

RV INVESTIGATOR

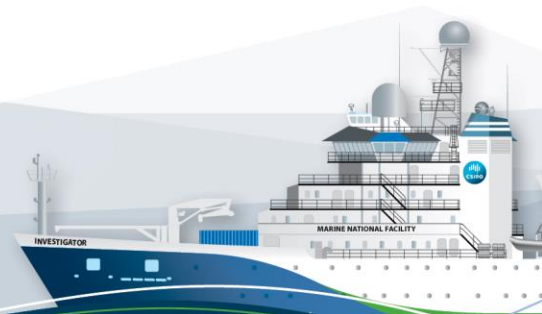
HYDROCHEMISTRY DATA PROCESS REPORT

Voyage: in2018_t01

Chief Scientist: Zanna Chase

Voyage title: Physical, chemical and biogeochemical gradients in the
EAC

Report compiled by: Kendall Sherrin & Mark Rayner



Contents

1	Executive Summary	4
2	Itinerary	5
3	Key personnel list	5
4	Summary.....	6
4.1	Hydrochemistry Samples Analysed.....	6
4.2	Rosette and CTD.....	6
4.3	Data Procedure Summary	7
5	Salinity Data Processing.....	8
5.1	Salinity Parameter Summary	8
5.2	Salinity Method.....	8
5.3	CTD vs Bottle Salinity – Absolute Difference Plot	9
5.4	Missing or Suspect Salinity Data and Actions taken	10
6	Dissolved Oxygen Data Processing	10
6.1	Dissolved Oxygen Parameter Summary.....	10
6.2	Dissolved Oxygen Method	10
6.3	CTD vs Bottle Dissolved Oxygen – Absolute Difference Plot	12
6.4	Dissolved Oxygen – Thiosulphate Normality and Blank over voyage.....	13
6.5	Missing or Suspect Dissolved Oxygen Data and Actions taken.....	14
7	Nutrient Data Processing.....	15
7.1	Nutrient Parameter Summary	15
7.2	Nutrient Methods	15
7.3	Instrument Calibration and Data Parameter Summary	16
7.4	Accuracy - Reference Material for Nutrient in Seawater (RMNS) Plots	17
7.4.1	Silicate RMNS: Measured Concentration over Voyage.....	19
7.4.2	Phosphate RMNS: Measured Concentration over Voyage	20
7.4.3	Nitrate + Nitrite (NO _x) RMNS: Measured Concentration over Voyage	21
7.4.4	Nitrite RMNS: Measured Concentration over Voyage.....	22
7.5	Analytical Precision	23
7.5.1	Nutrient Measurement Uncertainty	23
7.5.2	Method Detection Limit.....	23
7.5.3	Reference Material for Nutrients in Seawater.....	23
7.6	Sampling Precision	24
7.6.1	Silicate Duplicate/Replicates Difference	24
7.6.2	Phosphate Duplicate/Replicates Difference	25

7.6.3	Nitrate + Nitrite (NO _x) Duplicate/Replicates Difference	25
7.6.4	Nitrite Duplicate/Replicates Difference	26
7.6.5	Ammonia Duplicate/Replicates Difference.....	26
7.6.6	Redfield Ratio	27
7.7	Suspect or Bad Nutrient Calibration and Quality Control Data	27
7.8	Investigation of Missing or Flagged Nutrient Data and Actions taken.	28
7.9	Temperature & Humidity Change over Nutrient Analyses	28
8	Appendix.....	29
8.1	Salinity Reference Material.....	29
8.2	HyPro Flag Key for CSV & NetCDF file	29
8.3	GO-SHIP Specifications.....	30
8.3.1	Salinity.....	30
8.3.2	Dissolved Oxygen	30
8.3.3	Silicate (SiO ₂)	30
8.3.4	Phosphate (PO ₄).....	30
8.3.5	Nitrate (NO ₃)	30
8.3.6	Notes	30
8.4	RMNS Values for each CTD Deployment	31
9	References	32

1 Executive Summary

The main objective for this voyage was to characterize the contrasting physical, biological and chemical gradients associated with warm-core and cold-core EAC eddies. The voyage was also largely education, forming part of an assessment for IMAS university courses.

Nutrient data produced from the voyage was of very high quality, the data will be highly beneficial for biogeochemical study due to the high resolution of data points either side of the DCM. All 5 dissolved inorganic nutrients were analysed, Nitrate, Nitrite, Phosphate, Silicate and Ammonia. Ammonia data was very good, however extremely low level concentrations did have high than usual variability which may have been attributed to inexperienced sampling or unusual contamination.

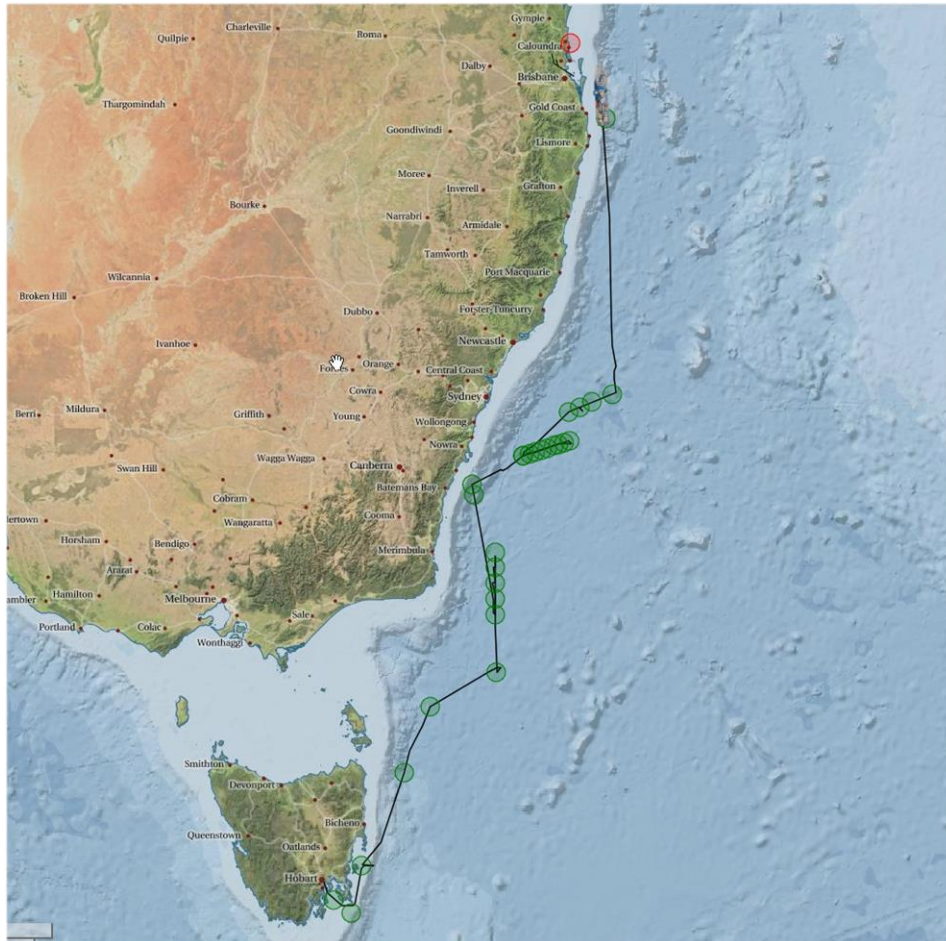
Dissolved Oxygen analysis was completed without any major issues. It was prudent to ensure that the samplers were collecting the sample correctly, however this proved difficult due to the educational benefit of rotating through different students for each deployment.

Salinity analysis was adequate, however the results showed a greater variability than expected, meaning many of the CTD casts had trouble with calibration. This could have been due to a couple of reasons, the simplest would be the lack of experience in sampling for the students and a lack of direction shown on correct practice. This could have also been an effect of a faulty salinometer, where the introduced variability degraded results by a considerable degree.

All finalized data can be obtained from the CSIRO data centre Contact:
DataLibrariansOAMNF@csiro.au.

2 Itinerary

Departed Hobart 5th of April, arrived Brisbane 14th of April.



3 Key personnel list

Name	Role	Organisation
Zanna Chase	Chief Scientist	UTAS/IMAS
Don McKenzie	Voyage Manager	CSIRO
Kendall Sherrin	Hydrochemist	CSIRO
Mark Rayner	Hydrochemist	CSIRO

4 Summary

4.1 Hydrochemistry Samples Analysed

Analysis	Number of Samples
Salinity (Guildline Salinometer)	128 CTD
Dissolved Oxygen (automated titration)	131 CTD
Nutrients (AA3)	533 CTD
	115 UWY

Note:

- Conductivity Temperature Density (CTD); samples collected from NISKIN bottles on the CTD rosette.
- Underway (UWY); samples collected from clean instrument seawater supply in the Underway lab.

4.2 Rosette and CTD

- 21 CTD stations were sampled with a 36 bottle rosette (12 L).
- See in2018_v01_HYD_VoyageReport.pdf (voyage report) for more details on sample collection.

4.3 Data Procedure Summary

The procedural workflow for data processing is outlined below.

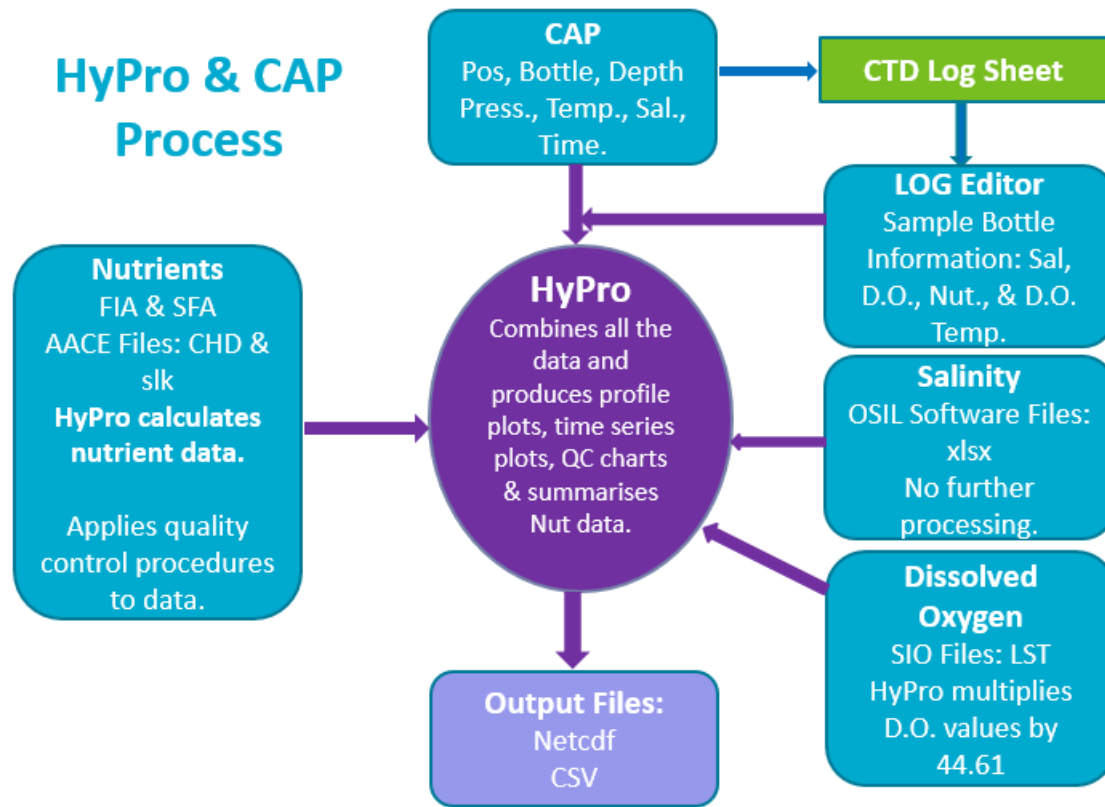


Figure 1: The processing steps for hydrology data following sample assay.

5 Salinity Data Processing

5.1 Salinity Parameter Summary

Details	
HyPro Version	5.3
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72151 and SN 71613
Software	OSIL Data Logger ver 1.2
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 practical salinity units
Analyst(s)	Mark Rayner, Kendall Sherrin
Lab Temperature (±0.5°C)	21.5 -23.5°C during analysis.
Bath Temperature	24.01°C
Reference Material	Osil IAPSO - Batch P161
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 held in Salt Room for 6 -12 hrs to reach 22°C before analysis
Comments	71613 was used for all samples

5.2 Salinity Method

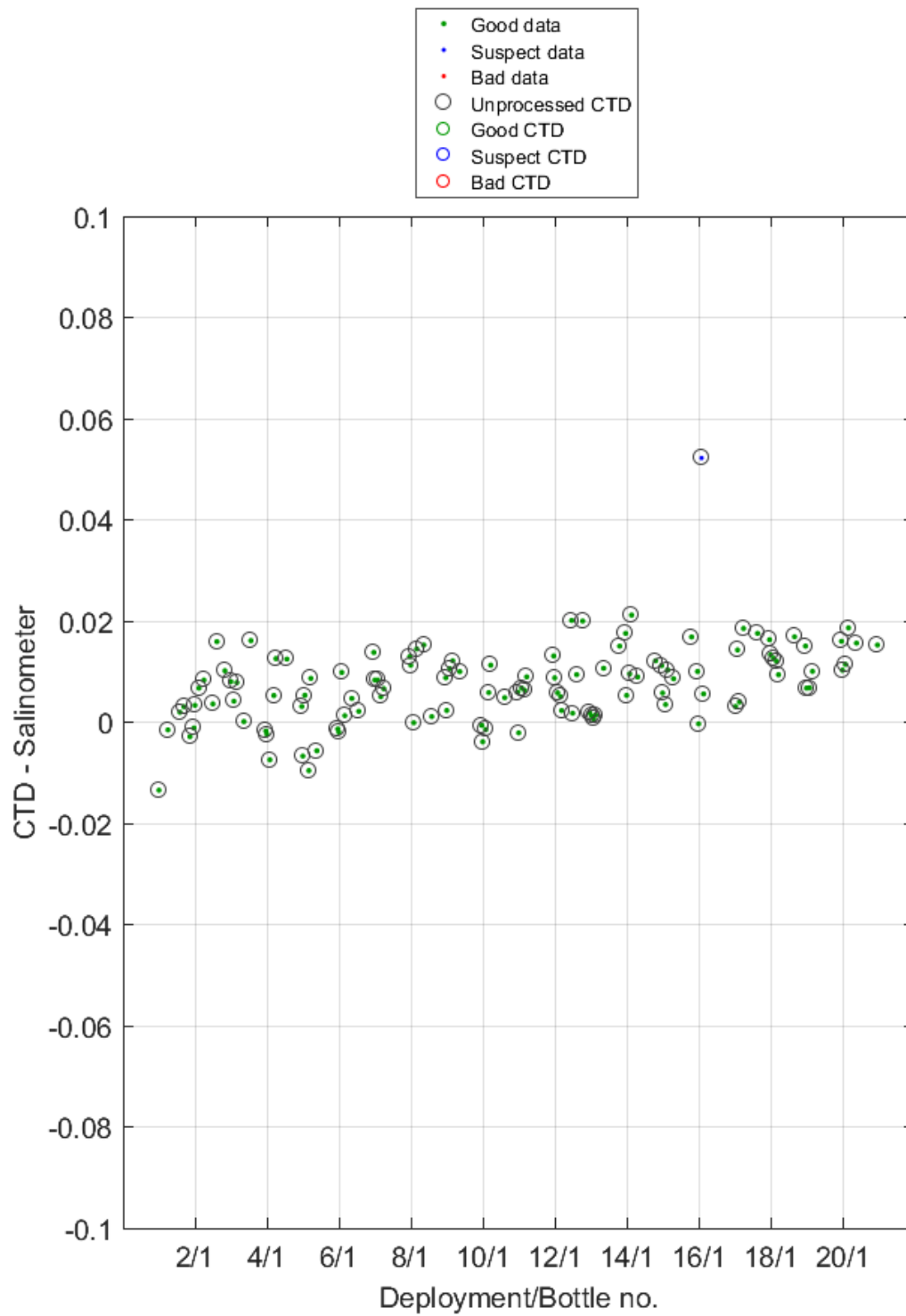
The method uses a high precision laboratory salinometer (Guildline Autosal 8400B) which is operated in accordance with its technical manual.

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 32.4356×10^{-3} .

The Autosal is calibrated with standard seawater (OSIL, IAPSO) of known conductivity ratio against which the samples are measured. The Autosal is calibrated before each batch run of samples.

Salinity samples are collected into 200ml OSIL bottles –from the bottom via a PTFE straw filled till overflowing. The sample is decanted to allow a headspace of approximately 25cm³. A plastic insert is fitted, the bottle inverted and rinsed then capped and stored cap-down until measured. To measure, the salinometer 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 conductivity ratio data is captured by the Osil data logger v1.2 program which then calculates the practical salinity.

5.3 CTD vs Bottle Salinity – Absolute Difference Plot



5.4 Missing or Suspect Salinity Data and Actions taken

Data is flagged based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots.

CTD	RP	Bottle	Run	Flag	Reason for Flag or Action
-	-	-	-	-	-

6 Dissolved Oxygen Data Processing

6.1 Dissolved Oxygen Parameter Summary

Details	
HyPro Version	5.3
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Kendall Sherrin & Mark Rayner
Lab Temperature ($\pm 1^{\circ}\text{C}$)	Variable, 20.0 - 23.0°C
Sample Container type	Pre-numbered glass 140 mL glass vial w/stopper, sorted into 18 per box and boxes labelled A to S.
Sample Storage	Samples were stored within Hydrochemistry lab under the forward starboard side bench until analysis. All samples were analysed within ~48 hrs
Comments	8 – 34 samples were collected from each deployment

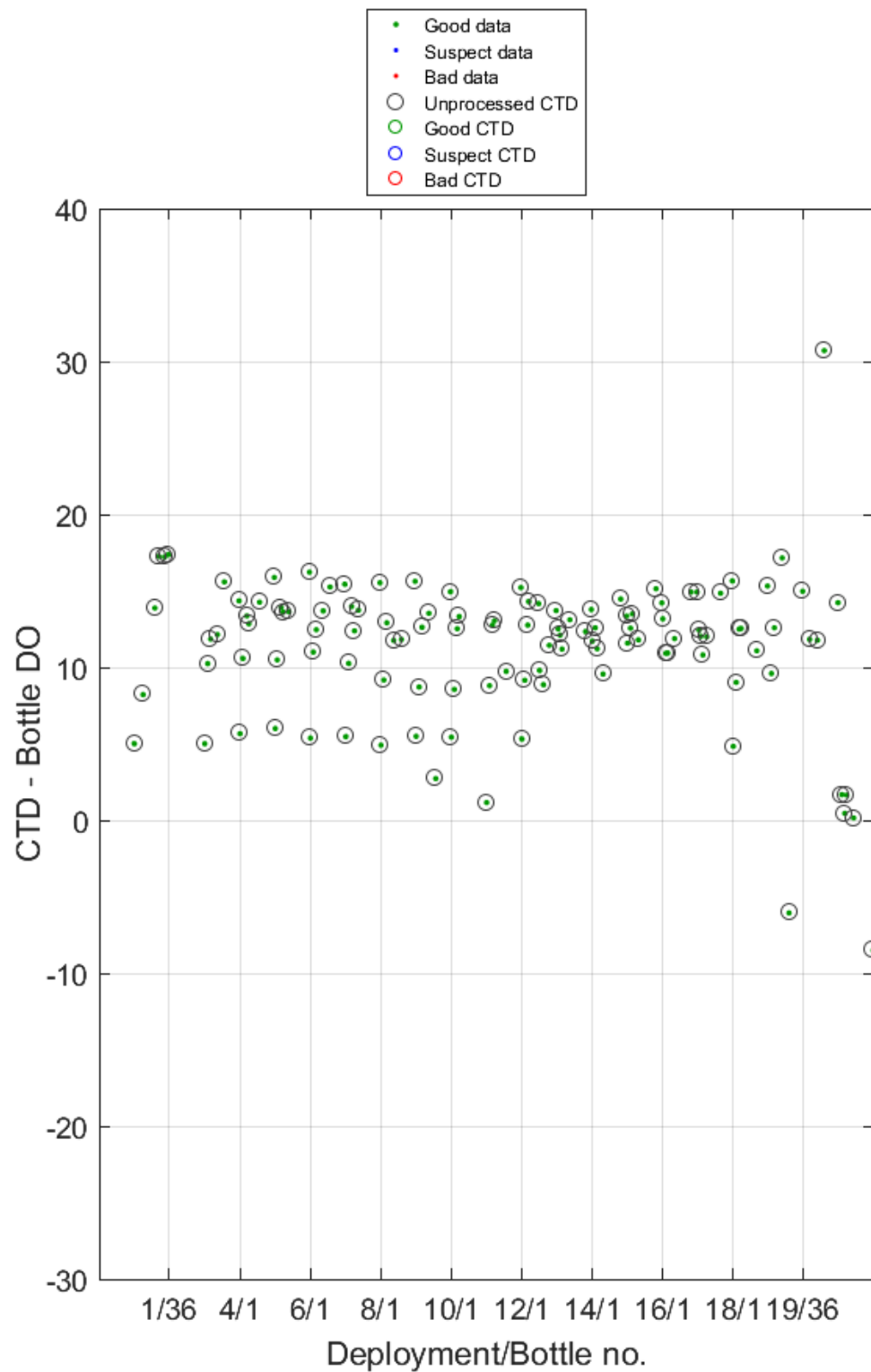
6.2 Dissolved Oxygen Method

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

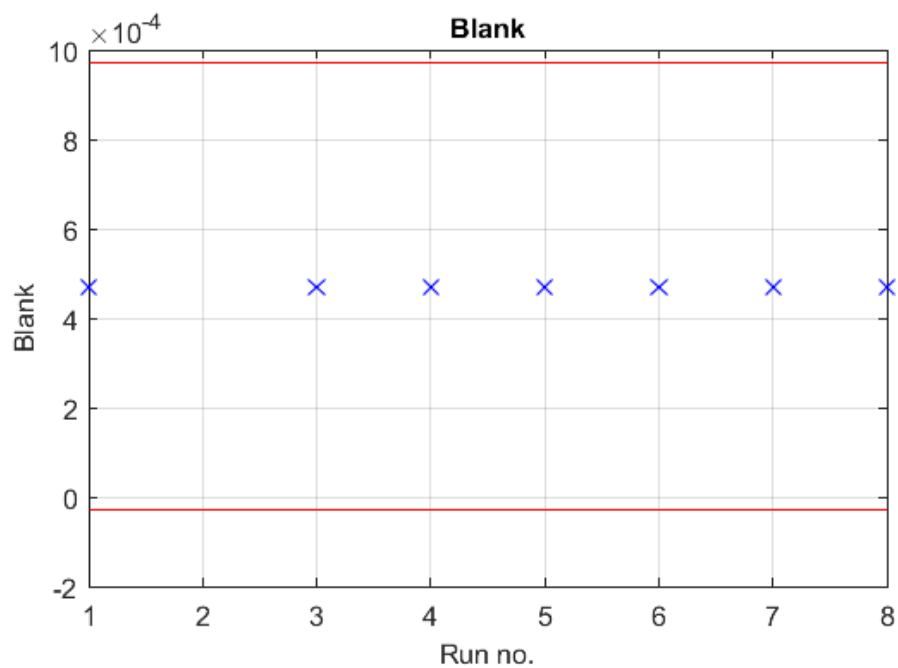
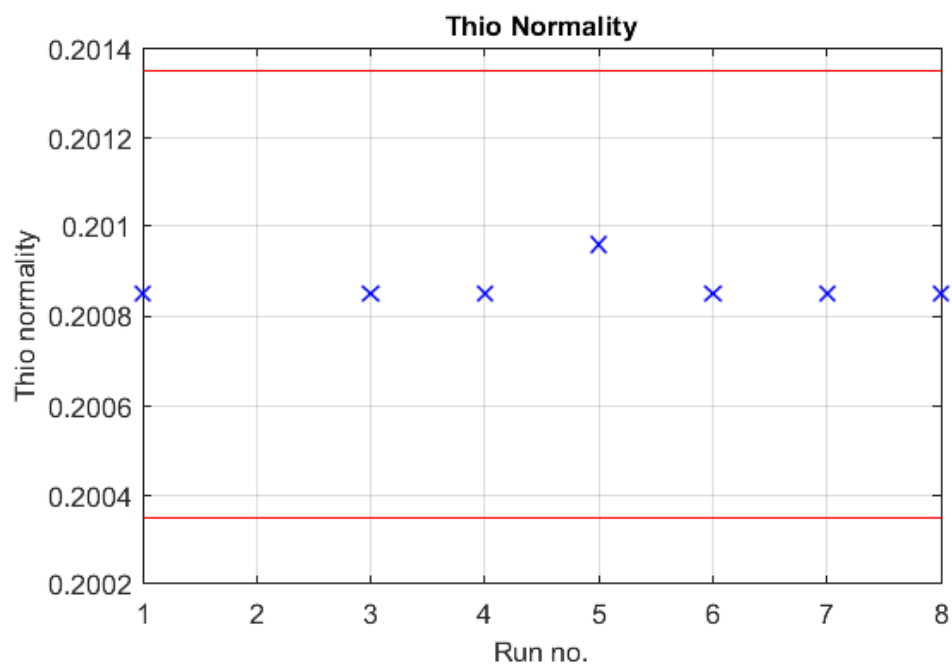
Manganese chloride followed by alkaline iodide, is added to the sample, and the precipitated manganous hydroxide is distributed evenly throughout the bottle by shaking. At this stage, the dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV). Just before titration, the sample is acidified, converting the Mn (IV) back to the divalent state liberating an amount of Iodine equivalent to the original dissolved oxygen content of the water. The Iodine is auto-titrated with a standardised thiosulphate solution using a Met Rohm 665 Dosimat 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.

The thiosulphate solution is standardised by titrating a 10ml aliquot of potassium iodate primary standard. The blank correction is determined from the difference between two consecutive titres for 1ml aliquots of the same potassium iodate solution.

6.3 CTD vs Bottle Dissolved Oxygen – Absolute Difference Plot



6.4 Dissolved Oxygen – Thiosulphate Normality and Blank over voyage



6.5 Missing or Suspect Dissolved Oxygen Data and Actions taken

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

CTD	RP	Run	Flag	Reason for Flag or Action
10	23	Oxy007	-	No result, sample compromised.
10	36	Oxy007	-	Bad result, titrator failure.

7 Nutrient Data Processing

7.1 Nutrient Parameter Summary

Details					
HyPro Version	5.3				
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients analysed	<input checked="" type="checkbox"/> Silicate	<input checked="" type="checkbox"/> Phosphate	<input checked="" type="checkbox"/> Nitrate + Nitrite	<input checked="" type="checkbox"/> Nitrite	<input checked="" type="checkbox"/> Ammonia
Concentration range	112 $\mu\text{mol l}^{-1}$	3 $\mu\text{mol l}^{-1}$	36.4 $\mu\text{mol l}^{-1}$	1.4 $\mu\text{mol l}^{-1}$	2.0 $\mu\text{mol l}^{-1}$
Method Detection Limit* (MDL)	0.2 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$
Matrix Corrections	N	N	N	N	N
Analyst(s)	Kendall Sherrin & Mark Rayner				
Lab Temperature	Reasonably stable, 19.0 – 22.0°C				
Reference Material	RMNS – CJ				
Sampling Container type	50 ml HDPE screw cap lids for CTD samples 10 ml polypropylene sample tubes for underway samples				
Sample Storage	< 2 hrs at room temperature or \leq 12 hrs @ 4°C (Underway samples)				
Pre-processing of Samples	None				
Comments					

7.2 Nutrient Methods

CSIRO Oceans and Atmosphere Hydrochemistry nutrient analysis is performed with a segmented flow auto-analyser – Seal AA3 HR – to measure silicate, phosphate, nitrite, nitrate plus nitrite (NO_x), and ammonium

Silicate: 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: 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: colourimetric analysis, Cu-Cd reduction – Naphthylenediamine photometric 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: colourimetric analysis, Naphthylenediamine photometric method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium: fluorescence analysis, 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.

Detailed SOPs can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group on request.

7.3 Instrument Calibration and Data Parameter Summary

All instrument parameters and reagent batch compositions are logged for each analysis run. This information is available on request.

The raw data from each analysis run on the Seal AA3HR is imported into HyPro for peak height determination, constructing the calibration curve, deriving the sample results and applying drift and carry-over corrections.

Following standard procedures, the operator may choose to not include bad calibration points (see section 7.7 for edited data). Below are the corrections and settings that HyPro applied to the raw data.

All runs have a corresponding "AA3_Run_Analysis_sheet" to record the following: sample details, LNSW batch, cadmium column, working standards, reagent information, instrumentation settings, and pump tube hours. The nut### file numbers that correspond to each analytical run and the CTD samples analysed are in table 8.4. The nut### file numbers for underway and experimental samples are available upon request. Calibration summary data for each analysis run are in the voyage documentation and available upon request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Data Reported as	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
Forced through zero?	N	N	N	N	N
# of points in Calibration	7	6	7	6	6

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Matrix Correction	N	N	N	N	N
Blank Correction	N	N	N	N	N
Carryover Correction (HyPro)	Y	Y	Y	Y	Y
Baseline Correction (HyPro)	Y	Y	Y	Y	Y
Drift Correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS	N	N	N	N	N
Window Defined*	HyPro	HyPro	HyPro	HyPro	HyPro
Medium of Standards	LNSW (bulk on deck of Investigator) collected on 28/9/2016. Sub-lot passed through a 10 micron filter and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω MQ				
Proportion of samples in duplicate?	Samples were collected in duplicate at the greatest depth either RP01 or RP02 on the CTD rosette.				
Comments	Calibration and QC data that was edited or removed is located in the table within section 7.7. The reported data is not corrected to the RMNS. Per deployment RMNS data can be found in appendix 8.4.				

7.4 Accuracy - Reference Material for Nutrient in Seawater (RMNS) Plots

Japanese KANSO certified reference materials (RMNS) for silicate, phosphate, nitrate and nitrite in seawater was used in each nutrient analysis run to determine the accuracy. For each analysis run, a new RMNS bottle was opened and used. The RMNS was assayed in quadruplicate after the calibration standards.

RMNS lot CJ was used. Their stated values in $\mu\text{mol/kg}$ are converted to $\mu\text{mol l}^{-1}$ at 21°C and are listed below. RMNS do not have certified ammonium values.

RMNS CJ Concentrations				
NO_3	NO_x	NO_2	PO_4	SiO_4
16.5 ± 0.205	16.621 ± 0.212	0.032 ± 0.007	1.219 ± 0.020	39.424 ± 0.410

Table 1: RMNS CJ concentrations with expanded uncertainty ($\mu\text{mol/L}$) at 21°C

The submitted nutrient results do NOT have RMNS corrections applied.

RMNS Correction

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

Or for smoothing data

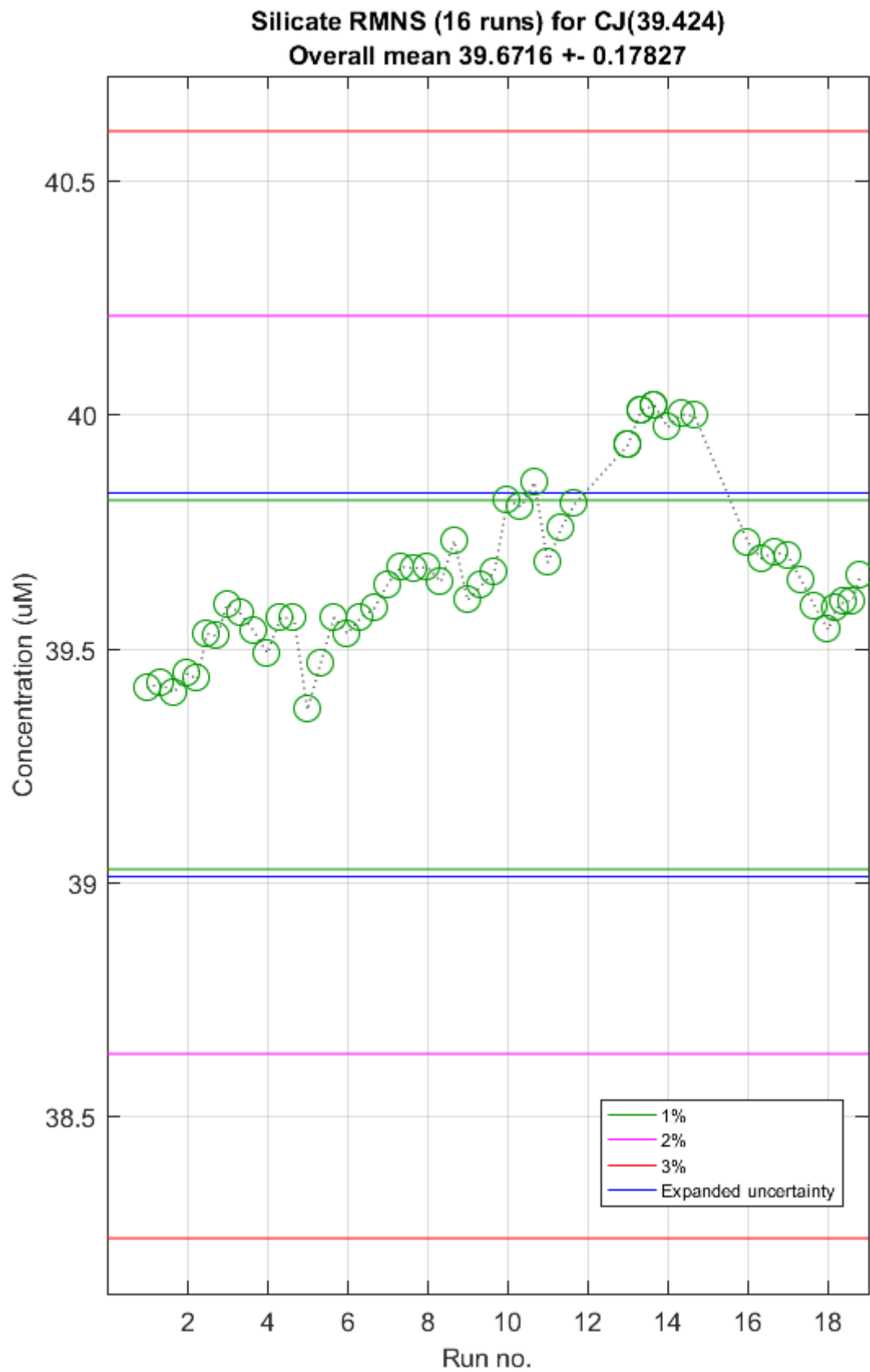
Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

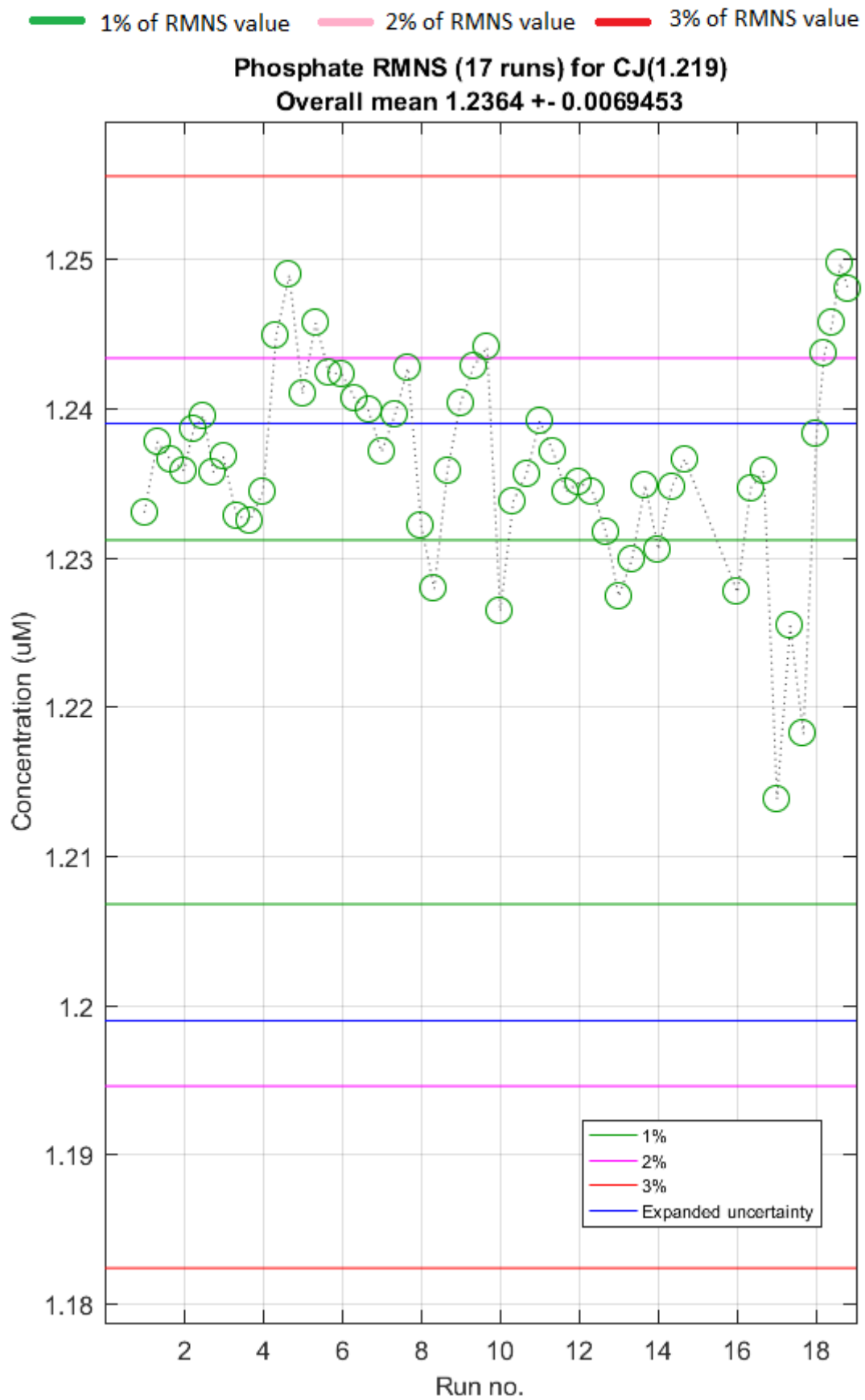
The following plots show RMNS values within 1% (green lines), 2% (pink lines) and 3% (red lines) of the published RMNS value except for nitrite. The nitrite limit is set to $\pm 0.020 \mu\text{M}$ (MDL) as 1% is below the method MDL. The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.3, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy. The assayed RMNS values per CTD deployment are reported in the table in appendix 8.4.

7.4.1 Silicate RMNS: Measured Concentration over Voyage

1% of RMNS value 2% of RMNS value 3% of RMNS value

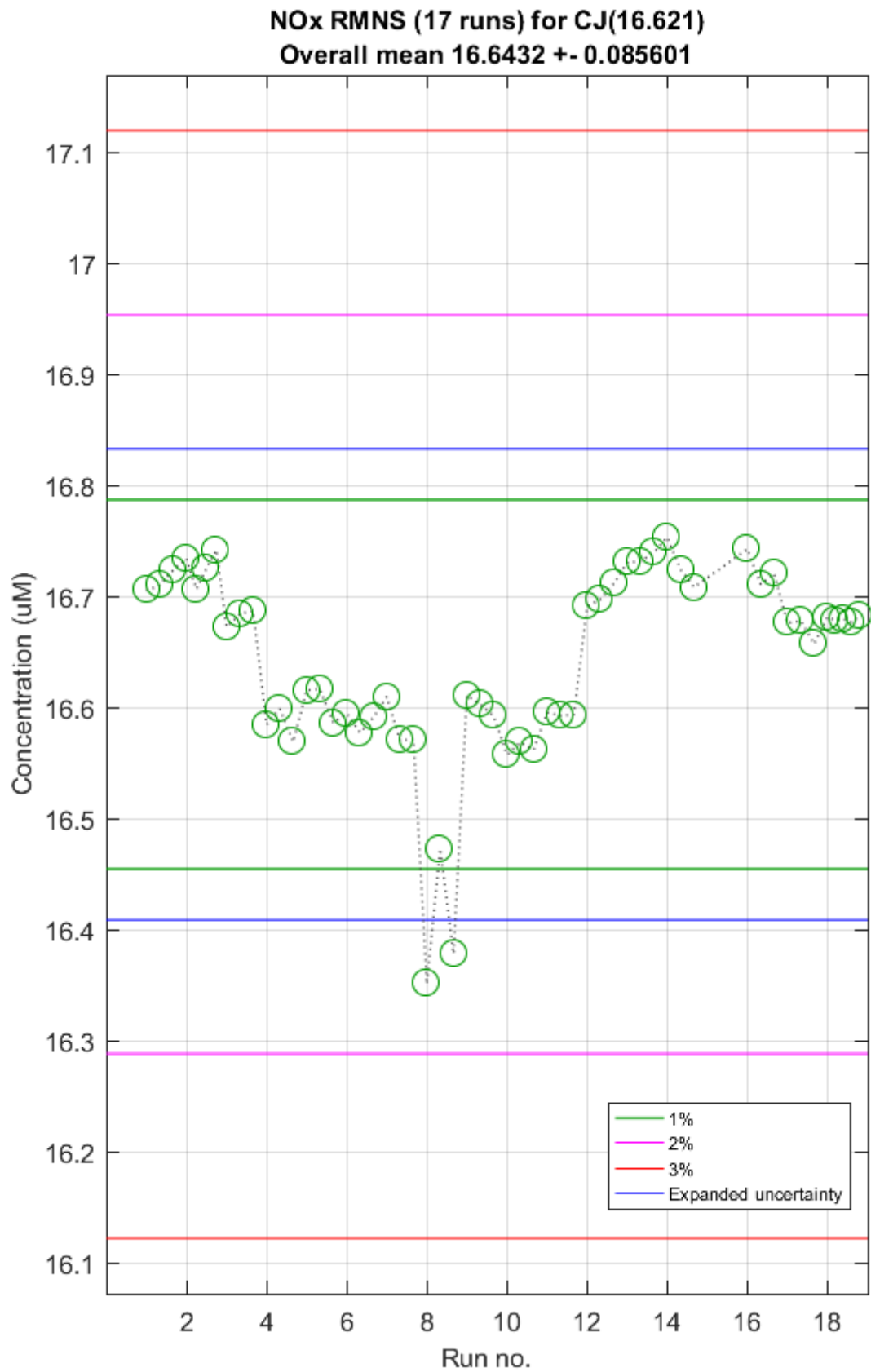


7.4.2 Phosphate RMNS: Measured Concentration over Voyage



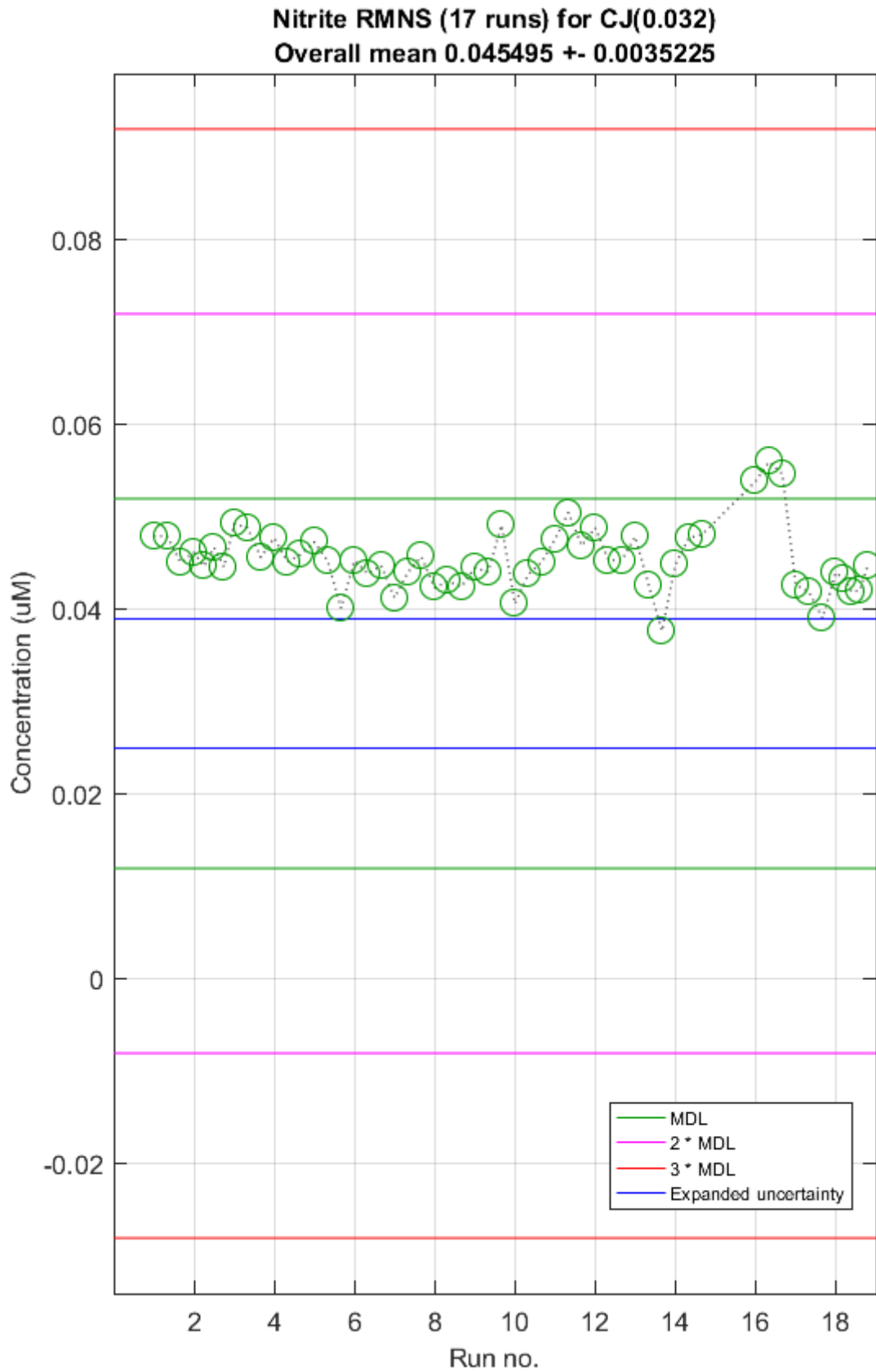
7.4.3 Nitrate + Nitrite (NOx) RMNS: Measured Concentration over Voyage

1% of RMNS value 2% of RMNS value 3% of RMNS value



7.4.4 Nitrite RMNS: Measured Concentration over Voyage

1% of RMNS value 2% of RMNS value 3% of RMNS value



7.5 Analytical Precision

7.5.1 Nutrient Measurement Uncertainty

The CSIRO Hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on 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	Nitrite	Ammonia
± 0.017	± 0.024	± 0.019	± 0.137	$\pm 0.296^{\text{‡}}$

*The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

‡The ammonia MU precision component does not include data on the RMNS.

7.5.2 Method Detection Limit

Method detection limits (MDL) achieved during the voyage were much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. RMNS and MDL precision data listed below. Results are $\mu\text{mol l}^{-1}$.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Min	-0.2	0.00	0.01	-0.015	-0.07
Max	0.2	0.05	0.05	0.016	0.16
Mean	0.009	0.019	0.03	0.006	0.013
Median	0.00	0.02	0.03	0.007	0.00
Precision of MDL (stdev)	0.02	0.004	0.004	0.003	0.002

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

7.5.3 Reference Material for Nutrients in Seawater

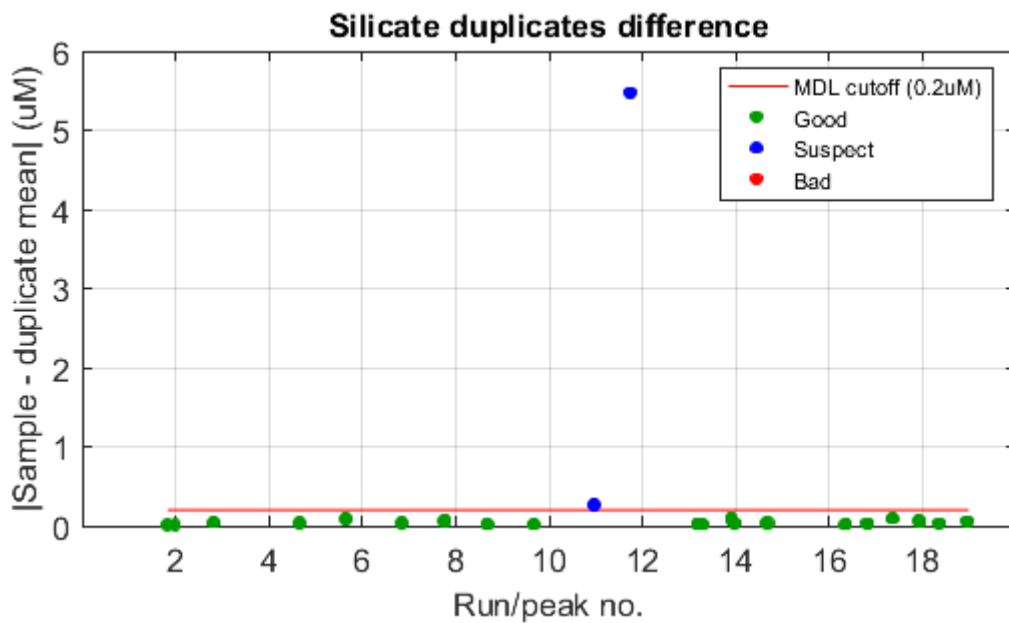
Precision values are calculated from intra-analysis measurements, multiple measurements are taken at a time, typically 3-4.

RMNS	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Published RMNS CJ ($\mu\text{mol l}^{-1}$)	39.424	1.219	16.621	0.032	-
w/uncertainty	± 0.41	± 0.02	± 0.21	± 0.007	-
Minimum	39.4	1.21	16.35	0.038	-
Maximum	40.0	1.25	16.75	0.056	-
Mean	39.66	1.23	16.64	0.045	-
Median	39.60	1.23	16.68	0.045	-
Precision of RMNS (stdev)	0.18	0.008	0.08	0.004	-

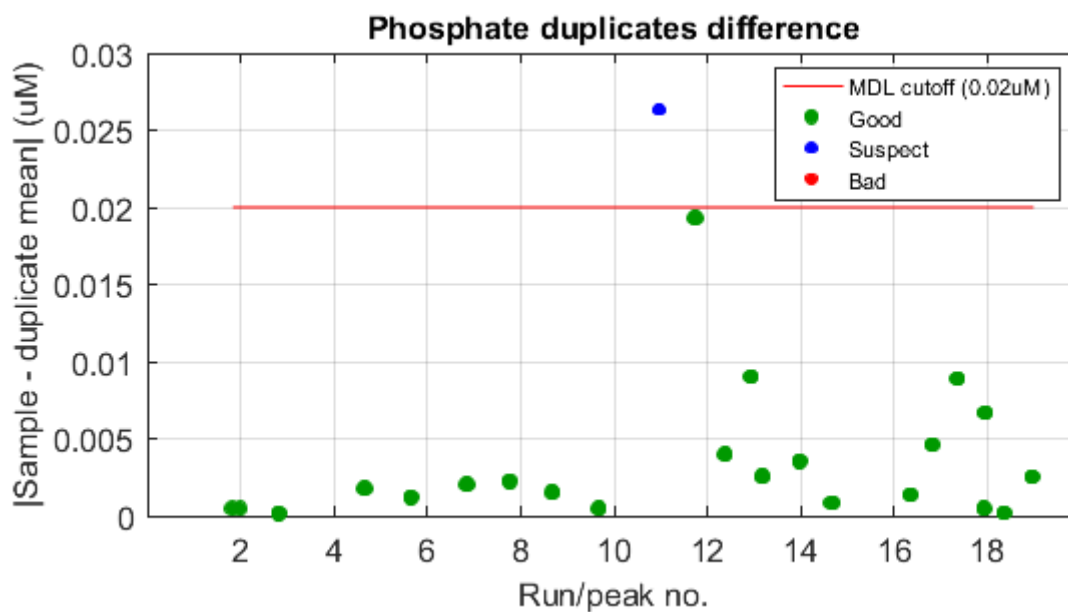
7.6 Sampling Precision

Duplicate samples were collected during CTD deployments from the NISKIN bottle in rosette position 01 or 02 to measure the sample precision. The multiple measurements are reported in the data as an average, when all measurements are flagged GOOD. The sampling precision is deemed good if the difference between the concentrations is below the MDL for silicate, phosphate and nitrite and within 0.06 μM for nitrate.

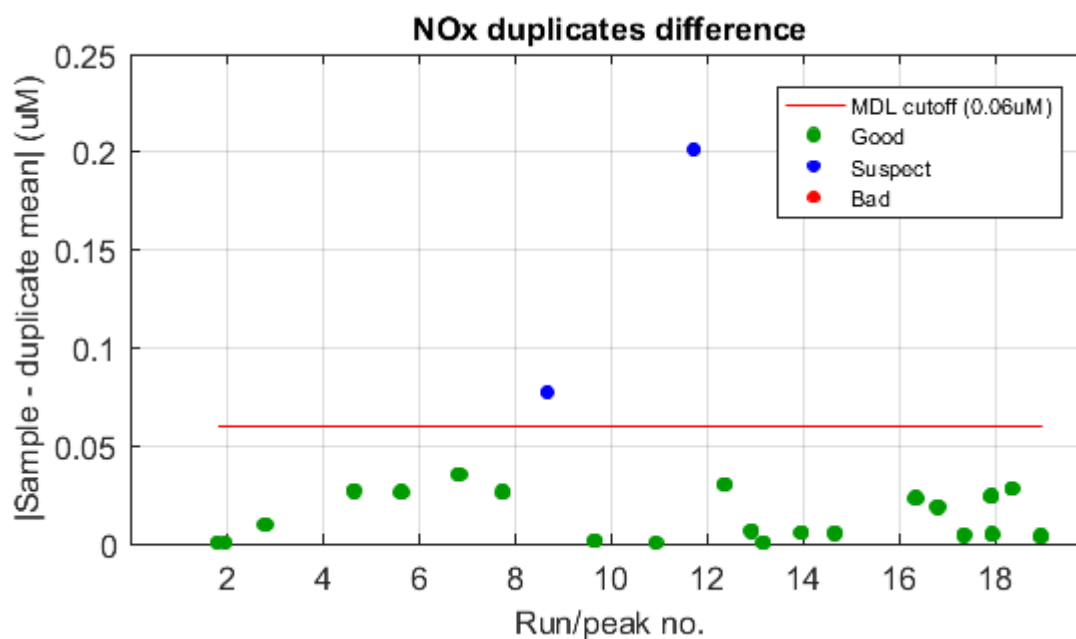
7.6.1 Silicate Duplicate/Replicates Difference



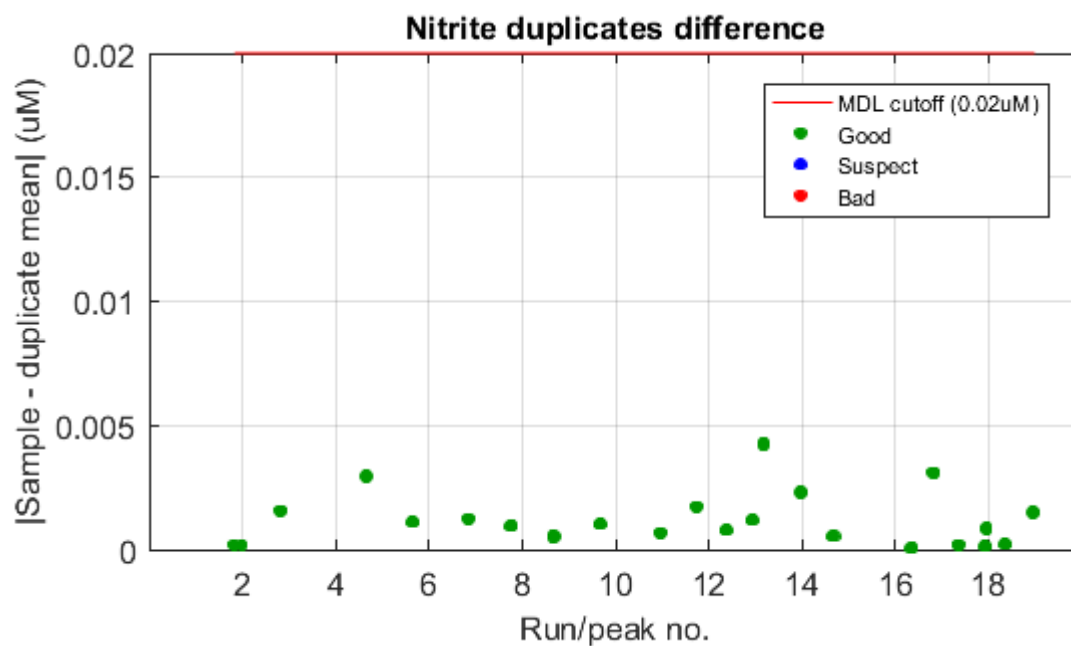
7.6.2 Phosphate Duplicate/Replicates Difference



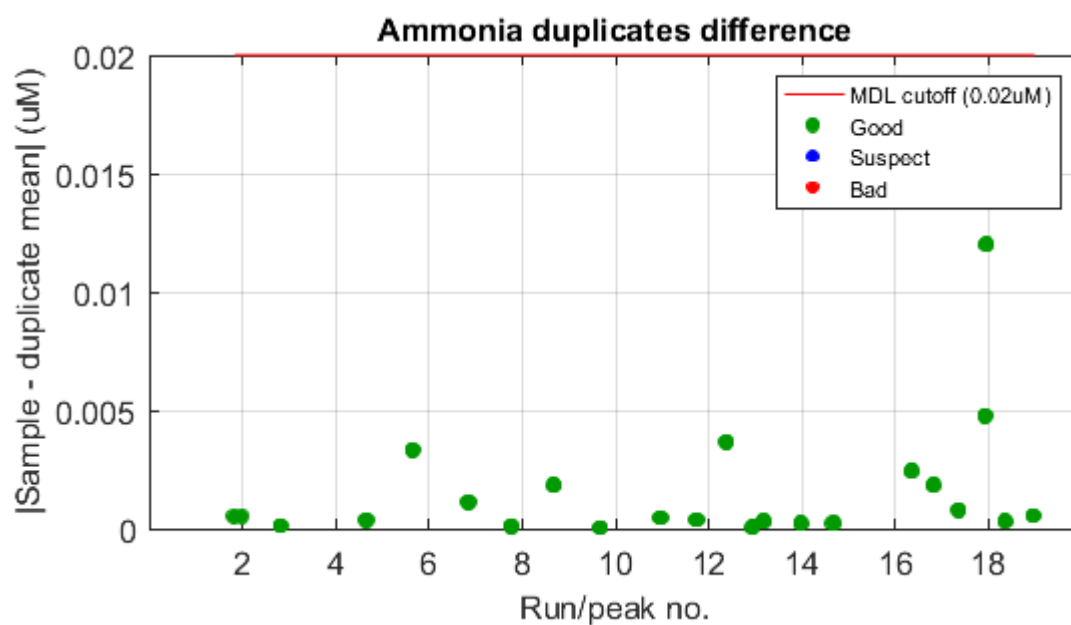
7.6.3 Nitrate + Nitrite (NOx) Duplicate/Replicates Difference



7.6.4 Nitrite Duplicate/Replicates Difference

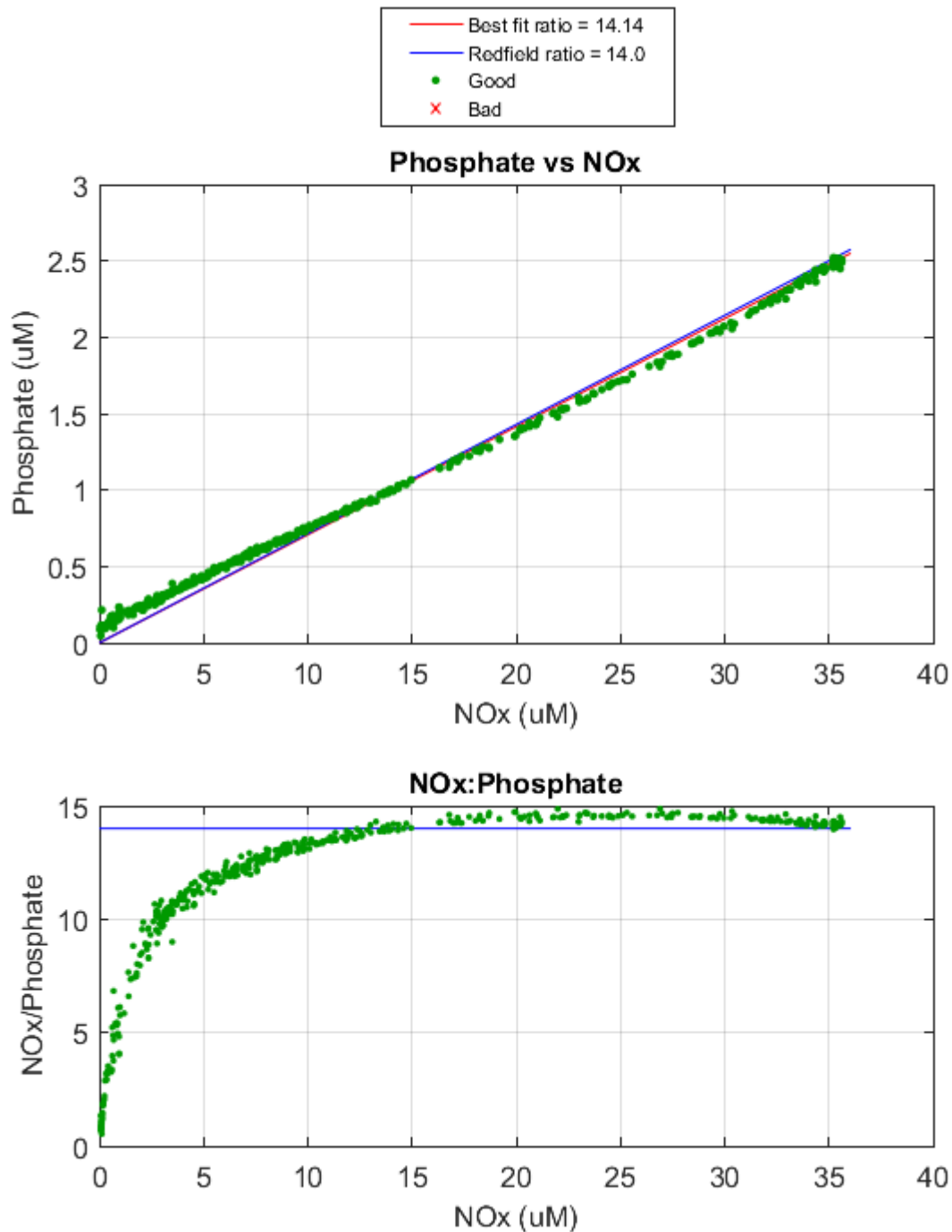


7.6.5 Ammonia Duplicate/Replicates Difference



7.6.6 Redfield Ratio

Plots consists of phosphate versus NOx, best fit ratio = 14.14.



7.7 Suspect or Bad Nutrient Calibration and Quality Control Data

The table below identifies all flagged data by HyPro. The calibration curve is fitted to the standards by performing several passes over each standard point and weighting its contribution to the curve depending on the magnitude of the difference between its measured and calculated value. The larger the difference, the less weighting is given to the

standard's contribution towards the curve construction. 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).
- 0.02uM for phosphate, nitrite and ammonium.

CTD	Peak	Run	Analysis	Reason for Flag or Action
1	Cal 4	Nut001	NH4	Both points BAD as greater than calibration error, not used in calibration.

7.8 Investigation of Missing or Flagged Nutrient Data and Actions taken.

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 within the .csv files. Suspect data (Flag 69) is exported in the .csv file. Refer to Appendix 8.2 for flag explanations.

CTD	RP	Run	Analysis	Flag	Reason for Flag or Action
7	1	Nut008	NO _x	69	Duplicate difference greater than nominal limit.
9	1	Nut010	PO ₄ , SiO ₂	69	Duplicate difference greater than nominal limit.
9	16	Nut010	All	69	Outlier on profiles, probable misfire or leak.
9	17	Nut010	All	69	Outlier on profiles, probable misfire or leak.
9	21	Nut010	All	69	Outlier on profiles, probable misfire or leak.
10	1	Nut011	NO _x , SiO ₂	69	Duplicate difference greater than nominal limit.
10	24	Nut011	All	69	Outlier on profiles, probable misfire or leak.
11	16	Nut012	All	69	Outlier on profiles, probable misfire or leak.
11	17	Nut012	All	69	Outlier on profiles, probable misfire or leak.
18	15	Nut017	All	69	Outlier on profiles, probable misfire or leak.
18	22	Nut017	All	69	Outlier on profiles, probable misfire or leak.
19	15	Nut018	All	69	Outlier on profiles, probable misfire or leak.
19	22	Nut018	All	69	Outlier on profiles, probable misfire or leak.
20	18	Nut018	All	69	Outlier on profiles, probable misfire or leak.

7.9 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_t01_hyd_voyagereport.docx" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.7°C.

8 Appendix

8.1 Salinity Reference Material

Osil IAPSO Standard Seawater	
Batch	P161
Use by date	03/05/2020
K ₁₅	0.99987
PSU	35.9950

8.2 HyPro Flag Key for CSV & NetCDF file

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.

8.3 GO-SHIP Specifications

8.3.1 Salinity

Accuracy of 0.001 is possible with Autosol™ salinometers and concomitant attention to methodology, e.g., monitoring Standard Sea Water. 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. High precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano (this manual) with great care and experience. Air temperature stability of $\pm 1^\circ\text{C}$ is very important and should be recorded.¹

8.3.2 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.

8.3.3 Silicate (SiO_2)

Approximately 1-3% accuracy[†], 2 and 0.2% precision, full-scale.

8.3.4 Phosphate (PO_4)

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

8.3.5 Nitrate (NO_3)

Approximately 1% accuracy[†], 2 and 0.2% precision, full scale.

8.3.6 Notes

- [†] If no absolute standards are available for a measurement then *accuracy* should be taken to mean the *reproducibility* presently obtainable in the better laboratories.
- 1. 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 batches is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.
- 2. 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 metadata.

8.4 RMNS Values for each CTD Deployment

ANALYSIS RUN	CTD #	SILICATE	PHOSPHATE	NITRITE	NOX (NO ₂ + NO ₃)
<i>CI reported</i>	-	<i>39.424</i>	<i>1.219</i>	<i>0.0320</i>	<i>16.621</i>
1	1	39.40	1.237	0.047	16.713
2	2	39.45	1.240	0.046	16.727
3	-	39.56	1.233	0.048	16.680
4	3	39.56	1.240	0.046	16.583
5	4	39.50	1.243	0.044	16.610
6	5	39.56	1.240	0.045	16.587
7	6	39.66	1.240	0.044	16.583
8	7	39.66	1.233	0.042	16.400
9	8	39.63	1.240	0.046	16.600
10	9	39.83	1.233	0.043	16.563
11	10	39.76	1.237	0.048	16.593
12	11, 12	*	1.233	0.046	16.700
13	13, 14	39.96	1.230	0.043	16.733
14	15	40.00	1.233	0.047	16.727
16	16, 17	39.70	1.233	0.055	16.723
17	18, 19	39.63	1.220	0.041	16.673
18	20, 21	39.60	1.240	0.043	16.680

*Analysis run 12 failed for Silicate analysis. CTD 11 and 12 were analysed for Silicate in analysis run 13, hence use Silicate RMNS values from run 13 if a correction is necessary.

9 References

- Armishaw, Paul, "Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty." *Accred Qual Assur*, 8, pp. 218-224 (2003).
- Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., "*The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment*," *Deep-Sea Research*, 14, pp.381-389 (1967).
- Hood, E.M. (2010). "*Introduction to the collection of expert reports and guidelines*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). "*Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- K  rouel, Roger and Alain Aminot, "*Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis*". *Journal of Marine Chemistry* 57 (1997) pp. 265-275.
- Murphy, J. And Riley, J.P., "*A Modified Single Solution Method for the Determination of Phosphate in Natural Waters*", *Anal.Chim.Acta*, 27, p.30, (1962)
- Wood, E.D., F.A.J. Armstrong, and F.A. Richards. (1967) "*Determination of nitrate in seawater by cadmium-copper reduction to nitrite*." *Journal of the Marine Biological Association of U.K.* 47: pp. 23-31.