Marine National Facility

RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage: IN2018_v01

Chief Scientist: Dr. Steve Rintoul

Voyage title: Detecting Southern Ocean change from repeat hydrography, deep Argo and trace element biogeochemistry & CAPRICORN

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1 Executive Summary

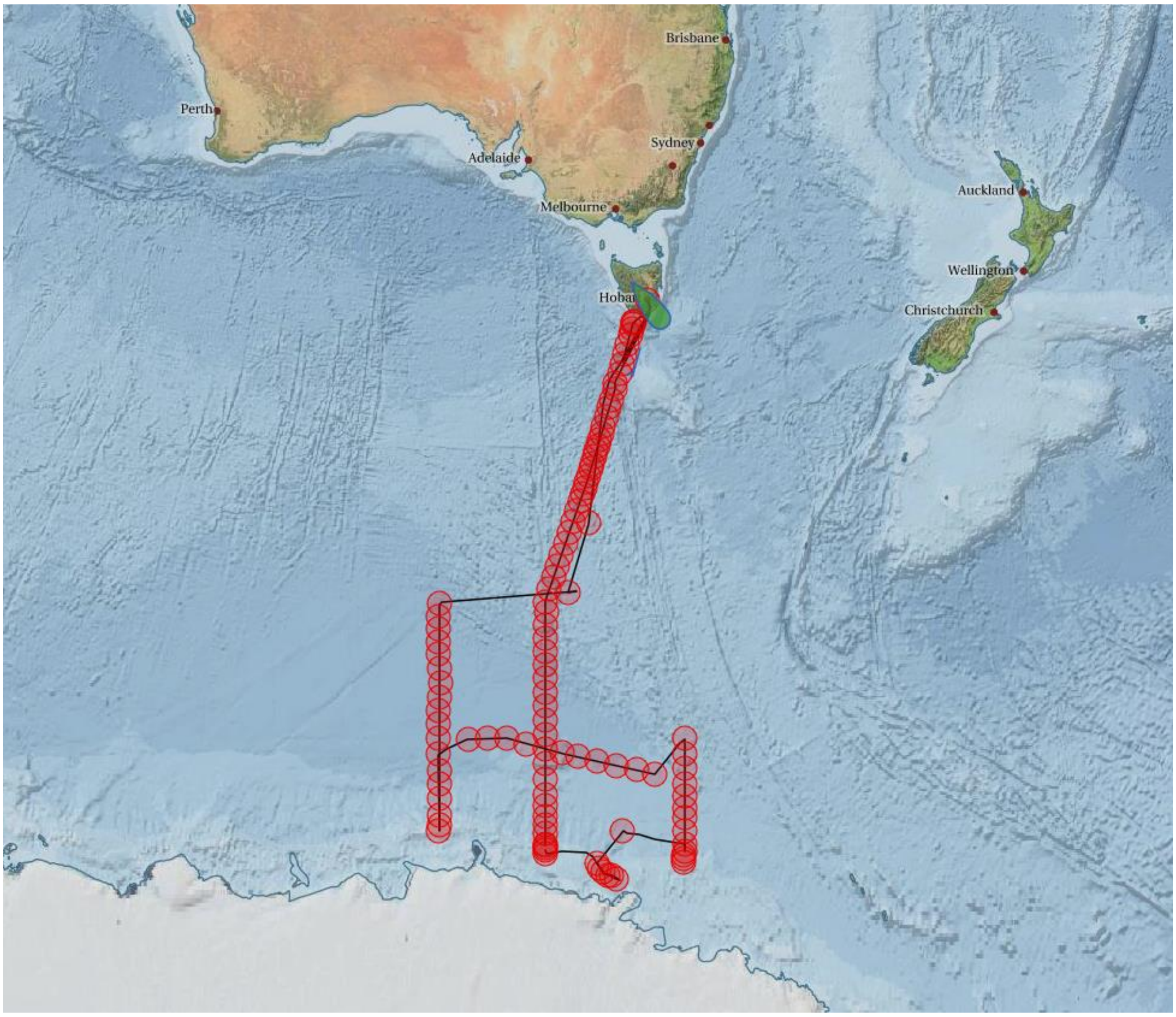
Nutrients, dissolved oxygen and salinity samples were collected and analysed through the full depth for climate studies and to quantify changes in the Antarctic Bottom Water in the Australian Antarctic Basin. The samples were collected along the GO-SHIP hydrographic reference sections SR3 and S4, on the Antarctic shelf near the Mertz glacier and along two transect lines at 150°E and 132°E. Five nutrients were analysed; silicate, phosphate, nitrate + nitrite, nitrite and ammonium. This was the first time ammonium has been measured successfully on every station for a hydrographic voyage.

High quality data was produced for the three measured parameters. Certified reference materials for nutrients in seawater were within the specified limits of the certified value.

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

2 Itinerary

Hobart to Hobart 11 January 2018 to 22 February 2018



3 Key personnel list

Name	Role	Organisation
Steve Rintoul	Chief Scientist	CSIRO & ACE CRC
Tegan Sime	Voyage Manager	CSIRO
Alain Protat	Principal Investigator	Bureau of Meteorology
Andrew Bowie	Principal Investigator	IMAS-UTAS/ACE CRC
Bronte Tilbrook	Principal Investigator	CSIRO & ACE CRC
Lev Bodrossy	Principal Investigator	CSIRO
Christine Rees	Hydrochemist	CSIRO
Kendall Sherrin	Hydrochemist	CSIRO
Stephen Tibben	Hydrochemist	CSIRO
Kristina Paterson	Hydrochemist	CSIRO

4 Summary

4.1 Hydrochemistry Samples Analysed

Analysis	Number of Samples
Salinity (Guildline Salinometer)	2819 CTD 30 TSG
Dissolved Oxygen (automated titration)	2824 CTD 38 UWY 1 EXP
Nutrients (AA3)	2825 CTD 63 UWY 108 EXP

Note:

- Conductivity Temperature Density (CTD); samples collected from NISKIN bottles on the CTD rosette.
- Underway (UWY); samples collected from underway clean instrument seawater supply in the PCO2 lab.

- Experimental (EXP): sample from microcosm experiments
- For sample information on UWY and EXP samples refer to the Hydrochemistry ELog from the voyage.

4.2 Rosette and CTD

- 108 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 procedure for data processing is outlined below.

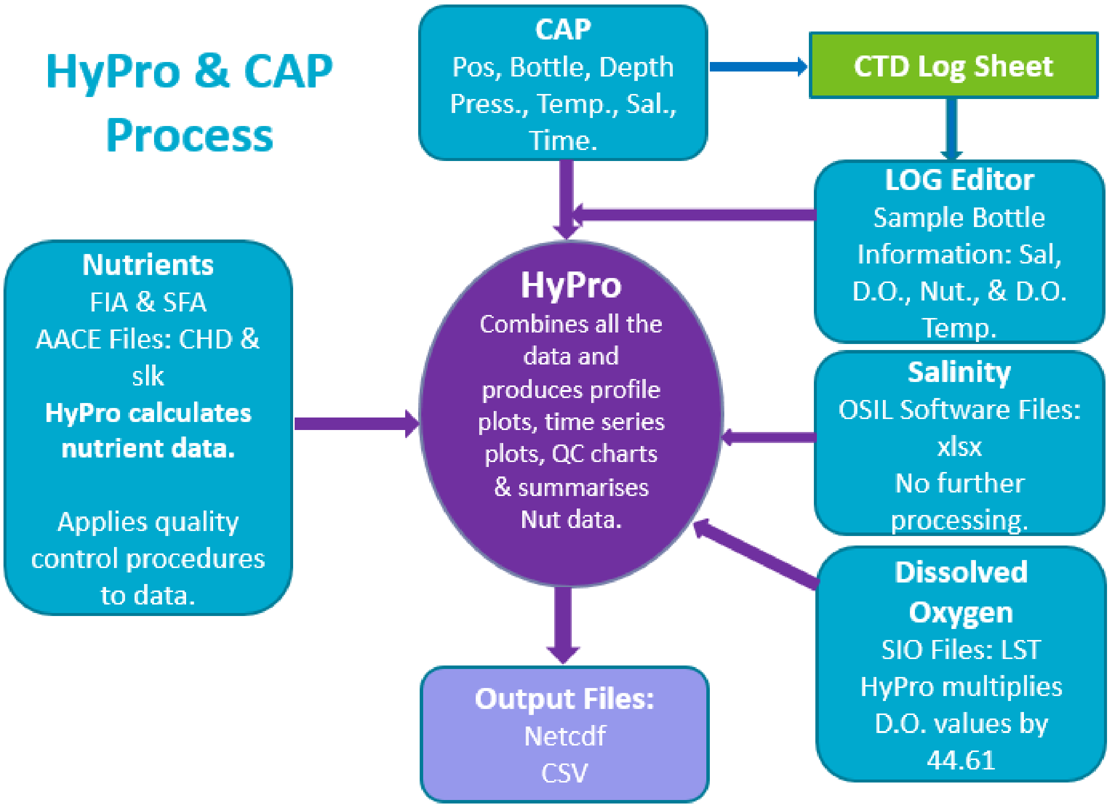


Figure 1: The processing steps for hydrology data following sample assay.

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)	Kristina Paterson
Lab Temperature (±0.5°C)	21.5 -23.5°C during analysis.
Bath Temperature	24.01°C
Reference Material	Osil IAPSO - Batch P161 and P158 (see appendix 8.1)
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	Both instruments were used interchangeably

5.2 Salinity Method

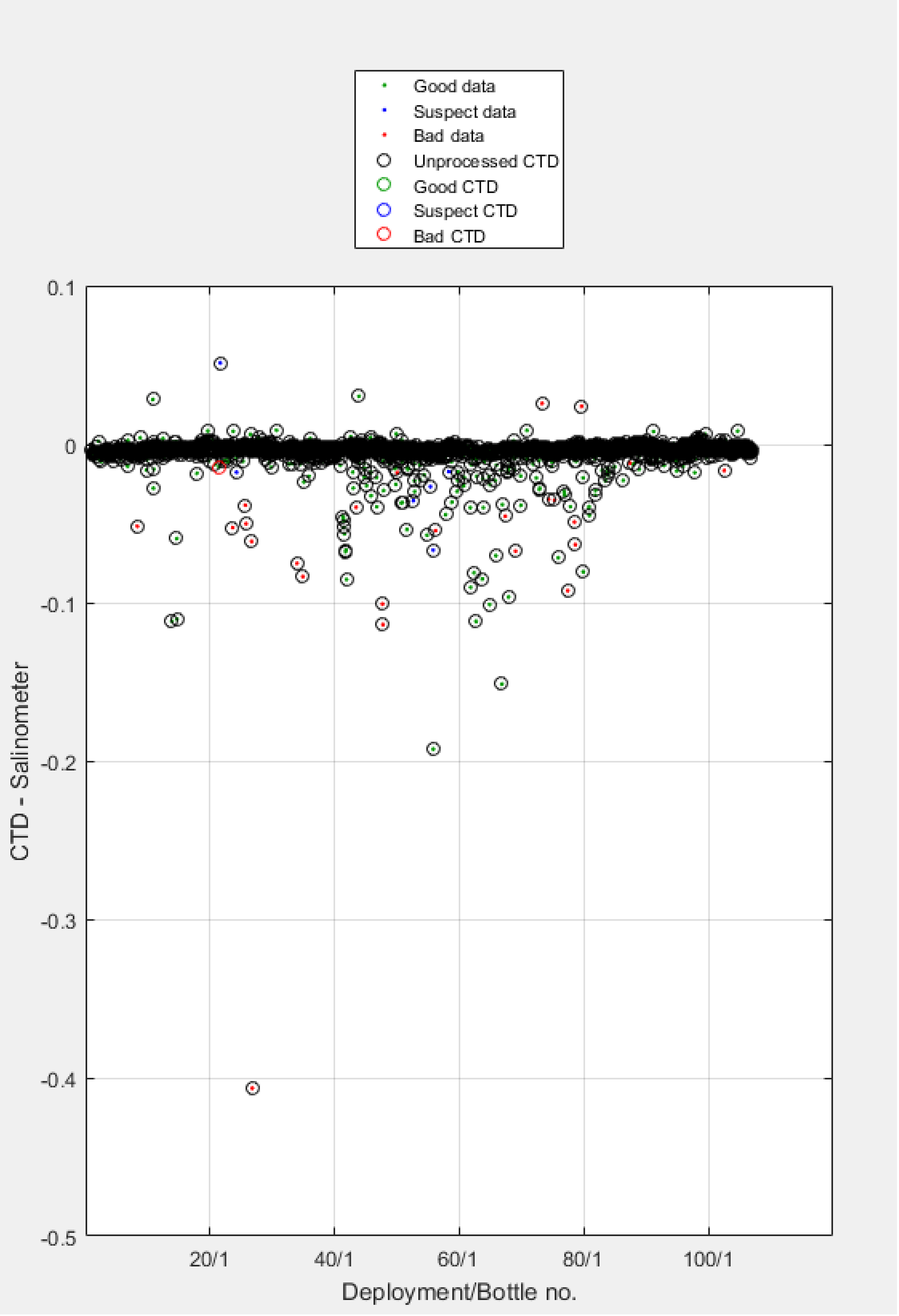
The method uses a high precision laboratory salinometer (Guildline Autosal 8400B) which is operated in accordance with its technical manual.

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 x 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 25cm^3. 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 Salinities vs Hydrochemistry Salinities Plot



5.4 Missing or Flagged 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	Run	Flag	Reason for Flag or Action
008	D12	8	133	Salinometer measurement was good, potentially sampled from the wrong niskin (niskin 11).
021	K16	021	133	Bottle was dropped/some sample spilled. The subsequent reading was at first unstable (poor agreement between readings) then stable but comparatively low salinity/out of profile.
021	K24	021	133	Salinometer measurement was good. Comparatively low salinity/out of profile.
023	E24	023	133	Comparatively high Salinity/out of profile, unusual nutrient and cfc data points suggests bottle fired at wrong depth
024	K10	024	69	First effort to sample was unstable, second effort was comparatively stable across 3 readings but high compared to CTD/out of profile.
025	C25	025	133	Out of profile (as is nuts and possibly other measurements) likely fired at wrong depth
025	C29	025	133	Out of profile (as is nuts and possibly other measurements) likely fired at wrong depth
026	E29	026	69	Sample was unstable during analysis (three attempts to make a stable measurement), cause unknown
026	E25	026	133	Sample was analysed ok, result out of profile cause unknown
033	C10	033	133	Salinometer measurement was good, high/out of profile.
033	C36	033	133	The first sample attempt was variable with a large difference between the two readings, the second sample was comparatively stable between the two readings but in comparison to the rest of the cast is out of profile/high
034	M34	034	133	Result is out of profile and comparatively high.
035	G03	035	133	Analysis was good and agreement good, sample is out of profile (high) cause unknown
043	E17	043	133	The sample was unstable and the result constantly increasing during analysis. The sample is high and out of profile
043	E10	043	133	Salinometer measurement was good. Result is high/out of profile.
043	E01	043	133	Salinometer measurement was good. Result is high/out of profile.

047	C26	046	133	Salinometer measurement was good. The result is out of profile, cause unknown, The measurement over the entire CTD was the most problematic to date, small bubbles forming on the electrodes and other unknown problems causing jumps of up to .003 units
047	C29	046	133	Salinometer measurement was good. The result is out of profile, cause unknown, The measurement over the entire CTD was the most problematic to date, small bubbles forming on the electrodes and other unknown problems causing jumps of up to .003 units
050	A03	050	133	High salinity/out of profile, measurement was erratic and difficult to obtain two readings within QC accepted range of each other.
052	E25	052	69	Salinity is comparatively high for the profile, but mimics/exaggerates a feature (spike/increase) seen in the CTD data. The sample needed two measurements, the first was low with poor agreement over two readings, the second reading was ok
055	M31	055	133	The sample ran poorly 2 times (significant difference between the two readings, internally stable for each of the 5 sub-readings within a reading), third try was stable but the value is high
055	M15	055	133	The sample ran poorly on the first attempt stepping up from 34.7044 to 34.7080, and remaining stable at the higher reading on the second attempt. Both results were significantly higher than the CTD.
056	G09	056	133	The sample analysed poorly on four attempts - one was within or close to acceptable limits but the final result is high/ out of profile. Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083). It was APPROXIMATELY at this point that inserts from the reserve bag of good/new inserts were introduced into circulation and which were later found to have approximately 50 with punctures near the top lip due to the insertion of a screwdriver to remove the inserts from the sample bottle. Some inserts with this problem may have been in circulation for the entire voyage, and may be the reason for anomalous high salinity readings.
058	C13	058	69	The sample had poor agreement during the first analysis attempt, and was low/out of profile.
067	E14	067	133	Salinometer measurement was good, high salinity/out of profile cause unknown. Could be

				related to salt inserts (conclusion post discovery of the lid holes after CTD 083)
069	C01	069	133	High salinity, cause unknown. Sample was run twice due to instability second reading was stable (but high compared to the rest of the profile and CTD salinity). Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
073	E11	073	133	Salinometer measurement was good. Results is low/out of profile. Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
074	M12	074	133	The sample analysed poorly on the first attempt and well on the second attempt, but the value is high/out of profile. Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
077	G15	077	133	Salinometer measurement was good. Results is low/out of profile. Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
078	M23	078	69	The sample analysed poorly and took 4 tries. Consensus was reached finally but there were significant differences between readings.
078	M18	078	133	The sample analysed poorly and took 3 tries. Consensus was reached but high compared to the CTD profile. Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
079	A23	079	133	Low/out of profile, sample ran poorly (three attempts). Could be related to salt inserts (conclusion post discovery of the lid holes on CTD 083)
083	M17	083	133	Analysed poorly. A hole was found in one insert from this CTD, not confirmed to be from this sample, but likely was from this sample based on the cluster of recent 'off' samples
086	C12	086	113	High salinity caused by small slit in insert.
087	J14	087	133	High salinity caused by small slit in insert.
101	M16	101	69	Sample analysed poorly on 1st attempt. High/ out of profile (not caused by hole in insert)
102	B20	201	133	High/ out of profile, potentially a misfire, suspect nutrient results also

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)	Stephen Tibben & Kendall Sherrin
Lab Temperature (±1°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

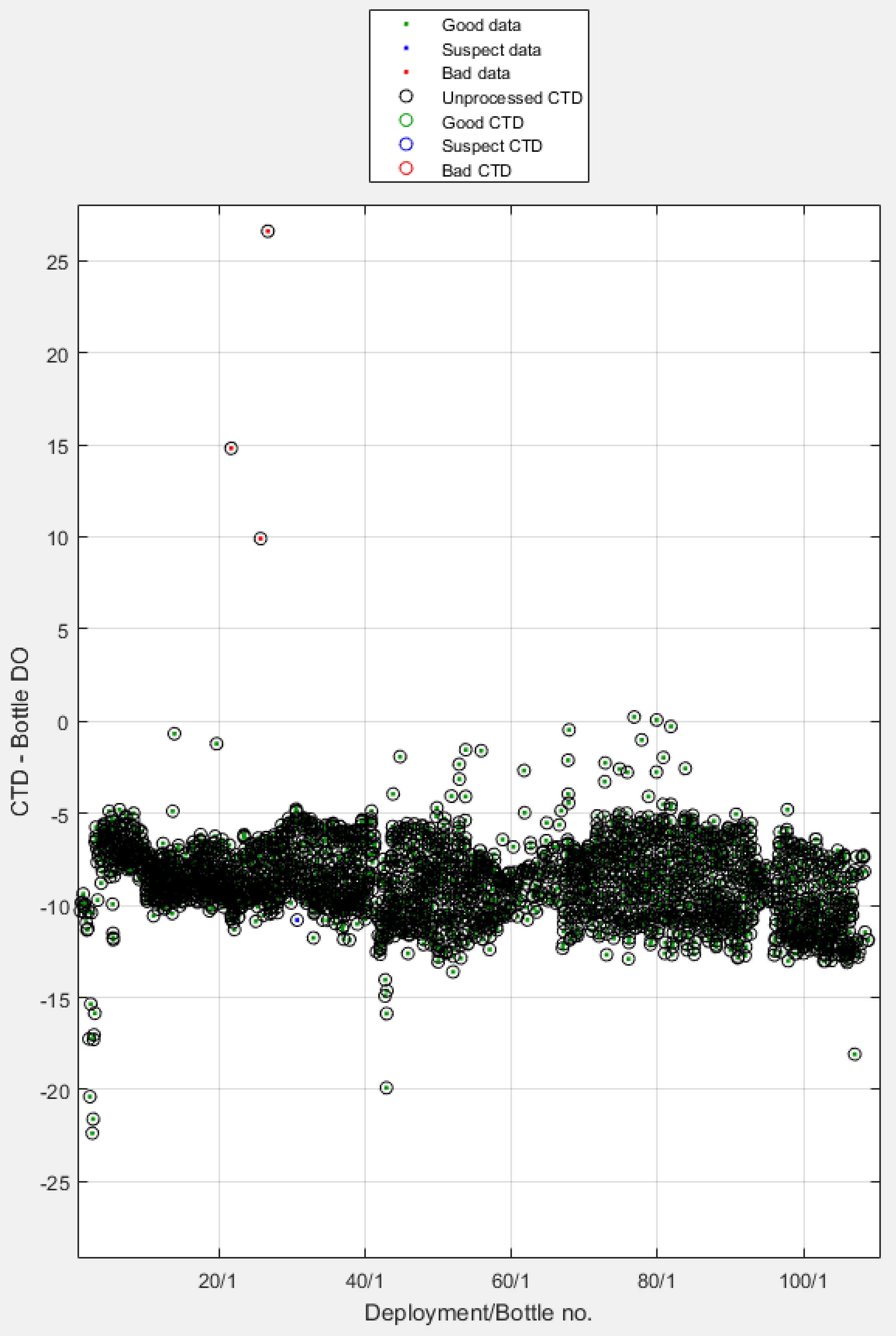
6.2 Dissolved Oxygen Method

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

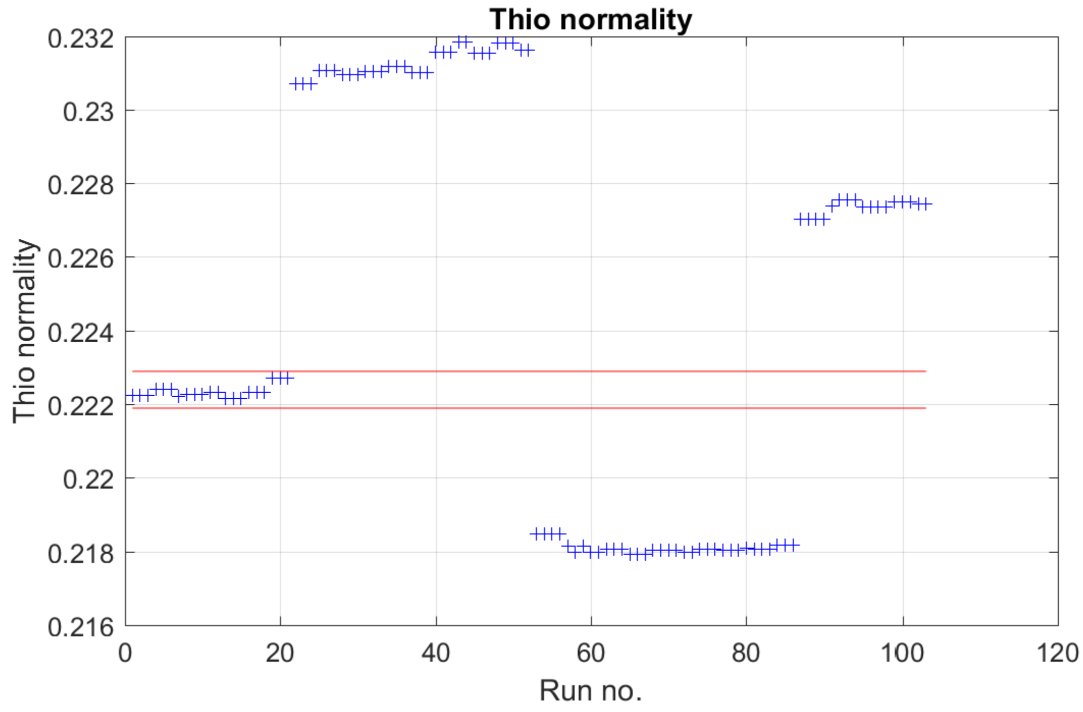
Manganese chloride followed by alkaline iodide, is added to the sample, and the precipitated manganous hydroxide is distributed evenly throughout the bottle by shaking. At this stage, the dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV). Just before titration, the sample is acidified, 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.

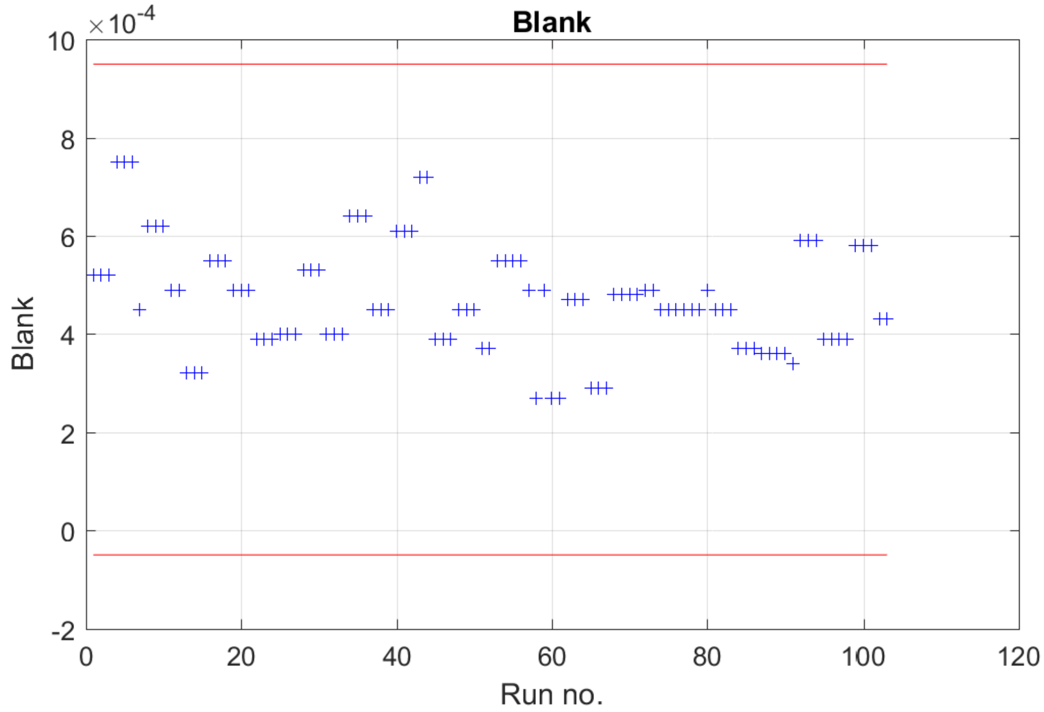
The thiosulphate solution is standardised by titrating a 10ml aliquot of potassium iodate primary standard. The blank correction is determined from the difference between two consecutive titres for 1 ml aliquots of the same potassium iodate solution.

6.3 CTD Dissolved Oxygen vs Hydrochemistry Dissolved Oxygen Plot



6.4 Dissolved Oxygen thiosulphate normality and blanks across voyage





6.5 Missing or Flagged 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
21	01	oxy020	141	Titrated sample with lamp off
21	24	oxy020	133	Outlier in vertical profile plot
23	24	oxy022	133	Outlier in vertical profile plot
25	25	oxy024	133	Outlier in vertical profile plot
25	29	oxy024	133	Outlier in vertical profile plot
97	4	oxy092	133	Titration end point bad, outlier in vertical profile plot
97	6	oxy092	133	Instrument failure. Burette dispensed air.
102	20	oxy097	133	Outlier in vertical profile plot

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	☒ Silicate	☒ Phosphate	☒ Nitrate + Nitrite	☒ Nitrite	☒ Ammonia
Concentration range	140 µmol l^{-1}	3 µmol l^{-1}	42.0 µmol l^{-1}	1.4 µmol l^{-1}	2.0 µmol l^{-1}
Method Detection Limit* (MDL)	0.2 µmol l^{-1}	0.02 µmol l^{-1}	0.02 µmol l^{-1}	0.02 µmol l^{-1}	0.02 µmol l^{-1}
Matrix Corrections	N	N	N	N	N
Analyst(s)	Christine Rees, Kendall Sherrin, Stephen Tibben				
Lab Temperature (±1°C)	Variable, 19.0 – 22.0°C				
Reference Material	RMNS – CC, CB, CD				
Sampling Container type	50 ml HDPE screw cap lids for CTD samples 30 ml polypropylene sample tubes for experimental samples 10 ml polypropylene sample tubes for underway samples				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
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 (NOx), 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 molybate. 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-naphthly-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-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.

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 7.8 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	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol 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
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 7.8. 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 lots CB, CC and CD were used. Their stated values in µ mol/kg are converted to µ mol l^{-1} at 21°C and are listed below. RMNS do not have certified ammonium values.

Table 1: RMNS CB, CC and CD concentrations with expanded uncertainty (µmol/L) at 21°C

RMNS	NO_3	NO_X	NO_2	PO_4	SiO_4
CB	36.65 ±0.28	36.77 ±0.28	0.119 ±0.006	2.58 ±0.02	111.82 ±0.64
CC	31.62 ± 0.25	31.74 ± 0.25	0.119 ± 0.006	2.13 ± 0.02	88.23 ± 0.49
CD	5.63 ± 0.05	5.65 ± 0.06	0.018 ± 0.005	0.46 ± 0.008	14.26 ± 0.10

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

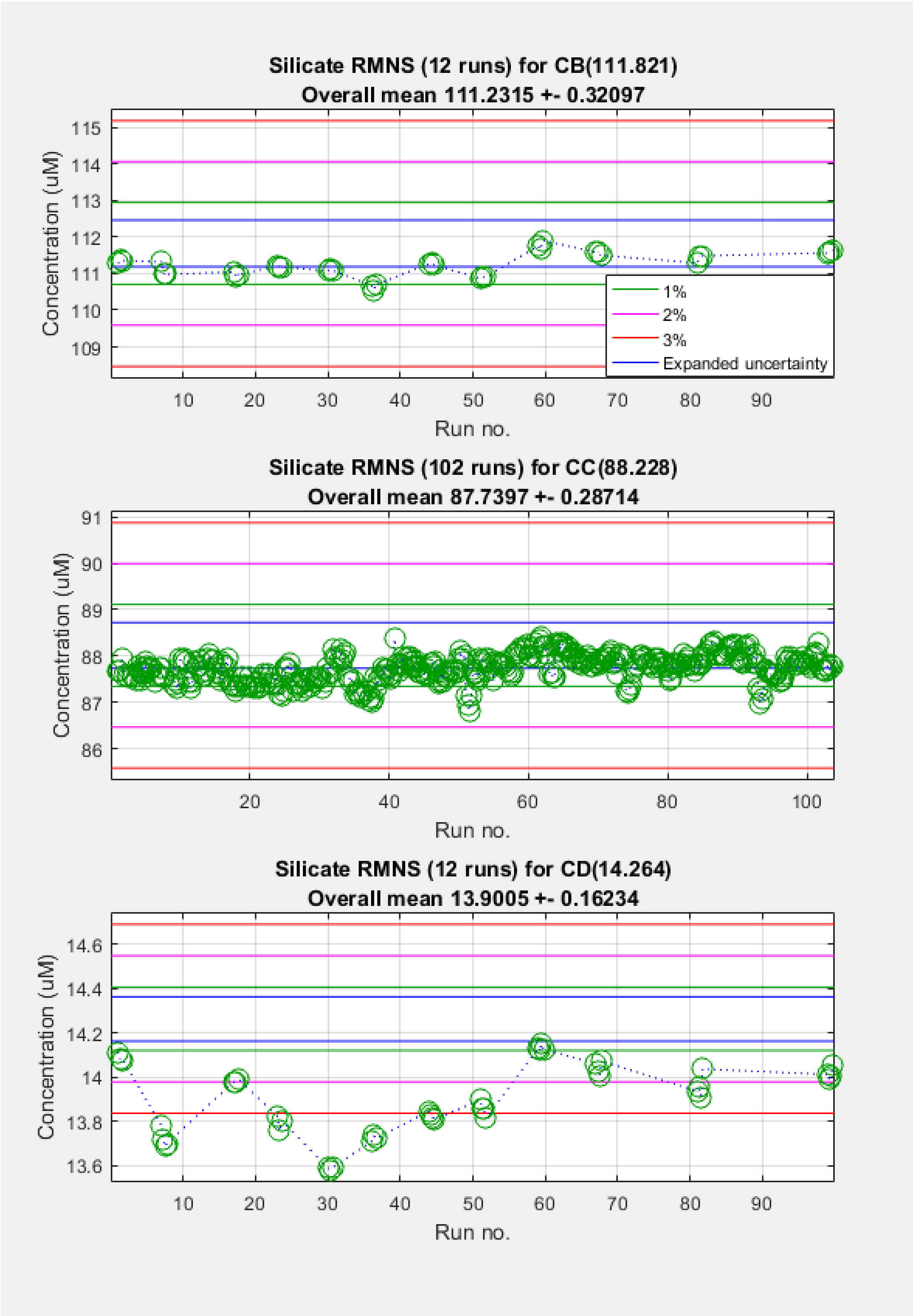
Or for smoothing data

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 ±0.020 µM (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.

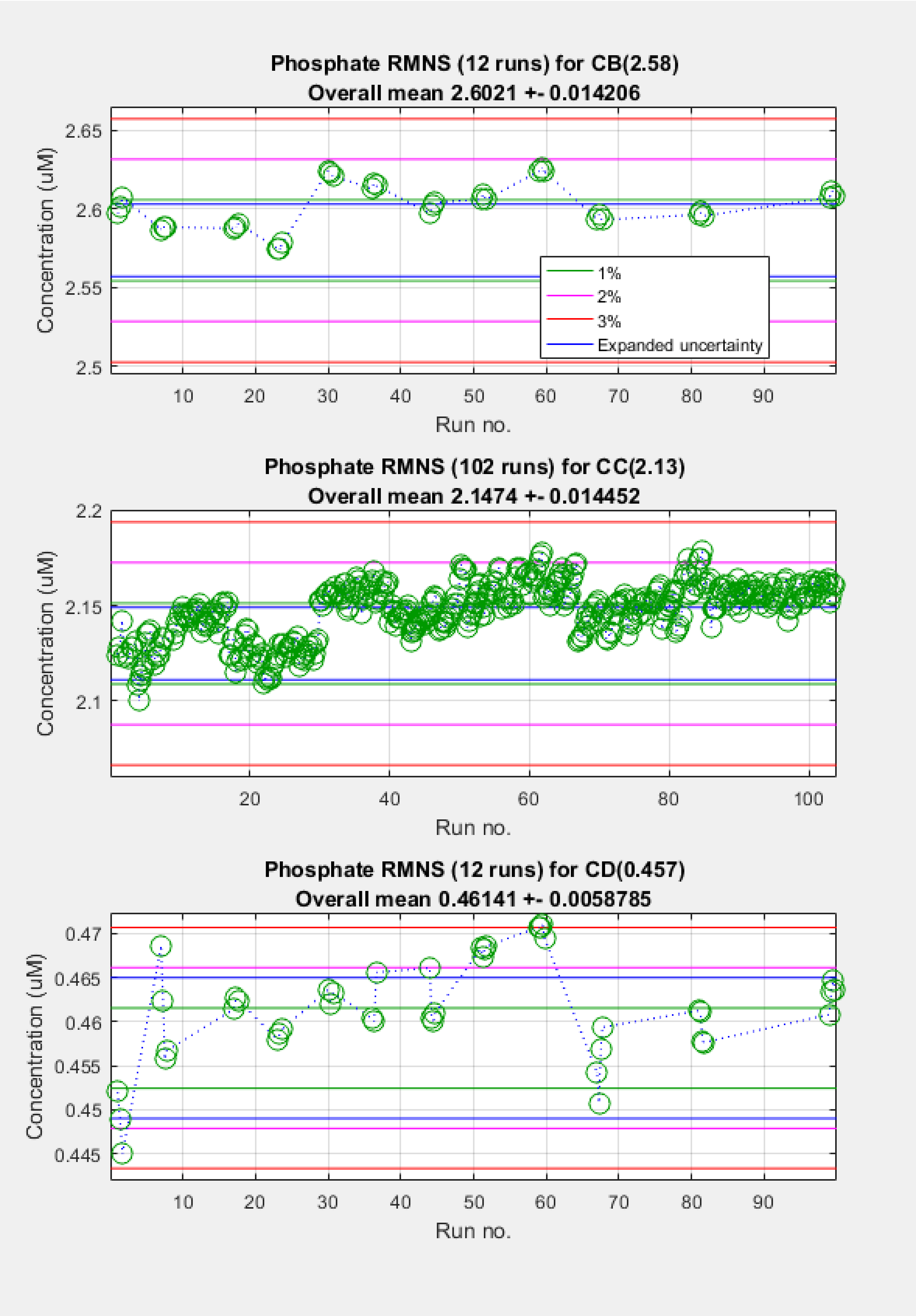
7.4.1 Silicate RMNS Plot

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



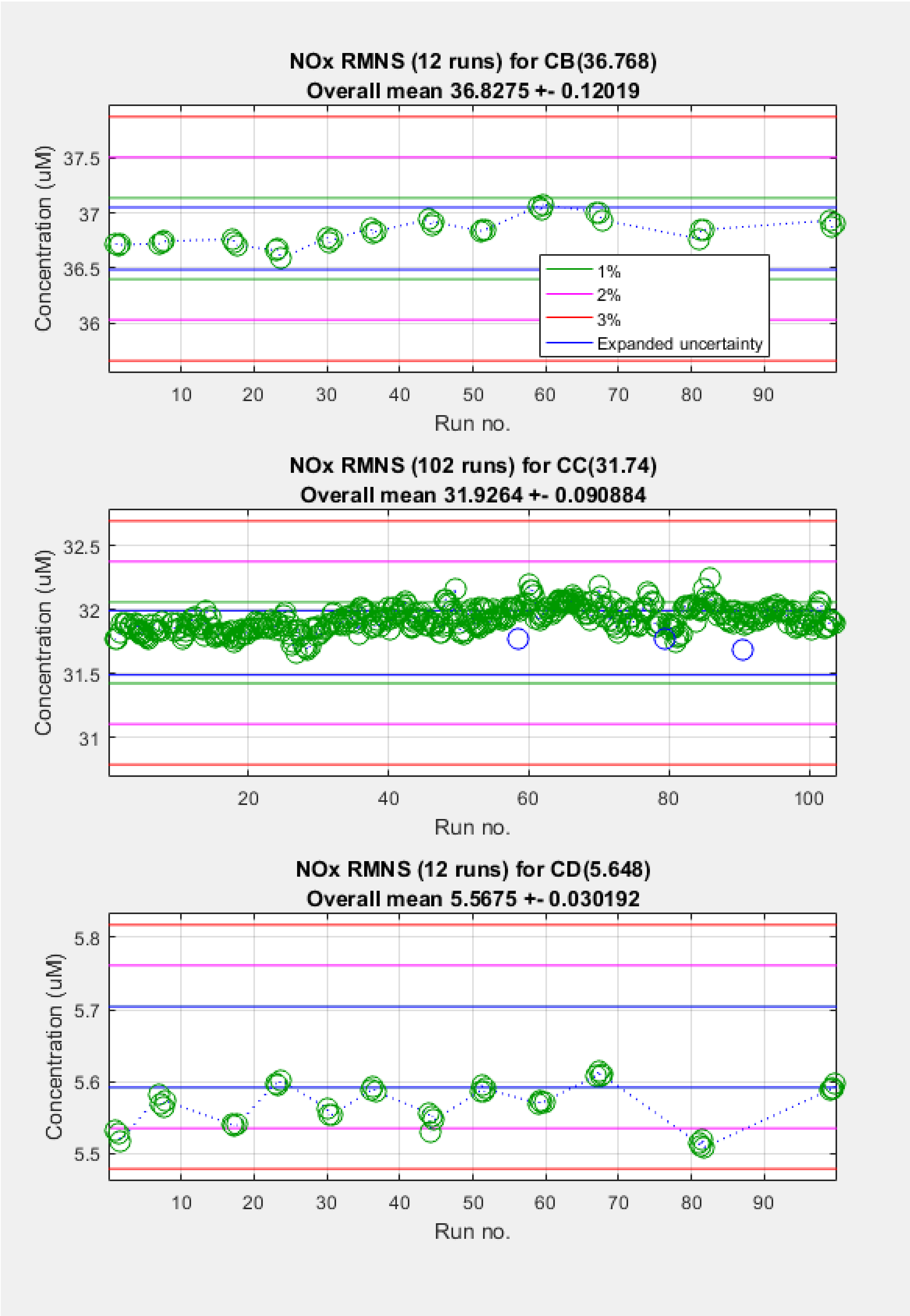
7.4.2 Phosphate RMNS Plot

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

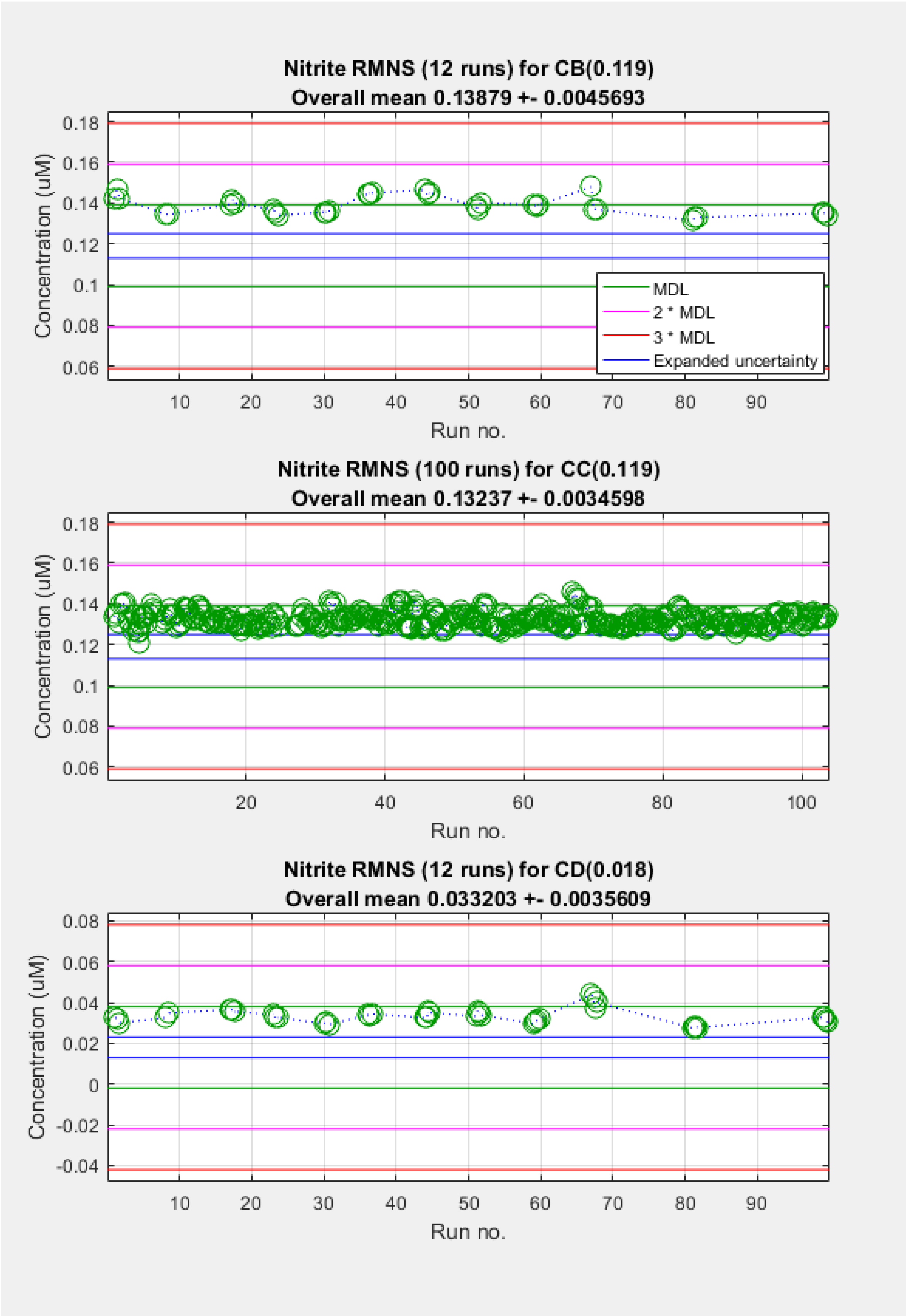


7.4.3 Nitrate + Nitrite (NOx) RMNS Plot

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



7.4.4 Nitrite RMNS Plot



7.5 Internal Quality Control

The internal quality control samples were prepared on the 28/9/2017 by filtering more than 2 litres of low nutrients seawater (LNSW) from a carboy through a 0.2 µM Acropak filter into HDPE square 1L bottles and then autoclaving.

A LNSW control was prepared to account for any nutrients already in the LNSW and also any nutrients picked up in the autoclaving. The autoclaved LNSW was well mixed and poured into an acid cleaned and dry HDPE square 1L bottle and lid screwed shut and wrapped with parafilm around the lid and stored at 4°C.

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

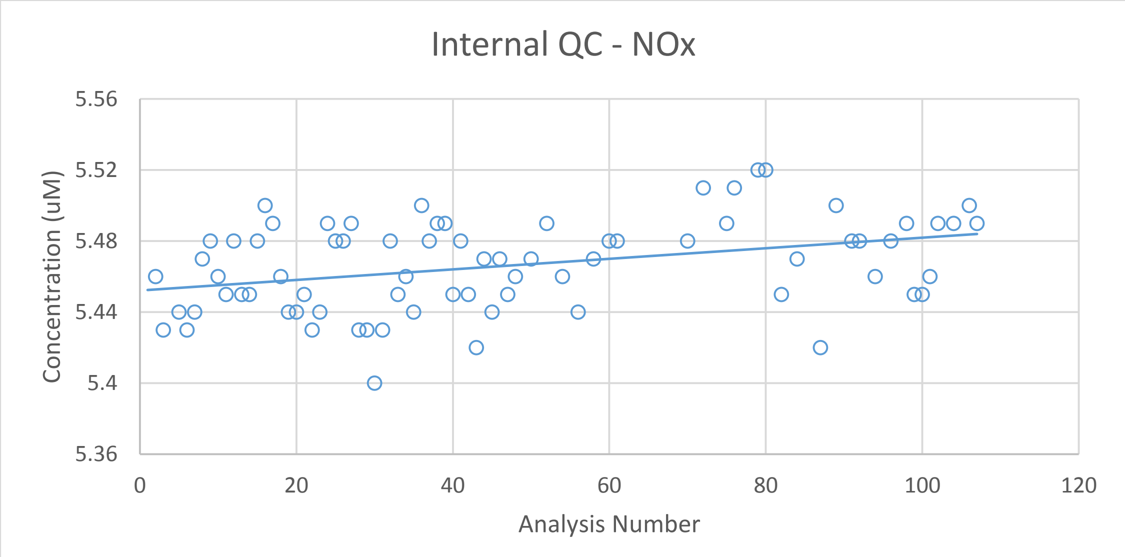
10 ml of silicate 1000 µmol/L = 10 µM

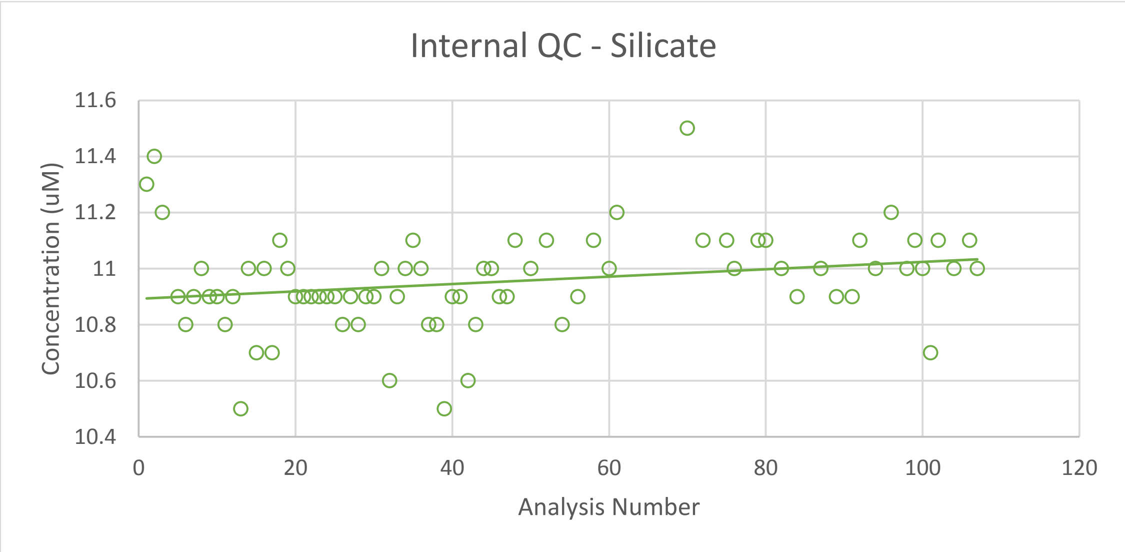
5 ml of nitrite 100 µmol/L = 0.5 µM

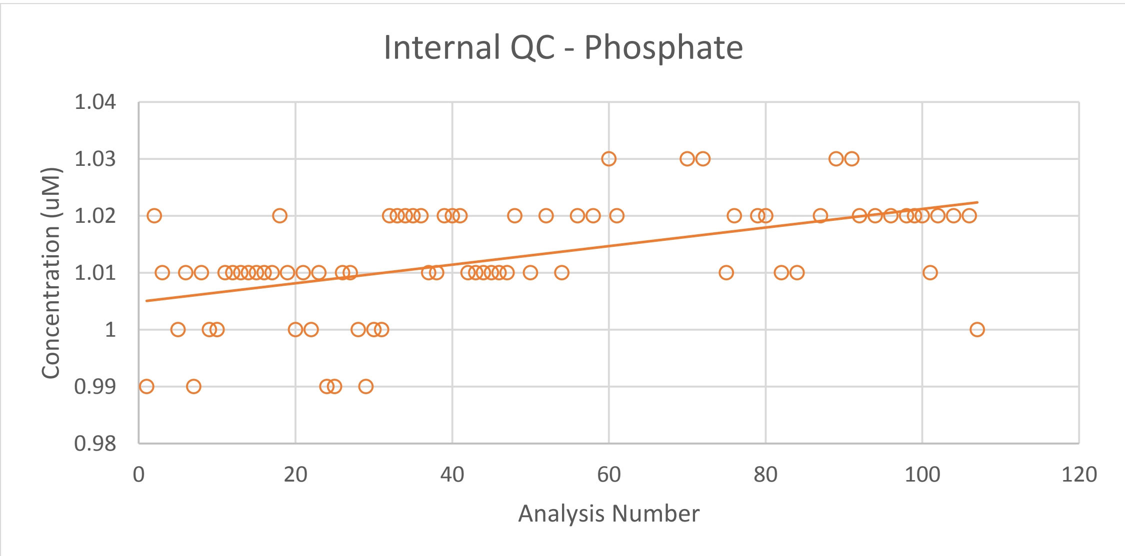
0.1 ml of ammonium 10,000 = 1µM

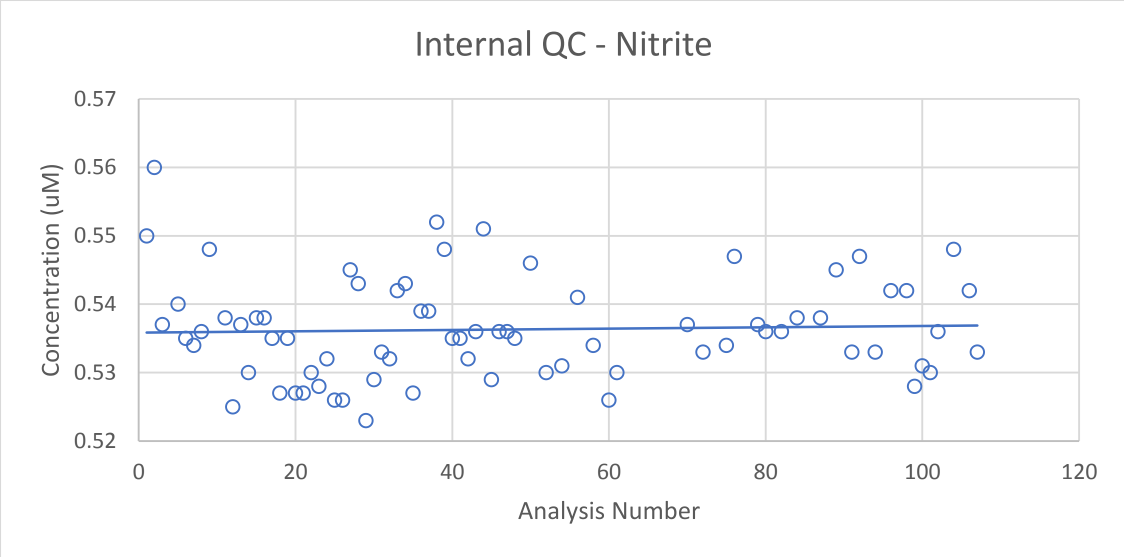
The flask was then made to volume with the autoclaved LNSW. It was mixed well and poured into an acid-cleaned and dry HDPE square 1L bottle with the lid screwed shut and parafilm wrapped around the lid and stored at 4°C.

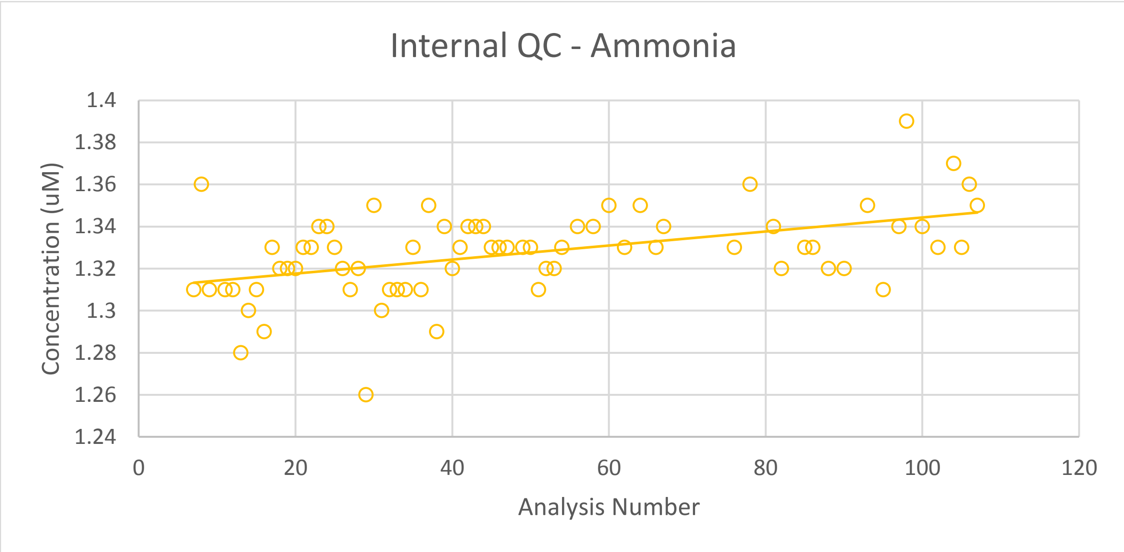
An initial measurement was made in October 2017 and another measurement was made in December 2017. It was determined that the standards were stable to be used on the voyage. The internal QC's were decanted into a number of 10 ml polypropylene screw lid sample tubes on three separate occasions and stored at 4°C. A sample tube of the control and the spike were analysed with the CTD samples, due to limited volume not all analytical runs contained an internal quality control.


Internal QC - NOx
Concentration (uM)
5.56
5.52
5.48
5.44
5.4
5.36
0
20
40
60
80
100
120
Analysis Number


Internal QC - Silicate
Concentration (uM)
11.6
11.4
11.2
11
10.8
10.6
10.4
0
20
40
60
80
100
120
Analysis Number


Internal QC - Phosphate
Concentration (uM)
1.04
1.03
1.02
1.01
1
0.99
0.98
0
20
40
60
80
100
120
Analysis Number





7.6 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 RMNS over time (Armishaw 2003).

	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Calculated MU* @ 1 µmol l^{-1}	±0.017	±0.024	±0.019	±0.137	±0.296[¥]

*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.

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 µmol l^{-1}.

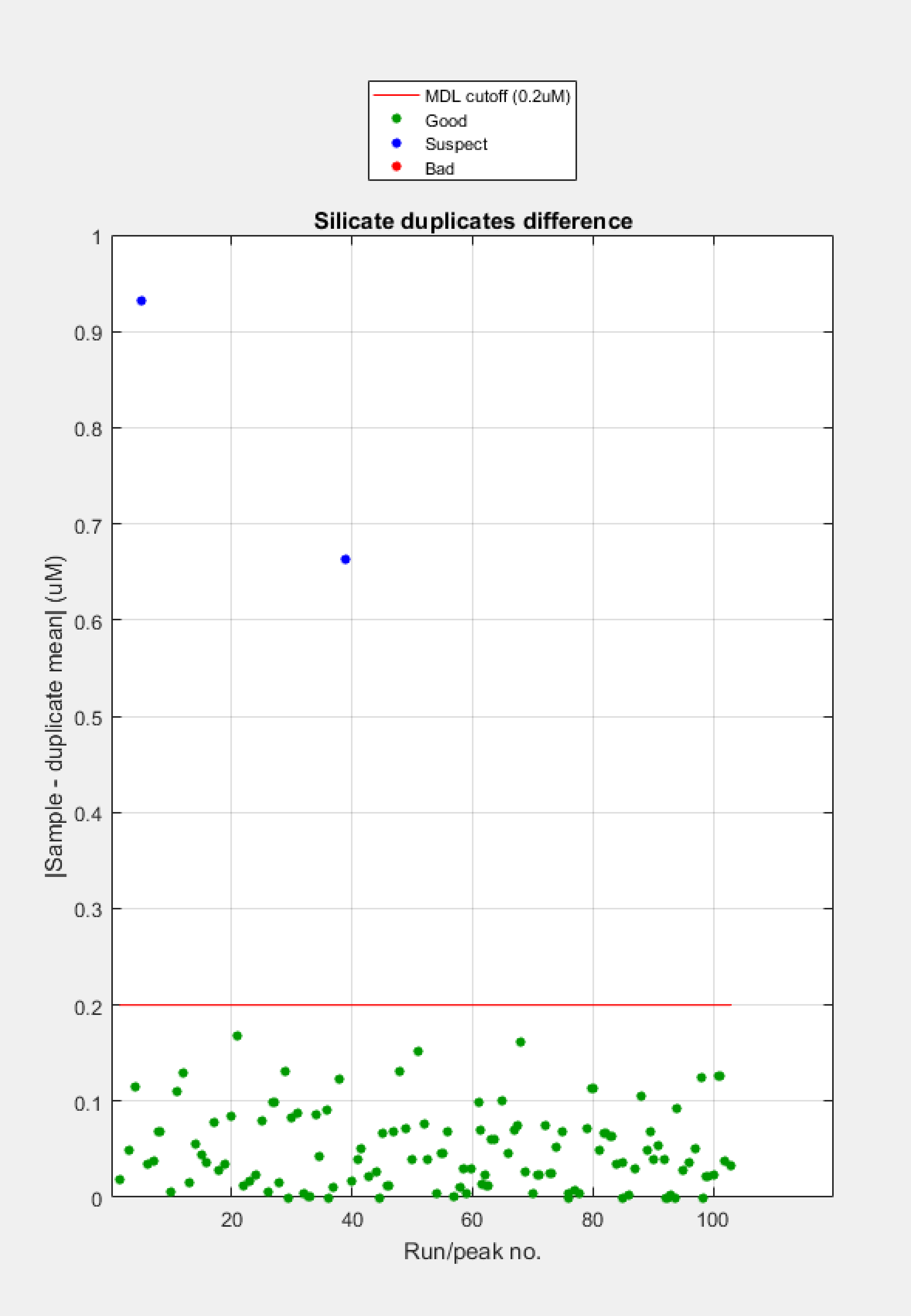
MDL	**Silicate**	**Phosphate**	**Nitrate + Nitrite (NOx)**	**Nitrite**	**Ammonia**
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Standard Dev. Min	0.00	0.00	0.00	0.000	0.00
Standard Dev. Max	0.057	0.010	0.0057	0.0040	0.0057
Standard Dev. Mean	**0.023**	**0.003**	**0.0053**	**0.0010**	**0.0007**
Standard Dev. Median	0.00	0.005	0.00	0.0005	0.00
Precision of MDL (stdev)	0.186	0.012	0.012	0.004	0.030
*MDL is based on 3 times the standard deviation of Low Nutrient Seawater (LNSW) analysed in each nutrient run.					
Published RMNS CD (µmol l^{-1})	14.26	0.46	5.65	0.018	-
w/std deviation	± 0.009	± 0.001	± 0.004	± 0.001	-
RMNS Min	13.6	0.44	5.51	0.028	1.43
RMNS Max	14.2	0.47	5.61	0.044	1.91
RMNS Mean	13.90	0.46	5.56	0.033	1.61
RMNS Median	13.90	0.46	5.57	0.033	1.56
RMNS Std Dev	0.16	0.006	0.03	0.003	0.14
Published RMNS CC (µmol l^{-1})	88.23	2.13	31.74	0.119	-
w/std deviation	± 0.053	± 0.005	± 0.029	± 0.002	-
RMNS Min	86.8	2.10	31.67	0.121	1.22
RMNS Max	88.5	2.18	32.45	0.141	2.35
RMNS Mean	87.74	2.14	31.92	0.132	1.60
RMNS Median	87.8	2.15	31.92	0.130	1.60
RMNS Std Dev	0.29	0.01	0.095	0.003	0.19

Published RMNS CB (μmol l^{-1})	111.82	2.58	36.768	0.119	-
w/std deviation	± 0.053	± 0.004	± 0.020	± 0.002	-
RMNS Min	110.5	2.57	36.59	0.131	1.16
RMNS Max	111.9	2.63	37.08	0.147	1.66
RMNS Mean	111.24	2.60	36.82	0.138	1.39
RMNS Median	111.25	2.60	36.83	0.138	1.38
RMNS Std Dev	0.32	0.01	0.12	0.004	0.13

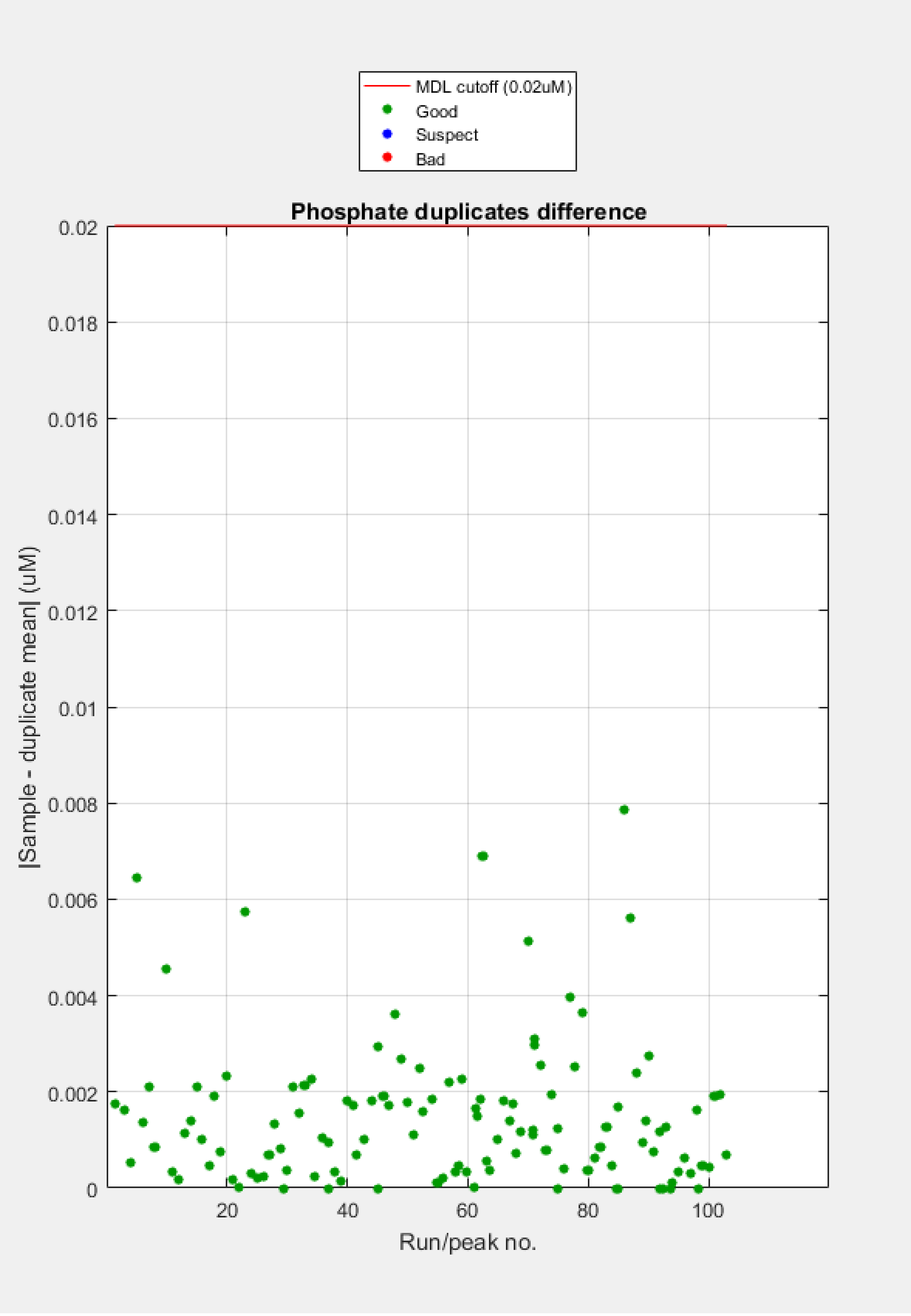
7.7 Sampling Precision

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.

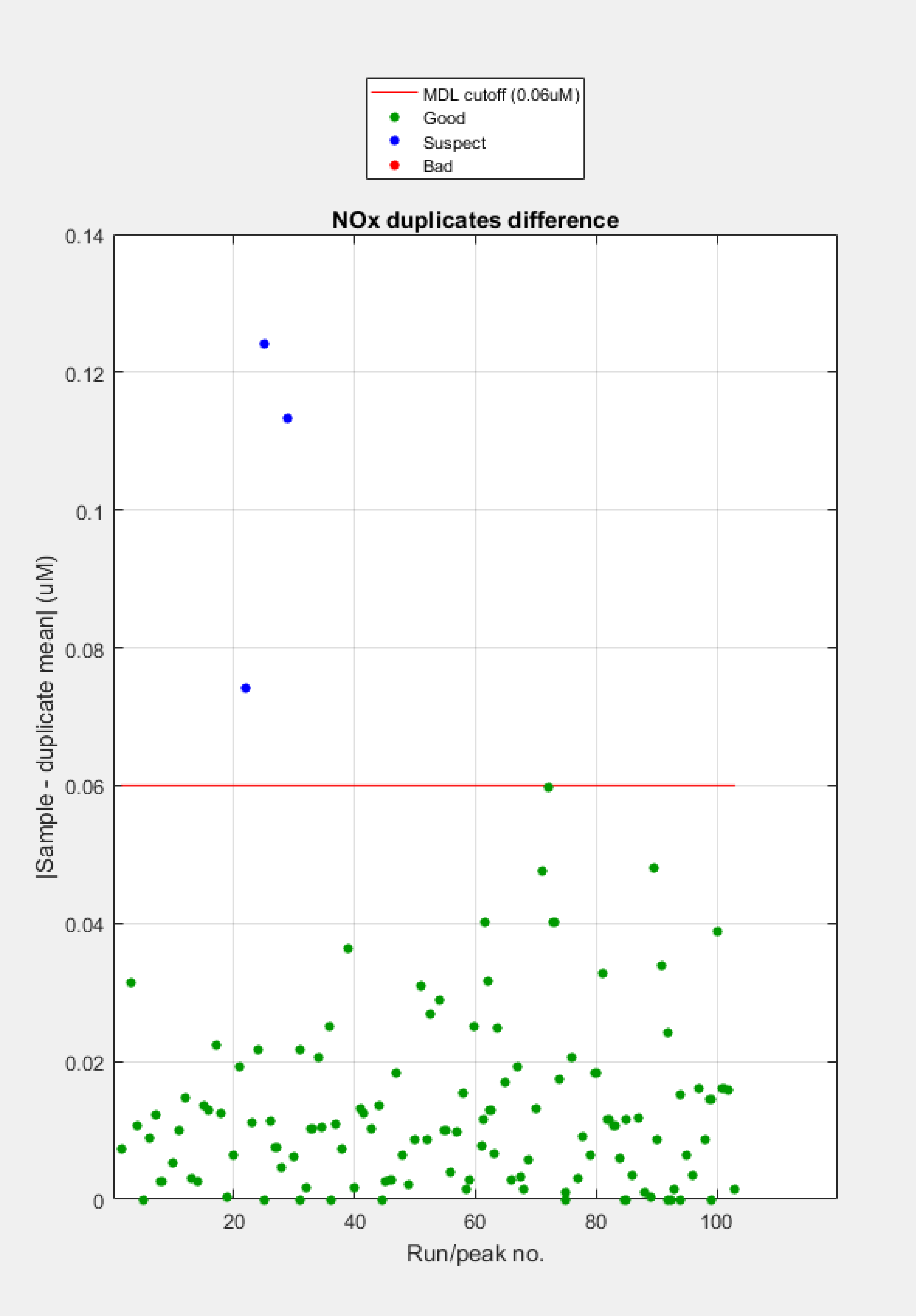
7.7.1 Silicate Duplicate/Replicates Plot



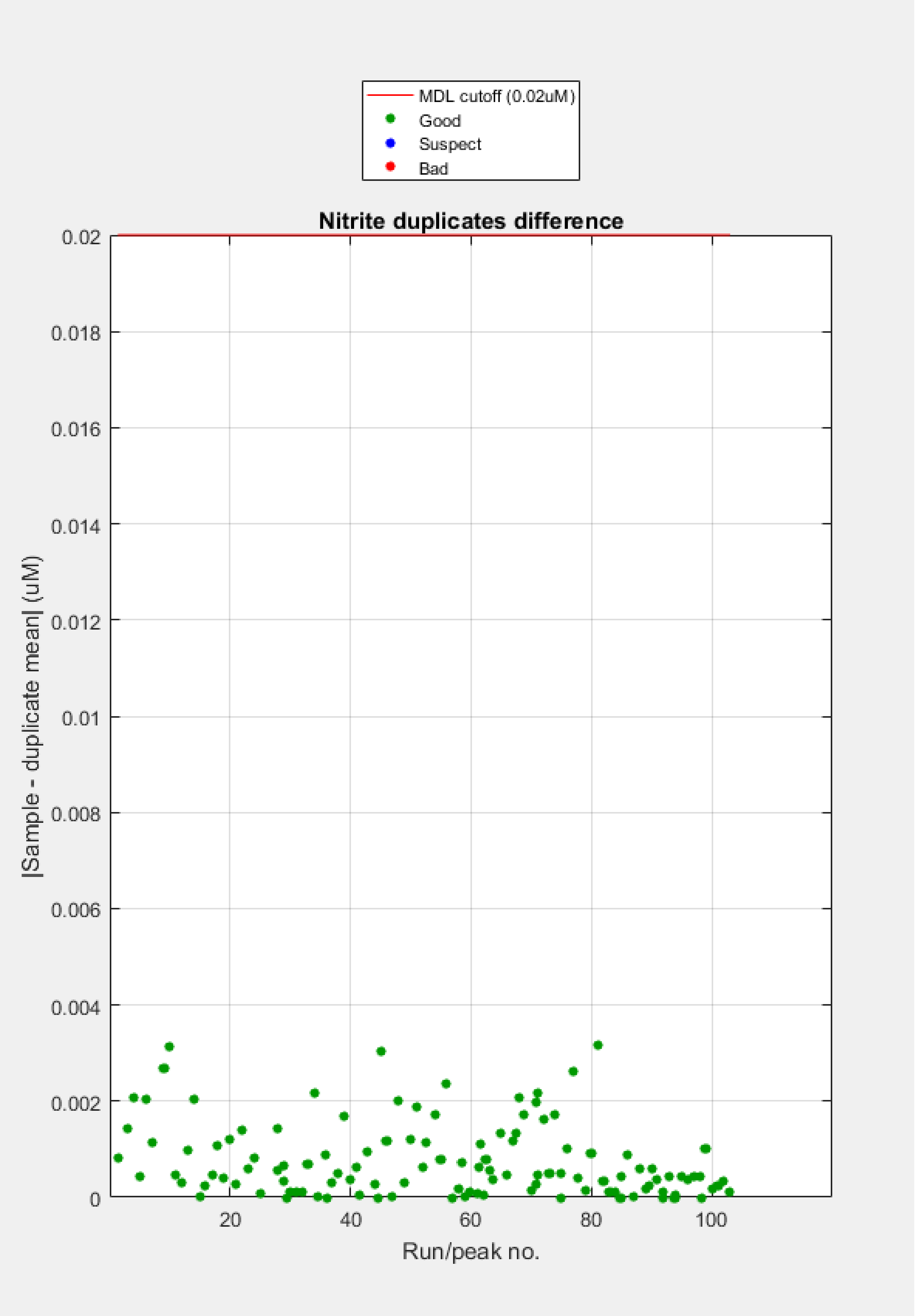
7.7.2 Phosphate Duplicate/Replicates Plot



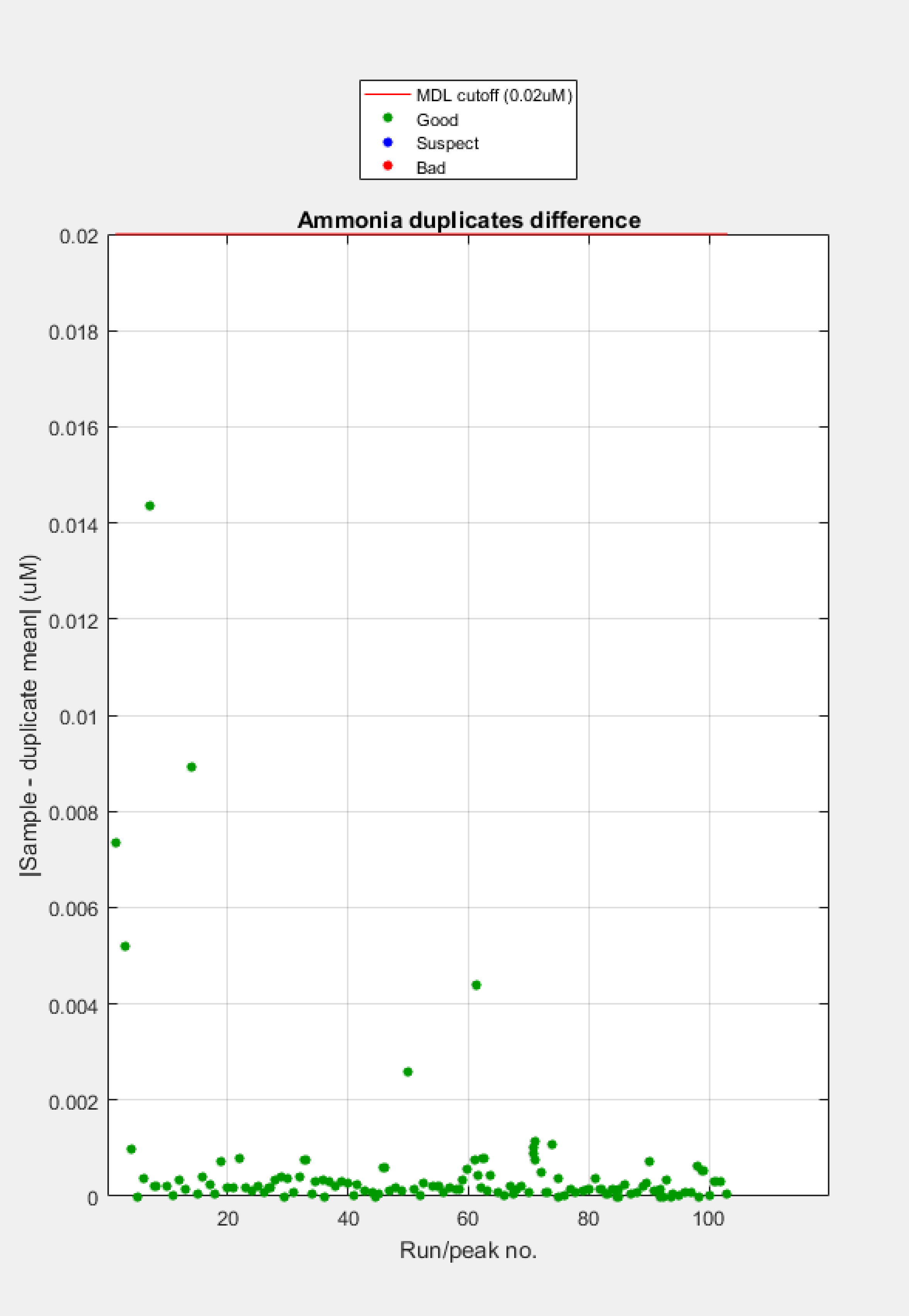
7.7.3 Nitrate + Nitrite (NOx) Duplicate/Replicates Plot



7.7.4 Nitrite Duplicate/Replicates Plot

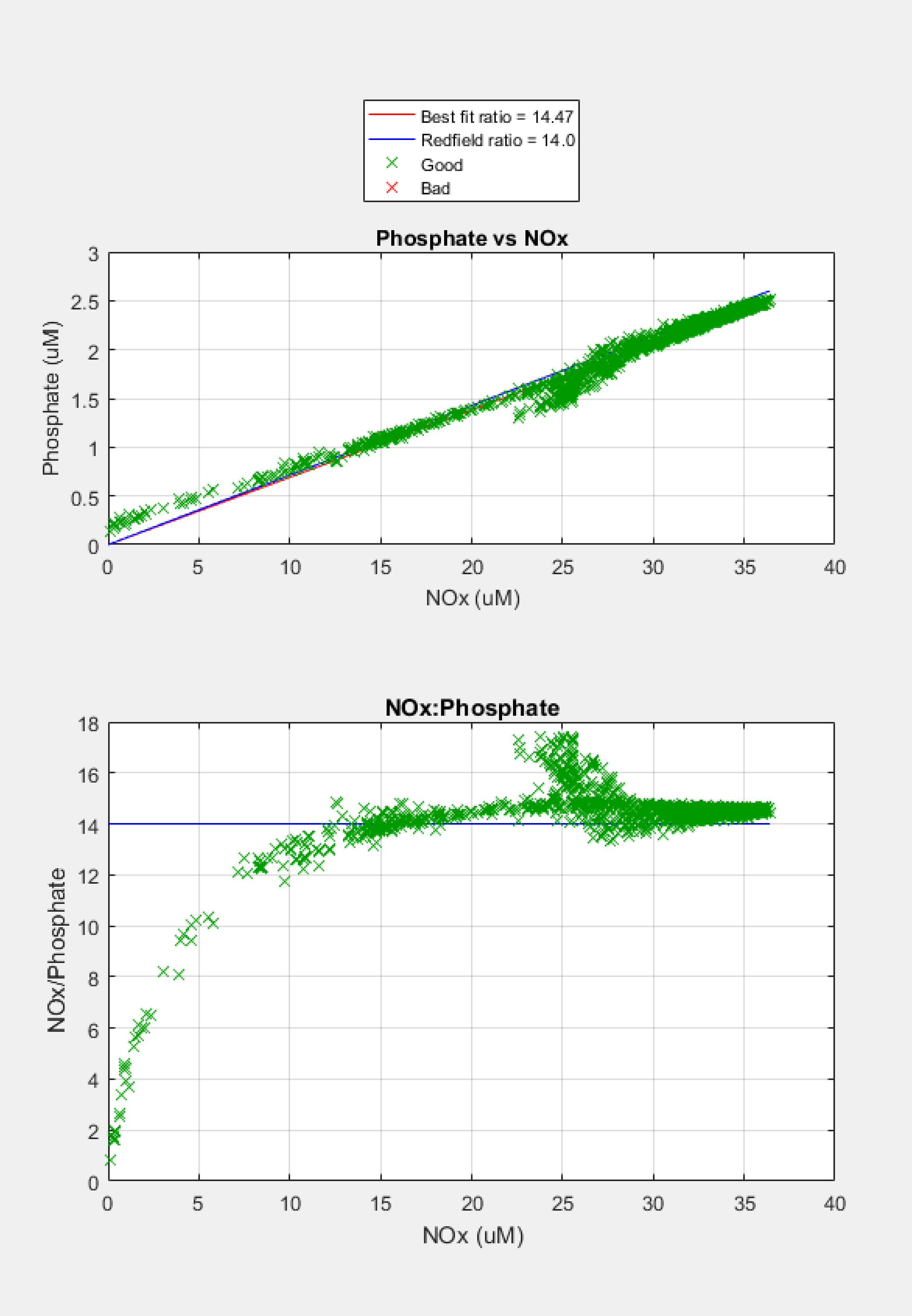


7.7.5 Ammonia Duplicate/Replicates Plot



7.7.6 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx, best fit ratio = 14.47.



7.8 Flagged 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

- ±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.
1	BQC	Nut001	All	Suspect (MAD) peak shape, placed test in front so not to be used in calculations.
3	Cal 4	Nut002	NH4	Both points BAD as greater than calibration error, not used in calibration.
4	BQC	Nut003	SiO2	3rd point flagged BAD (soft), large error compared to other 2 points.
5	Cal 2	Nut004	PO4	2nd Point suspect less weighting in calibration curve.
5	Cal 2&4	Nut004	NH4	<70% of calibration peaks are within calibration limits. Cal 2 & 4 suspect less weighting in calibration curve.
5	Duplicate RP02	Nut004	SiO2	Suspect, duplicate difference >0.2 µM. [First peak (lower concentration) is noisier than second].
5	Duplicate	Nut004	NOx	Second sample flagged as BAD (mad) peak shape. Duplicates much greater than 0.06 µM, due to bad peak shape exceed A/D value, peak window on side of peak.
5	Duplicate	Nut004	NH4	First sample flagged as BAD (op) peak window slipped down side of peak.
6	Cal 3&4	Nut005	NH4	<70% of calibration peaks are within calibration limits. Cal 3 & 4 suspect less weighting in calibration curve.
7	Cal 4	Nut006	NH4	Cal 4 both points suspect, less weighting in calibration curve.
8		Nut007	NO2	Base off set was higher than normal all results looked too high. Re-run samples for NO2 only in Nut008, results good. Also No High low sample for analysis Nut008 due to running out of volume. Hypro used previous high low measurement.
8	CC RMNS	Nut007	PO4	1st point suspect, greater than 2%
8	CD RMNS	Nut007	SiO2	All points greater than 3%
9	Cal 3	Nut009	NH4	Both points BAD as greater than calibration error, not used in calibration.
10	Cal 2 & 3	Nut010	NH4	Cal 2 1st point and cal 3 both points suspect less weighting in calibration curve.
11	Cal 3	Nut011	NH4	Both points BAD as greater than calibration error, not used in calibration.
12	Cal 3	Nut012	NH4	Both points BAD as greater than calibration error, not used in calibration.
16	Cal 5&6	Nut016	NOx	2nd points suspect, less weighting in calibration curve.
19	Cal 5	Nut019	NH4	Both points BAD greater than calibration error, not used in calibration.
21	Duplicate RP01	Nut021	NOx	Suspect, duplicate difference greater than 0.06 µM
22	CD RMNS	Nut022	SiO2	All points greater than 3%

24	Duplicate RP01	Nut024	NOx	First duplicate Suspect (MAD) peak shape.
25	All	Nut025	NO2	Bad data, hashed out of file, re-run in nut027, processed as nut027b
26	All	Nut026	NO2	Bad data, hashed out of file, re-run in nut028, processed as nut028b
26	Cal 4	Nut026	NH4	1st point suspect, less weighting in calibration curve.
28	Duplicates RP01	Nut028	NOx	Suspect, duplicate difference greater than 0.06 µM.
30	Cal 2,3 & 4	Nut030	NH4	Cal 2 suspect (both points), Cal 3 suspect (2nd point)- less weighting in calibration curve. Cal 4 BAD both points – not used in calibration.
30	CD RMNS	Nut030	SiO2	All points greater than 3%.
32	Cal 3	Nut032	NH4	Cal 3 suspect, less weighting in calibration curve.
35	Cal 2	Nut035	NOx	Cal 2, 1st point suspect, less weighting in calibration curve.
38	Duplicates RP01	Nut038	SiO2	Suspect duplicate difference greater than 0.2 µM.
42	Cal 2	Nut042	NOx	Cal 2 suspect, less weighting in calibration curve.
43	Cal 2	Nut043	NOx	Cal 2 suspect, less weighting in calibration curve.
44	Cal 2	Nut044	NOx	Cal 2 suspect, less weighting in calibration curve.
45	Cal 2	Nut045	NOx	Cal 2 suspect, less weighting in calibration curve.
45	Cal 6	Nut045	SiO2	Cal 6 2nd point greater than calibration error.
48	Cal 3	Nut048	NH4	Cal 3 2nd point suspect, less weighting in calibration curve.
51	Cal 2	Nut051	PO4	Cal 2 1st point suspect, less weighting in calibration curve.
52	Cal 2	Nut052	PO4	Cal 2 1st point suspect, less weighting in calibration curve.
54	Cal 5	Nut054	PO4	Cal 5 2st point suspect, less weighting in calibration curve.
54	BQC	Nut054	SiO2	1st point Suspect (MAD) peak shape.
54	Cal 4	Nut054	NH4	Cal 4 both points suspect, less weighting in calibration curve.
54	Drift	Nut052	NO2	Last drift has large spike in plateau, swapped the drift and drift sample check peaks around.
55	Cal 4	Nut055	NH4	Cal 4 both points suspect, less weighting in calibration curve.
56	Cal 4	Nut056	NH4	Cal 4 1st point suspect, less weighting in calibration curve.
58	RMNS	Nut058	NOx	2nd last RMNS peak is suspect (mad) peak shape.

61	Drift	Nut060	NOx	Last drift has large spike in plateau, swapped the drift and drift sample check peaks around.
70	Baseline	Nut066	NO2	Baseline stepped up on the Null before the BQC samples and then stepped down again on the uwy sample. # out all of those samples and stds etc. #peak start of No2 and it didn't work, had to # the AD value column.
70	Drift	Nut066	NO2	2nd Drift is BAD. Baseline stepped up on the Null before the BQC samples and then stepped down again on the uwy and ctd samples. # out all of the BQC and drift stds. All samples good.
71, 72	Cal 3	Nut067	NH4	Cal 3 both points suspect (MAD), less weighting in calibration curve.
75	Duplicates RP01	Nut070	NOx & SiO2	Bad peak shapes, re-ran samples at end of the run and they were OK.
76	Cal 6	Nut071	NOx	Cal 6 2nd point was flagged Bad (MAD) peak shape, not used in calibration.
78	Cal 2	Nut073	NO2	Cal 2 2nd point BAD greater than calibration error.
80	Cal 1	Nut075	NH4	Cal 1 2nd point suspect, less weighting in calibration curve.
81	Cal 1 & Cal 3	Nut076	NH4	Cal 1 both points suspect and Cal 3 1st point suspect, greater than calibration error.
82	Cal 1 & Cal 3	Nut077	NH4	Cal 1 both points suspect and Cal 3 1st point suspect, less weighting in calibration curve.
83	Cal 3	Nut078	NH4	Cal 3 both points suspect, less weighting in calibration curve.
84	Cal4 & 5	Nut079	NOx	Blockage occurred during the cals (cal 4-2 and 5-1 bad, rest perfect), this offset the timing, meaning the peaks were shifted. This only really affected the carryover (use from last run) and the first two RMNS (hashed out).... RMNS values good on peaks that are good. Magical. Second MDL also hashed out - the rest are good.
85	Cal 3	Nut080	NH4	Cal 3 both points Bad greater than calibration error.
86	RMNS	Nut081	SiO2	RMNS CD, 1 point flagged suspect outside of 3% line
87	Cal 3 & Cal 4	Nut082	NH4	Cal 3 2nd point and Cal 4 both points suspect greater than calibration error.
87	Cal 2	Nut082	NOx	Cal 2 both points suspect, less weighting in calibration curve.
88	Cal 4	Nut083	NH4	Cal 4 both points suspect, less weighting in calibration curve.
88	Cal 2	Nut083	NOx	Cal 2 both points suspect, less weighting in calibration curve.
89	Cal 2	Nut084	NOx	Cal 2 both points suspect, less weighting in calibration curve.

89	Cal 5	Nut084	NOx	Cal 5 2nd point suspect, less weighting in calibration curve.
89	Cal 3	Nut084	NH4	Cal 3 both points suspect, less weighting in calibration curve.
89	Cal 4	Nut084	NH4	Cal 4 both points suspect, less weighting in calibration curve.
90	Cal 2	Nut085	NOx	Cal 2 both points suspect, less weighting in calibration curve.
90	Cal 3	Nut085	NH4	Cal 3 both points suspect, less weighting in calibration curve.
91	Cal 3	Nut086	NH4	Cal 3 first point suspect, less weighting in calibration curve.
93	Cal 3	Nut088	NH4	Cal 3 both points are suspect, less weighting in calibration curve.
93	Cal 5	Nut088	NOx	Cal 5 2nd point suspect, less weighting in calibration curve.
94, 95	Cal 3	Nut089	NH4	Cal 3 first point suspect, less weighting in calibration curve.
96	Cal 3	Nut090	NOx	Cal 3 both points suspect greater than calibration error.
96	RMNS	Nut090	NOx	Fourth peak is suspect (mad) peak shape.
99	Cal 5	Nut093	NOx	Cal 5 2nd point suspect, less weighting in calibration curve.
100	Cal 2	Nut094	PO4	Cal 2 1st point suspect greater than calibration error.
101	Cal 5	nut095	NOx	Cal 5 1st point bad shape, 2nd point greater than calibration error.
102	Cal 6	Nut096	PO4	Cal 5 2nd point is suspect, less weighting in calibration curve.
uwy	Cal 1	Nut103	NH4	Cal 1 both points suspect, less weighting in calibration curve.

7.9 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
4	18	Nut003	All	133	Outliers on profiles, sampled from wrong Niskin.
5	02	Nut004	SiO2	69	Duplicates greater than MDL 0.2 [First peak (lower concentration) is noisier than second].
5	02	Nut004	NOx	129	Duplicates much greater than 0.06 µM, due to bad peak shape exceed A/D value, peak window on side of peak.
5	02	Nut004	PO4	133	BAD air spikes.
5	02	Nut004	NH4	133	First sample flagged as BAD peak window slipped down side of peak.
9	18	Nut009	NOx, PO4, SiO2	69	Outlier on profile [not seen on salinity or dissolved oxygen – same value as RP16, possible duplicate or sampled from wrong Niskin)
15	12	Nut012	SiO2, NO2	133	Outliers on profiles.
16	25	Nut016	All	141	Sample missing accidently not collected.
21	All	Nut021	NH4	N/A	Higher than usual background caused these samples to be slightly lower than expected, resulting in slightly negative values instead of 0. However results are good.
21	01	Nut021	NOx	69	Duplicates greater than 0.06 µM
21	24	Nut021	All	133	Outliers on profiles, Niskin misfire. Also seen in salinity data.
23	24	Nut023	All	133	Outliers on profiles, Niskin misfire. Also seen in salinity data.
24	01	Nut024	NOx	69	1st duplicate suspect peak shape.
25	All	Nut025	NO2	133	Bad data # out of file and re-run in nut027, processed as nut027b, this data is good.
25	25, 29	Nut025	All	133	Outliers on profiles, Niskin misfire. Also seen in salinity data.
26	29	Nut026	All	133	Outliers on profiles, Niskin misfire. Also seen in salinity data.
26	All	Nut026	NO2	N/A	The rmns, BQC and intQC all stepped up. The sample profiles were also offset from

					previous ctd profiles. CTD 25 & 26 were re-run for NO2 in the nut027b & nut028b. The initial NO2 results were # out of original files and second results used as they were good.
28	01	Nut028	NOx	69	Duplicates greater than 0.06 µM
28	29	Nut028	NOx	141	It's marked as Bad (soft) in trace. However error given in HyPro is exceeds A/D value 129, we do not have value for this one.
28	26, 27	Nut028	NOx	N/A	BAD peak shapes but were re-run at end of analysis and results OK.
29	21	Nut029	NOx	133	Bad peak shape, repeated in nut030 and result good. The repeated measurement for other nutrient data was # out of file as original results were good.
36	33	Nut036	PO4	133	Bad peak shape repeated in nut037 and result is good. The repeated measurement for other nutrient data was # out of file as original results were good.
38	01	Nut038	SiO2	69	Duplicates greater than 0.2 µM
44	23	Nut044	PO4	133	Bad peak shape repeated in nut045, and result is good. The repeated measurement for other nutrient data was # out of file as original results were good.
49	17	Nut49	NO2	69	Outlier on profile, bump on peak plateau.
56	All	Nut056	NO2	133/141	Nitrite baseline stepped up on sample 5627 and 5625, then stepped back down on 5624 and 5623 but then stepped back up on 5622 and stayed elevated. Drifts are also elevated and end baselines. Flagged all data for NO2 as bad.
75	02	Nut070	SiO4	133	Bad peak shape, repeated during run and result is OK, # out bad results.
75	02	Nut070	NOx	133	Bad peak shape, repeated during run and result is OK, # out bad results.
79	08	Nut074	SiO2	133	Bad peak shape, repeated in Nut075 and result is good. The repeated measurement for other nutrients data was # out of file as original results were good.
81	07	Nut076	SiO4, NOx, PO4	69	Outlier on profile, peak shapes good – not seen in salinity or dissolved oxygen.

89	09	nut084	SiO4	133	Bad peak shape. Outlier on profile. Re-run and replaced as new result is good. The repeated measurement for other nutrient data was # out of file as original results were good.
89	04	nut084	SiO4	133	Bad peak shape. Outlier on profile. Re-run and replaced. The repeated measurement for other nutrient data was # out of file as original results were good.
96	23	Nut090	NOx	69	Suspect peak shape was re-run later in the run and result was OK used that result for all nutrients and “tested” first one out.
97	06	Nut091	SiO4	133	Bad peak shape, re-run at end of the run and this result was OK and used. The repeated measurement for other data was # out of file as original results were good.
98	18 & 19	Nut092	NO2	133	Outliers on profile, re-run in nut094 results ok in nut094. The repeated measurement for other data was # out of file as original results were good.
98	34 & 35	Nut092	All	141	Samples missing accidently not collected.
99	14	Nut093	NOx	133	Bad outlier on profile, repeated in Nut94 this result good. The repeated measurement for other data was # out of file as original results were good.
102	20	Nut096	All	133	Bad, outlier in vertical profile plot (also when repeated in following run). Also seen as outlier in salinity and D.O. data.
104	29	Nut098	NOx	133	Bad peak shape, repeated and measurement OK. The repeated measurement for other nutrient data was # out of file as original results were good.
104	36	Nut098	All	141	Sample missing accidently not collected.
Uwy	08	Nut026	NO2	133	The rmns, BQC and intQC all stepped up. The sample profiles were also offset from previous ctd profiles. CTD 25, 26 and uwy were re-run and for NO2 in the nut027b & nut028b. The initial NO2 results were # out of original files and second results used as they were good.

7.10 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_v01_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	P158
Use by date	03/05/2020	25/03/2018
K_{15}	0.99987	0.99970

8.2 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.

8.3 GO-SHIP Specifications

Salinity Accuracy of 0.001 is possible with Autosal™ 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. Autosal 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 ± 1°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.

8.4 RMNS Values for each CTD Deployment

Analysis Run	CTD #	SiO4 measured	PO4 measured	NO2 measured	NOx measured
CB reported		**111.821**	**2.580**	**0.199**	**36.649**
1	1,2	111.367	2.603	0.144	36.713
7	8	111.100	2.590	-	36.730
8	8	-	-	0.135	-
17	17	110.967	2.590	0.140	36.737
23	23	111.200	2.573	0.135	36.640
30	30	111.100	2.620	0.136	36.753
36	36	110.633	2.613	0.145	36.833
44	44	111.267	2.600	0.145	36.917
51	51	110.900	2.610	0.138	36.843
59	60	111.767	2.623	0.139	37.057
67	71	111.567	2.593	0.141	36.983
81	86	111.433	2.600	0.132	36.823
99	105	111.600	2.610	0.135	36.900
CC reported		**88.228**	**2.130**	**0.119**	**31.740**
1	1,2	87.767	2.130	0.133	31.787
2	3	87.600	2.120	0.140	31.893
3	4	87.533	2.130	0.130	31.857
4	5	87.663	2.114	0.129	31.836
5	6	87.775	2.138	0.133	31.788
6	7	87.600	2.123	0.137	31.860
7	8	87.600	2.128	-	31.858
8	8	-	-	0.133	-
9	9	87.400	2.138	0.135	31.863
10	10	87.925	2.145	0.130	31.828
11	11	87.425	2.143	0.138	31.868
12	12	87.850	2.150	0.133	31.908
13	13	87.625	2.140	0.138	31.848
14	14	87.925	2.145	0.131	31.925
15	15	87.625	2.140	0.132	31.798
16	16	87.875	2.150	0.131	31.810
17	17	87.400	2.125	0.133	31.815
18	18	87.325	2.118	0.131	31.778

19	19	87.375	2.135	0.130	31.825
20	20	87.375	2.125	0.130	31.845
21	21	87.425	2.120	0.130	31.883
22	22	87.525	2.110	0.130	31.868
23	23	87.450	2.118	0.131	31.878
24	24	87.225	2.128	0.133	31.875
25	25	87.750	2.128	-	31.923
26	26	87.375	2.130	-	31.738
27	27	87.375	2.120	0.130	31.820
28	28	87.425	2.130	0.134	31.700
29	29	87.475	2.128	0.133	31.835
30	30	87.450	2.153	0.130	31.835
31	31	87.667	2.160	0.130	31.877
32	32	87.975	2.160	0.140	31.930
33	33	88.025	2.155	0.131	31.898
34	34	87.500	2.155	0.133	31.925
35	35	87.225	2.160	0.132	31.905
36	36	87.175	2.153	0.136	32.005
37	37	87.050	2.163	0.134	31.915
38	38	87.475	2.155	0.133	31.885
39	39	87.675	2.160	0.131	31.943
40	40	87.775	2.146	0.131	31.966
41	41	87.800	2.143	0.138	31.970
42	42	87.925	2.150	0.141	32.038
43	43	87.857	2.139	0.129	31.904
44	44	87.675	2.140	0.139	31.953
45	45	87.625	2.140	0.129	31.895
46	46	87.850	2.150	0.131	31.880
47	47	87.517	2.140	0.136	31.882
48	48	87.625	2.143	0.128	32.060
49	49	87.650	2.150	0.131	32.013
50	50	87.960	2.168	0.135	31.836
51	51	86.975	2.145	0.135	31.963
52	52	87.586	2.156	0.133	31.897
53	53	87.925	2.145	0.132	32.005
54	54	87.775	2.160	0.139	31.908

55	55	87.775	2.165	0.129	31.960
56	56	87.825	2.150	0.128	31.933
57	57	87.650	2.150	0.133	32.013
58	58, 59	88.025	2.168	0.130	32.000
59	60	88.175	2.168	0.131	32.035
60	61	88.050	2.163	0.133	32.153
61	62, 63, 64	88.250	2.175	0.133	31.935
62	65, 66	88.175	2.158	0.136	31.993
63	67	87.575	2.155	0.134	31.988
64	68	88.233	2.165	0.131	32.048
65	69	88.167	2.152	0.133	32.057
66	70	88.000	2.168	0.129	32.082
67	71, 72	87.880	2.132	0.143	32.022
68	73	87.925	2.140	0.130	31.960
69	74	87.825	2.148	0.138	32.020
70	75	87.900	2.148	0.132	32.058
71	76	88.025	2.135	0.130	32.008
72	77	87.775	2.150	0.129	31.868
73	78	87.975	2.153	0.129	31.993
74	79	87.275	2.138	0.128	31.915
75	80	87.750	2.150	0.131	31.875
76	81	88.000	2.150	0.133	31.995
77	82	87.800	2.150	0.132	32.090
78	83	87.900	2.158	0.133	31.880
79	84	87.800	2.145	0.131	31.890
80	85	87.667	2.155	0.134	31.863
81	86	87.800	2.140	0.128	31.780
82	87	87.875	2.168	0.138	32.018
83	88	87.825	2.163	0.134	31.995
84	89	87.800	2.173	0.134	32.000
85	90	88.000	2.160	0.132	32.140
86	91	88.250	2.148	0.128	32.050
87	92	88.000	2.158	0.133	31.973
88	93	88.100	2.158	0.131	31.938
89	94, 95	88.200	2.158	0.134	31.945

90	96	87.950	2.157	0.129	31.938
91	97	88.150	2.160	0.130	31.933
92	98	87.950	2.160	0.130	31.930
93	99	87.175	2.155	0.130	31.963
94	100	87.675	2.155	0.132	31.998
95	101	87.600	2.150	0.128	32.010
96	102	87.500	2.160	0.135	31.990
97	103	87.950	2.148	0.132	31.953
98	104	87.850	2.158	0.135	31.875
99	105	87.925	2.150	0.134	31.910
100	106	87.875	2.160	0.131	31.888
101	107	88.125	2.158	0.135	32.030
102	108	87.700	2.160	0.133	31.860
103	uwy	87.775	2.158	0.134	31.910
CD reported		**14.264**	**0.457**	**0.018**	**5.648**
1	1, 2	14.100	0.447	0.447	5.527
7	8	13.725	0.463	0.463	5.573
17	17	14.000	0.460	0.460	5.540
23	23	13.800	0.460	0.460	5.597
30	30	13.600	0.460	0.460	5.553
36	36	13.700	0.463	0.463	5.590
44	44	13.800	0.463	0.463	5.547
51	51	13.875	0.470	0.470	5.590
59	60	14.125	0.470	0.470	5.570
67	71	14.050	0.455	0.455	5.610
81	86	13.950	0.460	0.460	5.512
99	105	14.025	0.460	0.460	5.592

8.5 Internal Quality Control Values for each CTD Deployment

Measured concentrations (µM) of the internal quality control and the low nutrient seawater that were produced in the shore laboratory.

CTD/Date	LNSW	Spike	LNSW	Spike	LNSW	Spike	LNSW	Spike	LNSW	Spike
	NOx	NOx	PO4	PO4	SiO2	SiO2	NO2	NO2	NH4	NH4
Prepared Concentration	NA	5.5	NA	1.0	NA	10	NA	0.5	NA	1.0
	Measured Concentrations (µM)									
Oct-17	0.07	5.59	-0.001	0.99	0.9	11.3	0.06	0.55	0.34	1.31
Dec-17	0.1	5.46	0.017	1.02	1.0	11.4	0.041	0.56	0.39	1.36
CTD 1 & 2	0.09	5.43	0.01	1.01	0.7	11.2	0.037	0.537	0.35	1.31
CTD 3	0.09	5.44	0.01	1	0.5	10.9	0.04	0.54	0.36	1.31
CTD 4	0.09	5.43	0.02	1.01	0.4	10.8	0.037	0.535	0.37	1.31
CTD 5	0.09	5.44	0.01	0.99	0.5	10.9	0.037	0.534	0.34	1.28
CTD 6	0.1	5.47	0.02	1.01	0.5	11	0.043	0.536	0.34	1.3
CTD 7	0.09	5.48	0.01	1	0.4	10.9	0.046	0.548	0.36	1.31
CTD 8	0.09	5.46	0.01	1	0.4	10.9			0.34	1.29
CTD 9	0.1	5.45	0.02	1.01	0.4	10.8	0.038	0.538	0.39	1.33
CTD 10	0.1	5.48	0.01	1.01	0.5	10.9	0.038	0.525	0.39	1.32
CTD 11	0.11	5.45	0.01	1.01	0	10.5	0.043	0.537	0.36	1.32
CTD 12	0.1	5.45	0.02	1.01	0.5	11	0.035	0.53	0.36	1.32
CTD 13	0.11	5.48	0.02	1.01	0.2	10.7	0.042	0.538	0.37	1.33
CTD 14	0.1	5.5	0.01	1.01	0.5	11	0.034	0.538	0.36	1.33
CTD 15	0.11	5.49	0.01	1.01	0.2	10.7	0.0.36	0.535	0.37	1.34
CTD 16	0.11	5.46	0.03	1.02	0.7	11.1	0.033	0.527	0.38	1.34
CTD 17	0.09	5.44	0.02	1.01	0.6	11	0.038	0.535	0.37	1.33
CTD 18	0.1	5.44	0.02	1	0.5	10.9	0.04	0.527	0.37	1.32
CTD 19	0.1	5.45	0.02	1.01	0.5	10.9	0.041	0.527	0.37	1.31
CTD 20	0.1	5.43	0.01	1	0.4	10.9	0.032	0.53	0.36	1.32
CTD 21	0.1	5.44	0.02	1.01	0.5	10.9	0.037	0.528	0.32	1.26
CTD 22	0.09	5.49	0.02	0.99	0.5	10.9	0.039	0.532	0.38	1.35
CTD 23	0.09	5.48	0.02	0.99	0.4	10.9	0.038	0.526	0.36	1.3
CTD 24	0.09	5.48	0.02	1.01	0.4	10.8	0.039	0.526	0.36	1.31
CTD 25	0.09	5.49	0.02	1.01	0.4	10.9	0.048	0.545	0.36	1.31
CTD 26	0.1	5.43	0.01	1	0.1	10.8	0.046	0.543	0.36	1.31
CTD 27	0.09	5.43	0.01	0.99	0.4	10.9	0.034	0.523	0.37	1.33
CTD 28	0.11	5.4	0.02	1	0.5	10.9	0.038	0.529	0.37	1.31
CTD 29	0.1	5.43	0.02	1	0.6	11	0.04	0.533	0.38	1.35
CTD 30	0.1	5.48	0.01	1.02	0.1	10.6	0.033	0.532	0.36	1.29
CTD 31	0.09	5.45	0.02	1.02	0.5	10.9	0.041	0.542	0.38	1.34
CTD 32	0.09	5.46	0.02	1.02	0.5	11	0.044	0.543	0.35	1.32

CTD 33	0.09	5.44	0.03	1.02	0.6	11.1	0.033	0.527	0.37	1.33
CTD 34	0.12	5.5	0.02	1.02	0.6	11	0.043	0.539	0.36	1.34
CTD 35	0.13	5.48	0.02	1.01	0.4	10.8	0.039	0.539	0.37	1.34
CTD 36	0.12	5.49	0.01	1.01	0.4	10.8	0.044	0.552	0.38	1.34
CTD 37	0.12	5.49	0.02	1.02	0.1	10.5	0.045	0.548	0.37	1.33
CTD 38	0.11	5.45	0.02	1.02	0.5	10.9	0.04	0.535	0.37	1.33
CTD 39	0.12	5.48	0.01	1.02	0.4	10.9	0.038	0.535	0.37	1.33
CTD 40	0.11	5.45	0.01	1.01	0.3	10.6	0.038	0.532		
CTD 41	0.1	5.42	0.01	1.01	0.3	10.8	0.045	0.536	0.36	1.33
CTD 42	0.12	5.47	0.01	1.01	0.5	11	0.048	0.551	0.36	1.33
CTD 43	0.12	5.44	0.01	1.01	0.5	11	0.034	0.529	0.36	1.31
CTD 44	0.12	5.47	0.01	1.01	0.4	10.9	0.04	0.536	0.37	1.32
CTD 45	0.12	5.45	0.01	1.01	0.3	10.9	0.034	0.536	0.38	1.32
CTD 46	0.11	5.46	0.01	1.02	0.6	11.1	0.041	0.535	0.36	1.33
CTD 48	0.14	5.47	0.01	1.01	0.6	11	0.045	0.546	0.39	1.34
CTD 50	0.11	5.49	0.02	1.02	0.7	11.1	0.038	0.53	0.37	1.34
CTD 52	0.12	5.46	0.02	1.01	0.4	10.8	0.04	0.531	0.38	1.35
CTD 54	0.12	5.44	0.02	1.02	0.5	10.9	0.048	0.541	0.36	1.33
CTD 56	0.11	5.47	0.02	1.02	0.6	11.1	0.039	0.534	0.37	1.35
CTD 58	0.12	5.48	0.02	1.03	0.5	11	0.036	0.526	0.36	1.33
CTD 59	0.11	5.48	0.02	1.02	0.6	11.2	0.037	0.53	0.37	1.34
CTD 68	0.13	5.48	0.02	1.03	1	11.5	0.036	0.537	0.37	1.33
CTD 70	0.11	5.51	0.02	1.03	0.6	11.1	0.035	0.533	0.39	1.36
CTD 73	0.1	5.49	0.01	1.01	0.6	11.1	0.039	0.534	0.38	1.34
CTD 74	0.1	5.51	0.02	1.02	0.6	11	0.056	0.547	0.36	1.32
CTD 77	0.12	5.52	0.02	1.02	0.6	11.1	0.041	0.537	0.37	1.33
CTD 78	0.12	5.52	0.03	1.02	0.6	11.1	0.043	0.536	0.37	1.33
CTD 80	0.12	5.45	0.01	1.01	0.5	11	0.04	0.536	0.36	1.32
CTD 82	0.12	5.47	0.02	1.01	0.5	10.9	0.043	0.538	0.36	1.32
CTD 85	0.12	5.42	0.02	1.02	0.5	11	0.05	0.538	0.39	1.35
CTD 87	0.14	5.5	0.02	1.03	0.4	10.9	0.052	0.545	0.36	1.31
CTD 89	0.14	5.48	0.02	1.03	0.5	10.9	0.042	0.533	0.37	1.34
CTD 90	0.14	5.48	0.01	1.02	0.6	11.1	0.046	0.547	0.38	1.39
CTD 92	0.12	5.46	0.02	1.02	0.5	11	0.038	0.533	0.38	1.34
CTD 94	0.1	5.48	0.02	1.02	0.7	11.2	0.042	0.542	0.37	1.33
CTD 96	0.13	5.49	0.02	1.02	0.5	11	0.052	0.542	0.4	1.37
CTD 97	0.11	5.45	0.02	1.02	0.7	11.1	0.039	0.528	0.37	1.33
CTD 98	0.1	5.45	0.02	1.02	0.6	11	0.044	0.531	0.4	1.36

CTD 99	0.12	5.46	0.01	1.01	0.4	10.7	0.039	0.53	0.39	1.35
CTD 100	0.11	5.49	0.02	1.02	0.7	11.1	0.041	0.536	0.39	1.36
CTD 101	0.11		0.01		0.6		0.037		0.39	
CTD 102	0.16	5.49	0.02	1.02	0.5	11	0.048	0.548	0.39	1.33
CTD 103	0.12		0.02		0.6		0.045		0.41	
CTD 104	0.12	5.5	0.02	1.02	0.6	11.1	0.042	0.542	0.39	1.34
CTD 105	0.12	5.49	0.02	1	0.6	11	0.041	0.533	0.39	1.36

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