

RV INVESTIGATOR

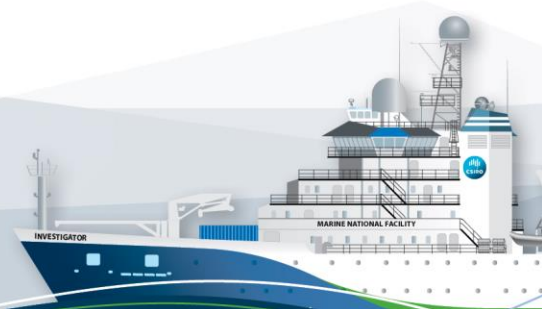
HYDROCHEMISTRY DATA PROCESS REPORT

Voyage: IN2017_t02

Chief Scientist: Dr Jochen Kaempf

Voyage title: Collaborative Australian Sea Training Alliance Network (CAPSTAN)

Report compiled by: Stephen Tibben



Contents

1	Itinerary	4
2	Key personnel list	4
3	Summary.....	4
	Hydrochemistry.....	4
3.1	Rosette and CTD.....	4
3.2	Procedure Summary	5
4	Salinity Data Processing.....	5
4.1	Salinity Parameter Summary	5
4.2	CTD vs Hydro Salinities Plot	5
4.3	Missing or Suspect Salinity Data and Actions taken	6
5	Dissolved Oxygen Data Processing	6
5.1	Dissolved Oxygen Parameter Summary.....	6
5.2	CTD vs Hydro DO Plot.....	7
5.3	Dissolved Oxygen thiosulphate normality and blank across voyage	8
5.4	Missing or Suspect Dissolved Oxygen Data and Actions taken.....	9
6	Nutrient Data Processing.....	9
6.1	Nutrient Parameter Summary	9
6.2	Nutrient calibration and data parameter summary	9
6.3	Accuracy - Reference Material for Nutrient in Seawater (RMNS)	10
6.4	Analytical Precision	11
6.5	Sampling Precision	11
6.5.1	Silicate Duplicate Plot	12
6.5.2	Phosphate Duplicate Plot.....	13
6.5.3	Nitrate + Nitrite (NO _x) Duplicate Plot	14
6.5.4	Nitrite Duplicate Plot	15
6.5.5	Ammonia Duplicate Plot	16
6.5.6	Redfield Ratio Plot (14.0)	17
6.6	Calibration and QC edited data.....	18
6.7	Investigation of Missing or Flagged Nutrient Data and Actions taken.	18
6.8	Temperature & Humidity Change over Nutrient Analyses	18
7	Appendix.....	19
7.1	Salinity Reference Material.....	19
7.2	Hypro Flag Key for CSV & NetCDF file	20
7.3	GO-SHIP Specifications.....	21

7.4	Nutrient Methods	22
8	References	23

1 Itinerary

Depart Leg 1	Date	Time
Henderson, WA	14 November	1000
Arrive	Date	Time
Hobart, TAS	26 November	1200

2 Key personnel list

Name	Role	Organisation
Dr Jochen Kaempf	Chief Scientist	Flinders University
Matt Kimber	Voyage Manager	CSIRO
Dr Leah Moore	Co-chief scientist	University of Canberra
Dr April Abbott	CAPSTAN director	Macquarie University
Stephen Tibben	Hydrochemist	CSIRO

3 Summary

All finalized data can be obtained from the CSIRO data centre. Nutrient data is not RMNS corrected.

Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	26 CTD 16 UWY (TSG)
Dissolved Oxygen (automated titration)	30 CTD
Nutrients (AA3)	100 CTD 13 UWY 1 EXP

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

3.1 Rosette and CTD

- 10 CTD stations were sampled with a 24 bottle rosette (10 L & 12 L).
- See in2017_t02_HydrochemistryReport.pdf (voyage report) for more details on sample collection.

3.2 Procedure Summary

The procedure for data processing is outline in Figure 1.

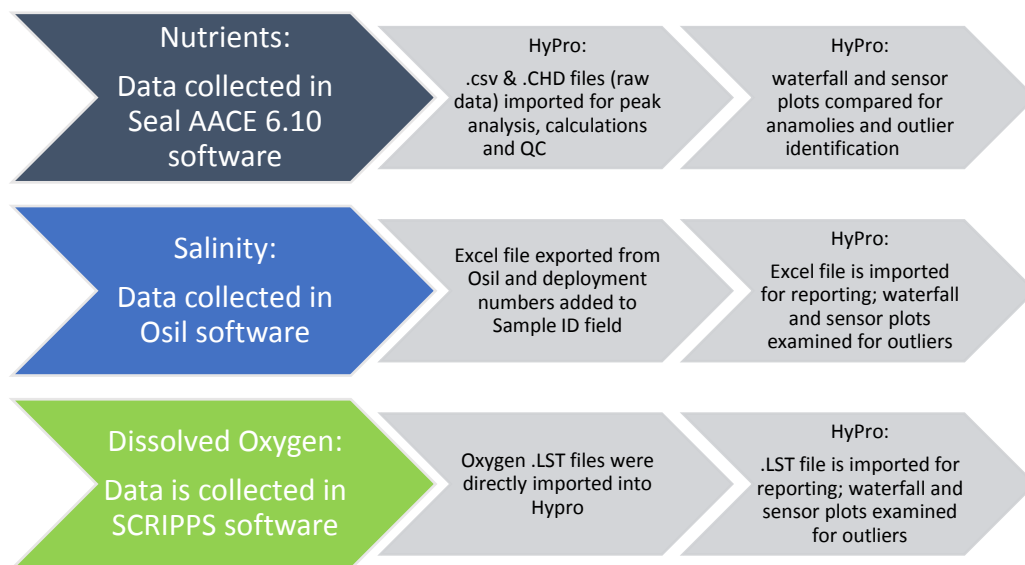


Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

4 Salinity Data Processing

4.1 Salinity Parameter Summary

Details	
HyPro Version	5.3
Instrument	Guildline Autosol Laboratory Salinometer 8400(B) – SN 71613
Software	OSIL Data Logger
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 salinity units
Analyst(s)	Stephen Tibben, Students under supervision
Lab Temperature (±0.5°C)	20.0 -20.5°C during analysis.
Bath Temperature	24.010°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 20°C before analysis
Comments	

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
01	07	C07	141	Sample not analysed. It is possible that it was not sampled.

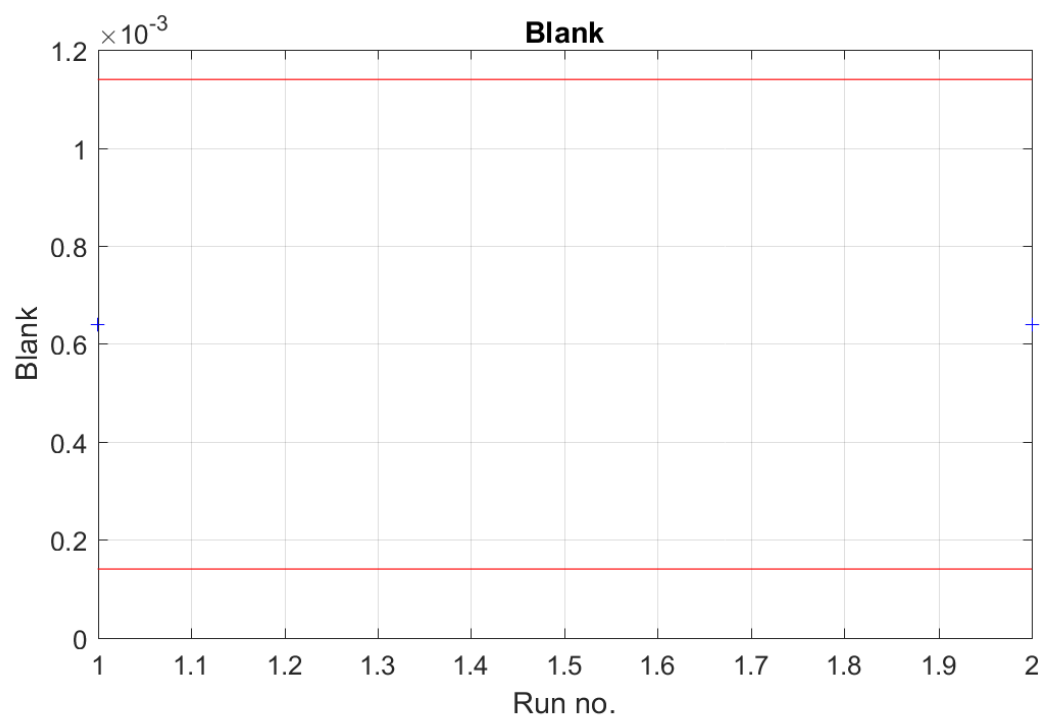
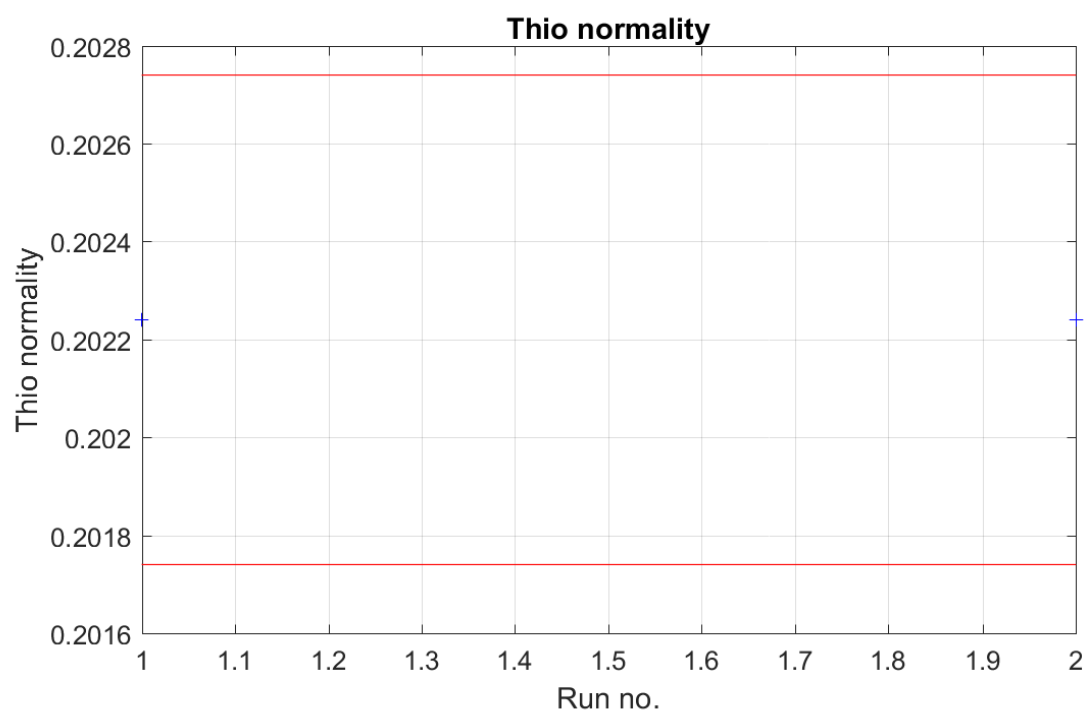
5 Dissolved Oxygen Data Processing

Typically only 2 – 3 dissolved oxygen samples were taken per deployment. This is sufficient for a slope/offset correction of CTD data, and student training was prioritised over data collection.

5.1 Dissolved Oxygen Parameter Summary

Details	
HyPro Version	5.3
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Stephen Tibben, Students under supervision
Lab Temperature ($\pm 1^{\circ}\text{C}$)	Variable, 19.0 - 21.0°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 ~72 hrs
Comments	

5.3 Dissolved Oxygen thiosulphate normality and blank across voyage



5.4 Missing or Suspect Dissolved Oxygen Data and Actions taken

N/A

6 Nutrient Data Processing

6.1 Nutrient Parameter Summary

Details					
HyPro Version	5.3				
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients analysed	<input checked="" type="checkbox"/> Silicate	<input checked="" type="checkbox"/> Phosphate	<input checked="" type="checkbox"/> Nitrate + Nitrite	<input checked="" type="checkbox"/> Nitrite	<input checked="" type="checkbox"/> Ammonia
Concentration range	112 $\mu\text{mol l}^{-1}$	3 $\mu\text{mol l}^{-1}$	36.4 $\mu\text{mol l}^{-1}$	1.4 $\mu\text{mol l}^{-1}$	2.0 $\mu\text{mol l}^{-1}$
Method Detection Limit* (MDL)	0.2 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$
Matrix Corrections	N	N	N	N	N
Analyst(s)	Stephen Tibben				
Lab Temperature ($\pm 1^\circ\text{C}$)	Variable, 19.0 – 21.0°C				
Reference Material	RMNS – CD, CB				
Sampling Container type	50 ml HDPE bottles				
Sample Storage	< 2 hrs at room temperature or \leq 12 hrs @ 4°C				
Pre-processing of Samples	None				
Comments	Non-CTD related samples were analysed and processed with the prefix-uwv and exp.				

6.2 Nutrient calibration and data parameter summary

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	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
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
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. 20 L carboys were filtered through 1µM by Stephen Tibben and Kendall Sherrin in March 2017 and stored in the hydrochemistry laboratory at 20°C.				
Medium of Baseline	18.2 Ω MQ				
Proportion of samples in duplicate?	1 duplicate for each CTD from NISKIN bottle 1				
Comments	The reported data is not corrected to the RMNS. Per run RMNS data can be found in Appendix Error! Reference source not found.				

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

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 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 CD was measured 4 times in runs 1 and 2. The RMNS Lot CB was measured 8 times in run 3. 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
CB	36.629	36.768	0.119	2.580	111.821
CD	5.630	5.648	0.018	0.457	14.264

The submitted nutrient results do **NOT** have RMNS corrections applied.

CTD	SiO ₄ measured	SiO ₄ expected	PO ₄ measured	PO ₄ expected	NO ₂ measured	NO ₂ expected	NO _x measured	NO _x expected
1	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
2	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
3	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
4	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
5	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
6	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
7	14.484	14.264	0.437	0.457	0.003	0.018	5.599	5.648
8	13.808	14.264	0.462	0.457	0.036	0.018	5.540	5.648
9	13.808	14.264	0.462	0.457	0.036	0.018	5.540	5.648
10	13.808	14.264	0.462	0.457	0.036	0.018	5.540	5.648

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

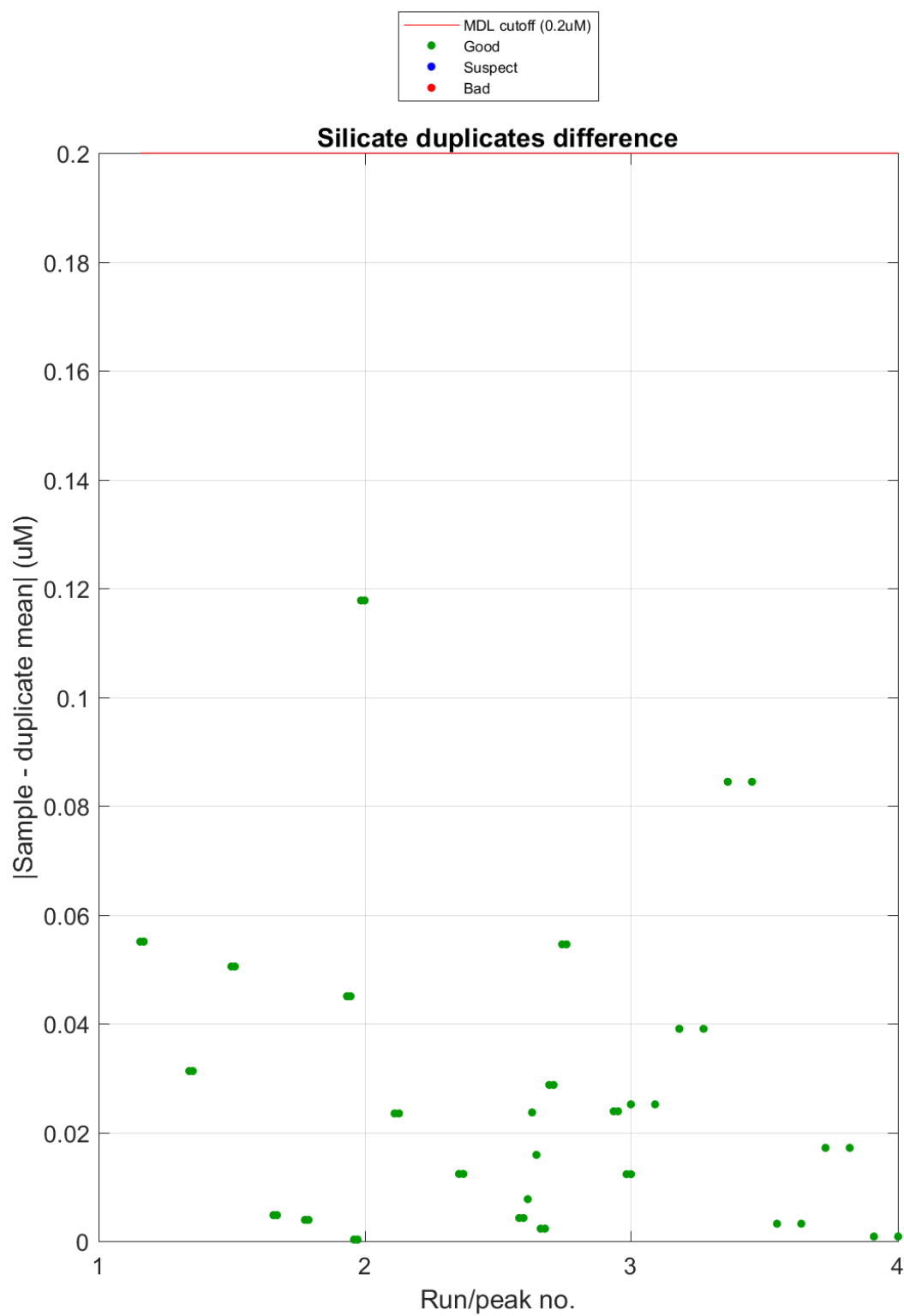
*The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

[‡]The ammonia MU precision component does not include data on the CRM.

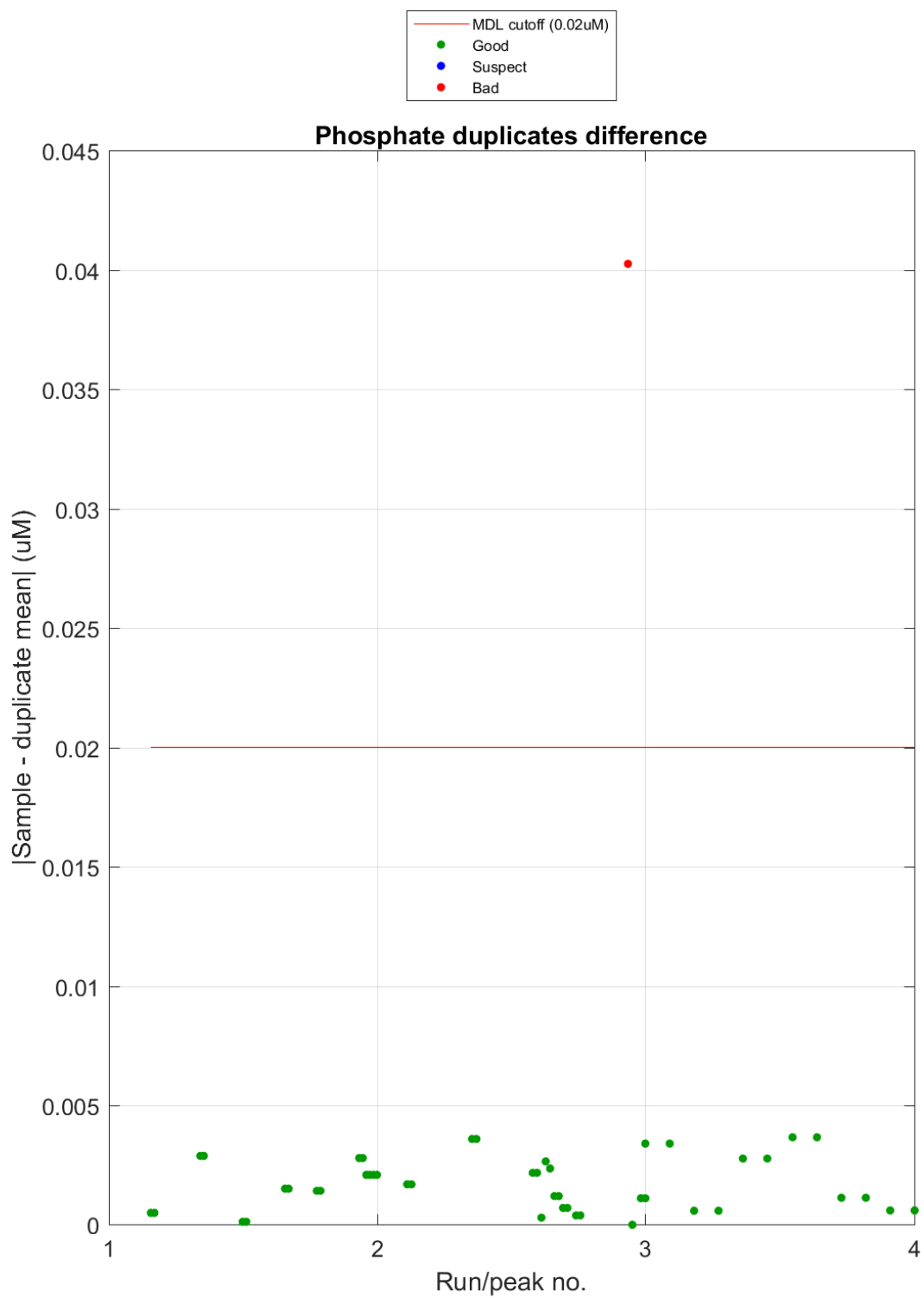
6.5 Sampling Precision

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.

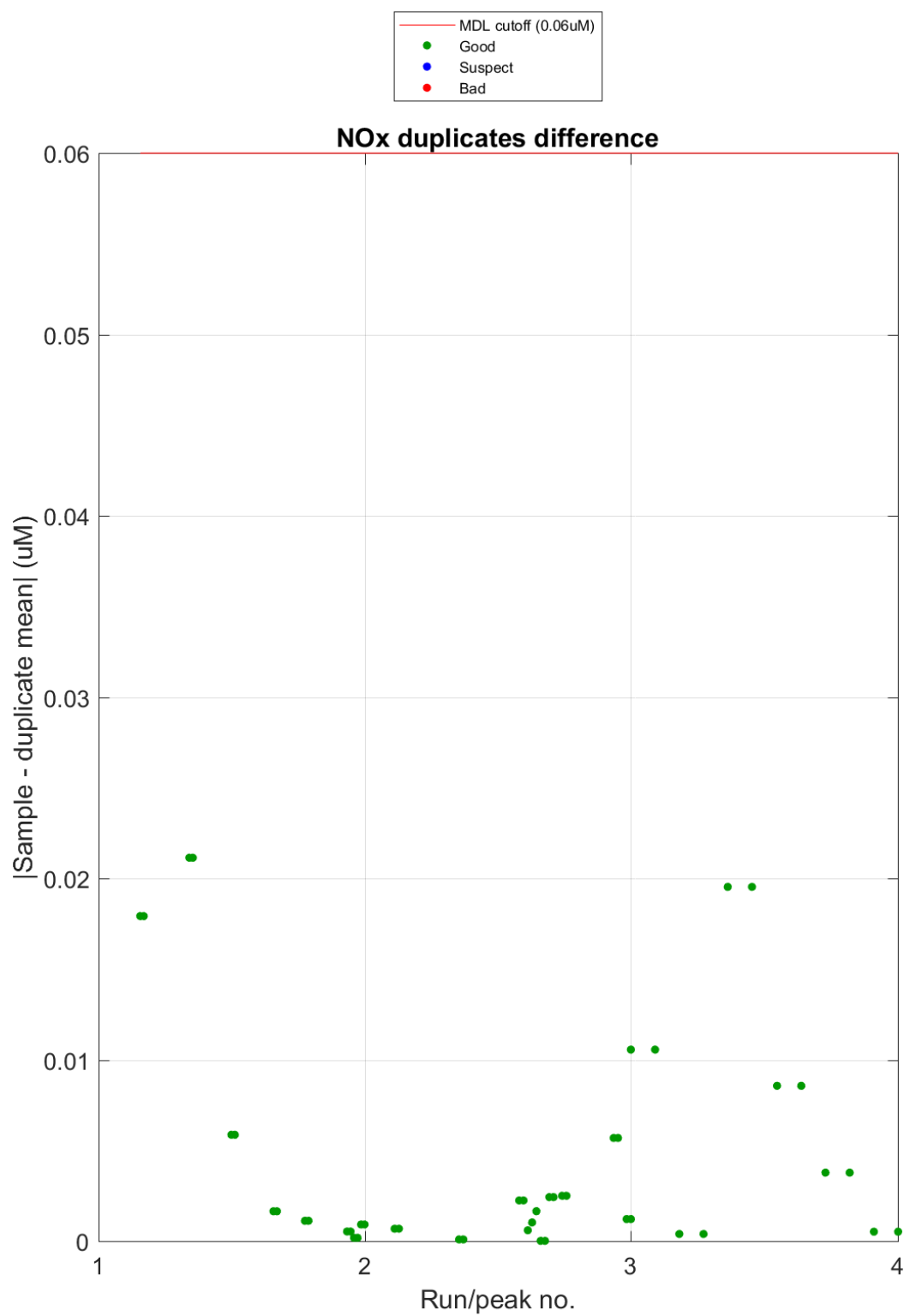
6.5.1 Silicate Duplicate Plot



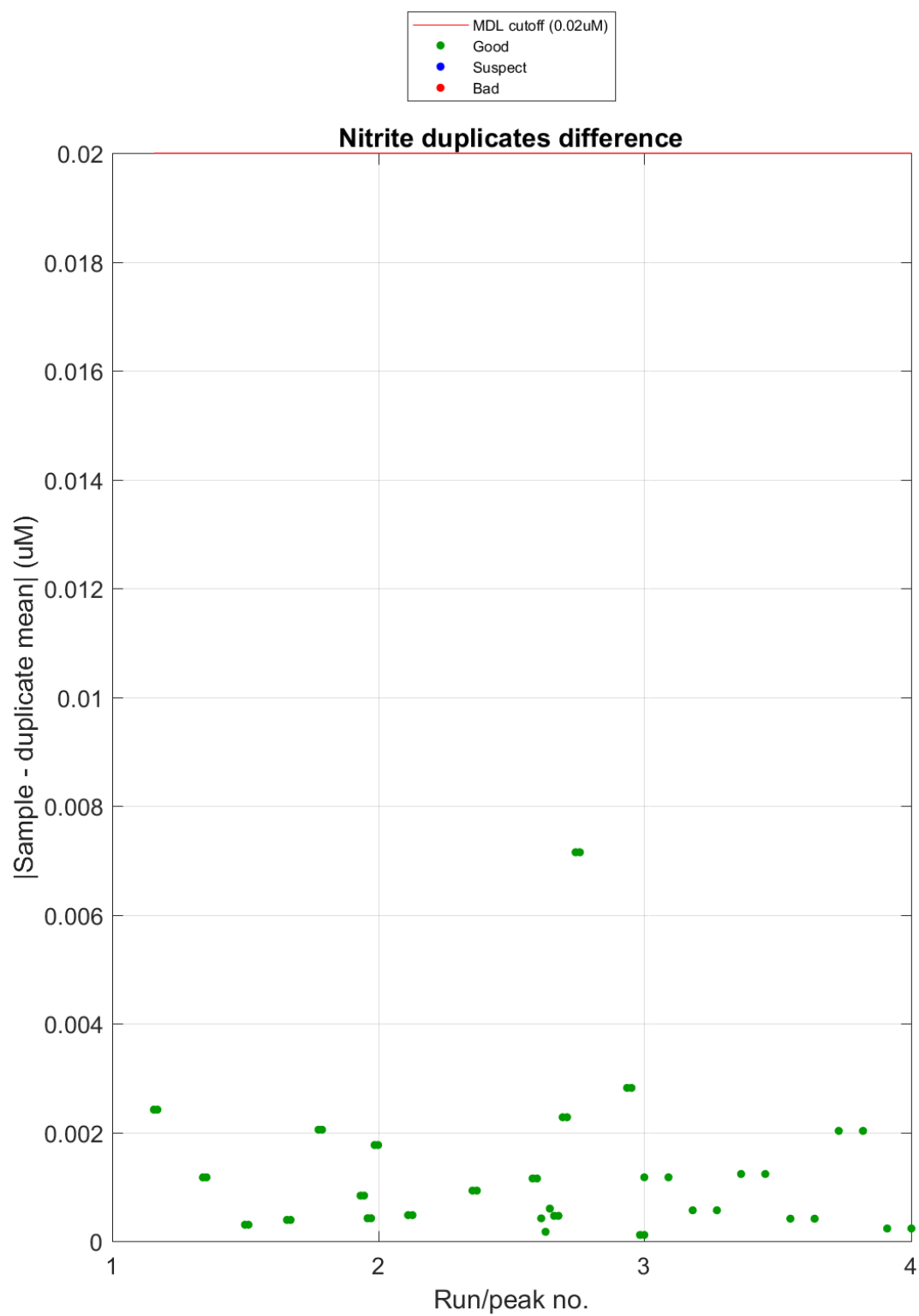
6.5.2 Phosphate Duplicate Plot



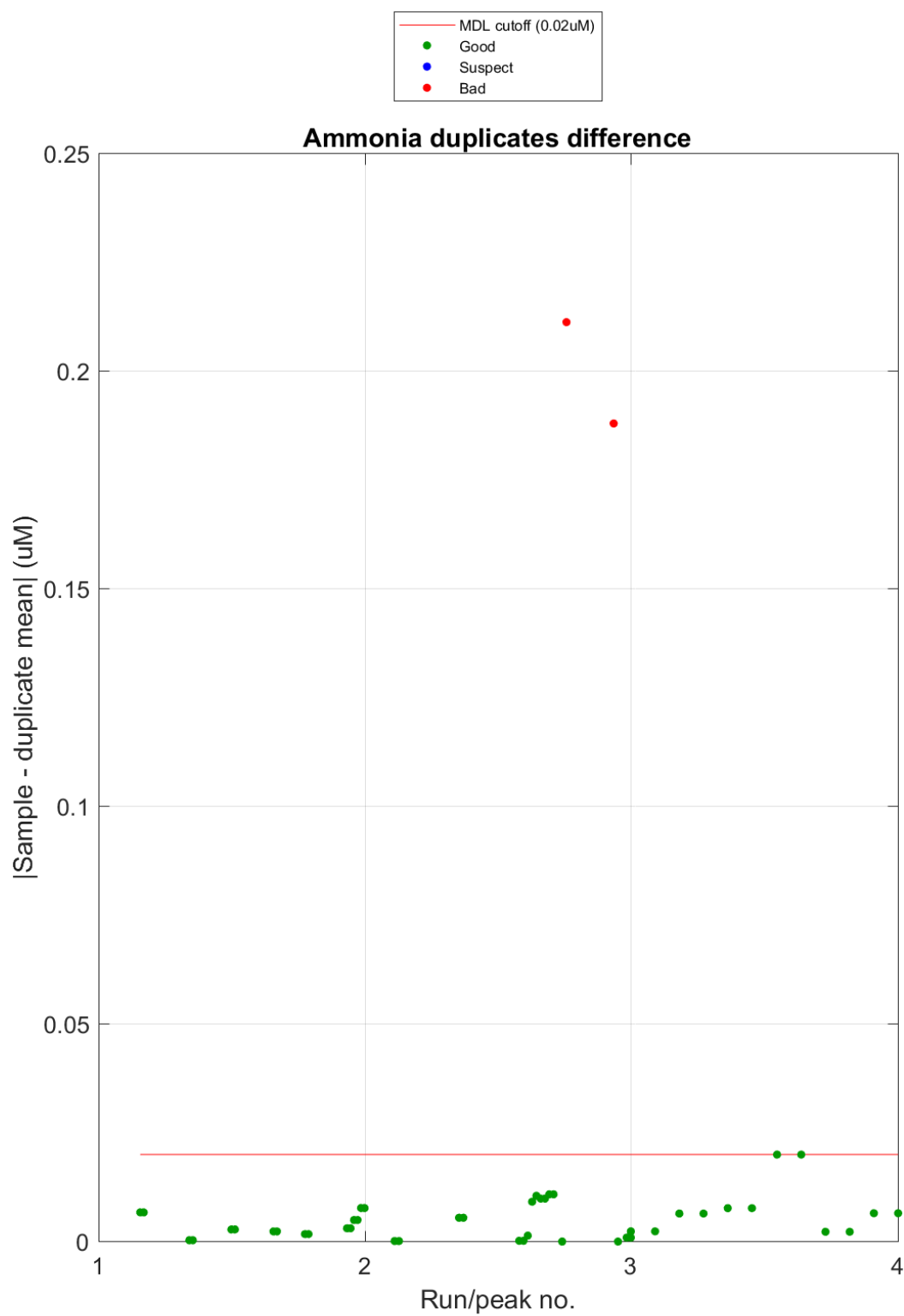
6.5.3 Nitrate + Nitrite (NOx) Duplicate Plot



6.5.4 Nitrite Duplicate Plot

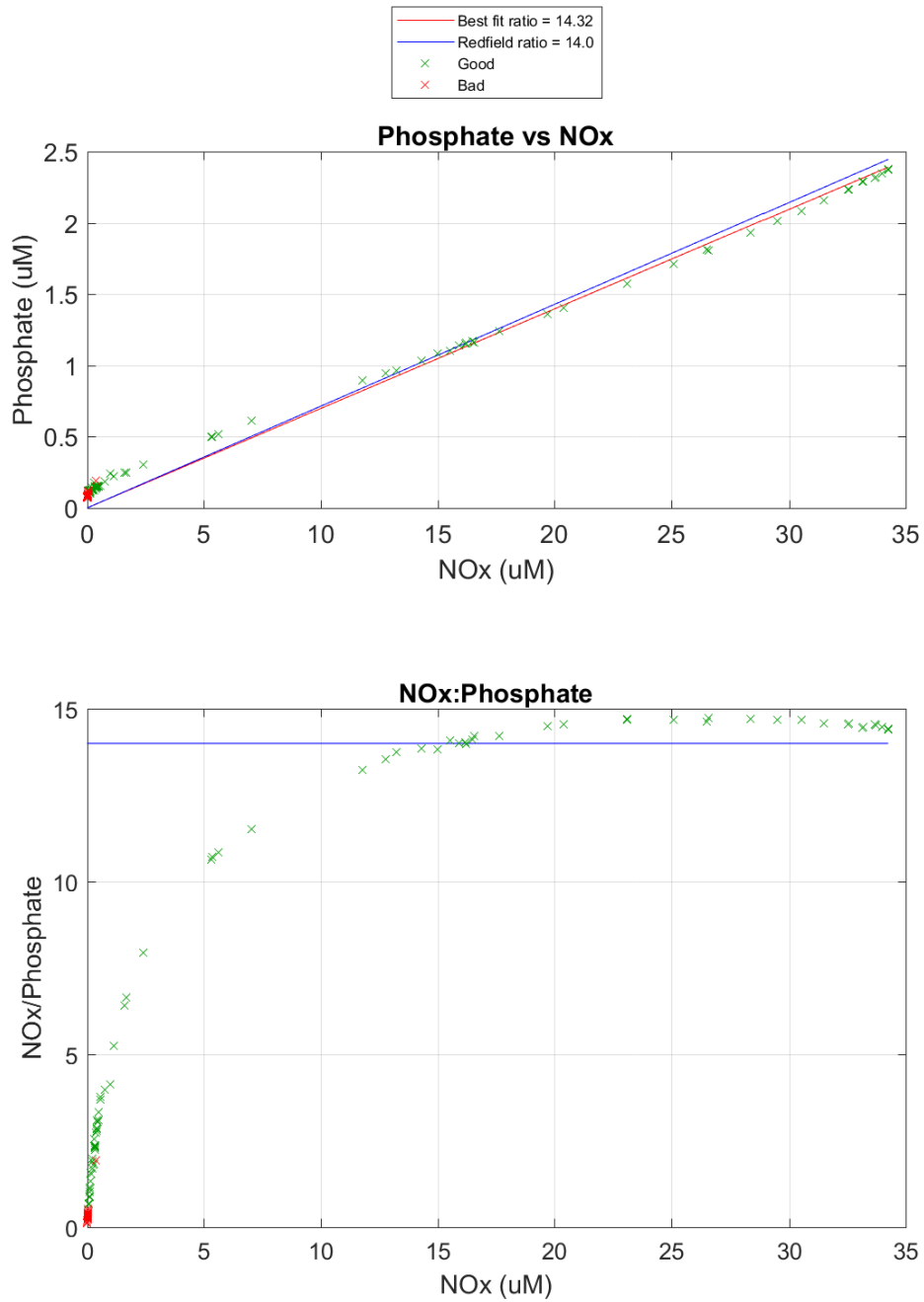


6.5.5 Ammonia Duplicate Plot



6.5.6 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx, best fit ratio = 14.32



6.6 Calibration and QC edited data

CTD	Peak	Analysis	Action
1-6	Cal 2	SiO4	First point greater than calibration error. Not used in calibration.
1-6	RMNS	SiO4	Suspect (MAD) peak shape, marked bad.
1-6	Cal 1	NH4	Both points greater than calibration error. Not used in calibration.
1-6	Cal 3	NH4	Both points greater than calibration error. Not used in calibration.
7-10	Cal 1	NH4	Both points greater than calibration error. Not used in calibration.
uwy008-013	Cal 2	NH4	Both points greater than calibration error. Not used in calibration.
uwy008-013	Cal 4	NH4	Both points greater than calibration error. Not used in calibration.

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
1	22	Nut001	All	141	Sample not analysed. It is possible that it was not sampled.
10	1	Nut002	PO4	133	Sample outlier in vertical profile plot. Possibly contaminated.
10	1	Nut002	NH4	133	Sample outlier in vertical profile plot. Possibly contaminated.
-	Exp001	Nut002	NH4	133	Sample contaminated.

6.8 Temperature & Humidity Change over Nutrient Analyses

The temperature/humidity logger QP6013 (Jaycar) malfunctioned before the voyage and was not used.

7 Appendix

7.1 Salinity Reference Material

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

7.2 Hypro Flag Key for CSV & NetCDF file

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

7.3 GO-SHIP Specifications

Salinity	Accuracy of 0.001 is possible with Autosol™ salinometers and concomitant attention to methodology, e.g., monitoring Standard Sea Water. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosol precision is better than 0.001 PSS-78. High precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano (this manual) with great care and experience. Air temperature stability of $\pm 1^{\circ}\text{C}$ is very important and should be recorded. ¹
O ₂	Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.
SiO ₂	Approximately 1-3% accuracy†, 2 and 0.2% precision, full-scale.
PO ₄	Approximately 1-2% accuracy†, 2 and 0.4% precision, full scale.
NO ₃	Approximately 1% accuracy†, 2 and 0.2% precision, full scale.

Notes: † If no absolute standards are available for a measurement then *accuracy* should be taken to mean the *reproducibility* presently obtainable in the better laboratories.

1 Keeping constant temperature in the room where salinities are determined greatly increases their quality. Also, room temperature during the salinity measurement should be noted for later interpretation, if queries occur. Additionally, monitoring and recording the bath temperature is also recommended. The frequent use of IAPSO Standard Seawater is endorsed. To avoid the changes that occur in Standard Seawater, the use of the most recent batches is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.

2 Developments of reference materials for nutrients are underway that will enable improvements in the relative accuracy of measurements and clearer definition of the performance of laboratories when used appropriately and the results are reported with the appropriate meta data.

7.4 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 $\mu\text{mol l}^{-1}$	3 $\mu\text{mol l}^{-1}$	42 $\mu\text{mol l}^{-1}$	1.4 $\mu\text{mol l}^{-1}$	2.0 $\mu\text{mol l}^{-1}$
Method Detection Limit (MDL)	0.2 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$	0.02 $\mu\text{mol l}^{-1}$

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

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

Nitrate is determined by first reducing to nitrite via a basic buffered copperized cadmium column before the colour reaction (Wood et al., 1967). Nitrite in seawater will react with sulphanilamide under acidic conditions to form a diazo compound. This compound couples with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex which can be detected at 520 nm.

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

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

8 References

- Armishaw, Paul, "Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty." *Accred Qual Assur*, 8, pp. 218-224 (2003).
- Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., "*The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment*," *Deep-Sea Research*, 14, pp.381-389 (1967).
- Hood, E.M. (2010). "*Introduction to the collection of expert reports and guidelines*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). "*Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- K  rouel, Roger and Alain Aminot, "*Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis*". *Journal of Marine Chemistry* 57 (1997) pp. 265-275.
- Murphy, J. And Riley, J.P., "*A Modified Single Solution Method for the Determination of Phosphate in Natural Waters*", *Anal.Chim.Acta*, 27, p.30, (1962)
- Wood, E.D., F.A.J. Armstrong, and F.A. Richards. (1967) "*Determination of nitrate in seawater by cadmium-copper reduction to nitrite*." *Journal of the Marine Biological Association of U.K.* 47: pp. 23-31.