# **BOFS Underway Data Documentation Index**

The BOFS underway data documentation contains one document file for each underway data file. These contain data from an entire cruise. The following documents are included:

## **1989 North Atlantic Bloom Experiment Cruises**

RRS Discovery	DI182	08 May 1989 to 08 June 1989
RRS Discovery	DI183	11 Jun 1989 to 11 Jul 1989
RRS Discovery	DI184	14 Jul 1989 to 14 Aug 1989

## **1990 BOFS Lagrangian Study Cruises**

RRS Discovery	DI190	14 Apr 1990 to 08 May 1990
RRS Charles Darwin	CD46	28 Apr 1990 to 23 May 1990
RRS Discovery	DI191	11 May 1990 to 08 Jun 1990
RRS Charles Darwin	CD47	25 May 1990 to 18 Jun 1990
RRS Discovery	DI192	09 Jun 1990 to 27 Jun 1990
RRS Charles Darwin	CD53	19 Sep 1990 to 24 Oct 1990

## **1991 BOFS North Atlantic Coccolithophore Study Cruises**

RRS Charles Darwin	<b>CD60</b>	13 Jun 1991 to 02 Jul 1991
RRS Charles Darwin	CD61	07 Jul 1991 to 29 Jul 1991

## **Sterna92 Antarctic Cruises**

RRS James Clark Ross	JCR2	28 Oct 1992 to 17 Dec 1992
RRS Discovery	DI198	11 Nov 1992 to 14 Dec 1992

<TIP> The hot links to the individual cruise documents are the BODC cruise mnemonics. These are used throughout the database to label data as belonging to that cruise.

# Surface Underway Data for Cruise Discovery DI182 (8<sup>th</sup> May to 8<sup>th</sup> June 1989)

## 1) Components of the Underway Data Set

The continuously logged underway data from cruise DI182 includes the following data channels. The single character at the end of each line is the parameter code used in the binary merge file.

Navigation:	Latitude (deg +ve N) Longitude (deg +ve E) Distance run (km)	A B K
Chemistry:	Dissolved Oxygen ( $\mu$ M) Dissolved inorganic carbon TCO <sub>2</sub> ( $\mu$ mol/kg) pCO <sub>2</sub> ( $\mu$ atmospheres i.e. ppm) pH (mol/kg) Temperature of pH determination (°C) Nitrate plus nitrite ( $\mu$ M) Silicate ( $\mu$ M)	Q H E M N T W
Biology:	Raw fluorescence (nominal mg/m <sup>3</sup> ) Chlorophyll (mg/m3)	D G
Physics:	Sea surface temperature (°C ) Surface salinity (PSU) Optical attenuance (per m)	C F I
Meteorology:	Wind speed (knots) Wind direction (degrees blowing from) Solar radiation (W/m <sup>2</sup> ) Barometric pressure (mB) Dry bulb air temperature (°C) PAR vector downwelling irradiance (W/m <sup>2</sup> )	Y Z O 1 a t

## 2) Methodology Overview

## 2.1) Plumbing

Instruments in the biology lab of RRS Discovery were connected to the ship's non-toxic pump (fixed to a pole amidships on the starboard side) via a black plastic header tank. The tank, approximate volume 130 litres, was located one deck above the biology lab and thus acted as a debubbling reservoir. From this reservoir, the flow was divided to feed the following instruments:

- a) pCO<sub>2</sub> to waste
- b) fluorometer to oxygen probe to sampling point
- c) autoanalyser to coulometer to waste
- d) pH electrode to waste

All waste tubes discharged below the level of the shelter deck.

### 2.2) Data Acquisition

Logging and initial processing of the data was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C. Here, the data records were sorted into files. Sampling rates varied from 10 seconds to several minutes.

In some cases the analytical equipment included an integral data logger (usually a PC) that supplied data to the Level C (a Sun workstation) on floppy disk.

The Level C ran a suite of calibration programs that was used for the initial conversion from raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigators post-cruise and subsequently submitted to BODC for incorporation into the underway data set.

## 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>, TCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data in raw form (e.g. nutrients) were calibrated to engineering units. Wind velocity was corrected for ship's motion and heading.

The output from each sensor was screened for spikes using a combination of editing software and manual editing on a graphics workstation. Wherever possible, comparative screening checks between channels were performed.

### 3) Methodology and Calibration Procedures

### 3.1) Navigation

Global Positioning System (GPS) was the primary navigation system used on this cruise. When no GPS fixes were available, the ship's position was determined by dead reckoning based upon the gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded 4 knots, the data were automatically flagged suspect. The positional error due to surface drift was retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry. This channel was recalculated by BODC, as frequent resets to zero (presumably due to ABC system crashes) were present in the original data channel.

At BODC a program was run that located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible into the gaps. These covered critical points such as course alterations and station arrivals/departures. Any remaining null values were filled by linear interpolation. The maximum duration of interpolated navigation data for this cruise was 1 hour 26 minutes.

## 3.2) Chemistry

## Dissolved oxygen

An Endeco type 1133 (sampling rate 2 minutes) oxygen probe was fitted to a flow cell and connected to the non-toxic supply. The sensor was electrically isolated from the ship's logging system by AD284J isolation amplifiers. Conversion from partial pressures and calibration against Winkler titration data (following the procedures of Carpenter 1965), was as follows:

OXobs (
$$\mu$$
M) = Sol\*(uAs-13.29) / (p1+p2\*OT)

given that:

uAs	=	-0.476+18.23*OXvolts
Sol	=	Cstar / (0.20946*(101.325-pH <sub>2</sub> O))
pH <sub>2</sub> O	=	exp((-216961/TK -3840.7) / TK+16.4754)
Cstar	=	exp(a1+a2/TK+a3/TK <sup>2</sup> +a4/TK <sup>3</sup> +a5/TK <sup>4</sup> -
		S*(a6+a7/TK+a8/TK <sup>2</sup> )
ΤK	=	absolute in-situ temperature
OT	=	oxygen sensor temp (tsg temp+0.77)

where:

a1	=	-135.90205
a2	=	157570.1
a3	=	-6.642308e7
a4	=	1.2438e10
a5	=	-8.621949e11
a6	=	0.017674
a7	=	-10.754
a8	=	2140.7

The calibration coefficients p1 and p2 varied as a function of time as shown in the following table:

Period	р1	p2
22:10 May 19 to 02:10 May 25	2.306	0.02977
02:10 May 25 to 07:05 May 28	1.632	0.1044
07:05 May 28 to 01:24 May 29	3.359	-0.0639
01:24 May 29 to 07:21 May 30	3.247	-0.06689
07:21 May 30 to 01:27 May 31	3.064	-0.05237
01:27 May 31to 06:19 Jun 01	2.674	-0.0151
06:19 Jun 01 to 20:03 Jun 05	2.376	0.01468

Calibration was done piecemeal because of changes in sensor response during the cruise.

### **Nutrients**

Nutrient analyses were performed on a Technicon Mark II Autoanalyser. Calibrations were undertaken with solutions made up from pre-weighed standards. The nutrient channels available on this cruise were nitrate plus nitrite and silicate; instrument problems resulted in the return of unusable data sets for nitrite and phosphate.

Silicate was analysed using stannous chloride reduction of silicomolybdic acid. Nitrate was reduced using a copper/cadmium coil and analysed as nitrite by diazotisation and coupling to form a dye (after Armstrong et. al. 1967).

Raw voltages were logged by connecting a Level A up to the chart recorder that monitored the colorimeter output voltage. These raw voltages were processed follows:

- The 30-second time-series of raw voltages was screened on a high-speed graphics workstation, to differentiate between signals due to baselines being run, standards run or actual ambient concentrations. Any spikes were flagged suspect.
- ii) The series was segmented into internally consistent subsets with linear baselines and consistent calibration, taking account of any instrumental changes such as gain or baseline alterations documented by the analyst.
- iii) The baseline was stripped off using the baseline drift equations determined for each segment.
- iv) For the silicate channel, which has particular problems associated with instrument drift, a linear regression of on-line drift for each segment was calculated by considering the difference between on-line readings immediately prior to and

after baselines.

- v) Calibration curves to convert voltage to concentration were determined for each segment and applied.
- vi) The data were synchronised to the other underway measurements, compensating for the time taken for the samples to run through the Autoanalyser tubing. Twelve minutes were subtracted for both the nitrate and silicate channels.
- vii) A time-series plot was examined to check the calibrated data and any remaining spikes were eliminated.

The standards were made up in Milli-Q purified water, but insufficient information on instrument gain settings was available to allow corrections to be made for the difference in optical density between the standards and seawater.

A modelling study was undertaken in the mid 1990s that looked at both carbon and nitrogen budgets. This concluded that the underway nitrate plus nitrite data from this cruise was significantly low. Subsequent investigations identified the problem as an error in the correction applied to take account of the nitrite present in the cocktail standards. This was corrected (subsequent to the publication of the original BOFS CD-ROM) but failed to completely make up the shortfall.

No detailed studies have been made of the silicate data and no specific comments on their quality have been received by BODC. However, there has been much general criticism of the entire 1989 BOFS nutrient data set. Consequently, users are advised to exercise caution when using the nutrient data from this cruise.

## <u>TCO</u>2

Total inorganic carbon was measured coulometrically. Sampling rate was one analysis every 8 minutes. The instrument used was a Coulometrics Inc. model 5011 coulometer. For more details of the techniques used, see Robinson et. al. (1990). Samples were preserved in mercuric chloride ( $250_{\mu}$ l per 250ml sample).

Mean analytical precision:	0.5-1 μmol/kg
Mean accuracy (by intercalibration):	1 μmol/kg

Data were converted to units of micromoles per kilogram using density derived from calibrated thermosalinograph data.

### <u>рН</u>

pH was measured by glass electrode potentiometry in a continuous automated flow system with a free diffusion liquid junction. The electrode was calibrated against 0.005M tris seawater buffer in accordance with the 1987 report of the Joint Panel on Oceanographic Tables and Standards. The resulting values are on the pH (Sea Water Scale) scale. National Bureau of Standards (NBS) buffers (pH 4 and 7) were used to confirm that the flat head glass electrode showed close to theoretical response (>99%).

Problems were encountered with the underway measurement of pH, which have been ascribed to the variable hydrostatic pressure on the inlet to the flow system, which caused unpredictable changes at the flowing liquid junction. This problem was partly overcome by alterations to the flow system, but the results were strongly dependent on the state of the peristaltic pump tubing. Good agreement with  $pCO_2$  and  $TCO_2$ , comparable to that found for discrete analyses, could be obtained for several hours after replacement of the pump tubing, following which significant drift was often observed. The suspect data were identified by the data originator and flagged by BODC.

The temperature of the pH measurement is included in a parallel channel for each data point.

### <u>pCO</u>2

The partial pressure of carbon dioxide (pCO<sub>2</sub>) was measured using a gas chromatographic method similar to that of Weiss (1981). Continuous measurements were carried out using a "shower head" type equilibrator from which the gas phase was sampled at approximately 7 minute intervals.

The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample. The equilibrated gas was carried in hydrogen, passed over a catalyst, which converted the  $CO_2$  to methane. The gas stream was passed to a flame ionisation detector (FID), Hewlett-Packard 5890A-GC that used compressed air as the combustion make-up gas.

Concentrations of  $CO_2$  in the equilibrated gas were compared every 15 minutes with marine air, dried to -30degC dew point (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data are given at in situ temperature and corrected for atmospheric pressure changes, in units of micro atmospheres. Precision studies show a standard deviation of no more than  $1.5\mu$  atms; repeated measurements of standards show a typical coefficient of variation to be no more than 0.2%.

### 3.3) Biology

### <u>Chlorophyll</u>

The underway chlorophyll data for this cruise have a somewhat complex history. As the data at various stages have entered the published literature, some explanation is required. A 'calibrated' chlorophyll data set was provided to BODC in 1990 and merged into the underway file.

In 1992, feedback was received that there were problems with this data set and a subsequent investigation showed that there was little resemblance between the

calibrated values and the extracted chlorophyll data set. It was concluded that the wrong version of the data file had been supplied to BODC but, as the scientist concerned had left, it wasn't possible to confirm or rectify the problem. As an interim measure, a crude recalibration against the extracted chlorophyll data set was undertaken by BODC.

In 1993, the data were reprocessed following the procedures described below and resubmitted to BODC in November. It is this recalibrated data that are present in the version of the underway file on the CD-ROM.

The extracted chlorophyll data set was obtained by taking samples from the non-toxic supply at approximately two hourly intervals whilst the ship was underway. These were filtered through GFF filters, extracted into 90 per cent acetone and assayed using a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards. The analysis was completed during the cruise.

Samples were only taken whilst the ship was underway between stations or engaged in localised surveys. The calibrated data are confined to these times. There are no data available whilst the ship was on station.

The calibration was done in 3 sections:

Calibration A	11/05/1989 20:24 - 12/05/1989 23:37
Calibration B	18/05/1989 23:39 - 25/05/1989 18:25
Calibration C	28/05/1989 07:08 - 03/06/1989 23:45

The data were originally logged at 10-second intervals from which 60-second averages were produced. Averaged values of fluorescence and irradiance (further smoothed by averaging over the three minutes prior to sampling) were selected to match the extracted chlorophyll sampling times.

These data were processed to derive values for components of a model that gives estimates for fluorescence yield at any point in the underway data set. The yield estimate comprised an estimate of the quenching factor, based on measured irradiance, and an estimate of the nighttime (unquenched) yield.

The quenching factor (Q) is given by:

 $Q(b,irrad) = 1 + b (Q_0(irrad) - 1)$ 

where

 $Q_0$  (irrad) = 1 + K1 (1- exp(K2 \* irrad)) b is a correction factor allowing for the daily variation in quenching response K1 = 0.96604 +/- 0.60759 K2 = -0.014581 +/- 0.016699

The yield reciprocal (chlorophyll per unit fluorescence) was used throughout to minimise errors in the chlorophyll estimates. The first approximation of the yield reciprocal was derived from the mean observed nighttime values (despiked using a 5

point median filter: spike size  $0.5 \text{ mg/m}^3$ ) linearly interpolated to give daytime values. Values of b were obtained by linear regression of the yield reciprocal against  $Q_0$  for each day.

The final estimate for the unquenched yield reciprocal, Xn2, was generated using the quenching factor to correct the observed data for the effects of light and then applying a 300km moving average to the corrected data. For calibration A, which was of short duration, the calibration was simplified by setting b=1 and Xn2 to the mean (over two nights) night time observed yield reciprocal.

The estimated unquenched yield reciprocal and the daily values of b were linearly interpolated onto the raw fluorescence values. The derived chlorophyll was then calculated using:

The calibrated data were compared with the extracted data set (error = (calibrated value - extracted value)/extracted value \* 100 per cent) with the following result:

Calibration A: mean error = 2.17% (sd 13.56%) Calibration B: mean error = -0.44% (sd 31.79%) Calibration C: mean error = 3.21% (sd 17.40%)

Regressions of calibrated chlorophyll against extracted chlorophyll, constrained to have an intercept of zero, gave the following result:

Claibration A: slope = 0.98+/-0.03 (r<sup>2</sup> = 85%) Calibration B: slope = 0.83+/-0.04 (r<sup>2</sup> = 44%) Calibration C: slope = 1.02+/-0.03 (r<sup>2</sup> = 49%)

Finally, the time channel was adjusted to allow for a two-minute delay between the water coming on board and it entering the fluorometer.

### 3.4) Physics

#### **Temperature and Salinity**

The instrument used was an ODEC (Ocean Data Equipment Corporation) model TSG-103 Thermosalinograph, incorporating a remote temperature sensor (thermilinear thermistor) and an inductive-type conductivity cell. Data acquisition was at a 3-second update rate and logging was done at 30-second intervals.

The remote temperature sensor was supplied by water from the intake side of the non-toxic pump. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply; the housing temperature was used to calculate salinity from conductivity according to the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1982).

The following calibration equations were derived on board by calibration against

Guildline Autosal salinity determinations on bottle samples drawn from the non-toxic supply.

Calibrated salinity = 0.09513\*Temperature - 0.0184\*Raw Salinity + 35.0085

Comparison by BODC with calibrated surface CTD temperatures revealed the thermosalinograph to be reading 0.06°C high. Both salinity and temperature corrections have been applied to the data.

Inspection of the data revealed the thermosalinograph record to be generally good with the exception of a few noisy patches in the temperature channel.

### **Optical Attenuance**

The instrument used was a SeaTech 660 nm (red) 25cm path-length transmissometer contained in a plastic water bath. The data were logged as voltages. These would normally be corrected by BODC for ageing of the light source but no air reading data were available. Consequently, the absolute values of attenuance may be overestimated.

Voltages were converted to percentage transmission (multiplied by 20) and any values outside the operational limits of the instrument (1-91.3%) were flagged suspect. Percentage transmission was converted to attenuance using the equation:

Considerable problems with noise were experienced during rough weather due to the formation of bubbles in the pond. The resulting spikes were easily identified during screening and have been flagged as suspect.

## 3.5) Meteorology

Discovery was fitted for this cruise with the 'Metpac' meteorological package, a prototype collection of meteorological instruments (currently superseded by Multimet). It was installed in 1978 and included the following sensors:

- port psychrometer (dry and wet bulb air temperatures)
- starboard psychrometer (dry and wet bulb air temperatures)
- port Vector anemometer (mean wind speed)
- port Vector wind vane (mean wind direction)
- barometer (air pressure)
- port Kipp and Zonen pyranometer (solar radiation)
- starboard Kipp and Zonen pyranometer (solar radiation)

In addition, for this and the following 1989 BOFS cruises a single Plessey photosynthetically available radiation (PAR) downwelling vector irradiance (cosine collector) sensor was also fitted.

### Air Temperature

The psychrometers, incorporating Pt100 resistance thermometers, were located in screens on the port and starboard side of the ship above the bridge. The Level A converted the thermometer output voltage to engineering units. This was based upon calibrations carried out periodically at the IOS Deacon Laboratory water bath. It is not known when the instruments were last calibrated prior to this cruise.

Both dry bulb temperature channels contained credible data and showed good agreement with occasional differences to 1°C maximum. Both channels were riddled with spikes that have all been flagged suspect. The CD-ROM data file contains a single dry bulb air temperature channel derived by averaging the port and starboard channels.

Both wet bulb air temperature channels contained total rubbish and have been scrapped.

#### Wind Velocity

The port anemometer was a Met. Office type Munro MK V. IOS Deacon Laboratory staff periodically calibrated the sensors at the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind speed and direction was undertaken by BODC using ship's heading and velocity over the ground. Checks were subsequently performed on the high-speed graphics workstation to ensure that the absolute wind velocity was independent of course changes and changes in ship'd speed.

During screening little or no evidence of shadowing from the ship's superstructure was observed but a curious cyclical oscillation (period approximately 30 minutes) was observed at times in the wind direction.

#### Barometric Pressure

The instrument used was a KDG aneroid barometer, calibrated to within 0.1mbar. The transmitter was a type TX 420 number 72291/1b and the transducer type ACT 30B number 72291/1a.

Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then converted to millibars. The instrument was calibrated by the manufacturers to within 0.1mB over the range 980-1050mB.

#### **Radiation**

The Metpac included two Kipp and Zonen type CM5/6 pyranometers mounted port and starboard. Output was in mV and was converted to W/m<sup>2</sup> by the Level A using the manufacturer's calibration. Instrument sensitivity was 0.00001119 Volts per W/m<sup>2</sup> and the temperature coefficient of sensitivity was 0.1%/°C. These instruments measure 'short wave radiation' from 300-3000nm (predominantly visible plus infrared) using a cosine collector. The data from these two instruments have been merged into a single channel by taking the maximum of the two readings to minimise the effects of shading.

In addition, a Plessey PAR cosine-collector vector irradiance meter (developed by IOS Deacon Laboratory in conjunction with Plessey Radar Research Centre, Havant, Hampshire) as described in Kahn et al. (1975) was mounted on the 'Monkey Island' to starboard, forward of the main mast.

The instrument is based on a Silicon photodiode and has a flat response over the range 350-700nm. Output frequency was converted to mW/cm<sup>2</sup> by the Level A, based on calibrations carried out by M. Jordan at the Plymouth Marine Laboratory.

Unlike the 2-pi PAR instruments used on the 1990 and 1991 BOFS cruises, this instrument was geometrically compatible with the Kipp and Zonen pyranometers. The empirical relationship below was determined as an approximate check on the relative performance of the two instruments:

solar = 3.47\*PAR - 0.72

## 4) Data Warnings

The pH data are of very mixed quality but have been flagged accordingly following the advice of the data originator.

Concerns have been expressed about the accuracy of the nutrient data.

The transmissometer data have not been corrected for decay of the light source.

## 5) References

Armstrong F.A.J., Stearns C.R. and Strickland J.D.H. 1967. The measurements of upwelling and subsequent biological processes by means of the Technicon AutoAnalyzer and associated equipment. *Deep Sea Research* <u>14</u>, 381-389.

Carpenter J.H. 1965. The Chesapeake Bay Institute techniques for the Winkler dissolved oxygen method. *Limnology and Oceanography* <u>10</u>, 141-143.

Fofonoff N.P. and Millard R.C. (1982). Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Kahn D.A., Pugh P.R., Fasham M.J.R. and Harris M.J. (1975). Underwater logarithmic irradiance meter for primary production and associated studies. In: *Institute of Electronic and Radio Engineers Conference proceedings* <u>32</u>: 81-90. Conference on Instrumentation in Oceanography, 23-25/9/75, UCNW, Bangor.

Robinson C. and Williams P.J.leB. 1991. Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chemistry* <u>34</u>, 157-175.

Weiss R.F. 1981. Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci* <u>19</u>, 611-616.

# Surface Underway Data for Cruise Discovery DI183 (11<sup>th</sup> June – 11<sup>th</sup> July 1989)

## 1) Components of the Underway Data Set

The continuously logged underway data from cruise DI183 includes the following data channels. The single character at the end of each line is the parameter code used in the binary merge file.

Navigation:	Latitude (deg +ve N) Longitude (deg +ve E) Distance run (km)	A B K
Chemistry:	Nitrate plus nitrite (μM) Nitrite (μM) Phosphate (μM) Silicate (μM)	T U V W
Biology:	Raw fluorescence (nominal mg/m <sup>3</sup> ) Chlorophyll (mg/m3)	D G
Physics:	Sea surface temperature (°C ) Surface salinity (PSU) Optical attenuance (per m)	C F I
Meteorology:	Wind speed (knots) Wind direction (degrees blowing from) Solar radiation (W/m <sup>2</sup> ) Barometric pressure (mB) Dry bulb air temperature (°C ) PAR vector downwelling irradiance (W/m <sup>2</sup> )	Y Z O 1 a t

## 2) Methodology Overview

## 2.1) Data Acquisition

Logging and initial processing of the data was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C. Here, the data records were sorted into files. Sampling rates varied from 10 seconds to several minutes.

The Level C ran a suite of calibration programs that were used for an initial conversion from raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing.

### 2.2) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Wind velocity was corrected for platform velocity and heading.

The output from each sensor was screened for spikes using a combination of editing software and manual editing on a graphics workstation. Wherever possible, comparative screening checks between channels were performed.

## 3) Methodology and Calibration Procedures

### 3.1) Navigation

Global Positioning System (GPS) was the primary navigation system used on this cruise. When no GPS fixes were available, the ship's position was determined by dead reckoning based upon the gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded 4 knots, the data were automatically flagged suspect. The positional error due to surface drift was retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible into the gaps. These covered critical points such as course alterations and station arrivals/departures. Any remaining null values were filled by linear interpolation. The largest gap interpolated for this cruise was 4 hours 48 minutes.

### 3.2) Chemistry

### Nutrients

The method used to collect underway nutrient data on this cruise differed significantly from most other BOFS cruises where underway nutrients were measured. The more common method was to plumb the autoanalyser into the non-toxic supply and use a Level A to log the chart recorder voltage every 30 seconds. The resulting voltage streams were then worked up into concentrations by BODC.

On this cruise, discrete water samples were drawn at regular intervals from the non-toxic supply and analysed using the autoanalyser with an automatic sample changer. The concentrations were then determined by manual measurement of the peak heights on the chart recorder output. This method produced much poorer spatial resolution, but the resulting analyses were undoubtedly of higher quality as the instrument was operating for a much shorter time and hence had less opportunity to

drift.

The instrument used was a Technicon Mark II. The chemistries used follow those described in Armstrong et al (1967) as summarised briefly below.

Nitrite:	Diazotisation and coupling to form an azo dye.
Nitrate:	Reduced using a Cu/Cd coil and then analysed as nitrite.
Silicate:	Stannous chloride reduction of silicomolybdic acid.
	Phosphate interference eliminated by using oxalic acid.
Phosphate:	Reduction of phosphomolybdate complex by ascorbic acid.
•	Sensitivity enhanced using antimony potassium tartrate catalyst.

The nutrient samples were taken every 15 minutes whilst the ship was underway between stations along the 20-West line.

### 3.3) Biology

### <u>Chlorophyll</u>

Chlorophyll was measured by a Turner Designs flow-through fluorometer calibrated against an extracted chlorophyll data set. This comprised 70 samples drawn from the non-toxic supply.

The samples were acetone extracted and measured on the Turner 112 bench fluorometer calibrated using absolute chlorophyll standards. More details of the procedure are given in the accompanying CTD document.

The raw fluorescence data were first corrected to eliminate steps produced when the instrument changed range. Once the data represented a common range, the raw reading was regressed against chlorophyll concentration giving the equation:

This was used to generate the chlorophyll channel present in the file.

### 3.4) Physics

Temperature and Salinity

The instrument used was an ODEC (Ocean Data Equipment Corporation) model TSG-103 Thermosalinograph, incorporating a remote temperature sensor (thermilinear thermistor) and an inductive-type conductivity cell. Data acquisition was at a 3-second update rate and logging was done at 30-second intervals.

The remote temperature sensor was supplied by water from the intake side of the non-toxic pump. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply. The housing temperature was used to calculate salinity from conductivity according to the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1982).

Salinity was calibrated at BODC by comparison with surface values taken from the calibrated CTD. The result showed the thermosalinograph to be reading 1.14 PSU low. This correction has been applied to the data but its magnitude causes some concern: usually corrections are significantly less than 0.5 PSU.

Comparison of the temperature channel with calibrated surface CTD temperatures revealed the thermosalinograph to be reading 0.22°C high. This correction has been applied to the data.

Inspection of the data revealed the thermosalinograph record to be reasonable after initial problems (which have been flagged out) on the first day of the cruise. At 47N, the temperature record becomes much noisier. However, this may be the result of a shallow thermocline rather than an indication of instrument malfunction.

### Optical Attenuance

The instrument used was a SeaTech 660 nm (red) 25cm path-length transmissometer contained in a plastic water bath. The data were logged as voltages. These would normally be corrected by BODC for ageing of the light source but no air reading data were available. Consequently, the absolute values of attenuance may be overestimated.

Voltages were converted to percentage transmission (multiplied by 20) and any values outside the operational limits of the instrument (1-91.3%) were flagged suspect. Percentage transmission was converted to attenuance using the equation:

#### Attenuance = -4log(%transmission/100)

This can only be described as a bad record. For much of the cruise, there were more spikes than signal. These have been completely flagged out. In addition, attenuance values at the start of the cruise are surprisingly high, which drop off alarmingly in a series of steps. These have been interpreted as instrumental malfunction and flagged out of the data set. Consequently, there is no attenuance data prior to 12.00 on 25/6/1989.

### 3.5) Meteorology

Discovery was fitted for this cruise with the 'Metpac' meteorological package, a prototype collection of meteorological instruments (currently superseded by Multimet). It was installed in 1978 and included the following sensors:

- port psychrometer (dry and wet bulb temperatures)
- starboard psychrometer (dry and wet bulb temperatures)
- port Vector anemometer (mean wind speed)
- port Vector wind vane (mean wind direction)
- barometer (air pressure)
- port Kipp and Zonen pyranometer (solar radiation)
- starboard Kipp and Zonen pyranometer (solar radiation)

In addition, for the 1989 BOFS cruises a single Plessey photosynthetically available

radiation (PAR) downwelling vector irradiance sensor was also fitted.

#### Air Temperature

The psychrometers, incorporating Pt100 resistance thermometers, were located in screens on the port and starboard side of the ship above the bridge. The Level A converted the thermometer output voltage to engineering units. This was based upon calibrations carried out periodically at the IOS Deacon Laboratory water bath. It is not known when the instruments were last calibrated prior to this cruise.

Both dry bulb temperature channels could only be described as awful: they contained at least 50 per cent instrumental spikes that have been flagged out. However, away from the spikes, the correspondence between the channels was reasonable with occasional differences to 1-2°C maximum. Both channels were riddled with spikes, which have all been flagged suspect.

The CD-ROM data file contains a single dry bulb air temperature channel derived by averaging the two data channels. Due to the high data loss through spikes, coverage is sporadic and, as only the worst of the spikes were flagged (otherwise very little data would remain), the merged channel has an unusually high noise level.

Both wet bulb channels contained total rubbish and have been scrapped.

### Wind Velocity

The port anemometer was a Met. Office type Munro MK V. The sensors were periodically calibrated by IOS Deacon Laboratory staff at the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind speed and direction was undertaken by BODC using ship's heading and velocity over the ground. Checks were subsequently performed on the high-speed graphics workstation to ensure that the absolute wind velocity was unaffected by changes ins ship's course and speed.

During screening no significant shadowing effects attributable to the ship's superstructure were observed. However, between 22:00 on 9th July to 09:00 on 10th July a curious cyclical signal with a period of approximately half an hour was observed in both wind speed and direction.

#### Barometric Pressure

The instrument used was a KDG aneroid barometer, calibrated to within 0.1mbar. The transmitter was a type TX 420 number 72291/1b. and the transducer type ACT 30B number 72291/1a.

Output was in the range 4-20 mA. This was converted to volts for input to the Level A and then converted to millibars using the manufacturer's calibration. This was within 0.1mB over the range 980-1050mB.

This channel contains an exceptionally high number of spikes that have been flagged

as suspect.

#### Radiation

The Metpac included two Kipp and Zonen type CM5/6 pyranometers, ,mounted port and starboard. Output was in mV and was converted to  $W/m^2$  by the Level A using the manufacturer's calibration. Instrument sensitivity was 0.00001119 Volts per  $W/m^2$  and the temperature coefficient of sensitivity was 0.1%/°C. These instruments measure 'short wave radiation' from 300-3000nm (predominantly visible plus infrared) using a planar collector.

The data from these two instruments have been merged into a single channel by taking the maximum of the two readings. This minimised shading artefacts.

In addition, a Plessey PAR cosine-collector vector irradiance meter (developed by IOS Deacon Laboratory in conjunction with Plessey Radar Research Centre, Havant, Hampshire) as described in Kahn et al. (1975) was mounted on the 'Monkey Island' to starboard, forward of the main mast.

The instrument was based on a Silicon photodiode and had a flat response over the range 350-700nm. Output frequency was converted to mW/cm<sup>2</sup> by the Level A, based on calibrations carried out by M. Jordan at the Plymouth Marine Laboratory.

Unlike the 2-pi PAR instruments used on the 1990 and 1991 BOFS cruises, this instrument was geometrically compatible with the Kipp and Zonen pyranometers. The following empirical relationship was determined as a check on the relative performance of the two sensors.

#### solar = 3.23\*PAR

The data from all radiometers contained a large proportion of spikes. These caused more problems than spikes on other channels because light data is, by nature, irregular. The method adopted to flag out spikes was to comparatively screen the solar and PAR channels. If the 'spike' could be identified in both channels, it was taken to be real. Otherwise it was flagged suspect.

This proved to be an extremely difficult task and it is quite possible that some real values have been flagged and some spikes missed. The radiation data from this cruise should therefore be used with caution.

## 4) Data Warnings

The transmissometer data have not been corrected for decay of the light source. The resulting channel has been heavily flagged due to huge numbers of spikes and a suspected instrument malfunction. The attenuance data from this cruise should be used with caution.

The thermosalinograph salinity was over 1 PSU low. Whilst a correction has been

possible, its magnitude should be borne in mind by users of the data.

All meteorology channels except wind velocity contained an exceptionally high proportion of spikes. As a result, the air temperature data are unusually noisy (small spikes were left in to give a usable data coverage) and the quality of the radiometer data was degraded because spikes in these channels could not be identified with certainty.

## 5) References

Armstrong F.A.J., Stearns C.R. and Strickland J.D.H. 1967. The measurements of upwelling and subsequent biological processes by means of the Technicon AutoAnalyzer and associated equipment. *Deep Sea Research* <u>14</u>, 381-389.

Fofonoff N.P. and Millard R.C. (1982). Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Kahn D.A., Pugh P.R., Fasham M.J.R. and Harris M.J. (1975). Underwater logarithmic irradiance meter for primary production and associated studies. In: *Institute of Electronic and Radio Engineers Conference proceedings* <u>32</u>: 81-90. Conference on Instrumentation in Oceanography, 23-25/9/75, UCNW, Bangor.

# Surface Underway Data for Cruise Discovery DI184 (14<sup>th</sup> July to 14<sup>th</sup> August 1989)

## 1) Components of the Underway Data Set

The continuously logged underway data from cruise DI183 includes the following data channels. The single character at the end of each line is the parameter code used in the binary merge file.

Navigation:	Latitude (deg +ve N) Longitude (deg +ve E) Distance run (km) Bathymetric depth (m)	A B K J
Physics:	Sea surface temperature (°C ) Surface salinity (PSU)	C F
Meteorology:	Wind speed (knots) Wind direction (degrees blowing from) Solar radiation (W/m <sup>2</sup> ) Barometric pressure (mB) Dry bulb air temperature (°C) PAR vector downwelling irradiance (W/m <sup>2</sup> )	Y Z O 1 a t

## 2) Methodology Overview

## 2.1) Data Acquisition

Logging and initial processing of the data was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C. Here, the data records were sorted into files. Sampling rates varied from 10 seconds to several minutes.

The Level C ran a suite of calibration programs that were used for an initial conversion from raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing.

## 2.2) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. The output from each sensor was screened for spikes using a combination of editing software and manual editing on a graphics workstation. Wherever possible, comparative screening checks between channels were performed.

## 3) Methodology and Calibration Procedures

## 3.1) Navigation

Global Positioning System (GPS) was the primary navigation system used on this cruise. When no GPS fixes were available, the ship's position was determined by dead reckoning based upon the gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded 4 knots, the data were automatically flagged suspect. The positional error due to surface drift was retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run that located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible into the gaps. These covered critical points such as course alterations and station arrivals/departures. Any remaining null values were then filled by linear interpolation. The largest gap filled by interpolation for this cruise was 23 hours 20 minutes. Users should be aware of the real possibility of positional error during this period, which commenced at 02:34 on 21st July.

Bathymetric depth was measured using a SimRad echo sounder logged via the ABC system. The Level C software applied Carter's Tables corrections to the data. The record looked clean but contained a lot of gaps.

### 3.2) Physics

### Temperature and Salinity

The instrument used was an ODEC (Ocean Data Equipment Corporation) model TSG-103 Thermosalinograph, incorporating a remote temperature sensor (thermilinear thermistor) and an inductive-type conductivity cell. Data acquisition was at a 3-second update rate and logging was done at 30-second intervals.

The remote temperature sensor was supplied by water from the intake side of the non-toxic supply. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply. The housing temperature was used to calculate salinity from conductivity according to the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1982).

Salinity was calibrated at BODC by comparison with surface values taken from the calibrated CTD. The result showed the thermosalinograph to be reading 1.15 PSU low. This correction has been applied to the data but its magnitude causes some concern: usually corrections are less than 0.5.

Due to the small number of CTD casts on this cruise, calibration points were infrequent. After 28th July, the salinity record exhibits a downwards drift falling to 33.8 (after a 1 PSU correction!). The instrument was obviously malfunctioning at a time when no calibration data were available, which left no option but to flag all data after this time suspect.

The magnitude of the instrumental drift and the sparsity of calibration points means that any salinity data from this cruise, even those points flagged good, should be

treated with caution.

Comparison of the temperature channel with calibrated surface CTD temperatures revealed the thermosalinograph to be reading 0.17°C high. This correction has been applied to the data.

Inspection of the data revealed the temperature record to be reasonable until after 08:00 on 11th August when it became extremely noisy. This problem persisted until the end of the cruise.

### 3.3) Meteorology

Discovery was fitted for this cruise with the 'Metpac' meteorological package, a prototype collection of meteorological instruments (currently superseded by Multimet). It was installed in 1978 and included the following sensors:

- port psychrometer (dry and wet bulb air temperatures)
- starboard psychrometer (dry and wet bulb air temperatures)
- port Vector anemometer (mean wind speed)
- port Vector wind vane (mean wind direction)
- barometer (air pressure)
- port Kipp and Żonen pyranometer (solar radiation)
- starboard Kipp and Zonen pyranometer (solar radiation)

In addition, for this and the other 1989 BOFS cruises a single Plessey photosynthetically available radiation (PAR) downwelling vector irradiance sensor was also carried.

#### Air Temperature

The psychrometers, incorporating Pt100 resistance thermometers, were located in screens on the port and starboard side of the ship above the bridge. The thermometer output voltage was converted to engineering units by the Level A. This was based upon calibrations carried out periodically at the IOS Deacon Laboratory water bath. It is not known when the instruments were last calibrated prior to this cruise.

Both dry bulb temperature channels were initially awful, containing more spikes than data, and required heavy flagging. However, the proportion of signal to noise improved, with just isolated patches of excessive noise lasting for a few hours. These have been flagged out completely.

The correspondence between the channels was reasonable with occasional differences to 1-2°C maximum. The CD-ROM data file contains a single dry bulb air temperature channel derived by averaging the two data channels. Due to the high data loss through spikes, coverage is sporadic.

Both wet bulb channels contained total rubbish and have been scrapped.

#### Wind Velocity

The port anemometer was a Met. Office type Munro MK V. IOS Deacon staff periodically calibrated the sensors at the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind speed and direction was undertaken by BODC using ship's heading and velocity over the ground. Checks were subsequently performed on the high-speed graphics workstation to ensure that the absolute wind velocity was independent of ship's motion.

During screening no evidence of shadowing by the ships superstructure was observed.

### Barometric Pressure

The instrument used was a KDG aneroid barometer, calibrated to within 0.1mbar. The transmitter was a type TX 420 number 72291/1b. and the transducer type ACT 30B number 72291/1a.

Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then converted to millibars. The instrument was calibrated by the manufacturer to within 0.1mB over the range 980-1050mB.

The channel contained clean data with a few spikes (flagged suspect) up until 10:00 on July 17th when the instrument expired.

### **Radiation**

The Metpac included two Kipp and Zonen type CM5/6 pyranometers, mounted port and starboard. Output was in mV and was converted to W/m<sup>2</sup> by the Level A using the manufacturer's calibration. Instrument sensitivity was 0.00001119 Volts per W/m<sup>2</sup> and the temperature coefficient of sensitivity was 0.1%/°C. These instruments measure 'short wave radiation' from 300-3000 nm (predominantly visible plus infrared) using a cosine collector.

The data from these two instruments have been merged into a single channel by taking the maximum of the two readings. This minimises shading artefacts.

In addition, a "Plessey" PAR irradiance meter (developed by IOS Deacon Laboratory in conjunction with Plessey Radar Research Centre, Havant, Hants.) as described in Kahn et al. (1975) was mounted on the 'Monkey Island' to starboard, forward of the main mast. The instrument was based on a silicon photodiode and had a flat response over the range 350-700nm. Output frequency was converted to mW/cm<sup>2</sup> by the Level A, based on calibrations carried out by M. Jordan at the Plymouth Marine Laboratory.

Unlike the 2-pi PAR instruments used on the 1990 and 1991 BOFS cruises, this instrument was geometrically compatible with the Kipp and Zonen pyranometers. The empirical relationship below was derived as a check on the relative performance of the two instruments.

#### solar = 3.31\*PAR

The data from all radiometers were initially plagued by spikes, but became much less noisy after July 28th. This noise, when present, caused more problems than spikes on

other channels because light data is, by nature, irregular. The method adopted to flag out spikes was to comparatively screen the solar and PAR channels. If the 'spike' could be identified in both channels, it was taken to be real. Otherwise it was flagged suspect.

This proved to be an extremely difficult task and it is quite possible that some real values have been flagged and some spikes missed. This should be borne in mind when using the radiation data from this cruise.

## 4) Data Warnings

The thermosalinograph salinity data from this cruise should be used with caution. Instrumental drift was exceptionally large and was based on a small quantity of data.

Air temperature and radiation channels contained a high proportion of spikes that still degrade the data quality to some degree despite BODC's best efforts at flagging the spikes suspect.

## 5) References

Fofonoff N.P. and Millard R.C. (1982). Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Kahn D.A., Pugh P.R., Fasham M.J.R. and Harris M.J. (1975). Underwater logarithmic irradiance meter for primary production and associated studies. In: *Institute of Electronic and Radio Engineers Conference proceedings* <u>32</u>: 81-90. Conference on Instrumentation in Oceanography, 23-25/9/75, UCNW, Bangor.

# Surface Underway Data for Discovery Cruise DI190 (14<sup>th</sup> April to 8<sup>th</sup> May 1990)

## 1) Components of the Underway Data Set

The underway data set for Discovery 190 contains the following data channels. The single character at the end of each line is the parameter code used in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance Run (km)	A B K
Chemistry:	Dissolved oxygen ( $\mu$ M) TCO <sub>2</sub> ( $\mu$ mol/kg) pCO <sub>2</sub> ( $\mu$ atm) Nitrate plus nitrate ( $\mu$ M) Nitrite ( $\mu$ M) Phosphate ( $\mu$ M) Silicate ( $\mu$ M)	Q H E T U V W
Biology:	Raw Fluorescence (nominal mg/m <sup>3</sup> ) Chlorophyll (mg/m <sup>3</sup>	D G
Physics:	Sea surface temperature (°C) Sea surface salinity (PSU) Optical Attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees blowing from) Solar radiation (W/m <sup>2</sup> ) Barometric Pressure (mB) Dry bulb air temperature °C Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> )	Y Z O 1 a L

## 2) Methodology Overview

## 2.1) Plumbing

Water from the non-toxic pump was fed into a 130 litre black plastic header tank situated above the laboratory to act as a debubbler. The supply from this tank was split to feed the underway chemistry measurements and the fluorometer. Each branch was equipped with a control valve and flow meter to enable the flow rates to each instrument to be controlled. The thermosalinograph and transmissometer pond were fed separately from the non-toxic supply.

### 2.2) Data Acquisition

For most parameters, data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp from a central master clock and transferred the data via the Level B disk buffer onto the Level C, where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

In some cases, for example dissolved oxygen, the analytical equipment included an integral data logger, such as a PC. In these cases, data were transferred to the Level C on floppy disk.

The level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set.

### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>, TCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR) were converted to engineering units. Wind velocity was corrected for ship's velocity and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data were not influenced by changes in ship's heading).

## 3) Methodology and Calibration Procedures

### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as

possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The largest gap interpolated on this cruise was 5 hours 53 minutes, commencing at 00:33 on 8/5/1990.

The distance run channel was checked to ensure it was progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary: distance run had reset to zero twice during the cruise.

### 3.2) Chemistry

### **Dissolved oxygen**

Dissolved oxygen was measured using an Endeco type 1125 pulsed dissolved oxygen controller multiplexed with two Endeco type 1128 dissolved oxygen probes. The probes were immersed in a Perspex cell (approx. 1 litre) fed at approximately 2 litres per minute.

The oxygen system had no way of determining salinity. Consequently, the data were logged and calibrated with an input salinity of zero for all computations. Calibration was achieved by regressing the output from the probe deemed more stable (designated probe 3) against measurements made using the Winkler method on samples taken from the probe outflow. Calibration samples were taken approximately every six hours.

Two calibration curves were established:

17/4/90 04:23 to 22/4/90 17:34 Calibrated = (Raw+223.219)/1.61711 (R<sup>2</sup>=96%) 23/4/90 15:24 to 25/4/90 10:10 Calibrated = (Raw- 61.957)/0.75511 (R<sup>2</sup>=92%)

The first calibration curve was applied to data prior to 04:23 on 17/4/90 (approximately 10 hours) and the second to data after 10:10 25/4/90 (approximately 10.5 days). Data falling in the interval between the two curves were calibrated using a linearly interpreted transition from one calibration equation to the other.

The calibrated data at zero salinity were corrected to in-situ salinity using the equations:

 $O_2$  (actual) =  $O_2$  (zero salinity) / Gamma

 $Gamma = \exp(S^*(A6 + A7/T + A8/T^2))$ 

where: S = Salinity (PSU) T = Absolute temperature (K) A6 = 0.017674 A7 = -10.754A8 = 2140.7

Due to the failure of the thermosalinograph conductivity sensor, there were a

significant number of data points for which no salinity data were available. A default value of 35.3 (the mean of the available salinity data) was used in these cases.

## <u>pCO</u>2

Continuous measurements of  $pCO_2$  were carried out using a "shower head" type equilibrator, similar to that described in Weiss (1981), from which the gas phase was sampled at approximately 7-minute intervals. The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample.

The equilibrated gas was carried in hydrogen, passed over a catalyst that converted the  $CO_2$  to methane. The gas stream was passed to a flame ionisation detector (FID), Hewlett-Packard 5890A-GC which used compressed air as the combustion make-up gas.

Concentrations of  $CO_2$  in the equilibrated gas were compared every 15 minutes with marine air, dried to -30°C dew point (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data are given at in-situ temperature and have been corrected for atmospheric pressure changes, in units of microatmospheres.

The apparatus worked faultlessly throughout the cruise, except for two minor breakdowns that caused data loss of the order of a couple of hours. The data are reported as being of high quality with precision to standards better than 0.1%.

## <u>TCO</u><sub>2</sub>

Total inorganic carbon (TCO<sub>2</sub>) was measured coulometrically. The sampling rate was approximately 1 sample every 6 minutes, achieved by improvements to the software. The instrument used was a Coulometrics Inc. model 5011 coulometer. For fuller details of the techniques used, see Robinson and Williams (1991). The mean analytical precision was estimated at 0.5-1  $\mu$ mol/kg and the mean accuracy, estimated for the method by intercalibration during the 1989 North Atlantic Bloom Experiment, was 1  $\mu$ mol/kg.

Potential drift in the coulometric titration was monitored frequently with sodium bicarbonate secondary standards and a 99.995% CO<sub>2</sub> gas reference. The drift was maintained in the range 0.02-0.15%.

The data are quoted in  $\mu$ mol/kg, which was computed from the measured data in  $\mu$ M by multiplying by (1000+sigmaT/1000). SigmaT was computed from calibrated thermosalinograph temperature and, due to problems with the thermosalinigraph, a default salinity of 35.3.

### **Nutrients**

The nutrients were measured using a Technicon AA2 autoanalyser connected to the pumped seawater supply by a continuous filter block (Morris et al, 1978). The chemistries used were:

- Nitrate: Reduced to nitrite by a Cu/Cd coil, then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish-purple azo dye.
- Nitrite: As for nitrate without the reduction step.
- Phosphate: Reduction of a phosphomolybdate complex in acid solution to 'molybdenum blue' by ascorbic acid with sensitivity enhanced by the catalytic action of antimony potassium tartrate.
- Silicate: Reduction of a silicomolybdate solution to 'molybdenum blue' by ascorbic acid with the addition of oxalic acid to eliminate interference from phosphates.

The colorimeter outputs were logged by a Level A connected to the chart recorder inputs. The system was calibrated by running distilled water washes to determine baseline and sets of four standards. Standards were run at least once per day.

The following processing procedures were adopted by BODC to convert the raw voltage streams into nutrient concentrations.

The raw voltages were screened on a graphics workstation to differentiate between signals due to baselines (flagged 'Z'), standards (flagged '1', '2', '3' or '4' according to concentration) or actual ambient concentrations. Any instrumental spikes or data logged whilst the instrument was non-operational were flagged suspect ('S').

The data were then segmented into internally consistent subsets (i.e. taking account of any instrumental change such as gain or baseline alterations documented by the analyst), with constant or linearly drifting baselines.

For each segment, the baseline as a function of time was fitted to a linear regression, which was applied to standardise the segment to a baseline of zero. For the silicate channel, which has particular problems associated with instrument drift, a linear regression of on-line drift for each segment was calculated by considering the difference between on-line readings immediately prior to and after baselines, providing the other data channels indicated no change in ambient nutrient concentration.

The standard voltages were then used to construct calibration curves to convert raw voltages into nutrient concentrations. These were then applied on a segment-by-segment basis to the data stream. All baseline and calibration equations were checked manually before they were used. Once concentrations had been calculated the custom baseline and standard flags were changed to suspect.

The data were subsequently quality controlled by inspection on a graphics workstation with particular attention paid to the concentrations obtained for the standards. Any data identified as suspect were flagged. These checks included comparative screening between the nutrient channels.

Two additional corrections were applied. First, the nutrient time channels were adjusted to correct for the delay incurred whilst the sample passed through the complex plumbing of the autoanalyser. Secondly, empirically determined corrections were applied to correct for the difference in optical density between the standards, made up in Milli-Q water, and seawater. The correction values used were:

Nutrient	Time Shift	Salt correction
NO <sub>3</sub>	-12 mins.	-0.03 μM
NO <sub>2</sub>	-8 mins.	-0.04 μM
PO <sub>4</sub>	-10 mins.	-0.07 μM
Si	-12 mins.	-0.10 μM

Note that the same autoanalyser gain setting was used throughout the cruise, which allowed the simplistic salt correction quoted above to be used. Due to the chemistry used for nitrate analysis, interference from nitrite is inevitable. The nitrate channel has been processed throughout as nitrate+nitrite and no attempt has been made to correct for nitrite.

As a final processing step, small negative values in the data were converted to zero to prevent them creating havoc with contouring software. Values of zero flagged 'G' should therefore be taken to mean 'below detection limit'.

Problems were encountered during the processing of two of the channels. The nitrate calibration contained much more scatter than is usually encountered. Consequently, accuracy is estimated to be no better than 10 per cent. The silicate channel did not contain sufficient baseline determinations to allow adequate correction for baseline drift. Consequently, some of the gradients observed in the data set may not be real.

## 3.3) Biology

### <u>Chlorophyll</u>

Chlorophyll was measured by a Turner Designs through-flow fluorometer calibrated against extracted chlorophyll data. Samples (100 ml) were drawn from the non-toxic supply and filtered through Whatman GFF filter papers. Two samples were filtered: one for immediate analysis and the other frozen. The samples analysed on board were extracted in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

The extractions were done in 10 ml Analar acetone and left refrigerated for 18-72 hours. During the extraction, the tubes were periodically shaken and centrifuged at 5000 rpm for 5-8 minutes.

Subsequent events showed that the instrument on board Discovery was malfunctioning and consequently the frozen samples were extracted and analysed post-cruise at PML. The calibration of the underway fluorometer was undertaken using the extracted data set obtained from the frozen samples.

The raw fluorometer data were first screened on a graphics workstation and any spikes flagged. Next, steps in the data set due to uncorrected range changes were identified and the data channel reduced to a single range.

The extracted data set comprised 50 samples. Calibration was achieved by multiple regression of the log of the extracted chlorophyll value against two predictors, the log of the raw fluorometer reading and calibrated, merged PAR ( $W/m^2$ ) averaged over a 3 minute interval. The cruise data were treated as a single population.

The calibration equation used was:

chlorophyll (mg/m<sup>3</sup>) = exp (0.599\*log(raw\_reading) + 0.00142\*PAR - 1.60)

The adjusted  $R^2$  for this regression was 72.4 per cent. If no PAR data were available (as was the case prior to 24th April), a PAR value of zero was assumed.

## 3.4) Physics

### Temperature and Salinity

The thermosalinograph conductivity sensor was inoperative for this cruise. Temperature was measured using the remote thermosalinograph temperature sensor (thermolinear thermistor), supplied by water from the intake side of the non-toxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system.

The raw ADC counts were calibrated to give temperature in engineering unit, based upon laboratory calibrations undertaken by RVS. The data were back calibrated against surface CTD and SeaSoar data. A correction of 0.02°C was determined and this has been applied to the data.

An underway salinity channel was derived from the calibrated SeaSoar data set. The top bin of the gridded data set (4km by 8m) was picked off and inserted into the appropriate time slot (determined by comparison of position channels) in the binary merge file. Calibration details are presented in a separate document.

The temperature sensor functioned well throughout the cruise, producing a data set of good quality by thermosalinograph standards. The surface salinity data set is severely limited in resolution and extent, as it had to be extracted from SeaSoar data.

### **Optical Attenuance**

Optical attenuance was measured using a SeaTech 660 nm (red) 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. The data were logged as voltages. These would normally be corrected for

light source decay using a ratio correction based on air voltage measured during the cruise and the air voltage measured when the instrument was new. However, neither the air voltage data nor the serial number of the instrument used could be obtained and hence no air correction was possible. The attenuance values are therefore overestimates.

Any values outside the operational limits of the instrument (1-91.3%) were automatically flagged suspect.

The percentage transmission (Volts\*20) was converted to attenuance using the equation:

Attenuance =  $-4.0 \log (\% \text{ Transmission}/100)$ .

Inspection of the data using a graphics workstation showed them to be relatively free from the 'bubble spikes' that can plague underway transmissometer data. The few spikes that were identified were flagged out.

### 3.5) Meteorology

### Air Temperature

The Metpac fitted to Discovery for this cruise included two psychrometers fitted to the port and starboard bridge wings. The instruments were calibrated periodically at the IOS Deacon Laboratory using a water bath. It is not known when the instruments were last calibrated prior to this cruise.

The psychrometer wicks were discovered on a subsequent cruise (Discovery 192) to be immersed in 'a foul yellow liquid'. It therefore came as no surprise when inspection of the wet bulb data set showed it to be total rubbish with no identifiable credible signal. Consequently, both wet bulb temperature channels were deleted from the data set.

A combined dry bulb temperature channel was generated by averaging the port and starboard channels. These showed good agreement (within a degree at worst and usually much better) throughout the cruise and consequently the source channels have been deleted from the data set.

### Wind Velocity

A Meteorological Office type Munro Mk V anemometer and wind vane located on the port side of the ship measured wind velocity. The sensors were calibrated periodically using the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly

independent of the ship's velocity and heading.

During these checks it was noted that some correlations could be seen between the ship's orientation relative to the wind and the wind speed. These were not consistently present and further investigation showed that wind speeds dropped noticeably if the ship turned to bring the wind off port onto starboard. This was interpreted in terms of shielding of the anemometer when the wind had certain orientations with respect to the ship.

The data were inspected on a graphics workstation and spikes flagged suspect.

### Radiation

Discovery was equipped with Kipp and Zonen type CM5/6 pyranometers and PML designed 2-pi PAR scalar irradiance meters mounted in pairs on the port and starboard side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the sensors in these instruments were quite different. The PAR meters had hemispherical domed sensors whilst the solarimeter sensors were fitted with cosine collectors. At midday on the equator, both types of instruments would produce comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters would be considerably higher. Consequently, simple comparisons between the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 7):	PAR = exp(Volts*4.996 + 6.7545)/10	0
Starboard (sensor 9):	PAR = exp(Volts*5.062 + 6.7874)/10	0

Merged solar and PAR channels were produced, after spikes had been flagged out, by taking the maximum of the port and starboard values to eliminate shading effects. PAR data are only available after 24th April.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

The PAR data return was particularly poor for this cruise as the instrumentation only functioned at low light levels.

### Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mbar over the range 980-1050 mB by the manufacturer. Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars.

The data were examined on a graphics workstation by BODC and any spikes were

flagged as suspect.

## 4) Data Warnings

The nitrate calibration was unusually poor. The silicate data may contain artificial gradients caused by uncorrected baseline drift.

No correction for light source decay has been applied to the optical attenuance data.

Wind speeds may be underestimated at times due to shielding of the anemometer.

No PAR data were available prior to April 24<sup>th</sup>. After this date the PAR data return was extremely poor as the instrumentation only functioned at low (crepuscular) light levels.

Chlorophyll data from the calibrated fluorometer could not be properly corrected for quenching due to the poor PAR data coverage.

## 5) References

Bradshaw, A.L., Brewer, P.G., Shafer, K. and Williams, R.T. 1981. Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program. *Earth Planet. Sci. Lett.* <u>55</u> : 99-115.

Morris, A.W., Howland, R.J.M., and Bale, A.J. 1978. A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. *Est. Coast. Mar. Sci.* <u>6</u>, 105-109.

Robinson, C. and Williams, P.J.IeB. 1991. Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chem* <u>34</u>: 157-175.

Weiss, R.F. 1981. Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci* <u>19</u> : 611-616

# Surface Underway Data for Cruise Charles Darwin CD46 (28<sup>th</sup> April – 23<sup>rd</sup> May 1990)

## 1) Components of the Underway Data Set

The underway data set for Charles Darwin 46 contains the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (deg +ve N) Longitude (deg +ve E) Distance run (km)	A B K
Biology:	Turner Designs raw fluorescence (nominal mg/m <sup>3</sup> ) Turner Designs chlorophyll (mg/m <sup>3</sup> ) Aquatracka raw fluorescence (Volts) Aquatracka chlorophyll (mg/m <sup>2</sup> )	D G ? !
Physics:	Temperature (°C) Salinity (PSU) Optical Attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees blowing from) Solar radiation (W/m <sup>2</sup> ) Dry bulb air temperature (°C) Wet bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> ) Long wave radiation (W/m <sup>2</sup> )	Y Z O a b L /

## 2) Methodology Overview

## 2.1) Plumbing

The ship was equipped with a pumped non-toxic supply with an inlet approximately 4m below the surface on the starboard side. All ship's wastewater was jettisoned to port to minimise the risk of contamination.

The Aquatracka fluorometer and the transmissometer were located in a light-tight pond fed continuously by this supply, tapped close to the inlet 'upstream' from the system header tank. This was unfortunate: the header tank acts as a debubbler that may have improved the quality of the transmissometer record.

The thermosalinograph and Turner Designs fluorometer were fed from 'downstream' of the header tank. The different plumbing of the two fluorometers produced a time offset with the Aquatracka reacting approximately 1-2 minutes faster to changes in the
ambient chlorophyll concentration.

#### 2.2) Data Acquisition

Data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

The Level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set.

#### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. the meteorology) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

## 3) Methodology And Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These cover critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap filled by interpolation was 3 hours 51 minutes from 04:58 on 6/5/1990.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary for this cruise.

#### 3.2) Biology

## <u>Chlorophyll</u>

Chlorophyll was measured by two fluorometers run in parallel, a Turner Designs through-flow and a Chelsea Instruments Aquatracka immersed in a light-tight pond. Both instruments were calibrated against extracted chlorophyll data. Samples were drawn from the non-toxic supply and filtered through GF/F filter papers. The samples were analysed on board by extraction in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

Fluorometer calibrations were done at BODC using both the underway sample set and the samples from the top water bottle on each CTD cast. Taken together, these sample sets provided good coverage at all stages of the daily light cycle.

Prior to calibration, both raw fluorometer channels were screened on a graphics workstation and any spikes flagged. Next, steps in the Turner Designs data set due to uncorrected range changes were identified and the data channel reduced to a single range. The Turner Designs data were supplied as raw ADC counts (large integers). These were scaled by a factor of 10,000 prior to processing to make them more manageable.

Calibration of the Aquatracka was done by multiple regression of the log of the extracted chlorophyll value against two predictors, voltage and calibrated, merged PAR ( $W/m^2$ ) averaged over a 3-minute interval. The entire cruise was treated as a single data set giving rise to the equation:

chlorophyll (mg/m<sup>3</sup>) = exp (
$$0.953^{*}V + 0.000832^{*}PAR - 2.71$$
) (n=84;r<sup>2</sup>=55.4%)

The Turner Designs calibration data failed to show any significant correlation between residual chlorophyll (difference between calibrated fluorometer chlorophyll and extracted value) and PAR. Consequently, the calibration equation below was derived by simple regression of chlorophyll against instrument reading:

chlorophyll (mg/m<sup>3</sup>) = 0.411\*Raw\_value + 0.485

After calibration, comparative screening checks (plots overlaid on identical scales) were done to see how the two independently calibrated channels compared. The correspondence between the two channels was most encouraging except for a few brief periods, associated with the highest chlorophylls, when the Aquatracka read significantly higher.

#### 3.3) Physics

#### Temperature and Salinity

Temperature and salinity were measured using an Ocean Data Equipment Corporation (ODEC) TSG-103 thermosalinograph, incorporating a remote temperature sensor (thermistor) and an inductive-type conductivity cell mounted next to a second thermistor.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1983).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. This showed that the instrument reading was steady but 0.39 PSU high. A correction of –0.39 PSU has been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A constant correction of 0.04°C was determined for the whole cruise and this has been applied to the data.

The salinity record looked good. The temperature was generally good but with noisy patches, particularly between 14-16 May. The noise from 10:00 to 16:00 on the 16th was so bad that the channel has been flagged out completely for this period.

An interesting feature of the temperature record are the sharp 'kicks' of up to 0.5°C in the early hours of most mornings. At first these were believed to be artefacts but their regularity in time prompted further investigation. When compared against the ship's logs they can be seen to be due to the ship repositioning onto the marker buoy once the tethered production rigs had been recovered. Their presence shows that the sea surface temperature in the area of the 'Lagrangian' study varied markedly over a relatively short distance.

#### **Optical Attenuance**

Optical attenuance was measured using a 660 nm 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. The data were logged as voltages. Normally, these would be corrected for light source decay, but this was not possible for this cruise due to lack of air correction data. Consequently, the attenuance values have been overestimated to some degree.

Voltages were converted to fractional transmission by dividing by 5 and then to

attenuance using the equation:

Attenuance = 
$$-4.0 \log (Transmission)$$
.

Inspection of the data using a graphics workstation showed them to be severely affected by spikes, presumably due to bubbles. The data required very heavy flagging. At 10:00 on 15/5/90, the attenuance record stepped up sharply from approximately 1-1.5 to 2.5-3, staying high for the rest of the cruise. All data from this point have been flagged suspect.

#### 3.4) Meteorology

#### Multimet System

The Multimet system fitted to Charles Darwin for this cruise contains a broad suite of sensors logged on an integral PC that was programmed to function as a Level A. The raw data were sent to the James Rennell Centre for working up and the calibrated data were sent to BODC to be merged into the underway file. It is not known when the instruments were last calibrated prior to this cruise.

#### Air Temperature

The Multimet on this cruise included three Vector Instruments type aspirated psychrometers. Two were fitted above the wheelhouse, one to port and one to starboard, with the third fitted to the foremast.

Combined wet and dry bulb temperature channels were generated by averaging data from all three instruments. These showed consistently good (within 1°C and usually much better) agreement: data from the mast instrument were systematically a little higher than the instruments on the bridge.

#### Wind Velocity

Wind velocity was measured by a Vector Instruments cup anemometer and vane located on the main mast. Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect.

#### **Radiation**

The multimet included two Kipp and Zonen type CM5/6 pyranometers and an Eppley longwave radiation sensor mounted on the forward mast. In addition, two PML designed 2-pi PAR meters were mounted on scaffold poles on either side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the sensors in these instruments are quite different. The PAR meters had hemispherical

domed collectors whilst the solarimeters had cosine collectors. At midday on the equator, both types of instruments would produce comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters was considerably higher. Consequently, simple comparisons between the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 11):	PAR = exp(Volts*-5.088 + 6.7478)/100
Starboard (sensor 12):	PAR = exp(Volts*-4.978 + 6.7770)/100

Merged solar and PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to eliminate shading effects.

It has been determined by empirical calibration that the PAR values in  $W/m^2$  may be converted to  $E/m^2/s$  by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

## 4) Data Warnings

The transmissometer data were excessively noisy and have been heavily flagged. These data have not been corrected for source decay and the data record included a large step. It is therefore recommended that the transmissometer data from this cruise be used with extreme caution.

## 5) Reference

Fofonoff, N.P. and Millard Jr., R.C. 1983. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

# Surface Underway Data for Cruise Discovery DI191 (11<sup>th</sup> May – 8<sup>th</sup> June 1990)

## 1) Components of the Underway Data Set

The underway data set for Discovery 191 contains the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N Longitude (degrees +ve E) Distance run (km)	A B K
Physics:	Temperature (°C) Salinity (PSU) Optical attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees blowing from) Barometric pressure (mB) Dry bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> )	Y Z 1 a L

## 2) Methodology Overview

#### 2.1) Plumbing

The thermosalinograph and transmissometer pond were fed from the non-toxic supply. A small header tank was included in the non-toxic system between the inlet and the instruments.

#### 2.2) Data Acquisition

Data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

The level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing.

#### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file)

using time as the primary linking key. Data logged as voltages (e.g. PAR) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

## 3) Methodology and Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap filled by interpolation was 1 hour 6 minutes.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary for this cruise.

#### 3.4) Physics

#### Temperature and Salinity

Temperature and salinity were measured using an ODEC (Ocean Data Equipment Corporation) model TSG-103 thermosalinograph, incorporating a remote temperature sensor (thermolinear thermistor) and an inductive-type conductivity cell mounted next to a second thermistor.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1983).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. From this analysis, the required correction was determined as +0.061 PSU. This correction has been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A correction of -0.3°C was determined and this has been applied to the data.

The instrument generally functioned well throughout the cruise, though the record is noisy in parts with several episodes of excessive noise that have been heavily flagged. The salinity record between May 17<sup>th</sup> and May 23<sup>rd</sup> has a curious, almost saw tooth, appearance with instantaneous jumps followed by a linear decrease over several hours. This may not be real. The temperature record indicates a failure of the non-toxic supply pump from 07.15 to 10.20 on 20/5/1990.

#### **Optical Attenuance**

Optical attenuance was measured using a SeaTech 660 nm (red) 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. The data were logged as voltages. These would normally be corrected for light source decay using a ratio correction based on air voltage measured during the cruise and the air voltage measured when the instrument was new. However, neither the air voltage data nor the serial number of the instrument used could be obtained and hence no air correction was possible. The attenuance values were therefore overestimates.

Any values outside the operational limits of the instrument (1-91.3%) were automatically flagged suspect.

The percentage transmission (Volts\*20) was converted to attenuance using the equation:

Attenuance =  $-4.0 \log (\% \text{ Transmission}/100)$ .

Inspection of the data using a graphics workstation showed the data set to have two distinct parts. Prior to 09:30 on May 19th, the record was extremely noisy with numerous spikes of the form usually associated with bubbles in the pond. These data have been heavily flagged. For the remainder of the cruise, the record was exceptionally smooth and clean. This dramatic change occurred after the non-toxic supply came back on line after the failure reported above.

An interesting feature of the record is the occurrence of a number of large peaks with attenuance values in the range 2-12 per metre. Similar peaks were observed in the transmissometer record from Discovery 192.

#### 3.5) Meteorology

#### Air Temperature

The Metpac fitted to Discovery for this cruise included two psychrometers fitted to the port and starboard bridge wings. The instruments were calibrated periodically at the IOS Deacon Laboratory using a water bath. It is not known when the instruments were last calibrated prior to this cruise.

The psychrometer wicks were discovered on the next cruise to be immersed in 'a foul yellow liquid'. It therefore came as no surprise when inspection of the wet bulb data set showed it to be total rubbish with no identifiable credible signal. Consequently, both wet bulb temperature channels were deleted from the data set.

Averaging the port and starboard channels, which generally showed good agreement except for occasional differences of up to 1°C, generated a combined dry bulb temperature channel. The individual channels have not been retained.

#### Wind Velocity

A Meteorological Office type Munro Mk V anemometer and wind vane located on the port side of the ship measured wind velocity. The sensors were calibrated periodically using the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect. No evidence of shadowing by the ship's superstructure was observed.

#### Radiation

Discovery was equipped for this cruise with two PML designed 2-pi PAR scalar irradiance meters mounted in pairs on the port and starboard side of the 'Monkey Island' above the bridge. It must be emphasised that these instruments hemispherical domed sensors, considerably enhancing their light collection efficiency, particularly when the sun was lower in the sky. Consequently, simple comparisons between data from these instruments and other equipment with different geometry must not be attempted.

The data were logged as voltages and calibrated in W/m<sup>2</sup> by BODC using coefficients

determined in February 1990. The calibration equations used were:

Port (sensor 7):	PAR = exp(Volts*4.996 + 6.7545)/100
Starboard (sensor 9):	PAR = exp(Volts*5.062 + 6.7874)/100

A merged PAR channel was produced, after spikes were flagged out, by taking the maximum of the port and starboard values to reduce shading effects.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75.

#### Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mbar over the range 980-1050 mB by the manufacturer. Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars.

The data were examined on a graphics workstation by BODC and any spikes were flagged as suspect.

## 4) Data Warnings

No correction for light source decay has been applied to the transmissometer data.

The thermosalinograph salinity between 17<sup>th</sup> and 23<sup>rd</sup> May exhibits a 'saw tooth' form that has the characteristics of an instrumental artefact.

## 5) Reference

Fofonoff, N.P. and Millard Jr., R.C. (1983). Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

# Surface Underway Data for Cruise Charles Darwin CD47 (25<sup>th</sup> May – 18<sup>th</sup> June 1990)

#### 1) Components of the Underway Data Set

The underway data set for Charles Darwin CD47 contains the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance run (km)	A B K
Biology:	Turner Designs raw fluorescence (nominal mg/m <sup>3</sup> ) Turner Designs chlorophyll (mg/m <sup>3</sup> ) Aquatracka raw fluorescence (Volts) Aquatracka chlorophyll (mg/m <sup>3</sup> )	D G ? !
Physics:	Temperature (°C) Salinity (PSU) Optical attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees from) Solar radiation (W/m <sup>2</sup> ) Dry bulb air temperature (°C) Wet bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> ) Long wave radiation (W/m <sup>2</sup> )	Y Z O a b L /

## 2) Methodology Overview

#### 2.1) Plumbing

The ship was equipped with a pumped non-toxic supply with an inlet approximately 4m below the surface on the starboard side. All ship's wastewater was jettisoned to port to minimise the risk of contamination.

The Aquatracka fluorometer and the transmissometer were located in a light-tight pond fed continuously by this supply, tapped close to the inlet 'upstream' from the system header tank. This was unfortunate: the header tank acts as a debubbler that may have improved the quality of the transmissometer record.

The thermosalinograph and Turner Designs fluorometer were fed from 'downstream' of the header tank. The different plumbing of the two fluorometers produced a time offset with the Aquatracka reacting approximately 1-2 minutes faster to changes in the ambient chlorophyll concentration.

#### 2.2) Data Acquisition

Data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

The Level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set.

## 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. the meteorology) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

## 3) Methodology and Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap filled by interpolation was 3 hours 38 minutes commencing at 16:00 on 15/6/1990.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure did not prove necessary for this cruise.

#### 3.2) Biology

#### <u>Chlorophyll</u>

Chlorophyll was measured by two fluorometers run in parallel, a Turner Designs through-flow and a Chelsea Instruments Aquatracka immersed in a light-tight pond. Both instruments would normally have been calibrated against extracted chlorophyll data. However, due to an oversight, no calibration samples were taken. A small extracted chlorophyll data was set collected as part of the biological process studies. However, these are totally unsuitable for calibration purposes being few in number and unevenly distributed in time.

Consequently, as a best approximation, the calibrations determined for Charles Darwin 46 were applied. The limitations of this are graphically illustrated if one overlays plots of both calibrated channels. Whilst there is reasonable agreement in parts, the Turner Designs value is often twice that of the Aquatracka. For the record, the equations applied were:

#### Aquatracka

chlorophyll (mg/m<sup>3</sup>) = exp (0.953\*V + 0.000832\*PAR - 2.71) (n=84;r<sup>2</sup>=55.4%)

Turner Designs

chlorophyll  $(mg/m^3) = 0.411*Raw_value + 0.485$ 

Prior to calibration, both raw channels were inspected on a graphical workstation and any spikes flagged suspect. Jumps in the Turner Designs data due to uncorrected range changes were eliminated by reducing the data to a common range. However, without the feedback from an extracted chlorophyll data set it is difficult to be sure that no errors have been made in this procedure.

Users of the underway chlorophyll data from this cruise should bear these problems very much in mind and use the data with extreme caution, particularly for applications where absolute rather than relative estimates of chlorophyll are required.

#### 3.3) Physics

#### Temperature and Salinity

Temperature and salinity were measured using an Ocean Data Equipment Corporation (ODEC) TSG-103 thermosalinograph, incorporating a remote temperature sensor (thermistor) and an inductive-type conductivity cell mounted next to a second thermistor.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1982).

Initially, there was a serious problem with the data for this cruise. For much of the cruise, the Level A was incorrectly configured. As a result, the 'calibrated' data produced on the Level C were total garbage. This was overcome at BODC by extensive reworking of the data back to its raw form (ADC counts), which were then reprocessed. This recovery was only possible through diligent work by RVS (including disassembly of the Level A EPROM) to obtain the necessary algorithms and constants. The reprocessing exercise was totally successful: this note is included to inform those who were aware of the problem at the time that it has been cured.

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. This showed a steady linear drift, which was corrected using the equation:

Corrected salinity = Salinity + (0.098 - Record number\*0.000002)

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A constant correction of 0.055°C was determined for the whole cruise and this has been applied to the data.

The salinity record looks good. The temperature is generally good but with noisy patches.

#### Optical Attenuance

Optical attenuance was measured using a 660 nm 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. The data were logged as voltages. Normally, these would be corrected for light source decay, but this was not possible for this cruise due to lack of air correction data. Consequently, the attenuance values have been overestimated to some extent.

Voltages were converted to fractional transmission by dividing by 5 and then to attenuance using the equation:

Attenuance = -4.0 log (Transmission)

Inspection of the data using a graphics workstation showed them to be severely affected by spikes, presumably due to bubbles. The data required very heavy flagging.

The attenuance values were generally higher than one would expect. Particularly worrying is a sudden drop by 0.5 per m when the instrument was cleaned at 12:00 on June 14th. The instrument had been cleaned once earlier in the cruise but it must be concluded that the high values were largely due to an accumulation of dirt on the transmissometer windows. These data should therefore be used with caution.

#### 3.4) Meteorology

#### Multimet System

The Multimet system fitted to Charles Darwin for this cruise contains a broad suite of sensors logged on an integral PC. The raw data were sent to the James Rennell Centre for working up and the calibrated data were sent to BODC to be merged into the underway file. It is not known when the instruments were last calibrated prior to this cruise.

#### Air Temperature

The Multimet on this cruise included three Vector Instruments type aspirated psychrometers. Two were fitted above the wheelhouse, one to port and one to starboard, with the third fitted to the foremast.

Averaging data from all three instruments generated combined wet and dry bulb temperature channels. These showed consistently good (within 1°C and usually much better) agreement. Data from the mast instrument were systematically a little higher than the instruments on the bridge.

#### Wind Velocity

Wind velocity was measured by a Vector Instruments cup anemometer and vane located on the main mast. Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect.

#### Radiation

The Multimet included two Kipp and Zonen type CM5/6 pyranometers and an Eppley longwave radiation sensor mounted on the forward mast. In addition, two PML designed 2-pi PAR scalar irradiance meters were mounted on scaffold poles on either side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the sensors in these instruments are quite different. The PAR meters had hemispherical domed sensors whilst the solarimeters were equipped with cosine collectors. At midday on the equator, both types of instruments would produce comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters was considerably higher. Consequently, simple comparisons between

the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 11):	PAR = exp(Volts*-5.088 + 6.7478)/100
Starboard (sensor 12):	PAR = exp(Volts*-4.978 + 6.7770)/100

Merged solar and PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to reduce shading effects.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

## 4) Data Warnings

The transmissometer data were excessively noisy and have been heavily flagged. There was strong evidence that the windows were dirty for much of the cruise. No correction for source decay was possible as no air readings were taken during the cruise.

Calibration of the fluorometers proved impossible as no calibration samples were collected. Calibrations determined from the previous cruise have been used. This has severely compromised the absolute accuracy and therefore the quality of the data.

## 5) References

Fofonoff, N.P. and Millard Jr., R.C. 1983. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

## Surface Underway Data for Cruise Discovery DI192 (9<sup>th</sup> to 27<sup>th</sup> June 1990)

## 1) Components of the Underway Data Set

The underway data set for Discovery 192 contains the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance Run (km)	A B K
Chemistry:	Dissolved oxygen ( $\mu$ M) TCO <sub>2</sub> ( $\mu$ mol/kg) pCO <sub>2</sub> ( $\mu$ atm) Alkalinity ( $\mu$ Eq/kg) Nitrate plus nitrite ( $\mu$ M) Nitrite ( $\mu$ M) Phosphate ( $\mu$ M) Silicate ( $\mu$ M)	Q H E T U V W
Biology:	Raw through-flow fluorescence (nominal mg/m <sup>3</sup> ) Chlorophyll (mg/m <sup>3</sup> )	D G
Physics:	Temperature (°C) Salinity (PSU Optical Attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees from) Solar radiation (W/m <sup>2</sup> ) Barometric Pressure (mB) Dry bulb air temperature (°C) Port dry bulb air temperature (°C) Starboard dry bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> )	Y Z 0 1 a 2 4 L

## 2) Methodology Overview

#### 2.1) Plumbing

Water from the non-toxic pump was fed into a 130 litre black plastic header tank situated above the laboratory to act as a debubbler. The supply from this tank was split to feed the underway chemistry measurements and the fluorometer. Each branch was equipped with a control valve and flow meter to enable the flow rates to each instrument to be controlled. The thermosalinograph and transmissometer pond were

fed separately from the non-toxic supply.

#### 2.2) Data Acquisition

For most parameters, data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

In some cases, for example dissolved oxygen, the analytical equipment included an integral data logger, such as a PC. In these cases, data were transferred to the Level C on floppy disk.

The level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set.

#### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>, TCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR, nutrients) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

## 3) Methodology and Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was

not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The largest gap interpolated was 10 hours 9 minutes, commencing at 13:52 on 10/6/1990.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure did not prove necessary for this cruise.

#### 3.2) Chemistry

#### **Dissolved oxygen**

Dissolved oxygen was measured using an Endeco type 1125 pulsed dissolved oxygen controller multiplexed with two Endeco type 1128 dissolved oxygen probes. The probes were immersed in a Perspex cell (approx. 1 litre) fed at approximately 2 litres per minute.

The oxygen system had no way of determining salinity. Consequently, the data were logged and calibrated with an input salinity of zero to all computations. Calibration was achieved by regressing the output from the probe deemed more stable (probe 1) against measurements made using the Winkler method on samples taken from the probe outflow. Calibration samples were taken approximately every six hours.

Two calibration curves were established:

12/6/90 17:52 to 15/6/90 18:04	Calibrated =	(Raw-212.688)/0.63369
		(R <sup>2</sup> =94%)
15/6/90 18:04 to 18/6/90 06:10	Calibrated =	(Raw+236.84)/1.96436
		$(R^2 = 88\%)$

The calibrated data at zero salinity were then corrected to in-situ salinity using the equations:

 $O_2 \text{ (actual)} = O_2 \text{ (zero salinity) / Gamma}$   $Gamma = \exp(S^*(A6 + A7/T + A8/T^2))$ where: S = Salinity (PSU) T = Absolute temperature (K) A6 = 0.017674 A7 = -10.754 A8 = 2140.7

Data were logged outside the time span covered by the above calibrations. These were flagged suspect during screening.

#### <u>Alkalinity</u>

Total alkalinity was measured by a potentiometric titration method. The system comprised a Metrohm 655 autoburette, a Metrohm 605 pH meter and a closed titration cell with a defined volume of 128.59 ml. The 5 ml burette and the cell were jacketed with a Lauda water bath set to maintain a stable temperature of 25°C.

The titration was driven by a Hewlett Packard 9825B desktop calculator, which also logged the titration curve (volume of 0.2M HCl versus Ingold combination electrode potential (mV)). Alkalinity was computed from the titration curve using a Hewlett Packard Language translation of the program of Bradshaw et al. (1981).

After the cruise, the cell and burette volumes were recalibrated and used to correct the results computed on board. Thermosalinograph salinities were used to convert the data into units of  $\mu$ Eq/kg.

#### <u>pCO</u>2

Continuous measurements of  $pCO_2$  were carried out using a "shower head" type equilibrator, similar to that described in Weiss (1981), from which the gas phase was sampled at approximately 7-minute intervals. The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample.

The equilibrated gas was carried in hydrogen, passed over a catalyst that converted the  $CO_2$  to methane. The gas stream was passed to a flame ionisation detector (FID), Hewlett-Packard 5890A-GC which used compressed air as the combustion make-up gas.

Concentrations of  $CO_2$  in the equilibrated gas were compared every 15 minutes with marine air, dried to -30°C dew point (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data are given at in-situ temperature and corrected for atmospheric pressure changes, in units of microatmospheres.

Precision studies have shown a standard deviation of no more than  $1.5\mu$  atms for the method. Repeated measurements of standards show a typical coefficient of variation to be no more than 0.2%.

#### <u>TCO</u><sub>2</sub>

Total inorganic carbon (TCO<sub>2</sub>) was measured coulometrically. Sampling rate was approximately one analysis every 6 minutes during a 7-day box grid survey. The instrument used was a Coulometrics Inc. model 5011 coulometer. For fuller details of the techniques used, see Robinson and Williams (1991). The mean analytical precision was estimated at 0.5-1  $\mu$ mol/kg and the mean accuracy estimated for the method by intercalibration during the 1989 North Atlantic Bloom Experiment was 1

 $\mu$ mol/kg. The data are quoted in  $\mu$ mol/kg, which was computed from the measured data in  $\mu$ M by multiplying by (1000+sigmaT/1000). SigmaT was computed from calibrated thermosalinograph temperature and salinity.

#### **Nutrients**

The nutrients were measured using a Technicon AA2 autoanalyser connected to the pumped seawater supply by a continuous filter block (Morris et al., 1978). The chemistries used were:

- Nitrate: Reduced to nitrite by a Cu/Cd coil, then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish-purple azo dye.
- Nitrite: As for nitrate without the reduction step.
- Phosphate: Reduction of a phosphomolybdate complex in acid solution to 'molybdenum blue' by ascorbic acid with sensitivity enhanced by the catalytic action of antimony potassium tartrate.
- Silicate: Reduction of a silicomolybdate solution to 'molybdenum blue' by ascorbic acid with the addition of oxalic acid to eliminate interference from phosphates.

The colorimeter outputs were logged by a Level A connected to the chart recorder inputs. The system was calibrated by running distilled water washes to determine baseline and sets of four standards. Standards were run at least once per day.

The following processing procedures were adopted by BODC to convert the raw voltage streams into nutrient concentrations.

The raw voltages were screened on a graphics workstation to differentiate between signals due to baselines (flagged 'Z'), standards (flagged '1', '2', '3' or '4' according to concentration) or actual ambient concentrations. Any instrumental spikes were flagged suspect ('S').

The data were then segmented into internally consistent subsets (i.e. taking account of any instrumental change such as gain or baseline alterations documented by the analyst), with constant or linearly drifting baselines.

For each segment, the baseline as a function of time was fitted to a linear regression, which was applied to standardise the segment to a baseline of zero. For the silicate channel, which has particular problems associated with instrument drift, a linear regression of on-line drift for each segment was calculated by considering the difference between on-line readings immediately prior to and after baselines.

The standard voltages were then used to construct calibration curves to convert raw voltages into nutrient concentrations. These were then applied on a segment-by-segment basis to the data stream. All baseline and calibration equations were checked

manually before they were used. Once concentrations had been calculated the custom baseline and standard flags were changed to suspect.

The data were subsequently quality controlled by inspection on a graphics workstation with particular attention paid to the concentrations obtained for the standards. Any data identified as suspect were flagged. These checks included comparative screening between the nutrient channels.

Two additional corrections were applied. First, the nutrient time channels were adjusted to correct for the delay incurred whilst the sample passed through the complex plumbing of the autoanalyser. Secondly, empirically determined corrections were applied to correct for the difference in optical density between the standards, made up in Milli-Q water, and seawater.

The correction values used were:

Nutrient	Time Shift	Salt correction
NO <sub>3</sub>	-12 mins.	-0.02 μM
NO <sub>2</sub>	-8 mins.	-0.04 µM
PO <sub>4</sub>	-10 mins.	-0.05 μM
Si	-12 mins.	-0.11 μM

Note that the same autoanalyser gain setting was used throughout the cruise, which allowed the simplistic salt correction quoted above to be used. Due to the chemistry used for nitrate analysis, interference from nitrite is inevitable. The nitrate channel has been processed throughout as nitrate+nitrite and no attempt has been made to correct for nitrite.

As a final processing step, small negative values in the data were converted to zero to prevent them creating havoc with contouring software. Values of zero flagged 'G' should therefore be taken to mean 'below detection limit'.

#### 3.3) Biology

#### <u>Chlorophyll</u>

Chlorophyll was measured by a Turner Designs through-flow fluorometer calibrated against extracted chlorophyll data. Samples were drawn from the non-toxic supply and filtered through GFF filter papers. Two samples were filtered: one for immediate analysis and the other frozen. The samples analysed on board were extracted in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

Subsequent events showed that the instrument on board Discovery was malfunctioning and consequently the frozen samples were extracted and analysed post-cruise at PML. The calibration of the underway fluorometer was undertaken using the extracted data set obtained from the frozen samples.

The raw fluorometer data were first screened on a graphics workstation and any spikes flagged. Next, steps in the data set due to uncorrected range changes were identified and the data channel reduced to a single range.

The extracted data set comprised 82 samples taken at all stages of the diel cycle. Calibration was achieved by multiple regression of the log of the extracted chlorophyll value against two predictors, the log of the raw fluorometer reading and calibrated, merged PAR ( $W/m^2$ ) averaged over a 3 minute interval. The cruise data were treated as a single population.

The calibration equation used was:

chlorophyll (mg/m<sup>3</sup>) = exp (0.690\*log(raw\_reading) + 0.000636\*PAR - 2.61)

The adjusted  $R^2$  for this regression was 61.4 per cent.

#### 3.4) Physics

#### Temperature and Salinity

Temperature and salinity were measured using an ODEC (Ocean Data Equipment Corporation) model TSG-103 Thermosalinograph, incorporating a remote temperature sensor (thermolinear thermistor) and an inductive-type conductivity cell mounted next to a second thermistor.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1983).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. From this analysis, the required correction was determined as +0.0273 PSU prior to the cleaning of the instrument on 21/6/1990 and -0.023 PSU after that operation. These corrections have been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A correction of -0.21°C was determined and this has been applied to the data.

The instrument functioned well throughout the cruise, producing a data set of good quality by thermosalinograph standards. The temperature record indicates a failure of the non-toxic supply pump from 12.30 to 13.00 on 19/6/1990 with intermittent problems until 15.00.

#### Optical Attenuance

Optical attenuance was measured using a SeaTech 660 nm (red) 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. The data were logged as voltages. These would normally have been corrected for light source decay using a ratio correction based on air voltage measured during the cruise and the air voltage measured when the instrument was new. However, neither the air voltage data nor the serial number of the instrument used could be obtained and hence no air correction was possible. The attenuance values were therefore overestimated.

Any values outside the operational limits of the instrument (1-91.3%) were automatically flagged suspect.

The percentage transmission (Volts\*20) was converted to attenuance using the equation:

Attenuance =  $-4.0 \log (\% \text{ Transmission}/100)$ .

Inspection of the data using a graphics workstation showed them to be relatively free from the 'bubble spikes' that can plague underway transmissometer data. The few spikes that were identified were flagged out.

A worrying feature of the data is a jump in attenuance from 0.4 per metre to 0.8 per metre after a continuous period of severe noise (flagged out as suspect) occupying the whole of 15/6/1990. In addition, the characteristics of the record change with considerably higher variance after 15/6. This may indicate that the transmissometer failed and was either repaired or replaced and not reported to BODC. Chlorophyll levels show no dramatic change over the period in question and users of the data should seriously consider whether this step is real.

An interesting feature of the record is the occurrence of a number of large peaks with attenuance values in the range 2-12 per metre. Comparing the peaks against the cruise track shows them to have a spatial consistency but they do not correlate with peaks in chlorophyll (indeed the largest peak shows a strong negative correlation with chlorophyll). Their cause is unknown.

#### 3.5) Meteorology

#### Air Temperature

The Metpac fitted to Discovery for this cruise included two psychrometers fitted to the port and starboard bridge wings. The instruments were calibrated periodically at the IOS Deacon Laboratory using a water bath. It is not known when the instruments were last calibrated prior to this cruise.

The psychrometer wicks were discovered on this cruise to be immersed in 'a foul yellow liquid'. It therefore came as no surprise when inspection of the wet bulb data set showed it to be total rubbish with no identifiable credible signal. Consequently, both

wet bulb temperature channels were deleted from the data set.

Averaging the port and starboard channels generated a combined dry bulb temperature channel. At times, the port and starboard readings differ by as much as 5°C, but for much of the cruise both instruments were in good agreement. Both source channels have been left in the data set to allow users to assess the uncertainty in the merged data channel.

Users would be well advised to use the air temperature data from this cruise with some degree of caution. At the very least, time series plots of all three channels should be examined prior to using the data.

#### Wind Velocity

A Meteorological Office type Munro Mk V anemometer and wind vane located on the port side of the ship measured wind velocity. The sensors were calibrated periodically using the Bracknell wind tunnel. It is not known when the instrument was last calibrated prior to this cruise.

Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect. An intercomparison, based on derived statistics, with data from Charles Darwin 47 (which was in the same area) showed the data to be encouragingly similar.

#### **Radiation**

Discovery was equipped with Kipp and Zonen type CM5/6 pyranometers and PML designed 2-pi PAR scalar irradiance meters mounted in pairs on the port and starboard side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the sensors in these instruments were quite different. The PAR meters had hemispherical domed sensors whilst the solarimeters were fitted with cosine collectors. At midday on the equator, both types of instruments would produce comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters was considerably higher. Consequently, simple comparisons between the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 7):	PAR = exp(Volts*4.996 + 6.7545)/100
Starboard (sensor 9):	PAR = exp(Volts*5.062 + 6.7874)/100

Merged solar and PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to reduce shading effects.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

#### Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mB over the range 980-1050 mB by the manufacturer. Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars.

The data were examined on a graphics workstation by BODC and any spikes were flagged as suspect.

## 4) Data Warnings

The transmissometer record exhibits a significant increase in attenuance after a marked break in the record. This may not be real. No correction for light source decay has been applied.

The air temperature data from this cruise should be used with caution. At the very least, the differences between the port and starboard instruments should be examined.

## 5) References

Bradshaw, A.L., Brewer, P.G., Shafer, K. and Williams, R.T. 1981. Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program. *Earth Planet. Sci. Lett.* <u>55</u> : 99-115.

Fofonoff, N.P. and Millard Jr., R.C. 1983. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Morris, A.W., Howland, R.J.M., and Bale, A.J. 1978. A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. *Est. Coast. Mar. Sci.* <u>6</u>, 105-109.

Robinson, C. and Williams, P.J.IeB. 1991. Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chem* <u>34</u>: 157-175.

Weiss, R.F. 1981 Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci* <u>19</u> : 611-616

# Surface Underway Data for Cruise Charles Darwin CD53 (18<sup>th</sup> September to 24<sup>th</sup> October 1990)

## 1) Components of the Underway Data Set

The underway data set for Charles Darwin 53 contains the following data channels. The single characters at the end of each line are the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance Run (km) Bathymetric depth (m)	A B K J
Chemistry:	pCO <sub>2</sub> (μatm) Nitrate plus nitrite (μΜ) Phosphate (μΜ) Silicate (μΜ)	E T V W
Biology:	Raw Aquatracka fluorescence (Volts) Chlorophyll (mg/m <sup>3</sup> )	? !
Physics:	Temperature (°C) Salinity (PSU)	C F
Meteorology:	Barometric Pressure (mB) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> )	1 L

## 2) Methodology Overview

#### 2.1) Plumbing

Water from the non-toxic pump was fed via a header tank (to act as a debubbler) to the  $pCO_2$  equilibrator and autoanalyser. The thermosalinograph was plumbed directly into the non-toxic supply. The fluorometer was placed in an enclosed pond fed from the non-toxic supply.

#### 2.2) Data Acquisition

Data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

The level C included a suite of calibration software that was used to apply initial

calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set. A separate PC logged the pCO<sub>2</sub> data.

#### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR, nutrients) were converted to engineering units.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels.

## 3) Methodology And Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined using dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap interpolated for this cruise was 3 hours 52 minutes, commencing at 19:44 on 18/9/1990.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary for this cruise.

Bathymetric depth was determined using a SimRad echo sounder logged automatically by the ABC system. The Level C software applied Carter's Tables corrections. The data set required heavy flagging during quality control, mainly as the result of large numbers of spurious shallow reflections.

## 3.2) Chemistry

#### <u>pCO</u>2

Continuous measurements of  $pCO_2$  were carried out using a "shower head" type equilibrator, similar to that described in Weiss (1981), from which the gas phase was sampled at approximately 7-minute intervals. The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample.

The equilibrated gas was carried in hydrogen, passed over a catalyst that converted the  $CO_2$  to methane. The gas stream was passed to a flame ionisation detector (FID), Hewlett-Packard 5890A-GC which used compressed air as the combustion make-up gas.

Concentrations of  $CO_2$  in the equilibrated gas were compared every 15 minutes with marine air, dried to -30°C dew point (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data were given at in-situ temperature and corrected for atmospheric pressure changes, in units of microatmospheres.

Precision studies have shown a standard deviation of no more than  $1.5_{\mu}$  atms for the method. Repeated measurements of standards show a typical coefficient of variation to be no more than 0.2%.

#### **Nutrients**

The nutrients were measured using a Technicon AA2 autoanalyser connected to the pumped seawater supply by a continuous filter block (Morris et al., 1978). The chemistries used were:

- Nitrate: Reduced to nitrite by a Cu/Cd coil, then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish-purple azo dye.
- Nitrite: As for nitrate without the reduction step.
- Phosphate: Reduction of a phosphomolybdate complex in acid solution to 'molybdenum blue' by ascorbic acid with sensitivity enhanced by the catalytic action of antimony potassium tartrate.
- Silicate: Reduction of a silicomolybdate solution to 'molybdenum blue' by ascorbic acid with the addition of oxalic acid to eliminate interference from phosphates.

The colorimeter outputs were logged by a Level A connected to the chart recorder inputs. The system was calibrated by running distilled water washes to determine baseline and sets of four standards. Standards were run at least once per day.

The following processing procedures were adopted by BODC to convert the raw voltage streams into nutrient concentrations.

The raw voltages were screened on a graphics workstation to differentiate between signals due to baselines (flagged 'Z'), standards (flagged '1', '2', '3' or '4' according to concentration) or actual ambient concentrations. Any instrumental spikes were flagged suspect ('S').

The data were then segmented into internally consistent subsets (i.e. taking account of any instrumental change such as gain or baseline alterations documented by the analyst), with constant or linearly drifting baselines.

For each segment, the baseline as a function of time was fitted to a linear regression, which was applied to standardise the segment to a baseline of zero. For the silicate channel, which has particular problems associated with instrument drift, a linear regression of on-line drift for each segment was calculated by considering the difference between on-line readings immediately prior to and after baselines.

The standard voltages were then used to construct calibration curves to convert raw voltages into nutrient concentrations. These were then applied on a segment by segment basis to the data stream. All baseline and calibration equations were checked manually before they were used. Once concentrations had been calculated the custom baseline and standard flags were changed to suspect.

The data were subsequently quality controlled by inspection on a graphics workstation with particular attention paid to the concentrations obtained for the standards. Any data identified as suspect were flagged. These checks included comparative screening between the nutrient channels.

The nutrient time channels were adjusted to correct for the delay incurred whilst the sample passes through the complex plumbing of the autoanalyser. Although the standards were made up in Millipore water, it proved impossible to apply any correction for difference in optical density ('salt correction'). This was because no record could be found of the gain settings used. The values are therefore overestimated to a small degree.

The time correction values used were:

Nutrient	Time Shif	ť
NO <sub>3</sub>	-12	mins.
PO <sub>4</sub>	-10	mins.
Si	-12	mins.

Due to the chemistry used for nitrate analysis, interference from nitrite is inevitable. The nitrate channel has been processed throughout as nitrate+nitrite. No nitrite channel is available: the logged autoanalyser channel only contained random noise.

As a final processing step, small negative values in the data were converted to zero to prevent them creating havoc with contouring software. Values of zero flagged 'G' should therefore be taken to mean 'below detection limit'.

## 3.3) Biology

#### <u>Chlorophyll</u>

Chlorophyll was measured by a Chelsea Instruments Aquatracka logarithmic response fluorometer calibrated against extracted chlorophyll data. Samples were drawn from the non-toxic supply and filtered through GFF filter papers. Two samples were filtered: one for immediate analysis and the other frozen. The samples analysed on board were extracted in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

The raw fluorometer data were first screened on a graphics workstation and any spikes flagged. A calibration was then undertaken by linear regression of fluorometer voltage against the log of the chlorophyll concentration. The cruise data were treated as a single population.

The calibration equation obtained was:

chlorophyll (mg/m<sup>3</sup>) = exp (
$$3.66^{*}(V) - 5.72$$
)

The adjusted  $R^2$  for this regression was 56.4 per cent.

There was a problem with this calibration. The samples taken for the calibration only span a narrow range of chlorophyll concentrations from 0.02 to 0.14 mg/m<sup>3</sup> that correspond to fluorometer voltages up to approximately 1 Volt. These adequately cover the biologically inactive waters sampled for the bulk of this cruise. However, the fluorometer record indicates two localised blooms encountered from 00:00 to 01:30 on October 16th (voltages up to 2.5V) and 14:30 to 15:00 on October 26th (voltages up to 2.0V).

Extrapolation of a logarithmic calibration to 2.5 times its determined limits inevitably results in erroneous results. As a consequence, all chlorophylls obtained from raw values in excess of 1 Volt have been flagged as suspect.

## 3.4) Physics

#### Temperature and Salinity

Temperature and salinity were measured using an ODEC (Ocean Data Equipment Corporation) model TSG-103 Thermosalinograph, incorporating a remote temperature sensor (thermolinear thermistor) and an inductive-type conductivity cell mounted next to a second thermistor.

The remote temperature sensor was supplied by water from the intake side of the non-

toxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1983).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. From this analysis, the required correction was determined as +0.079 PSU prior to the cleaning of the instrument on 22/9/1990 and -0.015 PSU after this operation. These corrections have been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD data. A correction of +0.03°C was determined and this has been applied to the data.

The instrument functioned well throughout the cruise, producing a data set of good quality by thermosalinograph standards.

#### 3.5) Meteorology

#### Radiation

Two PML designed 2-pi PAR meters were mounted on the port and starboard side of the 'Monkey Island' above the bridge. It must be emphasised that these instruments have hemispherical domed collectors and produce data that are not directly comparable with cosine collectors (vector irradiance sensors).

The meters were logged as voltages and calibrated in W/m<sup>2</sup> by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 11):	$PAR = exp(Volts^{(-5.088)} + 6.7478)/100$
Starboard (sensor 12):	$PAR = exp(Volts^{(-4.978)} + 6.7770)/100$

Note that these calibrations have negative slopes as the instruments were wired the wrong way round causing the sign of the voltage to be inverted.

Merged PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to eliminate shading effects. This procedure was only possible up until 27th September when the port sensor failed. The 'merged' channel from this point contains the data from the starboard sensor alone. A high pass filter, set at 605  $W/m^2$ , was applied to flag what are presumed to be erroneously high values as suspect.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75.

#### Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mB over the range 980-1050 mB by the manufacturer. Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars.

The data were examined on a graphics workstation by BODC and any spikes flagged. The instrument appears to have functioned well throughout the cruise.

## 4) Data Warnings

The 'merged' PAR channel only contained data from one sensor for much of the cruise. The data were therefore more susceptible to underestimation caused by shading events.

The chlorophyll calibration was inapplicable to small isolated patches of relatively high chlorophyll encountered during the cruise.

## 5) References

Fofonoff, N.P. and Millard Jr., R.C. 1983. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Morris, A.W., Howland, R.J.W. and Bale A.J. 1978. A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. *Est. Coast. Mar. Sci.* <u>6</u>, 105-109.

Weiss, R.F. 1981 Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci* <u>19</u> : 611-616

# Surface Underway Data for Cruise Charles Darwin CD60 (13<sup>th</sup> June – 2<sup>nd</sup> July 1991)

## 1) Components of the Underway Data Set

The underway data set for Charles Darwin 60 contained the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance Run (km) Bathymetric depth (m)	A B K J
Chemistry:	Dissolved oxygen ( $\mu$ M) TCO <sub>2</sub> ( $\mu$ mol/kg) pCO <sub>2</sub> ( $\mu$ atmospheres) Ammonia ( $\mu$ M) Nitrate plus nitrite ( $\mu$ M) Nitrite ( $\mu$ M) Phosphate ( $\mu$ M) Calcite (mg Ca/m <sup>3</sup> )	Q H E P T U V –
Biology:	Turner Designs raw fluorescence (nominal mg/m <sup>3</sup> ) Turner Designs chlorophyll (mg/m <sup>3</sup> ) Aquatracka raw fluorescence (Volts) Aquatracka chlorophyll (mg/m <sup>3</sup> )	D G ? !
Physics:	Temperature (°C) Salinity (PSU) Optical Attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees from) Solar radiation (W/m <sup>2</sup> ) Barometric Pressure (mB) Dry bulb air temperature (°C) Wet bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> ) Long wave radiation (W/m <sup>2</sup> )	Y Z O 1 a b L

## 2) Methodology Overview

#### 2.1) Plumbing

Water from the non-toxic pump was fed into a 130 litre black plastic header tank situated above the laboratory to act as a debubbler. The supply from this tank was split to feed the underway chemistry measurements and the Turner Designs fluorometer. Each branch was equipped with a control valve and flow meter to enable the flow rates to each instrument to be controlled. The thermosalinograph was fed separately from the non-toxic supply, via the non-toxic supply header tank. The pond containing the transmissometers and the Aquatracka fluorometer were fed from the non-toxic supply tap fitted between the inlet manifold and the header tank.

#### 2.2) Data Acquisition

For most parameters, data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

In some cases, for example dissolved oxygen, the analytical equipment included an integral data logger, such as a PC. In these cases, data were transferred to the Level C on floppy disk.

The level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set once this processing was complete.

#### 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>, TCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR, nutrients) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

## 3) Methodology and Calibration Procedures

#### 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap interpolated for this cruise was 8 hours 22 minutes, commencing at 00:06 on 14/6/1991.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary for this cruise.

Bathymetric depth was measured using a SimRad echo sounder logged by the ABC systems. Software on the Level C was used to apply Carter's Tables corrections to the data.

#### 3.2) Chemistry

#### **Dissolved oxygen**

Dissolved oxygen was measured using an Endeco type 1125 pulsed dissolved oxygen controller multiplexed with two Endeco type 1128 dissolved oxygen probes. The probes were immersed in a Perspex cell (approx. 1 litre) fed at approximately 2 litres per minute.

The oxygen system had no way of determining salinity. Consequently, the data were logged and calibrated with an input salinity of zero to all computations. Calibration was achieved by regressing the output from the probe deemed more stable against measurements made using the Winkler method on samples taken from the probe outflow. Calibration samples were taken approximately every six hours. The oxygen channel for this cruise has been derived by taking data at different times from both of the probes (designated probe 2 and probe 3 to reflect their logging channels).

Four calibration curves were established, the first taking data from probe 2 and the
other 3 from probe 3:

15/6/91 08:41 to 16/6/91 13:16	Calibrated =	(Raw+102.14)/1.6943 (R <sup>2</sup> =65%)
16/6/91 17:26 to 22/6/91 15:18	Calibrated =	(Raw-146.41)/0.6044 (R <sup>2</sup> =99%)
22/6/91 15:23 to 27/6/91 01:08	Calibrated =	(Raw-191.96)/0.5075 (R <sup>2</sup> =88%)
27/6/91 17:44 to 02/7/91 15:40	Calibrated =	(Raw-157.67)/0.6189 (R <sup>2</sup> =99%)

The first calibration was extrapolated in time to provide data between 13:16 and 17:26 on 16/6/91. Data for the interval from 01:08 to 17:44 on 27/6/91 were obtained by a linear interpolation between the calibrations on either side. The quality of the data from probe 3 is markedly better than that from probe 2 (clearly demonstrated by the regression statistics) but the former probe was not operational until June 16th.

The calibrated data at zero salinity were then corrected to in-situ salinity using the equations:

 $O_2 \text{ (actual)} = O_2 \text{ (zero salinity) / Gamma}$   $Gamma = \exp(S^*(A6 + A7/T + A8/T^2))$ where: S = Salinity (PSU) T = Absolute temperature (K) A6 = 0.017674 A7 = -10.754 A8 = 2140.7

From time to time gaps in the thermosalinograph record meant that no temperature or salinity data were available for the oxygen computations. In these cases, a default salinity of 35.0 and the probe temperature logged by the oxygen system were used. Initially, the points computed in this manner were flagged, but subsequent examination of the data set on a graphics workstation showed no anomalies in the flagged data points and consequently the flags were removed.

## <u>pCO</u>2

Continuous measurements of pCO<sub>2</sub> were carried out using a "shower head" type equilibrator, similar to that described in Weiss (1981), from which the gas phase was sampled at approximately 7-minute intervals. The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample.

The equilibrated gas was carried in hydrogen, passed over a catalyst that converted the CO<sub>2</sub> to methane. The gas stream was passed to a flame ionisation detector (FID),

Hewlett-Packard 5890A-GC which used compressed air as the combustion make-up gas.

Concentrations of CO<sub>2</sub> in the equilibrated gas were compared every 15 minutes with marine air, dried to -30°C dewpoint (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data were given at in-situ temperature and corrected for atmospheric pressure changes, in units of microatmospheres.

Precision studies have shown a standard deviation of no more than  $1.5\mu$  atms for the method. Repeated measurements of standards show a typical coefficient of variation to be no more than 0.2%.

## <u>TCO</u><sub>2</sub>

Total inorganic carbon (TCO<sub>2</sub>) was measured coulometrically. Sampling rate was one analysis approximately every 6 minutes. The instrument used was a Coulometrics Inc. model 5011 coulometer. For fuller details of the techniques used, see Robinson and Williams (1991). The mean analytical precision was estimated at 0.5-1  $\mu$ mol/kg and the mean accuracy estimated for the method by intercalibration during the 1989 North Atlantic Bloom Experiment was 1  $\mu$ mol/kg. The data were supplied in  $\mu$ mol/kg, which was computed from the measured data in  $\mu$ M by multiplying by (1000+sigmaT/1000). SigmaT was computed from calibrated thermosalinograph temperature and salinity.

This cruise was designed to study coccolithophores. Consequently, unlike any other BOFS cruise, the  $TCO_2$  apparatus was fed via a continuous filter block (Morris et al., 1978) to prevent calcite-rich particulate matter making equilibration times excessive.

## Nutrients

The nutrients were measured using a Technicon AA2 autoanalyser connected to the pumped seawater supply by a continuous filter block (Morris et al., 1978). The chemistries used were:

- Nitrate: Reduced to nitrite by a Cu/Cd coil, then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish-purple azo dye.
- Nitrite: As for nitrate without the reduction step.
- Phosphate: Reduction of a phosphomolybdate complex in acid solution to 'molybdenum blue' by ascorbic acid with sensitivity enhanced by the catalytic action of antimony potassium tartrate.

Ammonia: Production of an indophenol blue complex at optimum pH (10.6) and

#### temperature (55°C)

The colorimeter outputs were logged by a Level A connected to the chart recorder inputs. The system was calibrated by running distilled water washes to determine baseline and sets of four standards. Standards were run at least once per day.

The following processing procedures were adopted by BODC to convert the raw voltage streams into nutrient concentrations.

The raw voltages were screened on a graphics workstation to differentiate between signals due to baselines (flagged 'Z'), standards (flagged '1', '2', '3' or '4' according to concentration) or actual ambient concentrations. Any instrumental spikes were flagged suspect ('S').

The data were then segmented into internally consistent subsets (i.e. taking account of any instrumental change such as gain or baseline alterations documented by the analyst), with constant or linearly drifting baselines.

For each segment, the baseline as a function of time was fitted to a linear regression, which was applied to standardise the segment to a baseline of zero.

The standard voltages were then used to construct calibration curves to convert raw voltages into nutrient concentrations. These were then applied on a segment-by-segment basis to the data stream. All baseline and calibration equations were checked manually before they were used. Once concentrations had been calculated the custom baseline and standard flags were changed to suspect.

The data were subsequently quality controlled by inspection on a graphics workstation with particular attention paid to the concentrations obtained for the standards. Any data identified as suspect were flagged. These checks included comparative screening between the nutrient channels.

The nutrient time channels were adjusted to correct for the delay incurred whilst the sample passes through the complex plumbing of the autoanalyser. No salt corrections (corrections for difference in optical density between sample and standards) were applied as the standards were made up in nutrient-free seawater.

Nutrient	Time Shif	ť
NO <sub>3</sub>	-12	mins.
NO <sub>2</sub>	-8	mins.
PO <sub>4</sub>	-10	mins.
NH <sub>4</sub>	-9	mins.

Due to the chemistry used for nitrate analysis, interference from nitrite is inevitable. The nitrate channel has been processed throughout as nitrate+nitrite and no attempt has been made to correct for nitrite.

As a final processing step, small negative values in the data were converted to zero to

prevent them creating havoc with contouring software. Values of zero flagged 'G' should therefore be taken to mean 'below detection limit'.

## Calcite

The primary objective of this cruise was the study of coccolithophores. Consequently, a continuous measurement of the calcite concentration, i.e. an estimate of coccolith abundance, was required. This was achieved by calibration of the 531nm transmissometer against calcite determinations on discrete water samples (expressed as mg Ca/m<sup>3</sup>). A multiple regression technique incorporating chlorophyll to eliminate pigment interference was used.

The calibration equation derived was:

Calcite = (Attenuance<sub>531</sub> - (0.157 + 0.32\*Chlorophyll)/0.00191 (r<sup>2</sup>=86%)

When the calibration was applied any datacycles that did not have both attenuance and chlorophyll values had their calcite value set to null.

# 3.3) Biology

## <u>Chlorophyll</u>

Chlorophyll was measured by two fluorometers run in parallel, a Turner Designs through-flow and a Chelsea Instruments Aquatracka immersed in a light-tight pond. Both instruments were calibrated against extracted chlorophyll data. Samples were drawn from the non-toxic supply and filtered through GF/F filter papers. Two samples were filtered: one for immediate analysis and the other frozen. The samples analysed on board were extracted in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

No problems were reported with the bench fluorometer used on the cruise and the extracted chlorophyll data set obtained at sea was used for the fluorometer calibrations.

Prior to calibration, both raw fluorometer channels were screened on a graphics workstation and any spikes flagged. Next, steps in the Turner Designs data set due to uncorrected range changes were identified and the data channel reduced to a single range.

Due to the wide range of phytoplankton communities encountered on this cruise, the chlorophyll calibration was segmented empirically by grouping together calibration points of exhibiting similar fluorescence yields. Calibration equations were determined by multiple regression of the log of the extracted chlorophyll value against two predictors, the log of the raw fluorometer reading (Turner Designs) or voltage (Aquatracka) and calibrated, merged PAR (W/m<sup>2</sup>) averaged over a 3 minute interval.

The following calibration equations were determined:

**Turner Designs** 

14/6/1991 18:00 to 18/6/1991 12:00

chlorophyll (mg/m<sup>3</sup>) = exp  $(1.78*\log(raw_reading) + 0.0*PAR + 6.02)$ 

18/6/1991 12:01 to 23/6/1991 22:00

chlorophyll (mg/m<sup>3</sup>) = exp  $(1.31*\log(raw_reading) + 0.00176*PAR + 4.19)$ 

23/6/1991 22:01 to 30/6/1991 06:00

```
chlorophyll (mg/m^3) = exp (0.796*log(raw_reading) + 0.000984*PAR + 2.57)
```

30/6/1991 06:01 to 2/7/1991 16:00

chlorophyll (mg/m<sup>3</sup>) = exp  $(1.13*\log(raw_reading) + 0.00155*PAR + 2.7)$ 

Aquatracka

14/6/1991 20:00 to 23/6/1991 22:00

chlorophyll (mg/m<sup>3</sup>) = exp (3.27\*V + 0.00153\*PAR - 2.91)

23/6/1992 22:01 to 30/6/1991 03:00

chlorophyll (mg/m<sup>3</sup>) = exp ( $2.70^{*}V + 0.0018^{*}PAR - 2.33$ )

30/6/1991 03:01 to 2/7/1991 16:00

chlorophyll (mg/m<sup>3</sup>) = exp (3.61\*V + 0.000963\*PAR - 2.84)

## 3.4) Physics

## Temperature and Salinity

Temperature and salinity were measured using a SeaBird 'CTD in a bucket' incorporating a remote temperature sensor (Pt resistance thermometer) and an inductive-type conductivity cell mounted next to a second thermometer.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1983).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated CTD surface samples. This gave some surprising results. Initially, (until 00:50 on 17/6/91) the instrument was rock steady, exhibiting a constant offset requiring a correction of 0.02 PSU. This corresponded with the excellent performance of the instrument reported on the previous two cruises.

However, after this time, dramatic instrumental drift (reaching 0.45 PSU) commenced which was remarkably linear with cycle number and (hence time). A regression of cycle number against correction required yielded the equation:

Correction = Cycle number \* 0.000014 - 0.027 (R<sup>2</sup> = 94.4%)

This was valid until the system was thoroughly cleaned using Decon at 18:15 on 26/6/91. This cleaning eliminated the offset produced by the drift, but the instrument started to drift again immediately. This second period of drift was fitted to the equation:

Correction = Cycle number \* 000005 + 0.0879 (R<sup>2</sup> = 46.5%)

The poorer statistics reflect the fact that the drift after cleaning was less regular. The cause of this drift is unknown but it seems probable that it is related to the huge numbers of coccolithophores encountered during this cruise.

All the corrections described above have been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A constant correction of -0.05°C was determined for the whole cruise and this has been applied to the data.

Save for the salinity drift, the instrument functioned well throughout the cruise, producing a data set of good quality by thermosalinograph standards. When the height of the active coccolithophore bloom was sampled, both temperature and salinity became extremely noisy. The noise in salinity is an artefact resulting from the temperature noise, but whether the latter is real or an artefact is a moot point.

## **Optical Attenuance**

Optical attenuance was measured using a 531nm 25cm path-length transmissometer contained in a plastic water bath continuously flushed by the non-toxic supply. THIS IS NOT THE INSTRUMENT NORMALLY OPERATED BY RVS AND ABSOLUTE VALUES SHOULD NOT BE COMPARED WITH OTHER BOFS CRUISES. A 660 nm transmissometer was run in parallel, but did not function well and the data were rejected.

The data were logged as fractional transmission which were converted to attenuance using the equation:

Attenuance = -4.0 log (Transmission).

Inspection of the data using a graphics workstation showed them to be relatively free from the 'bubble spikes' that can plague underway transmissometer data. The few that were identified were flagged out.

## 3.5) Meteorology

### Multimet System

The Multimet system fitted to Charles Darwin for this cruise contained a broad suite of sensors logged on an integral PC programmed to function as a Level A. The system, at the request of the BOFS scientists, was calibrated before this cruise and again after Charles Darwin 61. The raw data were sent to the James Rennell Centre for working up and the calibrated data were sent to BODC to be merged into the underway file.

There was one problem with the data set supplied. The time channel on the Multimet data used the PC clock with no input from the ship's master clock. Unfortunately, no attempt had been made to synchronise the PC clock with the ship's master clock. Fortunately, the Multimet included light channels that could be compared with PAR data logged on the ABC system to work out a timing correction.

#### Air Temperature

The Multimet bristled with Vector Instruments type aspirated psychrometers. Two were fitted above the wheelhouse, one to port and one to starboard, with another pair fitted to the port and starboard foremast extensions.

Averaging data from the port wheelhouse and both mast instruments generated combined wet and dry bulb temperature channels. These showed consistently very good (within 0.5°C) agreement. The data from the starboard wheelhouse instrument were clearly anomalous and, consequently, were rejected.

#### Wind Velocity

Wind velocity was measured by a Vector Instruments cup anemometer and vane located on the main mast. Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect. No evidence of shadowing by the ship's superstructure was observed.

#### **Radiation**

The Multimet included two Kipp and Zonen type CM5/6 pyranometers and an Eppley longwave radiation sensor mounted on the forward mast. In addition, two PML designed 2-pi PAR meters were mounted on scaffold poles on either side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the

sensors in these instruments were quite different. The PAR meters had hemispherical domed sensors whilst the solarimeters were fitted with cosine collectors. At midday on the equator, both types of instruments would have produced comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters was considerably higher. Consequently, simple comparisons between the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 4):	PAR = exp(Volts*5.139 + 7.2376)/100
Starboard (sensor 9):	PAR = exp(Volts*5.062 + 6.7874)/100

Merged solar and PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to eliminate shading effects.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu E/m^2/s$  by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

## Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mB over the range 980-1050mB by the manufacturer. Output was in the range 4-20mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars. Note that this instrument was not part of the Multimet and was logged independently by the ABC system.

The data were examined on a graphics workstation by BODC and any spikes flagged.

# 4) Data Warnings

None

# 5) References

Bradshaw, A.L., Brewer, P.G., Shafer, K. and Williams, R.T. (1981). Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program. *Earth Planet. Sci. Lett.* <u>55</u> : 99-115.

Fofonoff, N.P. and Millard Jr., R.C. (1983). Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Morris, A.W., Howland, R.J.M., and Bale, A.J. (1978). A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. *Est. Coast. Mar. Sci.* <u>6</u>, 105-109.

Robinson, C. and Williams, P.J.leB. (1991). Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chem.* <u>34</u>: 157-175.

Weiss, R.F. (1981) Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci.* <u>19</u> : 611-616

# Surface Underway Data for Cruise Charles Darwin CD61 (6<sup>th</sup> to 29<sup>th</sup> July 1991)

# 1) Components of the Underway Data Set

The underway data set for Charles Darwin 61 contains the following data channels. The single character at the end of each line is the corresponding channel identifier in the binary merge file.

Navigation:	Latitude (degrees +ve N) Longitude (degrees +ve E) Distance Run (km) Bathymetric depth (m)	A B K J
Chemistry:	Dissolved oxygen ( $\mu$ M) pCO <sub>2</sub> ( $\mu$ atmospheres) Nitrate plus nitrite ( $\mu$ M) Nitrite ( $\mu$ M) Silicate ( $\mu$ M)	Q E T U W
Biology:	Turner Designs raw fluorescence (nominal mg/m <sup>3</sup> ) Turner Designs chlorophyll (mg/m <sup>3</sup> ) Aquatracka raw fluorescence (Volts) Aquatracka chlorophyll (mg/m <sup>3</sup> )	D G ? !
Physics:	Temperature (°C) Salinity (PSU) Optical Attenuance (per m)	C F I
Meteorology:	Absolute wind speed (knots) Absolute wind direction (degrees from) Solar radiation (W/m <sup>2</sup> ) Barometric Pressure (mB) Dry bulb air temperature (°C) Wet bulb air temperature (°C) Downwelling scalar 2-pi PAR irradiance (W/m <sup>2</sup> ) Long wave radiation (W/m <sup>2</sup> )	Y Z O 1 a b L

# 2) Methodology Overview

## 2.1) Plumbing

Water from the non-toxic pump was fed into a 130 litre black plastic header tank situated above the laboratory to act as a debubbler. The supply from this tank was

split to feed the underway chemistry measurements and the Turner Designs fluorometer. Each branch was equipped with a control valve and flow meter to enable the flow rates to each instrument to be controlled. The thermosalinograph was fed separately from the non-toxic supply, via the non-toxic supply header tank. The transmissometer and the Aquatracka fluorometer, unlike the previous cruise, were located in the non-toxic supply main header tank, which eliminated problems with noise due to air leaks.

# 2.2) Data Acquisition

For most parameters, data logging and initial processing was handled by the RVS ABC system. The Level A sampling microcomputer digitised an input voltage, applied a time stamp and transferred the data via the Level B disk buffer onto the Level C where the data records were assembled into files. Sampling rates varied from 10 seconds to several minutes.

In some cases, for example dissolved oxygen, the analytical equipment included an integral data logger, such as a PC. In these cases, data were transferred to the Level C on floppy disk.

The level C included a suite of calibration software that was used to apply initial calibrations to convert raw ADC counts into engineering units. At the end of the cruise, the Level C disk base was transferred to BODC for further processing. Some data sets were processed by the Principal Investigator post-cruise and submitted to BODC for incorporation into the underway data set.

## 2.3) BODC Data Processing Procedures

Data from the underway files were merged into a common file (the binary merge file) using time as the primary linking key. Data sets (e.g. pCO<sub>2</sub>) worked up post cruise were also merged, again using time as the primary link. Data logged as voltages (e.g. PAR, nutrients) were converted to engineering units. Wind velocity was corrected for ship's motion and heading.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to undertake all possible comparative screening checks between channels (e.g. to ensure corrected wind velocity data are not influenced by changes in ship's heading).

# 3) Methodology And Calibration Procedures

## 3.1) Navigation

GPS was the primary navigation system used on this cruise. When no GPS fixes were available the ship's position was determined by dead reckoning based upon the ship's gyro and EM log. Once a fix was obtained after a period of dead reckoning, the surface drift velocity was computed. If this exceeded four knots, the data were automatically flagged suspect. The positional error due to surface drift was then

retrospectively applied over the period of dead reckoning.

Distance run was computed from successive positional fixes using spherical trigonometry.

At BODC a program was run which located any null values in the latitude and longitude channels and checked to ensure that the ship's speed over the ground was not excessive. The bridge logs were used to manually enter as many positions as possible during periods when navigation wasn't automatically logged. These covered critical points such as course alterations and arrival/departure at stations. Any remaining null values were filled by linear interpolation. The maximum gap interpolated for this cruise was 26 hours 39 minutes, commencing at 17:20 on 8/7/1991. At this time the ship was in port undergoing emergency repairs.

The distance run channel was checked to ensure it is progressive. If this check showed resetting of the parameter to zero (caused by Level C crashes), the channel was recomputed from latitude and longitude. This procedure proved necessary for this cruise.

Bathymetric depth was measured using a Simrad echo sounder logged by the ABC system. Carter's Tables corrections were applied on the Level C.

## 3.2) Chemistry

#### Dissolved oxygen

Dissolved oxygen was measured using an Endeco type 1125 pulsed dissolved oxygen controller multiplexed with two Endeco type 1128 dissolved oxygen probes. The probes were immersed in a Perspex cell (approx. 1 litre) fed at approximately 2 litres per minute.

The oxygen system had no way of determining salinity. Consequently, the data were logged and calibrated with an input salinity of zero to all computations. Calibration was achieved by regressing the output from the probe deemed more stable against measurements made using the Winkler method on samples taken from the probe outflow. Calibration samples were taken approximately every six hours. The oxygen channel for this cruise has been derived by taking data at different times from both of the probes (designated probe 2 and probe 3 to reflect their logging channels).

Three calibration curves were established using probe 2. The data from probe 3 were rejected.

06/7/91	16:11 to	07/7/91	16:12	Calibrated	=	Raw*(-0.13) + 403.47
10/7/91	08:28 to	14/7/91	13:56	Calibrated	=	Raw*1.447 - 162.26
						$(R^2 = 76\%)$
15/7/91	09:01 to	25/7/91	19:54	Calibrated	=	Raw*0.9056 + 36.41
						(R <sup>2</sup> =85%)

The first calibration is based on two Winkler titrations and represents a small subset of the data on the initial outward leg before the ship was forced to return to port with mechanical problems. The other two calibrations were based on 12 and 25 titrations respectively.

Data for the interval from 14:01 on 14/7/91 to 08:45 on 15/7/91 were obtained by a linear interpolation between the calibrations on either side.

The calibrated data at zero salinity were then corrected to in-situ salinity using the equations:

 $O_2$  (actual) =  $O_2$  (zero salinity) / Gamma Gamma = exp(S\*(A6 + A7/T + A8/T<sup>2</sup>)) where: S = Salinity (PSU) T = Absolute temperature (K) A6 = 0.017674 A7 = -10.754 A8 = 2140.7

From time to time gaps in the thermosalinograph record meant that no temperature or salinity data were available for the oxygen computations. In these cases, a default salinity of 35.2 and the probe temperature logged by the oxygen system were used. Initially, the points computed in this manner were flagged, but subsequent examination of the data set on a graphics workstation showed no anomalies in the flagged data points and consequently the flags were removed.

<u>pCO</u>2

Continuous measurements of  $pCO_2$  were carried out using a "shower head" type equilibrator, similar to that described in Weiss (1981), from which the gas phase was sampled at approximately 7-minute intervals. The equilibrated sample was not dried prior to analysis; thus, no corrections were necessary for the partial pressure of water vapour within the sample.

The equilibrated gas was carried in hydrogen, passed over a catalyst that converted the CO<sub>2</sub> to methane. The gas stream was passed to a flame ionisation detector (FID), Hewlett-Packard 5890A-GC which used compressed air as the combustion make-up gas.

Concentrations of  $CO_2$  in the equilibrated gas were compared every 15 minutes with marine air, dried to -30°C dewpoint (using a dri-perm drier and a secondary standard of compressed air). The marine air was supplied by an intake mounted clear of the ship's superstructure to minimise possible contamination.

Primary calibration was by reference to a volumetrically prepared gaseous standard (pure  $CO_2$  in zero air). All data were given at in-situ temperature and corrected for atmospheric pressure changes, in units of microatmospheres.

Precision studies have shown a standard deviation of no more than  $1.5_\mu atms$  for the method. Repeated measurements of standards show a typical coefficient of variation

to be no more than 0.2%.

#### **Nutrients**

The nutrients were measured using a Technicon AA2 autoanalyser connected to the pumped seawater supply by a continuous filter block (Morris et al., 1978). The chemistries used were:

- Nitrate: Reduced to nitrite by a Cu/Cd coil, then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish-purple azo dye.
- Nitrite: As for nitrate without the reduction step.
- Silicate: Reduction of a silicomolybdate solution to 'molybdenum blue' by ascorbic acid with the addition of oxalic acid to eliminate interference from phosphates.

The colorimeter outputs were logged by a Level A connected to the chart recorder inputs. The system was calibrated by running distilled water washes to determine baseline and sets of four standards. Standards were run at least once per day.

The following processing procedures were adopted by BODC to convert the raw voltage streams into nutrient concentrations.

Initial inspection of the raw data showed the phosphate and ammonia channels to comprise total rubbish (random, mostly negative, numbers). This problem could not be resolved and consequently there are no data for these channels from this cruise.

The raw voltages were screened on a graphics workstation to differentiate between signals due to baselines (flagged 'Z'), standards (flagged '1', '2', '3' or '4' according to concentration) or actual ambient concentrations. Any instrumental spikes were flagged suspect ('S').

The data were then segmented into internally consistent subsets (i.e. taking account of any instrumental change such as gain or baseline alterations documented by the analyst), with constant or linearly drifting baselines.

For each segment, the baseline as a function of time was fitted to a linear regression, which was applied to standardise the segment to a baseline of zero. For the silicate channel, which has particular problems associated with instrument drift, a linear regression of on-line drift for each segment was calculated by considering the difference between on-line readings immediately prior to and after baselines.

The standard voltages were then used to construct calibration curves to convert raw voltages into nutrient concentrations. These were then applied on a segment by segment basis to the data stream. All baseline and calibration equations were checked manually before they were used. Once concentrations had been calculated the custom baseline and standard flags were changed to suspect.

The data were subsequently quality controlled by inspection on a graphics workstation with particular attention paid to the concentrations obtained for the standards. Any data identified as suspect were flagged. These checks included comparative screening between the nutrient channels.

The nutrient time channels were adjusted to correct for the delay incurred whilst the sample passes through the complex plumbing of the autoanalyser. No salt corrections (corrections for difference in optical density between sample and standards) were applied as the standards were made up in nutrient-free seawater.

Nutrient	Time Shift		
NO <sub>3</sub>	-12	mins.	
NO <sub>2</sub>	-8	mins.	
Si	-12	mins.	

Due to the chemistry used for nitrate analysis, interference from nitrite is inevitable. The nitrate channel has been processed throughout as nitrate+nitrite and no attempt has been made to correct for nitrite.

As a final processing step, small negative values in the data were converted to zero to prevent them creating havoc with contouring software. Values of zero flagged 'G' should therefore be taken to mean 'below detection limit'.

## 3.3) Biology

## <u>Chlorophyll</u>

Chlorophyll was measured by two fluorometers run in parallel, a Turner Designs through-flow connected to the non-toxic supply in the wet laboratory and a Chelsea Instruments Aquatracka immersed in the non-toxic supply header tank. Both instruments were calibrated against extracted chlorophyll data. Samples were drawn from the non-toxic supply and filtered through GFF filter papers. Two samples were filtered: one for immediate analysis and the other frozen. The samples analysed on board were extracted in acetone and determined on a Turner Designs bench fluorometer calibrated against absolute chlorophyll standards.

No problems were reported with the bench fluorometer used on the cruise and the extracted chlorophyll data set obtained at sea was used for the fluorometer calibrations.

Prior to calibration, both raw fluorometer channels were screened on a graphics workstation and any spikes flagged. Next, steps in the Turner Designs data set due to uncorrected range changes were identified and the data channel reduced to a single range.

Calibration equations were determined by regression techniques, against chlorophyll for the Turner Designs and log chlorophyll for the Aquatracka. Normally, a quench correction is included, but examination of the residuals showed insignificant correlation with PAR (Aquatracka r=0.069, Turner Designs r=-0.047). Consequently, no PAR

terms were computed. The apparent lack of quench effects may possibly be due to the relocation of the fluorometer to the header tank giving sufficient time for the phytoplankton to adapt to dark conditions.

The following calibration equations were determined for the whole cruise - the data set of 159 values was not deemed sufficient to allow the calibration to be segmented:

Turner Designs

chlorophyll (mg/m<sup>3</sup>) = 20.7\*raw\_reading + 0.002 (R<sup>2</sup> = 37.4%)

Aquatracka

chlorophyll (mg/m<sup>3</sup>) = exp ( $0.923^{*}V - 1.94$ ) (R<sup>2</sup> = 68.3%)

Comparative screening of the two calibrated channels shows the agreement to be very good at the start of the cruise. On July 10<sup>th</sup>, the Aquatracka record is significantly (a factor of 2) greater than than the Turner Designs record until 08:00 when the two instruments come back into line. From July 13<sup>th</sup>, the Turner record drifts steadily upwards from the Aquatracka record until by July 24<sup>th</sup> the Turner values are almost double those from the Aquatracka.

Looking at the calibration statistics, by far the better calibration was obtained for the Aquatracka. In the cruise report, it is stated that during the cruise the sensitivity of the Turner Designs instrument drifted upwards and this was corrected by insertion of tissue paper filters into the light path. From this one may conclude that the Aquatracka record is more reliable and it is recommended that this be the channel used for chlorophyll.

## 3.4) Physics

## Temperature and Salinity

Temperature and salinity were measured using a Sea Bird 'CTD in a bucket' incorporating a remote temperature sensor (Pt resistance thermometer) and an inductive-type conductivity cell mounted next to a second thermometer.

The remote temperature sensor was supplied by water from the intake side of the nontoxic supply; i.e. the sea surface temperature was measured at near-ambient temperature as opposed to the warming effects induced by the pumping system. The conductivity cell and housing temperature thermistor were supplied by a through-flow system from the non-toxic supply.

The raw ADC counts were calibrated to give conductivity and two temperature channels based upon laboratory calibrations undertaken by RVS. Salinity was computed from the housing temperature and conductivity using the UNESCO 1978 Practical Salinity Scale (Fofonoff and Millard, 1982).

Salinity was back calibrated using a combined data set comprising discrete salinity measurements on samples taken from the thermosalinograph outlet and calibrated

CTD surface samples. The spectacular drift noted on the previous cruise was totally absent adding weight to the hypothesis that the drift was due to the presence of huge numbers of coccolithorphores. The calibration showed the instrument to be reading 0.218 PSU low throughout the cruise. This correction has been applied to the data.

The remote (i.e. sea surface) temperature was back calibrated against surface CTD and SeaSoar data. A constant correction of -0.04°C was determined for the whole cruise and this has been applied to the data.

### **Optical Attenuance**

Optical attenuance was measured using a 660 nm 25cm path-length SeaTech transmissometer contained in the non-toxic supply header tank. The data were logged as a voltage in the range 0-5V. These were corrected for light source decay (cruise voltage in air 4.750V; manufacturer's figure 4.823V) and divided by 5 to give fractional transmission.

This was converted to attenuance using the equation:

Attenuance =  $-4.0 \log (Transmission)$ .

Inspection of the data using a graphics workstation showed that after implementation of regular instrument cleaning on 16/07/1991, the record was extremely good. The excellent correlation with the Aquatracka chlorophyll data is very encouraging. Data prior to July 16<sup>th</sup> were anomalously high and have been flagged suspect.

## 3.5) Meteorology

#### Multimet System

The Multimet system fitted to Charles Darwin for this cruise contains a broad suite of sensors logged on an integral PC. The system, at the request of the BOFS scientists, was calibrated before the previous cruise and again after this cruise. The raw data were sent to the James Rennell Centre for working up and the calibrated data were sent to BODC to be merged into the underway file.

There was one problem with the data set supplied. The time channel on the Multimet data used the PC clock. Unfortunately, no attempt had been made to synchronise this with the ship's master clock. Fortunately, the Multimet included light channels, which could be compared with PAR data logged on the ABC system to work out a timing correction.

#### Air Temperature

The Multimet bristled with Vector Instruments type aspirated psychrometers. Two were fitted above the wheelhouse, one to port and one to starboard, with another pair fitted to the port and starboard foremast extensions.

Averaging data from the port wheelhouse and both mast instruments generated combined wet and dry bulb temperature channels. These three instruments showed

consistent very good (within 0.5°C) agreement. The data from the starboard wheelhouse instrument were clearly anomalous and, consequently, were rejected.

## Wind Velocity

Wind velocity was measured by a Vector Instruments cup anemometer and vane located on the main mast. Conversion from relative to absolute wind velocity was undertaken at BODC. The ship's heading was added to the wind direction relative to the ship to give wind direction relative to compass coordinates. The ship's velocity over the ground was then subtracted from the relative wind velocity to give absolute wind velocity. Comparative screening checks were made to ensure that the absolute wind velocity was truly independent of the ship's velocity and heading.

The data were inspected on a graphics workstation and spikes flagged suspect. No evidence of shadowing by the ship's superstructure was observed.

#### **Radiation**

The Multimet includes two Kipp and Zonen type CM5/6 pyranometers and an Eppley longwave radiation sensor mounted on the forward mast. In addition, two PML designed 2-pi PAR meters were mounted on scaffold poles on either side of the 'Monkey Island' above the bridge. It must be emphasised that the geometries of the sensors in these instruments were quite different. The PAR meters had hemispherical domed sensors whilst the solarimeters were fitted with cosine collectors. At midday on the equator, both types of instruments would have produced comparable readings. However, at the latitude of this cruise, the collection efficiency of the PAR meters was considerably higher. Consequently, simple comparisons between the data sets from the two instrument types must not be attempted.

The Kipp and Zonen solarimeters were calibrated into  $W/m^2$  using the manufacturer's calibrations built into the Level A software. The PAR meters were logged as voltages and calibrated in  $W/m^2$  by BODC using coefficients determined in February 1990. The calibration equations used were:

Port (sensor 4):	PAR = exp(Volts*5.139 + 7.2376)/100
Starboard (sensor 9):	PAR = exp(Volts*5.062 + 6.7874)/100

Merged solar and PAR channels were produced, after spikes were flagged out, by taking the maximum of the port and starboard values to eliminate shading effects.

It has been determined by empirical calibration that the PAR values in W/m<sup>2</sup> may be converted to  $\mu$ E/m<sup>2</sup>/s by multiplying by 3.75. Please note that this factor is NOT applicable to the Kipp and Zonen solar radiation data.

#### Barometric Pressure

Barometric pressure was measured by a KDG aneroid barometer, calibrated to within 0.1mB over the range 980-1050 mB by the manufacturer. Output was in the range 4 - 20 mA, converted to volts for input to the Level A, which then applied the manufacturer's calibration to convert the data to millibars. Note that this instrument

was not part of the multimet and was logged independently by the ABC system.

The data were examined on a graphics workstation by BODC and any spikes flagged.

# 4) Data Warnings

The Turner Designs chlorophyll data (channel G) were the subject of a poor calibration and problems with the instrument were described in the cruise report. Consequently, it is recommended that the chlorophyll data from the Aquatracka (channel !) are used instead.

# 5) References

Bradshaw, A.L., Brewer, P.G., Shafer, K. and Williams, R.T. 1981. Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program. *Earth Planet. Sci. Lett.* <u>55</u> : 99-115.

Fofonoff, N.P. and Millard Jr., R.C. 1983. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* <u>44</u>.

Morris, A.W., Howland, R.J.M., and Bale, A.J. 1978. A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. *Est. Coast. Mar. Sci.* <u>6</u>, 105-109.

Weiss, R.F. 1981 Determination of carbon dioxide and methane by dual catalyst FID chromatography and nitrous oxide by ECD. *J. Chromatogr. Sci* <u>19</u> : 611-616

# Surface Underway Data for Discovery Cruise DI198 11<sup>th</sup> November to 14<sup>th</sup> December 1992

# 1) Components of the Underway Data Set

The following channels are present in the underway data files for cruise Discovery DI198. The characters at the end of each line are the channel identifiers in the binary merge file.

Navigation:	Latitude (°+ve N) Longitude (°+ve E) Ship's velocity N-S (knots +ve N) Ship's velocity E-W (knots +ve E) Ship's heading (°) Distance along track (km)	A B # ( ) K
Meteorology	<ul> <li>Bathymetric depth (m)</li> <li>PAR vector irradiance (W/m<sup>2</sup>) Relative wind speed (m/s) Relative wind direction (°) Absolute wind speed (knots) Absolute wind direction (° blowing from) Barometric pressure (mbar) Averaged dry bulb air temperature (°C) Averaged wet bulb air temperature (°C) Combined solar radiation (W/m<sup>2</sup>) Long-wave radiation (W/m<sup>2</sup>)</li> </ul>	t % & Y Z 1 a b O /
Physics:	Sea surface temperature (°C) Salinity (PSU) Optical attenuance (per m)	C F I
Biology:	Through-flow fluorometer output (nominal mg chl-a/m <sup>3</sup> ) Through-flow fluorometer chlorophyll (mg/m <sup>3</sup> ) Aquatracka fluorometer voltage (V) Aquatracka chlorophyll (mg/m <sup>3</sup> )	D G ? !
Chemistry:	Nitrate + nitrite ( $\mu$ M) Nitrite ( $\mu$ M) Phosphate ( $\mu$ M) Silicate ( $\mu$ M) pH (mol/kg) Dissolved oxygen ( $\mu$ M) Aqueous pCO <sub>2</sub> (ppm) Dissolved inorganic Carbon TCO <sub>2</sub> ( $\mu$ mol/kg)	T U V V W M Q E H

# 2) Underway Instruments and Methodology

# 2.1) Plumbing

The standard ship's non-toxic supply was deemed unsuited to the requirements of this cruise due to the presence of bubbles. Consequently, an independent debubbled system was set up.

The water was drawn from the standard inlet approximately 4m below the waterline through 2-inch stainless steel piping into a black plastic 50-litre header tank with a headspace connected to the atmosphere. The debubbled output was piped directly to the pCO<sub>2</sub>, dissolved oxygen, through-flow fluorometer, autoanalyser and pH systems plus taps for taking discrete water samples.

Two additional non-vented header tanks fed the thermosalinograph (with associated sampling tap) and the tank containing the transmissometer and Aquatracka fluorometer.

## 2.2) Instrumentation Summary

Discovery was equipped with five satellite navigation receivers, four of which operated with GPS. The primary scientific navigation came from a Trimble receiver. Data from a 24-channel Ashtech instrument was used for attitude measurements.

Bathymetry was collected using a Simrad EA500 scientific echo sounder.

The thermosalinograph consisted of a Falmouth Scientific Instruments Ocean Temperature Module (OTM) mounted in the hull at the non-toxic intake. A second OTM, together with an Ocean Conductivity Module, was mounted in a polyethylene tube connected to the modified non-toxic system as described above. The unit was located on the starboard side of the ' hangar' (a very large laboratory space designed to accommodate ROVs). A flow rate of approximately 20 litres per minute was achieved from the header tank located 2.5m above the instrument.

Additional sea temperature sensors were incorporated into the ADCP (a platinum resistance thermometer (PRT) mounted 5m below the waterline) and the meteorological package (a PRT mounted on the port side of the hull at a depth of approximately 3m).

Chlorophyll was measured by two fluorometers. A through-flow Turner Designs bench fluorometer was plumbed into the non-toxic supply and a Chelsea Instruments Aquatracka instrument was immersed in a tank flushed by the non-toxic. A SeaTech 660 nm (red) 25 cm path-length transmissometer measuring optical attenuance was also in the tank with the Aquatracka.

The meteorological package included the following instruments:

R.M. Young Instruments 05103 wind monitor (serial number 11277) incorporating a wind vane and cup anemometer that was situated on the

foremast.

Two Vector Instruments psychrometers, located port and starboard on the foremast (serial numbers 1072 and 1073 respectively).

Two Didcot PAR (400-700nm) vector irradiance meters, port and starboard on the foremast (serial numbers 27150 and 27151 respectively).

Two Kipp and Zonen CM6B solar radiometers, port and starboard (serial numbers 92015 and 92016 respectively).

A long wave pyrgeometer fitted to the foremast.

Vaisala DPA21 aneroid barometer (serial number 465569) located in the main laboratory.

Oxygen concentration was measured using an Endeco type 1125 pulsed dissolved oxygen electrode. Two electrodes were mounted in a Perspex container through which debubbled non-toxic water flowed at approximately two litres per minute. The PC data logger sampled the system every five minutes. Calibration samples were taken every two hours and analysed by the Winkler method.

pH was measured using a novel continuous technique based on multi-wavelength spectrophotometry that utilised the acid-base absorption properties of phenol red indicator.

 $pCO_2$  was measured continuously using a gas chromatograph and a showerhead equilibrator. Air for the GC system was supplied using a compressor in the laboratory and hydrogen through the piped gas supply. The equilibrator was located in an unheated laboratory annexe to keep the temperature as close as possible to ambient. The instrument cycle determined two aqueous concentrations bracketed by a standard and a measurement of the marine air concentration (determined as  $335\pm2$  ppm). This gave an aqueous pCO<sub>2</sub> measurement approximately every 6 minutes.

Total CO<sub>2</sub> or dissolved inorganic carbon was measured using a coulometric system. The seawater sample was fed into a calibrated pipette in which the DIC was quantitatively converted into carbon dioxide using orthophosphoric acid. The gas was purged by a nitrogen carrier stream into the reaction cell where it was quantified by coulometric titration. Further details are given in Robinson and Williams (1991).

Nutrients were measured using the Chemlab-based autoanalyser purchased for the North Sea Project survey cruises in 1988/89. The chemistries used were the standard wet chemical procedures developed at PML.

The colorimeter outputs were logged by a Siemens chart recorder and also an ABCsystem Level A interface.

No continuous filter block was mentioned in the cruise report and consequently it is concluded that the system was fed with unfiltered seawater. Due to the high nutrient

concentrations encountered in the area the seawater input was continuously diluted with four parts MilliQ water.

Standards made up in low-nutrient seawater and MilliQ blanks were run daily.

## 2.3) Data Acquisition

All data from the automatically logged sensors were acquired using the RVS ABC shipboard data logging system. Each instrument was connected to a microcomputer interface (the Level A), which captured and time-stamped (using a central master clock) the data at regular intervals. The information was transmitted to a logging workstation (the Level C) via a disk buffer (the Level B). Some Level C files were taken across into the P-EXEC system for further working up during the cruise.

Stand-alone PCs independently logged the data from the oxygen, pH,  $TCO_2$  and  $pCO_2$  systems. Care was taken to ensure that the PC clocks were synchronised to the central master clock.

# 3) Calibration and Quality Control Procedures

# **3.1) Introduction to BODC processing procedures**

Data from a number of sources were merged onto a common GMT time base in BODC's binary merge format. The data sets used were obtained as follows:

P-EXEC processed files

Navigation Meteorology Thermosalinograph

Level C data files

Bathymetry Transmissometer and raw fluorometer Autoanalyser colorimeter voltages

ASCII files from PC data loggers

Dissolved oxygen pCO<sub>2</sub> TCO<sub>2</sub> pH

ASCII files generated from Level C data

Calibrated fluorometers

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to carry out comparative screening checks between channels by overlaying data channels. A map of the cruise track was simultaneously displayed in order to take account of the oceanographic context.

## 3.2) Navigation and bathymetry

Scientific navigation was derived primarily from the Trimble GPS receiver. Accuracy for this system was determined over an 18-hour period whilst the ship was tied up in Port Stanley. The standard deviations of latitude and longitude were 32.5m and 25.8m respectively. Adequate GPS coverage was available for approximately 21 hours per day.

The ' best navigation' was determined from the raw 1-second GPS positions with data from poor fixes (pdop>5) rejected. The data were averaged to a sampling frequency of 1 minute. Gaps would normally have been filled by dead reckoning. However, this was compromised, as no electromagnetic speed log was available. Consequently, the gaps had to be filled by linear interpolation. Distance run and ship's velocity were computed from the interpolated 1-minute data.

The bathymetry data were corrected for sound velocity variation using Carter's Tables by software on the Level C, prior to supply to BODC. Inspection of the data showed them to be noisy, but this has been effectively eliminated through flagging the spikes as suspect.

## 3.3) Meteorology

## Barometric Pressure

Visual inspection of the data showed them to be clean and free from spikes. No attempt was made to correct the data to sea level.

#### Air Temperature

The air temperature data comprised port and starboard wet and dry bulb temperature channels from the psychrometers. The instruments were calibrated at IOS Deacon Laboratory prior to the cruise.

Visual inspection revealed that there were some problems with the data. The port dry bulb channel was extremely noisy. Agreement between the port and starboard channels (wet and dry bulb) varied from excellent (< $0.05 \circ C$ ) to very poor (>5  $\circ C$ ). The agreement of the wet bulb temperatures was generally better than the agreement for the dry bulb temperatures. Poor disagreement was almost always the result of the starboard sensor drifting high, indicating intermittent artificial heating (stack pollution or a light?) of the starboard psychrometer.

The following strategy was used to extract the final air temperature data. The individual wet bulb temperatures were screened and any spikes (very few) flagged as suspect. The channels were then screened overlain and the data from both

channels were flagged as suspect for periods when the difference between the channels exceeded 0.5 °C. Averaged wet bulb air temperatures were determined for those datacycles having both port and starboard values flagged as good.

The port dry bulb channel was screened, but ended up so heavily flagged that it was of little use. Consequently, the data presented as ' averaged' are from the starboard instrument. As a starboard sensor artifact caused the periods of poor wet bulb temperature agreement, data were taken out of the port wet bulb data set where the agreement between the two wet bulb sensors was poor.

#### Photosynthetically Available Radiation

The PAR vector irradiance data were supplied as two calibrated data channels (based on manufacturer's calibrations) in units of  $W/m^2$ . The individual data channels were screened and no problems were identified. There was acceptable agreement between the two instruments. Both instruments recorded negative values (down to  $-5 W/m^2$ ) in the dark. The cruise participants attributed this to non-linearity of the instruments at low light levels. It is a phenomenon that has been noted with Didcot light meters on other cruises.

The data were merged into a single irradiance channel, taking the maximum reading from the pair to eliminate shading artifacts.

#### Solar Radiation

The solar vector irradiance data were supplied as two calibrated data channels (based on manufacturer's calibrations) in units of  $W/m^2$ . No significant problems were identified with the data during screening. The port and starboard channels showed good agreement except for obvious effects of sensor shading. These were minimised by generating a merged solar radiation channel containing the maximum reading from the sensor pair on each time step.

#### Long Wave Radiation

The instrument was calibrated by IOS Deacon Laboratory and fitted to Discovery just before she left the UK for Antarctic waters. No problems were encountered other than intermittent spikes, attributed to communication errors between the instrument and the logging system. These have been flagged as suspect.

#### Wind Velocity

Both relative and absolute wind velocity data were provided in the worked up P\* data file. The relative wind velocities have been retained in the data file. Note that the absolute wind speeds have been converted by BODC from units of m/s into knots to facilitate comparison with the ship's velocity. The scaling factor used was 1.943845.

Inspection of the wind velocity channels did not reveal any problems with the data.

## 3.4) Physics

### Temperature

The sea temperature channel was generated from the FSI remote OTM until 12:09 on November 16<sup>th</sup> when the housing OTM failed and was replaced by the remote unit. After this time the sea surface temperature data were taken from the ADCP temperature sensor. The meteorological package temperature sensor was not used because it wasn't calibrated below 5 °C and the data acquisition system degraded resolution to 0.1 °C.

The thermosalinograph OTM was calibrated against surface SeaSoar temperature data. A correction of  $-0.008 \circ C$  (standard deviation 0.008  $\circ C$ ) was applied.

The ADCP temperature sensor used from 00:55 on November 16<sup>th</sup> was calibrated against surface SeaSoar temperature data. The following calibration function was applied to the data:

Corrected temperature = Raw temperature + 0.011 - (Raw temperature \* 0.014)

The standard deviation of this calibration was 0.031 °C. All calibration work was carried out before the data were supplied to BODC.

#### Salinity

The salinity data were calibrated against water bottle samples that were taken from the thermosalinograph output at hourly intervals. A correction of -0.091 PSU (standard deviation 0.019 PSU) was determined and applied to the data. All calibration work was carried out before the data were supplied to BODC.

#### **Optical Attenuance**

The transmissometer data were obtained as voltages. These were ratio corrected for source decay against a manufacturer's air voltage of 4.738V using the following air readings taken during the cruise:

11/11/1992 12:00:30 to 13/11/1992 12:00:304.547V13/11/1992 12:01:30 to 21/11/1992 12:00:304.543V21/11/1992 12:01:30 to 08/12/1992 14:59:304.537V08/12/1992 23:59:30 to 14/12/1992 23:59:304.540V

The instrument was thoroughly cleaned prior to each air reading.

The corrected voltages were divided by 5 to obtain fractional transmission and attenuance was computed using the equation:

Attenuance = -4 \* In (fractional transmission)

Inspection of the data showed them to be of exceptionally good quality with very few

bubble spikes.

## 3.5) Biology

## <u>Chlorophyll</u>

The data files included in the final data set came from two sources. The raw data (channels ' D' and ' ?') were taken directly from the ship's Level C data files.

The two fluorometers were independently calibrated against a set of almost 500 fluorometric extracted chlorophyll determinations on samples taken at regular intervals from the surface non-toxic supply. Prior to calibration the Turner Designs data were corrected for inadequacies in the Level A software corrections for the automatic changes in the instrument range.

Gerald Moore from PML, working with Alison Weeks from Southampton University, undertook the calibrations. The first stage of the calibration was to determine the chlorophyll yield using samples collected in darkness. Regional variations (to allow for variations in phytoplankton species assemblage) were then determined using cluster analysis. Several models were tried to correct for quench effects by incorporating underway PAR into a calibration. However, none of these were successful. An empirical quench correction was determined using an empirical fit of the daily yield to a smooth function and correcting the chlorophyll on a sample by sample basis.

The equations applied were:

**Turner Designs** 

Chl-a =  $0.009853 * \text{output} + 0.004236 * \text{output}^2$  (r<sup>2</sup> = 0.86)

Regional scaling factors:	6.0849 (Drake Passage)
	4.2519 (from Potter Cove)
	0.9622 (Seasoar survey)

Aquatracka

Chl-a =  $0.02772 * \exp(\text{output}) + 0.001753 * (\exp(\text{output}))^2$  (r<sup>2</sup> = 0.91)

Regional scaling factors:	3.4571 (Drake Passage)
	1.4859 (from Potter Cove)
	0.9416 (Seasoar survey)

Comparison of the two calibrated channels shows the agreement to vary between excellent and acceptable for most of the cruise. However, there were instances where feature magnitudes differed significantly and some features were present in one calibrated channel, but not in the other.

## 3.6) Chemistry

#### Nutrients

The logged data streams, including ambient measurements, standards, baselines and garbage logged when the instrument was off-line, were merged into the binary merge file as voltages. The components of the data stream were identified by applying different flags for standards, baselines, ambient data and garbage. Normal procedures were modified due to the non-linear instrument response reported by the analyst with the calibration modelled as a series of straight-line segments between standards.

A bespoke processing system at BODC subdivided the data into segments of uniform calibration, stripped off the baseline, computed calibration equations and applied them.

The delays due to the plumbing of the Chemlab system were unknown as this was the first time this system had been used in a continuous underway mode. Consequently, no delay corrections have been applied to the timings for the nutrient channels.

The calibrated data were quality controlled by visual inspection on a graphics workstation using procedures that incorporated cross-checking against the credible surface water discrete sample data set (surface bottles) and, wherever, intercomparison with data from the James Clark Ross Sterna cruise. This procedure was compromised because much of the Discovery discrete nutrient data had been discredited. However, it still led to a significant proportion of the ambient signal being flagged as suspect.

Many problems led this being a poor quality set of continuous underway nutrient data. The cruise report indicates that the analyst wasn't happy with the autoanalyser, reporting a non-linear response for nitrate+nitrite and silicate and the need for refurbishment. The presence of a dilution line in a continuous system is also a cause for concern. Short path-length flow cells were not available forcing the implementation of this potential source of error.

Other problems compromised the standard to which the data could be worked up. Standards and baselines were only run once per day. Whilst it is possible to obtain good data from daily standards, autoanalysers are extremely susceptible to baseline drift, particularly in areas of high ambient nutrient concentration. Baselines every couple of hours or so are required if this is to be adequately corrected. Evidence of this problem may be seen in parts of the data set as steady drifts followed by sudden jumps when the standards were run. The worst affected data have been flagged out, but the problem has not been totally eliminated.

The standards were run for an insufficient time considering that output voltages were only being logged every minute. In many cases, the apex of the standard peak was absent from the digital record. This was overcome to some extent by manual adjustments to the calibrations based on the paper chart recorder output. The nutrient processing is critically dependent on high quality information from the analyst on instrument setting adjustments and what was being run through the instrument, usually in logs or by annotations on the chart rolls. This information was often absent for this cruise. Even standard concentrations had to be best guessed at times.

Because of these concerns, it is strongly recommended that the nutrient data from this cruise be used with caution. The concerns are greatest for nitrate+nitrite and phosphate. Most of the latter data channel has been flagged as suspect.

## <u>pCO</u>2

The data were corrected post-cruise using a running standard and corrections for temperature and barometric pressure were applied.

No spikes requiring flagging were identified during screening.

#### **Dissolved Oxygen**

The data originator calibrated the dissolved oxygen data before they were submitted to BODC. Problems with the oxygen electrodes attributed to tarnishing of the gold electrodes meant that no data were available from the system until 30/11/1992.

The oxygen data were screened and noted as being clean with a small number of isolated spikes.

## <u>рН</u>

The pH measurements were made at temperatures between 20 and 25 °C. On November 17<sup>th</sup> the measurement temperatures varied over this full range. However, after this date all measurements were made at 23 °C.

Screening the pH revealed a small number of obvious spikes that have been flagged as suspect. In-situ temperature and salinity data were obtained from the calibrated thermosalinograph.

The data originator reported some problems with the equipment in areas of high particulate load due to flow cell contamination. It is uncertain whether the ' saw-tooth' form of the data towards the end of the cruise is real or was attributable to this cause. These features in the data have not been flagged.

Precision of the method was quoted at 0.005 pH units.

## Total CO<sub>2</sub>

The original plan was to measure  $TCO_2$  in a continuous underway mode to parallel pH and pCO<sub>2</sub>. However, the coulometer chemicals and DIC standards had been stored in the deck laboratory chill store for the transit passage from the UK to the Antarctic. During this period the temperature in the store fell from the expected value of 10°C to below freezing causing the standard bottles to shatter and

degradation of the reagents.

Consequently, a discrete sampling regime incorporating up to five replicates of each sample was adopted to assure data quality. However, problems with the system hardware, spikes on the ' clean' electrical supply and the premature demise of the reaction cell conspired to limit the number of samples analysed.

The data were converted from per litre to per kilogram units using density computed from calibrated thermosalinograph data. None of the data were flagged.

# 4) Data Warnings

There are concerns, described in detail above, about the quality of the nutrient data. Nitrate+nitrite and phosphate in particular should be used with caution.

# 5) Reference

Robinson C. and Williams P.J.leB. 1991. Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chemistry* <u>34</u>, 157-175.

# Surface Underway Data for James Clark Ross Cruise JCR2 28<sup>th</sup> October to 17<sup>th</sup> December 1992

# 1) Components of the Underway Data Set

The following channels are present in the underway data files for cruise James Clark Ross JCR2. The characters at the end of each line are the channel identifiers in the binary merge file.

Navigation:	Latitude (°+ve N) Longitude (°+ve E) Ship's velocity N-S (knots +ve N) Ship's velocity E-W (knots +ve E) Ship's heading (°) Distance along track (km)	A B # () K
Meteorology	: PAR vector irradiance (W/m <sup>2</sup> ) Relative wind speed (m/s) Relative wind direction (°) Absolute wind speed (knots) Absolute wind direction (° blowing from) Barometric pressure (mbar) Dry bulb air temperature (°C) Combined solar radiation (W/m <sup>2</sup> )	t & Y Z 1 a O
Physics:	Sea surface temperature (°C) Salinity (PSU) Optical attenuance (per m)	C F I
Biology:	Through-flow fluorometer output (nominal mg chl-a/m <sup>3</sup> ) Through-flow fluorometer chlorophyll (mg/m <sup>3</sup> )	D G
Chemistry:	Nitrate + nitrite ( $\mu$ M) Nitrite ( $\mu$ M) Phosphate ( $\mu$ M) Silicate ( $\mu$ M) Ammonium ( $\mu$ M) Urea ( $\mu$ M) Dissolved inorganic Carbon TCO <sub>2</sub> ( $\mu$ mol/kg)	T U V P 9 H

# 2) Underway Instruments and Methodology

# 2.1) Plumbing

Water for the non-toxic supply was drawn from two inlets, one in the prep laboratory

and one in the micro-radio laboratory. Both were approximately 5m below the sea surface. The system in the prep lab supplied the thermosalinograph.

## 2.2) Instrumentation Summary

James Clark Ross was equipped with several GPS receivers plus Sperry gyrocompasses and an electromagnetic log.

A SeaBird SBE-21 thermosalinograph with conductivity and housing temperature sensors was used to measure salinity. Sea surface temperature was obtained using a 4-wire platinum resistance thermometer in the ADCP transducer space.

Chlorophyll was measured by a through-flow fluorometer plumbed into the non-toxic supply. A SeaTech 660 nm (red) 25-cm path-length transmissometer measuring optical attenuance was located in a light-tight tank flushed by the non-toxic supply.

The meteorological package included the following instruments:

R.M. Young Instruments propeller vane anemometer situated on the foremast.

Vector Instruments psychrometer located on the foremast.

A Didcot PAR (400-700nm) vector irradiance meter and a Kipp and Zonen solar radiometer on the foremast.

Vaisala aneroid barometer.

Total  $CO_2$  or dissolved inorganic carbon was measured using a coulometric system in a continuous underway operational mode. The seawater sample was fed into a calibrated pipette in which the DIC was quantitatively converted into carbon dioxide using orthophosphoric acid. The gas was purged by a nitrogen carrier stream into the reaction cell where it was quantified by coulometric titration. Further details are given in Robinson and Williams (1991).

Nutrients were measured using a Technicon AA-II autoanalyser. The chemistries used were the standard wet chemical procedures developed at PML. The colorimeter outputs were logged by a chart recorder monitored by an ABC-system Level A interface. Standards made up in low-nutrient seawater and both seawater and MilliQ blanks were run.

## 2.3) Data Acquisition

All data from the automatically logged sensors were acquired using the RVS ABC shipboard data logging system. Each instrument was connected to a microcomputer (or Ocean Data Logger PC) interface (the Level A), which captured and time-stamped (using a central master clock) the data at regular intervals. The information was transmitted to a logging workstation (the Level C) via a disk buffer (the Level B).

A stand-alone PC independently logged the data from the  $TCO_2$  system. Care was taken to ensure that the PC clock was synchronised to the central master clock.

# 3) Calibration and Quality Control Procedures

## 3.1) Introduction to BODC processing procedures

Data from the ABC system Level C data files were merged onto a common GMT time base in BODC's binary merge format. The  $TCO_2$  data were further processed by the data originator (Carol Robinson) and submitted to BODC as a flat ASCII file, which was merged into the binary merge file.

Each data channel was inspected on a graphics workstation and any spikes or periods of dubious data were flagged. The power of the workstation software was used to carry out comparative screening checks between channels by overlaying data channels. A map of the cruise track was simultaneously displayed in order to take account of the oceanographic context.

## 3.2) Navigation

Scientific navigation was derived primarily from the GPS system. Dead reckoning was used when no satellite fixes were available. A navigation check program was run at BODC to locate any gaps in the navigation channels and to ensure that the ship's speed did not exceed 19 knots. A single gap with duration of 1 minute was found. This was filled by linear interpolation.

However, there were 102 speed check failures, mostly with speeds of 19-21 knots. The maximum erroneous speed located was 24.2 knots. These check failures were tracked down to small spikes in latitude or longitude that were replaced by interpolated values.

## 3.3) Meteorology

#### Barometric Pressure

Visual inspection of the data showed them to be clean and free from spikes. No attempt was made to correct the data to sea level.

#### Air Temperature

The air temperature data consisted of dry bulb and wet bulb channels. Visual inspection revealed that whilst the dry bulb channel looked credible, the wet bulb channel had serious problems. Wet bulb temperatures were higher than the corresponding dry bulb values for much of the cruise and the data channel included frequent long periods of absolutely constant data. Consequently, the wet bulb data channel has been excluded from the final data set. A small number of spikes and peaks interpreted as stack pollution events have been flagged as suspect on the dry bulb temperature channel.

### Photosynthetically Available Radiation

The PAR vector irradiance data were supplied as calibrated data (based on manufacturer's calibrations) in units of  $W/m^2$ . The data were screened and no problems were identified. Note that as there was only one sensor there is a higher risk of PAR underestimation due to shading events.

#### Solar Radiation

The solar radiation data were supplied as calibrated data (based on manufacturer's calibrations) in units of  $W/m^2$ . The data were screened and no problems were identified. Note that as there was only one sensor there is a higher risk of solar radiation underestimation due to shading events.

#### Wind Velocity

Both relative and absolute wind velocity data were provided in the data set from the cruise. The relative wind velocities have been retained in the data file. Note that the absolute wind speeds have been converted by BODC from units of m/s into knots to facilitate comparison with the ship's velocity. The scaling factor used was 1.943845.

Inspection of the wind velocity channels revealed the data to be exceptionally noisy. This has been reduced, but not eliminated by flagging the extreme values suspect. The record included periods when the wind speed dropped suddenly, which were interpreted as the anemometer stalling. The affected wind speeds have been flagged as suspect.

## 3.4) Physics

#### <u>Temperature</u>

The sea surface temperature thermometer was calibrated against surface CTD data. A correction of  $-0.091 \circ C$  (standard deviation 0.044) was determined and applied.

#### Salinity

The salinity data were calibrated against calibrated surface CTD data. A correction of 0.194 PSU was determined and applied.

A significant proportion of the data have been flagged as suspect, particularly when the ship was working in the Belinghausen Sea. This is believed to have been associated with ice in the non-toxic supply.

#### Optical Attenuance

The transmissometer data were obtained as voltages. These were ratio corrected for source decay against a manufacturer's air voltage of 4.768V using a cruise air reading of 4.754V.

The corrected voltages were divided by 5 to obtain fractional transmission and

attenuance was computed using the equation:

Attenuance = -4 \* In (fractional transmission)

A significant proportion of the data have been flagged as suspect, particularly when the ship was working in the Belinghausen Sea. This is believed to have been associated with ice in the non-toxic supply.

## 3.5) Biology

## <u>Chlorophyll</u>

The fluorometer was calibrated by linear regression of the raw signal against a set of over 200 fluorometric extracted chlorophyll determinations on samples drawn from the non-toxic supply.

The calibration was divided into two parts:

28/10/1992 07:27 to 10/11/1992 14:00

$$chl-a (mg/m^3) = raw_data * 0.134 - 1.49$$

10/11/1992 14:01 to 17/12/1992 23:03

```
chl-a (mg/m^3) = raw_data * 0.0648 - 0.108
```

## 3.6) Chemistry

## **Nutrients**

The logged data streams, including ambient measurements, standards, baselines and garbage logged when the instrument was off-line, were merged into the binary merge file as voltages. The analyst (Malcolm Woodward) subsequently spent a couple of days at BODC working up the data.

The processing strategy was to work through the chart recorder rolls for each channel. Malcolm identified periods when the autoanalyser output wasn't required, which were flagged as suspect. He then determined calibration functions for each segment of ambient data that were subsequently applied to convert voltages to nutrient concentrations.

These procedures worked well and there is confidence in all six nutrient parameters. Note that as a result of operational factors (medical evacuations to Port Stanley) the data set includes several sections across Drake Passage.

## Total CO<sub>2</sub>

The data originator (Carol Robinson) converted the data from per litre to per kilogram units using density computed from calibrated thermosalinograph data. Two obvious spikes in the data were flagged as suspect.

# 4) Data Warnings

Large quantities of data generated from the non-toxic supply have been flagged as suspect due to problems caused by ice in the system

# 5) Reference

Robinson C. and Williams P.J.leB. 1991. Development and assessment of an analytical system for the accurate and continual measurement of total inorganic carbon. *Marine Chemistry* <u>34</u>, 157-175.