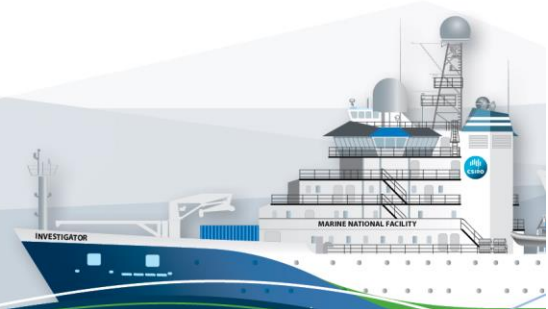# RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage: in2019_v07

Chief Scientist Emily Jateff

Voyage title: RAN Hydrographic and Maritime Heritage Surveys

Report compiled by: Stephen Tibben & Jack McDonald

Contents

1 Executive Summary

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NOx) and nitrite:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

The main objective of the voyage was to conduct a modern survey in the primary shipping route through the Bass Straight for the Australian Hydrographic Office (AHO). Also, in conjunction with Heritage Victoria and the Australian National Maritime Museum, historic shipwreck sites were surveyed using multibeam and drop camera techniques. Hydrochemistry testing and training were also completed on this voyage.

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity. The samples came from deployments of the conductivity temperature and depth (CTD) rosette and the underway system.

All data were compared with reference materials for the three measured parameters. It should be noted, however, that the main priority for this voyage was staff training. Five nutrients were analysed; silicate, phosphate, nitrate + nitrite, nitrite and ammonium. Certified reference materials for nutrients in seawater were within the specified limits of the certified value.

Results for nutrient samples from experiments issued to the science parties during the voyage.

Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2   Itinerary

Hobart to Hobart, April 11th – 23rd, 2019.

Voyage Track:
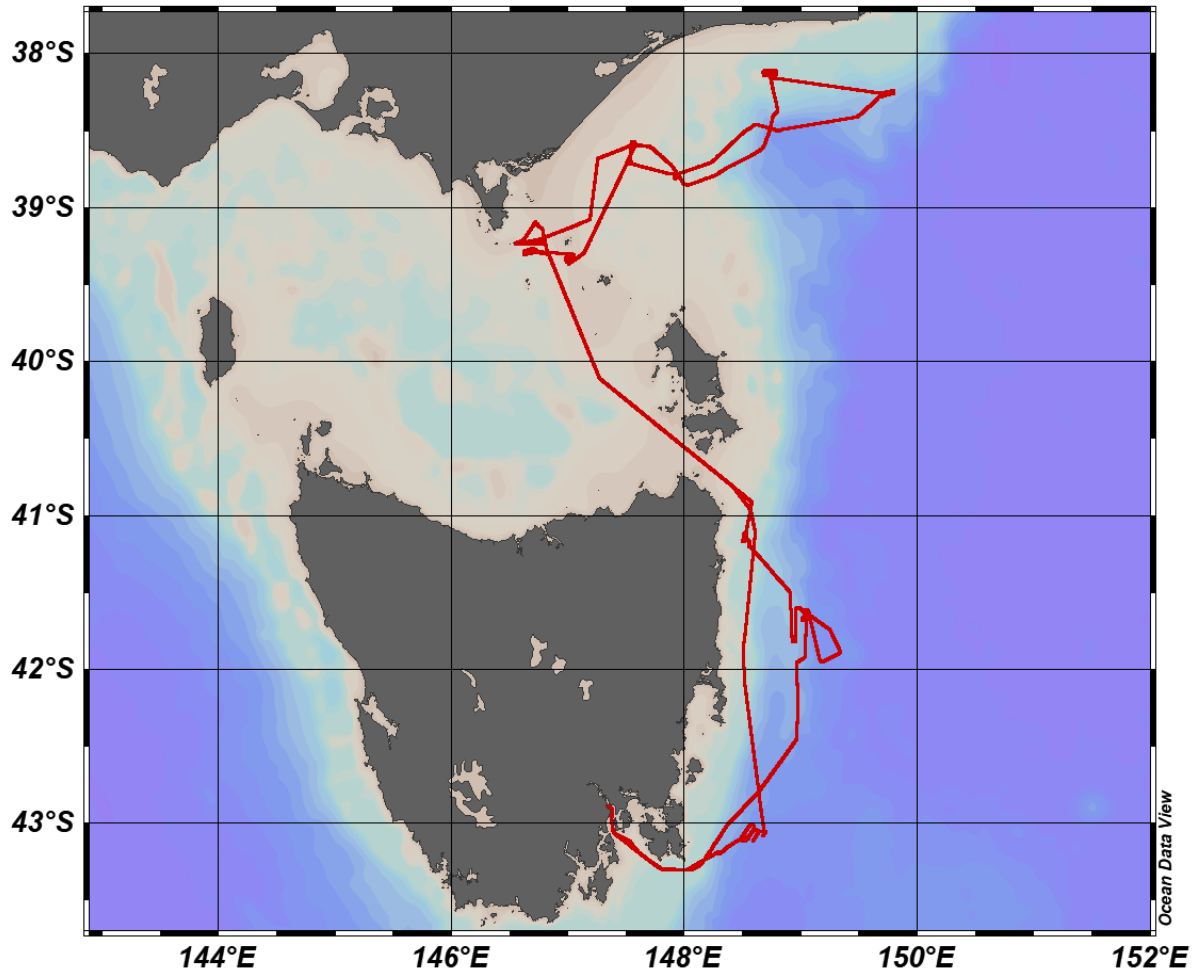
3   Key personnel list

Name	Role	Organisation
Emily Jateff	Chief Scientist	Australian National Maritime Museum
Max McGuire	Voyage Manager	CSIRO
Stephen Tibben	Hydrochemist	CSIRO
Jack McDonald	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	133 CTD
	22 TSG
Dissolved Oxygen (SIO automated titration)	133 CTD
Nutrients (Seal AA3HR segmented flow)	136 CTD

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.

- 7 CTD deployments in total. Deployments 4 through 10 - sampled by Hydrochemistry team.

4.1.2 TMR (Trace Metal Rosette)

- N/A

4.1.3 EXP (Experimental samples)

- N/A

4.1.4 TSG (Thermosalinograph)

- Samples collected by data acquisition and processing (DAP) and hydrochemistry staff from underway lab for calibration of thermosalinograph.

For TSG sample information refer to the voyage eLog.

4.2 Data Processing Overview

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated in figure 1.

CTD Deployment

CTD data converted to an xml file for HyPro

CTD Log Editor Software

Sampling log sheet data entered into the CTD deployment xml file. Imported into HyPro

CTD sampling log sheet - paper. Record sample ID and D.O. draw temp

Nutrient Results

Instrument output, two files: CHD (raw peak data) and SLK (peak meta-data). Both files imported into HyPro.

HyPro calculates the nutrient data and applies quality control criteria

HyPro Software

Combines all data and produces profile plots, time series plots, QC charts, sampling and assay summaries. It also compares the salt & D.O. bottle results against the CTD instrument data.

Salinity Results

Instrument output: xlsx file, imported into HyPro. Reported as is.

Dissolved Oxygen Results

Instrument output: LST file, imported into Hypro.

HyPro converts D.O. result from ml l^{-1} to µmole l^{-1} (multiply 44.66)

Output

Hydrology Data Set

Two formats: nc (netcdf), csv

Figure 1: Hydrology Data Processing Flow Diagram.

5   Salinity Data Processing

5.1   Salinity Parameter Summary

Details	
HyPro Version	5.7
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72151
Software	OSIL Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analyst	Stephen Tibben
Lab Temperature (±0.5°C)	21.5 -22.5°C during analysis.
Bath Temperature	24.01°C
Reference Material	OSIL IAPSO - Batch P161, use by 03/05/2020, K_{15} = 0.99987
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 stored in the Salt lab for a minimum of 8 hrs before measurement.
Comments	None.

5.2   Salinity Method

Salinity samples are measured on a high precision laboratory salinometer (Guildline Autosal 8400B) which is operated in accordance with its technical manual.

Practical salinity (S), is defined in terms of the ratio (K_{15}) of the electrical conductivity measured at 15°C 1atm of seawater to that of a potassium chloride (KCl) solution of mass fraction 32.4356×10^{-3}.

Before each batch of sample measurements, the Autosal is calibrated with standard seawater (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL solution is used for each calibration. The frequency of calibration is one per set of samples per CTD deployment.

Method synopsis: Salinity samples are collected into 200ml OSIL bottles, filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, till overflowing. The bottle is removed from the straw and the sample is decanted to allow a headspace of approximately $25cm^3$. A plastic insert is fitted, the bottle inverted and rinsed with water then capped and stored cap-down until measured. To measure, the Autosal cell is flushed three times with the sample and then measured after the fourth and fifth flush. The OSIL data logger software captures the conductivity ratio and calculates the practical salinity.

The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

5.3   CTD Salinity vs Bottle Salinity Plot

The difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities is generally less than 0.01 PSU.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the DataLibrariansOAMNF@csiro.au for corrected CTD data.

Note: dots = bottle samples, circles = CTD instrument (unprocessed)
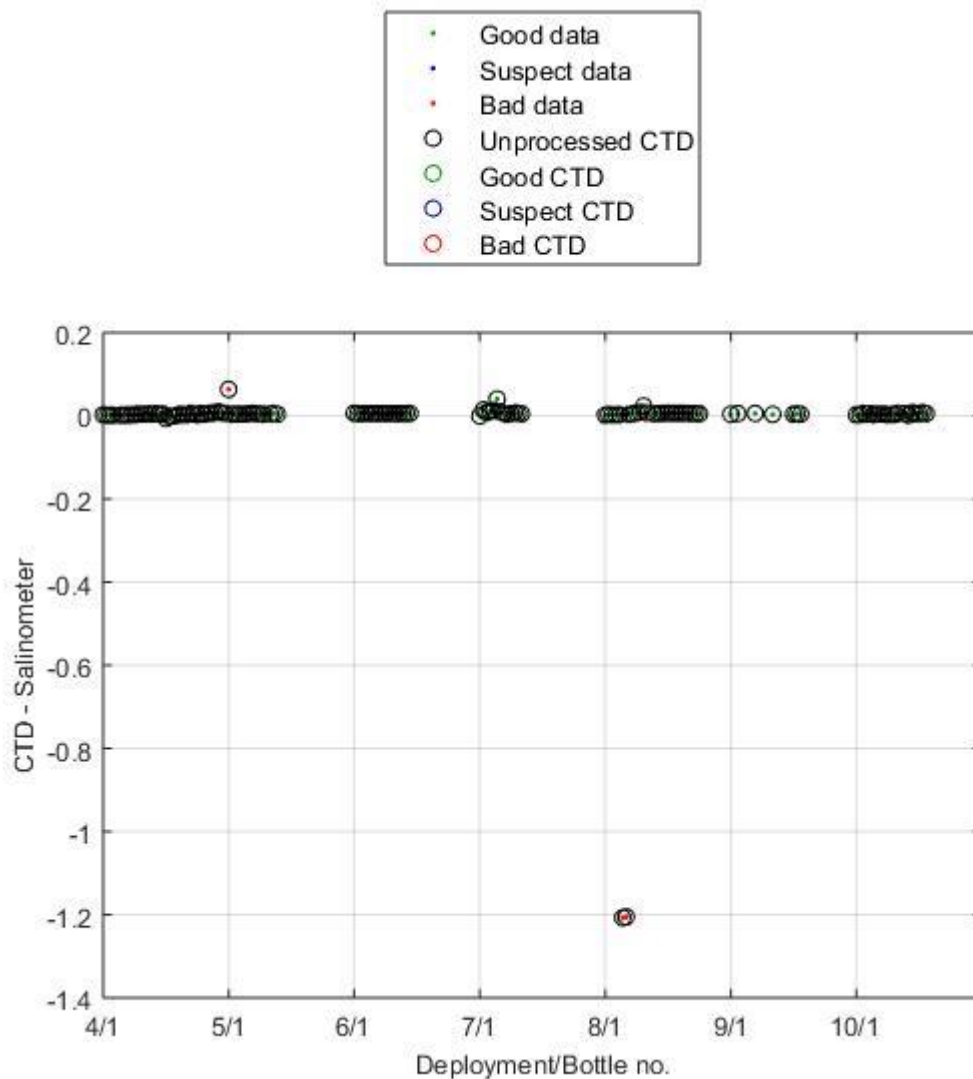
5.4   Missing or Suspect Salinity Data

Data is flagged based on notes from CTD sampling log sheet, observations during analysis, and examination of depth profile and waterfall plots (Flag key in appendix 8.5).

CTD	RP	Run	Flag	Reason for Flag or Action
5	1	sal001	133	Outlier in vertical profile plot
8	6, 7	sal004	133	Outliers in vertical profile plot

5.5   Salinity OSIL standard plot
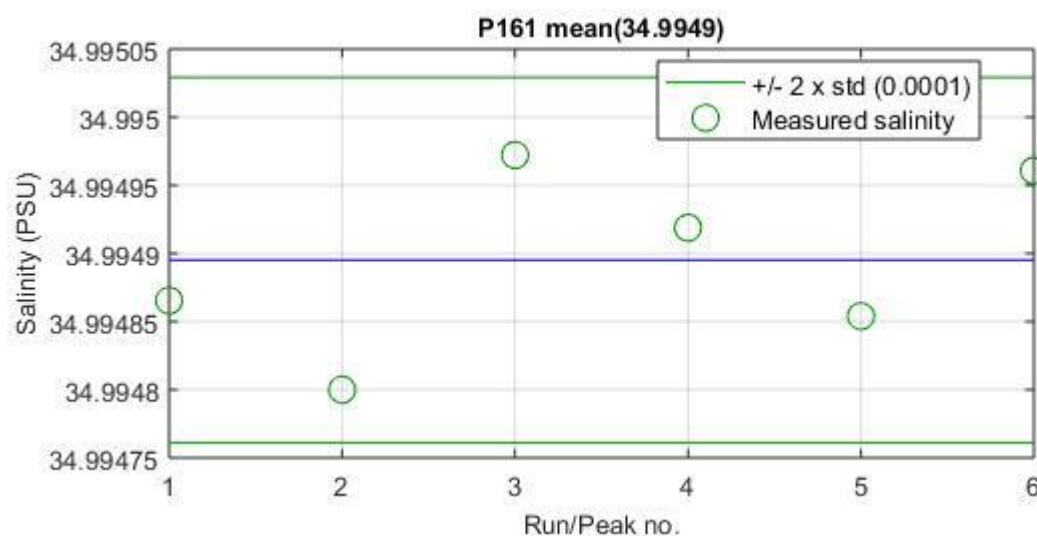
6 Dissolved Oxygen Data Processing

6.1 Dissolved Oxygen Parameter Summary

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 µM
Analyst	Jack McDonald
Lab Temperature (±1°C)	Variable, 20.2 - 23.2°C
Sample Container type	Pre-numbered 140 mL glass iodine determination flasks with glass stopper. 18 flasks per light-proof container.
Sample Storage	Samples stored in the hydrochemistry lab until analysis. All samples were analysed within ~48 hrs
Comments	None.

6.2 Dissolved Oxygen Method

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

Method synopsis: The sample is collected in an iodine determination flask of known volume. 1 mL of manganese (II) chloride solution followed by 1 mL of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum of 39 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, oxidizing the Mn (IV) back to the divalent state liberating iodine twice the original dissolved oxygen content of the sample. The tri-iodine is auto-titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1 mL 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.

Before each batch of sample assays, the thiosulphate solution is standardised by using it to titrate a 10 mL aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two consecutive titres for 1 mL aliquots of the same potassium iodate solution.

The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

6.3   CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

The CTD values in this plot are unprocessed raw data.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the DataLibrariansOAMNF@csiro.au for corrected CTD data.

Note: dots = bottle samples, circles = CTD instrument (unprocessed)
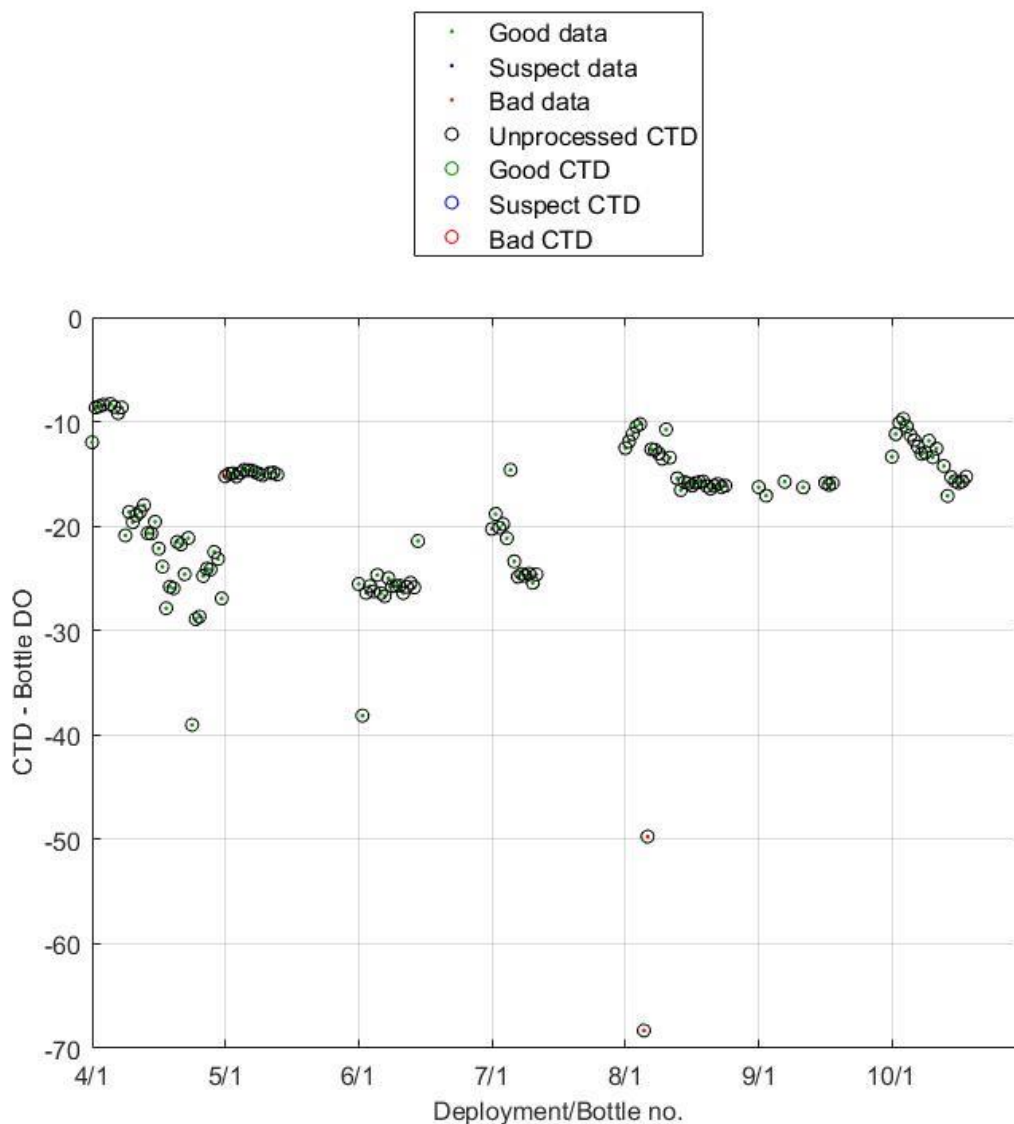
6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2 N) varied less than 0.0005 N for all dissolved oxygen sample titrations. The blank correction is less than 0.0008 mL with a voyage mean of 0.0005 mL and standard deviation of 0.0001mL (n=7).

Red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration and the blank concentration. The titrant should not vary more than 0.0005 N between analyses.
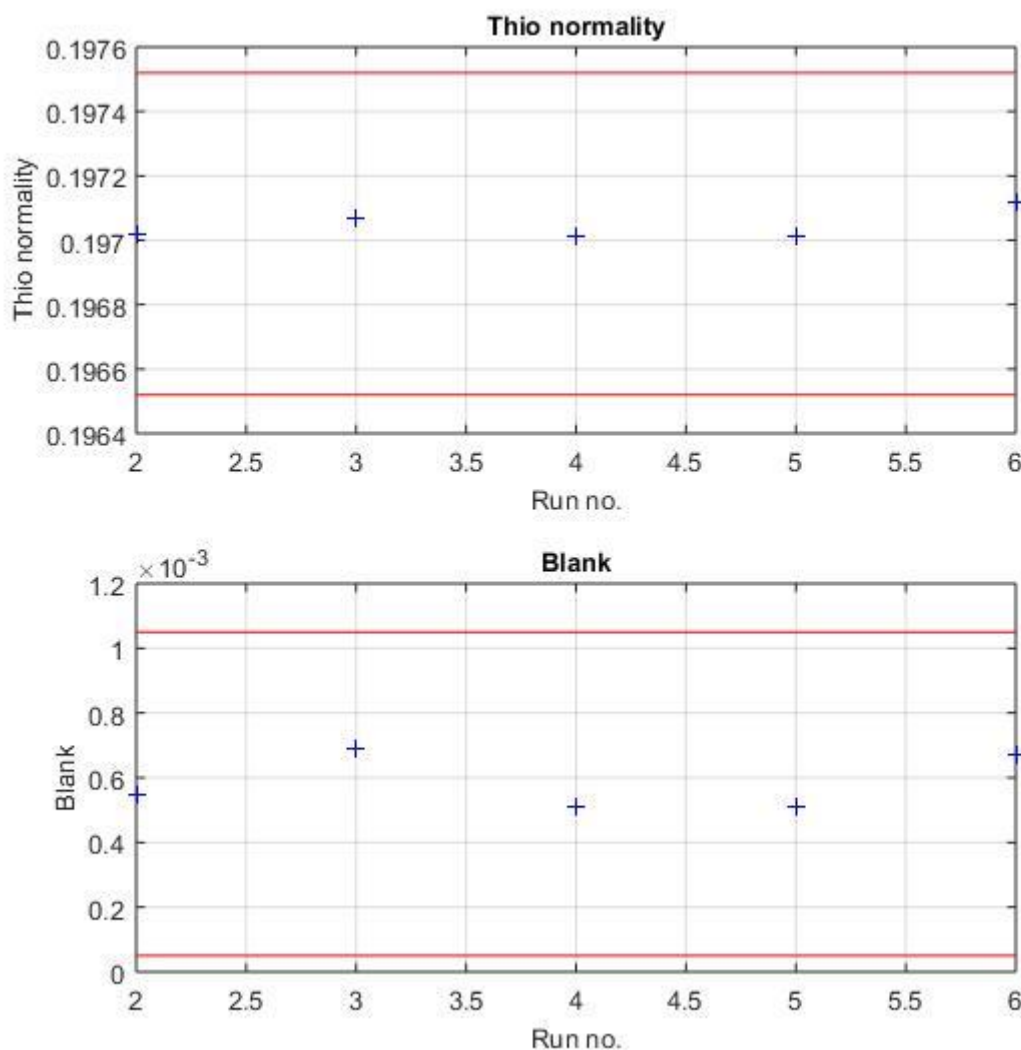
6.5 Missing or Suspect Dissolved Oxygen Data.

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 plots (Flag key appendix 8.5).

CTD	RP	Run	Flag	Reason for Flag or Action
5	1	oxy002	133	Outlier in vertical profile plot
8	6, 7	oxy005	133	Outliers in vertical profile plot

7   Nutrient Data Processing

7.1   Nutrient Assay Parameter Summary

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 7.09				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range	112 µM	3.0 µM	42 µM	1.4 µM	2.0 µM
Method Detection Limit (MDL)	0.2 µM	0.02 µM	0.02 µM	0.02 µM	0.02 µM
Matrix Corrections	none	none	none	none	none
Analysts	Stephen Tibben & Jack McDonald				
Lab Temperature (±1°C)	Variable, 20.2– 23.2°C				
Reference Material	KANSO, RMNS lot CA				
Sampling Container type	CTD: 50ml HDPE with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 24 hrs @ 4°C				
Pre-processing of Samples	CTD: None.				
Comments					

7.2   Nutrient Methods

When using silicate, phosphate, nitrate+nitrite (NOx) and nitrite data set for publication, please cite the paper:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/Iom3.10294

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1 cm flow-cells for colorimetric measurements and a JASCO FP2020 fluorescence instrument as the ammonium detector.

Silicate (SOP001): 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 (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS[1] Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine 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 (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Kérouel and Aminot (1997). 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.

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.
[1.] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

7.3   HyPro Processing Parameters

All instrument parameters and reagent batches and operation events are logged for each analysis run. This information is available on request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Data Reported as	$\mu mol\ l^{-1}$	$\mu mol\ l^{-1}$	$\mu mol\ l^{-1}$	$\mu mol\ l^{-1}$	$\mu mol\ l^{-1}$
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
# of points in Calibration	6	6	6	6	6
Forced through zero?	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	Low nutrient seawater (LNSW, bulk on deck of Investigator) collected on 28/9/2016. Sub-lot passed through a 10 micron filter on 15/10/2018 and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω water. Dispensed from Milli Q				
Proportion of samples in duplicate.	<10%. CTD: Niskin fired at the greatest depth sampled in duplicate. Single samples collected for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.1.				

7.4 HyPro Data Processing Summary

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and, duplicate sample results that do not match.

With suspect calibration points, their contribution to the curve is given less weighting dependent on their distance from the final curve. 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[1]).
- Within 0.02uM for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. The flagged nutrient calibration data is in appendix 8.2.

Missing or suspect nutrient data is tabulated in section 7.9, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.5.

[1.] World Ocean Circulation Experiment.

7.5 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Japanese KANSO certified RMNS lot CA was assayed in triplicate in each run to monitor accuracy. The certified values are in table 1.

For in2019_v07, the majority of RMNS results are within 3% of their certified mean and within 0.02μM for nitrite. Plots of RMNS values for all runs are below.

The assayed RMNS values per Analysis run and CTD deployments are listed in appendix 8.3.1

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.6, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

Table 1: RMNS concentrations with expanded uncertainty at 21°C

| RMNS	NO$_3$ (µmol L^{-1})	NO$_2$ (µmol L^{-1})	NO$_3$+ NO$_2$ (NO$_X$, µmol L^{-1})	PO$_4$ (µmol L^{-1})	SiO$_4$ (µmol L^{-1})
Lot CA	20.132 ± 0.154	0.065 ± 0.010	20.197 ± 0.164	1.441 ± 0.014	37.458 ± 0.225
Lot CD	5.629 ± 0.051	0.018 ± 0.004	5.647 ± 0.055	0.457 ± 0.008	14.264 ± 0.10
Lot CC	31.621 ± 0.246	0.119 ± 0.006	31.740 ± 0.252	2.130 ± 0.019	88.228 ± 0.492

KANSO publishes the RMNS nutrient values in µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C. The RMNS is not certified for ammonium. NO$_x$ is derived by summing the NO$_3$ and NO$_2$ values.

Plot key. The green pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µM increments from the certified value. The blue line is the expanded uncertainty of the certified value.
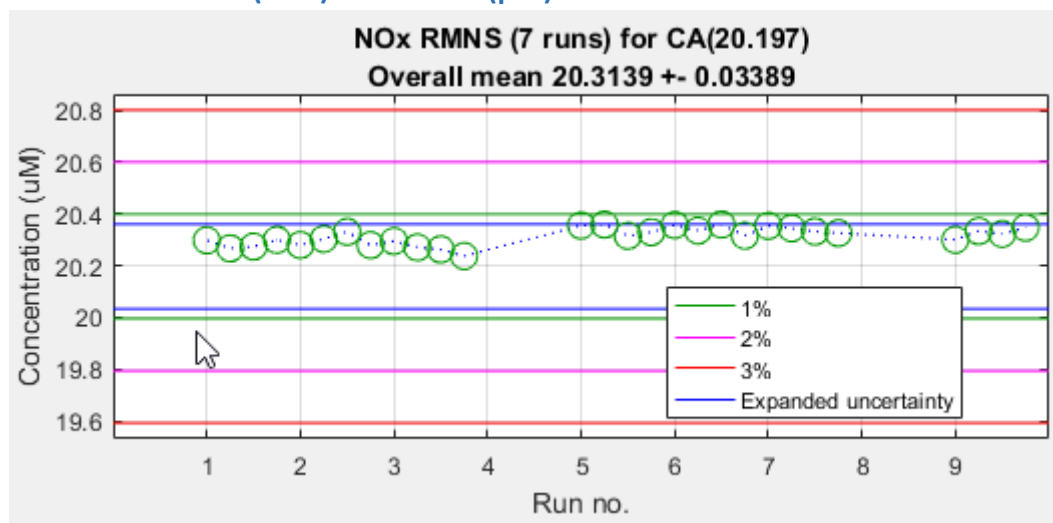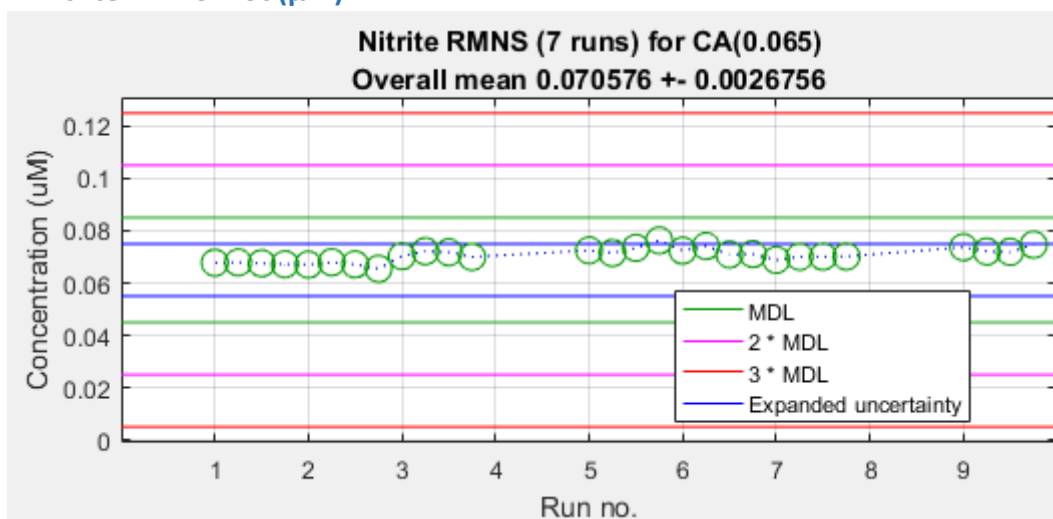
7.5.1 Silicate RMNS Plot (µM)
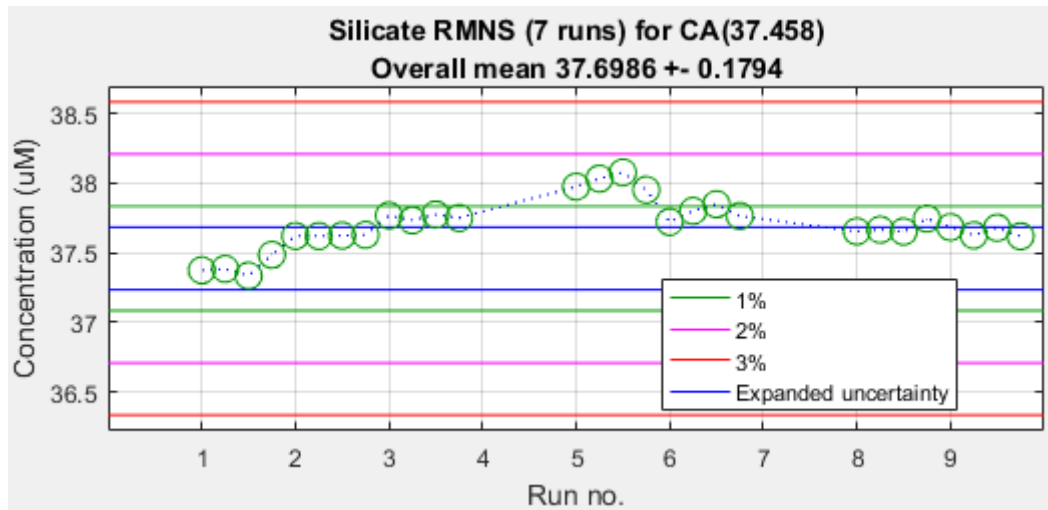
7.5.2 Phosphate RMNS Plot (µM)
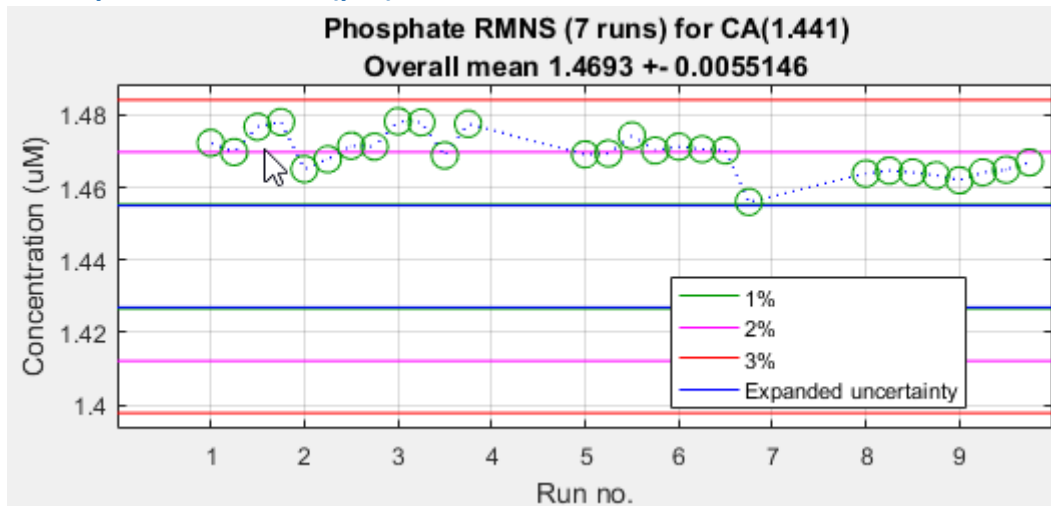
7.5.3   Nitrate + Nitrite (NOx) RMNS Plot (µM)

7.5.4   Nitrite RMNS Plot (µM)

7.6   Analytical Precision

7.6.1   Nutrient Measurement Uncertainty

The CSIRO Hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on the variation in the calibration curve, calibration standards, pipette and glassware calibration, and precision of the RMNS over time (Armishaw 2003).

Calculated Measurement Uncertainty @ 1 µmol L^{-1}				
Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
±0.017	±0.024	±0.019	±0.14	±0.30[¥]

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

¥The ammonia MU precision does not include data for the RMNS.

7.6.2   Nutrient Method Detection Limit

For in2019_v07, the measured detection limits (MDL) for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. The measured MDL is 3 times the standard deviation of three measurements of LNSW assayed in each nutrient run. See appendix 8.4 for the measured MDL per CTD deployments.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Nominal MDL	0.20	0.02	0.02	0.02	0.02
Standard Dev. Min	0.007	0.001	0.002	0.000	0.002
Standard Dev. Max	0.052	0.014	0.008	0.006	0.002
Standard Dev. Mean	**0.0297**	**0.0055**	**0.0048**	**0.004**	**0.002**
Standard Dev. Median	0.0330	0.0040	0.0050	0.004	0.002
Precision of MDL (stdev)	0.0167	0.00528	0.0024	0.0023	0.000

7.6.3   Reference Material for Nutrients in Seawater

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

| RMNS CA	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})	Nitrate + Nitrite (NOx, (µmol L^{-1})	Nitrite (µmol L^{-1})	Ammonia (µmol L^{-1})
Certified RMNS CA w/std deviation	37.458 ± 0.22	1.441 ± 0.014	20.197 ± 0.164	0.065 ± 0.010	- -
Minimum	37.394	1.464	20.266	0.067	
Maximum	38.007	1.476	20.352	0.073	
Mean	**37.7065**	**1.4702**	**20.313**	**0.0702**	
Median	37.7165	1.47	20.319	0.0705	
Precision (Stdev)	0.2020	0.0044	0.0351	0.0023	

7.7   Sampling Precision

Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate concentrations is less than the MDL value. The exception is nitrate+nitrite, which uses 0.06 µM as the MDL boundary.

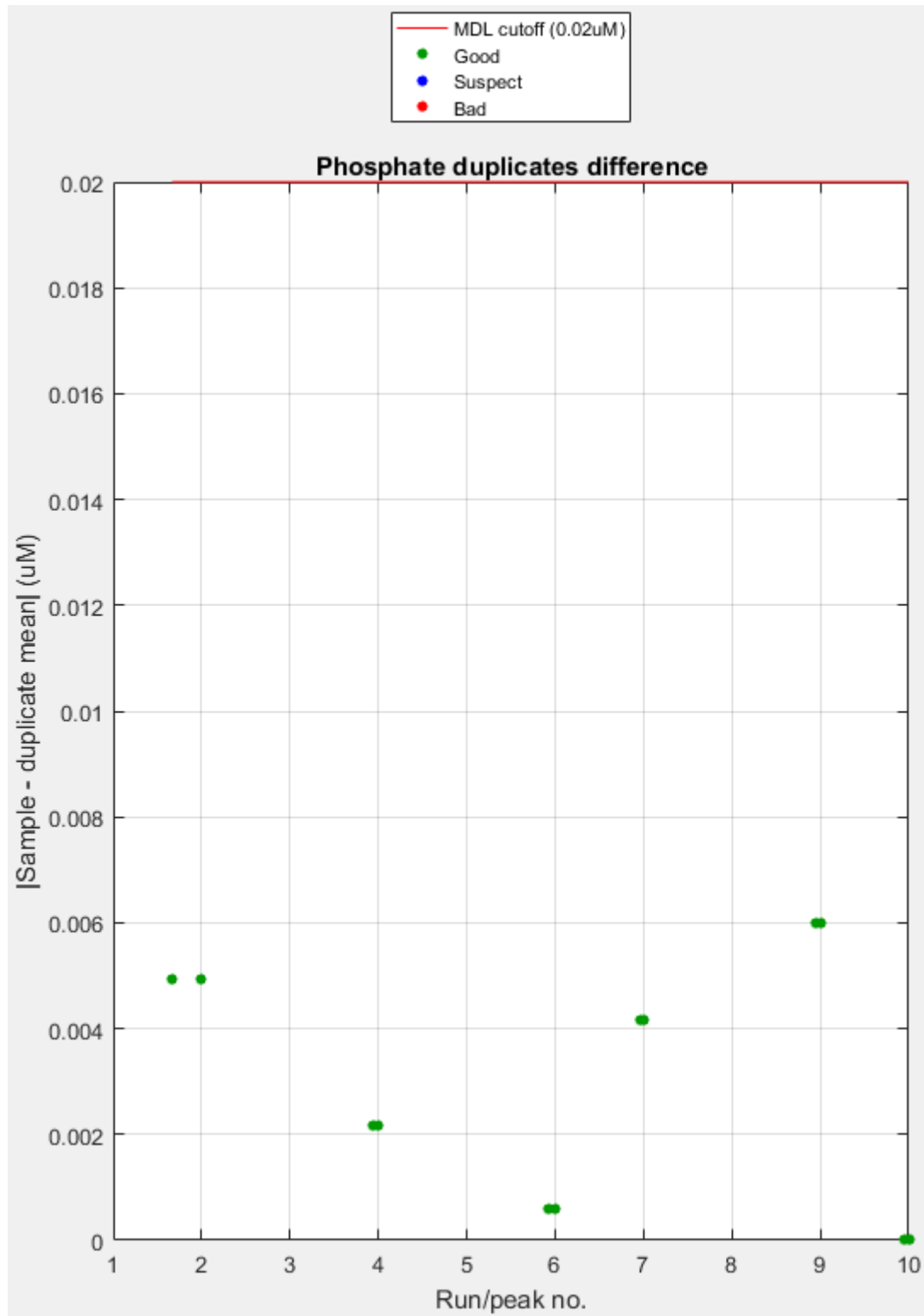Plots of the difference between the duplicate and their mean for the CTD deployments are below. The red line is the boundary below which sampling precision is deemed good.

For in2019_v07, the sampling precision is acceptable.
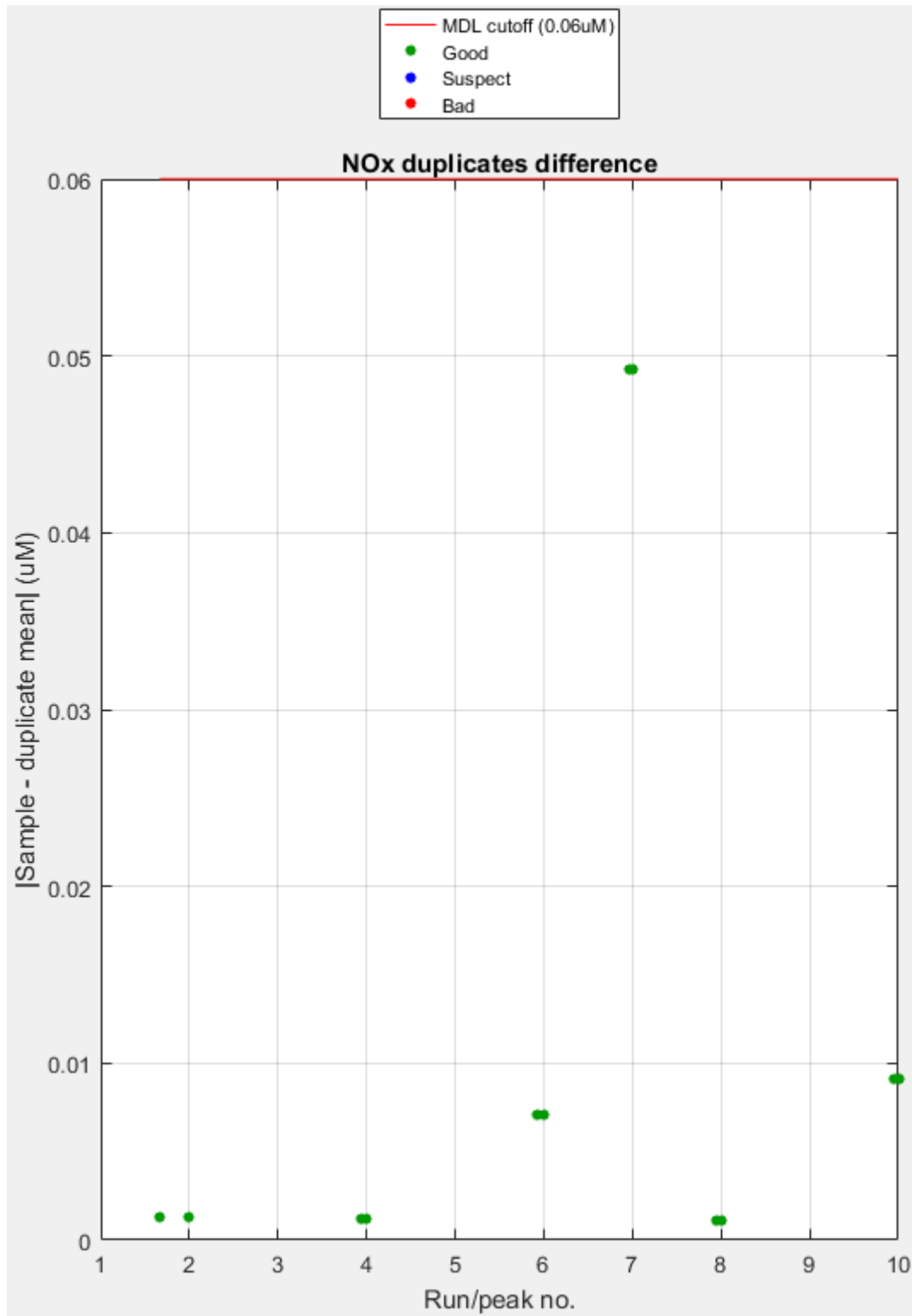
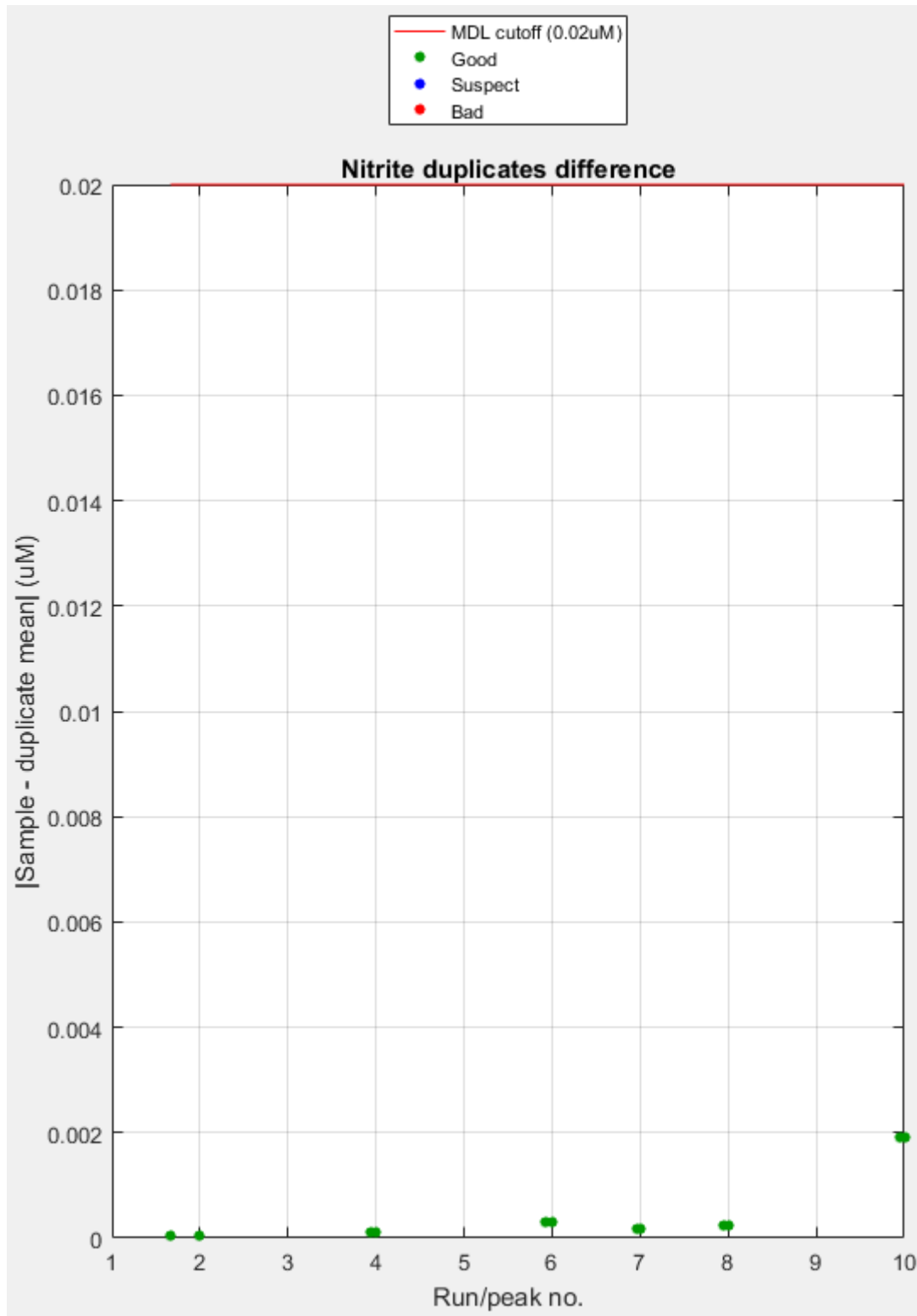### 7.7.1 Silicate Duplicates Plot
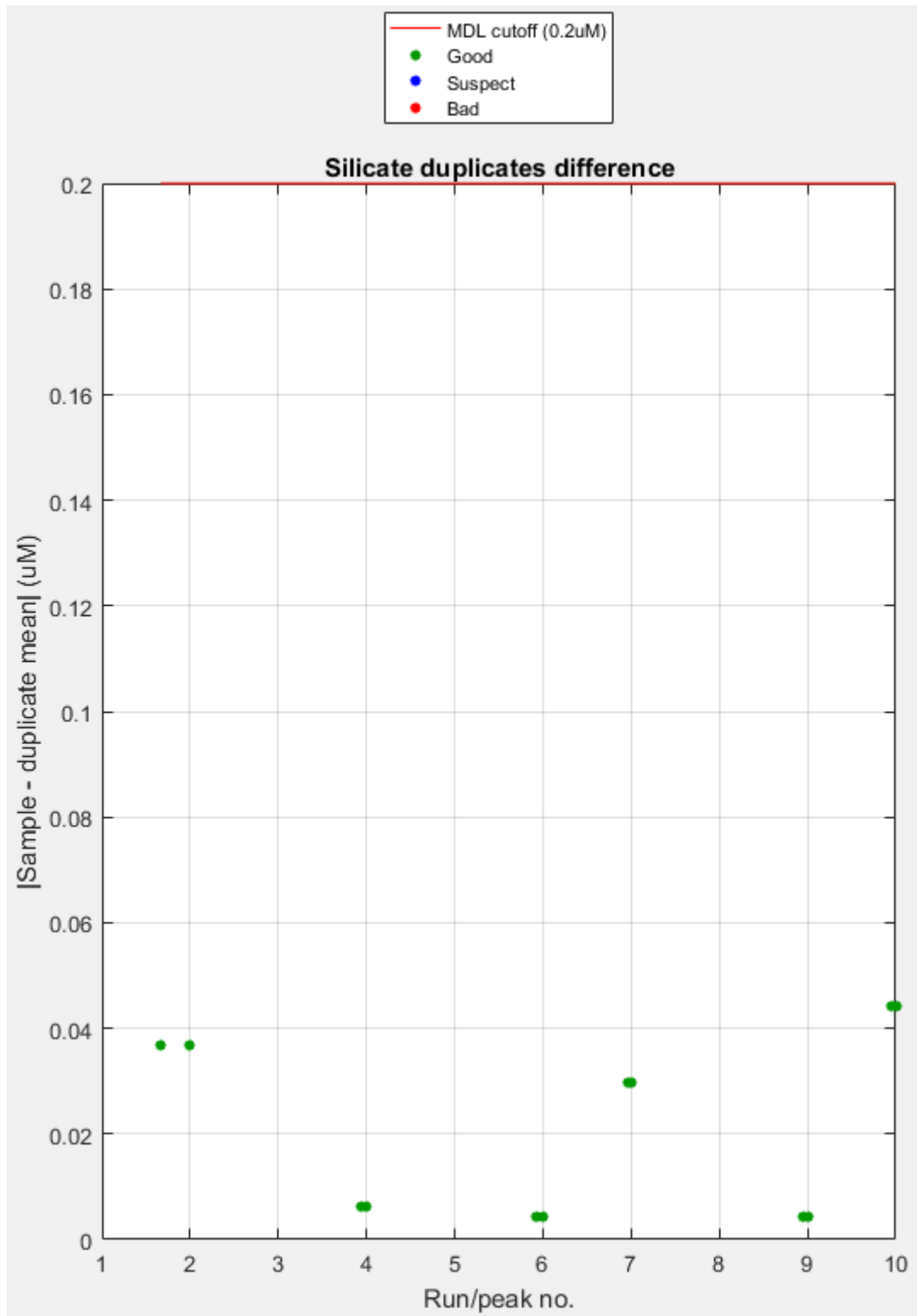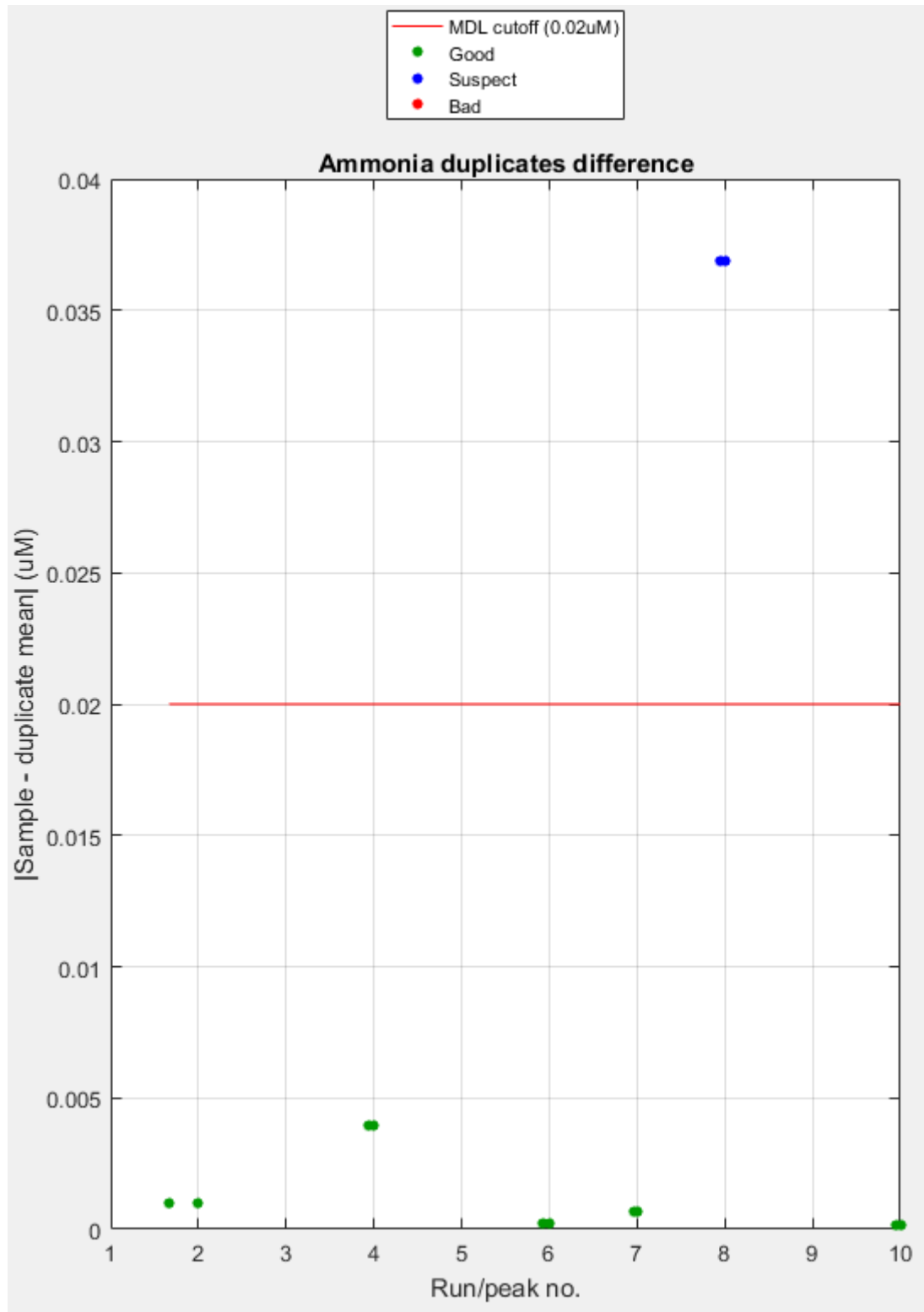
7.7.2   Phosphate Duplicates Plot

7.7.3 Nitrate + Nitrite (NOx) Duplicates Plot
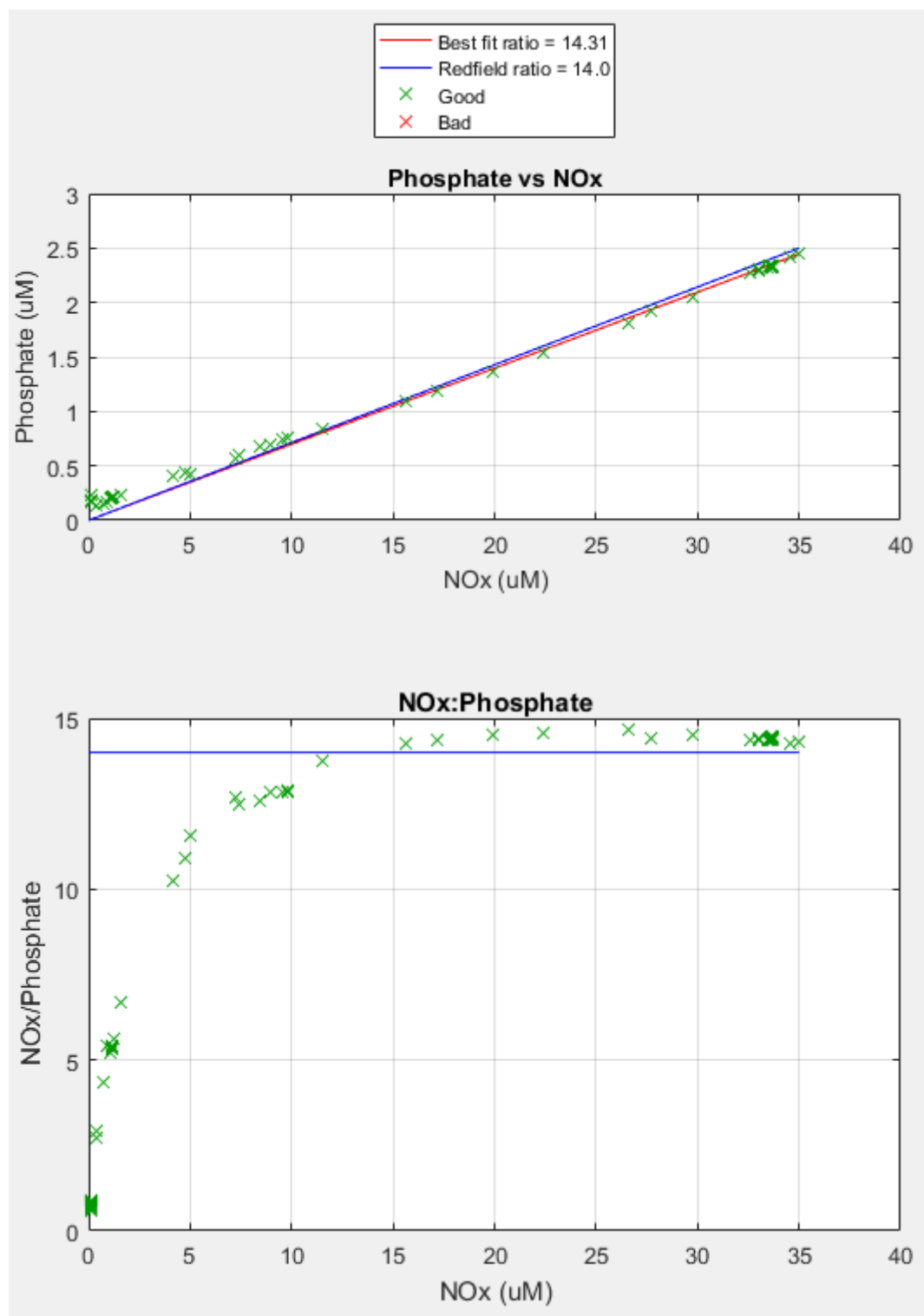
7.7.4 Nitrite Duplicates Plot

7.7.5 Ammonia Duplicates Plot

7.8   Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.31

7.9 Missing or Suspect Nutrient Data

The table below identifies all flagged data and any samples that had repeated analyses performed to obtain good data. Good data are flagged 0. Data flagged 63, below detection limit, are not included in the table below. Data flagged BAD (133) are not included in the .csv results files (in2019_v07HydroDep.csv). Flag Key in Appendix 8.5

CTD	RP	Run	Flag	Reason for Flag or Action
5	1	2	133	Outliers in vertical profile plot.
5	12	2	133	Outliers in vertical profile plot. Lanyard caught in top cap.
8	6, 7	6	133	Outliers in vertical profile plot.
9	1	7	69	NH_4 duplicates not within 0.02 µM.

7.10 Temperature & Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry lab and within the AA3HR instrument where measured and logged in the following locations:

(1) Directly above the AA3HR instrument, temperature only. Average 21.5°C.

(2) Above the AA3HR instrument, ship's instrument (Grafana). Data on request.

(3) On the deck of the nitrate & nitrite AA3HR chemistry module, beneath the instrument cover, temperature and humidity. Average temperature 22.5°C, standard deviation 1.3°C. Humidity data on request.

Refer to "in2019_v07_hyd_voyagereport.docx" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.5°C.

The laboratory temperature was measured and recorded on the nutrient run sheets at the start each analysis run. The temperature varied between 23.2°C and 20.2°C over the course of the voyage.

8 Appendix

8.1 Salinity: Reference Material Used

Osil IAPSO Standard Seawater	
Batch	P161
Use by date	03/05/2020
K_{15}	0.99987
PSU	35.995

8.2 Nutrients: Flagged Calibration and Quality Control Data

HyPro classifies the quality of data as good, suspect or bad and flags accordingly.

CTD	Peak	Run	Analysis	Reason for Flag or Action
4	Cal 2 & 3	Nut001	NH_4	Both points bad, not used in calibration curve.
7	Cal 1 & 3	Nut005	NH_4	Both points bad, not used in calibration curve.
8	Cal 1	Nut006	NH_4	Both points bad, not used in calibration curve.
8	Cal 3	Nut006	NH_4	Both points suspect, reduced weighting in calibration curve.
9	Cal 0	Nut007	PO_4	First point bad, not used in calibration curve.
9	Cal 0	Nut007	SiO_4	First point bad, not used in calibration curve.
9	Cal 1	Nut007	NH_4	Both points suspect, reduced weighting in calibration curve.
9	Cal 2	Nut007	NH_4	Both points bad, not used in calibration curve.
9	Cal 5	Nut009	NO_2	Both points off scale, not used in calibration curve.

8.3 Nutrients: RMNS results for each Analysis Run & CTD Deployment.

8.3.1 RMNS Lot CA Results

Analysis run	CTD #	Silicate (Si, $\mu mol\ L^{-1}$)	Phosphate (PO$_4$, $\mu mol\ L^{-1}$)	Nitrite (NO$_2$, $\mu mol\ L^{-1}$)	NOx (NO$_2$ + NO$_3$, $\mu mol\ L^{-1}$)
CA reported	-	37.458	1.441	0.065	20.197
1	4	37.394	1.474	0.068	20.285
2	5	37.622	1.469	0.067	20.298
3	6	37.755	1.476	0.071	20.266
5	7	38.007	1.471	0.073	20.340
6	8	37.783	1.467	0.072	20.352
7	9	-	-	0.070	20.339
8	9	37.678	1.464	-	-

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

How to use the RMNS for 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

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8.4   Nutrients: Measured Detection Limit for each Analysis Run & CTD Deployment.

Measured Detection Limit

Analysis Run	CTD #	Silicate (Si, $\mu mol\ L^{-1}$)	Phosphate (PO$_4$, $\mu mol\ L^{-1}$)	Nitrite (NO$_2$, $\mu mol\ L^{-1}$)	NOx (NO$_2$ + NO$_3$, $\mu mol\ L^{-1}$)	Ammonia (NH$_4^+$, $\mu mol\ L^{-1}$)
1	4	0.037	0.002	0.006	0.006	0.002
2	5	0.013	0.004	0.005	0.006	0.002
3	6	0.036	0.002	0.006	0.005	0.002
5	7	0.007	0.014	0.003	0.002	0.002
6	8	0.052	0.010	0.004	0.008	0.002
7	9	-	-	0.000	0.002	0.002
8	9	0.033	0.001	-	-	-

8.5   Flag Key for Hydrology Data Set

Flag	Description
0	Data is GOOD – nothing detected.
192	Data not processed.
63	Below nominal detection limit.
69	Data flagged suspect by operator. Set suspect by software if Calibration or Duplicate data is outside of set limits but not so far out as to be flagged bad.
65	Peak shape is suspect.
133	Error flagged by operator. Data is bad – operator identified by # in slk file or by clicking on point.
129	Peak exceeds maximum A/D value. Data is bad.
134	Error flagged by software. Peak shape is bad - Median Absolute Deviation (MAD) analysis used. Standards, MDL's and Duplicates deviate from the median, Calibration data falls outside set limits.
141	Missing data, no result for sample ID. Used in netcdf file as an array compiles results. Not used in csv file.
79	Method Detection Limit (MDL) during run was equal to or greater than nominal MDL. Data flagged as suspect.

8.6 GO-SHIP Specifications

8.6.1 Salinity

Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology. 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. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of ± 1°C is very important and should be recorded[2].

8.6.2 Dissolved Oxygen

Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.

8.6.3 SiO2

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

8.6.4 PO4

Approximately 1-2% accuracy[1], 0.4% precision[3], full scale.

8.6.5 NO3

Approximately 1% accuracy[1], 0.2% precision[3], full scale.

8.6.6 Notes

[1] If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.

[2] 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 batch is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.

[3] 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.

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