RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage: IN2016_v03 Leg 1/Leg2

Chief Scientist: Bernadette Sloyan/Susan Wijffels

Voyage title: Monitoring Ocean Change and Variability along 170°W from the ice edge to the equator

Report compiled by: Christine Rees, Peter Hughes, Stephen Tibben, Kelly Brown, Cassie Schwanger & Melissa Miller

Contents

1 Itinerary

Depart Leg 1	Date	Time
Hobart	26 April	0800
Arrive	Date	Time
Wellington (NZ)	26 May	1100
Depart Leg 2	Date	Time
Wellington (NZ)	27 May	1100
Arrive	Date	Time
Lautoka (Fiji)	30 June	0800

2 Key personnel list

Name	**Role**	**Organisation**
Dr. Bernadette Sloyan	Chief Scientist Leg 1	CSIRO
Dr. Susan Wijffels	Chief Scientist Leg 2	CSIRO
Don McKenzie	Voyage Manager Leg 1	CSIRO
Stephen Thomas	Voyage Manager Leg 2	CSIRO
Peter Hughes	Hydrochemist Leg 1	CSIRO
Christine Rees	Hydrochemist Leg 1 & 2	CSIRO
Stephen Tibben	Hydrochemist Leg 1 & 2	CSIRO
Kelly Brown	Hydrochemist Leg 1 & 2	CSIRO
Melissa Miller	Hydrochemist Leg 1	SCRIPPS
Cassie Schwanger	Hydrochemist Leg 2	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.

Dissolved Oxygen data has been corrected for Thiosulfate and blank concentration variation across the voyage (see section 5).

Nutrient experimental samples for ammonium were frozen and measured during transit at the end of each voyage leg.

3.1 Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	5740
Dissolved Oxygen (automated titration)	4690 CTD 94 UWY
Nutrients (AA3)	4705 CTD 94 UWY 245 EXP (NH_4)

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

- 140 CTD stations were sampled with a 36 bottle rosette (12 L), Dep 1 was the test cast to train samplers. However, salinities were analysed from this deployment.
- The following deployments failed either due to CTD malfunction or bottles not firing; deployment 7, 10, 14 (only 5 Niskin bottles closed), 16, 18, and 83.
- See in2016_v03_HydrochemistryReport.pdf (voyage report) for more details on sample collection.

3.3 Procedure Summary

The procedure for data processing is outline in Figure 1.

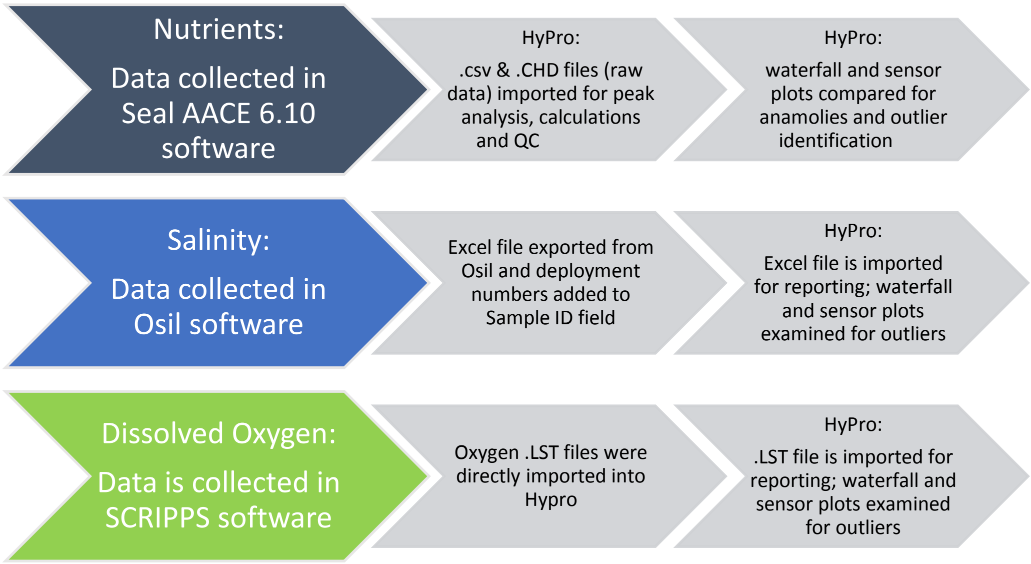


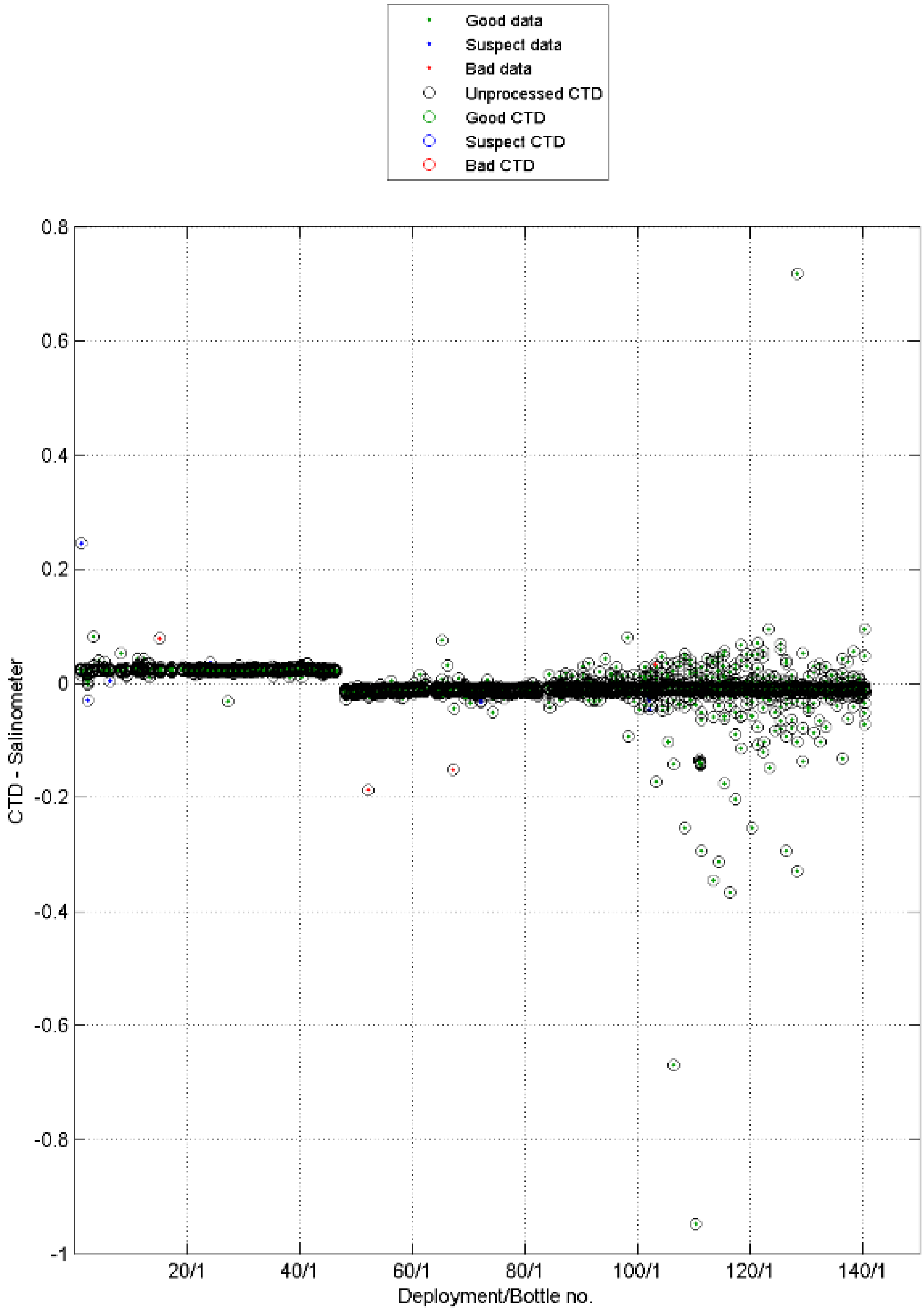
Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

4 Salinity Data Processing

4.1 Salinity Parameter Summary

Details	
HyPro Version	4.12
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71613
Software	Osil
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 salinity units
Analyst(s)	Stephen Tibben
Lab Temperature (±0.5°C)	21.0 -24.0°C during analysis.
Bath Temperature	24°C
Reference Material	Osil IAPSO - Batch P157
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. A duplicate sample from rosette position 2 was used to monitor the temperature of the samples to ensure temperature equilibration had occurred before analysis.
Comments	Principle investigators chose to use a smaller headspace within the salinity bottles (8 ml, compared with 25 ml recommended by Hydrochemistry team) from deployment 62 onwards. Experimental work during voyage showed no significant difference between salinity bottles with an 8 ml headspace compared to that of a 25 ml headspace.

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	Analysis	Flag	Reason for Flag or Action
1	26	C26	Salt	69	Sampling error? Training samplers/changed O-rings
1	5	C05	Salt	141	Niskin lid did not close, no sample
1	10	C10	Salt	69	Sampling error? Training
2	31	J32	Salt	69	Very high Niskin frozen
6	31	B31	Salt	69	Very high Niskin frozen
15	17	J17	Salt	133	Waterfall profile out
19	17,23		Salt	141	Niskin bottles did not fire.
24	7	E07	Salt	141	Niskin bottles did not fire.
24	13	E13	Salt	69	Waterfall profile out
38	all	all	Salt	0	All samples had less than recommended headspace.
44	20	E21	Salt	141	Niskin Lanyard caught in lid bottle leaking.
47	36		Salt	141	Niskin fired in air.
49	2, 3, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30,		Salt	141	Niskins not sampled
50	3, 7, 10, 12, 14, 16, 18, 20, 22, 24, 26, 29, 32		Salt	141	Niskins not sampled
52	20	H20	Salt	133	Outlier – lanyard was caught on bottle so possible leak
53	17		Salt	141	Niskin end cap didn't close
55	32		Salt	141	No data

CTD	RP	Bottle	Analysis	Flag	Reason for Flag or Action
67	25	K25	Salt	133	Waterfall profile out
72	10, 9	H10, H09	Salt	69	Waterfall profile out and also in error plot.
74	09		Salt	141	Niskin leaking did not sample
84	1, 2		Salt	141	Niskins not sampled
90	13	A13	Salt	0	Waterfall profile out
102	15,16,17	A15,A16, A17	Salt	69	Waterfall profile out RP15 was leaking
103	5	J05	Salt	133	Waterfall profile out, noted in sample log niskin rp 5 was warmer temperature than other bottles.
112	33-36		Salt	141	Niskins not sampled
113	10		Salt	141	Niskin not sampled
119	13		Salt	141	Niskin not sampled
124	10, 26		Salt	141	Niskin not sampled
134	11		Salt	141	Niskin not sampled
137	3	J03	Salt	0	Waterfall plot out
138	14		Salt	141	Niskin not sampled
139	14	C14	Salt	0	Waterfall plot out – niskin had just been majorly serviced
140	27	A27	Salt	133	Vertical profile plot out. Niskin Lanyard caught in lid - bottle leaking. Also bad for nutrients.

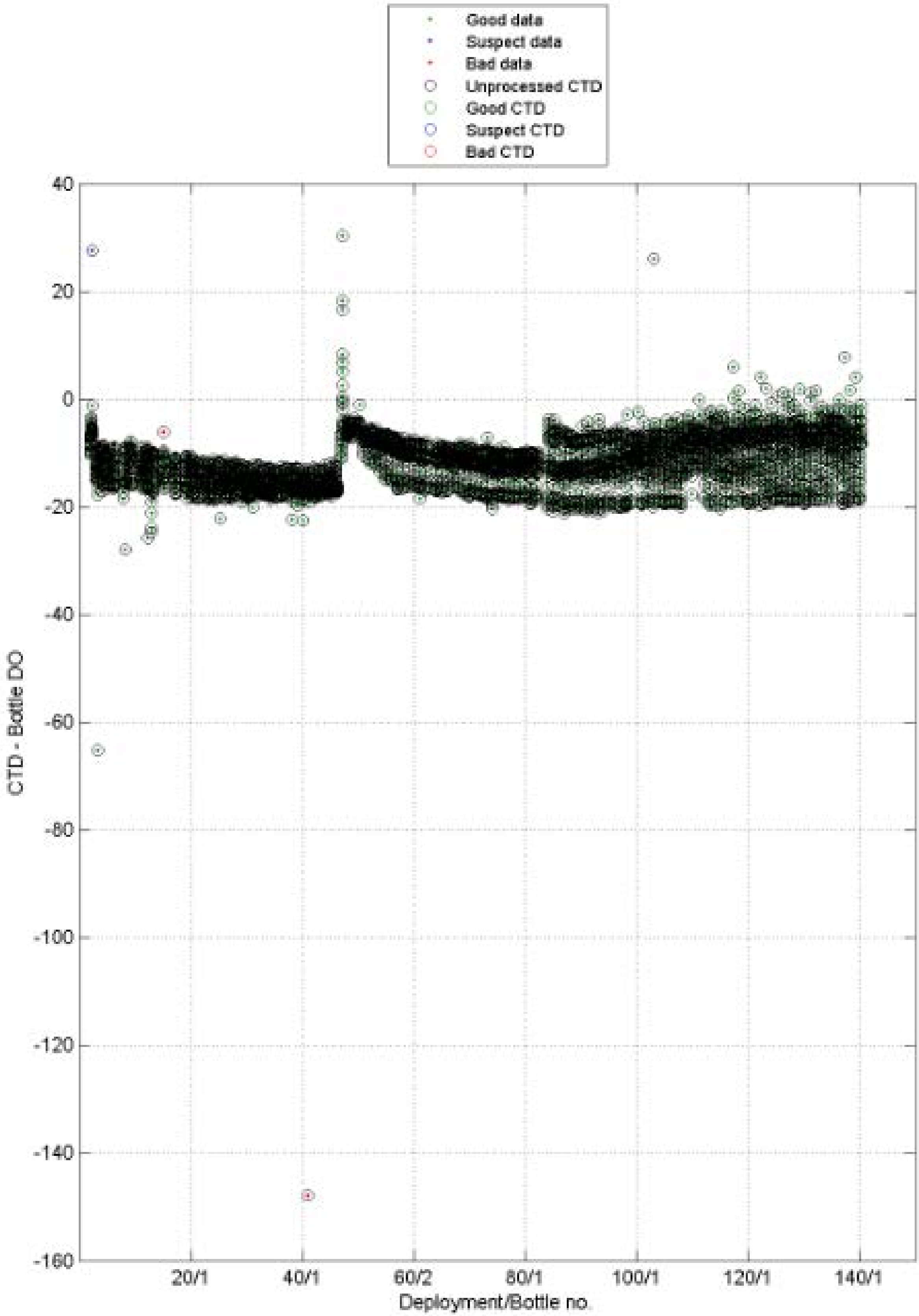
5 Dissolved Oxygen Data Processing

5.1 Dissolved Oxygen Parameter Summary

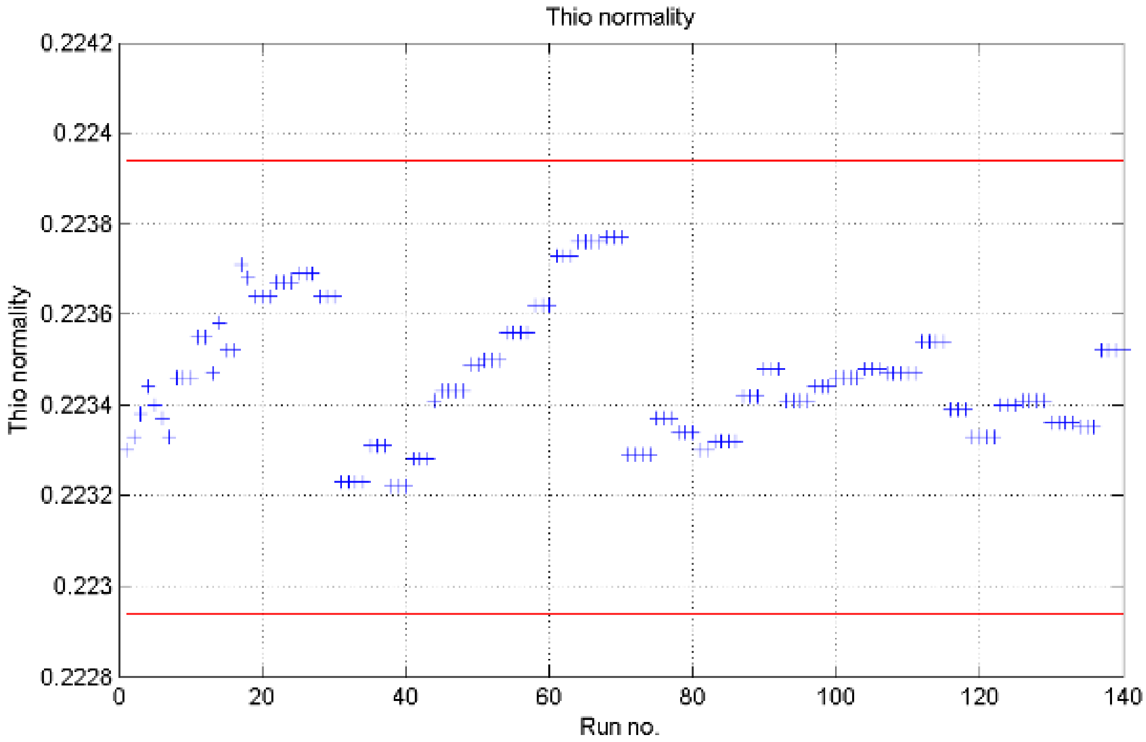
Details	
HyPro Version	4.12
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Kelly Brown
Lab Temperature (±1°C)	Variable, 20.0 - 23.0°C
Sample Container type	Pre-numbered glass 140 mL glass vial w/stopper, sorted into 18 per box and 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 ~18 hrs
Comments	Duplicate samples were collected randomly during every deployment to monitor sampling consistency. The duplicate sample was analysed as a test sample. There was some concern about the integrity of the tropical surface samples stored in the 21°C Hydrochemistry lab. An experiment was conducted to compare dissolved oxygen samples stored at 21°C and 30°C, no statistical difference was found between the dissolved oxygen concentrations. The samples continued to be stored in the hydrochemistry lab until analysis.

An extra calculation for the final dissolved oxygen concentration was implemented during the voyage. This calculation smoothed the data due to the day-to-day variation in the thiosulphate titrant concentration and blank values. Kelly Brown performed the calculation according to the Oxygen Titration Manual SIO/STS version: Jun-2015 section 7.1 Thiosulfate Smoothing Procedure. Steve vanGraas wrote a script that pulled the corrected data into the existing LST files which was then be re-read by HyPro.

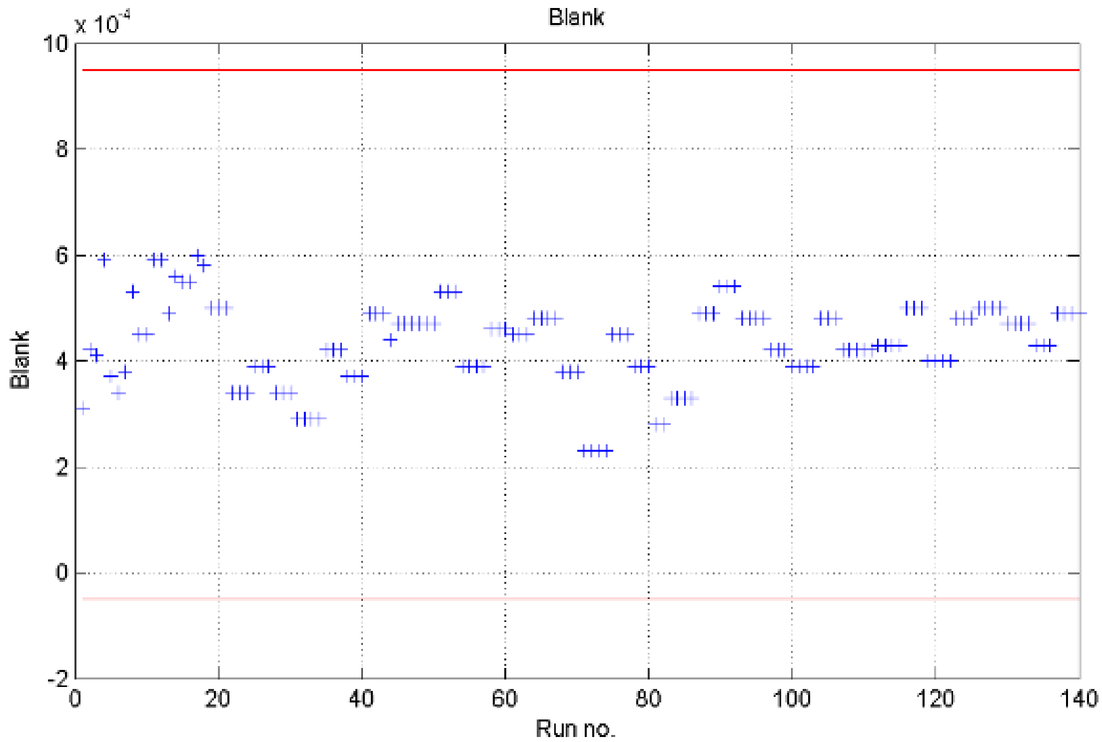
5.2 CTD vs Hydro DO Plot



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	Analysis	Flag	Reason for Flag or Action
2	31	187	D.O.	69	High Niskin bottle froze
uwy	017	647	D.O.	69	pCO2 system blowing air
4	11	252	D.O.	133	Incorrect volume possibly? Profile suspect
6	12	252	D.O.	133	Incorrect volume possibly? Profile suspect- flask pulled from box.
13	23	440	D.O.	141	Flask broke, lost sample, removed from file
15	17	430	D.O.	133	Profile is suspect, is also suspect for nuts, salt, cfc's.
19	17,23		D.O.	141	Bottles did not fire.
22	08	143	D.O.	141	Abort, titrator malfunction, lost sample removed from file
30	20	407	D.O.	141	Abort, titrator malfunction, lost sample removed from file
31	19	161	D.O.	141	Abort, titrator malfunction, lost sample removed from file
32	21	261	D.O.	141	Abort, titrator malfunction, lost sample removed from file
32	27	267	D.O.	141	Abort, titrator malfunction, lost sample removed from file
38	11	147	D.O.	141	Flask smashed while sampling
uwy	045	638	D.O.	69	NaOH/I bubble
39	01	232	D.O.	133	Draw Temp maybe incorrect, temperature probe was malfunctioning.
39	03	235	D.O.	141	Also sample 03 Abort, titrator malfunction, lost sample.
41	04	136	D.O.	133	2 magnets in flask bad endpoint
42	04	200	D.O.	69	Profile suspect in waterfall plot.
44	20		D.O.	141	Niskin Lanyard caught in lid bottle leaking.
47	36		D.O.	141	Niskin fired in air.

CTD	RP	Bottle	Analysis	Flag	Reason for Flag or Action
53	36	653	D.O.	141	Abort, not enough NaOH/I in sample to titrate.
56	01	728	D.O.	133	black particles in flask
59	01	161	D.O.	141	Abort, titrator malfunction, lost sample removed from file
60	01		D.O.	141	Stopper put in bottle upside down
74	09		D.O.	141	Niskin leaking did not sample
100	11	322	D.O.	141	Abort, titrator malfunction, lost sample removed from file
103	05	566	D.O.	133	Waterfall profile out noted in sample log niskin rp 5 warmer temperature than other niskins.
110	04	582	D.O.	133	Waterfall profile out.
112	02	279	D.O.	141	Abort, titrator malfunction, lost sample removed from file
128	13	687	D.O.	141	Abort, titrator malfunction, lost sample removed from file
134	11		D.O.	141	NISKIN leaking not sampled for D.O.
136	14,15		D.O.	141	NISKINS leaking not sampled for D.O.
138	14		D.O.	141	NISKIN leaking not sampled for D.O.
139	31		D.O.	141	NISKIN leaking not sampled for D.O.
140	19, 22, 27		D.O.	141	NISKINS leaking not sampled for D.O.

6 Nutrient Data Processing

6.1 Nutrient Parameter Summary

Details					
HyPro Version	4.12				
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)	Peter Hughes, Melissa Miller, Christine Rees and Cassie Schwanger				
Lab Temperature (±1°C)	Variable, 20.0 – 23.0°C				
Reference Material	RMNS – CA, BV, BW				
Sampling Container type	10 mL polypropylene				
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 samples were collected and frozen for ammonia analysis. Ammonia was measured at the end of Leg 1 and again at the end of Leg 2. Surface ammonia samples were collected from the CTD as well as a MDL that varied in depth. Underway samples were measured within a 24 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 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: http://www.cmar.csiro.au/datacentre/process/data_files/Investigator_NF/in2016_v03/data/in2016_v03Hydro_nc.zip

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 6.6 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	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 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 and stored in the constant temperature room 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 3.6.6. The reported data is not corrected to the RMNS. Per run RMNS data can be found in Appendix 5.4.				

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. 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.

The RMNS Lot CA (produced 22/02/2013) was measured 4 times in every CTD analysis. The RMNS Lot BV (produced 15/09/2011) was analysed every few days alongside the CA. The RMNS Lot BW was only measured once in 4 replicates during the voyage. 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
BV	36.21	36.26	0.048	2.56	104.6
BW	25.18	25.25	0.069	1.58	61.45

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

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

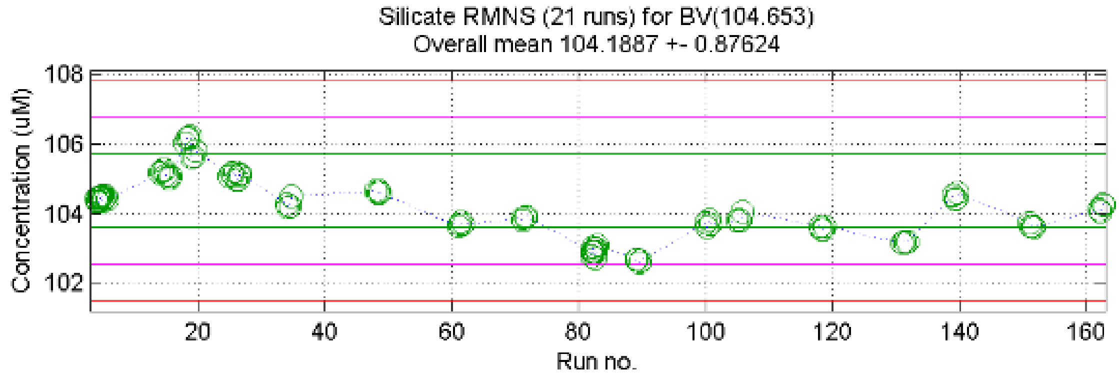
Corrected Nutrient Concentration = Nutrient measured – (nutrient measured x error)

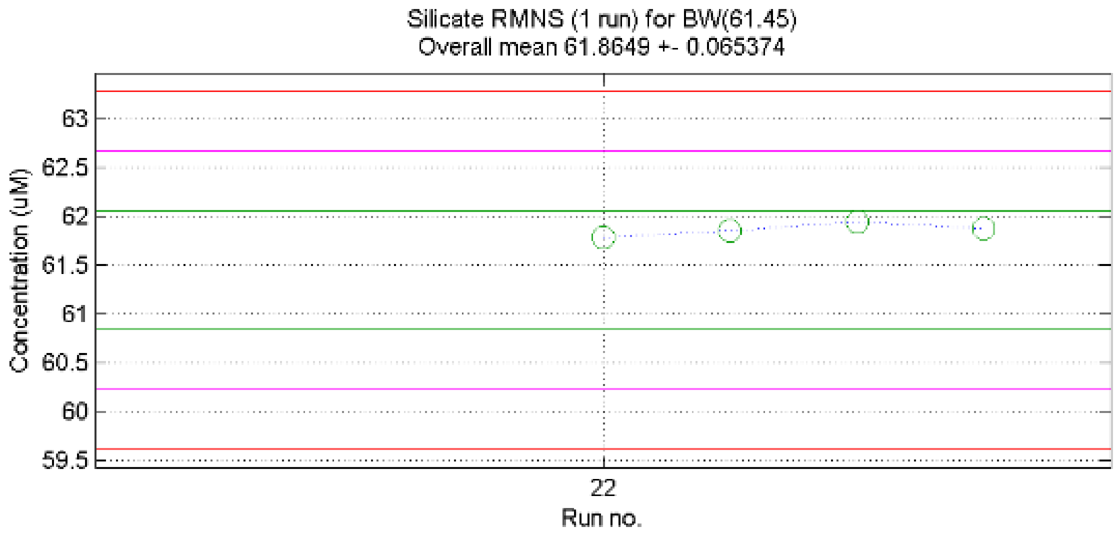
Note: NOx data should be corrected as NO_3 and NO_2.

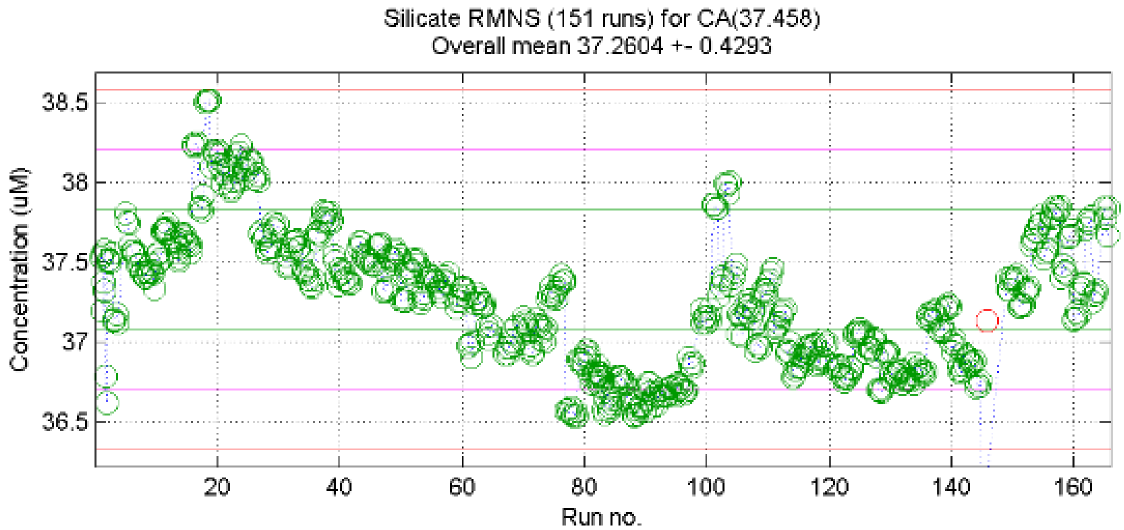
The following plots show RMNS values within 1% (green lines), 2% (pink lines) and 3% (red lines) of the published RMNS value except for nitrite. The nitrite limit is set to ±0.020 µM (MDL) as 1% is below the method MDL. The GO-SHIP criteria (Hyde *et al*., 2010), reference section 5.3, specifies using 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 5.4.

6.3.1 Silicate RMNS Plot

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

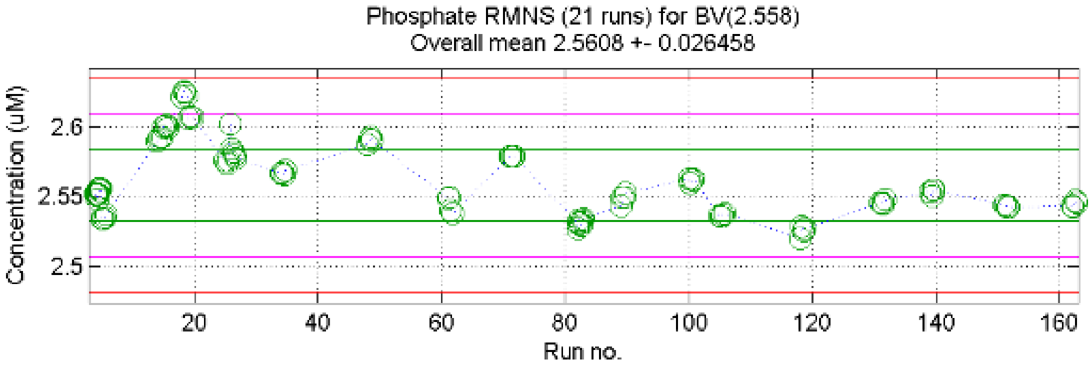


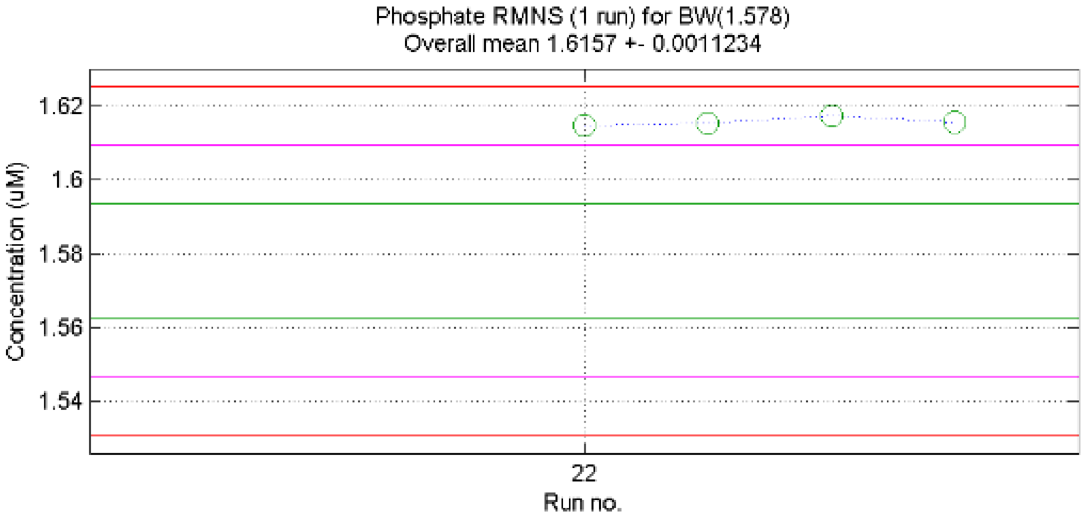


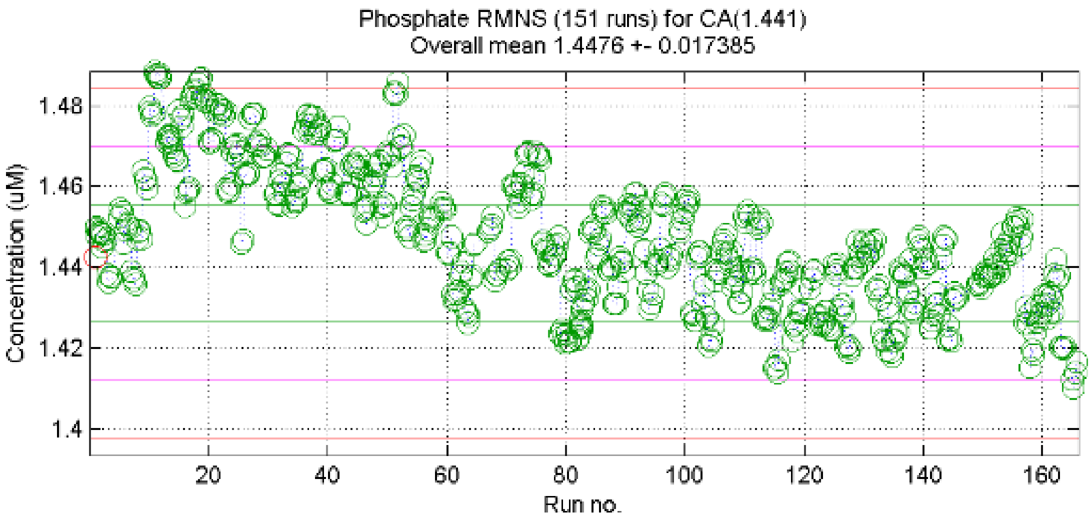


6.3.2 Phosphate RMNS Plot

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

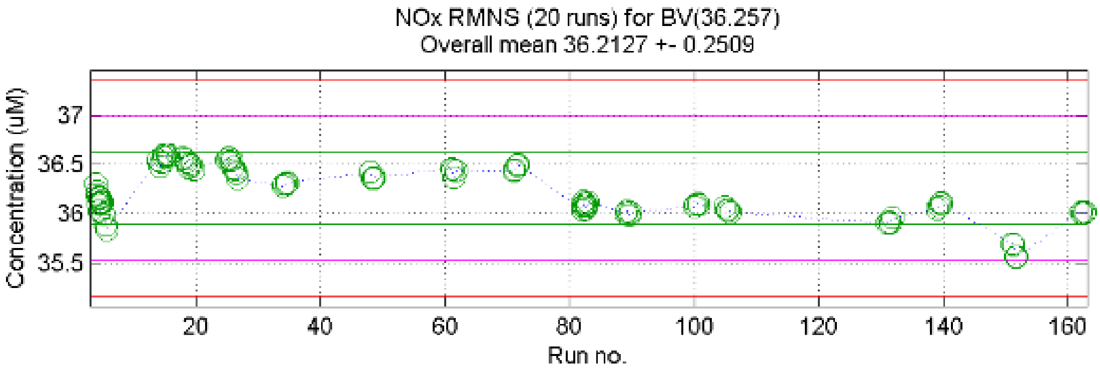


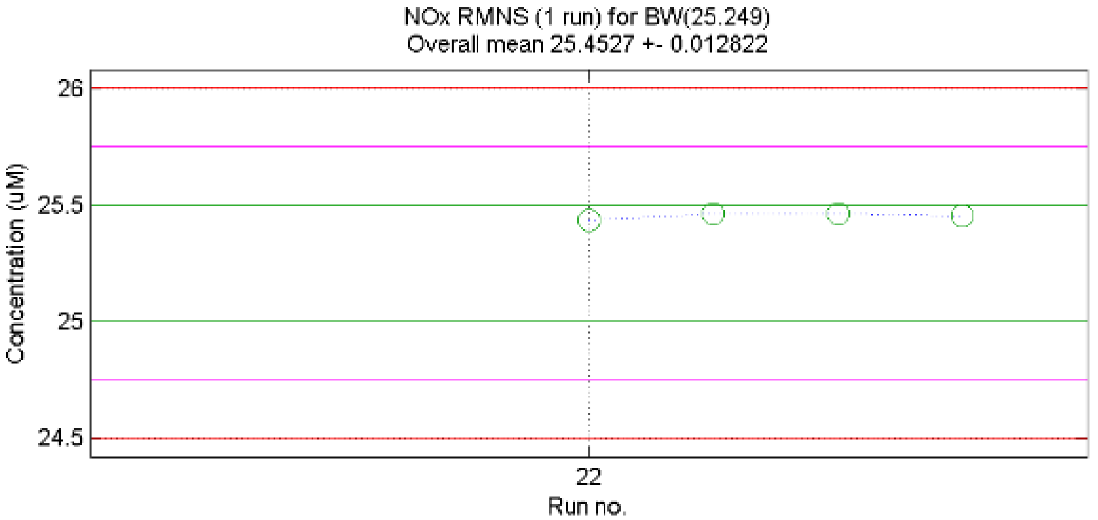


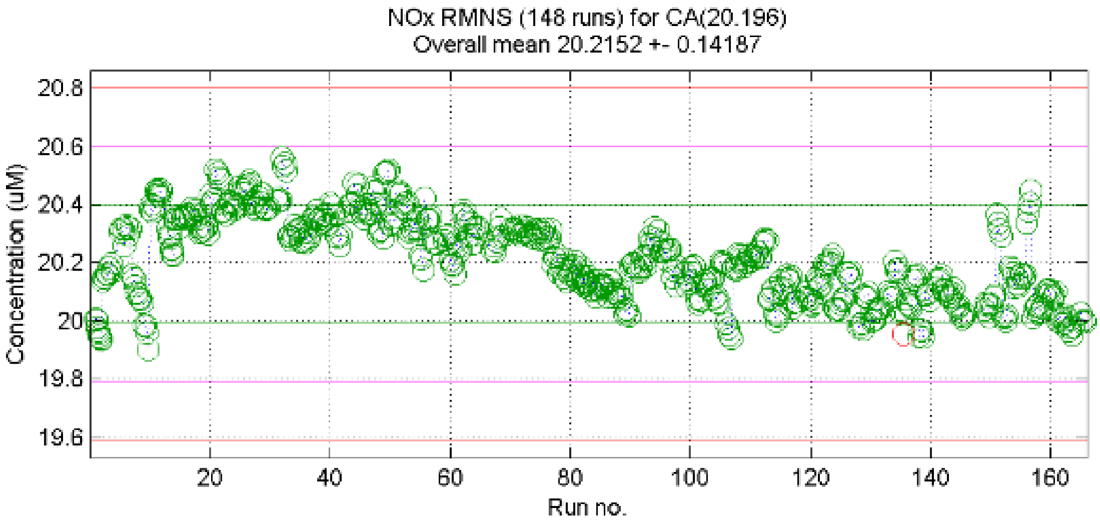


6.3.3 Nitrate + Nitrite (NOx) RMNS Plot

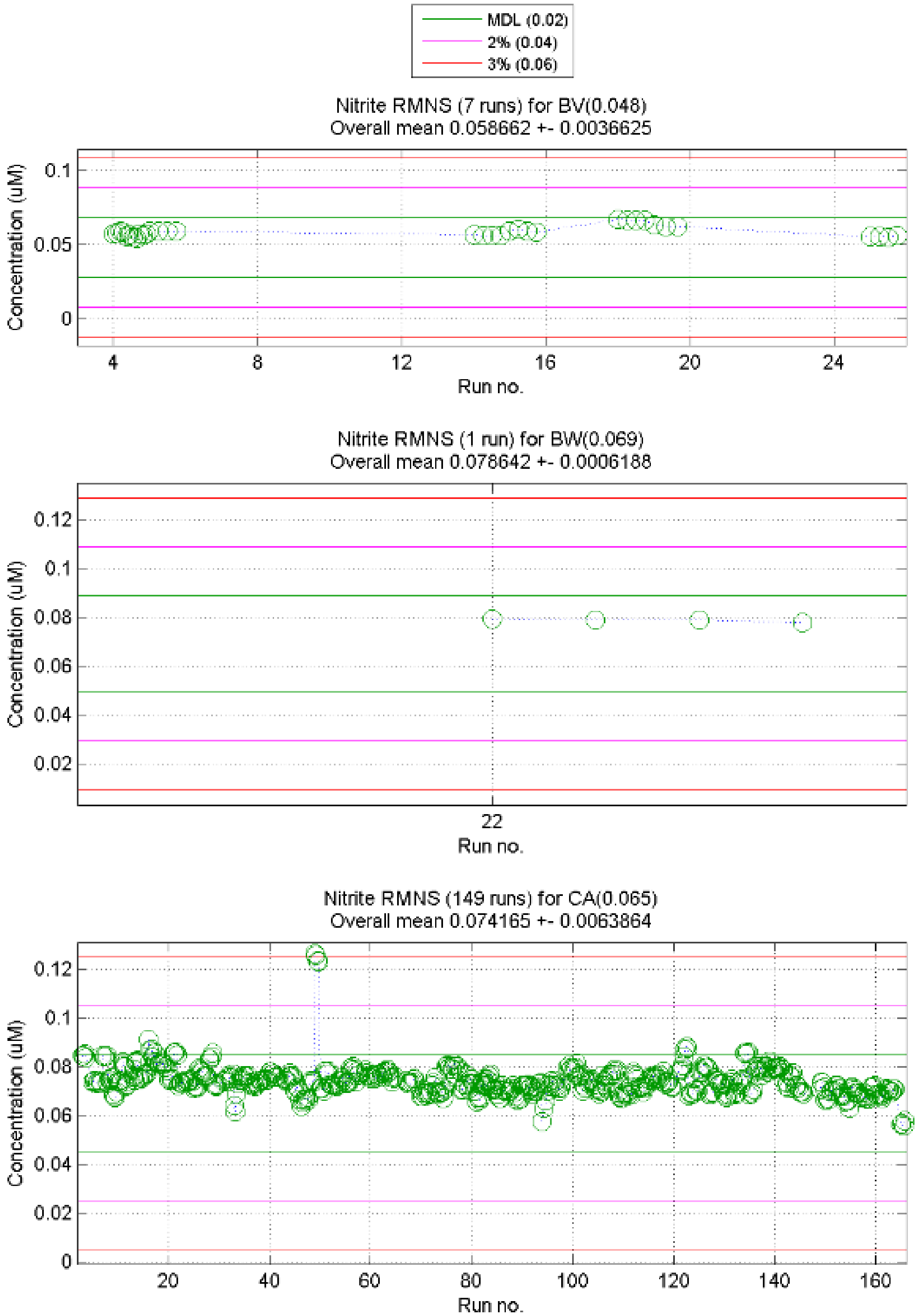
1% of RMNS value   2% of RMNS value   3% of RMNS value







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**	**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.

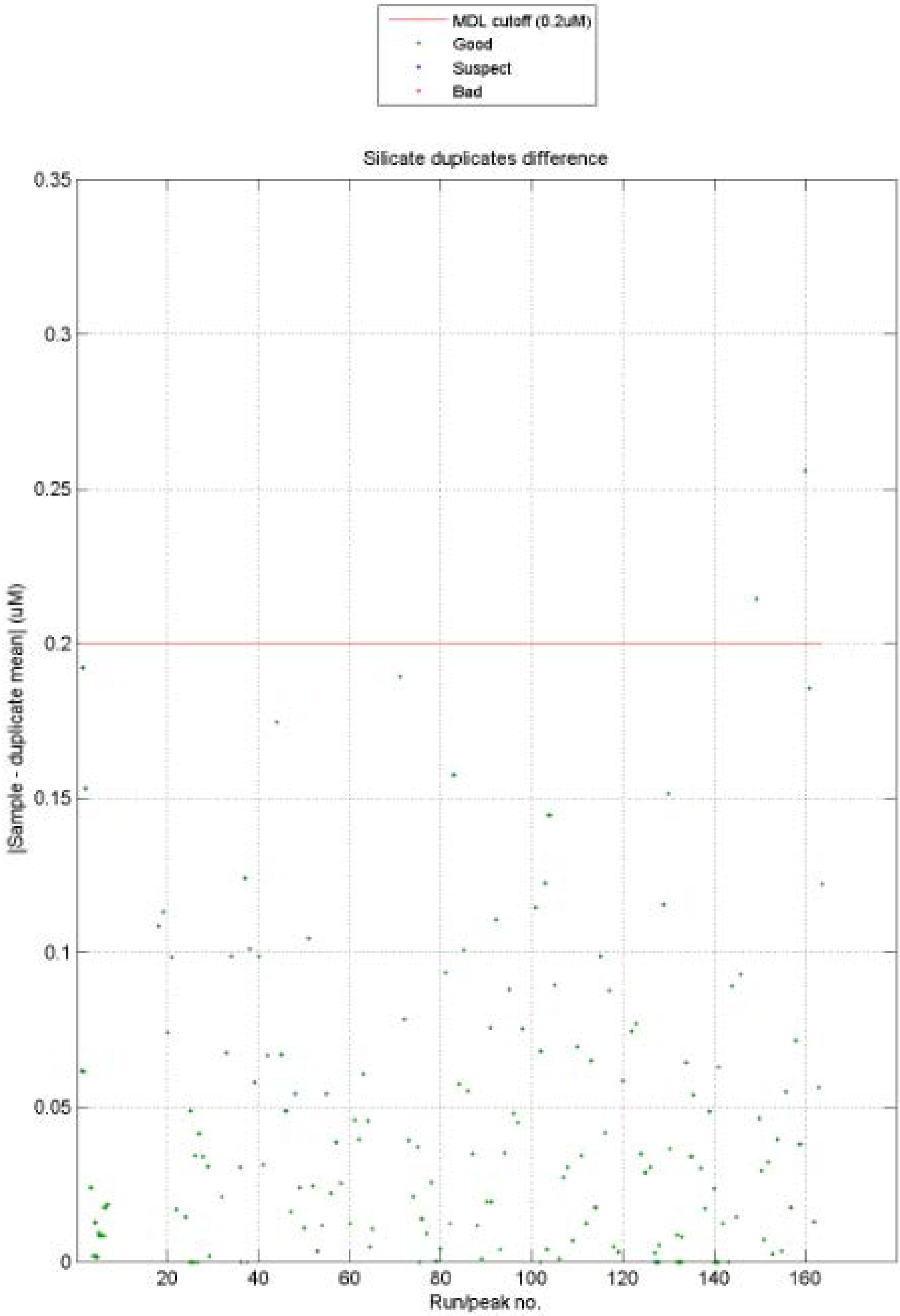
Method detection limits (MDL) achieved during the voyage were much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. Results are µmol l^{-1}. The precision of the RMNS is was also determined.

MDL	**Silicate**	**Phosphate**	**Nitrate + Nitrite (NOx)**	**Nitrite**	**Ammonia**
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Min	0.002	0.001	0.002	0.001	0.009
Max	0.227	0.015	0.032	0.011	0.009
Mean	**0.057**	**0.004**	**0.007**	**0.003**	**0.009**
Median	0.039	0.003	0.006	0.003	0.009
Precision of MDL (stdev)	0.050	0.003	0.005	0.002	NA
*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	36.03	1.413	19.96	0.062	-
RMNS Max	38.51	1.488	20.54	0.087	-
RMNS Mean	**37.26**	**1.447**	**20.29**	**0.074**	**-**
RMNS Median	37.26	1.445	20.31	0.073	-
RMNS Std Dev	0.43	0.017	0.12	0.005	-

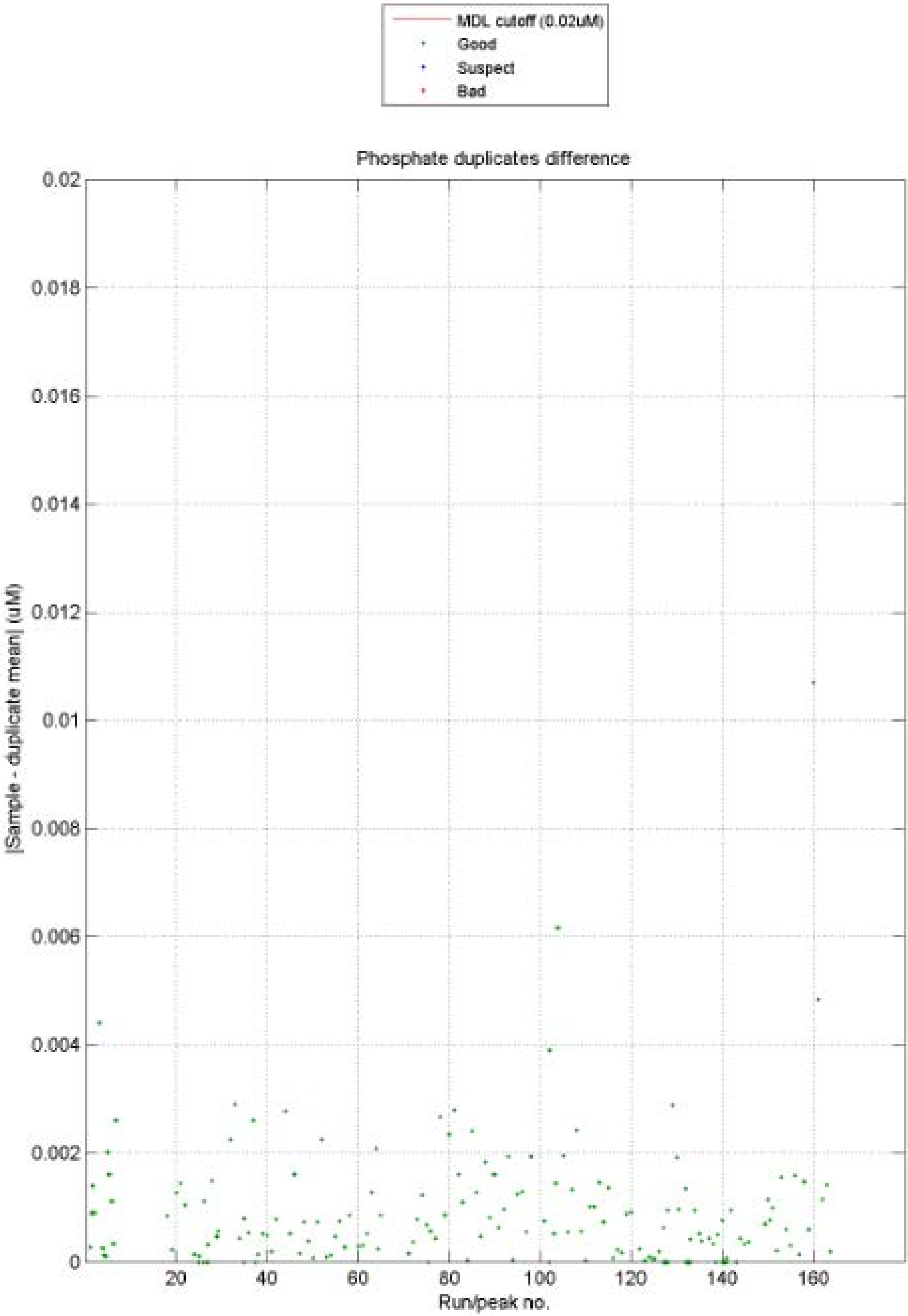
6.5 Sampling Precision

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 and nitrite and within 0.05 µM for nitrate.

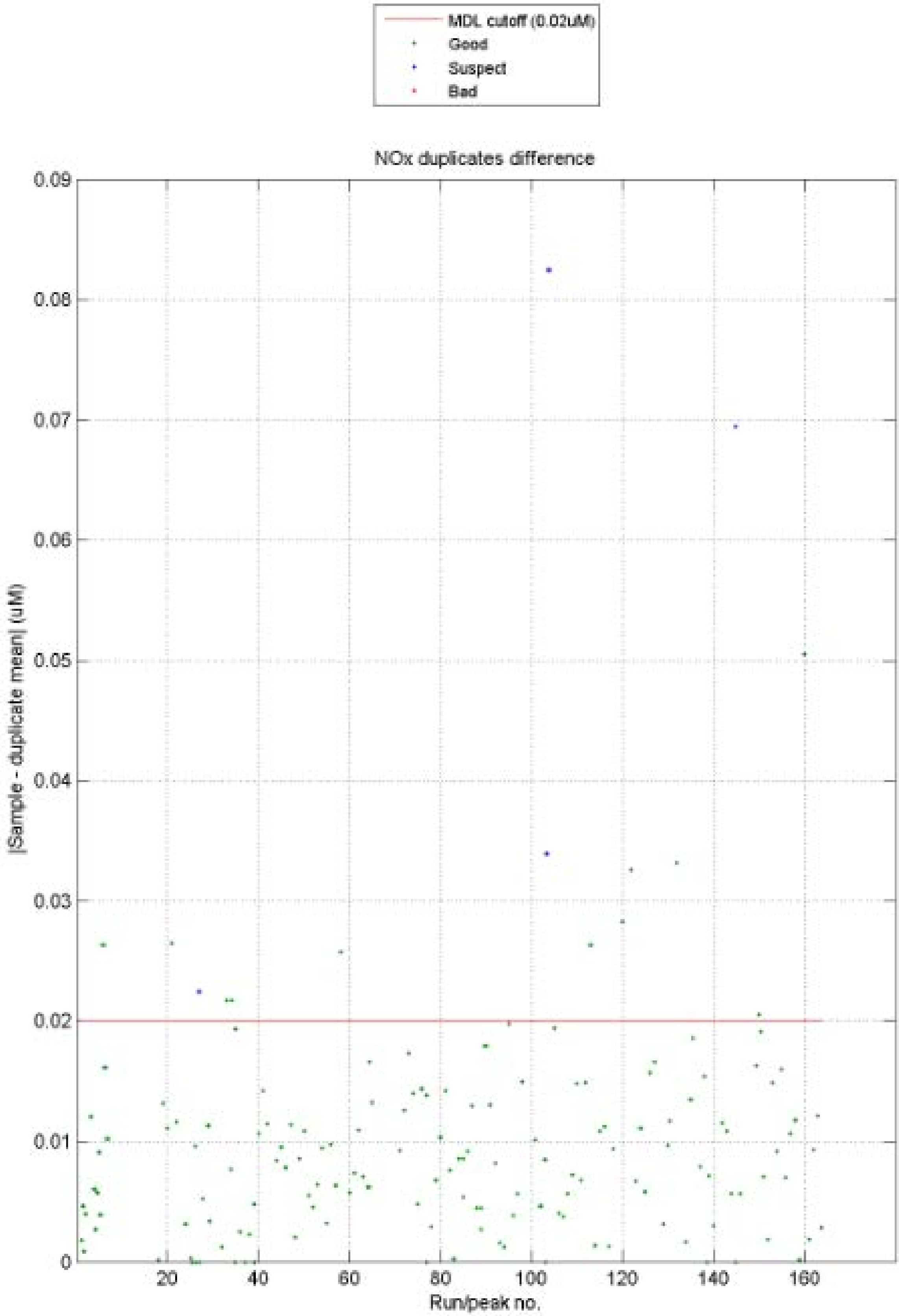
6.5.1 Silicate Duplicate Plot



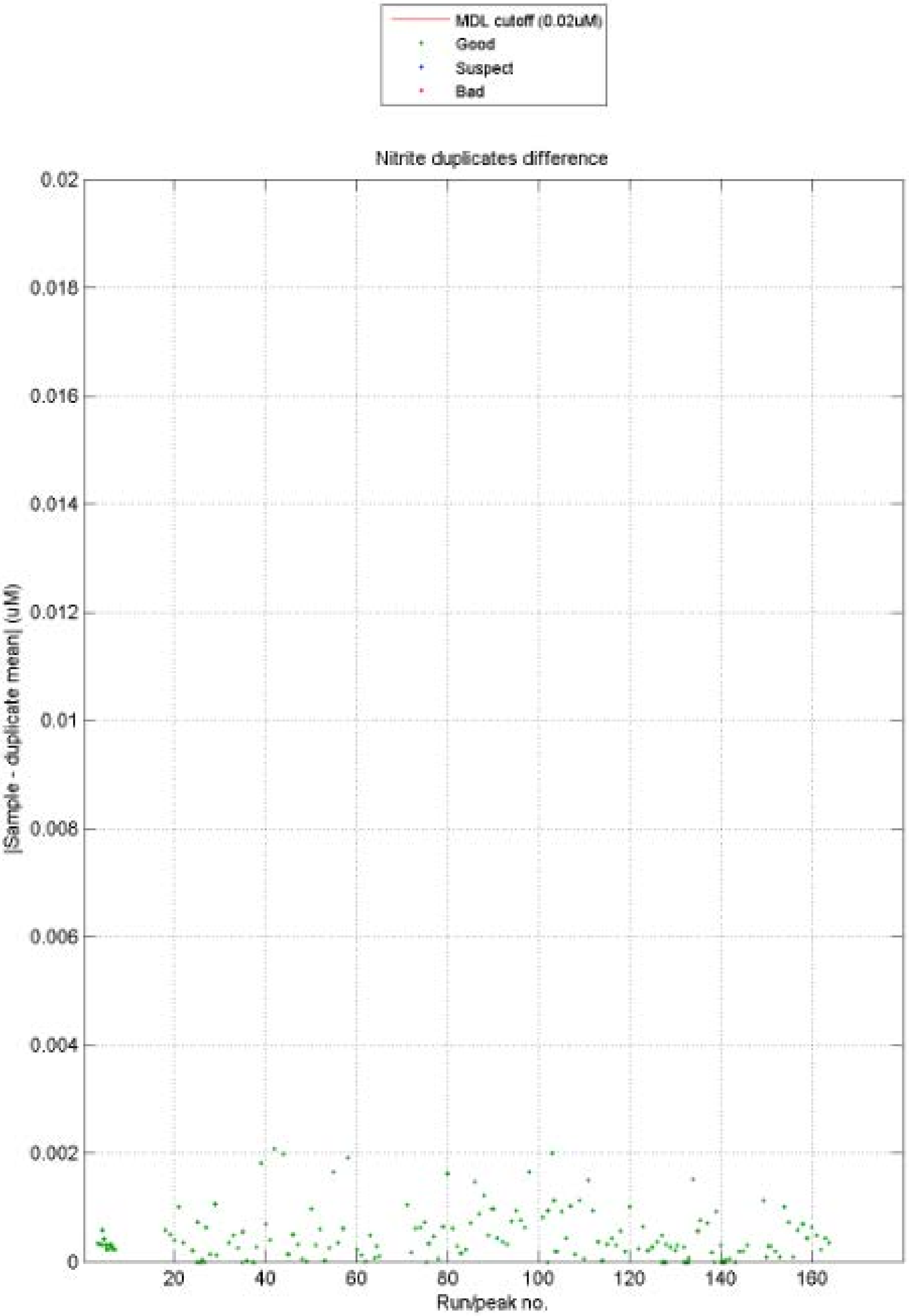
6.5.2 Phosphate Duplicate Plot



6.5.3 Nitrate + Nitrite (NOx) Duplicate Plot

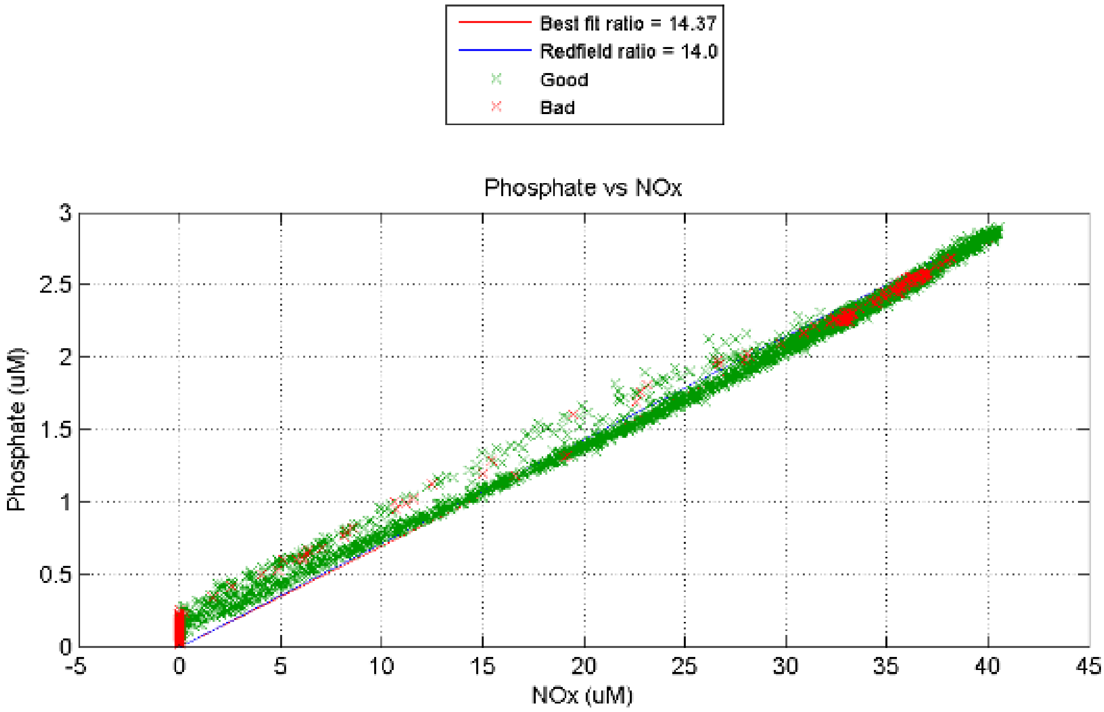


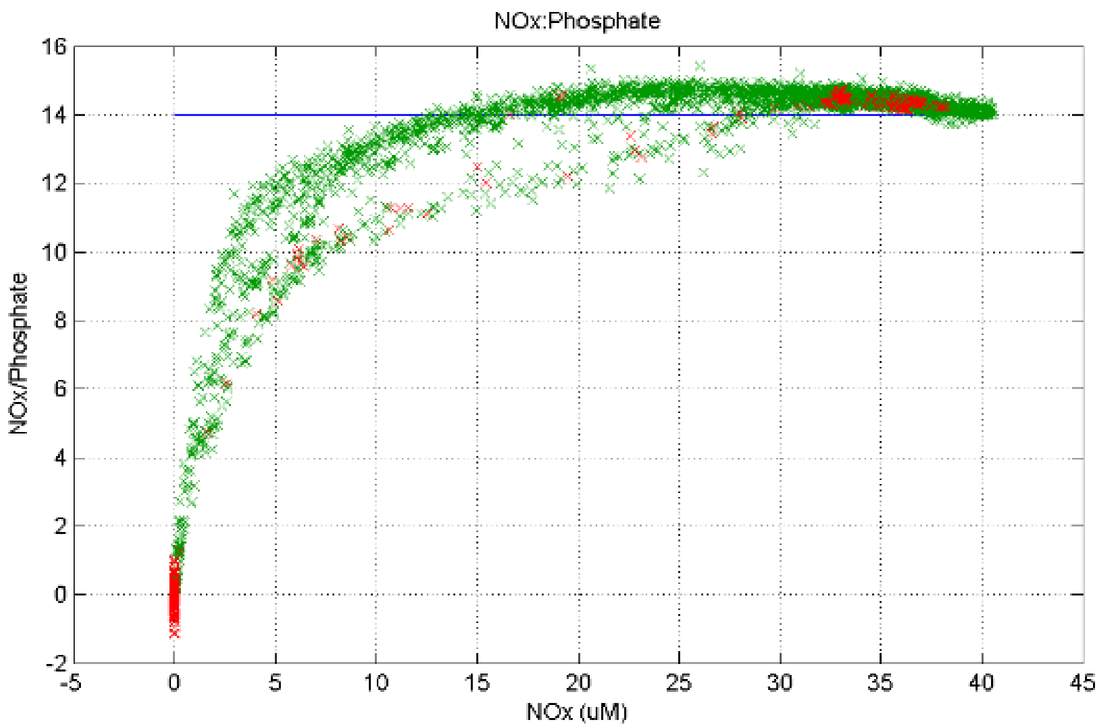
6.5.4 Nitrite Duplicate Plot



6.5.5 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx, best fit ratio = 14.37.





6.6 Calibration and QC edited data

CTD	Peak	Analysis	Action
29	Cal 5	NO2	Cal 5 was removed from curve, no carry over corrections were applied
30	Cal 5	NO2	Cal 5 was removed from curve, no carry over corrections were applied
108	Recovery	NOx	No cadmium column recovery determined
113	Cal 2	NOx	2nd Cal 2 removed due to spike on the peak
122	Cal 2	SiO4	Removed – outlier on curve
123	Cal 2	SiO4	Removed – outlier on curve
128	Cal 2	NOx	Removed – outlier on curve
128	Cal 4	SiO4	Removed – outlier on curve
129	Cal 1	NOx	Removed – outlier on curve
134	Cal 3	SiO4	Removed – outlier on curve
135	Cal 3	SiO4	Removed – outlier on curve
136	Cal 3	SiO4	Removed – outlier on curve
139	Cal 1, 2, 3, 4, 5	SiO4	Removed – outlier on curve
140	Cal 1, 2, 3, 4	SiO4	Removed – outlier on curve
140	Cal 1	NOx	Removed – outlier on curve

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	RP	Run	Analysis	Flag	Reason for Flag or Action
2	20	Nut017	NOx	65	Data good, hypro flag due to peak shape
3	11	Nut018	SiO4	65	Data good, hypro flag due to peak shape
4	03	Nut019	SiO4	65	Data good, hypro flag due to peak shape

CTD	RP	Run	Analysis	Flag	Reason for Flag or Action
9	07	Nut024	NOx	0	Outlier in waterfall profile for the first analysis, repeated and reported result from run nut025
11	04	Nut025	NOx	0	Outlier in waterfall profile, repeated in nut026, use result from nut026
11	28	Nut025	PO4	0	Outlier in waterfall profile, repeated in nut026, use result from nut026.
12	15	Nut026	NOx	0	Outlier in waterfall profile, repeated in nut027, use result from nut027.
15	17	Nut029	All Nuts	133	Does not follow water fall plot, flagged as bad. Niskin mistrip.
19	01	Nut032	NOx	0	Outlier in waterfall profile, repeated in nut033, use result from nut033
19	17,23	Nut032	All Nuts	141	Bottles did not fire, no samples collected
21	01,02	Nut034	Silicate	0	Odd Peak Shapes repeated in nut035 use results from nut035.
23	01	Nut036	NOx,NO2	0	2nd duplicate Flagged as Bad in HyPro – waterfall plot shows bad data. Duplicate >0.02.
24	21	Nut037	NOx	0	Suspect peak shape repeated in nut038 for final reported value.
27	22	Nut040	SiO4	65	Data good, hypro flag due to peak shape
41	11	All nuts		141	Emptied NISKIN before collecting nutrient samples.
48	01	Nut063	NOx	0	Difference between duplicates > 0.02µM (MDL), repeated in nut064 and use 2nd result.
49	2, 3, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30	Nut064	All Nuts	141	Niskins not sampled
50	3, 7, 10, 12, 14, 16, 18, 20, 22, 24, 26, 29, 32	Nut064	All Nuts	141	Niskins not sampled

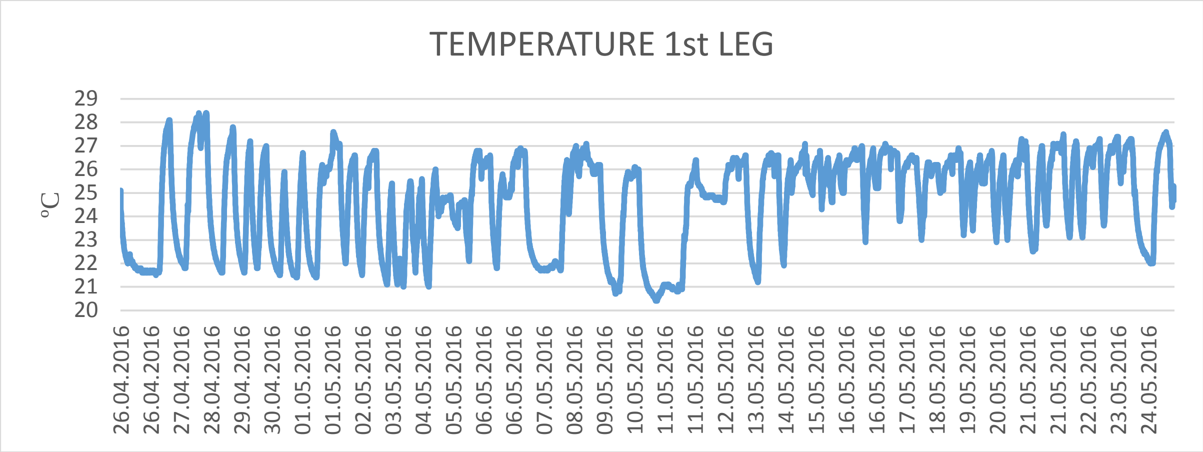
CTD	RP	Run	Analysis	Flag	Reason for Flag or Action
EXP 24	MLD	Nut065	NH4	0	Suspect peak shape; repeated in nut066 for final reported value.
52	20	Nut071	All Nuts	133	Outlier in waterfall profile, lanyard caught in top of NISKIN –lanyard pulled out. Repeated the analysis gave same result.
53	17	Nut072	All Nuts	141	Niskin end cap didn't close
56	26	Nut075	NOx	0	Suspect peak shape; repeated in nut076 for final reported value
64	01	Nut083	NOx	0	Difference between duplicates > 0.02µM (MDL), repeated in nut084 and use 2nd result.
68	01	Nut087	NOx	0	Difference between duplicates > 0.02µM (MDL), repeated in nut088 use this 2nd result.
70	10	Nut089	All Nuts	133	Outlier in waterfall plot, noted that vent popped off NISKIN.
70	01	Nut089	SiO4	0	Difference between duplicates > 0.20µM (MDL), repeated in nut090 use this 2nd result.
79	all	Nut098	NOx	0	Cd column blocked shifted peak windows and decreased NO3 conversion to NO2. Repeated samples in Nut099 for reported results.
81	03	Nut101	NOx	0	Blip on plateau, outlier in waterfall profile. Repeated in Nut102 for final result.
83	01, 02	Nut103	NOx	69	Bad duplicates >0.02, these NISKIN bottles were down at bottom of ocean floor. Crash Samples.
84	01, 02	Nut104	All Nuts	141	No samples collected
98	All	Nut118	NOx	0	BAD calibration curve causing RMNS to be above 3%. Data removed from slk file and re-ran in nut120 for reported results.
103	5	Nut124	All Nuts	133	The depth profile show an anomaly in this RP sample and a bottle temperature note was recorded on the sampling sheet. Salt and oxygen data also show an anomaly.
106	All	Nut127	NOx	0	RMNS low and results in profile much lower than previous runs. Repeated in nut 130.

CTD	RP	Run	Analysis	Flag	Reason for Flag or Action
111	All	Nut132	NOx	0	Results in profile much lower than all other runs. Repeated in nut135.
112	33-36	Nut133	All Nuts	141	Air valves not closed on niskins, no samples collected
113	10	Nut134	All Nuts	141	Niskin leaked, no samples collected
117	10	Nut138	SiO4	0	Large air spike on top of peak, repeated in nut139 for reported final results.
119	all	Nut140	NOx	0	RMNS 3% high, repeated run in nut142.
119	13	Nut142	All Nuts	141	No sample collected
121	30	Nut143	NOx	0	Bump in peak window –peak shape. Repeated in nut144 for reported result.
122	01	Nut144	NOx	69	Difference between duplicates 0.07µM (MDL = 0.02 µM), repeated in nut145 result not any better leave as is.
124	10, 26	Nut146	All Nuts	141	Niskins leaked, no samples collected
125	32	Nut149	NO2	129	The peak was off scale in AACE. Sample repeated with dilution 3mL sample + 6mL LNSW in run nut150 =(0.591-0.001)x3=1.77 µM updated csv file not netcdf
134	11	Nut157	All Nuts	141	Niskin leaked, no sample collected
138	14	Nut161	All Nuts	141	Niskin leaked, no sample collected
140	27	Nut163	All nuts	141	Lanyard caught in top cap-leaked.

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_v03_hyd_voyagereport.docx” for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.5°C.


TEMPERATURE 1st LEG
°C
29
28
27
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24
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21
20
26.04.2016
26.04.2016
27.04.2016
28.04.2016
29.04.2016
30.04.2016
01.05.2016
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05.05.2016
06.05.2016
06.05.2016
07.05.2016
08.05.2016
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10.05.2016
11.05.2016
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13.05.2016
14.05.2016
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22.05.2016
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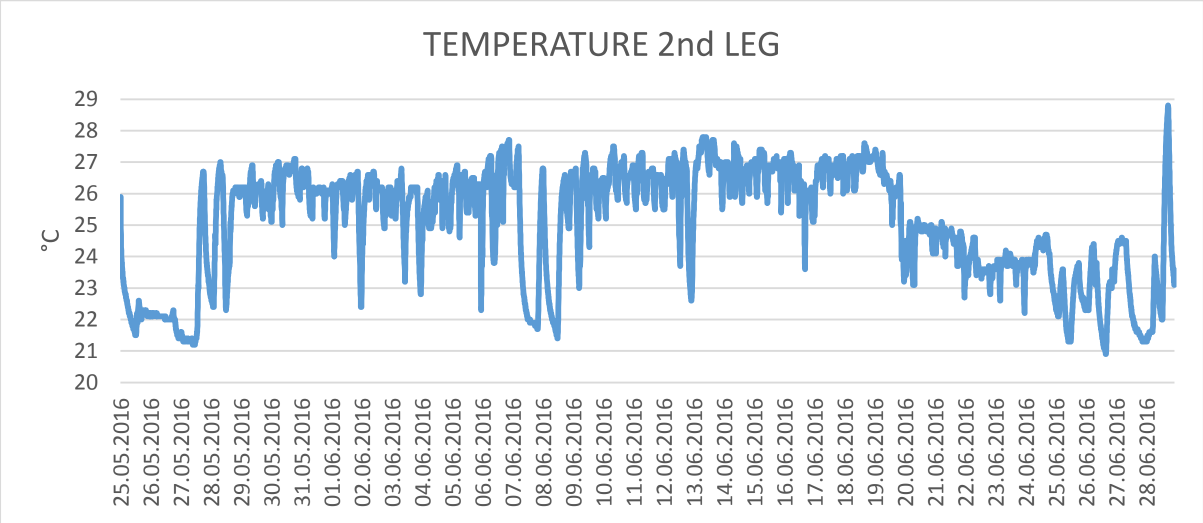
24.05.2016


TEMPERATURE 2nd LEG
°C
29
28
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25.05.2016
26.05.2016
27.05.2016
28.05.2016
29.05.2016
30.05.2016
31.05.2016
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15.06.2016
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17.06.2016
18.06.2016
19.06.2016
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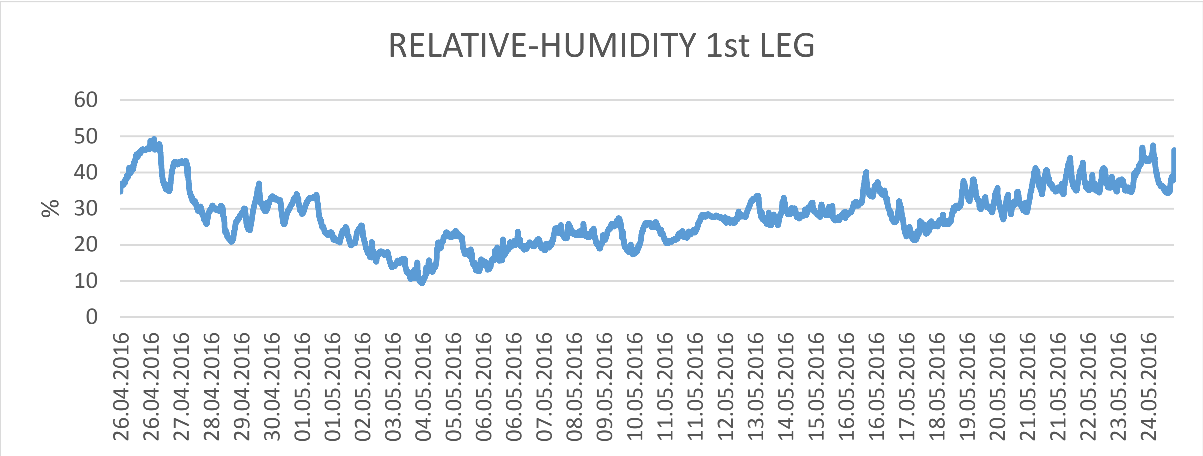
25.06.2016
26.06.2016
27.06.2016
28.06.2016


RELATIVE-HUMIDITY 1st LEG
%
60
50
40
30
20
10
0
26.04.2016
26.04.2016
27.04.2016
28.04.2016
29.04.2016
30.04.2016
01.05.2016
01.05.2016
02.05.2016
03.05.2016
04.05.2016
05.05.2016
06.05.2016
06.05.2016
07.05.2016
08.05.2016
09.05.2016
10.05.2016
11.05.2016
11.05.2016
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13.05.2016
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15.05.2016
16.05.2016
16.05.2016
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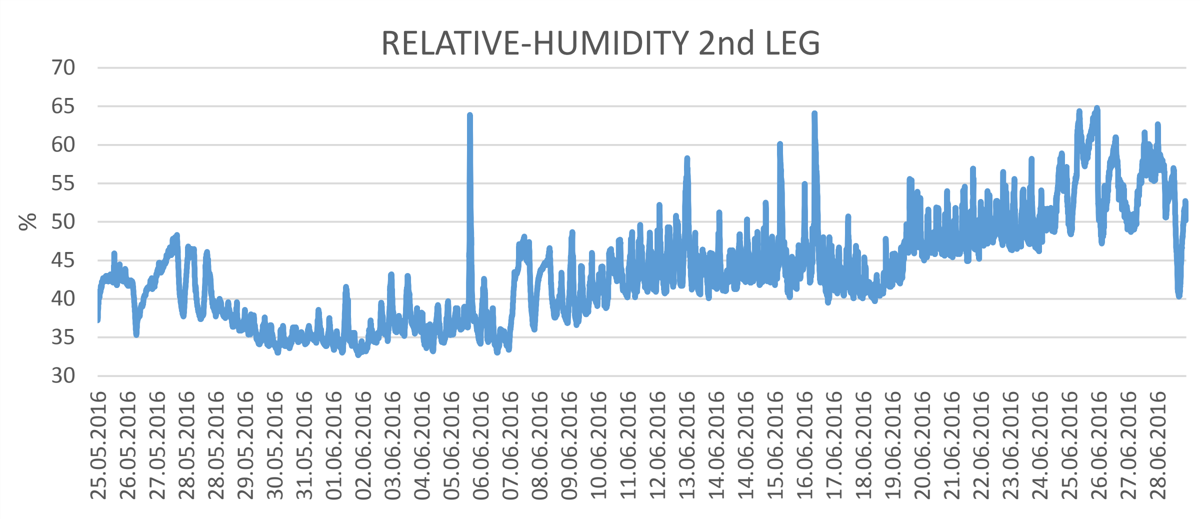
23.05.2016
24.05.2016



7 Appendix

7.1 Salinity Reference Material

Osil IAPSO Standard Seawater	
Batch	P157
Use by date	15/04/17
K_{15}	0.99985

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 CTD

CTD	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
2	**37.9**	37.5	**1.48**	1.44	**0.082**	0.065	**20.37**	20.20
3	**38.5**	37.5	**1.48**	1.44	**0.081**	0.065	**20.31**	20.20
3	**106.1**	104.7	**2.62**	2.56	**0.066**	0.048	**36.53**	36.26
4	**38.2**	37.5	**1.48**	1.44	**0.080**	0.065	**20.31**	20.20
4	**105.7**	104.7	**2.61**	2.56	**0.063**	0.048	**36.48**	36.26
5	**38.1**	37.5	**1.47**	1.44	**0.074**	0.065	**20.41**	20.20
6	**38.1**	37.5	**1.48**	1.44	**0.085**	0.065	**20.50**	20.20
8	**38.2**	37.5	**1.46**	1.44	**0.074**	0.065	**20.41**	20.20
9	**38.1**	37.5	**1.47**	1.44	**0.074**	0.065	**20.39**	20.20
11	**38.1**	37.5	**1.46**	1.44	**0.072**	0.065	**20.45**	20.20
11	**105.1**	104.7	**2.58**	2.56	**0.055**	0.048	**36.55**	36.26
12	**38.0**	37.5	**1.46**	1.44	**0.078**	0.065	**20.47**	20.20
12	**105.1**	104.7	**2.58**	2.56	**0.059**	0.048	**36.42**	36.26
13	**37.7**	37.5	**1.48**	1.44	**0.076**	0.065	**20.40**	20.20
14	**37.6**	37.5	**1.47**	1.44	**0.084**	0.065	**20.43**	20.20
15	**37.7**	37.5	**1.47**	1.44	**0.072**	0.065	**20.38**	20.20
17	**37.5**	37.5	**1.46**	1.44	**0.074**	0.065	**20.42**	20.20
19	**37.6**	37.5	**1.46**	1.44	**0.076**	0.065	**20.54**	20.20
20	**37.6**	37.5	**1.47**	1.44	**0.067**	0.065	**20.29**	20.20
21	**37.4**	37.5	**1.46**	1.44	**0.075**	0.065	**20.31**	20.20
21	**104.3**	104.7	**2.57**	2.56	**0.055**	0.048	**36.30**	36.26
22	**37.4**	37.5	**1.46**	1.44	**0.076**	0.065	**20.29**	20.20
23	**37.7**	37.5	**1.48**	1.44	**0.073**	0.065	**20.28**	20.20
24	**37.8**	37.5	**1.48**	1.44	**0.072**	0.065	**20.36**	20.20
25	**37.8**	37.5	**1.47**	1.44	**0.075**	0.065	**20.35**	20.20
26	**37.8**	37.5	**1.47**	1.44	**0.075**	0.065	**20.35**	20.20
27	**37.4**	37.5	**1.46**	1.44	**0.078**	0.065	**20.38**	20.20
28	**37.4**	37.5	**1.47**	1.44	**0.076**	0.065	**20.28**	20.20
29	**37.6**	37.5	**1.46**	1.44	**0.075**	0.065	**20.40**	20.20
30	**37.5**	37.5	**1.47**	1.44	**0.076**	0.065	**20.44**	20.20
31	**37.5**	37.5	**1.47**	1.44	**0.070**	0.065	**20.37**	20.20
32	**37.6**	37.5	**1.45**	1.44	**0.066**	0.065	**20.38**	20.20

CTD	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
33	**37.4**	37.5	**1.46**	1.44	**0.066**	0.065	**20.45**	20.20
34	**37.5**	37.5	**1.47**	1.44	**0.074**	0.065	**20.30**	20.20
34	**104.6**	104.7	**2.59**	2.56	**0.054**	0.048	**36.37**	36.26
35	**37.6**	37.5	**1.45**	1.44	**0.120**	0.065	**20.51**	20.20
36	**37.3**	37.5	**1.47**	1.44	**0.071**	0.065	**20.34**	20.20
37	**37.4**	37.5	**1.48**	1.44	**0.078**	0.065	**20.44**	20.20
38	**37.5**	37.5	**1.47**	1.44	**0.072**	0.065	**20.40**	20.20
39	**37.3**	37.5	**1.45**	1.44	**0.072**	0.065	**20.31**	20.20
40	**37.4**	37.5	**1.46**	1.44	**0.075**	0.065	**20.33**	20.20
41	**37.4**	37.5	**1.46**	1.44	**0.073**	0.065	**20.26**	20.20
42	**37.3**	37.5	**1.45**	1.44	**0.079**	0.065	**20.35**	20.20
43	**37.4**	37.5	**1.45**	1.44	**0.076**	0.065	**20.27**	20.20
44	**37.3**	37.5	**1.46**	1.44	**0.077**	0.065	**20.28**	20.20
45	**37.3**	37.5	**1.44**	1.44	**0.076**	0.065	**20.19**	20.20
46	**37.0**	37.5	**1.43**	1.44	**0.076**	0.065	**20.26**	20.20
46	**103.7**	104.7	**2.54**	2.56	**0.057**	0.048	**36.42**	36.26
47	**37.3**	37.5	**1.44**	1.44	**0.077**	0.065	**20.36**	20.20
48	**37.2**	37.5	**1.43**	1.44	**0.078**	0.065	**20.30**	20.20
49	**37.1**	37.5	**1.42**	1.44	**0.075**	0.065	**20.32**	20.20
50	**37.1**	37.5	**1.42**	1.44	**0.075**	0.065	**20.32**	20.20
51	**37.1**	37.5	**1.44**	1.44	**0.069**	0.065	**20.31**	20.20
52	**37.0**	37.5	**1.46**	1.44	**0.068**	0.065	**20.31**	20.20
52	**103.9**	104.7	**2.58**	2.56	**0.055**	0.048	**36.47**	36.26
53	**37.1**	37.5	**1.46**	1.44	**0.073**	0.065	**20.31**	20.20
54	**37.1**	37.5	**1.47**	1.44	**0.069**	0.065	**20.30**	20.20
55	**37.3**	37.5	**1.46**	1.44	**0.070**	0.065	**20.31**	20.20
56	**37.3**	37.5	**1.47**	1.44	**0.080**	0.065	**20.30**	20.20
57	**37.4**	37.5	**1.45**	1.44	**0.080**	0.065	**20.29**	20.20
58	**36.6**	37.5	**1.44**	1.44	**0.080**	0.065	**20.22**	20.20
59	**36.6**	37.5	**1.45**	1.44	**0.071**	0.065	**20.19**	20.20
60	**36.9**	37.5	**1.42**	1.44	**0.074**	0.065	**20.15**	20.20
61	**36.9**	37.5	**1.42**	1.44	**0.073**	0.065	**20.19**	20.20
61	**36.8**	37.5	**1.44**	1.44	**0.067**	0.065	**20.16**	20.20
62	**36.8**	37.5	**1.43**	1.44	**0.073**	0.065	**20.14**	20.20
62	**102.9**	104.7	**2.53**	2.56	**0.055**	0.048	**36.08**	36.26
63	**36.8**	37.5	**1.43**	1.44	**0.073**	0.065	**20.14**	20.20

CTD	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
64	**36.6**	37.5	**1.43**	1.44	**0.076**	0.065	**20.12**	20.20
65	**36.6**	37.5	**1.45**	1.44	**0.071**	0.065	**20.11**	20.20
66	**36.8**	37.5	**1.44**	1.44	**0.069**	0.065	**20.12**	20.20
67	**36.8**	37.5	**1.45**	1.44	**0.071**	0.065	**20.12**	20.20
68	**36.6**	37.5	**1.44**	1.44	**0.070**	0.065	**20.09**	20.20
69	**36.6**	37.5	**1.43**	1.44	**0.070**	0.065	**20.09**	20.20
70	**36.6**	37.5	**1.44**	1.44	**0.066**	0.065	**20.03**	20.20
70	**102.7**	104.7	**2.55**	2.56	**0.051**	0.048	**36.00**	36.26
71	**36.7**	37.5	**1.45**	1.44	**0.072**	0.065	**20.19**	20.20
72	**36.6**	37.5	**1.46**	1.44	**0.072**	0.065	**20.18**	20.20
73	**36.7**	37.5	**1.45**	1.44	**0.070**	0.065	**20.21**	20.20
74	**36.7**	37.5	**1.44**	1.44	**0.072**	0.065	**20.27**	20.20
75	**36.7**	37.5	**1.43**	1.44	**0.062**	0.065	**20.30**	20.20
76	**36.7**	37.5	**1.44**	1.44	**0.072**	0.065	**20.25**	20.20
77	**36.7**	37.5	**1.46**	1.44	**0.073**	0.065	**20.24**	20.20
78	**36.9**	37.5	**1.44**	1.44	**0.071**	0.065	**20.16**	20.20
79	**37.2**	37.5	**1.45**	1.44	**0.079**	0.065	**20.14**	20.20
80	**37.2**	37.5	**1.46**	1.44	**0.080**	0.065	**20.18**	20.20
80	**103.7**	104.7	**2.56**	2.56	**0.064**	0.048	**36.09**	36.26
81	**37.9**	37.5	**1.43**	1.44	**0.076**	0.065	**20.07**	20.20
82	**37.4**	37.5	**1.44**	1.44	**0.072**	0.065	**20.13**	20.20
83	**38.0**	37.5	**1.43**	1.44	**0.074**	0.065	**20.14**	20.20
84	**37.4**	37.5	**1.42**	1.44	**0.072**	0.065	**20.07**	20.20
85	**37.1**	37.5	**1.44**	1.44	**0.007**	0.065	**20.20**	20.20
85	**103.9**	104.7	**2.54**	2.56	**0.053**	0.048	**36.04**	36.26
86	**37.2**	37.5	**1.45**	1.44	**0.073**	0.065	**19.96**	20.20
87	**37.2**	37.5	**1.44**	1.44	**0.076**	0.065	**20.18**	20.20
88	**37.0**	37.5	**1.44**	1.44	**0.078**	0.065	**20.22**	20.20
89	**37.3**	37.5	**1.43**	1.44	**0.068**	0.065	**20.20**	20.20
90	**37.4**	37.5	**1.45**	1.44	**0.069**	0.065	**20.22**	20.20
91	**37.1**	37.5	**1.44**	1.44	**0.070**	0.065	**20.23**	20.20
92	**37.2**	37.5	**1.45**	1.44	**0.076**	0.065	**20.28**	20.20
93	**37.0**	37.5	**1.43**	1.44	**0.072**	0.065	**20.09**	20.20
94	**36.8**	37.5	**1.43**	1.44	**0.071**	0.065	**20.01**	20.20
95	**36.9**	37.5	**1.42**	1.44	**0.075**	0.065	**20.11**	20.20
96	**36.9**	37.5	**1.44**	1.44	**0.076**	0.065	**20.15**	20.20

CTD	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
97	**37.0**	37.5	**1.44**	1.44	**0.075**	0.065	**20.06**	20.20
98	**36.9**	37.5	**1.42**	1.44	**0.074**	0.065	**20.06**	20.20
99	**37.0**	37.5	**1.43**	1.44	**0.073**	0.065	**20.08**	20.20
100	**36.8**	37.5	**1.44**	1.44	**0.080**	0.065	**20.13**	20.20
101	**36.8**	37.5	**1.43**	1.44	**0.090**	0.065	**20.18**	20.20
102	**36.8**	37.5	**1.43**	1.44	**0.069**	0.065	**20.21**	20.20
103	**37.1**	37.5	**1.43**	1.44	**0.071**	0.065	**20.04**	20.20
104	**37.1**	37.5	**1.44**	1.44	**0.078**	0.065	**20.07**	20.20
105	**37.0**	37.5	**1.43**	1.44	**0.080**	0.065	**20.16**	20.20
106	**37.0**	37.5	**1.42**	1.44	**0.069**	0.065	**20.01**	20.20
107	**36.7**	37.5	**1.44**	1.44	**0.075**	0.065	**19.89**	20.20
108	**36.9**	37.5	**1.44**	1.44	**0.073**	0.065	**20.09**	20.20
109	**36.8**	37.5	**1.44**	1.44	**0.068**	0.065	**20.01**	20.20
110	**36.8**	37.5	**1.45**	1.44	**0.073**	0.065	**20.04**	20.20
110	**103.2**	104.7	**2.55**	2.56	**0.058**	0.048	**35.92**	36.26
111	**36.8**	37.5	**1.43**	1.44	**0.069**	0.065	**20.03**	20.20
112	**36.8**	37.5	**1.42**	1.44	**0.074**	0.065	**20.09**	20.20
113	**36.8**	37.5	**1.42**	1.44	**0.083**	0.065	**20.18**	20.20
114	**36.8**	37.5	**1.42**	1.44	**0.070**	0.065	**20.03**	20.20
115	**37.2**	37.5	**1.44**	1.44	**0.079**	0.065	**20.06**	20.20
116	**37.2**	37.5	**1.44**	1.44	**0.078**	0.065	**20.15**	20.20
117	**37.1**	37.5	**1.43**	1.44	**0.079**	0.065	**19.96**	20.20
118	**37.2**	37.5	**1.45**	1.44	**0.080**	0.065	**20.09**	20.20
118	**104.5**	104.7	**2.55**	2.56	**0.065**	0.048	**36.08**	36.26
119	**37.0**	37.5	**1.44**	1.44	**0.080**	0.065	**20.10**	20.20
120	**36.8**	37.5	**1.43**	1.44	**0.079**	0.065	**20.14**	20.20
120	**36.8**	37.5	**1.43**	1.44	**0.079**	0.065	**20.14**	20.20
121	**36.9**	37.5	**1.45**	1.44	**0.076**	0.065	**20.09**	20.20
122	**36.7**	37.5	**1.42**	1.44	**0.072**	0.065	**20.05**	20.20
123	**36.3**	37.5	**1.43**	1.44	**0.069**	0.065	**20.01**	20.20
124, 125	**37.4**	37.5	**1.44**	1.44	**0.072**	0.065	**20.04**	20.20
126, 127	**37.4**	37.5	**1.44**	1.44	**0.067**	0.065	**20.07**	20.20
128	**37.2**	37.5	**1.44**	1.44	**0.070**	0.065	**20.33**	20.20
128	**103.6**	104.7	**2.54**	2.56	**0.054**	0.048	**35.63**	36.26
129	**37.3**	37.5	**1.44**	1.44	**0.072**	0.065	**20.01**	20.20
130	**37.7**	37.5	**1.45**	1.44	**0.068**	0.065	**20.17**	20.20

CTD	SiO_4 measured	SiO_4 expected	PO_4 measured	PO_4 expected	NO_2 measured	NO_2 expected	NOx measured	NOx expected
131	**37.7**	37.5	**1.44**	1.44	**0.065**	0.065	**20.13**	20.20
132	**37.6**	37.5	**1.45**	1.44	**0.070**	0.065	**20.16**	20.20
133	**37.8**	37.5	**1.45**	1.44	**0.069**	0.065	**20.39**	20.20
134	**37.8**	37.5	**1.43**	1.44	**0.068**	0.065	**20.04**	20.20
134	**37.8**	37.5	**1.43**	1.44	**0.068**	0.065	**20.04**	20.20
135	**37.4**	37.5	**1.42**	1.44	**0.067**	0.065	**20.04**	20.20
136	**37.7**	37.5	**1.43**	1.44	**0.072**	0.065	**20.10**	20.20
137	**37.2**	37.5	**1.43**	1.44	**0.069**	0.065	**20.09**	20.20
138	**37.3**	37.5	**1.43**	1.44	**0.068**	0.065	**20.01**	20.20
139	**37.8**	37.5	**1.44**	1.44	**0.071**	0.065	**20.00**	20.20
139	**104.2**	104.7	**2.54**	2.56	**0.055**	0.048	**36.01**	36.26
140	**37.3**	37.5	**1.42**	1.44	**0.070**	0.065	**20.02**	20.20
uwy088-090	**37.8**	37.5	**1.41**	1.44	**0.057**	0.065	**20.00**	20.20
uwy091-094	**37.1**	37.5	**1.42**	1.44	**0.057**	0.065	**20.13**	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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