

RV INVESTIGATOR

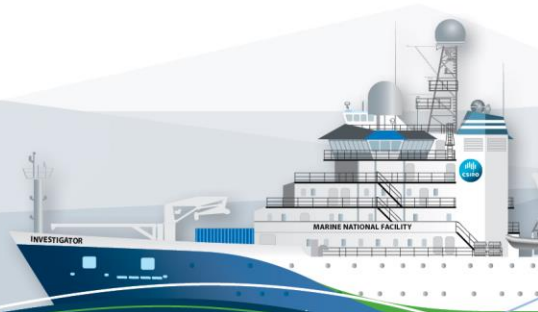
HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage: in2018_v07

Chief Scientist Eric Schultz

Voyage title: SOTS: Southern Ocean Time Series automated moorings for climate and carbon cycle studies southwest of Tasmania

Report compiled by: Peter Hughes



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1 Executive Summary

1. Deployed SOFS-7.5 meteorology/biogeochemistry mooring.
2. Carried out underway air sensor measurement comparison between ship and SOFS-7.5 mooring.
3. One CTD cast to 2250m at the SOFS-7.5 site, samples collected for nutrients, oxygen, dissolved inorganic carbon, alkalinity, POC and pigments.

Water samples collected for nutrients, dissolved oxygen, and salinity were assayed in the ship's hydrochemistry laboratory during the voyage. Data quality: GOOD.

Five nutrients determined: silicate, phosphate, nitrate + nitrite, nitrite and ammonium. The certified reference seawater results were within the specified limits.

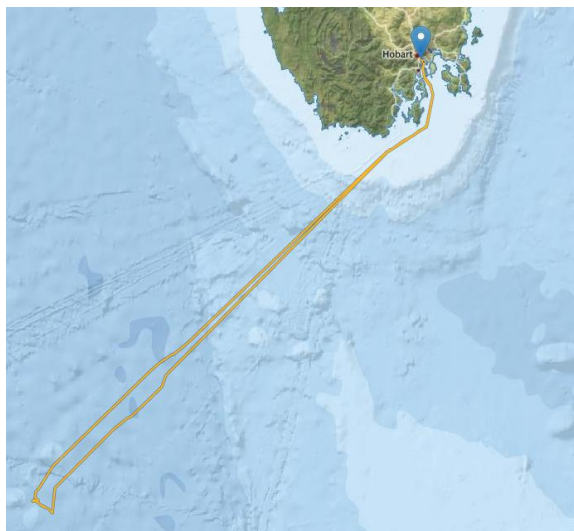
Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, August 20th – 25th, 2018.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Eric Schultz	Chief Scientist	BOM
Rod Palmer	Voyage Manager	CSIRO
Peter Hughes	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	21 CTD 13 TSG
Dissolved Oxygen (automated titration)	21 CTD 4 UWY
Nutrients (Seal AA3HR)	24 CTD 2 EXP 1 UWY

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles deployed at depth for water collection.
- 1 CTD deployment. Sampled by Peter Hughes, Hydrochemistry (HYD).

4.1.2 UWY (underway samples)

- Sampling point, underway seawater supply in the underway laboratory. Sampled by Peter Hughes (HYD).
- Type: Nutrients and dissolved oxygen. For comparison with the underway dissolved oxygen instrument and the CTD deployment surface bottle sample.

4.1.3 EXP (Experimental samples)

- Type: Nutrients. Prepared and sampled by the science group, Diana Davies (CSIRO).

4.1.4 TSG (Thermosalinograph)

- Sampling point, underway seawater supply in the underway laboratory. Samples collected by Peter Shanks (DAP) and Peter Hughes (HYD) to calibrate the thermosalinograph instrument.

UWY, EXP, and TSG sample meta-data recorded in the voyage elog.

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. Illustrated in Figure 1.

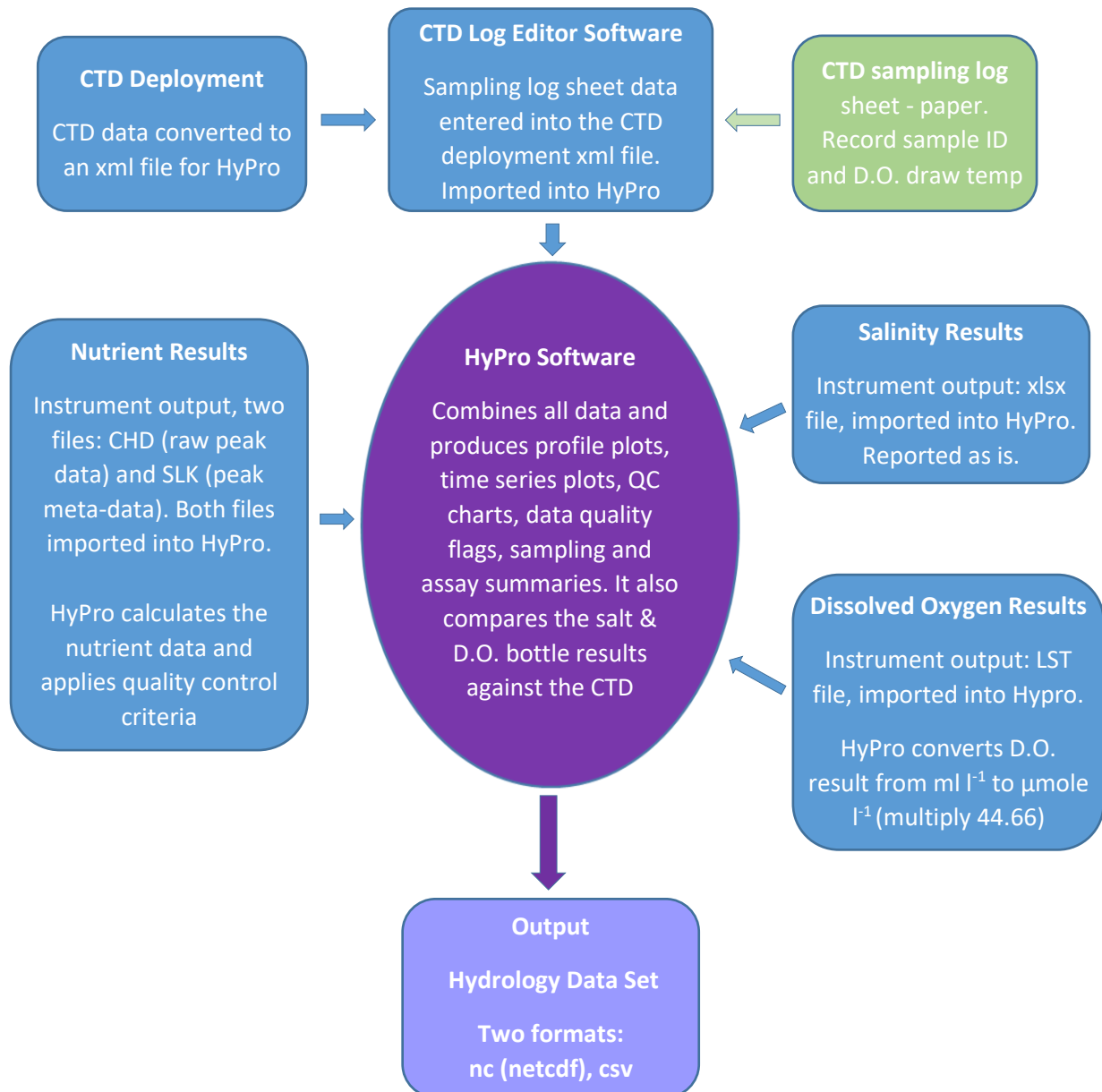


Figure 1: Hydrology Data Processing Flow Diagram.

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	Peter Hughes
Lab Temperature (±0.5°C)	21 -22°C during analysis.
Bath Temperature	24.02°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 as per its technical manual.

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

Before each batch of sample measurements, the 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.

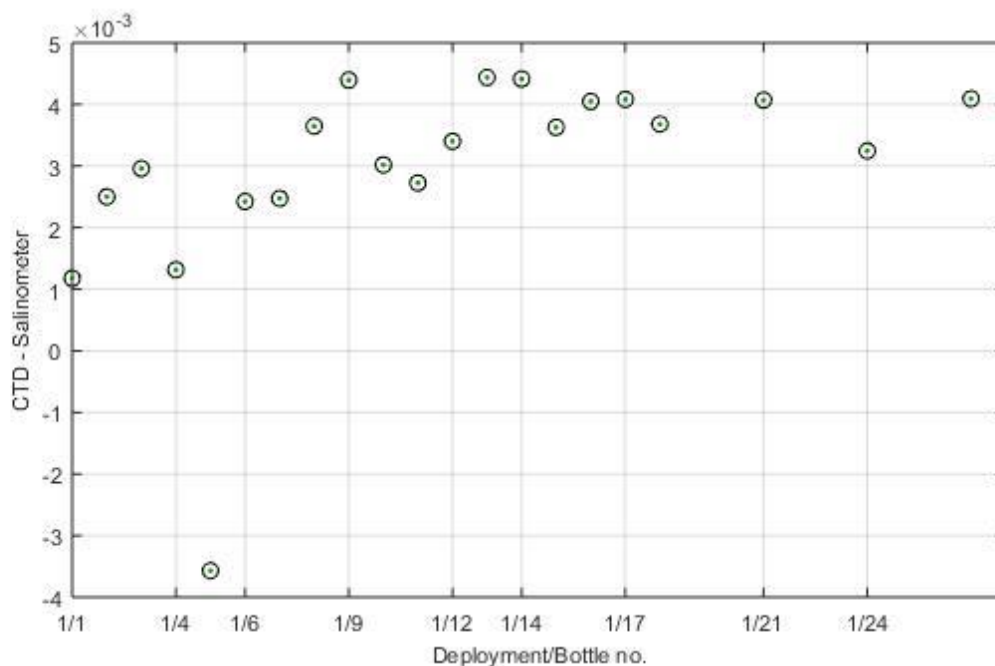
The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

5.3 CTD Salinity vs Bottle Salinity Plot

The difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities is less than 0.005 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)



5.4 OSIL Salinity Standard PSU across the Voyage

For this voyage, the Autosol instrument was calibrated once and the samples measured in one run. Thus, there is no multiple-run plot across the voyage.

5.5 Missing or Suspect Salinity Data

No missing or suspect data.

Data quality: GOOD.

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

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)	Peter Hughes
Lab Temperature (±1°C)	Variable, 21.0 - 22.0°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	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 solution. A blank correction is also determined from the difference between two consecutive titres for 1ml aliquots of the potassium iodate solution.

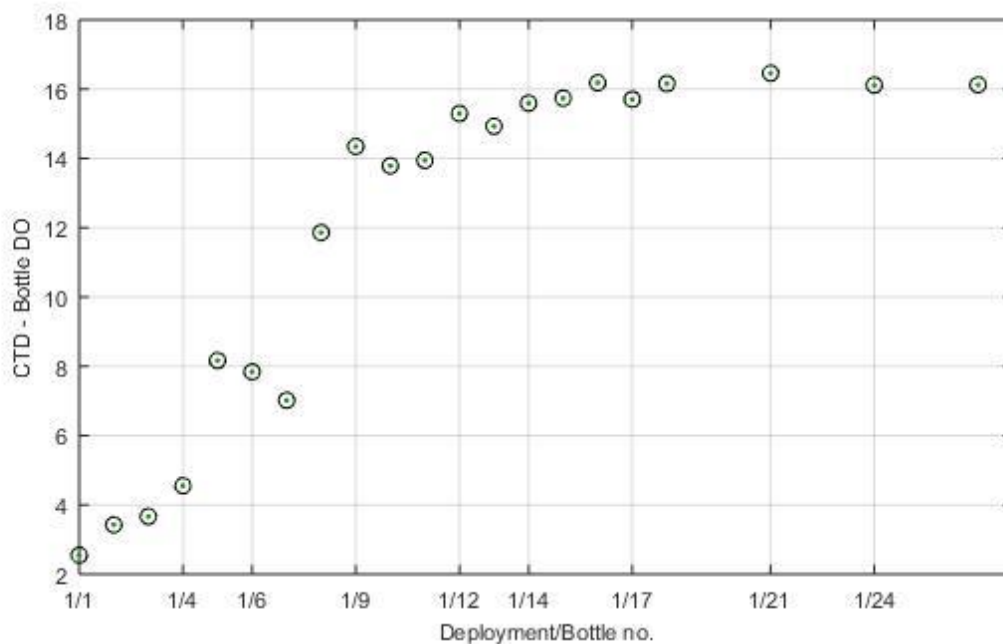
The output LST file from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

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). Units: $\mu\text{mole/L}$



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

For this voyage, the dissolved oxygen instrument was calibrated once and the samples assayed in two consecutive runs. Thus, there is one data point each for the thiosulphate normality and the blank correction volume. No multiple-run plot. The standardisation data are typical as evident when compared against the preceding voyage (in2018_v03) when the instrument was last used.

Voyage	Cal date	Thiosulphate	Blank
In2018_v03	6/5/2018	0.02024 N	0.0005 mL
In2018_v07	23/8/2018	0.02021 N	0.0007 mL

For reference, thiosulphate titre volumes for dissolved oxygen bottle samples lay in the range 0.48 to 0.76 ml.

6.5 Missing or Suspect Dissolved Oxygen Data.

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

No missing or suspect data.

Data quality: GOOD

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				
Lab Temperature (±1°C)	Variable, 21 - 22°C				
Reference Material	KANSO, RMNS lot BW				
Sampling Container type	CTD, EXP and UWY: 50ml HDPE with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD: and UWY: None. EXP: Prepared by the science party. Assayed as received				
Comments	None.				

7.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1cm flow-cells for colorimetric measurements and a JASCO FP2020 fluorescence instrument for 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-naphthyl-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-phthalaldehyde method. Based on Roger K  rouel and Alain Aminot, IFREMER (1997 Mar.Chem.57). Ammonium reacted with ortho-phthalaldehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460nm after excitation at 370nm.

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

7.3 HyPro Processing Parameters

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Data Reported as	��mol l ⁻¹	��mol l ⁻¹	��mol l ⁻¹	��mol l ⁻¹	��mol l ⁻¹
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
# of points in Calibration	6	6	6	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 var.	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 �� water. Dispensed from Milli Q unit.				
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 CTD deployment vs RMNS data is tabulated in appendix 8.3.				

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:

- $\pm 0.5\%$ 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 listed in section 7.9. This data is flagged in the final hydrology data set. Refer appendix 8.5 for Flag Key.

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

Japanese KANSO certified RMNS lot BW was assayed in quadruplicate to monitor accuracy. The certified values are in table 1.

For in2018v07, the majority of RMNS results are within 1% of their certified mean and within 0.02uM 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 8.3

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 ($\mu\text{mol L}^{-1}$) at 21°C

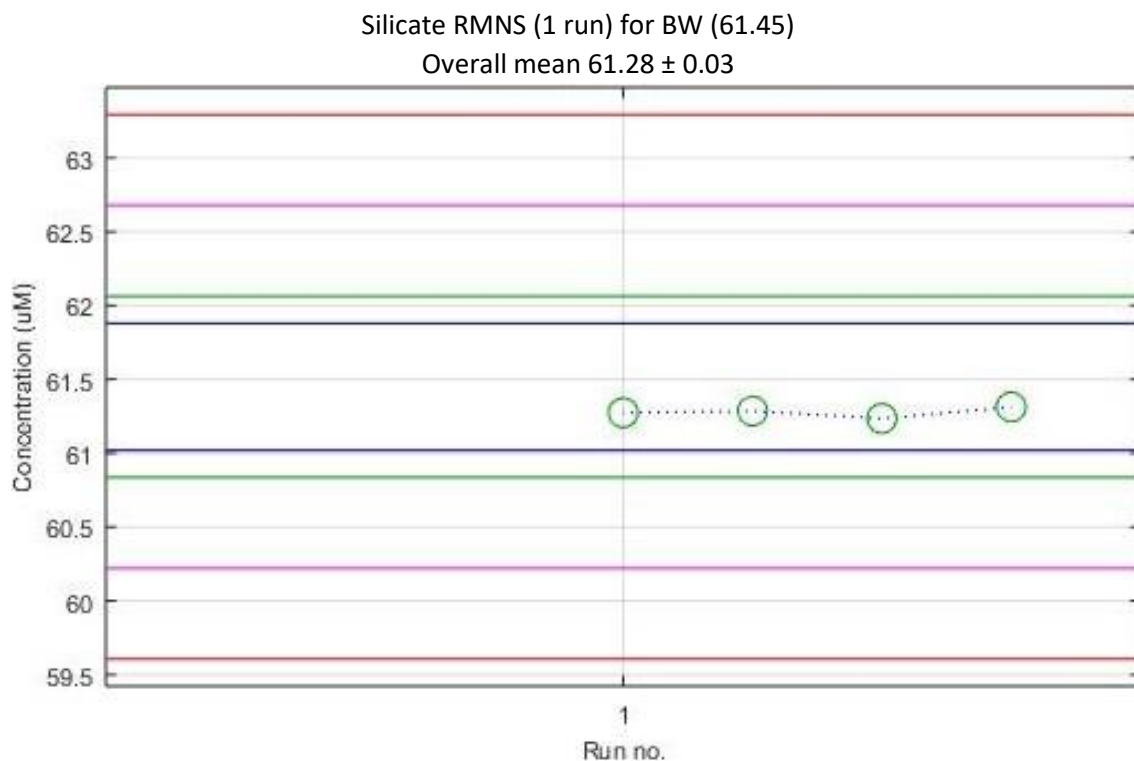
RMNS	NO ₃	NO ₂	NO ₃ + NO ₂ (NO _x)	PO ₄	SiO ₄
Lot BW	25.18 \pm 0.20	0.069 \pm 0.010	25.25 \pm 0.21	1.578 \pm 0.014	61.45 \pm 0.43

Note:

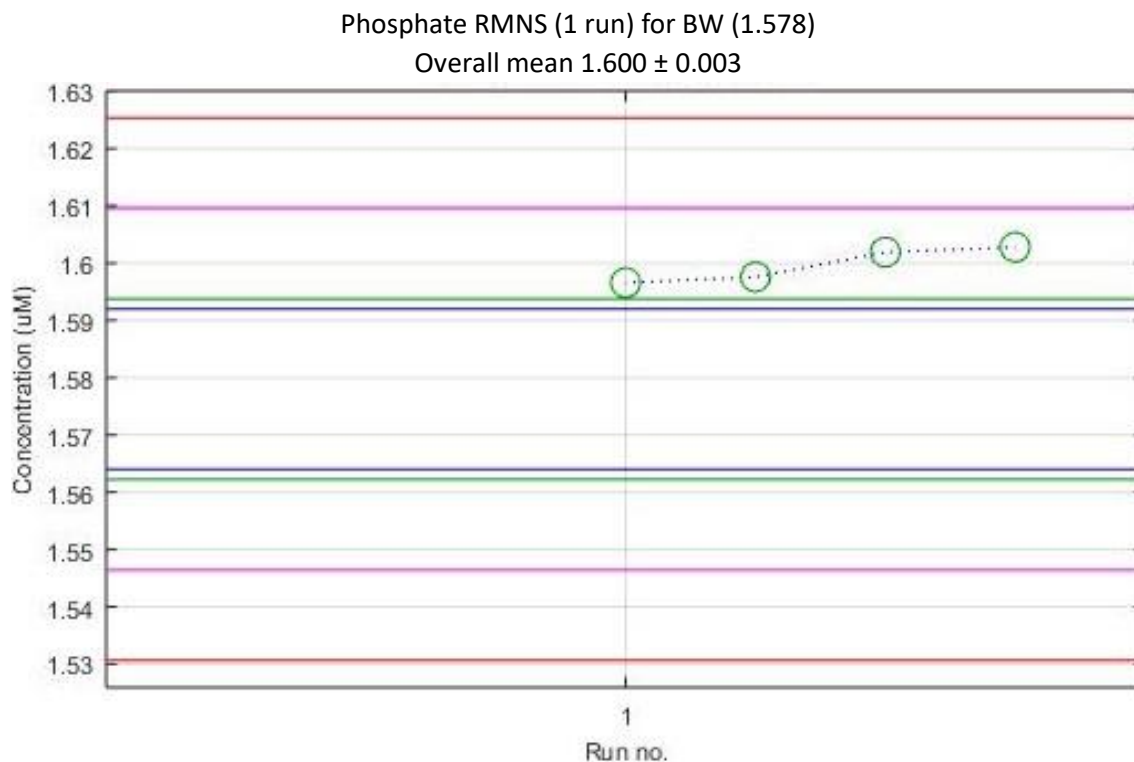
- (1) KANSO publishes the RMNS nutrient values in $\mu\text{mol kg}^{-1}$. These are converted to $\mu\text{mol l}^{-1}$ at 21°C by the hydrochemistry team.
- (2) Lot BW is not certified for ammonium.
- (3) NO_x is derived by adding the NO₃ and NO₂ values.

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



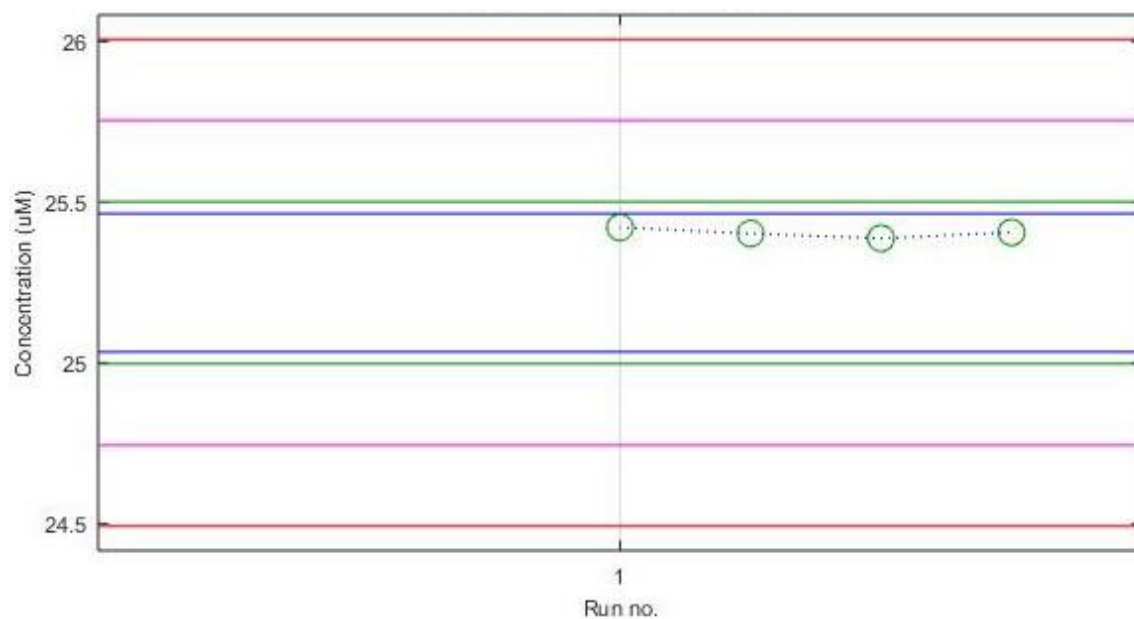
7.5.2 Phosphate RMNS Plot



7.5.3 Nitrate + Nitrite (NO_x) RMNS Plot

NO_x RMNS (1 run) for BW (25.25)

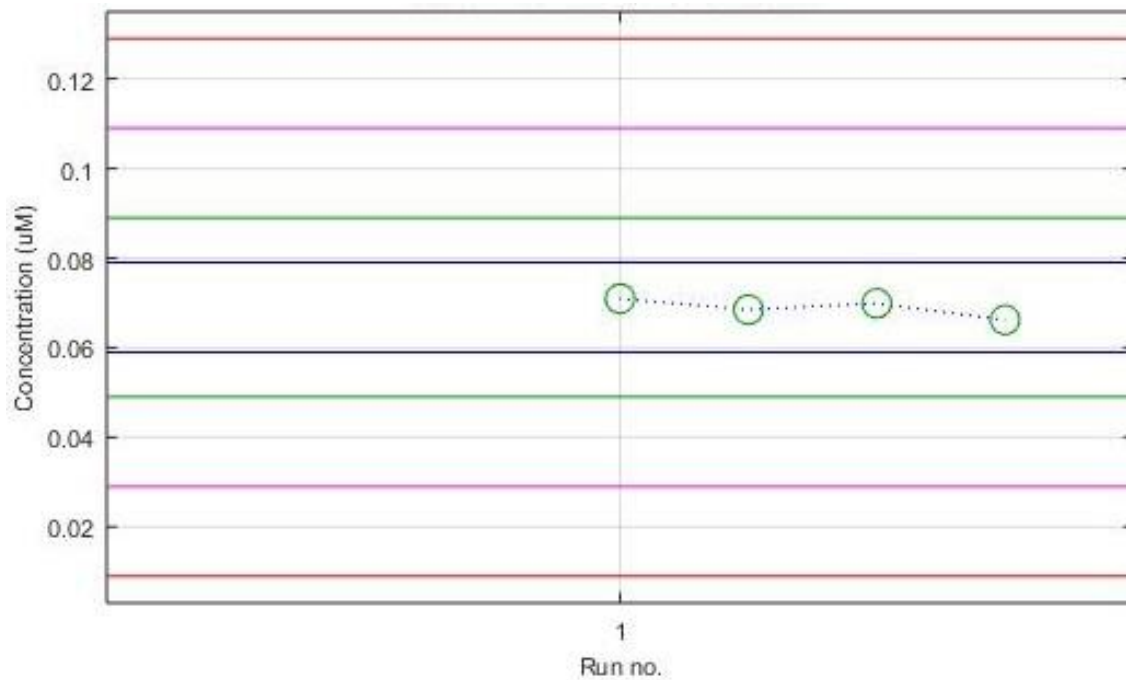
Overall mean 25.40 ± 0.01



7.5.4 Nitrite RMNS Plot

Nitrite RMNS (1 run) for BW (0.069)

Overall mean 0.069 ± 0.002



7.6 Analytical Precision

For in2018_v07, the analytical precision is GOOD.

7.6.1 Nutrient Measurement Uncertainty

The CSIRO Hydrochemistry method measurement uncertainty (MU) is 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 $\mu\text{mol L}^{-1}$				
Silicate	Phosphate	Nitrate + Nitrite (NO _x)	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 does not include RMNS data.

7.6.2 Nutrient Method Detection Limit

For in2018_v07, the measured detection limits are listed below:

Measured Detection Limit, MDL ($\mu\text{mol L}^{-1}$)						
Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NO _x (NO ₂ + NO ₃)	Ammonia
1	1	0.04	0.003	0.005	0.001	0.003

MDL value is 3 times the standard deviation of the Low Nutrient Seawater (LNSW) solution results assayed in quadruplicate during the run.

7.6.3 Reference Material for Nutrients in Seawater

Similar to the MDL measurement, the precision values derived from 4 assays only.

The measured precision is the same or better than the published RMNS lot BW value.

RMNS BW	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Published ($\mu\text{mol L}^{-1}$) w/std deviation	61.45 ± 0.12	1.58 ± 0.003	25.25 ± 0.04	0.069 ± 0.002	- -
Minimum	61.24	1.597	25.39	0.066	1.62
Maximum	61.31	1.603	25.42	0.071	1.63
Mean	61.28	1.600	25.41	0.069	1.625
Median	61.28	1.600	25.41	0.069	1.625
Precision (Stdev)	0.05	0.003	0.01	0.002	0.003

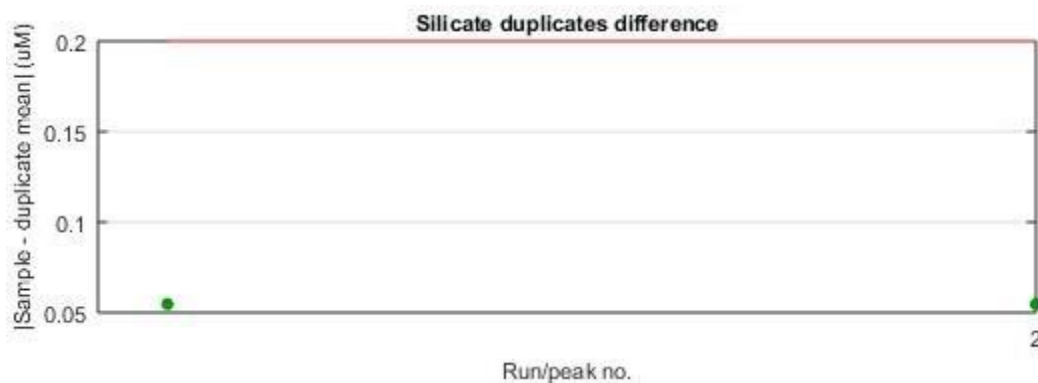
7.7 Sampling Precision

For in2018_v07, the sampling precision is GOOD.

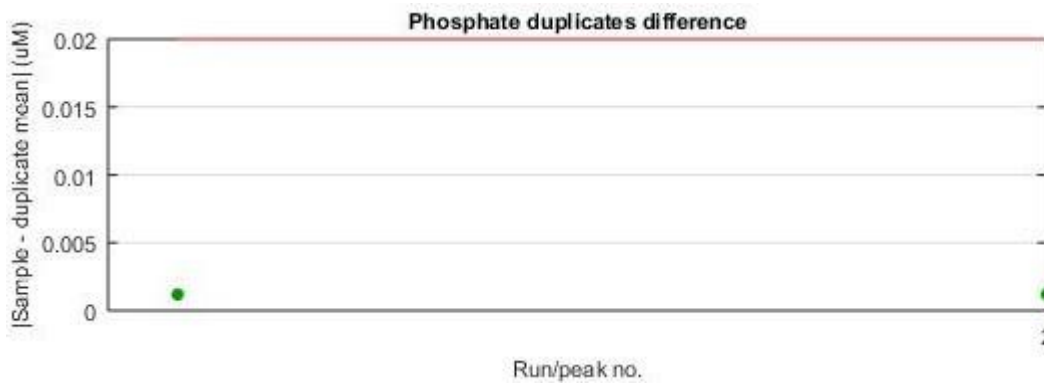
Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate concentrations is less than the MDL value. The exception is nitrate+nitrite which uses 0.06 μM as the MDL boundary.

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.

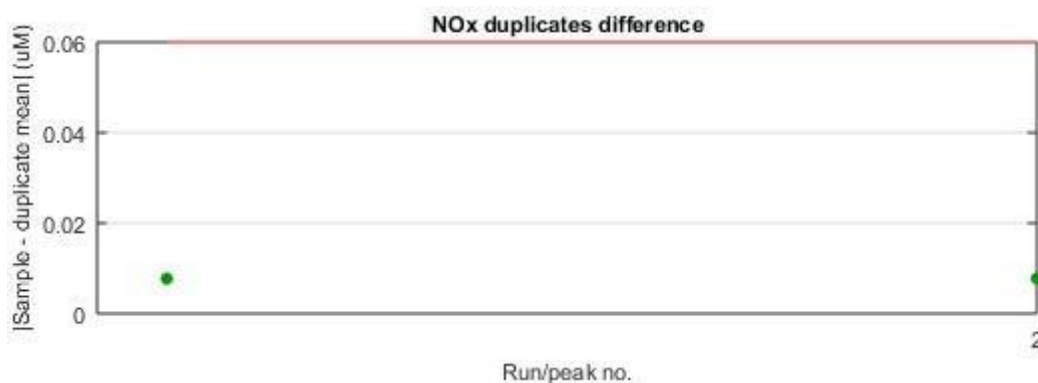
7.7.1 Silicate Duplicates Plot



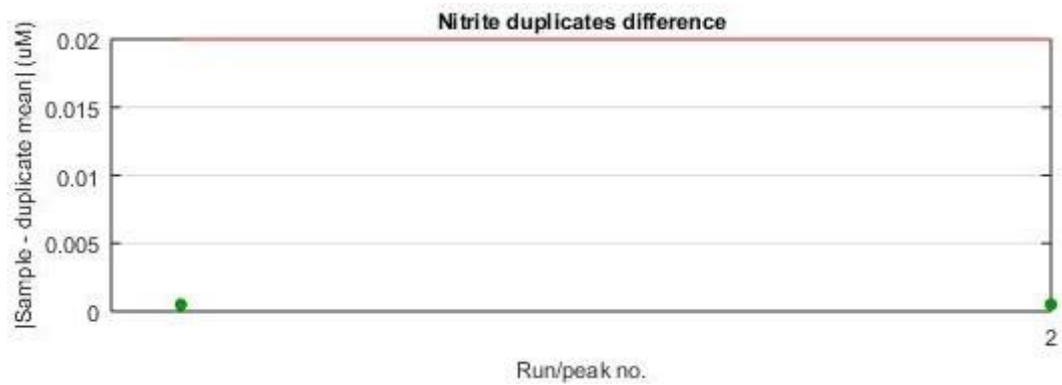
7.7.2 Phosphate Duplicates Plot



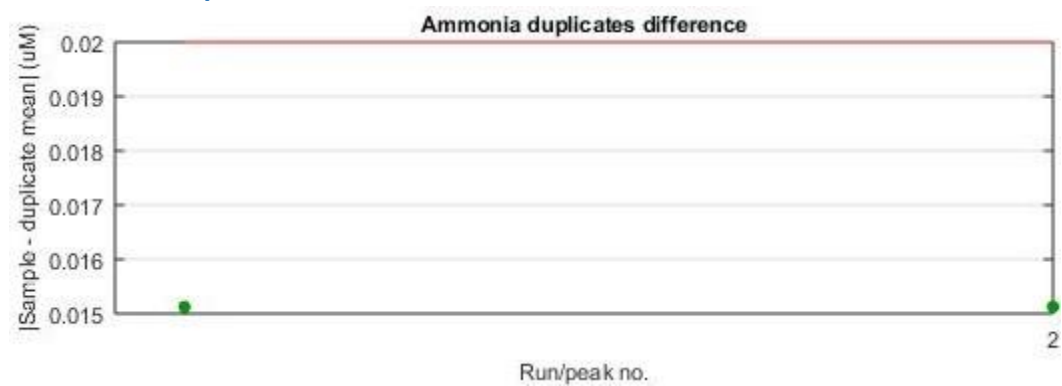
7.7.3 Nitrate + Nitrite (NOx) Duplicates Plot



7.7.4 Nitrite Duplicates Plot

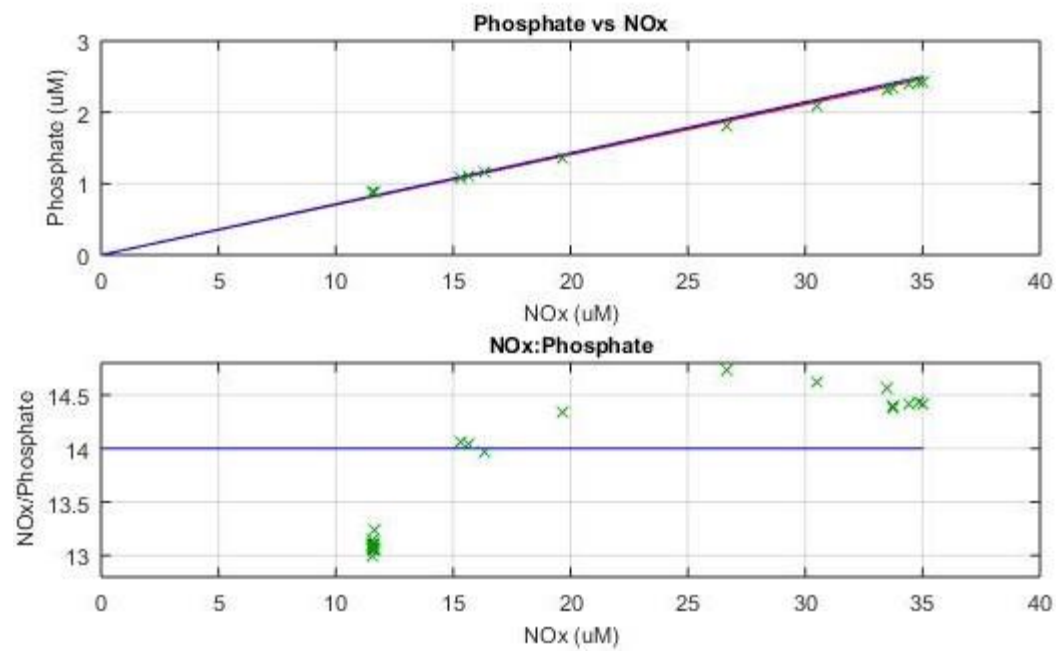


7.7.5 Ammonia Duplicates Plot



7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.2



7.9 Missing or Suspect Nutrient Data.

Missing or suspect data: none.

Data quality: GOOD

Good data is flagged 0 in the .csv and .netcdf files. Data that is flagged BAD is not included in the hydrology .csv file. See Appendix 8.5 for the flag key.

7.10 Temperature & Humidity Change over Nutrient Analyses

The temperature and humidity within the AA3 chemistry module was not logged for this voyage.

The laboratory temperature was measured and recorded on the nutrient run sheets at the start each analysis run. The temperature varied between 21 and 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: Flagged Calibration and Quality Control Data

HyPro classifies the quality of data as good, suspect or bad and flags accordingly.

CTD	Peak	Run	Analysis	Reason for Flag or Action
1	Cal 4	Nut001	NH ₄	Suspect, higher concentration due to contamination. Less weighting in calibration curve.

8.3 Nutrients: RMNS lot BW results for each CTD deployment.

RMNS Lot BW results (μmol L ⁻¹)						
Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NO _x (NO ₂ + NO ₃)	Ammonium
<i>BW reported</i>	-	61.45	1.578	0.069	25.25	-
1	1	61.28	1.600	0.069	25.40	1.63

8.4 Nutrients: Measured Detection Limit for each CTD Deployment.

Measured Detection Limit (μmol L ⁻¹)						
Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NO _x (NO ₂ + NO ₃)	Ammonium
1	1	0.04	0.003	0.005	0.001	0.003

8.5 Flag Key for Hydrology Data Set

Flag	Description
0	Data is GOOD.
63	Below nominal detection limit.
65	Peak shape is suspect.
69	Data is suspect. Flagged by operator or software. Various, MDL greater than the nominal MDL, Calibration or Duplicate data is outside of set limits.
129	Data is BAD. Peak exceeds maximum A/D value of AA3HR instrument.
133	Data is BAD. Flagged by operator.
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	No result to report. Flag used in the netcdf file. Not used in the csv file (final Hydrology data set)
192	Raw Data, not processed.

8.6 GO-SHIP Specifications

8.6.1 Salinity

Accuracy of 0.001 is possible with Autosol™ salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosol precision is better than 0.001 PSS-78. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of $\pm 1^\circ\text{C}$ is very important and should be recorded².

8.6.2 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% accuracy¹, 0.2% precision³, full scale.

8.6.4 PO₄

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

8.6.5 NO₃

Approximately 1% accuracy¹, 0.2% precision³, 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.

9 References

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