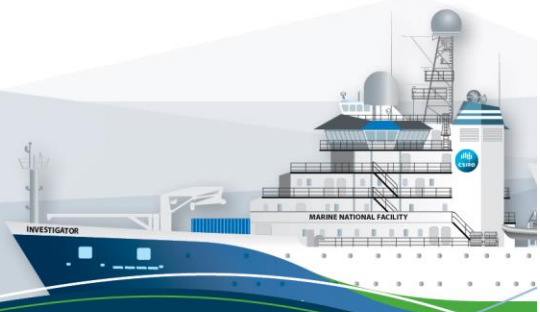
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2014_E03
Chief Scientist:	Iain Suthers
Voyage title:	Suthers Leg 1 Trial Voyage
Report compiled by:	Cassie Schwanger



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1 Itinerary

Mobilise	Date	
Hobart	10 November 2014	
Depart	**Date**	**Depart**
Hobart	11 November 2014	Hobart
Arrive	**Date**	**Arrive**
Hobart	17 November 2014	Hobart
Demobilise	**Date**	
Hobart	17 November 2014	

2 Key personnel list

Name	Role	Organisation
Iain Suthers	Chief Scientist	SIMS - UNSW
Tegan Sime	Voyage Manager	CSIRO
Carol Anstey	Hydrochemist	CSIRO
Peter Hughes	Hydrochemist	CSIRO
Mark Rayner	Hydrochemist	CSIRO
Christine Rees	Hydrochemist	CSIRO
Cassie Schwanger	Hydrochemist	CSIRO

3 Summary

3.1 Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	37
Dissolved Oxygen (automated titration)	38
Nutrients (AA3)	74

3.2 Rosette and CTD

- 34 CTD stations were completed with a 24 bottle rosette (10 L).

3.3 Nutrients

Details	
HyPro Version	3.21
Instrument	AA3

Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients anaylsed	☒ Silicate	☒ Phosphate	☒ Nitrate + Nitrite	☒ Nitrite	☒ Ammonia
Concentration range	140 µmol/L	3 µmol/L	36.4 µmol/L	1.4 µmol/L	2 µmol/L
Method Detection Limit (MDL)	0.2 µmol/L	0.02 µmol/L	0.02 µmol/L	0.02 µmol/L	0.02 µmol/L
Matrix Corrections	N	N	N	N	N
Analyst(s)	Carol Anstey, Peter Hughes, Christine Rees, & Cassie Schwanger				
Lab Temperature (±1°C)	Variable, 24 - 27°C				
Reference Material	BQC and RMNS – BW, CA and BV (Appendix 5.1)				
Sampling Container type					
Sample Storage	< 2 hrs at room temperature or < 24hrs @ 4°C				
Pre-processing of Samples	None				
Comments	This was the AA3 maiden voyage! Notes were taken for needed documentation and a standard voyage protocol was tested to determine work flow and maintenance schedules. Overall the instrument worked well.				

3.4 Salinities

Details	
HyPro Version	3.21
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)	Carol Anstey, Peter Hughes, Mark Rayner, & Cassie Schwanger
Lab Temperature (±0.5°C)	Variable, 24 - 27°C
Reference Material	Osil IAPSO - Batch P157
Sampling Container type	
Sample Storage	Samples held in Salt Room for 24 hrs before analysis within ~48 hrs
Comments	A new salinometer was set-up and worked well once the cell was wetted. A few changes were made to the cell outlet tube in order to prevent early draining of the cell. The Osil software was set-up to collect data. Files were exported into excel and uploaded into HyPro for processing. The cast number is posted edited into the data file under the Sample ID column.

3.5 Dissolved oxygen

Details	
HyPro Version	3.21
Instrument	Automated Photometric Oxygen system

Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Mark Rayner
Lab Temperature (±1°C)	Variable, 24 - 27°C
Sample Container type	
Sample Storage	Samples analysed within ~48 hrs
Comments	There were some issues with the configuration of the instrument software which are documented and fixed. It was also noted that the titration tip must be at the marked depth for proper mixing in the flask during titration.

4 Detailed processing

Delays in the data output for IN2014_E03 were due to assessing and updating HyPro to process AA3 profiles. A modification to accept salinity files exported from the Osil software, a new capability, was added to HyPro and tested with this voyage data. The nutrient .CHD and .SLK files were generated from the Seal AACE 6.10 software. In the future these files will automatically be duplicated into the voyage folder for post processing. The .CSV were created by HyPro.

4.1 Procedure

The procedure for data processing is outline in Figure 1.

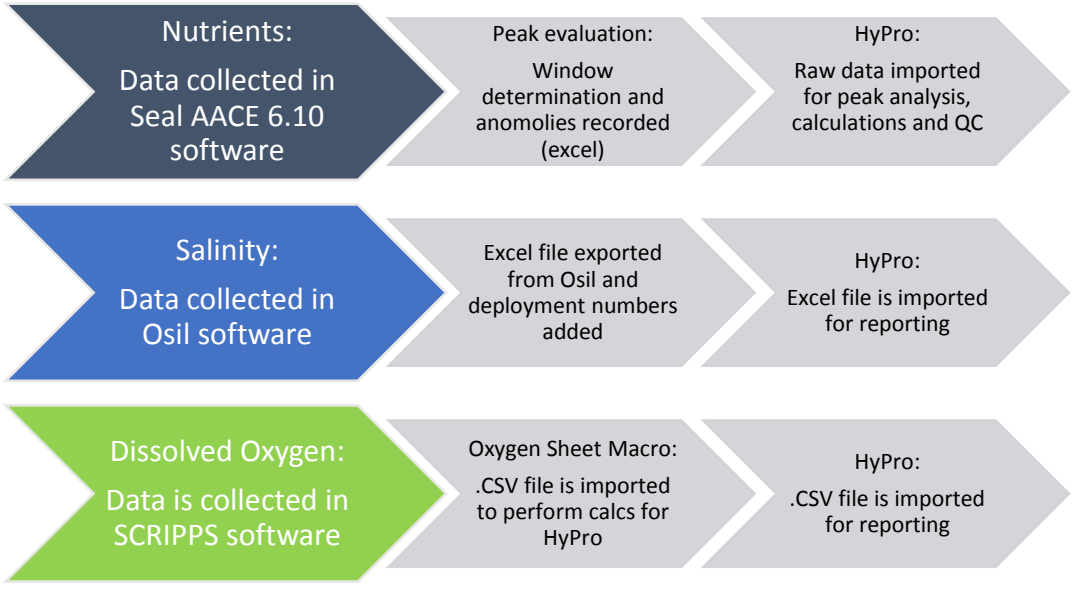


Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

4.2 Nutrients

- All runs have a corresponding AA3_Processing_Worksheet file to assist in characterizing data.

- The default peak window is a general estimate of peak timing and does not directly correlate to changes in data.
- Files for this voyage - nut003, nut 007-009, and nut011-015, all other files were test files.

Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Data Reported as	µM l^{-1}	µM l^{-1}	µM l^{-1}	NA	µM l^{-1}
Calibration Curve degree	>0.9995	>0.9995	>0.9995	NA	>0.9995
Forced through zero?	N	N	N	NA	N
# of points in Calibration	5	5	5	NA	5
Matrix Correction	N	N	N	NA	N
Blank Correction	N	N	N	NA	N
Carryover Correction	Y	Y	Y	NA	Y
Baseline Correction	Y	Y	Y	NA	Y
Drift Correction	Y	Y	Y	NA	Y
Data Adj for RMNS	N	N	N	NA	N
Medium of Standards	LNSW				
Medium of Blank	18.2 Ω MQ				
Proportion of samples in duplicate?	>10%				

Table 1: Nutrient data processing details

File	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia	Run Type
IN2014_E03nut003	☒	☒	☒	☒	☐	Set-up Char.
Peak window	50-90	50-90	90-100	60-90		
RMNS	<2%	BW = 1%	<2%	NA	NA	
Comments			Peak slipped in period		Blockage in flowcell – no data	
IN2014_E03nut007	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	50-105	50-100	60-110	55-100	60-105	
RMNS	<2%	BW = 1%	1%	NA	<2%	
Comments				High peaks had dips on plateau	MilliQ baseline was contaminated	
IN2014_E03nut008	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	50-90	55-95	80-105	60-95	60-95	
RMNS	NA	<2%	BW = 1%	NA	NA	
Comments						
IN2014_E03nut009	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	50-105	50-100	70-105	55-100	60-105	
RMNS	<2%	1%	1-2%	NA	NA	
Comments						
IN2014_E03nut011	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	50-100	50-105	60-105	50-95	50-105	
RMNS	NA	<2%	1%	NA	1%	
Comments	Top std was low 35 µmol/L; noisy peaks;			High peaks had dips on plateau		

File	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia	Run Type
	BQC and BW over scale					
IN2014_E03nut012	☒	☒	☒	☒	☒	CTD
Peak window	50-90	45-85	70-95	50-105	50-105	
RMNS	NA	1-2%	1-2%	NA	NA	
Comments		High peaks had dips on plateau				
IN2014_E03nut013	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	55-95	55-95	75-100	55-90	60-100	
RMNS	2%	1-2%	1%	NA	NA	
Comments				High peaks had dips on plateau		
IN2014_E03nut014	☒	☒	☒	☒	☒	CTD – all samples ran in duplicate
Peak window	85-120	60-110	80-100	40-80	50-85	
RMNS	NA	NA	NA	NA	NA	
Comments					3 peaks were bad due to rise on plateau	
IN2014_E03nut015	☒	☒	☒	☒	☐	CTD
Peak window	50-105	50-100	60-110	50-100		
RMNS	NA	NA	NA	NA	NA	
Comments	Gain was not re-set so top std was off scale; some spikes on peaks noted		Calibrant concentrations in AACE were wrong	Calibrant concentrations in AACE were wrong	Blockage in flowcell – no data	

4.3 Salinities

- Files for this voyage - sal002 and sal004; all other files are test runs
- First voyage using Osil software for data collection rather than manually recording results.
- Lab temperature unstable. Bath set at 27°C due to unstable lab temperature.

4.4 Dissolved oxygen

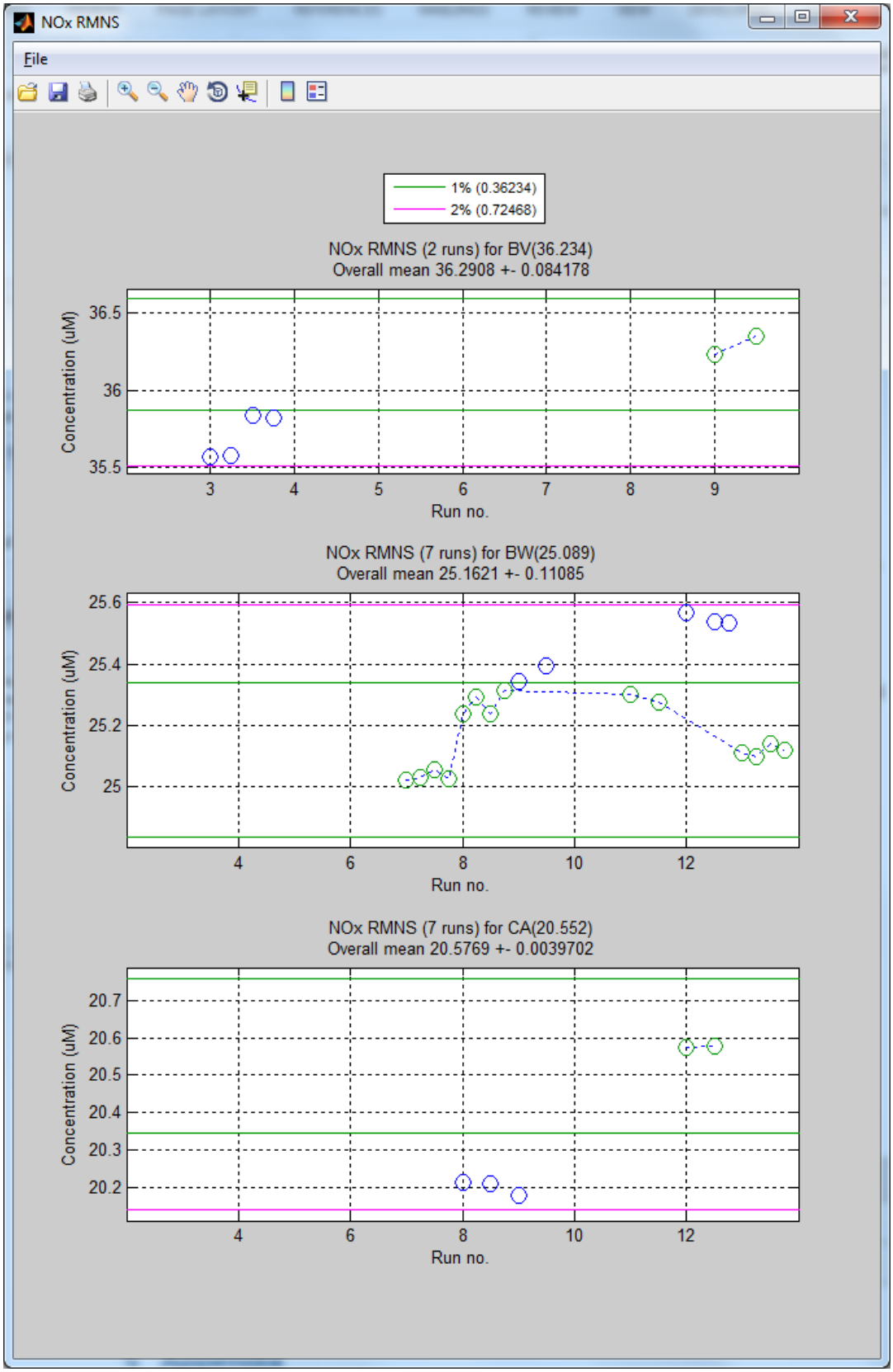
- The cast IDs were not properly recorded in the oxy file and required post process updating to go through HyPro.
- Files for this voyage – oxy003 and oxy008 - 011

4.5 Plots

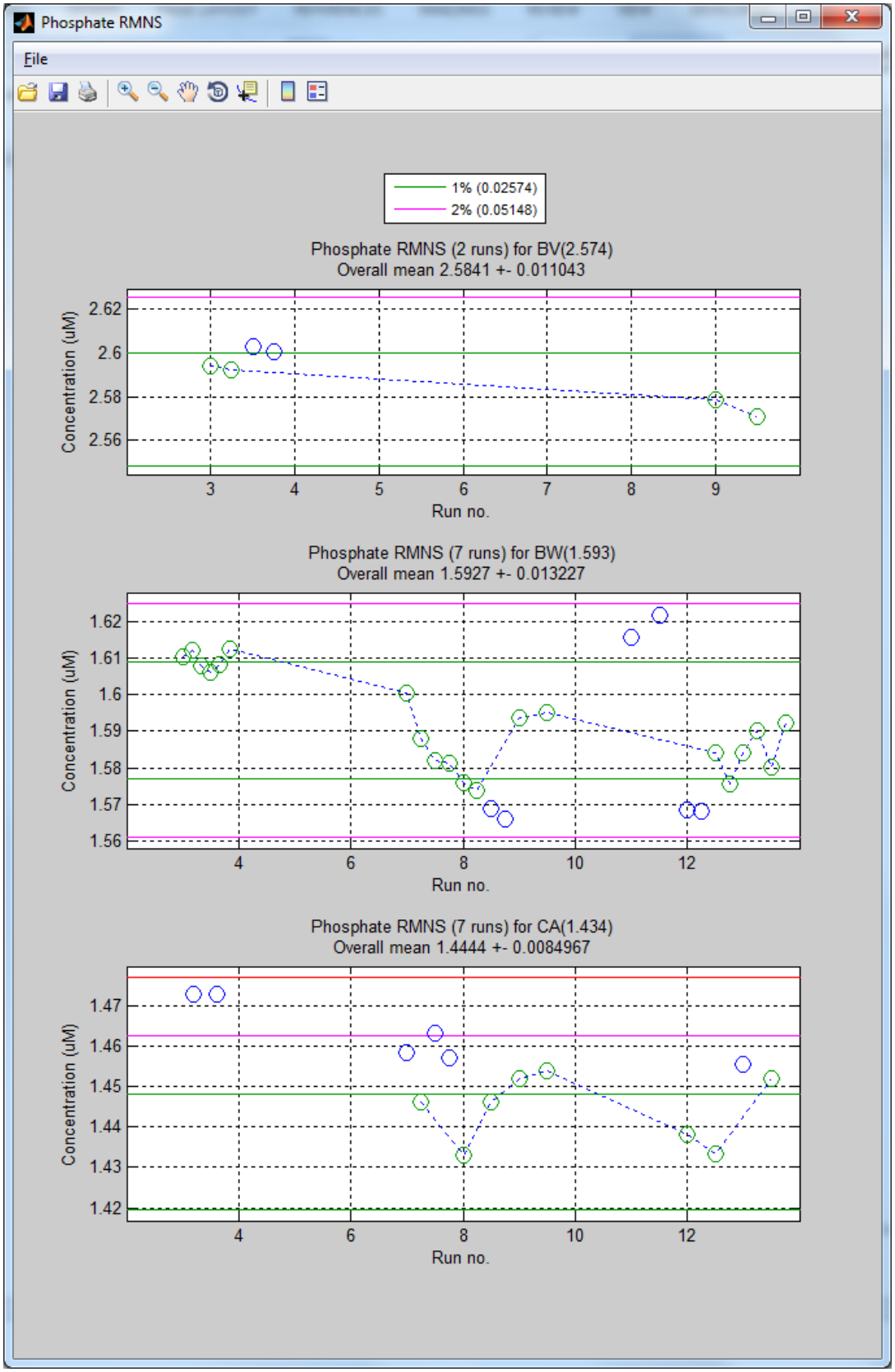
The following plots can be found in corresponding plots folder in the voyage – hypro folder: Hydro vs Salt, DO waterfall (no DO Hydro results this voyage), and Redfield Ratio.

4.6 HyPro checks

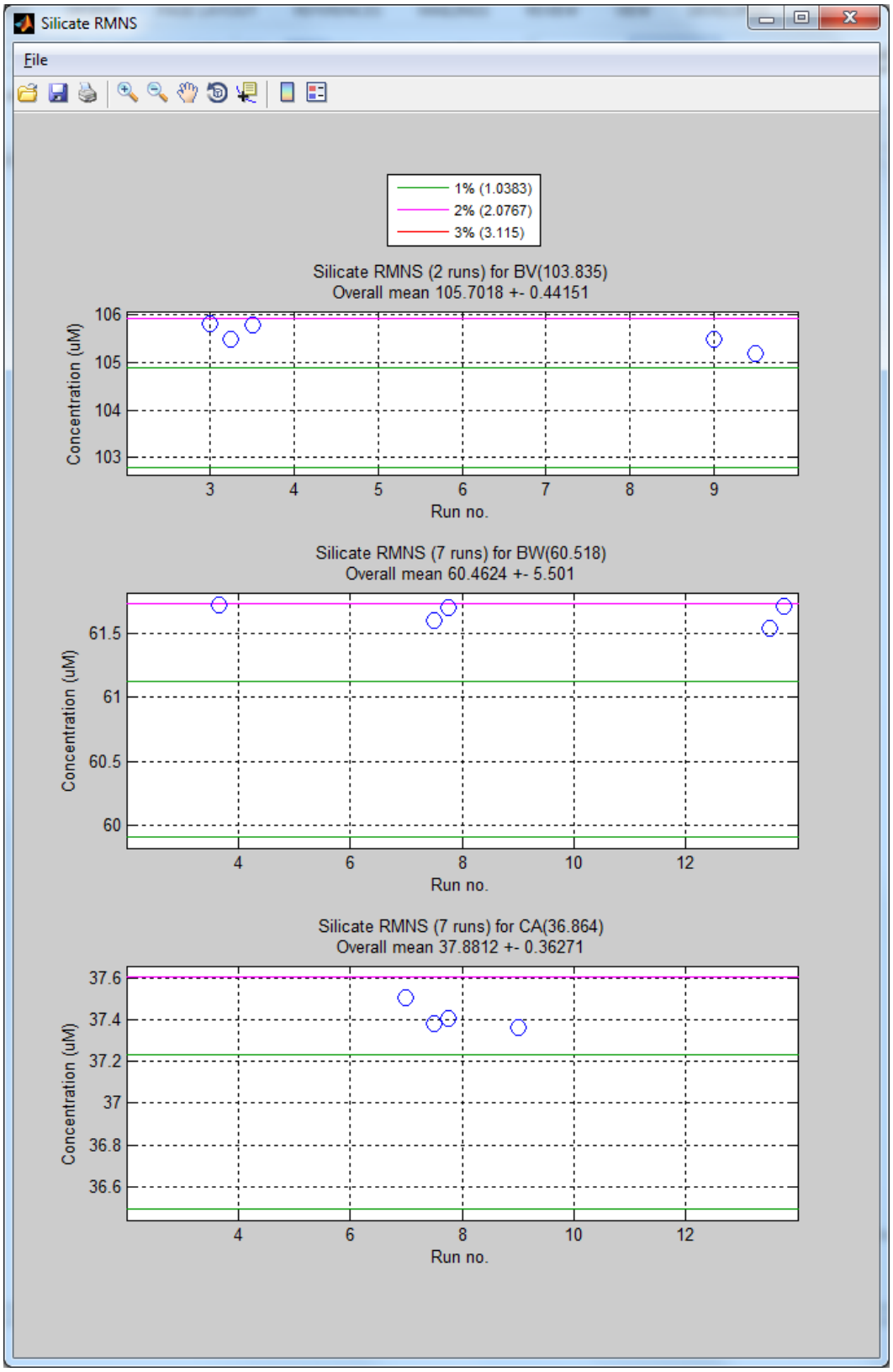
4.6.1 NOx RMNS plot



4.6.2 Phosphate RMNS plot


Phosphate RMNS
File
1% (0.02574)
2% (0.05148)
Phosphate RMNS (2 runs) for BV(2.574)
Overall mean 2.5841 +- 0.011043
Concentration (uM)
Run no.
Phosphate RMNS (7 runs) for BW(1.593)
Overall mean 1.5927 +- 0.013227
Concentration (uM)
Run no.
Phosphate RMNS (7 runs) for CA(1.434)
Overall mean 1.4444 +- 0.0084967
Concentration (uM)
Run no.

4.6.3 Silicate RMNS Plot



4.7 Investigation of missing data and actions required

Deployment	RP	Analysis	Reason for removal	Action taken
8	4	Salinity	Error in sampling	Data point marked BAD in HyPro
8	18	Nuts	No sample taken	No data to report
7, 8, 11, 14, 15	All	Nuts	Duplicate data	Data is removed from net CSV file

5 Appendix

5.1 Nutrient Reference Materials

RMNS	NO_X	NO_2	PO_4	SiO_4
BT	19.069	0.482	1.327	43.03
BF	41.388	0.02	3.114	157.932
CA	20.552	0.072	1.434	36.864
BU	4.052	0.07	0.381	21.517
BV	36.234	0.055	2.574	103.835
BW	25.089	0.052	1.593	60.518
BY	0.022	0.008	0.04	1.833

5.2 Salinity Reference Material

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

5.3 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
O2	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.
SiO2	Approximately 1-3% accuracy†, 2 and 0.2% precision, full-scale.
PO4	Approximately 1-2% accuracy†, 2 and 0.4% precision, full scale.
NO3	Approximately 1% accuracy†, 2 and 0.2% precision, full scale.