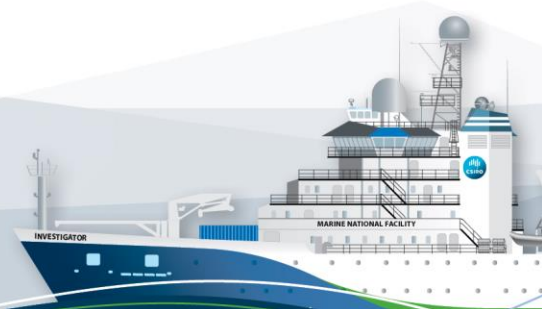


RV INVESTIGATOR

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2022_v06
Chief Scientist	Chris Chapman
Principal Investigator	Amandine Schaeffer
Voyage title:	Integrated Marine Observing System: monitoring of East Australian Current property transports at 27° S
Report compiled by:	Merinda McMahon and Pavie Nanthasurasak



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Executive Summary

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NO_x) 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

Objectives

The aims of this voyage were to recover an array of six full-depth current meter and property (temperature, salinity, and pressure) moorings from the continental slope (500 m depth) to the abyssal waters (5000 m depth) off Brisbane (27°S). This East Australian Current (EAC) deep-water mooring array is part of the Integrated Marine Observing System (IMOS) deployed with purpose of long-term ocean monitoring to promote a better understanding of climate variability in correlation with global ocean. The observing system is designed to capture the mean and time-varying flow of the EAC.

Biological and oceanography sampling from the CTD, Triaxus and Shipboard Acoustic Doppler Current Profiler (SADCP) were used to characterise the shelf waters off the Stradbroke Island National Reference Station (NRS) and to sample dynamic, ephemeral frontal eddies. These observations were used to determine the spatial and temporal variability of shelf water and plankton around the Stradbroke National Reference Station and Richmond Canyon.

In this voyage, 36-rosette CTD were used; however, only 18 niskin bottles were required for each deployment as empty spots on the rosettes were utilized to fit recovered instruments off the mooring array for post-recovery calibration. Nutrients, salinity, and dissolved oxygen samples were collected and analysed on this voyage, salinity and dissolved oxygen samples were used to calibrate sensors on the CTD. Underway nutrient samples were collected during the Triaxus tows and analysed to aid in the calibration of the nitrate sensor on the Triaxus.

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. Certified reference materials for nutrients in seawater (RMNS) were within 2% of their certified values. See table for the CTD deployment versus measured RMNS values.

Missing and suspect hydrology samples are listed in Appendix 8

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

Itinerary

Brisbane to Brisbane, 14th July – 30th July, 2022.

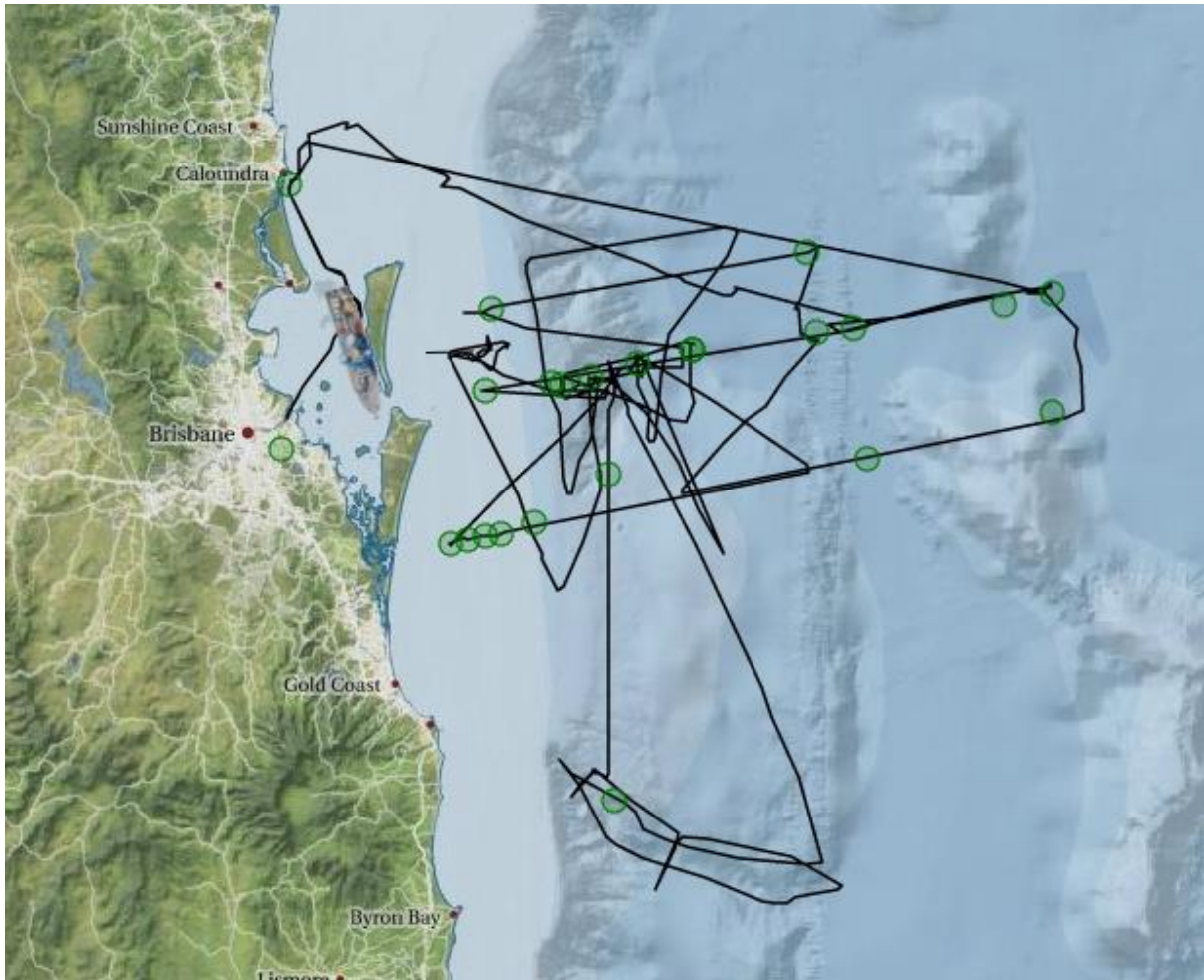


Figure 1: Voyage track

Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
Chris Chapman	Chief Scientist	CSIRO
Ben Arthur	Voyage Manager	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Pavie Nanthasurasak	Hydrochemist	CSIRO

Summary

Sample Type and Number Assayed

Table 2: Sample Type and Number Assayed

Analysis	Samples Assayed	Type
Salinity	230	CTD
	18	TSG
Dissolved Oxygen	230	CTD
Nutrients	199	CTD
	12	UWY

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.
- A total of 19 CTD deployments were sampled by
 - Hydrochemistry: Merinda McMahon and Pavie Nanthasurasak
 - Science party: Chris Chapman, Amandine Schaeffer, Julia Neme, Hannah Dawson, Megan Jeffers, Anne Crosby, Taleatha Pell and Lakiesha Wear.

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.

UWY (Underway)

- Taken from the same sampling point as per the TSG samples.
- Nutrients samples were collected from the underway system while the triaxus was being towed (uwy001-012).

Refer to voyage EVERLog for UWY and TSG sample information.

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).

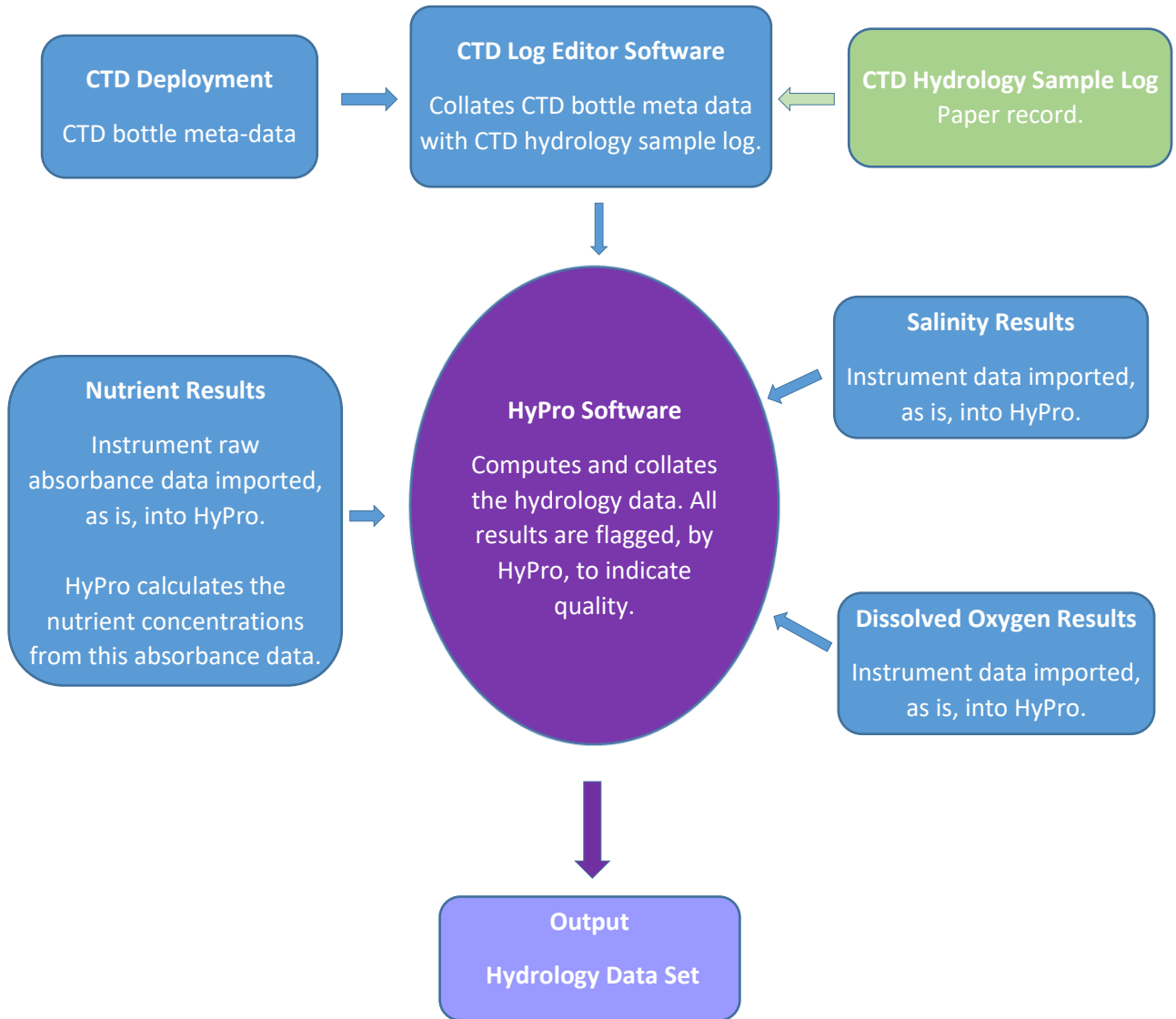


Figure 2: Hydrology Data Processing Flow Diagram.

Salinity

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 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 20.9°C SD 0.5
Analysts	Merinda McMahon and Pavie Nanthasurasak
Comments	See DAP report for CTD calibration details.

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.

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 25cm³. 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.

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. The larger differences are for shallow samples across the sudden changes in the thermohaline profile.

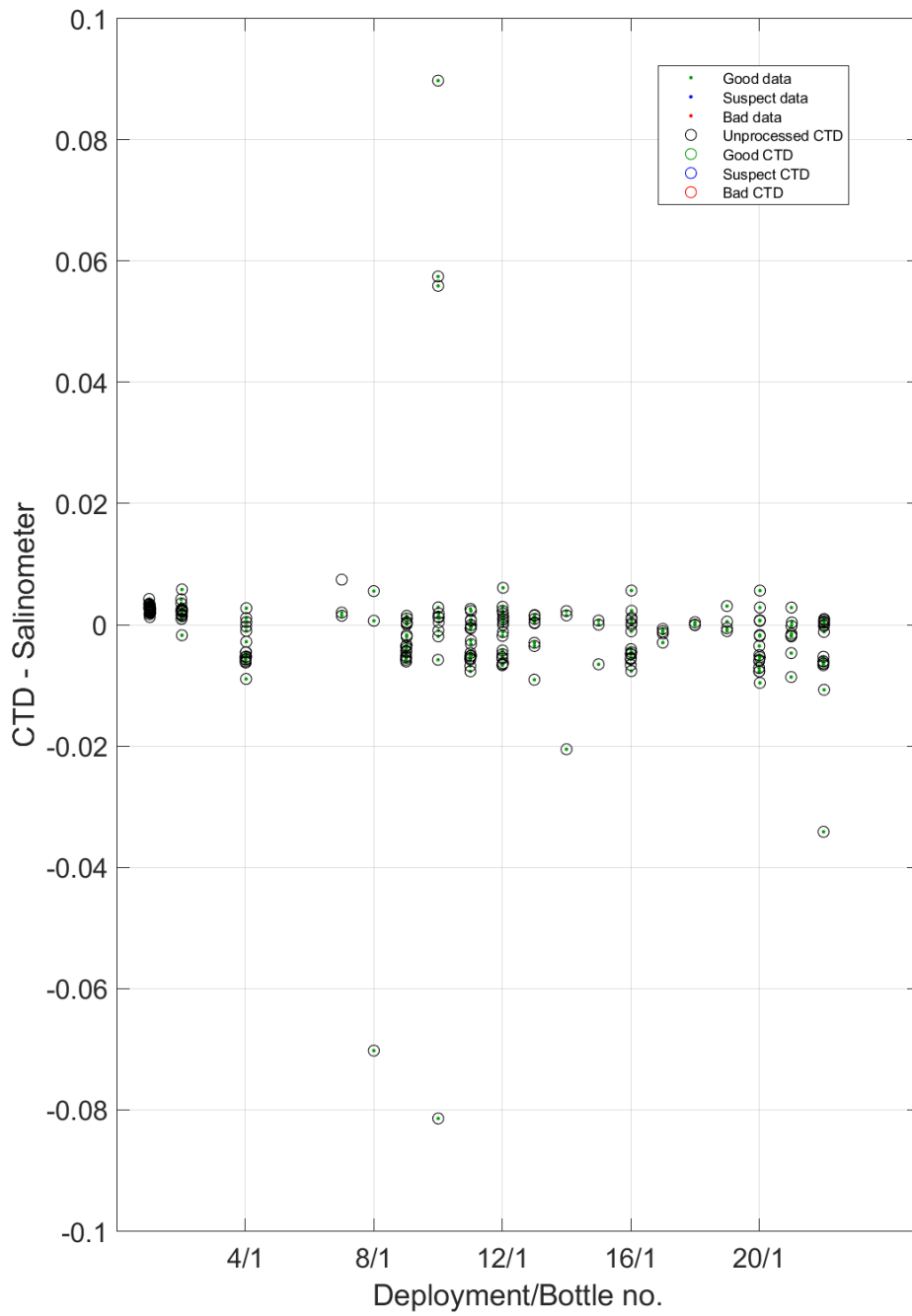


Figure 3: CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Black = UNPROCESSED. Units: PSU (dimensionless).

Dissolved Oxygen

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	$\pm 0.5 \mu\text{mol L}^{-1}$
Analysts	Merinda McMahon and Pavie Nanthasurasak
Lab Temperature ($\pm 1^\circ\text{C}$)	Mean 19.8°C SD 0.4
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.

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. 1 mL 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 24 hours when samples are being assayed.

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

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 $15 \mu\text{mol L}^{-1}$. The larger differences are for shallow samples across the sudden changes in the dissolved oxygen profile.

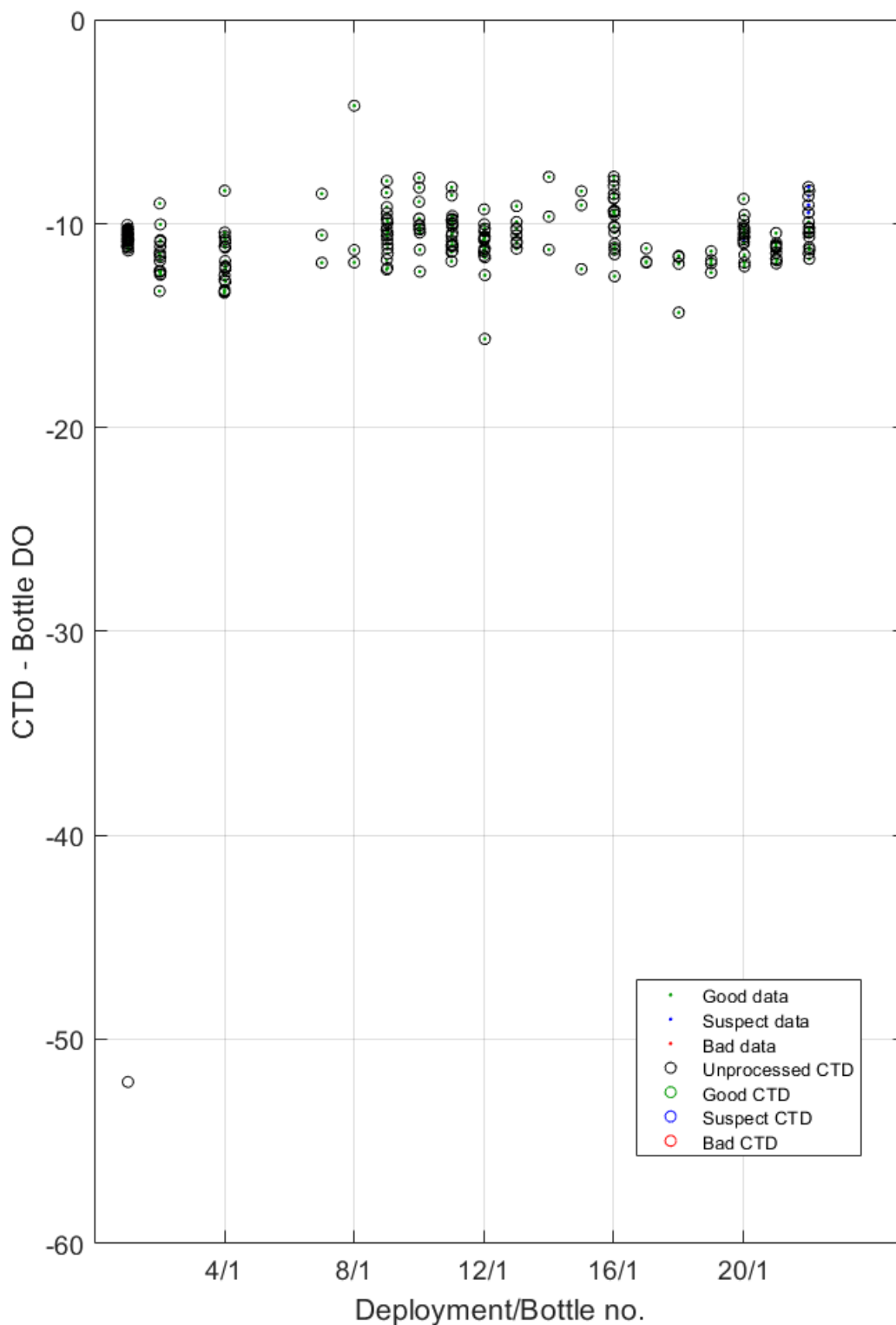


Figure 4. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Black = UNPROCESSED. Units: $\mu\text{mol L}^{-1}$. The outlier at approx. -52 is due to an air bubble in the sample, this sample was marked bad by the operator in HyPro.

Nutrients

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 ($\mu\text{mol L}^{-1}$)	112	3.0	42	1.4	2.0
Method detection limit ($\mu\text{mol L}^{-1}$)	0.2	0.02	0.02	0.02	0.02
Reference Material	KANSO RMNS lot CP				
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 19.8°C SD 0.4				
Analysts	Merinda McMahon and Pavie Nanthasurasak				
Comments	N/A				

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-SGNOS¹ Practical Workshop 2012 optimizing the antimony

catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum blue 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-phthaldialdehyde method. Based on K erouel and Aminot (1997). Ammonium reacted with ortho-phthaldialdehyde 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.

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 WOCE¹).
- 0.02µmol⁻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	Linear	Quadratic	Quadratic
# of points in Calibration	6	6	6	6	6

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
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.				

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 Table 7.

For in2022_v06, the certified reference material results for NOx, silicate and phosphate are within 2%, and nitrite within 0.06 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.

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

RMNS	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)
Lot CP	62.5687 ± 0.307	1.7951 ± 0.018	0.3175 ± 0.316	25.7136 ± 0.379

KANSO publishes the RMNS nutrient values in $\mu\text{mol kg}^{-1}$. These are converted to $\mu\text{mol L}^{-1}$ 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 CP statistics for of this voyage. Units: $\mu\text{mol L}^{-1}$

RMNS CP	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)
Minimum	62.3	1.80	0.312	25.56
Maximum	63.0	1.83	0.327	25.85
Mean	62.68	1.81	0.320	25.72
Median	62.70	1.81	0.320	25.72
Repeatability	0.088	0.009	0.003	0.084

Nutrient plots of RMNS

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

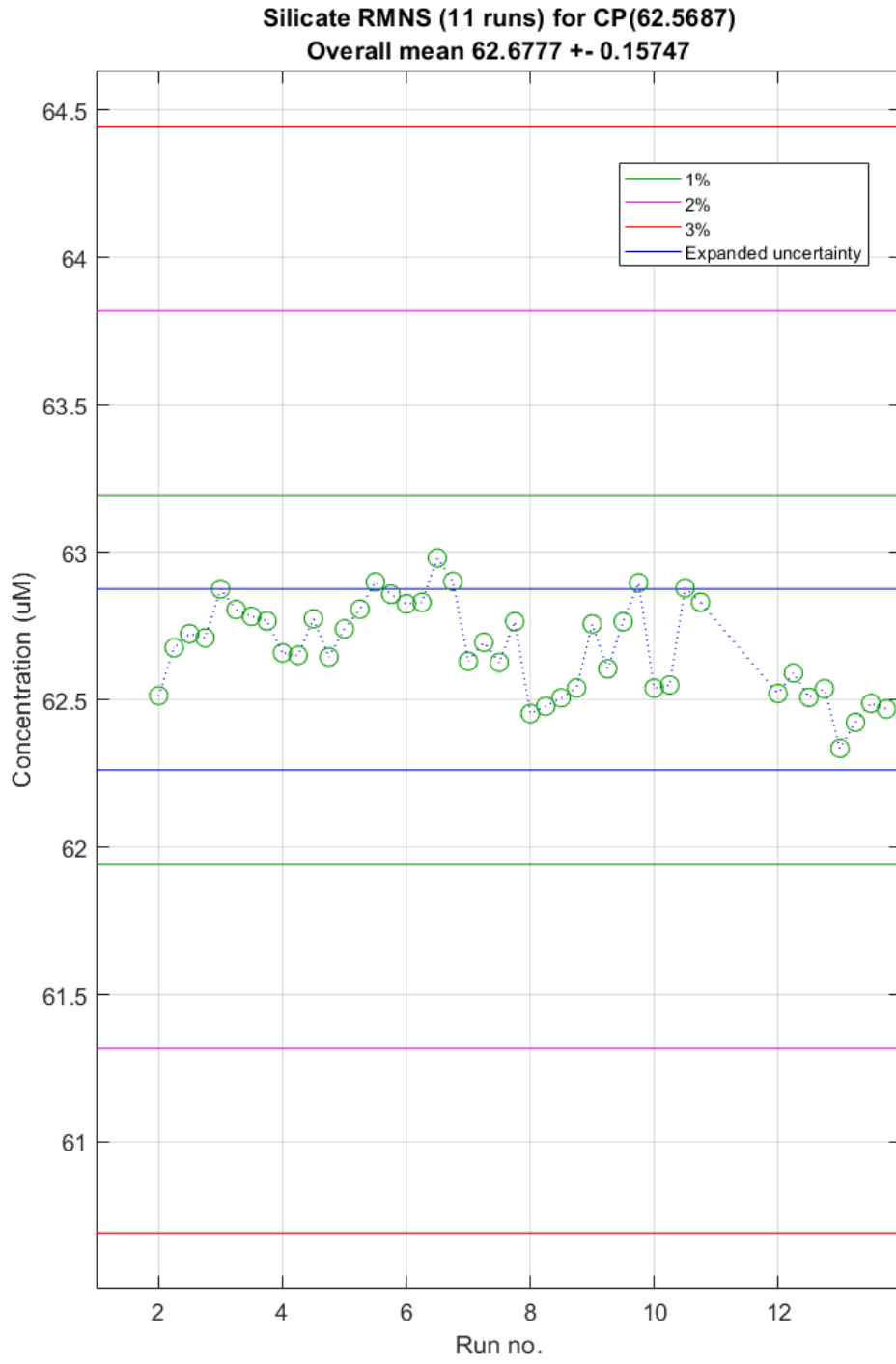


Figure 6: Silicate RMNS Plot ($\mu\text{mol L}^{-1}$)

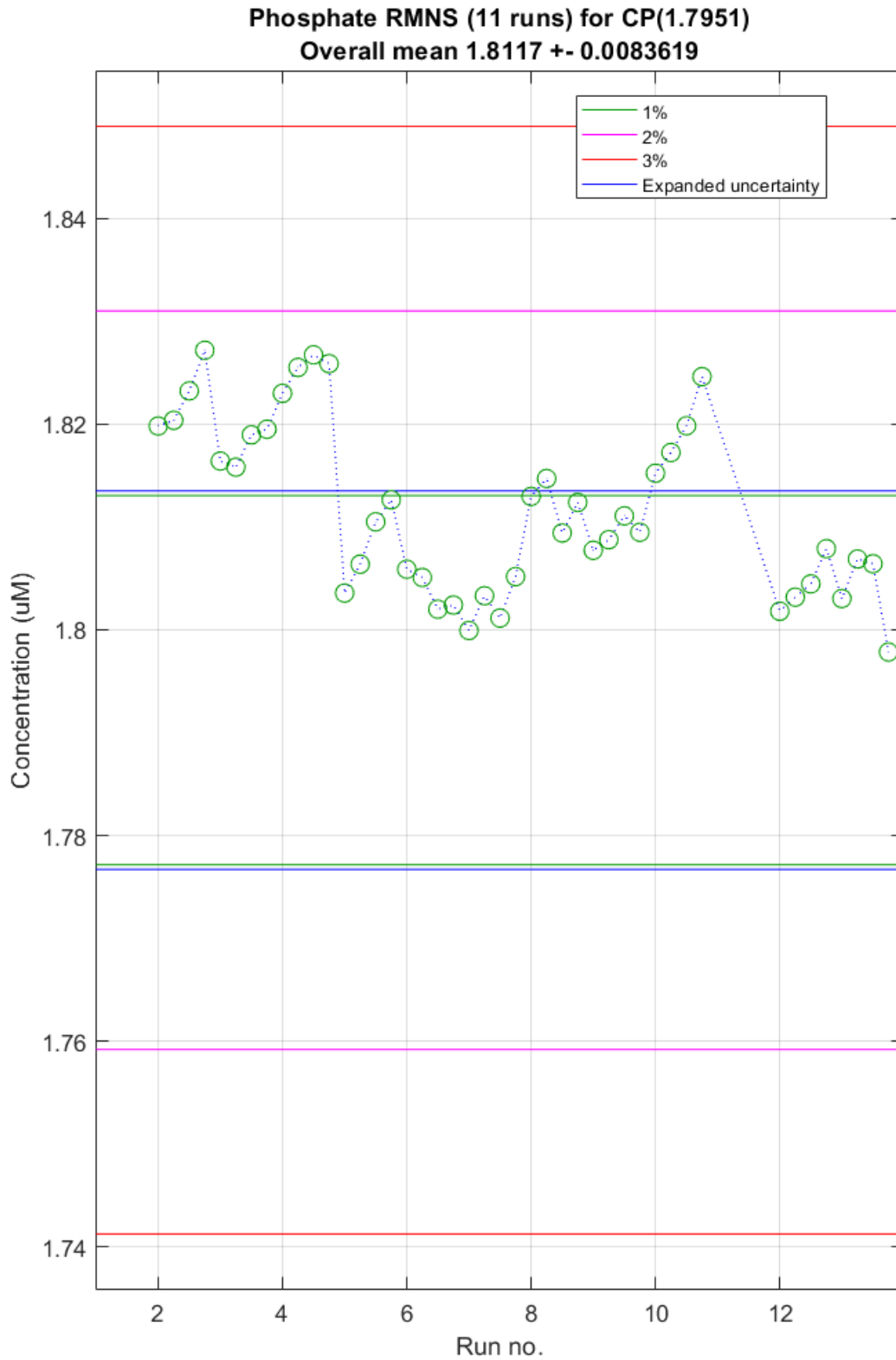


Figure 7: Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)

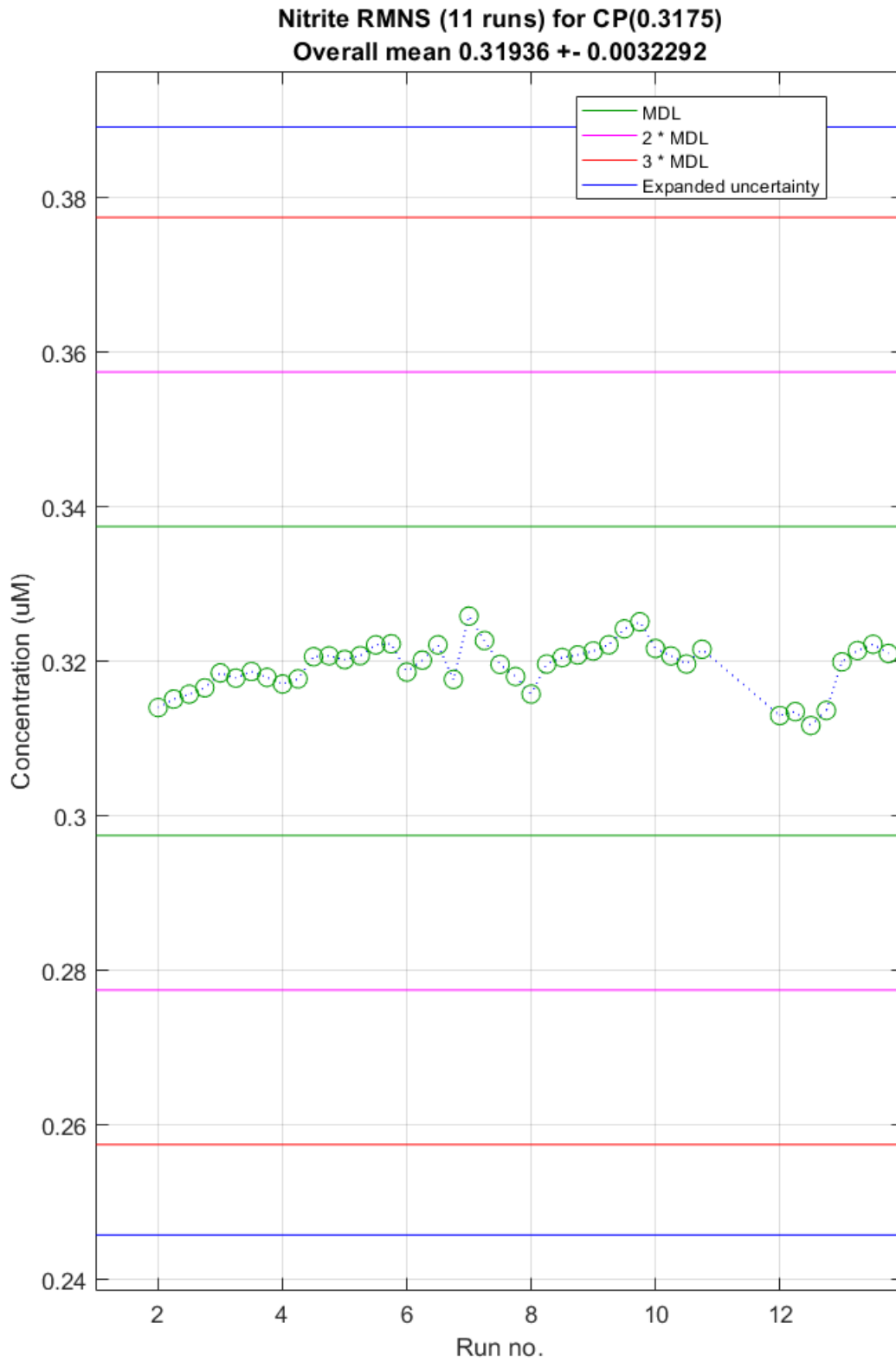


Figure 8: Nitrite RMNS Plot ($\mu\text{mol L}^{-1}$)

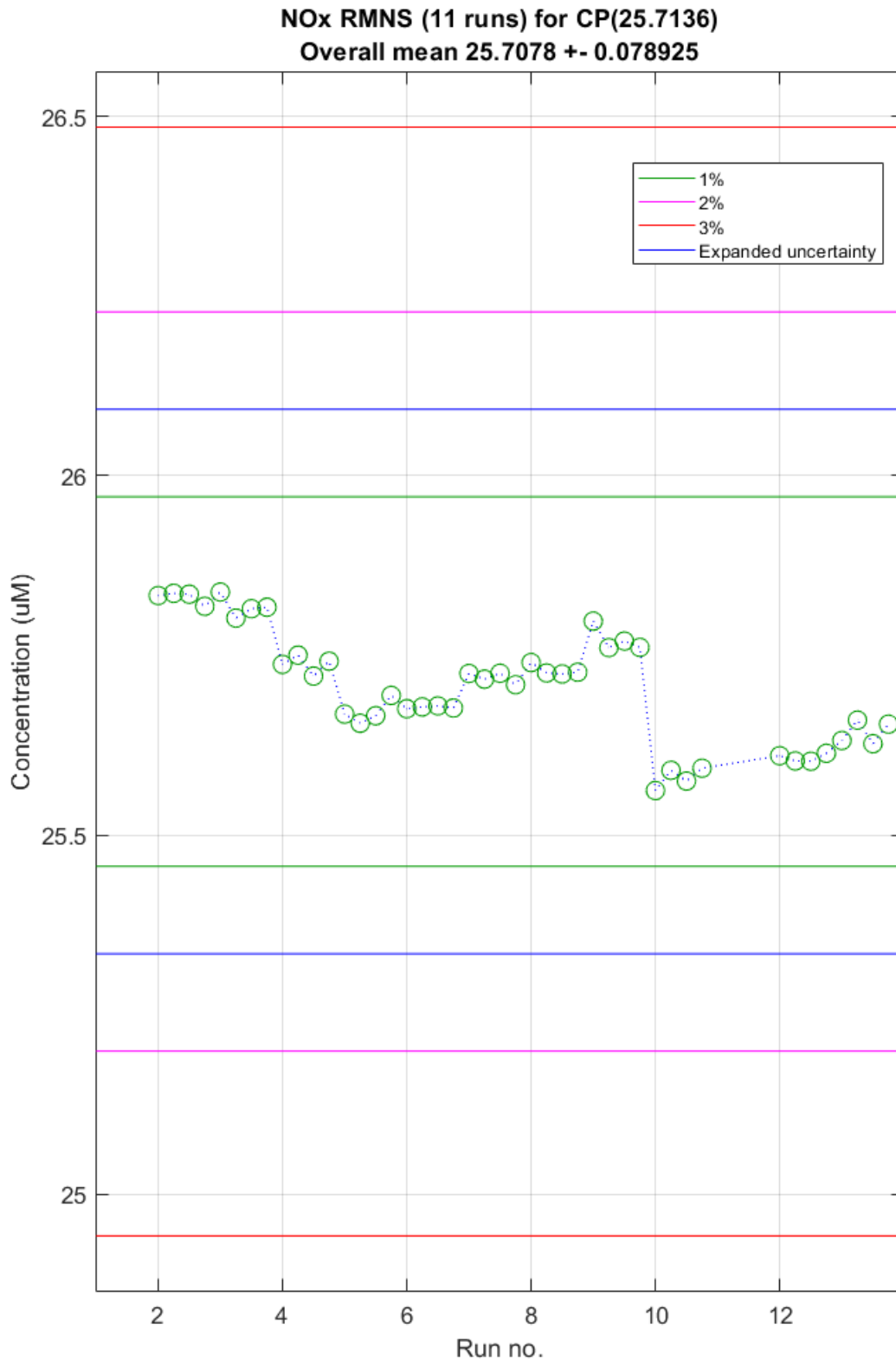


Figure 9: Nitrate + Nitrite (NOx) RMNS Plot ($\mu\text{mol L}^{-1}$)

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: $\mu\text{mol L}^{-1}$

Calculated Measurement Uncertainty @ 1 $\mu\text{mol L}^{-1}$				
Silicate	Phosphate	Nitrite	Nitrate + Nitrite (NO _x)	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.

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 for hydrochemistry (Table 13). 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: NO_x (nitrate+nitrite) which uses the limit 0.06 $\mu\text{mol L}^{-1}$

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 22 Units: $\mu\text{mol L}^{-1}$

	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _x)	Ammonia (NH ₄)
Minimum	0.00	0.00	0.00	0.00	0.00
Maximum	0.08	0.00	0.00	0.03	0.02
Mean	0.02	0.00	0.00	0.01	0.00
Variance	0.01	0.00	0.00	0.01	0.01

Table 13: CTD deployment 1. 34 bottles at 1000 dbar. Units: $\mu\text{mol L}^{-1}$.

	Salinity (PSU)	Dissolved Oxygen	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)
Minimum	34.430	196.87	30.90	2.01	0.000	29.30
Maximum	34.432	197.71	31.10	2.02	0.006	29.43
Mean	34.431	197.25	31.04	2.02	0.002	29.36
SD	0.001	0.18*	0.06	0.01	0.002	0.03

*Samples that were compromised during sampling process were excluded from this calculation.

Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: 14.37

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

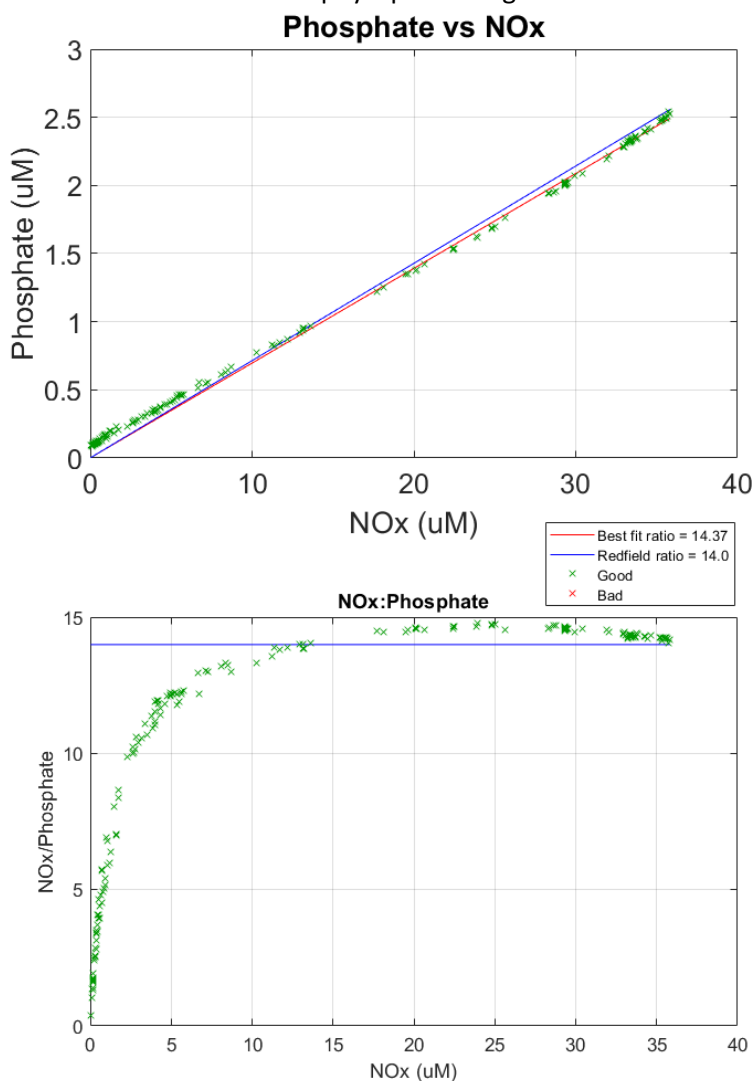


Figure 10. Redfield ratio plots.

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 19.8°C SD 0.4
- (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.

Appendix

Salinity: Reference Material Used

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

Nutrients: certified value for Reference Material Used

RMNS	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _x)
Lot CP	62.5687 ± 0.307	1.7951 ± 0.018	0.3175 ± 0.316	25.7136 ± 0.379

Nutrients: RMNS results for each CTD Deployment.

Analysis run number	CTD Deployment	Underway samples	Silicate (Si(OH) ₄) (μmol L ⁻¹)	Phosphate (PO ₄) (μmol L ⁻¹)	NOx (NO ₂ + NO ₃) (μmol L ⁻¹)	Nitrite (NO ₂) (μmol L ⁻¹)
2	1		62.656	1.823	25.831	0.315
3	2		62.808	1.818	25.818	0.318
4	4		62.682	1.825	25.738	0.319
5	7,8,9	1-5	62.826	1.808	25.671	0.321
6	11		62.885	1.804	25.678	0.320
7	12		62.679	1.802	25.719	0.322
8	13,14		62.494	1.812	25.729	0.319
9	15		62.756	1.809	25.772	0.323
10	17,18,19	6-9	62.700	1.819	25.580	0.321
12	20	10-12	62.539	1.804	25.607	0.313
13	21,22		62.429	1.804	25.643	0.321

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

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
7	2	133	Salinometer error – Bath temperature was recorded at 3 DegC
16	20	133	Niskin leaked
17	4	133	Niskin leaked (slightly)

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	25	133	Sampling error – air bubbles were observed around the stopper. Sample was marked as bad.
16	20	133	Niskin leaked
17	4	133	Niskin leaked slightly
20	1	133	Sampling error – small air bubbles were observed around the stopper. Sample was marked as suspect.
22	1	133	Sampling error – small air bubbles were observed around the stopper. Sample was marked as suspect.
22	2	133	Sampling error – small air bubbles were observed around the stopper. Sample was marked as suspect.
22	3	133	Sampling error – small air bubbles were observed around the stopper. Sample was marked as suspect.
22	4	133	Sampling error – small air bubbles were observed around the stopper. Sample was marked as suspect.

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
16	20	All	133	Niskin leaked
17	4	All	133	Niskin leaked slightly

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.

GO-SHIP Specifications

Salinity

Accuracy of 0.001 is possible with Autosol™ 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. Autosol 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 $\pm 1^\circ\text{C}$ is very important and should be recorded².

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.

Si(OH)₄

Approximately 1-3% accuracy¹, 0.2% precision³, full scale.

PO₄

Approximately 1-2% accuracy¹, 0.4% precision³, full scale.

NO₃

Approximately 1% accuracy¹, 0.2% precision³, full scale.

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.

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