RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2021_v03
Chief Scientist	Chris Chapman
Principal Investigator	Bernadette Sloyan, Iain Suthers & Amandine Schaeffer
Voyage title:	Integrated Marine Observing System: monitoring of East Australian Current property transports at 27° S Dynamics of larval fish diversity for ocean observing off North Stradbroke Island
Report compiled by:	Jack McDonald and Merinda McMahon

Contents

1 Executive Summary

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. 25-41.
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 primary aim of the voyage was to recover and re-deploy an array of six full-depth current meter and property (temperature, salinity, and pressure) moorings from the continental slope to the abyssal waters off Brisbane (27°S). The observing system is designed to capture the mean and time-varying flow of the EAC.

The aim of the piggy-back project was to complete two oceanographic surveys: one in the Fraser Island area between 28°S and 26°S; and the other on and over the continental shelf in the vicinity of the North Stradbroke Island IMOS NRS. These surveys included bongo net tows and Triaxus/SADCP sections and occurred in between the mooring operations and at the completion of the mooring operations. Finally, sampling from small scale ephemeral frontal eddies flowing down from Fraser Island and shelf – continental slope boundary exchanges was completed.

The following is a list of voyage objectives:

- Moorings recovery and deployment;
- Full depth CTD stations at each mooring recovery and deployment location with salinity, dissolved oxygen, and Nutrient water samples
- Pre-deployment CTD casts for calibration of Seabird 37 and 39 and mooring instrument calibration CTD
- Triaxus and Ship ADCP sections at various locations during the transit from Hobart to the mooring locations, across the mooring line, at the shelf-slope and Fraser Island survey regions
- Bongo net tows along the EAC mooring line, and as part of the shelf-slope and Fraser Island survey areas to study the significance of re-circulation features
- Bongo nets, CTD and bio-acoustic samplings at various locations during the transit from Hobart to the mooring sites; and surrounding the Stradbroke NRS site including opportunistic sampling of frontal eddies; and
- Deploy Surface Velocity Program drifters, XBTs and Argo (core and BGC) floats during the voyage, with supporting CTDs in the case of BGC Argo floats

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, phosphate, nitrate + nitrite, nitrite and ammonium. See Appendix 8.3 for the measured RMNS values for each CTD deployment.

Missing and suspect hydrology samples are listed 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

Hobart to Brisbane, May 5th – June 3rd, 2021.

Figure 1: Voyage track

3 Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
Chris Chapman	Chief Scientist	CSIRO
John Hooper	Voyage Manager	CSIRO
Jack McDonald	Hydrochemist	CSIRO
Merinda McMahon	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Table 2: **Sample Type and Number Assayed**

Analysis	Samples Assayed	Type
Salinity	359 24	CTD TSG
Dissolved Oxygen	360	CTD
Nutrients	369 86	CTD UWY

4.1.1 CTD Samples (Conductivity, Temperature, Density)

- Taken from 18 x 12L Ocean Test Equipment bottles on CTD rosette that is deployed at depth for water collection.
- A total of 24 CTD deployments were sampled by
    - Hydrochemistry: Jack McDonald and Merinda McMahon
    - Science party: Chris Chapman, Bernadette Sloyan, Amadine Schaeffer, Rebecca Cowley, Maurice Hugenin, Michael Hemming, Carolina Olguin Jacobson and Nur Arafeh Dalmau
- Hydrochemistry understands that the CTD rosette is typically held at each sampling depth for a minimum of 30 seconds before tripping bottles - as per GO-SHIP requirements. On this voyage, at up to three depths per cast, the CTD was held for 10 minutes upon request from the science party. Please see the CTD log sheets for more information.

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.

4.1.3 UWY (Underway)

- Taken from the same sampling point as the TSG samples.
- Triaxus calibration samples - nutrients were sampled at 1-hour intervals while the triaxus was being towed (uwy1-25, uwy34-37 and uwy42-46).
- Underway nutrients were collected and analysed in triplicate for each CTD dip of the two eddy “yoyo” transects. Transect 1 consisted of CTD 17-24 (uwy26-33) and transect 2 was CTD 27-29 (uwy38-39). Underway nutrients were not taken from the third CTD of transect 2 (CTD 29). However, triplicate underway nutrients (uwy040) were taken in what was believed to be the middle of the same eddy that was targeted by the second “yoyo” transect, and during the bongo net sampling (uwy041) later that evening.

Refer to voyage eLog for UWY and 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).

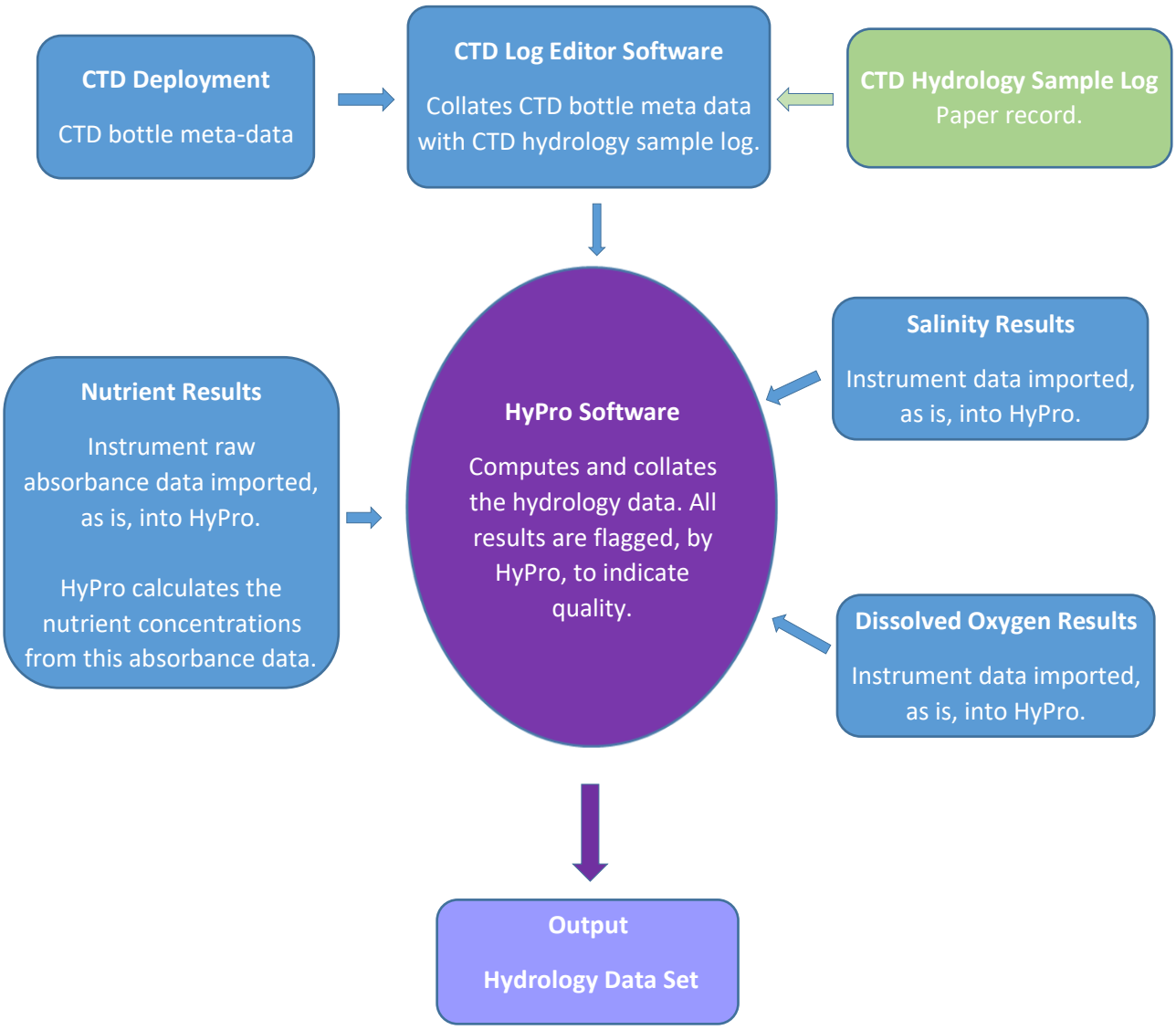


Figure 2: Hydrology Data Processing Flow Diagram.

5 Salinity

5.1 Salinity Measurement Parameters

Table 3: 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	Mean 22.2°C, SD 0.7
Analysts	Jack McDonald and Merinda McMahon
Comments	See DAP report for CTD 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 OSIL data logger software.

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 0.01 PSU.

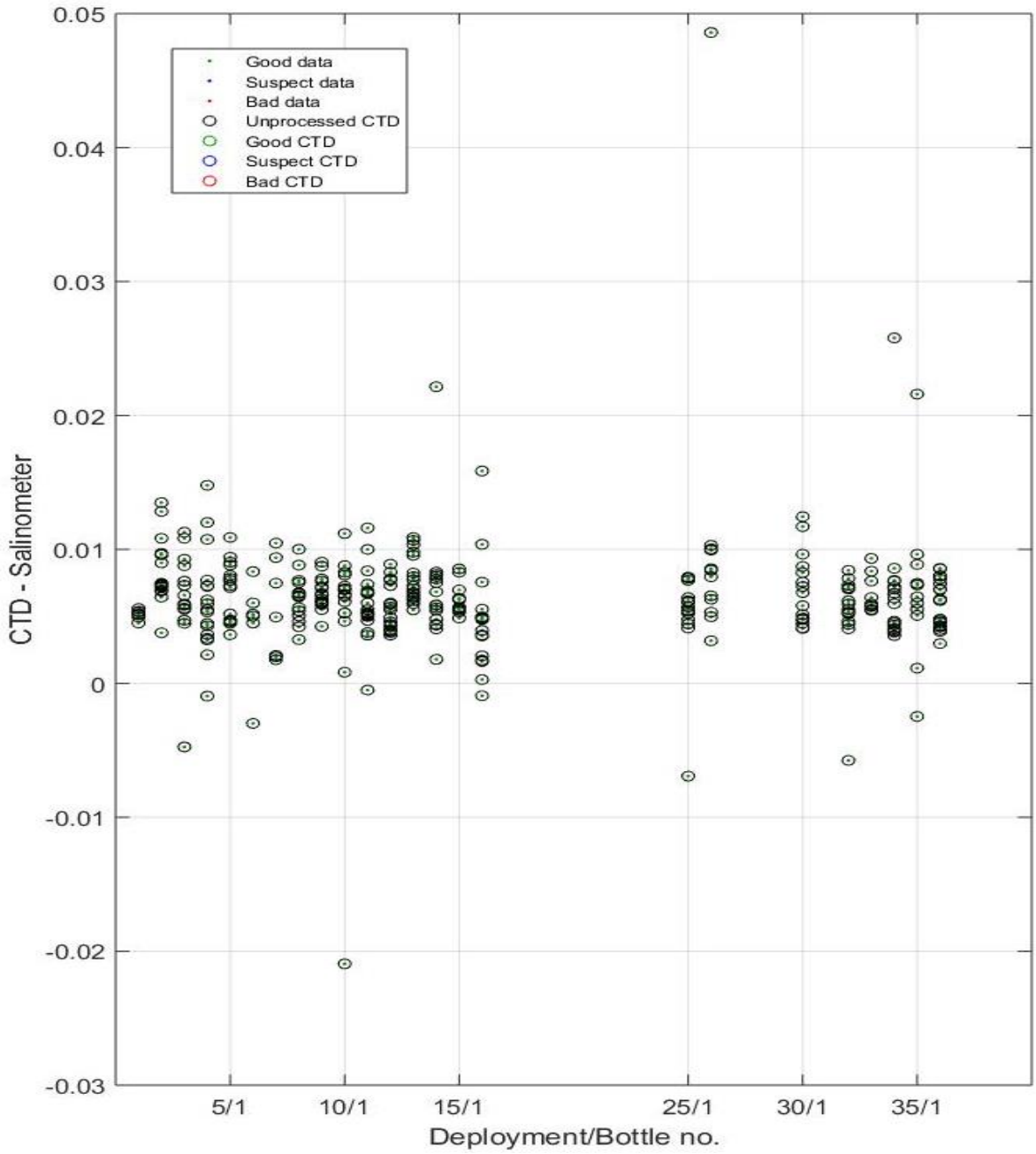


Figure 3: CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Black = UNPROCESSED. Units: PSU (dimensionless).

6 Dissolved Oxygen

6.1 Dissolved Oxygen Measurement Parameters

Table 4: 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	Jack McDonald and Merinda McMahon
Lab Temperature (±1°C)	Mean 20.0°C, SD 0.6
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 10 mL 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

For this voyage, the difference between the unprocessed CTD value and the measured bottle value is generally less than 10 µmol L^{-1}.

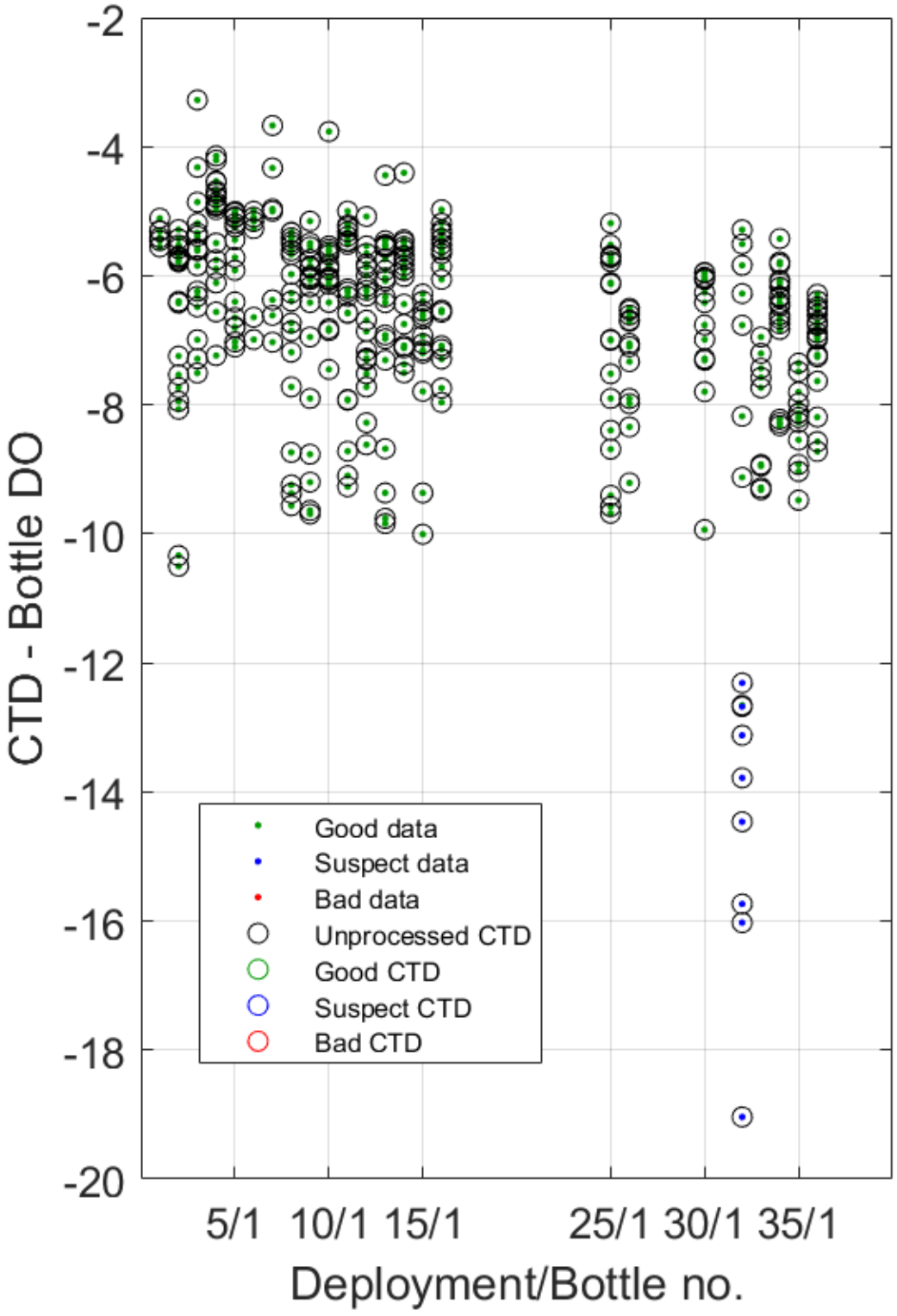


Figure 4. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Black = UNPROCESSED. Units: µmol L^{-1}

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

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

CTD Deployment 1 to 36: Mean: 0.22179 N
SD: 0.00013 (n=9)

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.

Note: KIO_3 was changed after run 9.

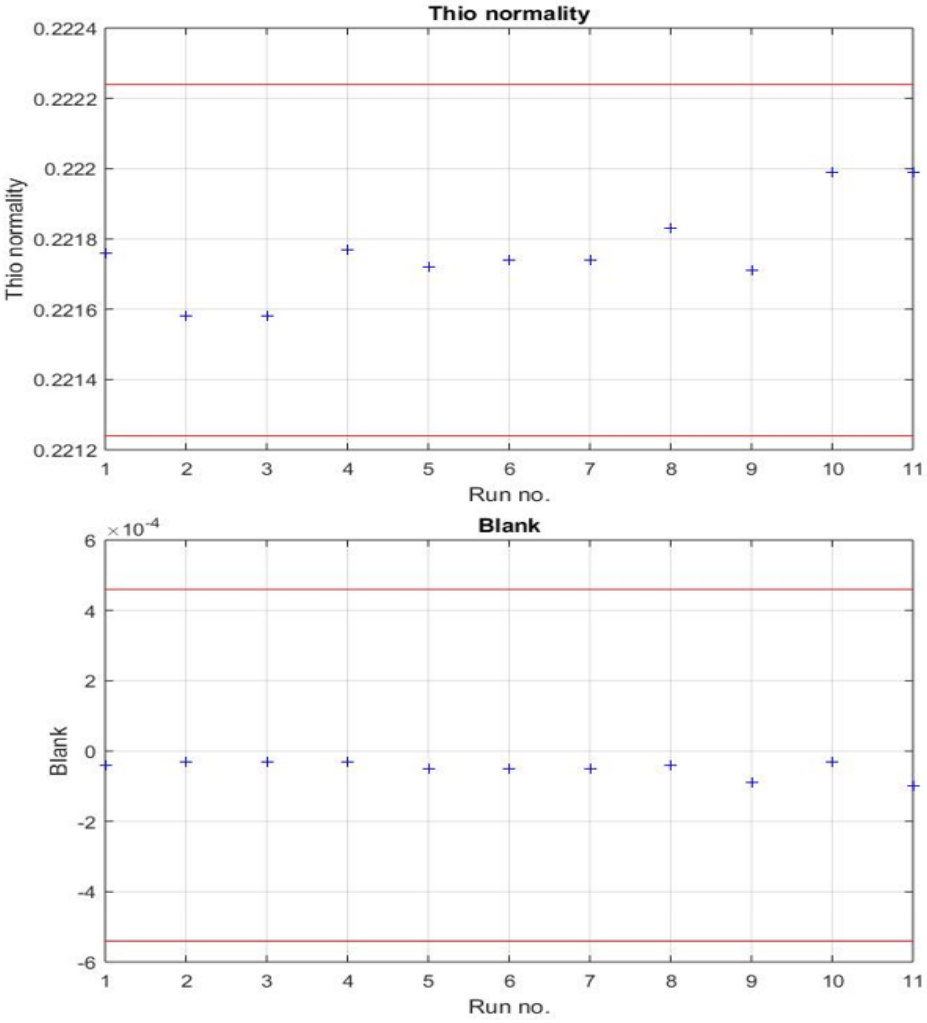


Figure 5. Thiosulphate standardisation and blank correction plots.

7 Nutrients

7.1 Nutrient Measurement Parameters

Table 5: 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})	161	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 CJ, CB and CL				
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)	Mean 20.0°C, SD 0.6				
Analysts	Jack McDonald, Merinda McMahon				
Comments	N/A				

7.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1 cm 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.

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 $umol^{-1}$ 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 6: 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-micron 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 Q Integral 10 unit.				
Duplicate samples.	CTD: Niskin fired at the greatest depth 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.				

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 CJ was assayed in triplicate in each run to monitor accuracy. The certified values are in Table 7.

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.8, specifies that the RMNS is within 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.

Table 7: RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: µmol L^{-1}

RMNS	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	Nitrate (NO_3)	NO_3+ NO_2 (NO_X)
Lot CJ	39.424 ± 0.410	1.219 ± 0.020	0.032 ± 0.007	31.621 ± 0.246	16.620 ± 0.212
Lot CB	111.821 ± 0.635	2.580 ± 0.022	0.119 ± 0.006	36.649 ± 0.276	36.768 ± 0.282
Lot CL	14.131 ± 0.012	0.435 ± 0.019	0.015 ± 0.006	5.601 ± 0.154	5.617 ± 0.160

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 CJ statistics for of this voyage. Units: µmol L^{-1}

RMNS CJ	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
Minimum	39.9	1.22	0.016	16.49
Maximum	40.5	1.25	0.104	16.78
Mean	**39.8**	**1.24**	**0.062**	**16.66**
Median	39.8	1.24	0.061	16.66
Repeatability	0.3	0.01	0.014	0.06

Table 9: RMNS CB statistics for of this voyage. Units: µmol L^{-1}

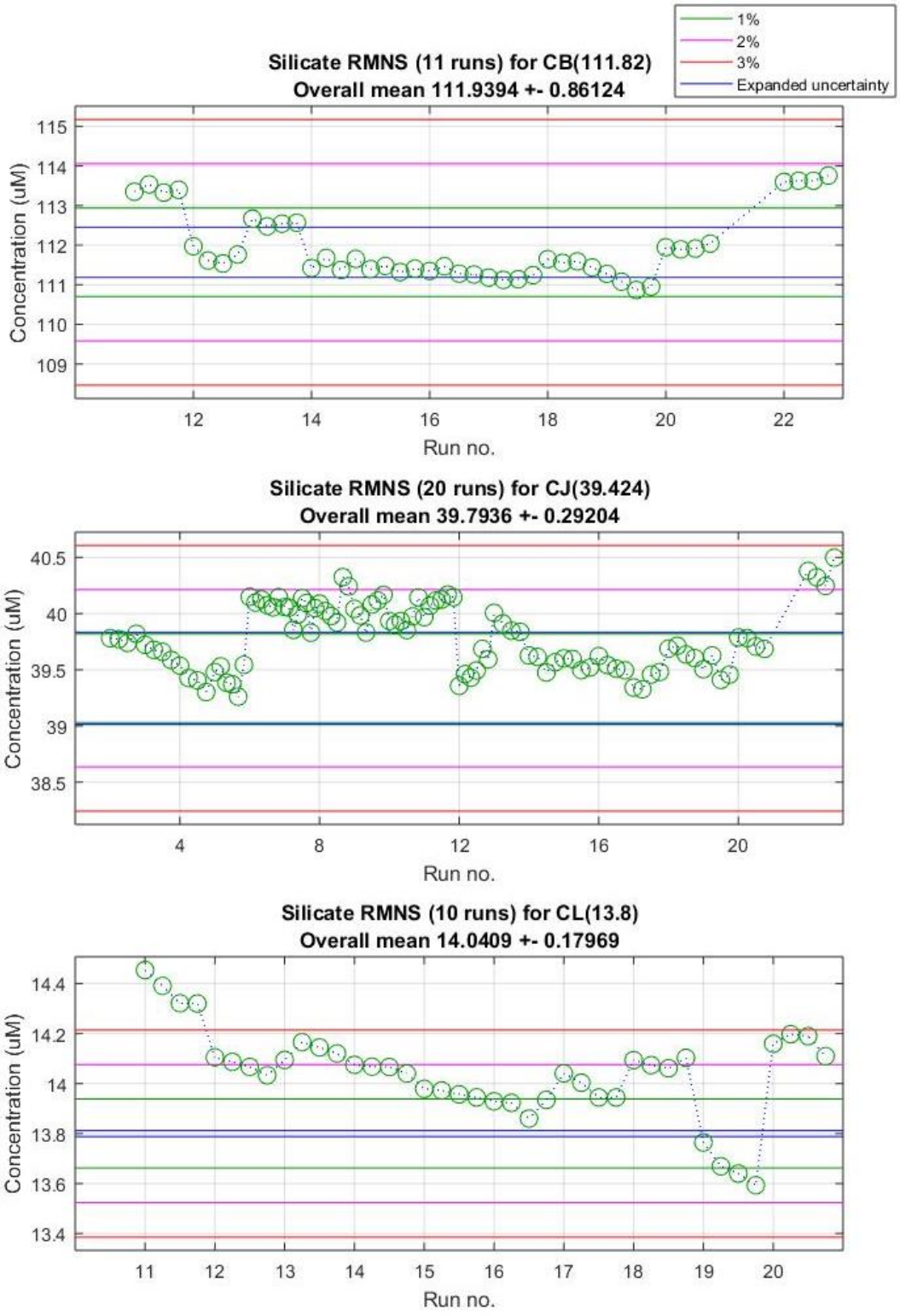
RMNS CB	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
Minimum	110.9	2.58	0.137	36.58
Maximum	113.8	2.62	0.211	37.10
Mean	**111.9**	**2.60**	**0.160**	**36.83**
Median	111.6	2.60	0.154	36.82
Repeatability	0.9	0.01	0.019	0.14

Table 10: RMNS CL statistics for of this voyage. Units: µmol L^{-1}

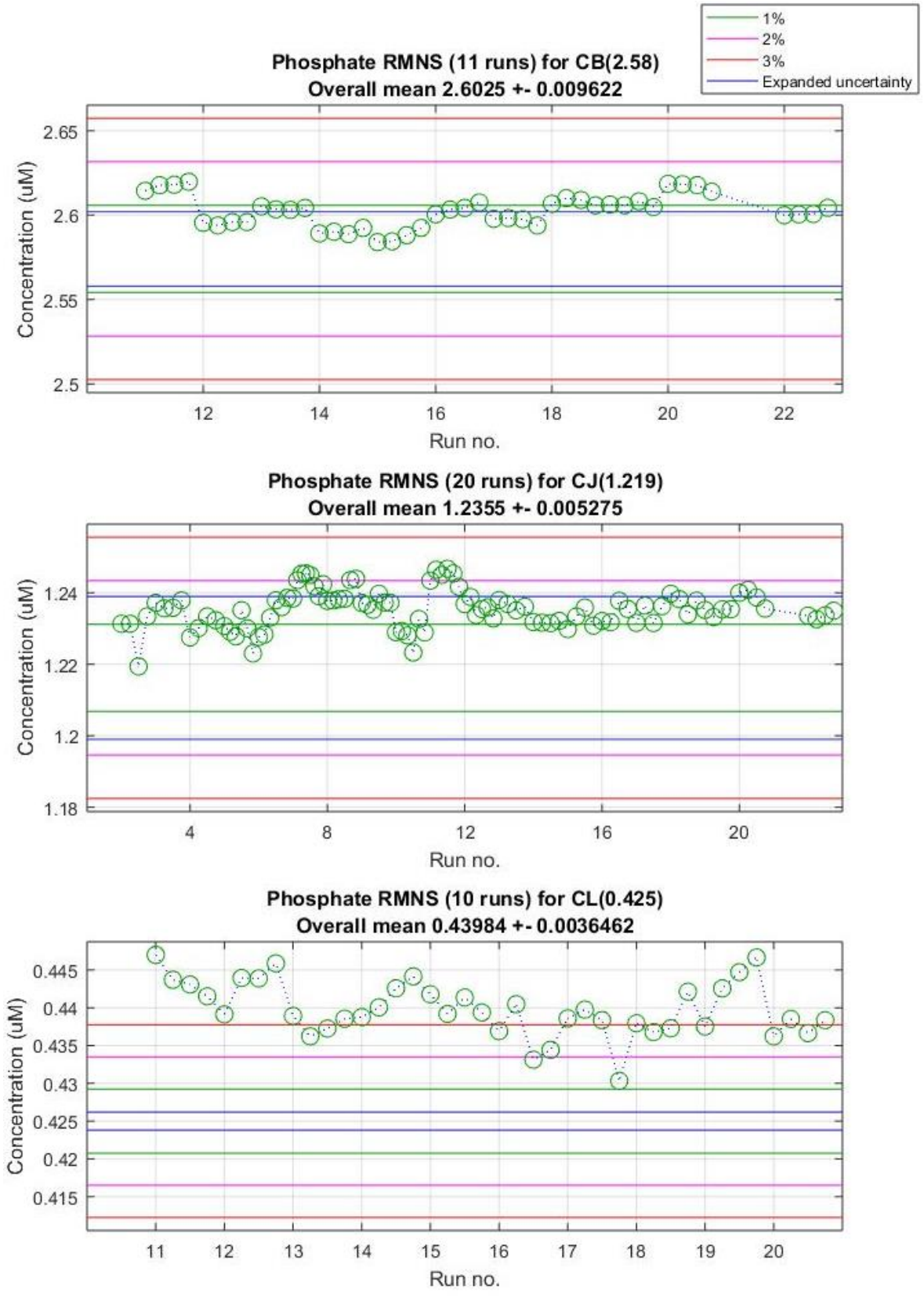
RMNS CL	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
Minimum	13.6	0.43	0.006	5.46
Maximum	14.5	0.45	0.081	5.55
Mean	**14.0**	**0.44**	**0.042**	**5.51**
Median	14.1	0.44	0.043	5.51
Repeatability	0.2	0.00	0.024	0.02

7.5 Nutrient plots of RMNS

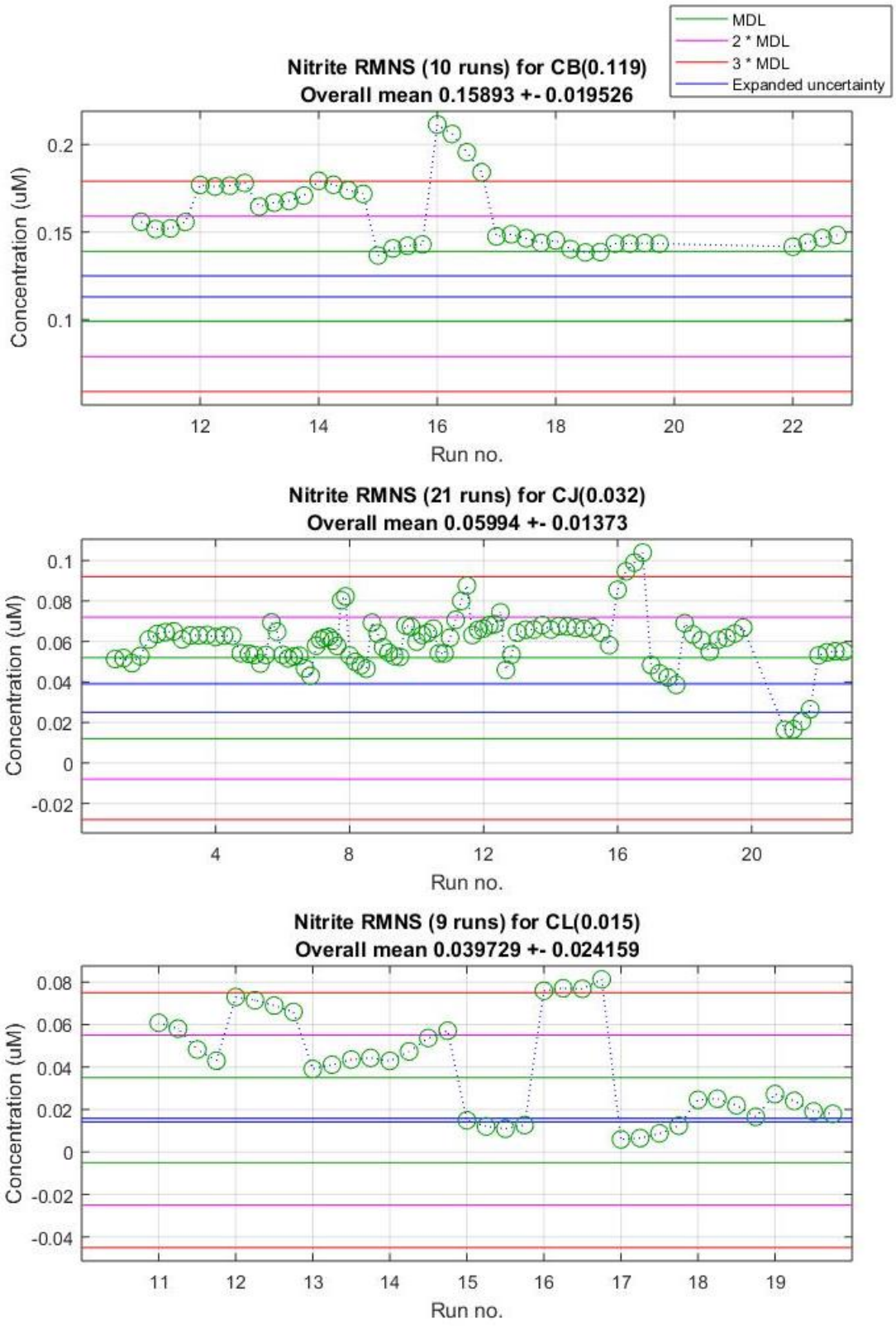
The green, pink and red contours are at 1%, 2% and 3% from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µmol L^{-1} increments from the certified value. The blue line is the certified value's expanded uncertainty. Plots are RMNS value versus instrument run number.



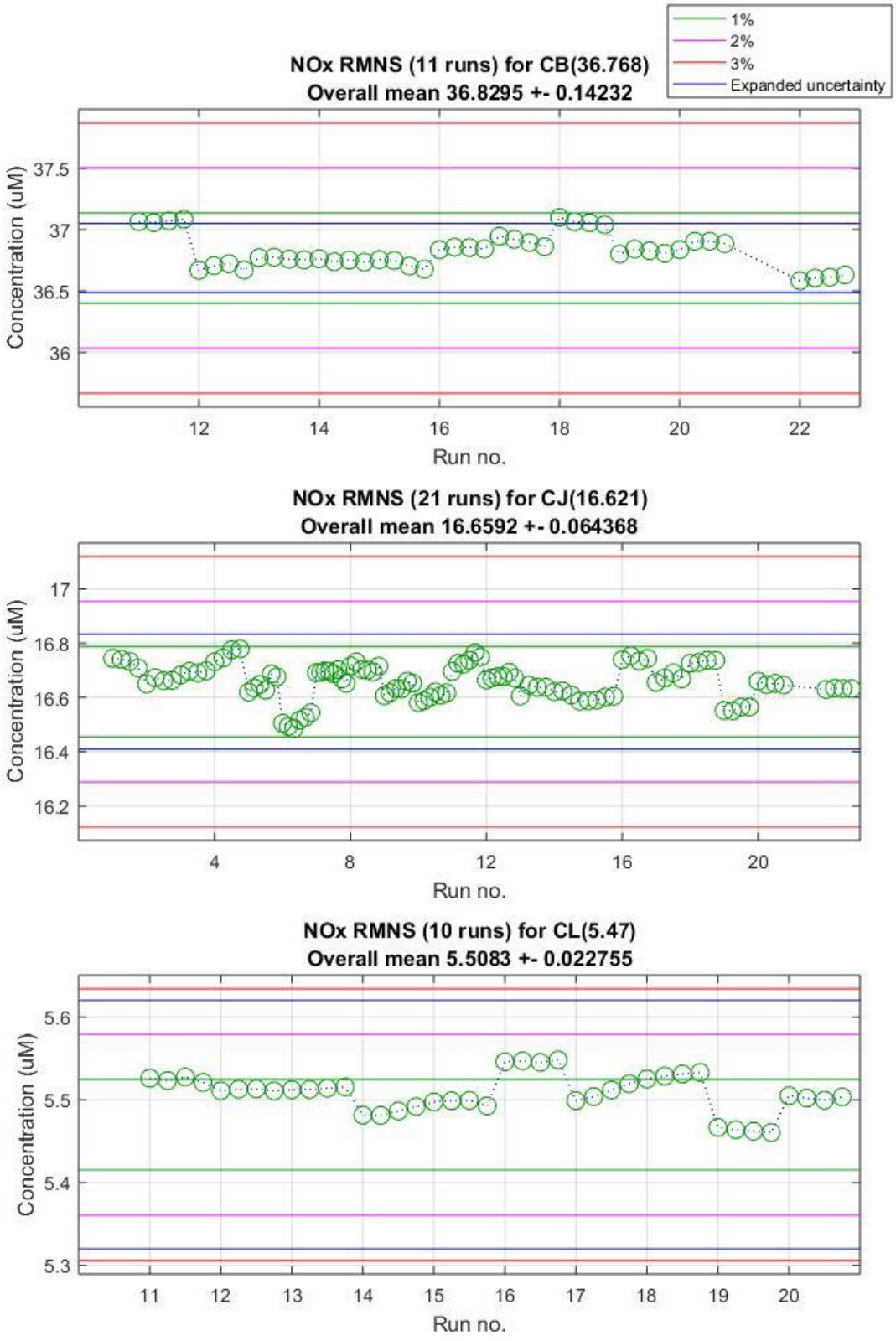
7.5.1 **Figure 6:** Silicate RMNS Plot (µmol L^{-1})



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 11: 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	±0.60¥

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.

Initial sampling precision is determined with the CTD test deployment (CTD 1) where multiple bottles are fired the same depth, each of which is then sampled by Hydrochemistry (Table 13). Half of the bottles are sampled from 1000 dbar, where the water is stable and has a reasonable concentration for Silicate, Phosphate, NOx, Dissolved Oxygen and Salinity. The other half of the bottles are fired at the chlorophyl max where the concentrations are typically higher for Nitrite and Ammonia. Duplicate nutrient samples are also collected from the greatest depth of subsequent CTD deployments (Table 12).

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.

Table 12: Difference between duplicate results. CTD 2 – CTD 36 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	0.3	0.01	0.01	0.05	0.01
Mean	0.1	0.00	0.00	0.02	0.00
Variance	0.1	0.00	0.00	0.01	0.00

Table 13: CTD deployment 1: 7 bottles at 1000 dbar used for sample precision for salinity, dissolved oxygen, silicate, phosphate and NOx. 7 bottles at 70 dbar (chlorophyl max) used for sample precision for nitrite and ammonia.

	Salinity (PSU)	Dissolved Oxygen (µmol L^{-1})	Silicate ($Si(OH)_4$) (µmol L^{-1})	Phosphate (PO_4) (µmol L^{-1})	Nitrite (NO_2) (µmol L^{-1})	NO_3+ NO_2 (NO_X) (µmol L^{-1})	Ammonia (NH_4) (µmol L^{-1})
Minimum	34.447	194.4	30.3	1.97	0.291	29.05	0.06
Maximum	34.449	194.9	30.4	1.98	0.296	29.06	0.07
Mean	34.448	194.5	30.3	1.97	0.294	29.06	0.06
SD	0.000	0.2	0.0	0.01	0.002	0.00	0.00

7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: 14.41

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.

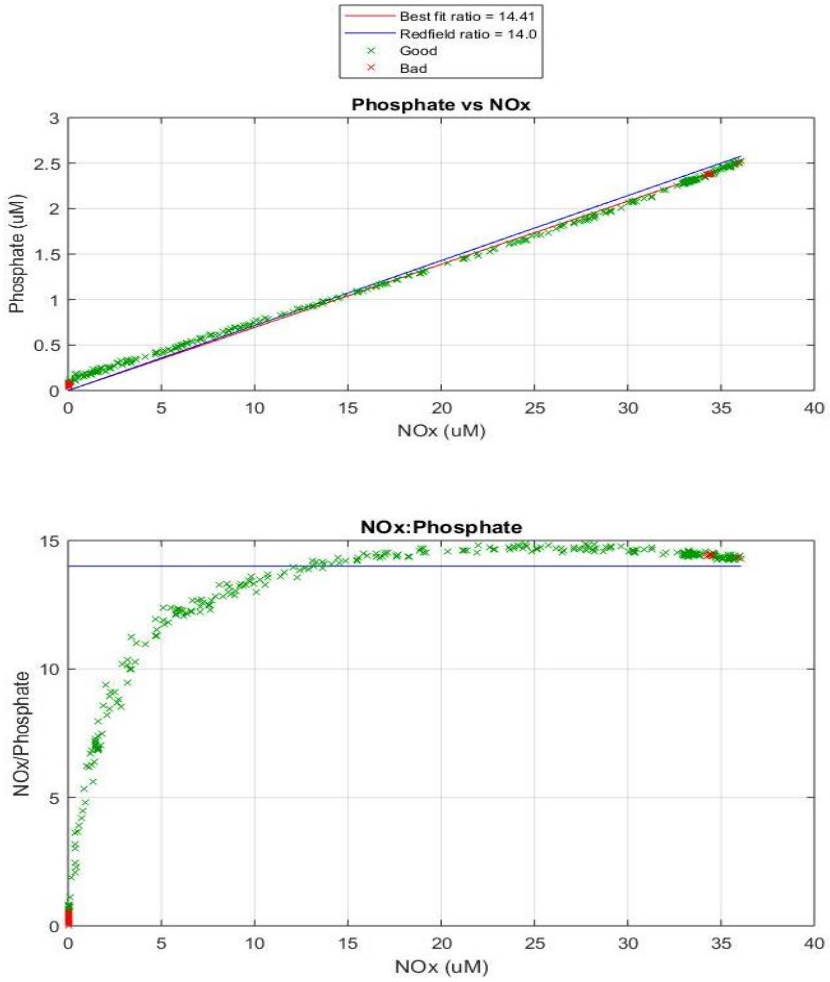


Figure 10. Redfield ratio plots.

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. Mean 20.0°C, SD 0.6

(2) On the deck of the nitrate & nitrite AA3HR chemistry module, temperature and humidity. Data on request.

(3) On the outboard bulkhead, Temperature, humidity and pressure. Data on request.

8 Appendix

8.1 Salinity: Reference Material Used

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

OSIL IAPSO Standard Seawater	
Batch:	P164
Use by date:	23/03/2023
K_{15}:	0.99985
PSU:	34.994

8.2 Nutrients: Reference Material Used

RMNS	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	Nitrate (NO_3)	NO_3+ NO_2 (NO_X)
Lot CJ	39.424 ± 0.410	1.219 ± 0.020	0.032 ± 0.007	31.621 ± 0.246	16.620 ± 0.212
Lot CB	111.821 ± 0.635	2.580 ± 0.022	0.119 ± 0.006	36.649 ± 0.276	36.768 ± 0.282
Lot CL	14.131 ± 0.012	0.435 ± 0.019	0.015 ± 0.006	5.601 ± 0.154	5.617 ± 0.160

8.3 Nutrients: RMNS results for each CTD Deployment.

8.3.1 RMNS Lot CJ Results per CTD Deployment

CTD Deployment	Underway samples	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	N/A	39.778	1.229	16.662	0.064
2	N/A	39.661	1.237	16.692	0.063
3	N/A	39.417	1.231	16.758	0.060
4	1-4	39.428	1.229	16.649	0.057
5, 6, 7	5-6	40.109	1.234	16.511	0.050
8, 9	N/A	40.008	1.243	16.686	0.065
10	7-12	40.096	1.240	16.710	0.055
11, 12	N/A	40.036	1.237	16.633	0.059
13	N/A	39.957	1.229	16.621	0.060
14	13-16	40.099	1.245	16.733	0.072
15	N/A	39.503	1.236	16.676	0.063
16	17-22	39.900	1.237	16.631	0.066
N/A	23-33	39.571	1.232	16.610	0.067
25	N/A	39.553	1.232	16.596	0.064
26	N/A	39.542	1.234	16.743	0.096
30	34-41	39.401	1.234	16.672	0.043
32	N/A	39.660	1.237	16.732	0.062
33, 34	N/A	39.500	1.235	16.558	0.063
35	N/A	39.740	1.239	16.651	0.020
36	42-46	40.362	1.234	16.632	0.054

8.3.2 RMNS Lot CB Results per CTD Deployment

CTD Deployment	Underway samples	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) ($\mu mol\ L^{-1}$)
14	13-16	113.404	2.617	37.070	0.154
15	N/A	111.722	2.595	36.692	0.177
16	17-22	112.564	2.604	36.765	0.167
N/A	23-33	111.532	2.590	36.747	0.175
25	N/A	111.400	2.587	36.721	0.141
26	N/A	111.339	2.604	36.848	0.199
30	34-41	111.173	2.597	36.906	0.147
32	N/A	111.557	2.608	37.065	0.141
33, 34	N/A	111.044	2.606	36.819	0.143
35	N/A	111.949	2.617	36.883	N/A
36	42-46	113.652	2.601	36.608	0.145

8.3.3 RMNS Lot CL Results per CTD Deployment

CTD Deployment	Underway samples	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) ($\mu mol\ L^{-1}$)
14	**13-16**	14.371	0.444	5.524	0.053
15	**N/A**	14.073	0.443	5.512	0.070
16	**17-22**	14.131	0.438	5.514	0.042
N/A	**23-33**	14.062	0.441	5.485	0.050
25	**N/A**	13.963	0.440	5.497	0.013
26	**N/A**	13.912	0.436	5.547	0.078
30	**34-41**	13.983	0.437	5.509	0.008
32	**N/A**	14.083	0.439	5.530	0.022
33, 34	**N/A**	13.667	0.443	5.463	0.022
35	**N/A**	14.164	0.437	5.503	N/A

The submitted nutrient results do <u>NOT</u> have RMNS corrections applied.

<u>How to use the RMNS for Correction</u>

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
4	5	NA	Salinometer error – incorrect bath temperature reading (3°C). Sample result not included in final data set.
10	5	NA	Niskin misfired. Sample result not included in final data set.
10	25	NA	Niskin misfired. Sample result not included in final data set.

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
10	5	NA	Niskin misfired. Sample result not included in final data set.
10	25	NA	Niskin misfired. Sample result not included in final data set.
32	9	69	Sampling error – air bubbles around stopper
32	19	69	Sampling error – air bubbles around stopper
32	20	69	Sampling error – air bubbles around stopper
32	22	69	Sampling error – air bubbles around stopper
32	23	69	Sampling error – air bubbles around stopper
32	24	69	Sampling error – air bubbles around stopper
32	25	69	Sampling error – air bubbles around stopper
32	26	69	Sampling error – air bubbles around stopper
32	27	69	Sampling error – air bubbles around stopper

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
10	5	All	NA	Niskin misfired. Sample result not included in final data set.
10	25	All	NA	Niskin misfired. Sample result not included in final data set.

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

8.8.1 Salinity

Accuracy of 0.001 PSU 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 precision or reproducibility (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, full scale.

8.8.4 PO_4

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

8.8.5 NO_3

Approximately 1% accuracy[1], 0.2% precision, 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. 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.

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