RV INVESTIGATOR
HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2018_v05
Chief Scientist	Prof. Nathan Bindoff
Principal Investigator	Dr. Steve Rintoul, Dr. Helen Phillips, Dr. Max Nikurashin, Dr. Kurt Polzin, Dr. Pete Strutton
Voyage title:	How does a standing meander southeast of Tasmania brake the Antarctic Circumpolar Current? Upper ocean biogeochemistry in the Macquarie Meander of the Antarctic Circumpolar Current
Report compiled by:	Peter Hughes, Julie Janssens, Mark Rayner and Dion Frampton

Contents

1 Executive Summary

Voyage objectives: combine a full-depth CTD/LADCP and bathymetric survey of the full meander, with targeted, rapid underway sampling of smaller-scale variability using the Triaxus towed CTD, a VMP-2000 microstructure profiler and underway instruments.

Water samples collected during the voyage were assayed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen (DO) and salinity. The nutrients determined: silicate, phosphate, nitrate+nitrite, nitrite and ammonium. The samples were collected from CTD rosette deployments, the underway seawater supply during Triaxus tows and from experiments run by the science party.

Sampling was done by the science party in accordance with our standard operating procedures (SOP). The CTD samplers were supervised by Benoit Legresy (CSIRO) and Mark Rosenberg (ACE), both experienced. The quality of samples submitted to the laboratory conformed to the SOP with few errors.

The hydrology data set is high quality. Outlier and suspect data are flagged and described in this report. For nutrients, the analytical accuracy was tracked using seawater certified reference materials (RMNS) made by KANSO, Japan. The RMNS data for each CTD deployment is tabulated in section 8.2.

The major anomalies in the in2018_v05 hydrology data are:

(1) CTD Deployment 18, bottle salinity data suspect. A large fluctuation in the ship's power impacted on the salinometer instrument, changing its operating conditions after it had been calibrated to measure the CTD 18 salinity samples. This change was identified after the samples had been measured. On inspection, the instrument was not plugged into the more stable uninterrupted power supply (UPS). The instrument was powered from the UPS for all subsequent analysis.

(2) CTD Deployment 69, CTD dissolved oxygen data suspect. The CTD DO instrument data above 230m deviates from the typical profile of adjacent CTD deployments as well as from the DO bottle data. Cause unknown. Refer CTD DO profile plot sec 6.2.1

(2) CTD Deployments 47 and 65. Surface bottles closed at depth, evident from the vertical profiles of nutrients and the difference between the CTD instruments and the measured bottle samples. All hydrology surface bottle data flagged as suspect.

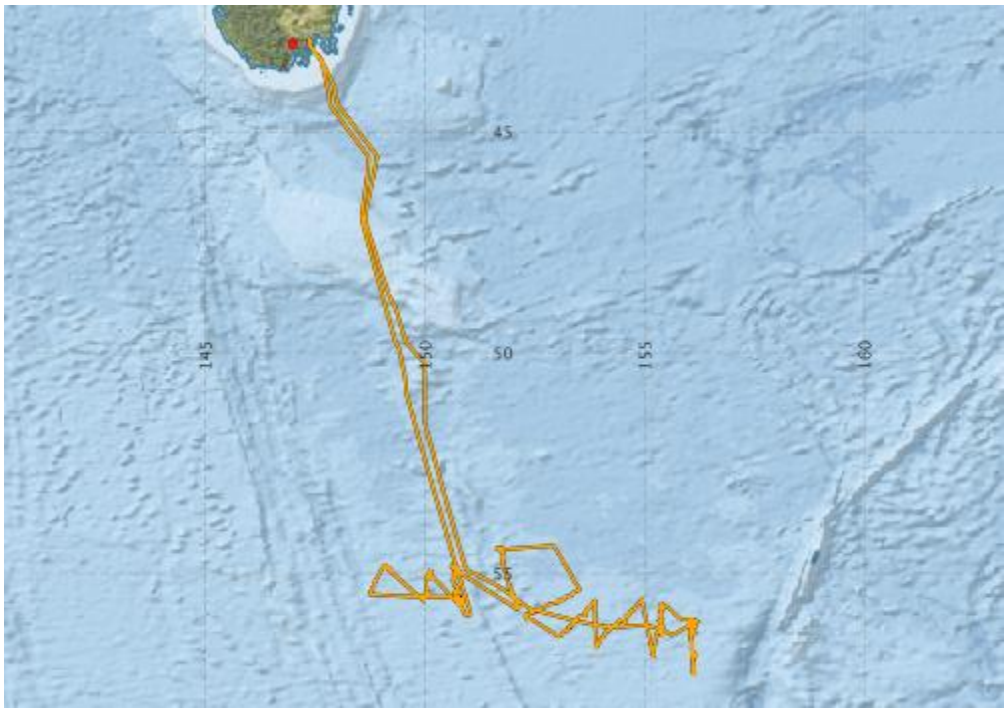
The issued hydrology data set, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, October 16th – November 16th, 2018.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Prof. Nathan Bindoff	Chief Scientist	UTAS/IMAS
Don McKenzie	Voyage Manager	CSIRO
Mark Rayner	Hydrochemist	CSIRO
Peter Hughes	Hydrochemist	CSIRO
Dion Frampton	Hydrochemist	CSIRO
Julie Janssens	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Autosal 8400B)	1941 CTD 15 TSG
Dissolved oxygen (SIO automated titration)	1944 CTD
Nutrients (Seal AA3HR segmented flow)	1971 CTD 191 EXP

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- 77 CTD deployments in total. Deployments sampled by the science party.

4.1.2 EXP (Experiment)

- Prepared and sampled by the science groups conducting the experiments.

4.1.3 TSG (Thermosalinograph)

- Sampling point, clean seawater supply in the underway lab. Sampled by MNF DAP personnel.

4.2 Data Processing Overview

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated in figure 1.

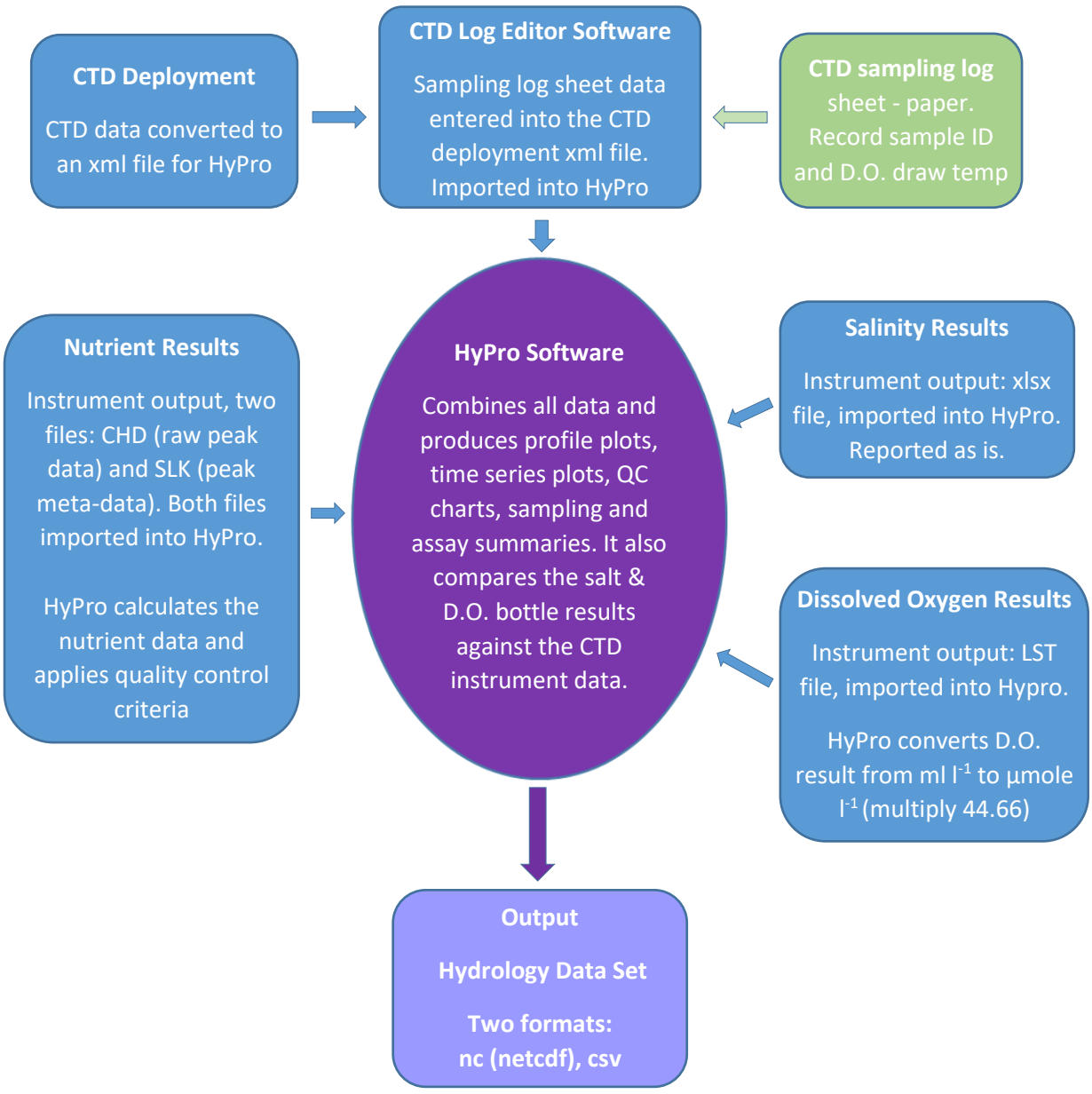


Figure 1: Hydrology Data Processing Flow Diagram.

5 Salinity Data Processing

5.1 Salinity Parameter Summary

Details	
HyPro Version	5.7
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72151
Software	OSIL Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analysts	Dion Frampton
Lab Temperature (±0.5°C)	21 -23°C during analysis.
Bath Temperature	24.01°C
Reference Material	Osil IAPSO - Batch P161, use by 03/05/2020, K_{15} = 0.99987
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	Autosal on ship's power until CTD deployment 18. Changed to ship's UPS power from deployment 19 on.

5.2 Salinity Method

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

The Autosal is calibrated with a seawater standard (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL seawater is used for each calibration. The frequency of calibration is one per CTD deployment.

Method synopsis: Salinity samples are collected into 200ml OSIL bottles, rinsed three times with the sample then filled from the bottom, via a polytetrafluoroethylene (PTFE) straw (ID 6mm), 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.

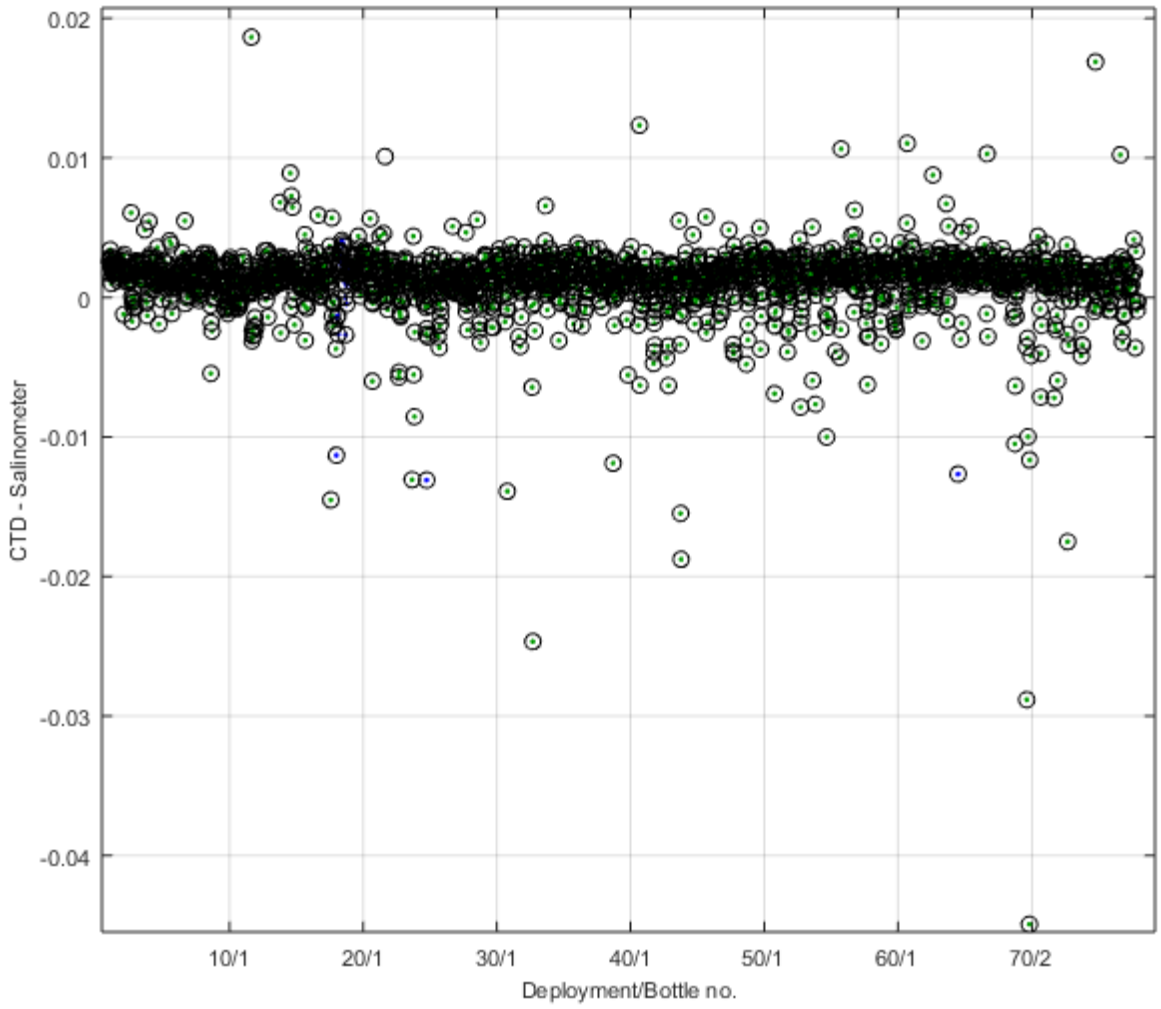
The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

5.3 CTD Salinity vs Bottle Salinity Plot

For this voyage, the difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities was generally less than 0.005 PSU. Plot below.

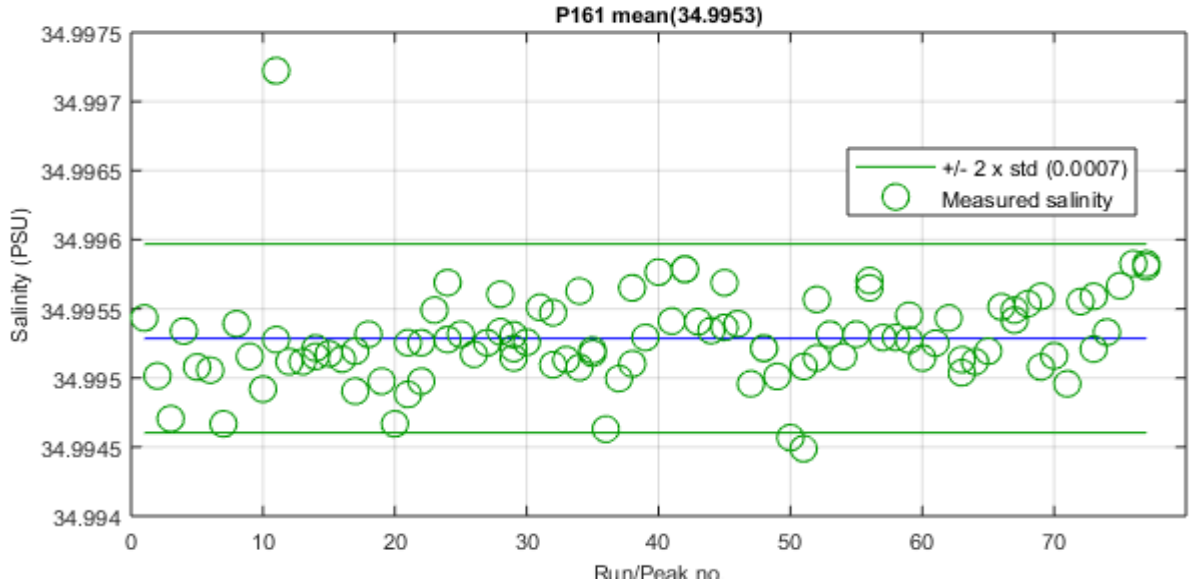
The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected CTD values are not reported in the hydrology set. Please contact the DataLibrarians@csiro.au for corrected CTD data.

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



5.4 OSIL Salinity Standard PSU across the Voyage

The instrument is calibrated with OSIL standard seawater lot P161 (PSU = 34.995). Once calibrated, the bottle used for that calibration is then measured as a sample. These measurements are plotted on the next page. The blue line represents the mean of all measurements.



5.5 Missing or Suspect Salinity Data

Data is flagged as Good, Suspect or Bad based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots. Flag key in appendix 8.4.

CTD	RP	Run	Flag	Reason for Flag or Action
4	17	sal004	-	No Result. Sampled but not measured. RP17 is the same depth as for the measured sample RP16
18	All	sal018	69	Results suspect. Instrument error, power fluctuation caused shift in calibration. See point (1) in executive summary.
21	32	sal021	-	No result. Sampled but not measured. RP32 is the same depth as for the measured sample RP31.
23	26	sal023	-	No result. Sampled but not measured. Niskin bottle leaking.
24	28	sal024	69	Result suspect. Multiple measurements of the sample vary by 0.002 PSU. Cause unknown.
30	25	sal030	133	Result bad. Multiple measurements of the sample vary by 0.003 PSU plus outlier in the vertical profile compared with CTD salinity. Cause unknown.
47	36	sal047	69	Result suspect. Outlier in vertical profile compared with CTD salinity. Probable cause: premature Niskin bottle closure at depth.
53	10	sal053	133	Result bad. Multiple measurements of the sample vary by 0.02 PSU plus outlier in vertical profile compared with CTD salinity. Cause unknown.
64	19	sal064	69	Result suspect. Multiple measurements of the sample vary by 0.006 PSU. Cause unknown.
65	35	sal065	69	Result suspect. Outlier in vertical profile compared with CTD salinity. Probable cause: premature Niskin bottle closure at depth
66	07	sal066	133	Result bad. Multiple measurements of the sample vary by 0.001PSU plus outlier in vertical profile compared with CTD salinity. Cause unknown.

6 Dissolved Oxygen Data Processing

6.1 Dissolved Oxygen Parameter Summary

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen system (SIO)
Software	SCRIPPS
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 µM
Analyst(s)	Mark Rayner
Lab Temperature (±1°C)	Variable, 21.0 - 23.0°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	Deployment 69. CTD instrument data suspect from RP24 up. See profile plot for CTD and bottle data, sec 6.5.1

6.2 Dissolved Oxygen Method

SCRIPPS 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 39 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before the sample is titrated, it is acidified, reducing the Mn (IV) back to the divalent state liberating iodine twice the original dissolved oxygen content of the sample. Iodine combines with the excess iodide and the resultant tri-iodine ion is auto-titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1ml 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.

The thiosulphate solution is standardised against a 10ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two consecutive titres for 1ml aliquots of the same potassium iodate solution.

Standardisation and blank determinations were done at the start of each 12 hour shift or when reagent solutions were changed.

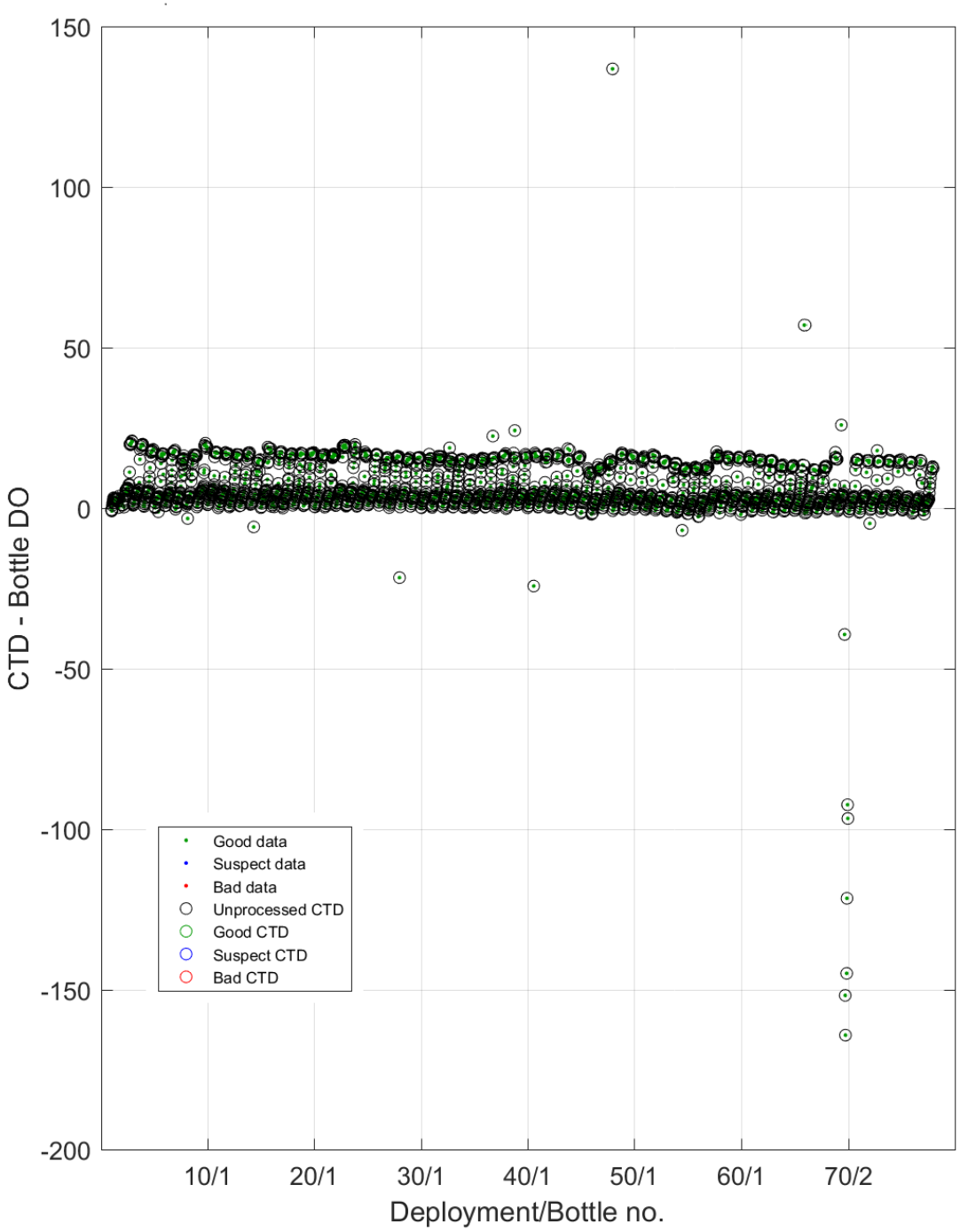
The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

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 DataLibrarians@csiro.au for corrected CTD data.

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

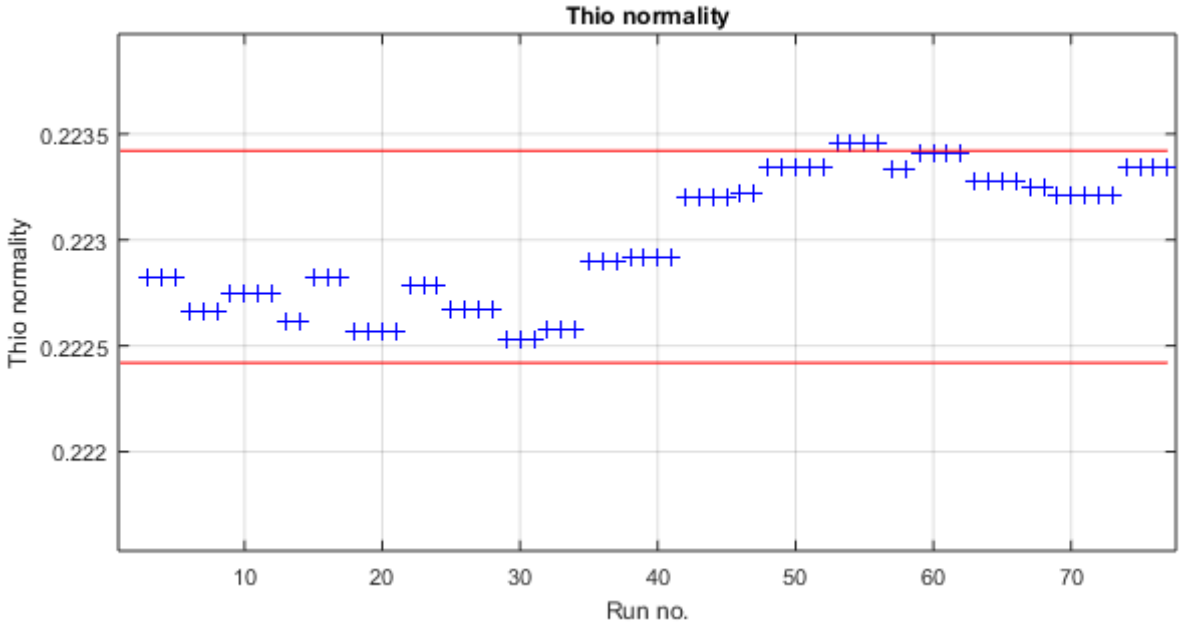


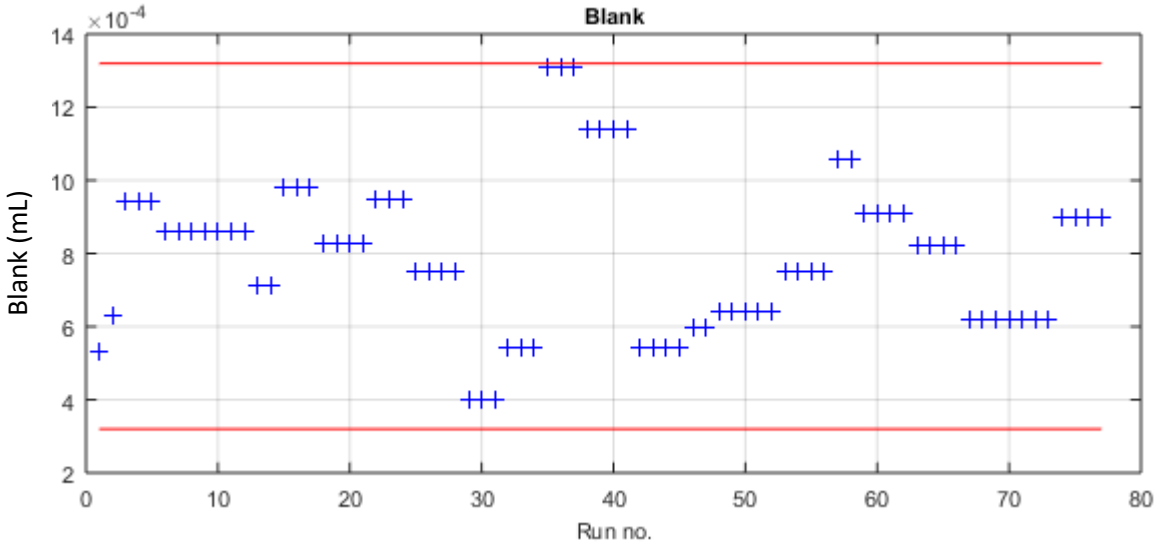
6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2N) varied less than 0.0004N for the first batch of secondary standard and less than 0.0003N for the second batch of secondary standard that covered all dissolved oxygen sample titrations. The blank correction is less than .0013 mL with a voyage mean of 0.0007 mL and standard deviation of 0.0002 mL

Red lines 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. The secondary thiosulphate standard was changed twice during the voyage. After CTD 2 and CTD 38.

For reference, titre volumes for dissolved oxygen bottle samples lay in the range 0.41 to 0.91 ml.



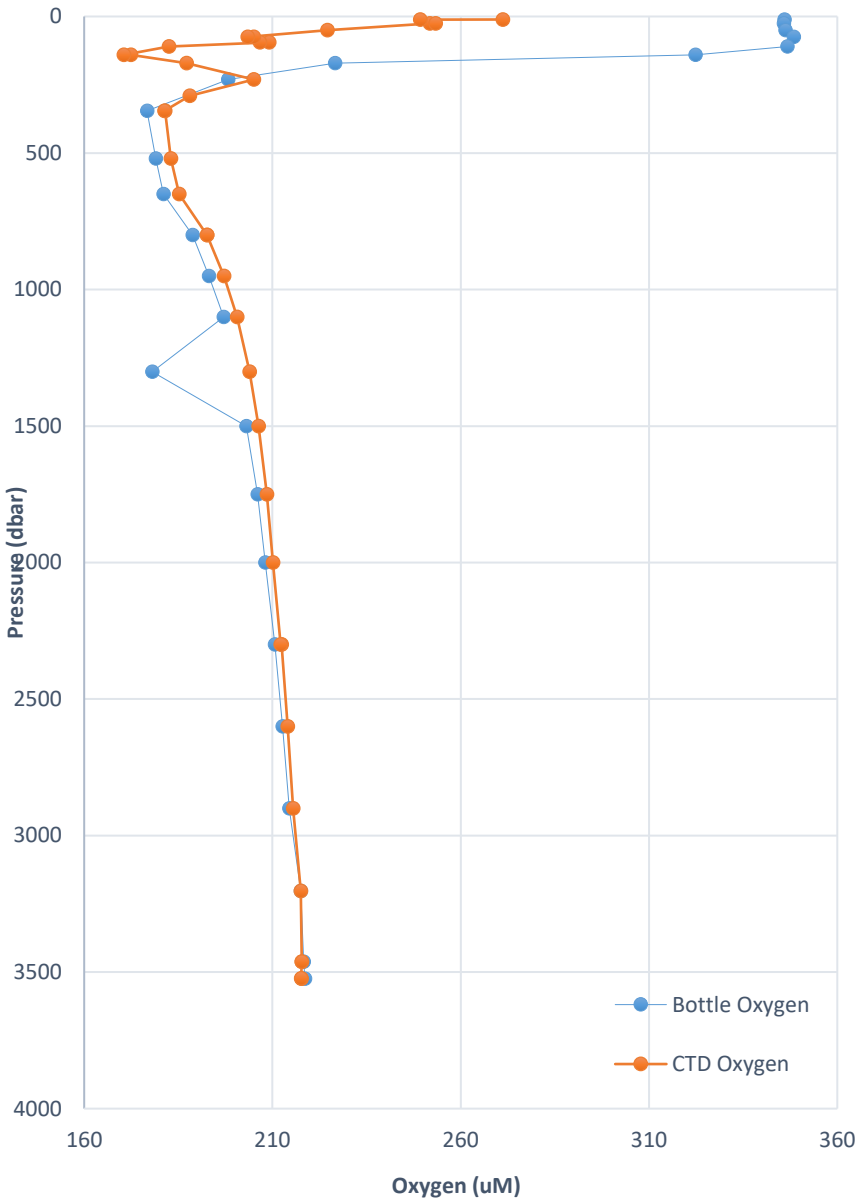


6.5 Missing or Suspect Dissolved Oxygen Data.

Data is flagged as Good, Suspect or Bad based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots. Flag key in Appendix 8.4.

CTD	RP	Run	Flag	Reason for Flag or Action
3	**18**	oxy003	-	No Result. Sample collected then lost due to breakage. Not assayed. Flagged in netcdf file only
39	**3**	oxy039	-	No result. Sample collected then lost due to breakage. Not assayed. Flagged in netcdf file only
47	**36**	oxy047	69	Result suspect. Outlier in vertical profile compared with CTD DO. Probable cause: premature Niskin bottle closure at depth
65	**35**	oxy065	69	Result suspect. Outlier in vertical profile compared with CTD DO. Probable cause: premature Niskin bottle closure at depth
69	**24 to 35**	oxy069	0	Results good. Large offset from the CTD oxygen instrument. Suspect CTD instrument data. Vertical profile plot below for reference, sec 6.5.1
69	**13**	oxy069	69	Result suspect. Outlier from vertical profile compared with CTD DO. Cause unknown.

6.5.1 Deployment 69 Bottle and CTD Oxygen vertical profile.



7 Nutrient Data Processing

7.1 Nutrient Assay Parameter Summary

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 6.10				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range	112 µM	3.0 µM	42 µM	1.4 µM	2.0 µM
Method Detection Limit (MDL)	0.2 µM[1]	0.02 µM	0.02 µM	0.02 µM	0.02 µM
Matrix Corrections	none	none	none	none	none
Analysts	Peter Hughes and Julie Janssens				
Lab Temperature (±1°C)	Variable, 21– 23°C				
Reference Material	KANSO, RMNS lot CC and CB (run 20 and 21)				
Sampling Container type	CTD: 50ml HDPE with screw cap lids. EXP: 12ml 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	CTD samples brought to room temperature in a water bath prior to assay.				

7.2 Nutrient Methods

When using the nutrient 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 (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 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 Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57). 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.

7.3 HyPro Processing Parameters

All instrument parameters and reagent batches and operation events are logged for each analysis run. This information is available on request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Data Reported as	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}
Calibration Curve degree	Linear	Linear	Quadratic	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	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				
Proportion of samples in duplicate.	<10%. CTD: Niskin fired at the greatest depth sampled in duplicate. Single samples collected for remaining depths.				
Comments	The reported data is not adjusted to the RMNS. Per deployment RMNS data tabulated in appendix 8.2.				

7.4 HyPro Data Processing Summary

After each 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:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE).
- Within 0.02uM for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. The flagged nutrient calibration data is in appendix 8.2.

Missing or suspect nutrient data is tabulated in section 7.8, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.4.

7.5 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Japanese KANSO certified RMNS lots CC and CB were assayed in triplicate in each run to monitor accuracy. The certified values are in table 1.

CSIRO reports nitrate+nitrite (designated NOx) and nitrite. The NOx values in table 1 are derived.

For this voyage, the majority of the measured RMNS analytes are within 2% of their certified mean. In the case of nitrite, within 0.02µM of its certified mean. Plots of RMNS values for all runs are below.

The assayed RMNS values per CTD deployment are listed in appendix 8.2

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.

Table 1: RMNS concentrations with expanded uncertainty (µmole L^{-1}) at 21°C

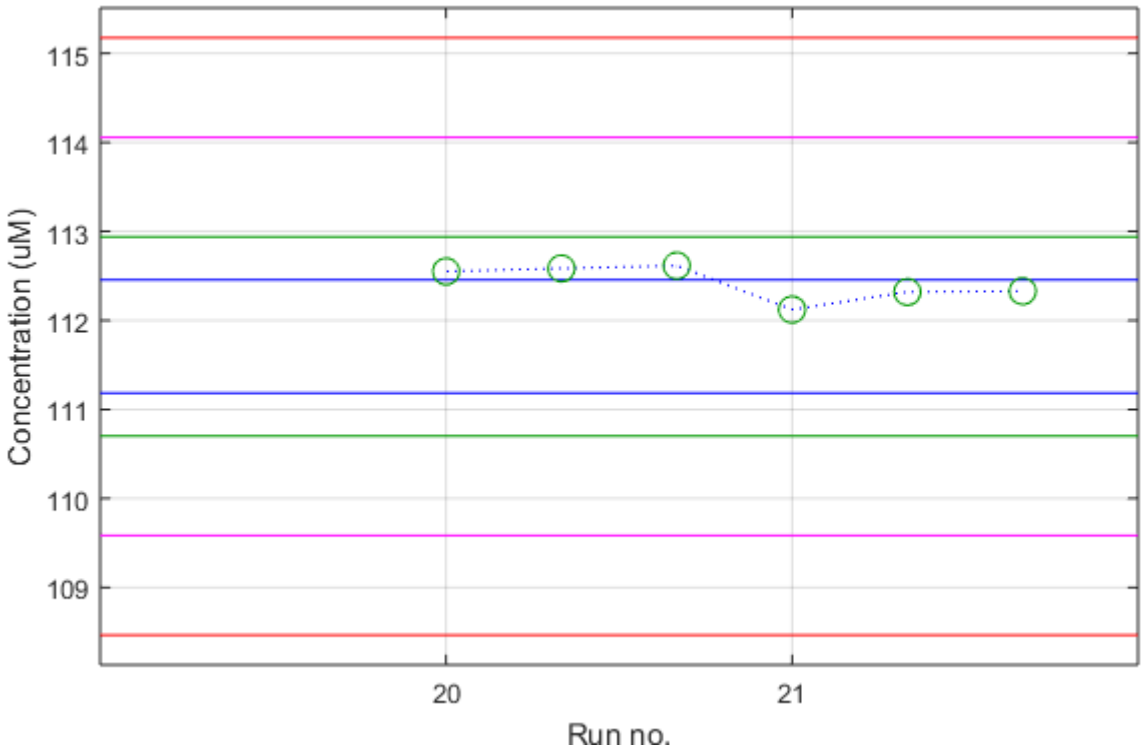
RMNS	Silicate	Phosphate	Nitrate: NO_3	Nitrite: NO_2	NO_3+ NO_2 (NO_X)
Lot CC	88.228 ± 0.492	2.130 ± 0.019	31.621 ± 0.246	0.119 ± 0.006	31.740 ± 0.252
Lot CB	111.821 ± 0.635	2.580 ± 0.022	36.649 ± 0.276	0.119 ± 0.006	36.768 ± 0.282

KANSO publishes the RMNS nutrient values in µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C (µM). The RMNS is not certified for ammonium. NO_x is derived by adding the NO_3 and NO_2 values.

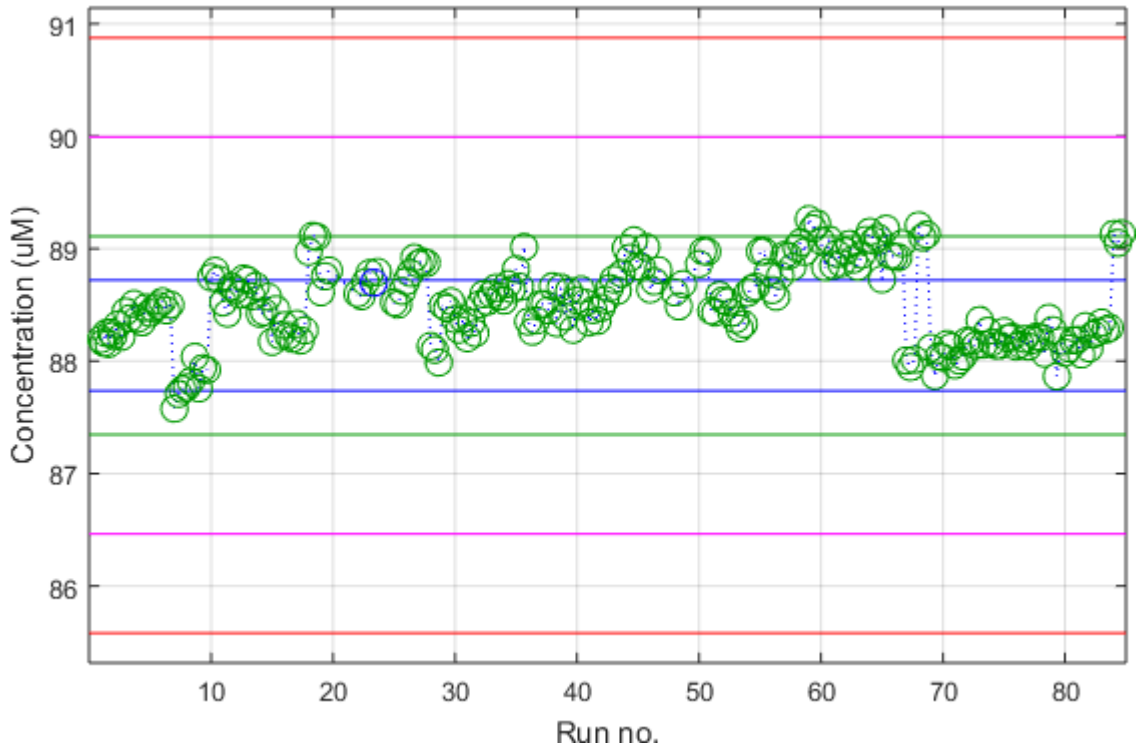
Plot key. The green, pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µM increments from the certified value. The blue line is the expanded uncertainty of the certified value.

7.5.1 Silicate RMNS Plot (µM)

Silicate RMNS (2 runs) for CB (111.82)
Overall mean 112.4 ± 0.2

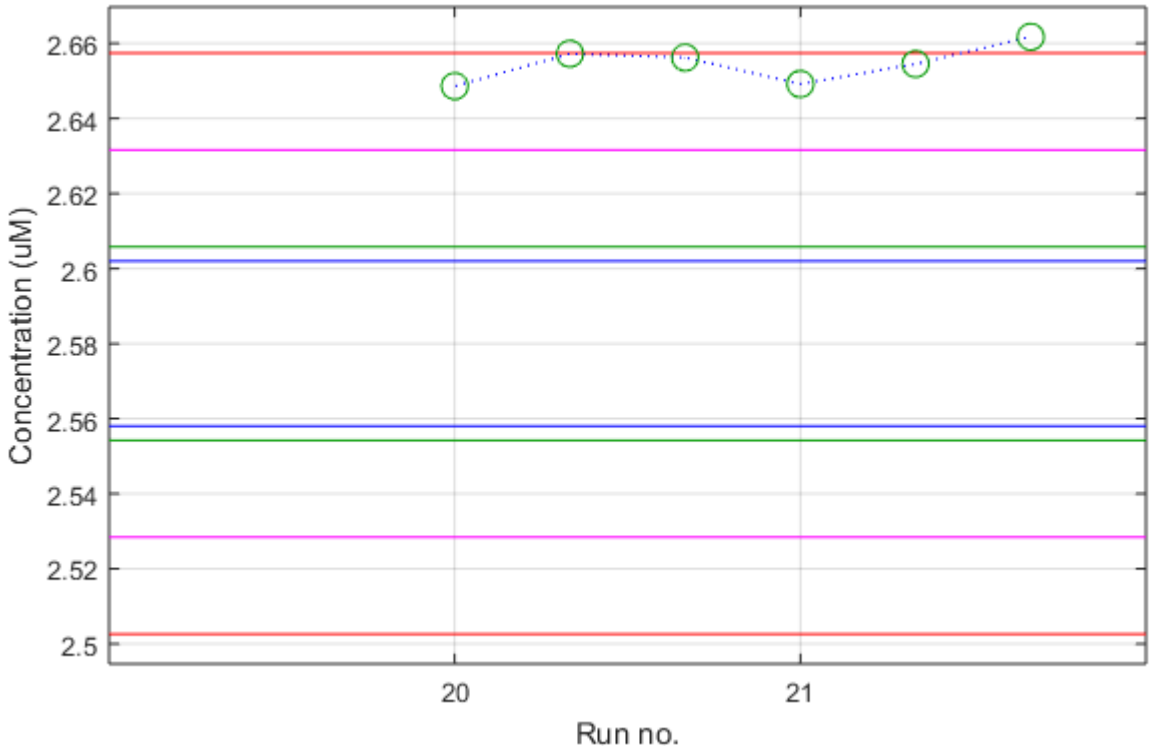


Silicate RMNS (79 runs) for CC (88.228)
Overall mean 88.5 ± 0.4

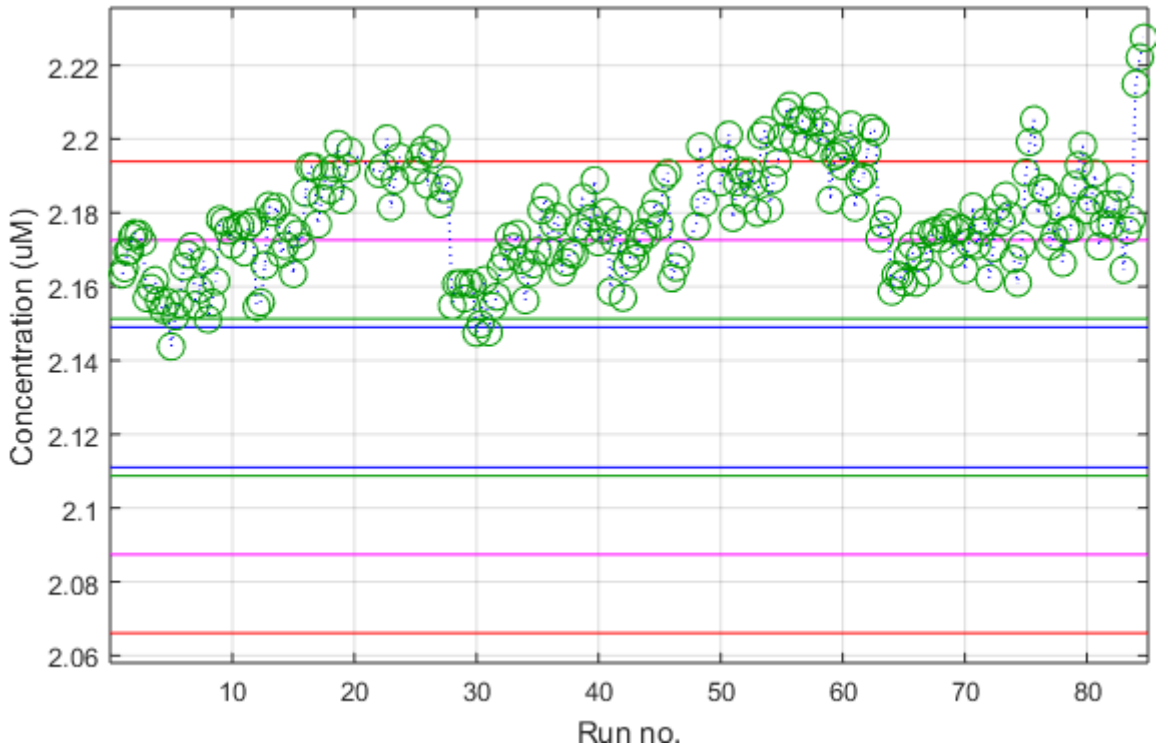


7.5.2 Phosphate RMNS Plot (µM)

Phosphate RMNS (2 runs) for CB (2.58)
Overall mean 1.655 ± 0.005

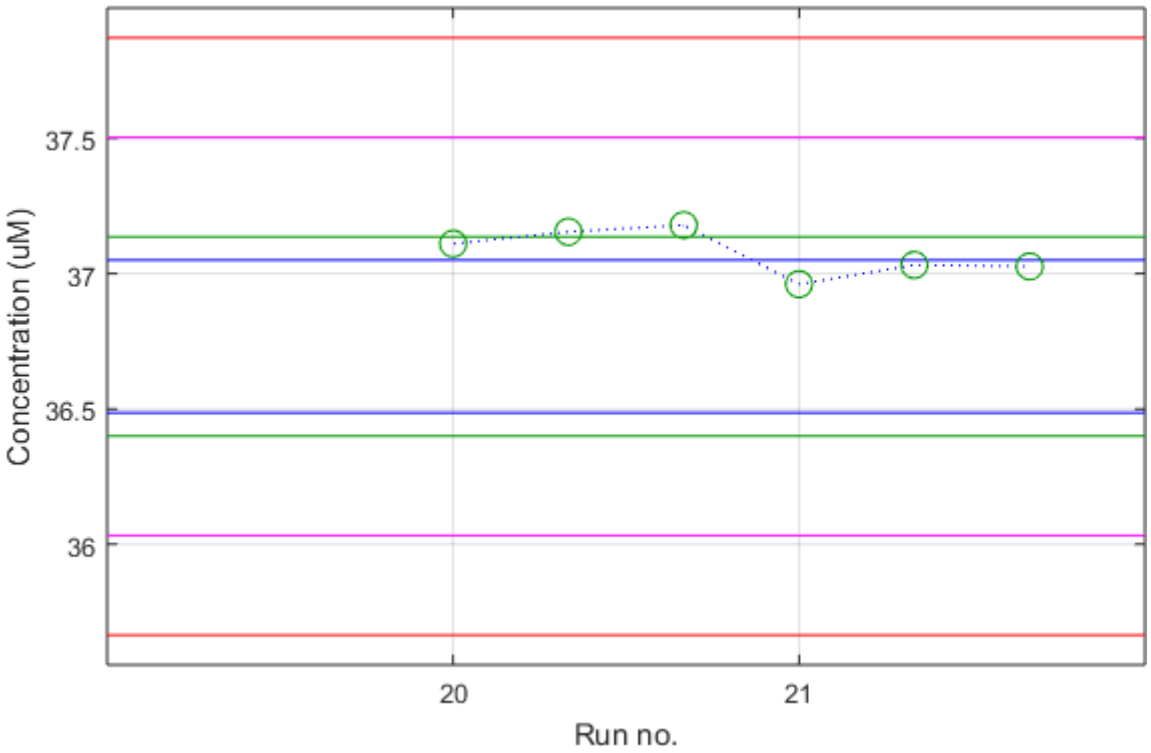


Phosphate RMNS (79 runs) for CC (2.13)
Overall mean 2.178 ± 0.015

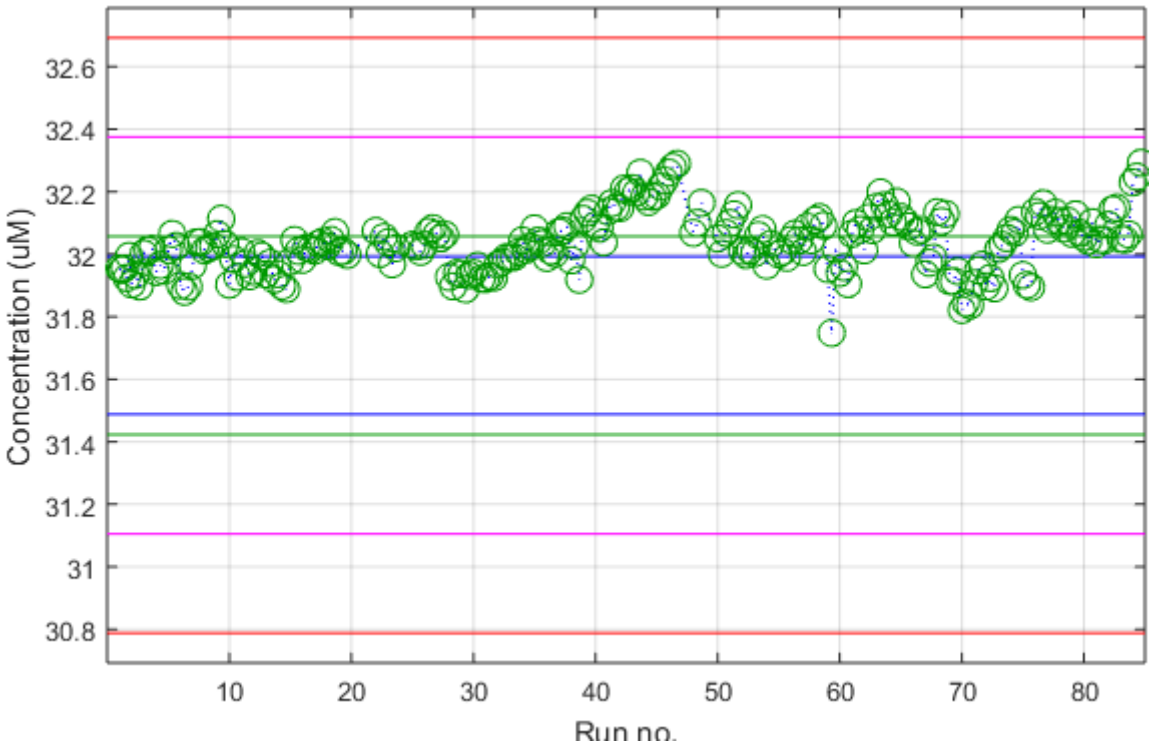


7.5.3 Nitrate + Nitrite (NOx) RMNS Plot (µM)

NOx RMNS (2 runs) for CB (36.768)
Overall mean 37.08 ± 0.08

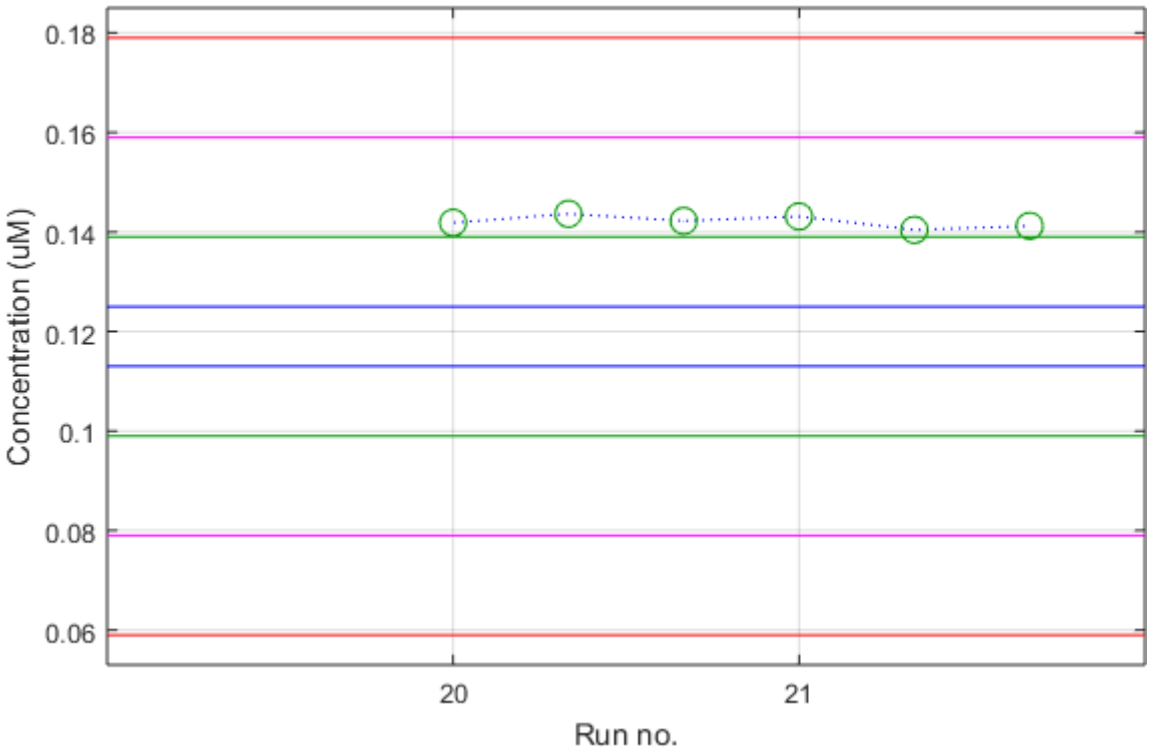


NOx RMNS (79 runs) for CC (31.74)
Overall mean 32.04 ± 0.09

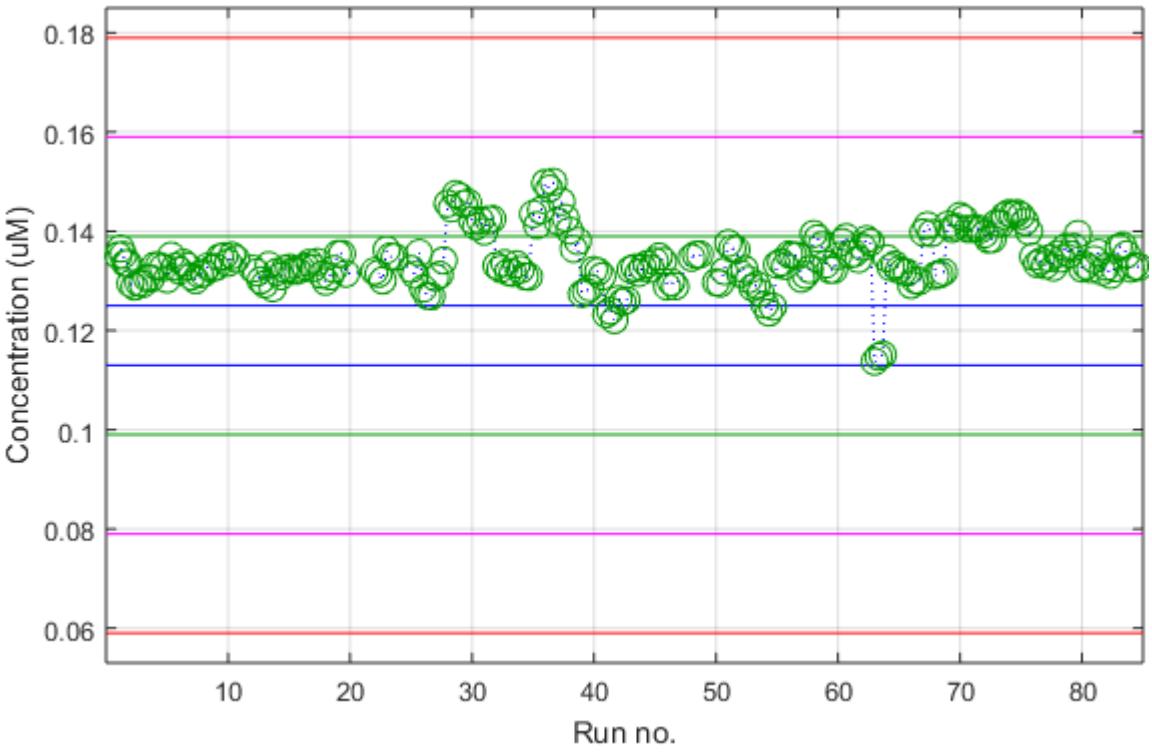


7.5.4 Nitrite RMNS Plot (µM)

Nitrite RMNS (2 runs) for CB (0.119)
Overall mean 0.142 ± 0.001



Nitrite (78 runs) for CC (0.119)
Overall mean 0.134 ± 0.006



7.6 Analytical Precision

7.6.1 Nutrient 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).

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

7.6.2 Nutrient Method Detection Limit

For this voyage, the measured detection limits (MDL)for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. The measured MDL is 3 times the standard deviation of three measurements of Low Nutrient Seawater (LNSW) assayed in each nutrient run. See appendix 8.4 for the measured MDL per CTD deployment.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Standard Dev. Min	0.000	0.000	0.000	0.000	0.000
Standard Dev. Max	0.058	0.006	0.006	0.006	0.006
Standard Dev. Mean	**0.064**	**0.003**	**0.002**	**0.001**	**0.001**
Standard Dev. Median	0.000	0.000	0.000	0.001	0.000
Precision of MDL (stdev)	0.17	0.009	0.008	0.005	0.06

7.6.3 Reference Material for Nutrients in Seawater

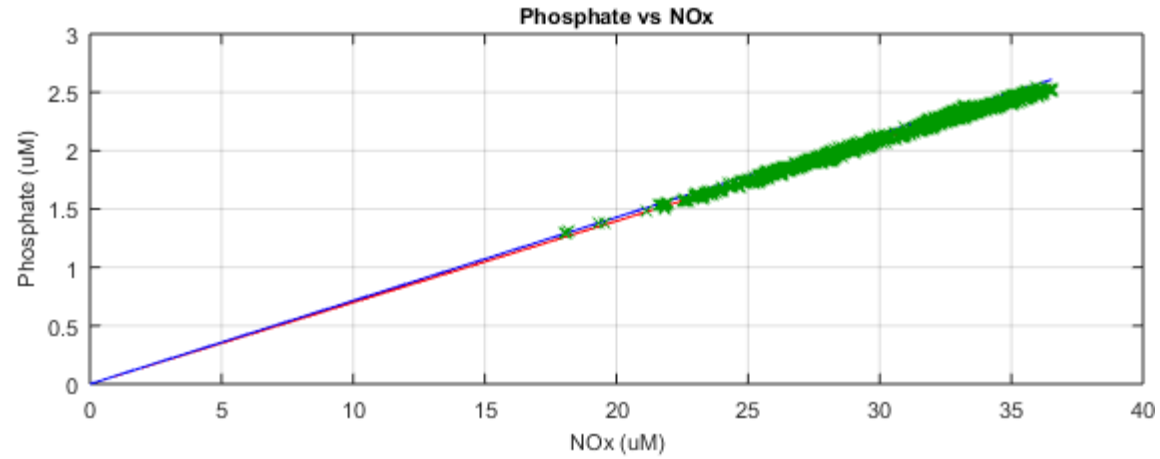
Precision values are calculated from intra-analysis measurements. The RMNS is assayed in triplicate within each run.

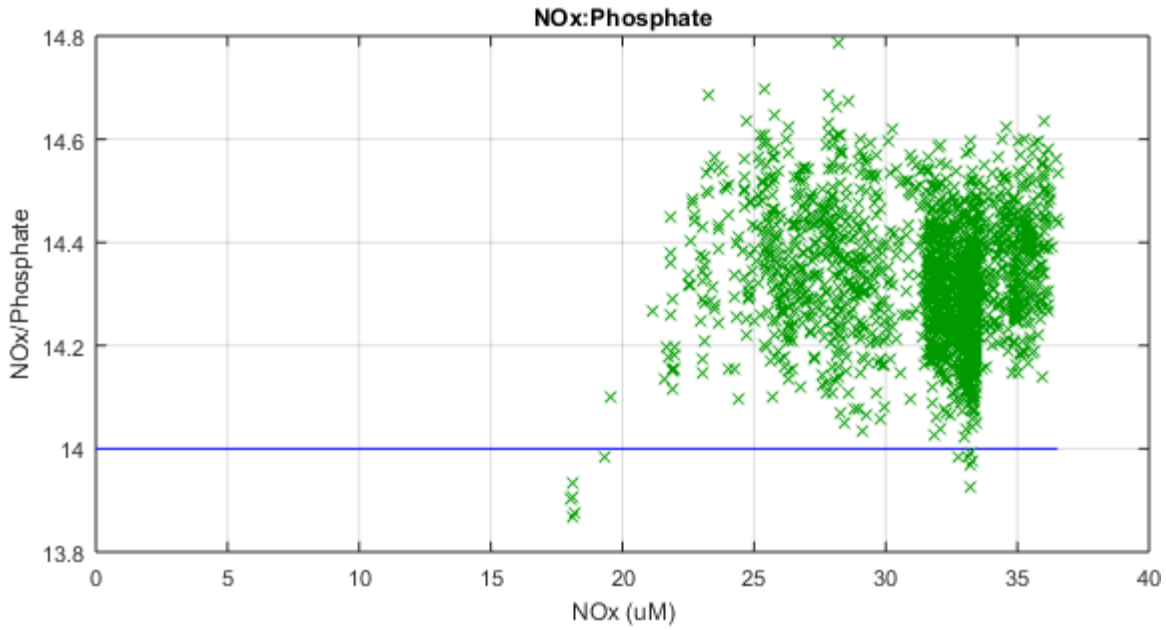
RMNS CC	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Certified RMNS CC (µmol L^{-1}) w/std deviation	88.228 ± 0.492	2.130 ± 0.019	31.740 ± 0.252	0.119 ± 0.006	- -
Minimum	87.6	2.14	30.96	0.114	1.31
Maximum	89.3	2.23	32.29	0.150	2.46
Mean	88.5	2.178	32.03	0.134	1.75
Median	88.5	2.18	32.03	0.133	1.71
Precision (Stdev)	0.3	0.015	0.12	0.006	0.2

RMNS CB	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Certified RMNS CB (µmol L^{-1}) w/std deviation	111.821 ± 0.635	2.580 ± 0.022	36.768 ± 0.282	0.119 ± 0.006	-
Minimum	112.1	2.65	36.96	0.140	1.85
Maximum	112.6	2.66	37.18	0.144	1.88
Mean	112.4	2.655	37.08	0.142	1.86
Median	112.5	2.655	37.07	0.142	1.86
Precision (Stdev)	0.2	0.005	0.08	0.001	0.01

7.7 Redfield Ratio Plot (14.0) for all CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.32





7.8 Missing or Suspect Nutrient Data.

Good data is flagged 0. Data flagged 63, below the detection limit, are not included in the table below. Data flagged BAD (133) are not included in the final csv result file (in2018_v05HydroDep.csv) archived in the CSIRO data centre. Flag Key in Appendix 8.4.

CTD	RP	Analyte	Flag	Reason for Flag or Action
4	03	Silicate	65	Result suspect. Instrument based, variation in the peak shape for the portion used to determine the concentration outside acceptable criteria used by HyPro. Cause unknown.
19	01	Silicate	69	Duplicate difference greater than 2 x MDL cutoff (0.4uM). Cause unknown. Duplicate assays (uM): 125.9, 125.5
20	12	All	144	No Result. Sample collected but not assayed due to operator error. Not flagged in csv data file.
39	06	NOx	65	Result suspect. Instrument based, variation in the peak shape for the portion used to determine the concentration outside acceptability criteria used by HyPro. Cause unknown.
47	36	ALL	69	Result suspect. Outlier in vertical profile. Probable cause: premature Niskin bottle closure at depth.
54	01	NOx	69	Duplicate difference greater than 2 x MDL cutoff (0.12uM). Cause unknown. Duplicate assays (uM): 33.18, 33.32
57	01	NOx	69	Duplicate difference greater than 2 x MDL cutoff (0.12uM). Cause unknown. Duplicate assays (uM): 33.54, 33.25
65	35	ALL	69	Result suspect. Outlier in vertical profile. Probable cause: premature Niskin bottle closure at depth.

7.9 Temperature & Humidity Change over Nutrient Analyses

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

(1) Above the AA3HR instrument, temperature only. Average 21.5°C, std 0.4.

(2) Against out-board bulkhead, temperature and pressure. Ship's instrument. Data on request.

(3) On the deck of the Nitrate & Nitrite AA3HR chemistry module, temperature and humidity. Data on request.

The laboratory temperature from (1) is also recorded on the nutrient run log sheet at the start and end of each analysis run. The laboratory temperature varied between 21 to 23°C over the course of the voyage.

8 Appendix

8.1 Salinity: Reference Material Used

Osil IAPSO Standard Seawater	
Batch	P161
Use by date	03/05/2020
K_{15}	0.99987
PSU	35.995

8.2 Nutrients: RMNS results for each CTD Deployment

8.2.1 RMNS Lot CC Results (µmol L^{-1})

Assay Run	CTD	Silicate (Si)	Phosphate (PO_4)	NOx (NO_3+NO_2)	Nitrite (NO_2)
CC value	**-**	***88.228 ± 0.492***	***2.130 ± 0.019***	***31.62 ± 0.25***	***0.119 ± 0.006***
1	**1**	88.20	2.168	31.96	0.135
2	**2**	88.26	2.174	31.91	0.129
3	**3**	88.44	2.159	32.01	0.130
4	**4**	88.39	2.155	31.95	0.133
5	**5**	88.46	2.150	32.03	0.133
multiple	**6**	Data tabulated in 8.2.2			
7	**7**	87.68	2.160	32.01	0.131
8	**8**	87.88	2.156	32.02	0.132
9	**9**	87.87	2.177	32.07	0.134
10	**10**	88.76	2.175	31.94	0.134
11	**11**	88.53	2.174	31.97	0.131
12	**12**	88.65	2.159	31.98	0.130
multiple	**13**	Data tabulated in 8.2.2			
14	**14**	88.48	2.172	31.91	0.132
16	**15**	88.25	2.190	32.01	0.133
17	**16**	88.26	2.184	32.03	0.133
18	**17**	89.06	2.192	32.05	0.131
19	**18**	88.72	2.191	32.00	0.134
20	**19**	RMNS lot CB. Data tabulated in 8.2.3			
21	**20**	RMNS lot CB. Data tabulated in 8.2.3			

22	**21**	88.63	2.194	32.04	0.131
23	**22**	88.76	2.189	32.01	0.135
25	**23**	88.55	2.195	32.02	0.133
26	**24**	88.80	2.194	32.06	0.127
27	**25**	88.87	2.186	32.06	0.132
28	**26**	88.07	2.159	31.92	0.146
29	**27**	88.50	2.159	31.92	0.146
30	**28**	88.34	2.153	31.94	0.142
31	**29**	88.26	2.153	31.93	0.142
32	**30**	88.54	2.169	31.98	0.133
33	**31**	88.61	2.171	32.00	0.132
34	**32**	88.62	2.162	32.03	0.131
36	**33**	88.33	2.175	32.00	0.149
multiple	**34**	Data tabulated in 8.2.2			
38	**35**	88.23	2.176	31.98	0.138
40	**36**	88.56	2.176	32.07	0.132
41	**37**	88.38	2.170	32.15	0.123
multiple	**38**	Data tabulated in 8.2.2			
multiple	**39**	Data tabulated in 8.2.2			
44	**40**	89.00	2.179	32.18	0.133
multiple	**41**	Data tabulated in 8.2.2			
46	**42**	88.72	2.165	32.28	0.129
48	**43**	88.60	2.186	32.11	0.135
50	**44**	88.94	2.195	32.04	0.130
51	**45**	88.49	2.186	32.13	0.137
52	**46**	88.50	2.188	32.01	0.131
53	**47**	88.33	2.194	32.05	0.128
54	**48**	88.64	2.188	32.00	0.125
55	**49**	88.92	2.206	32.00	0.133
56	**50**	88.66	2.203	32.05	0.135
57	**51**	88.91	2.204	32.05	0.131
58	**52**	89.01	2.202	32.11	0.138
multiple	**53**	Data tabulated in 8.2.2			

60	**54**	88.99	2.198	31.93	0.137
61	**55**	88.89	2.187	32.08	0.135
62	**56**	88.97	2.200	32.07	0.138
63	**57**	88.95	2.177	32.17	0.115
64	**58**	89.11	2.162	32.13	0.134
65	**59**	88.95	2.167	32.10	0.132
66	**60**	88.97	2.168	32.06	0.130
67	**61**	87.99	2.171	31.97	0.140
68	**62**	89.15	2.175	32.12	0.131
69	**63**	88.01	2.173	31.92	0.141
70	**64**	88.10	2.173	31.83	0.142
71	**65**	88.00	2.175	31.94	0.140
72	**66**	88.17	2.171	31.90	0.139
73	**67**	88.26	2.180	32.03	0.142
74	**68**	88.15	2.167	32.09	0.144
75	**69**	88.23	2.198	31.91	0.142
76	**70**	88.16	2.184	32.14	0.134
77	**71**	88.18	2.175	32.11	0.133
78	**72**	88.22	2.172	32.10	0.136
79	**73**	88.11	2.193	32.09	0.137
80	**74**	88.12	2.185	32.07	0.133
81	**75**	88.19	2.177	32.04	0.134
82	**76**	88.20	2.182	32.13	0.132
83	**77**	88.31	2.173	32.05	0.136

8.2.2 RMNS lot CC results where nutrients for a single CTD deployment are compiled from several assay runs. (µmole L^{-1})

Assay Runs	CTD	RP vs Analyte	Si	PO_4	NOx	NO_2
CC value		-	***88.23 ± 0.49***	***2.130 ± 0.019***	***31.62 ± 0.25***	***0.119 ± 0.006***
6,7	**6**	RP*: All except	88.50	2.168	31.89	0.133
		11 NOx	-	-	32.01	-
14,15	**13**	RP: All except	88.65	2.181	31.94	0.132
		16,18 NOx	-	-	31.91	-
37,38,39	**34**	RP: All except	88.43	2.181	32.13	0.144
		1 to 7 Si,PO_4,NOx	88.23	2.176	31.98	-
42,43	**38**	RP: All except	88.56	2.164	32.19	0.132
		5,12,26 PO_4	-	2.171	-	-
43,44	**39**	RP: All except	88.71	2.171	32.22	0.132
		1 Si,PO_4	89.00	2.179	-	-
45,46	**41**	RP: All except	88.90	2.186	32.21	0.134
		33 Si,PO_4,NOx,NO_2	88.72	2.165	32.28	0.129
59,60	**53**	RP: All except	89.22	2.192	31.91	0.133
		1,12,22,23 PO_4	-	2.198	-	-

8.2.3 RMNS lot CB Results (µmol L^{-1})

Assay Runs	CTD	RP vs Analyte	Si	PO_4	NOx	NO_2
CB value		-	***111.82 ± 0.64***	***2.580 ± 0.022***	***36.77 ± 0.28***	***0.119 ± 0.006***
20,21	**19**	RP*: All except	112.6	2.654	37.15	0.143
		3 Si	111.8	-	-	-
21	**20**	RP: All	111.8	2.655	37.00	0.142

*RP = Rosette Position

The nutrient results in the CSIRO data centre do NOT have RMNS adjustments applied.

8.3 Measured nutrient detection limit for each CTD Deployment (µmol L^{-1})

Assay Run	CTD	Silicate	Phosphate	NOx (NO_3+NO_2)	Nitrite	Ammonium
1	**1**	0.04	0.006	0.005	0.001	0.003
2	**2**	0.06	0.008	0.002	0.008	0.003
3	**3**	0.04	0.007	0.005	0.003	0.002
4	**4**	0.08	0.007	0.005	0.001	0.002
5	**5**	0.07	0.005	0.005	0.001	0.001
multiple	**6**	Data tabulated in 8.3.1				
7	**7**	0.06	0.002	0.006	0.004	0.002
8	**8**	0.04	0.006	0.001	0.005	0.004
9	**9**	0.06	0.002	0.008	0.003	0.002
10	**10**	0.05	0.001	0.002	0.000	0.002
11	**11**	0.01	0.013	0.009	0.003	0.006
12	**12**	0.02	0.004	0.004	0.003	0.005
13	**13**	Data tabulated in 8.3.1				
14	**14**	0.01	0.003	0.004	0.004	0.002
16	**15**	0.03	0.012	0.002	0.003	0.002
17	**16**	0.04	0.010	0.003	0.001	0.016
18	**17**	0.07	0.001	0.001	0.006	0.001
19	**18**	0.01	0.003	0.001	0.003	0.002
20	**19**	0.02	0.009	0.001	0.002	0.004
21	**20**	0.03	0.011	0.006	0.009	0.003
22	**21**	0.04	0.007	0.002	0.002	0.002
23	**22**	0.02	0.003	0.002	0.005	0.002
25	**23**	0.08	0.002	0.006	0.002	0.002
26	**24**	0.04	0.005	0.003	0.001	0.004
27	**25**	0.07	0.006	0.001	0.000	0.006
28	**26**	0.08	0.010	0.000	0.004	0.003
29	**27**	0.04	0.007	0.002	0.002	0.002
30	**28**	0.02	0.003	0.002	0.005	0.002
31	**29**	0.08	0.010	0.002	0.006	0.009
32	**30**	0.08	0.009	0.006	0.001	0.002

33	**31**	0.04	0.007	0.003	0.002	0.005
34	**32**	0.04	0.000	0.001	0.004	0.002
36	**33**	0.16	0.006	0.001	0.005	0.004
multiple	**34**	Data tabulated in 8.3.1				
38	**35**	0.02	0.003	0.009	0.001	0.003
40	**36**	0.05	0.008	0.003	0.001	0.011
41	**37**	0.06	0.002	0.002	0.003	0.003
multiple	**38**	Data tabulated in 8.3.1				
multiple	**39**	Data tabulated in 8.3.1				
44	**40**	0.05	0.004	0.003	0.003	0.003
multiple	**41**	Data tabulated in 8.3.1				
46	**42**	88.72	2.165	32.28	0.129	
48	**43**	0.17	0.008	0.003	0.001	0.013
50	**44**	0.02	0.008	0.002	0.001	0.003
51	**45**	0.08	0.003	0.012	0.002	0.001
52	**46**	0.06	0.001	0.003	0.002	0.004
53	**47**	0.06	0.002	0.003	0.006	0.004
54	**48**	0.11	0.016	0.010	0.018	0.004
55	**49**	0.03	0.008	0.006	0.002	0.006
56	**50**	0.01	0.013	0.002	0.003	0.003
57	**51**	0.05	0.011	0.002	0.004	0.002
58	**52**	0.03	0.005	0.005	0.003	0.002
multiple	**53**	Data tabulated in 8.3.1				
60	**54**	0.01	0.005	0.002	0.002	0.004
61	**55**	0.10	0.001	0.003	0.005	0.007
62	**56**	0.04	0.009	0.004	0.007	0.002
63	**57**	0.11	0.005	0.010	no result	0.002
64	**58**	0.08	0.003	0.002	0.005	0.002
65	**59**	0.03	0.006	0.004	0.003	0.004
66	**60**	0.04	0.007	0.003	0.003	0.004
67	**61**	0.02	0.012	0.005	0.002	0.003
68	**62**	0.03	0.004	0.005	0.004	0.003
69	**63**	0.09	0.001	0.008	0.009	0.002

70	**64**	0.04	0.003	0.002	0.001	0.003
71	**65**	0.11	0.003	0.001	0.001	0.004
72	**66**	0.08	0.009	0.003	0.002	0.004
73	**67**	0.04	0.011	0.002	0.003	0.002
74	**68**	0.03	0.004	0.003	0.003	0.002
75	**69**	0.07	0.009	0.007	0.008	0.013
76	**70**	0.04	0.007	0.003	0.002	0.010
77	**71**	0.03	0.005	0.004	0.004	0.002
78	**72**	0.01	0.007	0.010	0.003	0.002
79	**73**	0.05	0.008	0.003	0.001	0.002
80	**74**	0.04	0.007	0.003	0.005	0.005
81	**75**	0.06	0.005	0.005	0.001	0.004
82	**76**	0.10	0.005	0.007	0.003	0.002
83	**77**	0.04	0.007	0.001	0.007	0.002

8.3.1 Detection limits where nutrients for a single CTD deployment are compiled from several assay runs (µmol L^{-1})

Assay Runs	CTD	RP vs Analyte	Si	PO_4	NOx	NO_2	NH_4
6,7	**6**	RP*: All except	0.03	0.008	0.004	0.004	0.003
		11 NOx	-	-	0.006	-	-
13,14	**13**	RP: All except	0.01	0.004	0.006	0.004	0.004
		16,18 NOx	-	-	0.004	-	-
37,38,39	**34**	RP: All except	0.10	0.009	0.002	0.005	0.003
		1 to 7 Si,PO_4,NOx	0.02	0.003	0.009	-	-
42,43	**38**	RP: All except	0.03	0.010	0.002	0.002	0.002
		5,12,26 PO_4	-	0.006	-	-	-
43,44	**39**	RP: All except	0.02	0.006	0.006	0.001	0.002
		1 Si,PO_4	0.05	0.004	-	-	-
45,46	**41**	RP: All except	0.03	0.007	0.002	0.003	0.002
		33 Si,PO_4,NOx,NO_2	0.06	0.004	0.005	0.012	0.001
59,60	**53**	RP: All except	89.22	2.192	31.91	0.133	0.005
		1,12,22,23 PO_4	-	2.198	-	-	-

*RP = Rosette position

8.4 Flag Key for Hydrology Data Set

Flag	Description
0	Data is GOOD.
63	Data is below the nominal detection limit. Flagged by the processing software; HyPro.Applies only to nutrients.
65	Data is suspect. Flagged by HyPro. Applies only to nutrients. Relates to the shape of the measured portion of the absorbance peak. Criteria set in HyPro.
69	Data is suspect. Flagged by operator or HyPro.
133	Data is bad. Flagged by operator.
141	No data. Flag present in nc (netcdf) file only.
192	Data not processed. Raw data not adjusted by calibration.

8.5 GO-SHIP Specifications

8.5.1 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].

8.5.2 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 SiO2

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

8.5.4 PO4

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

8.5.5 NO3

Approximately 1% accuracy[1], 0.2% precision[3], 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

Armishaw, P. (2003). "*Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty."* Accred. Qual. Assur., 8: pp. 218-224

Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H. (1967) *"The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment.",* Deep-Sea Res., 14: pp.381-389. doi: 10.1016/0011-7471(67)90082-4

Hood, E.M. (2010). *"Introduction to the collection of expert reports and guidelines."* The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.

Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). *"Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers."* In the GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 12010. (UNESCO/IOC)

Kérouel, R. and Aminot A. (1997) *"Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis",* Mar. Chem., 57: pp. 265-275. doi: 10.1016/S0304-4203(97)00040-6

Murphy, J. And Riley, J.P. (1962)"*A Modified Single Solution Method for the Determination of Phosphate in Natural Waters"*, Anal. Chim. Acta, 27: p.30. doi: 10.1016/S0003-2670(00)88444-5

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

Wood, E.D., Armstrong, F.A.J., andRichards, F.A. (1967) *"Determination of nitrate in seawater by cadmium-copper reduction to nitrite."* Journal of the Marine Biological Association of U.K. 47: pp. 23-31. doi: 10.1017/S002531540003352X