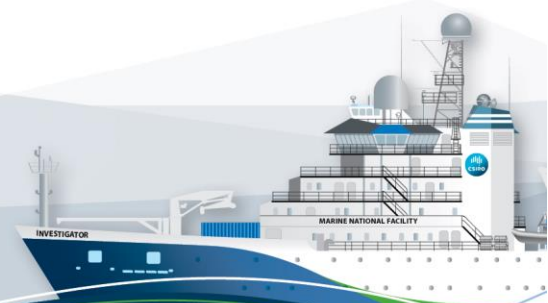


RV INVESTIGATOR

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	IN2023_V06
Chief Scientist	Professor Moninya Roughan
Voyage title:	Understanding Eddy Interactions and Their Impacts in the East Australian Current System
Report compiled by:	Narendra Pati, Peter Hughes, Maddy Lahm, Merinda McMahon



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1 Executive Summary

1.1 Objectives

This voyage focused on mesoscale eddies, the weather systems of the ocean, that move heat, salinity, and other tracers around. They impact the ocean, ecosystems, and climate, not much is known about how these eddies interact with each other or how they affect the environment. The aim of this voyage was to learn more about eddy-eddy interactions and their impact on the atmosphere, ocean, and marine life in the East Australian Current System.

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

Five nutrients were determined: silicate, phosphate, nitrate + nitrite, nitrite and ammonium using AA3HR autoanalyser. Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values. Missing and suspect hydrology samples are listed in Appendix section.

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	Sydney	Sydney
Date	09/10/2023	02/11/2023
Time	0900	1000

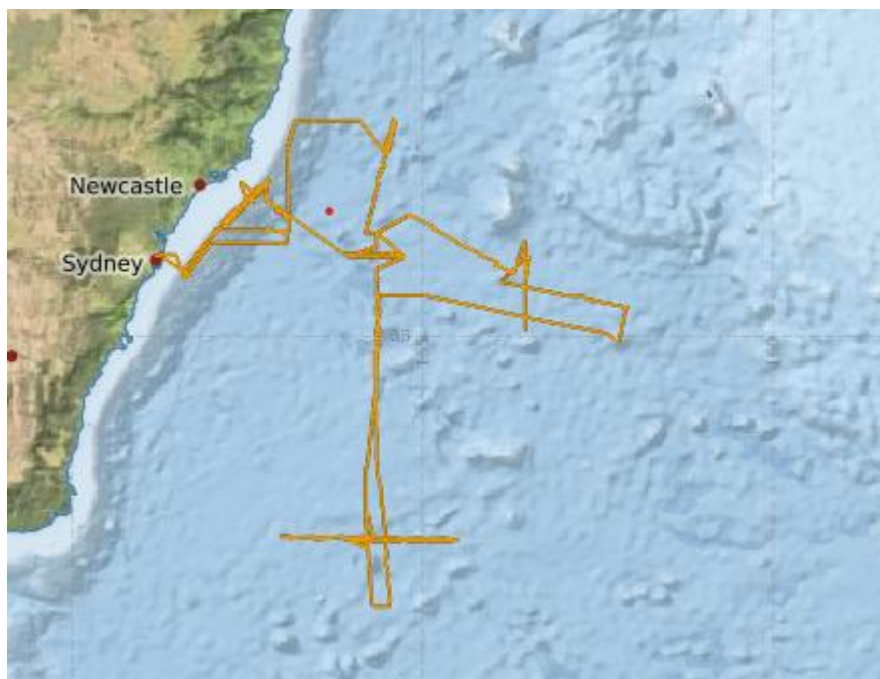


Figure 1. Voyage track

3 Key personnel list

Table 2: Key Personnel list

Name	Role	Organisation
Professor Moninya Roughan	Chief Scientist	UNSW
Linda Gaskell	Voyage Manager	CSIRO
Peter Hughes	Hydrochemist	CSIRO
Narendra Pati	Hydrochemist	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Maddy Lahm	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Table 3: Sample Type and Number Assayed

Analysis	Samples Assayed	Type
Salinity	1021	CTD
	18	TSG
Dissolved Oxygen	1019	CTD
Nutrients (AA3)	1872	CTD
	234	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 83 CTD deployments were sampled by:
 - Science participants lead by Amandine Schaeffer and Shane Keating.
 - No bottles were fired/data collected on CTD 2, 14 and 36 due to technical issues.

4.1.2 Thermosalinograph (TSG) samples

- 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.
- TSG sampling team: Narendra Pati and Peter Hughes
- Refer to voyage EVERlog for TSG sample information.

4.2 Data Processing Overview

4.2.1 Conventional hydrology data

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).

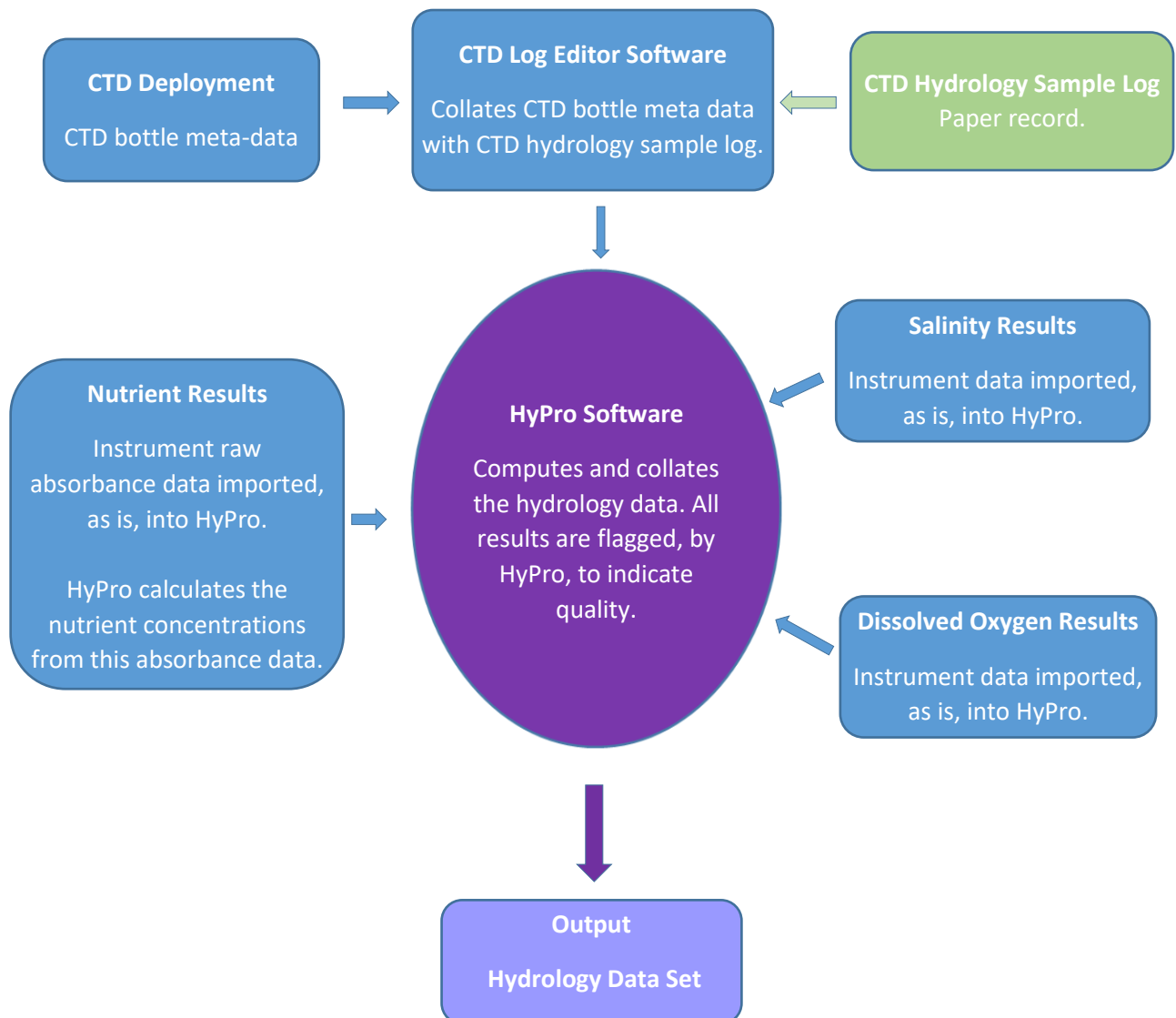


Figure 2. Hydrology Data Processing Flow Diagram.

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. Bath temperature 24.0°C
Software	Ocean Scientific International Ltd (OSIL) Data Logger version 1.2
Hydrochemistry Methods	Sampling: WI_Sal_002 Analysis: SOP 006
Accuracy	± 0.001 practical salinity units
Reference Material	OSIL IAPSO – Batch P166, use by 06/04/2025, $K_{15} = 0.99987$ 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 the measurement.
Lab Temperature	Mean 22.8°C SD 0.7°C
Analysts	Narendra Pati, Maddy Lahm, Peter Hughes and Merinda McMahon
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 0.05 PSU. The larger differences are for shallow samples across the sudden changes in the thermohaline profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the [NCMI DataLibrarians@csiro.au](mailto:NCMI_DataLibrarians@csiro.au) for corrected CTD data.

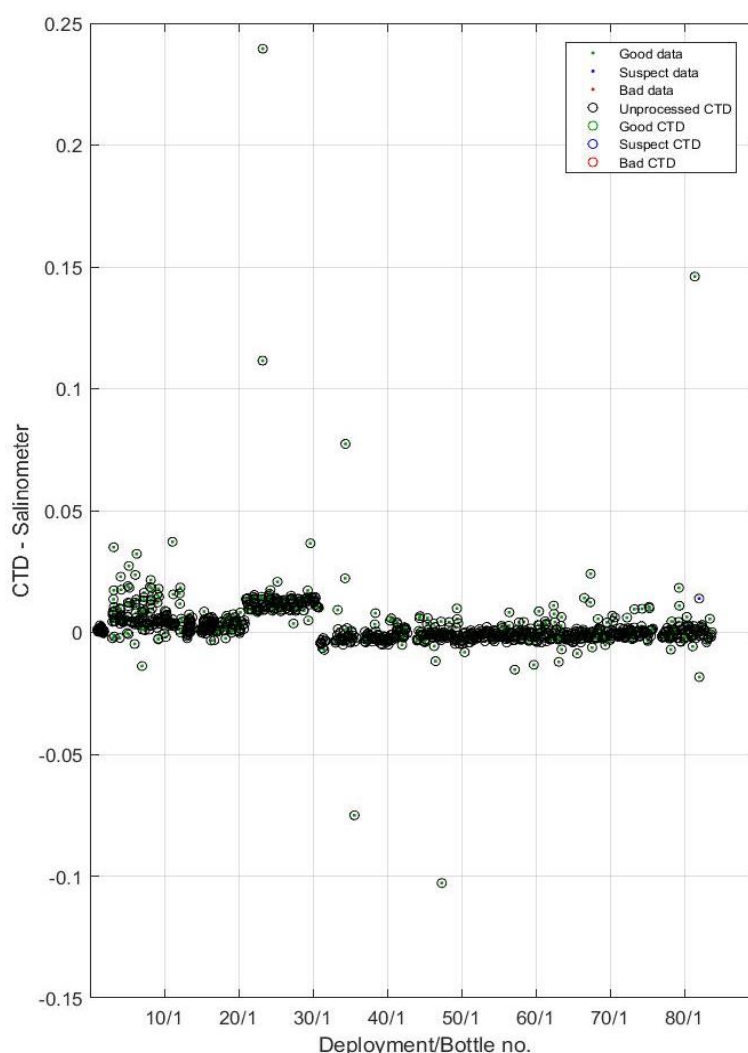


Figure 3. CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Black = UNPROCESSED. Units: PSU (dimensionless).

6 Dissolved Oxygen

6.1 Dissolved Oxygen Measurement Parameters

Table 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 Analysis: SOP 005
Accuracy	$\pm 0.5 \mu\text{mol L}^{-1}$
Lab Temperature	Mean 22.5°C SD 1.6°C
Sample Container type	140 mL glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis.
Analysts	Narendra Pati, Maddy Lahm, Merinda McMahon and Peter Hughes
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 $20 \mu\text{mol L}^{-1}$. The larger differences are for shallow samples across the sudden changes in the dissolved oxygen profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the [NCMI DataLibrarians@csiro.au](mailto:NCMI_DataLibrarians@csiro.au) for corrected CTD data.

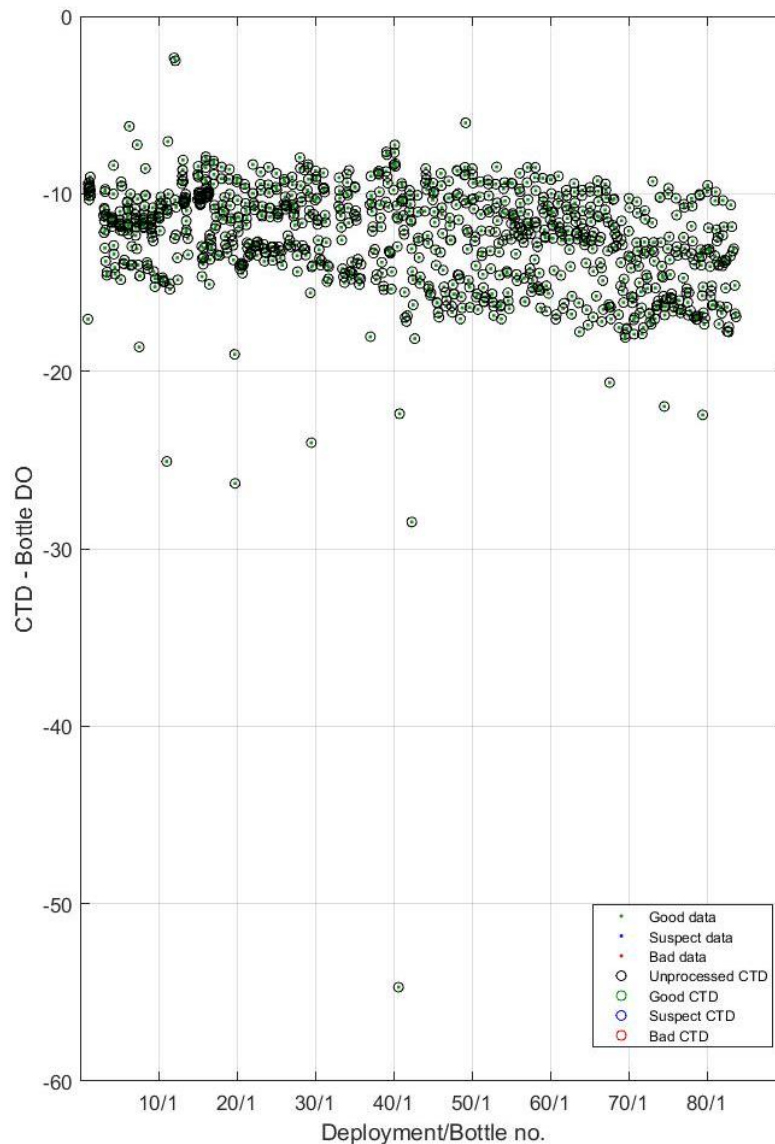


Figure 4. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Red = BAD. Black = UNPROCESSED. Units: $\mu\text{mol L}^{-1}$. *Note: Bad oxygen bottle data is listed in appendix 8.5.

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 as follows:

CTD Deployment 1 to 83: Mean: 0.201821 N
SD: 0.00017 (n=15)

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.

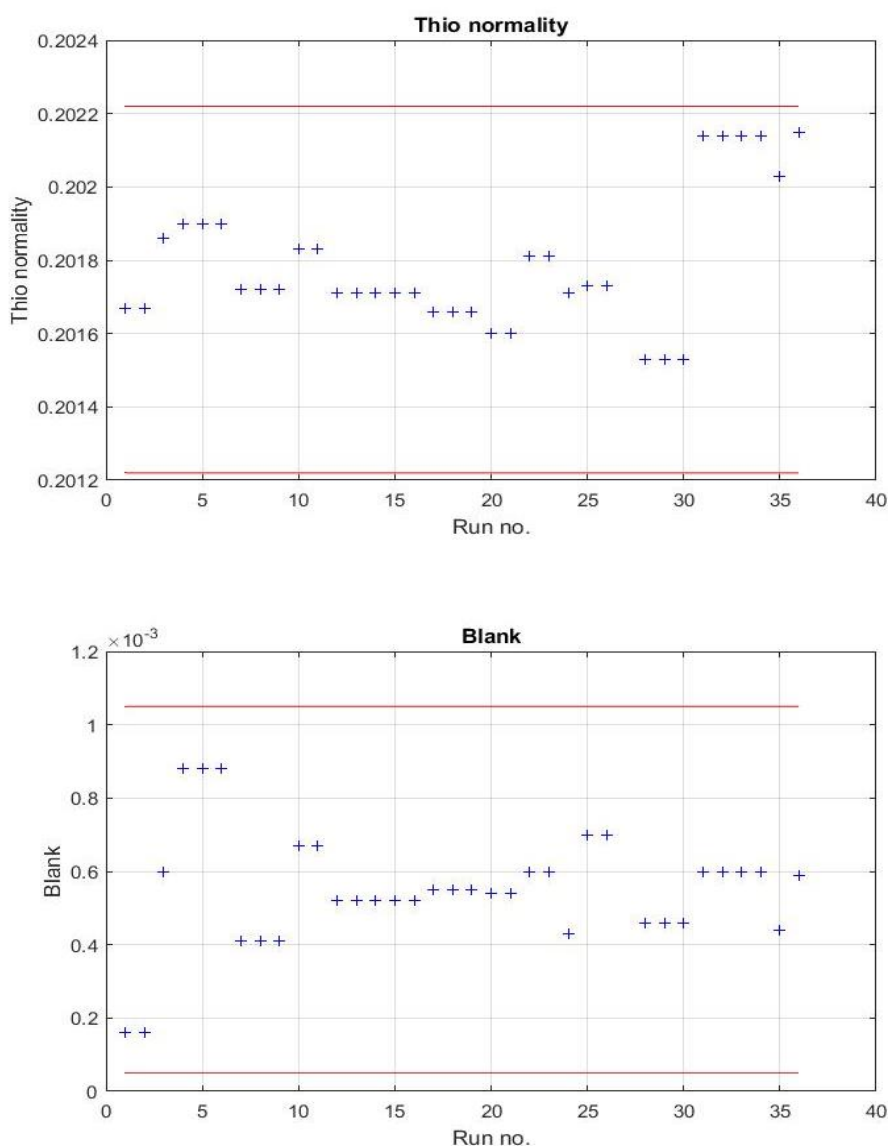


Figure 5. Thiosulphate standardisation and blank correction plots.

7 Nutrients

7.1 Nutrient Measurement Parameters

Table 6: Nutrient measurement parameters analysed with Seal AA3HR segmented flow analyser. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details					
Instrument	Seal AA3HR segmented flow analyser				
HyPro version	5.7				
Operating Software	AACE 7.10				
Hydrochemistry Sampling Method	WI_Nut_001				
Hydrochemistry analysis method	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrients	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Top concentration ($\mu\text{mol L}^{-1}$)	112.0	3.0	36.4	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 CO				
Sample Container	CTD: 50 mL HDPE with screw cap lids. Reused after acid wash with 10% HCl solution.				
Sample Storage	< 4 hours at room temperature after collection or < 12 hours at 4°C after collection				
Sample preparation	Assayed as neat. No filtration.				
Lab Temperature (°C)	Mean 22.5°C SD 1.6°C				
Analysts	Peter Hughes and Narendra Pati				
Comments	N/A				

7.2 Nutrient Methods

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

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

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-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 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 Kérouel 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.

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 WOCE¹).
- $0.02 \mu\text{mol L}^{-1}$ 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 Appendix 8.6.

¹ World Ocean Circulation Experiment

Table 7: HyPro 5.7 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	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 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 system.				
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 8.2.				

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_V06, Japanese KANSO certified RMNS lot CO was assayed in triplicate in each run to monitor accuracy. The certified values are listed in Table 8. Internal bulk quality control (BQC) was also analysed in each run for analysis on AA3HR segmented flow analyser.

For RMNS lot CO, NO_x, phosphate, and silicate were within 3% and nitrite within 0.04 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 8.2.

Table 8: RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: µmol L⁻¹

RMNS	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _x)
Lot CO	35.5515 ± 0.1638	1.2052 ± 0.0143	0.0410 ± 0.0410	16.2808 ± 0.1946

Table 9: RMNS CO statistics for of this voyage. Units: µmol L⁻¹

RMNS CO	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _x)
Minimum	35.1	1.19	0.05	16.02
Maximum	35.8	1.24	0.08	16.47
Median	35.4	1.22	0.07	16.37
Mean	35.4	1.22	0.07	16.34
Repeatability	0.048	0.004	0.002	0.014

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.

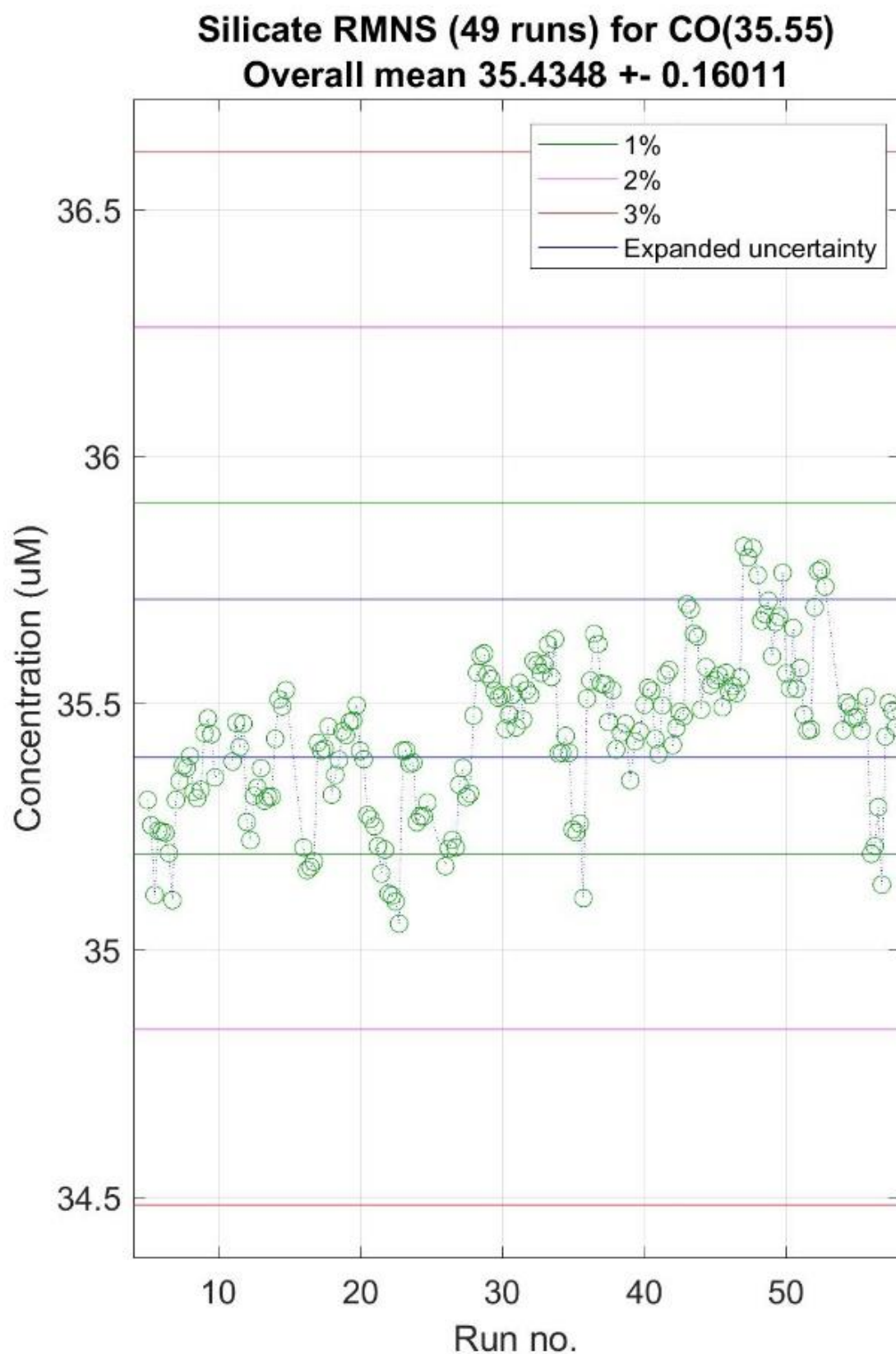


Figure 6. Silicate RMNS Plot ($\mu\text{mol L}^{-1}$)

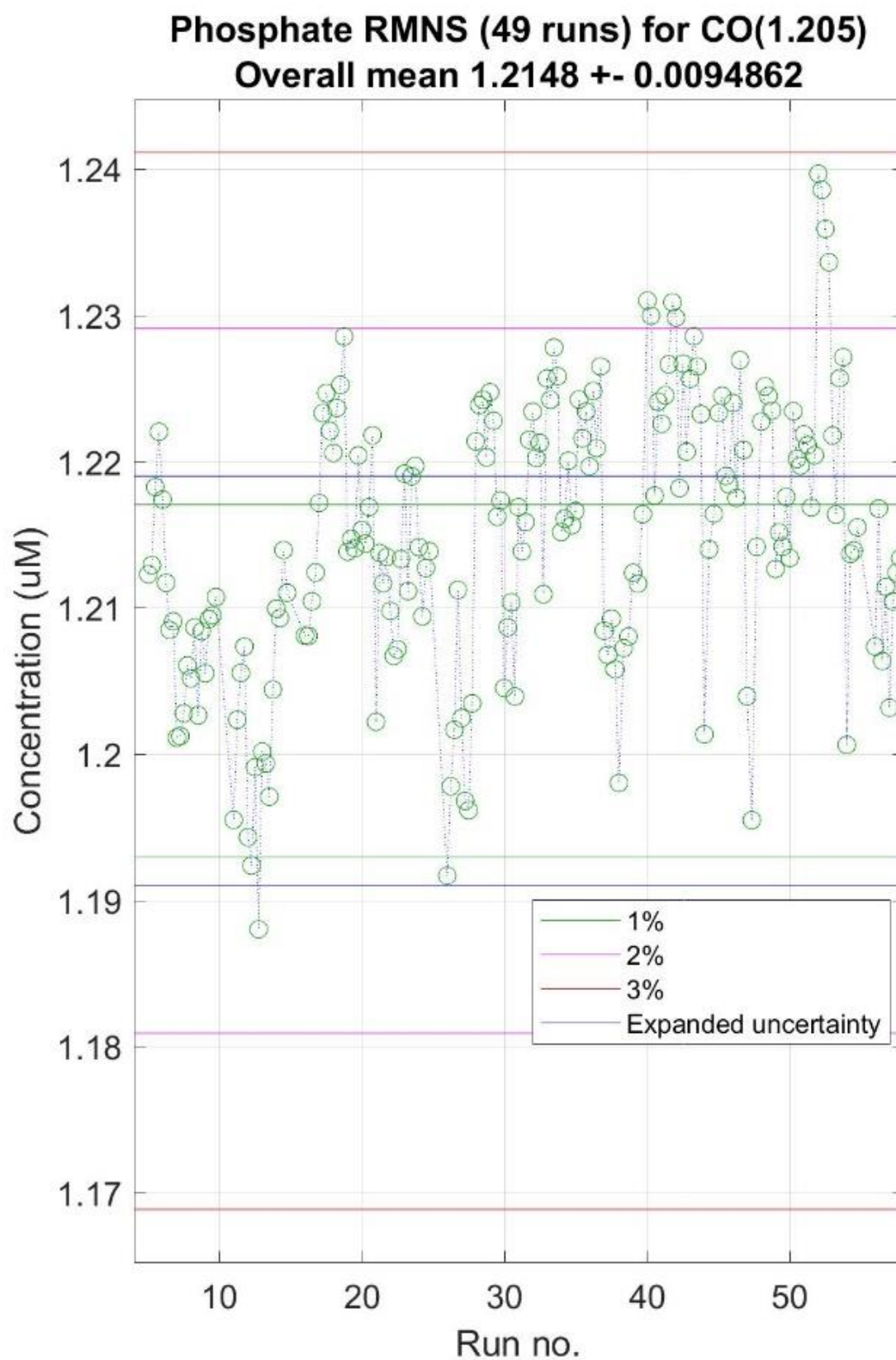


Figure 7. Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)

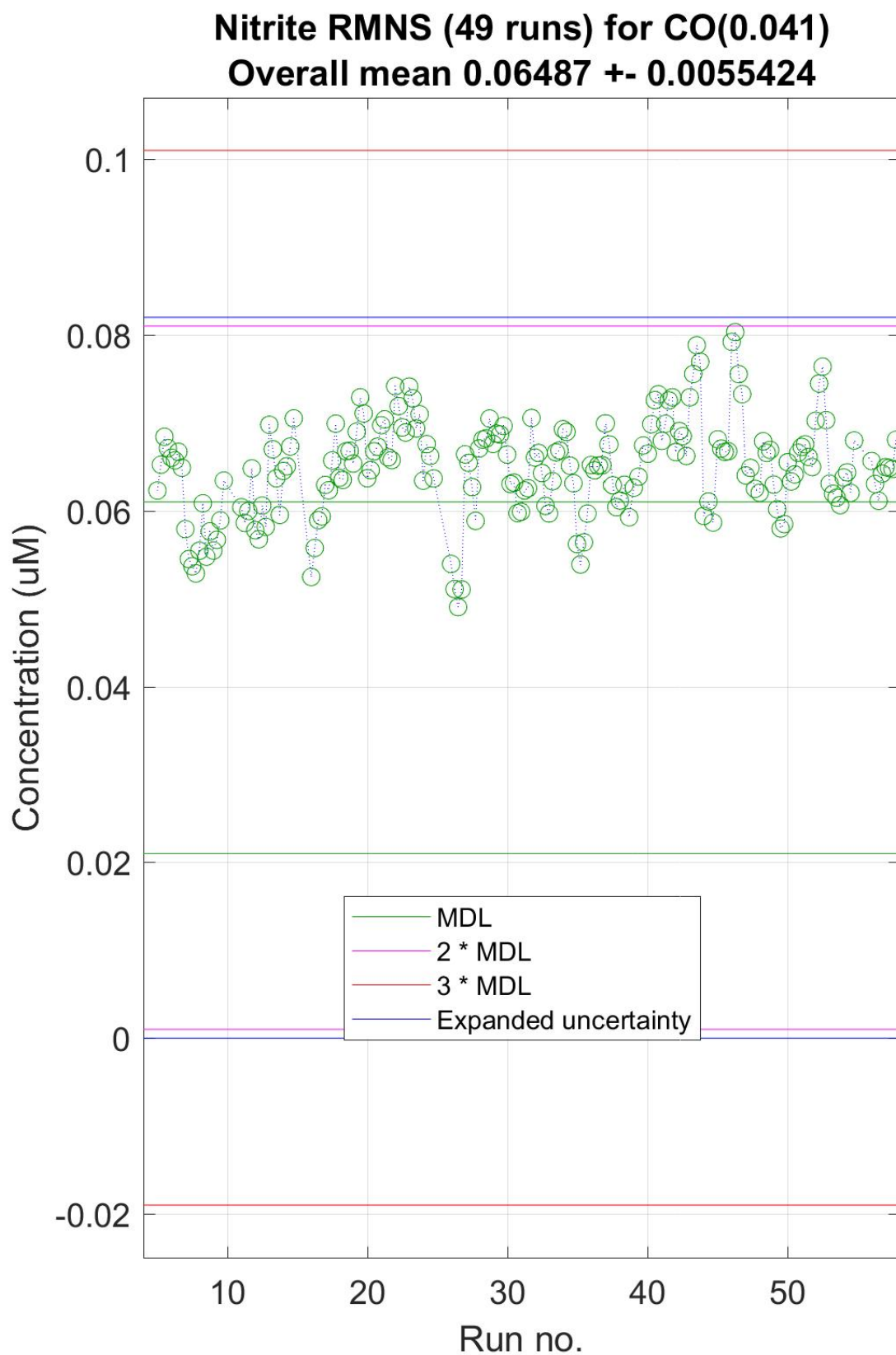


Figure 8. Nitrite RMNS Plot ($\mu\text{mol L}^{-1}$)

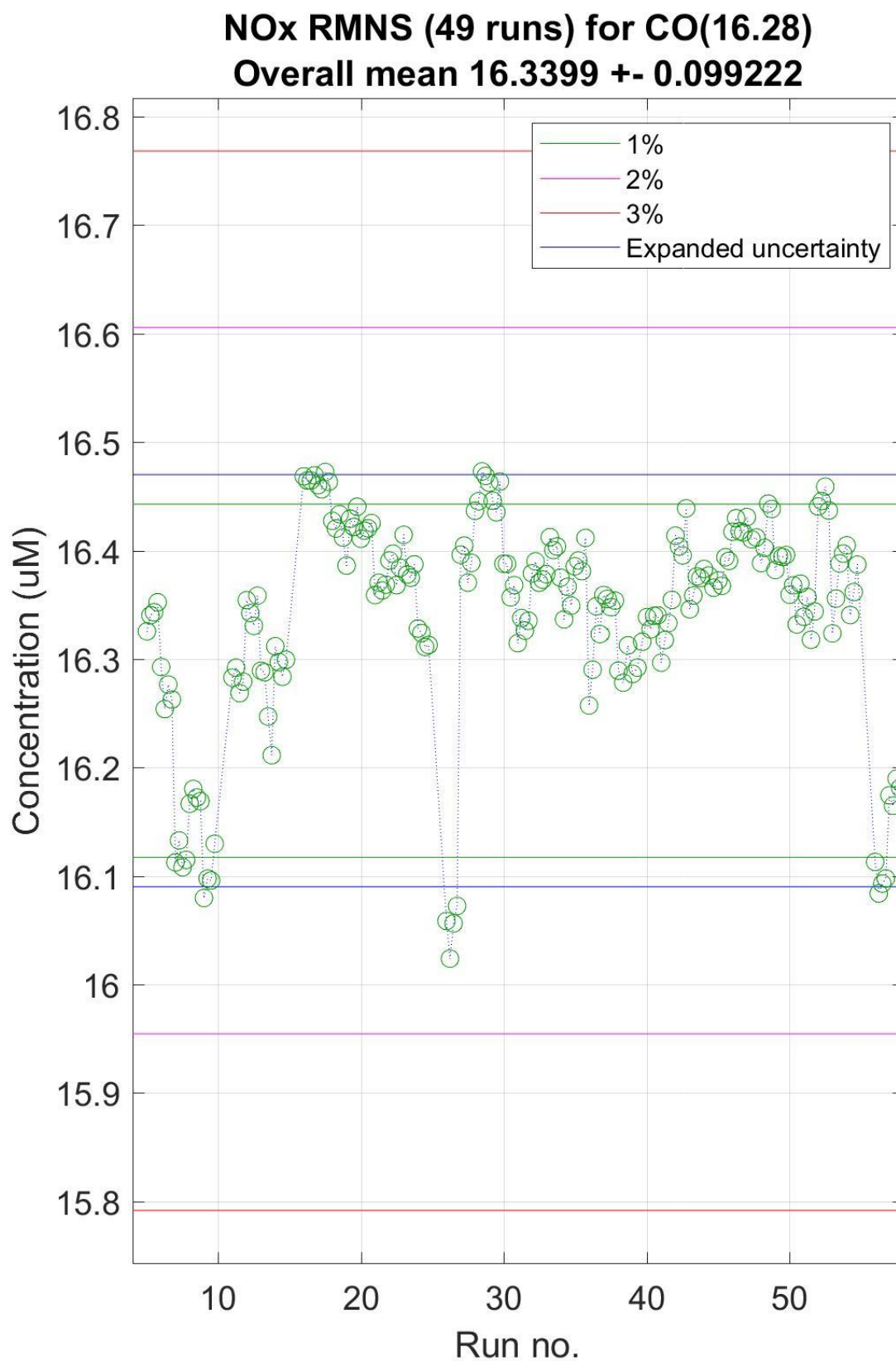


Figure 9. Nitrate + Nitrite (NOx) RMNS Plot ($\mu\text{mol L}^{-1}$)

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	±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	0.00	0.000	0.000	0.000	0.000
Standard Dev. Max	0.058	0.015	0.010	0.006	0.006
Standard Dev. Median	0.000	0.006	0.006	0.002	0.000
Standard Dev. Mean	0.024	0.004	0.003	0.002	0.001
Precision of MDL (stdev)	0.024	0.004	0.003	0.002	0.001

7.8 Sampling Precision

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 12).

Table 12: CTD deployment 1. 14 bottles at 1000 dbar. Units: $\mu\text{mol L}^{-1}$.

	Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrite (NO_2)	$\text{NO}_3 + \text{NO}_2$ (NO_x)	Ammonia (NH_4)
Minimum	47.90	2.17	0.01	31.74	0.00
Maximum	48.30	2.19	0.02	31.93	0.01
Mean	48.14	2.19	0.02	31.82	0.00
Variance	0.12	0.01	0.00	0.07	0.01

Duplicate nutrient samples were collected from the greatest depth 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. 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.

7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: **14.35**

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.

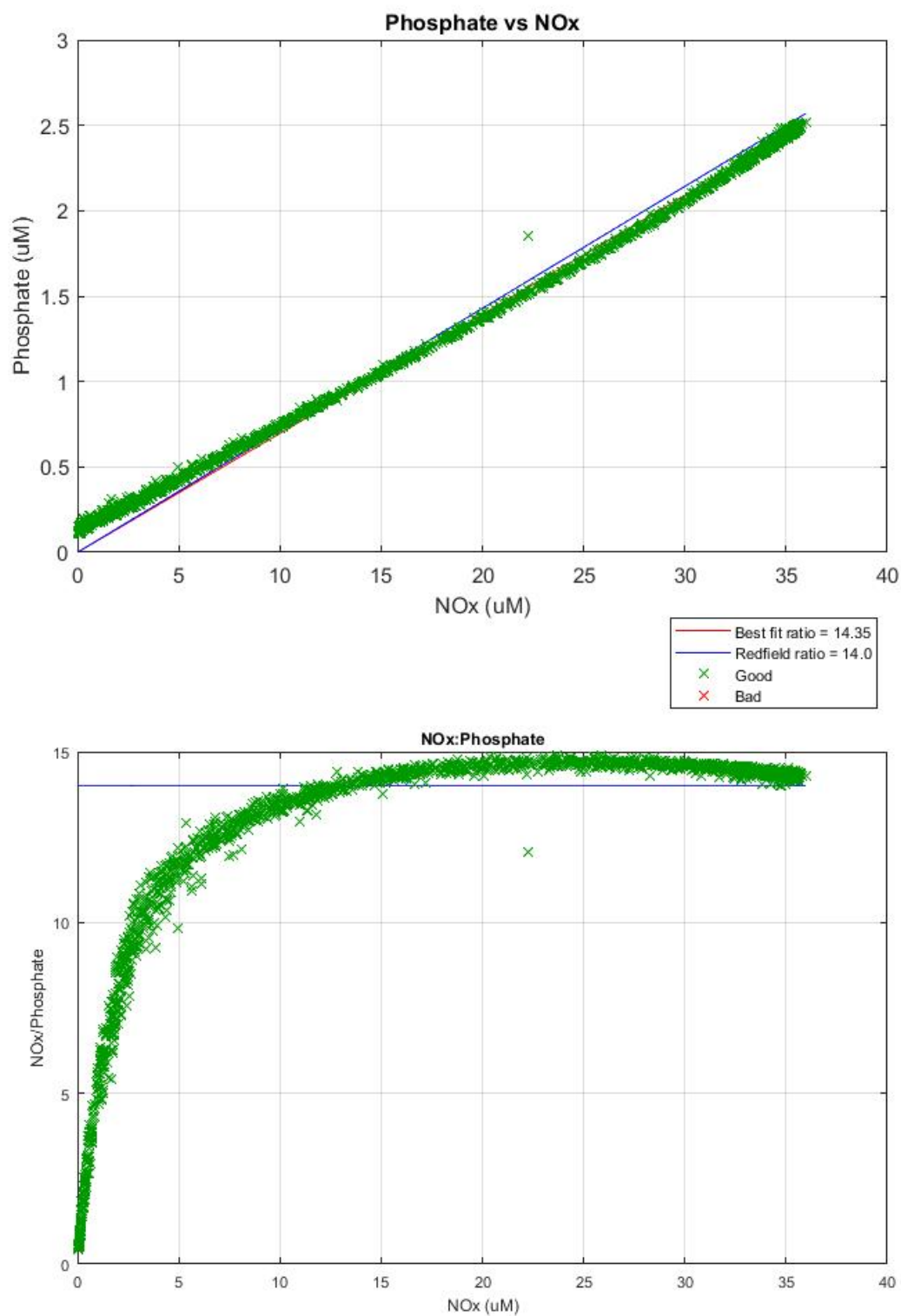


Figure 10. Redfield ratio plots. Note: please refer to appendix 8.6 for explanation of the outlier point in this plot.

7.10 Temperature and Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry laboratory and within the AA3HR instrument were measured and logged in the following locations:

- 1) Above the AA3 auto sampler
- 2) On each deck of the AA3 chemistry modules, post heater
- 3) Inside each detector of the AA3

Data was measured using Ruuvi temperature and humidity sensors and logged and monitored in Grafana. Measurements were recorded every 20 minutes for the duration of the voyage. If required, this data will be provided on request.

8 Appendix

8.1 Salinity: Reference material used

OSIL IAPSO Standard Seawater	
Batch	P166
Use by date	06/04/2025
K ₁₅	0.99987
PSU	34.995

OSIL IAPSO Standard Seawater	
Batch	P167
Use by date	21/02/2026
K ₁₅	0.99988
PSU	34.995

8.2 Nutrients: RMNS results for each CTD Deployment

8.2.1 Lot CO

Run analysis #	CTD Deployment #	UWY Samples	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)
5	1, 3	N/A	35.227	1.216	16.340	0.066
6	4, 5, 6	N/A	35.193	1.212	16.271	0.066
7	7, 8	N/A	35.347	1.203	16.117	0.055
8	9, 10	N/A	35.336	1.206	16.172	0.057
9	11, 12	N/A	35.424	1.209	16.101	0.059
11	13	N/A	35.428	1.203	16.281	0.061
12	15	24 – 32	35.280	1.193	16.346	0.058
13	16	33 – 48	35.322	1.200	16.259	0.065
14	17	49 – 53	35.489	1.211	16.298	0.067
16	18	N/A	35.179	1.210	16.467	0.057

17	19, 20	N/A	35.421	1.222	16.463	0.065
18	21	N/A	35.374	1.225	16.423	0.065
19	22	N/A	35.464	1.216	16.419	0.070
20	23, 24	N/A	35.332	1.217	16.419	0.066
21	25, 26	N/A	35.205	1.210	16.365	0.068
22	27, 28	N/A	35.094	1.209	16.385	0.071
23	29, 30	N/A	35.391	1.217	16.389	0.072
24	31	54 – 70	35.275	1.213	16.319	0.065
26	32, 33	N/A	35.201	1.201	16.053	0.051
27	34, 35	N/A	35.332	1.200	16.390	0.063
28	37, 38	N/A	35.558	1.222	16.456	0.068
29	39, 40	N/A	35.536	1.220	16.452	0.069
30	41, 42	N/A	35.489	1.207	16.375	0.063
31	43	71 – 73	35.496	1.217	16.328	0.064
32	44, 45	N/A	35.560	1.219	16.378	0.064
33	46, 47	84 – 89	35.595	1.226	16.399	0.064
34	48, 49	97 – 106	35.407	1.217	16.357	0.067
35	50, 51	107, 109	35.210	1.221	16.392	0.057
36	N/A	110 – 135 + 145	35.578	1.223	16.305	0.065
37	52	N/A	35.516	1.208	16.354	0.065
38	53	N/A	35.434	1.204	16.293	0.061
39	54	N/A	35.403	1.213	16.298	0.065
40	55, 56	N/A	35.495	1.226	16.337	0.071
41	57, 58	N/A	35.504	1.226	16.325	0.071
42	59	137 – 144 + 146 – 167	35.455	1.224	16.413	0.068
43	60	168 – 173	35.666	1.226	16.364	0.076
44	61	174 – 182	35.532	1.211	16.375	0.060
45	62, 63	N/A	35.539	1.221	16.381	0.067
46	64, 65	N/A	35.532	1.222	16.420	0.077
47	66, 67	N/A	35.809	1.205	16.418	0.064
48	68, 69	N/A	35.703	1.224	16.418	0.066
49	70, 71	183 – 187	35.674	1.215	16.392	0.060
50	72, 73	188 – 192	35.568	1.219	16.357	0.065
51	74, 75	193 – 199	35.484	1.220	16.339	0.066

52	76, 77	N/A	35.742	1.237	16.446	0.073
53	78, 79	N/A	N/A	1.223	16.366	0.062
54	80, 81	N/A	35.477	1.211	16.374	0.065
55	78, 79	N/A	35.476	N/A	N/A	N/A
56	82, 83	200 – 210	35.206	1.210	16.097	0.064
57	N/A	211 – 234	35.467	1.210	16.177	0.066

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

8.3 Measured MDL for each CTD deployment

Run analysis #	CTD Deploy ment #	UWY 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)	Ammonia (NH ₄)
5	1, 3	N/A	0.098	0.006	0.003	0.005	0.005
6	4, 5, 6	N/A	0.033	0.005	0.004	0.008	0.008
7	7, 8	N/A	0.076	0.007	0.010	0.006	0.006
8	9, 10	N/A	0.058	0.006	0.002	0.006	0.002
9	11, 12	N/A	0.026	0.024	0.018	0.014	0.002
11	13	N/A	0.045	0.014	0.011	0.003	0.001
12	15	24 – 32	0.102	0.004	0.010	0.005	0.002
13	16	33 – 48	0.073	0.002	0.004	0.012	0.002
14	17	49 – 53	0.057	0.007	0.009	0.005	0.002
16	18	N/A	0.031	0.007	0.012	0.018	0.042
17	19, 20	N/A	0.022	0.009	0.011	0.004	0.003
18	21	N/A	0.011	0.010	0.018	0.005	0.022

19	22	N/A	0.028	0.012	0.010	0.003	0.003
20	23, 24	N/A	0.133	0.004	0.006	0.001	0.005
21	25, 26	N/A	0.033	0.005	0.003	0.002	0.001
22	27, 28	N/A	0.040	0.017	0.006	0.003	0.001
23	29, 30	N/A	0.033	0.003	0.004	0.002	0.004
24	31	54 – 70	0.023	0.001	0.004	0.002	0.002
26	32, 33	N/A	0.036	0.014	0.012	0.007	0.002
27	34, 35	N/A	0.021	0.021	0.006	0.002	0.002
28	37, 38	N/A	0.083	0.002	0.005	0.002	0.003
29	39, 40	N/A	0.056	0.002	0.006	0.002	0.002
30	41, 42	N/A	0.038	0.011	0.005	0.004	0.004
31	43	71 – 73	0.042	0.012	0.001	0.007	0.003
32	44, 45	N/A	0.008	0.009	0.030	0.003	0.002
33	46, 47	84 – 89	0.037	0.011	0.012	0.006	0.002
34	48, 49	97 – 106	0.008	0.010	0.004	0.004	0.003
35	50, 51	107, 109	0.138	0.018	0.008	0.006	0.004
36	N/A	110 – 135 + 145	0.115	0.011	0.009	0.002	0.005
37	52	N/A	0.039	0.007	0.002	0.004	0.003
38	53	N/A	0.038	0.008	0.017	0.009	0.010
39	54	N/A	0.040	0.005	0.009	0.006	0.003
40	55, 56	N/A	0.058	0.014	0.005	0.007	0.002
41	57, 58	N/A	0.034	0.006	0.010	0.003	0.006
42	59	137 – 144 + 146 – 167	0.081	0.007	0.001	0.010	0.004
43	60	168 – 173	0.046	0.003	0.003	0.004	0.004
44	61	174 – 182	0.043	0.018	0.006	0.005	0.085
45	62, 63	N/A	0.059	2.983	0.015	0.005	0.036
46	64, 65	N/A	0.015	0.005	0.002	0.016	0.036
47	66, 67	N/A	0.137	0.039	0.013	0.005	0.032
48	68, 69	N/A	0.111	0.004	0.007	0.004	0.025
49	70, 71	183 – 187	0.014	0.014	0.011	0.002	0.003
50	72, 73	188 – 192	0.110	0.007	0.012	0.004	0.004
51	74, 75	193 – 199	0.049	0.004	0.007	0.003	0.006
52	76, 77	N/A	0.135	0.013	0.005	0.003	0.003

53	78, 79	N/A	N/A	0.015	0.005	0.003	0.003
54	80, 81	N/A	0.091	0.021	0.007	0.007	0.003
55	78, 79	N/A	0.055	N/A	N/A	N/A	N/A
56	82, 83	200 – 210	0.061	0.009	0.004	0.002	0.024
57	N/A	211 – 234	0.020	0.002	0.012	0.005	0.003

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
40	18	133	Missed measurement, analyst error

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	2	133	Lid placed in sample upside down therefore unable to achieve acceptable seal. Samples exposed to air.
10	3	133	Lid placed in sample upside down therefore unable to achieve acceptable seal. Samples exposed to air.
11	3	133	Sample re-collected at end as air bubble was in original sample. Re-sample is a an outlier – contaminated with oxygen that entered the niskin bottle once cracked open
13	28	133	Titration aborted, analyst error
19	30	133	Titration aborted, analyst error
28	1	133	Titration aborted, analyst error
46	21	133	Air bubble in sample
48	9	133	Titration aborted, analyst error
49	9	133	Titration aborted, analyst error

8.6 Missing or Suspect Nutrient 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	Analyte	Flag	Reason for Flag
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20	9	PO ₄	65	Phosphate looks like an outlier in the plots, especially in the Redfield ratio plot, however there is no indication from an analysis standpoint that this data point is bad.
33	47	All	65	All nutrients appear to be outliers in the waterfall plot. Indication of a potential bottle misfire.

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.

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