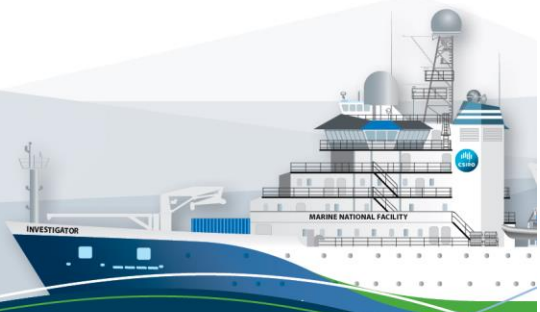
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2019_v01
Chief Scientist	Mike Double
Voyage title:	The availability of Antarctic krill to large predators and their role in biogeochemical recycling in the Southern Ocean / ENRICH
Report compiled by:	Kendall Sherrin



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1 Executive Summary

The main objective of this voyage was to increase understanding on the factors of krill (*Euphausia superba*) which influence the distributions of their predators, i.e. squid, fish, bird and mammal species. This voyage focused on using active acoustics to characterise krill swarms along with trawls to assess krill health and growth rates. Use of passive acoustic sonobuoys allowed the vessel to track and hone in on pods of Antarctic blue whales, with their sighting logged and recorded. Additionally the southern ocean iron fertilisation theory was field tested with on board experiments and a gridded field of CTD/TMR deployments completed.

Hydrochemistry water samples were primarily collected from the CTD, including nutrients, dissolved oxygen and salinity. Additional nutrient samples came from the incubation experiments undertaken.

The data produced was of very high quality, with no issues encountered throughout for any of the instrumentation. Deployments of the CTD rosette to shallow depths of 400m resulted in slightly noisier CTD calibration data, however this is to be expected when compared to a typical deep oceanographic deployment (>1000m).

Nutrient data for the voyage was extremely good all 5 dissolved macro nutrients were analysed, silicate, phosphate, NO_x (nitrate+nitrite), nitrite and ammonium. Ammonium data was particularly good this voyage due to the high resolution sampling regime in the top 200m of the water column. All nutrient data analysed from the CTD deployments was analysed along with a certified reference material to assess instrumentation accuracy.

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

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

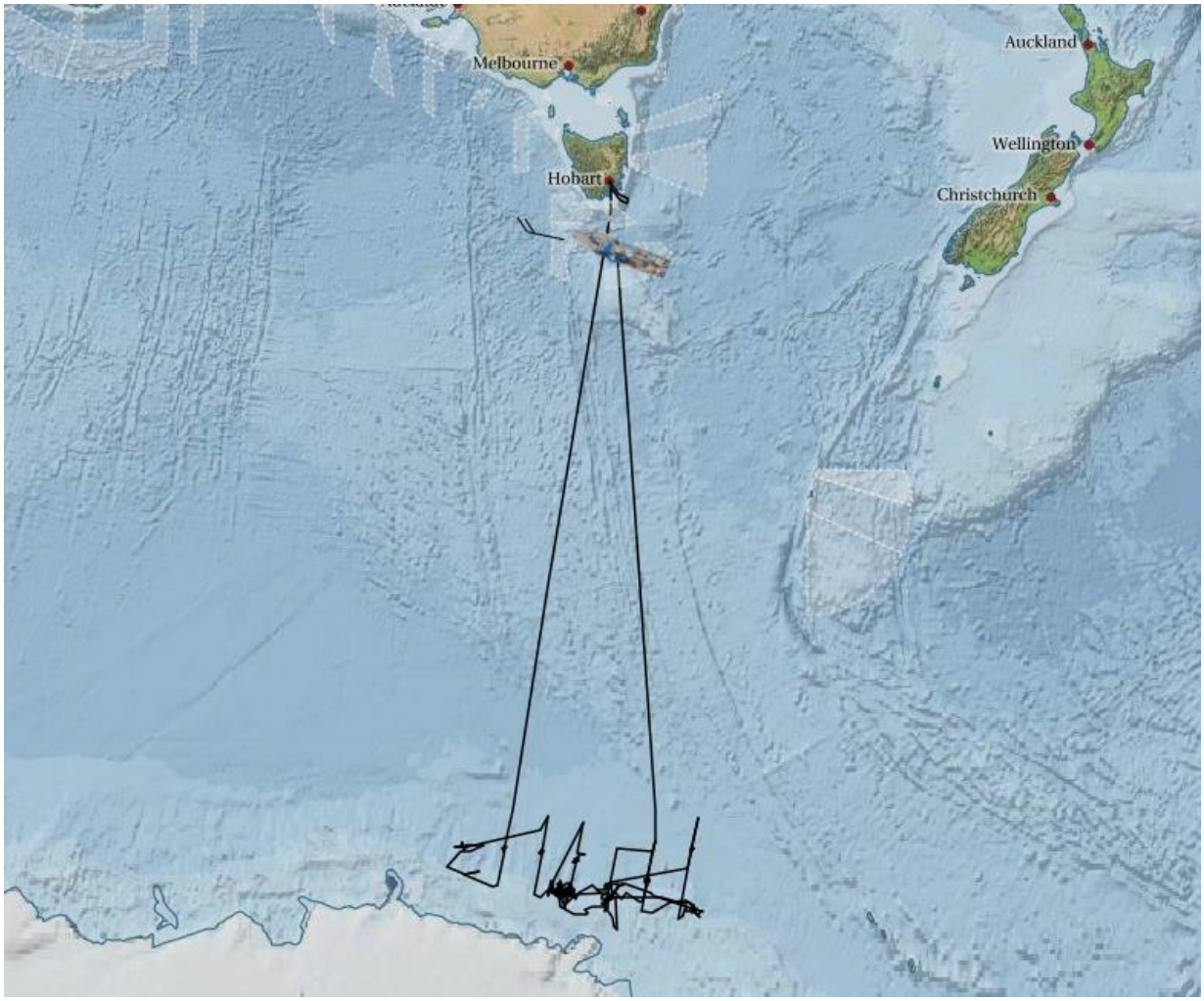
Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, January 16th – March 5th, 2019.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Mike Double	Chief Scientist	AAD
Lisa Woodward	Voyage Manager	CSIRO

Kendall Sherrin	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	260 CTD
	24 TSG
Dissolved Oxygen (automated titration)	260 CTD
Nutrients (Seal AA3HR)	431CTD
	11 TMR
	169 EXP

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.
- 31 CTD deployments in total. Not all deployments were successful, which is why there is not data for all 31.

4.1.2 TMR (Trace Metal Rossette)

- Sampling point, 12 bottle trace metal clean rosette.

4.1.3 EXP (Experimental samples)

- Prepared and sampled by the science groups conducting the experiments.
- Clara Rodriguez Vives & Abbie Smith completed experiments on in2019_v01 which these samples pertain to.

4.1.4 TSG (Thermosalinograph)

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

For UWY, EXP, 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.

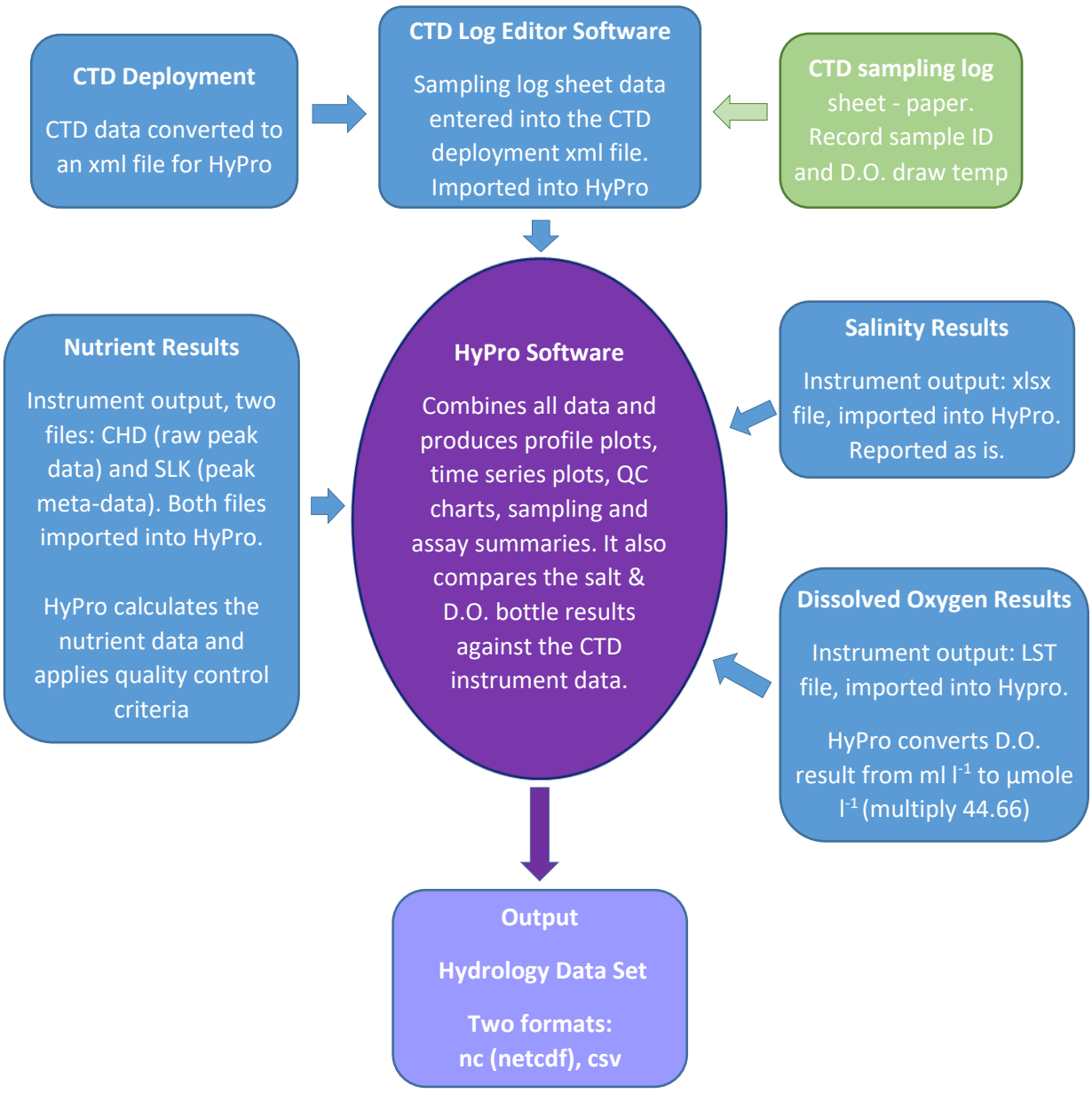


Figure 1: Hydrology Data Processing Flow Diagram.

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	Kendall Sherrin
Lab Temperature (±0.5°C)	20 – 22.5°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.

Method synopsis: Salinity samples are collected into 200ml OSIL bottles, filled from the bottom, via a 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. Further flush-measurement cycles are done where the initial values are more than 3 digits different. The Osil Data logger software captures the conductivity ratio and calculates the practical salinity.

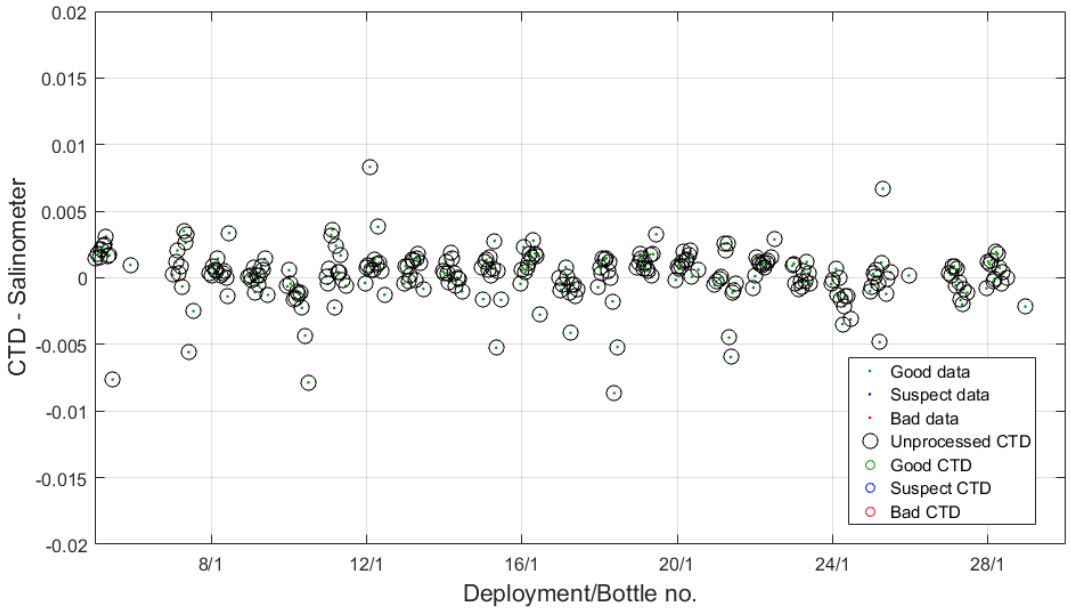
The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

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 DataLibrarians@csiro.au for corrected CTD data.

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



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.

CTD	RP	Run	Flag	Reason for Flag or Action
-	-	-	-	no bad samples from an analytical standpoint

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)	Kendall Sherrin
Lab Temperature (±1°C)	Variable, 20 - 24°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 1mL of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum ten 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.

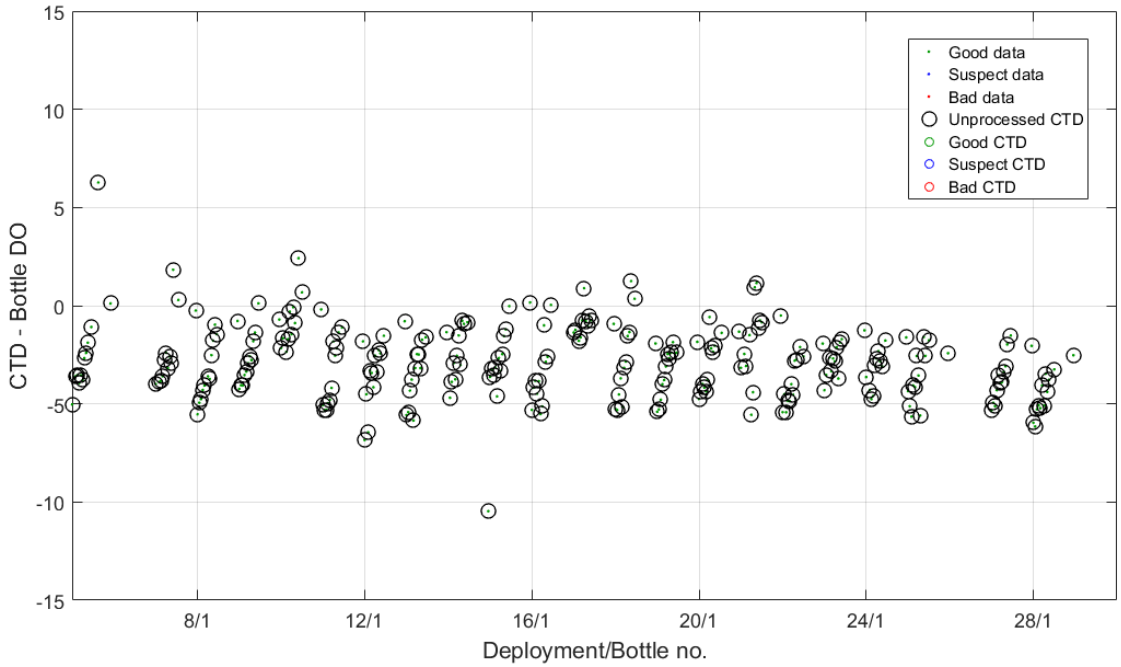
The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

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 DataLibrarians@csiro.au for corrected CTD data.

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

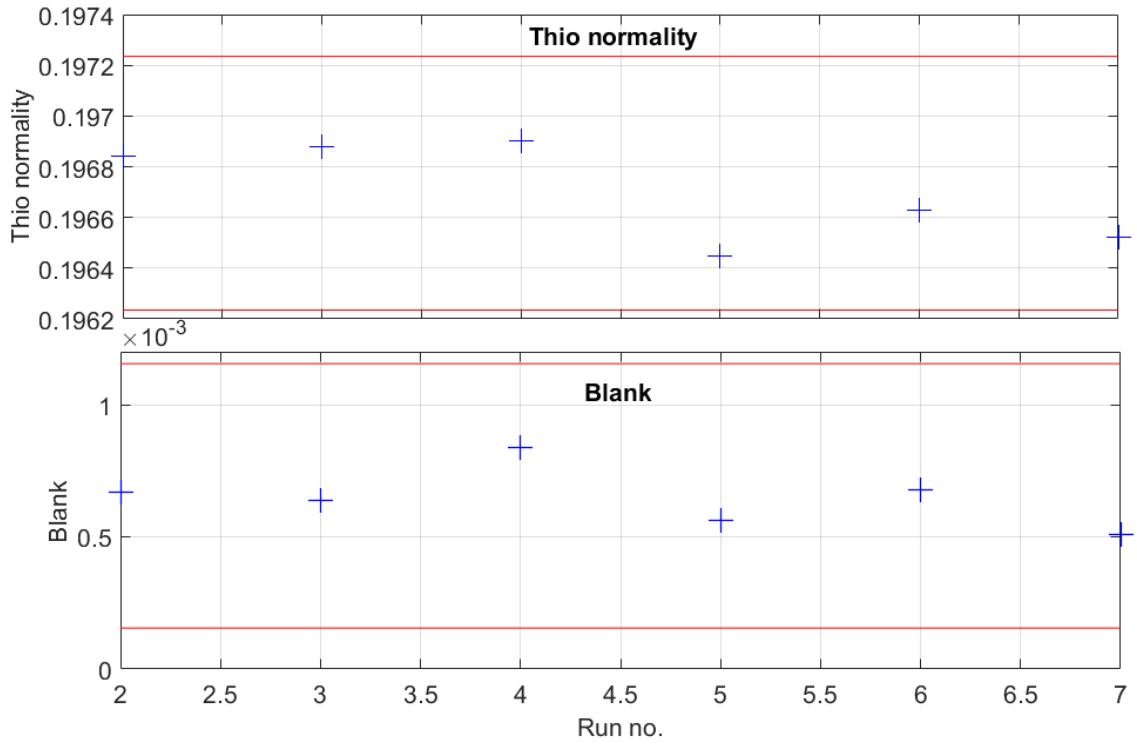


6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2N) varied less than 0.0005N for all dissolved oxygen sample titrations. The blank correction is less than 0.001ml.

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.

CTD	RP	Run	Flag	Reason for Flag or Action
10	4/5	3		Bottle 618 (RP4) and 620 (RP5) had lids swapped, calibrated volumes will differ affecting final O2 conc
10	9/11	3		Bottle 624 (RP9) and 625 (RP11) had lids swapped, calibrated volumes will differ affecting final O2 conc
14	1	5		Sample lost bad titration
14	2	5		Bubble in sample bottle
14	9	5		Bubble in sample bottle
16	24			Sample lost bad titration
17	11	5		Bubble in sample bottle

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	Kendall Sherrin				
Lab Temperature (±1°C)	Variable, 20– 24°C				
Reference Material	KANSO, RMNS lot CC				
Sampling Container type	CTD: 50ml HDPE with screw cap lids. Experimental: 12ml PP tubes with screw cap lids. TMR: 30ml PP tubes with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	EXP: dilution of some samples as required, dilutions were added as information to the Elog.				
Comments					

7.2 Nutrient Methods

When using silicate, phosphate and nitrate+nitrite (NOx) 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

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.	<10%. CTD: 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.				

7.4 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 0.02uM 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 7.9, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.3.

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

Japanese KANSO certified RMNS lot CC was assayed 9 times in each run to monitor accuracy. The certified values are in table 1.

For in2019_v01, the majority of RMNS results are within 1%, except Phosphate which was 1-2% high, of their certified mean and within 0.02µM 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 8.2.

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.

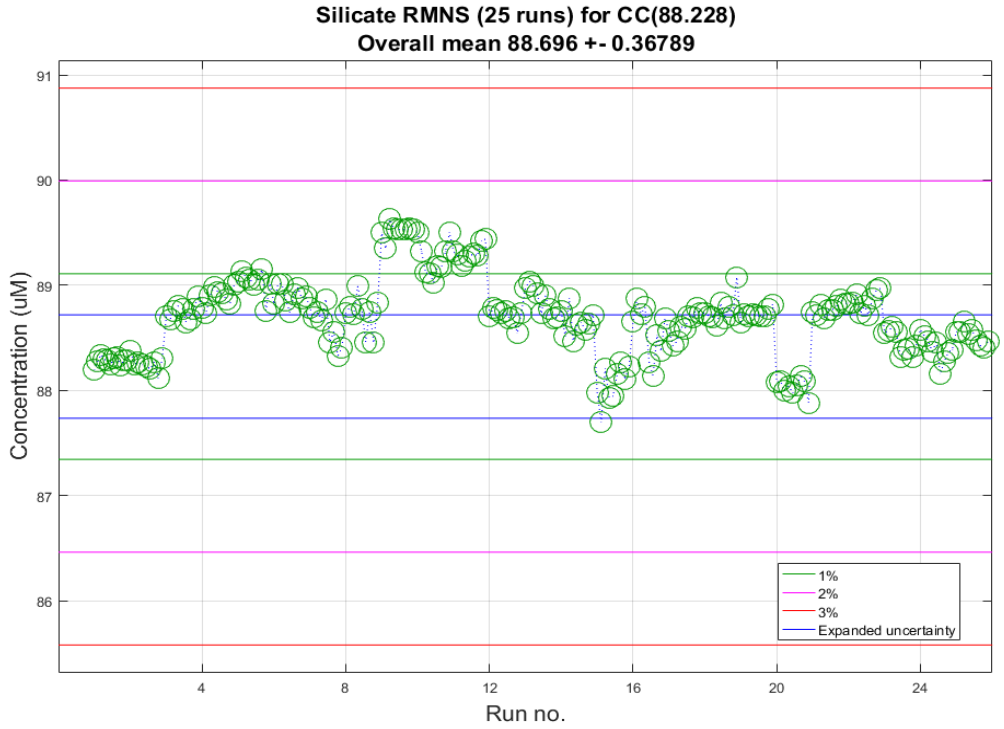
Table 1: RMNS concentrations with expanded uncertainty (µmol L^{-1}) at 21°C

RMNS	NO_3	NO_2	NO_3+ NO_2 (NO_X)	PO_4	SiO_4
Lot CC	31.621 ± 0.246	0.119 ± 0.006	31.740 ± 0.252	2.130 ± 0.019	88.228 ± 0.492

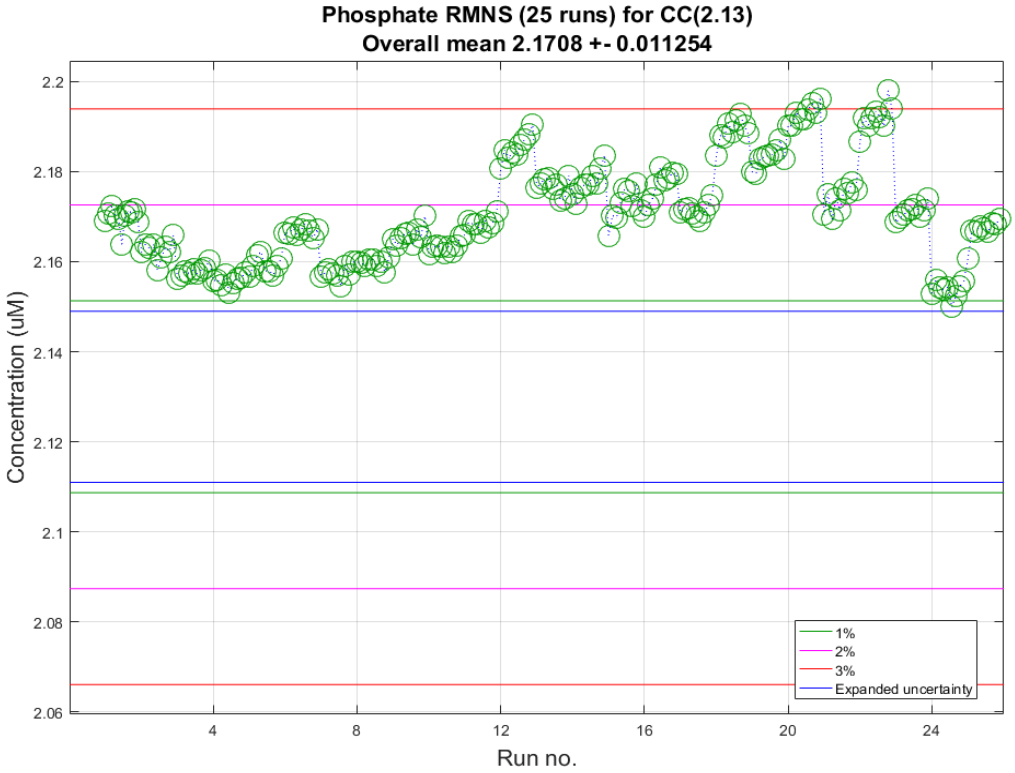
KANSO publishes the RMNS nutrient values in µ mol kg^{-1}. These are converted to µ mol l^{-1} at 21°C. Lot BW is not certified for ammonium. NO_x is derived by adding the NO_3 and NO_2 values.

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.

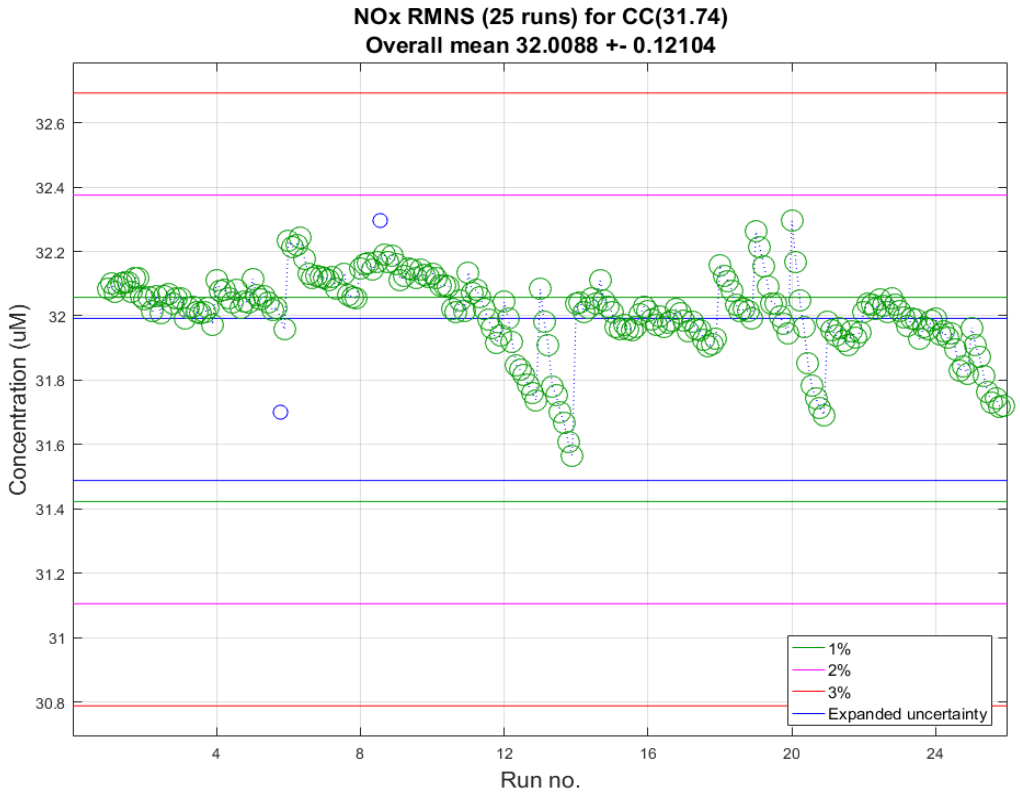
7.5.1 Silicate RMNS Plot



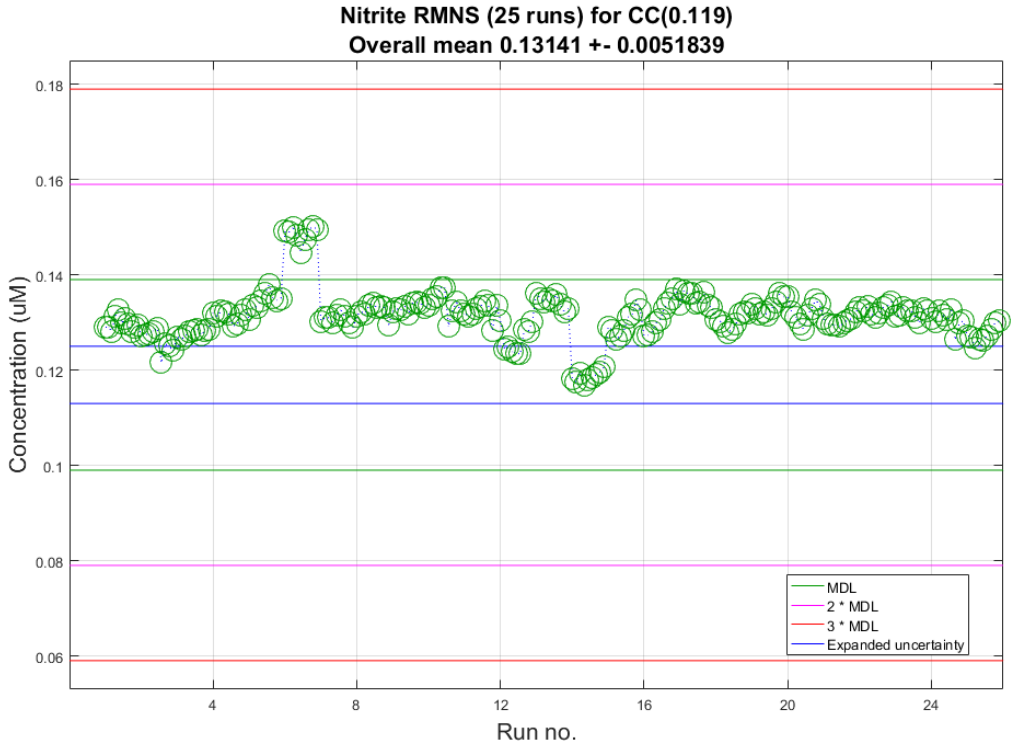
7.5.2 Phosphate RMNS Plot



7.5.3 Nitrate + Nitrite (NOx) RMNS Plot



7.5.4 Nitrite RMNS Plot



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_v01, the measured detection limits for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. See appendix 8.4 for the measured MDL per CTD deployments.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Standard Dev. Min	0.00	0.00	0.00	0.001	0.00
Standard Dev. Max	0.058	0.006	0.006	0.004	0.006
Standard Dev. Mean	**0.01**	**0.002**	**0.002**	**0.001**	**0.00**
Standard Dev. Median	0.00	0.00	0.00	0.001	0.00
Precision of MDL (stdev)	0.01	0.002	0.002	0.001	0.00

*MDL is based on 3 times the standard deviation of Low Nutrient Seawater (LNSW) analysed in each nutrient run.

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 CC	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Published RMNS CC (µmol l^{-1}) w/std deviation	88.23 ± 0.492	2.13 ± 0.019	31.62 ± 0.246	0.119 ± 0.006	- -
Minimum	87.7	2.15	31.57	0.117	0.50
Maximum	89.6	2.20	32.37	0.15	2.32
Mean	88.69	2.17	32.01	0.131	1.89

Median	88.70	2.17	32.02	0.132	1.91
Precision (Stdev)	0.36	0.01	0.12	0.005	0.215

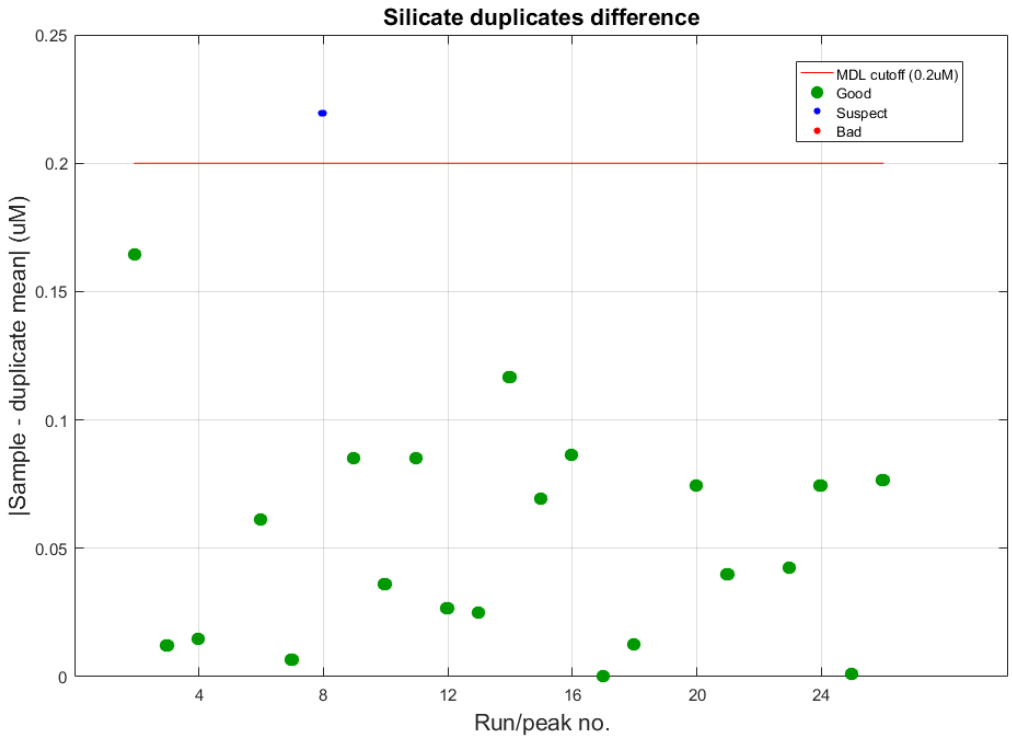
7.7 Sampling Precision

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 µM as the MDL boundary.

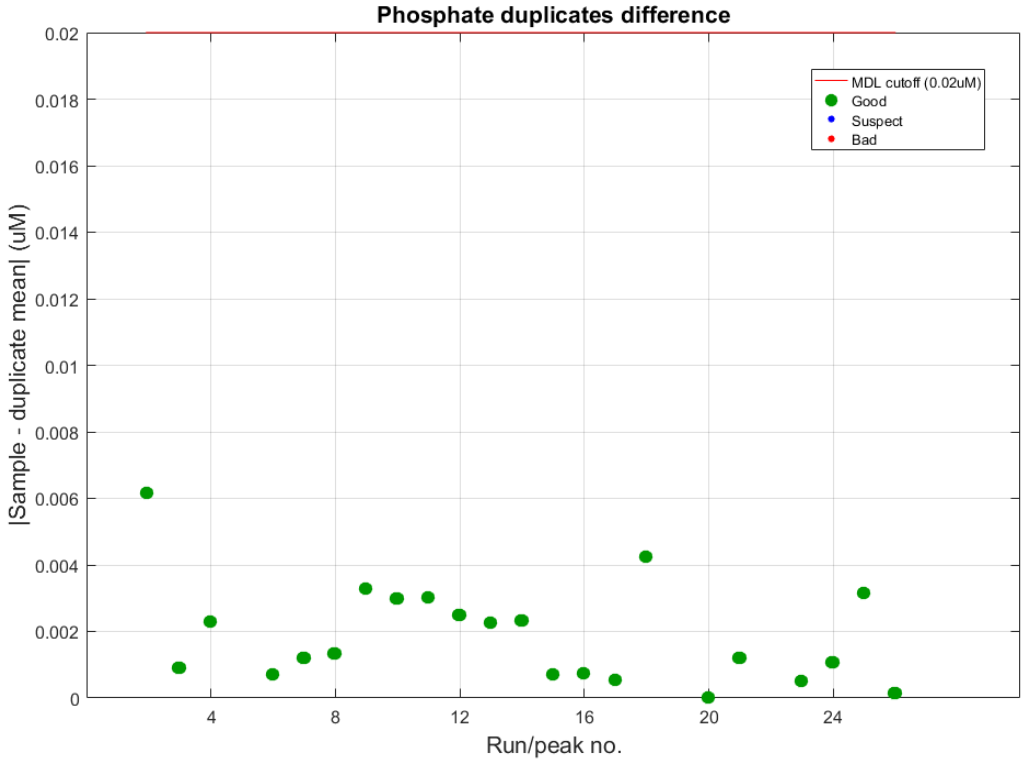
Plots of the difference between the duplicate and their mean for the CTD deployments are below. The red line is the boundary below which sampling precision is deemed good.

For in2019_v01, the sampling precision is good.

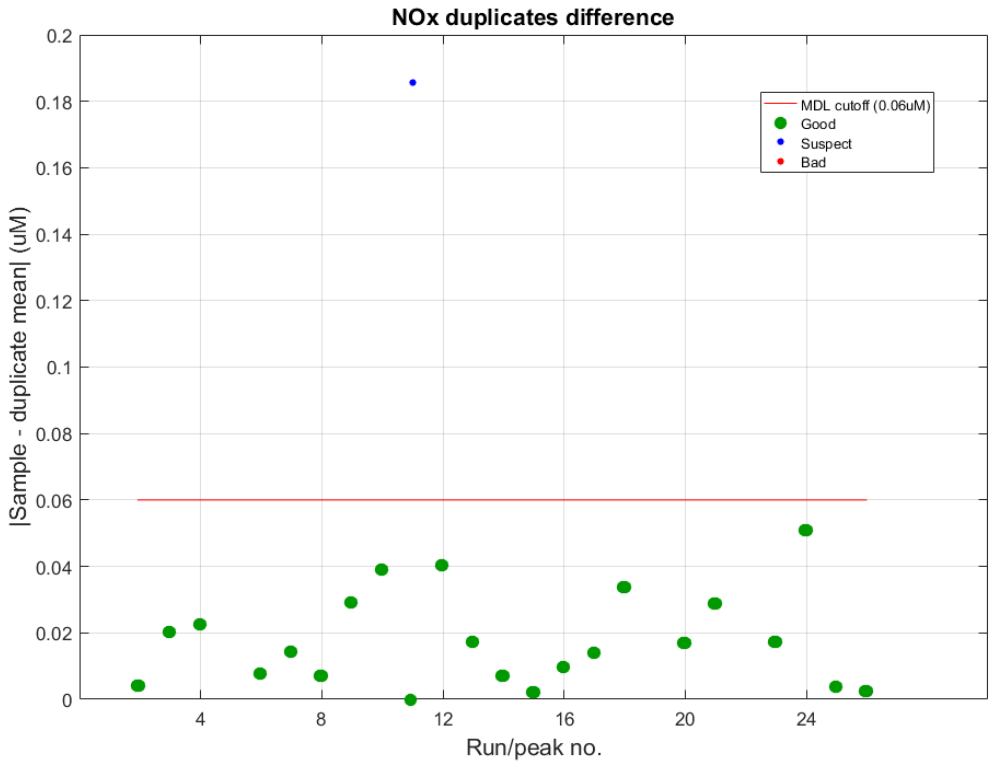
7.7.1 Silicate Duplicates Plot



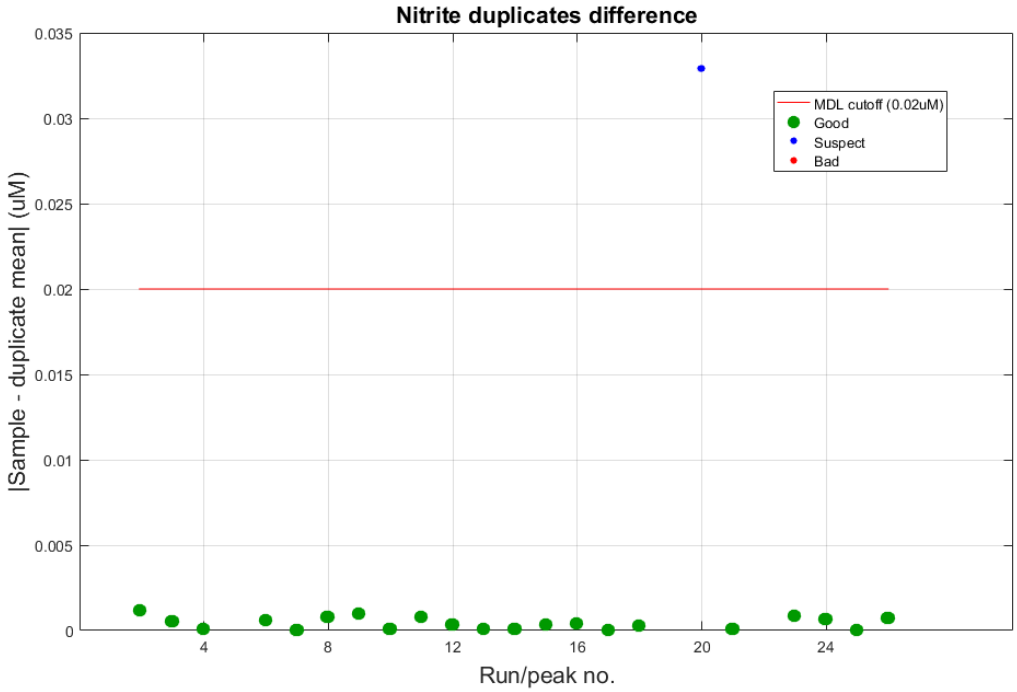
7.7.2 Phosphate Duplicates Plot



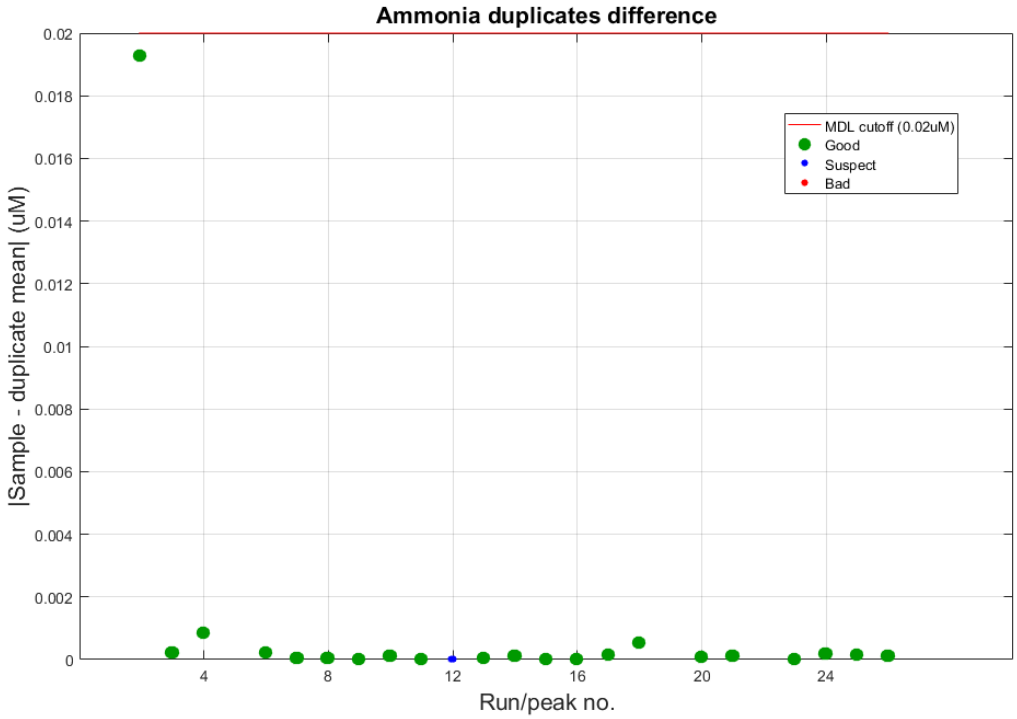
7.7.3 Nitrate + Nitrite (NOx) Duplicates Plot



7.7.4 Nitrite Duplicates Plot

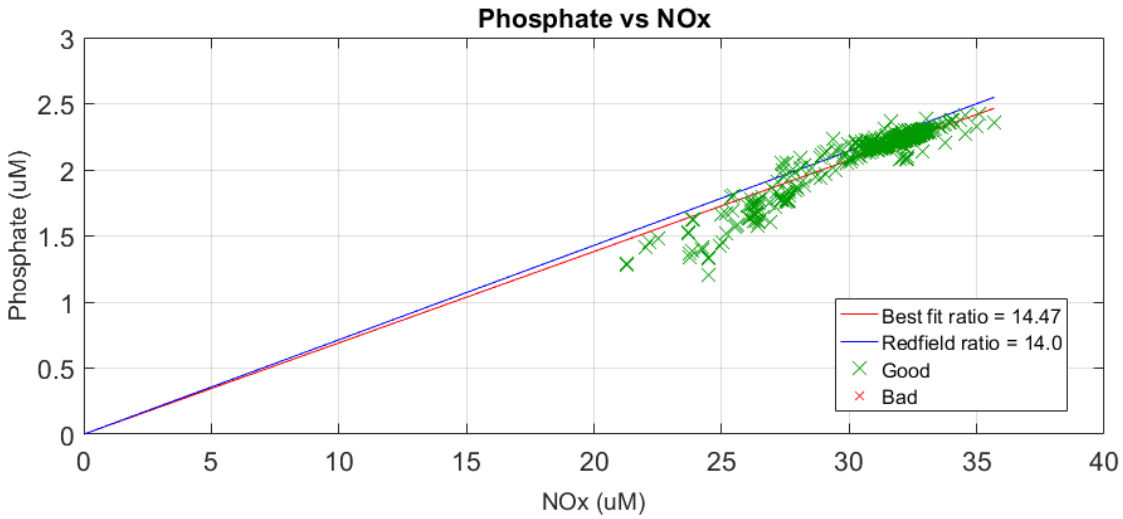


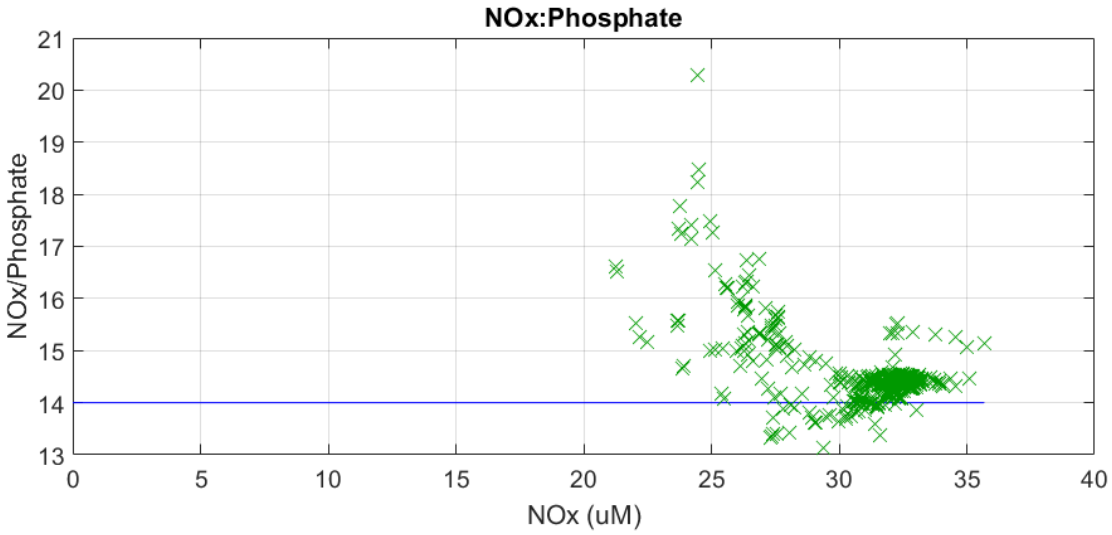
7.7.5 Ammonia Duplicates Plot



7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.47





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. Data that falls below the detection limit, Flag 63, is not captured in this table. All GOOD data is flagged 0 in the .csv and .netcdf files. Data that is flagged BAD is not exported to the .csv files. Flag Key in Appendix 8.5.

CTD	RP	Run	Flag	Nutrient	Reason for Flag or Action
11	1	7	69	Silicate	Flagged suspect due to duplicates being more different than expected limits
14	1	10	65	NOx	Suspect due to peak shape abnormality
15	1, 2, 3	11	69	Ammonia	Flagged due to concern samples were contaminated
22	1	19	69	Nitrite	Flagged suspect due to duplicates being more different than expected limits
25	9	23	69	Silicate	Suspect due to peak shape abnormality

7.10 Temperature & Humidity Change over Nutrient Analyses

The temperature and humidity within the AA3 chemistry module was logged using a temperature/humidity logger QP6013 (Jaycar) placed on the deck of the chemistry module.

Refer to “in2019_v01_hyd_voyagereport.docx” for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21°C.

The laboratory temperature was measured and recorded on the nutrient run sheets at the start each analysis run. The temperature varied between 20 and 24°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 Analysis Run & CTD Deployment.

8.2.1 RMNS Lot CC Results

Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NOx (NO2 + NO3)
CC reported	-	*88.23*	*2.130*	*0.119*	*31.621*
1	5	88.28	2.169	0.130	32.093
2	7	88.26	2.161	0.126	32.046
3	8	88.76	2.160	0.128	32.013
4	-	88.88	2.158	0.131	32.062
5	9	89.04	2.160	0.135	32.003
6	10	88.90	2.170	0.149	32.174
7	11	88.62	2.159	0.131	32.123
8	12	88.72	2.160	0.132	32.181
9	13	89.50	2.168	0.133	32.132
10	14	89.24	2.161	0.134	32.069
11	15	89.30	2.170	0.132	32.019
12	16	88.71	2.184	0.126	31.860
13	18	88.86	2.178	0.134	31.783
14	19	88.64	2.179	0.119	32.043
15	-	88.06	2.173	0.130	31.981
16	20	88.57	2.177	0.131	31.992
17	21	88.62	2.170	0.135	31.944
18	-	88.76	2.189	0.130	32.059
19	22	88.71	2.181	0.133	32.078
20	23	88.03	2.192	0.132	31.917
21	-	88.79	2.176	0.130	31.944
22	24	88.84	2.191	0.133	32.031
23	25	88.46	2.170	0.132	31.977
24	27	88.42	2.152	0.131	31.904
25	28	88.53	2.169	0.127	31.802

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

8.3 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.

8.4 GO-SHIP Specifications

8.4.1 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].

8.4.2 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.

8.4.3 SiO2

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

8.4.4 PO4

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

8.4.5 NO3

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

8.4.6 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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