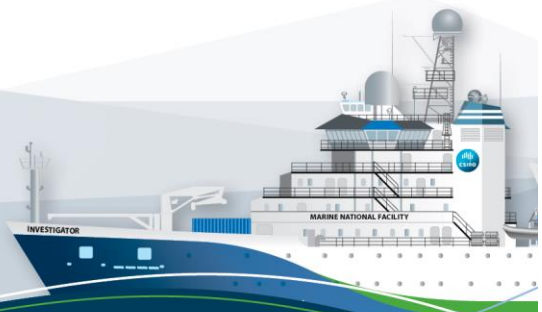
HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2022_v03
Chief Scientist	Elizabeth Shadwick
Principal Investigator	Ben Scoulding, Jay Mace, Craig Hanstein, and Scott Meyerink
Voyage title:	SOTS: Southern Ocean Time Series automated moorings for climate and carbon cycle studies southwest of Tasmania
Report compiled by:	Alicia Camac and Julie Janssens



Contents

1 Executive Summary

Overall data collected was of very high quality. No significant sample collection, analysis or data processing issues were encountered.

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NOx) and nitrite:
Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*."
Limnol. Oceanogr: Methods, 17(1): pp. 25-431.
doi:10.1002/lom3.10294

If publishing ammonium data, please cite the following:
Rees, C., Janssens, J., Sherrin, K., Hughes, P., Tibben, S., McMahon, M., McDonald, J., Camac, A., Schwanger, C. and Marouchos, A., (2021*) "Method for Reproducible Shipboard Segmented Flow Analysis Ammonium Measurement Using an In-House Reference Material for Quality Control."*
Frontiers in Marine Science, 8.
doi:10.3389/fmars.2021.581901

1.1 Objectives

The scientific aims of this voyage were to:

1. Deploy SOFS-11 meteorology/biogeochemistry mooring
2. Deploy SAZ-24 sediment trap mooring
3. Recover SOFS-10 meteorology/biogeochemistry mooring
4. Recover SAZ-23 sediment trap mooring
5. Do CTDs at the SOTS site, including collecting samples for nutrients, oxygen, dissolved inorganic carbon, alkalinity, and particulate matter analyses
6. Ship meteorological observations at SOFS buoy for comparisons
7. Tow MacArtney Triaxus on transit to SOTS site
8. Tow CPR on return to Hobart (not undertaken)
9. Carry out underway air and water sampling and sensor measurements, including bio-optics and bio-acoustics
10. Deploy 2-3 Biogeochemical-Argo autonomous profiling floats at the SOTS site, potentially augmented by casts of a bio-optical sensor package.
11. Collect Thorium isotopes samples in seawater and aerosol sampling on UTAS CTDs

1.2 General Hydrochemistry Information

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity.

Five nutrients were determined: silicate ($Si(OH)_4$), phosphate (PO_4), nitrate + nitrite (NOx), nitrite (NO_2) and ammonium (NH_4). Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values. See table for the CTD deployment versus measured RMNS values.

Missing and suspect data are in appendix 8.4, 8.5, and 8.6.

Final hydrology data, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre.

For Data, contact: NCMI_DataLibrarians@csiro.au

2 Itinerary

Table 1: Voyage itinerary

	Depart	Arrive
Port	Hobart	Hobart
Date	02/05/2022	15/05/2022
Time	09:30	08:30

Voyage track:

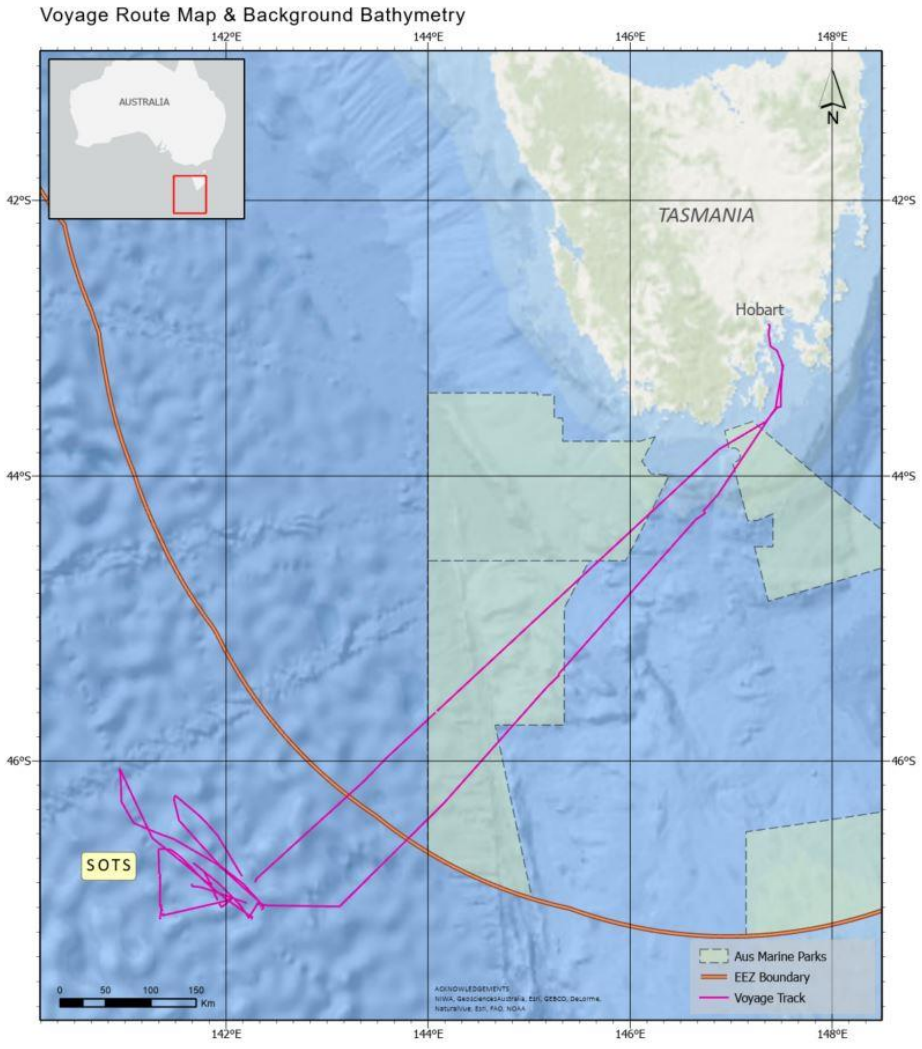


Figure 1: Voyage track

3 Key personnel list

Table 2: Key Personnel list

Name	Role	Organisation
Elizabeth Shadwick	Chief Scientist	CSIRO
Matt Kimber	Voyage Manager	CSIRO
David Flynn	Deputy Voyage Manager	CSIRO
Julie Janssens	Hydrochemist	CSIRO
Alicia Camac	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Table 3: Sample Type and Number Assayed

Analysis	Samples Assayed	Type
Salinity	119	CTD
	21	TSG
	21	EXP
Dissolved Oxygen	111	CTD
	20	EXP
Nutrients	111	CTD
	100	EXP

4.1.1 CTD Samples (Conductivity, Temperature, Density)

- Taken from the 12L Ocean Test Equipment bottles on the CTD rosette that is deployed at depth for water collection.
- 8 CTD deployments were sampled for Hydrology.

4.1.2 TSG Samples (Thermosalinograph)

- Taken from the underway instrument clean seawater line supplying the pCO2 instrument in the underway laboratory.
- TSG samples collected by Hydrochemistry. Results emailed to Vito Dirita (CSIRO) at the completion of the voyage.
- Refer to voyage everLog for TSG sample information.

4.2 Data Processing Overview

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated below (fig.2).

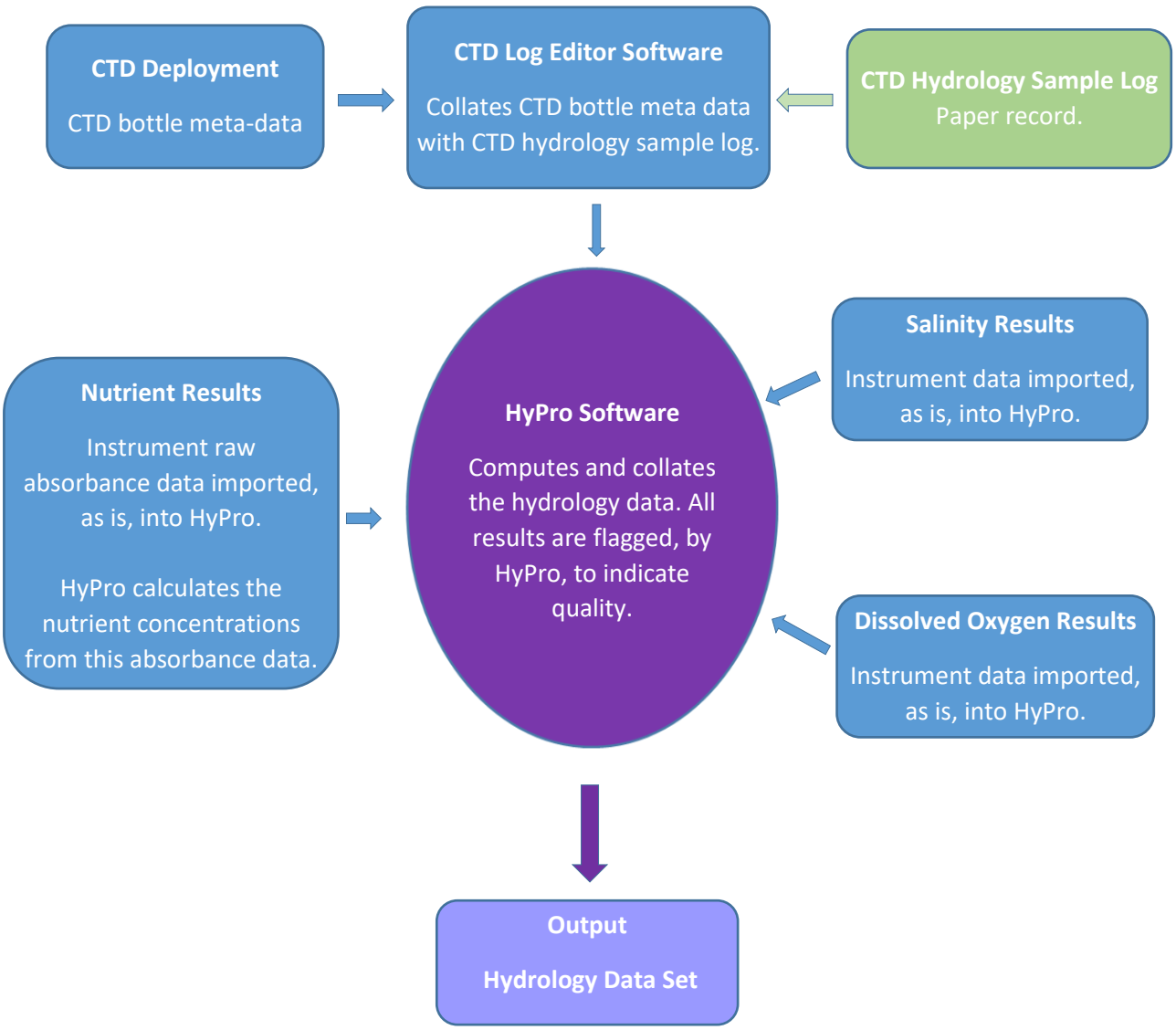


Figure 2: Hydrology Data Processing Flow Diagram.

5 Salinity

5.1 Salinity Measurement Parameters

Table 4: Salinity Measurement Parameters

Details	
HyPro Version	5.7
Instruments	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71611 Bath temperature 24.0°C
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2
Hydrochemistry Methods.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Reference Material	OSIL IAPSO - Batch P163, use by 10/04/2022, K_{15} = 0.99985 OSIL IAPSO – Batch P164, use by 23/03/2023, K_{15} = 0.99985
Sample Container	200 ml volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.
Sample Storage	Stored in Salinometer lab > 8 hrs before measurement.
Lab Temperature	Not recorded
Analysts	Julie Janssens
Comments	See DAP report for CTD processing and calibration details.

5.2 Salinity Method

Salinity samples were measured on a Guildline Autosal 8400B instrument operated in accordance with its technical manual. The measured value is recorded with an OSIL data logger.

Before each lot of sample measurements, the Autosal is calibrated with standard seawater (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL standard is used for each calibration. The frequency of calibration is at least one per run (one run consists of samples from up to two CTD deployments).

Method: The salinity sample is collected in a 200ml OSIL bottle. The bottle is rinsed then filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, till overflowing. The bottle is removed from the straw and the sample is decanted to allow a headspace of approximately 25cm^3. A dry plastic insert is fitted, the bottle inverted and rinsed with water then capped and stored cap-down until measured. To measure, the Autosal cell is flushed three times with the sample and then measured after the fourth and fifth flush. The OSIL data logger software captures the conductivity ratio and calculates the practical salinity.

The output from the data logger is imported into HyPro and collated with the CTD deployment meta-data.

5.3 CTD Salinity vs Bottle Salinity Plot

For this voyage, the difference between the unprocessed (uncorrected) CTD value and the measured bottle value is generally less than 0.002 PSU.

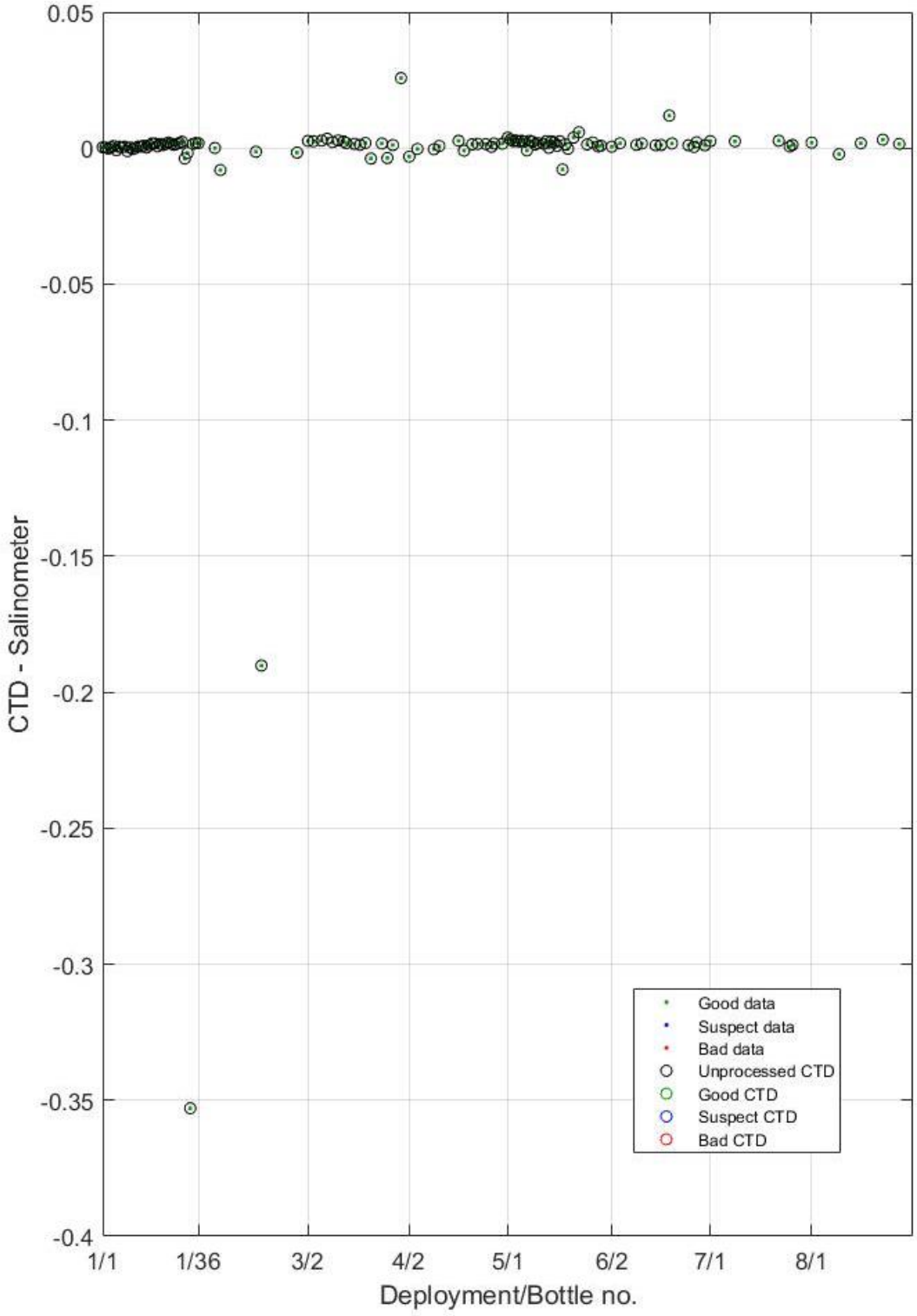


Figure 3: CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour, green indicating good bottle data. Please ignore the black ring, indicating unprocessed CTD data, this plot is generated using the pre-processed CTD output. Units: PSU.

6 Dissolved Oxygen

6.1 Dissolved Oxygen Measurement Parameters

Table 5: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
Hydrochemistry Methods	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 µmol L^{-1}
Analysts	Alicia Camac
Lab Temperature (±1°C)	See plot in appendix 7.9 (1)
Sample Container type	140 mL glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis.
Comments	See DAP report for CTD calibration details.

6.2 Dissolved Oxygen Method

SIO method used. The method is based on the whole bottle modified Winkler titration of Carpenter (1965) plus modifications by Culberson *et al* (1991).

Method: The sample is collected in an iodine determination flask of known volume. 1mL of manganese (II) chloride solution followed by 1 mL of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum of 15 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, Mn (IV) is reduced to the divalent state liberating iodine. The iodine is titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1 mL burette. The endpoint is determined by measuring the decrease in the UV absorption 365 nm.

The thiosulphate solution is standardised by with a 10ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two titres of consecutive additions of 1 mL aliquots of potassium iodate to the same blank sample. The standardisation is done at least once per 12-hour shift, when samples are being assayed.

The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

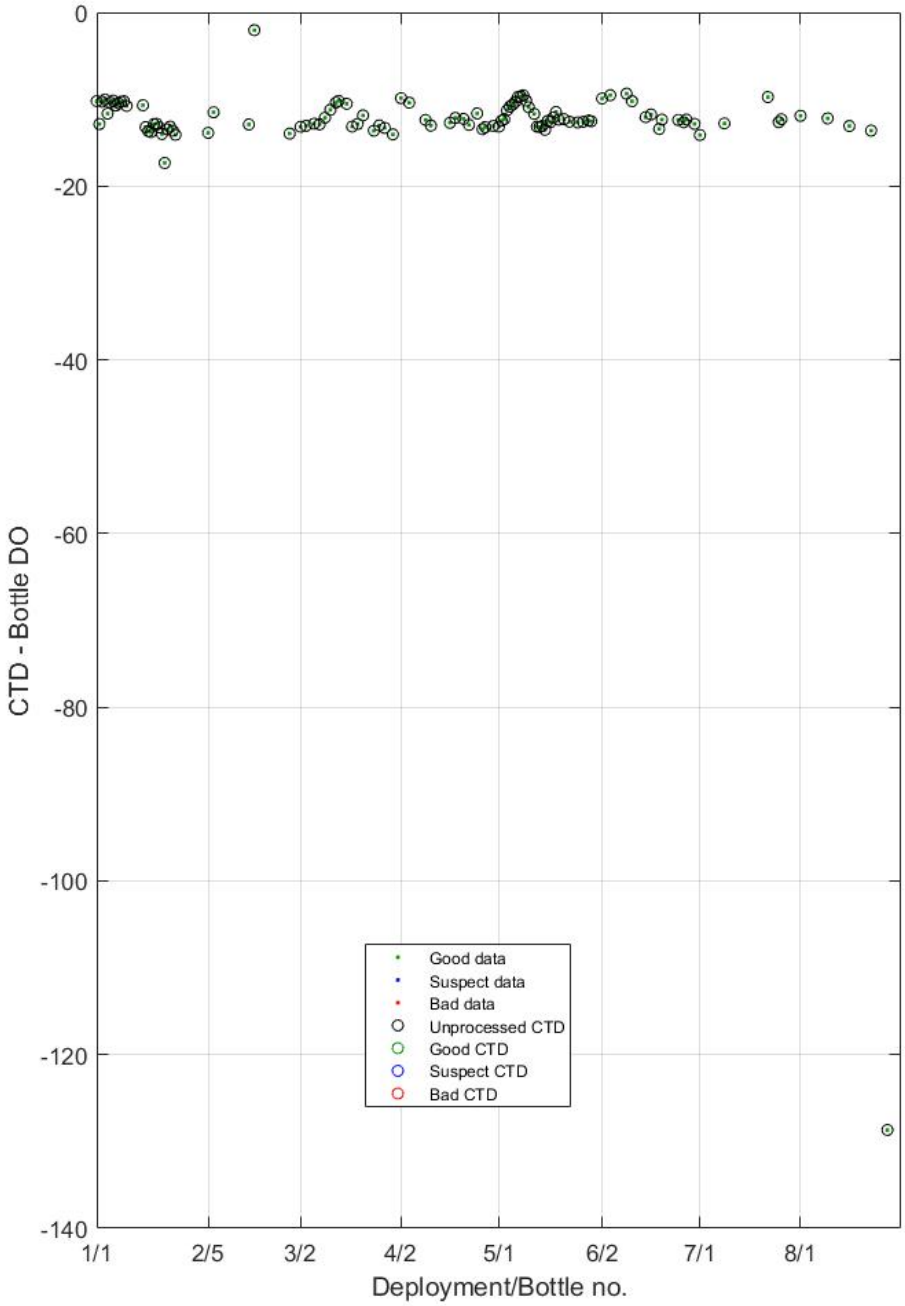


Figure 4. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour, green indicating good bottle data. Please ignore the black ring, indicating unprocessed CTD data, this plot is generated using the pre-processed CTD output. Units: µmol L^{-1}.

6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The variance in thiosulphate concentration is within our QC parameter of less than 0.0005N between standardisations. One batch of thiosulphate reagent was used during the voyage. The mean normality as follows:

CTD Deployment 1 to 8:	Mean:	0.206148 N
	SD:	0.00012 (n=5)

The blank correction is used in the calculation of the thiosulphate normality and is due to oxidisable species in the MQ water that is added to the KIO_3 aliquot before the titration.

The red lines in figure 5 indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration and the blank concentration. The titrant should not vary more than 0.0005 N between analyses.

The lines are centred on the mean normality for the voyage, and are used as a guide for the expected normality range.

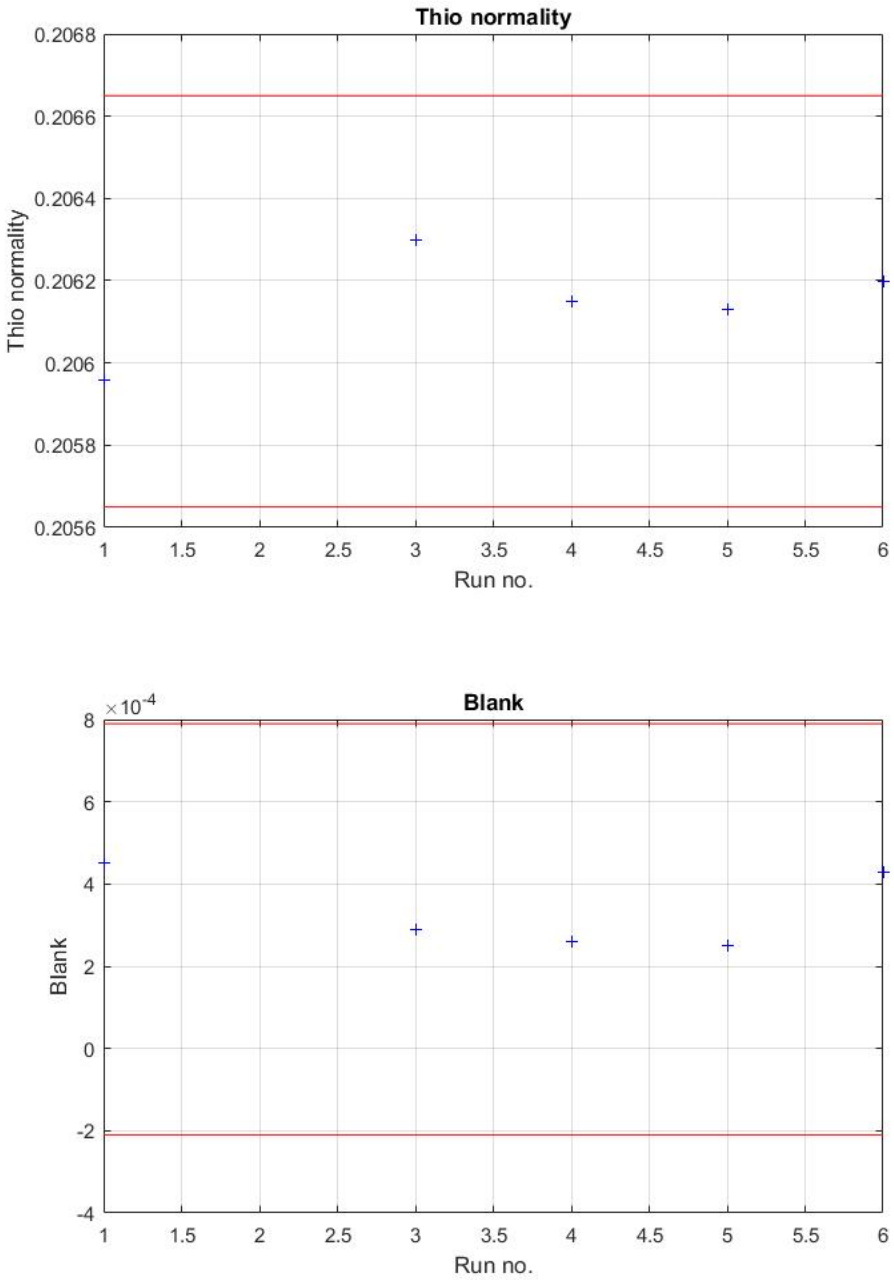


Figure 5. Thiosulphate standardisation and blank correction plots.

7 Nutrients

7.1 Nutrient Measurement Parameters

Table 6: Nutrient measurement parameters. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details					
Processing Software	CSIRO HyPro 5.7				
Instrument	Seal AA3HR segmented flow analyser.				
Operating Software	AACE 7.10				
Hydrochemistry. Methods	Sampling: WI_DO_001				
	Assay:				
	SOP001	SOP002	SOP003	SOP004	SOP005
	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Top concentration (µmol L^{-1})	140	3.0	42	1.4	2.0
Method detection limit (µmol L^{-1})	0.2	0.02	0.02	0.02	0.02
Reference Material	KANSO RMNS lot CH				
Sample Container	50 mL HDPE with screw cap lids. Reused after acid wash with 1M HCl				
Sample Storage	< 4 hrs at room temperature or < 12 hrs @ 4°C				
Sample preparation	Assayed as neat. No filtration.				
Lab Temperature (°C)	See plot in appendix 7.9 (1)				
Analysts	Julie Janssens, Alicia Camac				
Comments	N/A				

7.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1cm flow-cells for colorimetric measurements and a JASCO FP2020 fluorescence instrument as the ammonium detector.

Silicate (SOP001): colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660nm.

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS[1] Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper - cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 520 nm (run 1 - 3) and 540 nm (run 3 – 22).

Nitrite (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Kérouel and Aminot (1997). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460nm after excitation at 370nm.

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.
[1] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

7.3 HyPro Processing Summary for Nutrients

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and, duplicate sample results that do not match.

Suspect calibration points are weighted less when fitting the calibration curve. The cut-off limits for good calibration data are:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE[1]).
- 0.02 µmol L^{-1} for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. The Flag key is in Appendix 8.7. Missing or suspect nutrient data is tabulated in section 8.6

[1] World Ocean Circulation Experiment

Table 7: HyPro Processing Parameters. All instrument parameters and reagent batches and operation events are logged for each analysis run. This information is available on request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Data Reported as	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
# of points in Calibration	6	6	6	6	6
Forced through zero	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N

Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	Low nutrient seawater (LNSW, bulk on deck of Investigator) collected on in2019_v05. Sub-lot passed through a 10 µm filter and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω water. Dispensed from the Milli IQ7010.				
Duplicate samples.	CTD: Niskin fired at the greatest depth, Chl *a* max and subsurface were analysed in duplicate. Single samples were analysed for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.1				

7.4 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Descriptive statistics are used to ascertain the accuracy and precision of the analysis from the repetitive measurement of the RMNS for silicate, phosphate, NOx, and nitrite in seawater.

Japanese KANSO certified RMNS lot assayed in triplicate in each run to monitor accuracy. The certified values are in appendix 8.2.

For in2022_v03, RMNS CH was the main RMNS used across the voyage for CTDs. RMNS BY, CB, and CG were only used for the characterisation run at the start of the voyage. The certified reference material results for NOx, silicate and phosphate are within MDL, and nitrite within 0.02 µmol L^{-1} of their certified mean concentration.

The GO-SHIP criteria (Hyde *et al*., 2010), appendix 8.8, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

The assayed RMNS values per CTD deployments are listed in the appendix 8.3.1.

KANSO publishes the RMNS nutrient values in µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C. The RMNS is not certified for ammonium. NO_x is derived by summing the NO_3 and NO_2 values.

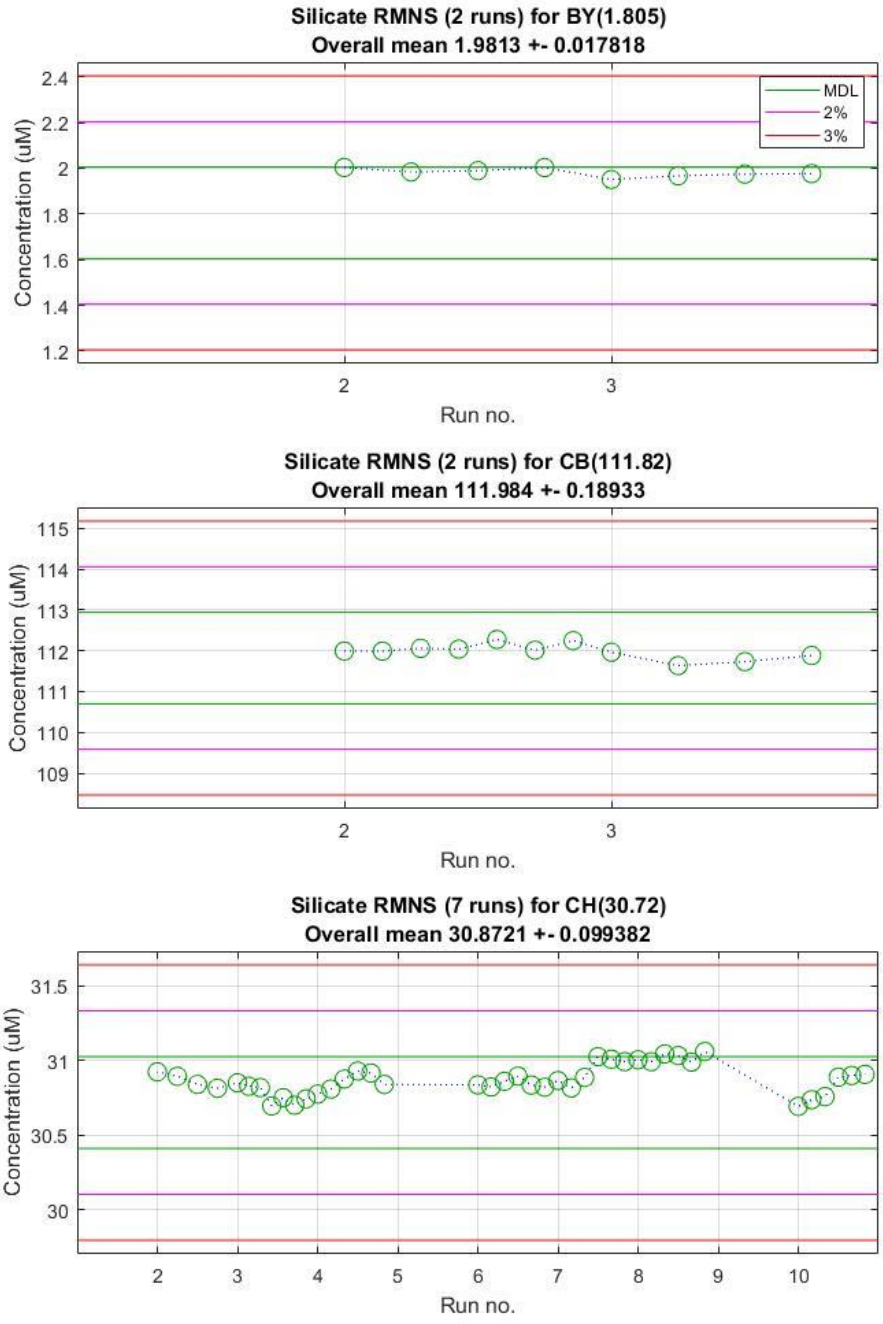
Table 8: RMNS CH statistics for of this voyage. Units: µmol L^{-1}

RMNS CH	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
Minimum	30.7	1.20	0.173	17.18
Maximum	31.1	1.22	0.183	17.5
Mean	30.866	1.206	0.178	17.365
Median	30.9	1.21	0.178	17.38
Repeatability	0.102	0.005	0.002	0.095

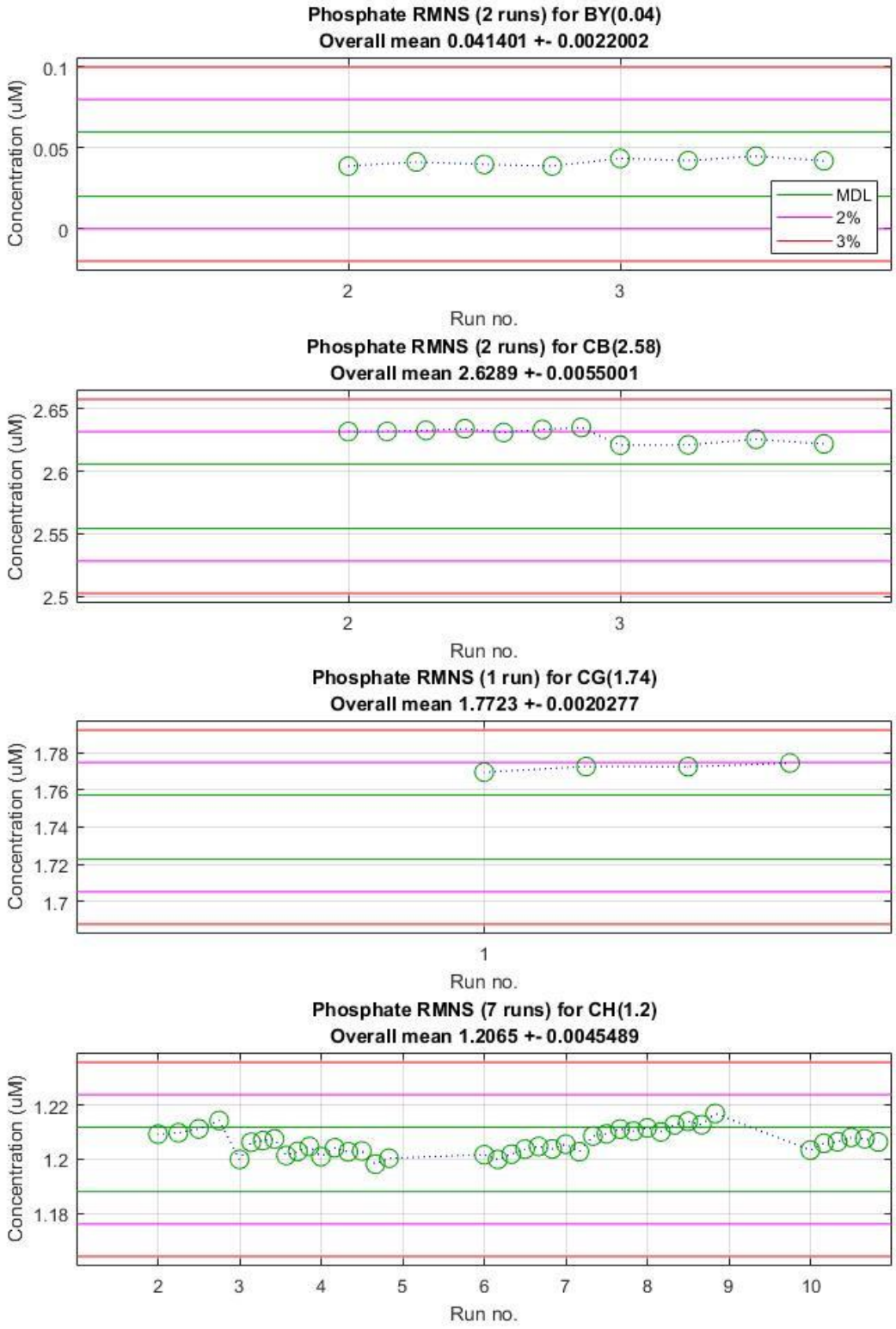
7.5 Nutrient plots of RMNS

The green pink and red contours are at 1%, 2% and 3% from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µmol L^{-1} increments from the certified value. The blue line is the certified value's expanded uncertainty. Plots are RMNS value versus instrument run number.

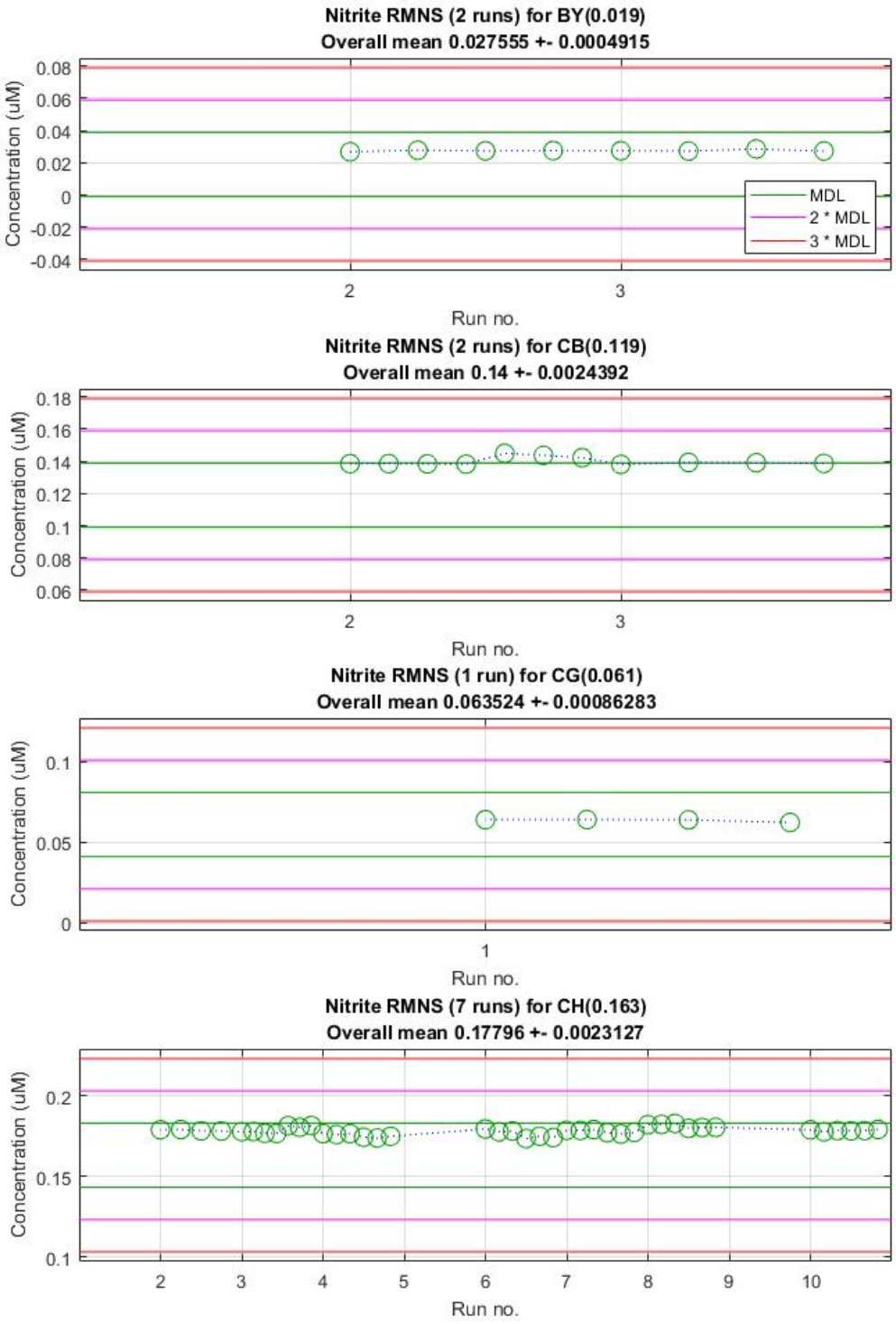
7.5.1 **Figure 6:** Silicate RMNS Plot (µmol L^{-1})



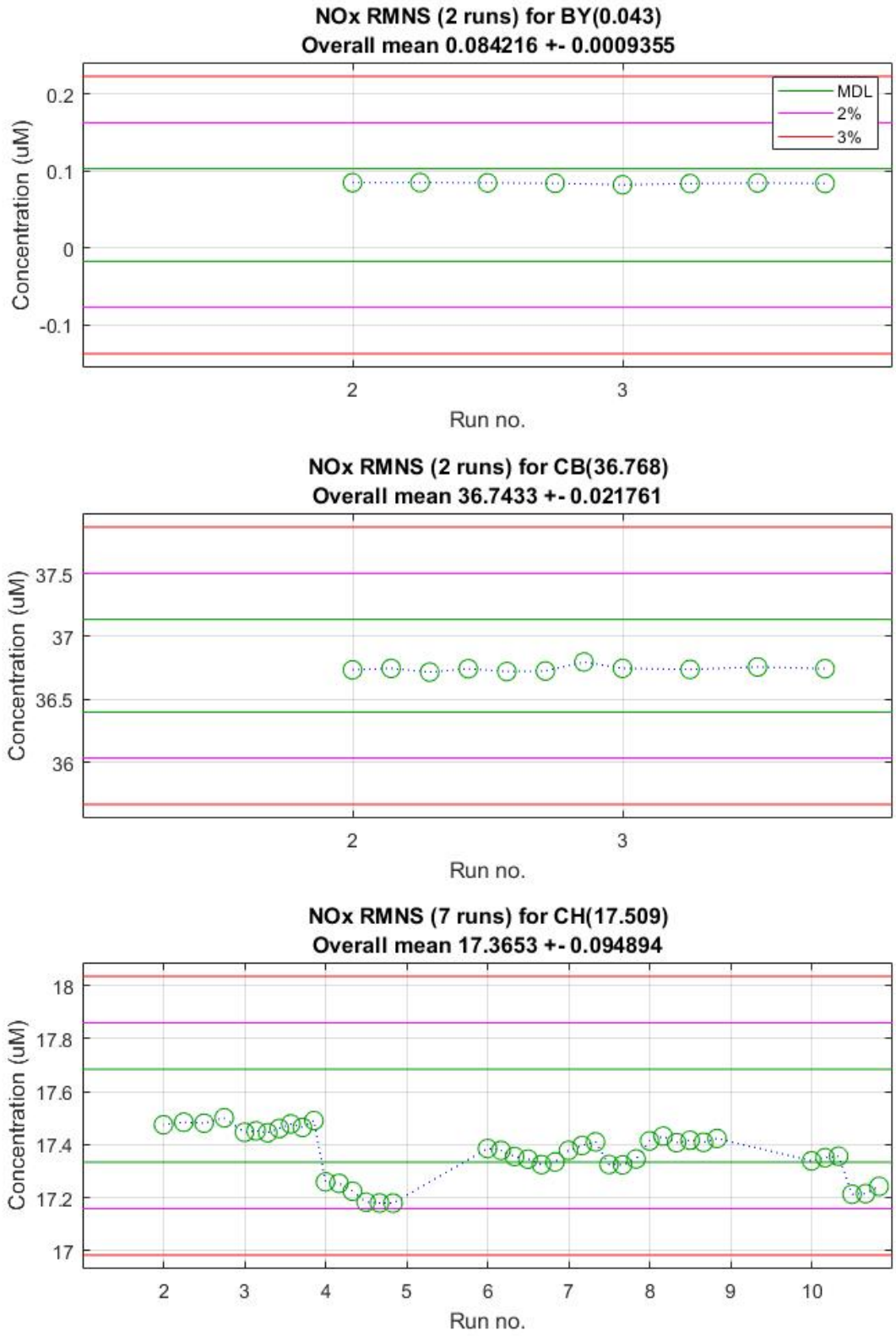
7.5.2 **Figure 7:** Phosphate RMNS Plot (µmol L^{-1})



7.5.3 **Figure 8:** Nitrite RMNS Plot (µmol L^{-1})



7.5.4 **Figure 9:** Nitrate + Nitrite (NOx) RMNS Plot (µmol L^{-1})



7.6 Measurement Uncertainty

The CSIRO hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on the variation in the calibration curve, calibration standards, pipette and glassware calibration, and precision of the RMNS over time (Armishaw 2003).

Table 9: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol L^{-1}

Calculated Measurement Uncertainty @ 1 µmol L^{-1}				
Silicate	Phosphate	Nitrite	Nitrate + Nitrite (NOx)	Ammonia
±0.017	±0.024	±0.14	±0.019	±0.30¥

The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

¥The ammonia MU precision does not include data for the RMNS.

7.7 Sampling Precision

The sampling precision for this voyage is good.

Duplicate nutrient samples are collected from the greatest depth for each CTD deployments and were also collected from the Chl *a* max depth and from the subsurface for CTD004 to CTD008.

For nutrients, the sampling precision is good if the difference from the mean of duplicate measurements is less than the nominal method detection limit. The exception: NOx (nitrate+nitrite) which uses the limit 0.06 µmol L^{-1}
Duplicate samples that exceed this limit are flagged 69 (suspect). These are tabulated in appendix 8.6. Duplicates plots available on request.

Table 10: Difference between duplicate results. CTD 1 – 8. Units: µmol L^{-1}

	Silicate ($Si(OH)_4$)	**Phosphate (PO_4)**	**Nitrite (NO_2)**	**NO_3+ NO_2 (NO_X)**	**Ammonia (NH_4)**
Minimum	0.0	0.00	0.00	0.00	0.00
Maximum	0.08	0.00	0.00	0.01	0.03

7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: 14.12

The Redfield Ratio is a check for the accuracy of phosphate and nitrate+nitrite (NOx) analysis. The ratio is the required amount of P to N for marine phytoplankton growth.

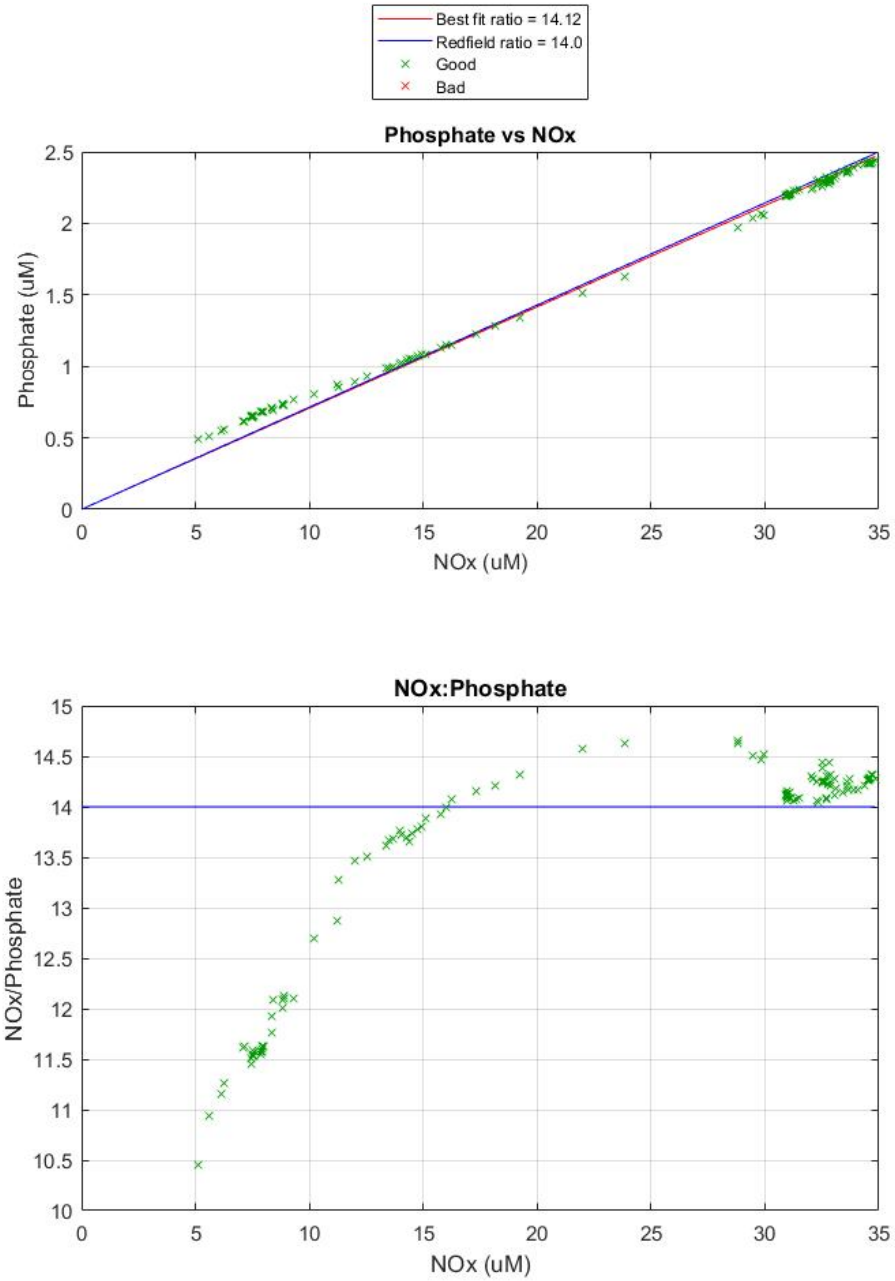
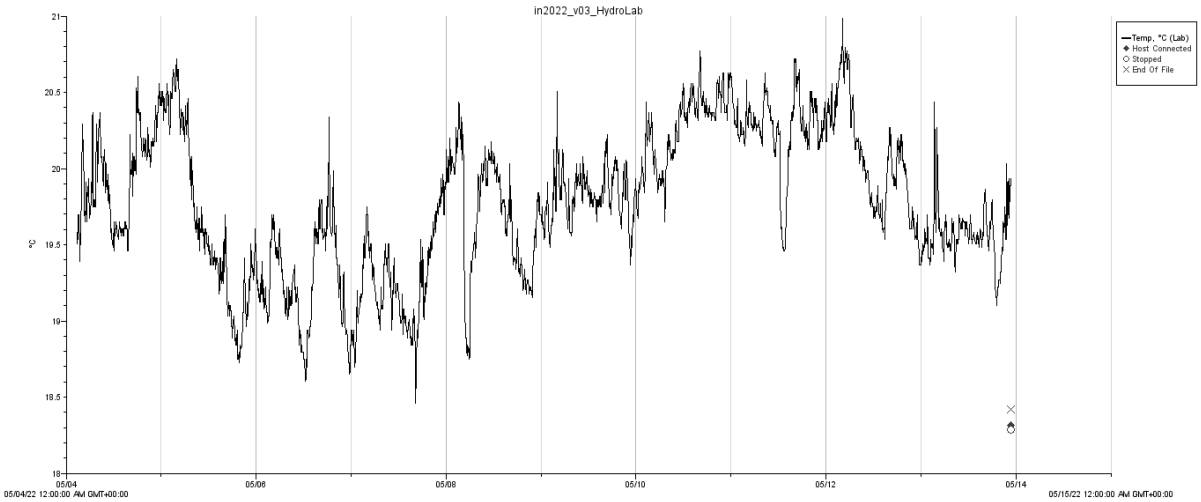


Figure 10. Redfield ratio plots.

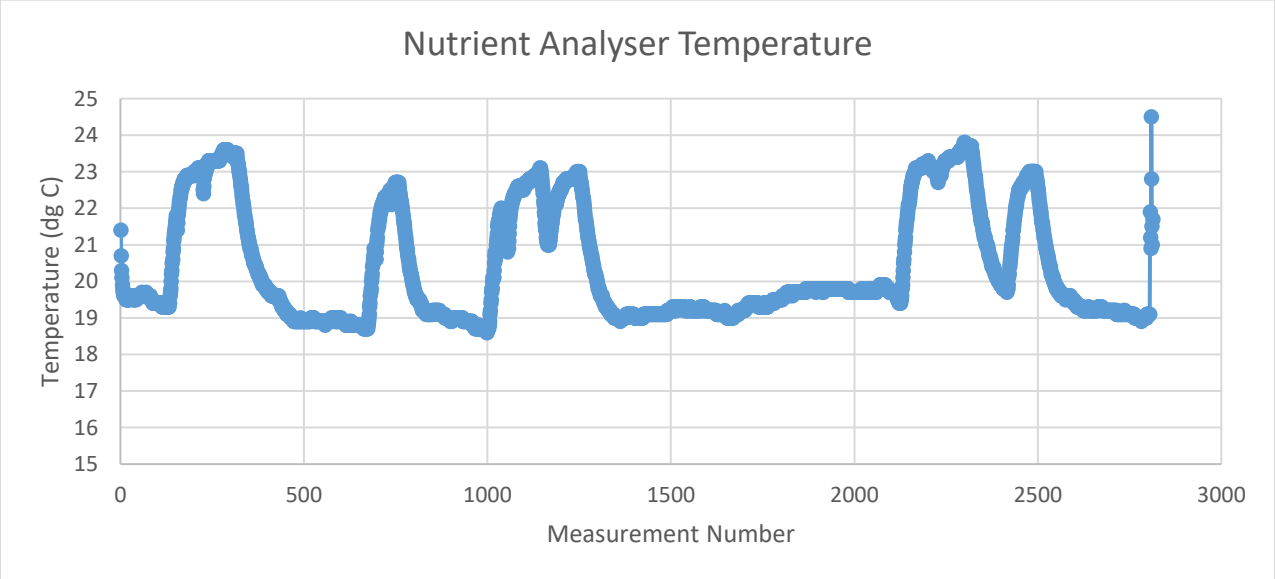
7.9 Temperature & Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry laboratory and within the AA3HR instrument were measured and logged as follows:

(1) Above the AA3HR instrument, temperature only**.**



(2) On the deck of the nitrate & nitrite AA3HR chemistry module, temperature and humidity. Mean 20.4°C, standard deviation: 1.56°C



8 Appendix

8.1 Salinity: Reference Material Used

OSIL IAPSO Standard Seawater		
Batch:	P163	P164
Use by date:	10/04/2022	23/04/2023
K_{15}:	0.99985	0.99985
PSU:	34.994	34.994

8.2 Nutrients: Reference Material Used

RMNS	Silicate ($Si(OH)_4$) µmol L^{-1}	Phosphate (PO_4) µmol L^{-1}	Nitrite (NO_2) µmol L^{-1}	Nitrate (NO_3) µmol L^{-1}	NO_3+ NO_2 (NO_X) µmol L^{-1}
Lot CH	30.735 ± 0.307	1.201 ± 0.015	0.163 ± 0.015	17.355 ± 0.184	17.518 ± 0.169
BY	1.806 ± 0.065	0.040 ± 0.010	0.020 ± 0.009	0.024 ± 0.037	0.044 ± 0.028
CB	111.823 ± 0.635	2.581 ± 0.023	0.119 ± 0.006	36.649 ± 0.288	36.768 ± 0.282
CG	57.752 ± 0.512	1.741 ± 0.021	0.061 ± 0.031	23.269 ± 0.267	24.330 ± 0.236

8.3 Nutrients: RMNS results for each CTD Deployment.

8.3.1 RMNS Lot CH Results per CTD Deployment

Analysis #	CTD Dep. #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)
1	NA	NA	NA	NA	NA
2	001	30.87	1.21	17.49	0.178
3	002	30.77	1.20	17.46	0.179
4	003	30.86	1.20	17.21	0.175
5	NA	NA	NA	NA	NA
6	004	30.85	1.20	17.35	0.176
7	005	30.93	1.21	17.36	0.178
8	006	31.02	1.21	17.42	0.181
9	NA	NA	NA	NA	NA
10	007	30.82	1.21	17.29	0.178

The submitted nutrient results do NOT have RMNS corrections applied.

How to use the RMNS for Correction

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run
Corrected Concentration = Ratio x Measured Nutrient Concentration

Or for smoothing data

Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run
Corrected Concentration = Ratio x Measured Nutrient Concentration

8.4 Missing or Suspect Salinity Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Flag key: appendix 8.7)

CTD	RP	Flag	Reason for Flag
NA	NA	NA	NA

8.5 Missing or Suspect Dissolved Oxygen Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of the depth profile (Flag key: appendix 8.7).

CTD	RP	Flag	Reason for Flag
1	19 & 18	NA	Experimental duplicate flask #337 and #328 missing for .LST file (still on the ship)
5	1	NA	Bottle sampled in duplicate (DO flask #410 and #332)

8.6 Missing or Suspect Nutrient Data.

Not included, Data flagged 63 (below detection limit). Data flagged 133 is not reported in the final hydrology dataset. (Flag key: appendix 8.7)

CTD	RP	Analyte	Flag	Reason for Flag
NA	NA	NA	NA	NA

8.7 Data Quality Flag Key

Flag	Description	
0	Data is GOOD	
63	Nutrients only.	Data below nominal detection limit.
65	Data is SUSPECT.	Nutrients only: Absorbance peak shape, measured by the instrument, is marginally outside set limits.
69	Data is SUSPECT.	Duplicate data is outside of set limits (software). Data point is an outlier on the depth profile plot (operator). Tagged by software or operator
79	Data is SUSPECT.	Nutrients only. Measured Method Detection Limit (MDL) for the analysis run is greater than the nominal MDL. All samples in that run tagged.
129	Data is BAD.	Nutrients Only. Absorbance peak exceeds the maximum value that can be measured by the instrument.
133	Data is BAD.	Set by operator.
134	Data is BAD.	Nutrients Only. Absorbance peak shape of calibrants, measured by the instrument, is outside of set limits (software).
141	NO Data.	Used in netcdf results file. Not used in csv results file.

8.8 GO-SHIP Specifications

GOSHIP specifications available here.

8.8.1 Salinity

Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosal precision is better than 0.001 PSS-78. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of ± 1°C is very important and should be recorded[2].

8.8.2 Dissolved Oxygen

Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.

8.8.3 $Si(OH)_4$

Approximately 1-3% accuracy[1], 0.2% precision[3], full scale.

8.8.4 PO_4

Approximately 1-2% accuracy[1], 0.4% precision[3], full scale.

8.8.5 NO_3

Approximately 1% accuracy[1], 0.2% precision[3], full scale.

8.8.6 Notes

[1] If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.

[2] Keeping constant temperature in the room where salinities are determined greatly increases their quality. Also, room temperature during the salinity measurement should be noted for later interpretation, if queries occur. Additionally, monitoring and recording the bath temperature is also recommended. The frequent use of IAPSO Standard Seawater is endorsed. To avoid the changes that occur in Standard Seawater, the use of the most recent batch is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.

[3] Developments of reference materials for nutrients are underway that will enable improvements in the relative accuracy of measurements and clearer definition of the performance of laboratories when used appropriately and the results are reported with the appropriate meta-data.

9 References

Armishaw, P. (2003) “Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty.” Accred Qual Assur, 8: pp. 218-224

Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H. (1967) “The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment,” Deep-Sea Res., 14: pp.381-389. doi: 10.1016/0011-7471(67)90082-4

Hood, E.M. (2010). “Introduction to the collection of expert reports and guidelines.” The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.

Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). "Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010. (UNESCO/IOC)

Kérouel, R., and Aminot, A. (1997) “Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis”. Mar. Chem., 57: pp. 265-275. doi: 10.1016/S0304-4203(97)00040-6

Murphy, J. And Riley, J.P. (1962)”A Modified Single Solution Method for the Determination of Phosphate in Natural Waters”, Anal. Chim. Acta, 27: p.30. doi: 10.1016/S0003-2670(00)88444-

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

Wood, E.D., Armstrong, F.A.J., and Richards, F.A. (1967) “Determination of nitrate in seawater by cadmium-copper reduction to nitrite.” Journal of the Marine Biological Association of U.K. 47: pp. 23-31.