrument used was an RDI 150 kHz unit, hull-mounted approximately 2 m to port of the keel of the ship and 33 in aft of the bow at the waterline. Data Acquisition Software (DAS), version 2.48, was run on a PC to acquire the data. With the exception of a few interruptions (see Problems section below) the instrument operated continuously from JD 114 to JD 15 1 in the water-tracking mode, and set to use 3 beam solutions for determining velocities as beam 3 (the forward beam) was not working. Ping data were averaged by the DAS into 2 minute ensembles, and 64 x 8 m depth bins were used for the entire cruise with a depth offset of 13 m included in the processing to allow for the ship's draught and the 'blank after transmit' period.

4.2 Daily Processing

- Acquisition of ADCP water-tracking velocities from Level C RVS files and conversion to PSTAR format using the PSTAR program adpexecO.
- Correction of the times of each ADCP ensemble to account for the linear, 18 second per 24 hour drift of the PC clock using program adpexec 1.
- Correction of ADCP heading data (which the DAS reads from the ship's gyrocompass) using the Ashtech minus gyro heading differences (program adpexec2).
- Calibration of the shear profiles, taking account of errors in signal amplitude and transducer alignment using a working calibration determined by a 'zig-zag' run in water-tracking mode at the end of cruise D232 (see Calibration section below). This was done with program adpexec3.
- Merging velocity profiles with navigation fixes obtained from the GPS4000 navigation files to effectively remove the ship's speed from the ADCP velocities, thus giving absolute velocities (program adpexec4).
- Separation of each day's ADCP data into 'on station' and 'underway' files. Each on station file corresponded to a CTD station and the velocities in these files were plotted as vectors, averaged over the period of time the ship held station and plotted against LADCP velocity profiles for comparison.

4.3. Calibration

The ADCP is calibrated to take account of the orientation of the transducer mounted in the hull (the transducer orientation is intended to be fore-aft). Ideally, the ADCP's bottom-tracking mode is employed in shallow (<500 m) water to determine the amplitude factor, A, and the alignment angle error, 0. However, the absence of beam 3 meant that the bottom-tracking mode of ADCP operation was unavailable throughout this cruise. Instead, a total of three zigzag runs in regions known to have fairly uniform currents were used to calibrate the ADCP; one conducted at the end of cruise D232 and the other 2 conducted on JDs 137 and 151 of cruise D233.

During each zig-zag run, the Bridge were asked to make an initial turn of 44° (either to port or starboard as preferred) away from the base course at between 10 to 15 seconds past the hour. The new heading was maintained at a steady speed of 10 knots for 20 minutes. At 20 minutes past the hour, a 90° turn back towards the base course was made, and thereafter alternate 90° turns were completed, with 20 minutes steaming between each turn. As far as possible, the same speed through the water was maintained throughout, and the entire calibration run lasted for about 3 hours in each case.

Data from the zig-zag runs were processed as described above but with A set to 1 and \varnothing set to 0° in adpexec3. Data recorded during the ship's turns were discarded, and the components of ship's velocity and ADCP velocity (i.e. 'water past the ship') were each averaged together for each of the 'zigs' or 'zags' between turns. The differences in each of these four averaged components were then calculated for before and after each turn such that:

- adpe = difference between averaged east-west component of ADCP velocity before and after turn.
- adpn = difference between averaged north-south component of ADCP velocity before and after turn.
- ve = difference between averaged east-west component of ship's velocity before and after turn.
- vn = difference between averaged north-south component of ship's velocity before and after turn.

So, a zig-zag run comprising eight 90° turns produces eight different values of each of these 4 quantities.

Equations 4.1 and 4.2 are then used to find \varnothing and A:

The 8 values of \emptyset and A were then averaged to give the best estimate of the true amplitude factor and transducer misalignment angle. The calculations were made using data from several bin depths to further reduce the likelihood of errors.

The zig-zag calibration at the end of D232 gave average values of \varnothing and A as 2.64° (with an sd of 0.0l°) and 0.9917 respectively and these values were used in adpexec3 to calibrate all data from this cruise. Data from the zig-zag run on JD 137 of this cruise have not been worked up due to the poor quality of ADCP data acquired on that day (see Problems below). The final run, conducted on the last day of the cruise (JD 151) will be worked up ashore.

4.4 Problems

Gaps in the otherwise continuous ADCP data set were as follows:

- JD 120, 19:17 to JD 121 04:45: ADCP was still working but logging to level C had stopped.
- JD 122, 17:20 to 17:30: ADCP was interrupted to retrieve missing data for the previous day from raw files on the P.C.'s hard disk.
- JD 127, 08:35 to 09:35: Power cut.
- JD 139, 04:37 to 04:40 ADCP interrupted to change settings in DAS.
- JD 140, 12:00 to 12:40: ADCP interrupted to change settings in DAS.
- JD 141, 07:30 to 08:42: ADCP stopped for testing.
- JD 144, 11:45 to 11:55: ADCP stopped to check settings in DAS.

The majority of these interruptions were necessary as a result of a persistent problem occurring with the DAS software prior to the data being logged in the RVS files.

As beam 3 was known not to be working, the DAS software was set to calculate 3 beam velocity solutions from the start of the cruise. However, it appeared that the DAS software was still using 4 beam solutions at certain times, such that 'bad' data from beam 3 were included which subsequently degraded the calculated velocities. The use of 4 beam solutions was identified in the ADCP data files by the presence of non-zero error velocities (error velocities being only determinable when all 4 beams are used). Throughout the cruise, the occasional non-zero error velocity in the data files occurred, but during the period from JD 133 to JD 145, the percentage of 4 beam solutions being used was large enough to produce many spurious velocities which considerably degraded the data set. JD 137 was perhaps the worst day in terms of poor data quality during this period.

4 beam solutions were particularly prevalent at depth and in the 'underway' data between CTD stations. On station velocity profiles were still reliable to about 150 in depth, as confirmed by comparisons with LADCP data. At depths greater than 150 in, large changes in current velocity (up to 60 cm s^{-1}) appeared to occur simultaneously throughout the water column whenever the ship's speed changed, which was clearly erroneous.

The abundance of 4 beam solutions at depth may indicate that whenever the DAS software receives back-scattered signals which it considers to be too low, it listens to all 4 beams in an attempt to improve the signal to noise ratio, and subsequently calculates velocity using ping data from all 4 beams. However, this problem will require further investigation ashore.

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5 NAVIGATION DATA

5.1 Differential GPS4000

Differential GPS4000 navigation data (ship position, heading, speed over ground, satellite fix parameters) were acquired every second throughout the cruise, giving the ship's position to within 5 in.

Daily Processing:

- Acquisition of GPS4000 data from RVS files using the gpsexec0 program.
- Quality control of data in which data are deleted wherever poor positioning accuracy is indicated by satellite fix parameters.
- Averaging ship velocity data into 2 minute bins for subsequent merging with ADCP data.

Data Quality

The percentage of 'good' data acquired during a 24 hour period ranged from a minimum of 97.5% on JD 108 to a maximum of 99.8% on JD 103.

5.2 Ship's Gyrocompass

Two SG Brown gyrocompass units are installed on the bridge. Ship heading was logged every second via a level A microprocessor.

Daily Processing

• Acquisition of gyro heading data from RVS files using the gyroexecO program.

Data Quality

The percentage of 'good' data acquired during a 24 hour period ranged from a minimum of 99. 1 % on JD 96 to a maximum of over 99.9% on JD 99.

5.3 Ashtech 3DF GPS Attitude Determination

The Ashtech 3DF GPS is a system comprising four satellite receiving antennae mounted on the boat deck and the roof of the bridge with a receiver unit in the bridge itself. Every second the Ashtech measures ship attitude (heading, pitch, roll) and these data are used in post-processing to correct ADCP current measurements for 'heading error'. This post-processing is necessary as the ADCP uses the less accurate but more continuous ship's gyro headings to resolve east and north components of current. With each attitude acquired are measures of the maximum measurement rms error and maximum baseline rms error which permit poorly determined attitudes to be flagged during processing.

Daily Processing:

- Acquisition of Ashtech data from RVS files using the ashexec0 program.
- Quality control of Ashtech data using ashexec 1.
- Averaging into 2 minute bins to be compatible with ADCP data and determination of the 'aghdg' parameter (the correction applied to gyro headings) using ashexec2.
- Plotting daily time series of a-ghdg and manually editing out any remaining outliers from the data using PLXYED and ashexec3.

Data Quality

The percentage of 'good' data acquired during a 24 hour period ranged from a minimum of 87.7% on JD 107 to a maximum of 98.3% on JD 103. Manual editing was required on JD's 103, 104, 105, 107 and 108 with a maximum of 9, 2 minute averaged data cycles being removed on JD 107. The largest gap in a-ghdg data was also on JD 107 and lasted approximately 2 hours.

5.4 Problems with Navigation Data

A power cut of approximately 30 minutes from 08:35 to 09:05 on JD 127 caused all navigation instruments to stop logging during that period. On the same day, the Ashtech stopped logging for 4 hours from 05:40 to 09:40, a loss of data initially unrelated to the power cut. It also stopped logging for 10 minutes at about 20:00 on JD 138.

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6 METEOROLOGICAL MEASUREMENTS

6.1 Aims

The primary goals of the surface meteorological and radiative flux measurements made on D233 were:

- i. To evaluate sources of error in the downwelling longwave flux as measured by an Eppley pyrgeometer using a circuit that allows the temperatures of various components of the pyrgeometer to be recorded.
- ii. To investigate the dependence of the corrected downwelling longwave on the amount of cloud cover, the air temperature and the humidity, and to develop a new parameterisation for this flux if existing ones prove insufficient. The large range of latitude, 20 - 63.5 °N, covered during the cruise provided an ideal opportunity for this investigation to be carried out under a wide variety of atmospheric conditions.

In addition, measurements of various meteorological variables were made with a range of sensors as standard. Finally, estimates of the surface wind stress were obtained by the inertial dissipation method using high frequency wind speed measurements made with a Research R2A sonic anemometer.

6.2 Sensors Deployed

Meteorological variables

Measurements from a combination of sensors mounted for this cruise alone and the standard RVS sensor suite were made during the cruise. Information from a total of 19 sensors giving the wind speed and direction, air and sea surface temperatures, atmospheric humidity and pressure, downwelling radiative fluxes and various component temperatures for one of the pyrgeometers was logged using the GrhoMet instrumentation system, details of these sensors are given in Table 6.1 and their deployment positions are shown schematically on Figure 6. 1. Prior to D232, modifications were made to the RVS sensor system such that data from the standard meteorological sensors is now recorded via the RVS Surfmet system which outputs data every 30 sec to the Level 'B' and every 5 sec via an RS232 serial link to the GrhoMet PC. GrhoMet separately acquires data from the cruise specific sensors at a 5 sec sampling rate from a new Rhopoint box mounted on the starboard rail of the foremast platform. The two data streams are merged by the GrhoMet PC every 5 sec and written to the level B.

Cloud observations

Observations of the total cloud amount and of the type and amount of low, medium and high altitude cloud were made at hourly intervals during daylight and typically three hourly intervals at night throughout the cruise using the Met. Office 'Cloud Types for Observers' guide as a reference. Over 600 observations were made in total covering a wide variety of cloud

Table 6.1 Variables and sensors logged by the GrhoMet system.

The variable names in the data files are shown [thus]. (RVS) indicates that the sensor is part of the standard ship's system; (SOC) that the instrument was added for the cruise.

Notes (1). Dry bulb reading noisy for significant fraction of cruise

(2). Wind speed persistently biased low by 10 - 15%

Figure 6.1. Plan view of the bow of the ship showing meteorological sensor positions for Discovery Cruise D233.

conditions, the resulting dataset will be used for an investigation of how the downwelling longwave flux may best be parameterised in terms of the cloud cover and other variables.

Wind stress

High frequency wind speed measurements were made with a Gill Instruments Solent Sonic Anemometer (R2 Asymmetric Model, serial no. 37) which was mounted on the starboard side of the foremast platform. The anemometer was operated in Mode 1 and the 21 Hz sampled data were logged using a PC system situated in the Plot that was also used for the GrhoMet output. Two programs were used to sample the data, standard sonic and Gill sonic the latter being a new program which provides additional parameters during the data processing cycle. In each case wind speed spectra and spectral levels are determined from the raw data. Standard sonic has a 10 minute sampling period starting each quarter hour. It derives a single PSD value in the range 2 - 4 Hz from the average of 12 data sections, each of which contains 1024 data points, taken within the sampling period. Gill sonic calculates PSD values in the sub-ranges 2 - 3 Hz, 3 - 4 Hz, 4 - 5 Hz and 5 - 6 Hz from each section. It was initially run with an 8 minute sampling period which was increased to 10 minutes on JD 142 to allow comparisons to be made with the standard sonic program.

6.3 Sensor Performance

Air temperature and humidity

Dry bulb air temperature measurements were obtained from the two psychrometers, the vector sensor and the RVS humidity sensor. An initial problem with the direction of the fan supply to the psychrometers led to them being biased high relative to the vector sensor by of order 0.5 °C for the first four days of the cruise. The fan supply was reversed on JD 118 and agreement between the three sensors to typically within 0. 1 °C was subsequently obtained with the exceptions due to noise noted below. The signal from the aft dry bulb sensor became increasingly noisy from JD 132 to 135, at which point the foremast connections were checked and sprayed with moisture repellent. No obvious problems were found but following the checks no further noise problems occurred until JD 138 and intermittently thereafter. The RVS sensor had an offset of about -0.4 °C with respect to the vector and the psychrometer values after the fan problem was corrected. Regarding the wet bulb temperatures, the aft psychrometer showed a positive bias, increasing with the amount of downwelling shortwave, of up to 0.2 °C with respect to the foreward sensor. Its cause remains uncertain ; there was no obvious effect of shortwave on the relative values of the psychrometer dry bulb measurements. Given the noise in the aft dry bulb values and the apparent bias in the wet bulb we suggest that the foreward sensor values be used in any subsequent analysis.

Radiative Fluxes-Longwave

Measurements of the downwelling longwave flux were obtained with two Eppley pyrgeometers mounted on top of the foremast. The first radiometer, No 27960, was operated in standard mode with output according to the manufacturers calibration; the second, No 31170, was fitted with a circuit, supplied by Dave Hosom of Woods Hole Oceanographic Institute, which allowed the dome and sensor temperatures and the thermopile voltage to be recorded. Given these parameters and pre-cruise laboratory calibrations for the effect of the domesensor temperature difference and shortwave leakage on the measured longwave flux a corrected longwave field was produced for 31170. The domesensor temperature difference was found to be a function of both the incident shortwave and the relative wind speed, typical values being 1.8 °K and 1.2 °K for a shortwave flux Of 1000 Wm^2 and relative wind speeds of 3 and 10 ms⁻¹ respectively. The magnitude of the required correction to the measured longwave for this effect was of order 10 Wm⁻². In post-cruise analysis we plan to develop an empirical correction for the dome-sensor temperature difference and assess the level of agreement of the longwave flux measured by the two instruments once it has been applied to 27960. A paper is being prepared on the results of the longwave study (Pascal and Josey, 1998).

Radiative Fluxes -Shortwave

Measurements of the shortwave flux were obtained with two RVS solarimeters mounted on the port and starboard sides of the foremast platform. Shadowing proved a problem as on previous cruises but in periods when the two sensors were clearly illuminated they were in good agreement e.g. to within 5 Wm⁻² for a downwelling flux of order 800 Wm⁻² on JD 122. At night, both sensors were typically within 2 Wm^{-2} of zero.

Wind Speed and Wind Stress

Wind speed measurements were made with two Solent Sonic anemometers (one Research R2A; one Windmaster) and an RVS cup anemometer. The RVS sensor was mounted on a pole projecting forward from the port side of the foremast platform with several other instruments in close proximity. The wind speeds that it recorded were typically biased low by 10- 15 % relative to those measured by the Windmaster Sonic. The Windmaster and Research Sonics agreed in the mean to within 0.2 in s^{-1} giving mean wind speeds of 8.03 and 8.20 in $s⁻¹$ respectively.

Output from the two sonic programs was compared for the period JD 1421445 - 1460915. Relative to the standard sonic output, Gill sonic gave mean wind speed values that were typically lower by 0.8% and PSD values higher by 5%. Generally both systems agreed well although the standard system was more prone to wayward data points particularly at low wind speeds; this being primarily due to vibration peaks in the spectrum affecting data in the 4 Hz region.

Preliminary determinations of the wind stress were carried out with the standard sonic output using only data obtained within 30° of the bow in order to avoid biases in the measured speeds arising from flow distortion by the ship. The following least squares fit (equation 6. 1) to the variation of the neutral drag coefficient with 10 in wind speed was found for wind speeds > 6 m s⁻¹,

$$
10^3 \, \text{C}_{\text{dn}} = 0.64 + 0.045 \, \text{u}_{10n} \tag{6.1}
$$

Sea Surface Temperature (SST).

Measurements of the bulk sea surface temperature were made with a trailing thermistor (soap) and the thermosalinograph (TSG). In addition the skin temperature was measured with the Scanning Infrared SST Radiometer (SISTeR) deployed by Tom Sheasby from the University of Leicester. The SISTeR measurements are covered in a separate section ; comparisons of all three sensors carried out as part of the SISTeR study showed that there was an intermittent slowly decaying offset in the SST as measured by the TSG remote sensor. The sensor was replaced on JD 134 at 1440 but the offset problem continued for the remainder of the cruise.

6.4. Summary of Measurements

A wide variety of atmospheric conditions were sampled as the cruise track took the ship from the tropics to the sub-Arctic. Summary time series for each of the measured variables are shown on Figure 6.2. During the first two weeks of the cruise, Trade wind conditions dominated with a steady flow of relatively warm, dry air from the North-East at typical speeds of $7-11 \text{ m s}^{-1}$. The winds slackened and veered to the south-west on JD 127 with the ship at latitude

38 °N. Several calm days followed, prior to the strongest winds of the cruise, in the range 18-20 m s⁻¹ on JD 130, caused by a low pressure system to the west of Portugal. A high pressure system centred on the UK ensured relatively calm conditions for the remainder of the leg to Iceland with increasing cloud cover and relative humidities. Along the section from Cape Verde to Iceland the air temperature dropped from 22 °C to 7.5 °C and the specific humidity ranged from 13.5 gkg⁻¹ to 5.5 gkg⁻¹. The winds increased again and shifted to the Northeast during the Rockall Section and survey of the Rockall Trough as a low pressure system developed over Scandinavia.

6.5 References

Pascal, R. W. and S. A. Josey (1998). Accurate radiometric measurement of the atmospheric longwave flux at the sea surface, J. Atmos. Oceanic Technol., in preparation.

Simon Josey and Robin Pascal

Figure 6.2. Summary plot of meteorological conditions experienced during the cruise. Time series show three hourly mean values of wind speed (speed), wind direction - from - (dirn), sea surface temperature (sst), atmospheric pressure (press), dry bulb temperature (psy2dry), specific humidity (QAIR), relative humidity (RH), downwelling longwave (Iwave1c) and downwelling shortwave (maxswvps).

7 SALINITY MEASUREMENTS

7.1 Salinity sampling

Salinity samples were drawn from each Niskin bottle plus a duplicate each from Niskins 1 and 5. The only exception to this was on the very shallow casts, where only one duplicate was taken (from bottle 1). Sample bottles used were the standard 200 ml glass bottles with disposable plastic inserts and screw caps.

7.2 Measurement

Two salinometers were installed in the constant temperature laboratory, (Guildline models 8400 and 8400A), but only the 8400A unit was used; the 8400 being carried as a backup. The salinometer tank temperature was set at 21 °C but to maintain a laboratory temperature of 20 °C degrees, the laboratory air conditioning unit was set at 19 °C.

The salinometer was standardised at the start of each crate of samples using batch P133 standard seawater (production date Nov '97) and salinity was calculated from the Guildline ratio using Microsoft Excel spreadsheet macros. Only 2 ampoules were found to be high in salinity, which was probably caused by imperfect sealing, allowing evaporation. Comparison of the CTD/bottle sample salinities showed that differences were better than 0.001.

The salinometer generally performed very well, except on 2 separate occasions when a reading was being taken the ratio display started counting down at approximately 0.00001 per second, and had dropped 0.00250 after 4 minutes. After the cell had been flushed and refilled, the display behaved normally and gave expected readings. No obvious reason could be found for this.

The only other problem encountered, was that the outlet tubing on the peristaltic pump came off on 2 occasions. In the first instance it was pushed back on to the outlet nipple, but it came off again after about 12 hours. This time the pump unit was replaced with the one fitted to the other salinometer. However this unit suddenly made the salinity readings go high. It was then noticed that the pump outlet tubing on this unit had cable ties fitted for extra security, but were missing from the original unit. The original pump was fined back on the salinometer with cable ties securing the tubes. The salinity readings then returned to normal and no further problems were experienced. It is suspected that some salt crystals may have been trapped in the spare pump, causing the salinity to go high when flushed through the cell.

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8 OXYGEN MEASUREMENTS

8.1 Sampling

Dissolved oxygen samples were drawn from each of the Niskin bottles following the collection of samples for CFC/halocarbon analysis. Between one and four duplicate samples were taken on each cast, from the deepest bottles. The samples were drawn through short pieces of silicon tubing into clear, precalibrated, wide necked glass bottles and were fixed immediately on deck with manganese chloride and alkaline iodide dispensed using precise repeat Anachem bottle top dispensers. Samples were shaken on deck for approximately half a minute, and if any bubbles were detected in the samples at this point, then a new sample was drawn. The samples were transferred to the constant temperature (CT) laboratory, and then shaken again thirty minutes after sampling and stored under water until analysed.

The temperature of the water in the Niskin bottles was measured using a hand held electronic thermometer probe. The temperature was used to calculate any temperature dependent changes in the sample bottle volumes.

8.2 Analysis

Samples were analysed in the constant temperature laboratory starting two hours after the collection of samples. The samples were acidified immediately prior to titration and stirred using a magnetic stirrer bar set at a constant spin. The Winkler whole bottle titration method with amperometric endpoint detection (Culberson 1987) was used with equipment supplied by Metrohm. The spin on the stir bar was occasionally disturbed by the movement of the ship and also by the uneven bases of the glass bottles, leading to less ineffective stirring of the sample and a longer titration time. This probably did not effect the accuracy of the endpoint detection. The Anachem dispensers were washed out with deionised water, each time the reagents were topped up, to avoid any problems caused by the corrosive nature of the reagent.

The normality of the thiosulphate titrant was checked against an in-house potassium iodate standard of 0.01 N at 20 °C at the beginning of each analytical run and incorporated into the calculations. A total of seven standards were used throughout the duration of the cruise. Blank measurements were also determined at the start of each run to account for the introduction of oxygen with the reagents and impurities in the manganese chloride, as described in the WOCE Manual of Operations and Methods (Culberson 1991). Thiosulphate standardisation was carried out by adding the iodate after the other reagents and following on directly from the blank measurements in the same flask, as on the cruises D227 and D230. The thiosulphate precision was consistent throughout the cruise for each batch used. Tests were also carried out on each batch of alkaline iodide used,

since some variability had been apparent on previous cruises when the iodide batch was changed.

The number of pairs of duplicate measurements taken during the cruise was 461. Duplicate differences > 1.0 µmol $I⁻¹$ accounted for 28.2% of these duplicate pairs and ignoring these high duplicate differences the mean (±SD) duplicate difference was 0.457 (\pm 0.282). The duplicate difference achieved was not related to any of the individual calibrated bottles and high duplicate differences seemed to occur at random.

8.3 Problems

Persistent bubbles in the tubing of the thiosulphate Titrino unit resulted in the replacement of some of the tubing at station 13480. The plastic dispenser was also replaced at station 13496. This seemed to solve the problem and the unit remained free of bubbles until the end of the cruise.

8.4 Acknowledgement

We would like to thank Russell Davidson, Simon Josey and Chris Wilson for their help in taking samples from the Niskin bottles.

8.5 References

Culberson, C. H. and S. Huang, 1987: Automated amperometric oxygen titration. Deep-Sea Research 34 875-880.

Culberson, C.H., 1991: WOCE Operations Manual (WHP Operations and Methods). WHPO 91/1 Woods Hole. 15pp

Elizabeth Rourke, Kate Day, Tom Sheasby.

9 NUTRIENT MEASUREMENTS

9.1 Sampling Procedures

Samples for the analysis of dissolved inorganic nutrients: dissolved silicon (also referred to as silicate and reported as $SiO₃$), nitrate and nitrite (referred to as nitrate or $NO₂+NO₃$) and phosphate($PO₄$), were collected after CFCs, oxygen, and $CO₂$ samples had been taken. All samples were collected into 30 ml "diluvial" sample cups, rinsed 3 times with sample before filling. These were then stored in a refrigerator (at 4 °C until analysed (between 1 and 12 hours after collection).

A total of 139 casts were sampled for nutrients during the cruise. Samples were transferred into individual 8 ml samples cups, mounted onto the sampler turntable and analysed in sequence. The nutrient analysis was performed using the SOC Chemlab AAII type AutoAnalyser coupled to a Digital-Analysis Microstream data capture and reduction system. The majority of sample was analysed in duplicate to ensure accuracy and increase precision.

9.2 Calibration

The primary calibration standards for dissolved silicon, nitrate and phosphate were prepared from sodium hexaflurosilicate, potassium nitrate, and potassium dihydrogen phosphate, respectively. These salts were dried at 110 °C for 2 hours, cooled and stored in a dessicator, then accurately weighed to 4 decimal places prior to the cruise. The exact weight was recorded aiming for nominal weight of 0.960 g, 0.510 g and 0.681 g for dissolved silicon, nitrate and phosphate respectively. When diluted using MQ water, in calibrated 500 ml. glass (or polyethylene for silicate) volumetric flasks these produced 10 mmol I^1 standard stock solutions. These were stored in the refrigerator to reduce deterioration of the solutions. Two standard stock solutions were required for each nutrient over the duration of the cruise, checked daily against OSI standards as described later.

Mixed working standards were made up once per day in 100 ml calibrated polyethylene volumetric flasks in artificial seawater ($@40g$ I⁻¹NaCl). The working standard concentrations, corrected for the weight of dried standard salt and calibrations of the 500 ml and 100 ml volumetric flasks are shown in Table 9. 1.

A set of working standards was run in duplicate on each analytical run to calibrate the analysis. The top standard was also run in duplicate at the start of each analytical run as it had been shown to increase the linearity of the standardisation (Holley, 1998).

9.2 Analysis

Silicon

Dissolved silicon analysis followed the standard AAII molybdate-ascorbic acid method with the addition of a 37 °C heating bath (Hydes, 1984). The colorimeter was fitted with a 50 mm. flow cell and a 660 nm filter. The gain was adjusted to 2.8 for a maximum response at 40 µmol $I⁻¹$.

Nitrate

Nitrate (and nitrite) analysis followed the standard AAII method using sulphanilamide and naphtylethylenediamine-dihydrochloride with a copperisedcadmium filled glass reduction column. A 15 mm flow cell and 540 nm filter was used with a gain setting of 2. 1, adjusted for concentrations of up to 40 μ mol I^{-1} . Nitrite standards equivalent in concentration to the third nitrate standard were prepared each day to test the efficiency of the column.

Phosphate

For phosphate analysis the standard AAII method was used (Hydes, 1984) which follows the method of Murphy and Riley (1962). A 50 mm flowcell and 880 mm filter were used and the gain set to 9 throughout the cruise, measuring concentrations of 0-2 μ mol I^{-1} .

There was a large amount of noise on this channel predominantly due to two reasons.

- Firstly, the photometer was very sensitive to light
- Secondly, it was sensitive to movement.

The light fitting above was removed and the entire photometer was covered with black sheeting, eliminating this problem. However when the ship rolled in rough weather the phosphate baseline noticeably shifted back and forth with the ship's roll. This resulted in an increase in error of peaks and is a problem that needs to be addressed for future cruises. It is of note that the photometer had not been safety tested since 9th August, 1996.

9.3 Operation and maintenance

Reagents for each of the nutrients analysed were made up as and when required from pre-weighed salts; some maintenance was also required. Position 38 on the rotating table occasionally was not sampled. This was temporarily eliminated by keeping the autostop switch off. The tubing on the peristaltic pump was fully replaced once a week throughout the cruise and all tubing was rinsed with dilute Decon solution. In addition the chart recorder had some loose connections (corresponding to the nitrate channel) which caused problems. This unit had also not been safety tested since 9th August, 1996.

9.4 Precision - Duplicate and quality control measurements

Samples were analysed in duplicate except for occasions where time was limited either due to problems (described above) or to large quantity of samples being collected.

Several quality control samples were also analysed on each run. Two quality control samples were made up from standard solutions supplied by OSI (prepared each day in plastic volumetric flasks using NaCl solution). The concentrations were adjusted to be equivalent to the 2nd and 4th working standard concentrations (so the QC material is referred to as QC2 and QC4 respectively). In addition a deep water sample was collected from the test station at \sim 3500 in. The deep water QC samples were decanted into clean rinsed plastic diluvial containers and stored in the cold store until required, using I per analytical run. Each QC sample was analysed in duplicate (except for where time was limited as described above), variations in the results are shown in Figures 9.1 - 9.3 (colours, indicate duplicates)

9.5 References

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10 HALOCARBONS MEASUREMENTS (inc CFC TRACERS)

There were two main aims to the halocarbon work on D233:

• the first was to collect a comprehensive CFC tracer data set to WOCE standards for CFC-11, CFC-12, CFC-113 and carbon tetrachloride in order to characterise the water masses of the region and make a study of their spreading, mixing and ventilation rates. Particular emphasis was placed on Labrador Sea Water, Mediterranean Water, waters of Southern Ocean origin (Antarctic Intermediate Water and Antarctic Bottom Water) and the circulation/recirculation patterns waters prevalent in the Rockall Trough.

Figure 9.1 Silicate QC Deep, QC2 and QC4.

Figure 9.2 Nitrate QC Deep, QC2 and QC4.

Figure 9.3 Phosphate QC Deep, QC2 and QC4.

• The second was to make measurements of as many halogenated compounds as practically possible in order to access the oceanic source/sink of compounds such as methyl bromide, methyl iodide, methyl chloride, methylene chloride, bromochloromethane and the anthropogenic CFC replacements (sink only).

10.1 Sample Collection

Samples were drawn from 10 1 Niskin bottles which had been checked for physical integrity and chemical cleanliness prior to the cruise; no contamination problems developed during the cruise. Samples were drawn first from the rosette, directly into 100 ml ground glass syringes and stored under a continuous flushing stream of surface seawater to keep gas tight. Occasionally 250 ml ground glass syringes were used to provide a larger sample for GC-MS analysis. Most samples were analysed within 12 hours of collection although the frequency of CTD stations sometimes led to a further delay of up to 12 hours, however there was no evidence of sample degradation when this occurred.

10.2 Analysis

Halocarbon analyses were carried out using a modified version of the GC-ECD system described in Boswell and Smythe-Wright (1996), with the same modifications as specified in Bacon (1998) for *RRS Discovery* cruise D230. The chromatography run time ranged from 38-41 minutes depending on the carrier gas flow. This enabled 16 compounds to be measured (up to and including carbon tetrachloride) after which time the chromogratographic run was terminated in order to achieve a balance between number of compounds measured and sample throughput. Measurements were made on 124 out of a total of 139 stations, approximately half to full depth and half to 200 m (to focus entirely on biogenic gases). Occasionally, were station frequency reduced the number of samples that could logistically be handled, it was necessary to focus on analysing samples taken from bottle depths which corresponded to bottom to mid waters to achieve the CFC tracer aims of the cruise.

10.3 Problems

The main problem occurred on JD 132 during the analysis of samples from station 13468 when the joint connecting the 'B' trap to the extraction board became loose allowing water to pass into the precolumn. Despite immediately action, water percolated through the column to the detector causing irreparable damage which resulted in the entire 'B' channel (column, precolumn and detector) being replaced. Because of the water ingress three valves later became blocked and had to be cleared. As a result of these problems some stations were incompletely analysed.

10.4 GC-MS

When time permitted a newly purchased HP GC-MS system was used to analyse surface samples. This new system had been set up in the laboratory prior to the cruise using gas samples but had not been previously tested for seawater. First results with regard to achieving the detection limits of the GC-ECD system were very encouraging, but due to pressure on personnel the system was not used routinely for the analysis of samples. It did however prove very useful in identifying a number of peaks observed with the GC-ECD system. (Further fine tuning of the GC-MS methodology since the cruise has resulted in the system being adopted for future work at sea).

10.5 Automated GC-MS trials

A fully automated GC-MS system for continuous sea water measurement was tested during the cruise but due to pressure of other work and problems with the control software only limited success was achieved with its operation and no data collected.

10.6 Calibration and Precision

CFC tracers were calibrated using a 20 point calibration from a gas standard prepared by the NOAA CMDL laboratory which had been cross calibrated to the SIO 1993 scale. Biogenic gases were calibrated using similar techniques but with gases supplied by a Kintek gas standards generator. Duplicate measurements were made at a number of stations and showed precision and accuracy of CFC tracers to be within WOCE requirements: less than 1% or $+0.005$ pmol kg⁻¹ for CFC-11 and CFC-12 at low levels.

10.7 Acknowledgements

We would like to thank Russell Davidson, Ben Schazmann and Alex Megann for their much appreciated help with the collection of CFC samples.

10.8 References

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Cristina Peckett, Iris Soler-Aristigui, Claudia Dimmer, Denise Smythe-Wright

11 CARBON DIOXIDE MEASUREMENTS

The aim of the $CO₂$ work was to make full depth measurements of pH, and alkalinity in order to calculate the total inorganic carbon present in the ocean at the time of the cruise and to make underway measurements of the partial pressure of $CO₂ (PCO₂)$ in surface seawater from the ship's non-toxic supply and air. Such studies are becoming increasingly important in detecting the changes in the carbonate system in the oceans as a result of the increases of $CO₂$ in the atmosphere due to the burning of fossil fuels. The components of the carbonate system: pH, alkalinity, partial pressure of $CO₂$ (PCO₂) and total inorganic carbon are interrelated by the thermodynamics of the carbonate system in seawater and the buffers used to determine the pH. By measuring two of these variables it is possible to calculate the other two by means of a set of equations deduced from thermodynamic equilibrium. During the CHAOS cruise, samples were collected at every second station, and analysed for pH and alkalinity; $PCO₂$ calculated from this data was compared with the continuous surface measurements from the non-toxic supply. In addition, the continuous measurements of $PCO₂$ in air and surface sea samples were combined to estimate the $CO₂$ gradient across the sea surface and together with the wind speed, piston velocity and solubility of $CO₂$ used to calculate the $CO₂$ flux between ocean and atmosphere.

11.1 pH measurements

Sample Collection

pH samples were collected directly into 100 ml glass bottles which were kept in the dark until analysed. A total of 62 stations were sampled following behind the collection of CFC/halocarbons and oxygen samples.

Analysis

pH measurements were made using a triple-wavelength spectrophotometric technique (Byrne, 1987). This required measuring the sample adsorption after the dye-solution addition, at the acid indicator species wavelength (434 nm), at the basic indicator species wavelength (578 nm) and at a wavelength with no adsorption from any of the two referred species (730 nm) to correct the base line. The indicator used was Aldrich m-cresol purple sodium salt $(C_{21}H_{17}O_5Na)$ prepared in seawater to avoid changes in the sample salinity. Prior to analysis all samples were stabilised in a thermostatic bath to 25 °C; this sample temperature was monitored with a platinum resistance Pt-probe. The samples were then individually pumped into the flow cell of a Hewlett-Packard -array spectrophotometer via a mixing channel; the temperature of the cell holder being controlled by a Peltier system to 25 °C. A blank reading was taken before the indicator solution was added to the mixing channel and the two solution mixed. During the analysis the sample flow was stopped three times and three different measurements of pH were made at three different indicator concentrations using equation 11.1 (Clayton and Byrne, 1993):

 pH_t =1245.69/T+3.8275+2.11 x 10-3(35-s)+ $log[(R-0.0069) / (2.222-0.133R)]$ 11.1

To eliminate the pH indicator perturbation in the sample a linear fit regression was made to the three pH measurements to give a pH value at zero indicator concentration. This result is the hydrogen ion concentration in total scale.

11.2 pC02 measurements

Sample Collection

 $pC0₂$ samples were obtained continuously from a depth 2-3 m though the ship's non toxic seawater supply. Seawater was pumped directly into a 'debubbling' tank and then fed at a rate of 4 1 min⁻¹ to a 'shower head' type equilibrator.

Analysis

The none dried gas phase was sampled from this equilibrator and passed into an IR CO2/H20 analyzer model LI-6262. Simultaneously an air sample was taken and passed via a soda lime/Mg(ClO)₂ filter to clean it of $CO₂$ and H₂O into a different channel of the analyser to give a zero $CO₂/H₂O$ IR. spectra. The result is a continuous estimate of the $CO₂$ mole fraction in the surface seawater in matmospheres of $CO₂$ (when referenced to atmospheric pressure). Data from the ship's global position system was used to locate and date all the $CO₂$ data.

Calibration and standardisation

Every 60 minutes marine air was pumped from an intake mounted clear of the ship's superstructure to minimize the possible contamination from the ship, into the analyzer to obtain the $CO₂$ mole fraction in the air. A standard of $CO₂$ made up in synthetic air was also run every 6 hours to detect changes in the zero channel value.

Problems

Unfortunately severe problems with the data transmission card prevented the continuous logging of the data file and so it was necessary to write down position, time and $pCO₂$ data every 10 minutes or less during the entire cruise.

Luis Laglera-Baquer and Maria Somoza-Rodriguez

11.3 Alkalinity Measurements

Sample Collection

Seawater samples for alkalinity measurement were collected from all depths at a total of 62 stations following behind those for CFCs, oxygen and pH. The samples were drawn directly into 300 ml plastic bottles and stored in the dark until analysed either the same day or one day later.

Analysis

Alkalinity was measured using an automatic potentiometric Titrino Metrohm, titrator fitted with a Metrohm Combination glass electrode. Potentiometric titrations were carried out with hydrochloric acid to a final pH of 4.44 (Perez and Fraga, 1987b). The hydrochloric acid was made up from an ampoule of Fixanal HCL to give a molarity of 0.5 M when dissolved in 5 1 of milli-Q water (the exact molarity was established later in the laboratory).

The electrodes were standardised with three buffers according to the following sequence:

- i calibration of the combined electrode with NBS buffers of pH 7.413;
- ii checking of the electrode response with a pH 4.008 NBS buffer solution
- iii adaptation of the electrode to the strong ionic strength of seawater by means of a pH 4.4 seawater buffer containing 4.0846 g of $C_2H_5KO_4$ and 1.52568 g of $B_4O_7Na_2H_2O$ in 1 Kg of CO_2 - free seawater.

At each station, samples of $CO₂$ reference material for oceanic measurements, batch 42 (CRM) and of a seawater substandard (SSS) and were analysed at the beginning and end of each series of samples. The SSS is a quasy-steady surface de-aerated 25 1 seawater sample taken from the non-toxic supply and stored in the dark. The variations in the measured SSS and CRM alkalinity during the cruise will be used to correct the electrode deviations over time and so refer the alkalinity results to the same line base. All concentrations are calculated in mmol kg^{-1}

Iris S. Aristegui and Maria J. R. Somoza.

11.4 References

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12 PHYTOPLANKTON AND PIGMENT STUDIES

There is some evidence to suggest that phytoplankton are natural producers of halocarbons which are involved in ozone depletion. The work carried on the cruise forms part of the SOC SASHES project, investigating the sources and sinks of halogenated environmental substances and was carried out to compliment the seawater and atmospheric halocarbon studies. The primary aim was to collect biological samples during the spring phytoplankton bloom period for algal pigment and speciation studies back at SOC and to make shipboard measurements of chlorophyll.

12.1 Pigment studies

Sample collection

Chlorophyll and HPLC sampling focused on the surface layer with the top 6 Niskin bottles from the CTD (usually fired at around 120,75, 50, 25, 10 and 5 m) being sampled at 117 stations. Samples were collected in 5 1 carboys which were rinsed in the sample prior to being filled.

For HPLC analysis, water samples (2 1) and duplicates were filtered through 25 mm Whatman GF/F filters using a specially developed positive pressure filtration unit TOPPFUN. The filter papers were immediately placed in cryovials and stored in liquid nitrogen for subsequent HPLC algal pigment analysis at SOC.

For chlorophyll analysis, two 100 ml aliquots were filtered through 25 mm. Whatman GF/F filters at low pressure. The papers were then placed in glass vials containing 10 ml of 90% acetone and immediately stored in the dark at -5 °C for 24 hr in order to extract the chlorophyll.

Chlorophyll analysis

Samples were warmed to room temperature before the fluorescence was measured using a Turner Designs Fluorometer. To measure the phaeopigments in the sample, 4 drops of 10% hydrochloric acid were added and the fluorescence remeasured. Chlorophyll standard solutions (Sigma) covering the expected range of samples were used for calibration of the fluorometer and were made up and measured along with blanks for each set of samples. Throughout the cruise three primary standards were used to make up the calibration standards. The chlorophyll concentration of these were calculated from the absorbance measured before and after acidification at 665 nm. and 750 nm in a Camspec UV-visible spectrophotometer. Chlorophyll and phaeopigment concentrations were calculated using equations from the JGOFS protocols (1994) in Microsoft Excel.

Chlorophyll concentrations ranged from 0.001 to 8.72 mg $m⁻³$; the highest concentrations being found in the sub-polar gyre, around the Iceland coast where there was evidence of the spring bloom taking place. High concentrations were also seen off the coast of Africa due to the upwelling event. The chlorophyll maximum shifted from around 50 to 100 m in the subtropical gyre to between the surface and 20 m in the sub-polar gyre.

Problems

The main area of inaccuracy was due to filtering leakages on the filtering bottles and this problem will be addressed at SOC.

12.3 Phytoplankton studies

Sample collection

Phytoplankton samples for microscope speciation studies at SOC were taken at the surface, the chlorophyll maximum and a sample in between these two depths. Two 100 ml amber glass bottles were filled for each depth and preservative agents (Lugol's iodine and Formalin) added to each. In addition, samples were collected at these depths and also at around 90 m for picoplankton identification and enumeration. A total of 702 phytoplankton and 468 picoplankton samples were taken from 117 stations.

Russell Davidson and Ben Schazmann

12.4 Culture Studies

Previous work has shown that phytoplankton species differ in the halocarbons they produce, and indeed many do not seem to give off any volatile halogenated compounds at all. The aim this work was to isolate the most common species of phytoplankton in the surface waters when concentrations of either chlorophyll and/or halocarbons such as methyl bromide, methyl iodide and methyl chloride were high, with the assumption that it is those species that are primarily responsible for the high halocarbon levels seen. These species will subsequently be grown and cultured back in the lab at SOC in a specially adapted gas-tight culture flask and the headspace gas sampled and analysed for halocarbons using the GC-ECD.

Sample collection Surface water samples of approximately 15 1 were collected whilst on station using the bucketover-the-side method and filtered through a 20 µm nylon mesh to concentrate the phytoplankton into a smaller volume of water.

At a few stations seawater from the chlorophyll maximum was collected by firing an extra bottle on the CTD rosette. Small sterile Petri dishes of seawater were examined under a Zeiss compound microscope at x 100 and individual cells of the most prolific species picked up into sterile capillary pipettes (pulled from Pasteur pipettes using a Bunsen flame). Cells were isolated into sterile polyethylene tubes containing 1 ml artificial seawater media and placed in a Mercia Scientific illuminated incubator at 15 °C on a 16 hour light: 8 hour dark cycle. Filtered seawater was used in later isolations.

Due to time constraints for this work only stations occupied in the late afternoon could be sampled. Water samples were taken from 34 stations and isolates collected from 14 of them, with a total of 122 isolates taken.

Cristina Peckett

12.5 References

JGOFS, 1994. Protocols for the JGOFS. Intergovernmental Oceanographic Commission Manual and Guides 29 170 pp

13 DISSOLVED ORGANIC NITROGEN

Samples were collected along the 20 °W section for dissolved organic nitrogen measurement on a ship of opportunity basis as part of an SOC study of dissolved organic nitrogen in the North Atlantic. Samples were drawn directly into 100 ml acid washed plastic bottles and stored frozen for subsequent analysis at SOC.

14 ATMOSPHERIC GAS MEASUREMENTS

Production of halocarbons by the chemical industry is now restricted under terms laid out in the Montreal Protocol and subsequent revisions. Controlled substances include CFCs, halons, carbon tetrachloride, methyl chloroform, HCFCs, HBFCs and methyl bromide. Long term monitoring of all such species is therefore important to verify the expected decrease in the atmospheric halogen burden, and to assess the environmental impact of the new substitute compounds.

There are also a variety of halocarbons known to be produced biogenically, including methyl chloride, methyl iodide, bromoform, dibromomethane, chloroform and methyl bromide. These species provide a significant contribution to the total atmospheric halogen load and are synthesised predominantly by oceanic biota, fungi, or released during biomass burning. Detailed information about the sources, sinks, and seasonal and annual cycles for many of these naturally occurring halocarbons is sparse, and high frequency, high precision measurements are needed from a range of biospheres to quantify their global atmospheric budgets.

14.1 Analysis

The fully automated instrumentation as described by Bassford (1998) consisting of a novel twin ECD gas chromatograph (HP 6890) with sample enriching Adsorption-Desorption System (ADS) (Simmonds, 1995) enabled halocarbon concentrations at pptv levels to be determined at hourly intervals. The effluent from the first electron capture detector (ECD) passes into the second ECD which has enhanced sensitivity due to oxygen doping of the detector make-up gas. Such a unique serial detection system was designed to be extremely sensitive for determination of both strong and weakly electron capturing species. Strongly electronegative compounds efficiently attach electrons during passage through the first detector and produce an attenuated

response in the second oxygen doped detector. This results in a decrease in peak width, and consequently the potential for an increase in resolution for other less responsive compounds. The procedure allows precise quantification of a suite of 27 halocarbons, including compounds such as $CH₃Cl$ and $CH₃Br$, which are poorly detected by normal ECDs.

The system performed routine analysis of air and standard samples in a continuous three hour cycle (two air runs followed by a standard analysis).

14.2 Sample collection

The air sample was obtained using a length of 1/4 copper tubing from the deck lab to the top of the foremast, through which air was pumped for 10 minutes before a 200 ml sample was taken.

14.3 Standardisation and calibration

The bracketing of air runs by standards enabled quantification of the atmospheric measurements and allowed for any drift in sensitivity. The working standard containing halocarbons at near ambient concentrations was obtained from a gravimetrically prepared calibration standard containing 16 atmospheric halocarbons present at ppm concentrations with a stated accuracy of ± 1 % (Linde Gases, UK). The final calibration standard will be compared with absolute calibration standards maintained by the Scripps Institute and NOAA in the USA, and the standard used to determine the concentration of CFCs in the water on this cruise.

For those compounds which are known or suspected to be unstable in a gaseous mixture at low concentrations, such as methyl iodide, atmospheric mixing ratios are calculated retrospectively using C_2Cl_4 (PCE) as a surrogate standard. A liquid standard is prepared by performing a volumetric (verified gravimetrically) dilution of either an EPA calibration mixture (Supelco EPA 624) or pure components into HPLC grade heptane. The standard is then either injected into an evacuated 3.5 1 elecropolished stainless steel flask and pressurised to the required concentration using ultra high purity zero air (Air Products Ltd.), or injected directly on column through the purged packed injection port. Assuming the chromatographic peak height (H) is proportional to concentration (C) of an uncalibrated compound in a sample, the relationship between compound x andC₂Cl₄ (PCE) can be expressed in terms of relative response ratios (13.1 and 13.2).

> $\text{Hs}_x = \text{k}_x \cdot \text{C}_x$ $\text{H}_{c2c|4} = \text{k}_{c2c|4} \cdot \text{C}_{c2c|4}$ 13.1 $k_x = H_x \cdot C_{C2C14}$ K = ------ ------------ 13.2 k_{C2C14} \bullet C_x

To assess system precision, each standard run was compared with standard runs before and after, therefore correcting for any drift in detector sensitivity. The standard ratio was calculated by dividing each run by the mean of its bracketed standards.

14.4 Problems

Much of the deviation observed on the cruise was due to the variations in laboratory temperature, particularly in the tropics where the daytime lab temperature often reached 30 °C. As sample trapping occurs at room temperature, high temperatures tend to lead to a slight decrease in trapping efficiency. The amount of water reaching the detectors through the system also affected the detector sensitivity.

The high laboratory temperature at the start of the cruise also made it necessary to change the GC temperature programme to a run start temperature of 35 $^{\circ}$ C instead of 30 °C as previously used. However, the higher start temperature still gave satisfactory peak separation for the early eluting compounds.

Further problems encountered with the utilisation of the instrumentation in a shipboard environment were mainly associated with the removal of water from the air sample. Initially a three stage drying system was planned, comprising an ice trap (which removes water through condensation), a Nafion dryer (which removes water through a membrane due to a counter flow of dry nitrogen) and a potassium carbonate drying agent trap. However, after initial standard runs through the system doubts were expressed about the integrity of an air or standard sample having passed through the drying agent. Both contamination and removal of halocarbons by the potassium carbonate appeared to be a problem. Thereafter, only the ice trap and Nafion dryer were used. The ice trap design successfully utilised in previous land-based field campaigns consisted of 1/16" tubing immersed in an ice bath, however with the volume of water collected in the marine environment, ice blockages became a problem with this trap and a trap comprising 1/4" tubing was utilised with twice daily drainage of water. The

length of 1/4" coiled tubing had to be extended by Iceland in order to cope with the increased volume of water to be trapped out during foggy weather. Additional minor problems involved two misaligned valves which temporarily prevented air flow through the system, and three crashes of the HP Chemstation software which runs the gas chromatograph and is responsible for data collection, resulting in two nights without data acquisition. Frequent system leak checking was necessary as the motion of the ship loosened fittings particularly into valves.

The data obtained will allow comparison with atmospheric data acquired on campaigns at Mace Head Atmospheric Research Station, Ireland and Ny-Ålesund, Spitzbergen. Concentrations monitored will be correlated with local meteorological data recorded on board the ship, wind trajectories, and the surface water halocarbon concentrations. The data will help to determine the extent of global tropospheric mixing of the anthropogenic halocarbons and to compare global source strengths of the naturally produced compounds.

14.5 References

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Simmonds P.G. O'Doherty SJ, Nickless G, Sturrock G.A, Swaby R, Knight P, Ricketts J, Woffendin G, Smith R., 1995. Anal. Chem. 34, 717-723. Claudia Dimmer.

15 SISTeR INSTRUMENT

The Scanning Infra-red Sea-surface Temperature Radiometer (SISTeR) is a thermal infra-red radiometer designed and built by Dr. Tim Nightingale at the Rutherford Appleton Laboratory (RAL) in Didcot, Oxford. It weighs approximately 20 Kg and is roughly 30 x 30 x 60 cm. The instrument was designed for the validation of the 2nd Along Track Scanning Radiometer (ATSR-2) instrument on board ERS-2. The infra-red filter used during the cruise is centred on 10.8 µm. The radiometer can be programmed to look forward at any given angles from 0° (nadir) to 180° (zenith), and at its two internal black-bodies.

15.1 Aims

The data collected during this cruise will be mainly used in studying the so-called 'skin-effect' by comparing the radiometric 'skin' sea temperature with the 0 cm bulk sea temperature from the 'soap' instrument. This measured 'skin-effect' and other meteorological data will then be used to test various models of this effect. Also using these data the effect of validating satellite radiometers (which measure the skin temperature) with bulk temperature will be investigated. A further aim is the validation of the ATSR-2 instrument by comparing coincident radiometric sea temperatures measured from the ship to those measured by the satellite.

15.2 Instrument Deployment

The instrument was mounted on the bow of the *RRS Discovery* on a 10 mm. aluminium plate bolted on through 6 holes drilled on previous cruises. Cables were made to connect the instrument through the ship's loom to a laptop in the main lab using the junction box on the starboard side of the bow. It was mounted such that it was looking at an angle of 45° to starboard to avoid looking at the ship's wake or shadow. SISTeR was programmed to look at the sea at 30° (from nadir), then at three sky angles of 120°, 150° and 170° respectively. It then looked at its two on board black-bodies (one heated) for calibration and the measurement cycle repeated.

A second mount for SISTeR was built and installed on the port side of the foremast, using the junction box on the starboard side of the mast. Due to the need to cover the instrument during bad weather, it was decided that the bow mount was more suitable as access to the foremast is restricted during bad weather.

15.3 Preliminary Results

The instrument was deployed for most of the cruise and performed well. Additionally two calibration runs, using an external black-body source, were performed at the start and half way through the cruise, with a third planned to be done at the end. From the first calibration the instrument had an accuracy of better that 0.05 °K and a peak to peak noise of 0.1 °K as expected (see Figure 15 1).

Halfway through the cruise the accuracy was still 0.05 but the noise had increased to 0.2 °K peak to peak as the mirror degraded due to salt corrosion etc. There was one clear day coincident with an ERS-2 overpass that could result in a validation point and one partially cloudy day that may also yield a validation.

Thomas Sheasby

Figure 15.1 Graph showing a detail of the first SISTeR calibration. The SISTeR data are the dots, the actual temperature the line.

16 THERMOSALINOGRAPH MEASUREMENTS

Surface temperature and salinity were measured continuously throughout the cruise using a Falmouth Scientific Inc (FSI) shipboard thermosalinograph (TSG). The TSG comprises two FSI sensor modules, an Ocean Conductivity Module (OCM) and an Ocean Temperature Module (OTM), both fitted within the same laboratory housing. Sea surface temperature is measured by a second OTM situated on the suction side of the non-toxic supply in the forward hold. The nontoxic intake is 5 m below the sea surface. Data from the OCM and the OTM modules are passed to a PC, which imitates the traditional level A system, passing it to level B at 30 second intervals.

The temperature modules are installed pre-calibrated to a laboratory standard and laboratory calibration data are used to obtain four polynomial coefficients. A similar procedure is employed for the conductivity module. Salinity samples were drawn from the non-toxic supply at approximately four-hourly intervals for calibration of computed TSG salinity. These samples were then analysed on a Guildline 8400A salinometer in the usual way. The four hourly bottle salinities from the non-toxic supply are used as true salinity from which to calculate an offset to be applied to the TSG salinities. TSG salinity is usually calculated from the measured conductivity (cond) and temperature at the housing located in the

water bottle annexe (htemp). The temperature of the surface water is measured by the remote or marine sensor (rtemp).

16. 1 Daily data processing

- Acquisition of raw TSG data (htemp, rtemp, cond) from level A and conversion to level C PSTAR format (executable: tsgexecO).
- Averaging of raw TSG data over a basis of 2 minutes and merging with navigation data from the RVS Bestnav file (tsgexec 1).

After analysis, bottle salinity data was recorded in Excel and saved as a tabdelimited text file, which is ftp'ed from a Mac, converting the data to PSTAR format and time is converted to seconds (tsg.exec, tsgexec2).

16.2 Calibration and validation

Calibration was initiated by merging the bottle file (tsg233.samples) and TSG file (tsg233) on time using PSTAR. The differences (bottle salinities - TSG salinities) were calculated and 3 outlying data points were removed from outside the range [-0.5, 0.5] psu. The differences were plotted against bottle salinity, conductivity and distance run. The most linear scatter was the plot of difference against bottle salinity, increasing with increasing salinity. A quadratic calibration was then applied to the TSG data (PEXEC : plreg2) and the calibrated data was compared with the bottle salinities to produce a mean difference to 4 decimal places of - 0.0629 (s.d.=0.3770). After the removal of the 3 rogue data points, the new statistics were mean=0.0000 psu (s.d.=0.0310).

It must be noted that bottle salinities after JD 144 (24th May) were not included in the calibration, leaving 93 bottle samples for the calibration of the 2 minute TSG data set.

Thanks to Steve Alderson for his help with calibration.

Penny Holliday and Chris Wilson

17 EXPENDABLE BATHYTHERMOGRAPH MEASUREMENTS

A total of 35 Expendable Bathythermographs (XBTs) were deployed. These were kindly provided by the Hydrographic Office (MoD) in Taunton on the condition that a copy of the data would be returned to them after the cruise for incorporation into their database. In 0, 36 probes were supplied, being one box (12 probes) of T5s (depth rated to 1830 m) and two boxes (24 probes) of T7s (depth rated to 780 in). It was found to be necessary to slow the ship speed to approximately 6 kts, to deploy the T5s, although the T7s could be deployed at full speed (11- 12 kts).

One probe was deployed as a trial of the system on the preceding cruise (D232), and one probe failed to record to the data disk for an unknown reason. Consequently, 34 probes were successfully deployed (11 T5s and 23 T7s), representing a high degree of reliability (for example, on previous cruises it has often been the case that some 10% of probes have failed). The probes were deployed from the aft port quarter of the ship and this is therefore clearly a good place for such deployments, and for avoiding contacts between the wire and the ship's hull. The data were transferred to the RVS and PSTAR systems via floppy disk. Appendix B gives information on the XBT stations.

The only problem concerned the transmission of the data to satellite via the GOES system. The GOES buffer became full after the first four XBT drops, and the system then failed to upload the data to the satellite at the synoptic hours, so that no more XBTs could be sent to the buffer. This problem has been encountered on previous cruises. Although this was investigated on the present cruise, no solution could be found. This will be looked at further by the technical staff after the ship has returned to port.

The XBTs were deployed during the survey of the Rockall Trough area (between 53-58 °N, 9-16 °W) and gave useful additional data to provide increased resolution between the CTD stations, and to fill in sections between the ends of the CTD lines. An example is shown in Figure 17. 1. As well as revealing the mixed layer structure in the upper ocean (at 55° 58'N, 10° 30'W), this figure also indicates the detailed nature of the data coverage obtained. The data from the 34 successful drops will be sent to the Hydrographic Office as required.

Adrian New

Figure 17.1. XBT profile from Station 13

18 PRECISION ECHOSOUNDER

The Simrad EA500 Hydrographic Echosounder was used in bottom detection mode throughout the cruise. Depth values were passed via an RVS Level A interface to the Level C system for processing, with a nominal transducer depth of 11.5 m used. A visual display of the return signal was displayed in the Simrad VDU. Hardcopy output was produced on a colour inkjet printer. The amount of cable submerged whilst on station was approximately 11.5 m, and while steaming the echosounder was 2 m shallower. So during steaming the measured depth is 2 m deeper than the real depth.

Raw data were corrected for the speed of sound using Carter Tables (RVS Level C stream prodep) and transferred into the pstar format (executable: depO). Data quality was consistently poor while steaming, but improved on station. Editing consisted of the removal of major spikes (plxyed), merging with daily GPS navigation (dep I) and averaging to 10 minute intervals (dep2) to smooth the multitude of small spikes which remained after the manual de-spiking stages. It should be noted that the quality of the resulting data files is somewhat dubious. Table 18.1 shows a comparison of the actual depth (as measured by the CTD pressure and altimeter with echo-sounder depth).

The echosounder data suffered over steep topography and large spikes were seen in the raw data. At times, it was difficult to separate noise from data, in which cases linear interpolation was used to fill gaps produced by removal of such data. The echosounder underestimated depth in regions of steep topography, but, apart from that and a few occasions on which there was inexplicable strange behaviour, the edited bathymetry compared quite well to CTD pressure-derived plus altimeter depth on station.

The mean difference (CTD minus echosounder) for all points is -55.15 m (s.d. 341.97). Excluding all points with absolute difference greater than 38 m, the mean difference is -2.95 m (s.d. 8.87, N=120).

Chris Wilson and Penny Holliday

Table 18.1 Comparison of actual depth with echo-sounder depth on station. Max press is maximum pressure (dbar) measured by the CTD, Max depth is max press converted to depth (metres), Alt is altimeter height off bottom at closest approach (metres), Est depth is max depth plus Alt (metres), PES depth is depth measured by echosounder, corrected for sound speed variation via Carter's Tables (metres), and Diff is Est depth minus PES depth (metres).

19 SCIENTIFIC INSTRUMENTATION

19.1 Surfmet

The Surfmet system, which combines the old Met and TSG systems ran continuously for the duration of the cruise with data logged to level B and also sent to the OTD Met system via a serial link.

The remote temperature sensor measuring incoming non-toxic water temperature was suspected of jumping and drifting. This was replaced with a spare but this too was found to jump at certain times. This may be attributable to the physical properties of the non-toxic system which may cause some heat generation/loss whilst on/off station. It was not always apparent though and requires further observation.

Prior to cruise D232 a new non-toxic pipe system was installed. This is plastic coated piping and there is a direct feed to the TSG flow-through system. The old header tank is now replaced by a vortex debubbler which operates at 40-50 1 $min⁻¹$. with small volume, thus reducing lag time. A flow-through transmissometer and fluorometer are fed from the same supply as the TSG.

The output from the TSG was modified to provide an output to the $CO₂$ measuring equipment, although flow to the TSG was reduced it appears to have had no detrimental effect.

The windvane of the Met system is oriented so that zero degrees is to Port. For this cruise however, the crossarm which supports it and the anemometer was rotated so that zero degrees was forward.

19.2 ADCP

The previous cruise showed that although one of the transducers four beams was defective, the ADCP could still operate using three beams. At first the data appeared to be good but halfway into the cruise, the defective third beam appeared to be producing some bad signals. This meant that data signals of bins deeper than 200 m were corrupted. The third beam signals were then grounded at the receiver board in the deck unit and the problem was resolved. Data down to 400 m then appeared to be good and matched closely with the LADCP which was being used on the cruise.

19.3 EchoSounder

During the early part of the cruise the echosounder suffered from considerable noise. This meant that there were a lot of drop outs and false depths given on the digital output, although it was still possible to see what the depth was from the scrolling display. About two weeks into the cruise this noise seemed to disappear but was replaced by weak signals, which also produces a lot of depth errors. This problem was less apparent in depths less than 2500 m where the soundings were consistently good. The problem appeared to be with the transmission from the deck unit but since the latter part of the cruise was shallow no further investigations were carried out.

19.4 SBWR

The system was reinstalled prior to this cruise after calibration and fitting of valves to the inlets. A fault was found with the Port Pressure transducer but this was eventually traced to a broken wire in the signal circuit. The SBWR ran continuously throughout the cruise with a change of sampling parameters midway through in order to optimise the statistical analysis.

19.5 XBT

The XBT system was used to deploy about 35 probes, including T5s and T7s in the latter part of the cruise. The launching and data collection worked fine but the GOES transmitter buffer was full and didn't empty at the scheduled transmission time.

Dave Jolly

20 SCIENTIFIC ENGINEERING

Cruise 233 consisted of a 139 CTD deployments through the starboard gantry, using the 20 ton Cobra winch system and the 10 ton Cobra winch system. Also in use were the Non toxic systems and Milii pore water plant. A few minor problems occurred during the cruise but none led to any major loss of equipment or scientific down time.

20.1 Starboard Gantry

The gantry worked well and caused no problems throughout the cruise.

20.2 20 ton Cobra winch system

This system was used with the deep tow electrical conducting wire for the deepest casts. There were no problems with this system after the initial setting up of the back tension loads on the storage drum. Trials were undertaken by RVS technicians to try to determine an intermittent fault with one of the boost pumps, however this did not interfere with the scientific cruise programme.

20.3 10 ton Cobra winch system

This system was used for the majority of the casts and in general worked well. There were, however, a few small problems.

Winch spooling

The recovery of the wire had to be slowed on a few occasions to help to prevent wire distortion. This problem seemed to cure itself after a few deep casts and there were no more problems encountered.

Diverter sheave bearing

One of the inboard sheaves bearings collapsed and needed repair. These repairs were undertaken by the RVS technicians. A new bearing was turned on the lathe, fitted, and the unit reassembled. The sheave gave no more problems.

Retermination of the CTD wire

An electrical fault on the termination was found. The wire was cropped at 135 m and reterminated. After being load tested the wire was put into service and gave no more problems.

20.4 Non toxic

A few leaks followed the refit modifications but no serious problems occurred.

20.5 Milii Q water plant

The system was serviced by RVS technicians and a circuit board replaced, no major problems were encountered.

Chris Rymer, Tony Poole and Rhys Roberts

APPENDIX A

CHAOS CTD STATION INFORMATION

The following table gives information for all CTD stations. The data headings are as follows

Comments

APPENDIX A (continued)

APPENDIX B

CHAOS XBT STATION INFORMATION

The following table gives information for all XBT stations. The data headings are as follows

Stn nbr: station number Date: date format is mmddyy throughout Day: Julian Day
Time: format is hh format is hhmm throughout Lat, Long: positions corresponding to the above in deg min Speed: in knots Heading: degrees North Depth: uncorrected depth from the echosounder (PES fish) in metres

APPENDIX C

LADCP COMMAND FILE

