RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2017_t01
Chief Scientist:	Hugh Barker
Voyage title:	Transit
Report compiled by:	Cassie Schwanger

Contents

1   Executive Summary

Nutrient were collected from the underway seawater supply. Good quality data was produced for the measured parameters. Certified reference materials for nutrients in seawater were within the specified limits of the assigned value.

2   Itinerary

Inset voyage track.

Depart	Date	Time
Sydney	24/9/2017	2000
Arrive	Date	Time
Broome	8/10/2017	1300

3   Key personnel list

Name	Role	Organisation
Hugh Barker	Voyage Manager	CSIRO
Cassie Schwanger	Hydrochemist	CSIRO

4   Summary

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

4.1   Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	NA
Dissolved Oxygen (automated titration)	NA
Nutrients (AA3)	20 UWY

Note:

- UWY - samples collected from underway clean instrument seawater supply in the PCO2 lab and/or trace metal clean in wet clean lab or PCO2 lab. See Elog.

4.2   Rosette and CTD

- NA

4.3   Data Procedure Summary

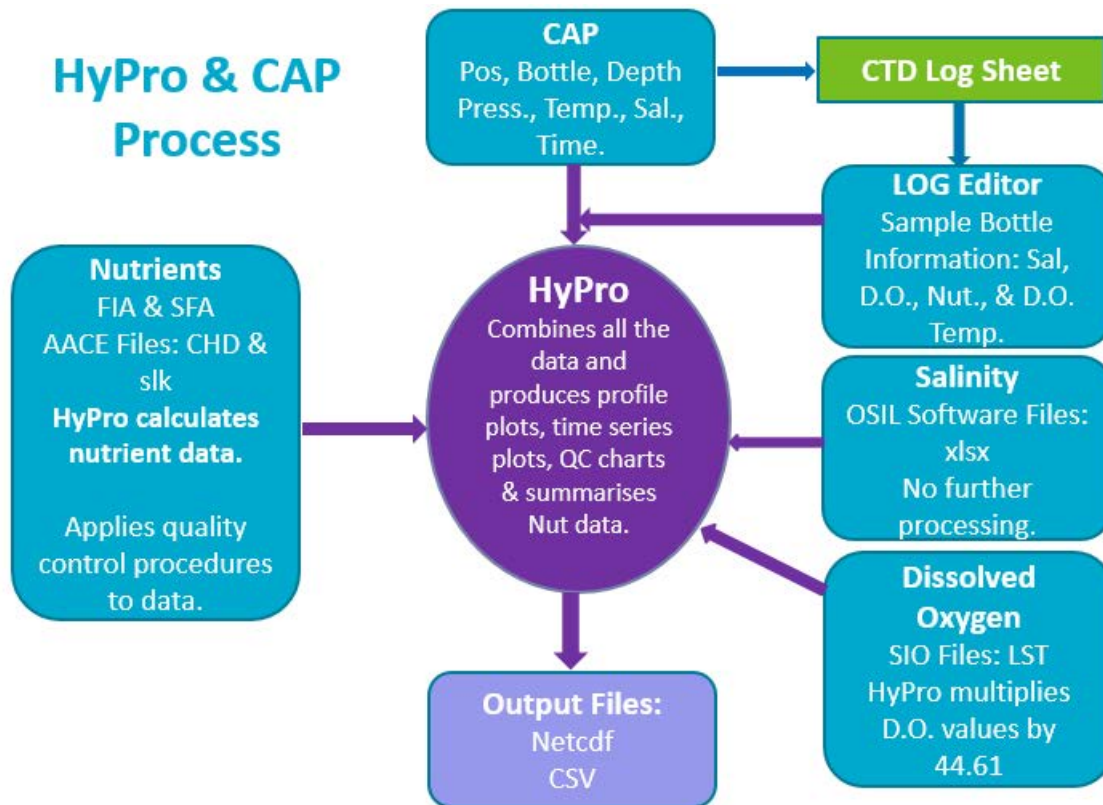The procedure for data processing is outlined below.

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

5   Nutrient Data Processing

5.1   Nutrient Parameter Summary

Details					
HyPro Version	4.17				
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)	Cassie Schwanger				
Lab Temperature (±1°C)	Variable, 20.0 – 23.0°C				
Reference Material	RMNS – CD				
Sampling Container type	50 mL HDPE sample tubes				
Sample Storage	< 2 hrs at room temperature or ≤ 24 hrs @ 4°C				
Pre-processing of Samples	None				
Comments					

5.2   Nutrient Methods

CSIRO Oceans and Atmosphere Hydrochemistry nutrient analysis is performed with a segmented flow auto-analyser – Seal AA3 HR – to measure silicate, phosphate, nitrite, nitrate plus nitrite (NOx), and ammonium

Silicate: colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660nm.

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

Nitrate: colourimetric analysis, Cu-Cd reduction – Naphthylenediamine photometric method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper - cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 520 nm.

Nitrite: colourimetric analysis, Naphthylenediamine photometric method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium: fluorescence analysis, ortho-phtaldiadehyde method. Based on Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460nm after excitation at 370nm.

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

5.3   Instrument Calibration and Data Parameter Summary

All instrument parameters and reagent batch compositions are logged for each analysis run. This information is available on request.

The raw data from each analysis run on the Seal AA3HR is imported into HyPro for peak height determination, constructing the calibration curve, deriving the sample results and applying drift and carry-over corrections. The calibration curve is fitted to the standards by performing several passes over each standard point and weighting its contribution to the curve depending on the magnitude of the difference between its measured and calculated value. The larger the difference, the less weighting is given to the standard's contribution towards the curve construction. The cut-off limits for good calibration data are

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE).

- 0.02uM for phosphate, nitrite and ammonium.

Following standard procedures, the operator may choose to not include bad calibration points (see section 6.7 for edited data). Below are the corrections and settings that HyPro applied to the raw data.

All runs have a corresponding "AA3_Run_Analysis_sheet" to record the following: sample details, LNSW batch, cadmium column, working standards, reagent information, instrumentation settings, and pump tube hours. The NUT### file numbers that correspond to each analytical run and the

details of the samples analysed are in "Nut_AACE_LogLin2017_v02.doc". These files along with calibration summary data for each analysis run are in the voyage documentation and available upon request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Data Reported as	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}	µmol l^{-1}
Calibration Curve degree	Linear	Linear	Quadratic	Quadratic	Quadratic
Forced through zero?	N	N	N	N	N
# of points in Calibration	5	5	5	5	5
Matrix Correction	N	N	N	N	N
Blank Correction	N	N	N	N	N
Carryover Correction (HyPro)	Y	Y	Y	Y	Y
Baseline Correction (HyPro)	Y	Y	Y	Y	Y
Drift Correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS	N	N	N	N	N
Window Defined*	HyPro	HyPro	HyPro	HyPro	HyPro
Medium of Standards	LNSW (bulk on deck of Investigator) collected on 28/9/2016. Sub-lot passed through a 10 micron filter and stored in 20 L carboys in the hydrochemistry laboratory at 22°C.				
Medium of Baseline	18.2 Ω MQ				
Proportion of samples in duplicate?	No duplicates collected.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data can be found in appendix 6.4.				

5.4 Accuracy - Reference Material for Nutrient in Seawater (RMNS) Plots

Japanese KANSO certified reference materials (RMNS) for silicate, phosphate, nitrate and nitrite in seawater was used in each nutrient analysis run to determine the accuracy. For each analysis run, a new RMNS bottle was opened and used. The RMNS was assayed in quadruplicate after the calibration standards.

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

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

RMNS	NO$_3$	NO$_X$	NO$_2$	PO$_4$	SiO$_4$
CD	5.63 ± 0.003	5.65 ± 0.004	0.018 ± 0.001	0.46 ± 0.01	14.26 ± 0.05

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

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), appendix 7.3, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy. The assayed RMNS values per CTD deployment are reported in the table in appendix 7.4.

5.4.1 Silicate RMNS Plot
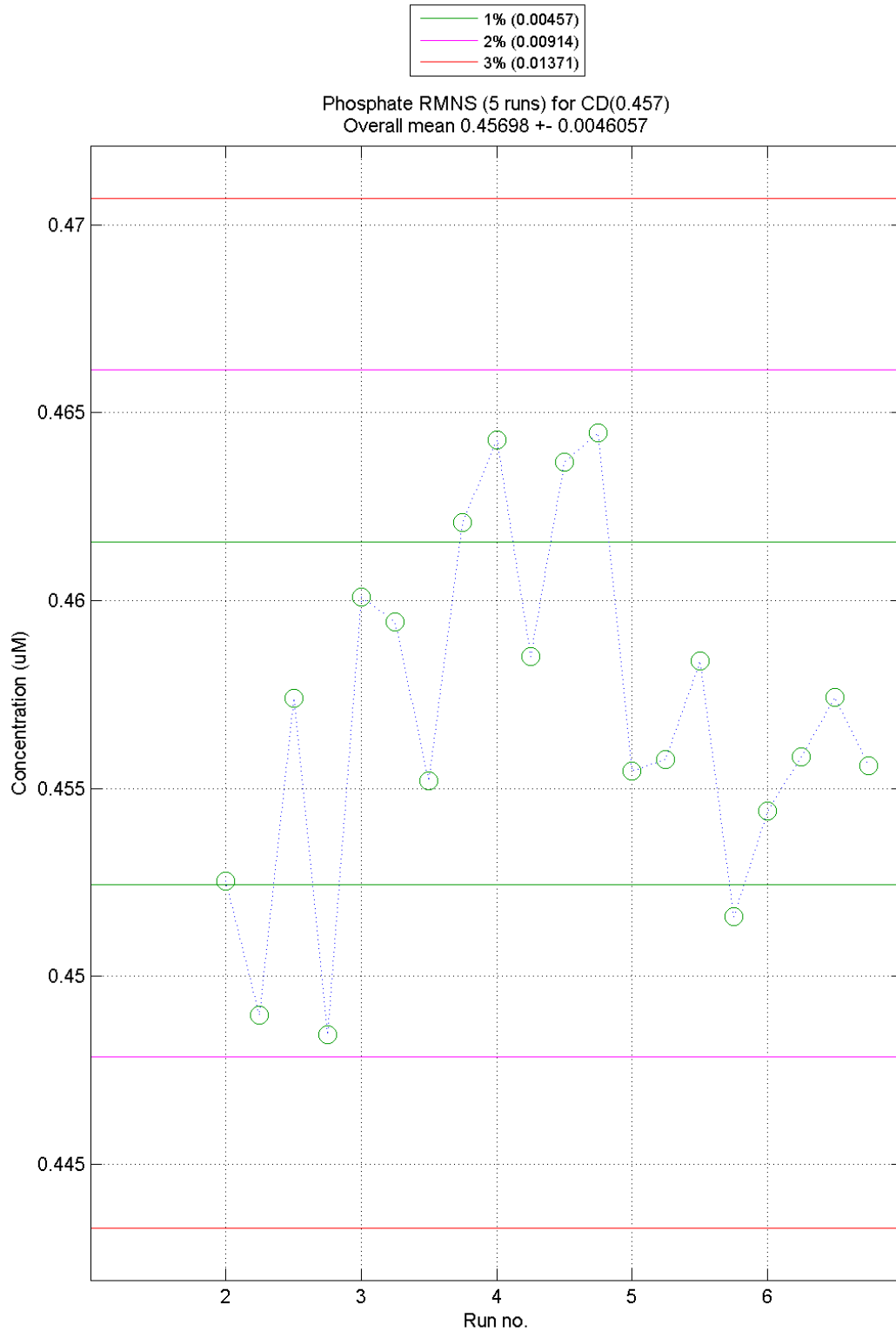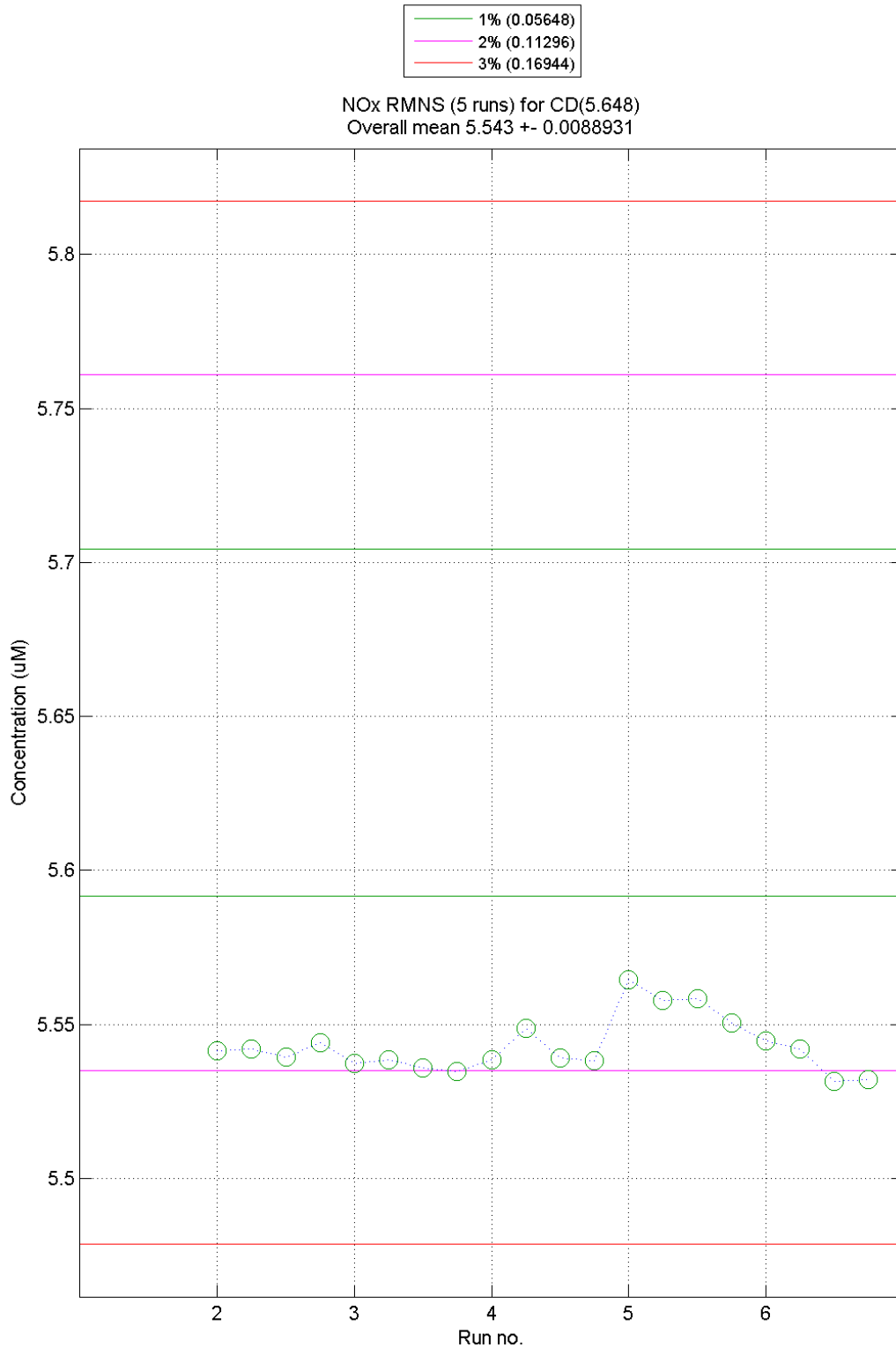
5.4.2 Phosphate RMNS Plot

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

5.4.3 Nitrate + Nitrite (NOx) RMNS Plot

NOx RMNS (5 runs) for CD(5.648)
Overall mean 5.543 +- 0.0088931

5.4.4 Nitrite RMNS Plot
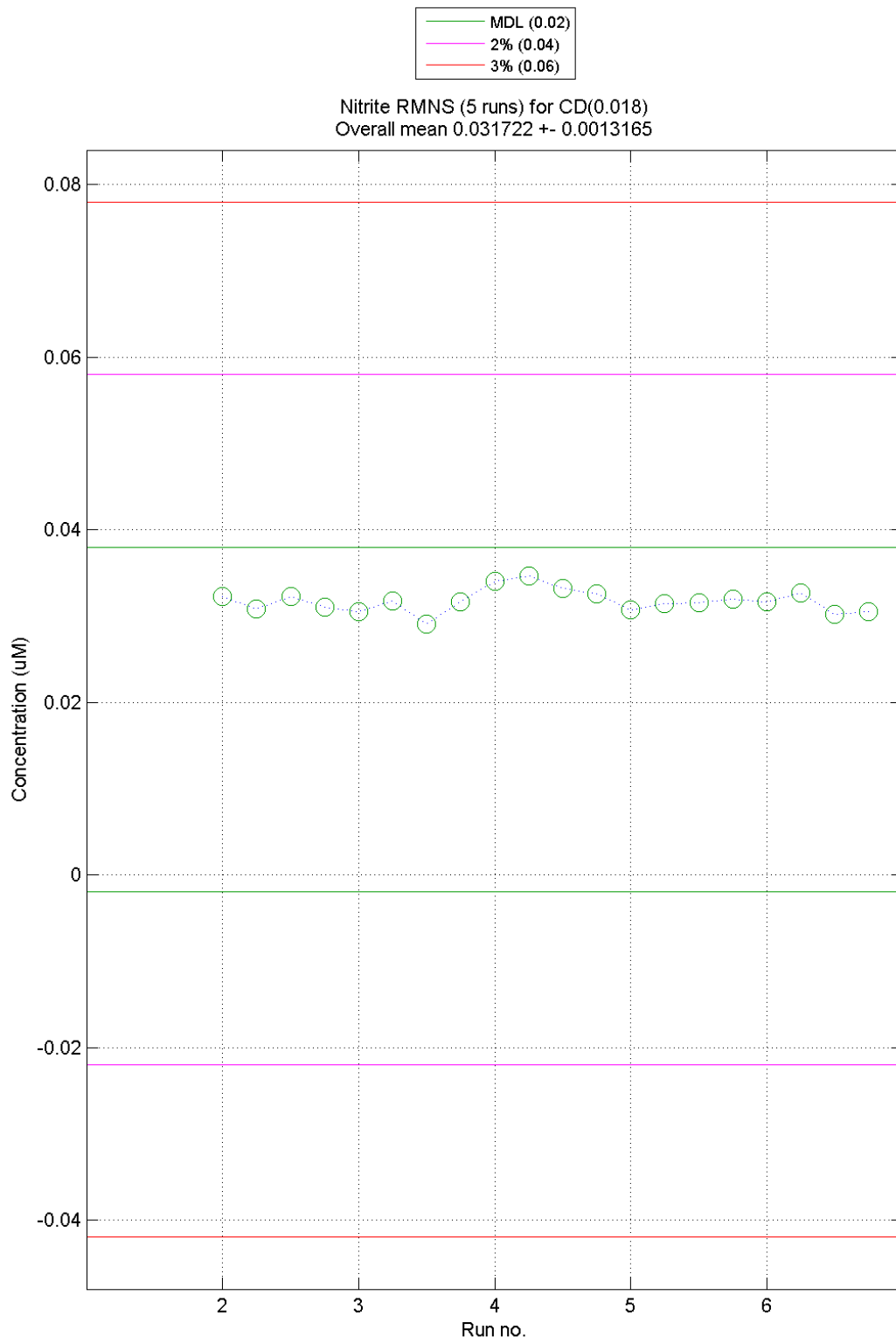
5.5   Analytical Precision

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

	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Calculated MU* @ 1 µmol l^{-1}	±0.017	±0.020	±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 RMNS.

Method detection limits (MDL) achieved during the voyage were much lower than the nominal detection limits, indicating high analytical precision at lower concentrations. RMNS and MDL precision data listed below. Results are µmol l^{-1}.

MDL	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Nominal MDL*	0.20	0.02	0.02	0.02	0.02
Min	0.008	0.004	0.002	0.003	0.003
Max	0.066	0.013	0.007	0.005	0.004
Mean	**0.038**	**0.007**	**0.005**	**0.004**	**0.003**
Median	0.043	0.006	0.006	0.003	0.003
Precision of MDL (stdev)	0.026	0.004	0.002	0.001	0.0004

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

	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia
Published RMNS CD (µmol l^{-1})	14.26	0.46	5.65	0.018	-
w/uncertainty	± 0.05	± 0.01	± 0.004	± 0.001	-
RMNS Min	14.15	0.45	5.54	0.031	1.28
RMNS Max	14.37	0.46	5.56	0.034	1.61
RMNS Mean	**14.30**	**0.46**	**5.54**	**0.032**	**1.56**
RMNS Median	14.37	0.46	5.54	0.032	1.57
RMNS Std Dev	0.09	0.005	0.009	0.001	0.003

5.6   Calibration and QC edited data

No edits made.

5.7   Investigation of Missing or Flagged Nutrient Data and Actions taken

The table below identifies all flagged data and any 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.

UWY	Run	Analysis	Flag	Reason for Flag or Action
007	Nut003	All	133	Possible contamination in sample from underway supply water

5.8   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 "in2017_t01_hyd_voyagereport.docx" for room temperature graphs, nutrient samples were placed on XY3 auto sampler at the average room temperature of 21.5°C.

6   Appendix

6.1   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.

6.2 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.

6.3   RMNS Values for each nutrient run

CTD	SiO$_4$	PO$_4$	NO$_2$	NOx	NH$_4$
	measured	measured	measured	measured	*measured*
CD reported	**14.26**	**0.457**	**0.018**	**5.648**	*NA*
2	14.15	0.452	0.032	5.542	*1.563*
3	14.27	0.459	0.031	5.537	*1.566*
4	14.37	0.463	0.034	5.541	*1.611*
5	14.37	0.455	0.032	5.558	*1.594*
6	14.37	0.456	0.031	5.538	*1.284*

7   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).

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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.

Kérouel, 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.