RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2020_v08
Chief Scientist:	Philip Boyd
Voyage title:	SOLACE – Southern Ocean Large Areal Carbon Export: quantifying carbon sequestration in subpolar and polar waters
Report compiled by:	Jack McDonald & Stephen Tibben

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

1.1 Objectives/Proposal

First, to improve water column measurement of the downward export flux of carbon of the biological pump using an integrated suite of new technological advances – from particle decomposition to mesopelagic vertical migrations.

Second, to integrate these improved estimates of the functioning of the biological export with bio-optical properties, used as proxies of biogeochemical (BGC) properties, and which can be remotely sensed using satellite sensors. A combination of conventional passive "ocean colour radiometry" and active "CALIOP" LIDAR (that 'sees through clouds' and also senses below the surface) will be validated on SOLACE to provide a comprehensive regional extrapolation of carbon export fluxes.

Third, to cross-link larger scale estimates of the biological pump (termed the BGP – biological gravitational pump - in a Review paper at Nature by Boyd, Claustre, Levy, Siegel and Weber, under revision) with those of PIPs (Particle Injection Pumps, Boyd et al., 2019, Nature) such as the Mixed Layer Pump (Llort et al., 2018) than can be assessed using profiling biological-floats (i.e., BGC-ARGO) as part of the US S. Ocean SOCCOM mission (www.soccom.edu), as well as the individual programmes of France, Australia and others.

Fourth, to link these S. Ocean findings with those of international programmes on this topic, working on N. Hemisphere analogues, via data synthesis and modelling (co-collaborator Dave Siegel, UCSB) to produce large areal maps of carbon export by both the BGP and PIPs. These programmes sit under the JETZON umbrella - http://jetzon.org/ .

1.2 General Hydro Info

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity.

Five nutrients were analysed; silicate, phosphate, nitrate + nitrite, nitrite and ammonium. Certified reference materials for nutrients in seawater were within the specified limits of the certified value.

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

Hydrochemistry oversaw the collection of salinity, oxygen and nutrient samples (silicate, phosphate, nitrate + nitrite (NOx), nitrite, and ammonium) from the CTD.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, December 4th 2020 – January 16th, 2020.

Figure 1: Voyage Track:

3 Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
Dr Philip Boyd	Chief Scientist	UTAS
Lisa Woodward	Voyage Manager	CSIRO
Jack McDonald	Hydrochemist	CSIRO
Stephen Tibben	Hydrochemist	CSIRO

4 Sample Summary

Table 2: Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	163 CTD
	39 TSG
Dissolved Oxygen (SIO automated titration)	169 CTD
	8 UWY
Nutrients (Seal AA3HR segmented flow)	483 CTD
	132 UWY
	154 EXP
	149 TMR

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12 L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- 29 CTD deployments were sampled in total on this leg. Deployments were sampled by Hydrochemistry personnel, Jack McDonald and Stephen Tibben, as well as members from the science party: Margot Hind, Stephanie Pastula-Ramadier, Tyler Rohr, Yaojia (Bobby) Sun, Inessa Corney, Annabelle Erskine, David Green, Phil Butterworth, Charlotte Robinson, Jakob Weis, and Sam Eggins.
- A 12-bottle TMR CTD rosette (CSIRO's) was sampled by Michael Elwood and Sam Eggins. There were 15 TMR deployments sampled for Nutrients.

4.1.2 TSG (Thermosalinograph)

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

For TSG sample information, please refer to 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. An overview of this process is illustrated in figure 1.

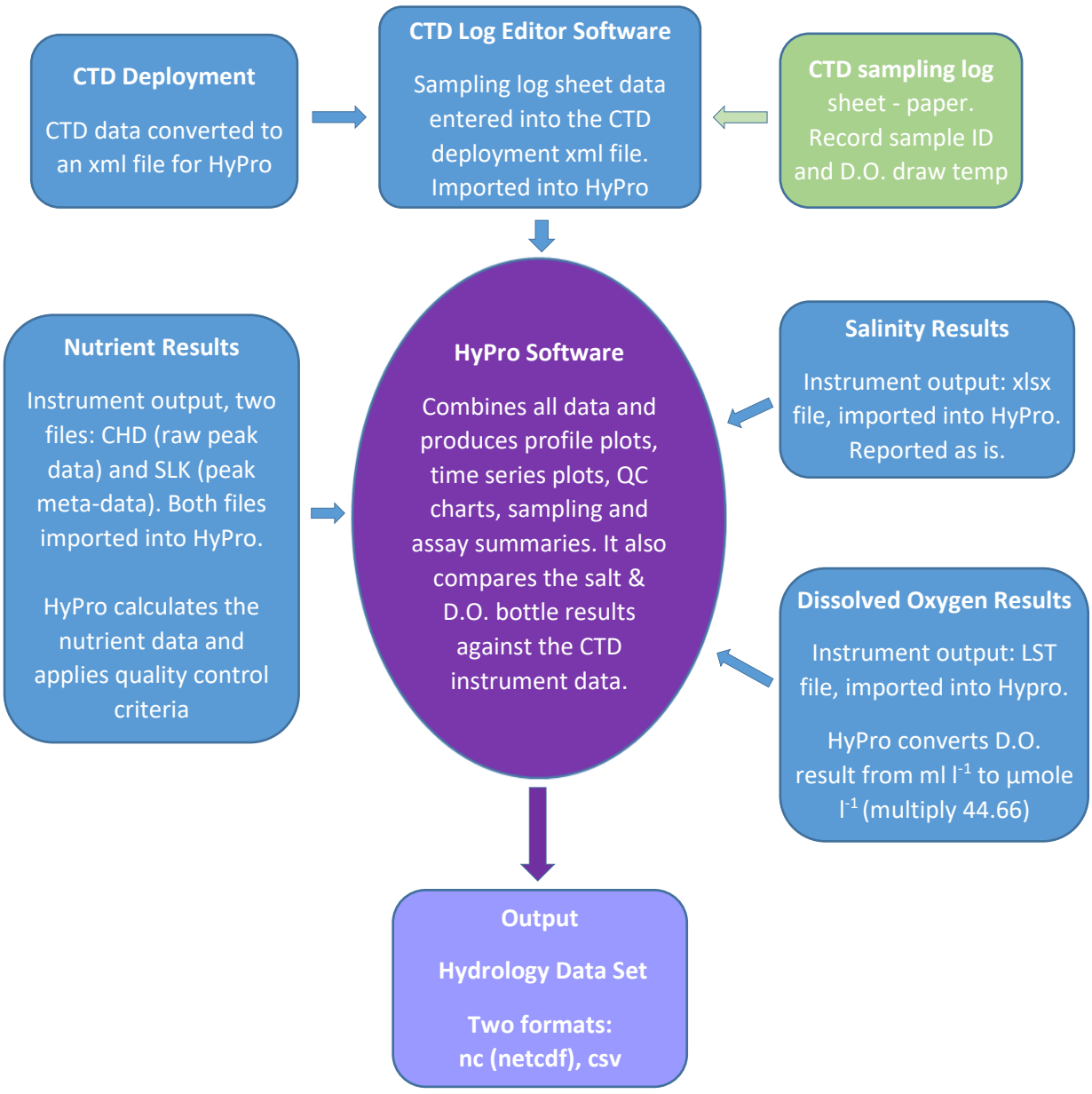


Figure 2: Hydrology Data Processing Flow Diagram.

5 Salinity Data Processing

Table 3: Salinity Parameter Summary

Details	
HyPro Version	5.7
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72151
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analysts	Stephen Tibben & Jack McDonald
Lab Temperature (±0.5°C)	Not recorded – HOBO malfunctioned
Bath Temperature	23.997°C
Reference Material	OSIL IAPSO[1] - Batch P162, use by 16/04/2021, K_{15} = 0.99983 OSIL IAPSO[1] - Batch P163, use by 10/04/2022, K_{15} = 0.99985
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 salinometer room for a minimum of 8 hrs before measurement.
Comments	None.

5.1 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 the shoulder of the bottle ~11-12 cm from bottom of bottle. 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.

[1] International Association for the Physical Sciences of the Oceans

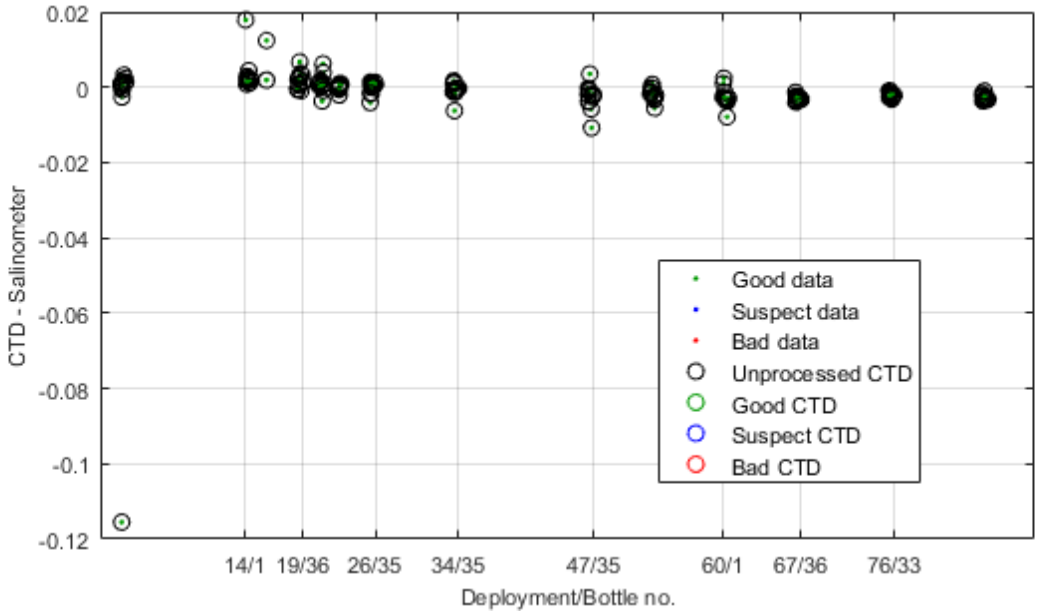
5.2 CTD Salinity vs Bottle Salinity Plot

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

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

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

Figure 3: CTD Salinity vs Bottle Salinity Plot. Deployment/Bottle number (x-axis). Difference of Salinity bottle data from the corresponding CTD salinity value (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: PSU (dimensionless).



5.3 Missing or Suspect Salinity Data

Table 4: 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 8.4

CTD	RP	Run	Flag	Reason for Flag or Action
N/A	N/A	N/A	N/A	N/A

5.4 Stability of Salinity Standard over Voyage

The salinometer was standardised with IAPSO standard seawater lot P162 (PSU = 34.993) for analytical runs 1 – 9. Figure 4 shows the readings for lot P162 used to standardise the instrument before each run. The blue line represents the mean of all standard measurements

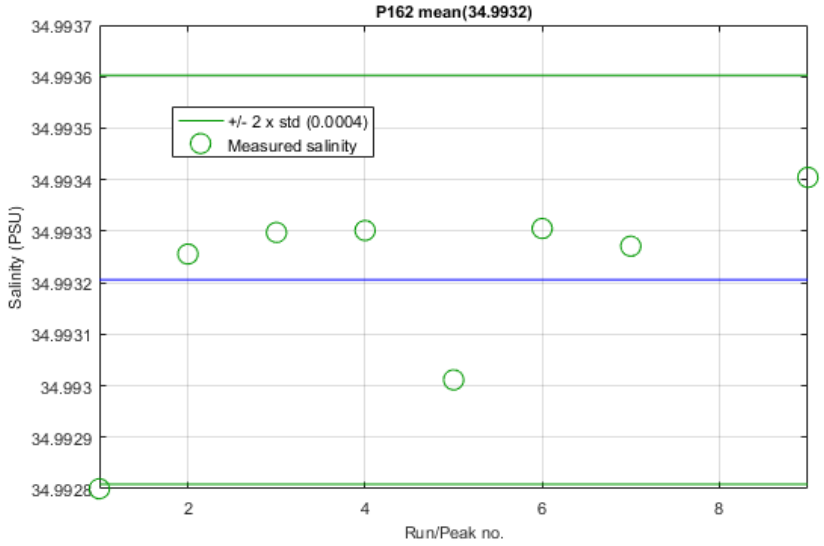


Figure 4: Measured salinity of P162 IAPSO salinity standard for instrument standardization prior to each run 1 – 9 (note: run 8 does not exist)

The salinometer was standardised with IAPSO standard seawater lot P163 (PSU = 34.994) for analytical runs 9 – 15. Figure 5 shows the readings for lot P163 used to standardise the instrument before each run. The blue line represents the mean of all standard measurements

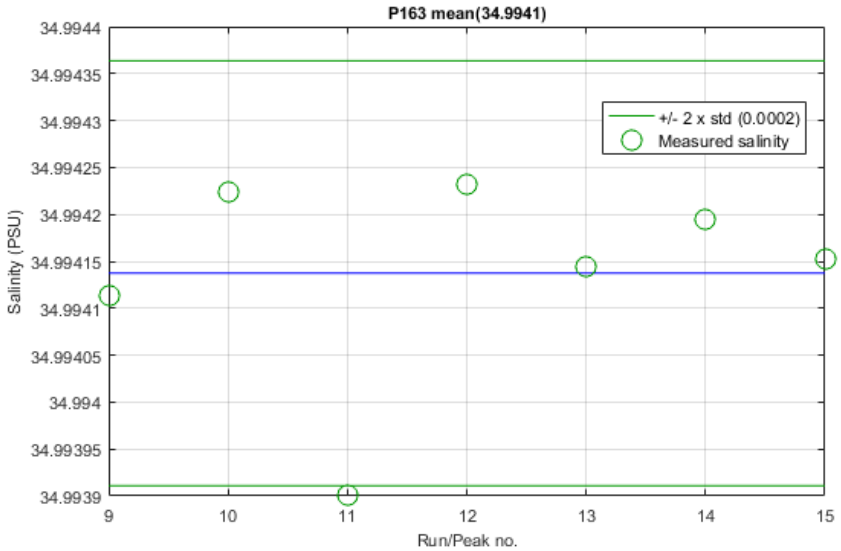


Figure 5: Measured salinity of P163 IAPSO salinity standard for instrument standardization prior to each run 9 – 15

6 Dissolved Oxygen Data Processing

6.1 Dissolved Oxygen Parameter Summary

SIO method used. The method is based on the whole-bottle modified Winkler titration of Carpenter (1965) plus modifications by Culberson *et al* (1991).

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

Before each batch of sample assays, 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 1 mL aliquots of the same potassium iodate solution.

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

Table 5: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 µmol L^{-1}
Analyst(s)	Jack McDonald + Stephen Tibben
Lab Temperature (±1°C)	Not recorded – HOBO malfunctioned
Sample Container type	Pre-numbered 140 mL glass iodine determination flasks with glass stopper. 18 flasks per light-proof container.
Sample Storage	Samples stored in the hydrochemistry lab until analysis. All samples were analysed within ~48 hrs
Comments	None.

6.2 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

The CTD values in this plot are unprocessed raw data.

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

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

Figure 6. CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot. Deployment/Bottle number (x-axis). Difference in dissolved oxygen results from the bottle sample to its corresponding CTD measurement (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: µmol L^{-1}

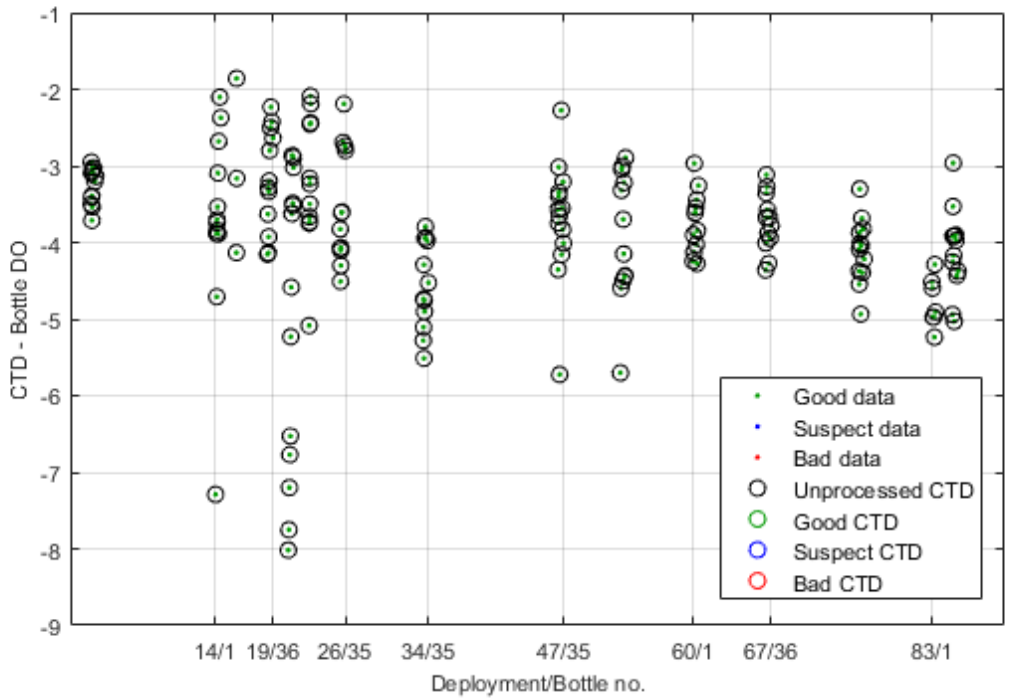


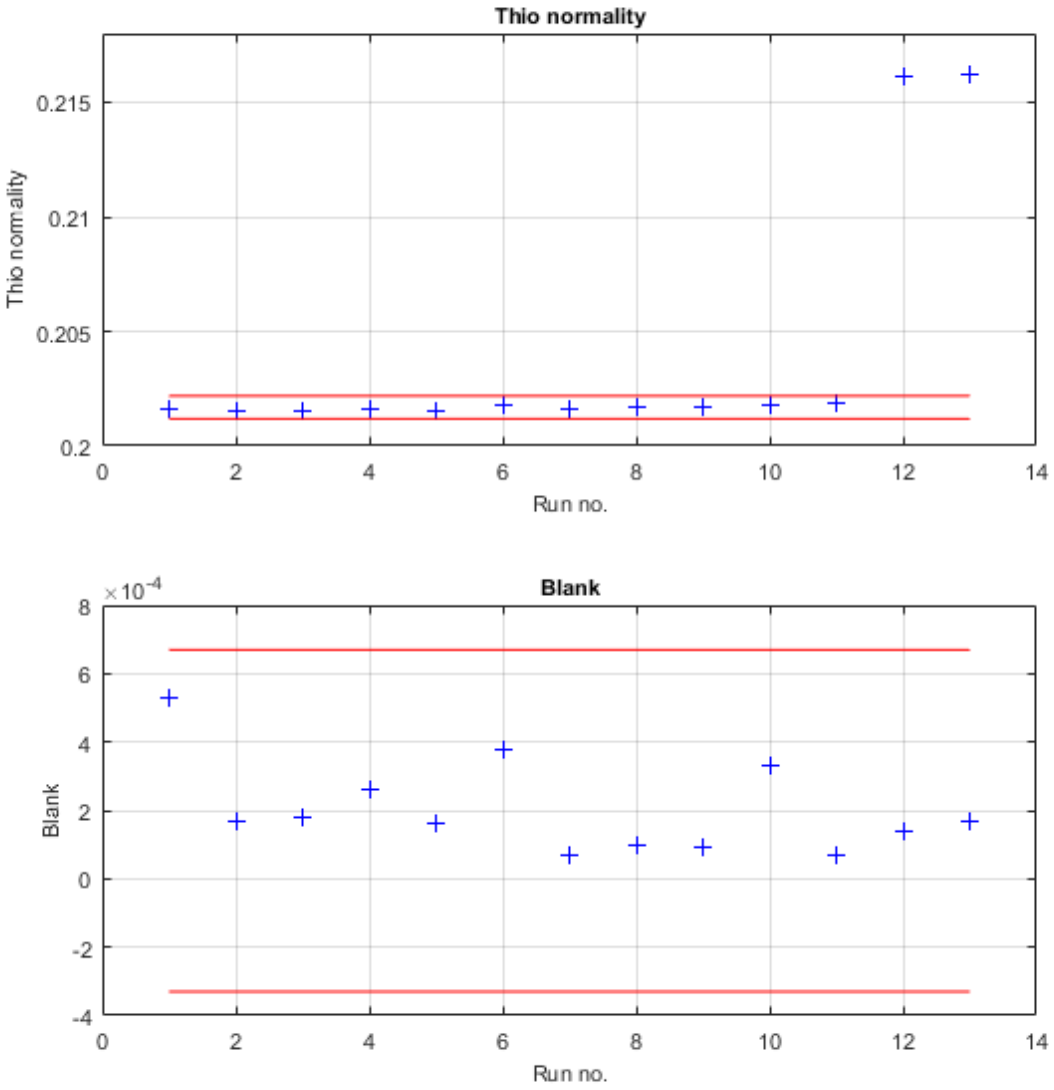
Table 6: Missing or suspect dissolved oxygen bottle data. Data is flagged based on CTD sampling log sheet notes, observations during analysis, and examination of the depth profile (Flag key in appendix 8.4).

CTD	RP	Run	Flag	Reason for Flag or Action
N/A	N/A	N/A	N/A	N/A

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

The thiosulfate titrant was changed after run 11. At this point, a new thiosulfate concentration was determined by the KIO_3.

Figure 7. Auto-titrator calibration plots. In Figure 5a the red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration. In Figure 5b red lines indicate acceptable variation either side of the mean blank concentration. The titrant should not vary more than 0.0005 N between analyses. The variance for the last two points is due to swapping the Thiosulfate titrant out for a new batch. Plots from now on will centre the variance on the new thiosulfate concentration.



7 Nutrient Data Processing

7.1 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[1] 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 Kérouel and Aminot (1997). 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.

[1] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

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

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 7.09				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range (µmol L^{-1})	112	3.0	42	1.4	2.0
Method Detection Limit (MDL) (µmol L^{-1})	0.2	0.02	0.02	0.02	0.02
Matrix Corrections	none	none	none	none	none
Analysts	Jack McDonald and Stephen Tibben				
Lab Temperature (±1°C)	Not recorded – HOBO malfunctioned				
Reference Material	KANSO, RMNS lot CC				
Sampling Container type	CTD: 50mL HDPE with screw cap lids.				
Sample Storage	< 4 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD and UWY: None.				
Comments					

7.2 HyPro Processing Summary for Nutrients

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and, duplicate sample results that do not match.

With suspect calibration points, their contribution to the curve is given less weighting dependent on their distance from the final curve. The cut-off limits for good calibration data are:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE[1]).
- Within 0.02uM for phosphate, nitrite and ammonium.

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

Missing or suspect nutrient data is tabulated in section 7.7, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.5.

[1] World Ocean Circulation Experiment

Table 8: 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	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 variance.	N	N	N	N	N
Medium of Standards	Low nutrient seawater was collected in oligotrophic waters off Queensland on a previous voyage and aged for 12+ months. LNSW is measured in triplicate within each analytical run to ensure no contamination in standards. Sub-lot passed through a 10 micron filter and was 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 collected1 for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.				

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

Descriptive statistics are used to ascertain the accuracy and precision of the analysis from the repetitive measurement of the RMNS for silicate, phosphate, NOx, and nitrite in seawater.

Japanese KANSO certified RMNS lot CC was assayed in triplicate in each run to monitor accuracy. The certified values are in Table 9.

For in2020_v08, the certified reference material results (mean of mean-of-triplicates for each run during voyage) for NOx, Phosphate and Silicate are within 1% of the certified values. Nitrite was within 0.04 µmol L^{-1} of the certified value.

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

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

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

RMNS	Nitrate (NO_3)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)	Phosphate (PO_4)	Silicate ($Si(OH)_4$)
Lot CD	5.629 ± 0.051	0.018 ± 0.004	5.647 ± 0.055	0.457 ± 0.008	14.264 ± 0.10
Lot CJ	16.588 ± 0.205	0.032 ± 0.007	16.620 ± 0.212	1.219 ± 0.020	39.424 ± 0.410
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 µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C. The RMNS is not certified for ammonium. NO_x is derived by summing the NO_3 and NO_2 values.

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

RMNS CC	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)	Phosphate (PO_4)	Silicate ($Si(OH)_4$)
Minimum	0.12	31.11	2.07	87.00
Maximum	0.16	32.36	2.18	89.40
Mean	0.14	31.90	2.14	88.20
Median	0.14	31.86	2.15	88.19
Reproducibility	0.01	0.19	0.02	0.35

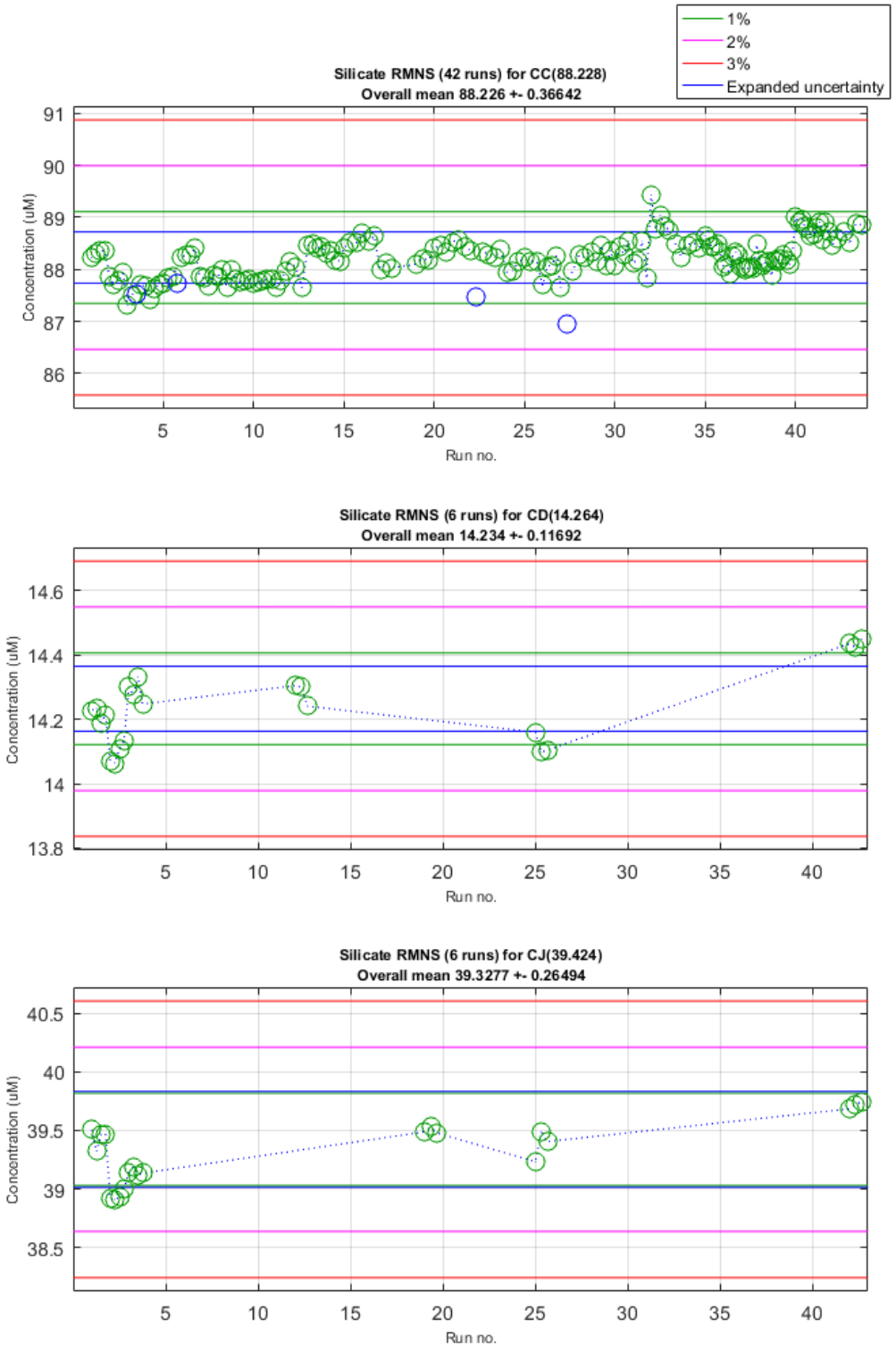
RMNS CJ	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)	Phosphate (PO_4)	Silicate ($Si(OH)_4$)
Minimum	0.02	16.40	1.20	38.90
Maximum	0.06	16.70	1.25	39.70
Mean	0.05	16.59	1.23	39.34
Median	0.05	16.60	1.24	39.45
Reproducibility	0.01	0.10	0.02	0.05

RMNS CD	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)	Phosphate (PO_4)	Silicate ($Si(OH)_4$)
Minimum	0.019	5.50	0.46	14.10
Maximum	0.048	5.60	0.48	14.40
Mean	0.035	5.55	0.47	14.23
Median	0.033	5.55	0.47	14.23
Reproducibility	0.001	0.03	0.01	0.10

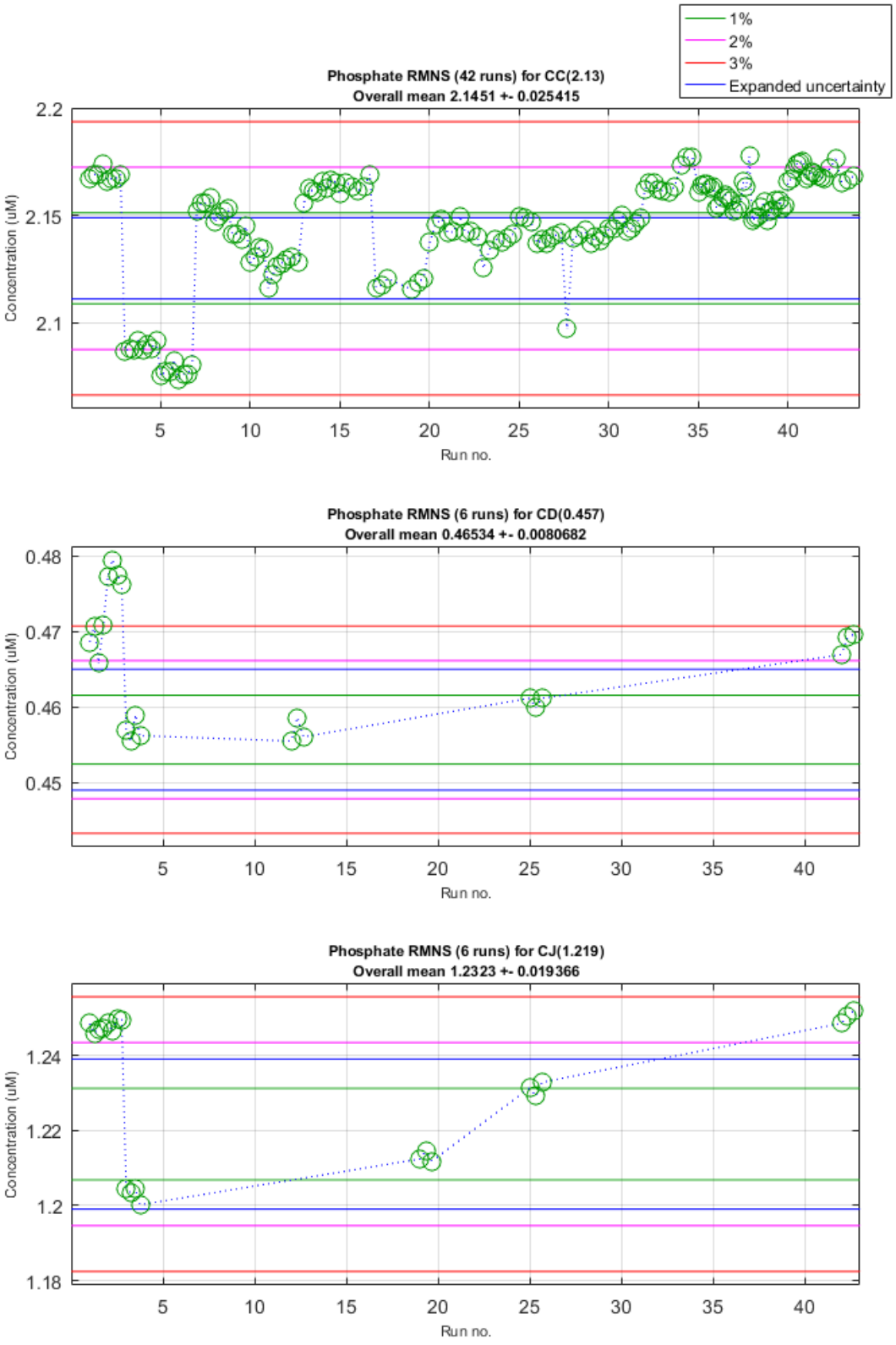
7.4 Nutrient plots of RMNS

The green pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µmol L^{-1} increments from the certified value. The blue line is the certified value's expanded uncertainty.

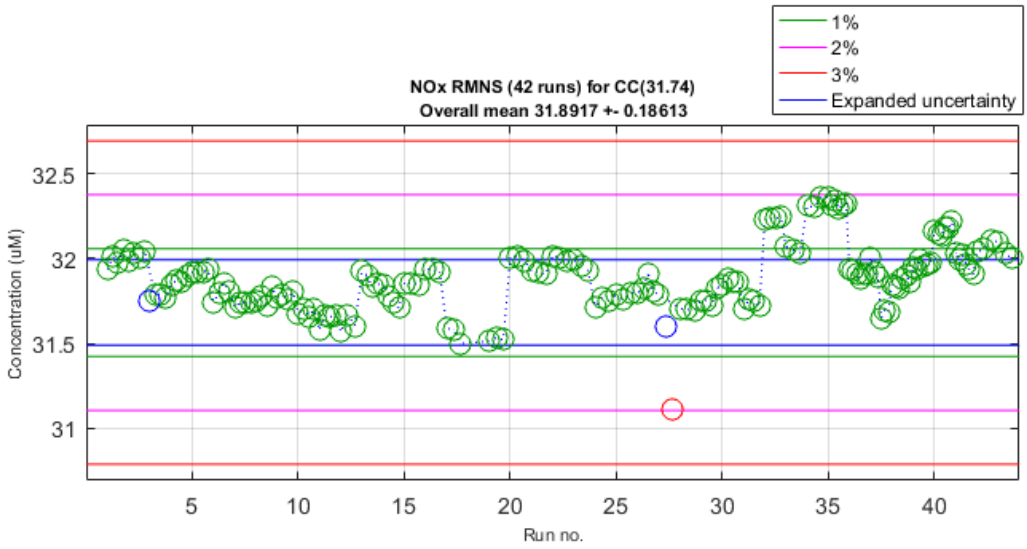
7.4.1 **Figure 8:** Silicate RMNS Plot (µmol L^{-1})

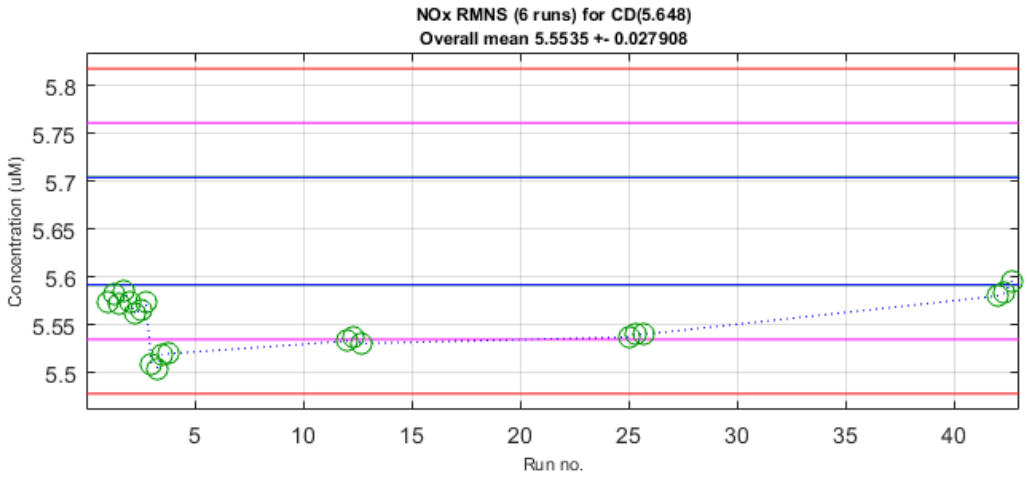


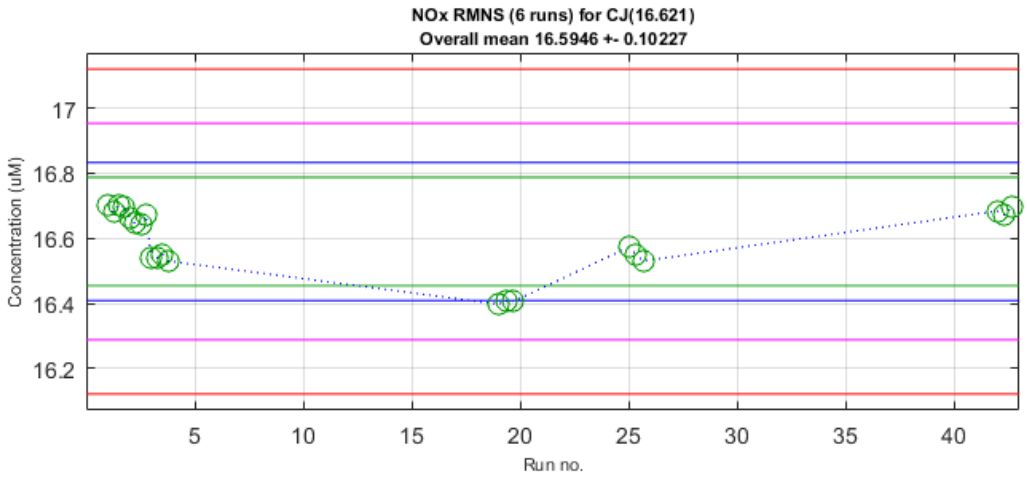
7.4.2 **Figure 9:** Phosphate RMNS Plot (µmol L^{-1})



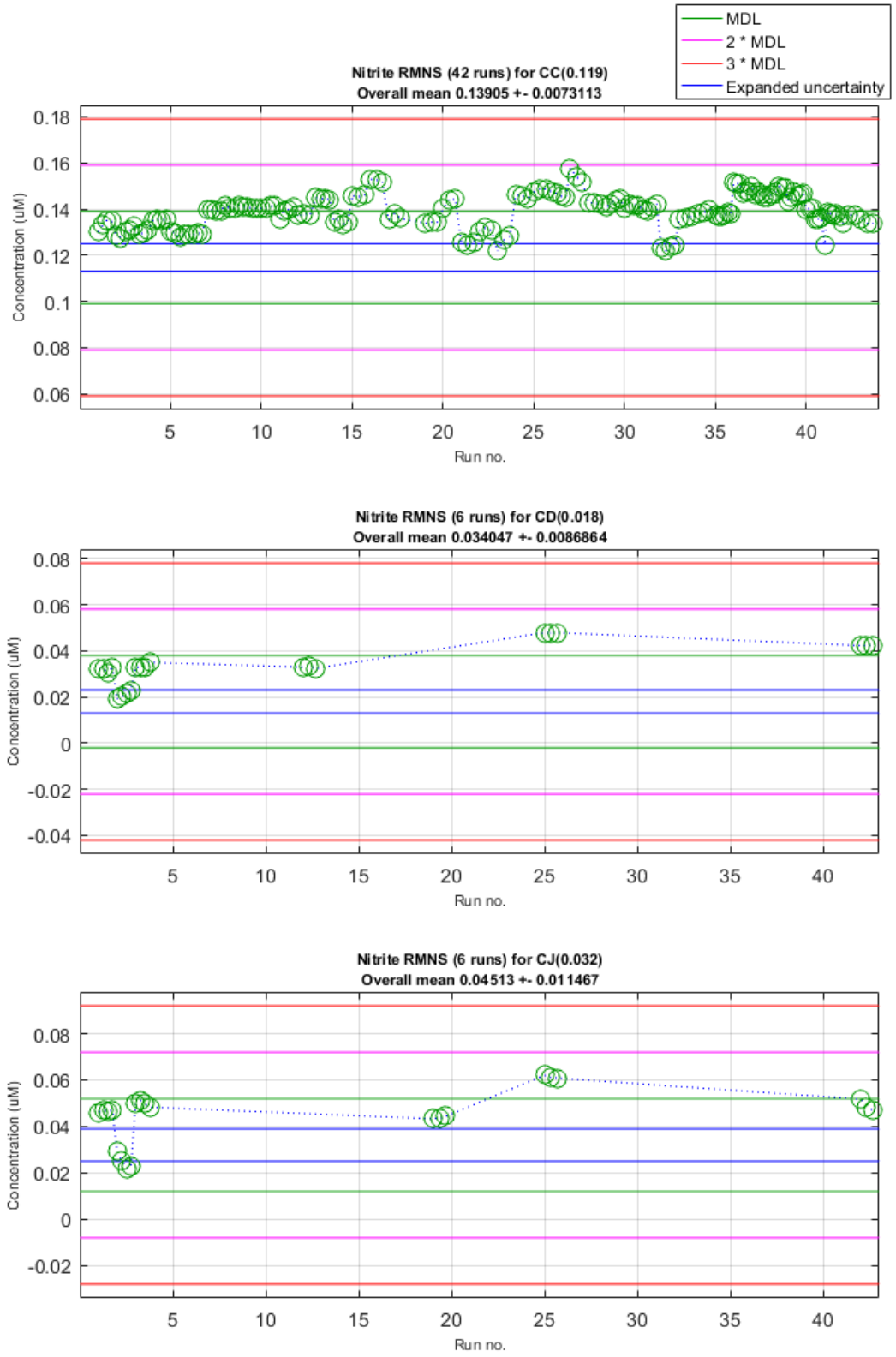
7.4.3 **Figure 10:** Nitrate + Nitrite (NOx) RMNS Plot (µmol L^{-1})







7.4.4 **Figure 11:** Nitrite RMNS Plot (µmol L^{-1})



7.5 Measurement Uncertainty

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

Table 11: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol L^{-1}

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 Sampling Precision

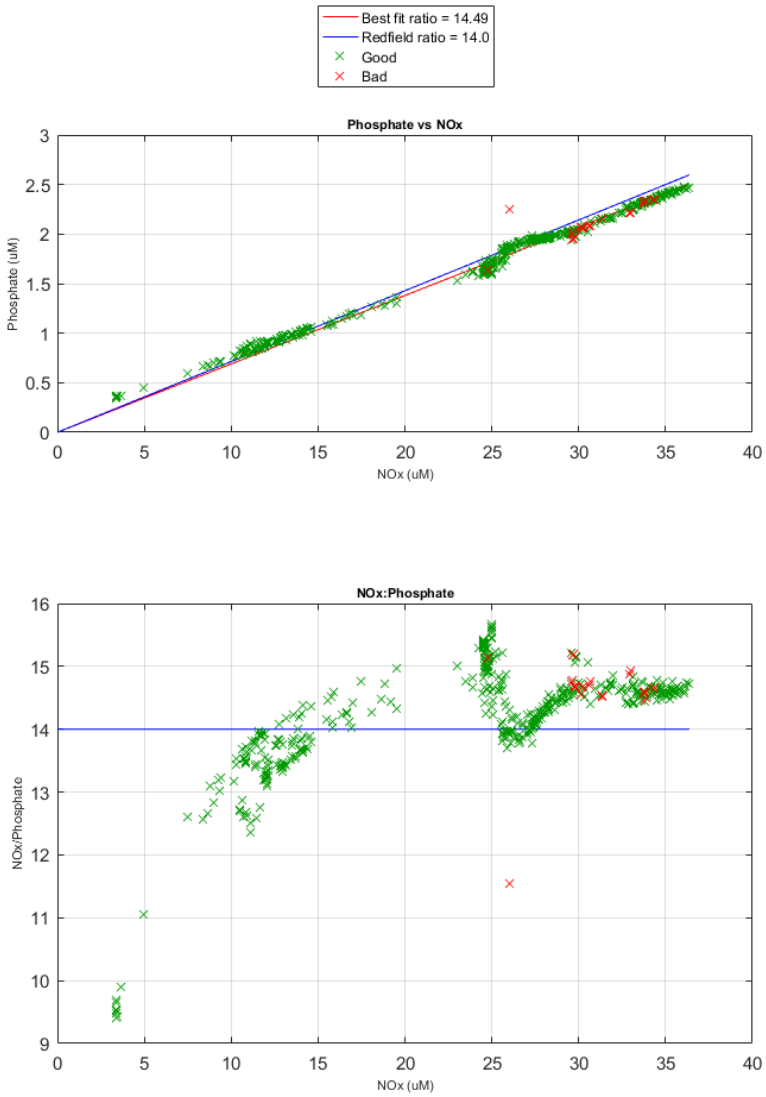
Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate concentrations is less than the MDL value. The exception is nitrate+nitrite, which uses 0.06 µmol L^{-1} as the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

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

7.7 Redfield Ratio Plot (14.0) for CTD Deployments.

Calculating and plotting the Redfield Ratio is a check for the accuracy of phosphate and nitrate+nitrite (NOx) analysis. The ratio is the required amount of P to N for marine phytoplankton growth. The ratio is very consistent in the deep ocean with phosphate to nitrate equalling 14. The ratio for leg this voyage was 14.49.

Figure 12. Redfield ratio plots.



7.8 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 (in2020_v08_HydroDep.csv). Flag Key in Appendix 8.4.

Table 12: Missing or Suspect Nutrient Data

CTD	RP	Run	Flag	Reason for Flag or Action
47	22	nut022	Suspect	Outlier in depth plot
77	18	nut035	Suspect	Outlier in depth plot

7.9 Temperature & Humidity Change over Nutrient Analyses

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

(1) Above the AA3HR instrument on the other side, ship's instrument (Grafana). Data on request.

(2) On the deck of the nitrate & nitrite AA3HR chemistry module, temperature, and humidity. Data on request.

Refer to "in2020_v08_hyd_voyagereport.docx" for room temperature graphs.

The laboratory temperature was measured and recorded on the nutrient run sheets at the start each analysis run.

8 Appendix

8.1 Salinity: Reference Material Used

OSIL IAPSO Standard Seawater	
Batch:	P162
Use by date:	16/04/2021
K_{15}:	0.99983
PSU:	34.993
Batch:	P163
Use by date:	10/04/2022
K_{15}:	0.99985
PSU:	134.994

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

8.2.1 RMNS Lot CC Results

Analysis Run	CTD #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)
1		88.325 ± 0.096	2.17 ± 0	0.133 ± 0.002	31.993 ± 0.048
2		87.825 ± 0.096	2.17 ± 0	0.13 ± 0.001	32.015 ± 0.024
3		87.5 ± 0.163	2.09 ± 0	0.131 ± 0.001	31.775 ± 0.019
4		87.6 ± 0.141	2.09 ± 0	0.135 ± 0	31.87 ± 0.022
5		87.775 ± 0.096	2.08 ± 0	0.129 ± 0.001	31.923 ± 0.005
6		88.3 ± 0.082	2.078 ± 0.005	0.129 ± 0.001	31.8 ± 0.045
7		87.825 ± 0.096	2.158 ± 0.005	0.14 ± 0.001	31.733 ± 0.015
8		87.9 ± 0.141	2.15 ± 0	0.141 ± 0.001	31.768 ± 0.046
9		87.775 ± 0.05	2.143 ± 0.005	0.141 ± 0.001	31.78 ± 0.018
10		87.775 ± 0.05	2.133 ± 0.005	0.141 ± 0.001	31.683 ± 0.021
11		87.825 ± 0.126	2.125 ± 0.006	0.139 ± 0.002	31.645 ± 0.044
12		87.9 ± 0.265	2.13 ± 0	0.137 ± 0.001	31.613 ± 0.051
13		88.45 ± 0.058	2.16 ± 0	0.145 ± 0.001	31.878 ± 0.046
14		88.275 ± 0.096	2.168 ± 0.005	0.135 ± 0.001	31.768 ± 0.056
15		88.467 ± 0.058	2.163 ± 0.006	0.146 ± 0.001	31.853 ± 0.006
16		88.6 ± 0.1	2.163 ± 0.006	0.152 ± 0.001	31.93 ± 0.01
17		88.033 ± 0.058	2.12 ± 0	0.136 ± 0.002	31.557 ± 0.049
19		88.167 ± 0.058	2.12 ± 0	0.134 ± 0	31.52 ± 0.01
20		88.4 ± 0.1	2.147 ± 0.006	0.143 ± 0.002	32.003 ± 0.012
21		88.5 ± 0.1	2.143 ± 0.006	0.125 ± 0.001	31.92 ± 0.01
22		88.067 ± 0.493	2.14 ± 0	0.131 ± 0.001	32 ± 0.02
23		88.3 ± 0.1	2.133 ± 0.006	0.125 ± 0.003	31.96 ± 0.03
24		88 ± 0.1	2.14 ± 0	0.146 ± 0.001	31.747 ± 0.025
25		88.167 ± 0.058	2.15 ± 0	0.148 ± 0.001	31.783 ± 0.021
26		88.05 ± 0.252	2.14 ± 0	0.146 ± 0.001	31.833 ± 0.053
27		87.533 ± 0.503	2.127 ± 0.023	0.155 ± 0.003	31.5 ± 0.351
28		88.267 ± 0.058	2.14 ± 0	0.142 ± 0.001	31.7 ± 0
29		88.275 ± 0.206	2.14 ± 0	0.143 ± 0.002	31.76 ± 0.042
30		88.325 ± 0.171	2.145 ± 0.006	0.141 ± 0.001	31.865 ± 0.013

31	88.15 ± 0.289	2.145 ± 0.006	0.141 ± 0.001	31.733 ± 0.028
32	89 ± 0.283	2.165 ± 0.006	0.123 ± 0.001	32.238 ± 0.01
33	88.5 ± 0.3	2.16 ± 0	0.136 ± 0.001	32.05 ± 0.02
34	88.467 ± 0.058	2.177 ± 0.006	0.139 ± 0.001	32.323 ± 0.032
35	88.467 ± 0.121	2.16 ± 0	0.137 ± 0.001	32.325 ± 0.024
36	88.133 ± 0.163	2.157 ± 0.005	0.149 ± 0.002	31.913 ± 0.021
37	88.083 ± 0.204	2.162 ± 0.012	0.147 ± 0.002	31.808 ± 0.15
38	88.117 ± 0.117	2.152 ± 0.004	0.148 ± 0.002	31.858 ± 0.03
39	88.217 ± 0.075	2.153 ± 0.005	0.146 ± 0.002	31.965 ± 0.022
40	88.85 ± 0.152	2.172 ± 0.004	0.138 ± 0.002	32.17 ± 0.03
41	88.767 ± 0.121	2.17 ± 0	0.136 ± 0.005	31.973 ± 0.051
42	88.6 ± 0.1	2.173 ± 0.006	0.136 ± 0.002	32.07 ± 0.036
43	88.767 ± 0.231	2.17 ± 0	0.134 ± 0.001	32.043 ± 0.051

8.2.2 RMNS Lot CJ Results

Analysis Run	CTD #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)
1		39.45 ± 0.1	1.25 ± 0	0.047 ± 0.001	16.695 ± 0.01
2		38.925 ± 0.05	1.25 ± 0	0.025 ± 0.003	16.655 ± 0.013
3		39.125 ± 0.05	1.2 ± 0	0.05 ± 0.001	16.54 ± 0.008
19		39.5 ± 0	1.21 ± 0	0.044 ± 0.001	16.407 ± 0.006
25		39.367 ± 0.153	1.23 ± 0	0.061 ± 0.001	16.55 ± 0.02
42		39.7 ± 0	1.25 ± 0	0.049 ± 0.003	16.683 ± 0.015

8.2.3 RMNS Lot CD Results

Analysis Run	CTD #	Silicate ($Si(OH)_4$) ($\mu mol\ L^{-1}$)	Phosphate (PO_4) ($\mu mol\ L^{-1}$)	Nitrite (NO_2) ($\mu mol\ L^{-1}$)	NOx ($NO_2 + NO_3$) ($\mu mol\ L^{-1}$)
1		14.2 ± 0	0.47 ± 0	0.032 ± 0.001	5.578 ± 0.01
2		14.1 ± 0	0.48 ± 0	0.021 ± 0.002	5.568 ± 0.005
3		14.275 ± 0.05	0.46 ± 0	0.034 ± 0.001	5.513 ± 0.01
12		14.267 ± 0.058	0.46 ± 0	0.033 ± 0.001	5.533 ± 0.006
25		14.133 ± 0.058	0.46 ± 0	0.048 ± 0	5.54 ± 0
42		14.4 ± 0	0.47 ± 0	0.042 ± 0	5.587 ± 0.012

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 $Si(OH)_4$

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

8.4.4 PO_4

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

8.4.5 NO_3

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.

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