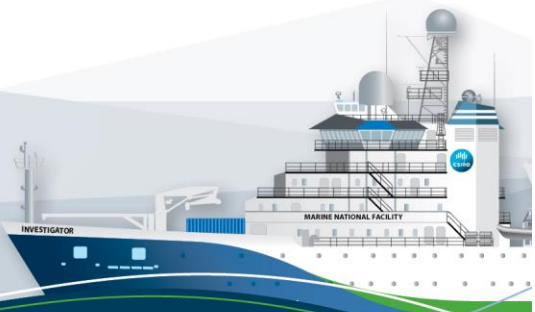
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	IN2023_V02
Chief Scientist	Martin Jutzeler
Voyage title:	Gigantic submarine landslide offshore western Tasmania: risk mitigation for shelf derived tsunami in Australia
Report compiled by:	Pavie Nanthasurasak and Maddy Lahm



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1 Executive Summary

1.1 Objectives

The scientific purpose of in2023_v02 was to investigate the nature of the continental shelf off the coast of western Tasmania, a 20-40km wide shelf disrupted by small canyons and a particular 450 km3 submarine landslide deposit over a 50km stretch. At this time, this probe of what has been determined to be a head scarp failure resulting from the land sliding downslope 30-120km at 2000-4500m underwater is the first highly detailed examination of this feature.

Four main research aims have been outlined for this voyage. First, the morphology and internal structure of the landslide will be evaluated to better model the transport and sedimentation process of submarine landslide. Second, the numerical model of tsunami inundation will be constructed based on the quantitative data collected on this voyage to further explain the potential causes of failure of marine landslide as well as prediction of plausible collapse of similar shelf around Australia. Third, the major fault zones, highly mineralised Mount Read Volcanics, and shallow shelf will be extensively mapped for better understanding of geology and tectonism of Tasmania. Fourth, biodiversity around this region will be studied to enhance the knowledge on relationship between seafloor habitat features and spatial distribution of nutrients, ocean currents, and geomorphological variables.

Voyage activities including piston coring, dredging, seismic reflection, sub-bottom profiler, bathymetry, deep-towed camera, CTD, underway hydrochemistry analysis, water column surveying, epibenthic sleds and nets will be extensively utilised to accomplish the research aims. Apart of main voyage priority, piggyback projects including Blythe Star Shipwreck survey and ARGO floats deployment was also accomplished.

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.

On this voyage, AA100 auto analyser was setup in the Hydrochemistry Laboratory for continuous underway measurement during deep tow camera operation along the shelf and slope and storm bay transit. The AA100 measured Nitrate and Phosphate off the general clean seawater intake of RV Investigator. The underway measurements were made continually, but due to the nature of method and data processing this results in a calibrated data point every 120 seconds.

Underway nutrient analysis data points were matched using UTC time stamps, no time correction was applied to account for the residence time in the ships piping or in the instrument, meaning all data is offset by 7:35. The matching timestamp (.nc) file was generated by ship underway system and this timestamp file will be stored in CSIRO data centre and forwarded to scientist in charge of nutrient

analysis for this voyage. Discrete underway samples were also taken on this voyage (when possible) in times where AA100 components encounter issues resulting in missed timing of underway analysis with deep tow camera operations and/or transit. The discrete underway were taken every 15 minutes throughout the duration of the deep tow camera and/or transit, and they were analysed using AA3HR auto analyser.

Overall underway nutrients data analysed using AA100 was of medium to high quality. Undefined occasional issues with analysis channels resulted in higher nominal detection limit and higher RMNS value than expected in some analysis runs. However, actual concentration of the underway nutrients can be corrected using the method provide in appendix 8.2. *Please note that final data reported by hydrochemistry team has no data correction applied.*

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

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*."

Limnol. Oceanogr: Methods, 17(1): pp. 25-41.

doi:10.1002/lom3.10294

If publishing ammonium data, please cite the following:

Rees, C., Janssens, J., Sherrin, K., Hughes, P., Tibben, S., McMahon, M., McDonald, J., Camac, A., Schwanger, C. and Marouchos, A., (2021*) "Method for Reproducible Shipboard Segmented Flow Analysis Ammonium Measurement Using an In-House Reference Material for Quality Control."*

Frontiers in Marine Science, 8.

doi:10.3389/fmars.2021.581901

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	24/03/2023	30/04/2023
Time	0800	0730

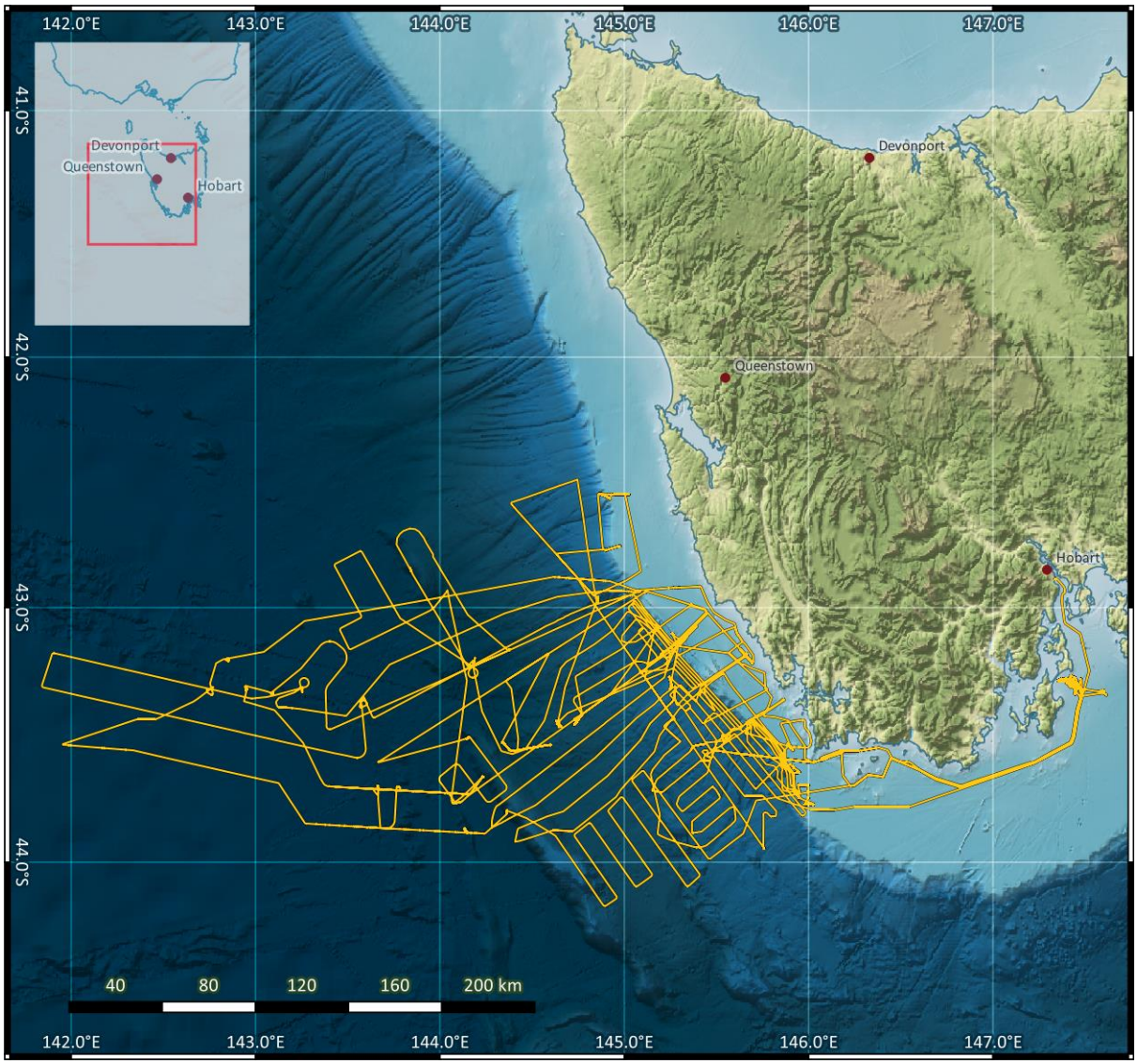


Figure 1. Voyage track

3 Key personnel list

Table 2: Key Personnel list

Name	Role	Organisation
Martin Jutzeler	Chief Scientist	UTAS
David Flynn	Voyage Manager	CSIRO
Margot Hind	Alternate Voyage Manager	CSIRO
Pavie Nanthasurasak	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	221	CTD
	11	TSG
Dissolved Oxygen	221	CTD
Nutrients (AA3)	221	CTD
	19	UWY
Underway nutrients (AA100)	402	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 21 CTD deployments were sampled by
    - Hydrochemistry: Pavie Nanthasurasak and Maddy Lahm
    - Science party: Claire Kain, Gabrielle King, Jack Dent, Ella Clausius, Frida Home, Shannon Frey, Stannislaus (Glen) Fabian, Peter Puskic, Benjamin Viola, Grace Cumming, Michaela Durston, Bronwyn Davies

4.1.2 Underway (UWY) and Thermosalinograph (TSG) samples

- Taken from the underway instrument clean seawater line supplying the pCO2 instrument in the underway laboratory. UWY samples were collected during deep tow camera operations.
- UWY and TSG samples collected by hydrochemistry. Results emailed to Vito Dirita (CSIRO) at the completion of the voyage.
- TSG sampling team: Pavie Nanthasurasak and Maddy Lahm
- UWY sampling team: Pavie Nanthasurasak and Maddy Lahm

Refer to voyage EVERLog for UWY and TSG sample information.

4.1.3 AA100 samples

- Continuously fed directly into the AA100 instrument through general clean seawater tap in hydrochemistry laboratory. No discrete samples were taken from this tap.

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).

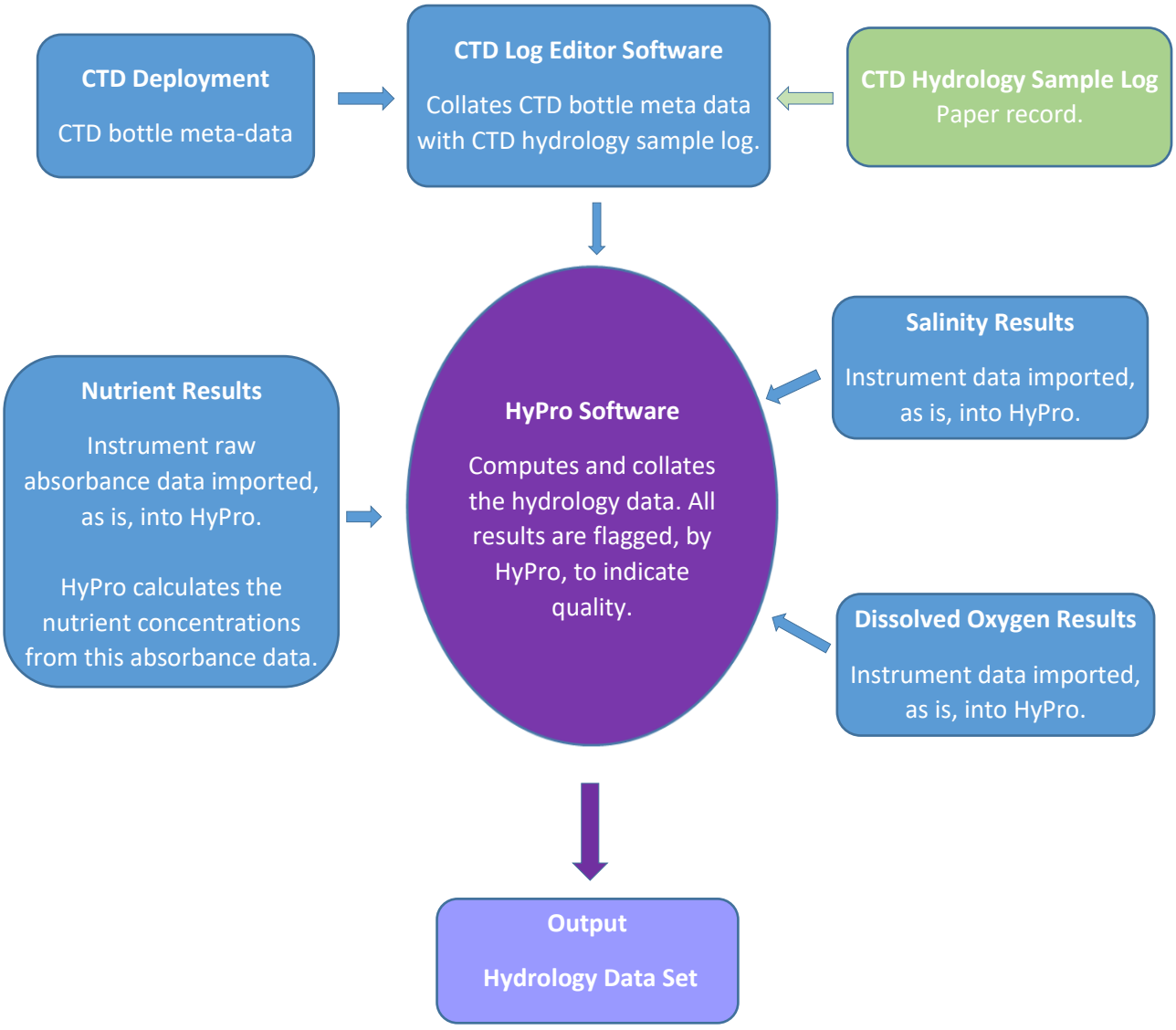


Figure 2. Conventional Hydrology Data Processing Flow Diagram.

4.2.2 AA100 auto analyser

The following flowchart provides an overview of how the AA100 was setup to analyse the underway seawater on the ship. Also outlined is the process of how the data is automatically matched with the ship underway data to provide latitude and longitude for the data points, which will again be offset by 7:35 due to length of underway piping and analysis time.

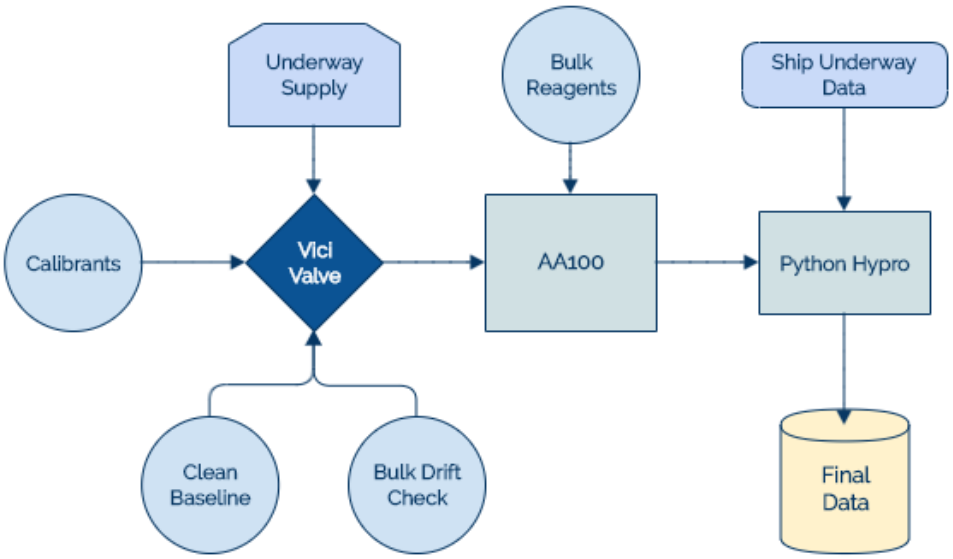


Figure 3. AA100 Hydrology Data Processing Flow Diagram.

5 Salinity

5.1 Salinity Measurement Parameters

Table 4: Salinity Measurement Parameters

Details	
HyPro Version	5.7
Instruments	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72088. Bath temperature 24.0°C
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 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
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 20.7°C SD 0.9°C
Analysts	Pavie Nanthasurasak and Maddy Lahm
Comments	See DAP report for CTD calibration details.

5.2 Salinity Method

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

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

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 set of samples per CTD deployment.

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

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

5.3 CTD Salinity vs Bottle Salinity Plot

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

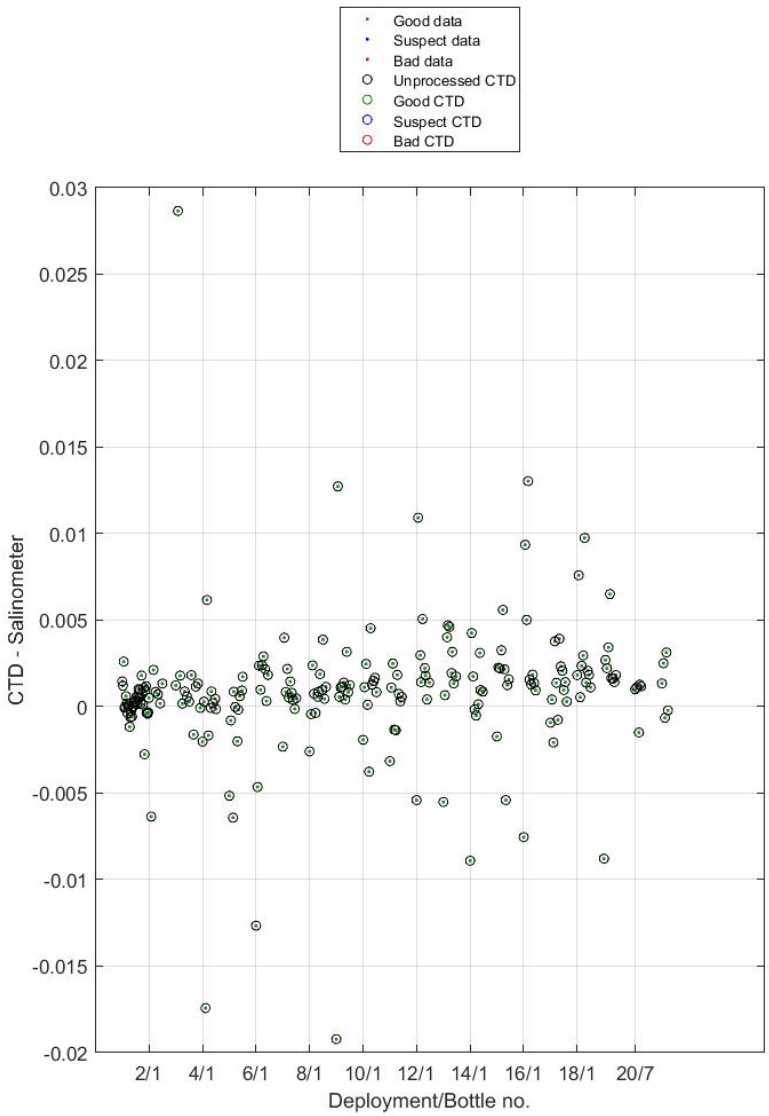


Figure 4. CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Black = UNPROCESSED. Units: PSU (dimensionless).

6 Dissolved Oxygen

6.1 Dissolved Oxygen Measurement Parameters

Table 5: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Scripps Automated Photometric Oxygen System (SIO)
Software	LVO2 ver 2.36 Scripps Institution of Oceanography (SIO)
Hydrochemistry Methods	Sampling: WI_DO_001 Analysis: SOP 005
Accuracy	± 0.5 µmol L^{-1}
Analysts	Pavie Nanthasurasak and Maddy Lahm
Lab Temperature (±1°C)	Mean 19.6°C SD 0.4°C
Sample Container type	140 mL glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis. All samples were analysed within ~48 hrs
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 15 µmol 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 for corrected CTD data.

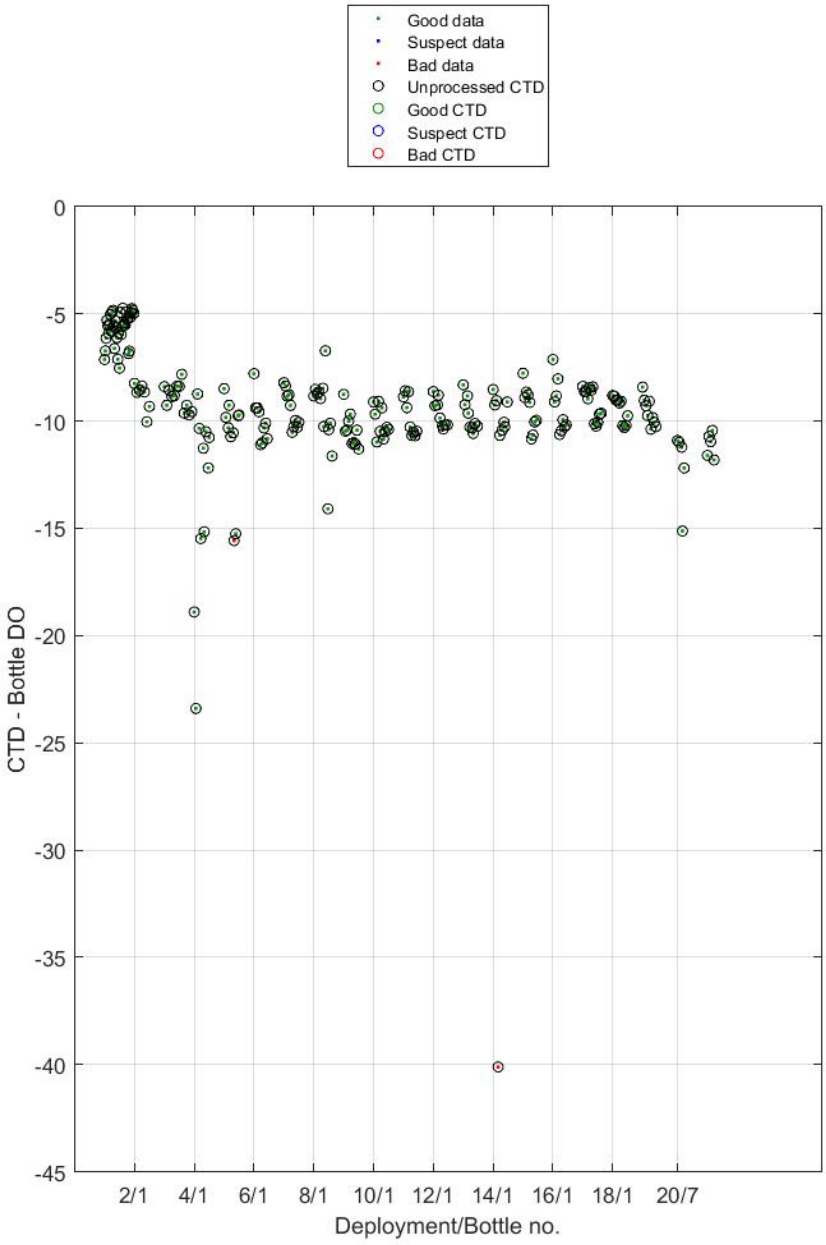


Figure 5. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot**.** The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Red = BAD. Black = UNPROCESSED. Units: µmol L^{-1}. **Note: Bad oxygen bottle data is listed in appendix 8.5.*

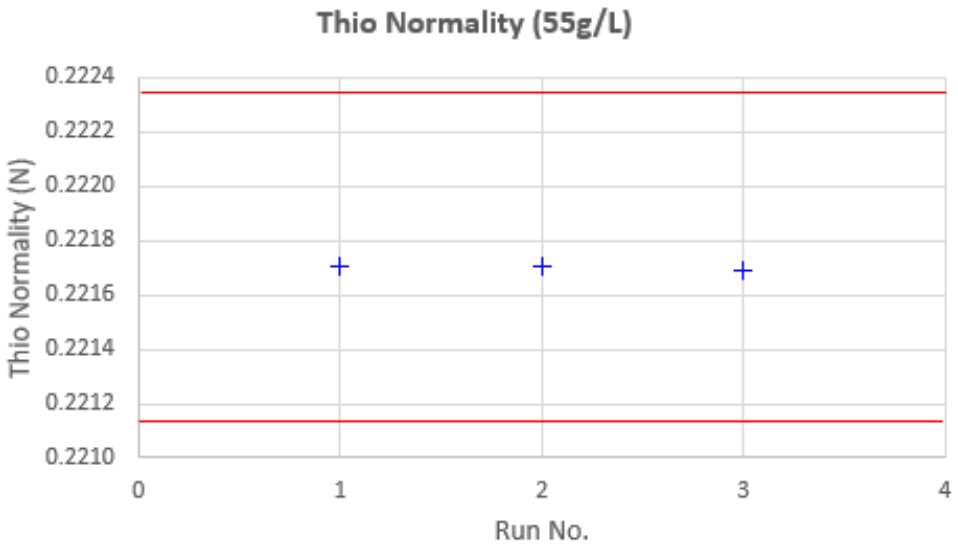
6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The variance in thiosulphate concentration is within our QC parameter of less than 0.0005 N between standardisations. Two batches of thiosulphate reagent were used during the voyage, one was 0.22 N (55 g/L) used for CTD deployment 1 to deployment 3 and another was 0.20 N (50 g/L) used for the rest of CTD deployment for this voyage. The mean normality as follows:

CTD Deployment 1 to 3:	Mean:	0.221661 N
	SD:	0.000008 (n=3)
CTD Deployment 4 to 21:	Mean:	0.202841 N
	SD:	0.000048 (n=7)

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.

For thiosulphate normality plots, the red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration. For blank plot, red lines indicate acceptable variation either side of the mean blank concentration. The titrant should not vary more than 0.0005 N between analyses.



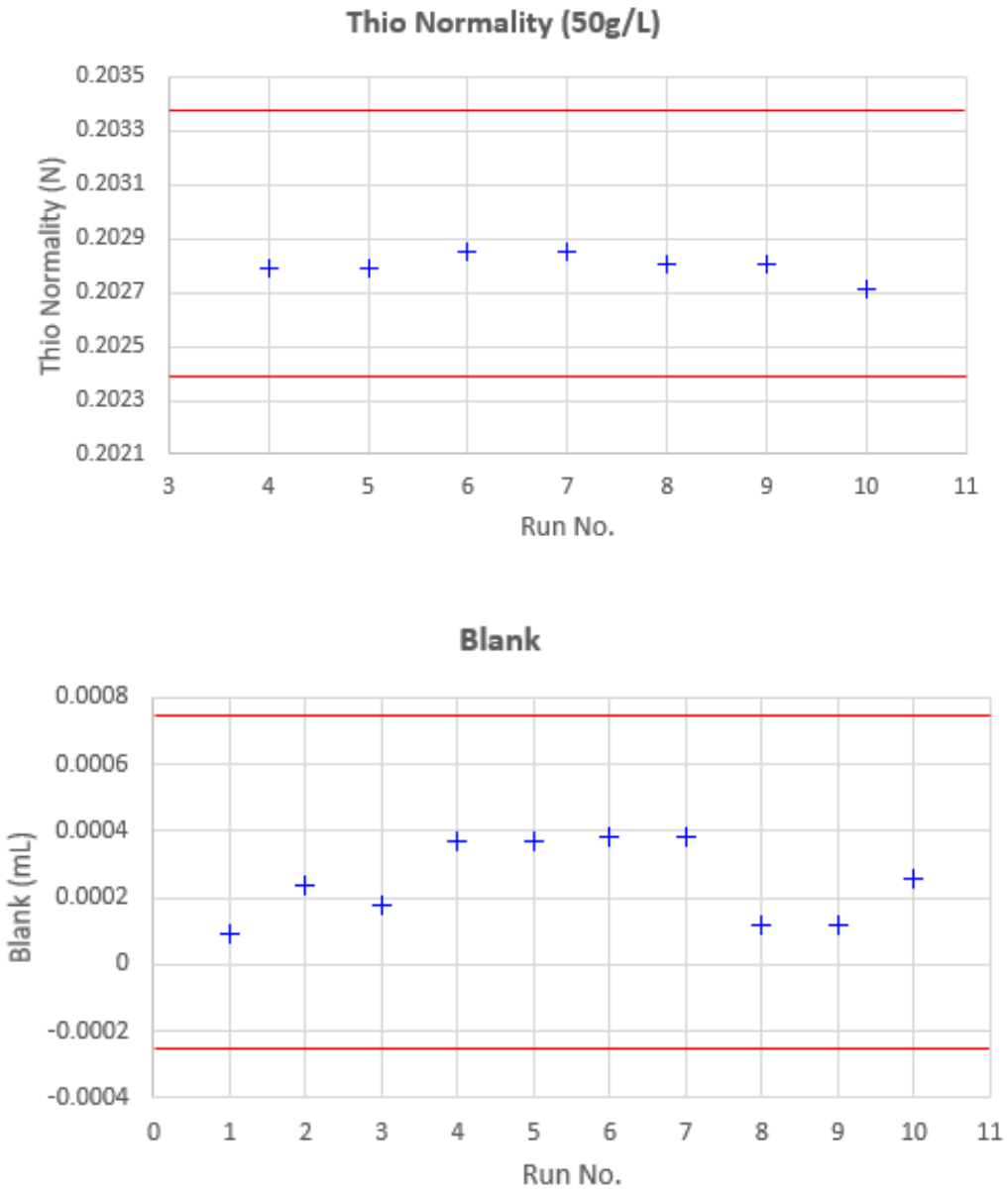


Figure 6. Thiosulphate standardisation and blank correction plots.

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 (µmol L^{-1})	140.0	3.0	42.0	1.4	2.0
Method detection limit (µmol L^{-1})	0.2	0.02	0.02	0.02	0.02
Reference Material	KANSO RMNS lot CP				
Sample Container	CTD: 50 mL HDPE with screw cap lids. Reused after acid wash with 10% HCl solution. UWY: 12 mL PP tubes with screw cap lids.				
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 19.6°C SD 0.4°C				
Analysts	Pavie Nanthasurasak and Maddy Lahm				
Comments	N/A				

Table 7: Nutrient measurement parameters analysed with Seal AA100 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 AA100 segmented flow analyser	
HyPro version	0.70	
Operating Software	AACE 7.10	
Hydrochemistry Sampling Method	N/A	
Hydrochemistry analysis method	AA100 SOP 01	AA100 SOP 02
Nutrients	Phosphate	Nitrate + Nitrite (NOx)
Top concentration (µmol L^{-1})	3.0	14.0
Method detection limit (µmol L^{-1})	0.02	0.02
Reference Material	KANSO RMNS lot CL	
Sample Container	N/A	
Sample Storage	N/A	
Sample preparation	Assayed as neat. No filtration.	
Lab Temperature (°C)	Mean 19.6°C SD 0.4°C	
Analysts	Pavie Nanthasurasak and Maddy Lahm	
Comments	UWY samples for AA100 was directly sampled from UWY tap in Hydrochemistry lab. The analysis was continuous without any discrete samples collected.	

7.2 Nutrient Methods

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

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

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS[1] Practical Workshop 2012 optimizing the antimony

catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

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

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

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

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.

[1] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

Nutrient samples are assayed on a Seal AA100 segmented flow auto-analyser fitted with 15 mm flow-cells for colorimetric measurements. Both channels are heated to 37°C on the manifold, and 40°C on the photometers. Underway water was fed into the AA100 via a cup that was continually overflowing, allowing the AA100 to draw an unpressurised sample. The cup only held a volume of approximately 20mL, with the seawater flowrate between 3.5-4.0L/min. With such a small dead volume and high flowrate, the sample could be as true as possible.

Phosphate (AA100 SOP 01): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS[1] Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

Nitrate (AA100 SOP 02): 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.

7.3 HyPro Processing Summary for Nutrients

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

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

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

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE[1]).
- 0.02umol^{-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

For AA100 auto analyser, HyPro was used to automatically assign latitude and longitude values to the data points. The latitude and longitude coordinates were extracted from the ships underway file by matching the UTC time stamps. Again, please note the offset of 7:35, which was not applied. Meaning the matching latitude and longitude for samples was when the measurement was recorded on the computer. To match this back to the original surface water the offset of 7:35 will need to be subtracted from all sample time stamps.

Table 8: 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	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}
Calibration Curve fit	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 on 14/03/2023) 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.

Table 9: HyPro 0.70 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	**Phosphate**	**Nitrate + Nitrite (NOx)**
Data Reported as	µmol L^{-1}	µmol L^{-1}
Calibration Curve fit	Linear	Linear
# of points in Calibration	6	6
Forced through zero	N	N
Matrix correction	N	N
Blank correction	N	N
Peak window defined by	HyPro	HyPro
Carryover correction (HyPro)	Y	Y
Baseline drift correction (HyPro)	Y	Y
Sensitivity drift correction (HyPro)	Y	Y
Data Adj for RMNS variance.	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 on 14/03/2023) 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.	N/A	
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, NOx, and nitrite in seawater.

Japanese KANSO certified RMNS lot CP (AA3 HR segmented flow analyser) and CL (AA100 segmented flow analyser) were assayed in triplicate in each run to monitor accuracy. The certified values are in Table 10. Internal bulk quality control (BQC) was also analysed in each run in triplicates for analysis on AA3HR segmented flow analyser.

For in2023_v02, the certified reference material results lot CP for NOx and silicate are within 1%, phosphate is within 2% and nitrite within 0.04 µmol L^{-1} of their certified mean concentration. For lot CL, both phosphate and NOx are around the range of expanded uncertainty 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 NO_3 and NO_2 values. The assayed RMNS values per CTD deployments are listed in the appendix 8.2.

Table 10: 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 CP	62.5687 ± 0.307	1.7951 ± 0.018	0.3175 ± 0.316	25.7136 ± 0.379
Lot CL	14.1347 ± 0.307	0.4353 ± 0.020	0.0154 ± 0.006	5.618 ± 0.160

Table 11: RMNS CP statistics for of this voyage. Units: µmol L^{-1}

RMNS CP	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
Minimum	62.500	1.790	0.312	25.460
Maximum	62.900	1.830	0.345	25.800
Mean	62.643	1.813	0.325	25.599
Median	62.650	1.820	0.325	25.585
Repeatability	0.094	0.011	0.008	0.094

Table 12: RMNS CL statistics for of this voyage. Units: µmol L^{-1}

RMNS CL	Phosphate (PO_4)	NO_3+ NO_2 (NO_X)
Minimum	0.448	5.474
Maximum	0.468	5.943
Mean	0.459	5.662
Median	0.457	5.553
Repeatability	0.006	0.204

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. Please note that plots for lot CL are representing only certified values and expanded uncertainty.

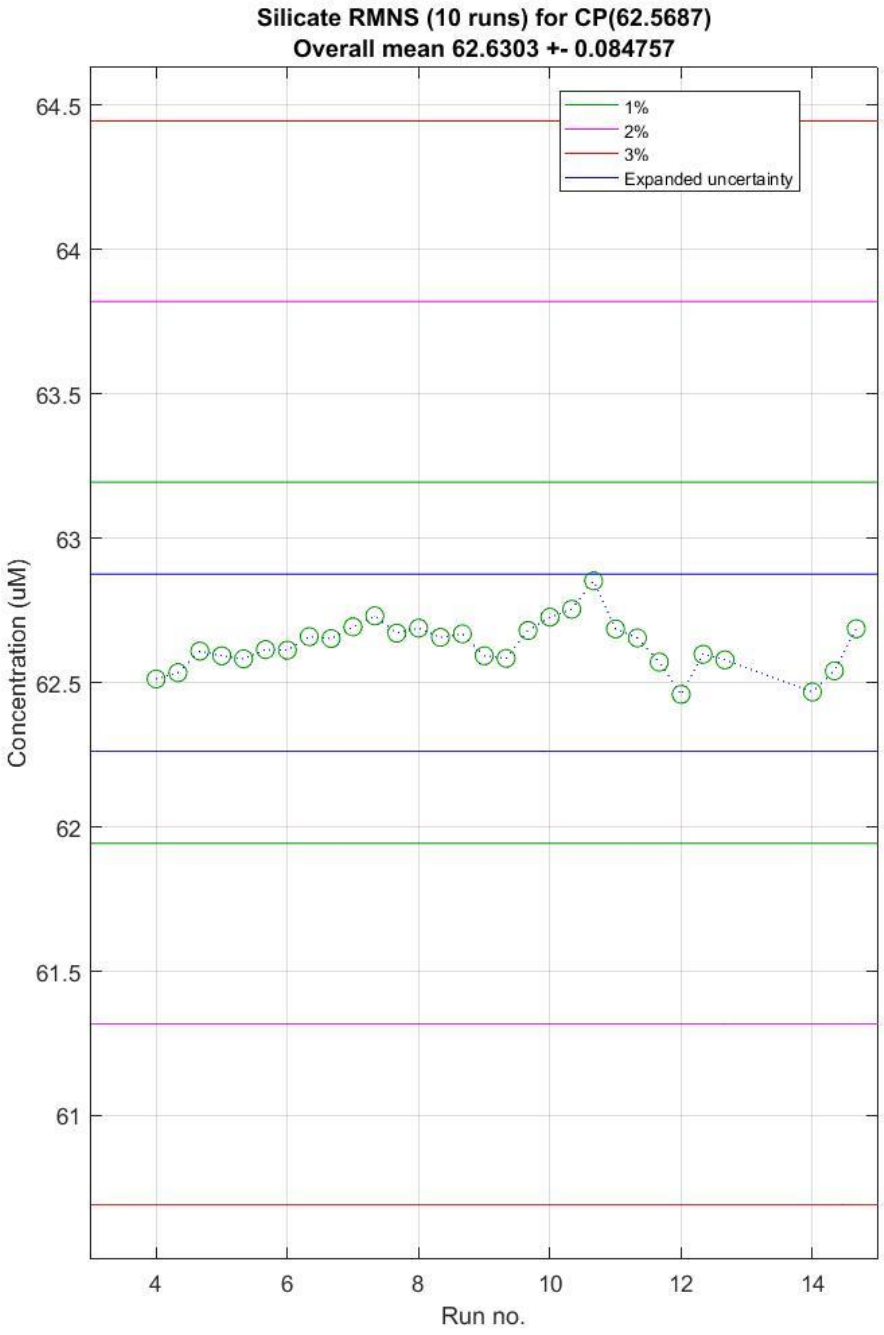


Figure 7. Silicate RMNS lot CP Plot (µmol L^{-1})

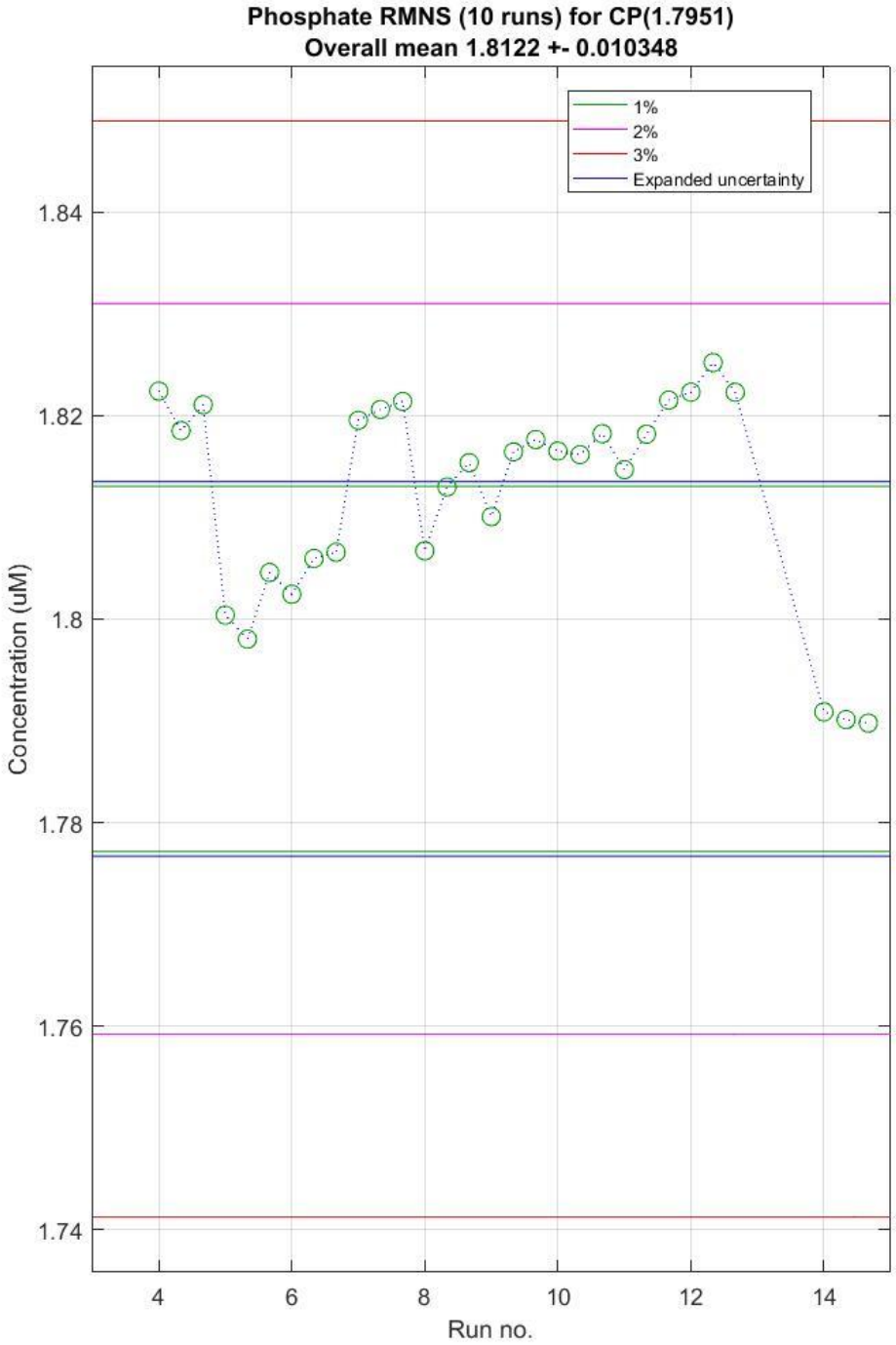


Figure 8. Phosphate RMNS lot CP Plot (µmol L^{-1})

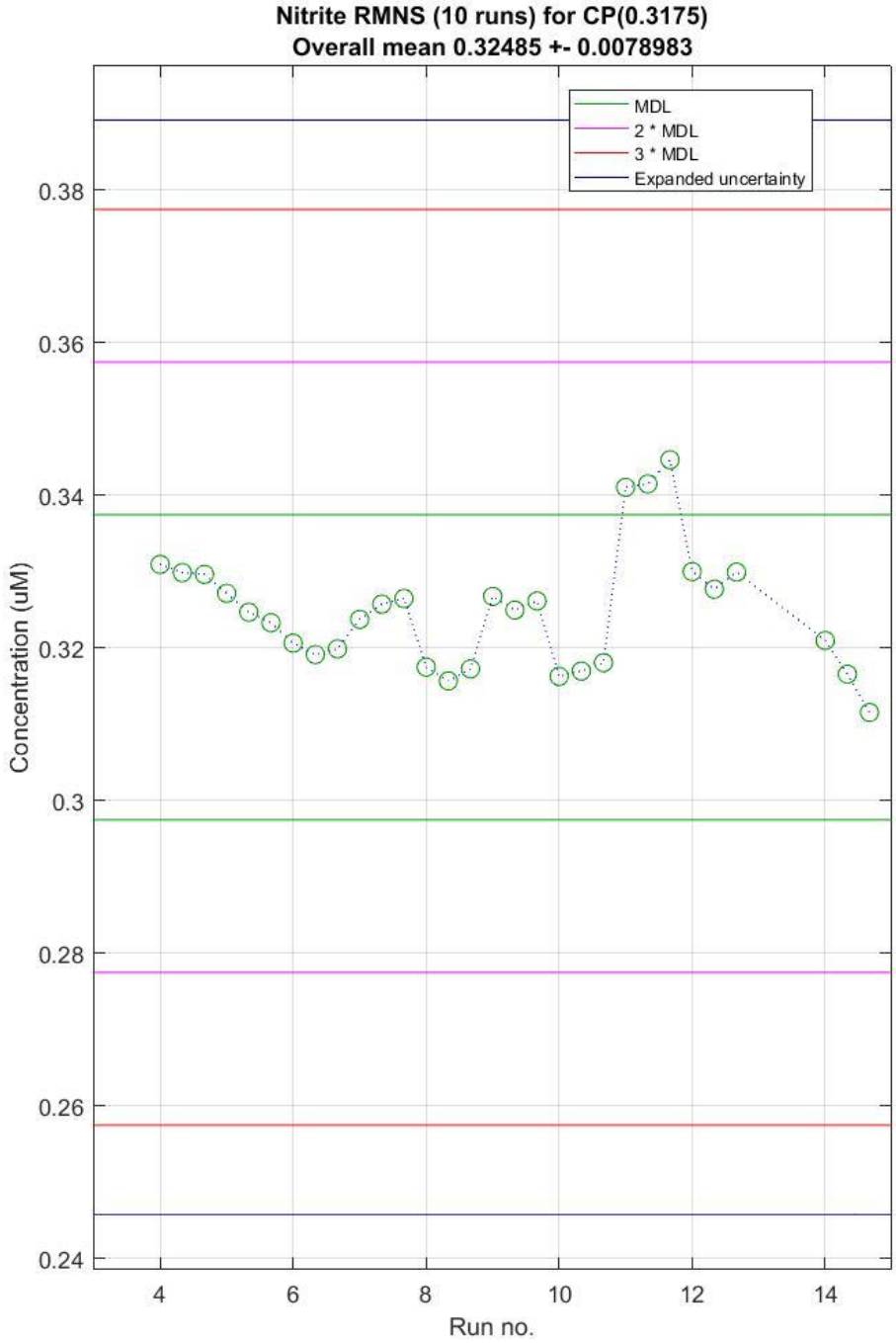


Figure 9. Nitrite RMNS lot CP Plot (µmol L^{-1})

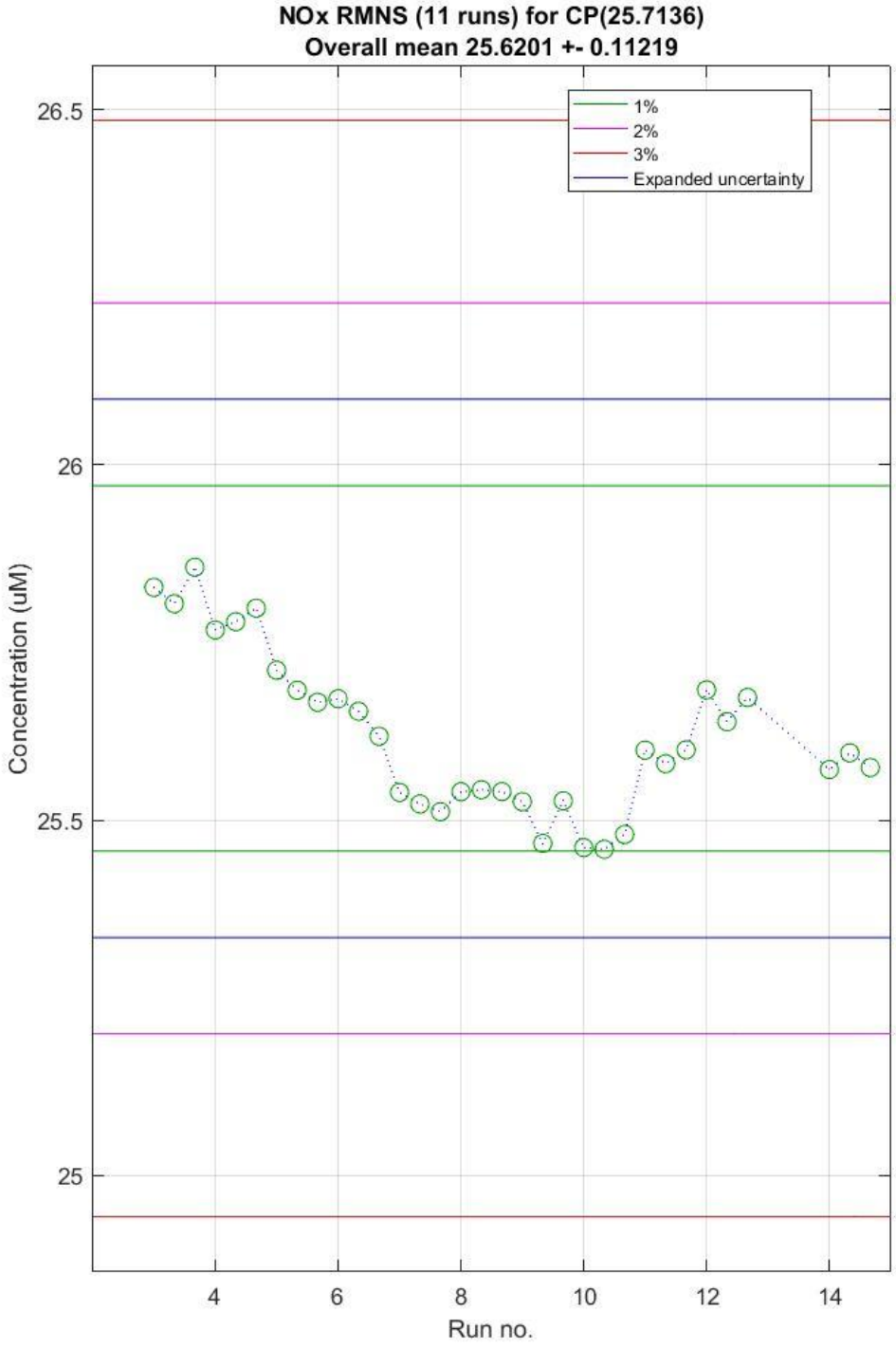


Figure 10. Nitrate + Nitrite (NOx) RMNS lot CP Plot (µmol L^{-1})

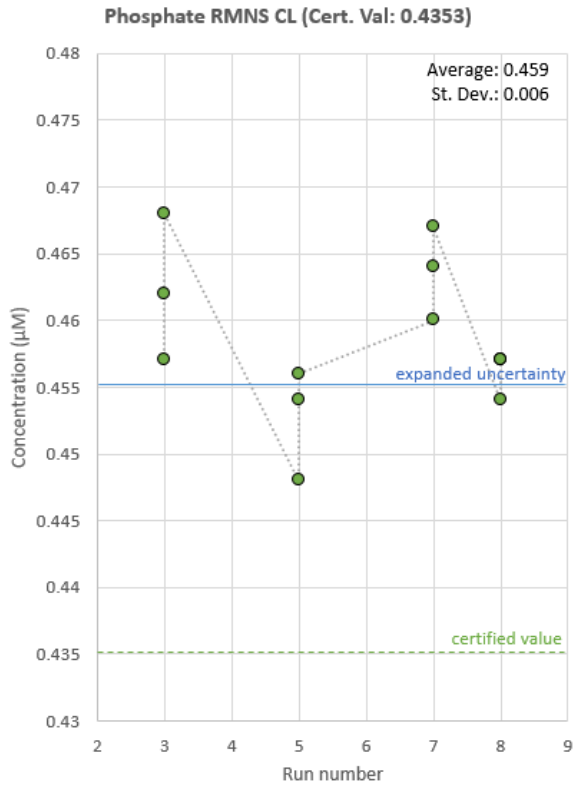


Figure 11. Phosphate RMNS lot CL Plot (µmol L^{-1})

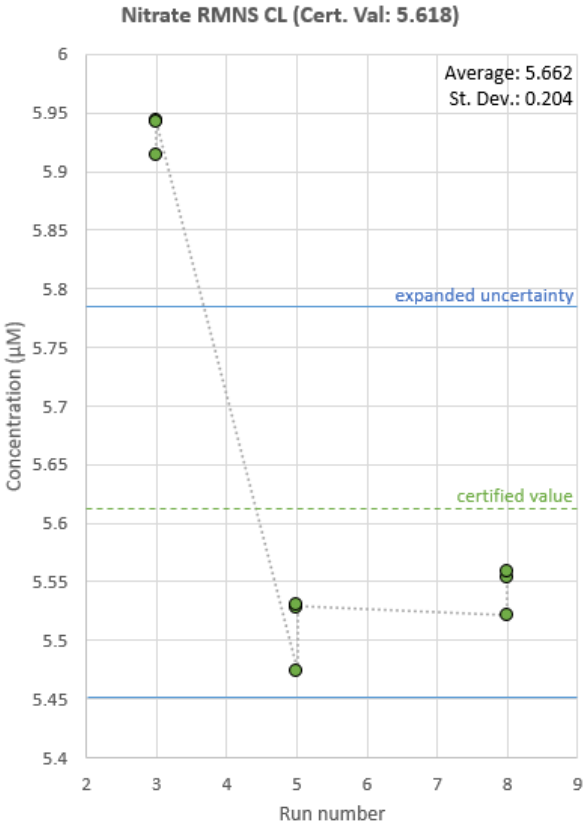


Figure 12. Nitrate + Nitrite (NOx) RMNS lot CL Plot (µmol L^{-1})

7.6 Measurement Uncertainty

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

Table 13: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol L^{-1}

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

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

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

7.7 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 14: AA3HR auto analyser MDL statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are of all analytical measurements. Units: µmol L^{-1}

MDL	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrate + Nitrite (NOx)	Nitrite (NO_2)	Ammonia (NH_4)
Nominal MDL	0.200	0.020	0.020	0.020	0.020
Standard Dev. Min	0.008	0.002	0.002	0.001	0.003
Standard Dev. Max	0.076	0.018	0.012	0.006	0.006
Standard Dev. Mean	0.050	0.009	0.006	0.003	0.004
Standard Dev. Median	0.056	0.007	0.005	0.003	0.004
Precision of MDL (stdev)	0.021	0.006	0.004	0.002	0.001

Table 15: AA100 auto analyser MDL statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are of all analytical measurements. Units: µmol L^{-1}

MDL	Phosphate (PO_4)	Nitrate + Nitrite (NOx)
Nominal MDL	0.020	0.020
Standard Dev. Min	0.004	0.019
Standard Dev. Max	0.009	0.049
Standard Dev. Mean	0.006	0.037
Standard Dev. Median	0.006	0.043
Precision of MDL (stdev)	0.002	0.016

7.8 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 17). Duplicate nutrient samples are also collected from the greatest depth of subsequent CTD deployments (Table 16).

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 16). The exception: NOx (nitrate+nitrite) which uses the limit 0.06 µmol L^{-1}

Duplicate samples that exceed this limit are flagged 69 (suspect). These are tabulated in appendix 8.6.

Table 16: Difference between duplicate results. CTD 2 – CTD 21 Units: µmol L^{-1}

	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)	Ammonia (NH_4)
Minimum	0.000	0.000	0.000	0.000	0.000
Maximum	0.100	0.010	0.010	0.040	0.020
Mean	0.011	0.003	0.002	0.011	0.004
Variance	0.032	0.005	0.002	0.011	0.007

Table 17: CTD deployment 1. 36 bottles at 1000 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	34.432	185.120	49.600	2.260	0.003	32.560
Maximum	34.439	187.933	50.300	2.270	0.017	32.840
Mean	34.436	186.162	50.000	2.266	0.012	32.711
SD	0.001	0.811	0.151	0.005	0.003	0.049

7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: **13.86**

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

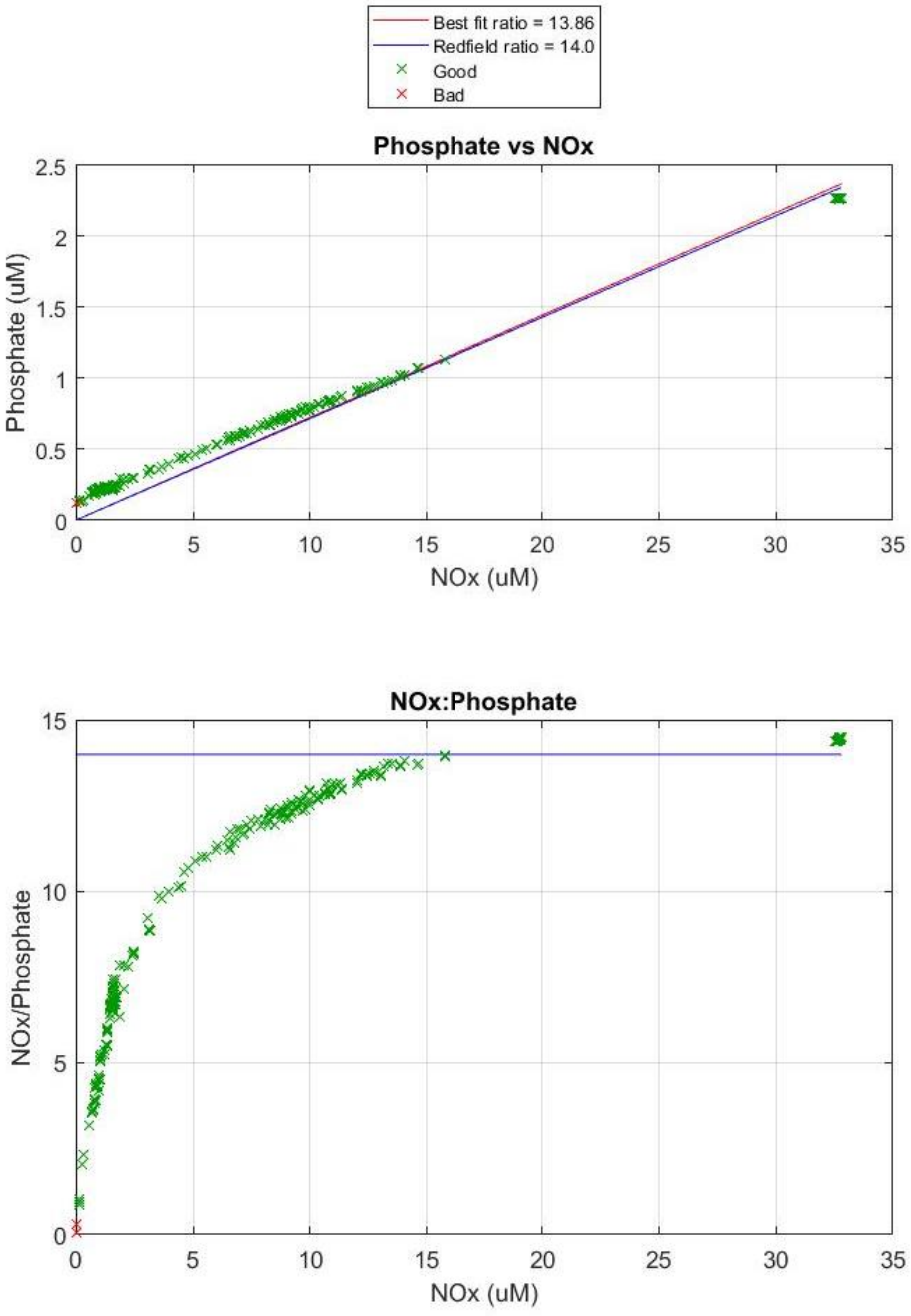


Figure 13. Redfield ratio plots. Red = Data below nominal detection limit (see bad data listed in appendix 8.6).

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:

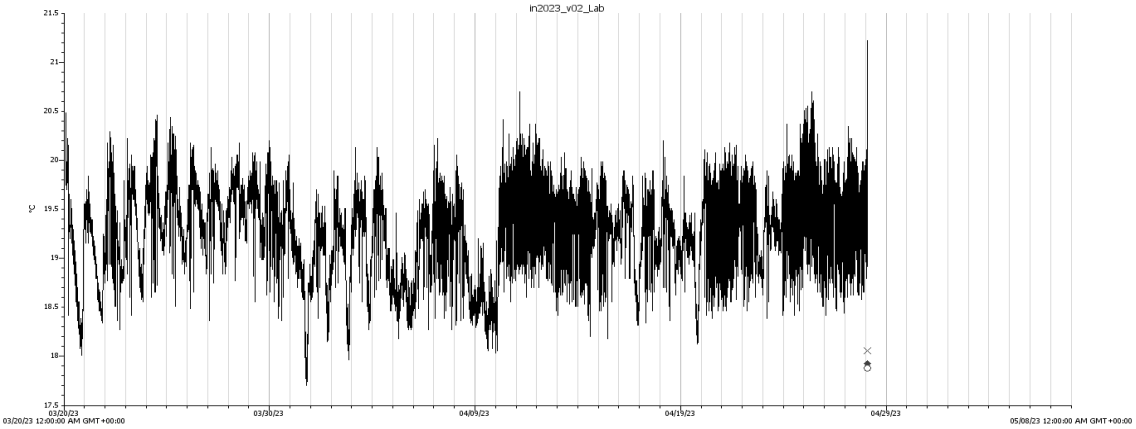


Figure 14. Above the AA3HR instrument, temperature only. Mean 19.3°C SD 0.5°C.

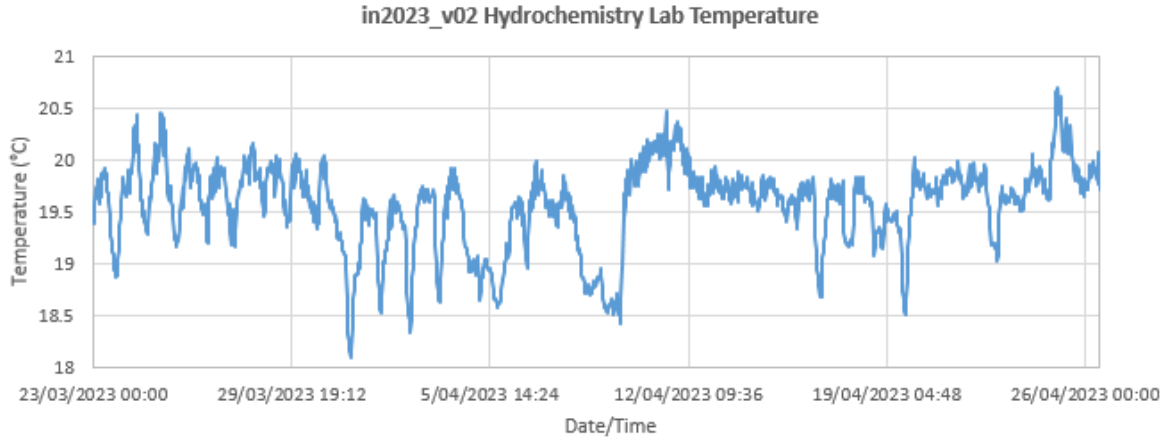


Figure 15. On the left side of AA3HR auto sampler, temperature only. Mean 19.6°C SD 0.4°C.

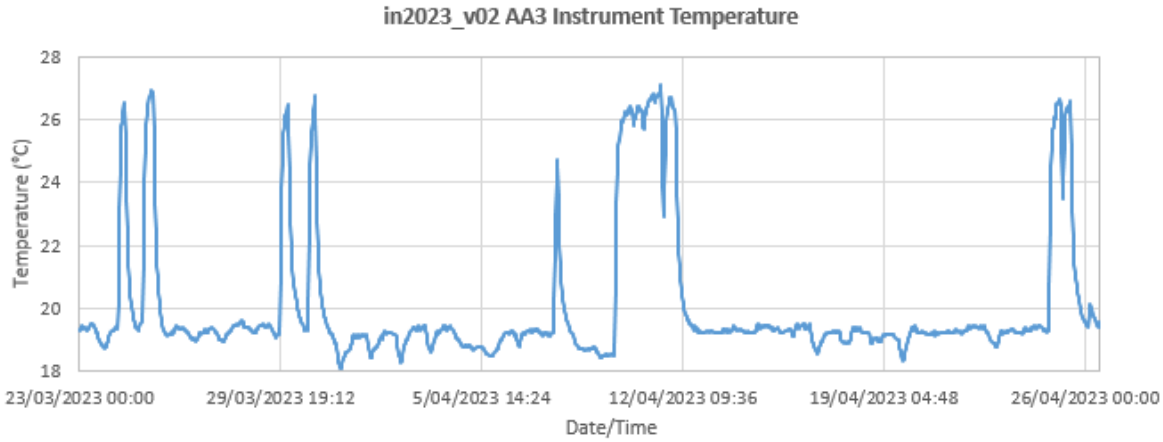


Figure 16. On the deck of the AA3HR silicate and phosphate channel chemistry module, temperature only. Mean 20.1°C SD 2.2°C.

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

8.2 Nutrients: RMNS results for each CTD Deployment.

8.2.1 Lot CP

Run analysis #	CTD Deployment #	UWY sample #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)
4	1	1-11	62.552	1.821	25.782	0.330
5	2		62.596	1.801	25.687	0.325
6	3		62.641	1.805	25.647	0.320
7	4, 5, 6		62.698	1.756	25.525	0.325
8	7, 8, 9		62.671	1.812	25.541	0.317
9	10, 11		62.619	1.815	25.507	0.326
10	12, 13, 14		62.778	1.817	25.467	0.317
11	15, 16, 17		62.637	1.818	25.592	0.342
12	18, 19		62.545	1.823	25.665	0.329
14	20, 21	12-19	62.565	1.790	25.580	0.316

8.2.2 Lot CL

Run analysis #	Run analysis # (post-processing)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)
3	031 (PO_4) , 032 (NOx)	0.462	5.934
5	051 (PO_4) , 052 (NOx)	0.453	5.510
7	071 (PO_4) , 072 (NOx)	0.464	N/A*
8	081 (PO_4) , 082 (NOx)	0.456	5.544

**NOx result is not reported for run analysis number 7 due to issue with analysis channel.*

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

8.3.1 AA3HR Auto analyser

CTD Deployment #	UWY sample #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)	Ammonia (NH_4) ($\mu mol\ L^{-1}$)
1	1-11	0.042	0.002	0.003	0.002	0.003
2		0.021	0.007	0.003	0.001	0.005
3		0.061	0.007	0.007	0.003	0.003
4, 5, 6		0.059	0.016	0.006	0.003	0.004
7, 8, 9		0.064	0.003	0.005	0.002	0.005
10, 11		0.008	0.004	0.002	0.001	0.004
12, 13, 14		0.076	0.010	0.011	0.003	0.006
15, 16, 17		0.053	0.015	0.002	0.005	0.004
18, 19		0.050	0.003	0.012	0.001	0.003
20, 21	12-19	0.064	0.018	0.005	0.006	0.003

8.3.2 AA100 Auto analyser

Run analysis #	Run analysis # (post-processing)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)
3	031 (PO_4) , 032 (NOx)	0.009	0.049

5	051 (PO_4) , 052 (NOx)	0.004	0.019
7	071 (PO_4) , 072 (NOx)	0.005	N/A*
8	081 (PO_4) , 082 (NOx)	0.006	0.043

**NOx result is not reported for run analysis number 7 due to issue with analysis channel.*

8.4 Missing or Suspect Salinity Data

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

CTD	RP	Flag	Reason for Flag
NA	NA	NA	NA

8.5 Missing or Suspect Dissolved Oxygen Data

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

CTD	RP	Flag	Reason for Flag
5	13	133	DO lid was put upside down resulting in small loss of sample volume and air gap under the stopper. Data was marked as BAD by operator
14	7	133	DO lid was put upside down resulting in small loss of sample volume and air gap under the stopper. Data was marked as BAD by operator

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
3	31	NOx	63	NOx concentration is below nominal detection limit
3	34	NOx	63	NOx concentration is below nominal detection limit

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

8.8.2 Dissolved Oxygen

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

8.8.3 $Si(OH)_4$

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

8.8.4 PO_4

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

8.8.5 NO_3

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

8.8.6 Notes

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

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

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

9 References

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