

RV INVESTIGATOR

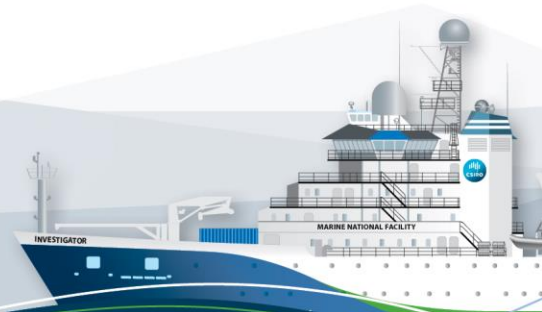
HYDROCHEMISTRY DATA PROCESS REPORT

Voyage: in2017_v02

Chief Scientist: Tom Trull

Voyage title: Southern Ocean Time Series

Report compiled by: Christine Rees, Kendall Sherrin & Cassie Schwanger



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1 Itinerary

Depart Leg 1	Date	Time
Hobart	17/3/2017	0800
Arrive	Date	Time
Hobart	30/3/2017	0800

2 Key personnel list

Name	Role	Organisation
Tom Trull	Chief Scientist	CSIRO
Tegan Sime	Voyage Manager	CSIRO
Christine Rees	Hydrochemist	CSIRO
Kendall Sherrin	Hydrochemist	CSIRO
Cassie Schwanger	Hydrochemist	CSIRO

3 Summary

All finalized data can be obtained from the CSIRO data centre. RMNS corrected nutrient data will be provided at a later date to the data centre.

3.1 Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	CTD 152
Dissolved Oxygen (automated titration)	CTD 116
Nutrients (AA3)	CTD 319 EXP 45 UWY 10

Note: CTD-samples collected from NISKIN bottles on CTD rosette, UWY-underway samples collected from underway seawater intake and EXP-experimental samples.

3.2 Rosette and CTD

- 9 CTD stations were sampled with a 36 bottle rosette (12 L), Dep 1 was the test cast to train samplers. However, salinities, dissolved oxygen and nutrients were collected and analysed.

- The following deployments were not sampled for hydrochemistry: **1 & 3**
- See in2017_v02_HYD_VoyageReport.pdf (voyage report) for more details on sample collection.

3.3 Procedure Summary

The procedure for data processing is outline in Figure 1.

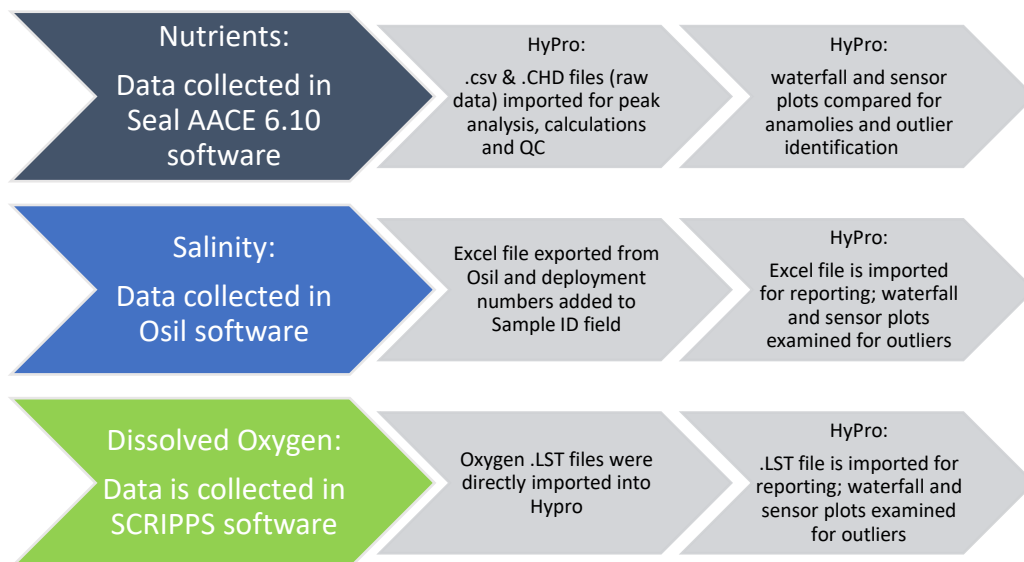


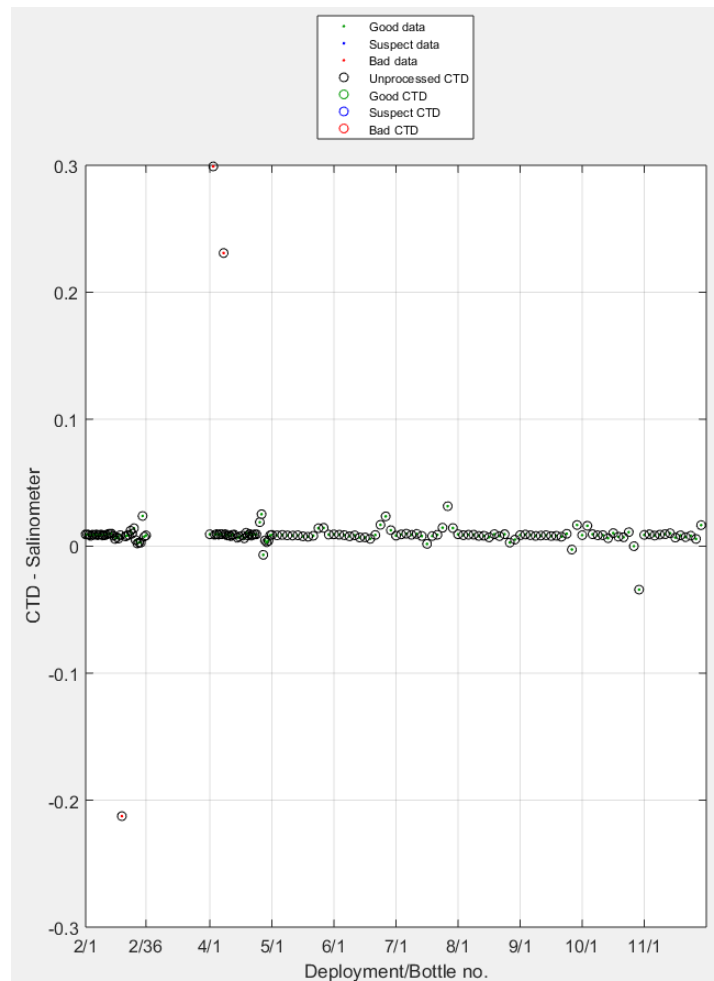
Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

4 Salinity Data Processing

4.1 Salinity Parameter Summary

Details	
HyPro Version	4.13
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71611
Software	OSIL Data Logger
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 salinity units
Analyst(s)	Christine Rees, Kendall Sherrin, Cassie Schwanger
Lab Temperature (±0.5°C)	21.0 -22.5.0°C during analysis.
Bath Temperature	23.996°C
Reference Material	Osil IAPSO - Batch P158
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 7-8 hrs to reach 22°C before analysis
Comments	New inserts were received from OSIL due to the originally supplied inserts being of lesser quality. All inserts on board are new and were found to be much more ridged.

4.2 CTD vs Hydro Salinities Plot



4.3 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.

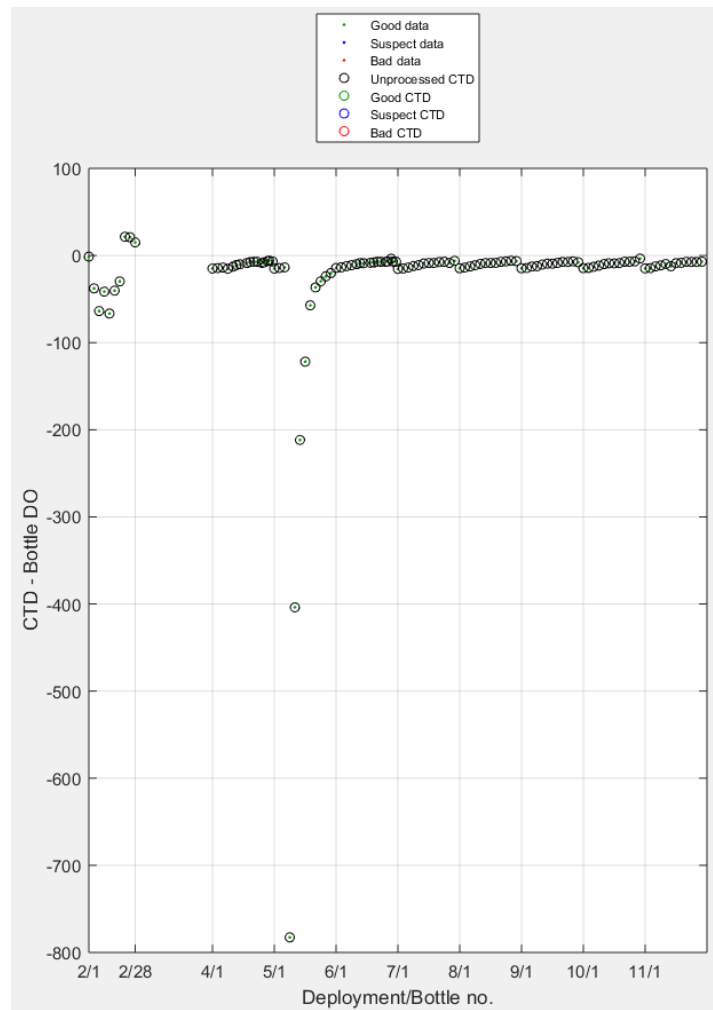
CTD	RP	Bottle	Flag	Reason for Flag or Action
2	22	A22	133	Outlier on profile
4	3	J03	133	Outlier on profile
4	9	J09	133	Outlier on profile

5 Dissolved Oxygen Data Processing

5.1 Dissolved Oxygen Parameter Summary

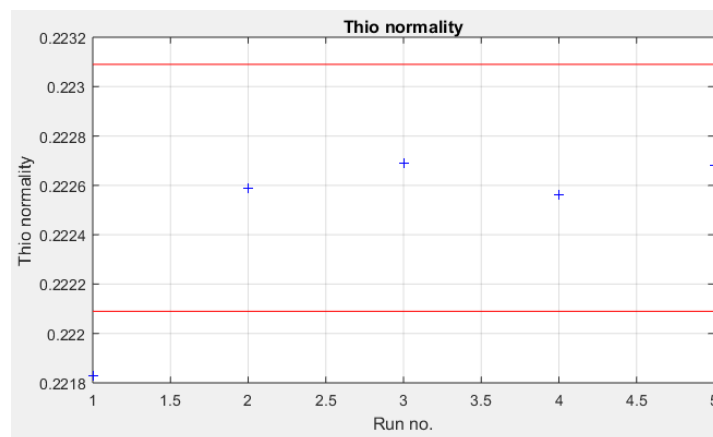
Details	
HyPro Version	4.13
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Christine Rees, Kendall Sherrin, Cassie Schwanger
Lab Temperature ($\pm 1^{\circ}\text{C}$)	Variable, 19.0 - 21.5°C
Sample Container type	Pre-numbered glass 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	

5.2 CTD vs Hydro DO Plot

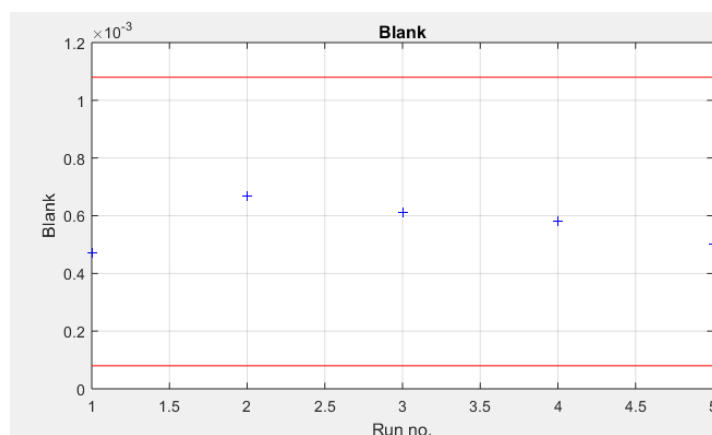


The large depicted error between dissolved oxygen samples and the CTD sensor was due to an issue with the primary dissolved oxygen sensor for deployment 5. Bottle results are correct.

5.3 Dissolved Oxygen thiosulphate normality across voyage



5.4 Dissolved Oxygen blank concentration across voyage



5.5 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.

No dissolved oxygen bottle data is flagged as suspect or bad. All results are of good quality.

6 Nutrient Data Processing

6.1 Nutrient Parameter Summary

Details					
HyPro Version	4.13				
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)	Christine Rees, Kendall Sherrin, Cassie Schwanger				
Lab Temperature ($\pm 1^\circ\text{C}$)	Variable, 19.0 – 21.5°C				
Reference Material	RMNS – CC, BW, CD				
Sampling Container type	30 ml polypropylene sample tubes				
Sample Storage	< 2 hrs at room temperature or ≤ 18 hrs @ 4°C				
Pre-processing of Samples	None				
Comments					

6.2 Methods Summary

Silicate analysis is based on a modified Armstrong et al. (1967) method. Silicate in seawater reacts with acidified ammonium molybdate to produce silicomolybdic acid. This solution will also react with phosphate producing a phosphomolybdic acid. Tartaric acid is introduced to remove this interference. Finally, Stannous Chloride (Tin II Chloride) is added to reduce silicomolybdic acid to the blue compound silicomolybdous acid which can be detected at 660 nm or 820 nm.

Phosphate measurement is based on the original Murphy and Riley (1962) method with some modifications developed at the NIOZ-SGNOS Practical Workshop 2012 optimizing antimony catalyst/phosphate ratio and reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum blue complex with acidified ammonium molybdate reduced by ascorbic acid which can be detected at 880 nm.

Nitrate is determined by first reducing to nitrite via a basic buffered copperized cadmium column before the colour reaction (Wood et al., 1967). Nitrite in seawater will react with sulphanilamide under acidic conditions to form a diazo compound. This compound couples with 1-N-naphthly-

ethylenediamine di-hydrochloride to produce a reddish purple azo complex which can be detected at 520 nm.

The ammonia method, developed by Roger K  rouel and Alain Aminot, IFREMER (1997 Mar.Chem.57), is based on the reaction of ammonium with orthophthaldialdehyde and sulfite at a pH of 9.0-9.5 producing an intensely fluorescent product; excitation 370 nm, emission 460 nm.

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

6.3 Nutrient calibration and data parameter summary

During the course of the voyage all run information was logged - LNSW batch, new cadmium column, new stock standard, daily standard information, fresh reagent information, instrumentation settings, pump tube changes and pump tube hours. This information along with calibration summary data and calibration plots for each analysis run are available in the following zip folder consisting of files containing; mdl, drift, baseline, carry-over, calibration & RMNS results:

All NUT#### file numbers with each ctd deployment analysed per analysis run can be viewed in the pdf file "AA3FileLog.pdf" in the above location. The latitude, longitude and time (UTC) that matches the UWY samples is located in file "IN2016 V03 UWY.pdf". All runs have a corresponding AA3_Run_Analysis_sheet and AA3_Processing_Worksheet file to assist in characterizing data and note questionable peaks. This information is contained in the voyage documentation and available upon request.

The raw data is imported into Hypro for peak determination. For each analysis run (indicated by a NUT####), HyPro fits the best calibration curve to the standards by performing several passes over each standard point. If the measured value is different from the calculated value it will allocate less weighting to the point in the calibration curve. HyPro will mark these points as suspect or bad within the calibration curve. Following standard procedures, the operator may choose to remove bad calibration points by placing a # in front of the peak start column within the data file (see section 6.7 for edited data). Below are the standard corrections and settings that Hypro applies to the raw data.

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	6	6	6	6	6
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

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
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 17/5/2015 off shore from Brisbane (-27.1S, 155.2E) using the clean instrument seawater supply inlet. Twenty five carboys were filtered through 1µM by Stephen Tibben and Kendall Sherrin on the 21 st and 22 nd of April 2016. Four containers were stored in the hydrochemistry laboratory at 21°C.				
Medium of Baseline	18.2 Ω MQ				
Proportion of samples in duplicate?	1 duplicate for each CTD from NISKIN bottle 1				
Comments	Calibration and QC data that was edited or removed is located in the table in section 6.7. The reported data is not corrected to the RMNS. Per run RMNS data can be found in Appendix 7.4.				

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

The certified reference materials (CRM) for silicate, phosphate, nitrate and nitrite in seawater produced by KANSO – Japan was used in each nutrient analysis to ensure the accuracy of results. The RMNS was run 4 times after the calibration standards. No QC data is supplied for the experimental ammonia samples as there is not a CRM. Accuracy is determined by comparing the new standard batch with the old and tracking to ensure the concentration is within 1% accuracy between batches.

Table 1: RMNS CC, BW and CD concentrations (µM) at 21°C

RMNS	NO ₃	NO _x	NO ₂	PO ₄	SiO ₄
CD	5.63 ± 0.0051	5.65 ± 0.055	0.018 ± 0.004	0.457 ± 0.008	14.26 ± 0.101
BW	25.180 ± 0.205	25.249 ± 0.215	0.069 ± 0.010	1.578 ± 0.014	61.450 ± 0.430
CC	31.621 ± 0.246	31.740 ± 0.252	0.119 ± 0.006	2.13 ± 0.019	88.228 ± 0.492

The submitted nutrient results do NOT have RMNS corrections applied.

During the voyage principal researchers corrected the data within each nutrient analysis using the CA RMNS. The following calculation was performed:

RMNS Correction

$$\% \text{ error} = (RMNS \text{ measured} - RMNS \text{ Published}) / RMNS \text{ Published}$$

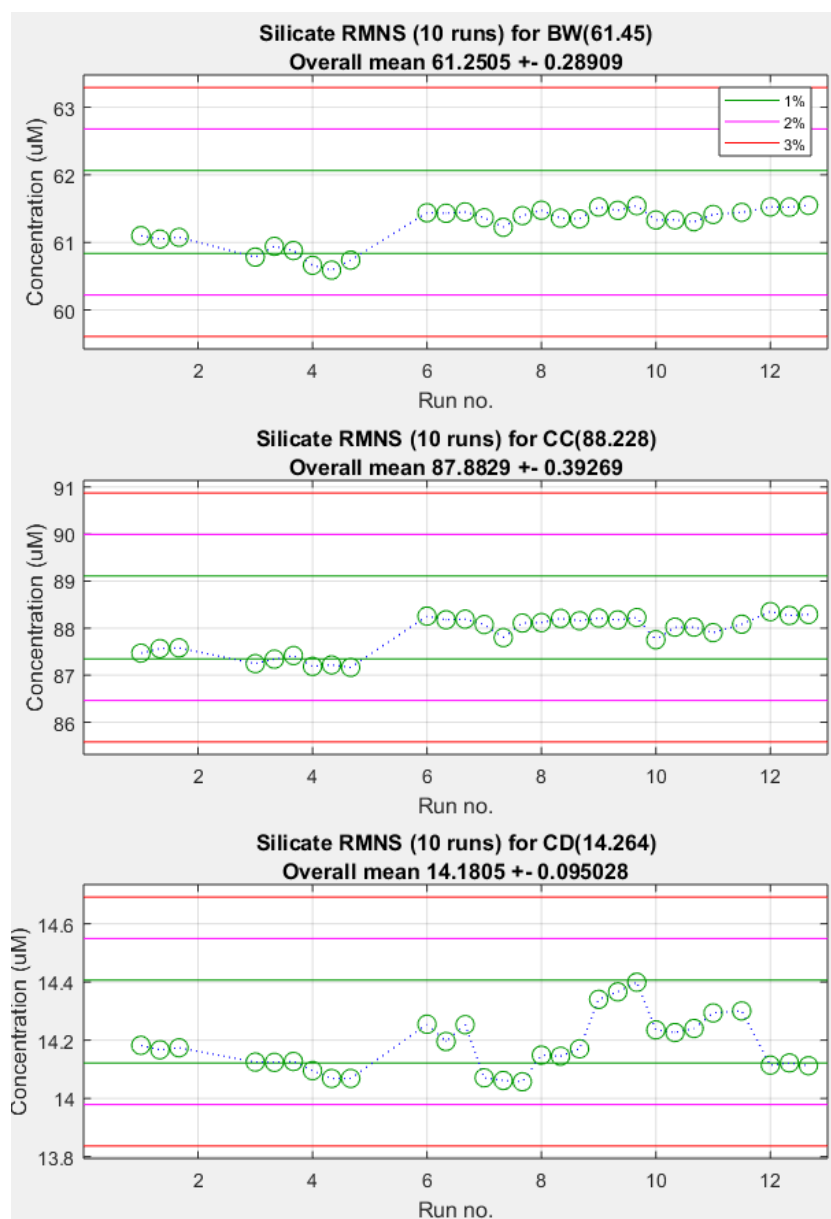
$$\text{Corrected Nutrient Concentration} = \text{Nutrient measured} - (\text{nutrient measured} \times \text{error})$$

Note: NO_x data should be corrected as NO₃ and NO₂.

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), reference section 7.3, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy. The calculated RMNS values per CTD are reported in the table in section 7.4.

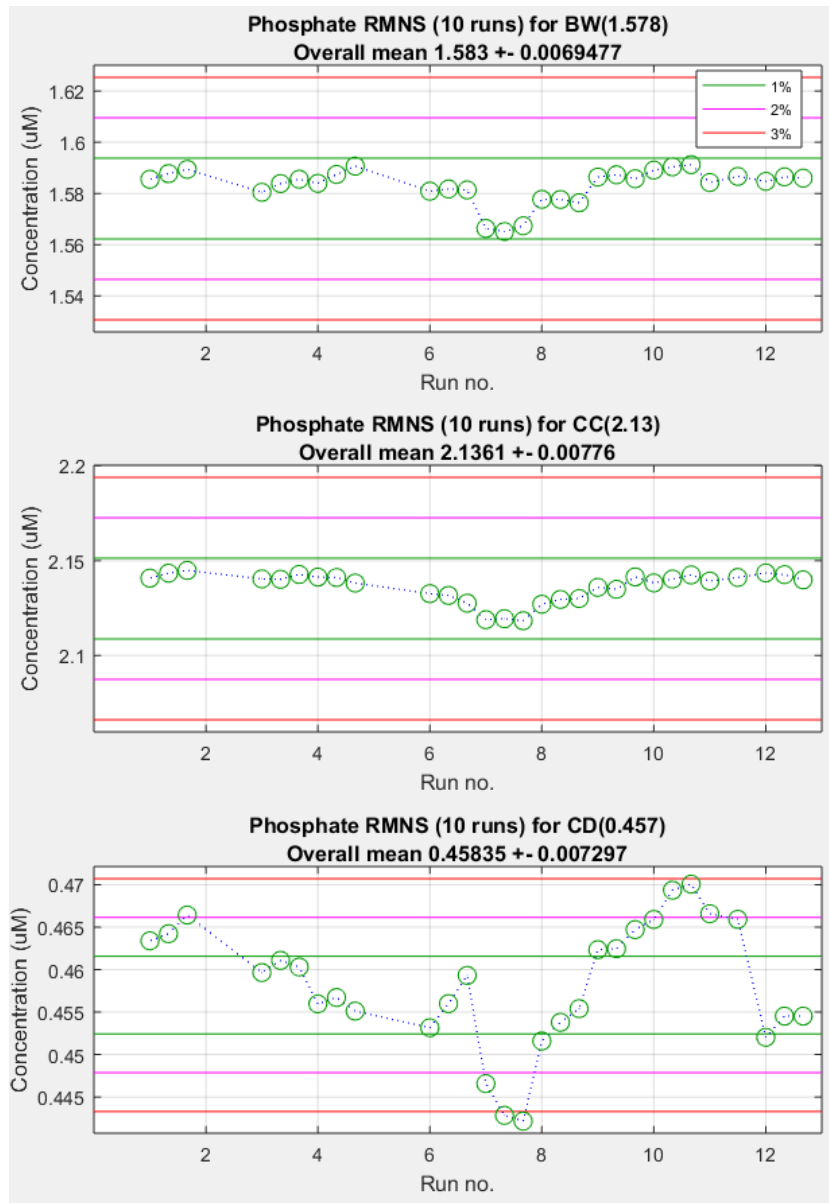
6.4.1 Silicate RMNS Plot

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



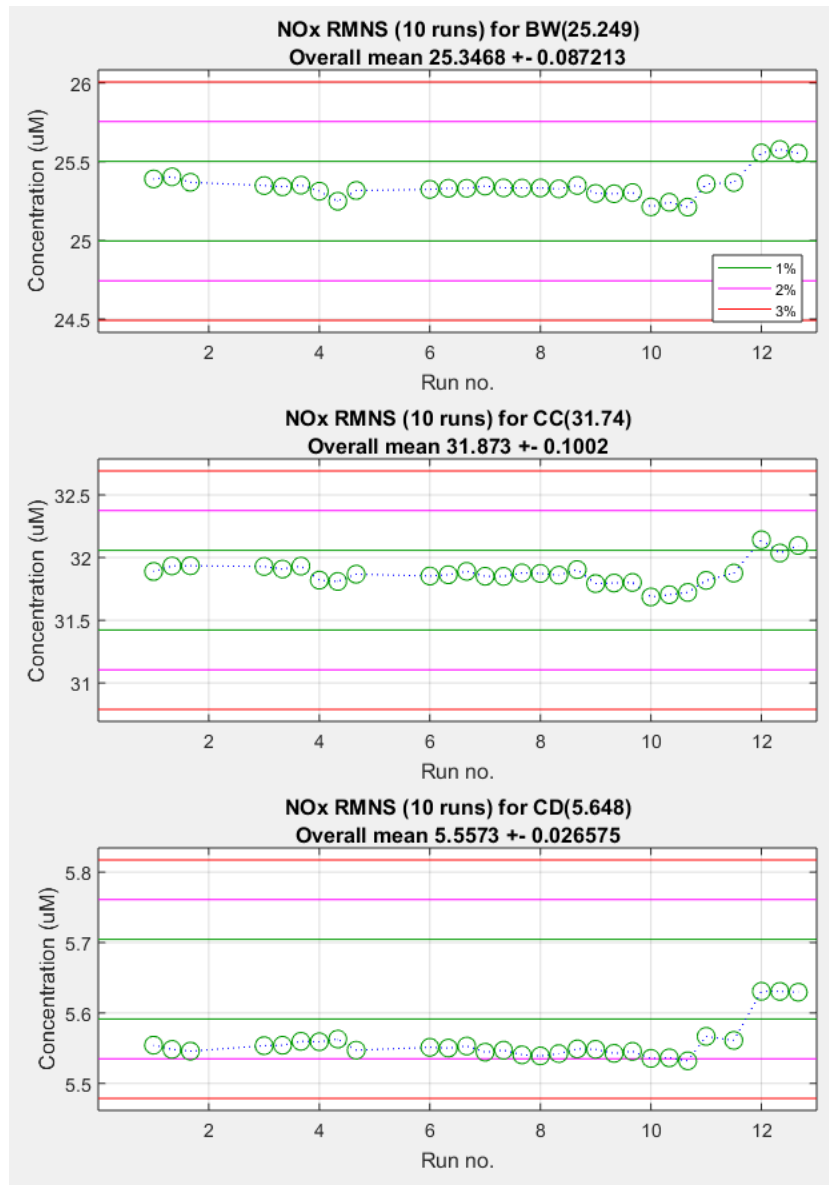
6.4.2 Phosphate RMNS Plot

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

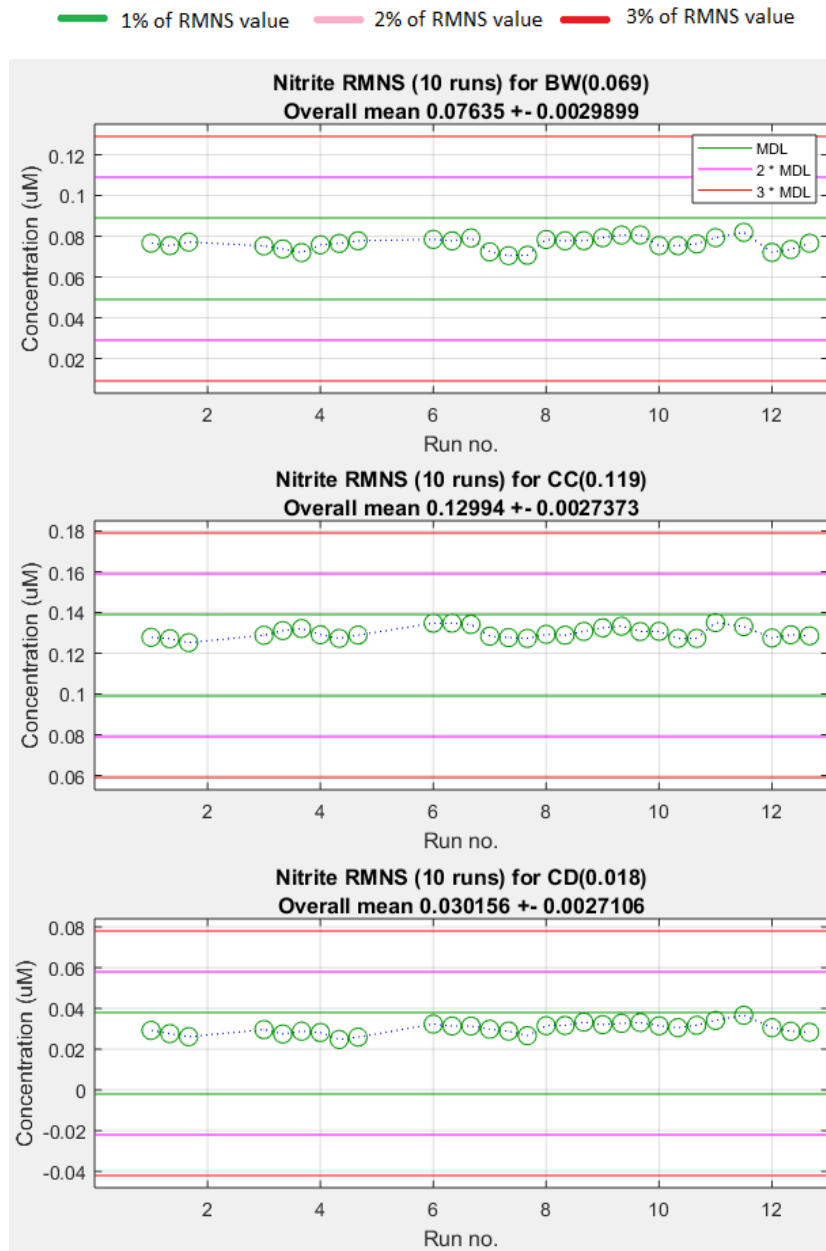


6.4.3 Nitrate + Nitrite (NO_x) RMNS Plot

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



6.4.4 Nitrite RMNS Plot



6.5 Analytical Precision

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 CRM over time (Armishaw 2003).

	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Calculated MU* @ 1 µmol l ⁻¹	±0.017	±0.020	±0.017	±0.108	±0.066 [‡]

*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 CRM.

Method detection limits (MDL) achieved during the voyage were much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. Results are µmol l⁻¹. The precision of the RMNS is was also determined.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Min	0.00	0.00	0.02	0.001	0.00
Max	0.3	0.04	0.05	0.01	0.04
Mean	0.17	0.019	0.03	0.005	0.007
Median	0.2	0.02	0.004	0.006	0.005
Precision of MDL (stdev)	0.10	0.011	0.011	0.002	NA

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

Published CD RMNS (µmol l ⁻¹)	37.46	1.441	20.20	0.065	-
w/uncertainty	± 0.22	± 0.014	± 0.16	± 0.010	
RMNS Min	14.1	0.44	5.53	0.025	-
RMNS Max	14.4	0.47	5.63	0.037	-
RMNS Mean	14.183	0.458	5.556	0.03	-
RMNS Median	14.2	0.46	5.55	0.031	-
RMNS Std Dev	0.097	0.008	0.026	0.003	-

Published CC RMNS	37.46	1.441	20.20	0.065	-
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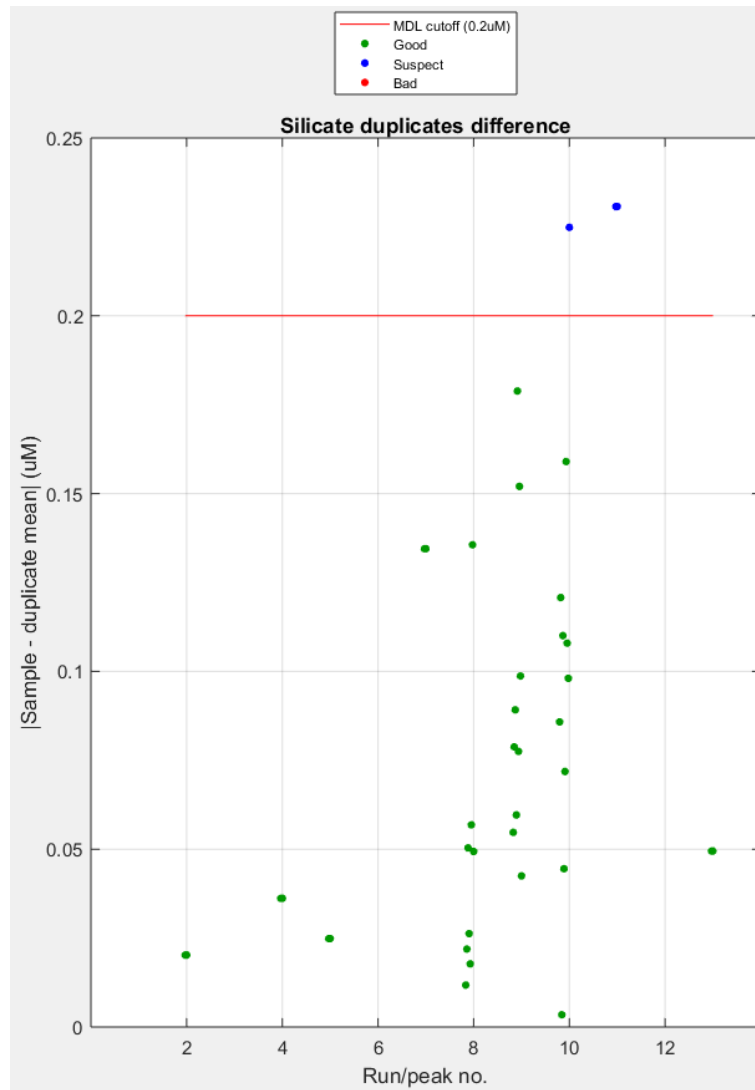
($\mu\text{mol l}^{-1}$)	± 0.22	± 0.014	± 0.16	± 0.010	
w/uncertainty					
RMNS Min	87.2	2.12	31.69	0.125	-
RMNS Max	88.4	2.14	32.14	0.135	-
RMNS Mean	87.89	2.136	31.873	0.13	-
RMNS Median	88.1	2.14	31.87	0.129	-
RMNS Std Dev	0.39	0.007	0.10	0.003	-

Published BW RMNS	37.46	1.441	20.20	0.065	-
($\mu\text{mol l}^{-1}$)	± 0.22	± 0.014	± 0.16	± 0.010	
w/uncertainty					
RMNS Min	60.6	1.57	25.21	0.07	-
RMNS Max	61.5	1.59	25.58	0.082	-
RMNS Mean	61.241	1.584	25.347	0.076	-
RMNS Median	61.4	1.59	25.33	0.077	-
RMNS Std Dev	0.283	0.007	0.087	0.003	-

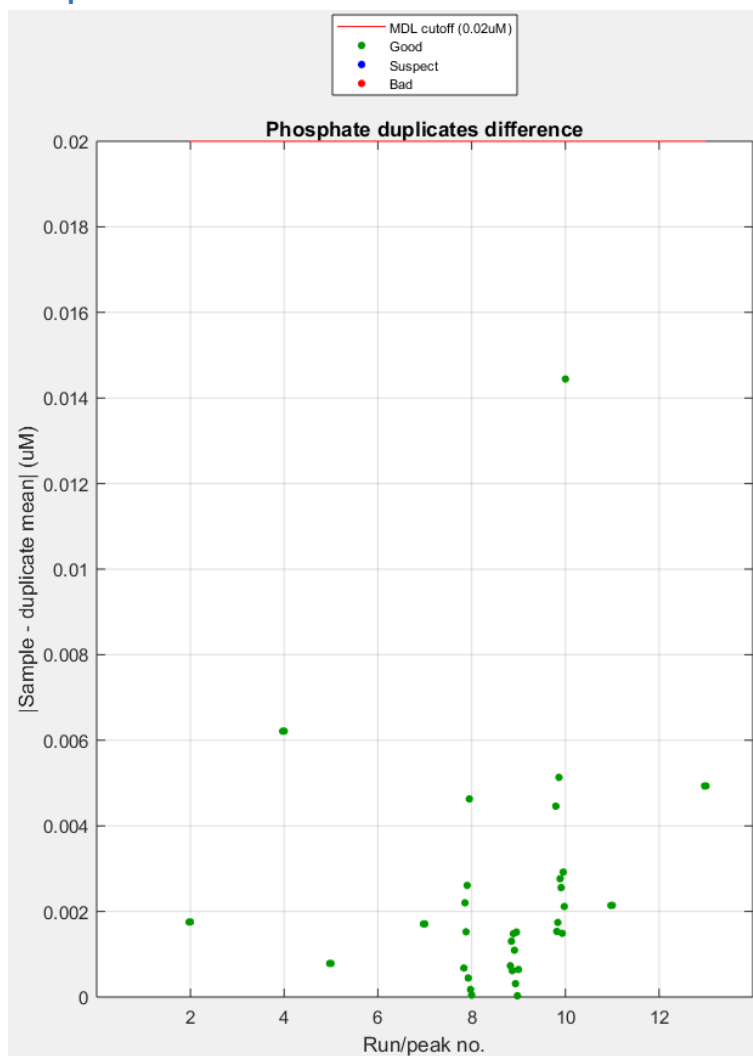
6.6 Sampling Precision

Duplicates samples were collected from NISKIN bottle 1 to measure the precision of nutrient sampling (this is not a measurement of analytical precision). The duplicate measurements are reported in the data as an average when the duplicates are flagged GOOD. The sampling precision is deemed good if difference between duplicate concentrations is below the MDL for silicate, phosphate and nitrite and within 0.05 μM for nitrate.

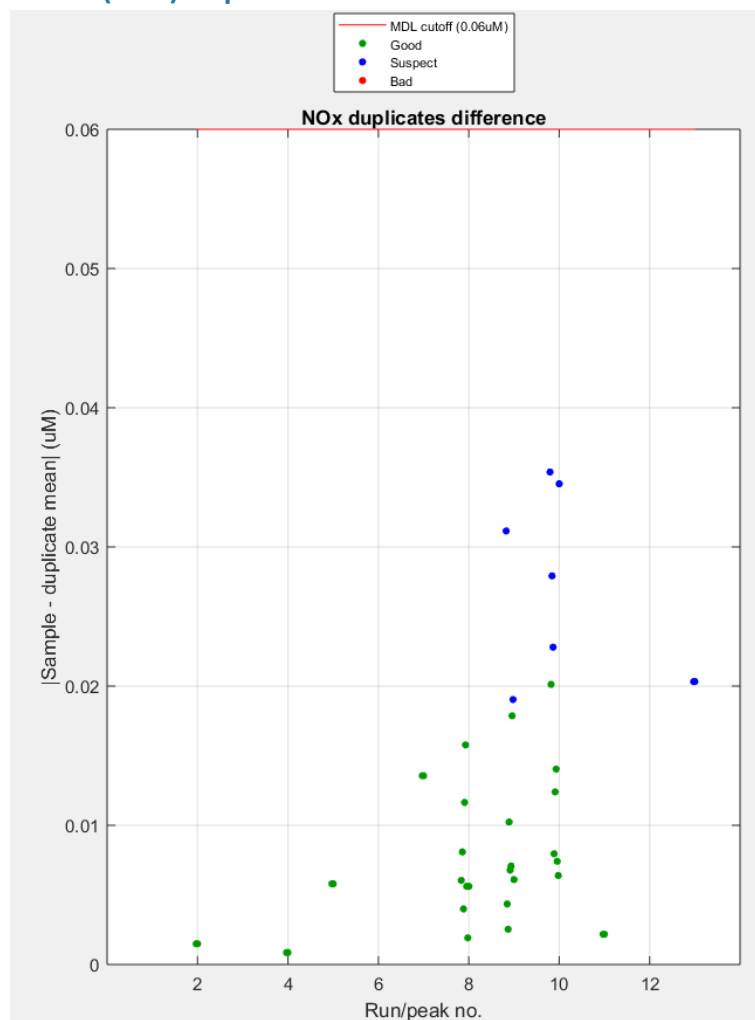
6.6.1 Silicate Duplicate Plot



6.6.2 Phosphate Duplicate Plot

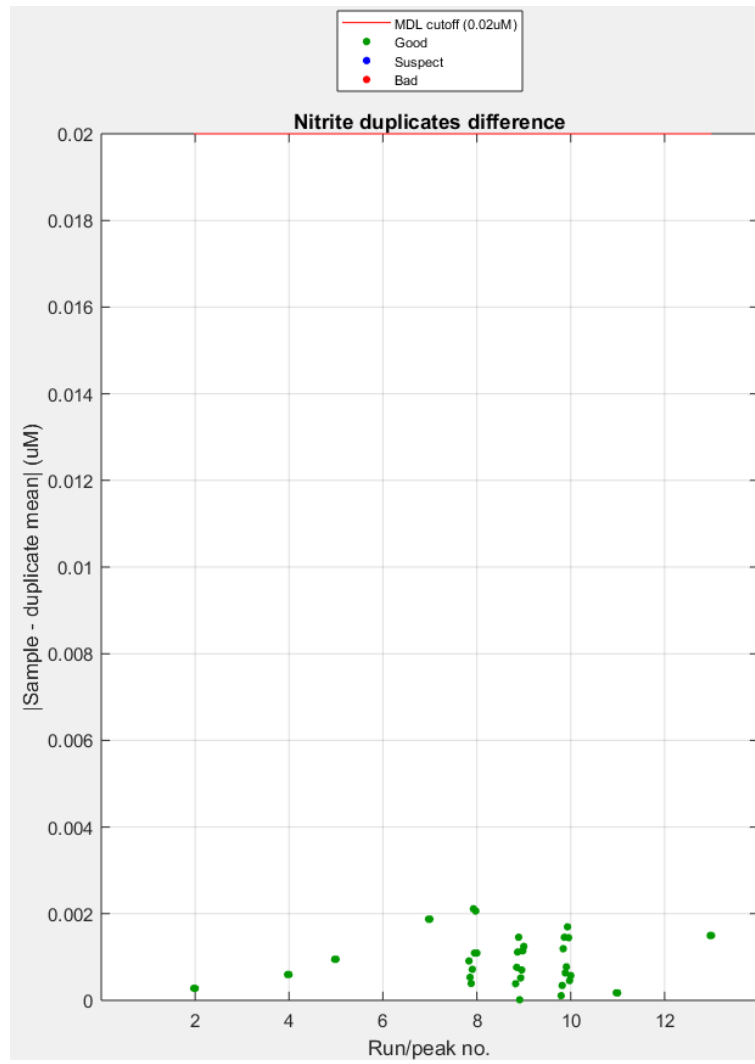


6.6.3 Nitrate + Nitrite (NOx) Duplicate Plot

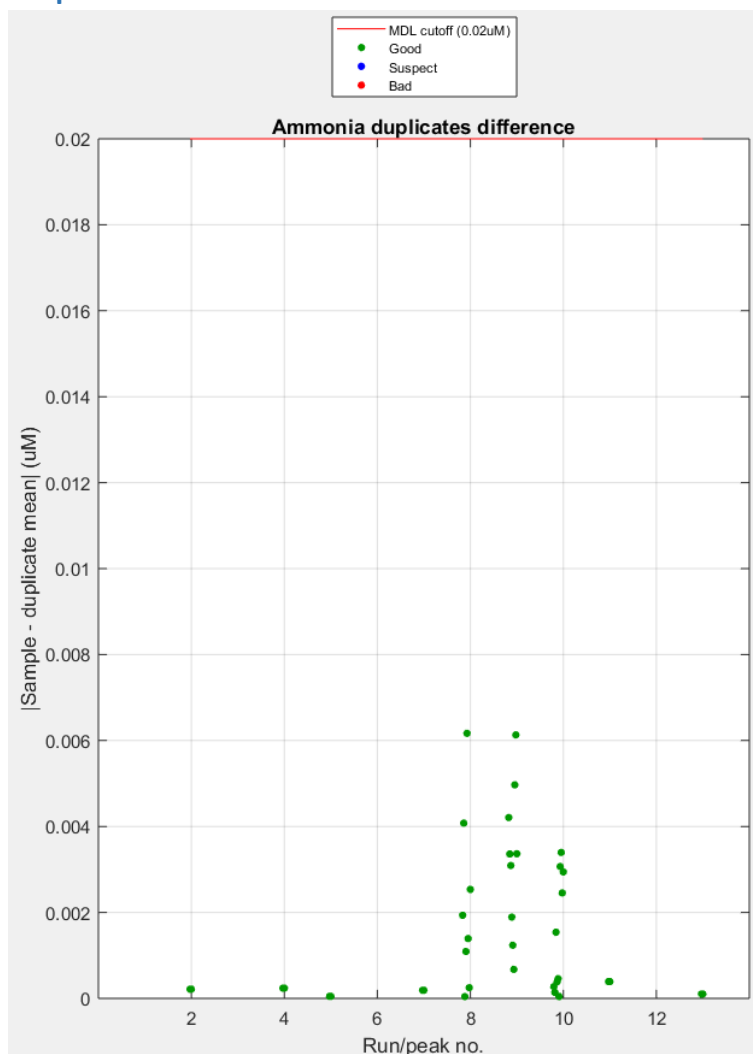


A number of points here are shown as suspect however this is incorrect. The colouring is incorrect for the plot. In the dataset these points should be regarded as good.

6.6.4 Nitrite Duplicate Plot

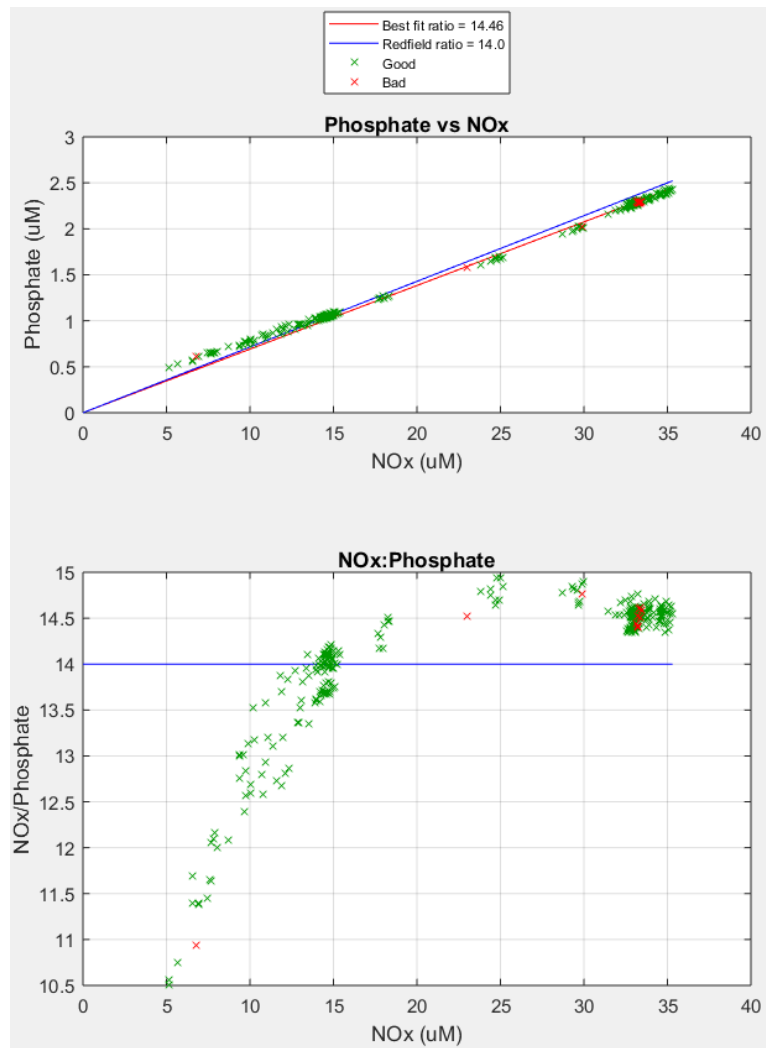


6.6.5 Ammonia Duplicate Plot



6.6.6 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx, best fit ratio: 14.46.



6.7 Calibration and QC edited data

CTD	Peak	Analysis	Reason for Flag or Action
2	Cal 1	NH4	Suspect greater than calibration error
4	TesCal 5	PO4	Over range
5	Test BZ	SiO2	Over range
6	Final Drift	SiO2	Spike on plateau
8	High	SiO2	Marked bad – carryover from previous run used
8	Cal 6 #2	NOx	Odd peak shape due to low sample aspiration – excluded from Cal curve by Hypro; data good
9	Cal 5	NOx	Suspect
10	Cal 5	NOx	Suspect (1 st point)
10	BQC	SiO2	Suspect (MAD) peak shape
TMR	Cal 5	NOx	Suspect
	Cal 6	NOx	1 st point Suspect
11	Cal 1	NH4	Suspect

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

The table below identifies all flagged data and data that was repeated. 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. Refer to Appendix 7.2 for flag explanations.

CTD	RP	Run	Analysis	Flag	Reason for Flag or Action
2	22	Nut001	All	133	Outlier on profile
4	3, 9	Nut003	All	133	Outlier on profile
8	1	Nut008	NOx		Duplicates > 0.03 – but fine; first peak and 8th peak
10	1	Nut010	SiO2		Duplicates > 0.2
11	1	Nut011	NOx		Duplicates > 0.02 –OK as < 0.06 µmol/L

6.9 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 “in2017_v02_hyd_voyagereport.docx” for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the **average room temperature of 20.5°C**.

7 Appendix

7.1 Salinity Reference Material

Osil IAPSO Standard Seawater	
Batch	P158
Use by date	25/03/18
K ₁₅	0.99940

7.2 Hypro Flag Key for CSV & NetCDF File

Flag	Meaning
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.

7.3 GO-SHIP Specifications

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
O ₂	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.
SiO ₂	Approximately 1-3% accuracy†, 2 and 0.2% precision, full-scale.
PO ₄	Approximately 1-2% accuracy†, 2 and 0.4% precision, full scale.
NO ₃	Approximately 1% accuracy†, 2 and 0.2% precision, full scale.

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 meta data.

7.4 RMNS Values for each CTD

7.4.1 RMNS CD

		SiO4 Certified	PO4 Certified	NOx Certified	NO2 Certified
		14.264	0.457	5.647	0.018
Run	CTD	SiO4 Measured	PO4 Measured	NOx Measured	NO2 Measured
1	2	14.20	0.46	5.55	0.0277
3	4	14.10	0.46	5.55	0.0287
4	5	14.10	0.46	5.56	0.0263
6	6	14.27	0.46	5.55	0.0313
7	7	14.10	0.44	5.54	0.0287
8	8	14.13	0.45	5.54	0.0323
9	9	14.37	0.46	5.55	0.0327
10	10	14.20	0.47	5.54	0.0313
11	-	14.30	0.47	5.56	0.0355
12	11	14.10	0.45	5.63	0.0293

7.4.2 RMNS BW

		SiO4 Certified	PO4 Certified	NOx Certified	NO2 Certified
		61.45	1.578	25.25	0.069
Run	CTD	SiO4 Measured	PO4 Measured	NOx Measured	NO2 Measured
1	2	61.07	1.59	25.39	0.0763
3	4	60.87	1.58	25.35	0.0737
4	5	60.67	1.59	25.29	0.0770
6	6	61.43	1.58	25.33	0.0783
7	7	61.33	1.57	25.34	0.0710
8	8	61.40	1.58	25.34	0.0780
9	9	61.50	1.59	25.30	0.0803
10	10	61.30	1.59	25.22	0.0753
11	-	61.40	1.59	25.37	0.0805
12	11	61.50	1.59	25.56	0.0740

7.4.3 RMNS CC

		SiO4 Certified	PO4 Certified	NOx Certified	NO2 Certified
		88.228	2.13	31.74	0.119
Run	CTD	SiO4 Measured	PO4 Measured	NOx Measured	NO2 Measured
1	2	87.57	2.14	31.92	0.1267
3	4	87.30	2.14	31.92	0.1307
4	5	87.20	2.14	31.83	0.1283
6	6	88.23	2.13	31.87	0.1347
7	7	88.00	2.12	31.86	0.1277
8	8	88.17	2.13	31.88	0.1297
9	9	88.20	2.14	31.80	0.1320
10	10	87.93	2.14	31.70	0.1283
11	-	88.00	2.14	31.85	0.1340
12	11	88.33	2.14	32.09	0.1283

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