Plume Cruise Pumped Stations

Introduction

During the North Sea Project Plume Cruises (CH42, CH46, CH65 and CH69), the ship was fitted with a clean pumped sampling system to allow samples for trace metal analysis to be collected whilst the ship was underway. This system comprised a Teflon pump with polyethylene tubing. The inlet was attached to the precision echo sounder fish on the port side in line with the forecastle and the outlet was in the RVS clean chemistry container where the samples were handled (Morley et al., 1988).

At regular intervals during the plume surveys, a large volume of water was drawn off this system into clean plastic containers. The time of sampling was noted and the water sample designated as a 'P' station. During Challenger 65, technical problems were encountered with the clean pumped system and a high volume Flygt pump had to be used to obtain a number of samples. As this was not an 'ultra-clean' system, the stations have been designated 'F' stations to clearly distinguish them from the Teflon pumped samples.

Three files of data pertaining to these stations are included on the CD-ROM, termed PSTATN1, PSTATN2 and PSTATN3. The protocols used to obtain the data in each of these tables are described below.

File PSTATN1

This file contains data extracted from the ship's automatically logged sensors contemporaneous with the P-station sampling. It is important to note that these systems were plumbed into the ship's general non-toxic supply which includes a header tank. Consequently, the two plumbing systems had a different lag time. All data included in PSTATN1 were averaged over a four minute interval to minimise the effects of this difference. The data used had been quality controlled by visual examination on a graphics workstation: only data flagged as good were included in the averages.

Navigation

The ship's position was logged every 30 seconds during each cruise. In general, the navigation system used was Decca updated every two minutes and filled by linear interpolation. Gaps when the Decca system was down or radio reception was too poor were filled using SatNav fixes interpolated by dead reckoning based on an em-log below the ship's hull.

Plots of the cruise track against a reliable coastline show no overland incursions even at the higher reaches of river estuaries.

Salinity and Temperature

Salinity and temperature were measured using a thermosalinograph logged every 30 seconds. On cruises CH42 and CH46 the instrument was a TSG103 whilst on CH65 and CH69 the instrument fitted was a Grundy Environmental Systems 6620. Temperature was measured by a thermistor in the non-toxic supply inlet manifold located 2m below the surface. Conductivity (plus an additional temperature measurement for the computation of salinity) or salinity were measured by a unit in the ship's wet laboratory.

The TSG103 instrument has two advantages. First, conductivity and temperature are independently logged. Consequently, they may be independently calibrated and salinity computed digitally using the practical salinity (Fofonoff and Millard (1983)) algorithm. The 6620 uses an internal analogue computation and outputs salinity directly. The salinity algorithm used is unknown (no manual can be found for the instrument) but as the instrument dates from 1979 it is certain to differ from the one used for the TSG103 data.

The consequence of this is a systematic salinity error which increases in magnitude as salinity deviates from 35.0. This will be partially, though not completely, corrected by the intercalibration with the CTD.

Secondly, the TSG103 has an autoranging facility whereas ranges on the 6620 have to be set manually by switches on the thermosalinograph unit. If the data moved out of range, a constant, incorrect value was logged. Significant amounts data were lost in this manner.

In all cases, the thermosalinograph was intercalibrated against surface values taken from the calibrated CTD. The corrections applied to the thermosalinograph, together with the 'P' stations to which they apply, are tabulated below:

Cruise	Start	End	Salinity Correction	Temperature Correction
CH42	P001	P054	0.17	0.01
CH46	P100	P104	0.34	0.00
CH46	P105	P167	0.34	0.01
CH65	P201	P204	0.10	-0.04
CH65	P205	P218	0.04	0.06
CH65	P219	P230	0.13	0.06
CH69	P301	P347	0.07	0.04
CH69	P348	P349	0.05	0.04
CH69	P350	P369	0.07	0.04

Density was computed from salinity and temperature using the algorithm in Fofonoff and Millard (1983).

Dissolved Oxygen

Dissolved oxygen was measured on one cruise only (CH42) using an Endeco 1125 pulsed dissolved oxygen sensor controller multiplexed with 2 Endeco type 1128 D.O. probes. The probes were immersed in a perspex cell (approx 1 litre volume) supplied from the general non-toxic supply via a constant head device at 2 litres/minute. Dissolved oxygen and probe temperature were logged at 15 minute intervals by a PC connected to the controller.

The data were corrected for temperature but as the software was unable to cope with salinity variation were computed at zero salinity. At regular intervals triplicate samples were drawn off from the probe outflow into 60 ml borosilicate glass stoppered bottles and analysed for oxygen by Winkler titration.

These values, recomputed to zero salinity, were used to select the most accurately responding of the two electrodes and then calibrate it by linear regression. Once calibrated, the data were recomputed to in-situ salinity using the equations:

O_2 (actual) = O_2 (zero salinity) / γ

γ = 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

Oxygen saturation was computed using the equation of Weiss (1970).

Chlorophyll

Chlorophyll concentrations were measured using an Aquatracka logarithmic response fluorometer mounted in a light tight box on the starboard deck plumbed into the ship's non-toxic sea water supply. Voltages induced by the receiving photodiode were logged every 30 seconds.

On Challenger 65 and 69, extracted chlorophyll concentrations were determined by spectrophotometric analysis of chlorophyll extracts in 90% acetone from frozen GFF filter papers.

For these cruises, the fluorometer was calibrated by regressing the natural log of the chlorophyll concentration against the fluorometer voltage. Chlorophyll concentrations were then computed using the equation:

Chlorophyll (mg/m^3) = exp ($a*V + c$)

where V = fluorometer voltage and a and b are the slope and intercept of the regression line. The constants determined were:

CH65: a = 1.314, b = -2.453 (n=121, r^2=74.8%)
CH69: a = 2.705, b = -6.904 (n=39, r^2=51.6%)

No extracted chlorophylls were taken on CH42 and CH46. For CH42 values of a and b of 1.156 and -2.097 were obtained by interpolation of the calibrations from CH41 and CH43. Both of these were poor calibrations (r^2 values of 33.43 and 13.63 respectively), possibly due to the small range of chlorophyll concentrations encountered in winter conditions.

For CH46, the calibration from CH47 was used (there was no calibration for CH45). This gave values for a and b of 0.717 and -0.6205 (n=98, r^2=59.04%).

Attenuance and Total Suspended Matter

Attenuance was measured using a SeaTech transmissometer mounted in a light tight housing on the starboard deck, plumbed into the general non-toxic sea water supply. The transmissometer had a red (661 nm) light source and an optical path length of 25 cm.

The photodiode voltage was logged every 30 seconds. This was corrected for decay of the light source using the ratio of the voltage measured in air during the cruise to the voltage specified by the manufacturer. Path length independence was achieved by converting the air corrected voltage to attenuance using the equation:

Attenuance (per m) = $-4.0*\log_e(\text{voltage}/5.0)$

Total suspended matter was determined by regressing attenuance against gravimetric suspended matter determinations and applying the equation:

Total suspended matter (mg/l) = (Attenuance-a)/b

where a is the slope of the regression and b its intercept. The results of the regressions were as follows:

Cruise	a	b	n	r^2
CH42	0.46	1.08	49	N/A
CH46	0.51	0.53	38	N/A
CH65	0.51	-0.10	119	86.8
CH69	0.45	0.00	65	62.0

Nutrients

The nutrient values were determined using a Technicon AA2 autoanalyser connected to the general non-toxic sea water supply via a continuous filtration block (Morris et al., 1978).

The method used for phosphate was based on the 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.

The method used for silicate was based on the reduction of a silicomolybdate in acidic solution to 'molybdenum blue' by ascorbic acid. Oxalic acid is introduced into the sample stream before the addition of ascorbic acid to eliminate interference from phosphates.

Nitrate was reduced to nitrite by a Cu/Cd reduction coil. The nitrite was 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. With this method nitrite interference cannot be eliminated and consequently the parameter measured is nitrate plus nitrite.

Nitrite was analysed by the same method as nitrate with no reduction prior to complexing.

In all cases the colorimeter output was as a voltage to a chart recorder which was tapped off and logged automatically at either 30 second or 1 minute intervals.

Calibration was achieved by running four standard concentrations through the system once or twice a day. Distilled water washes were passed through the system at approximately six-hourly intervals.

The processing of autoanalyser data is complex. The voltage channels were screened on a graphics workstation and suspect data points, baselines (voltages logged for a distilled water wash) and standards were given discrete flags.

The data were subdivided into segments using the analyst's notes and the chart records for which a the baseline was linear and a single calibration curve applied.

The processing system computed a baseline drift equation for each segment and, in a second pass, stripped off the baseline. Calibration equations were computed and applied to each segment. The calibration program additionally converted all baseline and standard flags to suspect.

Silicate required an additional processing step prior to baseline correction. Running a distilled water wash caused the silicate signal voltage to drop, sometimes by as much as 100 per cent. This voltage drop was assumed to be a linear drift between baselines and corrected on this basis.

Post-processing quality control comprised checking time series plots for any spikes which have been overlooked and checking the concentrations computed for the standards.

The internal processes of an autoanalyser involve considerable delays between the collection of a water sample and the logging of the data point for that sample. Time corrections were applied to synchronise nitrate to salinity and the other three nutrients to nitrate.

File PSTATN2

This file contains the dissolved trace metal data, together with salinity and extracted chlorophyll data.

Salinity

Water samples were drawn into a screw topped glass bottles with an airtight plastic seal and transferred to Southampton where salinity was determined using an 'Autosal' salinometer.

Chlorophyll and Phaeopigment

Up to 2 litres of water for each sample were filtered through glass fibre filters (GFF) and frozen quickly on board ship. The samples were returned frozen to the laboratory where they were extracted with 90% acetone and assayed in a scanning spectrophotometer. The concentrations of chlorophyll and phaeopigments were calculated using the SCOR-UNESCO algorithms (Strickland and Parsons, 1968).

Dissolved metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn)

Each sea water sample was pressure-filtered (ca. 0.7 bar) in-line through a 0.4 µm Nuclepore membrane filter. Samples for dissolved metal analysis were acidified to ca. pH 2 by the addition of sub-boiled nitric acid (1 ml per litre of sea water) in order to stabilise the total-dissolved concentrations of metals.

For a substantial proportion of the samples large volume filtration systems were used to obtain sufficient suspended particulate material for trace metal analysis.

Analysis was undertaken using the specialised clean facilities in the Department of Oceanography, University of Southampton. Dissolved metals were extracted and preconcentrated following the dithiocarbamate complexation-freon extraction method of Danielsson et al. (1978), as modified by Statham (1985) and Tappin (1988), and were determined by graphite furnace atomic absorption spectrophotometry (GFAAS).

Within batch analytical precision of the method is generally less than 10% (coefficient of variation) for each metal. Fuller details of the method are given in Tappin et al. (1992).

Quality control (i.e.. accuracy and between batch analytical precision) of the data was assessed by regularly analysing aliquots of the CASS-1 coastal sea water reference sample for dissolved trace metals and a bulk filtered acidified sea water sample which was used for batch-to-batch quality control.

Results of these analyses were satisfactory, with very few exceptions, and ensure that the data are of high quality.

Additionally, the data set was examined to identify any values which appeared to have been affected by contamination on the basis of supporting data; it was necessary to reject an insignificant fraction of the total data.

Dissolved Al

A separate aliquot of the pumped sea water sample was filtered through a 0.4 µm Nucleopore membrane using a small vacuum unit and analysed using the method of Hydes and Liss (1976).

The complete analytical procedure was completed at sea in the ship's general laboratory.

Dissolved Arsenic Species

A separate aliquot of water was filtered, in the clean laboratory, through a 0.45 µm Millipore filter for arsenic analysis. The samples were stored at 4°C to reduce biological activity and keep losses of monomethyl arsenic (MMA) and dimethyl arsenic (DMA) to a minimum. Nevertheless, some losses were inevitable as the samples had to be stored on board ship for the cruise duration (up to 2 weeks) and subjected to a 2-3 week analytical procedure. These losses have been quantified for samples from the Tamar Estuary in Kitts (1991).

The technique used for inorganic arsenic was to add 6M Analar HCl and 2 per cent Spectrosol $NaBH_4$ solution to the water sample to generate arsines. These were purged from the apparatus by a stream of nitrogen for analysis by flame atomic absorption spectroscopy.

MMA and DMA were analysed using a similar technique using a lower acid concentration (1M) to favour the formation of organic arsines. The lower concentrations required the incorporation of an arsine trapping procedure. The nitrogen purgative, dried by NaOH traps, was passed through a glass U tube packed with glass beads cooled to -196°C by liquid nitrogen. The trap was allowed to gradually warm to room temperature giving up the trapped arsines as a series of pulses, thus achieving separation of the arsenic species. Each species was analysed by flame atomic absorption spectroscopy.

A full description and discussion of the analytical techniques is given in Kitts, 1991.

Dissolved Mercury

Reactive mercury, i.e. mercury which can be determined without prior oxidation, was determined by the reduction of the mercury in the acidified sample to elemental form by the addition of tin (II) chloride. This was then removed from solution by purging with oxygen-free nitrogen and the mercury vapour trapped as an amalgam on gold chips. Once purging was complete, the gold chips were inductively heated to vaporize the mercury as a pulse which was quantified by atomic absorption spectroscopy.

Total mercury was measured by the above method on samples which had been oxidised by addition of hydrochloric acid, potassium bromide and potassium bromate. Samples were left to oxidise for at least an hour before the bromine was reduced by the addition of excess hydroxylammonium chloride solution.

Both mercury determinations were on sea water which had been filtered through an ashed (450°C for 24 hours) GFF filter paper. Full details of the methodology are given in Harper et al (1989).

File PSTATN3

This file contains the particulate trace metal data together with two independent measurements of suspended matter.

Suspended matter

Two independent estimates of total suspended matter were obtained. The first was a determination of the weight of material deposited on the Nucleopore filter to be used as the analytical sample.

A further two litres of water were drawn into a large measuring cylinder and filtered using a vacuum filtration system onto a pre-weighed GFF filter. Each sample was carefully washed with distilled water to remove salt, removed from the filtration system and air dried.

In some cases where samples had a large sediment load it proved impossible to filter two litres. In these cases, as much of the sample as possible was filtered and the volume filtered determined by noting the volume of water remaining in the measuring cylinder.

After the cruise, each sample was reweighed to constant weight and the total suspended matter concentration determined by subtracting the pre-cruise filter paper weight and dividing by the volume of water filtered.

Particulate trace metals

The preparation of the sample membranes is described above. Prior to analysis, the samples were stored frozen. Once thawed, they were leached using 1M HCl at room temperature for 8 hours under clean conditions. The leachate was decanted into volumetric flasks and made up to volume. Metals were determined by either flame AAS or GFAAS.

The data were supplied to BODC in units of µg/g dry weight or per cent in the case of aluminium. The metals supplied in µg/g were converted to nmoles per litre of water by multiplying by the suspended matter concentration (included with the data) and dividing by the atomic weight (Cd 112.4; Co 58.933; Cr 51.996; Cu 63.54; Fe 55.847; Mn 54.938; Ni 58.69; Pb 207.19; Zn 65.37).

Aluminium was converted to µmoles per litre of water by multiplying by 10 times the suspended matter concentration and dividing by the atomic weight (26.982).

N.B. In all computations, the suspended matter concentration determined from the Nucleopore filter as part of the trace metal analytical procedure was used.

References

Danielsson, L.-G., B. Magnusson and S. Westerlund (1978) An improved metal extraction procedure for the determination of trace metals in sea water by trace metals in sea water by atomic absorption spectrometry with electrothermal atomization. Analytica Chimica Acta 98, 47-57.

Fofonoff N.P. and R.C. Millard Jr. (1983) Algorithims for computation of fundamental properties of sea water. UNESCO Tech. Pap. mar. sci. 44: 53 pp.

Harper, D.J., C.F. Fileman, P.V. May and J.E. Portmann (1989). Methods of analysis for trace metals in marine and other samples. Aquatic environment protection: analytical methods number 3. MAFF Directorate of Fisheries Research, 38pp.

Hydes, D.J. and P.S. Liss (1976). A fluorometric method for the determination of low concentrations of dissolved aluminium in natural waters. The Analyst 101, 922-931.

Kitts, H. (1991). Estuaries as sources of methylated arsenic to the North Sea. Ph.D. thesis, Polytechnic South West.

Morley, N.H., P.J. Statham and C. Fay (1988) Design and use of a clean shipboard handling system for sea water samples. In: Advances in Underwater Technology, Ocean Science and Offshore Engineering, Volume 16 (Oceanology '88), Graham and Trotman, London, 283-290.

Morris, A.W., R.J.M. Howland and A.J. Bale (1978). A filtration unit for use with continuous autoanalytical systems applied to highly turbid waters. Est. coast. mar. sci. 6, 105-109.

Statham, P.J. (1985) The determination of dissolved manganese and cadmium in sea water at low nmol/l concentrations by chelation and extraction followed by electrothermal atomic absorption spectrophotometry. Analytica Chimica Acta 169, 149-159.

Strickland, J.D.H. and Parsons, T.R. (1968). A practical handbook of sea water analysis. Bull.Fish.Res.Bd.Can.:167.

Tappin, A.D. (1988) Trace metals in shelf seas of the British Isles, Ph.D. Thesis, University of Southampton, 279pp.

Tappin A.D., D.J. Hydes, P.J. Statham and J.D. Burton (1992) Concentrations, distributions and seasonal variability of dissolved Cd, Co, Cu, Mn, Ni, Pb and Zn in the English Channel. Continental Shelf Research (vol 12, in press).

Weiss R.F. The solubility of nitrogen, oxygen and argon in water and sea water. Deep Sea Research 17, 721-735.