RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2016_v04
Chief Scientist:	Dr. Martina Doblin
Voyage title:	Influence of temperature and nutrient supply on the biogeochemical function and diversity of ocean microbes.
Report compiled by:	Christine Rees and Stephen Tibben.

Contents

1 Itinerary

Depart Leg 1	Date	Time
Sydney	31 August	1400
Arrive	Date	Time
Brisbane	22 September	1600

2 Key personnel list

Name	Role	Organisation
Dr. Martina Doblin	Chief Scientist	University of Technology
Hugh Barker	Voyage Manager	CSIRO
Christine Rees	Hydrochemist	CSIRO
Stephen Tibben	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	Total
Salinity (Guildline Salinometer)	243 CTD 5 EXP
Dissolved Oxygen (automated titration)	225 CTD
Nutrients (AA3)	458 CTD 53 UWY 317 EXP

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

- 55 CTD stations were sampled with a 24 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; **6, 20, 34, 41, 47**.
- See in2016_v04_HydrochemistryReport.pdf (voyage report) for more details on sample collection.

3.3 Procedure Summary

The procedure for data processing is outline in Figure 1.

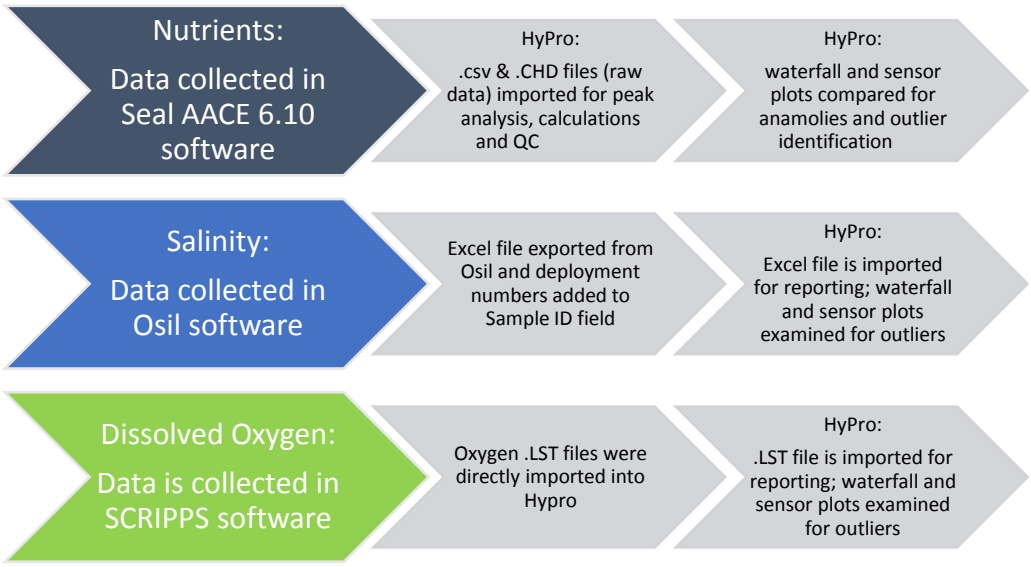


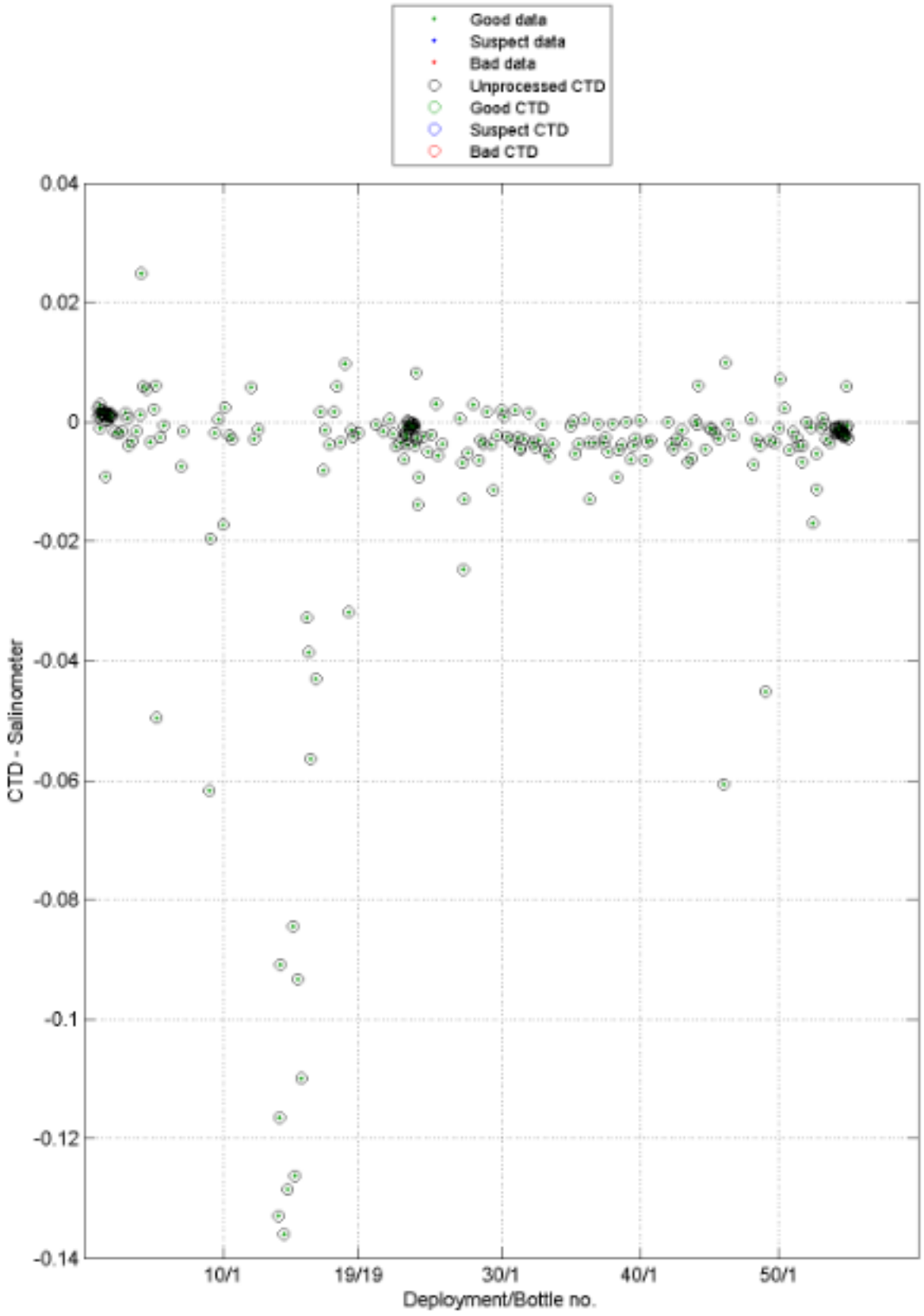
Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

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)	Stephen Tibben
Lab Temperature (±0.5°C)	20.5 -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, all samples analysed within 48 hrs.
Comments	Instrument worked well accept for the occasional import of the incorrect temperature refer to “in2016_v04_HydrochemistryReport.pdf” for further details.

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.

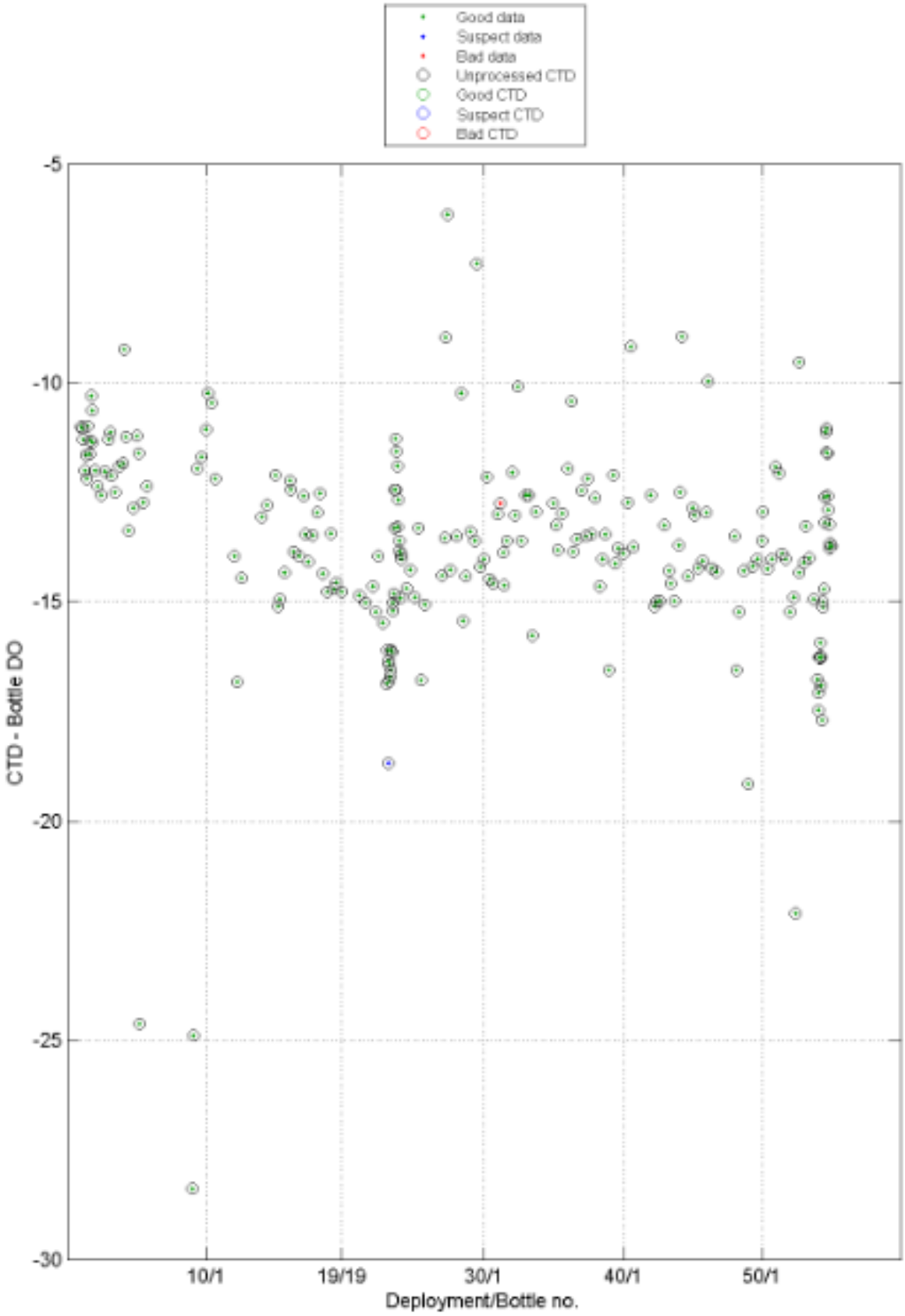
CTD	RP	Bottle	Flag	Reason for Flag or Action
8	All	-	141	Salinity samples not collected.
11	All	-	141	Salinity samples not collected.
13	All	-	141	Salinity samples not collected.
26	All	-	141	Salinity samples not collected.
55	All	-	141	Salinity samples not collected.

5 Dissolved Oxygen Data Processing

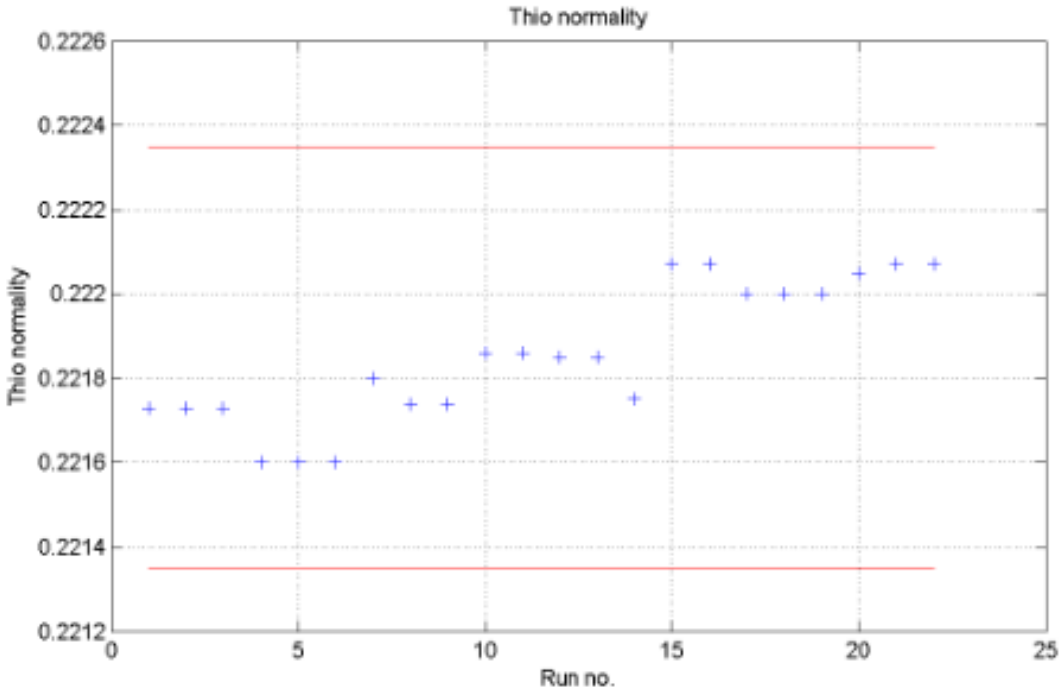
5.1 Dissolved Oxygen Parameter Summary

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
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	Instrument worked well on two occasions there was difficulty in calibrating the system, however this was resolved –refer to "in2016_v04_HydrochemistryReport.pdf" for further details.

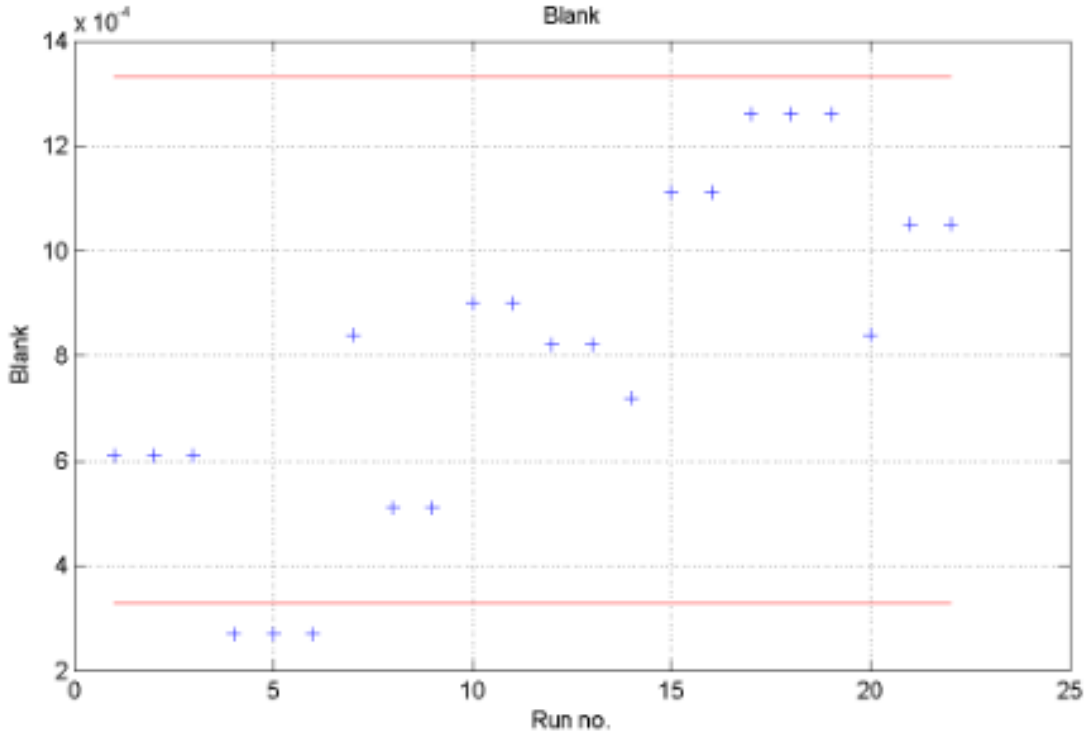
5.2 CTD vs Hydro DO Plot



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.

CTD	RP	Bottle	Flag	Reason for Flag or Action
7	All	-	141	Oxygen samples not collected.
8	All	-	141	Oxygen samples not collected.
11	All	-	141	Oxygen samples not collected.
13	All	-	141	Oxygen samples not collected.
23	04	660	69	Outlier in waterfall plot.
26	All	-	141	Oxygen samples not collected.
31	06	279	133	Incorrect flask number and volume entered
55	All	-	141	Oxygen samples not collected.

6 Nutrient Data Processing

6.1 Nutrient Parameter Summary

Details					
HyPro Version	4.13, reprocessed back on shore with 4.16				
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients analysed	☒ Silicate	☒ Phosphate	☒ Nitrate + Nitrite	☒ Nitrite	☒ Ammonia
Concentration range	112 µmol l^{-1}	3 µmol l^{-1}	36.4 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 and Stephen Tibben				
Lab Temperature (±1°C)	Variable, 20.0 – 23.0°C				
Reference Material	RMNS – CA, CD				
Sampling Container type	50 ml HDPE bottles (CTD & exp) and 30 ml polypropylene sample tubes (uwy).				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	None				
Comments	Non-CTD related samples were analysed and processed with the prefix-uwy and exp. Exp and uwy samples were measured within a 12 hour period of sample collection.				

6.2 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 is contained in the voyage documentation and is available upon request. All analysis 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 also available upon request.

Additional information is contained in the following folder;
http://www.cmar.csiro.au/datacentre/process/data_files/Investigator_NF/in2016_v04/data/in2016_v04_Hydro_Additional_Calibration_info.zip

The link is available through Marlin, within the folder there are 4 more folders “Calibration_Plots” and “Calibration_Summary” contain information regarding the calibrations, drift, baseline and MDL. The folder “Analysis_Run_Sheets” contains the analysis run file numbers (NUT### file) which correspond to the CTD deployment, underway and experimental samples analysed within each run. The folder “Sample_Log_Files” contains the time (EST) and date that matches the **uwy** samples and the experimental details that match the **exp** data.

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 6.6 for edited data). Below are the standard corrections and settings that HyPro applies to the raw data. Once data processing is completed the output files (CSV and NetCDF) are run through the HydroNcChecker programme to ensure all correct data has entered into these files.

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	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
Data Adj for RMNS	N	N	N	N	N
Window Defined*	HyPro	HyPro	HyPro	HyPro	HyPro

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
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 21st and 22nd 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 6.6. The reported data is not corrected to the RMNS. Per run RMNS data can be found in Appendix 7.4.				

6.3 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. QC data is not supplied for the experimental ammonium 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.

The RMNS Lot CA (produced 22/02/2013) was measured 4 times in every CTD analysis. The RMNS Lot CD (produced 08/04/2015) was analysed twice with the CA. RMNS results were converted from µ mol/kg to µ mol l^{-1} at 21°C in the following table.

Table 1: RMNS CA, BV and BW concentrations (µM) at 21°C

RMNS	NO_3	NO_X	NO_2	PO_4	SiO_4
CA	20.13	20.20	0.065	1.44	37.46
CD	5.63	5.65	0.018	0.457	14.26

The submitted nutrient results do <u>NOT</u> have RMNS corrections applied.

The following equation can be used to correct the data for each nutrient analysis using the CA RMNS.

<u>RMNS Correction</u>

% error = (RMNS measured – RMNS Published)/RMNS Published

Corrected Nutrient Concentration = Nutrient measured – (nutrient measured x error)

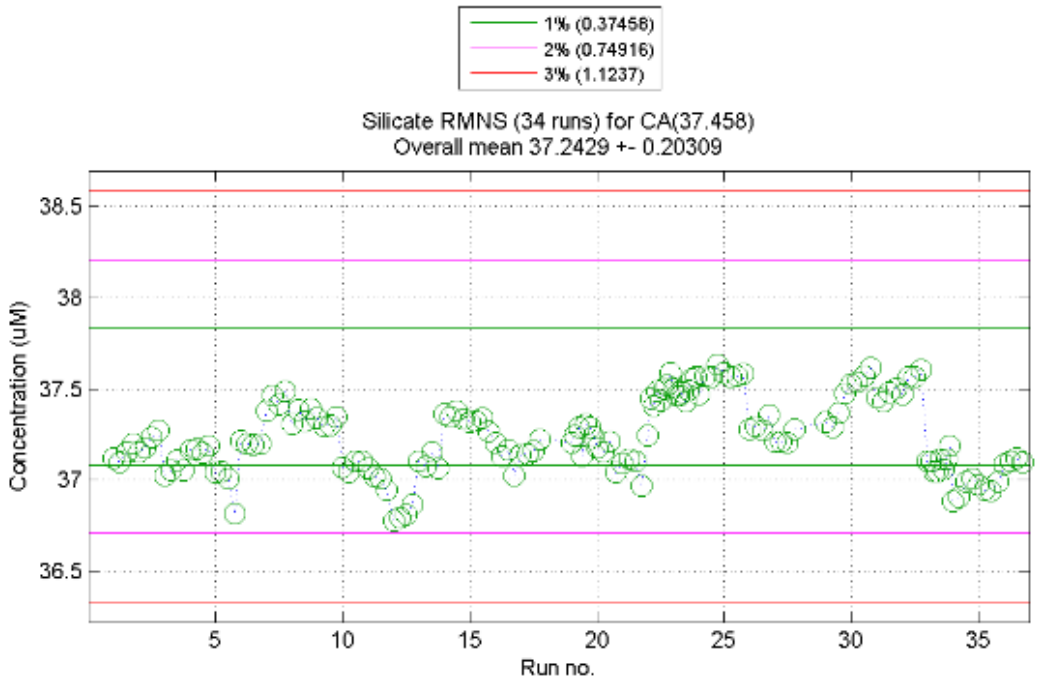
Note: NOx data should be corrected as NO_3 and NO_2.

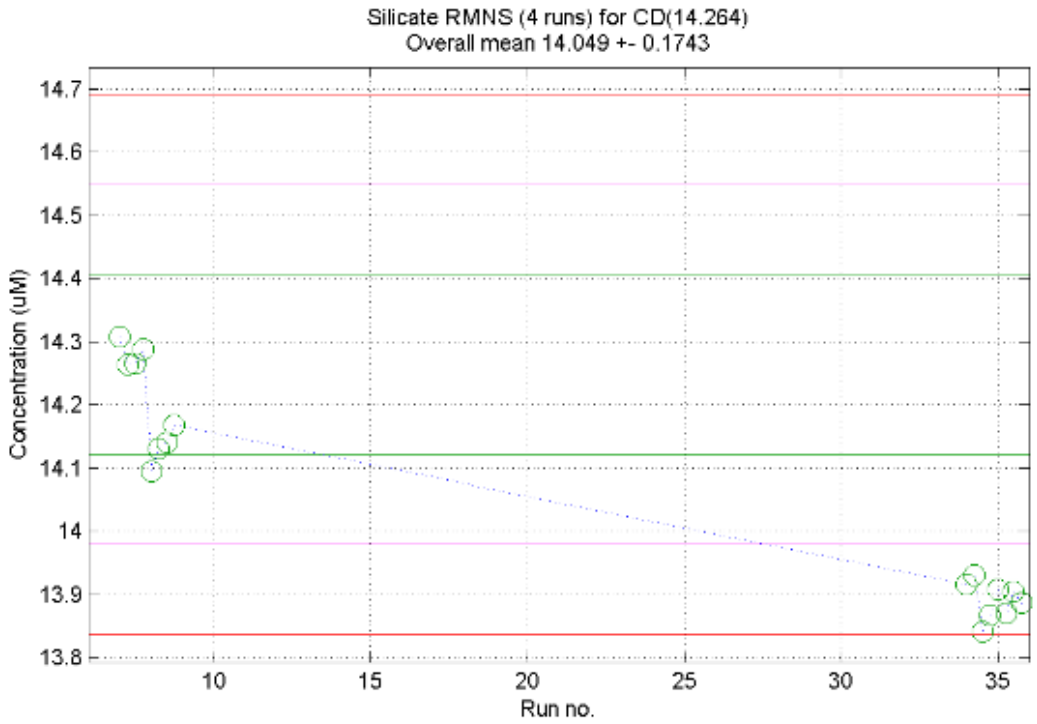
The following plots show RMNS values within 1% (green lines), 2% (pink lines) and 3% (red lines) of the published RMNS value except for nitrite. The nitrite limit is set to ±0.020 µM (MDL) as 1% is

below the method MDL. The GO-SHIP criteria (Hyde *et al*., 2010), reference section 7.3, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy. The measured RMNS values per CTD are reported in the table in Appendix 7.4. The CD RMNS Plots are under review as 1% of the published RMNS value is below the detection limit for SiO_4, PO_4 and NO_2. The lines are to be changed to the MDL value.

6.3.1 Silicate RMNS Plot

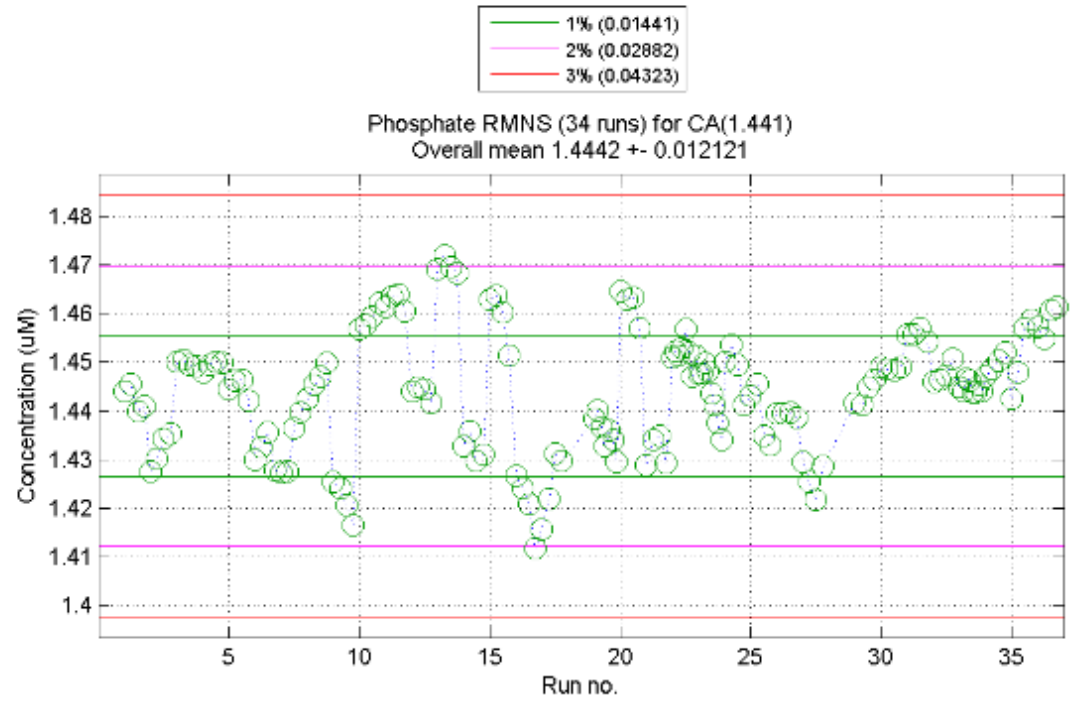
1% of RMNS value 2% of RMNS value 3% of RMNS value

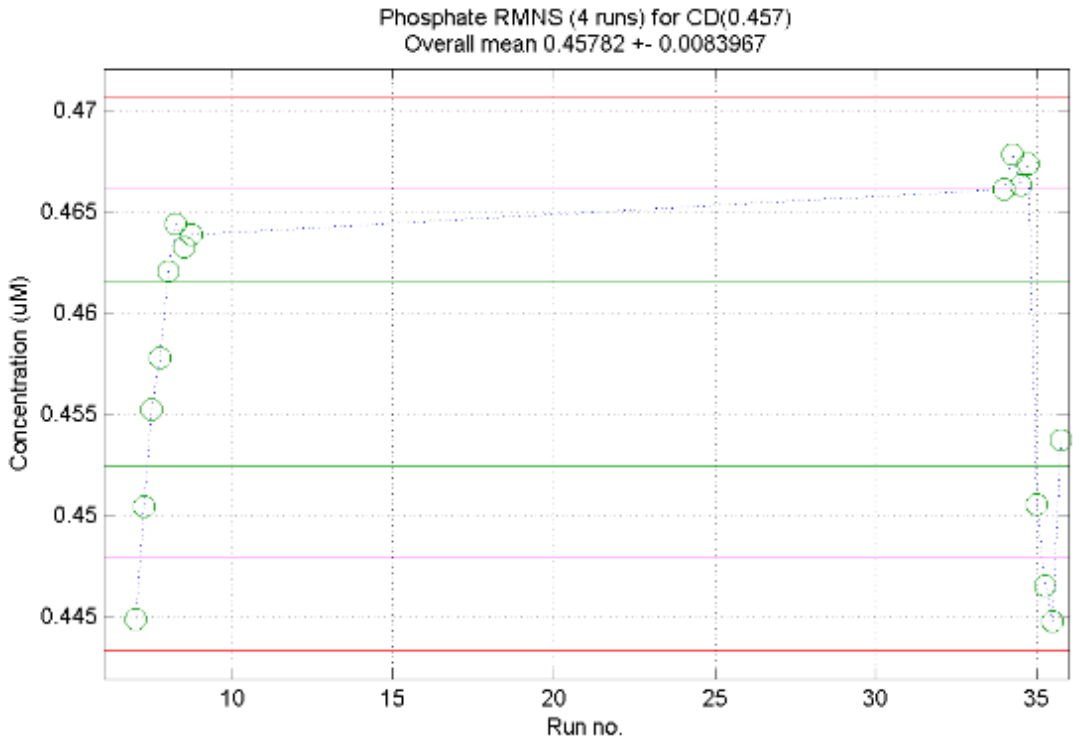




6.3.2 Phosphate RMNS Plot

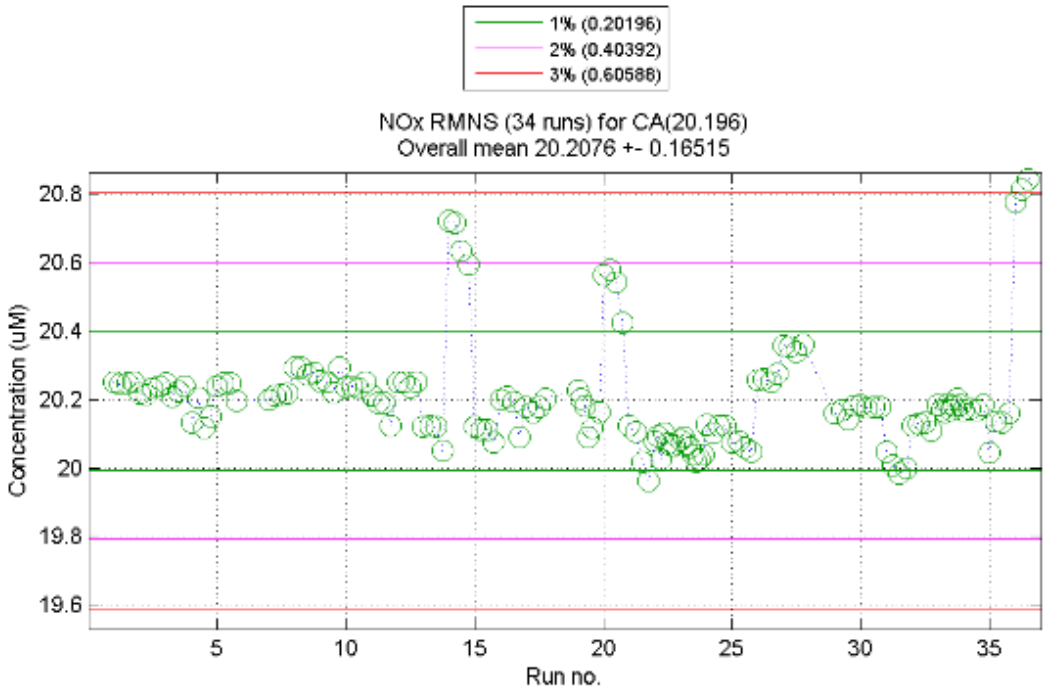
1% of RMNS value 2% of RMNS value 3% of RMNS value

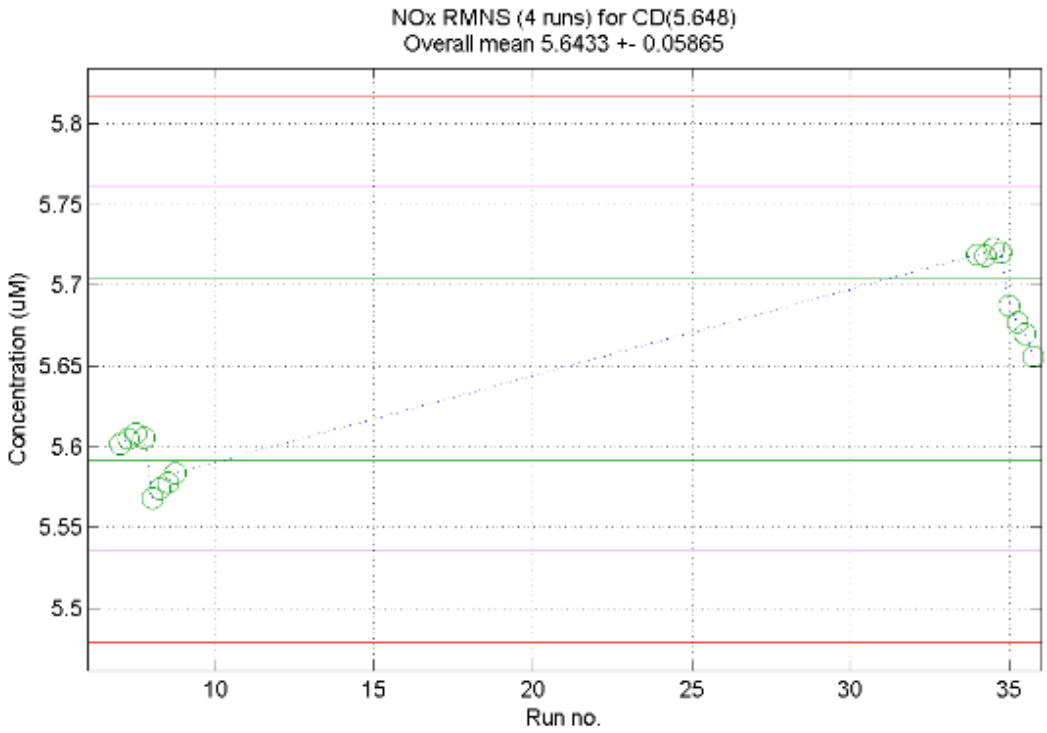




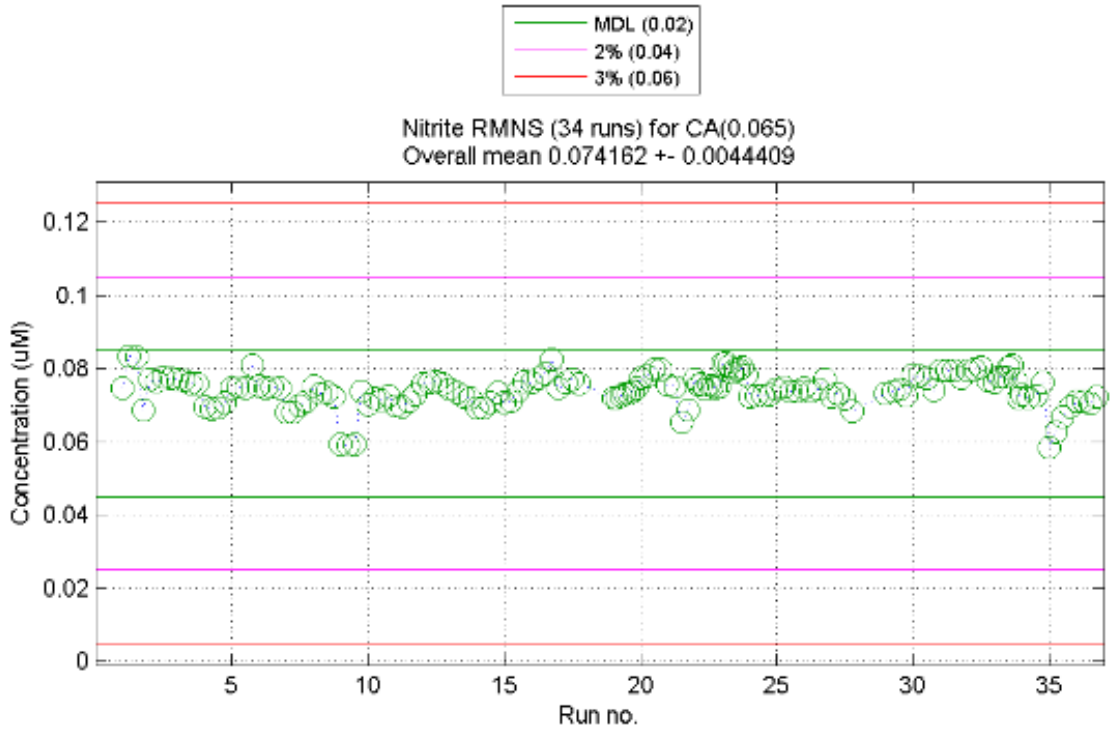
6.3.3 Nitrate + Nitrite (NOx) RMNS Plot

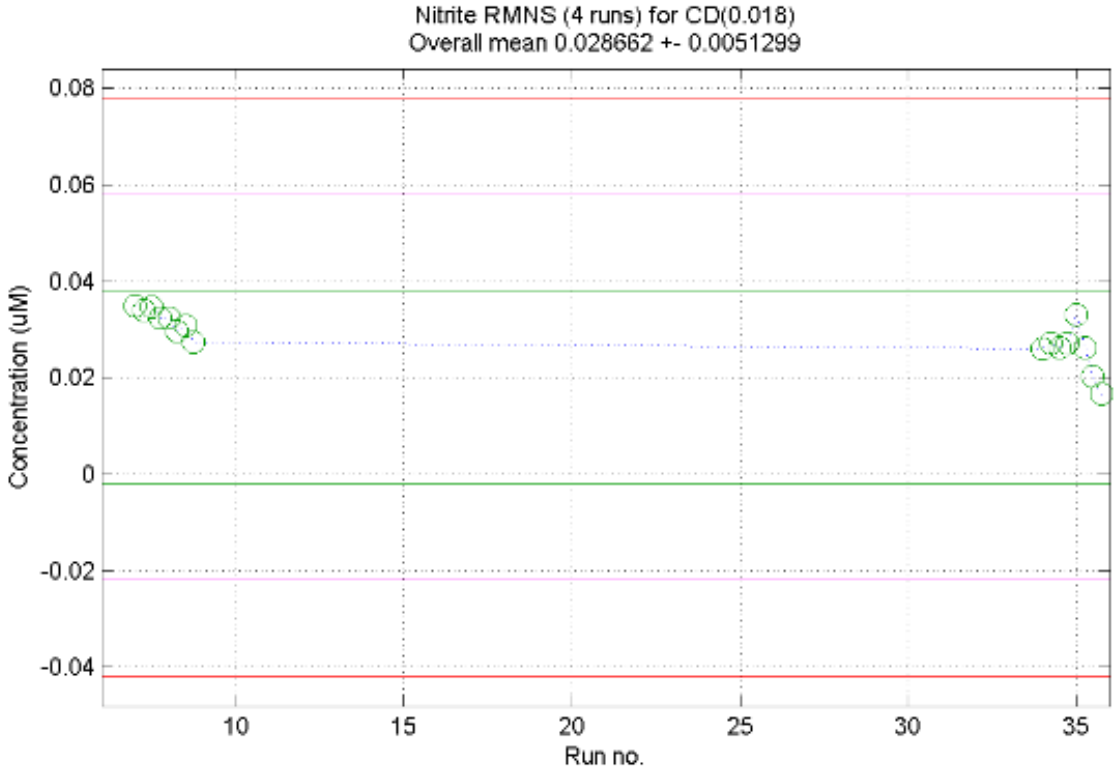
1% of RMNS value 2% of RMNS value 3% of RMNS value





6.3.4 Nitrite RMNS Plot





6.4 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 (NOx)	Nitrite	Ammonium
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 (NOx)	Nitrite	Ammonium
Nominal MDL*	*0.20*	*0.02*	*0.02*	*0.020*	*0.02*
Min	0.016	0.001	0.003	0.000	0.002
Max	0.128	0.011	0.068	0.018	0.005
Mean	**0.045**	**0.005**	**0.012**	**0.004**	**0.003**
Median	0.037	0.005	0.010	0.003	0.004
Precision of MDL (stdev)	0.025	0.002	0.012	0.003	0.001

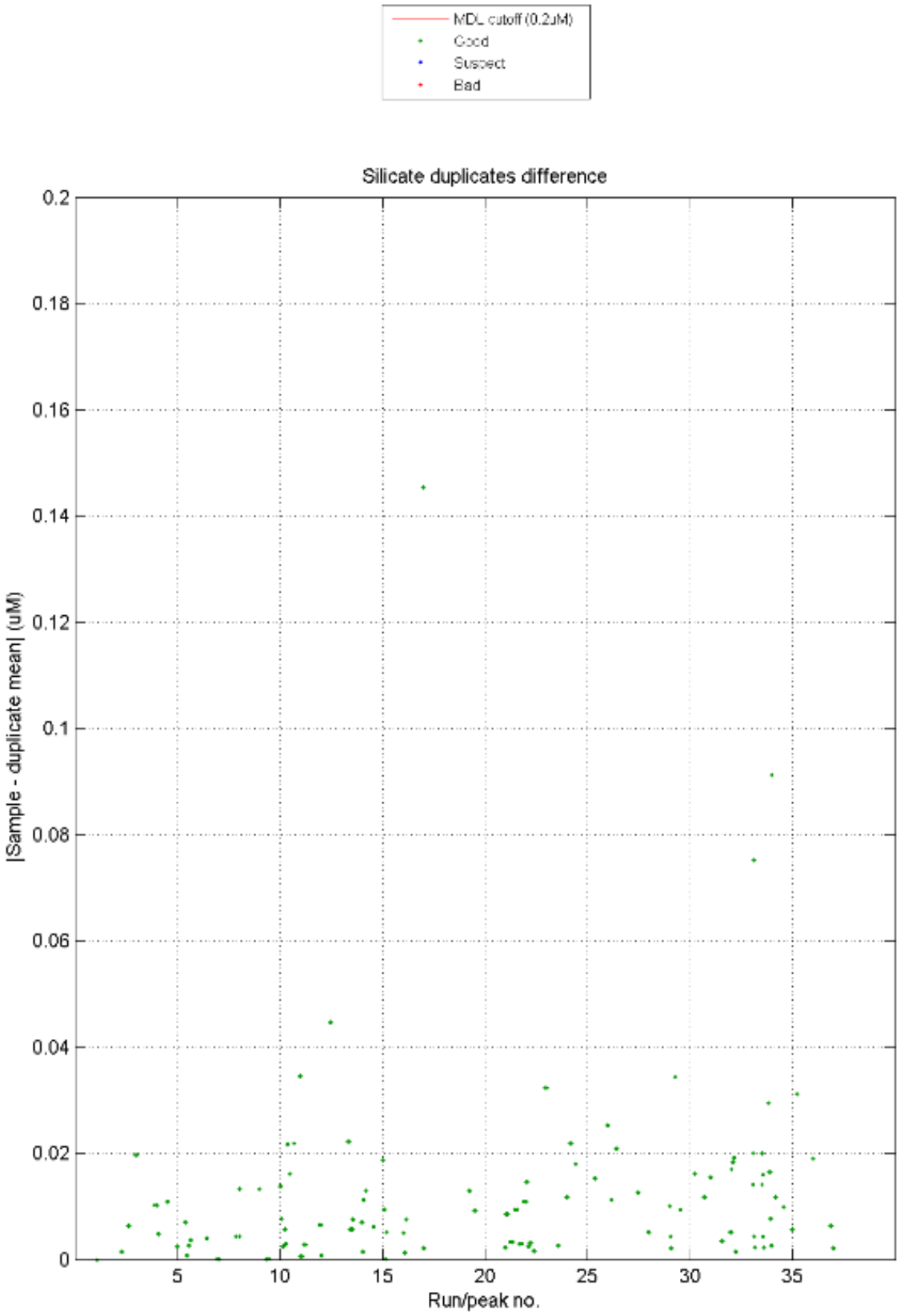
*MDL is based on 3 times the standard deviation of Low Nutrient Seawater (LNSW) analysed in each nutrient run.

Published RMNS (µmol l^{-1})	37.46	1.441	20.20	0.065	-
w/uncertainty	± 0.22	± 0.014	± 0.16	± 0.010	
RMNS Min	36.80	1.420	20.01	0.063	-
RMNS Max	37.60	1.470	20.82	0.080	-
RMNS Mean	**37.24**	**1.444**	**20.22**	**0.074**	**-**
RMNS Median	37.20	1.440	20.18	0.074	-
RMNS Std Dev	0.21	0.013	0.17	0.004	-

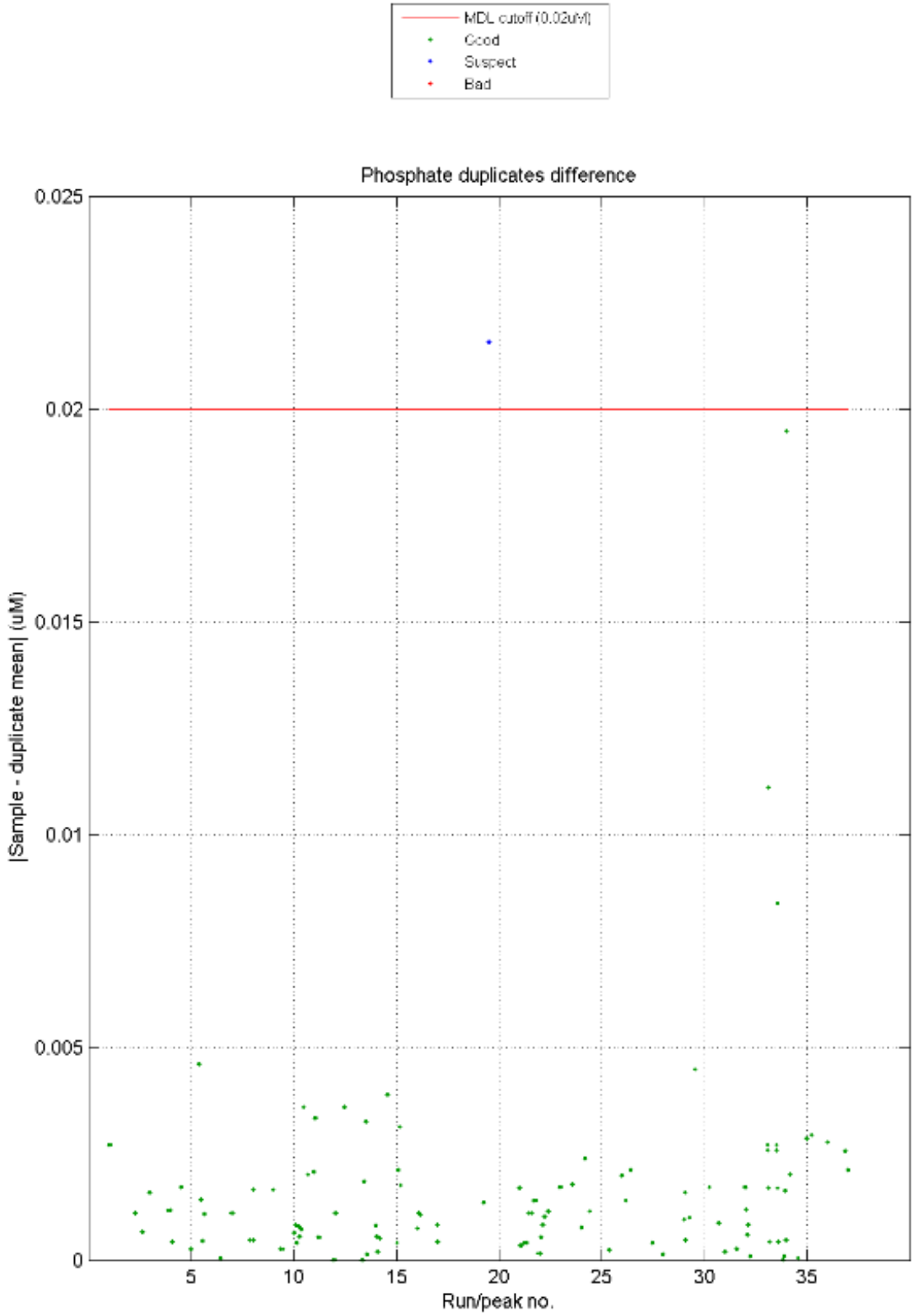
6.5 Sampling Precision

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, NOx[1] and nitrite.

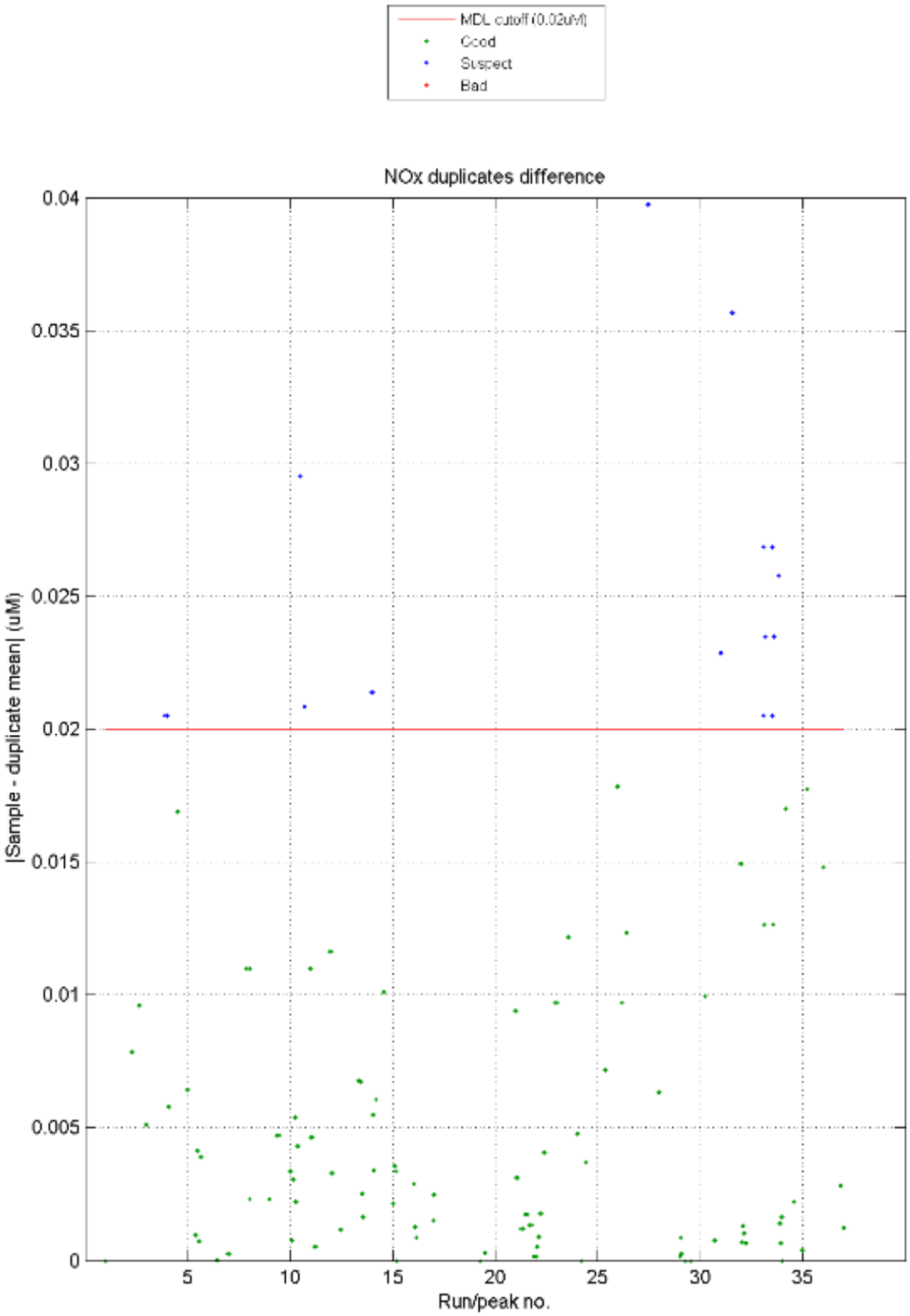
6.5.1 Silicate Duplicate Plot



6.5.2 Phosphate Duplicate Plot

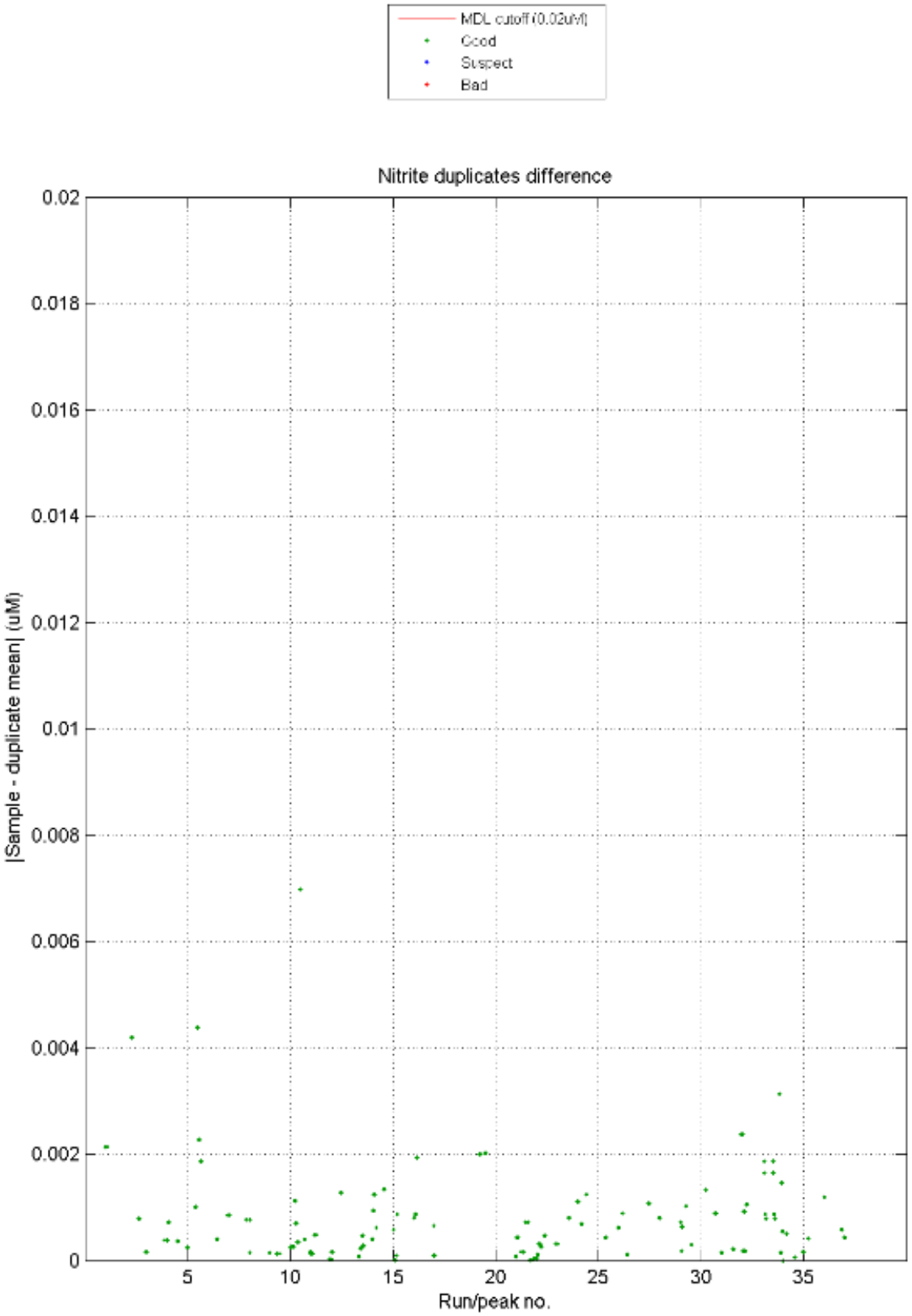


6.5.3 Nitrate + Nitrite (NOx) Duplicate Plot

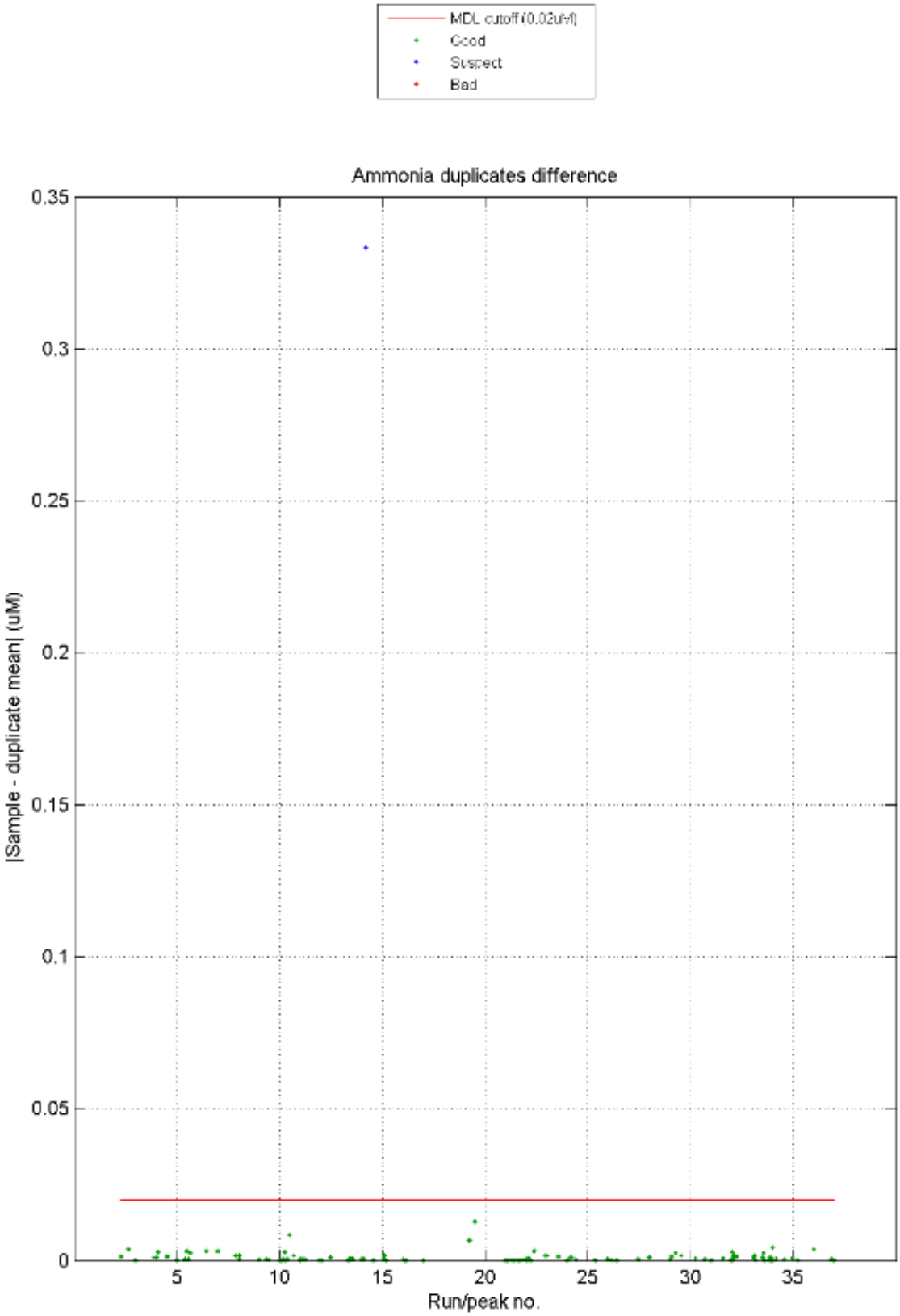


[1] **The value of 0.02µM for NOx is under review and may be changed to 0.05 µM within HyPro.**

6.5.4 Nitrite Duplicate Plot

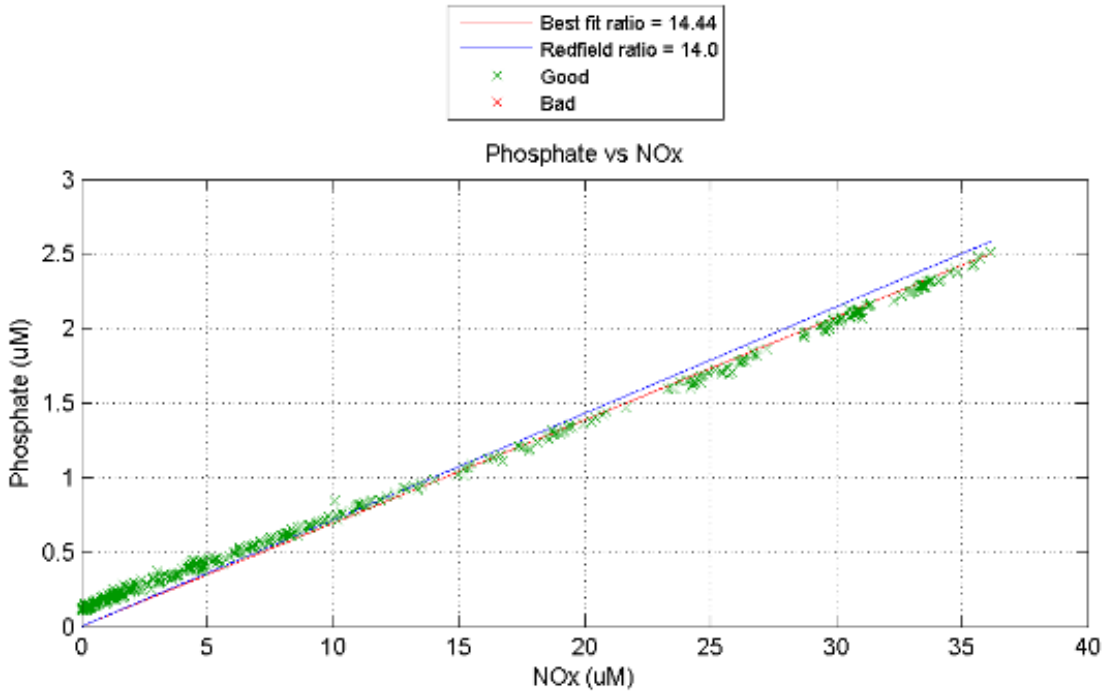


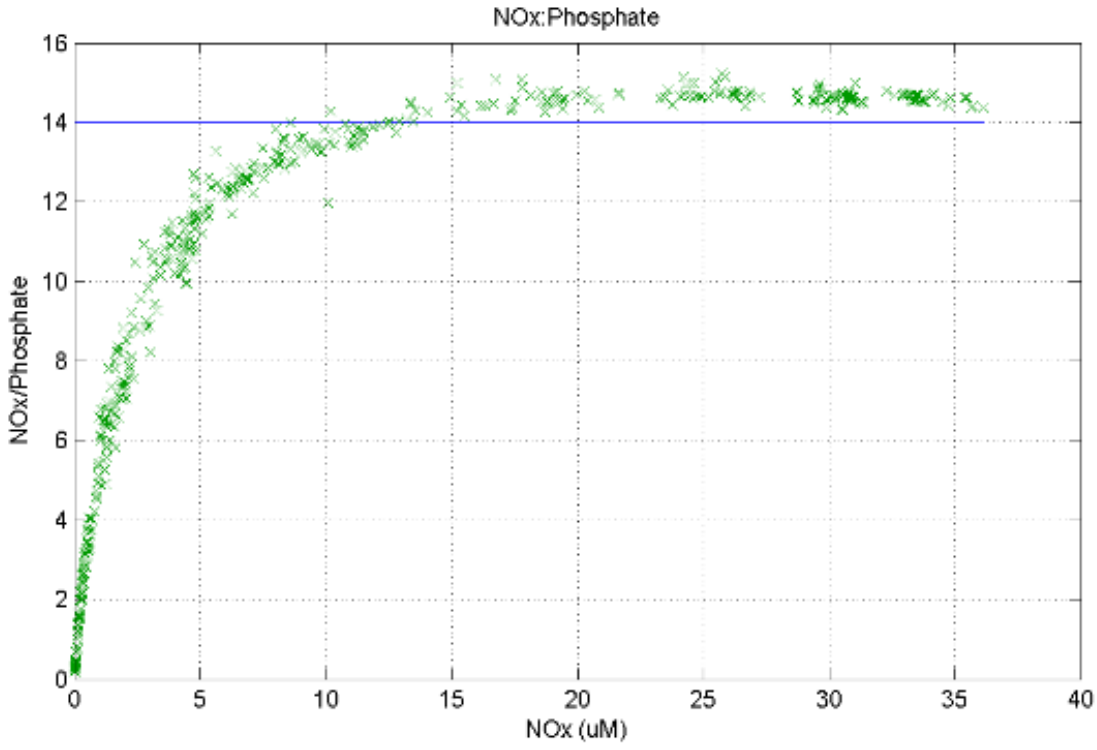
6.5.5 Ammonium Duplicate Plot



6.5.6 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx, best fit ratio = 14.44.





6.6 Calibration and QC edited data

During this voyage a number of analysis runs had peak time slippage occur due to partial blockage within the Cadmium column these were analysis runs nut005, nut006, nut010, nut017 and nut019. The timing was adjusted within the peak start column of the slk file to ensure the peak plateau occurred within the correct position. All data is good within these adjusted files.

CTD, exp, uwy	Peak	Run #	Analysis	Action
01	RMNS CA	Nut001	SiO4	First value marked bad due to spike in plateau.
01	BQC	Nut001	SiO4	Second value marked bad dip in peak plateau.
02, 03 & 04	-	Nut002	NH4	<70% of calibrants used in the calibration curve.
exp001-012, uwy001-004	Baseline	Nut005	NH4	2nd baseline marked as bad – contaminated.
exp013-030	RMNS & BQC	Nut006	NOx	Marked bad in slk file – peak time slippage.
13, 14, 15, exp031-033, uwy011-013	Cal 1	Nut010	NOx	1st marked suspect – peak shape.
18, 19, uwy017-019	Cal 5	Nut013	SiO4	2nd marked suspect – peak shape.
exp058-068, uwy022	BQC	Nut015	NOx	1st marked suspect – peak shape.
23, uwy023-025	BQC	Nut016	NOx	Last marked suspect – peak shape.
23, uwy023-025	BQC	Nut016	NH4	Last marked bad – peak time slippage.
23, uwy023-025	Drift	Nut016	All	Removed – drift, drift correction did not occur on 2nd half of run. Ran out of volume.
exp069-104, uwy026	Cal 1	Nut017	NOx	Removed – as suspect in calibration curve.

CTD, exp, uwy	Peak	Run #	Analysis	Action
exp069-104, uwy026	Cal 5	Nut017	All	2nd one Removed – bad peak shape due to running out of volume.
exp069, uwy026	High	Nut017	All	Removed – bad peak shape due to running out of sample. Carryover correction used from run Nut016.
24, exp105-128, uwy027-030	Cal 1	Nut019	NOx	Removed – as outside acceptable calibration error.
24, exp105-128, uwy027-030	Cal 5	Nut019	NOx	2nd one marked suspect – peak shape.
24, exp105-128, uwy027-030	RMNS	Nut019	NOx	2nd one removed –bad peak shape.
26, 27, uwy040-042	RMNS	Nut022	NOx	Last one marked bad – bad peak shape.
35, 36, exp182-205	Cal 3	Nut026	SiO4	Removed – as outside acceptable calibration error.
39, 40, exp206-234, uwy043-045	Cal 3	Nut029	SiO4	2nd one Removed – bad peak shape.
42,43,44, exp235-240	Cal 1	Nut030	NOx	Removed – as outside acceptable calibration error.

6.7 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.

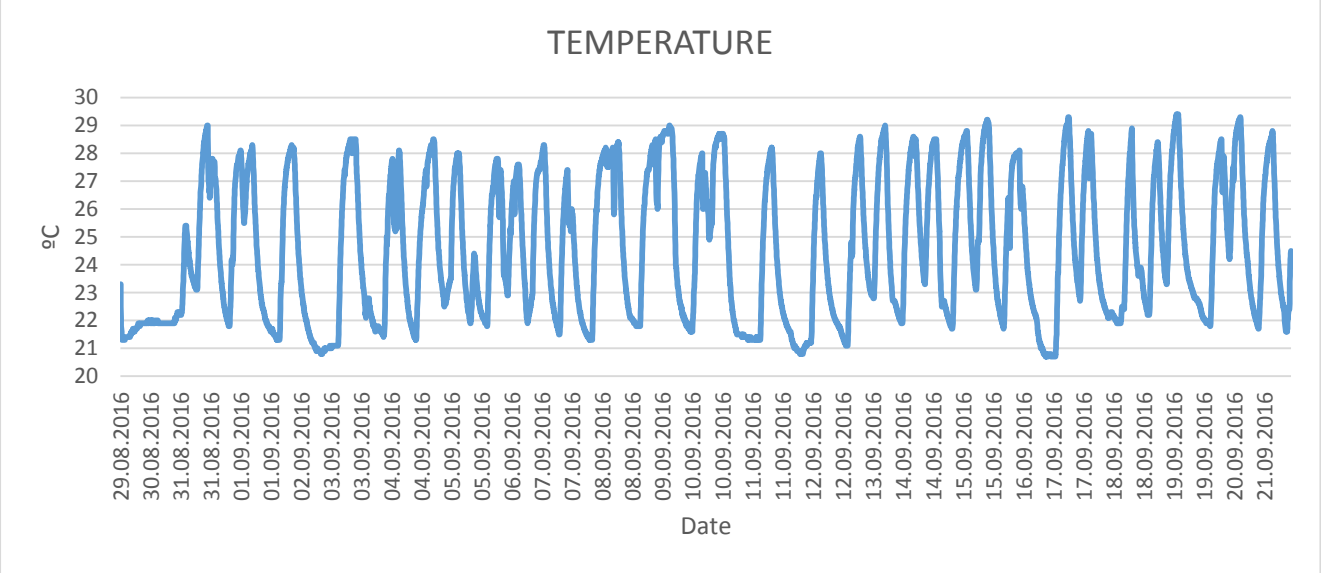
CTD, exp, uwy	RP	Run	Analysis	Flag	Reason for Flag or Action
1	All	Nut001	NH4	141	All NH4 data removed due to leak in NH4 chemistry module.
1	1	Nut001	SiO4	133	First duplicate marked bad due to spike in peak plateau.
1	1	Nut001	NOx	134	Second duplicate marked bad due to spike causing bad peak shape.
1	19	Nut001	NOx	65	Data good, HyPro flag due to peak shape.
5	1	Nut003	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
7	All	-	All	141	Nutrient samples not collected.
13	1	Nut010	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
14	1	Nut010	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
19	1	Nut013	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
21	1	Nut014	NH4	69	Data good, difference between duplicates > 0.02µM (MDL).
24	1	Nut019	NOx	133	First duplicate marked bad due to spike in peak plateau.
30	1	Nut024	NOx	133	First duplicate marked bad due to bad peak shape.
37	1	Nut027	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
39, 40	1	Nut029	NOx	69	First duplicate marked bad due to bad peak shape.
44	1	Nut030	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).
45	1	Nut031	NOx	69	Data good, difference between duplicates > 0.02µM (MDL).

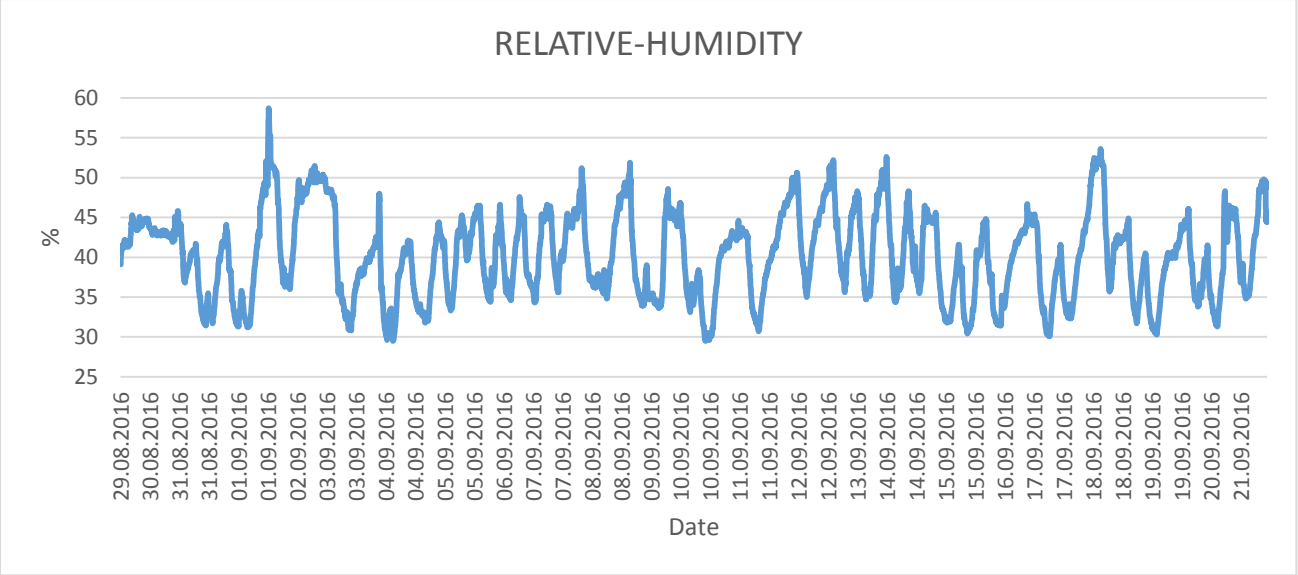
CTD, exp, uwy	RP	Run	Analysis	Flag	Reason for Flag or Action
48	1	Nut033	NOx	69	Data good, difference between duplicates >0.02µM (MDL).
exp066	-	Nut015	NOx	133	2nd duplicate flagged bad due to air going through the column.
exp066 – 104 & uwy026	-	Nut017	NH4	141	All NH4 data missing due to extreme negative shift in baseline.
exp111	-	Nut019	PO4	69	Data good, difference between duplicates > 0.02µM (MDL).
exp268, 269, 272	-	Nut033	NOx	69	Data good, difference between duplicates > 0.02µM (MDL). These samples were measured twice due to the odd peak shapes.
exp270	-	Nut033	NOx	133	Removed – measured 3 times the third result Ok, bad peak shape for first two results.
exp270	-	Nut033	NO2	129 &133	Measured 3 times, 1st time spike in plateau went over A/D range, 2nd time removed bad peak shape, 3rd time result OK.

6.8 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 "in2016_v04_HydrochemsistryReport.pdf" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.5°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 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.

7.4 RMNS Values for each Analytical Run

Run #	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
1	**37.1**	37.5	**1.44**	1.44	**0.077**	0.065	**20.25**	20.20
2	**37.2**	37.5	**1.43**	1.44	**0.077**	0.065	**20.23**	20.20
3	**37.1**	37.5	**1.45**	1.44	**0.076**	0.065	**20.23**	20.20
4	**37.2**	37.5	**1.45**	1.44	**0.070**	0.065	**20.15**	20.20
5	**37.0**	37.5	**1.44**	1.44	**0.076**	0.065	**20.20**	20.20
6	**37.2**	37.5	**1.43**	1.44	**0.075**	0.065	**N/A**	20.20
7	**37.4**	37.5	**1.43**	1.44	**0.069**	0.065	**20.21**	20.20
8	**37.4**	37.5	**1.45**	1.44	**0.073**	0.065	**20.28**	20.20
9	**37.3**	37.5	**1.42**	1.44	**0.063**	0.065	**20.26**	20.20
10	**37.1**	37.5	**1.46**	1.44	**0.071**	0.065	**20.24**	20.20
11	**37.0**	37.5	**1.46**	1.44	**0.071**	0.065	**20.18**	20.20
12	**36.8**	37.5	**1.44**	1.44	**0.076**	0.065	**20.25**	20.20
13	**37.1**	37.5	**1.47**	1.44	**0.073**	0.065	**20.10**	20.20
14	**37.4**	37.5	**1.43**	1.44	**0.071**	0.065	**20.67**	20.20
15	**37.3**	37.5	**1.46**	1.44	**0.073**	0.065	**20.10**	20.20
16	**37.1**	37.5	**1.42**	1.44	**0.079**	0.065	**20.17**	20.20
17	**37.2**	37.5	**1.43**	1.44	**0.076**	0.065	**20.18**	20.20
19	**37.2**	37.5	**1.44**	1.44	**0.073**	0.065	**20.16**	20.20
20	**37.1**	37.5	**1.46**	1.44	**0.079**	0.065	**20.53**	20.20
21	**37.1**	37.5	**1.43**	1.44	**0.071**	0.065	**20.05**	20.20
22	**37.4**	37.5	**1.45**	1.44	**0.075**	0.065	**20.07**	20.20
23	**37.5**	37.5	**1.44**	1.44	**0.080**	0.065	**20.05**	20.20
24	**37.6**	37.5	**1.45**	1.44	**0.073**	0.065	**20.12**	20.20
25	**37.6**	37.5	**1.44**	1.44	**0.074**	0.065	**20.07**	20.20
26	**37.3**	37.5	**1.44**	1.44	**0.075**	0.065	**20.26**	20.20
27	**37.2**	37.5	**1.43**	1.44	**0.071**	0.065	**20.35**	20.20
29	**37.4**	37.5	**1.44**	1.44	**0.073**	0.065	**20.16**	20.20
30	**37.6**	37.5	**1.45**	1.44	**0.077**	0.065	**20.18**	20.20
31	**37.5**	37.5	**1.46**	1.44	**0.079**	0.065	**20.01**	20.20
32	**37.6**	37.5	**1.45**	1.44	**0.079**	0.065	**20.12**	20.20
33	**37.1**	37.5	**1.44**	1.44	**0.077**	0.065	**20.18**	20.20
34	**36.9**	37.5	**1.45**	1.44	**0.073**	0.065	**20.17**	20.20
35	**37.0**	37.5	**1.45**	1.44	**0.064**	0.065	**20.12**	20.20
36	**37.1**	37.5	**1.46**	1.44	**0.071**	0.065	**20.82**	20.20

7.5 Nutrient Methods

CSIRO Oceans and Atmosphere Hydrochemistry nutrient analysis is performed with a segmented flow auto-analyser – Seal AA3 – to measure silicate, phosphate, nitrite, nitrate plus nitrite, and ammonia.

Table 2: Calibration range and detection limits of nutrient analysis

Details					
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Concentration range	140 µmol l^{-1}	3 µmol l^{-1}	42 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}

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 Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57), is based on the reaction of ammonium with orthophtaldialdehyde 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.

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