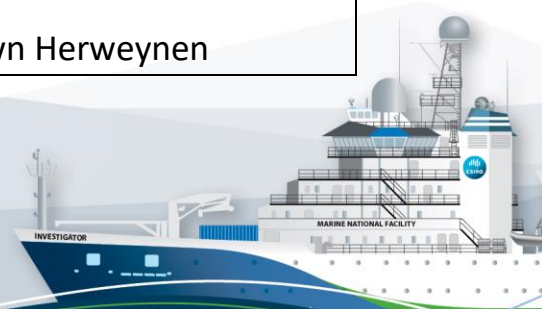


RV INVESTIGATOR

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	IN2023_V07
Chief Scientist	Benoit Legresy
Principal Investigator	Lennart Bach (UTAS), Kyla Drushka (APL), Annie Foppert (UTAS), Rosemary Morrow (LEGOS), Maxim Nikurashin (UTAS), Beatriz Pena-Molino (CSIRO), Helen Phillips (UTAS), Kurt Polzin (WHOI), Stephen Rintoul (CSIRO), Elizabeth Shadwick (CSIRO), and Andrew Thompson (CALTECH)
Voyage title:	SWOT-ACC : Smaller Scales Of The Antarctic Circumpolar Current In A Meander South Of Tasmania
Report compiled by:	Julie Janssens and Dawn Herweynen



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1 Executive Summary

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

Concentration of ammonia were extremely low in most water samples measured. Lots of concentrations measured were within 3x of method detection limit. Some results are negative due to the concentration being lower than the instrument MilliQ wash water. These negative values should be treated as 0 $\mu\text{mol/L}$.

1.1 Objectives

The Fine-scale Observations of the (Antarctic Circumpolar) Current Under SWOT (FOCUS) voyage was aimed to using a Surface Water Ocean Topography (SWOT) satellite to collect data along a swath in a meander of the Antarctic Circumpolar Current (ACC) that has been identified as a gateway for heat to travel through to cold Antarctic waters. FOCUS around this meander aims to:

1. Characterise small scale variability
2. Relate small scale variability in sea surface height to subsurface ocean structure
3. Quantify how small scale processes facilitate heat and carbon transport both between the surface ocean and interior and across the ACC
4. Investigate physical, biogeochemical and biological coupling at small and temporal scales.

The hydrochemistry team analysed dissolved oxygen (DO), salinities from the 110 CTD casts, and nutrients (PO_4 , NO_x , NO_2 , Si, and NH_4) from 106 CTD casts. CTD001 was the MNF test cast. CTDs 002, 003, and 004 were test casts for mooring sensors. No Nutrients were taken from these “mooring” casts. CTD030 was aborted and not sampled. They also measured DO, salinities and nutrients from the underway samples collected by the science party during the Triaxus tows.

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 (SiO_4), phosphate (PO_4), nitrate + nitrite (NO_x), nitrite (NO_2) and ammonium (NH_4). Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values. See Appendix 8.3 for the CTD deployment versus measured RMNS values.

Missing and suspect hydrology samples are listed in Appendix 8

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

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	15/11/2023	20/12/2023
Time	09:30 AM	08:30 AM

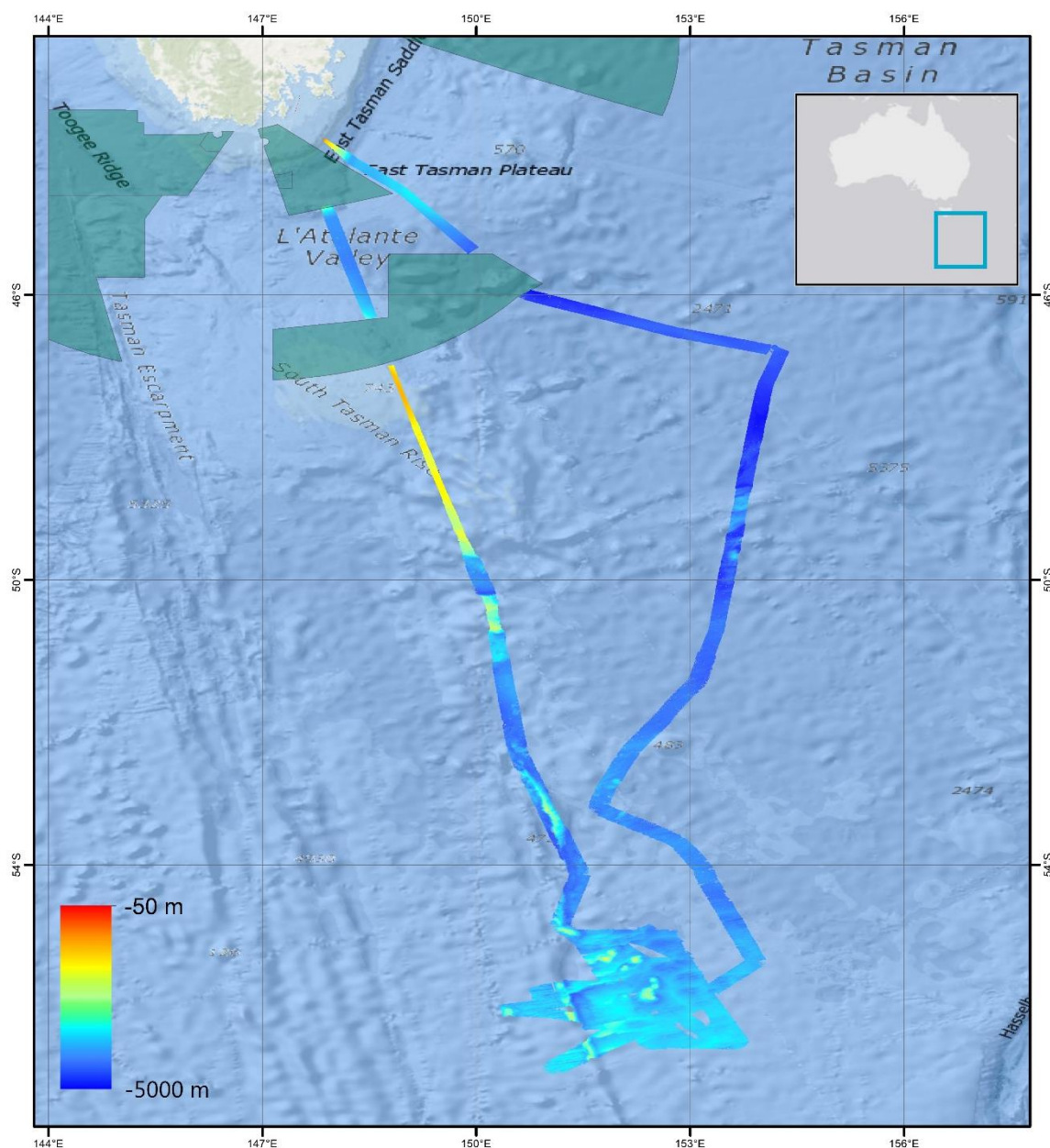


Figure 1: Voyage track

3 Key personnel list

Table 2: Key Personnel list

Name	Role	Organisation
Benoit Legresy	Chief Scientist	CSIRO
Claire Grubb	Voyage Manager	CSIRO
Julie Janssens	Hydrochemist	CSIRO
Dawn Herweynen	Hydrochemist	CSIRO
Matthew Corkill	Hydrochemist	CSIRO
James McLaughlin	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Table 3: Sample Type and Number Assayed

Analysis	Samples Assayed	Type
Salinity	1564	CTD
	101	UWY
	42	TSG
Dissolved Oxygen	1565	CTD
	101	UWY
Nutrients	1557	CTD
	101	UWY

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.
- A total of 110 CTD deployments were sampled by
 - Hydrochemistry: Julie Janssens, Matthew Corkill, Dawn Herweynen, James McLaughlin
 - Science party: Benoit Legresy, Helen Phillips, Yann-Treden Tranchant, Felipe Da Silva, Maya Jakes, James Wyatt, Andrea Hay, Yue (Luna) Bai, Polina Sholeninova, Camila Cataldo Mendez, Sylvie King, Paige England, Xihan Zhang, Luis Ackerman
- 110 CTD casts were sampled for DO and salinities. 106 casts were sampled for nutrients (PO₄, NO_x, NO₂, Si, and NH₄). CTD001 was the MNF test cast. CTDs 002, 003, and 004 were test casts for mooring sensors. No Nutrients were taken from these “mooring” casts. CTD030 was aborted and not sampled.

4.1.2 TSG Samples (Thermosalinograph)

- Taken from the underway instrument clean seawater line supplying the pCO₂ instrument in the underway laboratory.
- TSG (TSG001 to TSG041) samples collected by hydrochemistry. Results emailed to Vito Dirita (CSIRO) at the completion of the voyage.
- TSG sampling team: Julie Janssens and Dawn Herweynen

Refer to voyage EVERLog for TSG sample information

4.1.3 Underway samples (UWY)

- Taken from the underway instrument clean seawater line supplying the pCO₂ instrument in the underway laboratory.
- DO, nutrients, and salinity UWY samples were taken hourly during Triaxus tows
- Underway sampling team: Yann-Treden Tranchant, Felipe Da Silva, Maya Jakes, James Wyatt, Andrea Hay, Yue (Luna) Bai, Polina Sholeninova, Camila Cataldo Mendez, Sylvie King, Paige England, Xihan Zhang, Luis Ackerman

Refer to voyage EVERLog and IN2023_V07_UWY sampling logsheets.pdf for UWY 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).

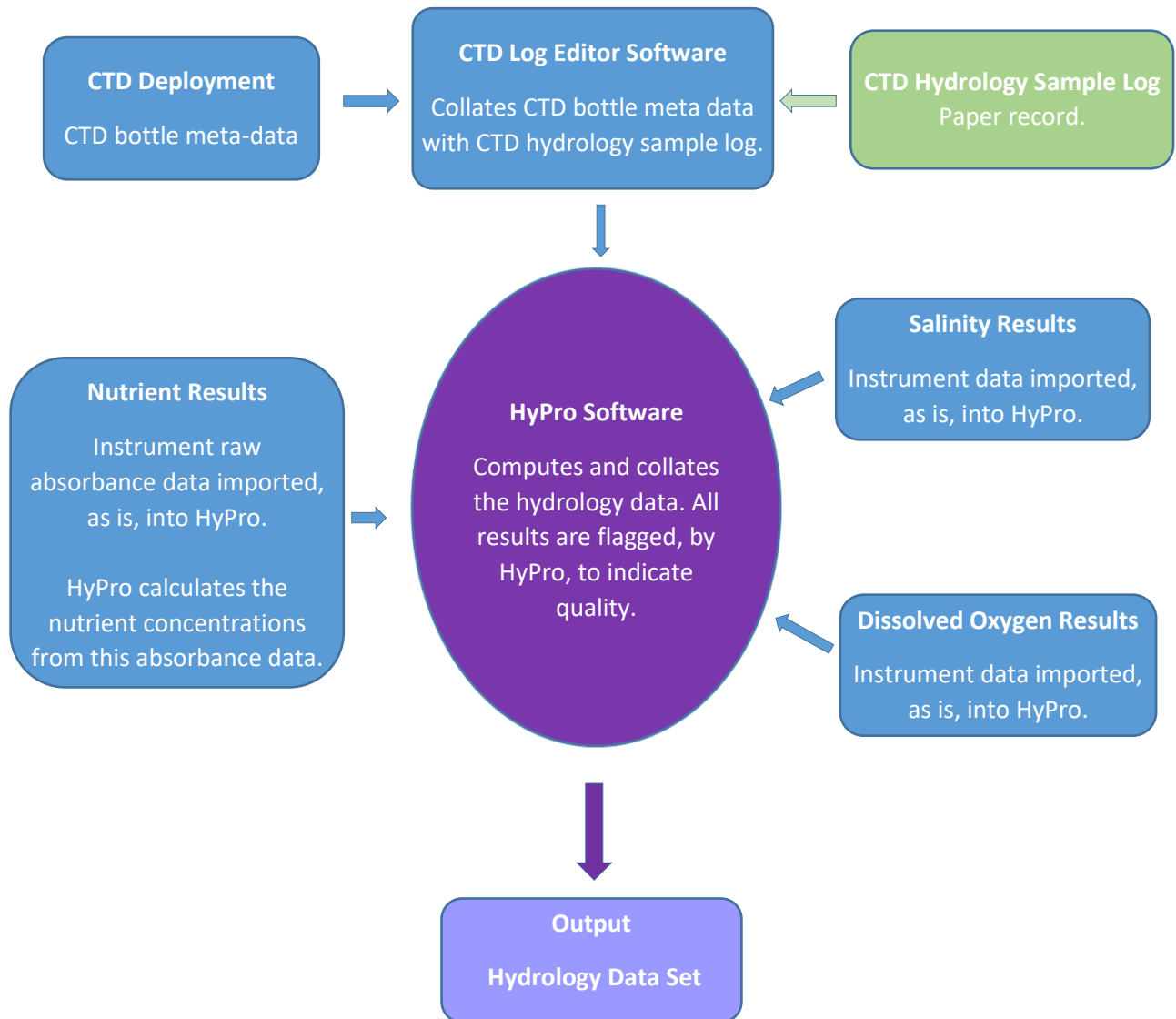


Figure 2: Hydrology Data Processing Flow Diagram.

5 Salinity

5.1 Salinity Measurement Parameters

Table 4: Salinity Measurement Parameters

Details	
HyPro Version	5.7
Instruments	Guildline Autosol Laboratory Salinometer 8400(B) – SN 72088 and SN 71613. Bath temperature 24.0°C
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2
Hydrochemistry Methods	Sampling: WI_Sal_002 Measurement: SOP 006
Accuracy	± 0.001 practical salinity units
Reference Material	OSIL IAPSO – Batch P167, use by 21/02/2026, $K_{15} = 0.99988$
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 for minimum of 8 hrs before measurement.
Lab Temperature	Mean 21.6°C SD 0.82°C
Analysts	James McLaughlin
Comments	See DAP report for CTD calibration details.

5.2 Salinity Method

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

Practical salinity (S) is defined in terms of the ratio (K_{15}) of the electrical conductivity measured at 15°C 1 atm of seawater to that of a potassium chloride (KCl) solution of mass fraction 32.4356×10^{-3} .

Before each lot of sample measurements, the Autosol 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 Autosol 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 0.02 PSU. The larger differences are for shallow samples across the sudden changes in the thermohaline profile.

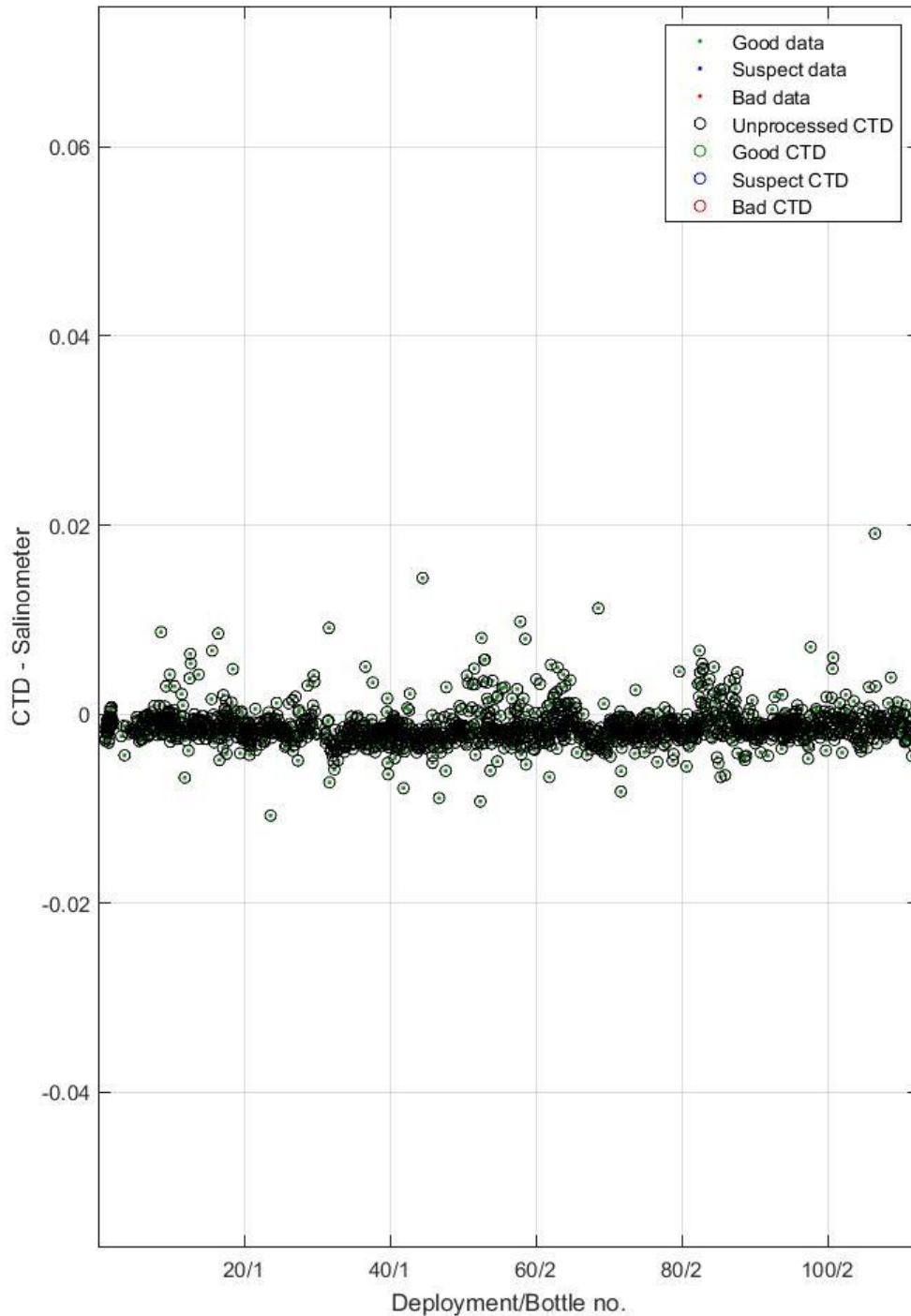


Figure 3: CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Black = UNPROCESSED. Units: PSU (dimensionless). Cast 090, RP20 has been removed from the data set due to being a significant outlier.

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: SOP 005
Accuracy	$\pm 0.5 \mu\text{mol L}^{-1}$
Lab Temperature	Mean 19.7°C SD 0.3°C
Sample Container type	140 mL glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis.
Analysts	Matthew Corkill
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. One mL of manganese (II) chloride solution (reagent 1) followed by 1 mL of alkaline iodide solution (reagent 2) 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 using a solution of 5.15 M sulfuric acid (reagent 3), 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 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 $20 \mu\text{mol L}^{-1}$. The larger differences are for shallow samples across the sudden changes in the dissolved oxygen profile.

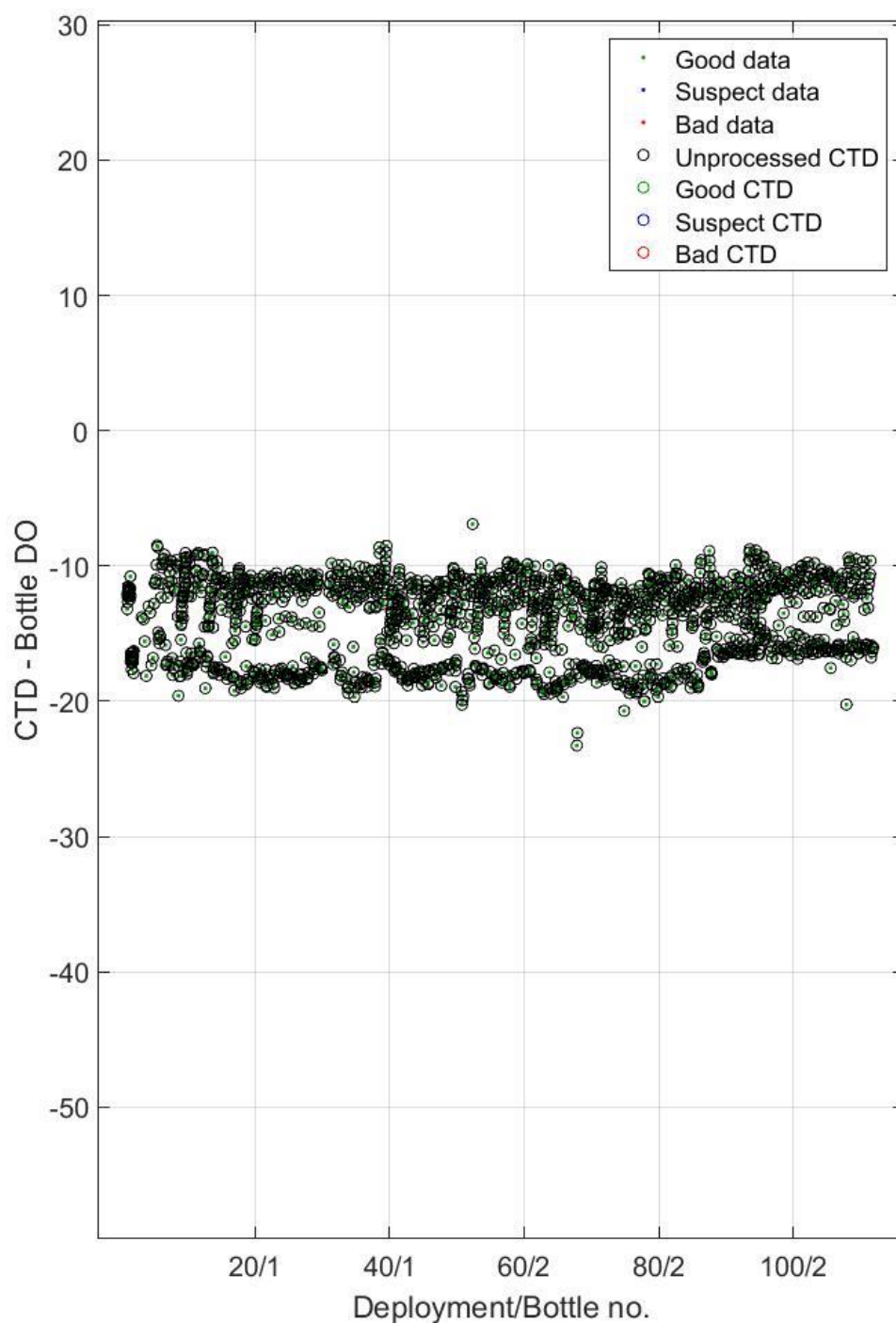


Figure 4. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Black = UNPROCESSED. Units: $\mu\text{mol L}^{-1}$. Cast 087 on RP19, cast 024 on RP02 and cast #20 on RP30 have been removed from the data set as they are large outliers.

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. Two batches of thiosulphate reagent was used during the voyage. The mean normality as follows:

CTD Deployment 1 to 111: Mean: 0.221049 N
SD: 0.000142 (n=25)

The blank correction is used in the calculation of the thiosulphate normality and is due to oxidisable species in the Milli-Q water that is added to the KIO_3 aliquot before the titration. A new batch of alkaline iodate (reagent 2) gave negative blanks and reduced the KIO_3 titre, indicating reducing species contamination. The blank correction accounted for this and thiosulfate normality remained within tolerance so no further action was taken.

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.

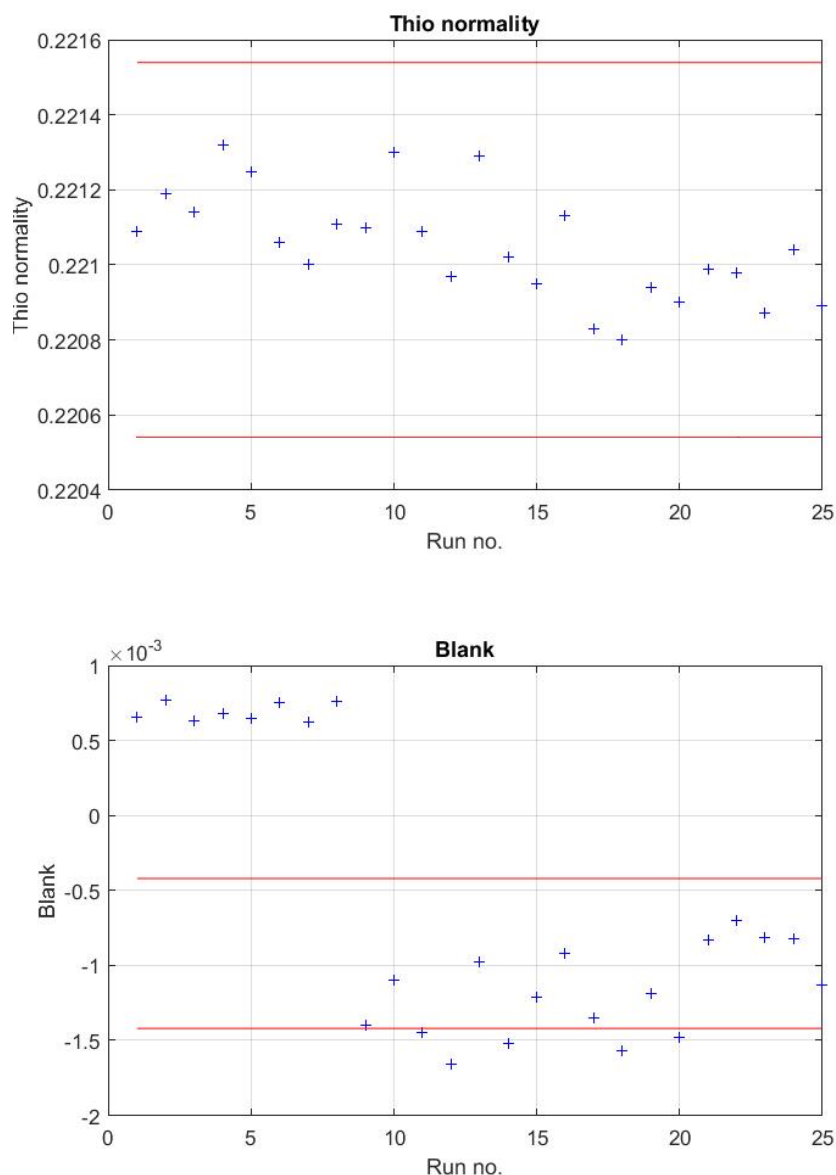


Figure 5. Thiosulphate standardisation and blank correction plots. Blank measurement values change significantly from run 008 to run 009 due to a change in alkaline iodate (reagent 2).

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					
Instrument	CSIRO HyPro 5.7				
HyPro version	Seal AA3HR segmented flow analyser.				
Operating Software	AACE 7.10				
Hydrochemistry Sampling Method	WI_DO_001				
Hydrochemistry analysis method	SOP001	SOP002	SOP003	SOP004	SOP005
Nutrients	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Top concentration ($\mu\text{mol L}^{-1}$)	140	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 1 M HCl				
Sample Storage	< 4 hrs at room temperature or < 12 hrs @ 4°C				
Sample preparation	Assayed as neat. No filtration.				
Lab Temperature (°C)	Mean 19.7°C SD 0.3°C				
Analysts	Julie Janssens and Dawn Herweynen				
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 660 nm.

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 complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880 nm.

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-naphthyl-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-phthalaldehyde method. Based on K  rouel and Aminot (1997). Ammonium reacted with ortho-phthalaldehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460 nm after excitation at 370 nm.

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:

- $\pm 0.5\%$ of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE²).
- $0.02 \mu\text{mol L}^{-1}$ 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

² 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	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$
Calibration Curve degree	Linear	Linear	Linear	Quadratic	Quadratic

# of points in Calibration	7	6	7	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 PW1 wharf, CSIRO Hobart) collected in June 2021. Sub-lot passed through a 10-micron filter (filtered in May 2023) 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 IQ 7010.				
Duplicate samples.	CTD: Niskin fired at the greatest and shallowest depths were analysed in duplicates. 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, NO_x, and nitrite in seawater.

For IN2023_V07, Japanese KANSO certified RMNS lot CP were assayed in triplicate in each run to monitor accuracy. The certified values are in Table 8. Internal bulk quality control (BQC) was also analysed in each run in duplicates for analysis on AA3HR segmented flow analyser.

For IN2023_V07, most of the certified reference material results for NO_x, silicate, and Nitrite are within 1%. Most Phosphate RMNS are within 3%. As RMNS were measured in quadruplicates per run, the few exceptions beyond 3% were able to be rejected as 3 RMNS measurements within 3% are satisfactory to deem a run successful. Nitrite RMNS fell within 0.35 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.

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 NO₃ and NO₂ values. The assayed RMNS values per CTD deployments are listed in the appendix 8.3.

Table 8: RMNS CP certified concentrations $\pm$ expanded uncertainty (U) at 21°C. Units: $\mu\text{mol L}^{-1}$

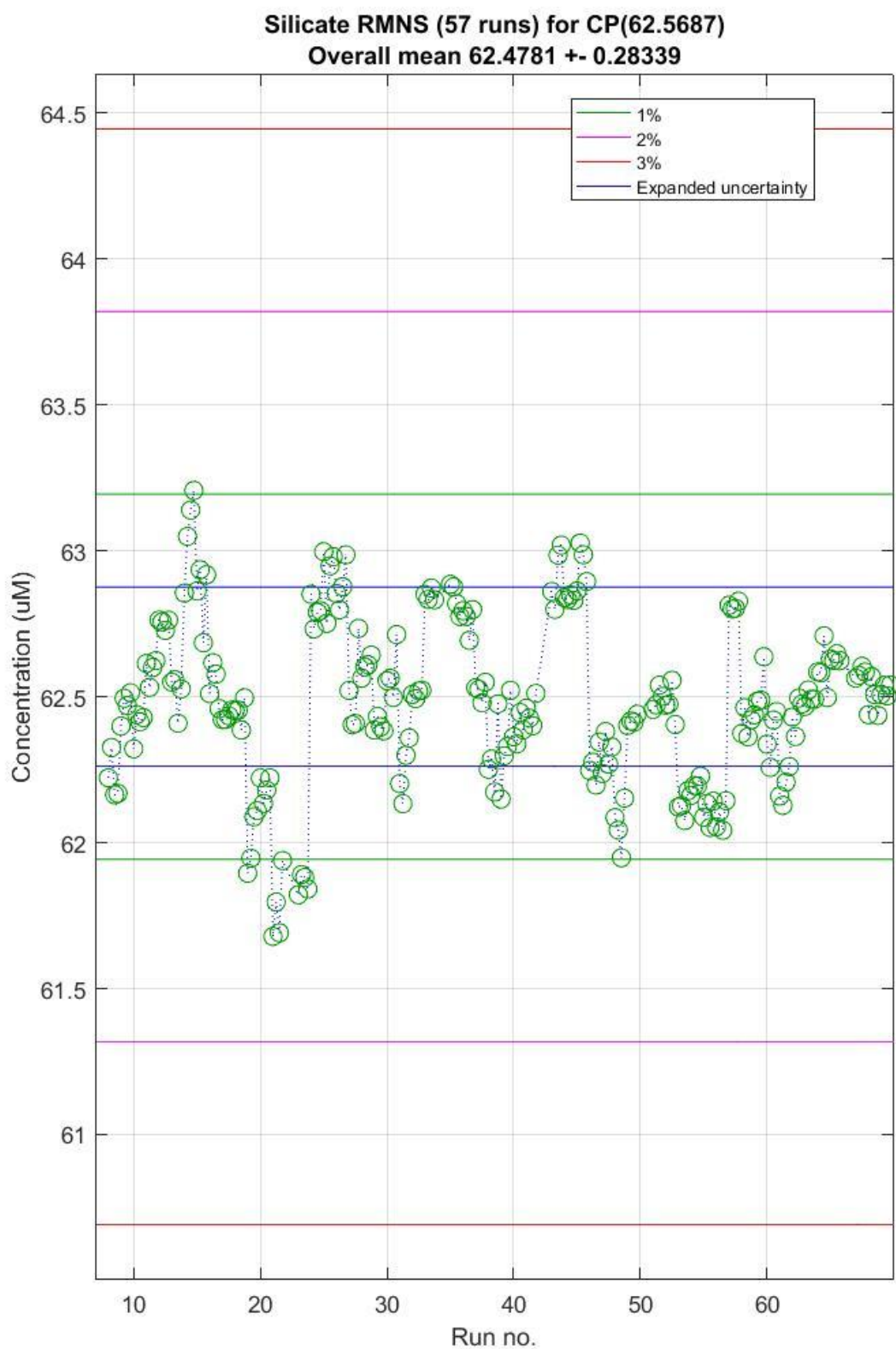
RMNS	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)
Lot CP	62.5687 ± 0.307	1.7951 ± 0.018	0.3175 ± 0.316	25.7136 ± 0.379

Table 9: RMNS CP statistics for the IN2023_V07 voyage. Units: $\mu\text{mol L}^{-1}$

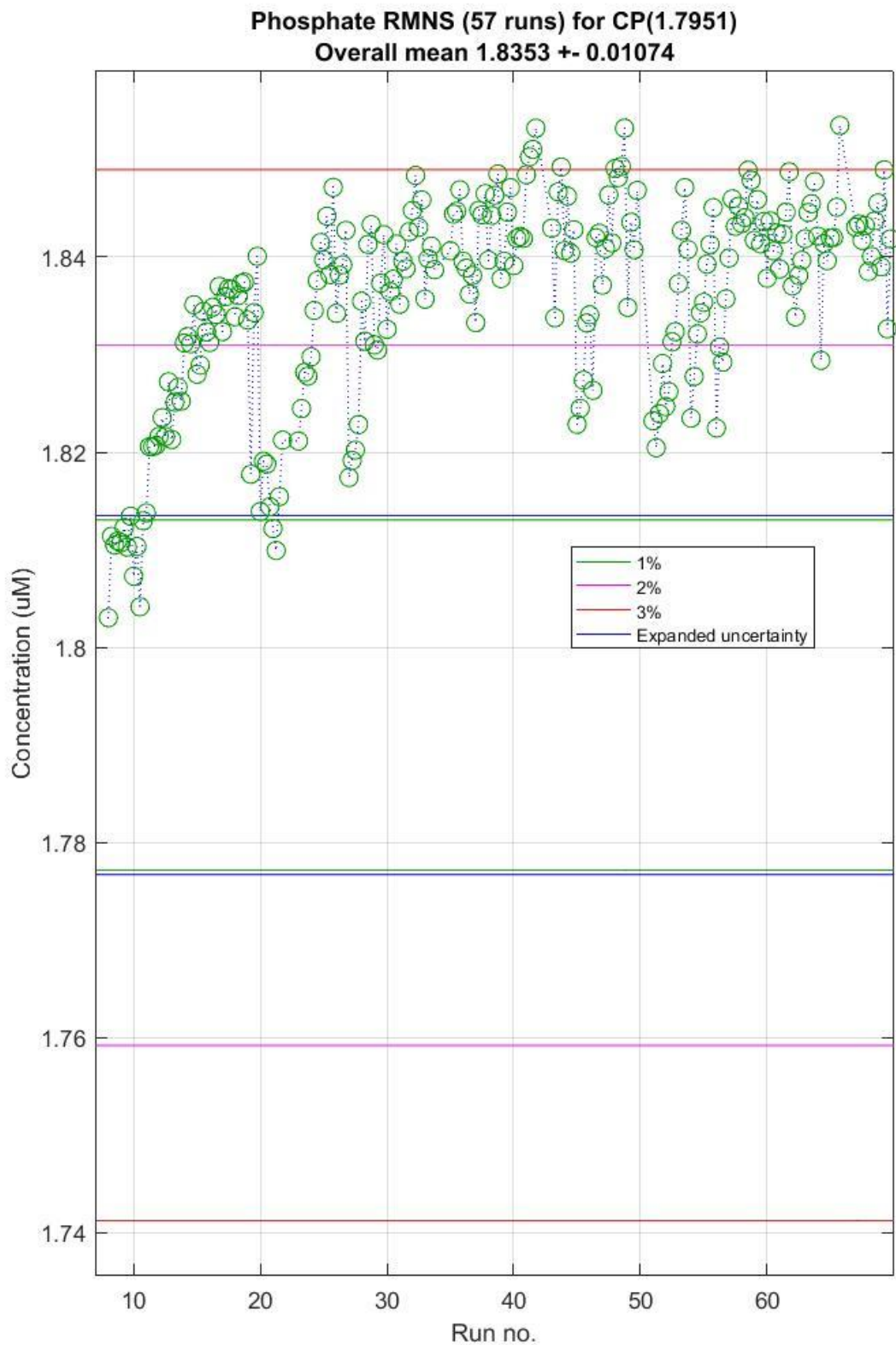
RMNS CP	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)
Minimum	61.7	1.8	0.304	25.31
Maximum	63.2	1.85	0.345	26.23
Median	62.477	1.835	0.325	25.651
Mean	62.5	1.84	0.325	25.65
Repeatability	0.059	0.005	0.002	0.027

7.5 Nutrient plots of RMNS

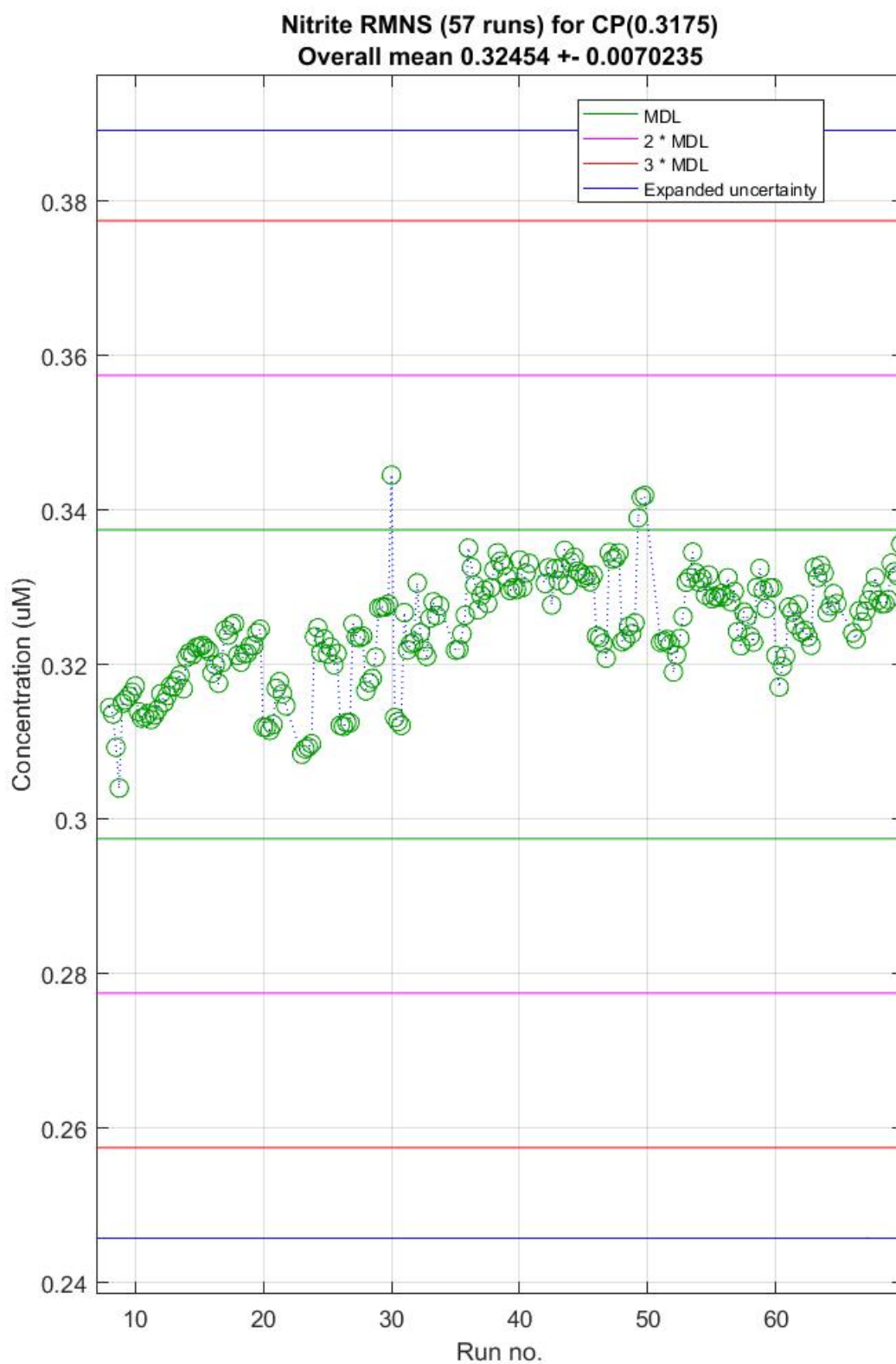
The green, pink, and red contours are at 1%, 2%, and 3% from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 $\mu\text{mol L}^{-1}$ increments from the certified value. The blue line is the certified value's expanded uncertainty. Plots are RMNS value versus instrument run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



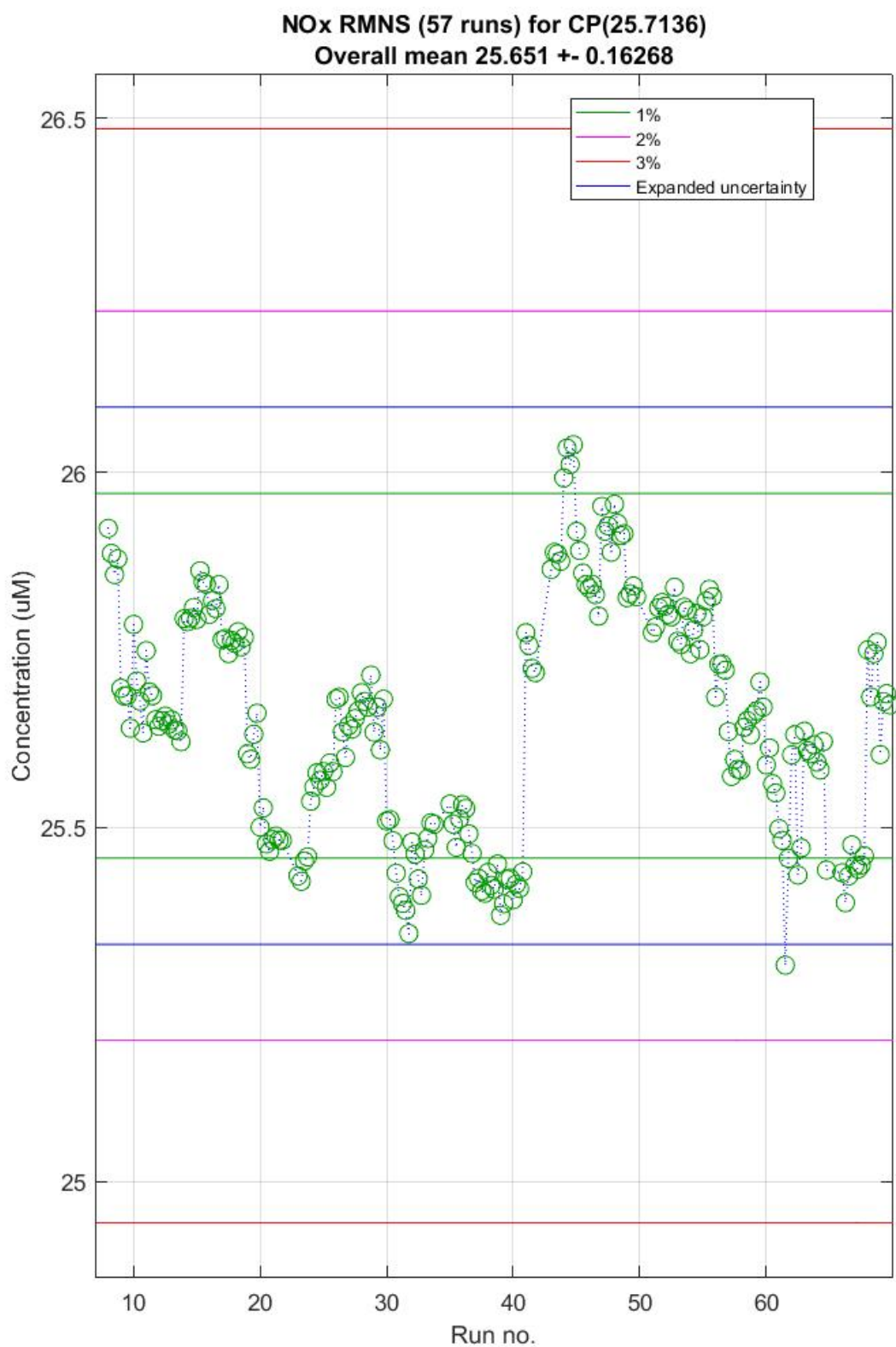
7.5.1 Figure 6: Silicate RMNS Plot ($\mu\text{mol L}^{-1}$)



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



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



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

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 10: 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	$\pm 0.30^*$

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 Method Detection Limit for Nutrients

Low nutrient seawater (LNSW) was measured 3 times in each run to determine its method detection limit (MDL). The nominal MDL was determined previously by measuring nutrients in LNSW 10 times. The MDL is set to three times the standard deviation of the LNSW results (National Association of Testing Authorities 2013). The resultant MDL was used to assess the analysis precision at low concentrations. The MDLs for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. See appendix 8.3 for the measured MDL per CTD deployments.

Table 11: AA3HR auto analyser MDL statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are of all analytical measurements. Units: $\mu\text{mol L}^{-1}$

MDL	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrate + Nitrite (NO _x)	Nitrite (NO ₂)	Ammonia (NH ₄)
Nominal MDL	0.200	0.020	0.020	0.020	0.020
Standard Dev. Min	0.0	0.0	0.0	0.0	0.0
Standard Dev. Max	0.058	0.006	0.006	0.004	0.006
Standard Dev. Median	0.0	0.0	0.0	0.001	0.0
Standard Dev. Mean	0.021	0.002	0.002	0.001	0.001
Precision of MDL (stdev)	0.021	0.002	0.002	0.001	0.001

7.8 Sampling Precision

The sampling precision for this voyage is GOOD.

Initial sampling precision is determined with the CTD test deployment (CTD 001) where multiple bottles are fired the same depth, each of which is then sampled for hydrochemistry (Table 12).

Duplicate nutrient samples are also collected from the greatest and shallowest depths of subsequent CTD deployments.

For nutrients, the sampling precision is good if the difference from the mean of duplicate measurements is less than the nominal method detection limit (Table 6). The exception: NO_x (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: CTD deployment 1. 17 bottles (18 samples) at 100 dbar.

	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
Minimum	34.774	275.07	2.891	0.839	0.366	12.35
Maximum	34.775	276.32	5.059	0.970	0.417	12.43
Mean	34.775	275.34	3.292	0.932	0.382	12.41
SD	0.0003	0.2871	0.592	0.024	0.015	0.017

Table 13: CTD deployment 1. 17 bottles (18 samples) at 2000 dbar.

	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
Minimum	34.660	177.26	82.51	2.360	0.160	33.65
Maximum	34.663	179.09	83.09	2.400	0.304	33.85
Mean	34.661	177.75	82.81	2.375	0.236	33.77
SD	0.0007	0.4278	0.179	0.008	0.054	0.058

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

7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: **14.33**

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.

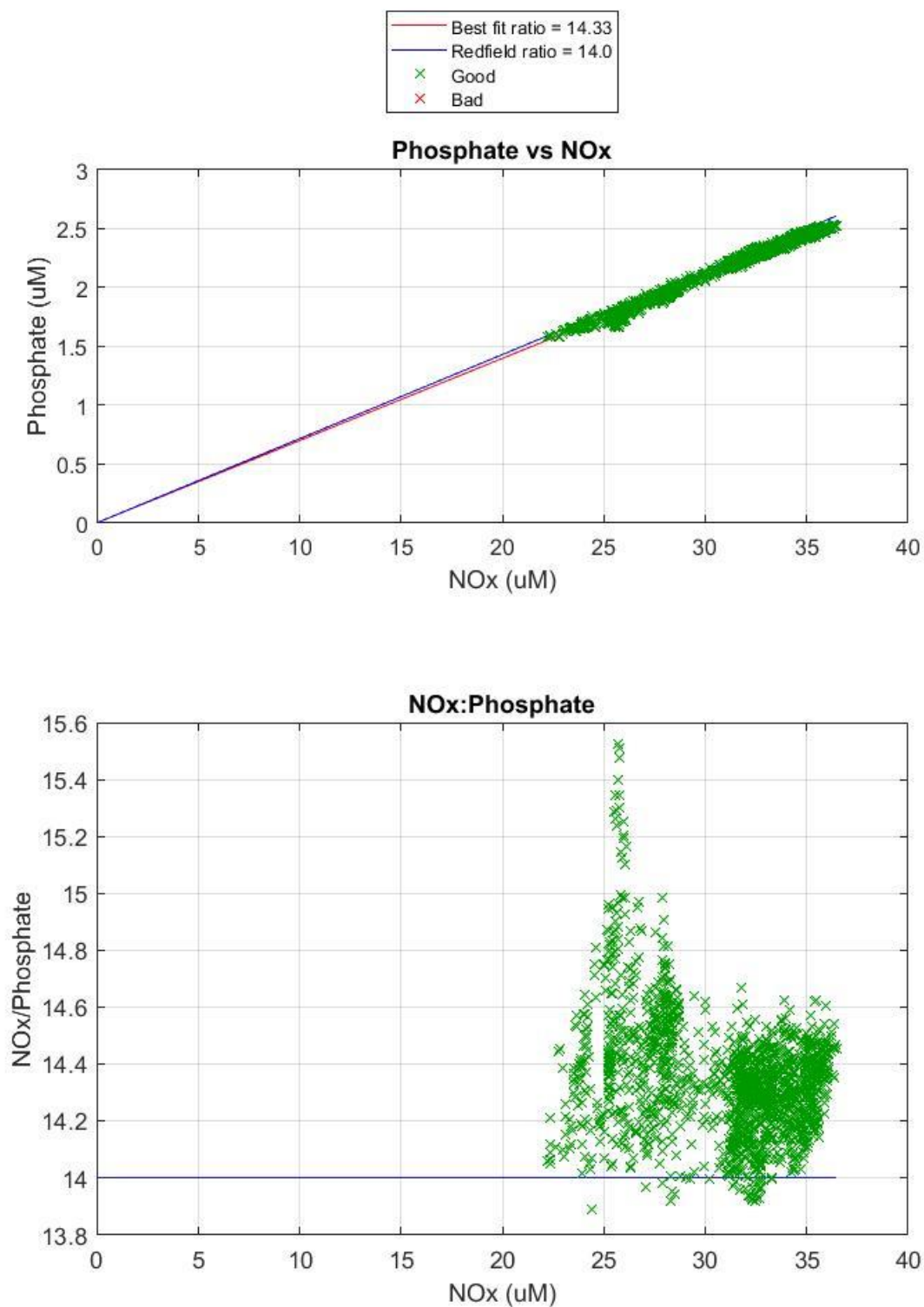


Figure 10. Redfield ratio plots.

7.10 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 19.4°C SD 0.4°C
- (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:	P167
Use by date:	21/02/2026
K ₁₅ :	0.99988
PSU:	34.995

8.2 Nutrients: 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

8.3 Nutrients: RMNS lot CP results

8.3.1 CTD Deployments

Run analysis #	CTD Deployment #	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)
8	1	62.225	1.808	25.888	0.310
9	5	62.475	1.810	25.678	0.316
10	6,7	62.375	1.808	25.703	0.314
11	8	62.575	1.818	25.695	0.314
12	9	62.775	1.823	25.650	0.316
13	10,11,12	62.525	1.828	25.638	0.318
14	13,14	63.050	1.833	25.795	0.322
15	15,16	62.850	1.830	25.835	0.322
16	17,18	62.550	1.833	25.818	0.319
17	19	62.425	1.838	25.758	0.325
18	20	62.475	1.838	25.765	0.321
19	21,22	62.000	1.830	25.623	0.323
20	23,24,25	62.175	1.815	25.495	0.312
21	26,27	61.775	1.815	25.483	0.317
23	28,29	61.850	1.825	25.440	0.309
24	31,32,33	62.800	1.835	25.563	0.324
25	34 and 35 (NOx, PO ₄ , Si(OH) ₄ , NH ₄), 36	62.925	1.843	25.578	0.321
26	37, 34 and 35 (NO ₂ only)	62.900	1.838	25.648	0.313
27	38	62.500	1.820	25.648	0.324
28	39	62.600	1.838	25.688	0.319
32	40	62.500	1.845	25.443	0.325
33	41,42,43	62.850	1.840	25.490	0.327
35	44,45,46	62.850	1.843	25.503	0.324
36	47,48	62.775	1.840	25.503	0.331
37	49,50	62.500	1.840	25.418	0.329
38	51,52	62.325	1.845	25.430	0.333
39	53,54	62.300	1.843	25.408	0.330
40	55,56	62.375	1.840	25.418	0.332
41	57,58,59 (NOx, PO ₄ , Si(OH) ₄ , NH ₄)	62.450	1.850	25.743	-
42	57,58,59, (NO ₂ only)	-	-	-	0.331

43	60	62.925	1.843	25.880	0.332
44	61,62	62.800	1.843	26.018	0.333
45	63,64	62.950	1.825	25.878	0.332
46	65,66,67	62.250	1.835	25.828	0.323
48	68,69	62.050	1.850	25.928	0.324
49	70,71	62.400	1.840	25.828	0.337
51	72,73,74	62.500	1.823	25.795	0.323
52	75,76,77	62.500	1.828	25.813	0.322
53	78,79,80	62.125	1.843	25.785	0.332
54	81,82,83	62.200	1.828	25.768	0.331
55	84,85	62.100	1.843	25.822	0.329
56	86,87	62.075	1.830	25.715	0.330
57	88,89	62.800	1.845	25.595	0.325
58	90,91	62.425	1.845	25.625	0.327
59	92	62.500	1.843	25.673	0.329
60	93,94	62.350	1.840	25.578	0.320
61	95,96	62.200	1.843	25.438	0.327
62	97,98,99	62.450	1.838	25.533	0.324
63	100,101,102	62.500	1.845	25.618	0.332
64	103,104,105	62.600	1.838	25.558	0.328
65	106,107 (Si(OH) ₄ , PO ₄ , and NH ₄)	62.600	1.845	-	-
66	106,107, (NO _x & NO ₂)	-	-	25.450	0.325
67	108,109,110	62.600	1.840	25.733	0.329
68	111	62.475	1.843	25.880	0.328

8.3.2 CTD Deployment repeats for individual samples

Run analysis #	Sample #	Silicate (Si(OH) ₄) (μmol L ⁻¹)	Phosphate (PO ₄) (μmol L ⁻¹)	NO _x (NO ₂ + NO ₃) (μmol L ⁻¹)	Nitrite (NO ₂) (μmol L ⁻¹)
14	1408, 1411, 1420	-	1.833	25.795	0.322
15		62.850	-	-	-
27	3801 dups	-	1.820	25.648	0.324
28		62.600	-	-	-
36	4802 dups	62.775	1.840	-	0.331
37		-	-	25.418	-
40	5602 dups	62.375	1.840	25.418	-
42		-	-	-	0.331

49	7001 dups, 7101 dups	-	1.840	25.828	0.337
51		62.500	-	-	-
51	7235 dups, 7435 dups	62.500	1.823	-	0.323
52		-	-	25.813	-
52	7702 dups	-	-	-	0.322
53		62.125	1.843	25.785	-
54	8102, 8201, 8135	62.200	1.828	-	0.331
55		-	-	25.822	-
64	10435 dups	62.600	1.838	-	0.328
66		-	-	25.450	-

8.3.3 Underway samples during Triaxus tow

Run analysis #	Tow #	Sample #	Silicate (Si(OH) ₄) (μmol L ⁻¹)	Phosphate (PO ₄) (μmol L ⁻¹)	NO _x (NO ₂ + NO ₃) (μmol L ⁻¹)	Nitrite (NO ₂) (μmol L ⁻¹)
29	1	001-012	62.400	1.835	25.648	0.327
30	1,2	013-024	62.600	1.838	25.485	0.321
31	2	025-039	62.250	1.840	25.380	0.324
47	3	040-062	62.300	1.843	25.920	0.335
57	4	063-089	62.800	1.845	25.595	0.325
69	5	090-100	62.500	1.840	25.660	0.333

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 and underway (UWY) sampling log notes, observations during analysis, and examination of depth profile plots (Flag key: appendix 8.7)

CTD #	UWY sample #	RP #	Flag	Reason for Flag
90	-	20	133	Large outlier. Data was marked as BAD by operator.
-	052	-	133	No insert in salt bottle. Data was marked as BAD by operator.

8.5 Missing or Suspect Dissolved Oxygen Data

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

CTD #	UWY sample #	RP #	Flag	Reason for Flag
20	-	30	133	Large outlier – no stirring was initiated when sample was undergoing titration. Data was marked as BAD by operator.
24	-	2	133	Large outlier – a large bubble was present under the DO stopper; sample was tipped out by the science party. Data was marked as BAD by operator.
87	-	19	133	Large outlier. Data was marked as BAD by operator.
96	-	32	133	Titration error. Data was marked BAD by operator.
96	-	35	133	Titration error. Data was marked BAD by operator.
-	088	-	133	Precipitate was floating at top of flask – suspect reagents added in reverse order. Data was marked BAD by operator.

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
11	8	Ammonia	65	Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.
20	8	Ammonia	65	Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.
29	29	Nitrite	133	Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.

57	1	Ammonia	69	Duplicate of this bottle did not match. Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.
77	2	NO _x , Silicate and Phosphate	69	Duplicate of this bottle did not match. Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.
99	5	Nitrite	133	Abnormal vertical profile plot. Operator suspected sampling contamination. The data was marked as SUSPECT by operator.

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 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.

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% accuracy¹, 0.2% precision³, full scale.

8.8.4 PO_4

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

8.8.5 NO_3

Approximately 1% accuracy¹, 0.2% precision³, 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

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