

RV INVESTIGATOR

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage: in2019_t02

Chief Scientist Dr Robin Beaman

Principal Investigator Dr Robin Beaman

Voyage title: Deep seascapes of the Great Barrier Reef: Uncovering submarine canyons and landslides

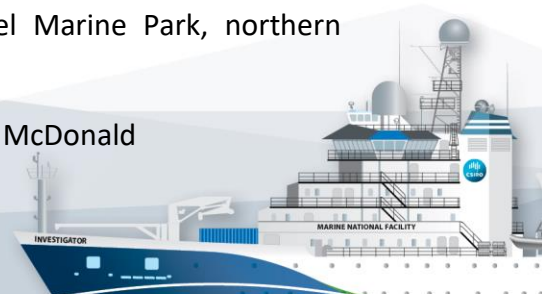
First measurements of nitrate isotopic composition in the Coral Sea

Spatial and temporal variability in the distribution and abundance of seabirds

ORCA: Using the Investigator radar as a moving reference for the Australian operational radar network

Environmental baselines for Wessel Marine Park, northern Australia

Report compiled by: Peter Hughes & Jack McDonald



Contents

1	Executive Summary	4
2	Itinerary and Personnel	5
3	Sample Summary	6
3.1	CTD (Conductivity, Temperature, Density)	6
3.2	EXP (Experimental samples)	6
3.3	TSG (Thermosalinograph)	6
4	Data Processing Overview	7
5	Salinity Analysis and Data Processing	8
5.1	Salinity Method	8
5.2	CTD Salinity vs Bottle Salinity Plot	9
6	Dissolved Oxygen Analysis and Data Processing	10
6.1	Dissolved Oxygen Method	10
6.2	CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot	11
6.3	Dissolved Oxygen Instrument Calibration.	12
7	Nutrient Analysis and Data Processing	13
7.1	Nutrient Methods	13
7.2	HyPro Data Processing Summary for Nutrients	14
7.3	Accuracy and Precision - Reference Material for Nutrient in Seawater (RMNS).....	16
7.4	Nutrient plots of RMNS.....	17
7.4.1	Figure 6. Silicate RMNS Plot ($\mu\text{mol L}^{-1}$).....	17
7.4.2	Figure 7a. RAW Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)	17
7.4.3	Figure 7b. ADJUSTED Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)	18
7.4.4	Figure 8. Nitrate + Nitrite (NO _x) RMNS Plot ($\mu\text{mol L}^{-1}$)	18
7.4.5	Figure 9. Nitrite RMNS Plot ($\mu\text{mol L}^{-1}$).....	19
7.5	Measurement Uncertainty.....	20
7.6	Method Detection Limit for Nutrients	20
7.7	Sampling Precision	21
7.8	Redfield Ratio.....	21
7.9	Temperature & Humidity Change over Nutrient Analyses	22
8	Appendix.....	23
8.1	Salinity: Reference Material Used.....	23
8.2	Nutrients: RMNS lot CG results for each CTD Deployment.	24
8.3	Nutrients: Measured Detection Limit for each CTD Deployment.....	25

8.4	Flag Key for Hydrology Data Set.....	26
8.5	GO-SHIP Specifications.....	27
8.5.1	Salinity.....	27
8.5.2	Dissolved Oxygen	27
8.5.3	Si(OH) ₄	27
8.5.4	PO ₄	27
8.5.5	NO ₃	27
8.5.6	Notes.....	27
9	References.....	28

1 Executive Summary

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

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." *Limnol. Oceanogr: Methods*, 17(1): pp. 25-41. doi:10.1002/lom3.10294

This voyage was a transit voyage from Brisbane to Darwin. There were five supplementary projects carried out along the way. Titles and custodians of these projects are listed here. Out of these projects, the hydrology data will be of primary use to Dr Dirk Erler's project.

1. Deep seascapes of the Great Barrier Reef: Uncovering submarine canyons and landslides. Dr Robin Beaman.
2. First measurements of nitrate isotopic composition in the Coral Sea. Dr Dirk Erler.
3. Spatial and temporal variability in the distribution and abundance of seabirds. Dr Eric Woehler.
4. ORCA: Using the Investigator radar as a moving reference for the Australian operational radar network. Dr Alain Protat.
5. Environmental baselines for Wessel Marine Park, northern Australia. Dr Rachel Przeslawski.

The first CTD deployment was accompanied with the release of two BGC-Argo floats. The CTD salinity, dissolved oxygen and nitrate bottle data from this deployment will be used to check the BGC-Argo float data. Similarly, Total Alkalinity, Total CO₂, POC (particulate organic carbon) and Pigments samples were collected from this CTD deployment by Dirk Erler, which will also be used for float calibration.

Hydrochemistry oversaw the collection of salinity, oxygen and nutrient samples (silicate, phosphate, nitrate + nitrite (NO_x), nitrite, and ammonium) from the CTD. All samples were analysed in the ship's hydrochemistry laboratory.

High quality data were produced for the three measured parameters. Certified reference materials for nutrients in seawater (RMNS) were mostly within the specified limits of the certified value. Note: Phosphate results are adjusted to bring the RMNS within 1% of its certified value. Measured RMNS values per CTD deployment are listed in section 8.2 of this report.

Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary and Personnel

Brisbane to Darwin, October 4th – 14th, 2019

Figure 1: Voyage Track



Table 1: Key personnel list

Name	Role	Organisation
Dr Robin Beaman	Chief Scientist	James Cook University
Stephen Thomas	Voyage Manager	CSIRO
Peter Hughes	Hydrochemist	CSIRO
Jack McDonald	Hydrochemist	CSIRO

3 Sample Summary

Table 2: Total samples collected and assayed.

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	48 CTD
	21 TSG
Dissolved Oxygen (SIO automated titration)	48 CTD
Nutrients (Seal AA3HR segmented flow)	49 CTD
	5 EXP

3.1 CTD (Conductivity, Temperature, Density)

- Samples collected from the 12L Ocean Test Equipment bottles on the 24 bottle CTD rosette.
- 6 CTD deployments in total. Deployments were sampled by Peter Hughes and Jack McDonald.

3.2 EXP (Experimental samples)

- Sampled and prepared by Dirk Eler and Thomas Glaze. Samples taken from the underway system.

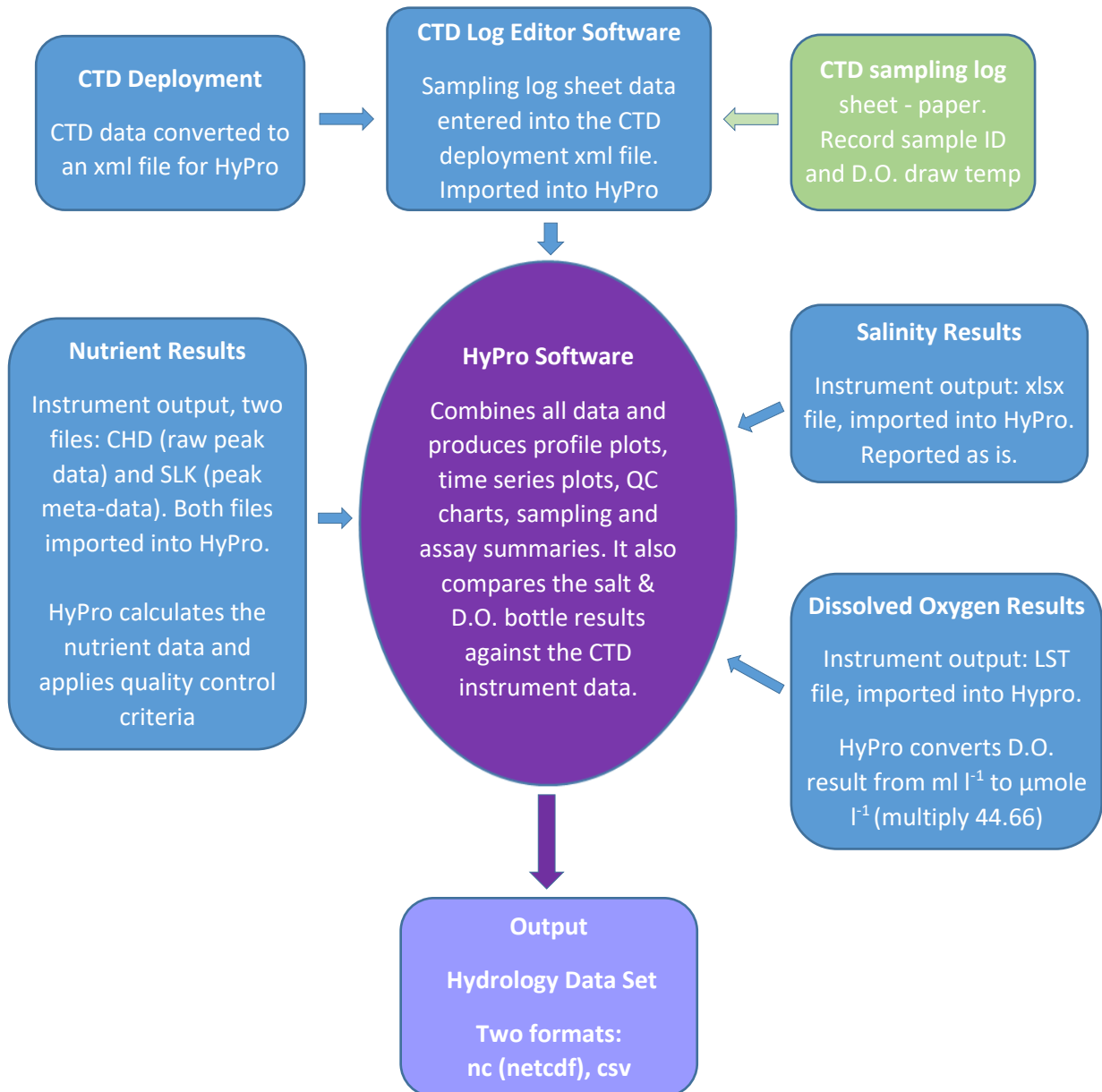
3.3 TSG (Thermosalinograph)

- Samples collected by hydrochemistry from the instrument clean seawater supply in the underway lab.
- TSG sampling times recorded in the voyage elog.

4 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 in figure 1.

Figure 2: Hydrology Data Processing Flow Diagram.



5 Salinity Analysis and Data Processing

5.1 Salinity Method

Salinity samples are measured on a high precision laboratory salinometer (Guildline Autosol 8400B) which is operated in accordance with its technical manual.

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 32.4356×10^{-3} .

Before each batch of sample measurements, the Autosol is calibrated with standard seawater (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL solution is used for each calibration. The frequency of calibration is one per set of samples per CTD deployment.

Method synopsis: Salinity samples are collected into 200 mL OSIL bottles, 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 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 software is imported into HyPro and collated with the CTD deployment meta-data.

¹ International Association for the Physical Sciences of the Oceans

Table 3: Salinity measurement parameters.

Details	
HyPro Version	5.7
Instrument	Guildline Autosol Laboratory Salinometer 8400(B) – SN 72089
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analysts	Peter Hughes, Jack McDonald
Lab Temperature (±0.5°C)	22.1 -22.5 °C during analysis.
Bath Temperature	24.00°C
Reference Material	OSIL IAPSO ¹ - Batch P162, use by 16/04/2021, $K_{15} = 0.99983$, PSU = 35.993
Sampling Container type	200 mL volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.
Sample Storage	Samples stored in the Salt lab for a minimum of 8 hrs before measurement.
Comments	None.

5.2 CTD Salinity vs Bottle Salinity Plot

The difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities is generally less than 0.01 PSU.

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 DataLibrariansOAMNF@csiro.au for corrected CTD data.

Note: dots = bottle samples, circles = CTD instrument (unprocessed)

Figure 3: CTD Salinity vs Bottle Salinity Plot. Deployment/Bottle number (x-axis). Difference of Salinity bottle data from the corresponding CTD salinity value (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: $\mu\text{mol L}^{-1}$

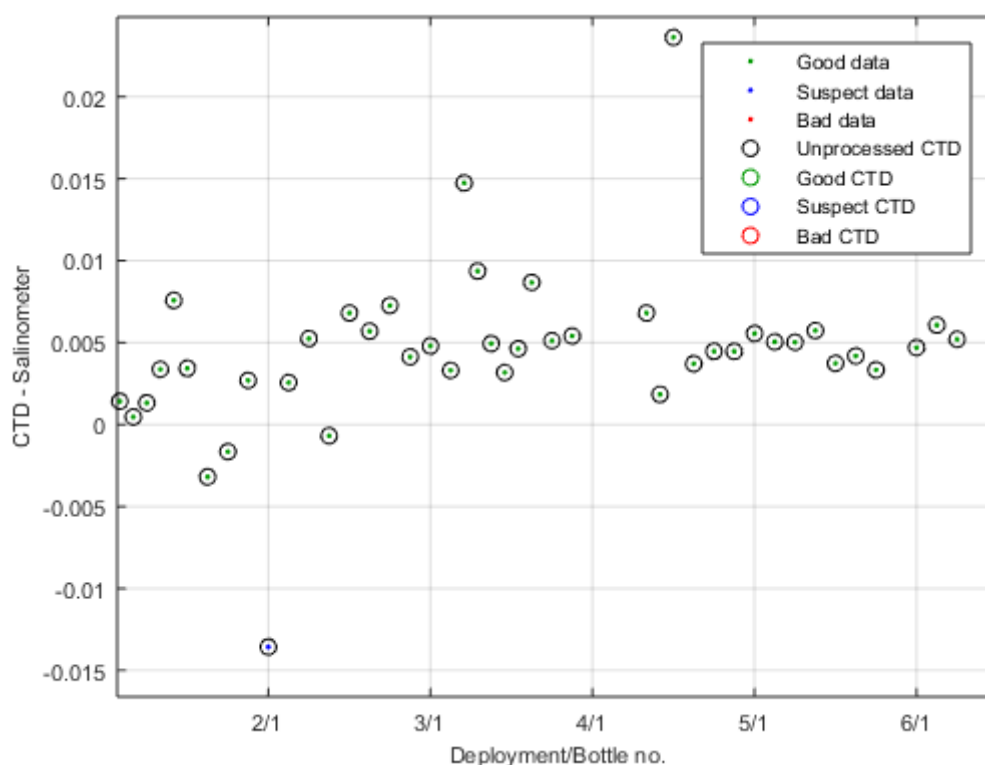


Table 4: Missing or Suspect Salinity Data. Data is flagged based on CTD sampling log sheet notes, observations during analysis, and examination of the depth profile (Flag key in appendix 8.4).

CTD	RP	Flag	Reason for Flag or Action
2	1	69	Flagged suspect by operator. Initial sample measurement rejected due to variable readings. Sample capped, instrument re-calibrated and the sample measured again. Difference between this value and the CTD instrument is 0.014 PSU. Flagged as suspect due to difference and the reduced sample volume when second measurement taken.
4	01 to 07	0	Bottle salinity good. CTD primary salinity suspect, values < 8 PSU. Communication issues with CTD instrument during deployment. Cause unknown. Values not included in Figure 3.

6 Dissolved Oxygen Analysis and Data Processing

6.1 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 synopsis: 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 20 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, oxidizing the Mn (IV) back to the divalent state liberating iodine twice the original dissolved oxygen content of the sample. The tri-iodine is auto-titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1 mL burette. The endpoint is determined by measuring changes in the UV absorption of the tri-iodide ion at 365 nm. The point at which there is no change in absorbance is the endpoint.

Before each batch of sample assays, 10 mL aliquots of potassium iodate primary standard are used to standardise the thiosulphate titrant. A blank correction is also determined from the difference between two consecutive titres for 1 mL aliquots of the same potassium iodate solution.

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

Table 5: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	$\pm 0.5 \mu\text{mol L}^{-1}$
Analyst(s)	Peter Hughes, Jack McDonald
Lab Temperature ($\pm 1^\circ\text{C}$)	Variable, 19.3 - 22.5 °C
Sample Container type	Pre-numbered 140 mL glass iodine determination flasks with glass stopper. 18 flasks per light-proof container.
Sample Storage	Samples stored in the hydrochemistry lab until analysis. All samples were analysed within ~48 hrs
Comments	None.

6.2 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

The CTD values in this plot are unprocessed raw data.

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 DataLibrariansOAMNF@csiro.au for corrected CTD data.

Figure 4. CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot. Deployment/Bottle number (x-axis). Difference in dissolved oxygen results from the bottle sample to its corresponding CTD measurement (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: $\mu\text{mol L}^{-1}$

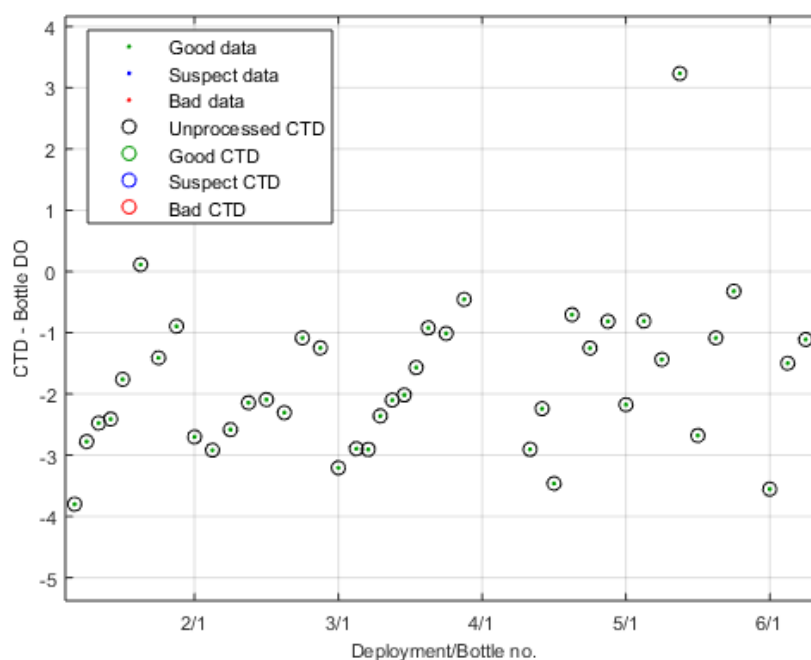


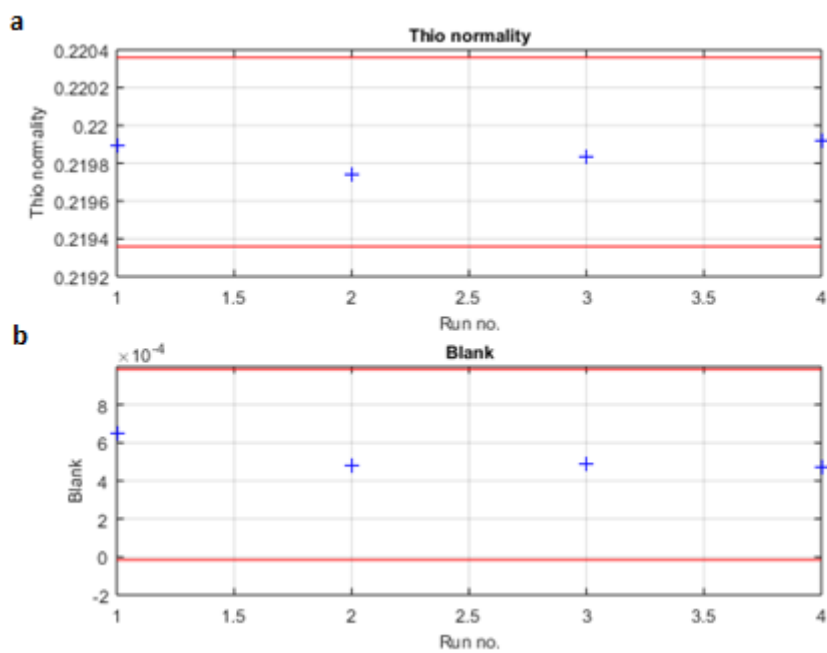
Table 6: Missing or suspect dissolved oxygen bottle data. Data is flagged based on CTD sampling log sheet notes, observations during analysis, and examination of the depth profile (Flag key in appendix 8.4).

CTD	RP	Flag	Reason for Flag or Action
4	01 to 07	0	Bottle dissolved oxygen good. CTD primary dissolved oxygen suspect, values $> 530 \mu\text{mol L}^{-1}$. Communication issues with CTD instrument during deployment. Cause unknown. Values not included in Figure 4.

6.3 Dissolved Oxygen Instrument Calibration.

The normality of the thiosulphate titrant (0.22N) varied less than 0.0002N for all dissolved oxygen sample titrations. The blank corrections are less than 0.0007 mL with a voyage mean of 0.0005 mL and standard deviation of 0.00007 mL (n=4). For reference, titre volumes for dissolved oxygen bottle samples lay in the range 0.31 to 0.58 mL

Figure 5. Auto-titrator calibration plots. In Figure 5a the red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration. In Figure 5b red lines indicate acceptable variation either side of the mean blank concentration. The titrant should not vary more than 0.0005 N between analyses.



7 Nutrient Analysis and Data Processing

7.1 Nutrient Methods

When using silicate, phosphate, nitrate+nitrite (NO_x) and nitrite data set for publication, please cite the paper:

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

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/Si(OH)₄ (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/PO₄ (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/NO₃ (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/NO₂ (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium/NH₄ (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 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.

Table 7: Nutrient measurement parameters. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 7.09				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrate + Nitrite (NO _x)	Nitrite (NO ₂)	Ammonium (NH ₄)
Concentration range (μmol L ⁻¹)	112	3.0	36.4	1.4	1.0
Method Detection Limit (MDL), (μmol L ⁻¹)	0.2	0.02	0.02	0.02	0.02
Matrix Corrections	none	none	none	none	none
Analysts	Peter Hughes, Jack McDonald				
Lab Temperature (±1°C)	Variable, 19.3 - 22.5 °C				
Reference Material	KANSO, RMNS lot CG				
Sampling Container type	CTD: 50ml HDPE with screw cap lids. EXP: 30ml PP tubes with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD: None. EXP: as prepared by the science parties.				
Comments	None				

No missing data. All reported nutrient data flagged GOOD.

7.2 HyPro Data 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.

With suspect calibration points, their contribution to the curve is given less weighting dependent on their distance from the final 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).
- Within $0.02 \mu\text{mol L}^{-1}$ for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. Missing or suspect nutrient data is tabulated in section 7.1, table 8. The Flag key is in Appendix 8.4.

¹ World Ocean Circulation Experiment

Table 8: HyPro software processing parameters.

Result Details	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrate + Nitrite (NO _x)	Nitrite (NO ₂)	Ammonia (NH ₄)
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	5	5	5	5	5
Forced through zero?	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	Low nutrient seawater (LNSW, bulk on deck of Investigator) collected on 28/9/2016. Sub-lot passed through a 10 micron filter and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω water. Dispensed from Milli Q				
CTD deployment sampling regime.	Niskin fired at the greatest depth sampled in duplicate. Single samples collected for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.2.				

7.3 Accuracy and Precision - 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.

Japanese KANSO certified RMNS lot CG was assayed in triplicate in each run to monitor accuracy. The certified values are in Table 10.

For in2019_t02, the certified reference material results for NO_x and silicate are within 1%, phosphate is within 2% and nitrite within 0.02 μmol L⁻¹ of their certified mean concentration.

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.5, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

The assayed RMNS values per CTD deployments are listed in the Appendix 8.2.

Table 9: RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: μmol L⁻¹

RMNS	Nitrate (NO ₃)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _x)	Phosphate (PO ₄)	Silicate (Si(OH) ₄)
Lot CG	24.27 ± 0.205	0.061 ± 0.03	24.330 ± 0.24	1.74 ± 0.02	57.75 ± 0.51

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.

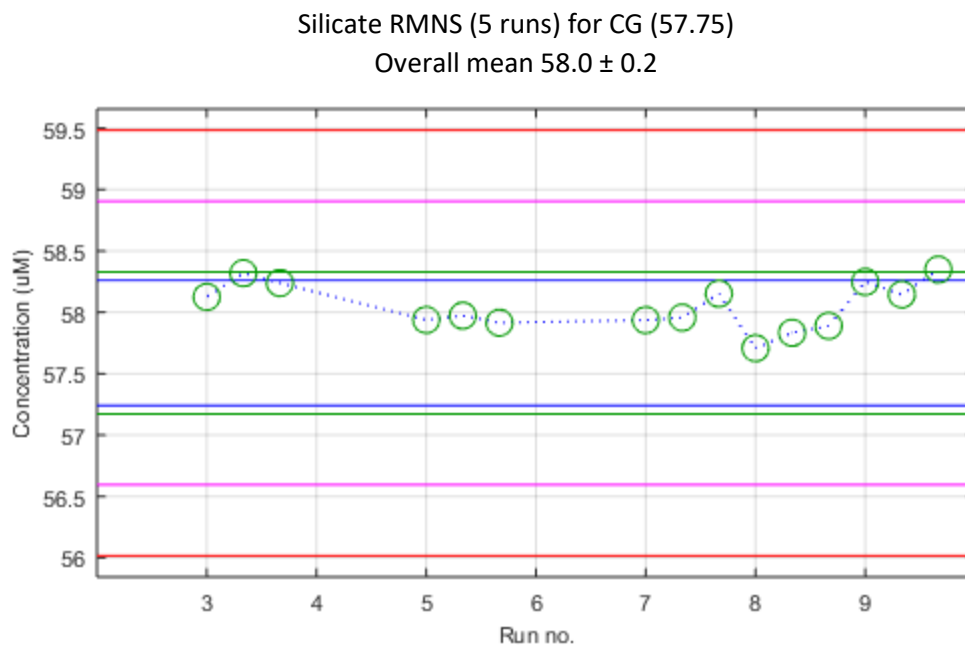
Table 10: RMNS statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are of all analytical measurements. Units: μmol L⁻¹

RMNS CG	Silicate (Si(OH) ₄)	RAW Phosphate (PO ₄)	Nitrate + Nitrite (NO _x)	Nitrite (NO ₂)
Minimum	57.50	1.68	23.87	0.062
Maximum	58.30	1.73	24.56	0.076
Mean	57.97	1.71	24.40	0.068
Median	57.95	1.71	24.50	0.068
Reproducibility	0.22	0.01	0.23	0.004

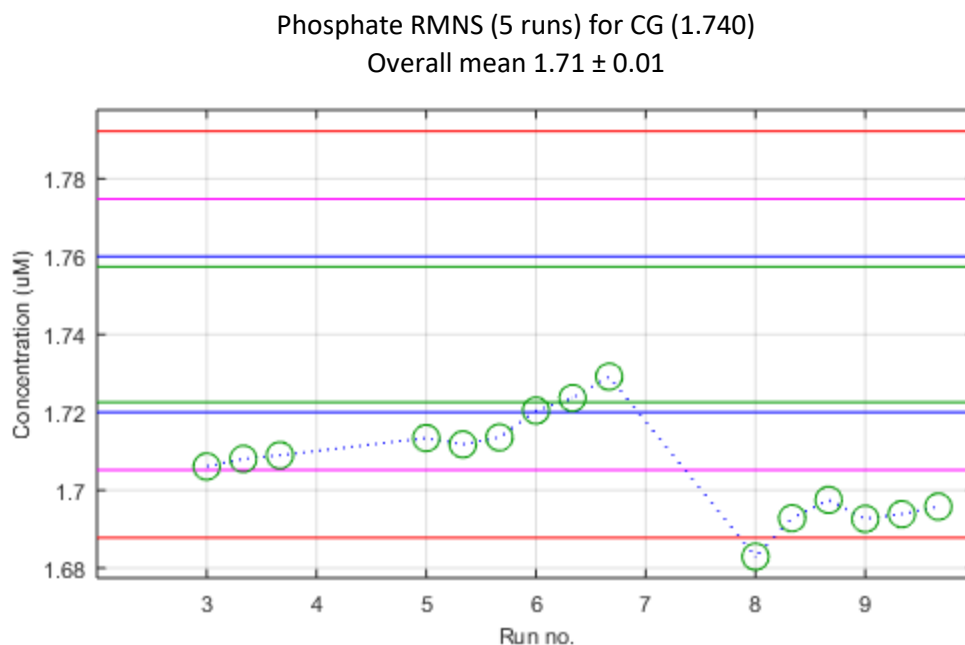
7.4 Nutrient plots of RMNS

The green pink and red lines are the 1%, 2% and 3% contours 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.

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

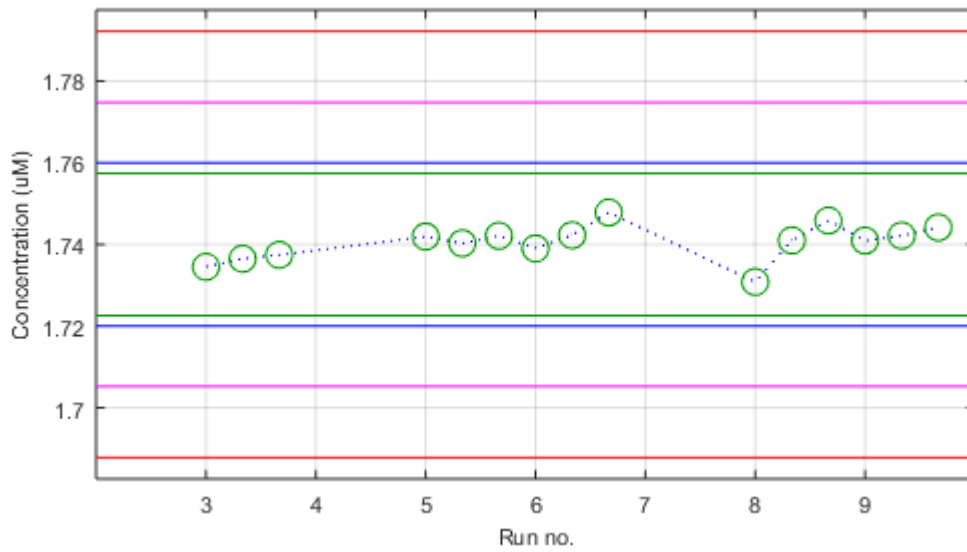


7.4.2 Figure 7a. RAW Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)



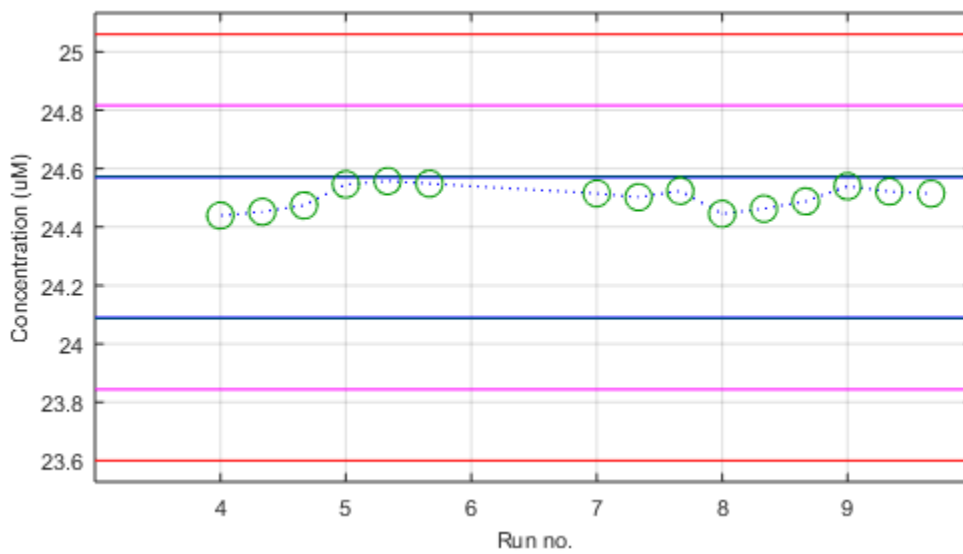
7.4.3 Figure 7b. ADJUSTED Phosphate RMNS Plot ($\mu\text{mol L}^{-1}$)

Adjusted Phosphate RMNS (5 runs) for CG (1.740)
Overall mean 1.740 ± 0.004



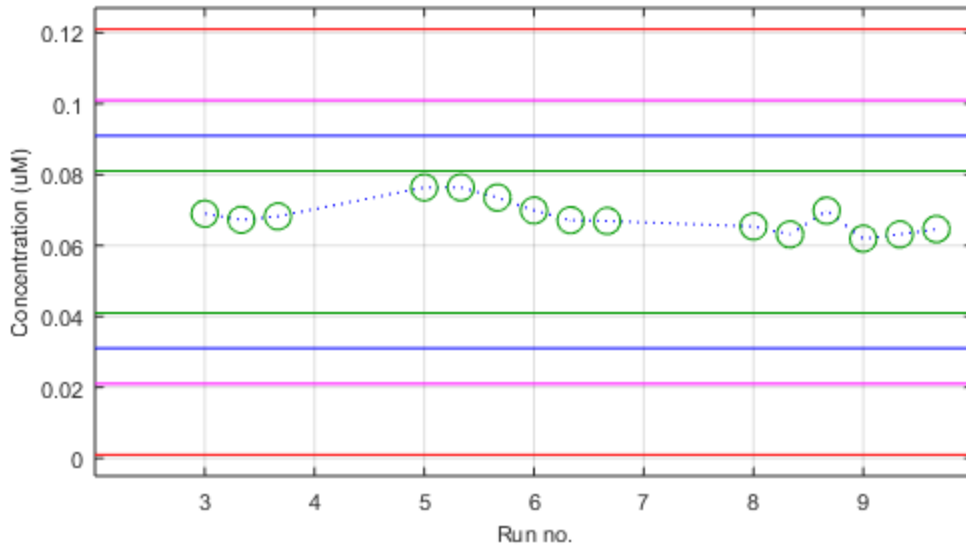
7.4.4 Figure 8. Nitrate + Nitrite (NO_x) RMNS Plot ($\mu\text{mol L}^{-1}$)

NO_x RMNS (5 runs) for CG (24.33)
Overall mean 24.4 ± 0.2



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

Nitrite RMNS (5 runs) for CG (0.061)
Overall mean 0.068 ± 0.004



7.5 Measurement Uncertainty

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

Table 11: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: $\mu\text{mol L}^{-1}$

Calculated Measurement Uncertainty @ 1 $\mu\text{mol L}^{-1}$				
Silicate (Si(OH)_4)	Phosphate (PO_4)	Nitrate + Nitrite (NOx)	Nitrite (NO_2)	Ammonia (NH_4)
± 0.017	± 0.024	± 0.019	± 0.14	$\pm 0.30^\ddagger$

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

‡The ammonia MU precision does not include RMNS data.

7.6 Method Detection Limit for Nutrients

Low nutrient seawater (LNSW) was measured 4 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 12: 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 (NOx)	Nitrite (NO_2)	Ammonia (NH_4)
Nominal MDL	0.20	0.02	0.02	0.02	0.02
Min	0.028	0.002	0.002	0.002	0.001
Max	0.132	0.012	0.012	0.007	0.003
Mean	0.074	0.007	0.006	0.004	0.002
Median	0.078	0.008	0.005	0.004	0.002
Reproducibility	0.036	0.003	0.003	0.002	0.001

7.7 Sampling Precision

Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate concentrations is less than the MDL value. The exception is nitrate+nitrite, which uses $0.06 \mu\text{mol L}^{-1}$ as the MDL boundary.

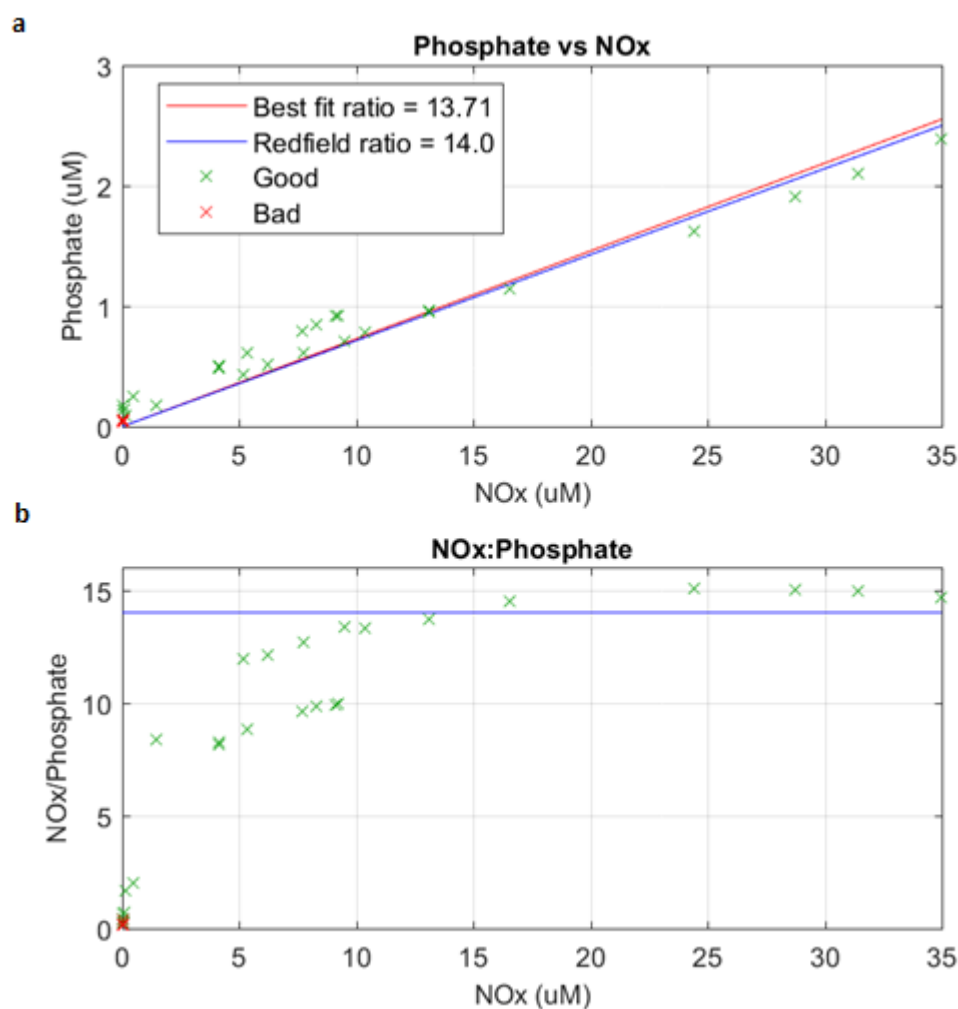
Plots of the difference between the duplicate and their mean for the CTD deployments are below. The red line is the boundary below which sampling precision is deemed good.

For in2019_t02, the sampling precision is within acceptable criteria.

7.8 Redfield Ratio

Calculating and plotting 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. The ratio is very consistent in the deep ocean with phosphate to nitrate equalling 14. The ratio for this voyage was 13.7. Note, only two CTD deployments went deeper than 1000m, the remaining deployments were less than 500m

Figure 10. Redfield ratio plots.



7.9 Temperature & Humidity Change over Nutrient Analyses

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

- (1) Above the AA3HR instrument, temperature only. Average 21.5 °C.
- (2) Above the AA3HR instrument on the other side, ship's instrument (Grafana). Data on request.
- (3) On the deck of the nitrate & nitrite AA3HR chemistry module, temperature and humidity. Data on request.

Refer to "in2019_t02_hyd_voyagereport.docx" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.5 °C. The laboratory temperature was recorded on the nutrient run sheets at the start each analysis run. The temperature varied between 20.5 and 22.1°C over the course of the voyage.

8 Appendix

8.1 Salinity: Reference Material Used

OSIL IAPSO Standard Seawater	
Batch	P162
Use by date	16/04/2021
K ₁₅	0.99983
Practical Salinity Units (PSU)	35.993

8.2 Nutrients: RMNS lot CG results for each CTD Deployment.

CTD deployment #	Silicate (Si(OH) ₄) μmol L ⁻¹	RAW Phosphate (PO ₄) μmol L ⁻¹	ADJUSTED Phosphate (PO ₄) μmol L ⁻¹	Nitrite (NO ₂) μmol L ⁻¹	NOx (NO ₂ + NO ₃) μmol L ⁻¹
RMNS lot CG	57.75	1.74	1.74	0.061	24.33
1	58.21	1.71	1.74	0.068	24.46
2	57.96	1.71	1.74	0.076	24.51
3	58.00	1.72	1.74	0.067	24.52
4	57.86	1.69	1.74	0.066	24.51
5, 6	58.25	1.69	1.74	0.063	24.53

Submitted phosphate nutrient results ARE adjusted based on the RMNS measurements.

Submitted Silicate, Nitrite and NOx DO NOT have adjustments applied based on the RMNS measurements.

How to use the RMNS for Correction (adjustment)

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 Nutrients: Measured Detection Limit for each CTD Deployment.

Measured Detection Limit					
CTD deployment #	Silicate (Si(OH) ₄) μmol L ⁻¹	Phosphate (PO ₄) μmol L ⁻¹	Nitrite (NO ₂) μmol L ⁻¹	NO _x (NO ₂ + NO ₃) μmol L ⁻¹	Ammonia (NH ₄) μmol L ⁻¹
1	0.07	0.005	0.007	0.004	0.001
2	0.09	0.002	0.004	0.003	0.002
3	0.03	0.009	0.004	0.003	0.001
4	0.03	0.007	0.012	0.007	0.003
5, 6	0.09	0.009	0.002	0.006	0.002

8.4 Flag Key for Hydrology Data Set

Flag	Description
0	Data is GOOD – nothing detected.
63	Below nominal detection limit. Nutrients only.
69	Data flagged suspect by operator. Set suspect by HyPro software if Calibration or Duplicate data is outside of set limits but not so far out as to be flagged bad. Nutrients only.
79	AA3HR instrument response, measured method detection limit (MDL) during run was equal to or greater than nominal MDL. Data flagged as suspect. Nutrients only.
129	AA3HR instrument response, absorbance peak exceeds maximum detector value. Data is bad. Nutrients only.
133	Data is BAD. Error flagged by operator.
141	Missing data, no result for sample ID. Used in netcdf file. Not used in csv file.
192	Data not processed.

8.5 GO-SHIP Specifications

8.5.1 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.

8.5.2 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.

8.5.3 Si(OH)_4

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

8.5.4 PO_4

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

8.5.5 NO_3

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

8.5.6 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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