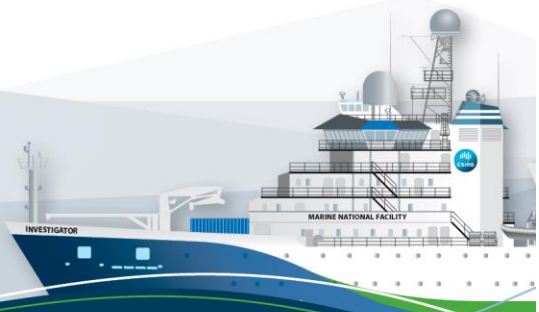
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2018_v04
Chief Scientist	Michael Ellwood
Principal Investigator	April Abbott
Voyage title:	Constraining external iron inputs and cycling in the southern extension of the East Australian Current.
Report compiled by:	Christine Rees & Stephen Tibben



Contents

1 Executive Summary

The primary objective of the voyage was to characterize the sources and biogeochemical cycling of iron and associated nutrients and their impact on productivity southwest, southeast and northeast of Tasmania. Hydrochemistry analysed salinity, oxygen and nutrient samples collected from the conductivity temperature depth (CTD) rosette, trace metal rosette (TMR), underway (UWY) seawater supply and experiments (EXP) conducted on board. Underway nitrate plus nitrite (NOx) and phosphate was analysed continuously using the AA100 nutrient analyser while transiting between stations. The AA100 was connected to the underway seawater supply surface water (7 m) in the underway lab. Please refer to the separate report for the data processing of the AA100 data.

Five nutrients were analysed; silicate, phosphate, nitrate + nitrite, nitrite and ammonium. Certified reference materials for nutrients in seawater were analysed within each analytical run. The reference materials were within GO-SHIP specified limits.

High quality data was produced for salinity and dissolved oxygen analyses and were also within specified limits of quality control.

Results for nutrient samples from experiments issued to the science parties during the voyage.

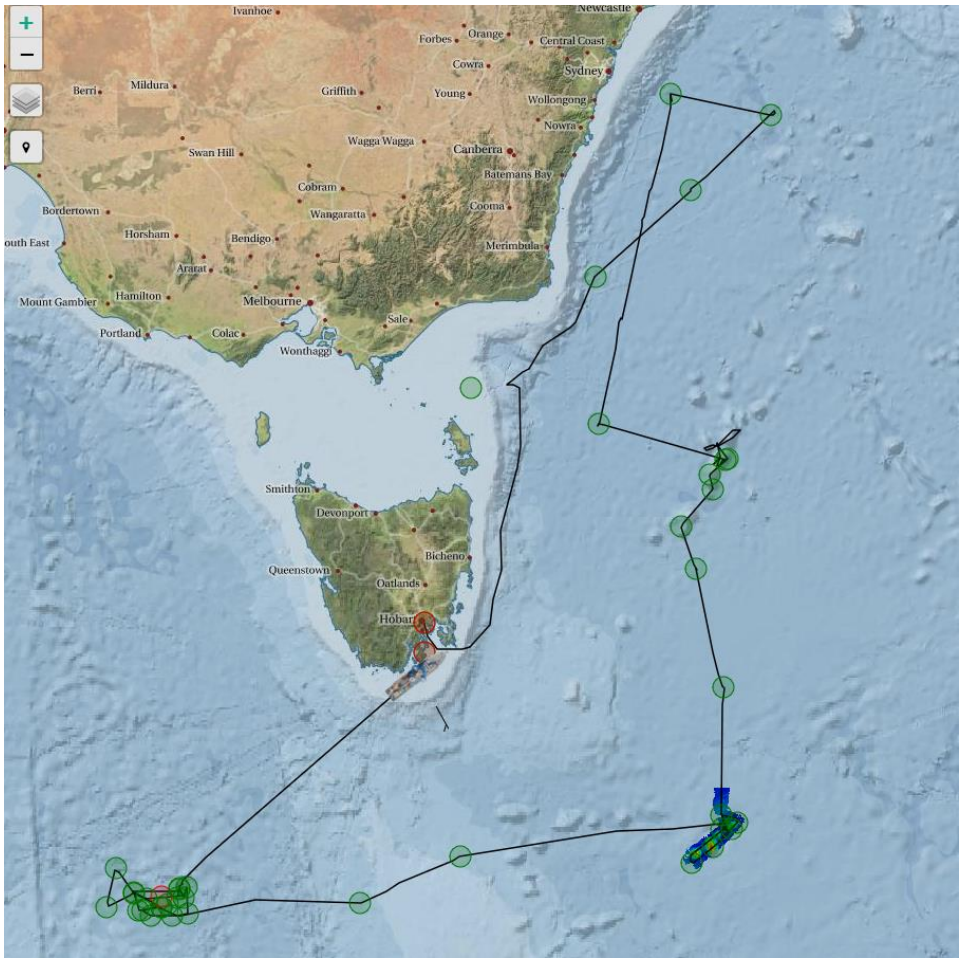
Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Hobart to Hobart, September 11th to October 8th, 2018.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Michael Ellwood	Chief Scientist	ANU
Max McGuire	Voyage Manager	CSIRO
Christine Rees	Hydrochemist	CSIRO
Stephen Tibben	Hydrochemist	CSIRO
Kendall Sherrin	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	348 CTD 21 TSG
Dissolved Oxygen (automated titration)	348 CTD
Nutrients (Seal AA3HR)	630 CTD 217 TMR (including 13 PP) 108 EXP 128 UWY

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- **25** CTD deployments in total. Deployments were sampled by:
- Sarah Andrew, Hanneloor Heynderickx, Riteshma Deva, Dave Janssen, Phil Butterworth, and Svenja Halfter

4.1.2 TMR (Trace Metal Rossette)

- Sampling point, 12 bottle trace metals rosette.
- **21** deployments in total, 18 TMR & 3 primary production (PP). Sampled by the trace metals team.

4.1.3 EXP (Experimental samples)

- Prepared and sampled by the science groups conducting the experiments.
    - Pauline Latour (Pauline.latour@utas.edu.au)
    - Riteshma Devi (riteshma.devi@anu.edu.au)
    - Prayna Maharaj (prayna.maharaj@anu.edu.au)

4.1.4 TSG (Thermosalinograph)

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

4.1.5 UWY (Underway)

- Samples were collected by Kendall Sherrin.

For UWY, EXP, and TSG sample information refer to the eLog's from the voyage. TMR & TMRPP information is included in the file: TMR & PP Log.xlsx.

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.

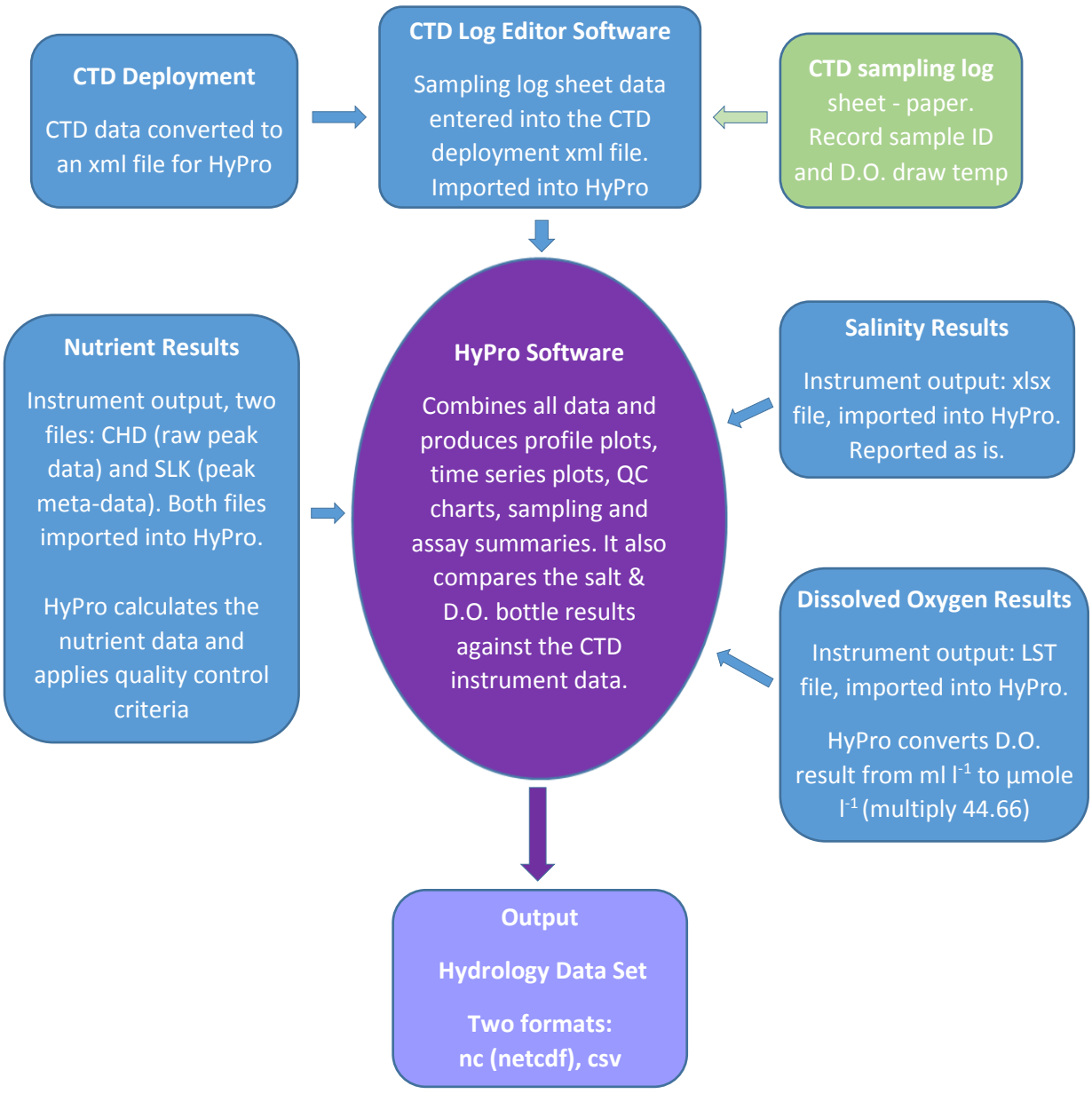


Figure 1: Hydrology Data Processing Flow Diagram.

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	Stephen Tibben
Lab Temperature (±0.5°C)	20° - 23°C during analysis, average 21°C.
Bath Temperature	24.01°C
Reference Material	OSILIAPSO - Batch P162, use by 16/04/2021, K_{15} = 0.99983
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.

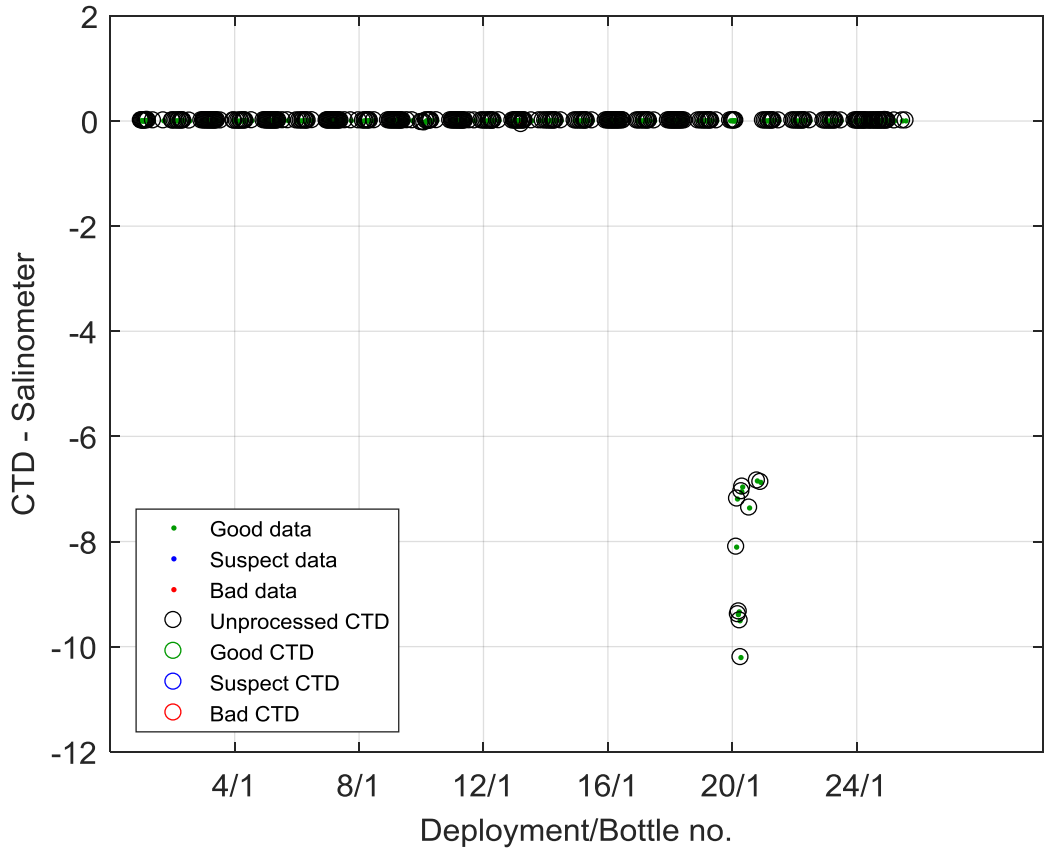
The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

5.3 CTD Salinity vs Bottle Salinity Plot

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

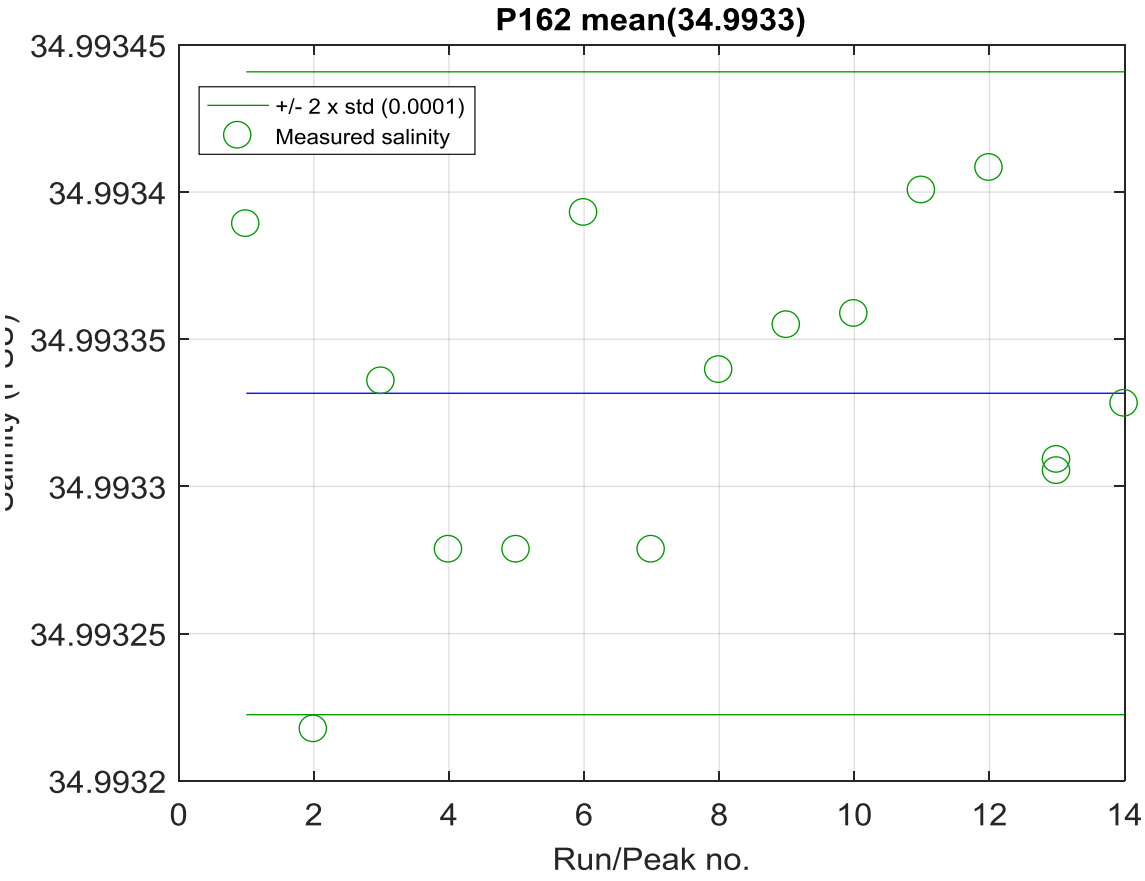
The large offset seen at deployment 20 was due to biological material entering the primary conductivity cell and causing erroneous readings.

The unprocessed CTD values were 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.



5.4 OSIL Salinity Standard PSU across the Voyage

Practical salinity (PSU) of P162 is 34.993, the blue line is the mean of all standards measured which were used to standardise the salinometer.



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
08	04	sal00x	141	Missing, was not sampled.
13	09	sal006	133	Outlier on vertical profile plot. Same salinity as next bottle so probably mis-sampled.

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)	Christine Rees & Kendall Sherrin (CTD019 & 020)
Lab Temperature (±1°C)	Variable 20.0 - 23.0°C Average 21°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.

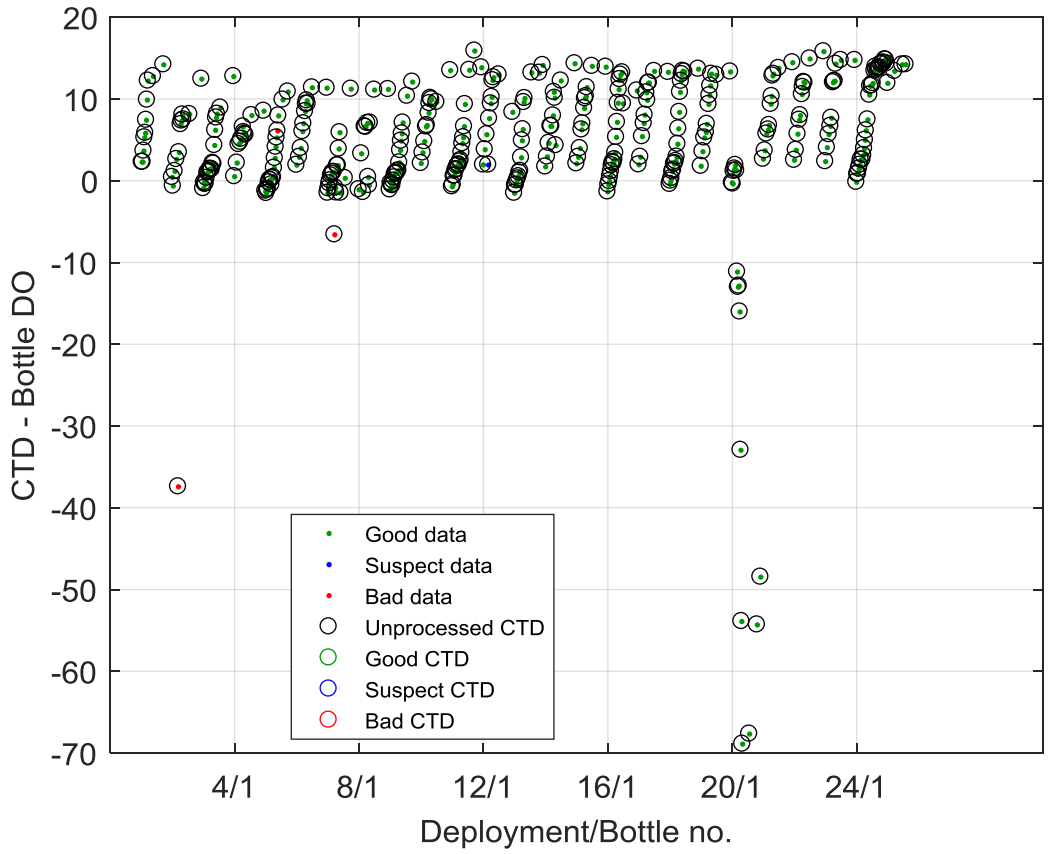
6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

The CTD values in this plot are unprocessed raw data.

The large offset seen at deployment 20 was due to biological material entering the primary conductivity cell and causing erroneous readings.

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)

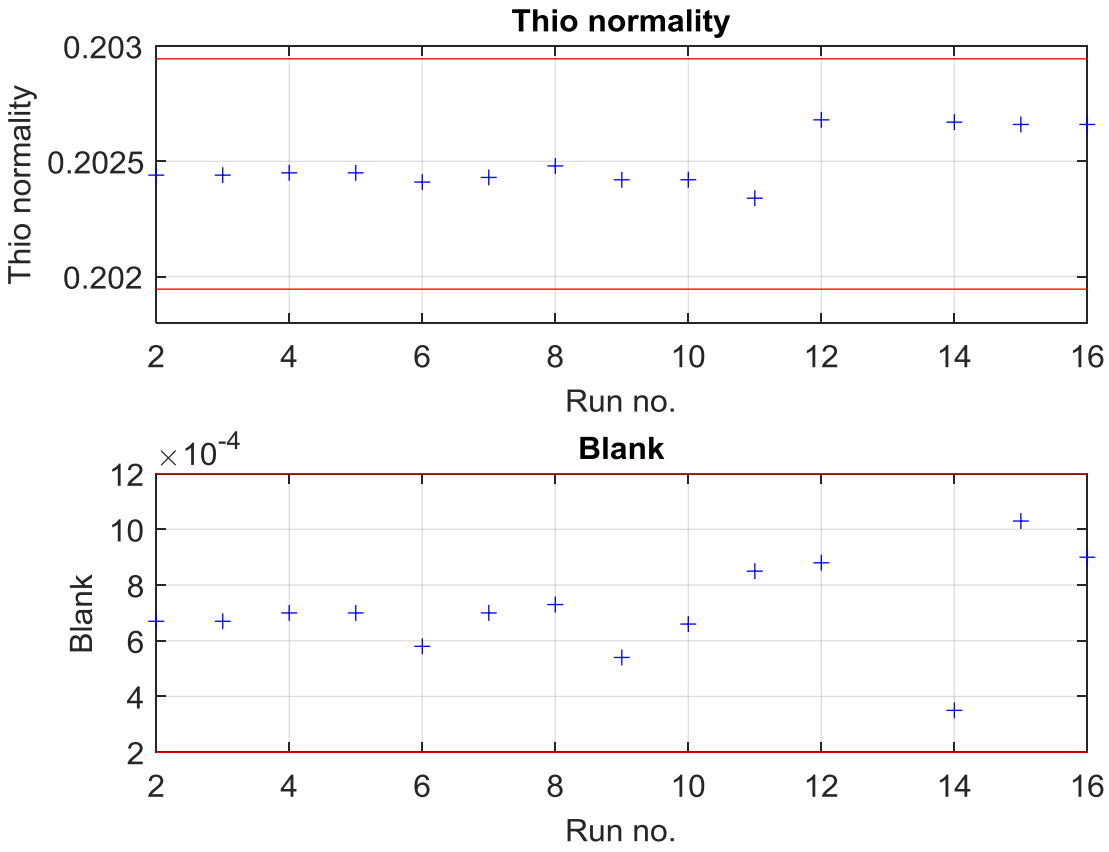


6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2N) varied less than 0.0004 for all dissolved oxygen sample titrations. The blank correction is less than 0.001 ml.

Red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration and the blank concentration. The titrant should not vary more than 0.0005 N between analyses.

For reference, titre volumes for dissolved oxygen bottle samples lay in the range 0.44 to 0.81 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
1	1	oxy001	141	Missing due to the flask volumes not in file: O2 flask file. Sat too long with acid in it, before being titrated.
2	8	oxy002	133	Lid placed in upside down, bubble trapped underneath.
5	15	oxy005	133	Accidently removed flask before end of titration.
7	9	oxy006	133	Outlier in profile
12	7	oxy009	69	Suspect outlier in profile.

7 Nutrient Data Processing

7.1 Nutrient Assay Parameter Summary

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 6.10				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range	140 µM	3.0 µM	42 µM	1.4 µM	2.0 µM
Method Detection Limit (MDL)	0.2 µM[1]	0.02 µM	0.02 µM	0.02 µM	0.02 µM
Matrix Corrections	none	none	none	none	none
Analysts	Christine Rees & Stephen Tibben				
Lab Temperature (±1°C)	Variable, 20 – 23°C Average 21°C				
Reference Material	KANSO, RMNS lot CJ				
Sampling Container type	CTD & TMR: 50ml HDPE with screw cap lids. EXP and UWY: 12ml PP tubes with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD, UWY & TMR: None. EXP: as prepared by the science parties.				
Comments					

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 as the ammonium detector.

Silicate (SOP001): colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660nm.

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater

forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper - cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 520 nm.

Nitrite (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460nm after excitation at 370nm.

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

7.3 HyPro Processing Parameters

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

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Data Reported as	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
# of points in Calibration	7	6	7	6	6
Forced through zero?	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	LNSW (bulk) filtered through 5 micron filter into 20 L carboys and stored in the clean dry laboratory at 22°C. Filtration occurred January and September 2018.				
Medium of Baseline	18.2 Ω water. Dispensed from Milli Q				

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
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 8.3.				

7.4 HyPro Data Processing Summary

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

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

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

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

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

Japanese KANSO certified RMNS lot CJ was assayed in triplicate in each run to monitor accuracy in the middle ranges of the calibration curve. RMNS lot CB was analysed at the beginning of the voyage and lot CD was analysed 3 times during the voyage, to determine accuracy at the high and low ranges of the calibration curves. The certified values are in table 1.

For in2018_v04, the RMNS lot CJ results for NOx and silicate were within 1% of the certified mean, nitrite within 1 MDL (0.02µM) and phosphate within 3%. 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.

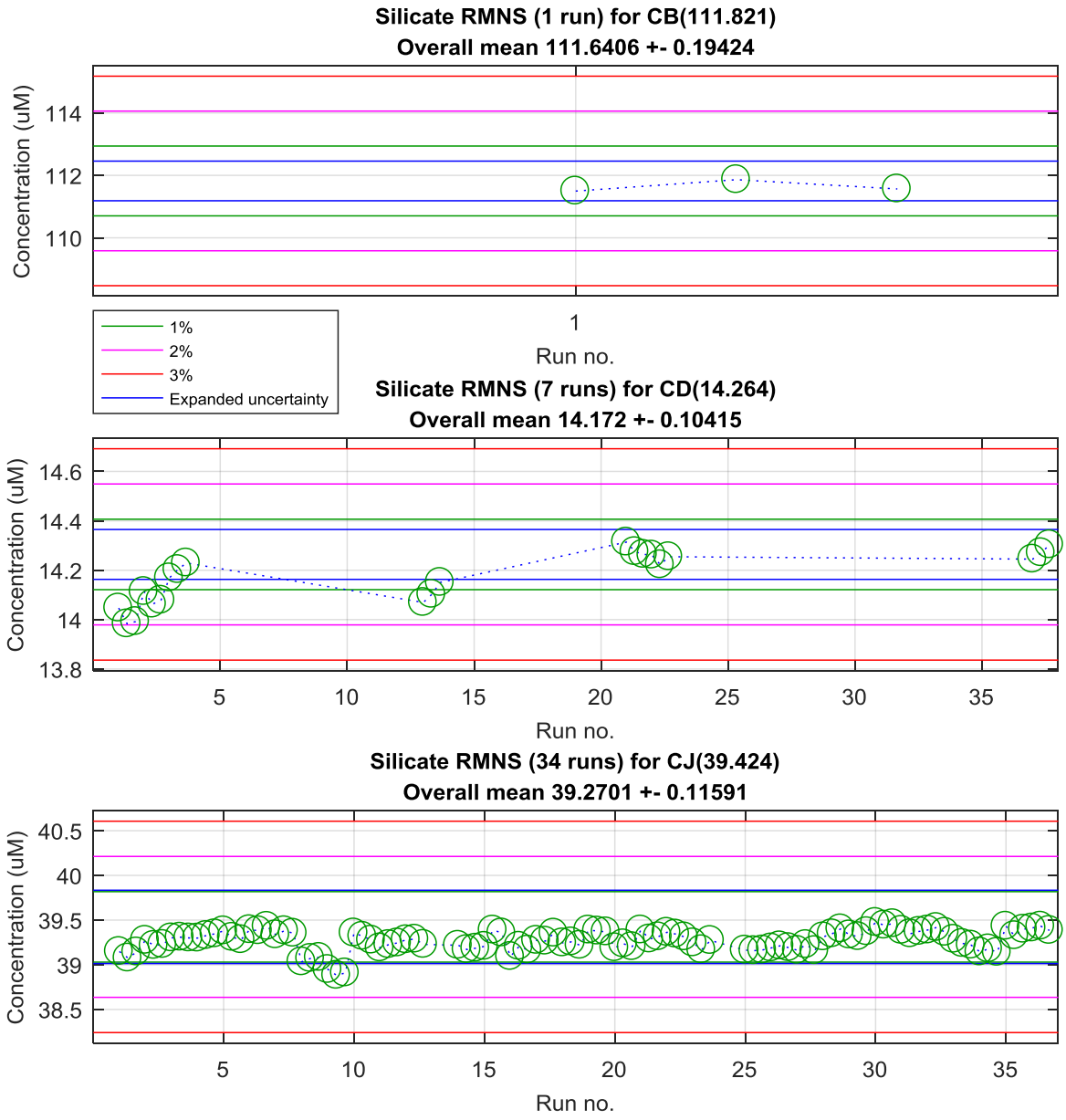
Table 1: RMNS concentrations with expanded uncertainty (µmol L^{-1}) at 21°C

RMNS	NO_3	NO_2	NO_3+ NO_2 (NO_X)	PO_4	SiO_4
Lot CD	5.629 ± 0.051	0.018 ± 0.004	5.647 ± 0.055	0.457 ± 0.008	14.264 ± 0.10
Lot CB	36.649 ± 0.276	0.119 ± 0.006	36.768 ± 0.282	2.580 ± 0.022	111.821 ± 0.635
Lot CJ	16.588 ± 0.205	0.032 ± 0.007	16.620 ± 0.212	1.219 ± 0.020	39.424 ± 0.410

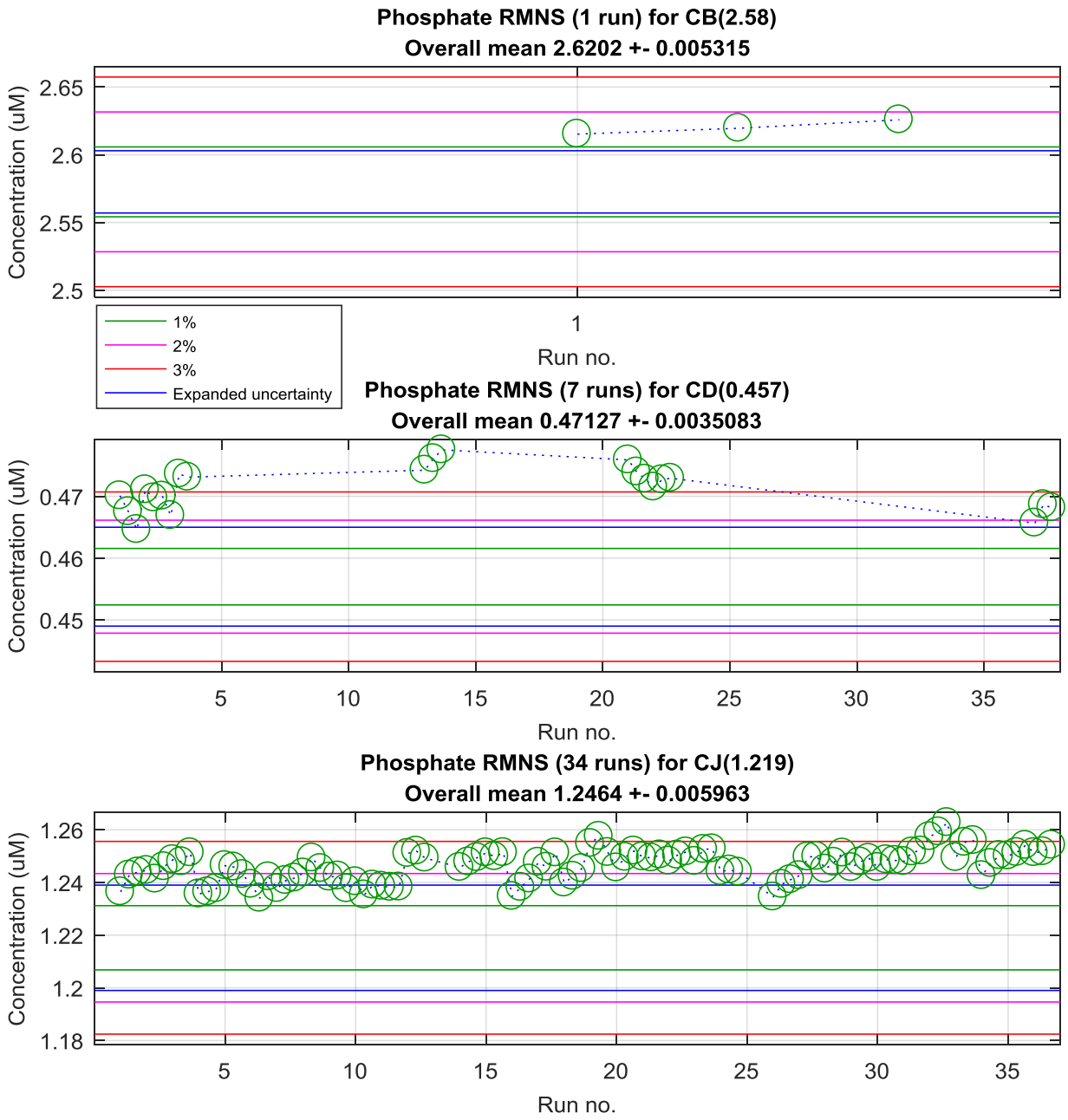
KANSO publishes the RMNS nutrient values in µ mol kg^{-1}. These are converted to µ mol l^{-1} at 21°C. RMNS is not certified for ammonium. NO_x is derived by adding the NO_3 and NO_2 values.

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

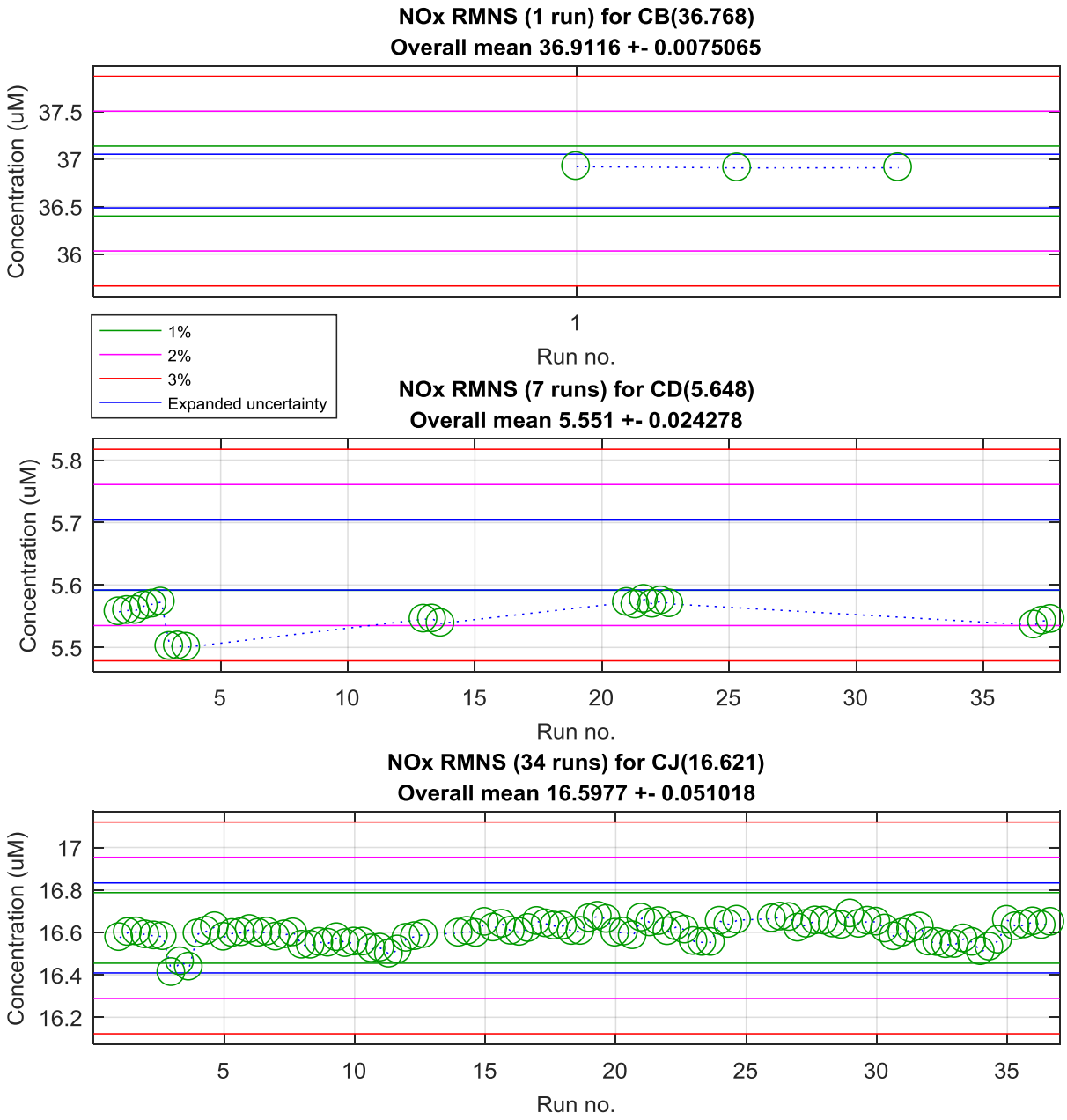
7.5.1 Silicate RMNS Plot



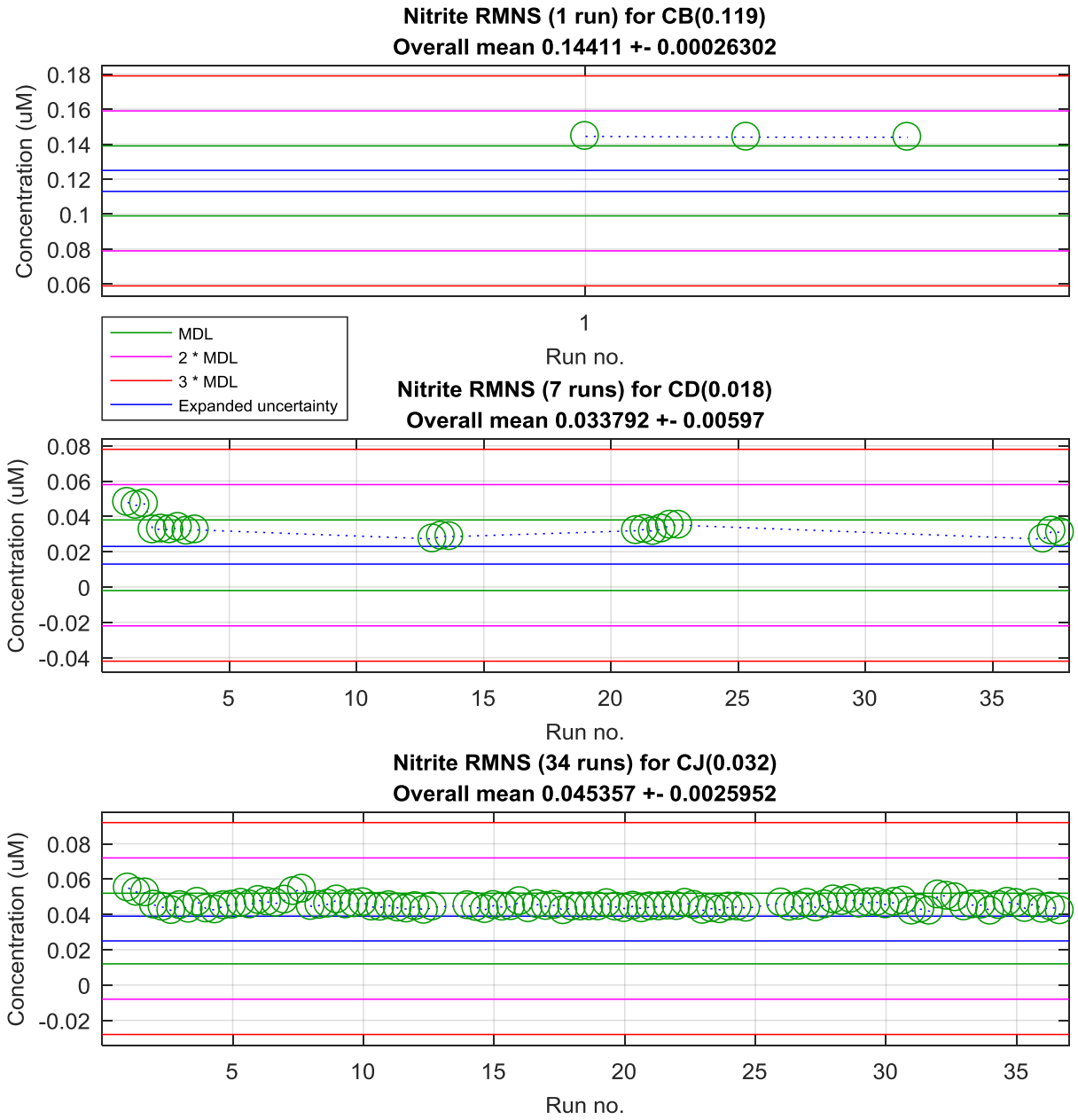
7.5.2 Phosphate RMNS Plot



7.5.3 Nitrate + Nitrite (NOx) RMNS Plot



7.5.4 Nitrite RMNS Plot



7.6 Internal Quality Control

The internal quality control (QC) samples were prepared on the 05/11/2018 by filtering approximately 8 litres of low nutrients seawater (LNSW) from a carboy through a 0.2 µM Acropak filter into 2 4 L polycarbonate bottles and then autoclaving.

The following processes were conducted inside a laminar flow cabinet.

A LNSW control was prepared to account for any nutrients already in the LNSW and also any nutrients picked up in the autoclaving and decanting process. The autoclaved LNSW was well mixed and poured into an acid cleaned and dry 1 L volumetric flask then mixed before decanting into a HDPE square 1 L bottle with lid and screwed shut with parafilm wrapped around the lid and stored at 4^{o}C in the dark. The same process was used except the LNSW was then poured from the 1 L HDPE bottle into 100 new 10 ml polypropylene sample tubes with HDPE screw caps which were also wrapped with parafilm and stored at 4^{o}C in the dark.

The Spiked internal quality control was prepared by spiking nutrients into the autoclaved LNSW from an OSIL kit containing 5 nutrients each in separate bottles containing 50 ml. The concentrations of the each bottle were as follows: Silicate 1000 µmol/L, Phosphate 100 µmol/L, Nitrate 1000 µmol/L, Nitrite 100 µmol/L and Ammonia 10,000 µmol/L.

The following amounts were pipetted into a calibrated 1 L volumetric flask.

10 ml of phosphate 100 µmol/L = 1 uM

5 ml of Nitrate 1000 µmol/L = 5 µM

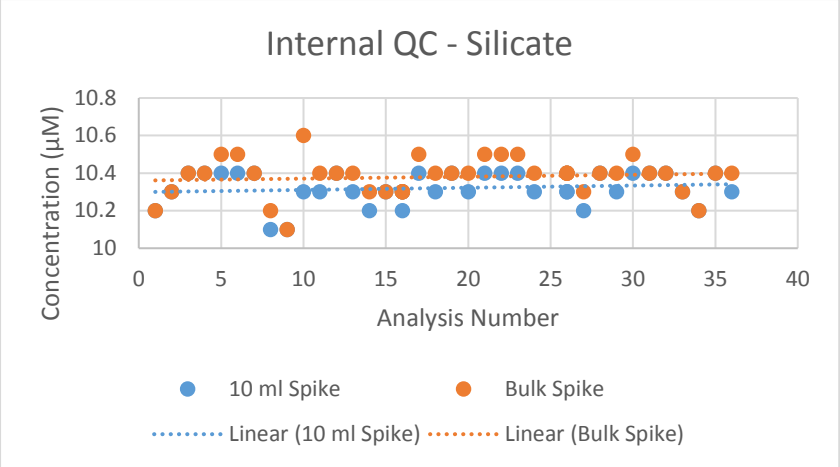
10 ml of silicate 1000 µmol/L = 10 µM

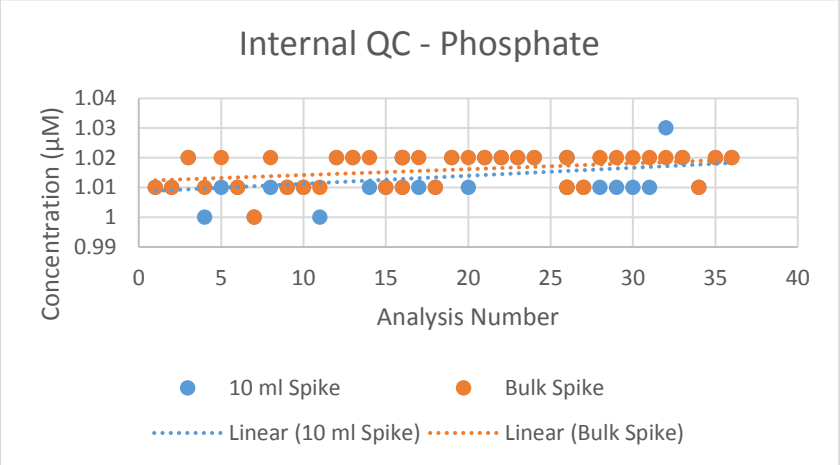
5 ml of nitrite 100 µmol/L = 0.5 µM

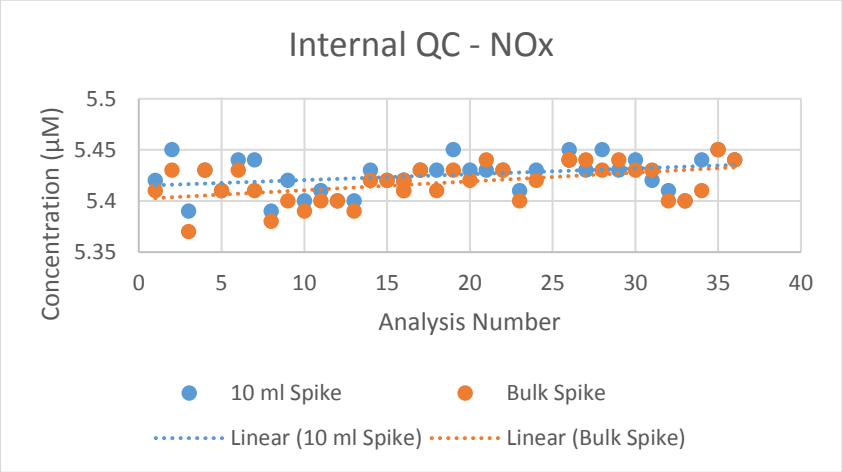
0.1 ml of ammonium 10,000 = 1µM

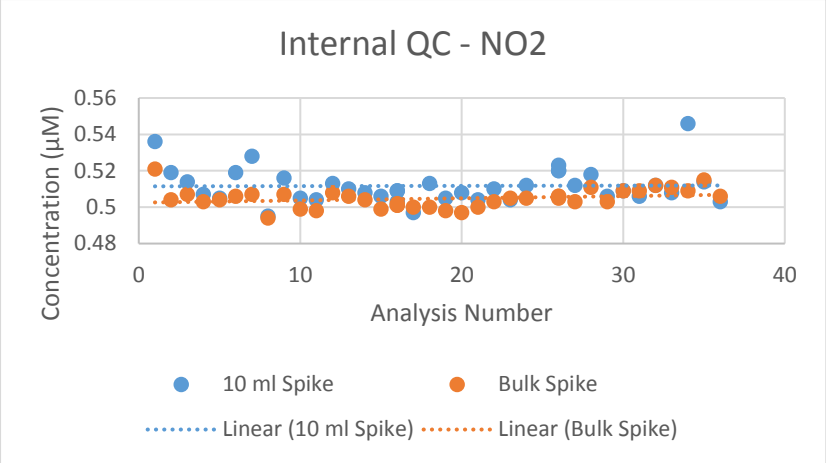
The volumetric flask was then made to volume with the autoclaved LNSW. It was mixed well and poured into an acid-cleaned and dry HDPE square 1 L bottle with the lid screwed shut and parafilm wrapped around the lid and stored at 4^{o}C. The same process was used except the spiked LNSW was then poured from the 1 L HDPE bottle into 100 new 10 ml polypropylene sample tubes with HDPE screw caps which were also wrapped with parafilm and stored at 4^{o}C in the dark.

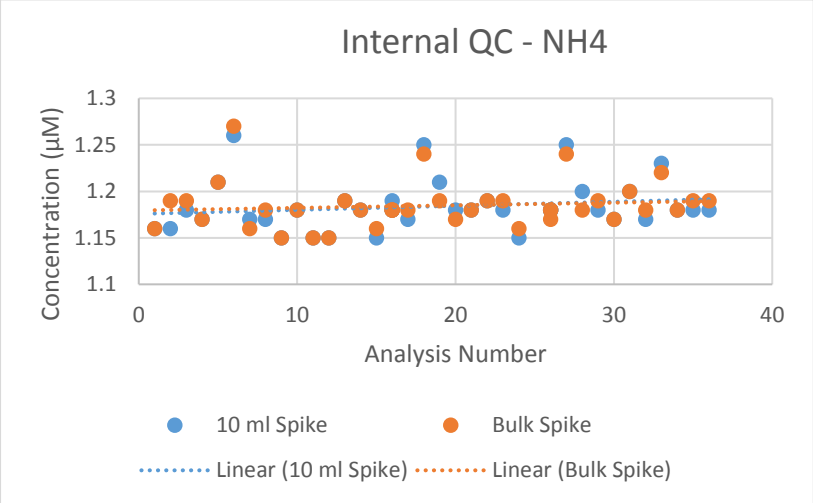
Initial measurements were made on shore on the 7 September 2018, and a comparison was made between the QC's stored in 1 litre container (bulk) and the QC's stored in 10 ml sample tubes. The bulk QC's were decanted into 2 30 ml polypropylene sample tubes, each sample tube was analysed 3 times. The other QC's had 6 10 ml samples tubes analysed, i.e. 6 controls and 6 spiked. The standards were analysed in every analyses during the voyage. A 10 ml sample tube of the control and spike and also the bulk QC's (spike and control) decanted into 10 ml samples tubes were analysed with every analysis run during the voyage. There was found to be no statistical difference between the bulk stored QC's versus the samples stored in 10 ml sample tubes


Internal QC - Silicate
Concentration (µM)
10.8
10.6
10.4
10.2
10
0
5
10
15
20
25
30
35
40
Analysis Number
10 ml Spike
Bulk Spike
Linear (10 ml Spike)
Linear (Bulk Spike)


Internal QC - Phosphate
Concentration (µM)
1.04
1.03
1.02
1.01
1
0.99
0
5
10
15
20
25
30
35
40
Analysis Number
10 ml Spike
Bulk Spike
Linear (10 ml Spike)
Linear (Bulk Spike)


Internal QC - NOx
Concentration (µM)
5.5
5.45
5.4
5.35
0
5
10
15
20
25
30
35
40
Analysis Number
10 ml Spike
Bulk Spike
Linear (10 ml Spike)
Linear (Bulk Spike)





7.7 Analytical Precision

7.7.1 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.

7.7.2 Nutrient Method Detection Limit

For in2018_v04, 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	0.02	0.00	0.00	0.001	0.000
Standard Dev. Max	0.24	0.02	0.01	0.007	0.004
Standard Dev. Mean	**0.05**	**0.01**	**0.00**	**0.001**	**0.001**
Standard Dev. Median	0.04	0.01	0.01	0.003	0.002
Precision of MDL (stdev)	0.06	0.01	0.01	0.003	0.002

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

7.7.3 Reference Material for Nutrients in Seawater

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

RMNS CD	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Published RMNS CD (µmol l^{-1}) w/std deviation	14.26 ± 0.009	0.46 ± 0.001	5.65 ± 0.004	0.018 ± 0.001	- -
Minimum	14.01	0.47	5.50	0.03	1.39
Maximum	14.29	0.48	5.57	0.05	1.91
Mean	14.17	0.47	5.55	0.03	1.63
Median	14.20	0.47	5.56	0.03	1.64
Precision (Stdev)	0.11	0.00	0.03	0.01	0.20

RMNS	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Published RMNS CJ (µmol l^{-1}) w/std deviation	39.42 0.020	1.219 ±0.002	16.62 ±0.009	0.032 ±0.001	- -
Minimum	38.91	1.24	16.44	0.04	0.77
Maximum	39.46	1.26	16.67	0.05	1.03
Mean	39.27	1.25	16.60	0.05	0.90
Median	39.30	1.25	16.61	0.05	0.91
Precision (Stdev)	0.11	0.01	0.05	0.00	0.06

7.8 Sampling Precision

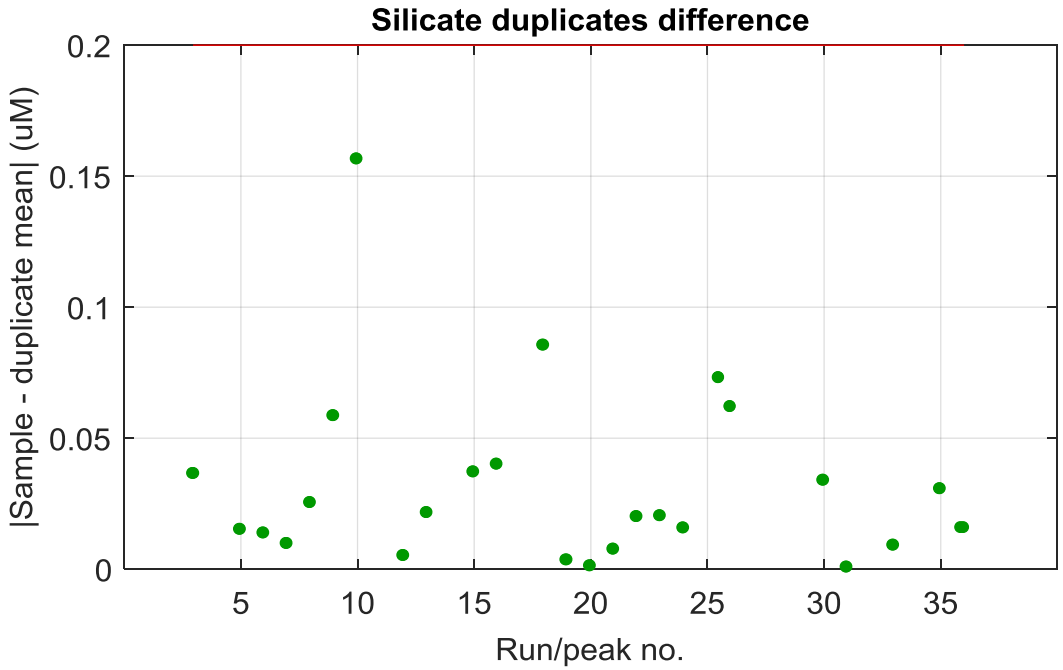
Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate

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

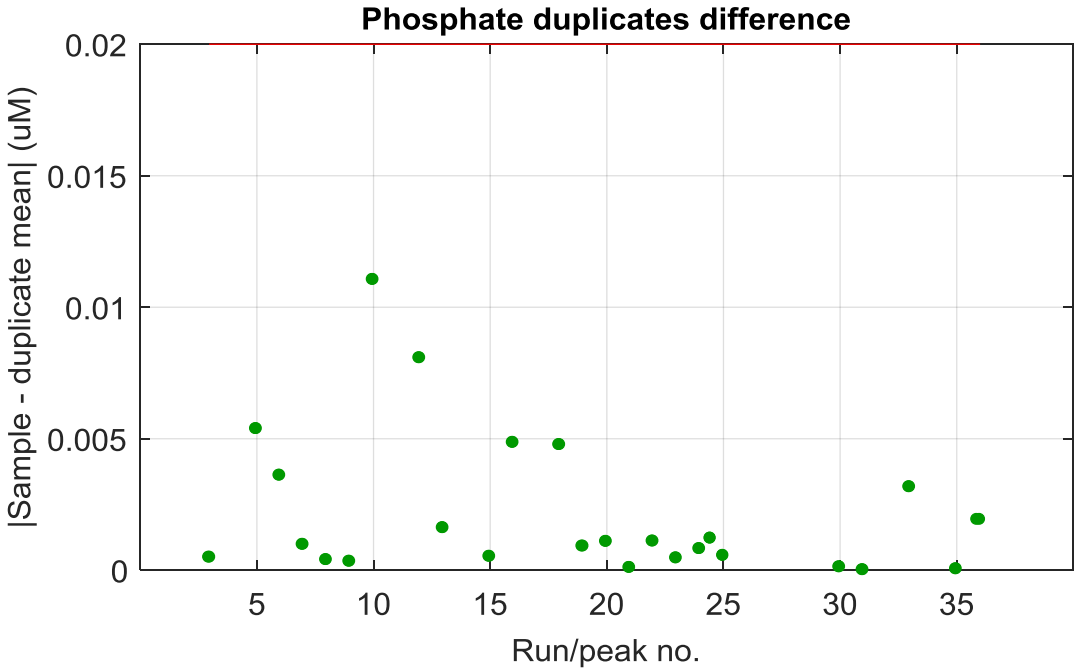
Plots of the difference between the duplicate and their mean for the CTD deployments are below. The red line is the boundary below which sampling precision is deemed good.

For in2018_v04, the sampling precision is good.

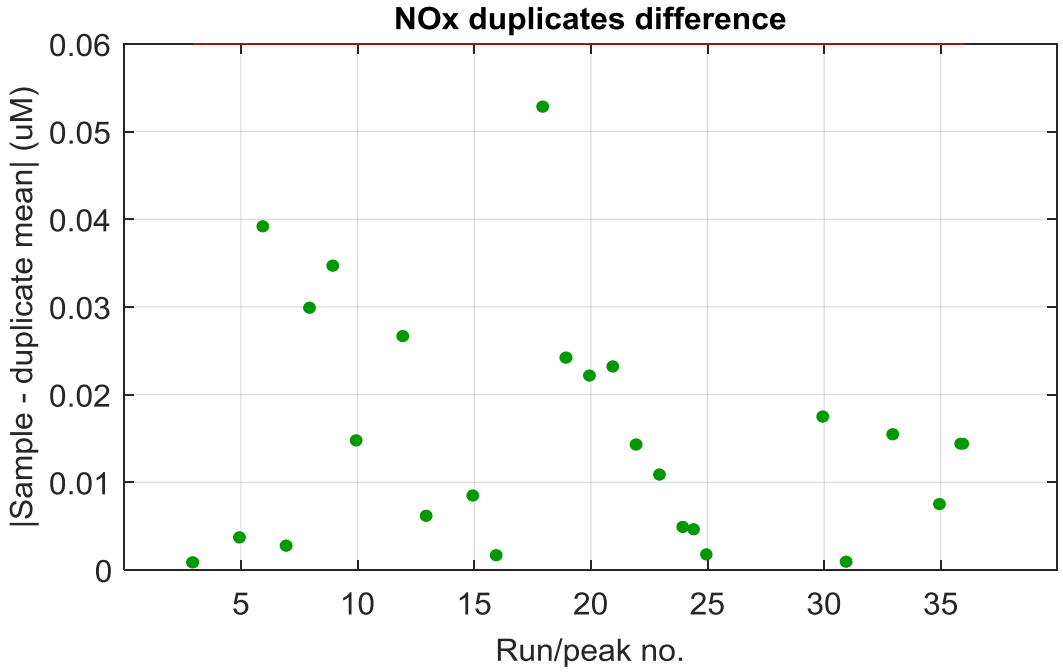
7.8.1 Silicate Duplicates Plot



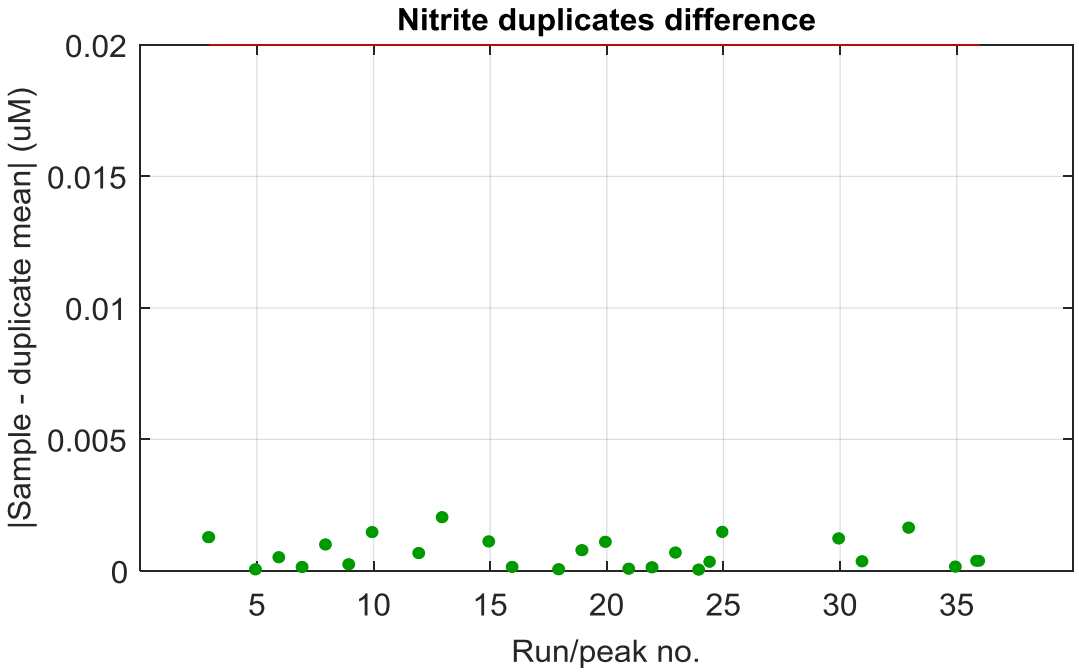
7.8.2 Phosphate Duplicates Plot



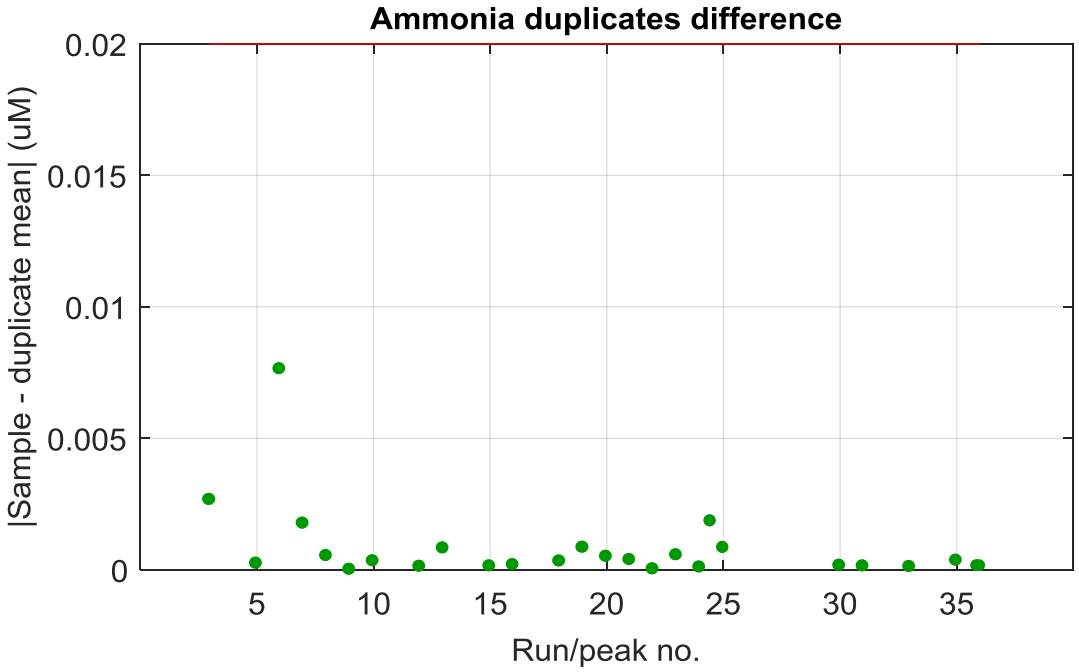
7.8.3 Nitrate + Nitrite (NOx) Duplicates Plot



7.8.4 Nitrite Duplicates Plot

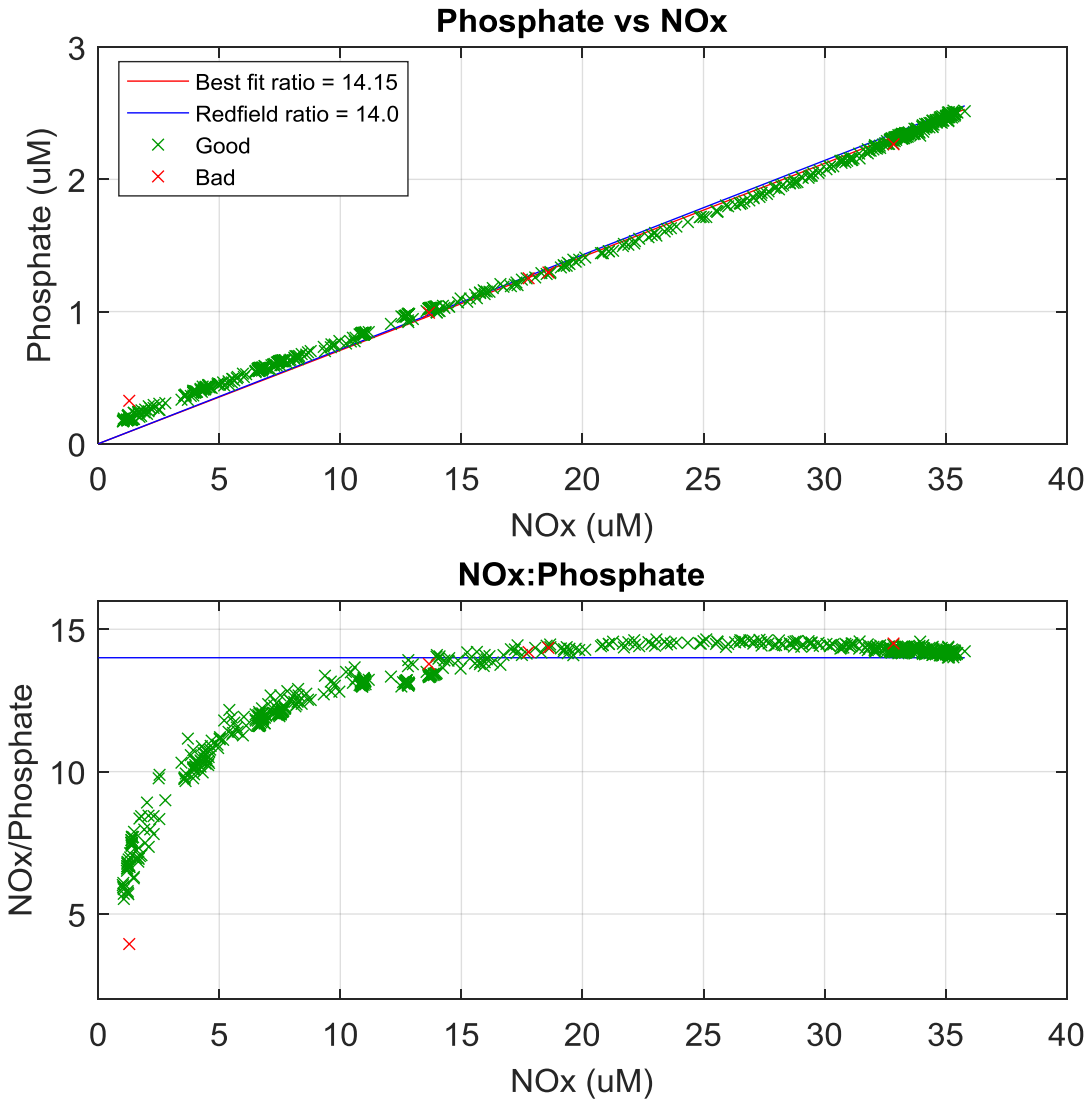


7.8.5 Ammonia Duplicates Plot



7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.15



7.10 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	Analytes	Reason for Flag or Action
1	3	nut002	69	NH4	Outlier in profile unusually high concentration for depth
5	26	nut007	69	PO_4	Outlier in vertical profile
7	15, 22, 26	nut009	133	All	Outlier in vertical profile
9	22	nut012	133	All	Outlier in vertical profile
tmr001	12	nut003	133	All	Misfire of Niskin bottle
tmr004	7	nut006	69	NOx, PO4, SiO4	Outlier in vertical profiles
tmr005	7, 8, 12	nut008	69	NOx, PO4, SiO4	Outliers in vertical profiles
tmr011	8 & 9	nut017	69	NOx, PO4, SiO4	Outliers in vertical profiles
tmr015	8	nut028	69	NOx, PO4, SiO4	Outliers in vertical Profiles

7.11 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 “in2018_v04_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 23°C over the course of the voyage.

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

8.2 Nutrients: Flagged Calibration and Quality Control Data.

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

	Peak	Run	Analysis	Reason for Flag or Action
1	Cal 3 & Cal 5	Nut002	NH4	Suspect, less weighting in calibration curve.
3	Cal 3	Nut005	NH4	2nd point suspect, less weighting in calibration curve.
4	Cal 1	Nut006	NH4	Both points suspect, less weighting in calibration curve.
6	Cal 2	Nut008	NH4	Both points suspect, less weighting in calibration curve.
7	Cal 1 & 4	Nut009	NH4	Both points suspect, less weighting in calibration curve.
TMR006	Cal 1	Nut010	NH4	Both points suspect, less weighting in calibration curve.
8	Cal 5	Nut011	PO4	2nd point suspect, less weighting in calibration curve.
8	Cal 4	Nut011	NH4	Both points suspect, less weighting in calibration curve.
9	Cal 5	Nut012	PO4	1st point Bad (MAD) peak shape, not used in calibration.
9	Cal 5	Nut012	NH4	2nd point suspect, less weighting in calibration curve.
uwy	Cal 5	Nut013	NOx	2nd point suspect, less weighting in calibration curve.
uwy	Cal 2 & 3	Nut013	NH4	<70% of calibration peaks are within calibration limits, less weighting in calibration curve.
10	Cal 2	Nut014	PO4	Both points suspect, less weighting in calibration curve
10	Cal 2	Nut014	NH4	<70% of calibration peaks are within calibration limits, less weighting in calibration curve.
11	Cal 6	Nut015	NOx	1st point suspect less weighting in calibration curve.
11	Cal 2	Nut015	PO4	Both points suspect, less weighting in calibration curve.
PPTMR002	Cal 2	Nut016	PO4	1st point suspect, less weighting in calibration curve.
PPTMR002	Cal 2 & 4	Nut016	NH4	All points suspect, less weighting in calibration curve.

12	Cal 6	Nut017	SiO4	2nd point suspect (MAD) peak shape, less weighting in calibration curve.
12	Cal 4	Nut017	NH4	Both points suspect, less weighting in calibration curve.
13	Cal 5	Nut018	NH4	Both points suspect, less weighting in calibration curve.
14	Cal 3	Nut019	NH4	Both points bad not used in calibration curve
14	Cal 4	Nut019	NH4	2nd point suspect, less weighting in calibration curve.
15	Cal 5	Nut020	PO4	2nd point suspect, less weighting in calibration curve.
15	Cal 4	Nut020	NH4	Both points bad not used in calibration curve.
17	Cal 5	Nut022	PO4	2nd point suspect, less weighting in calibration curve.
19	Cal 6	Nut025	SiO4	1st point suspect, less weighting in calibration curve.
TMR014	Cal 1	Nut027	NH4	Both points suspect, less weighting in calibration curve.
TMR015	Cal 5	Nut028	PO4	2nd point suspect, less weighting in calibration curve.
22	Cal 1 & 3	Nut030	NH4	<70% of calibration peaks are within calibration limits, Cal 1 both points suspect less weighting in calibration curve. Cal 3 bad not used in calibration.
exp	Cal 2	Nut031	PO4	1st point suspect, less weighting in calibration curve.
23	Cal 2	Nut032	NOx	2nd point suspect, less weighting in calibration curve.
23	Cal 1	Nut032	NH4	Both points BAD not used in the calibration curve.
TMR017	Cal 6	Nut033	NOx	2nd point suspect (MAD) peak shape, less weighting in calibration curve.
24	Cal 2	Nut034	NOx	1st point suspect, less weighting in calibration curve.
25	Cal 5 & 6	Nut035	SiO4	All points suspect, less weighting in calibration curve.
exp	Cal 2	Nut036	PO4	Both points suspect, less weighting in calibration curve.
exp	Cal 5 & 6	Nut036	SiO4	All points suspect, less weighting in calibration curve.
uwy	Cal 5 & 6	Nut037	SiO4	All points suspect, less weighting in calibration curve.

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

8.3.1 RMNS Lot CJ Results

Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NOx (NO2 + NO3)
CJ certified	-	*39.424*	*1.219*	*0.032*	*16.621*
1		39.122	1.241	0.053	16.592
2	1	39.239	1.244	0.044	16.584
3		39.303	1.249	0.045	16.436
4	2	39.324	1.237	0.043	16.608
5	3	39.323	1.245	0.046	16.59
6	4	39.401	1.238	0.047	16.604
7	5	39.357	1.24	0.052	16.588
8	6	39.062	1.246	0.045	16.544
9	7	38.913	1.241	0.047	16.557
10		39.317	1.238	0.045	16.544
11	8	39.22	1.238	0.044	16.513
12	9	39.265	1.251	0.044	16.581
13		-			
14	10	39.191	1.248	0.044	16.598
15	11	39.317	1.251	0.045	16.635
16		39.155	1.238	0.045	16.608
17	12	39.297	1.248	0.044	16.64
18	13	39.24	1.242	0.044	16.613
19	14	39.378	1.255	0.045	16.667
20	15	39.21	1.249	0.044	16.594
21	16	39.33	1.25	0.044	16.654
22	17	39.34	1.25	0.045	16.613
23	18	39.229	1.251	0.043	16.554
25	19 & 20	39.163	1.244	0.044	16.649
26		39.197	1.238	0.045	16.669
27		39.182	1.247	0.045	16.637
28		39.354	1.248	0.048	16.642
29	21	39.34	1.248	0.046	16.659
30	22	39.459	1.248	0.047	16.614

31		39.369	1.251	0.042	16.612
32	23	39.39	1.26	0.05	16.549
33		39.248	1.254	0.045	16.555
34	24	39.154	1.247	0.045	16.534
35	25	39.385	1.252	0.045	16.64
36		39.409	1.252	0.043	16.643

The submitted nutrient results do NOT have RMNS corrections applied.

How to use the RMNS for Correction

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

Or for smoothing data

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

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

Measured Detection Limit (µmol L^{-1})						
Analysis Run	CTD #	Silicate	Phosphate	Nitrite	NOx (NO2 + NO3)	Ammonia
1		0.088	0.019	0.002	0.008	0.002
2	1	0.058	0.018	0.002	0.012	0.002
3		0.04	0.002	0.004	0.007	0.002
4	2	0.032	0.014	0.003	0.008	0.003
5	3	0.049	0.018	0.003	0.008	0.002
6	4	0.024	0.003	0.003	0	0.003
7	5	0.042	0.021	0.003	0.004	0.002
8	6	0.065	0.01	0.002	0.006	0.002
9	7	0.106	0.007	0.006	0.002	0.003
10		0.235	0.004	0.004	0.007	0.002
11	8	0.056	0.008	0.004	0.007	0.002
12	9	0.034	0.004	0.002	0.007	0.002
13		0.139	0.002	0.005	0.004	0.002
14	10	0.049	0.008	0.002	0.007	0.002
15	11	0.026	0.006	0.004	0.005	0.002
16		0.065	0.002	0.002	0.005	0.002
17	12	0.078	0.003	0.001	0.011	0.003
18	13	0.02	0.006	0.001	0.008	0.002
19	14	0.073	0.022	0.002	0.004	0.003
20	15	0.022	0.002	0.005	0.006	0.002
21	16	0.026	0.008	0.007	0.007	0.002
22	17	0.153	0.017	0.002	0.005	0.003
23	18	0.088	0.002	0.005	0.006	0.002
24	19 & 20	0.028	0.004	0.003	0.003	0.002
26		0.032	0.003	0.003	0.006	0.001
27		0.031	0.003	0.005	0.008	0.003
28		0.03	0.002	0.003	0.009	0.003
29	21	0.02	0.007	0.002	0.009	0.003

30	22	0.039	0.014	0.003	0.005	0.003
31		0.034	0.006	0.001	0.007	0.003
32	23	0.024	0.006	0.004	0.009	0.003
33		0.057	0.011	0.002	0.004	0.003
34	24	0.167	0.007	0.002	0.003	0.003
35	25	0.05	0.006	0.002	0.003	0.004
36		0.112	0.017	0.002	0.004	0.002
37		0.034	0.003	0.001	0.005	0

8.5 Flag Key for Hydrology Data Set

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

8.6 GO-SHIP Specifications

8.6.1 Salinity

Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosal precision is better than 0.001 PSS-78. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of ± 1°C is very important and should be recorded[2].

8.6.2 Dissolved Oxygen

Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.

8.6.3 SiO2

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

8.6.4 PO4

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

8.6.5 NO3

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

8.6.6 Notes

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

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

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

9 References

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