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RRS *James Clark Ross* Cruise JR18002

3 - 22 NOVEMBER 2018

Repeat hydrographic measurements on GO-SHIP line SR1b

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ABSTRACT

The 24th complete occupation of the Drake Passage section SR1b obtained full-depth temperature, salinity, dissolved oxygen, and lowered ADCP velocity profiles at 29 stations between Burdwood Bank and Elephant Island, along with water column samples of salinity, dissolved oxygen, nutrients, carbonate system parameters, oxygen and carbon isotopes, and CFCs and SF6, and underway surface ocean and meteorological data and vessel mounted current measurements. The aims of these decadal repeat hydrographic measurements are to monitor the Antarctic Circumpolar Current's properties and transports and contribute to understanding the Southern Ocean's role in heat and carbon storage and transports and the contribution of ocean circulation to regional patterns of warming and sea level rise. They contribute to the international Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) and were funded by NERC through the Ocean Regulation of Climate by Heat and Carbon Sequestration and Transports (ORCHESTRA) National Capability programme and Transient tracer-based Investigation of Circulation and Thermal Ocean Change (TICTOC) large grant. At approximately half the stations large-volume samples were taken to measure radium and actinium isotopes to constrain iron fluxes as part of the NERC-funded RaCE:TraX project. The cruise also included opportunistic measurements of water column microplastics (funded by the Collaborative Antarctic Science Scheme) and nutrient isotopes, and experiments on phytoplankton nutrient limitation.

KEYWORDS

Repeat hydrography, CTD, LADCP, VMADCP, nutrients, carbon, transient tracers, CFC, isotopes, radioisotopes, radium, iron, phytoplankton, microplastics, ocean observation

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Clément Vic	U. Southampton	Physics

Ship's Personnel

Graham Chapman	Master	Simon Evans	Chief Officer
Samuel Vargas	2nd Officer	Scott Cramman	3rd Officer
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Aleksander Hardy	3rd Engineer	Steven Eady	4th Engineer
Lloyd Sutton	Purser	Amber Chadwick	Doctor
Thomas Biggs	Deck Engineer	Oliver Vivian	Deck Engineer
Clifford Mullaney	Bosun Sci Ops	Noel Littlehales	Bosun
John O'Duffy	Bosun's Mate		
Mark McMahon	AB	Martins Neilands	AB
Christopher Devitt	AB	Paula Muñoz Garcia	AB
Carlos Vargas Leon	Motorman	Stephen Pictor	Motorman
Brian Robertson	Chief Cook	David Tucker	2nd Cook
Derek Lee	Senior Steward	Oliver Burch	Steward
Michael Anderson	Steward		

2 Itinerary and Cruise Track

Cruise JR18002 departed Mare Harbour, Falkland Islands, on 3 Nov 2018, crossed Drake Passage to the vicinity of Elephant Island, and returned to Port Stanley, Falkland Islands, on 22 Nov 2018. The cruise track and CTD/LADCP cast sites are shown in Figure 2.1. GO-SHIP CTDs were conducted working south from Burdwood Bank to 59.3 S, then recommenced working north from Elephant Island, along with RaCE:TraX CTDs.

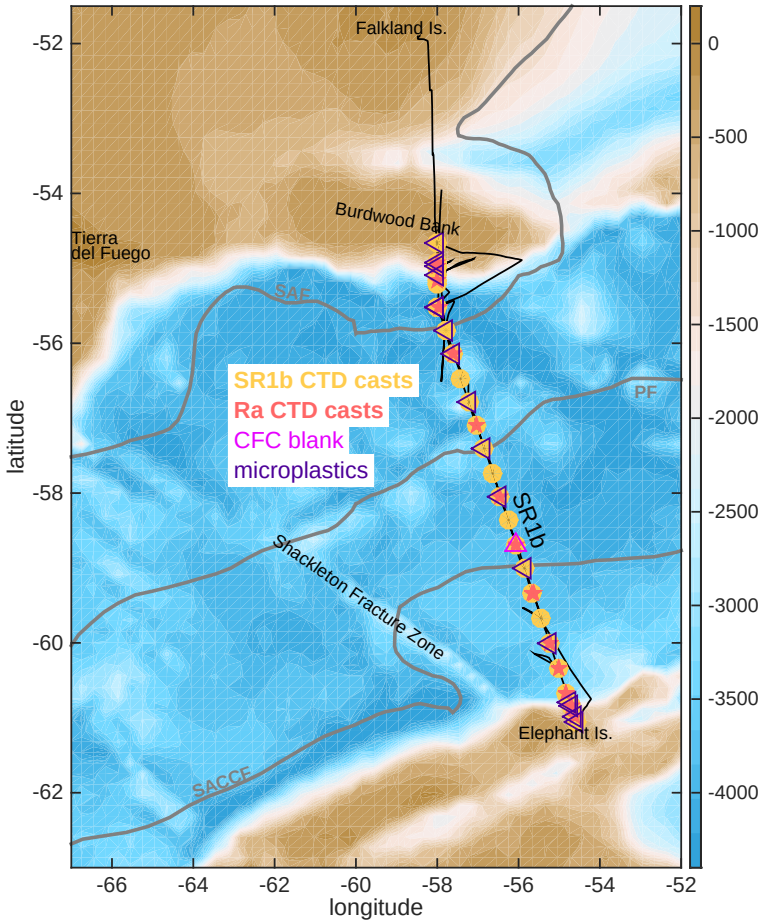

Figure 2.1: JR18002 cruise track and locations of GO-SHIP CTD casts (yellow circles), RaCE:TraX repeat casts (orange stars), CFC bottle blank (pink triangle), and casts with collection of microplastics samples (purple triangles), overlaid on bathymetry from IBCSO and *Smith and Sandwell* and climatological locations of the Subantarctic Front (SAF), Polar Front (PF), and Southern ACC Front (SACCF) from *Orsi et al.* (1995).

3 Objectives

RRS *James Clark Ross* cruise JR18002 included programmed fieldwork related to three projects, as well as opportunistic sampling for three more:

- ORCHESTRA (Ocean Regulation of Climate by Heat and Carbon Sequestration and Transports)
  Lead: Y. Firing, NOC
  NERC LTS-M NE/N018095/1
  ORCHESTRA aims to quantify and understand how the Southern Ocean and its interactions with the atmosphere and ice affect the ocean's uptake and storage of heat and carbon. Cruise aim: To make high-quality decadal repeat hydrographic measurements on GO-SHIP line SR1b, repeating similar measurements made in 2009 as well as continuing a near-annual time series of physical measurements ongoing since 1993.

- TICTOC (Transient Tracer-Based Investigation of Circulation and Thermal Ocean Changed)
  Lead: M.-J. Messias, Exeter
  NERC Large Grant NE/P019064/1
  TICTOC aims to understand the contribution of ocean circulation to regional patterns of ocean warming and sea level rise. Cruise aim: To make transient tracer (CFC and SF6) measurements on GO-SHIP line SR1b, repeating similar measurements made in 2009.

- RaCE:TraX (Radium in Changing Environments: A Novel Tracer of Iron Fluxes at Ocean Margins)
  Lead: A. Annett, U. Southampton
  NERC Independent Research Fellowship
  RaCE:TraX aims to reduce the uncertainties in iron fluxes to the ocean using Radium and Actinium isotopes as a chronometer. Cruise aim: to measure Ra and Ac isotope ratios from samples across Drake Passage, to be used along with samples from the Western Antarctic Peninsula (cruise JR18003) to determine the origin of iron in the Antarctic Circumpolar Current.

- Microplastics in Drake Passage
  Lead: A. Mountford, Newcastle (PI: M. Morales Maqueda, Newcastle)
  Collaborative Antarctic Science Scheme
  Aim: make repeat measurements of microplastic concentrations across Drake Passage to validate numerical model of microplastic dispersion.

- Phytoplankton productivity in high-nutrient, low-chlorophyll (HNLC) regions
  Lead: T. Browning, GEOMAR
  Aim: measure nutrient co-limitation of phytoplankton sampled from the HNLC Drake Passage.

- Nutrient isotopes
  Lead: R. Tuerena, U. Edinburgh
  Aim: quantify N and Si regeneration within the mixed layer.

ORCHESTRA and TICTOC sampling were both contributions to the Global Ship-based Hydrographic Investigation Program (GO-SHIP), with transient tracers measured by TITOC and the other GO-SHIP level 1 variables by ORCHESTRA.

4 Narrative

Yvonne Firing and Alice Marzocchi

JR18002 started on a less than promising note, with 3 members of the ship's complement sent home the day before sailing due to an incident in port, and the NMF LN2 generator tech disembarking with the pilot for medical reasons. We then ran into a concentration of both weather and technical delays in the first part of the cruise, with some technical issues persisting or recurring throughout, and another batch of weather about halfway through.

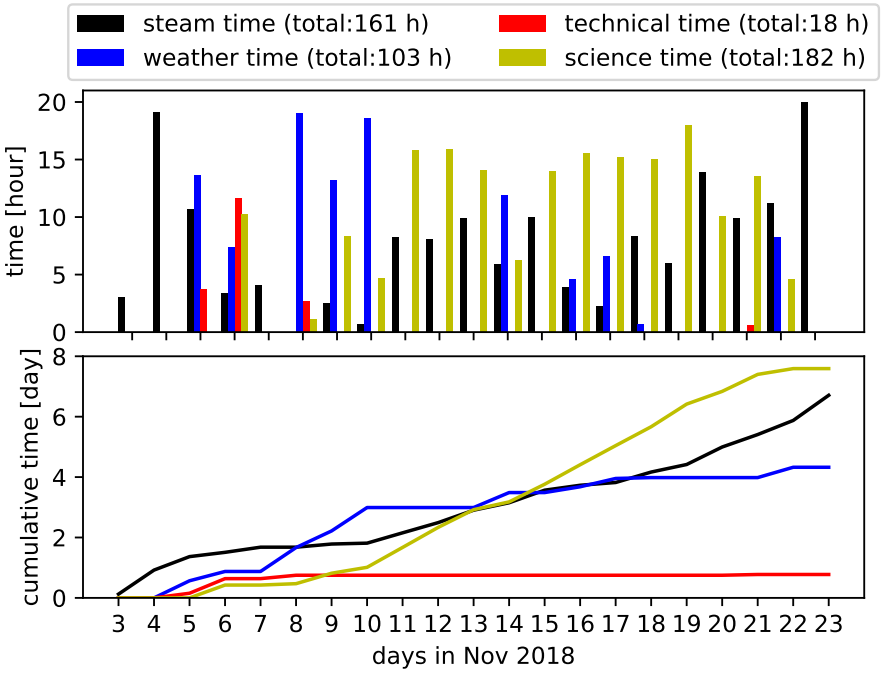

Figure 4.1: Daily and cumulative time spent on science, steaming, weather delays, and technical delays (not including pauses/slowdowns during CTD casts for winch testing), based on the bridge log.

28^{th} departure of most of the science party from Brize Norton
29^{th} arrival in Stanley
30^{th} Oct "tropical" swimming at Surf Bay + walk to Gypsy Cove
31^{st} Oct move onto the JCR, unpacking, very still evening with beautiful sunset
1^{st} Nov physics team found penguins at Bertha's Beach, everyone else setting up, science party complete (i.e. Matthew and Amber arrive)
2^{nd} Nov everyone else also found penguins + more setting up + Clement's birthday drinks at glamorous MPA bar
3^{rd} Nov set sail in the morning (less 1 NMF tech, 1 3rd officer, 1 AB, and 1 steward) + first tow fish deployment + start of greasy nightmares
4^{th} Nov weather day
5^{th} Nov first CTD attempt and sampling practice; lost comms on upcast after firing 5 bottles, plus wire was slipping despite degreasing
6^{th} Nov first wildlife sighting (pod of pilot whales) + second CTD/first full test CTD (still with greasy cable) and more sampling practice
7^{th} Nov weather and more greasy cable nightmares + first SR1b station (with "new" old cable)
8^{th} Nov picking up pace with CTDs, then paused by massive waves (i.e. flooded aft deck night)
9^{th} Nov back to CTDing, dropping a station due to time
10^{th} Nov shrinking cups day, deepest station (wire confirmed to only reach to 4300 m)

11^{th} Nov Remembrance Day
12^{th} Nov giant iceberg, sunny day, up to more than 20 CTDs
13^{th} Nov long steam to Elephant Island to avoid weather + demise of bottle 19 + start of Amber's casts
14^{th} Nov humpback whales show
15^{th} Nov bad weather, then back to CTDs late in the day
16^{th} Nov more pilot whales following the ship + getting close to finishing SR1b CTDs
17^{th} Nov last SR1b CTD in the snow! Back on deck just before midnight
18^{th} Nov full attention to Amber's casts and long steam north
19^{th} Nov morning pilot whales and surfing penguins + getting smug: now CTDs are only at convenient(ish) times + fluffying party in Ambers container
20^{th} Nov end of Amber's casts and end of science!
21^{st} Nov start packing, steaming, end of cruise dinner
22^{nd} Nov return to Port Stanley

4.1 Major technical issues

The overall impact of the issues noted below on the data obtained was relatively little. One SR1b GO-SHIP cast was dropped (by replacing two adjacent stations with one at the mid-point). The deepest site was not sampled to full depth on a continuous cast; fortunately, however, this is in a relatively quiet isolated basin in the northern part of the passage. The section was broken about 2/3 of the way through, producing a 4-day discontinuity, fortunately in a relatively quiescent area; satellite altimetry along with the repeat of the last southbound site on our way north conforms that a continuous section can still be constructed. One RaCE:TraX site was dropped and sampling was reduced by 1/3 at another site (by dropping a cast; most RaCE:TraX profiles required 3 casts). Niskin issues led to not sampling or discarding results from 109 (out of 712) sets of attempted Niskin samples on GO-SHIP casts, to reducing microplastics sample volumes being reduced from 10 L to 5 L, and to 28 (out of 94) RaCE:TraX samples being short of the target volume of 150 L, although only 4 were substantially smaller. The uncertainty about sample quality due to the many additional possibly- or slightly- leaking Niskins is partially mitigated by generally good comparisons between sample and CTD values and between neighbouring sample profiles.

The impact on personnel was more significant. The wire problems at the start interferred with training CTD watchstanders and samplers on the test casts. The initial plan was to perform all the casts southbound, with the RaCE:TraX repeat casts interspersed with the SR1b casts, giving time for RaCE:TraX PI Annett to process samples and prepare sampling supplies in between (space did not permit preparing everything before). Because of the accumulation of delays early on, and the concern over the reach and life of the CTD wire (see below), we decided to postpone starting the RaCE:TraX casts until reaching the northbound leg. This rearrangement meant that the last 4 days of the cruise were extremely intensive for Annett.

4.1.1 CTD wire

The new CTD wire turned out to be impregnated with grease; an attempt to degrease it on a deadweight cast appeared productive, so following discussions over what measures to take on a real cast (including stoppers able to get hauling started if necessary, and quasi-continuous cleaning), the ship side and PSO decided to try a test cast with the CTD. The failed both because the wire was slipping on hauling and because CTD comms were lost; it turned out that there was both a short in the wire and damage to a CTD connector cable (due to lines used during handling of the rosette over the rail and the fact that the cable was run along the outside of the rosette due to the 20 L Niskins). Given feedback from NMF that a high number of washes would be required to make the wire useable on the JCR's winch, we decided to switch to the old wire, even though it was too short to reach full ocean depth on one of the stations, and the need

for additional reterminations and further shortening was anticipated; fortunately this was not necessary and the AABW-containing deep southern part of the section was not out of reach. Throughout the cruise there were a number of shorter delays associated with testing and repairing one of the winch pumps.

4.1.2 Niskins

The 20 L Niskins were troublesome, leaking both consistently (2-4 per cast) and irregularly (for the most part, different bottles each time), making it difficult to troubleshoot specific problems. They were the SDA's newly acquired trace metal clean bottles, loaned because NMF was not able to provide them. NMF did provide a frame. When the Niskins were first tested on JR18001, it proved difficult to get them to seal, so new springs and lanyards were installed during mobilisation for JR18002; however, it was still difficult to get the tension right, resulting in several snapped lanyards and many instances of bottles not closing due to low tension. The Niskins were installed on the usual JCR rosette normally used for 12 L bottles; it is not clear why the larger, NMF-suppled frame was not used, since the 20 L bottles barely fit on the smaller frame and this caused difficulties with instrument cable placement, rosette handling, Niskin closing and sealing (due to end caps hitting the frame as well as lanyards becoming trapped in neighbouring bottle endcaps), and general working around the rosette. The securement of the Niskins to the rosette was also problematic; when one was lost due to an impact against the side of the ship, it became evident that the mounting brackets for several others had loose or missing bolts and in some cases were warped. More detail is given in Appendix 20. It may be that customised springs and an appropriately sized frame can solve these problems, but otherwise the use of these bottles is not recommended.

4.1.3 Salinometers

The salinometers, despite having been serviced shortly before the previous cruise, revealed serious problems on that cruise, and on JR18002 were initially completely unreliable. The AME tech and the lab manager managed to repair one and keep it running for most of the cruise, and then to repair it again once ashore, at which point the rest of the salt samples could be run. The 2nd machine still showed jumps of 10s to 100s of counts (compared to a desired +/-2) about half the time, and was therefore not useable. More detail is given in Section 5.5 and Appendix 20.

4.1.4 LN2 generators

Tom Biggs

Due to the medevac of the NMF LN2 technician, the two LN2 generators (needed by the CFC team) had to be looked after by the deck engineer. The green plant failed around half way through the trip. It had a few issues leading up to this: The motor issue that was temporarily fixed in Stanley. Then it tripped a few times and stopped running early on in the cruise. Eventually though it failed entirely and took the ship's 32A supply with it. I assume this was probably motor related also.

The yellow plant was in the most part good and trouble free. It was only a couple of days before the end of the cruise that it started to play up. It seemed to not produce any LN2, then started slowly then eventually got up to full speed again. It initially looked like there was an issue with the filters and the helium compressor/chiller. On further investigations and discussions with NMF via email I found that the filters were absolutely fine and although the helium pressures were a little out from where they should be, they didn't seem to be having a detrimental effect on the production now that it's up and running again.

The slow production is quite likely to have been caused by users drawing too much from the dewar and the plant having to effectively 'use' the LN2 it was producing to chill the dewar down to the temp where it could store what was being produced. The electronic gauges are not particularly accurate and the 'Minimum' mark written on the gauge is perhaps not clear enough.

5 CTD and LADCP

Yvonne Firing, Louis Clément, Morgan Dibb, Tomas Jonathan, Alice Marzocchi, Andrew Twelves, Clément Vic

NOC, NOC, U Southampton, Oxford, NOC, U Edinburgh, U Southampton

The 71 CTD/LADCP casts, and water samples collected, are summarised in Table 5.1.

One stainless steel CTD system was prepared with a 24-way carousel. Details of the instrumentation are given in Section 20. Operation was normal on the 71 stations conducted during the cruise, except for CTD 23 when the rosette was smashed on the ship's hull during recovery, due to an outstanding wave that suddenly rocked the ship; the impact sheared Niskin 19 from the frame and it was lost.

5.1 CTD operation

Data were acquired with SeaSave V 7.22.3. After each cast, BAS_SVP was run. It prepares a sound velocity profile and a CTD listing for transmission to the UK Met Office. Then, three operations were run through the SBE Data Processing version 7.22.2 software. First, *Run/Data Conversion* was run using the program setup file DatCnv.psa. It converts raw data (.hex file) into engineering units (.cnv and .ros files). The .ros file contains data for each scan associated with a bottle firing, and data for user-selected range of scans before and after each bottle firing. Second, *Run/Align CTD* was run using the program setup file AlignCTD.psa. It inputs an X.cnv file and outputs an X_align.cnv file. It aligns parameter data in time, relative to pressure. This ensures that calculations of salinity, dissolved oxygen concentration and other parameters are made using measurements from the same parcel of water. Third, *Run/Cell Thermal Mass* was run using the program setup file CellTM.psa. It inputs an X_align.cnv file and outputs an X_align_ctm.cnv file. It uses a recursive filter to remove conductivity cell thermal mass effects from the measured conductivity.

SBE35 temperature data were uploaded using SeaTerm after finishing a cast or, for later stations with multiple casts at one site, for several casts at once. SBE35 temperature data can be logged when a Niskin bottle is fired. If the SBE35 is set to 8 samples, it requires approximately 13 seconds to make a measurement, calculated as 8 * 1.1 seconds plus an overhead; the procedure followed for bottle firing was therefore to wait 30 s for equilibration, fire a bottle, and wait 15 s to ensure the SBE35 measurement had been taken. Data are stored internally and must be downloaded at the CTD deck unit as a separate process from the CTD data transfer. The SBE35 data are then transferred as a collection of ASCII files. The SBE35 cable was damaged by handling lines during deployment or recovery of the rosette in the early casts, so the SBE35 was removed before cast 11 and refitted, with a new cable, on cast 23.

All output files were copied from the local drive (D) to the network drive (U).

5.2 Lowered Acoustic Doppler Current Profiler (LADCP) operation

The 300-kHz Workhorse LADCP was installed in a downward-looking configuration on the CTD rosette (see Section 20). The instrument was configured (right) to sample 25 x 8-m bins, with data collected in beam co-ordinates and rotated to earth co-ordinates during processing.

The LADCP was connected to a charger and by a serial cable to the CTD computer in the UIC for programming prior to each station and data download after each station, using BBTalk. Pre-deployment tests were performed prior to each deployment.

Data downloaded after each station were copied to the network data drive (V), with names of the form JR18002_NNN.000. On two casts more than one LADCP file was produced; the additional files were added to processing (see below) but appeared to be very short, with the whole in-water deployment contained in the main file.

5.3 Water sample collection

Seawater samples for analysis were drawn from the Niskin bottles in the following order: CFCs, dissolved oxygen; dissolved inorganic carbon, carbon isotopes, oxygen isotopes, nutrients, nitrogen and silicon isotopes, salinity, microplastics, eDNA, particulates.

Microplastics and carbon 14 were only sampled at selected stations. Microplastics were only sampled at selected depths (surface, bottom and 1 to 3 additional intermediate depths). eDNA was only sampled at stations deeper than 2750 m and 1 or 2 samples were drawn, as close as possible to 2750 m and 1000 m.

Nutrients and dissolved inorganic carbon samples were always taken as duplicates. CFCs and dissolved oxygen isotopes were taken as duplicates only at selected depths. In all cases, unless otherwise noted in the sampling log sheets, the duplicates were taken consecutively.

Niskin bottles firing depths were chosen based on the downcast profiles in an attempt to cover the pressure, temperature, salinity, and oxygen ranges, while taking samples both in regions of low variability (for calibration), and at extrema (including the bottom layer, the surface mixed layer, and subsurface temperature, salinity, and oxygen extrema, where these features appeared in the profile).

After each cast all bottles were checked to ensure they had fired properly and any issues with misfires, leaking or dribbling were noted in the sample log and, where appropriate, annotated in the mbot_01 case of the opt_jc18002.m script. All bottles started with an initial flag of 2 and during CTD processing new quality control flags were assigned to bottles that had been flagged either during sampling or during data checks described below.

For each bottle, initial quality control flags were assigned based on visual inspection:

- Flag 3 : possibly leaking or questionable based on visual inspection (49 Niskins)
- Flag 4 : empty, end caps clearly not seated, heavily leaking, or open spigot (73 Niskins)
- Flag 9 : did not fire (e.g. line did not release, 18 Niskins) or broken Niskin (1 Niskin, see below)

Heavily leaking (from the end caps, not just the spigot) bottles were not sampled. Overall, we had persistent leakage issues, ranging from minor dribbling, to moderate leaking, and all the way to heavy gushing when some bottles were opened, in almost all casts and for several bottles. A number of bottles (e.g. 7, 10, 12, 21) were consistently leaking and/or had issues with pushed-in spigots. Therefore, two bottles were generally fired at the same depth as backups. Bottle 24 often did not fire or fired during recovery/on deck; also in this case, bottles 23 and 24 were often fired at the same depth as a backup.

All Niskin bottles on the rosette intially had 20 L capacity. Two spares were available, but the spigot from one spare had to be used to replace one damaged during cocking of the bottles in the first casts, leaving one complete spare. Upon recovery of the CTD on cast 23, the rosette frame hit the hull of the ship pushing out bottle 19, which consequently also hit the hull of the ship and shattered. The Niskin was replaced before the following cast, but the bottom of the new one repeatedly failed to close, apparently because it was hitting the rosette frame at the bottom. On cast 45, bottle 19 was replaced again with a smaller 12 L bottle, to be used for the remaining casts for Ra sample collection.

Where the Niskin was flagged as 3 or 4, all bottle samples were given a flag at least as high. Niskin flags were later re-evaluated using the sample values, as described below, resulting in final totals of 58 questionable, 75 bad, 18 did-not-fire (attempted), and 1526 good.

5.4 Data Processing

5.4.1 CTD processing for each cast

The CTD data processing followed the methods used on previous SR1b and other NOC OCP cruises, using the Mexec software suite. The Mexec processing steps run following the initial SeaBird conversions and corrections described above are listed in Figure 5.1; cruise-specific options were set in opt_jr18002.m. More information can be found in the JC159 cruise report and in "A User Guide for Mexec, v3.2" (available from the NOC Ocean Circulation and Processes subgroup of the Marine Physics and Ocean Climate group).

On stations 36 to 39, the primary CTD gave bad values for several hundred meters. Secondary sensors looked fine and were set as main sensor for those stations. Subsequently, the secondary sensor was set as the main sensor for all stations (and earlier stations were reprocessed) because it was more reliable overall and was also the sensor the oxygen was plumbed into.

For station 15, automatic out-of-range editing was applied at the mctd_02a.m stage, and the cell thermal mass correction applied after that. For stations 29, 36, 39, and 40-43, automatic out-of-range editing was applied at the mctd_rawedit.m stage. In the case of stations 36 and 39, this was to remove obvious stretches of bad temperature and conductivity data. For the others, relatively small negative pressures were leading to values outside the permitted range for the subsequent GSW calculations, so the minimum allowed pressure was set to -1.495.

5.4.2 Sample ingestion, quality control, and CTD data calibration

Figure 5.2 shows the locations of Niskin samples from SR1b stations, both along the section (top panel) and in time (bottom panel). Niskin sample data were read in to files also containing the CTD data at bottle firing times using smallscript_load_botcaldata.m. As sample data accumulated, we compared sample and CTD data, as well as individual sample values with smoothed, gridded profiles, to detect sample or Niskin flags that needed to be changed (either undetected bad values or bad Niskins, or Niskins flagged as questionable that looked fine). Flags assigned in the laboratory were usually not lowered based on this analysis. Inspection of profiles aboard the ship led to the assignment of bad or questionable flags to 41 salinity, 56 oxygen, 13 DIC, 17 alkalinity, 1 nitrate+nitrite, 2 silicate, and 3 phosphate values (these totals do not include values that were flagged because the Niskin was bad or questionable).

This initial quality control procedure was carried out using two functions:

- msam_checkbottles_01([a:b], var, sr1b) plots one sample of the type var for a range of stations [a:b], alongside residuals from the CTD values (for salinity and oxygen) or from the mapped values (for other quantities). Already flagged points are marked, and points for further investigation are selected using the GUI interface.
- msam_checkbottles_02(n, var) plots profiles of several sample types for a single station n, as well as neigbouring stations values and the CTD/mapped profiles.

A record of all post-comparison flag alterations was kept in the text document bottle_data_flags.txt within the CTD data directory. For oxygen and salinity, some good samples may yet be inappropriately flagged as questionable if they were taken at points in the profile with strong gradients/high variability. To detect these flags on bottles, the script ctd_evaluate_sensors.m plots their values against both the the CTD at firing times and the CTD 1 Hz data stream. Where the latter shows variance encompassing the bottle sample value, the 3 or 4 flag may be altered. Flags in bottle_data_flags.txt are applied to data files by running msam_02b.m. At the conclusion of this process only those results with 2 flags were used for calibration purposes.

Temperature, salinity, and oxygen were calibrated, using ctd_evaluate_sensors.m to compare calibration (SBE35 or bottle sample analysis values) with CTD data and determine calibration functions.

Temperature calibration

Comparisons between 1334 SBE35 readings and values recorded by each of the two CTD temperature sensors showed an apparent scale factor in addition to pressure dependence and, for sensor two, a very small drift in time. The calibration functions used were:

$$\begin{aligned} T_{1,cal} &= T_1(1.00016) + interp([0, 800, 5000], [0.1, -0.2, 0.0] \times 10^{-3}, p) + 1 \times 10^{-5}, \\ T_{2,cal} &= T_2(1.00017) + interp([0, 2000, 5000], [-1, -1.3, -1.8] \times 10^{-3}, p) - n \times 10^{-5} + 2.8 \times 10^{-4}, \end{aligned}$$

where p is pressure and n is station number, and $interp(a, b, c)$ indicates linear interpolation of $b(a)$ to c. The existence of very similar best fit scale factors for each sensor may be a cause for concern, but the correction is quite small in any case.

Conductivity calibration

Conductivities (at Niskin bottle firing temperatures) calculated from 441 good bottle salinity analyses were compared with the two CTD sensors. The calibrations applied were:

$$\begin{aligned} C_{1,cal} &= C_1(1 + interp([0, 1800, 5000], [-0.8, -2.0, -1.5] \times 10^{-3}, p) + 6 \times 10^{-4}/35), \\ C_{2,cal} &= C_2(1 + interp([0, 1500, 5000], [-1.8, -2.8, -4.5] \times 10^{-3}, p)/35). \end{aligned}$$

These conductivity scale factors are approximately equivalent to adding the quantity in curly brackets to salinity.

Oxygen calibration

Using the calibrated salinity and temperature to compute density and convert oxygen concentrations to μmol kg^{-1}, 444 good dissolved oxygen values were compared with the corresponding CTD readings. Scale and additive dependence on CTD oxygen, pressure, station number, and temperature were considered; simple functions of pressure seemed to reduce the bottle-CTD differences without over-fitting, resulting in a final calibration of

$$O_{cal} = O(interp([0, 5000], [1.036, 1.062], p) + 3n \times 10^{-5}) + interp([0, 500, 5000], [-1.50.5 - 0.9], p).$$

5.4.3 Gridded sections

Calibrated temperature, salinity, and dissolved oxygen were gridded using msec_run_mgridp.m (Figure 5.3). The stations used for constructing these sections, from north to south, were: 3 through 22, 44, 40, 36, 32, 31, 27, 26, 25, 23. Station 11, which was not full-depth, was used instead of station 1 for increased temporal continuity. Station 22 (the first cast at this site) was used rather than station 45 (the second cast at this site) because when the section was joined up with station 45, an eddy happened to be occupying this site. The effect of both of these choices, and generally of the discontinuity in the section, should be further evaluated before making any averages or transport calculations, however.

5.4.4 LADCP processing for each cast

Data for each station were processed on fola using the LDEO-IX v 12 software package, developed at Lamont-Doherty Earth Observatory (LDEO). The software uses an inverse method to calculate velocity profiles, optionally including LADCP bottom tracking and/or VMADCP (called Surface ADCP or SADCP within the software) upper ocean velocities as constraints. At-sea processing was performed using four sets of constraints:

1. ship navigation (ladcp/ix/DL_GPS),
2. ship navigation and bottom tracking (ladcp/ix/DL_GPS_BT),
3. ship navigation and VMADCP (ladcp/ix/DL_GPS_SADCP), and
4. ship navigation, bottom tracking and VMADCP (ladcp/ix/DL_GPS_BT_SADCP).

Directories, links, and parameter files for LADCP processing were set up at the beginning of the cruise using conf_script_jr18002, and by running lad_linkscript_ix after each cast. As part of ctd_all_part1, a 1-hz ctd file is generated (mout_1hzasc) with CTD data to be used by the LDEO software. Additionally, mvad_for_ladcp was run to export time, lat, lon, u, v and depth from the VMADCP into mat files to be used by the LDEO processing; ladctd_linkscript_ix makes links to these files. CTDs 2,11,49,50, and 52-64 did not go deep enough to see the bottom, so the bottom tracking constraint could be applied to the LADCP processing and we considered the SADCP-constrained solutions as the most realistic ones. Apart from these CTDs, we considered the bottom-track and SADCP-constrained solutions as the most realistic ones. An example of profiles obtained for different processing options is shown in Fig. 5.4.

JR18002		CTD station number						
	script	**example outfiles**						
	DatCnv.psa	ctd_cruise_nnn.cnv						
	AlignCTD.psa	ctd_cruise_nnn_align.cnv						
	CellTM.psa	ctd_cruise_nnn_align_ctm.cnv						
T	ctd_linkscript	ASCII_FILES/ ctd_cruise_nnn_ctm.cnv						
M	stn = *nnn*; ctd_all_part1							
	msam_01	sam_cruise_nnn.nc						
	mctd_01	ctd_cruise_nnn_raw.nc						
	mctd_02a	ctd_cruise_nnn_raw.nc						
	mctd_02b							
	mctd_03	ctd_cruise_nnn_1hz.nc ctd_cruise_nnn_psal.nc						
	mdcs_01	dcs_cruise_nnn.nc						
	mdcs_02	dcs_cruise_nnn.nc						
	mout_1hzasc							
M	stn = *nnn*; mdcs_03g	dcs_cruise_nnn.nc, ctd_cruise_nnn_surf.nc						
M	stn = *nnn*; ctd_all_part2							
	mctd_04	ctd_cruise_nnn_2db.nc						
	mfir_01	fir_cruise_nnn_bl.nc						
	mfir_02	fir_cruise_nnn_time.nc						
	mfir_03	fir_cruise_nnn_ctd.nc						
	mfir_04	sam_cruise_nnn.nc						
	mwin_01	win_cruise_nnn.nc						
	mwin_03	fir_cruise_nnn_winch.nc						
	mwin_04	sam_cruise_nnn.nc						
M	mctd_checkplots							
M	mctd_rawshow							
M	mctd_rawedit	ctd_cruise_nnn_24hz						
M	smallscript_postedit	set klist first (only if mctd_rawedit run)						
T	lad_linkscript_ix							
M	cfgstr.orient = 'DL'; cfgstr.constraints = {'GPS'}; process_cast_cfgstr(*nnn*, cfgstr); cfgstr.constraints = {'GPS';'BT'}; process_cast_cfgstr(*nnn*, cfgstr);							
	If cast wasn't full-depth: edit populate_station_depths case in opt_*cruise*.m to set water depths Set niskin flags in mbot_01 case in opt_*cruise*.m							
M	klist = nnn; smallscript_botnav	summary .csv files can be synced to legwork						

Steps marked T are to run in terminal; steps marked M are to run in matlab.
It is critical that the SBE DatCnv exports scan and time variables as well as other CTD variables.
NMEA lat and lon are also desirable. Conductivity in mS/cm (approx 30-40) rather than S/m (approx 3-4) is preferred.
If there are large spikes in temperature, you should set the mctd_01 case of opt_*cruise*.m and rerun from the beginning, so that the noctm version is processed, automatically despiked, and then run through the cell thermal mass conversion.

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Figure 5.1: Logsheet for Mexec CTD processing.

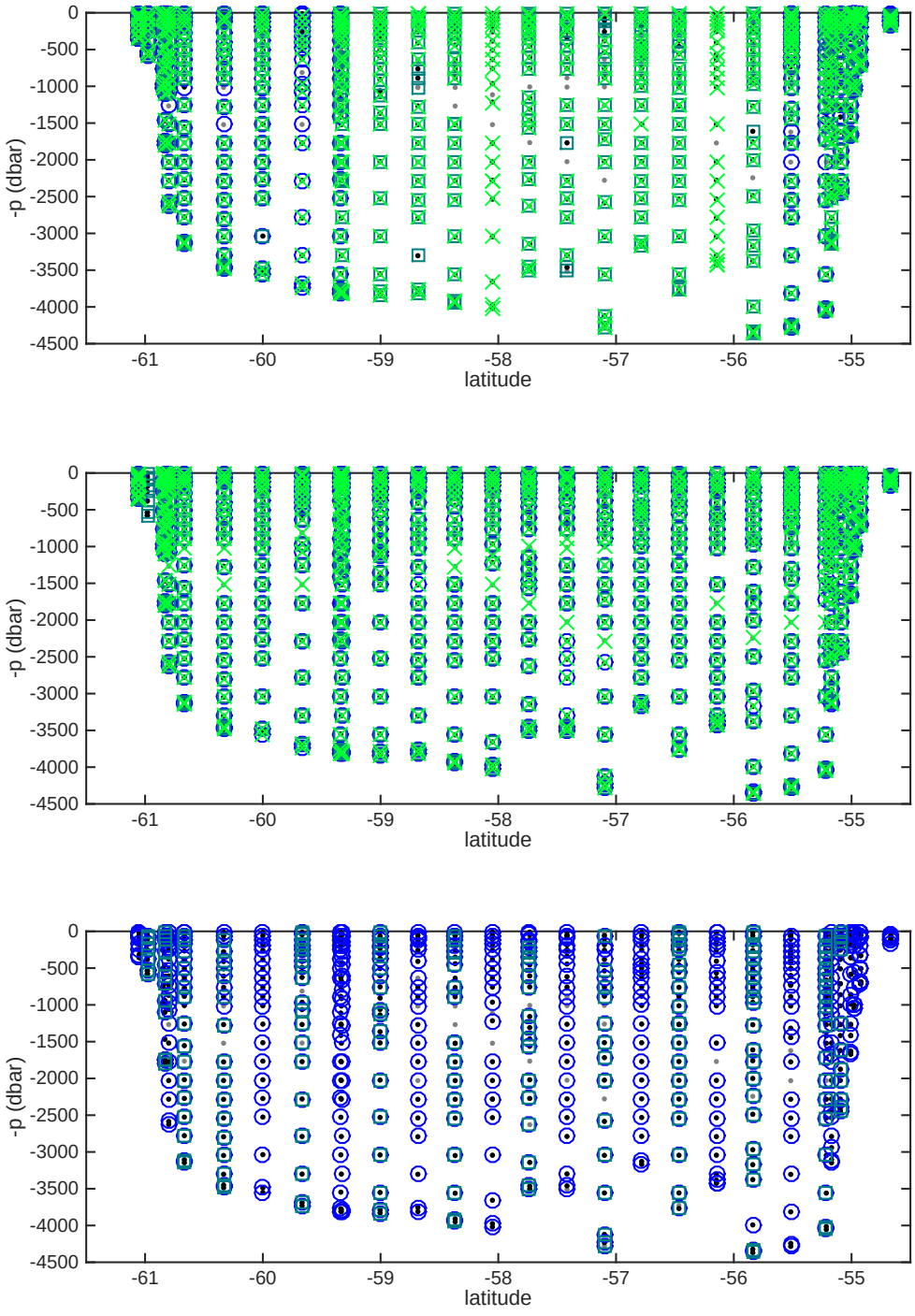

Figure 5.2: Latitudes and depths of Niskin bottle fire attempts (gray dots), completed fires (black dots), and successful samples for SBE35 temperature (top, blue circles), salinity (top, teal squares), dissolved oxygen (top, green Xes), nutrients (middle, blue circles), carbon (middle, teal squares), CFCs (middle, green Xes), d18O (bottom, blue circles), radiocarbon (bottom, teal squares).

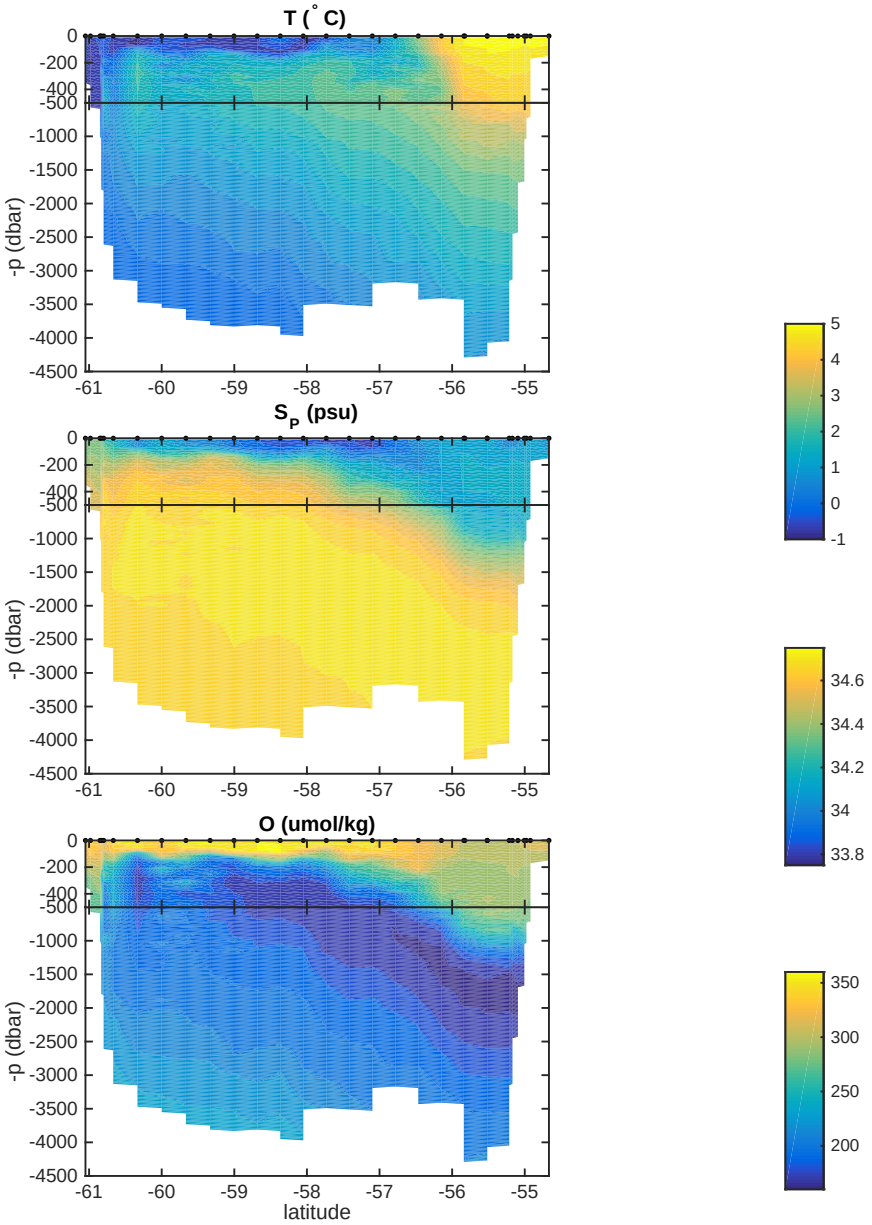

Figure 5.3: Gridded temperature, salinity, and dissolved oxygen from SR1b section (see text for stations used).

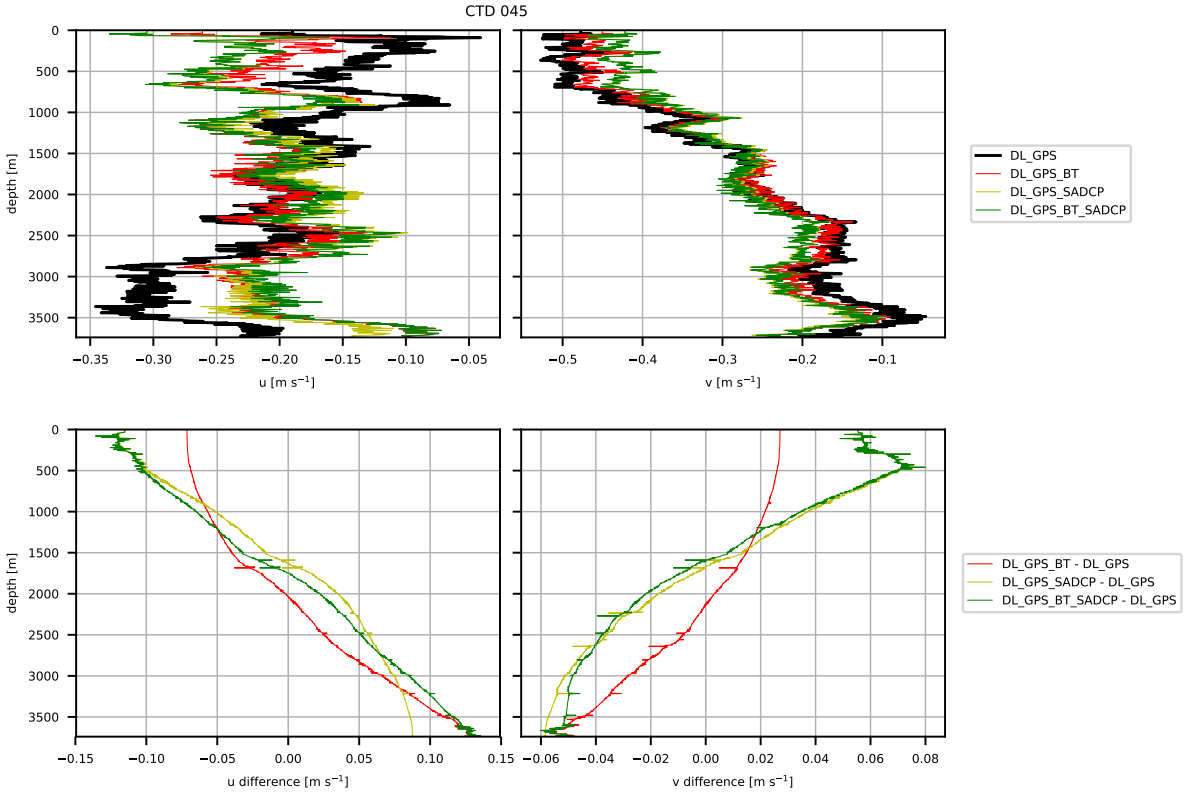

Figure 5.4: (top) Zonal (u) and meridional (v) velocity profiles from the LADCP for CTD 045. Black, red, yellow and green lines represent the profiles for processing options 1,2,3 and 4 from the list in section 5.4.4, respectively. (bottom) Velocity difference between the profiles on corresponding to processing options 2,3,4 and the profile corresponding to processing option 1.

Table 5.1: CTD stations and Niskin sampling. Stn is sequential CTD cast number (repeat casts at the same site have different numbers). Cast start, bottom, and end times are given (UTC). Wat dep and CTD max in m. RaCE:TraX casts are marked Ra; the rest are GO-SHIP casts. Notes: [a]Test cast, aborted on upcast due to multiple shorts and wire slipping; [b]Test cast for replacement wire; aborted on downcast due to weather; [c]Start of SR1b section; [d]Full depth repeat of cast 2; [e]Partial depth (wire-limited) repeat of cast 1; [f]Section broken after this cast to procede to Elephant Island due to weather; [g]Repeat of cast 22 to join up SR1b section; [h]C14 samples taken; [i]Microplastics; [j]eDNA samples taken; [k]CFC bottle blank.

Stn	yy/mm/dd HHMM	Lat (S)	Lon (W)	Wat Dep	CTD max	sal	oxy	nut	CO2	CFC	O18	C13	Note
001	2050 18/11/05 2222 0130	55 49.54	57 48.26	4703	4742	5	5	0	4	5	5	5	a,i
002	1923 18/11/06 1947 2019	55 30.98	57 59.01	5000	708	23	23	23	16	13	0	0	b,i
003	2048 18/11/07 2053 2109	54 40.01	57 59.00	168	160	8	8	8	6	8	6	6	c,i
004	0014 18/11/08 0028 0102	54 55.34	57 59.00	711	706	18	20	19	8	23	20	20	i
005	0800 18/11/08 0819 0852	54 58.67	57 59.01	1045	1037	9	7	10	7	24	10	10	i
006	1046 18/11/08 1117 1213	55 00.40	57 59.00	1668	1650	12	12	24	12	24	12	12	
007	0947 18/11/09 1030 1144	55 05.70	57 59.01	2421	2411	22	17	17	17	23	11	11	h,i
008	1348 18/11/09 1441 1607	55 10.20	57 58.98	3107	3097	23	23	23	18	24	24	24	
009	1810 18/11/09 1918 2055	55 12.86	57 59.00	3996	3983	21	19	21	17	24	21	21	h,j
010	2336 18/11/10 0047 0226	55 31.00	57 59.00	4216	4206	21	19	20	20	24	21	21	d,i,j
011	0701 18/11/10 0817 1015	55 50.33	57 47.54	4789	4290	22	21	21	19	24	22	22	e,h,j
012	1303 18/11/10 1409 1538	56 08.88	57 36.79	3382	3368	0	22	22	20	23	22	22	i,j
013	1823 18/11/10 1927 2055	56 27.95	57 25.48	3719	3705	21	20	21	19	22	19	19	h,j
014	2358 18/11/11 0051 0215	56 46.96	57 13.68	3146	3118	21	21	22	18	23	21	21	i
015	0548 18/11/11 0703 0853	57 05.94	57 02.15	4210	4198	20	16	21	18	24	18	18	h,j

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Table 5.1 – *Continued from previous page*

Stn	yy/mm/dd HHMM	Lat (S)	Lon (W)	Wat Dep	CTD max	sal	oxy	nut	CO2	CFC	O18	C13	Note
016	18/11/11 1138 1236 1417	57 25.00	56 50.34	3468	3454	20	15	20	14	24	21	21	i,j
017	18/11/11 1700 1757 1924	57 44.00	56 38.57	3458	3446	20	20	20	18	24	20	20	h,j
018	18/11/11 2153 2300 0040	58 03.00	56 26.79	3957	3947	0	20	21	18	24	19	19	i,j
019	18/11/12 0355 0501 0646	58 22.00	56 15.03	3890	3879	21	20	21	18	24	20	20	h,j
020	18/11/12 0937 1041 1233	58 41.00	56 03.24	3753	3742	20	18	22	20	24	21	21	j
021	18/11/12 1508 1612 1741	59 00.27	55 50.85	3772	3761	21	20	21	20	24	20	20	h,i,j
022	18/11/12 2011 2114 2247	59 20.00	55 39.07	3754	3743	22	21	22	20	24	22	22	f,j
023	18/11/13 2326 2336 0000	61 03.00	54 35.24	361	353	7	11	7	12	22	8	8	i
024	18/11/14 0226 0239 0300	60 58.86	54 37.79	580	572	0	0	7	0	24	0	0	Ra
025	18/11/14 0347 0358 0425	60 58.86	54 37.79	581	573	8	8	24	8	0	8	8	h,i
026	18/11/14 0556 0614 0645	60 51.02	54 42.66	1006	1001	7	8	6	8	24	0	0	i
027	18/11/14 0813 0844 0940	60 49.99	54 43.30	1789	1772	12	12	12	12	24	12	12	h
028	18/11/14 1122 1137 1207	60 49.99	54 43.30	1789	802	0	0	24	0	0	0	0	Ra
029	18/11/14 1257 1330 1414	60 49.99	54 43.30	1789	1771	0	0	24	0	0	0	0	Ra
030	18/11/14 1453 1503 1523	60 49.99	54 43.30	1789	403	0	0	24	0	0	0	0	Ra
031	18/11/14 1637 1725 1835	60 47.97	54 44.56	2607	2586	22	22	22	19	24	20	20	i
032	18/11/14 2027 2119 2234	60 40.00	54 49.49	3104	3096	19	19	20	19	24	21	22	h,j
033	18/11/15 0021 0045 0118	60 40.00	54 49.49	3104	1248	0	0	21	0	0	0	0	Ra

Continued on next page

Table 5.1 – *Continued from previous page*

Stn	yy/mm/dd HHMM	Lat (S)	Lon (W)	Wat Dep	CTD max	sal	oxy	nut	CO2	CFC	O18	C13	Note
034	0201 18/11/15 0237 0322	60 40.00	54 49.49	3104	1996	0	0	21	0	0	0	0	Ra
035	0411 18/11/15 0425 0442	60 40.00	54 49.49	3104	500	0	0	21	0	0	0	0	Ra
036	0739 18/11/15 0838 1020	60 20.00	55 01.88	3437	3428	20	19	20	20	23	20	20	h,j
037	2349 18/11/16 0011 0045	60 19.94	55 01.71	3437	1197	0	0	24	0	0	0	0	Ra
038	0132 18/11/16 0208 0254	60 20.00	55 01.88	3437	1998	0	0	22	0	0	0	0	Ra
039	0341 18/11/16 0359 0417	60 20.00	55 01.88	3437	602	0	0	21	0	0	0	0	Ra
040	0724 18/11/16 0822 0956	60 00.00	55 14.28	3500	3490	19	19	20	19	24	20	20	i
041	1204 18/11/16 1233 1307	60 00.00	55 14.28	3500	1248	0	0	24	0	0	0	0	Ra
042	1349 18/11/16 1427 1514	60 00.00	55 14.28	3500	1995	0	0	24	0	0	0	0	Ra
043	1556 18/11/16 1609 1632	59 59.99	55 14.28	3500	602	0	0	24	0	0	0	0	Ra
044	1919 18/11/16 2021 2144	59 40.00	55 26.67	3674	3664	0	16	18	13	24	19	19	h,i
045	0033 18/11/17 0135 0315	59 20.25	55 39.36	3754	3743	19	19	19	15	24	20	20	g
046	0537 18/11/17 0559 0637	59 20.03	55 38.99	3754	1266	0	0	0	0	0	0	0	Ra
047	0756 18/11/17 0834 0926	59 20.41	55 39.23	3754	1990	0	0	0	0	0	0	0	Ra
048	1031 18/11/17 1048 1108	59 19.92	55 39.02	3754	600	0	0	0	0	0	0	0	Ra
049	1718 18/11/17 1733 1756	58 40.96	56 03.22	3752	604	0	0	0	0	0	0	0	Ra
050	1849 18/11/17 1931 2002	58 41.00	56 03.25	3752	1702	0	24	0	0	24	0	0	k
051	2147 18/11/17 2256 0010	58 41.00	56 03.25	3752	3744	0	0	0	0	0	0	0	Ra

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Table 5.1 – *Continued from previous page*

Stn	yy/mm/dd HHMM	Lat (S)	Lon (W)	Wat Dep	CTD max	sal	oxy	nut	CO2	CFC	O18	C13	Note
052	0058 18/11/18 0156 0309	58 41.00	56 03.24	3752	3458	0	0	0	0	0	0	0	Ra
053	0401 18/11/18 0429 0508	58 41.00	56 03.25	3752	1499	0	0	0	0	0	0	0	Ra
054	0546 18/11/18 0626 0708	58 41.00	56 03.25	3752	1997	0	0	0	0	0	0	0	Ra
055	1207 18/11/18 1245 1330	58 03.00	56 26.79	3961	2001	0	0	0	0	0	0	0	Ra
056	1417 18/11/18 1447 1522	58 03.00	56 26.78	3962	1201	0	0	0	0	0	0	0	Ra
057	2147 18/11/18 2226 2309	57 05.96	57 02.09	4210	1997	0	0	0	0	0	0	0	Ra
058	0000 18/11/19 0024 0055	57 05.92	57 02.07	4210	1195	0	0	0	0	0	0	0	Ra
059	0843 18/11/19 0922 1007	56 09.00	57 37.45	3382	2000	0	0	0	0	0	0	0	Ra
060	1144 18/11/19 1159 1229	56 09.00	57 37.45	3381	802	0	0	0	0	0	0	0	Ra
061	1314 18/11/19 1321 1344	56 09.00	57 37.45	3381	302	0	0	0	0	0	0	0	Ra
062	1826 18/11/19 1906 1949	55 30.89	57 58.57	4216	1983	0	0	0	0	0	0	0	Ra
063	2038 18/11/19 2101 2130	55 30.72	57 58.41	4216	994	0	0	0	0	0	0	0	Ra
064	2242 18/11/19 2303 2318	55 30.74	57 58.46	4216	300	0	0	0	0	0	0	0	Ra
065	0717 18/11/20 0754 0841	55 10.20	57 59.01	3107	1992	0	0	0	0	0	0	0	Ra
066	0936 18/11/20 1002 1041	55 10.20	57 59.00	3107	1196	0	0	0	0	0	0	0	Ra
067	1216 18/11/20 1232 1252	55 10.20	57 59.01	3107	522	0	0	0	0	0	0	0	Ra
068	2354 18/11/21 0015 0045	54 58.67	57 59.00	1050	1032	0	0	0	0	0	0	0	Ra
069	0121 18/11/21 0138 0203	54 58.68	57 59.00	1050	752	0	0	0	0	0	0	0	Ra

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Table 5.1 – *Continued from previous page*

Stn	yy/mm/dd HHMM	Lat (S)	Lon (W)	Wat Dep	CTD max	sal	oxy	nut	CO2	CFC	O18	C13	Note
070	18/11/21 0235 0249 0304	54 58.68	57 59.00	1050	402	0	0	0	0	0	0	0	Ra
071	18/11/21 0413 0431 0454	54 55.36	57 59.04	717	711	0	0	0	0	0	0	0	Ra

5.5 Salinity sampling and analysis

Salinity samples were taken from all successfully-closed Niskin bottles (including duplicate depths) for all SR1b CTD casts. The salinity samples were taken in 200 ml glass sample bottles, using a plastic tube for convenience. Each bottle was rinsed three times, neck first to remove any salt crystals, and then filled up to the shoulder. The sample bottles rims were then wiped dry and fitted with a clean plastic stopper and capped with a screw cap. (Stoppers and screw caps were rinsed with milli-Q water and dried before use.) After a crate of 24 bottles was full (usually after each cast), it was moved into the rad lab and left for 24 hours to equilibrate to the ambient temperature of the laboratory.

Samples were also taken from the underway system every 4 hours as part of the routine watchkeeping checks, using the same method as described above for the CTD. This was done to enable calibration of the TSG system. The underway samples were stored together in a separate crate and analysed once the crate had been filled, but were otherwise treated in the same way as the CTD samples.

5.5.1 Salinity analysis and salinometer performance

Both salinometers aboard, although serviced before the previous cruise, were not working at the start of the cruise, and even after repair were prone to functioning erratically or not at all throughout the cruise. Issues with the salinometers were reported during JR18001, but it was not appreciated how serious they were until mobilisation for JR18002.

Salinity sample analysis was performed, by each of the physics watch-standers, on the BAS Guildline 8400B Salinometers, Serial No.s 65763 (most crates) and 68533 (crates 8 [CTD010], 14 [CTD012], 15 [CTD017]), , in the Rad Lab, using a bath temperature of 24 C and keeping the room temperature between 20 and 24 C.

Standard procedures were followed: A sample of IAPSO Standard Seawater, batch P160 (K15= 0.99983) was run before each set of up to 24 samples, and a new standard was run after each set, to calculate the salinometer offset including a possible linear drift over the course of the crate. Before starting new sets of runs, the volume was flushed with old standard (P158) or previously opened bottles of P160, to bring it closer to the standard salinity. For intervals between runs, it was flushed with milli-Q water. For each sample (or standard), the cell was flushed and filled 3 times before taking the 1st reading and once before subsequent readings. Three readings were taken unless there was an outlier, in which case a 4th reading was taken. For most crates the Autosal software was used to record the readings; when the software was not working and in any case as a backup, the value at the end of the 10 second reading interval was logged by hand.

Because the salinometers were behaving erratically, we sometimes re-ran the initial standard half way through the crate to check for large drifts. The salinometers had to be repaired before running the final crates (after the cruise), leading to a large change in standardisation; therefore we have given statistics for the two sets of standards separately below.

5.5.2 Standards offsets

Before comparison with the CTD data, the sample readings must be adjusted for the salinometer offset, or the difference between the standard reading and its label value. Standards and samples were inspected using msal_standardise_avg.m to discard outliers and detect questionable standards. Two sets of standards recorded substantially lower values than the rest (despite three internally-consistent readings for each one); the corresponding crates (CTDs 12 and 18) were flagged as questionable. Where both initial and final standards were run and flagged as good, we linearly interpolated between their offsets; otherwise we used a constant offset for the crate.

After application of flags, the standards offsets used were in the range $\pm 2.5 \times 10^{-4}$ (median 0, standard deviation 1.1×10^{-4} over 33 standards) for the runs during the cruise, and -8×10^{-4} to -4.5×10^{-4} (median -7.3×10^{-4}, standard deviation 1.1×10^{-4} over 14 standards) for the post-repair runs after the cruise. Drifts within a sample set were up to 4.0×10^{-4} (during) or 1.2×10^{-4} (after), with a median absolute value of 1.0×10^{-4} (during) or 0.2×10^{-4} (after).

6 Chlorofluorocarbons (CFCs) and sulpher hexafluoride (SF_6) measurements

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A series of three halocarbons (dichlorodifluoromethane CFC-12, trichlorofluoromethane - CFC-11, and trichlorotrifluoroethane - CFC-113), carbon tetrachloride (CCl4) and sulphur hexafluoride (SF_6) were measured by shipboard electron capture gas chromatography (EC-GC) coupled to an extraction-and-trap system. The method combines the Lamont Doherty Earth Observatory CFC method [Smethie et al., 2000] and the Plymouth Marine Laboratory SF_6 method [Law et al. 1994] tied together with a common valve for the introduction of gas and water samples. This system has the advantage of a simultaneous analysis of SF_6, CFCs and CCl4 from the same water sample with a running time per sample of 20 minutes. The system was set up in the temperature controlled Exeter container # which was installed on the after deck of the James Clark Ross (JCR) to reduce the possibility of contamination from high levels of CFCs and radio waves frequently present inside research vessels.

6.1 Sample collection

Water samples were collected from the 20-litre Niskin bottles as soon as the CTD sampling rosette was on board. When taken, water samples for CFC analysis were the first samples drawn from the bottle. The Niskin nitrile 'O' rings were conditioned by a isopropanol wash and a baking in a vacuum oven for 24 hours to remove susceptible contamination before installation in Niskin bottles. The trigger system of the bottles was external stainless steel springs. Water samples were collected in 500 ml ground glass stoppered bottles that were filled from the bottom using conditioned Tygon tubing and overflowed 3 times to expel all water exposed to the air. Immediately after sampling, the samples were immersed in a cool box of clean cold deep seawater and stored in the cold room ($\sim$5°C) to prevent degassing and hydrolysis of the CCl4 and CFC-113 until their analysis.

For air sampling, $\frac{1}{4}$" o.d. Dekabon tubing was run from the JCR monkey island into the container. Air was pumped through the line to the instrument using a DA1 SE Charles Austen pump, with the line being flushed for approximately 30 minutes before beginning analysis.

6.2 Analysis technique

Sample analysis was performed on board using a coupled SF_6 and CFCs system with a common valve for the introduction of gas and water samples. Samples were introduced to the system by applying nitrogen (N2) pressure to the top of the sample bottles, forcing the water to flow through and fill a 27 cm^3 calibrated volume for CFCs and a 300 cm^3 volume for SF_6. The measured volumes of seawater were then transferred to separate purge and trap systems, before being stripped with N2 and trapped at -100°C on a Unibeads 3S trap (for CFCs) and at -80°C on a Porapak Q trap (for SF_6) each immerged in the headspace of liquid nitrogen. Each purge and trap system was interfaced to an Agilent 6890N gas chromatograph with electron capture detector (GC-ECD). The traps were heated to 100°C for CFCs and 65°C for SF_6 and injected into the respective gas chromatographs. The SF_6 separation was achieved using a molecular sieve packed 2 meters main column and 1meter buffer column. The CFCs separation was achieved using a 1m Porasil B packed pre-column and a 1.5m carbograph AC main column. The carrier gas was pure nitrogen, which was cleaned by a series of purity traps. Liquid nitrogen was used as the cryogenic cooling material for the sample traps, and was provided by two on-board liquid nitrogen generator located in the workshop of the JCR.

6.3 Calibrations

The CFCs and SF_6 concentrations in air and water were calculated using two external gaseous standard supplied by NOAA (Brad Hall, December 2015) in 29-L Aculife-treated aluminum cylinders (Table 6.1)). The final data set will be converted to mol/kg on the SIO-98 scale using NOAAs comparison tables. The calibration curves were made by multiple injections of different volumes (0.1, 0.25, 0.3, 0.5, 1, 2, 3, 5, 8 ml) of standard to span the range of tracers measured in the water (Figure 6.1). The changes in the sensitivity of the system for each compound were tracked by injections of a fixed volume of standard gas and used to adjust the calibration curves respectively.

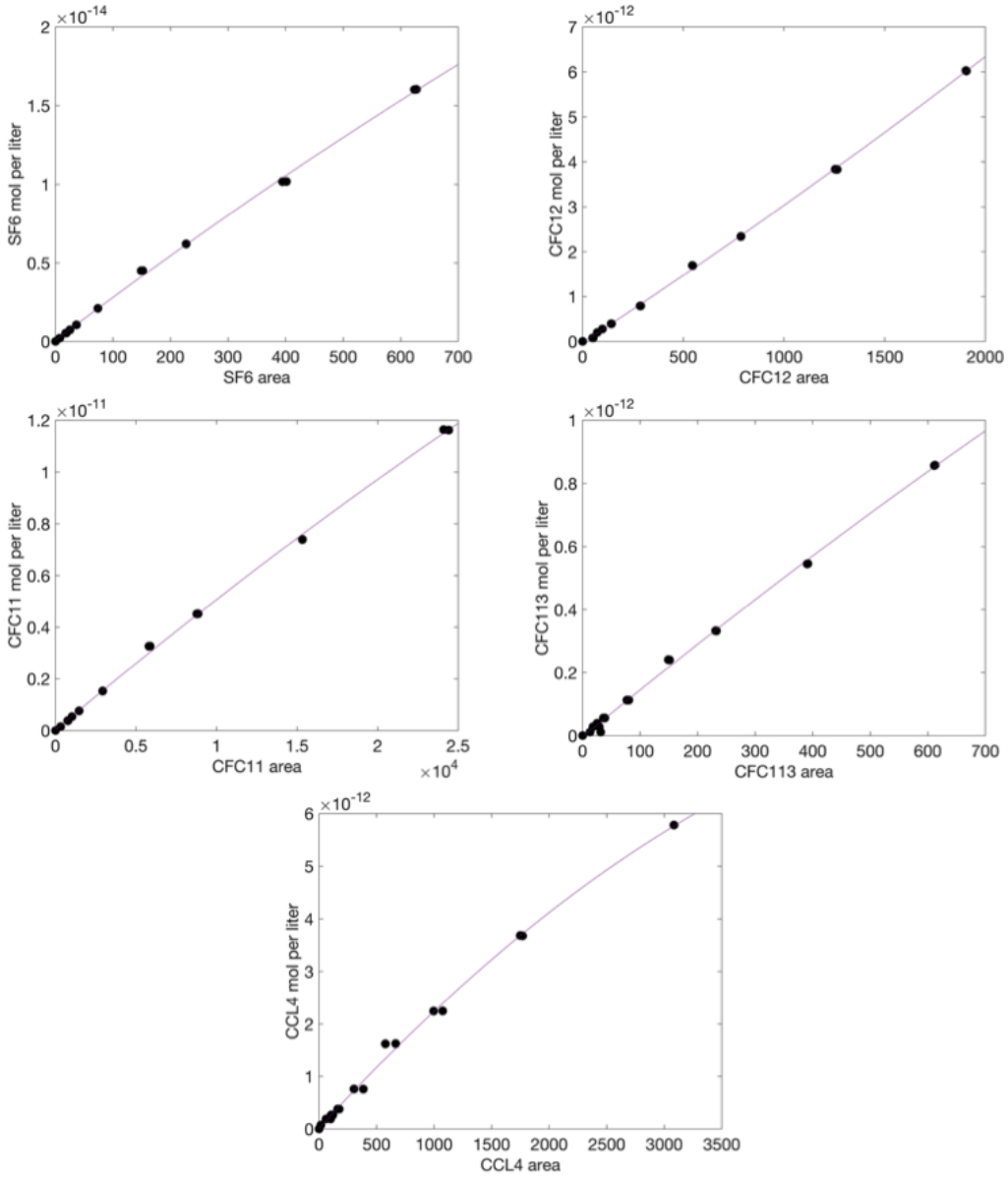

Figure 6.1: Calibration curves for CFC-11, CFC-12, CFC-113, CCl4 and SF_6 on the 4th of November.

Table 6.1: Concentrations of the NOAA 2017 CFC and SF_6 standards used, in ppt.

	NOAA2017 CC456893 - spiked for CFC-11 , CCl4, SF_6	NOAA2017 CC456907
SF_6	17.61	8.70
CFC-11	1031	232.4
CFC-12		516.6
CFC-113	75.2	73.5
CCl4	521	83.1

6.4 Detection limit and precision

6.4.1 Precision or reproducibility

The precision (or reproducibility) for the water samples measurements can be determined from two samples drawn from the same Niskin bottle. In total, 100 duplicates (200 samples) were drawn along the cruise with results shown in Table 6.2.

Table 6.2: The preliminary standard deviations from CFC duplicate samples.

SF_6	$\pm$1.24%	for surface values
	$\pm$ 0.015 fmol kg^{-1}	for values ¡ 0.25 fmol kg^{-1}
CFC-12	$\pm$0.86 %	for surface values
	$\pm$ 0.0029 pmol kg^{-1}	for values ¡ 0.25 pmol kg^{-1}
CFC-11	$\pm$0.85%	for surface values
	$\pm$ 0.0046 pmol kg^{-1}	for values ¡ 0.50 pmol kg^{-1}
CFC-113	$\pm$3.07%	for surface values
	$\pm$ 0.0076 pmol kg^{-1}	for values ¡ 0.1 pmol kg^{-1}
CCl4	$\pm$1.51%	for surface values
	$\pm$ 0.070 pmol kg^{-1}	for values ¡ 0.3 pmol kg^{-1}

6.4.2 Test stations and sample blank correction

The blank correction is to compensate for any contamination of CFCs/SF_6 originating from the sampling bottles, handling and from the measurements procedure. This correction is normally best estimated from analysis of CFC-free water when available. Here, we used samples from a full 20L Niskin discharge of its gases through a continual sparge $\sim$ until concentrations have reached a steady-state value. Based on the measurements of a 4 hours sparged full Niskin, blank corrections of 0.003 pmol kg^{-1} for CFC-11, 0.006 pmol kg^{-1} for CFC-12 and 0.006 pmol kg^{-1} for CFC-113 will be applied to the data set. No blank corrections were required for the SF_6 data. If the measured CFC concentration for a sample is very low, subtracting a blank can result in a very small negative number reported. Additionally, a test station (station 51) was carried out in CFC-low deep waters to test the blank of the Niskin bottle and sampling procedure by firing all the Niskins at the same depth (Table 6.3).

6.4.3 Sparging efficiency

The sparging efficiency was evaluated by re-stripping high concentration surface water samples until results did not change (having reached the system blank) at a number of different flow rates. Comparing those residual concentrations to the initial concentrations, the re-sparge values were approximately $<$2%

Table 6.3: Results of the Niskin blank test at station 51 (58° 41.00' S 56° 3.24' W) in mol kg^{-1}, where all the Niskins were closed at a same depth of 1700 dbar. Highlighted values indicate leaking Niskins (bottle numbers 13/16/17) or suspicious values (bottle number 21).

NISKIN	SF_6	CFC12	CFC11	CFC113	CCL4
1	7.846×10^{-17}	1.126×10^{-13}	2.266×10^{-13}	2.168×10^{-14}	1.294×10^{-12}
1	7.790×10^{-17}	1.284×10^{-13}	2.343×10^{-13}		1.379×10^{-12}
2	7.282×10^{-17}	1.176×10^{-13}	2.237×10^{-13}		1.377×10^{-12}
3	8.579×10^{-17}	1.151×10^{-13}	2.268×10^{-13}	1.714×10^{-14}	1.310×10^{-12}
4	8.692×10^{-17}	1.214×10^{-13}	2.383×10^{-13}	1.969×10^{-14}	1.287×10^{-12}
5	7.959×10^{-17}	1.160×10^{-13}	2.319×10^{-13}	1.302×10^{-14}	1.306×10^{-12}
6	6.097×10^{-17}	1.182×10^{-13}	2.345×10^{-13}	1.467×10^{-14}	1.299×10^{-12}
7	8.749×10^{-17}	1.272×10^{-13}	2.365×10^{-13}	1.324×10^{-14}	1.303×10^{-12}
8	1.010×10^{-16}	1.117×10^{-13}	2.318×10^{-13}	1.297×10^{-14}	1.298×10^{-12}
9	1.115×10^{-16}		2.253×10^{-13}	1.588×10^{-14}	1.299×10^{-12}
10	9.285×10^{-17}		2.170×10^{-13}	1.451×10^{-14}	1.337×10^{-12}
11	8.354×10^{-17}		2.349×10^{-13}	1.477×10^{-14}	1.299×10^{-12}
12	9.680×10^{-17}	1.166×10^{-13}	2.397×10^{-13}	2.097×10^{-14}	1.081×10^{-12}
13	1.862×10^{-16}	2.351×10^{-13}	4.515×10^{-13}	3.602×10^{-14}	1.544×10^{-12}
14	7.592×10^{-17}	1.164×10^{-13}	2.321×10^{-13}	2.387×10^{-14}	1.269×10^{-12}
15	9.200×10^{-17}	1.171×10^{-13}	2.296×10^{-13}	2.404×10^{-14}	1.308×10^{-12}
16	2.126×10^{-16}	2.446×10^{-13}	4.641×10^{-13}	3.755×10^{-14}	1.589×10^{-12}
17	1.185×10^{-16}	1.628×10^{-13}	3.174×10^{-13}	2.991×10^{-14}	1.415×10^{-12}
18	9.454×10^{-17}	1.212×10^{-13}	2.474×10^{-13}	1.647×10^{-14}	1.295×10^{-12}
19	9.764×10^{-17}	1.213×10^{-13}	2.397×10^{-13}	1.202×10^{-14}	1.327×10^{-12}
20	9.397×10^{-17}	1.240×10^{-13}	2.435×10^{-13}	2.468×10^{-14}	1.375×10^{-12}
21	1.247×10^{-16}	1.247×10^{-13}	2.399×10^{-13}	1.546×10^{-14}	1.263×10^{-12}
22	1.092×10^{-16}	1.224×10^{-13}	2.411×10^{-13}	1.712×10^{-14}	1.310×10^{-12}
23	1.002×10^{-16}	1.149×10^{-13}	2.331×10^{-13}	1.404×10^{-14}	1.319×10^{-12}
24	8.523×10^{-17}	1.169×10^{-13}	2.330×10^{-13}	1.449×10^{-14}	1.328×10^{-12}
Mean	8.815×10^{-17}	1.191×10^{-13}	2.337×10^{-13}	1.704×10^{-14}	1.303×10^{-12}
STD	1.203×10^{-17}	4.715×10^{-15}	7.082×10^{-15}	4.023×10^{-15}	5.849×10^{-14}

of the initial sample concentration for CFC-12 and CFC-11 and below <6% for CFC-113 and CCl4 for a sparging of 4 min at 85 mL/min. The SF_6 re-sparge value was zero for a 3 min sparging going up to 120 mL/min. A fit of the re-sparging efficiency as a function of temperature and flow rate will be applied to the final data set.

Additional factors affecting accuracy include chromatographic considerations, such as interferences and baseline variation. Those will be checked for the final data set.

6.5 Preliminary data

Samples were drawn at all the stations totaling 810 analyses for CFCs and SF_6. Preliminary results are presented below in Figure 6.2. The distributions of the CFCs and SF_6 seen here are largely consistent with previous studies, showing a broad near surface maximum and in the mode waters, relatively high concentration in the ventilated Antarctic Bottom Water at the bottom, and lower concentration in the deep circumpolar waters.

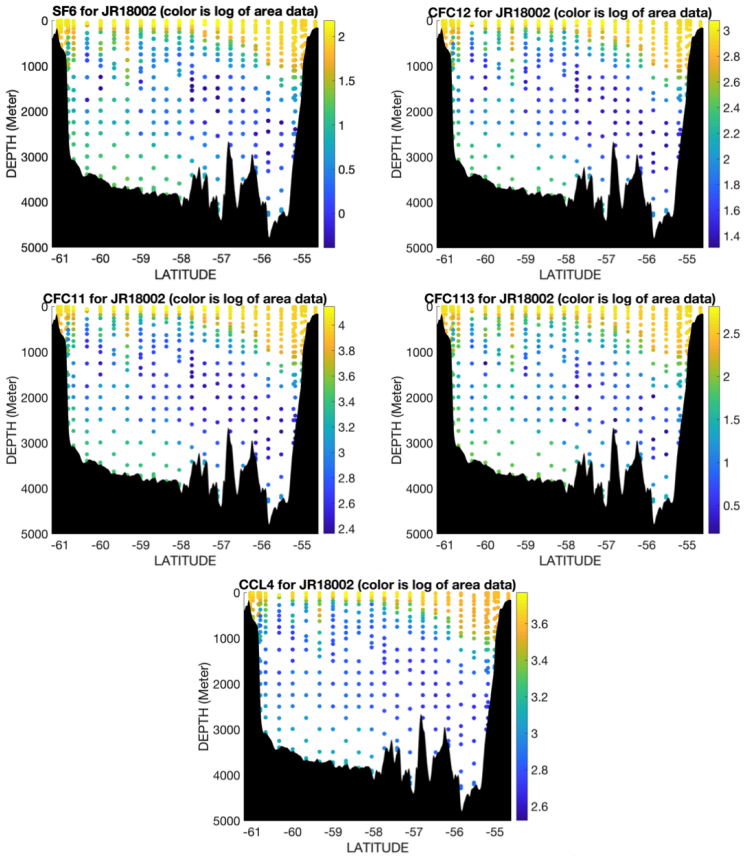

Figure 6.2: Preliminary vertical distributions of CFC-12, CFC-11, CFC-113, CCl4 and SF_6 along the JR18002 transect across Drake Passage ($\log_{10}$ of the chromatographic area, uncalibrated).

6.6 References

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7 Inorganic Carbon Parameters

Neill Mackay, Maria de la Fuente Ruiz, Aimee Coggins

7.1 Analysis Background

The analytical equipment for the carbon parameters was set up in the main laboratory, with discrete CTD samples being analysed for both total dissolved inorganic carbon (DIC) and total alkalinity (TA). Two Versatile Instruments for the Detection of Titration Alkalinity (VINDTA) systems (Mintrop, 2004), version 3C serial numbers 11 & 24 coupled to UIC coulometers were used to this end during JR18002. These systems draw water from a single sample and autonomously separate it into two independent analysis lines, one analysing for total alkalinity by potentiometric acid titration, the other quantifying for DIC by the acid-derived extraction of carbon dioxide and subsequent coulometric titration (Johnson et al, 1985; Johnson et al, 1987; Johnson et al, 1993).

7.2 CTD Sampling Strategy for Inorganic Carbon

Water samples for the determination of DIC and TA were drawn from the 20L Niskin bottles on the CTD rosette and collected in 250ml and 500 ml glass bottles according to the Standard Operating Procedure (SOP) 01 (Dickson et al., 2007), to avoid gas exchange with the air. All samples were poisoned with mercuric chloride (20 l per 50 ml of sample) to kill all organisms that may alter the chemistry of the sample. Samples were kept at room temperature in the dark until shortly before being placed into a 25C water bath to bring to this temperature prior to analysis. A total of 1032 samples were drawn from 31 CTD stations (first station number 2, last station number 45, several stations in between were designated for Radium sampling). Samples for DIC and alkalinity were taken from up to 20 different Niskin bottles on each station, sampling every depth when there were 20 or fewer unique depths. All samples had duplicates collected, such that there were 516 A samples and 516 duplicate B samples. All A samples and 10% of the B samples were analysed during the cruise; the remainder are being transported back to NOC. Figure 7.1 shows the depth-latitude grid of samples analysed for DIC and TA during the cruise.

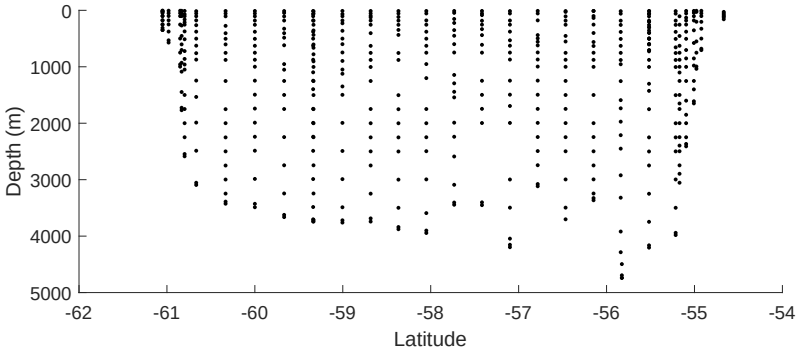

Figure 7.1: Locations of sampling for the dissolved inorganic carbon system on JR18002

7.3 Total Dissolved Inorganic Carbon

Total inorganic carbon was analysed by coulometry. All inorganic carbonate was converted to CO_2 (gas) by addition of excess phosphoric acid (1 M, 8.5%, made by dilution on ship of 85% phosphoric acid) to a calibrated volume of seawater sample. Oxygen-free-Nitrogen (OfN) gas was passed through a soda lime trap to remove any traces of CO_2 prior to entry into the system; the gas was then used to both empty the

DIC pipette, and to flush and carry the evolving CO_2 from the sample to the coulometer cell. Here, CO_2 is quantitatively absorbed by a dimtheylsulfoxide-ethanolamine mixture forming an acid and changing the colour of the solution, which is coulometrically titrated to return it to its original transmittance.

The coulometry solutions accumulate CO_2 over time and thus need to be changed regularly to ensure high performance. Cell preparation was conducted by the addition of cathode and anode solutions (UIC Corp.) to their individual chambers, solid potassium iodide to the anode chamber and a stirrer bar to the main chamber. On JR18002 cells that were performing well were run for approximately 24 hours, with a set of 4 cells being used in rotation. Cells were sometimes changed more often when they were found to not be performing well, or if the potassium iodide had been used up. Platinum (cathode) and silver (anode) electrodes were also used in rotation. As the silver anode is consumed during the analysis, one of these had to be replaced with new during the cruise. Cells were rinsed by Milli-Q water, before passing Milli-Q water through the glass frit under vacuum 3 times and then a final Milli-Q rinse. Cells were then dried in an oven prior to next use. Silver anodes and platinum electrodes were cleaned with milli-Q water and dried in the oven.

1.5 bottles of anode and 2 bottles of cathode solution were used during the cruise, using approximately 6 and 1 litres of each substance respectively.

The oxygen-free nitrogen gas was piped from 90L cylinders located on deck. The pressure of the gas cylinder in use was checked when possible (weather conditions allowed for only occasional checks) to ensure that sufficient pressure was available for normal operation and that the inlet pressure did not exceed 1.5 bar. In between whiles, regular checks of the gas flow were carried out on VINDTA 24, which has a flow meter, to ensure the flow remained at 150 ml/min. Only one gas cylinder was used and lasted the whole cruise.

7.3.1 Issues encountered - VINDTA 11

There were often a number of zeros in the blank from the DIC titration. The cause of this was unknown, but a note was made in the lab book and results spreadsheet when it was seen in the log file. The instances of zeros in the blank seemed to reduce as the cruise progressed. A bad USB connection at one point caused the left hand side of the instrument to stop working; this was fixed by removing and replacing the USB cable connecting to the VINDTA PC. The fill sensor for the pipettes was triggering before they had filled due to rusty contacts. This was resolved by cleaning the contacts.

7.3.2 Issues encountered - VINDTA 24

The water bath gave persistent errors during rough weather due to a water level sensor triggered each time the ship rolled. When this error occurred the water bath needed to be reset in order for water to circulate around the VINDTA; this had a knock-on effect that the Peltier cooler would stop cooling, affecting the DIC readings. Generally therefore only VINDTA 11 was used to run samples in rough seas. Occasionally low counts were seen on the coulometer 10000 below what was normally expected. The cause was unknown but may have been moisture in the tube between the stripper and the coulometer cell, or possibly movement of the cell within the coulometer housing, which has a broken clip, changing the transmittance. The outlet from the stripper was dried periodically and some blu-tak was used to attempt to secure the cell in place. At one point the tube became flooded due to a sample left in the stripper after an aborted run; this tube was replaced. Valve 2 had a bad connection which meant water was pouring into waste during the filling of the AT cell, resulting in a 250 ml sample bottle being entirely used up for a standard run. This was resolved by stripping back and re-connecting the valve wire.

7.4 Standardisation

The accuracy of the DIC analyses was determined regularly by measuring certified reference material (CRM), supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), Batches 161, 170 and 175. One CRM was run twice on one instrument when a coulometer cell was settled down and ready to use, and another after completing the analysis for a CTD cast. When possible a CRM bottle was run 3 times, splitting the runs across both VINDTA instruments; however this could only be done when both VINDTAs were running well at the same time, which was not generally the case. Control charts for the outputs of the CRMs analyses (in counts per mole of CO_2) are shown in Figure 7.2, suggesting the analysis was within control, with a few outliers. Quality control for DIC is thus ongoing.

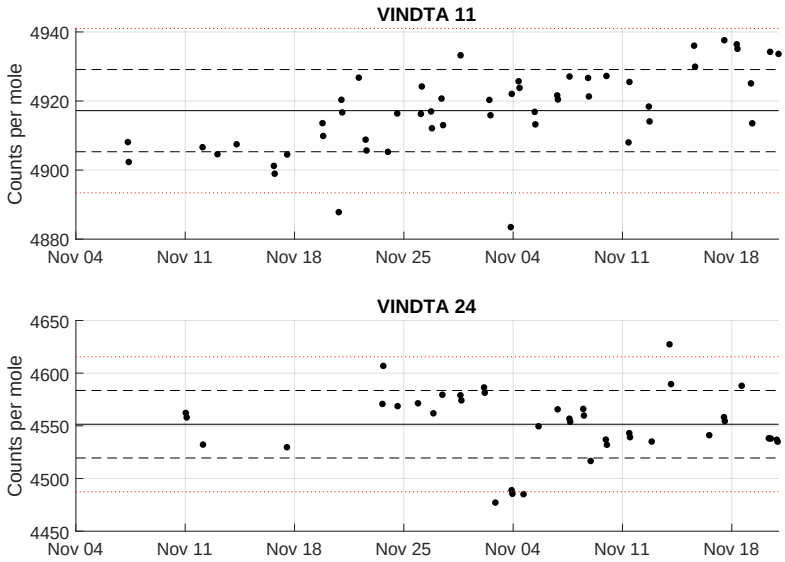

Figure 7.2: DIC CRM control charts.

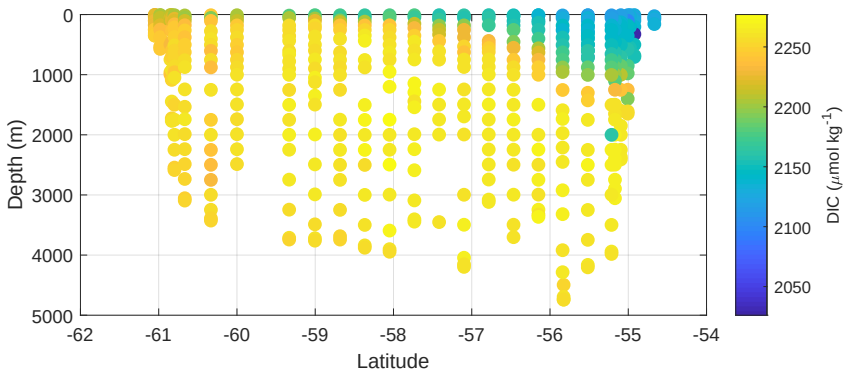

Figure 7.3: Preliminary DIC distribution across SR1b.

7.5 Total Alkalinity

The alkalinity measurements were made by potentiometric titration, following Dickson et al. (2007) SOP3a, closed cell titration. The s-shaped titration curve produced by potential of a proton sensitive electrode shows two inflection points, characterising the protonation of carbonate and bicarbonate, respectively. The acid consumption up to the second point is equal to the titration alkalinity. From this

value, the carbonate alkalinity is calculated by subtracting the contributions of other ions present in the seawater, i.e. nutrients. The systems use highly precise Metrohm Titrinos for adding acid, an ORION-Ross pH electrode and a Metrohm reference electrode. The burette, the pipette (volume approximately 100 ml), and the analysis cell have a water jacket around them that house constantly flowing 25°C water. One batch of acid titrant (0.1 M HCl) was used; the batch was made on board and a small sample is being taken back to NOC to verify the concentration. Electrodes were refilled with 3M KCl and 0.7M NaCl solutions daily. Midway through the cruise the electrode solutions were completely removed and replaced with fresh.

Alkalinity data was calibrated with CRMs, shown in Figure 7.4. However, the calculation method is dependent on a realistically estimated ratio of acid factor and pipette calibration, since the same calibration factor can also be obtained with various combinations of these two parameters, but the quality of the curve fit will be different. Therefore a re-calibration of the pipette and exact calculation of the acid factor will be processed post cruise. Changes that would exceed the mean standard deviation of the method are not likely.

7.5.1 Issues encountered - VINDTA 11

As there is no gas flow meter on VINDTA 11 the flow was checked on VINDTA 24 and assumed to be the same for both. A white residue was found collecting in the AT pipette which was found to be due to the tube going through the peristaltic pump which feeds the pipette having perished. The AT pipette was replaced before the cause of the residue was diagnosed; when it reappeared in the new pipette the tube was replaced with a new one. This should have no effect on the TA measurement save for a small error in the calibrated volume due to the rubber collected inside the pipette.

7.5.2 Issues encountered - VINDTA 24

Bubbles were collecting in the tube feeding HCl to the AT cell while setting up to run the last set of samples on the cruise. The problem was resolved by replacing the tube with a new one.

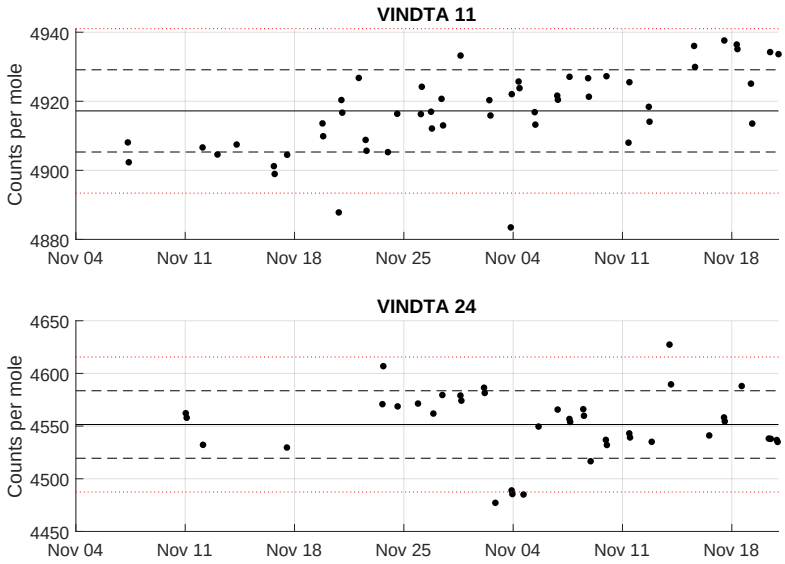

Figure 7.4: Control charts for NOC acid titrant batch acid factor.

An initial estimate of the alkalinity distribution is given in Figure 7.5. Final alkalinity data await further quality control and final nutrient data.

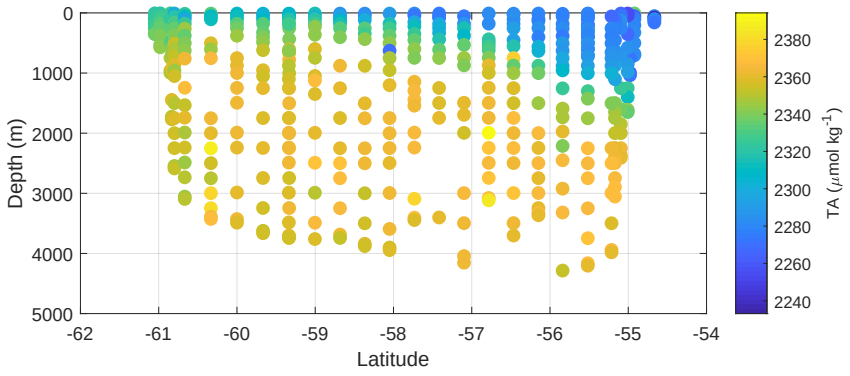

Figure 7.5: Preliminary alkalinity distribution across SR1b.

7.6 References

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8 Dissolved oxygen

Ed Mawji, Francesca Carr, Matthew Humphreys and Robyn Tuerena

8.1 Sampling and analysis

8.1.1 Sampling strategy

Dissolved oxygen (DO) samples were collected during JR18002 in order to calibrate the DO sensor on the CTD rosette, and to help identify misfired or leaking Niskin bottles.

Samples were collected from every cast except for those designated exclusively for radium measurements. Every Niskin bottle was sampled on each cast, excluding known misfires and those with obvious leaks. We aimed to sample 2 Niskins in duplicate for each cast.

8.1.2 Sample collection

DO samples were collected as soon as possible, second in the sampling order after CFCs. Seawater was collected directly into pre-calibrated Pyrex Iodine titration flasks. Before the sample was drawn, bottles were flushed with seawater for several seconds (approximately 3 times the volume of the bottle) while the temperature of the water was recorded using a handheld digital thermometer (Hanna Instruments) and recorded on a log sheet. Throughout the sampling process, care was taken to avoid bubble formation inside the sampling tube and sampling bottle.

The fixing reagents (i.e. manganous chloride and sodium hydroxide/sodium iodide solutions) were then immediately added, and the bottle sealed with a glass stopper, taking care not to introduce any air bubbles. Sample bottles were then thoroughly mixed by shaking in order to homogenise the contents, and were then stored in a dark plastic crate for 30 to 40 minutes to allow the precipitate to settle. After collection, a Milli-Q water seal was applied to the neck of the sample flasks in order to prevent ingress of air.

Once the precipitate had settled all samples were thoroughly mixed for a second time in order to ensure that the reaction was complete, and the Milli-Q seal was replaced. Analyses were carried out as soon as possible, and normally within two to ten hours of sample collection.

8.1.3 Analysis

The chemical reagents were prepared in advance at NOCS following the procedures described by Dickson (1994). 5 litres of each reagent were prepared and homogenised using 5-litre glass volumetric flasks, this reduce the batch effect and allowed us to change reagent during analysis. Thiosulfate was weighed into 27.4 g portions at NOCS and all solutions were made during the cruise. Thiosulfate solutions were made at least two days in advance.

When ready to titrate, the Milli-Q seal was dried and the stopper of the flask carefully removed. A 1 ml aliquot of 5 M sulfuric acid was dispensed into the flask, immediately followed by a clean magnetic stirrer. The flask was placed on the stir plate and the electrode and burette were carefully inserted to place the tips in the lower-middle depth of the sample flask. The initial volume of sodium thiosulfate ($Na_2S_2O_3$) for each sample was 0.3-0.6 ml before continuing to be titrated at 0.0005 ml intervals using an electrode with amperometic end-point detection (Culberson and Huang, 1987) with an end current of 0.1×10^{-6} A. The resultant volume of titrant was recorded both by manual logging and on the Titrino (Metrohm). Following this the value was converted to a DO concentration.

Thiosulfate calibrations and reagent blank checks were carried out for each sampling station following the GO-SHIP protocols (Langdon, 2010). At least 3 blank checks of the reagents and 4 standardisations of the sodium thiosulfate were completed using a 1.667 mol l^{-1} certified iodate standard (OSIL) every cast (Fig. 8.1).

8.2 Problems encountered

During a couple of casts (in particular casts 21 and 22) bubbles were noted in the manganous chloride dispensed during sample collection. This may have reduced the volume of this reagent dispensed and consequently rendered the final DO determination unreliable. Where these bubbles were observed they were noted in the sampling log sheet and the corresponding final data were flagged as suspect. The problem was caused by a loose joint within the pump mechanism inside the dispenser and fixed by tightening this connection.

As the entire sample is used in the thiosulfate titration, the volume of each oxygen sampling bottle is critical to the final measurement, so these are individually calibrated. Each bottle and stopper was labelled to ensure they are kept together as a pair with a known volume. However, due to continual wetting of the bottle exteriors during sampling, and also the Milli-Q seal soaking into the label for several hours before analysis, the labels did sometimes become detached from the bottles. This was anticipated from previous experience, and we attempted to prevent the issue by relabelling all bottles at the start of the cruise with waterproof sticker labels coated with nail varnish. However this was did not solve the problem and a more permanent labelling solution should be found prior to future expeditions.

The burettes in the thiosulfate and iodate dispensers were prone to air bubble formation. This is a previously identified problem for these dispensers that the manufacturer (Metrohm) has been unable to resolve. We followed their suggestion of dismantling and cleaning the inside of the burette but the bubbles persisted. As the bubbles were generally trapped at the top of the burette (i.e. away from where the reagent was dispensed), and we made sure that bubbles did not pass through the dispensing tubing, this probably did not cause significant problems for our analysis.

Occasional blanks and standardisation runs returned unexpectedly low values that were not noticed prior to beginning measurement of the samples (e.g. cast 14). However, each time these were found to be due to the potassium iodate solution having run out. This reagent is not used in the actual sample measurements so this should not lead to any problems for those data. The issue arose in part because the iodate bottle was secured to the lab bench in an opaque container so the amount of its contents could not easily be seen.

8.3 Results

8.3.1 Blanks and standards

We performed 3 blank measurements and 4 standard determinations before the start of each cast of measurements (Fig. 8.1). Excluding where specific analytical problems were identified (e.g. the potassium iodate standard running out, or bubbles in the thiosulfate dispenser, see Section 8.2 for details) the results were generally consistent across the cruise.

The blank was evaluated separately for each cast (Fig. 8.1a). The average values that we used are shown in Table 8.1.

Two batches of thiosulfate titrant were used, with the batch changed at the start of cast 25 analysis. We used average thiosulfate standardisation values of 0.46323 ml from the start of the cruise up to cast 24 inclusive, and 0.46392 ml from cast 25 onwards to calibrate all of the DO measurements (Fig. 8.1b).

Table 8.1: Dissolved oxygen blank values, as shown in Fig. 8.1a.

Cast	Blank (mL)		Cast	Blank (mL)
1	0.00758		18	0.00717
2	0.00958		19	0.00383
3	0.00350		20	0.00342
4	0.00550		21	0.00317
5	0.00308		22	0.00808
6	0.00467		23	0.00933
7	0.00150		25	0.00367
8	0.00688		26	0.00308
9	0.00583		27	0.00158
10	0.00133		31	0.00533
11	0.00650		32	0.00558
12	0.00242		36	0.00425
13	0.00500		40	0.00500
14	0.00763		44	0.00642
15	0.00683		45	0.00717
16	0.00483		50	0.00550
17	0.00558			

8.3.2 Precision and accuracy

We collected 48 pairs of duplicate samples from the same Niskin in total (Fig. 8.2). Two of these had very large differences between the duplicates (over 50 mmol m^{-3}) due to analytical issues and were excluded from further consideration here. The remaining 46 had a mean absolute difference of 1.2 mmol m^{-3}, which corresponds to a 1σ precision of 1.1 mmol m^{-3} (Humphreys et al., 2016).

For cast 50, all 24 Niskins on the rosette were fired at the same depth (nominally 1700 m), for the benefit of the CFC team. We also collected and analysed DO samples from every Niskin. The standard deviation of these 24 measurements was 2.7 mmol m^{-3} although this was somewhat skewed by a single outlier (Niskin 4) without which the standard deviation dropped to 1.6 mmol m^{-3} (Fig. 8.3).

The first precision estimate (from duplicates) indicates measurement precision within individual casts, as duplicates were always analysed in the same session. The latter (from cast 50) provides an estimate of our overall measurement precision, also restricted to within a single cast, but also including the effect of sampling from different Niskin bottles. The greater value for the cast 50 estimate suggests that different Niskins fired at the same nominal depth have real differences in their DO concentrations on the order of up to 2 mmol m^{-3}.

8.3.3 SR1b transect

The DO measurements plotted across the SR1b transect are shown in Fig. 8.4. They show the expected patterns of variation with depth and latitude and are quantitatively consistent with historical data from this region, within the measurement uncertainty.

8.4 References

Culberson, C.H. and Huang, S. (1987). Automated amperometric oxygen titration. *Deep-Sea Res. Pt A* **34**(5-6), 875-880. doi:10.1016/0198-0149(87)90042-2

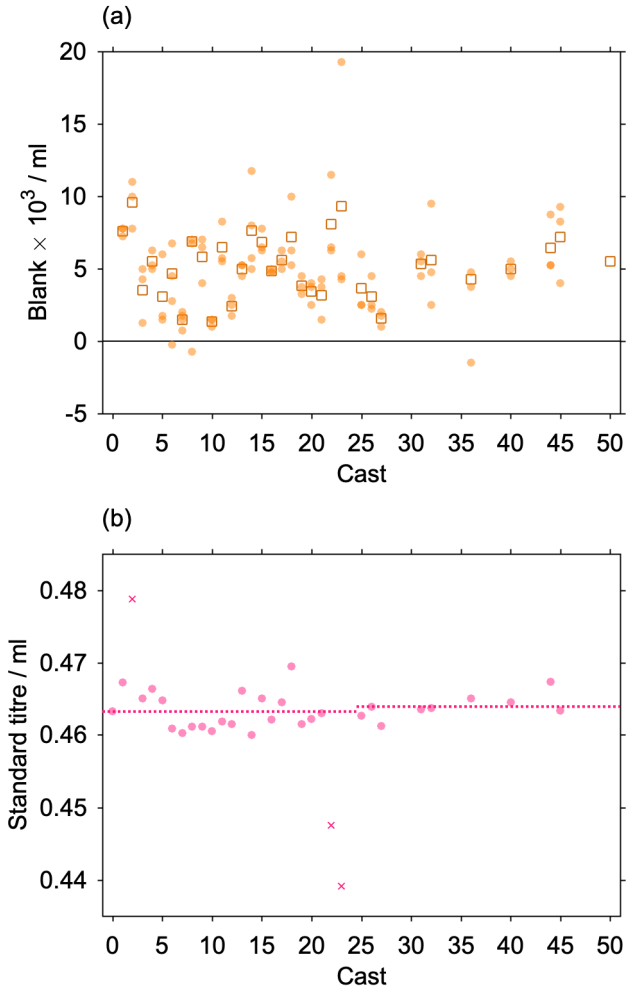

Figure 8.1: Results of all (a) blank and (b) calibration standard titrations throughout cruise JR18002. (a) The square markers show the average blank value for each cast, as listed in Table 8.1. (b) The dotted line shows the two average values for the different thiosulfate batches (0.46323 ml up to cast 24 inclusive, 0.46392 for cast 25 onwards). The crosses show points that were excluded from evaluating these mean values.

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9 Inorganic nutrients

Ed Mawji, Matthew Humphreys and Robyn Tuerena

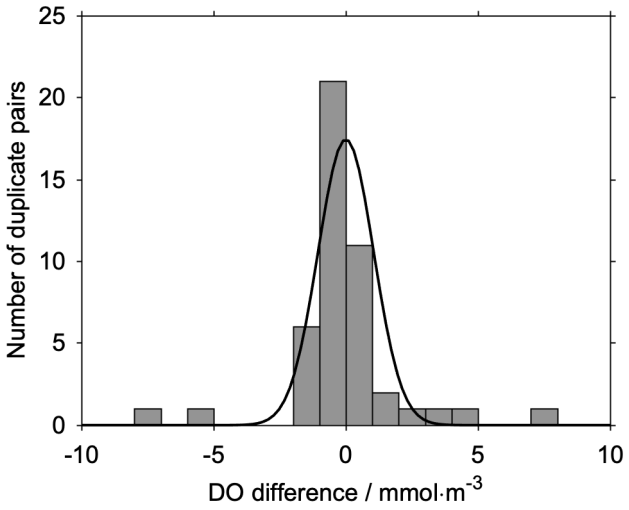

Figure 8.2: Histogram of differences between DO duplicate analysis results. Black line shows normal distribution with mean $\pm$ standard deviation of 0 ± 1.1 mmol m^{-3}.

A 4-channel Seal Analytical AA3 autoanalyser was set up in the Main lab of the RRS James Clarke Ross for the analysis of micro-molar concentrations of dissolved inorganic nutrients (silicate, phosphate, nitrate plus nitrite and nitrite). As part of the ORCHESTRA fieldwork programme the objectives of JR18002 was to measure the special and temporal variation of dissolved inorganic nutrient along Drake Passage in accordance with GO-SHIP protocols.

9.1 Method

Samples were collected directly from the 24 x 20 L stainless steel rosette after the TA/DIC into pre-labelled sterile 15 mL centrifuge tubes (rinsed three times with water from the same Niskin). Samples were analysed directly from the collection tubes within 2-15 hour and measured from the lowest to the highest concentration (surface to deep) to reduce any carry over effects. Milli-Q water was used for the baseline and wash solution during each run. All unique sampling depths were sampled.

Seal Analytical chemistry and cleaning procedure protocols used during JR18002 were:

1. Silicate in seawater method No. G-177-96 Rev 10 (Multitest MT19).
2. Phosphate in water method No. G-175-96 Rev. 15 (Multitest MT 18).
3. Nitrate and nitrite in seawater method No. G-172-96 Rev. 13 (Multitest MT19).
4. Nitrite in seawater method No. G-062-92 Rev. 3.

Standards were prepared fresh every day by diluting the stock solutions of the different nutrients (Table 9.1) in artificial seawater (ASW) (35 g/L sodium chloride plus 0.2 g/L sodium hydrogen carbonate).

Each run of the system had a 6-point calibration series. Prior to analysis all samples and standards were brought to room temperature of $\sim$20°C. Concentrations of the working standards was adjusted throughout the cruise depending on the high values measured in the bottom waters (Table 9.2).

9.2 Maintenance

At the start of the cruise, installation of the AA3 took approximately two days, involving; the fitting of new pump tubing, new cadmium column and making all regents. Prior to JR18002 all lab equipment (volumetric flasks, measuring cylinders, reagent bottles and carboys) had been washed with 1% decon 90 followed by 10% HCl (24 hours) and rinsed with Milli-Q water. Once on board, all labware was

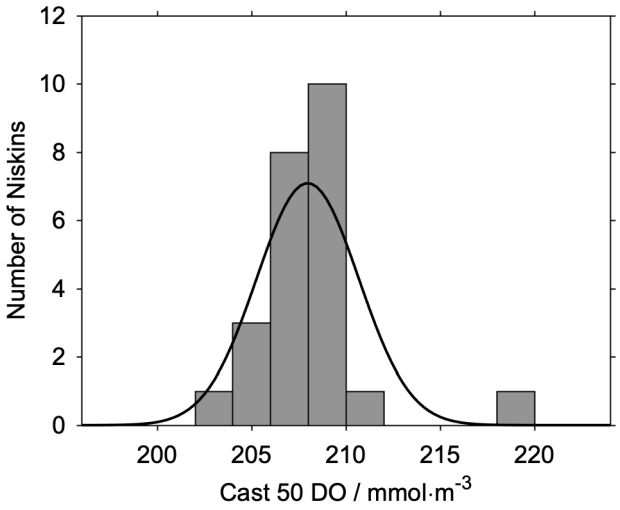

Figure 8.3: Histogram of DO analysis results from cast 50 (all Niskins fired at nominal depth of 1700 m). Black line shows normal distribution with mean ± standard deviation of 208.0 ± 2.7 mmol m^{-3}.

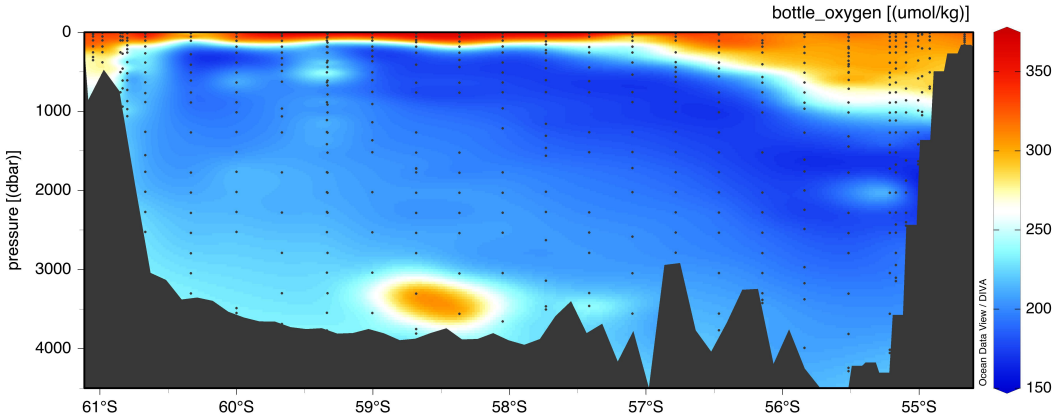

Figure 8.4: Cross-section of preliminary DO data as measured across the SR1b transect (eastern Drake Passage, Southern Ocean) on cruise JR18002.

re-rinsed several times before use. Following each run, each analytical channel was flushed with wash solutions and the autosampler with Milli-Q water following Seal Analytical cleaning protocols.

At least once per week the instrument was re-tubed and thoroughly cleaned with sodium hypochlorite for approximately 30 minutes (nitrite, nitrate, phosphate and silicate line).

Batches of ASW were prepared every days and the different chemical reagents were prepared as required.

Halfway through JR18002 the sensitivity of the Si channel decreased with the gain increasing from approximately 9 to 11, using a silicate standard of 130 μM L-1. No samples were analysed until the issue was resolved. Rather than trying to isolate the problem it was decided to remove and flush the flow cell with 1M NaOH followed by dilute sodium hypochlorite solution in addition all small bore transition tubing on the Si manifold was replaced. Sensitivity was restored suggesting the probably was caused by a partial blockage.

Table 9.1: Compounds used to prepare stock standard solutions, weight dissolved in 1 L or 500 ml of Milli-Q water and Molarity of the solution.

Compound	Weight (g)	Molarity stock solution
Potassium Nitrate	0.50655 in 1 L	5.0102
Sodium Nitrite	0.34294 in 1 L	4.9705
Potassium Dihydrogen Phosphate	0.67815 in 1 L	4.9832
Sodium Metasilicate pentahydrate (St. 1-86)	2.13015 in 500 mL	20.0829

Table 9.2: The standard concentrations used for each chemistry during JR18002.

Chemistry	CTD	Standard 1 (μM/L)	Standard 2 (μM/L)	Standard 3 (μM/L)	Standard 4 (μM/L)	Standard 5 (μM/L)	Standard 6 (μM/L)
NO3+NO2	1-45	1.00	2.00	10.01	20.02	30.03	40.04
SiO2	1-45	1.03	10.03	25.10	50.49	75.11	130.53
NO2	1-45	0.049	0.099	0.199	0.397	0.697	0.994
PO4	1-2	0.05	0.10	0.399	0.79	1.59	2.49
	3-21	0.39	0.59	0.79	1.59	1.99	2.49
	22-45	0.20	0.39	0.79	1.59	1.99	2.49

9.3 Quality Controls (QCs) / Analyser Performance

Cadmium column reduction efficiency: The reduction of the nitrate (NO3-) present in a sample to nitrite (NO2-), is achieved by passing the sample through a column filled with granular cadmium (cadmium column); cadmium is oxidised and nitrate is reduced. With use, the capacity of the cadmium column to reduce nitrate diminishes. The reduction efficiency was determined in every run by measuring nitrite and nitrate standards of similar concentrations (10 μM L^{-1}). The ratio of nitrate to nitrite expressed as a percentage provides an indication of the reduction efficiency of the cadmium column. For the analysis to produce reliable results, the oxidation efficiency needs to be $>$90%. When the efficiency is lower, the cadmium column needs replacing. New cadmium columns are conditioned by passing through a high nitrite standards (2 mM L^{-1}) followed by flushing with ammonium chloride. Throughout JR18002 the efficiency of the columns did not drop below 95% however in total we used 3 Cd columns. In each case, the column was replaced due to a build-up of backpressure probably caused by air entering the column.

CRM: In order to test the accuracy and precision of the analyses, CRMs from The General Environmental Technos Co., Ltd., (KANSO) were measured in triplicate in every run (normally at the start, middle and end). For the duration of JR18002 KANSO CRMs lot CD, CJ and CB were used; certified concentrations are shown in Table 9.3. Throughout JR18002 we had an issue with nitrite contamination in the baseline; this increased our limit of detection.

Table 9.3: Certified concentrations converted from μmol kg^{-1} to μmol L^{-1} of KANSO CRMs used during JR18002 and our results for each lot (in mmol L^{-1}).

	Nitrate	Nitrite	Silicate	Phosphate
KANSO CB	36.7 0.27	0.119 0.0057	111.9 0.62	2.6 0.022
KANSO CJ	16.6 0.2	0.032 0.007	39.43 0.4	1.22 0.02
KANSO CD	5.6 0.050	0.018 0.0044	14.3 0.099	0.46 0.0082
Measured CB	37.3 0.26	0.131 0.01	112.0 1.2	2.6 0.04
Measured CJ	16.8 0.14	0.038 0.01	39.8 0.66	1.25 0.02
Measured CD	5.6 0.07	0.037 0.01	14.6 0.21	0.47 0.01

The units of the CRMs (CD, CJ and CB) were converted from μmol/kg to μmol/L and the measured

values throughout the cruise were plotted in control charts, showing trends in data with time (Figure 9.1).

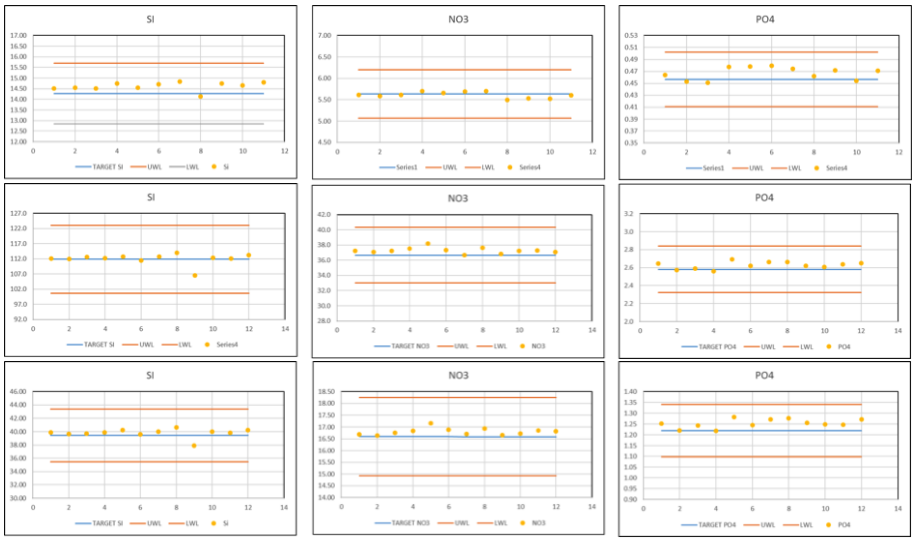

Figure 9.1: The certified value (vn-blue line) for A) CRM CD, B) CRM CJ, C) CRM CB plotted against measured values throughout JR18002 (yellow dots). Red lines are upper and lower warning levels (UWL and LWL = vn +/- 2*5/100*vn (5%)). In all cases the measured CRM values lie between the UWL and LWL.

9.4 Correlation Coefficient

The correlation coefficient shows how close the standards are to a true linear calibration. Seal Analytical protocols recommend a correlation coefficient greater than 0.9990. As can be seen in Figure 9.2 the correlation coefficient for all chemistries during JR18002 was higher than 0.9990. In fact, the lowest value seen throughout the cruise was 0.9993 for NO2.

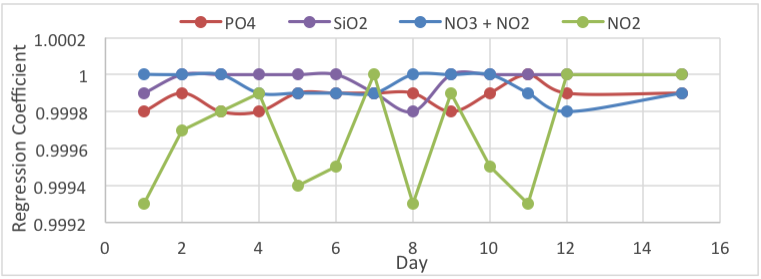

Figure 9.2: Correlation coefficients for all the nutrient chemistries during JR18002.

9.5 References

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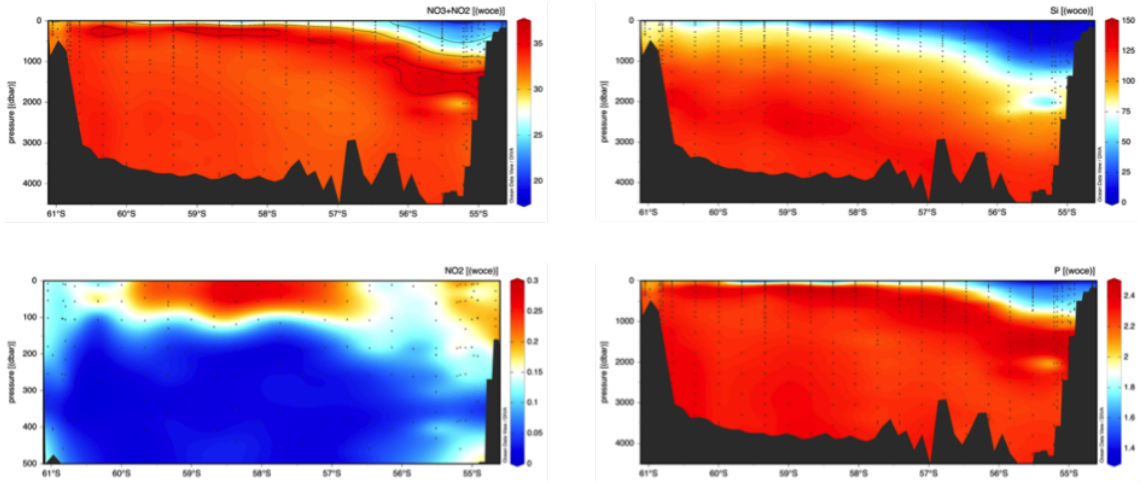

Figure 9.3: Plot of the raw nutrient values measured during JR18002. The data in these plots has not been QC for bottle misfires.

10 Nutrient isotopes

Robyn Tuerena
University of Edinburgh

10.1 Objectives

To characterise the variability in nitrogen and silicon isotope signatures across the Drake Passage. The data will be used to investigate how the mechanisms of nutrient uptake and recycling change across the Polar frontal and subantarctic zones. Stable isotope signatures will be used as tracers for the relative proportion of preformed and remineralised nitrate and silicate in intermediate water masses. This work will be part of a larger compilation of stable isotope data from ORCHESTRA, GEOTRACES and UKOA cruises.

10.2 Nutrient isotopes (dissolved)

Samples were collected throughout the transect (CTDs 1-7, 9-11, 13-15, 17-19, 21-22, 25, 27, 36, 40, 44-45), across the SR1b line. Full water column profiles were collected with higher resolution in the upper 500 m. Samples were filtered inline from the CTD using an acropak filter.

Nitrate isotope samples were collected into 30 mL bottles and frozen at -20°C. Si isotope samples were collected into 250 mL bottles and acidified with 230 μL of 20% HCl (trace metal clean). Sample caps were parafilmed and then stored at +4°C.

All isotope analyses on water samples will be carried out at the University of Edinburgh (Isotope Ratio Mass Spectrometry for nitrate N & O analysis; Multicollector ICP-MS for Si isotope analysis) following standard GEOTRACES protocols (Tuerena et al., 2015, GEOTRACES International Data Product).

10.3 Particulate organic matter isotopes (d13C, d15N and d30Si)

Water samples were collected from both the underway system (5 m) and the CTD casts (upper 200 m). Water was collected into 10 L carboys and the organic matter was pressure filtered onto filters (precombusted GF/F for N and polycarbonate for Si). Filters were stored in pre-combusted foil and flash-frozen in the -80°C freezer to be transported back in the -20°C storage.

For any further information regarding analysis, please contact Robyn Tuerena (rtuerena@ed.ac.uk).

11 Stable isotopes

Mel Leng

BGS

11.1 Radiocarbon

11.1.1 Sample Collection and Storage

Water samples for onshore (Woods Hole Oceanographic Institute, WHOI, USA) radiocarbon analysis were collected from 20-litre Niskin bottles attached to the CTD sampling rosette. This report covers the ship-based sampling procedure as supplied by 14C PI and TICTOC project partner Prof Bob Key. The radiocarbon (14C) data are expected between six months to two years after the cruise. Data will be reported in Δ14C notation, which represents the sample 14C/C ratio normalized to the Modern standard and corrected for fractionation and sample age (Δ in Stuiver and Polach, 1977).

The sample collection bottles (plus other equipment) and method were provided by WHOI. These samples will be analysed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) laboratory at WHOI. The recommended sampling procedure followed exactly the McNichol et al. (2010) guidance.

We collected 210 flask samples, including 8 in duplicate. A sampling strategy was developed in advance to ensure good coverage both horizontally and vertically across the SR1b transect. The sampling strategy was basically to sample every other cast between approximately the 2000 m isobaths, and as many depths of possible, taking care not to undertake too many duplicate depths (where multiple Niskins were fired at one depth) or waste samples on leaking Niskins. The samples were collected from 13 stations.

At each sampling station 1 or 2 crates of flasks (each containing 16 preprepared flasks) were number ordered. Each vessel has its own WHOI number and we sampled in increasing number order within each crate (all crates had a different set of numbers). At most of the stations only 1 crate of flasks were used but there are a few crates which contain flasks from 2 sampling stations. The flasks in WHOI number order were also given their cast and Niskin number. This and additional information about maximum depth, date, time were recorded on the log sheets and subsequently transferred to electronic logs.

Our method:

1. Collect the upcoming station depths to decide how many flasks will be needed at the station.
2. Order the flasks and add the cast and Niskin number to the vessel lids (note some of this additional information may be lost after securing the lids with the elastic band).
3. Take the following to the CTD:
   (a) The crate of ordered flasks
   (b) The sampling tube (tubing provided by WHOI)
   (c) Wear nitrile gloves (provided by WHOI) for sampling.
4. Select correct vessel from crate for each station/Niskin and go to CTD.
5. Attach open end of sampling tube to the Niskin spigot.
6. Turn on spigot and flush sampling tube with Niskin water for approx. 10 seconds (50 ml).
7. While the sampling tube is being flushed, work along the length of tube squeezing to ensure there are no air bubbles fixed to the inside of the tube.
8. Insert tube into bottom of the vessel, and fill with approx. 50ml of water, gently swirl around the sides of the bottle and discard, repeat.
9. With the tube still in the bottom of the vessel, fill the vessel 1.5 times (ie overflow).
10. Carefully remove the tube from the vessel, rinse the vessel top, and stopper the vessel.
11. Turn off Niskin spigot, and remove the tube.

12. Ensure sampling tube is empty of Niskin water in preparation for next sample.
13. Return the vessel to the crate.
14. Once all samples from a cast have been obtained remove the crate to a bench to continuing the preparation of the sample. For each vessel in turn, dry the outside of the vessel, remove the stopper, wipe clean and dry (with lab wipes provided by WHOI), apply a thin layer of grease (provided by WHOI) in a wavy pattern around the stopper, set aside. Pour away c. 10mls of sample water to create a headspace in the vessel. Using the Eppendorf pippette (tips provided by WHOI), add 100ul of the standard HgCl2 solution (provided by NOC) to the vessel. Carefully wipe the inside of the ground glass joint using lab wipes and place the stopper in the vessel. Twist the stopper while applying pressure to ensure a good seal with an even layer of grease. Secure the vessel top with a rubber band (provided by WHOI) over the entire vessel.
15. After all the samples have been sealed, the data sheets should be completed and checked, ensuring the correct Niskin, depth, sample bottle. The flasks in the shipping crates should be packed with all original packing material, the Bol information and sealed. The Bill of Lading should indicate cool stow across the Tropics (ie not above 25°C to ensure the working temperature of the grease seal). Away from the tropics the crates will likely be stored in the ships hold.

11.2 Oxygen and carbon isotopes

11.2.1 Sample Collection and Storage

Water samples for oxygen isotopic ratio ($^{18}O/^{16}O$, or δ18O) and stable carbon isotopic ratio ($^{13}C/^{12}C$, or δ13C) were collected from 20 litre niskin bottles attached to the CTD sampling rosette. Samples were collected using 30 ml wide-mouth HDPE bottles, and then poisoned using 8 μL of saturated mercuric chloride ($HgCl_2$) solution (provided by BGS) to inhibit biological activity and reliably preserve the carbon isotope ratios for later analysis. Pre-printed labels were filled out per station with a unique incrementing sample number, the cast number and the Niskin bottle number. Samples will be shipped back to the BGS labs in Nottingham to determine their δ18O and δ13C via isotope ratio mass spectroscopy, with both variables being measured from the same individual 30 mL sample bottle. This report only details the ship-based sampling procedure and preservation, not the final results.

The following sampling procedure was used to collect, preserve and store the δ18O and δ13C samples.

1. Collect the upcoming station depths to decide how many bottles will be needed at the station, as is best to complete the labels and log sheet in advance of sampling to save time while at the station, and because the labels can be difficult to write on after they get wet.
2. Pre-label 24 sample bottles for their Niskin number and place in a holder to carry to the CTD.
3. Wear nitrile gloves while sampling (this protects the hands from the cold water).
4. Select correct sample bottle to match with appropriate Niskin bottle.
5. Begin bottle rinsing by half filling sample bottle to the top with Niskin water directly from the small spigot (i.e. no need to use a sampling tube), replace lid, shake sample bottle and discard contents, repeat.
6. Collect sample. Fill sample bottle as full as possible with Niskin water, it may be necessary to reduce the flow from the Niskin bottle to achieve this and to ensure no bubbles in the bottle. Surface tension will allow a large dome of water to form in the top of the sample bottle, but a couple of droplets from this were poured away, as otherwise when poisoning, the mercuric chloride solution had a tendency to overflow the bottle.
7. Screw on sample bottle lid, and try to limit the time when the sample in the bottle does not have a lid on.
8. Place sample back in holder.
9. If a Niskin has failed for any reason, just leave the sample bottle empty, make a note on the log sheet of what has happened, then move onto the next niskin and sample bottle.

10. When all samples have been collected, transfer sample bottles to a fridge to keep cold until poisoning can be carried out, or continue immediately with poisoning.
11. When ready to begin poisoning, put on lab coat and nitrile gloves.
12. Transfer 30 ml sample bottles to a fume cupboard, or appropriately ventilated space.
13. Lay down sample tray with spill mat, gather mercuric chloride solution and pipette for use, and add new tip to pipette (an Elkay Exelpette variable volume 10-100l pipette was used).
14. Remove 30ml sample bottle lid (recall that the lid should stay off for as short a time as possible).
15. Pipette 8l of mercuric chloride solution into sample (hover the pipette over the top of the water but dont touch it, to avoid cross-contamination between samples).
16. Replace bottle lid, ensure is hand tight.
17. Repeat steps 15-17 for all samples.
18. After poisoning, clear away mercuric chloride solution and pipette tips, and ensure surface working area is wiped down. Any used pipette tips, or tissues used to wipe down the surface or come into contact with the mercuric chloride should be disposed of in a hazardous (UN) waste bin.
19. Use electrical tape (c. 2 times around the cap) cover the seal. Add a vertical mark which will indicate if any movement occurs during transport.
20. Stack bottle samples in appropriate storage container to be shipped back to the UK, include BoL information.

The sampling strategy for δ18O and δ13C was to collect a sample at every cast and every unique water depth, so if two Niskin bottles were fired at the same depth, a sample was only taken from the first of the Niskin bottles or whichever Niskin bottle was sampled by the other teams for comparison. However, 17 duplicate Niskins were collected. Samples were labelled sequentially from 1 to 691 (note leaking or misfired Niskins and some duplicates were not sampled). The final 30 sampled casts resulted in 523 samples including 17 duplicates.

11.3 References

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12 Microplastics

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Microplastics sampling was conducted along the SR1b transect in Drake Passage, with samples taken at a total of 17 stations at depths ranging from 5 to over 4000 metres (as summarised in Table 12.1). Seawater samples were collected from CTD rosette Niskin bottles; Tygon tubing was placed over the spigots and fed into 5-L translucent white plastic bottles. The use of Tygon tubing was for ease of collection and to minimise atmospheric contamination. Initially 10 litres of water were collected per depth. However, due to the variety of sampling taking place as well as leaking Niskin bottles, the total volume collected was reduced to 5 L per depth from station SR1b09 onwards. Samples were stored in a cool laboratory in the dark until they could be processed as soon as possible after collection to prevent algal and other biological growth.

The seawater was filtered using 1.2-μm gridded filter (Merck Millipore S-Pak Filters) and a desktop peristaltic pump (MasterFlex) attached to a 5-L Bchner flask and glass filter holder (Millipore). To minimise contamination, all equipment was thoroughly rinsed with a high-powered stream of MilliQ water in between each sample. The open bottle and glass filter holder were both kept covered with aluminium foil throughout the filtering, although an airtight natural rubber bung was introduced from station SR1b26. 5-L MilliQ blanks were conducted regularly throughout the filtering process in order to account for any contamination. A damp filter paper was kept out during the filtering of each stations samples to monitor atmospheric contamination. Filters were then stored in labelled glass petri dishes sealed with tape.

Analysis of the samples will be conducted when back in the UK using a compound microscope.

Table 12.1: Microplastics collection locations and times of filtering.

Date	Latitude	Longitude	Time (UTC)	Station	Cast
05/11/2018	55° 49.102 S	57° 41.768 W	22:22	Test cast	CTD001
06/11/2018	55° 30.990 S	57° 59.011 W	19:46	Test cast	CTD002
			19:56		
			20:17		
07/11/2018	54° 40.006 S	57° 58.993 W	20:55	SR1b01	CTD003
			21:02		
			21:06		
07/11/2018	54° 55.332 S	57° 58.967 W	00:29	SR1b02	CTD004
			00:38		
			00:43		
			00:59		
08/11/2018	54° 58.671 S	57° 59.005 W	08:18	SR1b03	CTD005
			08:21		
			08:31		
			08:39		
			08:49		
09/11/2018	55° 05.451 S	57° 58.681 W	10:30	SR1b5.5	CTD007
			11:02		
			11:16		
			11:38		

Continued on next page

Table 12.1 – *Continued from previous page*

Date	Latitude	Longitude	Time (UTC)	Station	Cast
			11:42		
09/11/2018	55° 10.760 S	57° 59.230 W	00:47	SR1b09	CTD010
			01:09		
			01:40		
			02:07		
			02:23		
10/11/2018	56° 08.874 S	57° 36.781 W	14:10	SR1b11	CTD012
			14:45		
			15:16		
			15:19		
			15:37		
10/11/2018	56° 47.000 S	57° 13.892 W	00:50	SR1b13	CTD014
			01:19		
			01:48		
			02:07		
			02:14		
11/11/2018	57° 24.939 S	56° 50.322 W	12:36	SR1b15	CTD016
			13:17		
			13:55		
			14:09		
			14:15		
11/11/2018	58° 02.95 S	56° 26.766 W	23:01	SR1b17	CTD018
			23:39		
			00:03		
			00:21		
			00:39		
12/11/2018	59° 00.0219 S	55° 51.4148 W	16:12	SR1b20	CTD021
			16:47		
			17:07		
			17:25		
			17:40		
13/11/2018	61° 02.974 S	54° 35.127 W	23:38	SR1b30	CTD023
			23:47		
			23:57		
14/11/2018	60° 58.861 S	54° 37.796 W	03:58	SR1b29	CTD025
			03:45		
			04:17		
			04:23		
14/11/2018	60° 57.115 S	54° 38.864 W	06:13	SR1b28	CTD026
			06:23		
			06:28		
			06:38		
			06:44		
14/11/2018	60° 49.991 S	54° 43.298 W	17:26	SR1b26	CTD031
			17:44		
			18:02		
			18:15		

Continued on next page

Table 12.1 – *Continued from previous page*

Date	Latitude	Longitude	Time (UTC)	Station	Cast
			18:34		
16/11/2018	59° 59.901 S	55° 14.102 W	08:22	SR1b23	CTD40
			08:57		
			09:20		
			09:35		
			09:54		

13 eDNA sampling and filtering

Alice Marzocchi and Yvonne Firing

eDNA samples were taken directly from the Niskin bottles using 1.2 L sealable plastic bags, which were first rinsed with seawater. The sampling was done using rubber glove to reduce samples contamination. One to three samples were generally collected, depending on the station and depth (Table **??**).

The initial processing of the samples (filtering) was done onboard the ship by several watch-standers, using rubber gloves to reduce human-derived degradation and contamination of eDNA. A plastic container was used to hold the bag with the seawater sample, a syringe was used for drawing seawater from the sample bag, and a Stervix column was used for filtering. The equipment was rinsed between samples as follows :

- The plastic container used to hold the seawater sample bag and the syringe used for filtering were rinsed with the ships tap water.
- Some of the sampled seawater was poured into the plastic container to rinse it, as well as the outside of the syringe. The water was then discarded.
- Some of the sampled seawater was poured into the small container and drawn into the syringe to rinse the inside of it. The water was then discarded.

1 L of seawater was filtered for every sample (unless otherwise indicated in the filtering log sheets) by iteratively drawing a 50 mL aliquot into the syringe, attaching the syringe to a single-use Stervix column and then forcing the seawater through the column. The syringe was then detached and more seawater drawn into it and filtered through the column. This process was repeated 20 times per sample and seawater was drawn directly from the sample bag, which was held inside the rinsed plastic container. Once 1 L of seawater had been filtered, residual seawater in the filter was removed by pushing air through it using the syringe. The Stervix filters were then labelled and put back into their original folded packaging, and stored in the freezer at -80C.

Plastic sample bags were rinsed with the ships tap water before the next use.

Table 13.1: List of eDNA samples taken by CTD cast (station), Niskin, depth (from CTD record), sample bag number, filterer, date and time (UTC), and volume filtered (mL).

station	niskin	depth (m)	bag	filterer	date	time	volume
9	1	3980		YF	09/11/18		1000
9	4	2995	3	YF	09/11/18		1000
9	23	58	12	YF	09/11/18		1000
10	2	4162	1	CV	09/11/18	07:15	1000
10	5	2748	3	CV	09/11/18	07:15	1000
10	6	2500	15	CV	09/11/18	07:15	1000
10	13	1003	13	CV	09/11/18	07:15	1000
11	6	2922	1	YF	10/11/18	12:00	1000
11	13	955	3	YF	10/11/18	12:00	1000
12	6	2747	1	AM	10/11/18		1000
13	4	2995	11	AM	10/11/18		1000
13	5	2497	5	AM	10/11/18		1000
15	6	2545	11	YF	11/11/18	11:38	1000
16	4	2745	6	AM	11/11/18		1000
16	10	1248	15	AM	11/11/18		1000
17	4	2589	6	CV	11/11/18	21:30	1000
18	5	2495	9	AM	12/11/18	02:36	1000
19	5	2501	9	CV/LC	12/11/18	08:20	1000
20	4	2749	6	MD	12/11/18	15:03	1000
21	14	599	9	AM	12/11/18	21:40	900
22	1	3742	6	CV	13/11/18	00:40	1000
22	4	2746	10	AM	13/11/18	01:35	1000
22	10	1003	15	AM	13/11/18	01:55	1000
32	3	2734	8	AM	14/11/18	00:06	1000
32	9	1245	14	AM	14/11/18	00:26	1000
36	5	2750	8	MD	15/11/18	12:14	1000
36	13	879	14	MD	15/11/18	12:44	1000
44	4	2745	8	AM	16/11/18	23:15	1000
44	11	953	14	AM	16/11/18	23:35	1000

14 Radium Sampling

Amber Annett

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14.1 Objectives

In quantifying timescales of heat and carbon fluxes, measurements of naturally occurring radium (Ra) and actinium (Ac) isotopes offer unique information and observational data to complement physical measurements. Dissolved Ra and Ac act as natural chronometers providing sediment fluxes and contact times of water parcels integrating over a range of timescales from weeks to years. On this expedition, Ra and Ac isotopes are used to investigate pathways and time scales of sediment input both locally, from the South American shelf and subantarctic islands, as well as upstream from the western Antarctic Peninsula.

Radium is produced continuously from lithogenic material by the decay of thorium (Th) and thus displays elevated concentrations near any sediment-water interface. Radium is present in the ocean as four naturally-occurring radioactive isotopes: ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra, with half-lives (11.4 d, 3.66 d, 1600 y and 5.75 y, respectively) spanning a range of time scales relevant to both vertical fluxes of (micro)nutrients out of sediments into the overlying water column, as well as horizontal advection. As Ra is not particle reactive, the decrease in concentration of each short-lived isotope away from the source (sediments) can be used to trace pathways of advection as well as constrain time scales of transport. ^{224}Ra and ^{228}Ra are derived from sedimentary material and can track sedimentary inputs along ocean margins recently they have been used to demonstrate hotspots of slope sediment Fe flux and with inverse modeling to estimate basin-scale trace metal inputs, respectively. Sourced from deep sea sediments, Ac has a half-life of 22 years and displays increasing concentrations with depth, such that Ac distributions can trace and constrain rates of upwelling over large vertical and temporal scales relevant to deep ocean ventilation.

14.2 Sampling Protocols

14.2.1 Radium isotopes

Ra sampling requires very large volumes of water, as Ra activities are typically very low away from sediment sources. Samples of ∼150 L were collected from the CTD by combining water from Niskin bottles fired at the same depth.

Samples were collected in 20 L collapsible plastic containers and transferred to large 160L plastic bins. Using a submersible pump, the entire 150 L sample was then passed through a column holding 20 g of MnO2-coated acrylic fiber, which strongly binds Ra. The Ra and parent isotopes are thus retained on the fiber and the filtrate is not kept. The fibers were then rinsed with Milli-Q and loaded into a Ra Delayed Coincidence Counter (RaDeCC; Scientific Computer Instruments, USA) system purged with He gas, and decay of Ra was counted for 10-12 h to quantify ^{223}Ra and ^{224}Ra content. Following decay of these short-lived isotopes, the fibers will be re-analysed using the RaDeCC to determine the activity of the parent isotopes (^{227}Ac, ^{228}Ra and ^{228}Th).

For most sampling events, a subsample was collected into acid-clean 250 mL LDPE bottles for analysis of the long-lived ^{226}Ra isotopes by mass spectrometry to calibrate the recovery of isotopes on sample fiber.

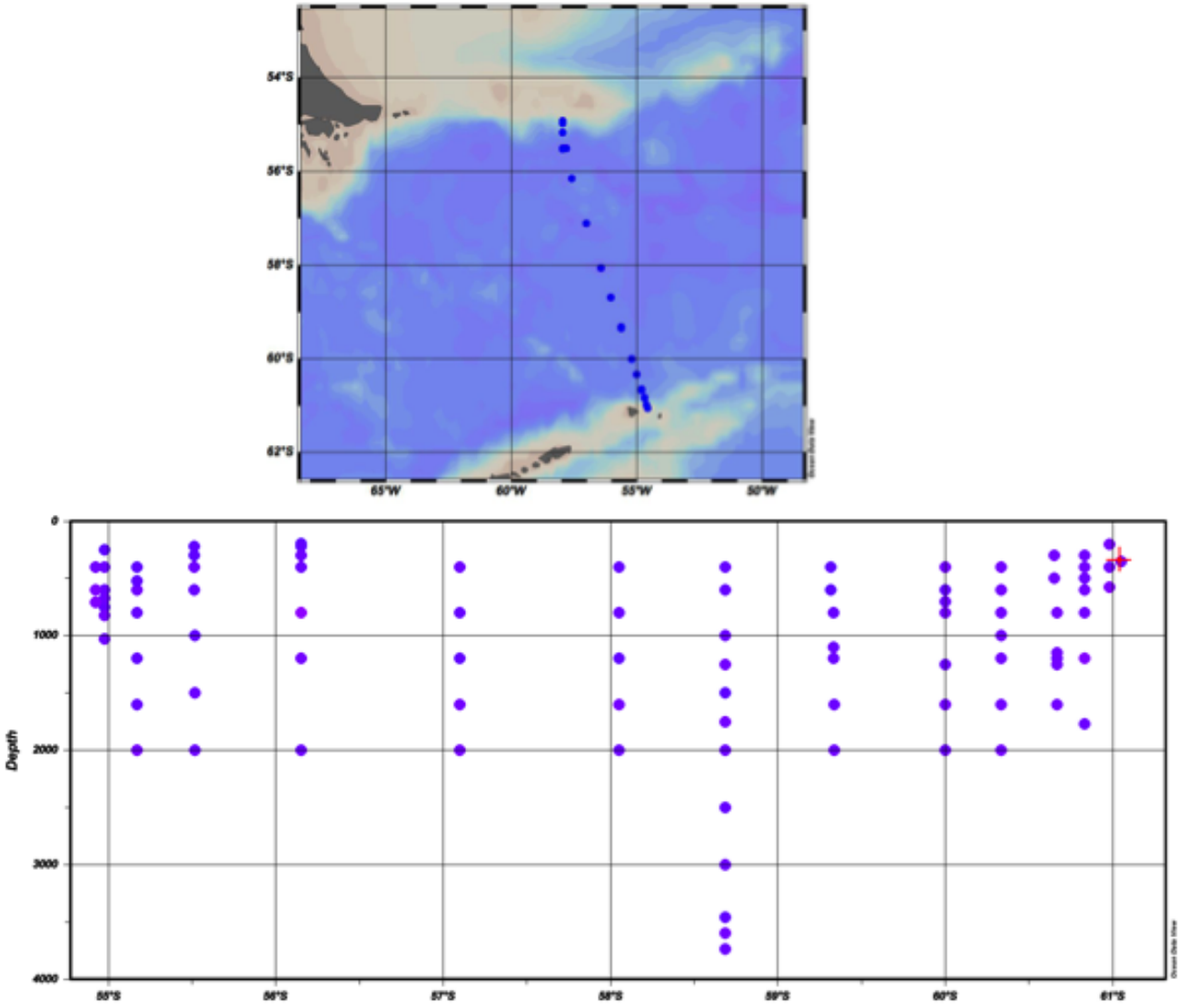

Figure 14.1: Map of Ra sampling stations along the SR1b section (left) and showing sampling depths (right, x-axis is latitude).

14.2.2 Towfish sample collection

On three occasions, large volume samples were also collected from the trace-metal clean towfish system when the ship was on station. The water was pumped directly into the large-volume plastic bins, and processed as for CTD samples. Because the rough weather resulted in the towfish spinning around while on station, wrapping the tubing around the wire and often stopping flow or damaging tubing, the decision was made not to continue surface water sampling for Ra from the towfish.

14.3 Samples collected

A total of 94 samples were collected for Ra isotopes, from 15 stations. Profiles consisted of 4-7 samples between the surface and 2000 m, as the continental shelves and slopes at 400-2000 m depth are the key potential sediment sources. Stations were chosen with closer spacing near the slopes. At one station, the profile was extended to the seafloor to constrain activities in deep water masses with an additional 5 depths sampled. Table 14.1 gives a summary of large-volume Ra samples collected, and Table 14.2 lists

the 250 mL samples collected for ^{226}Ra calibration.

Table 14.1: Summary of Ra sampling events. Sample names are given as DPddmm-xxx where ddmm is the latitude of the sampling station in 2 digit degrees and minutes, and xxx is sample depth, with corresponding CTD cast number. Also given are date and time of sampling (taken from when the CTD reached maximum depth) sample mass, and water column depth (Bot. Dep.).

Sample	CTD	Date	Time	Lat (S)		Long (W)		Mass	Bot. Dep.
			(bottom)	(deg)	(min)	(deg)	(min)	(kg)	(m)
DP6103-350	23	13/11/2018	23:33	61	3.003	54	35.157	155	361
DP6100-575	24	14/11/2018	02:37	60	58.862	54	37.792	134	584
DP6100-400	24	14/11/2018	02:37	60	58.862	54	37.792	153	584
DP6100-200	24	14/11/2018	02:37	60	58.862	54	37.792	149	584
DP6050-600	28	14/11/2018	11:38	60	49.999	54	43.295	151	1762
DP6050-500	28	14/11/2018	11:38	60	49.999	54	43.295	166	1762
DP6050-1768	29	14/11/2018	13:28	60	49.992	54	43.298	171	1762
DP6050-1200	29	14/11/2018	13:28	60	49.992	54	43.298	125	1762
DP6050-800	28, 29	14/11/2018	11:38	60	49.999	54	43.295	154	1762
DP6050-400	30	14/11/2018	15:02	60	49.992	54	43.297	155	1762
DP6050-300	30	14/11/2018	15:02	60	49.992	54	43.297	156	1762
DP6040-1150	33	15/11/2018	00:43	60	40	54	49.498	153	3102
DP6040-800	33	15/11/2018	00:43	60	40	54	49.498	146	3102
DP6040-1200	34	15/11/2018	02:34	60	40.001	54	49.487	172	3102
DP6040-1600	34	15/11/2018	02:34	60	40.001	54	49.487	153	3102
DP6040-1250	33, 34	15/11/2018	00:43	60	40	54	49.498	152	3102
DP6040-500	35	15/11/2018	04:21	60	39	54	49.495	155	3102
DP6040-300	35	15/11/2018	04:21	60	39	54	49.495	154	3102
DP6020-1200	37, 38	16/11/2018	00:10	60	19.888	55	1.571	156	3442
DP6020-1000	37	16/11/2018	00:10	60	19.888	55	1.571	157	3442
DP6020-800	37	16/11/2018	00:10	60	19.888	55	1.571	154	3442
DP6020-2000	38	16/11/2018	02:05	60	20.004	55	1.88	153	3442
DP6020-1600	38	16/11/2018	02:05	60	20.004	55	1.88	153	3442
DP6020-600	39	16/11/2018	03:52	60	20.004	55	1.88	153	3442
DP6020-400	39	16/11/2018	03:52	60	20.004	55	1.88	156	3442
DP6000-1250	41, 42	16/11/2018	12:29	59	59.993	55	14.283	172	3502
DP6000-800	41	16/11/2018	12:29	59	59.993	55	14.283	153	3502
DP6000-700	41	16/11/2018	12:29	59	59.993	55	14.283	172	3502
DP6000-2000	42	16/11/2018	14:22	59	59.995	55	14.28	172	3502
DP6000-1600	42	16/11/2018	14:22	59	59.995	55	14.28	153	3502
DP6000-600	43	16/11/2018	16:08	59	59.993	55	14.28	191	3502
DP6000-400	43	16/11/2018	16:08	59	59.993	55	14.28	153	3502
DP5920-1200	46	17/11/2018	06:01	59	19.9	55	38.923	172	3764
DP5920-1100	46	17/11/2018	06:01	59	19.9	55	38.923	172	3764
DP5920-800	46, 47	17/11/2018	06:01	59	19.9	55	38.923	185	3764
DP5920-2000	47	17/11/2018	08:31	59	20.276	55	39.149	165	3764
DP5920-1600	47	17/11/2018	08:31	59	20.276	55	39.149	172	3764
DP5920-600	48	17/11/2018	10:44	59	18.945	55	38.964	225	3764
DP5920-400	48	17/11/2018	10:44	59	18.945	55	38.964	215	3764
DP5840-600	49	17/11/2018	17:31	58	40.985	56	3.198	190	3755
DP5840-400	49	17/11/2018	17:31	58	40.985	56	3.198	190	3755

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Table 14.1 – *Continued from previous page*

Sample	CTD	Date	Time	Lat (S)		Long (W)		Mass	Bot. Dep.
			(bottom)	(deg)	(min)	(deg)	(min)	(kg)	(m)
DP5840-3740	51	17/11/2018	22:48	58	40.999	56	3.245	172	3755
DP5840-3600	51	17/11/2018	22:48	58	40.999	56	3.245	152	3755
DP5840-3460	51, 52	17/11/2018	22:48	58	40.999	56	3.245	205	3755
DP5840-3000	52	18/11/2018	01:55	58	40.999	56	3.25	172	3755
DP5840-2500	52	18/11/2018	01:55	58	40.999	56	3.25	188	3755
DP5840-1500	53, 54	18/11/2018	04:27	58	41	56	3.245	220	3755
DP5840-1250	53	18/11/2018	04:27	58	41	56	3.245	153	3755
DP5840-1000	53	18/11/2018	04:27	58	41	56	3.245	172	3755
DP5840-2000	54	18/11/2018	06:20	58	40.998	56	3.245	172	3755
DP5840-1750	54	18/11/2018	06:20	58	40.998	56	3.245	152	3755
DP5803-2000	55	18/11/2018	12:40	58	3.002	56	26.785	172	3961
DP5803-1600	55	18/11/2018	12:40	58	3.002	56	26.785	150	3961
DP5803-1200	55, 56	18/11/2018	12:40	58	3.002	56	26.785	200	3961
DP5803-800	56	18/11/2018	14:43	58	3.001	56	26.878	172	3961
DP5803-400	56	18/11/2018	14:43	58	3.001	56	26.878	188	3961
DP5706-2000	57	18/11/2018	22:21	57	5.989	57	2.113	152	4233
DP5706-1600	57	18/11/2018	22:21	57	5.989	57	2.113	152	4233
DP5706-1200	57, 58	18/11/2018	22:21	57	5.989	57	2.113	203	4233
DP5706-800	58	19/11/2018	00:22	57	5.935	57	2.068	190	4178
DP5706-400	58	19/11/2018	00:22	57	5.935	57	2.068	164	4178
DP5609-2000	59	19/11/2018	09:17	56	9.001	57	37.447	172	3383
DP5609-1200	59	19/11/2018	09:17	56	9.001	57	37.447	152	3383
DP5609-800	59, 60	19/11/2018	09:17	56	9.001	57	37.447	102	3383
DP5609-400	60	19/11/2018	11:59	56	9.002	57	37.447	172	3383
DP5609-300	60	19/11/2018	11:59	56	9.002	57	37.447	164	3383
DP5609-220	61	19/11/2018	13:22	56	9.004	57	37.452	209	3383
DP5609-195	61	19/11/2018	13:22	56	9.004	57	37.452	219	3383
DP5530-2000	62	19/11/2018	19:01	55	30.998	57	58.916	171	4193
DP5530-1500	62	19/11/2018	19:01	55	30.998	57	58.916	171	4193
DP5530-1000	62, 63	19/11/2018	19:01	55	30.998	57	58.916	198	4193
DP5530-600	63	19/11/2018	20:58	55	30.778	57	50.525	182	4193
DP5530-400	63	19/11/2018	20:58	55	30.778	57	50.525	164	4193
DP5530-300	64	19/11/2018	22:58	55	30.635	57	58.223	210	4193
DP5530-220	64	19/11/2018	22:58	55	30.635	57	58.223	200	4193
DP5510-2000	65	20/11/2018	07:52	55	10.199	57	59.005	152	3106
DP5510-1600	65	20/11/2018	07:52	55	10.199	57	59.005	190	3106
DP5510-1200	65, 66	20/11/2018	07:52	55	10.199	57	59.005	197	3106
DP5510-800	66	20/11/2018	09:58	55	10.201	57	59.006	190	3106
DP5510-600	66	20/11/2018	09:58	55	10.201	57	59.006	160	3106
DP5510-520	67	20/11/2018	12:27	55	10.2	57	59.008	209	3106
DP5510-400	67	20/11/2018	12:27	55	10.2	57	59.008	217	3106
DP5458-1030	68	21/11/2018	00:14	54	58.673	57	58.997	171	1042
DP5458-825	68	21/11/2018	00:14	54	58.673	57	58.997	152	1042
DP5458-750	68, 69	21/11/2018	00:14	54	58.673	57	58.997	197	1042
DP5458-675	69	21/11/2018	01:36	54	58.671	57	59	171	1042
DP5458-600	69	21/11/2018	01:36	54	58.671	57	59	179	1042

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Table 14.1 – *Continued from previous page*

Sample	CTD	Date	Time (bottom)	Lat (S) (deg)	Lat (S) (min)	Long (W) (deg)	Long (W) (min)	Mass (kg)	Bot. Dep. (m)
DP5458-400	70	21/11/2018	02:44	54	58.676	57	59.001	171	1042
DP5458-250	70	21/11/2018	02:44	54	58.676	57	59.001	217	1042
DP5455-707	71	21/11/2018	04:27	54	55.363	57	59.035	128	716
DP5455-600	71	21/11/2018	04:27	54	55.363	57	59.035	133	716
DP5455-400	71	21/11/2018	04:27	54	55.363	57	59.035	159	716
Total:								15668	

14.4 Preliminary results

Preliminary activities measured by RaDeCC include both short-lived Ra isotopes (^{223}Ra and ^{224}Ra) and their parents (Ac and Th, respectively). For this cruise most samples were collected far from sediment sources, such that there is likely no excess of short-lived radioisotopes and the activity is fully supported by the parent isotope within the water column. In this case, the preliminary data should give an indication of the activity of Ac and Th in each sample. Figure 14.2 shows uncorrected Ac and Th activities at the full-depth station (DP5840). For both isotopes, the range of values is reasonable, and increases towards the seafloor, consistent with a deep sedimentary source for these isotopes (or, in the case of ^{228}Th, a deep sediment source of its parent, ^{228}Ra). Fully corrected results for Th and Ac will take ~4 months to allow for decay of the short-lived daughters. ^{228}Ra will be measured by ingrowth of ^{228}Th over 12-18 months.

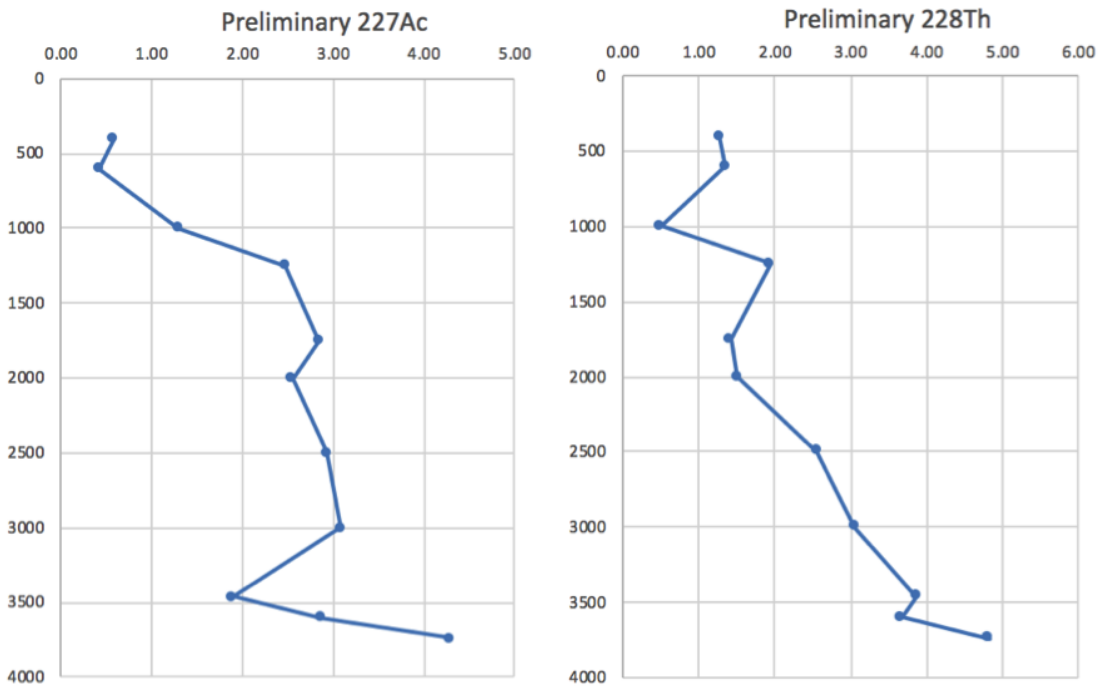

Figure 14.2: Uncorrected Ac and Th activities at full-depth station.

14.5 Amber's acknowledgements

Thank you to the officers, engineers, technicians and crew of the JCR. I'm very grateful to the many people who helped me with lugging around bottles of water, in particular the tireless Team Physics (Yvonne, Alice, Morgan, Clement, Louis, Twm and Andrew) who were there to help with every cast and kept the sampling going when I needed to sleep, as well as Robyn and Matt who did more than their share of manual labour. Thanks also to everyone who helped with the fluffing parties in the container lab, it would have been impossible to collect so many samples without such a great team. Finally, I'm very grateful to chief scientist Yvonne Firing for her support and organization that made this sampling effort a success.

Table 14.2: Small-volume ^{226}Ra samples collected, listing CTD cast and niskin bottle. Sample name format is the same as for Table 14.1.

CTD-Niskin	Sample		CTD-Niskin	Sample
n/a	fish1		51-11	dp5840-3600
24-01	dp6100-575		51-20	dp5840-3460
24-08	dp6100-400		52-06	dp5840-3000
23-01	dp6100-350		52-12	dp5840-3000
24-16	dp6100-200		52-22	dp5840-2500
29-01	dp6050-1768		54-05	dp5840-2000
29-10	dp6050-1200		54-14	dp5840-1750
28-01	dp6050-800		54-21	dp5840-1500
28-08	dp6050-600		53-13	dp5840-1250
28-15	dp6050-500		53-23	dp5840-1000
30-01	dp6050-400		53-05	dp5840-1000
30-13	dp6050-300		49-12	dp5840-600
34-04	dp6040-2000		49-19	dp5840-400
34-18	dp6040-1600		55-08	dp5803-2000
33-01	dp6040-1250		55-10	dp5803-1600
33-11	dp6040-1150		55-20	dp5803-1200
33-15	dp6040-800		56-12	dp5803-800
35-11	dp6040-500		56-17	dp5803-400
35-14	dp6040-300		57-09	dp5706-2000
38-09	dp6020-2000		57-13	dp5706-1600
38-17	dp6020-1600		57-20	dp5706-1200
38-20	dp6020-1200		58-02	dp5706-1200
38-23	dp6020-1000		58-18	dp5706-800
39-06	dp6020-600		58-10	dp5706-400
39-18	dp6020-400		59-08	dp5609-2000
42-01	dp6000-2000		59-16	dp5609-1200
42-11	dp6000-1600		59-21	dp5609-800
42-20	dp6000-1250		60-11	dp5609-400
41-13	dp6000-800		60-23	dp5609-300
41-23	dp6000-700		61-12	dp5609-220
43-07	dp6000-600		61-23	dp5609-195
43-16	dp6000-400		62-04	dp5530-2000
47-01	dp5920-2000		62-15	dp5530-1500
47-10	dp5920-1600		62-19	dp5530-1000
46-01	dp5920-1200		63-11	dp5530-600
46-13	dp5920-1100		63-17	dp5530-400
46-20	dp5920-800		65-04	dp5510-2000
48-02	dp5920-600		65-15	dp5510-1600
48-20	dp5920-400		65-21	dp5510-1200
51-01	dp5840-3740		66-12	dp5510-800

15 Underway Data Collection and Processing

Yvonne Firing and Morgan Dibb

15.1 Configuration of linux workstation koaeula

The NOC MPOC OCP group brought a workstation, koaeula, running CentOS7 Linux, which was the primary platform for data analysis during the cruise. The JCR cruise data directory was made available by mounting on koaeula. That directory includes SCS data streams, data from other sources such as CTD, LADCP, VMADCP, and the legwork directory. The network data directory was mounted on koaeula so that /mnt/data/jcr was the parent directory of the individual cruise data directories identified by date. Cruise jr18002 was current → 20181031.

The script conf_script_jr18002 set up the data and processing directories, symbolic links, and templates required for data syncing and processing in Mexec and otherwise, including links to the legdata directory and its legwork subdirectory.

Workstation koaeula was backed up regularly during the cruise. The legwork and current directories were also copied to backup disk at the end of the cruise.

Near the end of the cruise the koaeula directory structure was synced over to a second, similarly configured workstation, ewaewa, and all processing steps were tested there in order to leave ewaewa for use on JR18003. Some final processing and sample data ingestion in port was done only on ewaewa.

15.2 SCS data streams

A selection of underway data streams on the JCR are made available on the ship network through the SCS system. The SCS data streams (ea600 [sim], anemometer [met/surfmet], oceanlogger [ocl], gyro [nav/gyros], seatex-gll [nav/seapos], seatex-hdt [nav/seahead]) were processed on koaeula during the cruise. The emlog, gravity, usbl, tsshrp and furuno navigation data were collected but not processed. The em122 multi-beam echosounder was run much of the time but sometimes turned off on CTD upcasts; since the SR1b track has been traversed many times, em122 data were not logged. More details on SCS data streams on the JCR are given in the cruise reports for JR306 and JR15003. anemometer.mat emlog-vhw.mat furuno-rmc.mat netmonitor.mat seatex-gll.mat tsshrp.mat dopplerlog.mat emlog-vlw.mat furuno-vtg.mat oceanlogger.mat seatex-hdt.mat usbl-gga.mat ea600.mat furuno-gga.mat furuno-zda.mat seaspy.mat seatex-vtg.mat winch.mat em122.mat furuno-gll.mat gyro.mat seatex-gga.mat seatex-zda.mat

Preliminary stream parsing was started at the beginning of the cruise by running sedexec_startall. Most SCS data were processed in 24-hour segments, using m_daily_proc, which processes and averages each day's data (including vector averaging for wind), producing averaged, appended files for the SCS streams. Winch data were processed by CTD station as part of standard CTD processing (ctd_all_part2.m). Additional processing for thermosalinograph data is described below. At the end of the cruise data parsing on koaeula was stopped by sedexec_stopall.

15.3 Underway surface thermosalinograph and salinity calibration

TSG data read in as part of the daily procssing were set to absent when the pumps were off, or where flowrate indicated unreliable supply. At the end of the cruise the full record was cleaned by running mtsg_medav_clean_cal to perform initial processing; mtsg_findbad to interactively find bad times, and mtsg_medav_clean_cal again to remove them from ocl/ocl_jr18002_01_medav_clean.nc.

A total of 70 good underway samples were analysed for oceanlogger salinity calibration. Samples were drawn from the underway supply in the Prep Lab as often as every 4 hours during science time in ice-free areas, following the same procedure as for Niskin bottle samples, and the time noted in a logsheet to the nearest minute. They were analysed following the procedure described for CTD salinity samples in Section 5.5. TSG and bottle salinities were compared using mtsg_bottle_compare.m, and based on smoothed differences a linear drift ranging from -5×10^{-3} to $+14 \times 10^{-3}$ was applied.

15.4 Other underway data

Given that the SR1b track has been traversed many times, the EM122 multi-beam (swath) echo sounder was set to ping (for accurate depths to be used for CTD casts and by the bridge) but not to log, while EA600 single-beam echosounder data were logged but not examined.

The Simrad EK60 is a multifrequency echosounder designed to detect different species of zooplankton or fish. Acoustic backscatter data at 38, 70, 120, and 200 kHz were collected opportunistically for most of the cruise. These data have not been processed in any way.

15.5 Vessel Mounted ADCP

A vessel-mounted 75-kHz Teledyne RD Instruments (RDI) OceanSurveyor Acoustic Doppler Current Profiler (ADCP) was run throughout the cruise to measure horizontal ocean velocity. The ADCP had a beamangle of 30°, a transducer depth of 5 m, and a nominal transducer alignment of 60.08°.

The ADCP was configured with external trigger by the Simrad K-Sync unit, which was set to trigger it every 4 seconds (the minimum ping interval for this ADCP and range is about 3.5 seconds). The range of the instrument was up to 800 m, depending on scatterers, sea state, and the ships motion. Two modes were applied depending on the water depth: bottom track and water track. When in water depths approximately 1000 m or shallower the instrument was configured in bottom tracking mode, where each second ping is a bottom-tracking ping which is used to calibrate the heading alignment. In greater depths the water track mode was used to maximize the number of water pings.

There were 30 sequences in total but sequences 000-006 were very short and were discarded, leaving 007 through 029. There were six bottom track mode sequences: 007, 008, 015, 017, 022, and 029. The remaining sequences were in water track mode. Sequence 009 had errors due to too many ensemble resets but was still processed.

The data was processed using the University of Hawaii currents groups python CODAS software to process the ping (ENR) data files. Configuration files were set to use the PRDID heading messages listed as 'rdinc' in the N1R files, an initial alignment angle of 60.08 degrees, and a transducer depth of 6.5 m, and data were processed into 300 s ensembles. In addition to the automatic edits (including a percent good threshold, error velocity threshold, and bottom detection) ping data were edited manually taking a relatively light touch approach. In most cases the automatic editing removed bad ensembles (profiles) at sharp heading changes as well as bad bins due to ringing, but in a few cases manual edits were required. After editing, the median phase value was obtained from the bottom track data (from 38 points) while the median amplitude value was obtained from the water track data (from 65 estimates). Both phase and amplitude values were consistent between methods. In the end an amplitude scale factor of 1.02 and a rotation of -0.03° were applied.

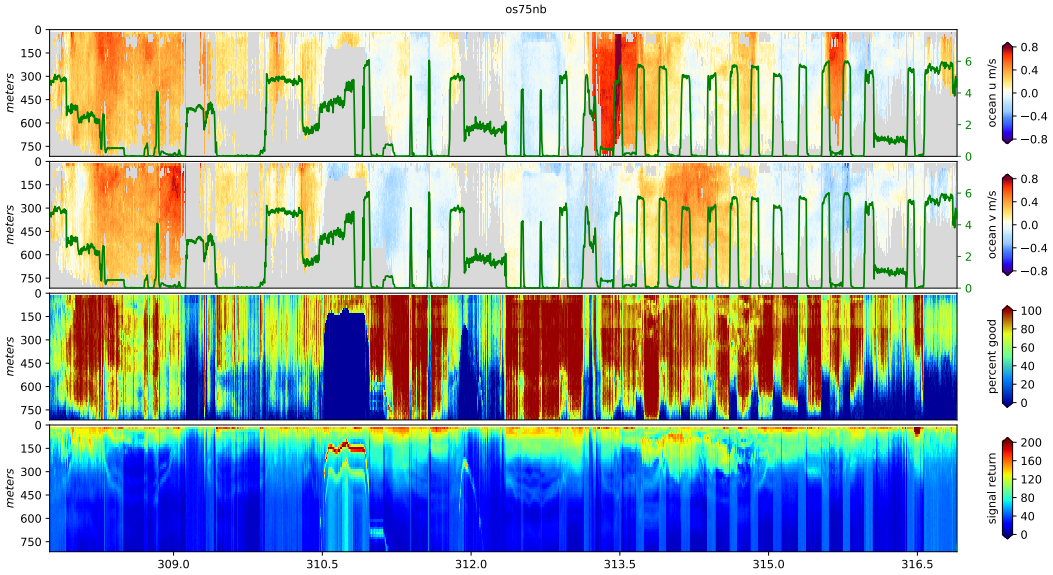

Figure 15.1: Edited, calibrated VMADCP data from southbound track: zonal (top panel) and meridional (second panel) velocity, overlaid with ship speed (green line); percent good (third panel) and amplitude (bottom panel).

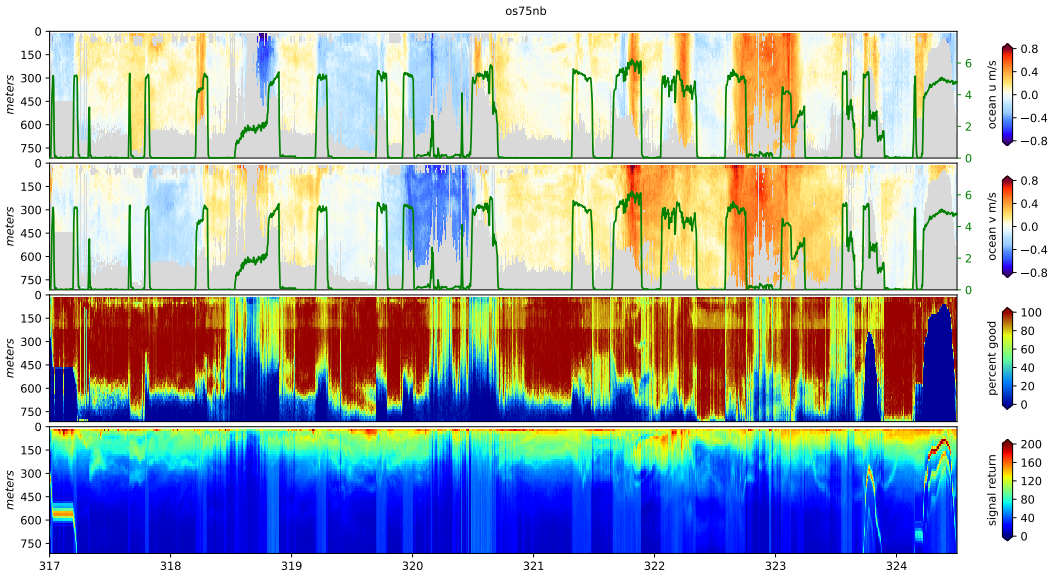

Figure 15.2: As in Figure 15.1, from northbound track.

16 Seawater trace elements, phytoplankton pigments, community structure and physiological status

Tom Browning

GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

16.1 Samples from the trace-metal-clean towed fish

Surface (2-3 m depth) seawater was sampled from a custom-built towed fish via acid washed 1-cm diameter tubing with suction provided by a Teflon bellows pump powered by filtered compressed air from the ship supply. Water was pumped directly into a section of the RRS James Clark Ross wet lab that was surrounded in plastic sheeting. Positive air pressure was maintained within this plastic bubble via a continuous inward airflow, with dust particles in this airflow removed by a HEPA filter.

35 discrete sampling sites were sampled for dissolved macronutrient (nitrate/phosphate/silicate) concentrations, trace element concentrations, phytoplankton pigment composition, phytoplankton cell counts, particulate organic carbon, biogenic silicate, chlorophyll-a concentrations, and active fluorescence physiological measurements. Further details for each of these are outlined below.

Table 16.1: Towed fish samples were collected at the following dates/times (includes experiment start points)

UTC Date	UTC Time		UTC Date	UTC Time
03/11/18	20:00:00		12/11/18	23:15:00
06/11/18	03:45:00		14/11/18	04:48:00
06/11/18	04:06:00		14/11/18	05:11:00
06/11/18	06:00:00		15/11/18	02:15:00
06/11/18	07:54:00		15/11/18	07:15:00
06/11/18	08:08:00		16/11/18	05:00:00
07/11/18	22:20:00		16/11/18	06:30:00
07/11/18	22:40:00		16/11/18	23:28:00
08/11/18	03:45:00		18/11/18	19:00:00
10/11/18	03:50:00		19/11/18	01:25:00
10/11/18	04:13:00		19/11/18	04:20:00
10/11/18	21:56:00		19/11/18	07:35:00
10/11/18	22:53:00		20/11/18	01:15:00
11/11/18	03:00:00		16/11/18	22:15:00
11/11/18	03:50:00		16/11/18	22:35:00
12/11/18	01:20:00		18/11/18	07:50:00
12/11/18	02:18:00		18/11/18	08:08:00
12/11/18	07:15:00			

16.2 Trace elements

Samples were collected in acid washed 125 mL LDPE sample bottles for dissolved (0.45/0.2 μm Sartorius filter capsule) trace metal concentrations (metals: Fe, Zn, Mn, Mg, Cu, Co, Cd, Al).

These samples will be returned in July to GEOMAR and acidified with 140 μL concentrated (10 M) high purity hydrochloric acid, whereupon they will left for approximately 6 months. Following this period

they will be pre-concentrated on a SeaFAST system (Thermo scientific) and subsequently analysed on an Element XR ICP-MS following the method of Milne et al. (2010).

16.3 Macronutrients

Samples were collected for dissolved (0.2 μm filter capsule) nitrate, phosphate, and silicate concentration analysis (15 mL). Samples were transferred to a 4°C laboratory and analysed on ship within 48 h by Dr. Ed Mawji.

16.4 Phytoplankton measurements

- Chlorophyll-a concentrations: 100 mL samples were filtered onto Machery Nagel GFF filter papers and extracted for 12-24 hours in 10 mL 90% HPLC-grade acetone in a -20 °C freezer in the dark before measurement on a Turner Designs trilogy fluorometer following the method of Welschmeyer (1994).

- High Performance Liquid Chromatography (HPLC): 1-1.5L seawater was filtered onto Machery Nagel GFF filter papers and placed directly into a -80°C freezer. These will be analysed on return to GEOMAR following the method of Gibb et al. (2000). Chlorophyll-a concentrations determined by HPLC will be used to verify those determined by fluorimetry (above).

- Analytical flow cytometry: 1.87 mL of seawater was mixed with 0.125 mL 16% paraformaldehyde yielding a final paraformaldehyde concentration of 1%. Mixing was carried out using vortex, after which samples were left for 10 minutes at room temperature in the dark before transfer to a -80°C freezer. Samples will be analysed on a FACSort flow cytometer (Beckton-Dickinson, UK) following the method of Davey et al. (2008), with the intention of analysing for nanophytoplankton, picophytoplankton, and total bacterial cell counts.

- Fast Repetition Rate fluorometry (FRRf): A FASTOcean fluorometer (Sensor ID: 14-9740-003) with integrated FASTact laboratory system (both Chelsea Technologies LTD., UK) was used to measure in vitro variable fluorescence of phytoplankton samples after a 30 minute dark acclimation period (with temperature maintained by submersion in continuously flowing water from the ships underway system). Fluorescence light curves were also ran following a protocol of progressively increasing light intensities between 20 and 2000 μmol photons m^{-2} s^{-1} (as described in Browning et al., 2014). Blank filtrates (0.2 μm filtrates) were also measured for most samples. All FRRf data will be blank-corrected and fluorescence parameters recalculated.

- POC/N. 0.30.6 L seawater was filtered through pre-combusted (6 hours at 450°C) 25 mm diameter GFF filters. Filter papers were then frozen at -80°C. Upon return to a shore based laboratory, samples will be subject to acid fuming, re-dried and then pelleted in tin boats (Elementar). Samples will be analyzed with an elemental analyzer (Euro Elemental Analyser), using a set of known masses of acetanilide as standards.

- BSi. 0.254 L seawater was filtered through 25 mm diameter 0.8 μm pore size polycarbonate filters (Whatman Nuclepore) and then frozen. Upon return to a shore-based laboratory samples will be digested in 4 mL 0.2 M NaOH (Sigma-Aldrich) at 90°C for 2 hours in acid-washed 15 mL polypropelene tubes. Following cooling, samples will be neutralised with 10 mL 0.1 M HCl and analysed for dissolved silicate on a SEAL QuAAtro nutrient autoanalyzer system (SEAL Analytical).

16.5 Incubation experiments

Ten 48120 hour duration on-deck incubation experiments were carried out in 1 L trace-metal-clean Nalgene polycarbonate bottles, following protocols described in Browning et al. (2017). Seawater was collected in bottles generally at dusk/night time, using the trace-metal-clean towed-fish described previously. Filling times were approximately 20 min to 1 hour depending on the pump flow rate. Bottled seawater was spiked with the following combinations of nutrients/trace metals: Fe, Mn, FeMn, FeZnCdCu. Initial conditions were sampled from triplicate bottles. Triplicate control bottles with no nutrients added were also collected and incubated alongside all nutrient treated bottles.

Bottles were placed in an on-deck (aft deck) incubator connected to the ships underway flow-through system, to continuously maintain temperatures at that of sea surface waters. Incubators were screened with Blue Lagoon screening (Lee Filters), which maintained irradiance at 30% of that of the surface. After incubation, experiments were taken down and measurements made for: macronutrient concentrations, chlorophyll-a concentrations (1 replicate per treatment bottle), FRRf, analytical flow cytometry (1 replicate per treatment bottle), HPLC pigments (pooled treatments), particulate organic carbon (pooled treatments), and biogenic silica (pooled treatments).

Table 16.2: Water for incubation experiments was collected at the following dates/times

Experiment	UTC date	UTC time
1	6/11/18	03:45
2	6/11/18	07:54
3	7/11/18	22:20
4	10/11/18	03:50
5	10/11/18	21:59
6	11/11/18	03:00
7	12/11/18	01:20
8	14/11/18	04:48
9	16/11/18	22:15
10	18/11/18	07:50

16.6 References

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17 Social media outreach

Mel Leng

BGS

A concerted effort was made to increase the outreach and engagement for the cruise and the ORCHESTRA project as a whole. 10 members of the science team were actively engaged with Twitter (using the hashtag #JR18002) resulting in 1500 likes and retweets (as of the end of the cruise) and we posted on the ORCHESTRA Facebook page which as of the end of the cruise resulted in over 4,000 interactions with followers. 10 blogs were written by the science team and cross posted on drakepassageblog.wordpress.com, the ORCHESTRA blog page at orchestra.ac.uk, and the BGS Geoblogy site, britgeopeople.blogspot.com.

Figure 17.1: A popular tweet.

18 Acknowledgments

We gratefully acknowledge the assistance of the Master, officers, crew, technical support personnel, and volunteers in making the cruise and data collection possible. Especial thanks are due to Aisling Smith, Seth Thomas, and Tom Biggs for extensive time and effort put into troubleshooting and repairs, and is Aisling's case for her help with everything from lab procedures to running samples to paperwork.

19 Appendix A: JR18002 IT Engineers Report

Andrew England

BAS

19.1 Data Logging/SCS

The SCS server and data logging systems worked well throughout the cruise, with no additional logging events apart from the start & stop occurring.

Time & Date (GMT)	Event
2018/10/31 11:08	ACQ started, newleg run (Leg: 20181031)
2018/11/26	ACQ stopped, end of leg

19.2 Other systems

The other systems on board the JRLB unix fileserver, SABRIS systems and ESX server all worked without any serious issues.

20 Appendix B: AME report

Seth Thomas

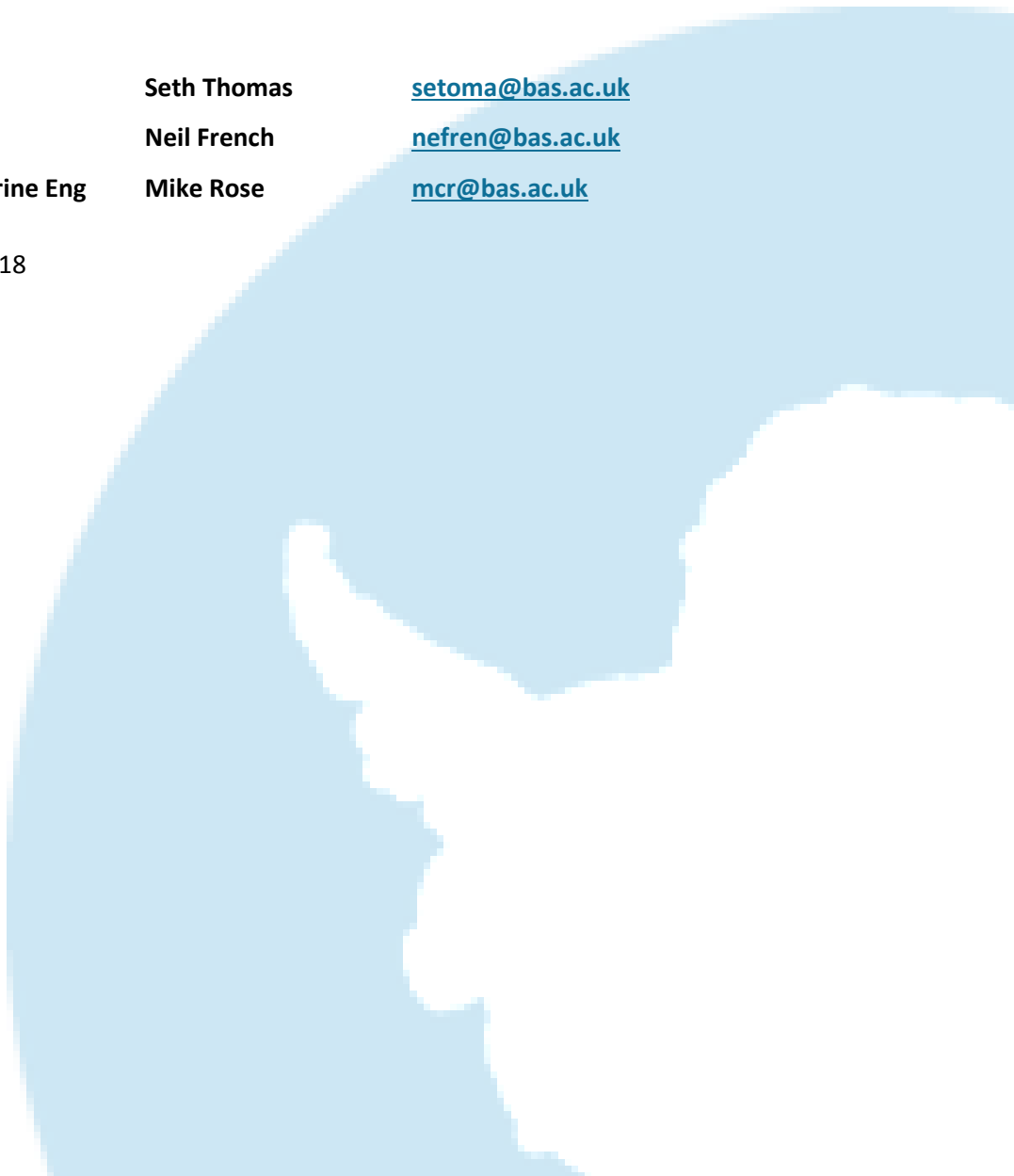
BAS

AME Scientific Ship Systems Cruise Report

Ship Science Engineer	**Seth Thomas**	setoma@bas.ac.uk
BAS Instrument Contact	**Neil French**	nefren@bas.ac.uk
Head of Antarctic and Marine Eng	**Mike Rose**	mcr@bas.ac.uk

Compiled on: 24 NOV 2018

For Cruise: JR18002



Contents

1 Cruise Summary

Cruise	Departure	Arrival	AME Engineer(s)
JR18002	03/10/18 (Falklands)	22/11/18 (Falklands)	Seth Thomas(setoma@bas.ac.uk)

This cruise is part of the science program, with 60 odd CTDs with large scale sampling for radium detection. (and normal salts, nutrients etc.)

Additional underway sampling was made using a hose attached towfish.

2 Instrumentation

2.1 Systems used on cruise

Instrument	#SN if Used	Make and Model	Comments
Lab Instruments			
AutoSal	68533	OSIL 8400B	
AutoSal	65753	OSIL 8400B	
Scintillation counter	No	PERKINELMER TRI-CARB 2910TR	
XBT	No		
Acoustic			
ADCP	Yes		
EM122	Yes		
TOPAS	No		
EK60/80	No		
K-Sync	Yes		
SSU	No		
USBL	No	Sonardyne Ranger 1	
10kHz IOS Pinger	No		
Benthos 12kHz Pinger	No		
Benthos 14kHz Pinger	No		
Mors 10kHz Transponder	No		
EA600	Yes		Bridge Equipment but logged
Oceanlogger			
Barometer1	V145002	VAISALA PTB210B1A2B	Inside the UIC
Barometer2	V145003	VAISALA PTB210B1A2B	Inside the UIC
Air humidity & temp1	61019333	Rotronic Hygroclip 2	On Foremast
Air humidity & temp2	61019251	Rotronic Hygroclip 2	On Foremast
TIR1 sensor (pyranometer)	172882	Kipp & Zonen Sp Lite2	On Foremast
TIR2 sensor (pyranometer)	172883	Kipp & Zonen Sp Lite2	On Foremast
PAR1 sensor	160959	Kipp & Zonen PQS-1	On Foremast
PAR2 sensor	160960	Kipp & Zonen PQS-1	On Foremast
Thermosalinograph	0018	SBE45	PrepLab
Transmissometer	1497DR	CST-846DR	PrepLab
Fluorometer	1498	WSCHL-1498	PrepLab
Flow meter	05/811950	LitreMeter F112-P-HC-AP-OR-PP	PrepLab
Seawater temp 1	0765	SBE38	Sea Inlet
Seawater temp 2	0771	SBE38	Sea Inlet

(Continued on next page)

Instrument	#SN if Used	Make and Model	Comments
CTD			
Deck unit 1	0548	SBE11plus	
Underwater ACD/ Depth	1225	SBE9plus	
Temp1	5645	SBE3plus	
Temp2	2191	SBE3plus	
Cond1	3248	SBE 4C	
Cond2	4126	SBE 4C	
Pump1	1807	SBE5T	
Pump2	7966	SBE5T	
Standards Thermometer	0061	SBE35 0024	
Transmissometer	527DR	C-Star	
Oxygen sensor	0620	SBE43	
PAR sensor	70442	QCP2350	
Fluorometer	12.8513-001	CTG Aqua Tracker MkIII	
Altimeter	10127.244739	Tritech	
CTD swivel linkage	1961018	Focal Technologies Group	
LADCP Master Down	14443	TeleDyne WHM300	
LADCP Slave Up	No	TeleDyne WHM300	
Pylon	0636	SBE32	
Other ship's systems (non-AME)			
Anemometer	Yes		Bridge Equipment, logged
Ships Gyro	Yes		Bridge Equipment, logged
System(s) brought by science team (non-AME)			
EXTRA NOTEWORTHY Sensors	No	MAKE	SEE YYY NOTES

2.2 Notes for Heading and Course Instruments

2.2.1 Seatex

2.2.2 Ships Gyro

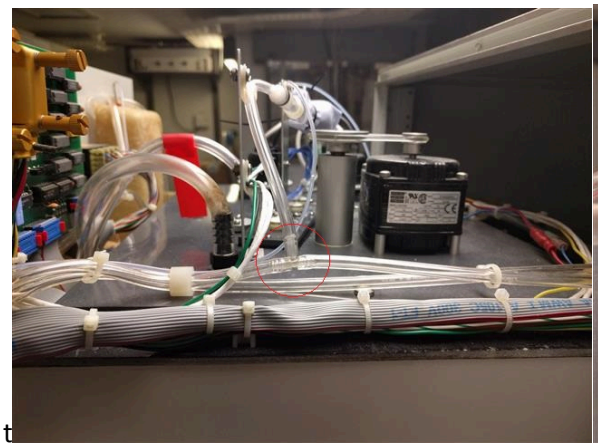
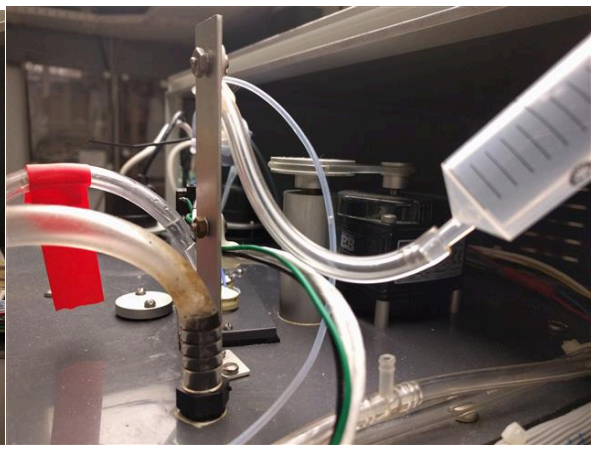
2.3 Notes for Lab Instruments used

2.3.1 AutoSal

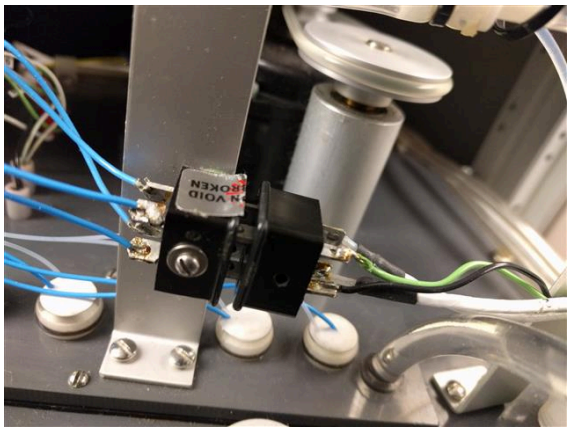
Following on from JR18001, both AutoSals have been problematic.

#65763 has been reading well enough, but has on 2 occasions leaked inside the case, thankfully without flooding any electronic components. This was seen to be coming from the flush manifold which had allowed water to creep up the flush vent tubes. In addition, water in the flush tubes leaves a salt residue which blocks the tube and prevents air from leaving the conductivity cell

resulting in trapped bubbles in the cell rendering the instrument inoperable. It was this symptom which prompted the case being opened and the internal leaks discovery. The vent tubes were cleaned by use of a medical syringe with a fine needle forcing milliQ and then dry air thrugh the tubes to clear them. This made the instrument workable for a while, then the same symptoms returned. Later, the flush pump stopped working entirely. It did start working again later, though it was noticed that the noise and pressure generated by this pump were both much less than the pump on the other AutoSal. Research of the technical manual showed that the inlet pump and the flush pump are identical models, and given that scientists always use an external peristaltic inlet pump, it was decided to swap the faulty flush pump for the seemingly operation inlet pump. This was implemented and now the unit seems to be working well. It is however, worth periodically opening up the front of the instrument and checking for fluid build-up in the flush manifold. If the manifold has accumulated water inside, then the t-junction should be removed and air forced into the flush manifold to clear it, and the vent tubes back through the conductivity cell. (The tube should then be reconnected to the t-junction before use.)

#68533 has been giving readings that fluctuate wildly over a few hundred counts. Variations of around 20 counts will make the data useless and rejected by the acquisition software. Initial inspection of the inside of the instrument showed no obvious damage but upon opening the connector (marked ‘calibration invalid if seal is broken’) it was noticed that the conductivity cell leads were not particularly well soldered to the connector, with two of the leads hanging by a few strands. Some solder was added to these connections making them a bit more robust, but still the values read were fluctuating. The connector was then tested while being partially withdrawn to check for contact quality/oxidation etc. The fluctuations stopped, although the count reading had been reduced (as expected).



The contacts were then given a rub down (as best as could be achieved in-situ) and reconnected.

Now the unit gives stable reading, although it is noted that the zero reading is now -0008 counts (the other unit gives +0002). I am unsure if this will detract from the instruments efficacy and am awaiting standardization checks by the lab manager to see if the unit can be considered fit. These instruments are calibrated against standard seawater every time they are used so a light offset shouldn't really be a problem.

25th November: The serial interface between the laptop and the AutoSal has stopped working. It was working consistently, and has now stopped.

I have not been able to re-establish communication from the salinometer to the laptop. Using putty to read serial messages from the interface box has now revealed the fault to within the salinometer-interface box connection. Both ribbon cables appear to be at fault (the incumbent one has a broken connector that was bound to fail at some point. Replacements have been ordered and will hopefully arrive before JR18003.

2.3.2 Scintillation Counter

2.3.3 XBT

Basic Stats			
Number Deployed		Number of Successful Casts	
		Number of Failures	

2.4 Notes for Acoustic Systems used

2.4.1 ADCP

2.4.2 EM122

2.4.3 Topas

2.4.4 EK60/80

2.4.5 K-Sync

2.4.6 SSU

2.4.7 USBL

2.4.8 10 KHz Pinger

2.4.9 Benthos Pingers

2.4.9.1 12kHz Pinger

2.4.9.2 14kHz Pinger

2.4.10 MORS 10 KHz Transponder

2.4.11 EA600

2.5 Notes about the Oceanlogger

2.6 Notes about the CTD

Basic Stats			
Number Of Casts	71	Number of Successful Casts	70
Max Depth	3700	Min Depth	
Cable Removed (m)		Number of Re-terminations (elect.)	2

2.6.1 Information about CTD configuration

CTD Conducting Cable: The shiny new CTD cable was terminated for use at the start of the cruise. It was noticed that the cable was very greasy. During the 1st (test) deployment, some of the sheaves on the traction winch were seen to be slipping a little. Hauling and recovery was achieved by degreasing the sheaves when they started to slip.

On the 2nd deployment, the traction winch failed to haul the cable back in. It was successfully brought it slowly by constant powerwashing the cable as it was hauled, and constant degreasing of the sheaves and powered rollers. The amount of blue grease coming off the cable was impressive and made a substantial mess of the deck and gantry area. During this slow upcast, the CTD stopped reporting (and sounding its ear piercing alarm) having presented an 'unable to communicate with water sampler' message. Upon recovery, it was noticed that there was some damage to the y-cable that connects the SBE9 main CTD body to the SBE35 thermometer and the SBE32 water sampler pylon. This cable was replaced but the problem persisted.

Following a failed insulation (megger) test of the CTD cable path, it was assumed that the termination had failed. The wet end termination was cut off and tested. This passed the insulation test showing over 4000MOhm. The CTD cable path was then test in parts to isolate the faulty section. All the shipside scientific wiring was good, so the slip rings were disconnected from the winch cable, and the cable tested. There was a dead short in the main cable. Resistance checks from the top and bottom showed:

~150 Ohms from the top (inboard end) ~50 Ohms from the bottom (outboard end)

This presents the assumption that the cable insulation has failed approximately ¼ of the way up the cable from the outboard end (roughly 2km). This fault occurred when the CTD was around 3500m below. Rather than start cutting huge amounts of cable while testing the remainder until an insulation test was passed, it was decided to re-terminate the old cable and curtail the deep CTD deployments to around 3700m depth (as the old cable is very short).

20litre Sampling Bottles: The springs that were delivered to go in the new 20l bottles are a mismatched collection of 3 different spring types. Hence making extension lanyards to go inside the bottles with the springs was a bit on an empirical guesswork exercise. Initial concerns that the knots tying these monofilament loops together (the normal method of using copper crimps to secure monofilament lines was not permissible due to concerns about sample contamination of copper inside the bottles.) may slip and let go were quickly replaced by the observed fear that the lanyards themselves would snap. This has happened on 4 occasions, one of which resulted in a scientist being struck on the chin as the top cap shot upwards as he was cocking bottles. No apparent injury was sustained. Luckily, this only seems to occur during the bottle cocking procedure, so no caps or other parts have been lost as a result.

The bottles themselves are too bit to comfortably fit in our 24 bottle frame. The length of the bottles means that some of them (aligned with the lower upright frame sections) are not allowed to close fully due to the lower caps striking the frame. This was partially alleviated by the addition of a

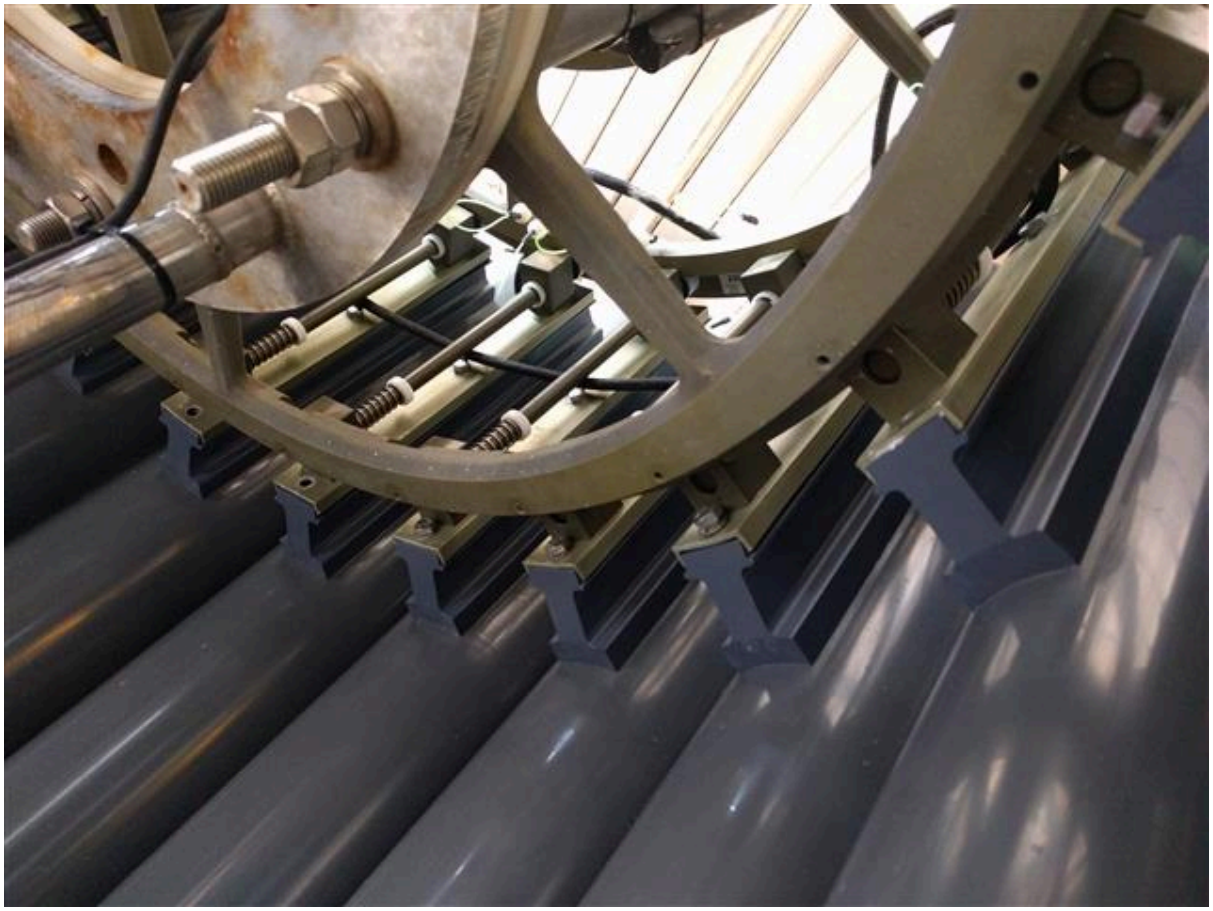
second isolation spacer washer between the upper and lower frame sections but one of the bottles (19) is perfectly in line with the lower frame rail and still fouls the frame. A 12l bottle was used here.

It is important to note here that our spare frame cannot be properly assembled currently as it needs this washer, hence if the primary frame were to be lost, it would be very difficult to fabricate a replacement with any haste. We have aboard a spare complete frame from NOC, but a conversation with Jez yesterday has me believing that NOC may take this back as their other spare frame has been damaged beyond serviceability.

One of our 20l bottles was completely destroyed when the CTD frame swung against the side of the ship during recovery in rough weather. As this was being replaced, it was noticed that a couple of the bottles had very stiff release pins making it very difficult to remove the bottle from the frame. Further inspection showed that the anodized aluminium mounting brackets on these (and a few other) bottles were visibly bent. Also the lowest of the bolts holding these brackets on the bottles were loose. All of these were tightened, and the worst of the bent brackets replaced with the bracket from the destroyed bottle. (Which was just about all that remained of it.)

Throughout the cruise there have been bottles failing to seal properly and leaking when recovered. This has been seemingly at random, so addressing the fault for specific bottles has not been possible. Hopefully when new product specific springs are attained, bottle closure will be a bit more constant, and dependable (and there will no longer be issues relating to internal 'spring extension lanyards' snapping.)

At the end of the cruise, when bottles were removed to allow access to the sensors to install a couple of missing spacers, is was again noticed that many of the bottle bracket bolts had again worked themselves loose, and a goodly few had fallen out altogether.



This presents even greater risk of bent brackets, smashed bottles, or lost bottles (specifically as the ‘safety rope’ used to ensure bottles do not fall off, is threaded through the insides of the brackets.

Also, being procured from the U.S.A. these bolts are 3/8inch UNC and we do not have stocks of these aboard. (The ship’s engineering store has some but they are slot headed, but could be used in time of need.)

3 Additional work completed on cruise

Coring Winch

Outboard load cell on the 30T coring winch has been recalibrated. If needed the new coefficients are: Gain = 0.035 Offset = -55.16

When inputting these values into CLAM it appears as though the system rounds to the nearest 0.01 though empirical measurements post calibration show this not to be the case. (I have not checked in the software to see how this is processed but it’s worth investigating at a later date.)

4 AME Department notes

4.1 Pre-cruise tasks

Task	Status
Download AME_Eng/Platform_Specific/JCR	N
Check cruise planning meeting notes	N
Number of hours hand over with previous ships AME Engineer	0.16

4.2 Daily & weekly tasks

Task	Frequency	Status
Sanity check the Oceanlogger data	Daily	Y
Check the Following Fans: Oceanlogger Acoustic Rack Seapath EM122 (Tween) Topas (Tween)	Daily	Y
Mega test CTD cable	Weekly	Y
Clean Underway System	Weekly	Y

4.3 End of cruise checks

Task	Status
XBT left in cage, in a suitable state	Y
The salinity bottles have been cleaned, if used	Y
CTD left in suitable state - Ducts cleaned with Triton and deionised water, blanking plugs installed and system washed with water	Y/N
CTD Slip Ring have been cleaned	Y
SVP is left in a good state and not left on deck (never leave this on deck)	Y
Office is tidy, with manuals and files returned and items stowed for sea	Y/N
Clean the following fans: Oceanlogger Acoustic Rack Seapath EM122 (Tween) Topas (Tween)	Y/N

4.4 Items to be purchased

4.5 Additional notes and changes/future work

4.6 End of cruise Notes