RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2019_v02
Chief Scientist	Tom Trull
Principal Investigator	Philip Boyd
Voyage title:	SOTS: Southern Ocean Time Series automated moorings for climate and carbon cycle studies southwest of Tasmania; Subantarctic Biogeochemistry of Carbon and Iron, Southern Ocean Time Series site.
Report compiled by:	Christine Rees, Merinda McMahon and Jack McDonald

Contents

1 Executive Summary

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

The primary objective was to deploy a new set of Southern Ocean Time Series (SOTS) moorings; Southern Ocean Flux Station (SOFS-8) and Sub-Antarctic Zone sediment trap (SAZ-21) and recover the existing SOTS moorings (SOFS-7.5 and SAZ-20). Ancillary work was to obtain supporting information on atmospheric and oceanographic conditions using Conductivity, Temperature and Depth (CTD) casts for samples and bio-optical sensor data, underway measurements, Triaxus towed body, continuous plankton recorder and autonomous profiling biogeochemical-Argo floats. The secondary object was to enhance the understanding of the interlinked biogeochemical cycles of iron and carbon in the Southern Ocean.

Water samples were collected for salinity, dissolved oxygen and nutrient measurement from the CTD and trace metal rosette (TMR) deployments, as well as the underway instrument water supply. Experiments were conducted on board by the science party producing additional nutrient samples. All samples were analysed during the voyage in the Hydrochemistry laboratory. The salinity and dissolved oxygen samples were used to calibrate the sensors on the CTD rosette and the underway nutrient samples were used to calibrate the nitrate (SUNA) sensor on the Triaxus. Additional salinity samples were collected and analysed during the voyage from the underway water supply to calibrate the Thermosalinograph (TSG).

Five nutrients were analysed; silicate, phosphate, nitrate + nitrite (NOx), nitrite and ammonium. Certified reference materials for nutrients in seawater (RMNS) were analysed in every nutrient analyses to ensure data quality.

All data (salinity, dissolved oxygen and nutrients) reported are within specified criteria and GO-SHIP compliant.

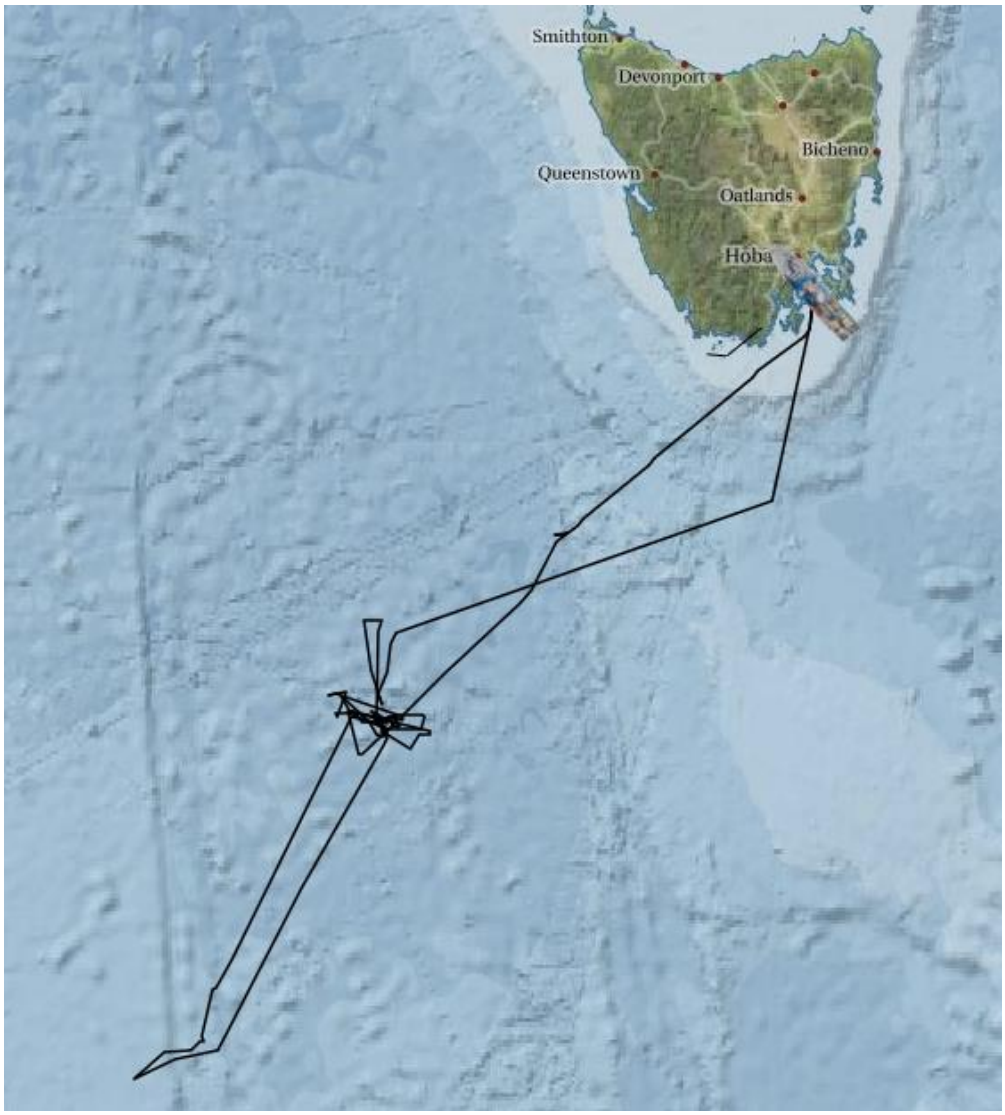
Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, March 14th – 05th, 2019.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Tom Trull	Chief Scientist	CSIRO-ACE
Tegan Sime	Voyage Manager	CSIRO
Christine Rees	Hydrochemist	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Jack McDonald	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	155 CTD 27 TSG
Dissolved Oxygen (SIO automated titration)	155 CTD
Nutrients (Seal AA3HR segmented flow)	155 CTD 117 TMR 114 EXP 13 UWY

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 24 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- 22 CTD deployments in total however only 16 CTD stations had water samples collected. Sampling conducted by the hydrochemistry team for dissolved oxygen, nutrients and salinity.

4.1.2 TMR (Trace Metal Rosette)

- Sampling point, 12 bottle trace metals rosette.
- 12 deployments in total, 11 deployments had nutrient samples collected. Sampled by the trace metals team.

4.1.3 EXP (Experimental samples)

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

4.1.4 TSG (Thermosalinograph)

- Samples collected by hydrochemistry from underway lab for calibration of thermosalinograph.

For UWY, EXP, TMR and TSG sample information refer to the eLog's from the voyage.

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.

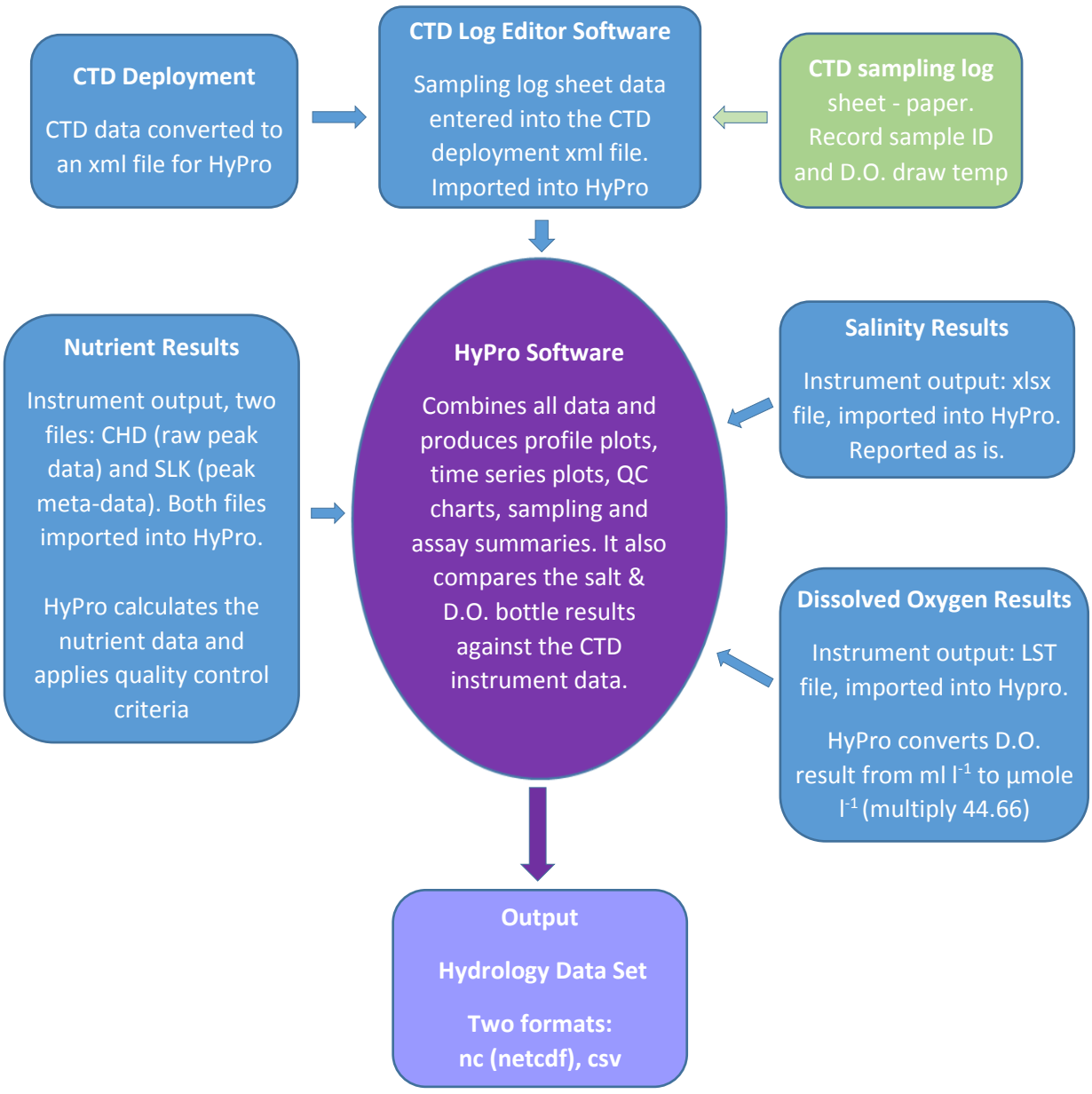


Figure 1: Hydrology Data Processing Flow Diagram.

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	Jack McDonald, Merinda McMahon and Christine Rees
Lab Temperature (±0.5°C)	Average, 21.5°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	None.

5.2 Salinity Method

Salinity samples are measured on a high precision laboratory salinometer (Guildline Autosal 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 x 10^{-3}.

Before each batch of sample measurements, the Autosal 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 200ml 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 25cm^3. A 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

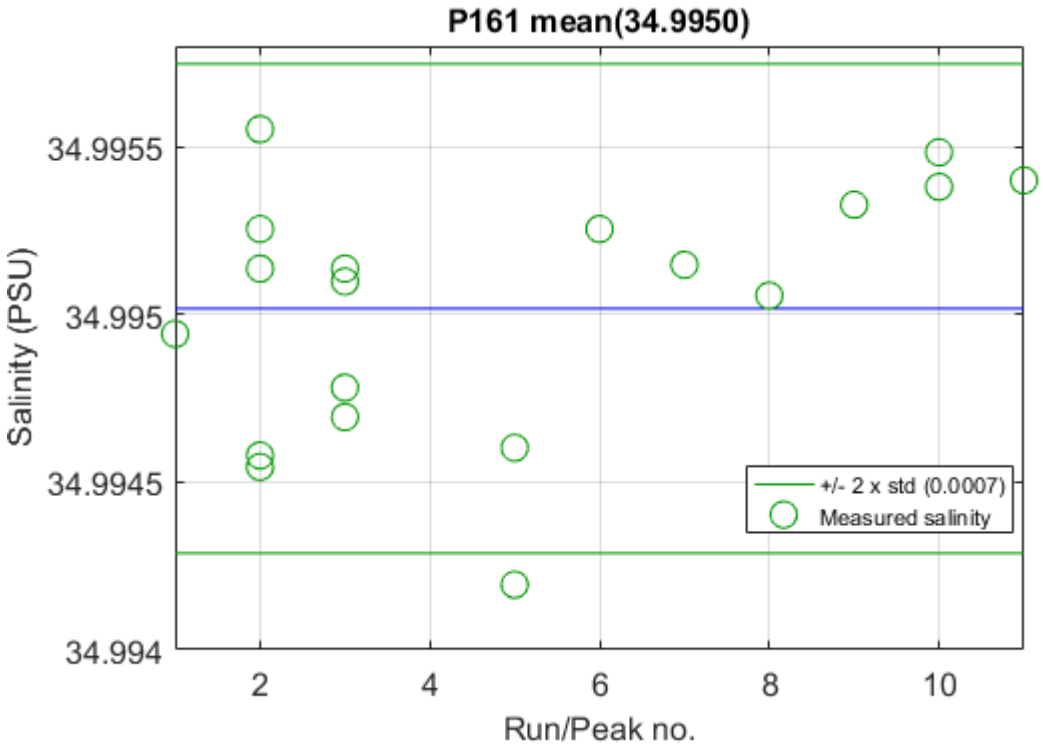
The difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities is generally less than 0.01 PSU.

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)

5.4 OSIL Salinity Standard PSU across the Voyage

The instrument is calibrated with OSIL standard seawater lot P161 (PSU = 34.995). The graph below shows the OSIL lot P161 measured results after the same bottle was used for the calibration. The blue line represents the mean of all standards measured for standardisation.



5.5 Missing or Suspect Salinity Data

Data is flagged based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots (Flag key in appendix 8.5).

CTD	RP	Run	Flag	Reason for Flag or Action
18	24	sal008	133	Outlier in depth profile plot, the Niskin bottle misfired at depth, dissolved oxygen and nutrient data also outliers.

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)	Merinda McMahon & Jack McDonald
Lab Temperature (±1°C)	Average, 20.4°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 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 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 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.

Before each batch of sample assays, the thiosulphate solution is standardised by using it to titrate 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.

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

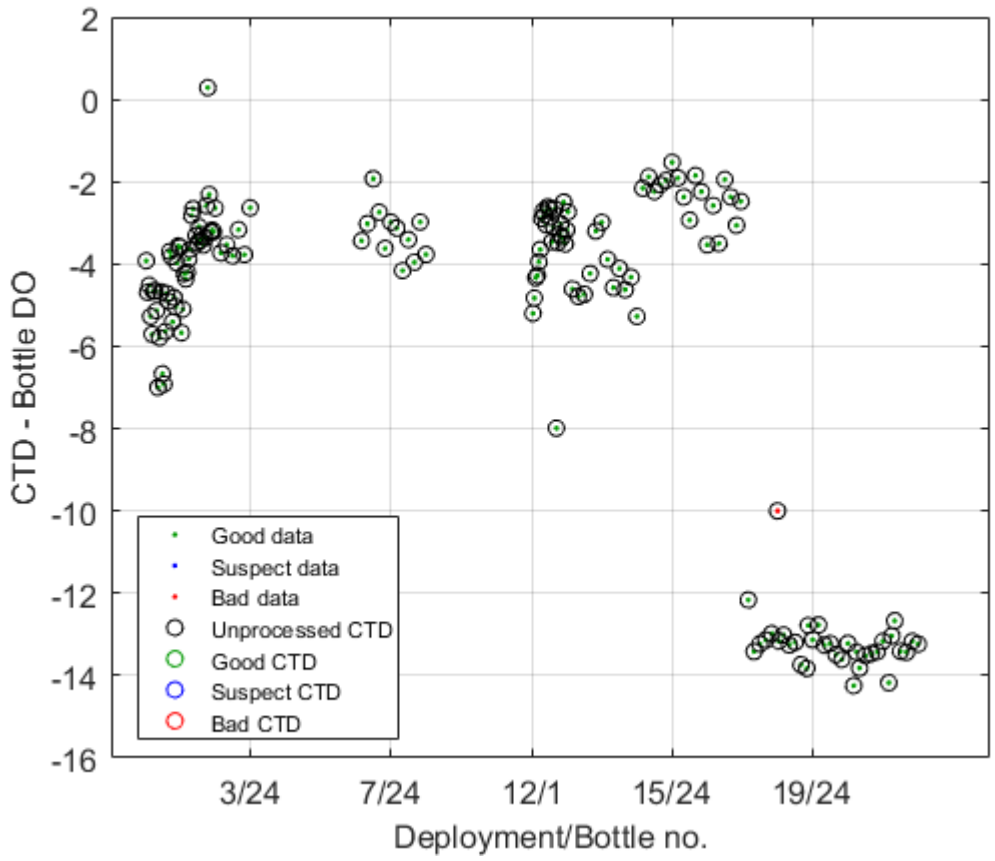
6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

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 DataLibrariansOAMNF@csiro.au for corrected CTD data.

The change in the data from deployment 18 onwards corresponds to the primary sensor being swapped with sensor 3154 which had been recently calibrated by Seabird, including a membrane replacement.

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

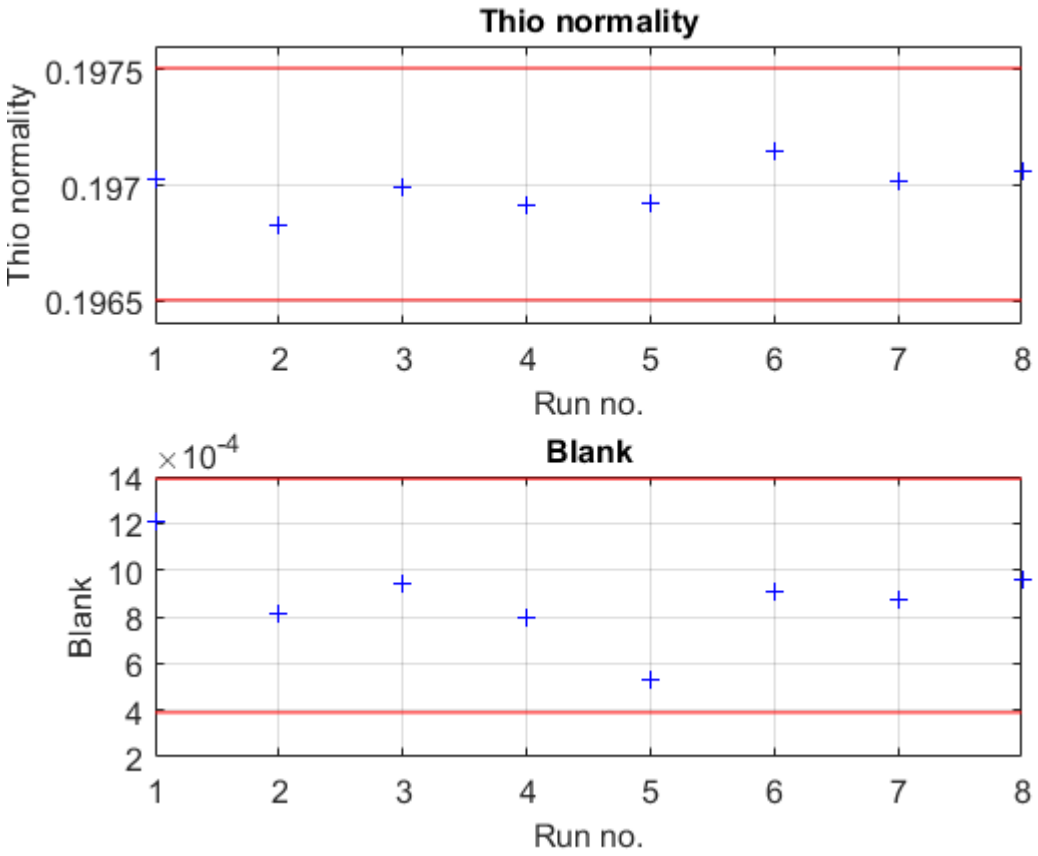


6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2N) varied less than 0.0003 N for all dissolved oxygen sample titrations. The blank correction is less than 0.001 mL with a voyage mean of 0.1970 mL and standard deviation of 0.0001 mL (n=8).

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.

For reference, titre volumes for dissolved oxygen bottle samples lay in the range 0.46 to 0.80 mL



6.5 Missing or Suspect Dissolved Oxygen Data.

Data is flagged as Good, Suspect or Bad in HyPro based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots (Flag key appendix 8.5).

CTD	RP	Run	Flag	Reason for Flag or Action
2	10	oxy002	141 (nc file)	Missing data. Operator error. Flask knocked over.
18	24	oxy007	133	Outlier in depth profile plot, the Niskin bottle misfired at depth, salinity and nutrient data also outliers.

7 Nutrient Data Processing

7.1 Nutrient Assay Parameter Summary

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	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range	140 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	Christine Rees, Merinda McMahon & Jack McDonald				
Lab Temperature (±1°C)	Average, 20.4°C				
Reference Material	KANSO, RMNS lot CJ, CD & CC				
Sampling Container type	CTD & TMR: 50ml HDPE with screw cap lids. EXP and UWY: 12ml PP tubes with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD, TMR and UWY: None. EXP: as prepared by the science parties.				
Comments	An extra calibration standard was added into calibration curve on request from the chief scientist. The calibrant was ½ the concentration of the usual calibrant 1.				

7.2 Nutrient Methods

When using silicate, phosphate, nitrate+nitrite (NOx) 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 (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	8	7	8	7	7
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

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
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.	CTD 2 & 12: 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 8.3.				

7.4 HyPro Data Processing Summary

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:

- ±0.5% of the concentration of the top standard for silicate and nitrate + nitrite (as per WOCE).
- Within 0.02 µM 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 7.9, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.5.

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

Japanese KANSO certified RMNS lot CJ was assayed in triplicate in each run to monitor accuracy. The certified values are in table 1.

For in2019_v02, the majority of RMNS results are within 1% of their certified mean and within 0.02 µM for nitrite. Plots of RMNS values for all runs are below.

The assayed RMNS values per Analysis run and CTD deployments are listed in appendix 8.4

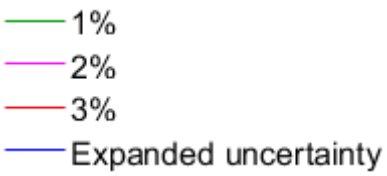
The GO-SHIP criteria (Hyde *et al*., 2010), appendix 8.6, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

Table 1: RMNS concentrations with expanded uncertainty at 21°C

RMNS	NO_3 (µmol L^{-1})	NO_2 (µmol L^{-1})	NO_3+ NO_2 (NO_X, µmol L^{-1})	PO_4 (µmol L^{-1})	SiO_4 (µmol L^{-1})
Lot CD	5.629 ± 0.0051	0.018 ± 0.004	5.647 ± 0.055	0.457 ± 0.008	14.264 ± 0.10
Lot CC	31.621 ± 0.246	0.119 ± 0.006	31.740 ± 0.252	2.130 ± 0.019	88.228 ± 0.492
Lot CJ	16.588 ± 0.205	0.032 ± 0.007	16.620 ± 0.212	1.219 ± 0.020	39.424 ± 0.410

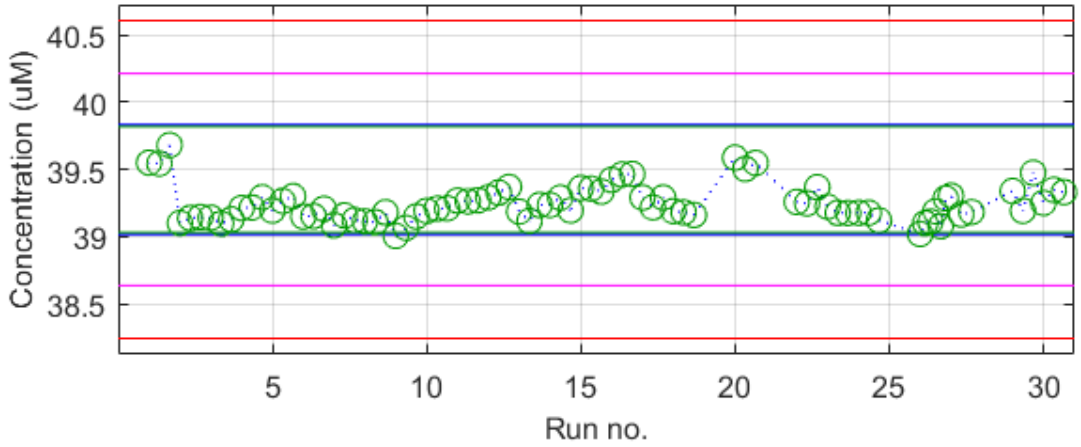
KANSO publishes the RMNS nutrient values in µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C. The RMNS is not certified for ammonium. NO_x is derived by adding the NO_3 and NO_2 values.

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.



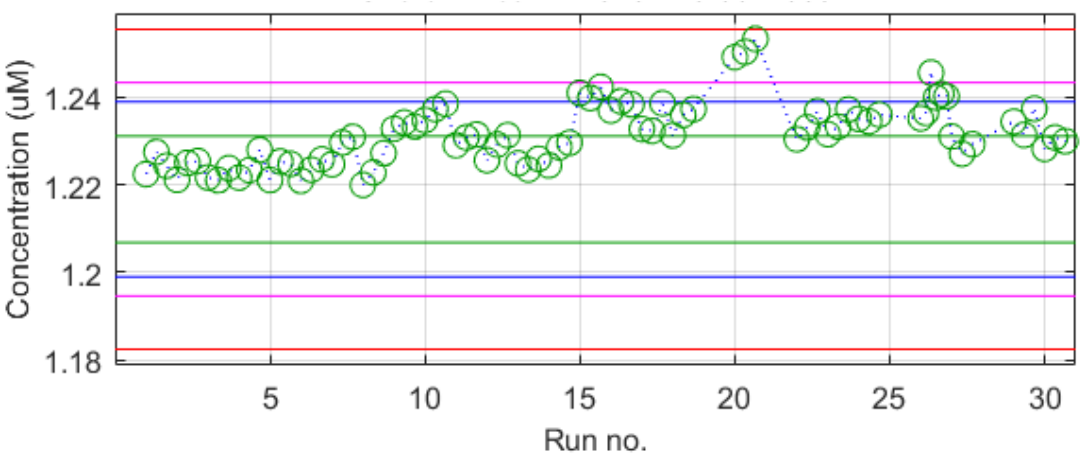
7.5.1 Silicate RMNS Plot (µM)

Silicate RMNS (26 runs) for CJ (39.42)
Overall mean 39.24 ± 0.14

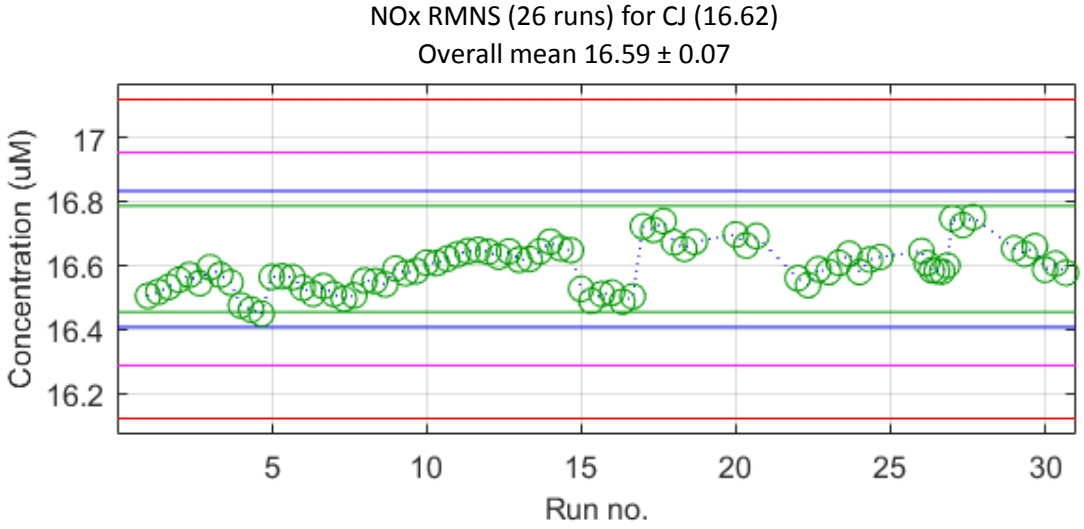


7.5.2 Phosphate RMNS Plot (µM)

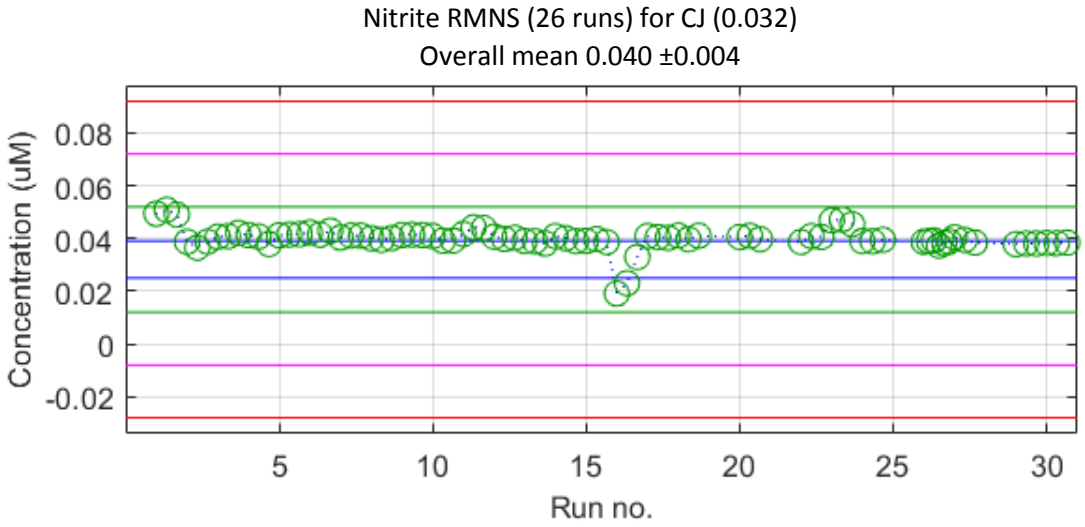
Phosphate RMNS (26 runs) for CJ (1.219)
Overall mean 1.232 ± 0.007



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



7.5.4 Nitrite RMNS Plot (µM)



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 in2019_v02, 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 deployments.

MDL	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})	Nitrate + Nitrite (NOx, µmol L^{-1})	Nitrite (µmol L^{-1})	Ammonia (µmol L^{-1})
Nominal MDL	0.20	0.02	0.02	0.02	0.02
Standard Dev. Min	0.010	0.001	0.000	0.000	0.001
Standard Dev. Max	1.121	0.008	0.017	0.009	0.003
Standard Dev. Mean	**0.101**	**0.004**	**0.006**	**0.002**	**0.002**
Standard Dev. Median	0.041	0.004	0.005	0.002	0.002
Precision of MDL (stdev)	0.223	0.002	0.004	0.002	0.001

7.6.3 Reference Material for Nutrients in Seawater

Precision values are calculated from intra-analysis measurements, multiple measurements are taken at a time, typically 3-4.

RMNS CD	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})	Nitrate + Nitrite NOx, (µmol L^{-1})	Nitrite (µmol L^{-1})	Ammonia (µmol L^{-1})
Certified RMNS CD w/std deviation	14.26 ± 0.009	0.46 ± 0.001	5.65 ± 0.004	0.018 ± 0.001	- -
Minimum	14.07	0.46	5.48	0.007	1.64
Maximum	14.37	0.46	5.48	0.007	1.85
Mean	14.22	0.46	5.52	0.025	1.73
Median	14.21	0.46	5.532	0.029	1.69
Precision (Stdev)	0.14	0.004	0.03	0.010	0.11

RMNS CC	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})	Nitrate + Nitrite NOx, (µmol L^{-1})	Nitrite (µmol L^{-1})	Ammonia (µmol L^{-1})
Certified RMNS CC w/std deviation	88.23 ± 0.005	2.13 ± 0.004	31.74 ± 0.030	0.119 ±0.002	- -
Minimum	87.63	2.13	31.58	0.126	1.39
Maximum	88.84	2.14	32.04	0.138	2.12
Mean	88.06	2.14	31.77	0.130	1.83
Median	87.70	2.13	31.69	0.127	1.80
Precision (Stdev)	0.68	0.003	0.24	0.007	0.29

RMNS CJ	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})	Nitrate + Nitrite (NOx, (µmol L^{-1})	Nitrite (µmol L^{-1})	Ammonia (µmol L^{-1})
Certified RMNS CJ w/std deviation	39.424 ± 0.020	1.219 ± 0.002	16.620 ± 0.009	0.032 ± 0.001	- -
Minimum	39.07	1.222	16.46	0.025	0.84
Maximum	39.59	1.251	16.74	0.050	1.03
Mean	39.24	1.232	16.59	0.040	0.92
Median	39.21	1.232	16.59	0.040	0.89
Precision (Stdev)	0.13	0.007	0.07	0.004	0.05

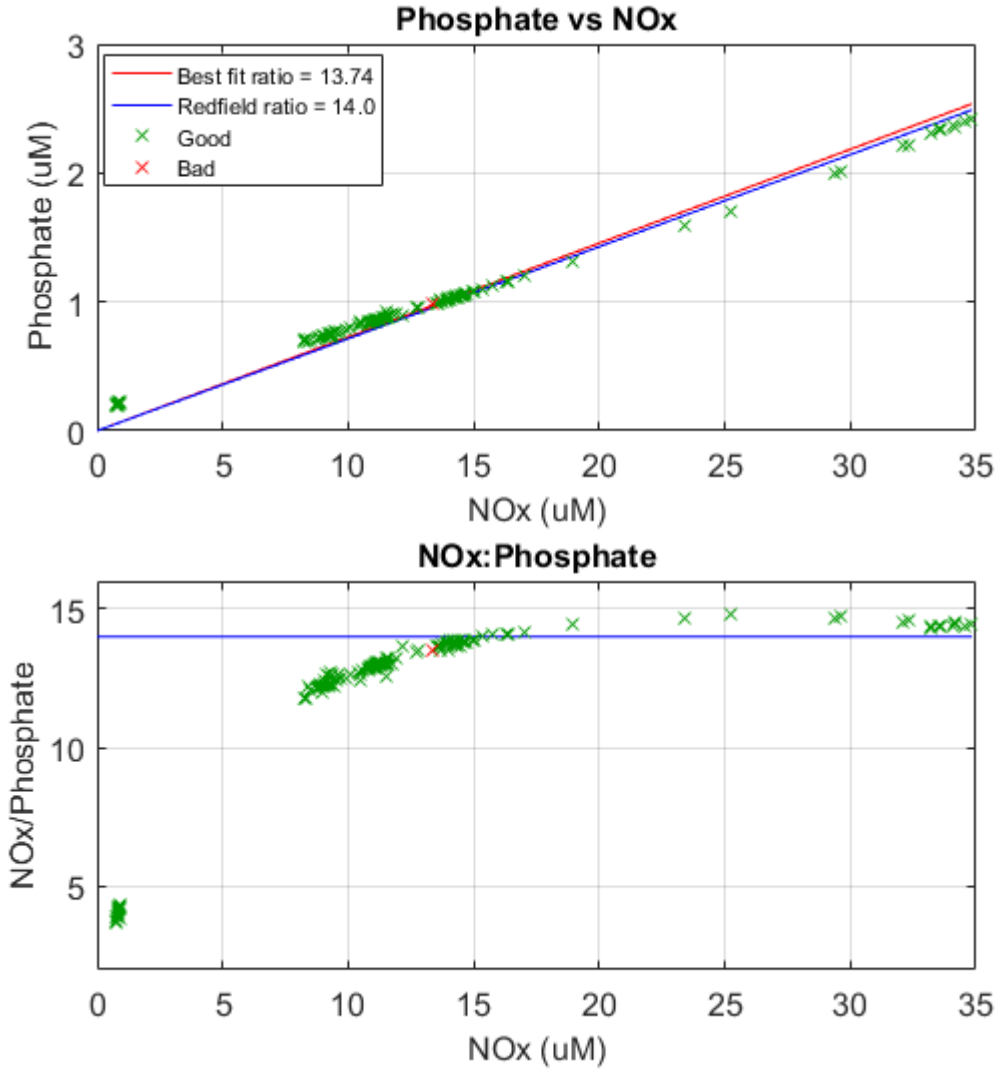
7.7 Sampling Precision

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 and their mean is less than the MDL value. The exception is nitrate+nitrite, which uses 0.06 µM as the MDL boundary.

For in2018_v02 duplicate samples were collected from deployment 1, 2 &12 the sampling precision was within the accepted limits.

7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 13.74.



7.9 Missing or Suspect Nutrient Data.

The table below identifies all flagged data and any samples that had repeated analyses performed to obtain good data. Good data are flagged 0. Data flagged 63, below detection limit, are not included in the table below. Data flagged BAD (133) are not included in the .csv results files (in2019_v02HydroDep.csv). Flag Key in Appendix 8.5.

CTD	RP	Nutrient	Run	Flag	Reason for Flag or Action
1	14	NH4	nut001	133	Sample was contaminated as much higher concentration compared to all other samples.
12	2	SiO4	nut007	69	Sample is an outlier in depth profile, contamination possible.
18	24	All	nut020	133	Outlier in depth profile plot, the Niskin bottle misfired at depth, salinity and dissolved oxygen data also outliers.
CTD 22/ EXP69-80	All	NH4	nut024	N/A	The baseline for NH_4 was contaminated resulting in the MDL being negative as well as the very low concentrated CTD samples. The data does look slightly offset in the depth profile compared to the other CTD deployments. However measurements are very low for ammonium so no correction applied.

7.10 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. Median 20.4°C, Average 20.4°C, standard deviation 0.6°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_v02_hyd_voyagereport.docx" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 20.4°C.

The laboratory temperature was measured and recorded on the nutrient run sheets at the start each analysis run. The temperature varied between 18.1°C and 23.8°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: Flagged Calibration and Quality Control Data

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. Data points marked as suspect or bad will have less weighting in the calibration curve.

Sample	Peak	Run	Analysis	Reason for Flag or Action
CTD 1	Cal 2, 4 & 6	Nut001	NOx	<70% of calibration peaks are within calibration limits. Cal 2, 4 & 6 suspect.
CTD 1	Cal 4, 5 & 6	Nut001	SiO4	<70% of calibration peaks are within calibration limits. Cal 4, 5 & 6 suspect.
CTD 1	Cal 0, 1 & 3	Nut001	NH4	<70% of calibration peaks are within calibration limits. Cal 1, 3 and second point cal 0 suspect.
UWY 1-8	Cal 1	Nut002	NH4	Both points suspect, less weighting in calibration curve.
CTD 2	Cal 3	Nut003	PO4	2nd point suspect.
CTD 2	Cal 1 & 4	Nut003	NH4	Both points at cal 1 and 4 marked suspect.
CTD 3	Cal 1	Nut004	NH4	Both cal 1 points marked as suspect
CTD 8	Cal 3 & 4	Nut006	NH4	Both cal 3 and 4 points parked as suspect.
CTD 12	Cal 3	Nut007	NH4	Both cal 3 points marked as suspect.
TMR 3	Cal 2 & 3	Nut008	NH4	Both cal 3 points and 2nd cal 2 point marked as suspect.
EXP6-22	Cal 3 & 4	Nut009	NH4	Both cal 3 points and 1st cal 4 point marked as suspect.
TMR 4	Cal 3 & 4	Nut010	NH4	Both cal 3 and 4 points were marked as suspect.
CTD 13	Cal 2 & 4	Nut013	NH4	Both cal 2 and 4 points were marked as suspect.
CTD 15/ TMR 7	Cal 2 & 4	Nut016	NOx	Both cal 2 and 4 points were marked as suspect.
CTD 15/ TMR 7	Cal 5	Nut016	PO4	One point of cal 5 was marked as suspect.

Sample	Peak	Run	Analysis	Reason for Flag or Action
CTD16/ TMR 8	Cal 3, 5 & 6	Nut017	NH4	<70% of calibration peaks are within calibration limits. Both cal 3 and 5 points and the first cal 6 point were marked as suspect.
EXP45-68	Cal 3 & 5	Nut018	NH4	Both cal 3 and 5 points were marked as suspect.
CTD 17&18	Cal 1	Nut020	NH4	Both cal 1 points were marked as suspect.
CTD 19/ TMR 9	Cal 3	Nut022	PO4	One point of cal 3 marked as suspect.
CTD19/ TMR 9	Cal 2 & 5	Nut022	NH4	Both cal 2 points marked as bad, both cal 5 points marked as suspect.
CTD 21	Cal 3	Nut023	PO4	Both cal 3 points were marked as suspect.
CTD 21	Cal 2	Nut023	NH4	Both cal 2 points were marked as suspect.
CTD 22/ EXP69-80	Cal 3	Nut024	PO4	Both cal 3 points were marked as suspect.
TMR10/ EXP81-92	Cal 3	Nut026	PO4	First cal 3 point was marked as suspect.
TMR 11/ EXP93-104	Cal 3	Nut027	PO4	First cal 3 point was marked as suspect.
TMR 11/ EXP93-104	Cal 3	Nut027	NH4	Second cal 0 point was marked as suspect.
TMR 12	Cal 3	Nut029	PO4	Both cal 3 points were marked as suspect.
EXP105-114/UWY9-13	Cal 1, 2 & 5	Nut030	NH4	Both points for cal 1 and 2 are marked as bad and both points for cal 5 was marked as suspect.
CTD 15/TMR 7	RMNS CJ	Nut016	NO2	Lower than normal but still within 1 MDL, the data looks ok.
CTD 17 & 18	RMNS CJ	Nut020	PO4	Much higher than normal just within 3%, however the data looks ok.

8.3 Nutrients: RMNS results for each Analysis Run & CTD Deployment.

8.3.1 RMNS Lot CJ Results

Analysis Run	CTD #	Silicate (Si, µmol L^{-1})	Phosphate (PO_4, µmol L^{-1})	Nitrite (NO_2, µmol L^{-1})	NOx (NO_2 + NO_3, µmol L^{-1})
CJ reported	-	*39.424*	*1.219*	*0.0320*	*16.620*
1	CTD 1	39.591	1.225	0.05	16.518
2	UWY 1-8	39.127	1.224	0.038	16.556
3	CTD 2	39.121	1.222	0.041	16.57
4	CTD 3/ EXP 1	39.24	1.219	0.032	16.462
5	CTD 7/ TMR 2	39.253	1.219	0.032	16.564
6	CTD 8/ EXP 2	39.169	1.219	0.032	16.525
7	CTD 12/ EXP 3-5	39.121	1.219	0.032	16.504
8	TMR 3	39.133	1.219	0.032	16.548
9	EXP 6-22	39.073	1.219	0.032	16.583
10	TMR 4	39.203	1.219	0.032	16.612
11	TMR 5	39.266	1.219	0.032	16.642
12	TMR 6/ EXP 23-34	39.329	1.219	0.032	16.638
13	CTD 13/ EXP 35-44	39.178	1.219	0.032	16.627
15	Inter calibration	39.350	1.241	0.039	16.509
14	CTD 14	39.239	1.219	0.032	16.658
16	CTD 15/ TMR 7	39.449	1.238	0.025	16.501
17	CTD 16/ TMR 8	39.266	1.235	0.032	16.62
18	EXP 45-68	39.176	1.235	0.032	16.62
20	CTD 17&18	39.546	1.251	0.032	16.62
22	CTD 19&20/ TMR 9	39.291	1.233	0.032	16.62
23	CTD 21	39.191	1.234	0.032	16.62
24	CTD 22	39.158	1.235	0.032	16.62
26	TMR 10/EXP 81-92	39.129	1.24	0.032	16.62
27	TMR 11/EXP 93-104	39.217	1.229	0.032	16.62
29	TMR 12	39.335	1.234	0.032	16.62
30	EXP 105-114/UWY 9-13	39.309	1.23	0.032	16.62

The submitted nutrient results do <u>NOT</u> have RMNS corrections applied.

<u>How to use the RMNS for Correction</u>

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run
Corrected Concentration = Ratio x Measured Nutrient Concentration

Or for smoothing data

Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run
Corrected Concentration = Ratio x Measured Nutrient Concentration

8.4 Nutrients: Measured Detection Limit for each Analysis Run & CTD Deployment.

Measured Detection Limit						
Analysis Run	Samples	Silicate (Si, µmol L^{-1})	Phosphate (PO_4, µmol L^{-1})	Nitrite (NO_2, µmol L^{-1})	NOx (NO_2 + NO_3, µmol L^{-1})	Ammonia (NH_4^+, µmol L^{-1})
1	CTD 1	0.033	0.008	0.009	0.005	0.001
2	UWY 1-8	0.042	0.003	0.002	0.014	0.003
3	CTD 2	0.035	0.002	0.003	0.002	0.002
4	CTD 3/ EXP 1	0.041	0.005	0.003	0.004	0.002
5	CTD 7/ TMR 2	0.046	0.006	0.001	0.017	0.002
6	CTD 8/ EXP 2	0.021	0.003	0.001	0.007	0.002
7	CTD 12/ EXP 3-5	0.058	0.002	0.001	0.003	0.002
8	TMR 3	0.01	0.003	0.001	0.008	0.001
9	EXP 6-22	0.072	0.007	0.003	0.003	0.002
10	TMR 4	0.035	0.003	0.002	0.009	0.002
11	TMR 5	0.036	0.002	0.000	0.005	0.002
12	TMR 6/ EXP 23-34	0.028	0.004	0.001	0.003	0.001
13	CTD 13/ EXP 35-44	0.049	0.003	0.005	0.003	0.002
14	CTD 14	0.053	0.005	0.002	0.005	0.002
15	Inter calibration	1.121	0.006	0.002	0.007	0.002
16	CTD 15/ TMR 7	0.026	0.002	0.001	0.003	0.002
17	CTD 16/ TMR 8	0.026	0.003	0.002	0.008	0.002
18	EXP 45-68	0.041	0.004	0.004	0.002	0.001
20	CTD 17&18	0.399	0.001	0.003	0.005	0.001
22	CTD 19&20/ TMR 9	0.014	0.007	0.004	0.005	0.001
23	CTD 21	0.027	0.003	0.001	0.008	0.002
24	CTD 22	0.033	0.004	0.002	0.007	0.001
26	TMR 10/EXP 81-92	0.041	0.004	0.001	0.005	0.001
27	TMR 11/EXP 93-104	0.057	0.006	0.002	0.000	0.001
29	TMR 12	0.238	0.001	0.001	0.003	0.001
30	EXP 105-114/UWY 9-13	0.041	0.004	0.002	0.004	0.001

8.5 Flag Key for Hydrology Data Set

Flag	Description
0	Data is GOOD – nothing detected.
192	Data not processed.
63	Below nominal detection limit.
69	Data flagged suspect by operator. Set suspect by software if Calibration or Duplicate data is outside of set limits but not so far out as to be flagged bad.
65	Peak shape is suspect.
133	Error flagged by operator. Data is bad – operator identified by # in slk file or by clicking on point.
129	Peak exceeds maximum A/D value. Data is bad.
134	Error flagged by software. Peak shape is bad - Median Absolute Deviation (MAD) analysis used. Standards, MDL's and Duplicates deviate from the median, Calibration data falls outside set limits.
141	Missing data, no result for sample ID. Used in netcdf file as an array compiles results. Not used in csv file.
79	Method Detection Limit (MDL) during run was equal to or greater than nominal MDL. Data flagged as suspect.

8.6 GO-SHIP Specifications

8.6.1 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].

8.6.2 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.

8.6.3 SiO2

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

8.6.4 PO4

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

8.6.5 NO3

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

8.6.6 Notes

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

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

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

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