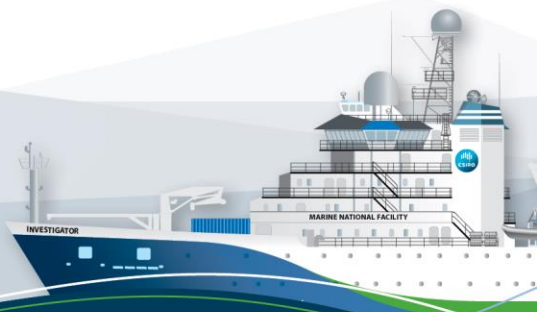
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2015_v03
Chief Scientist:	Iain Suthers
Voyage title:	Submesoscale processes – billows and eddies – along the productive shelf by the East Australian Current
Report compiled by:	Mark Rayner, Christine Rees and Cassie Schwanger



Contents

1 Itinerary

Depart	Date	Time
Brisbane	3 June 2015	0800
Arrive	**Date**	**Time**
Sydney	18 June 2015	0800

2 Key personnel list

Name	Role	Organisation
Iain Suthers	Chief Scientist	CSIRO
Max McGuire	Voyage Manager	CSIRO
Mark Rayner	Hydrochemist	CSIRO
Christine Rees	Hydrochemist	CSIRO
Cassie Schwanger	Hydrochemist	CSIRO

3 Summary

All data finalized data can be obtained from the CSIRO data centre…

3.1 Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	328
Dissolved Oxygen (automated titration)	342 8 UWY
Nutrients (AA3)	341 CTD 198 UWY

3.2 Rosette and CTD

- 48 CTD stations were completed with a 24 bottle rosette (10 L).
- See in2015_v03_HydrochemistryReport.pdf for more details on sample collection.
- Samplers – blue and green teams as specified in voyage plan.

3.3 Procedure

The procedure for data processing is outline in Figure 1.

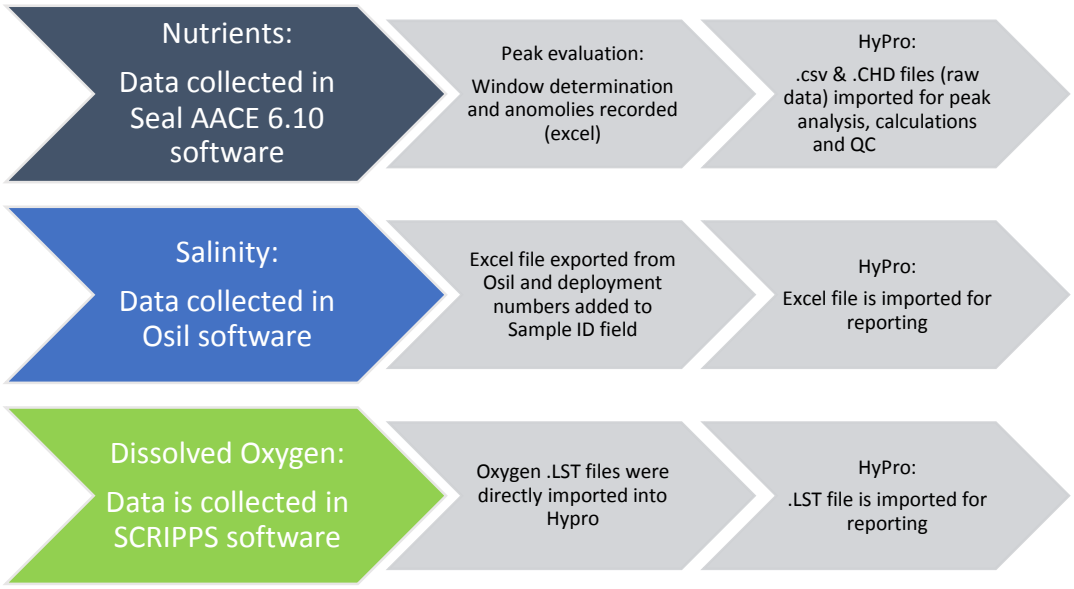


Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

3.4 Nutrients

Details					
HyPro Version	3.27 and 4.0				
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients anaylsed	☒ Silicate	☒ Phosphate	☒ Nitrate + Nitrite	☒ Nitrite	☒ Ammonia
Concentration range	112 µmol l^{-1}	3 µmol l^{-1}	36.4 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)	Christine Rees & Cassie Schwanger				
Lab Temperature (±1°C)	Variable, 21.5 -25.3°C				
Reference Material	RMNS – BW & CA				
Sampling Container type	10 mL polypropylene				
Sample Storage	< 2 hrs at room temperature or < 24hrs @ 4°C				
Pre-processing of Samples	None				
Comments	A number of non-CTD related samples underway and experimental samples were analysed and processed with the prefix “uwy” and the date (ddmm collected & analysed) added into the sample id. A number of analysis runs for Ammonia had high baselines which indicated that the matrix wash had been contaminated with Ammonia. This caused the Cal 0 to be negative (nut 012 & 015) and occasionally the MDL’s and samples with very low NH4 concentrations. The samples that were negative were below the nominal detection limit. The files affected were; nut 003, 005, 012, 015, 018, 020, 024, 025 & 026.				

All runs have a corresponding AA3_Run_Analysis_sheet and AA3_Processing_Worksheet file to assist in characterizing data and note questionable peaks. These are found within the voyage documentation. Also refer to section 4.8 Nutrient Processing.

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	quadratic	quadratic	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 (MAI 25-2-2015)				
Medium of Blank	18.2 Ω MQ				
Proportion of samples in duplicate?	>10%				

* The default peak window is a general estimate of peak timing and does not directly correlate to changes in data.

3.5 Salinities

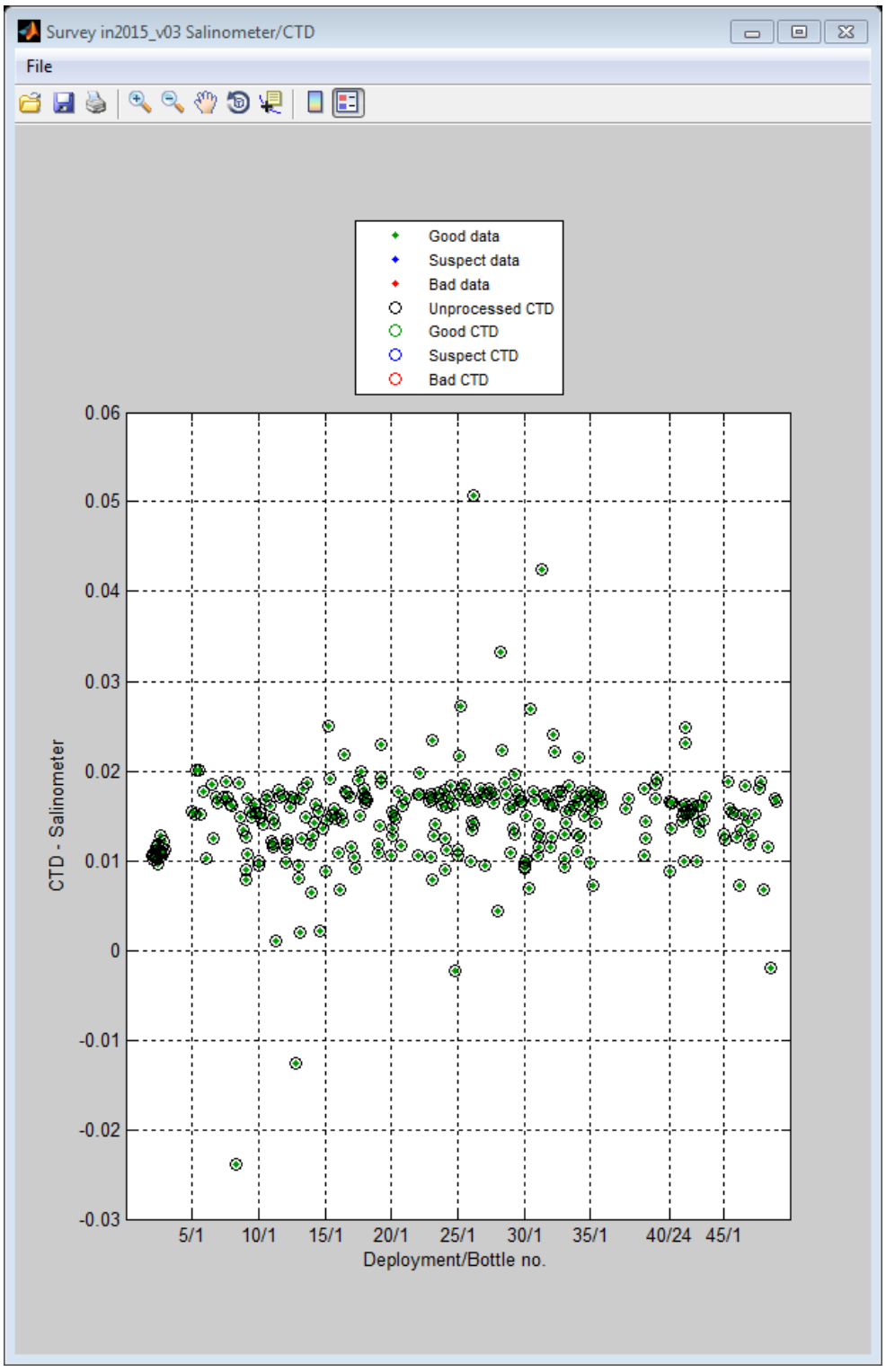
Details	
HyPro Version	3.27 and 4.0
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71613
Software	Osil
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 salinity units
Analyst(s)	Mark Rayner
Lab Temperature (±0.5°C)	21.5-25.0°C
Bath Temperature	24°C
Reference Material	Osil IAPSO - Batch P157
Sampling Container type	Square 250mL borosilicate with GL32 lids; torque closed to 7.4Nm AND Round 250 mL amber borosilicate w/Teflon cone insert in lids
Sample Storage	Samples held in Salt Room for 24 hrs before analysis within ~48 hrs
Comments	There were several problems with sample collection 1) over filling the square bottles and 2) under filling the round bottles. Samplers were re-trained.

3.6 Dissolved oxygen

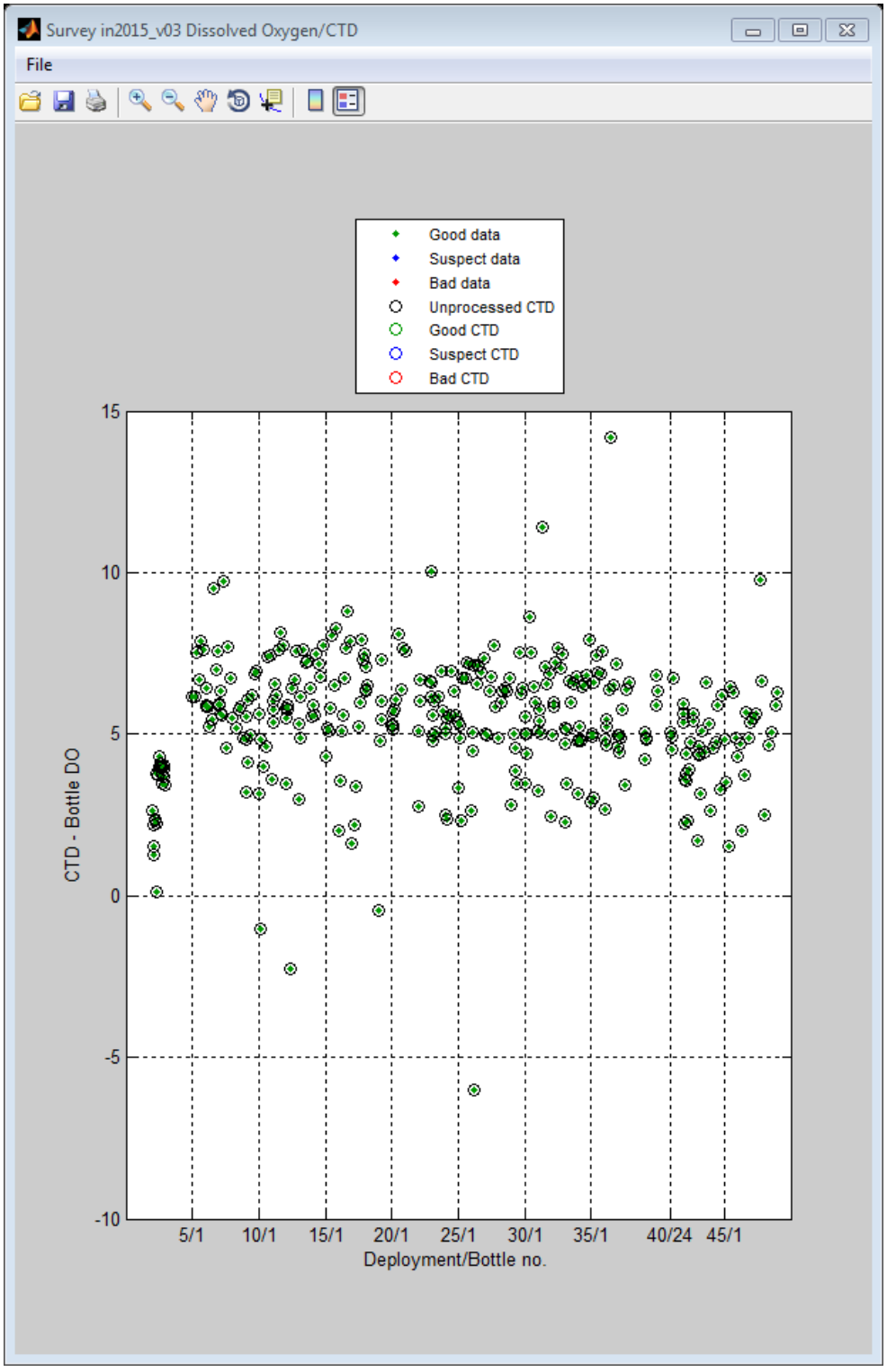
Details	
HyPro Version	3.27 and 4.0
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Mark Rayner
Lab Temperature (±1°C)	Variable, 21.5-25.3°C
Sample Container type	Pre-numbered glass 140 mL glass vial w/stopper
Sample Storage	Samples analysed within ~48 hrs
Comments	CTD #21 was combined with CTD#22 for Hypro due to error in loading file. Standardization for voyage ranged 0.202669 to 0.202998. Blank average = 0.0004. There several configuration errors which required the re-start procedure (DO_Ops_Guide_V01.pdf)

4 Quality Control

4.1 CTD vs Hydro Salinities Error Plot



4.2 CTD vs Hydro DO Error Plot



4.3 Waterfall Plots

All waterfall plots consist of good data, without any outliers. This indicates the Niskin bottles did not leak.

4.4 Redfield Ratio Plot (14.0)

Plots consists of phosphate versus NOx all good data, without any outliers, best fit ratio = 14.24. Plot can be viewed;
http://www.cmar.csiro.au/datacentre/process/data_files/Investigator_NF/in2015_v03/doc/RedfieldRatio.pdf

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

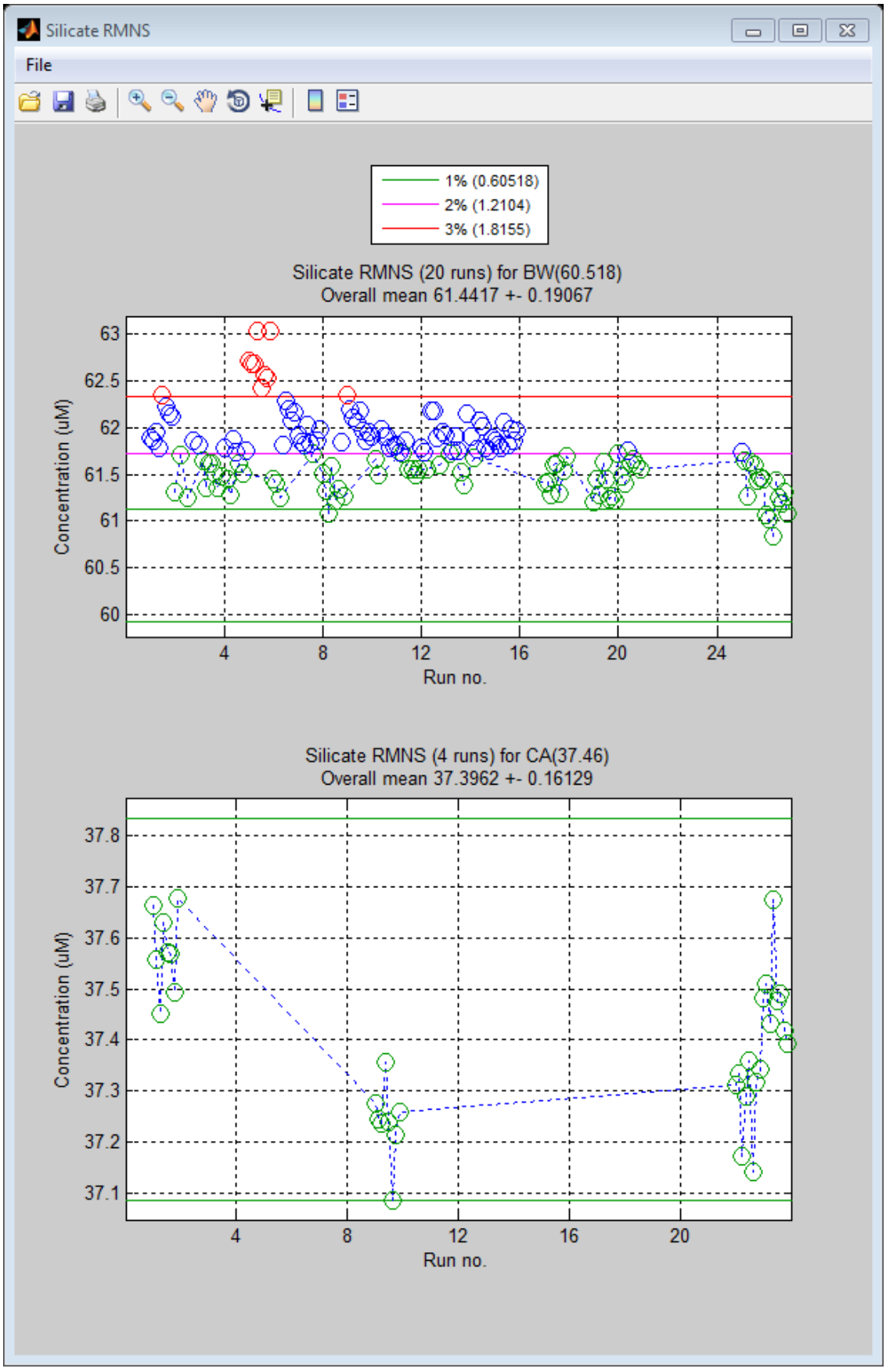
The certified reference materials (crm) for silicate, phosphate, nitrate and nitrite in seawater produced by KANSO – Japan was used in each nutrient analysis to ensure the accuracy of results.

The Lot BW (produced 03/04/2012) was run in every analysis and the Lot CA (produced 22/02/2013) was ran occasionally. RMNS results were converted from µ mol/kg to µ mol l^{-1} at 21°C.

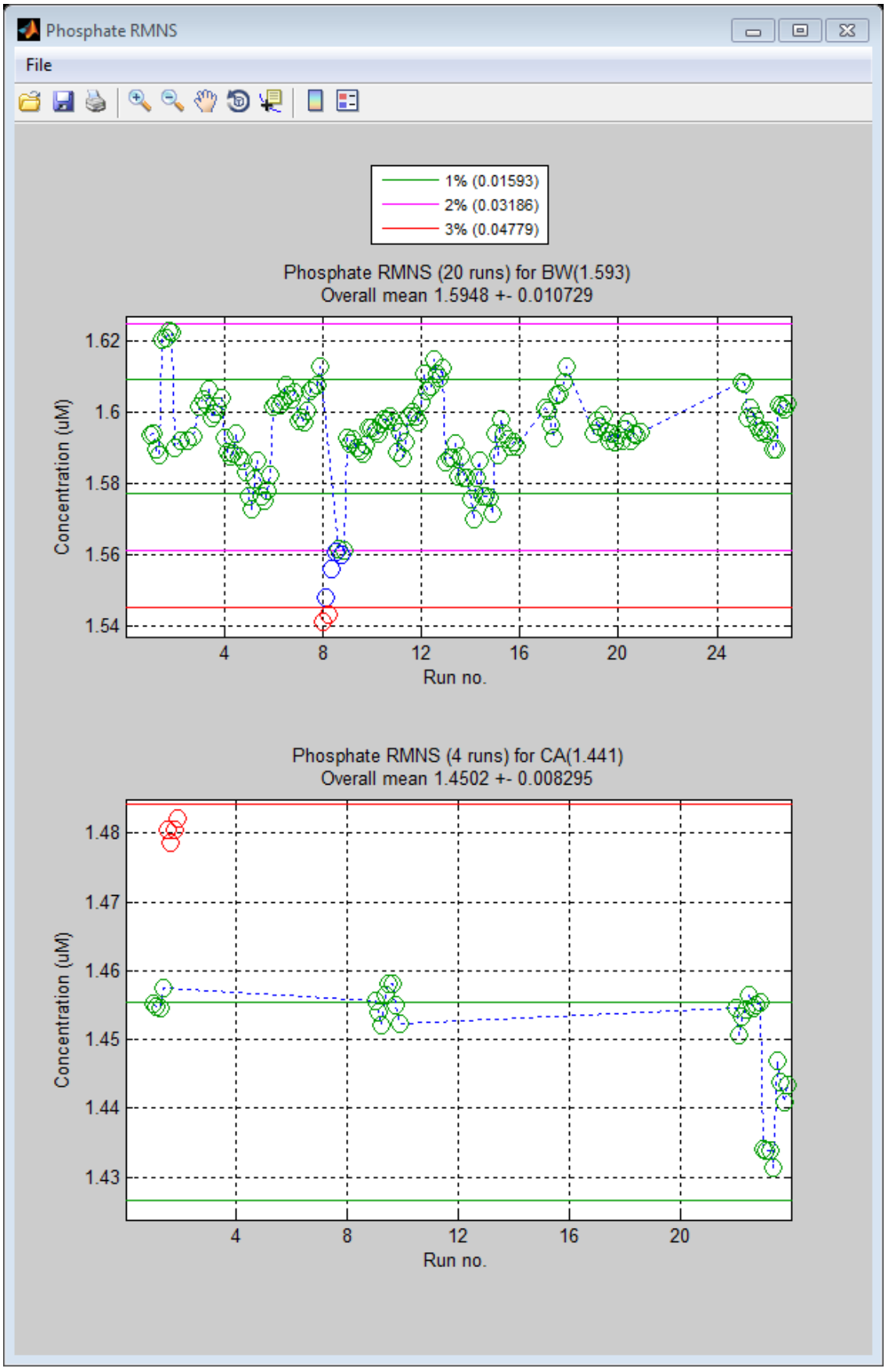
4.5.1 RMNS BW & CA µ mol l^{-1} at 21°C.

RMNS	NO_X	NO_2	PO_4	SiO_4
CA	20.19	0.064	1.441	37.46
BW	25.089	0.052	1.593	60.518

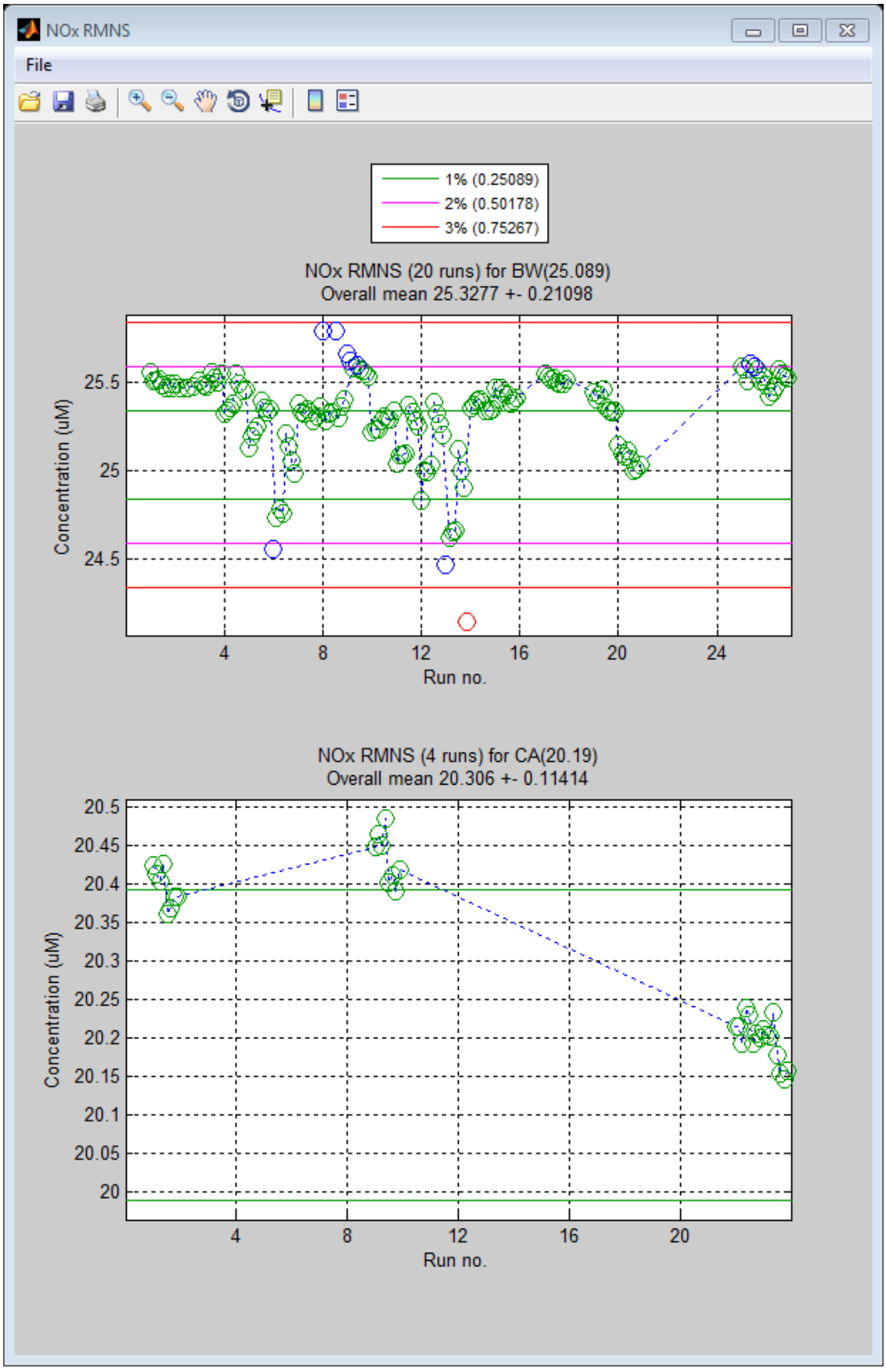
4.5.2 Silicate RMNS Plot



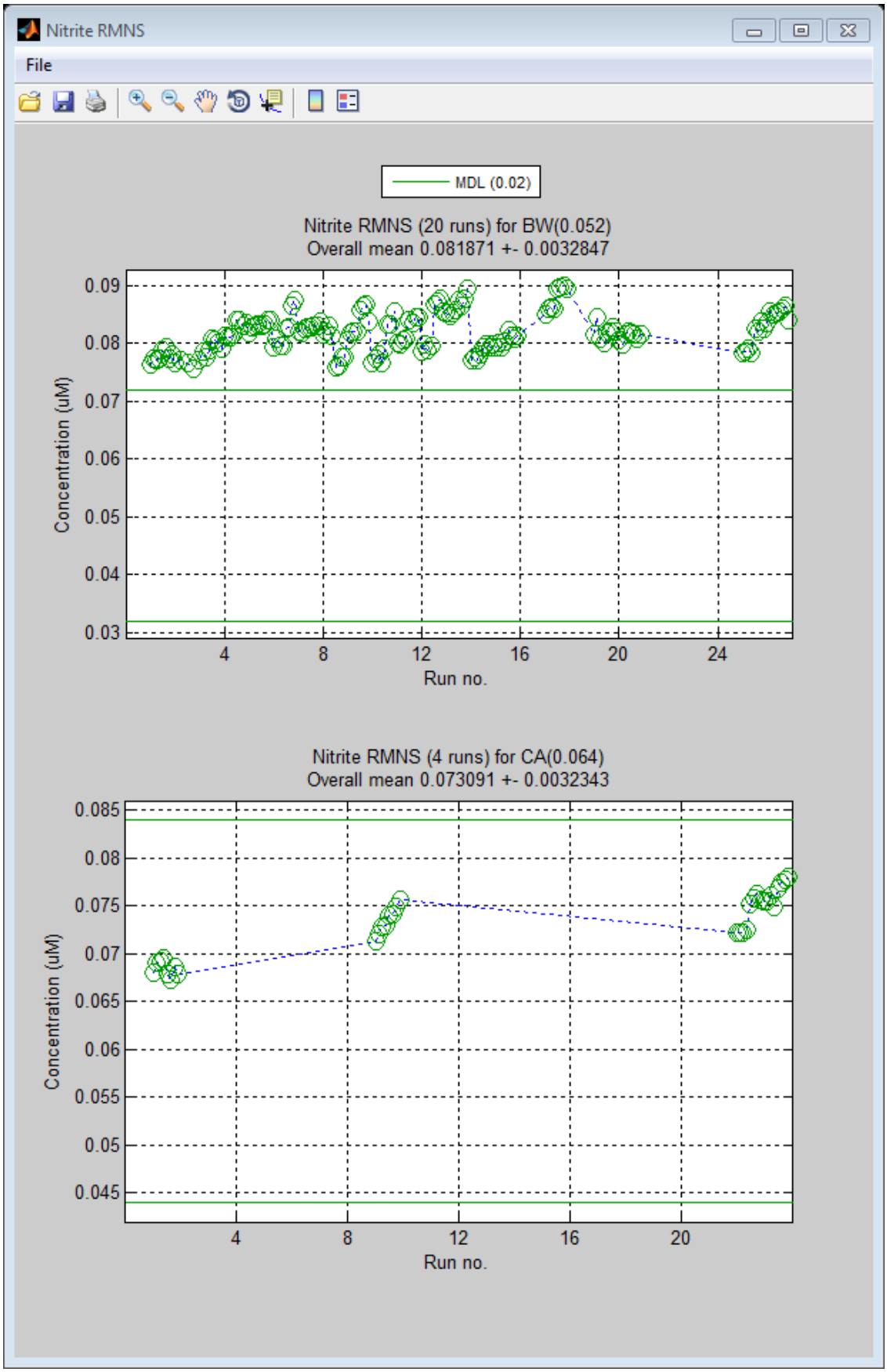
4.5.3 Phosphate RMNS Plot



4.5.4 Nitrate + Nitrite (NOx) RMNS Plot

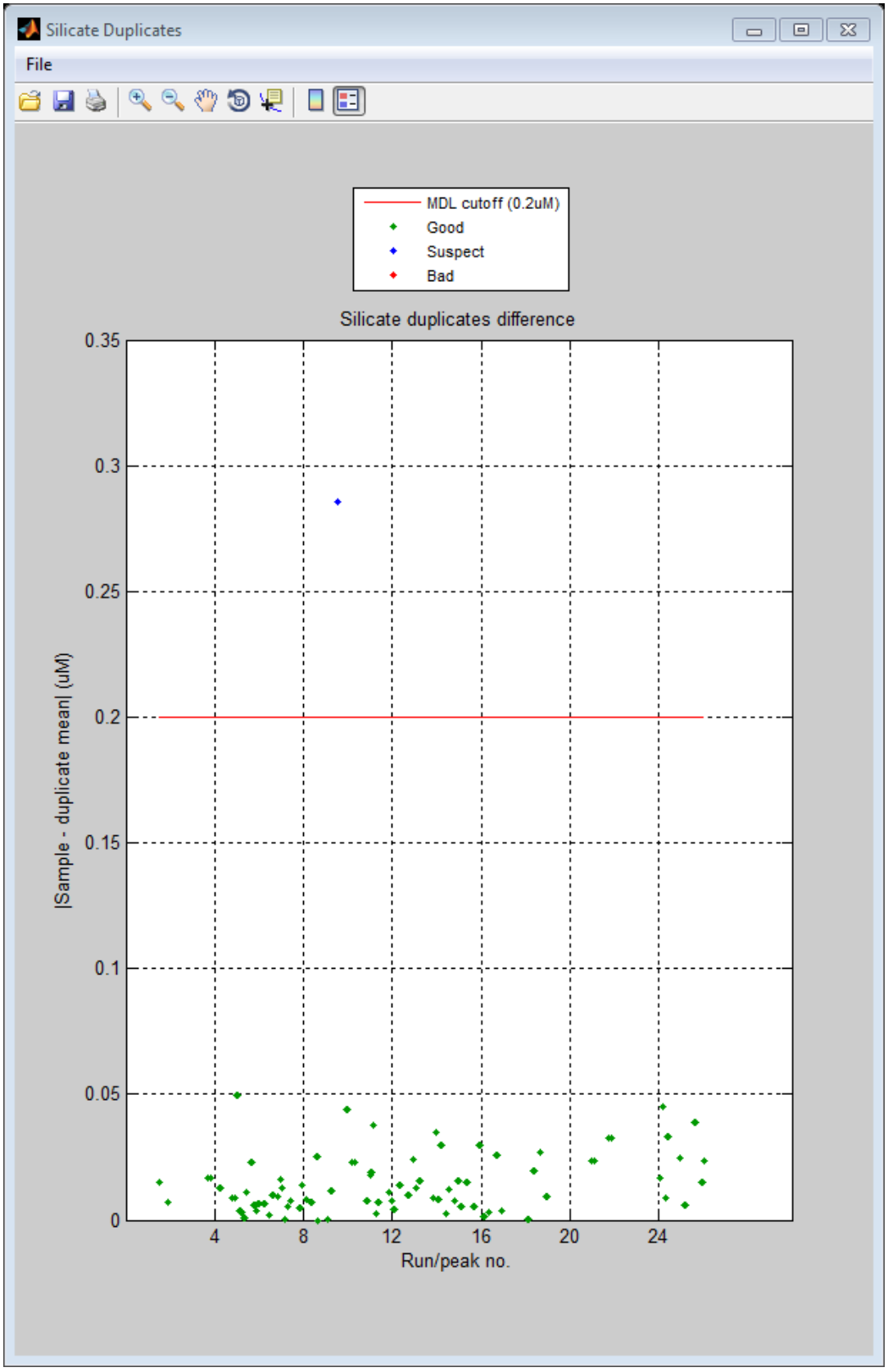


4.5.5 Nitrite RMNS Plot

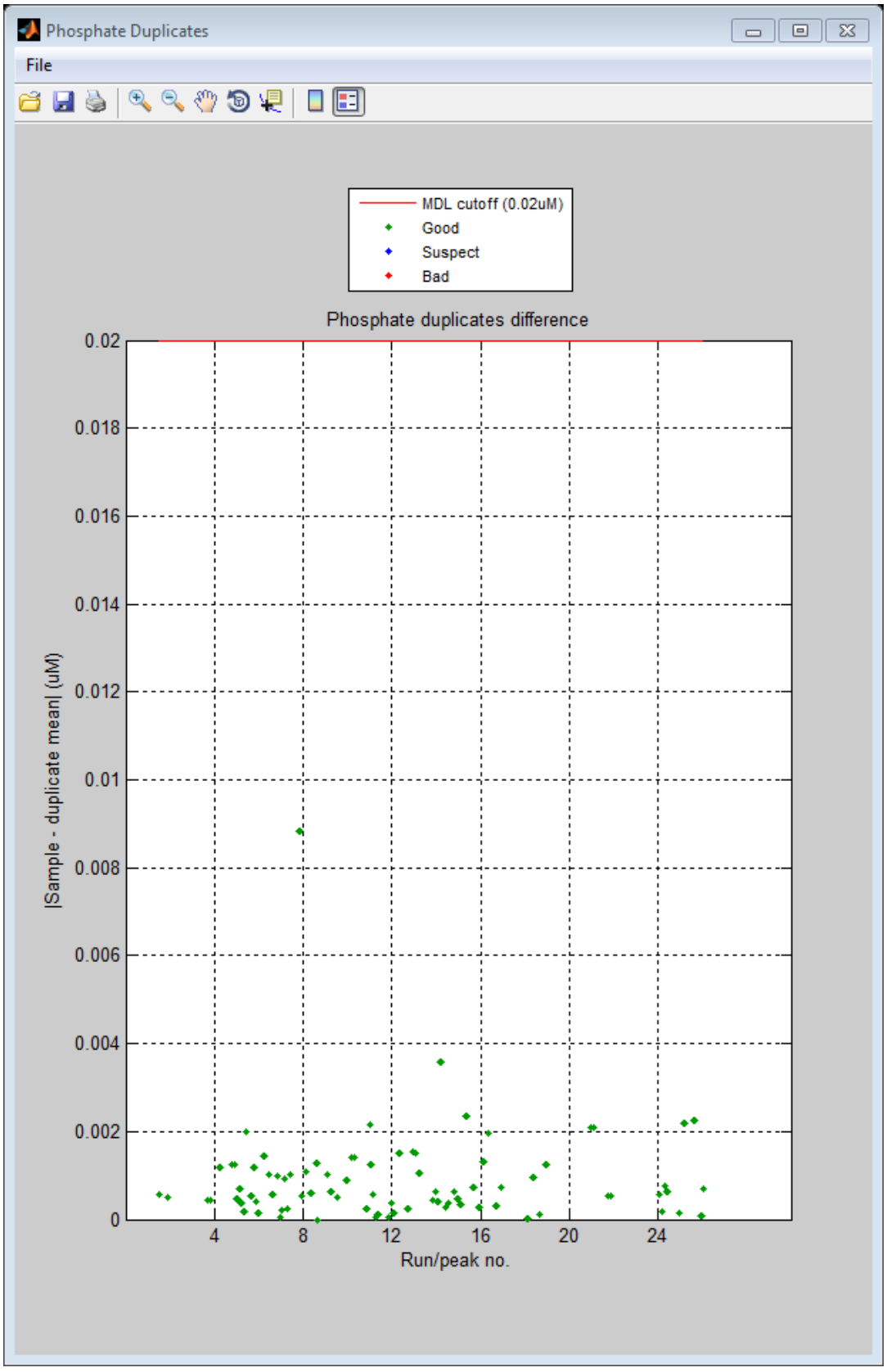


4.6 Duplicate Plots – Sampling Precision

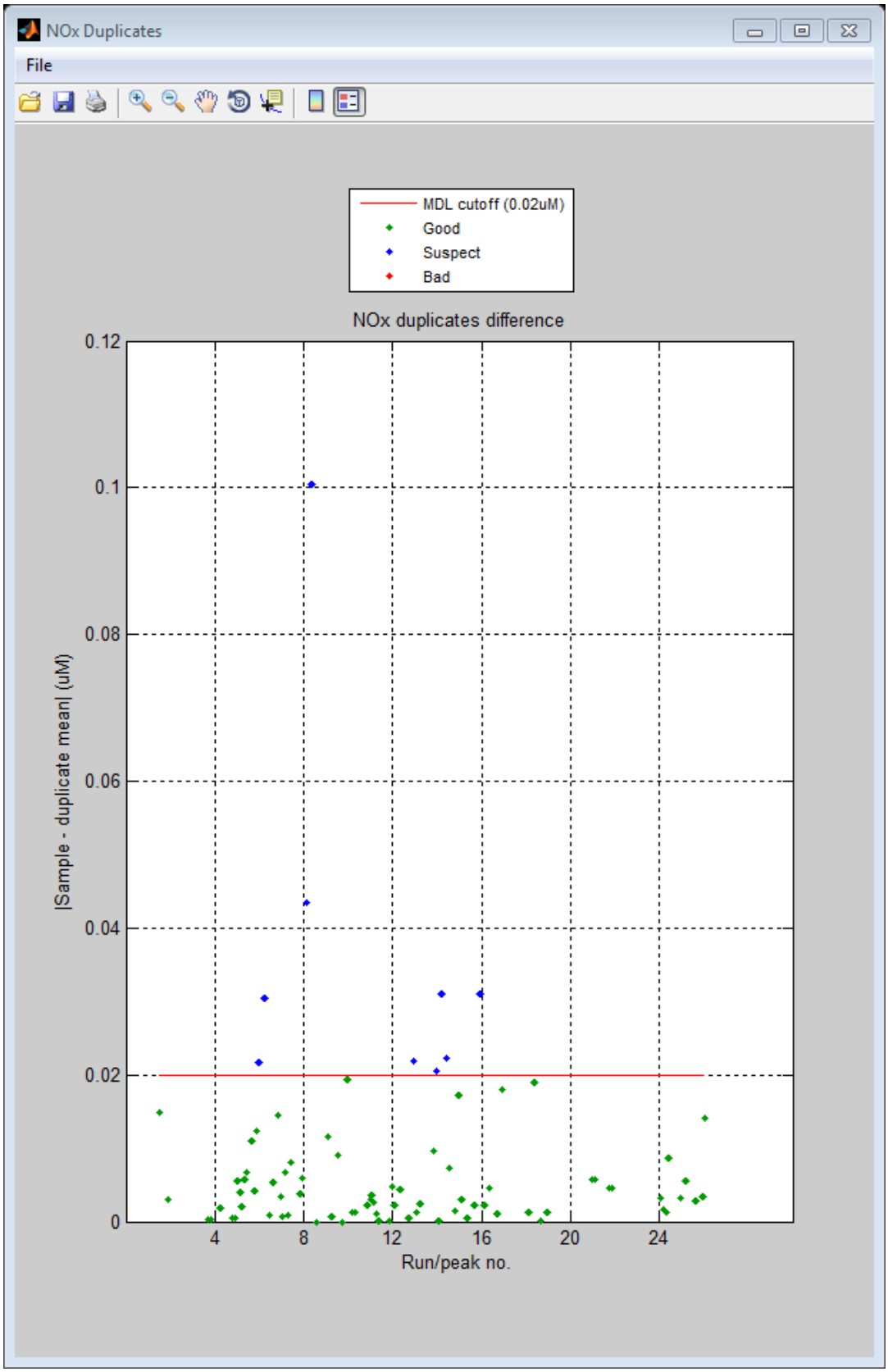
4.6.1 Silicate Plot



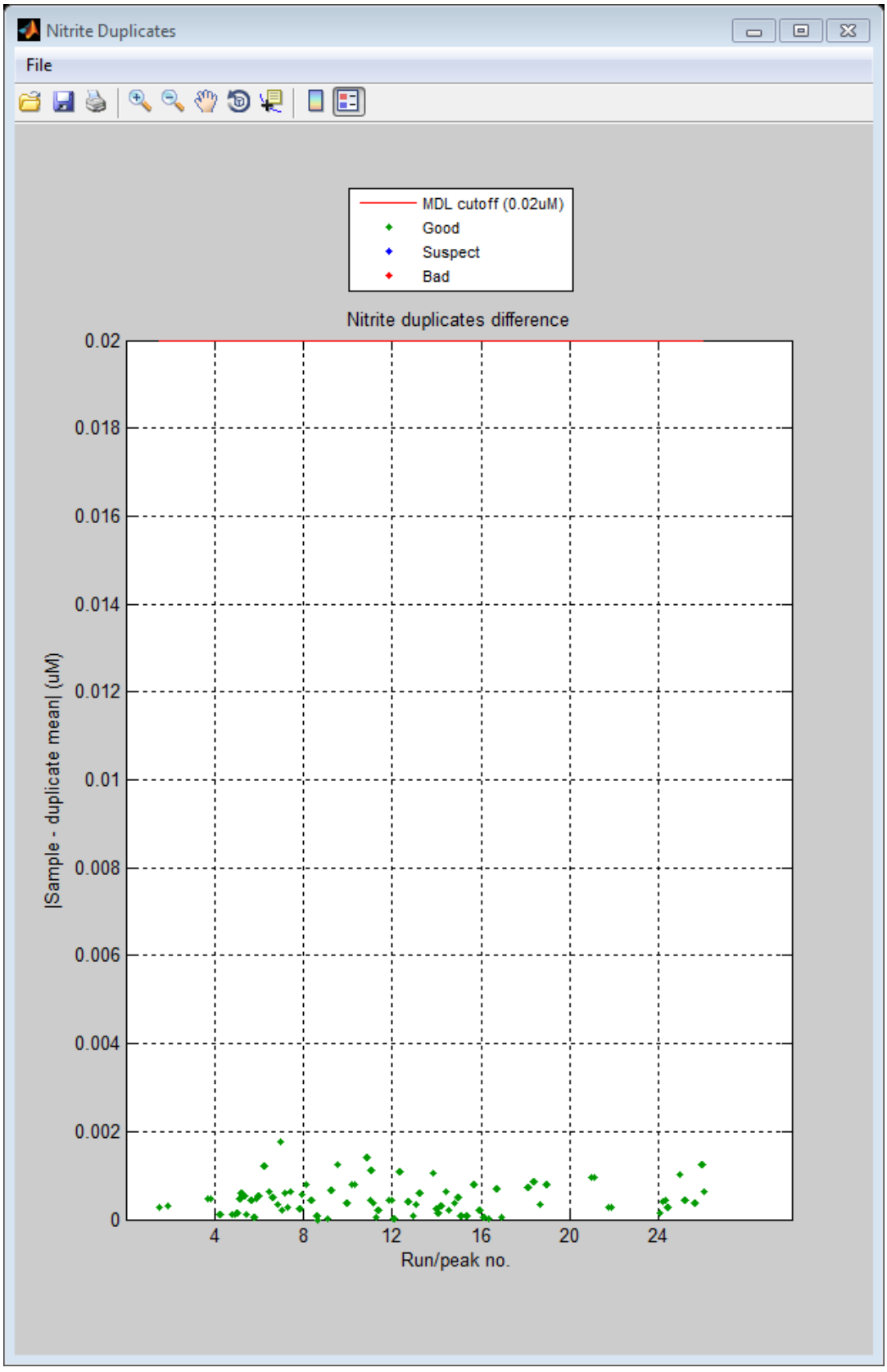
4.6.2 Phosphate Plot



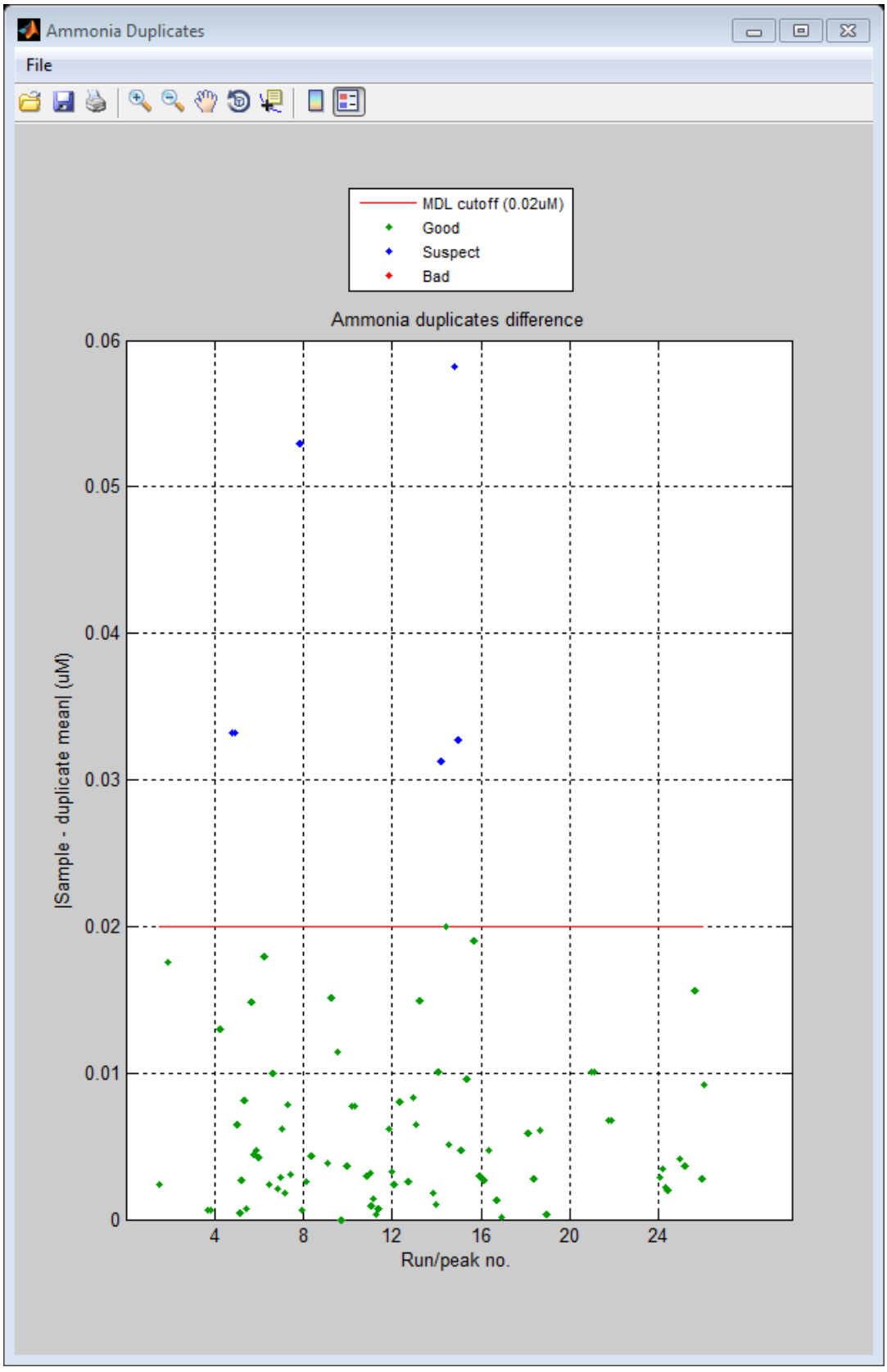
4.6.3 Nitrate + Nitrite (NOx) Plot



4.6.4 Nitrite Plot



4.6.5 Ammonia Plot



4.7 Precision

Method detection limits (MDL) achieved during the voyage were much lower than the nominal detection limits, indicating high precision at lower concentrations. At full scale precision was more variable however within GO-Ship specifications except for silicate which was slightly above. Results are µmol l^{-1}.

MDL	**Silicate**	**Phosphate**	**Nitrate + Nitrite (NOx)**	**Nitrite**	**Ammonia**
Nominal MDL	0.2	0.02	0.02	0.02	0.02
Min	0.032	0.002	0.003	0.000	0.002
Max	0.155	0.014	0.025	0.007	0.102
Median	0.09	0.005	0.007	0.002	0.016
Precision of MDL (stdev)					
Min	0.011	0.001	0.001	0.000	0.001
Max	0.052	0.005	0.008	0.003	0.034
Median	0.030	0.002	0.002	0.001	0.006
Drift Concentration (µmol l^{-1})	112	3.0	36.4	1.4	2.0
Precision of Drift (stdev)					
Min	0.068	0.001	0.007	0.000	0.003
Max	0.654	0.027	0.148	0.007	0.150
Median	0.233	0.005	0.038	0.002	0.020

*MDL is based on 3 times the standard deviation of Low Nutrient Seawater (LNSW) analysed 12 times in each nutrient run.

4.8 Nutrient Data Processing

Calibration summary data for each analysis run is available in the following zip folder; http://www.cmar.csiro.au/datacentre/process/data_files/Investigator_NF/in2015_v03/doc/calibrations.zip. The data consists of txt files containing; mdl, drift, baseline, carry-over, calibration & RMNS results, and a summary table of the nutrient processing actions. The calibration plots are available in the following zip folder; http://www.cmar.csiro.au/datacentre/process/data_files/Investigator_NF/in2015_v03/doc/calibration_plots.zip.

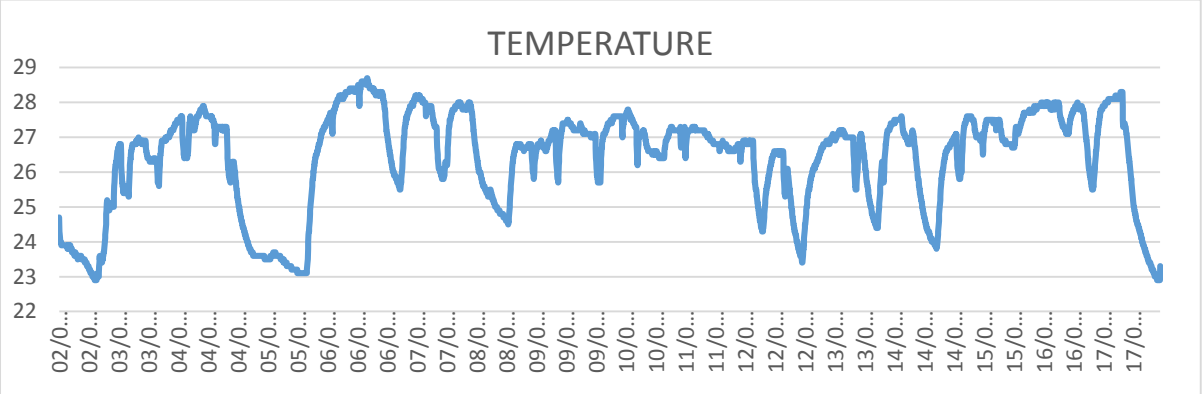
4.9 Investigation of Missing or Suspect Data and Actions taken.

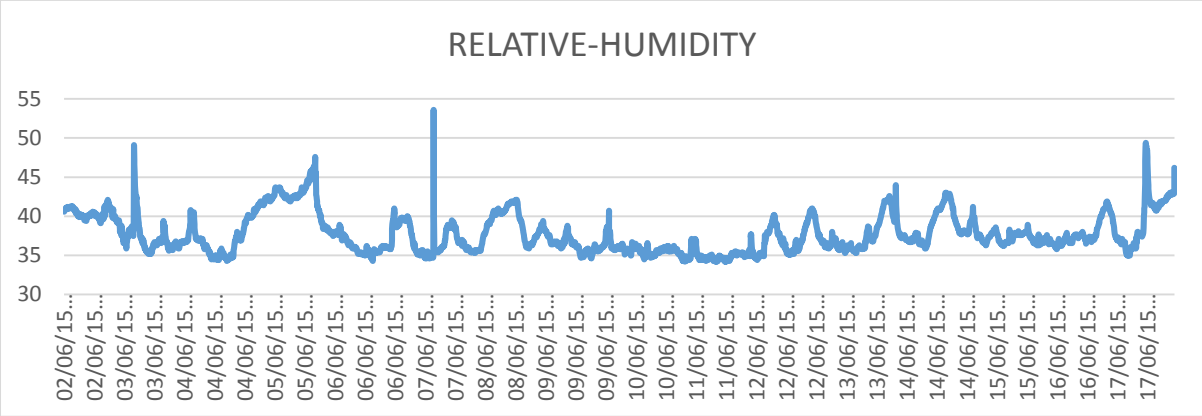
Deployment	RP	File	Analysis	Flag	Reason for Flag or Action
6	2	NUT 004	NH4	Suspect	Differences b/w duplicates > MDL
7	1	NUT 005	NOx	Suspect	Differences b/w duplicates > MDL
8	9	NUT 006	NOx	Suspect	Differences b/w duplicates > MDL
13	13	NUT 007	NH4	Suspect	Differences b/w duplicates > MDL
14, 15	4	NUT 008	NOx	Suspect	Differences b/w duplicates > MDL
17	5	NUT 009	SiO4	Suspect	Differences b/w duplicates > MDL
26	2	NUT 012	NOx	Suspect	Differences b/w duplicates > MDL
29	5	NUT 013	NOx	Suspect	Differences b/w duplicates > MDL
30	2	NUT 014	NOx	Suspect	Differences b/w duplicates > MDL
30, 32	2	NUT 014	NH4	Suspect	Differences b/w duplicates > MDL
31	13	NUT 014	NOx	Suspect	Differences b/w duplicates > MDL
32	13	NUT 014	NH4	Suspect	Differences b/w duplicates > MDL
34	2	NUT 015	NOx	Suspect	Differences b/w duplicates > MDL
16	1 & 4	NUT 008	NH4	Bad	#/removed, air in line caused an offset in peak position; sample was re-analysed in NUT009
16	1 & 4	Nut 008	NOx	Bad	#/removed, air in line caused an offset in peak position; RP1 re-analysed in NUT009; RP4 was ran in duplicate, 2nd measurement was removed so no duplicates
UWY	XLLC1, XHLNB1, XHLNC1, XLLNB1, XLLNC1, XCC1 - 1306	NUT 020	NH4	Bad	#/removed, XLLC1 was contaminated - the results were off scale for reportable concentrations which carried over into the following samples.
6	1, 2, 4, & 8		Salt	Missing	Samples were not measureable, bottles were overfilled and the torqued lid caused the bottles to crack.
7	1, 2, 3, 4 & 6		Salt	Missing	Samples were not measureable, bottles were overfilled and the torqued lid caused the bottles to crack. Sampling after this point for salinity was performed using the old style bottles and the samplers were re-trained.
12	3		Salt	Missing	Sample was not measureable, broken bottle – neck was cracked.
19	2		Oxygen	Bad	Sample result removed, stopper in upside down.
32	3		Oxygen	Missing	Sample not measured, incorrect addition of reagents.
36	ALL		Salt	Missing	No data, sampling bottle mix up.

37	1-5, 9, 13		Salt	Missing	No data, sampling bottle mix up.
44	ALL		Salt	Bad	Sample results removed, unsure – possible sampling bottle mix up.

4.10 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.





5 Appendix

5.1 Salinity Reference Material

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

5.2 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.

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]
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.