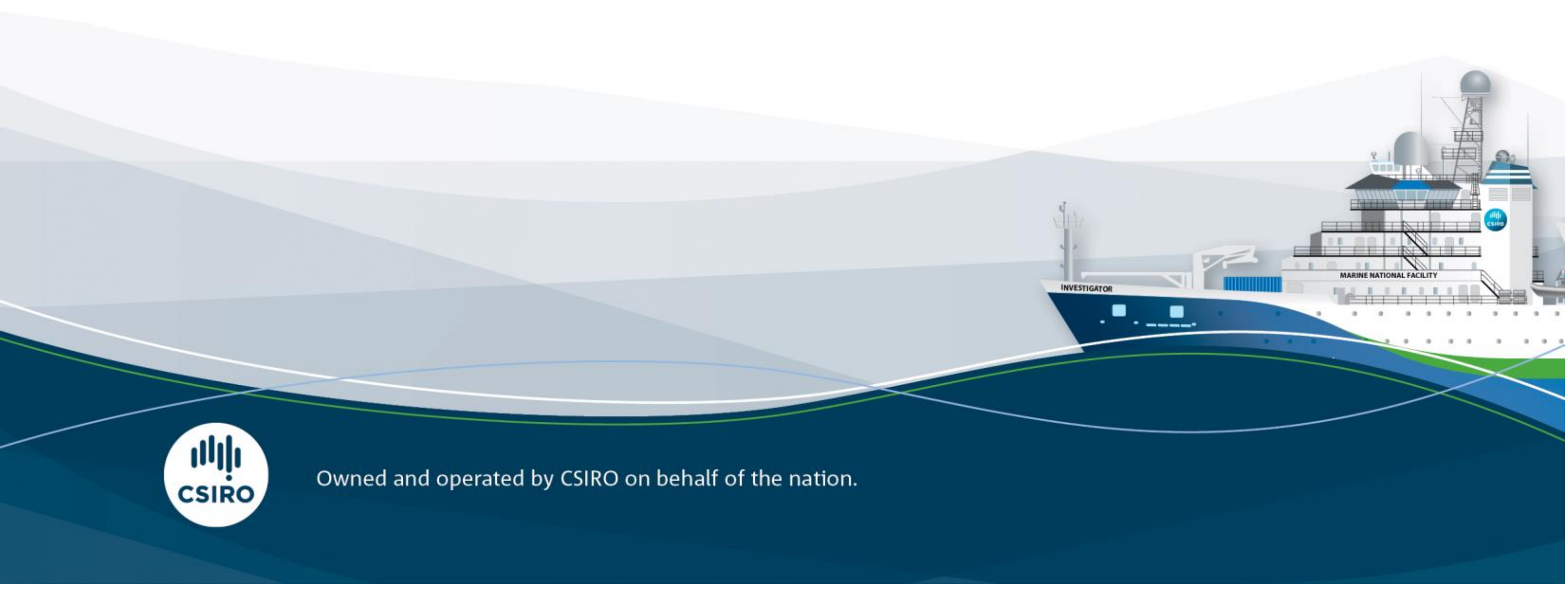
Marine National Facility

RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2015_V01
Chief Scientist:	Dr Tom Trull
Voyage title:	IMOS Southern ocean times series
Report compiled by:	Rayner and Rees



Contents

1 Itinerary

Mobilise	**Date**	
Hobart	19-20 March 2015	
Depart	**Date**	**Depart**
Hobart	21 March 2015	Hobart
Arrive	**Date**	**Arrive**
Hobart	30 March 2015	Hobart
Demobilise	**Date**	
Hobart	30-31 March 2015	

2 Key personnel list

Name	Role	Organisation
Dr Tom Trull	Chief Scientist	SIMS - UNSW
Max McGuire	Voyage Manager	CSIRO
Christine Rees	Hydrochemist	CSIRO
Mark Rayner	Hydrochemist	CSIRO

3 Summary

3.1 Hydrochemistry

Analysis	Sampled
Salinity (Guildline Salinometer)	86
Dissolved Oxygen (automated titration)	73
Nutrients (AA3)	70

3.2 Rosette and CTD

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

3.3 Nutrients

Details					
HyPro Version	3.20				
Instrument	AA3				
Software	Seal AACE 6.10				
Methods	AA3 Analysis Methods internal manual				
Nutrients anaylsed	☒ Silicate	☒ Phosphate	☒ NOx	☐ Nitrite	☐ Ammonia

Concentration range	140 µmol/L	3 µmol/L	35.0 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		
Analyst(s)	Christine Rees & Mark Rayner				
Lab Temperature (±1°C)	Variable, 19.0 – 24.0°C				
Reference Material	RMNS – BW (Appendix 5.1)				
Sampling Container type	Sample tube: polypropylene, lid: High density polyethylene				
Sample Storage	≤ 2 hrs at room temperature				
Pre-processing of Samples	None				
Comments	The temperature was logged using a temperature/humidity logger QP6013 (Jaycar) placed on the deck of the chemistry module. See appendix 5.4				

3.4 Salinities

Details	
HyPro Version	3.20
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)	21.0 -23.8°C
Reference Material	Osil IAPSO - Batch P157
Sampling Container type	Old sample bottles, duplicate sample taken in new salt bottles
Sample Storage	Samples held in Salt Room for 24 hrs before analysis within ~48 hrs
Comments	Salinometer was set-up and worked well. The Osil software was used 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	3.20
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Christine Rees
Lab Temperature (±1°C)	Variable, 19.0 - 24.0°C
Sample Container type	Glass Erlenmeyer flask with glass stopper.
Sample Storage	Samples analysed within ~48 hrs

Comments	There were some issues with communication between the dosimat and computer, software freezing, and the software picking the incorrect file to obtain the Thiosulphate Normality as well as the calibrated flask volumes. Further work is required to sort this file issue out. There was also issues with obtaining a good blank during the second analyses

4 Detailed processing

Oxygen and salinity data where imported into Hypro. There was no evidence of any outliers or bad data points required to be flagged in Hypro.

All nutrient data was processed starting from Aace and Hypro version 3.20.

4.1 Procedure

The procedure for data processing is outline in Figure 1.

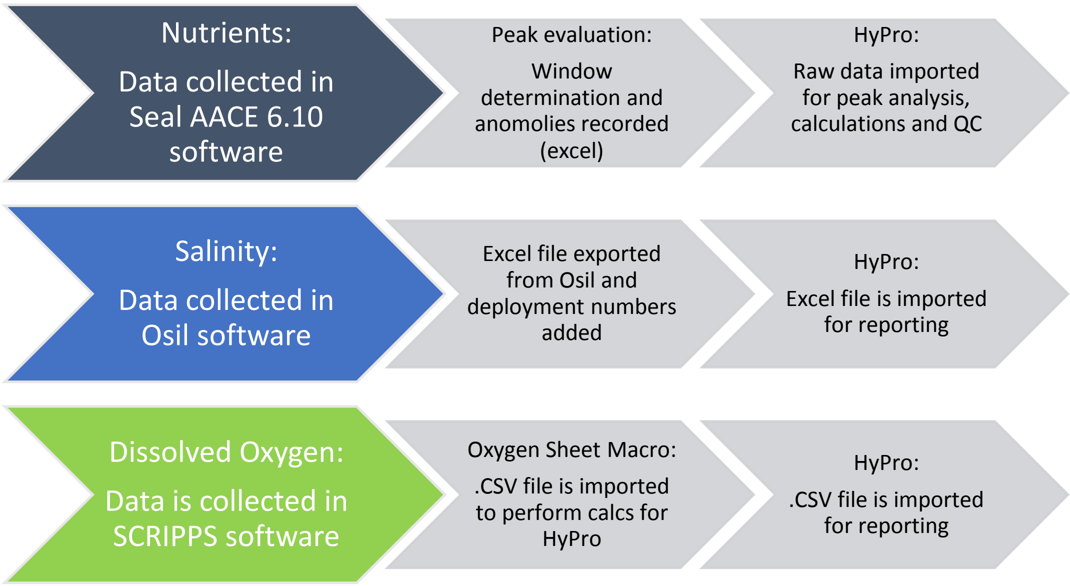


Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

4.2 Nutrients

- Silicate, phosphate and Nitrate + Nitrite analysis was carried out during the voyage. The AA3 was set up with a master file IN2015_V01 (24 sample tray protocol) the AA3 worked well producing high quality data. AACE files were sent directly to the IN2015_V01 current directory where they were then copied into the SEAL program file directory on the processing computer.
- All runs have a corresponding AA3 Run_ Analysis_Worksheet file & AA3_Processing_Worksheet file to assist in characterising data.
- The final slk and chd file produced from AACE were copied into Hypro directory for calculation of nutrient concentrations. Hypro uses the median of the peak window to calculate the concentration of each peak.
- During the voyage analysis run nut004 had a high MDL for silicate and phosphate. Further processing determined that the high MDL is most likely an artefact of the baseline shifting during the analysis of the MDL's. Phosphate RMNS at the end of the run also changed from

2% to 3%. Comparison of the surface silicate samples with the other analysis runs indicated they were also higher. The silicate samples were repeated from refrigerated samples the next day. Comparison of phosphate samples indicated that the results from nut004 were OK. The repeated run nut005 results had an improved MDL for silicate and the surface samples were of similar concentrations to the other analyses. The silicate results from nut005 were the reported concentrations to the chief scientist on board. Further investigation is required into why analysis run nut004 had a lower than normal precision.

- Files for this voyage - nut001 - 006.

Details	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Data Reported as	µM l^{-1}	µM l^{-1}	µM l^{-1}	N/A	N/A
Calibration Curve degree	>0.9995	>0.9995	>0.9995		
Forced through zero?	N	N	N		
# of points in Calibration	5 or 6	5	5		
Matrix Correction	Y	Y	Y		
Blank Correction	N	N	N		
Carryover Correction	Y	Y	Y		
Baseline Correction	Y	Y	Y		
Drift Correction	Y	Y	Y		
Data Adj for RMNS	N	N	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
IN2015_v01nut001	☒	☒	☒	☐	☐	Set-up Char.
Peak window	50-105	50-100	60-105			
RMNS	≤2%	≤2%	≤2%			
Comments	Peak Period Moved in AACE					
IN2015_v01nut002	☒	☒	☒	☐	☐	Testing file exporting, Cd column & sample needle position
Peak window	50-105	50-100	60-105			
RMNS	≤1%	≤2%	≤2%			
Comments	Peak Period Moved in AACE, baseline noisy forced					
IN2015_v01nut003	☒	☒	☒	☐	☐	CTD 5 3 samples ran in duplicate
Peak window	50-105	50-100	60-105			
RMNS	≤1%	≤1%	≤1%			
Comments	Baseline noisy forced	Peak Period Moved in AACE				
IN2015_v01nut004	☒	☒	☒	☐	☐	CTD 7 3 samples ran in duplicate
Peak window	50-105	50-100	60-105			
RMNS	≤1%	≤2%	≤1%			
Comments	New pump tubes, very high MDL.	New pump tubes	New pump tubes			
IN2015_v01nut005	☒	☐	☐	☐	☐	CTD – Silicate repeat of deployment 7
Peak window	50-105					
RMNS	≤1%					

File	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia	Run Type
Comments	Peak Period Moved in AACE					
IN2015_v01nut006	☒	☒	☒	☐	☐	CTD 9 3 samples ran in duplicate
Peak window	50-105	50-100	60-105			
RMNS	≤1%	≤2%	≤1%			
Comments	Baseline slight noise, New reagents except tartaric acid					

4.3 Salinities

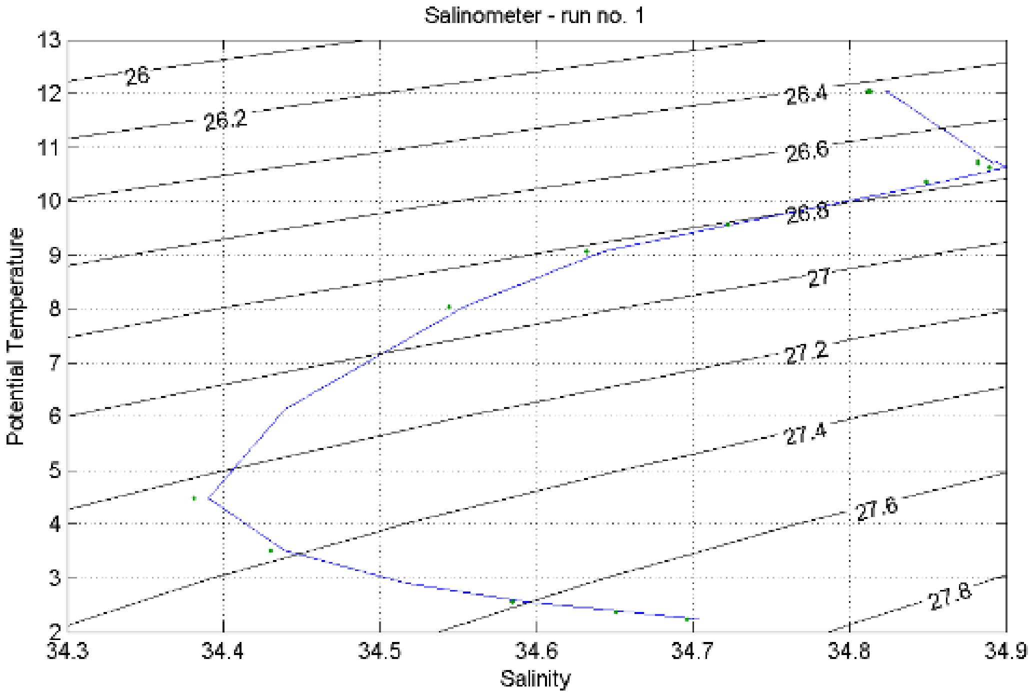
- Files for this voyage - sal001, sal003 sal004; in addition; samples for a storage experiment T-0 were also analysed (16).
- Salinity data was collected using Osil software.
- Lab temperature stable. Bath set at 24°C. Lab temperature and bath temperature was measured before both analyses, both temperature were suitable for analyses to proceed.

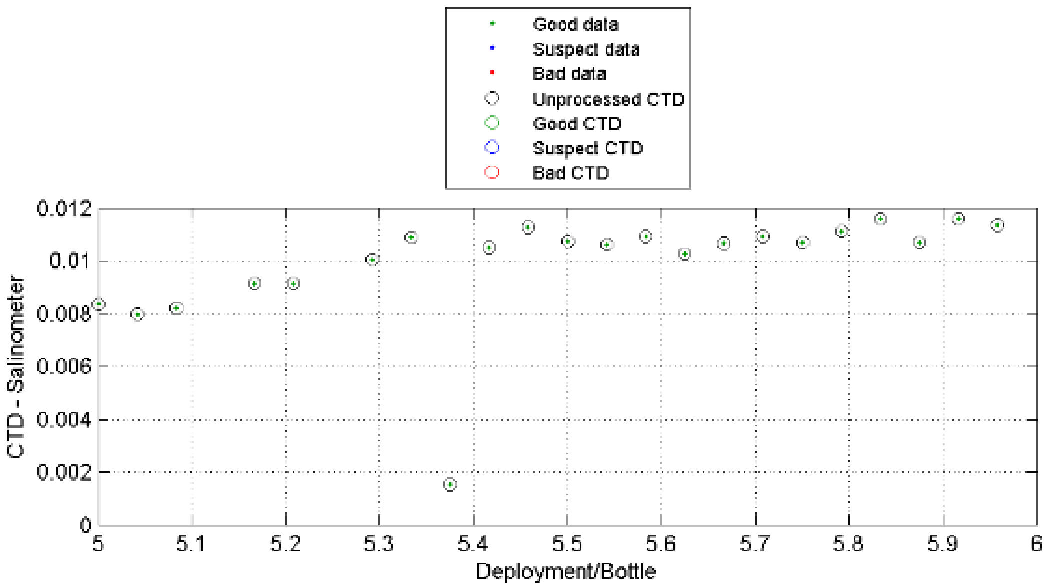
4.4 Dissolved oxygen

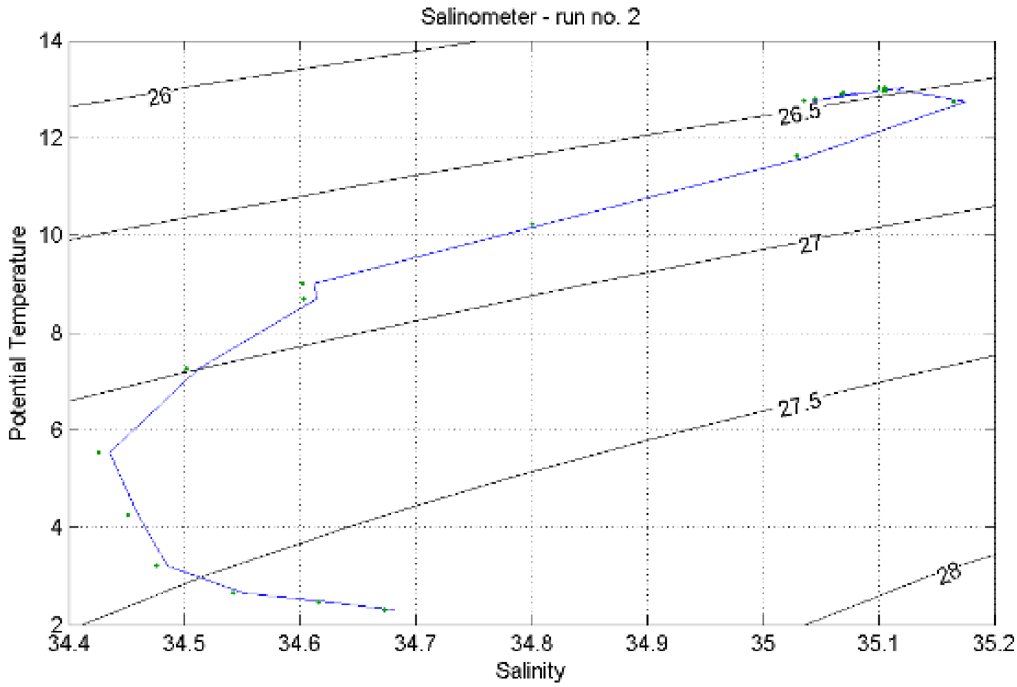
- The DO system was problematic with a number of issues; com port identification, software freezing, communication with the dosimats, the program picking the incorrect thiosulphate normality and difficulties in obtaining a good blank reading (during second calibration). To try and correct the blank readings the following was performed; both burettes flushed, detector windows cleaned, bath cleaned, thiosulphate dispensing tip re-orientated and only one flask #225 was used. To correct the program from picking the incorrect thiosulphate normality was difficult to resolve, as we are not sure which file it was reading.
  We managed to get it to select the right concentration (not sure how) in the end.
  Communication between the dosimats and computer were resolved by following the written protocol.
- Comparison between the underway samples and the CTD surface samples indicated there was a problem with the dissolved oxygen results for the oxy001-003 files. Further investigation by plotting the dissolved oxygen results against the CTD results indicated there was an offset between these results, with the filesoxy001-003 having incorrect oxygen concentrations. Investigation found that the programme was using the incorrect volumes for calculating the concentration of dissolved oxygen. This problem has been resolved by placing a new copy of the volume file into the directory. The oxygen data was re-calculated using the correct flask volumes in Hypro.
- Files for this voyage – oxy001 – 003. Plus oxy099 for 3 underway samples.

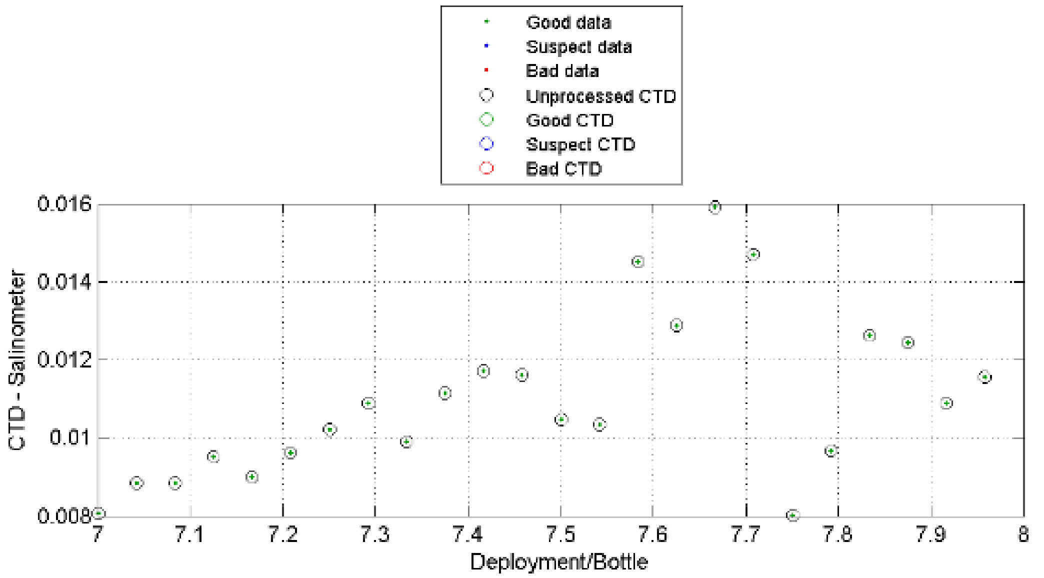
4.5 CTD vs Hydro salinities

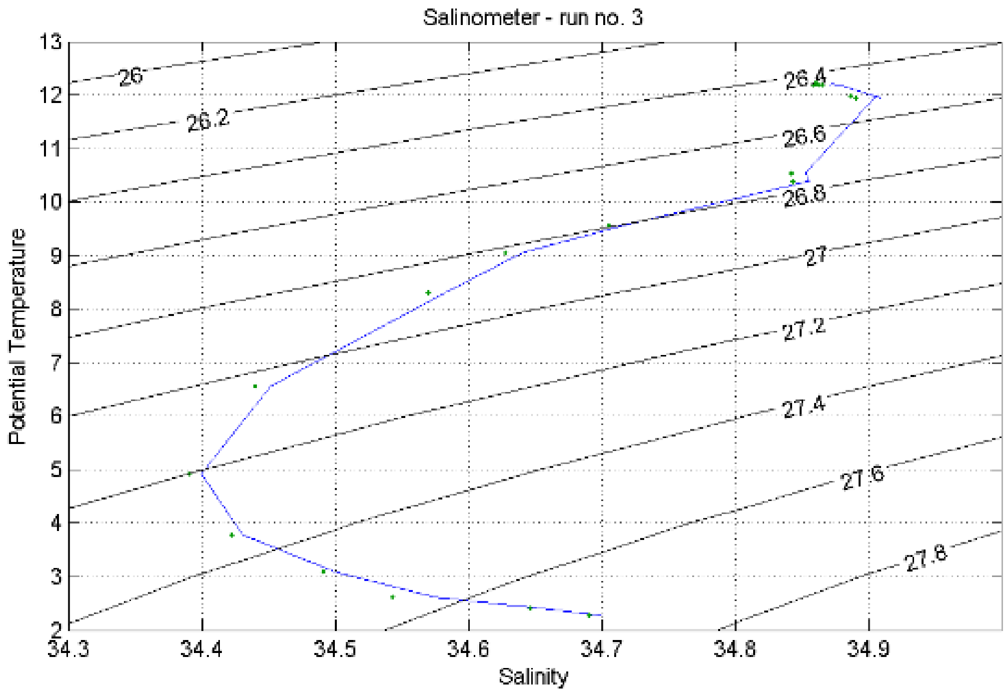
The following plots can be viewed in the following location (Mark to add in link).

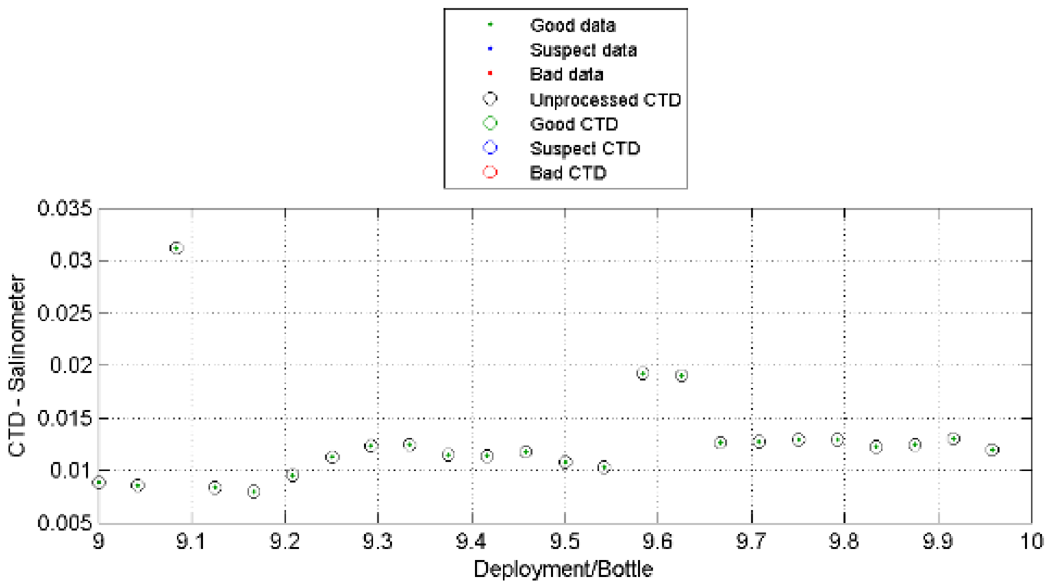

Salinometer - run no. 1
Potential Temperature
Salinity
26
26.2
26.4
26.6
26.8
27
27.2
27.4
27.6
27.8


Good data
Suspect data
Bad data
Unprocessed CTD
Good CTD
Suspect CTD
Bad CTD
CTD - Salinometer
Deployment/Bottle


Salinometer - run no. 2
Potential Temperature
Salinity
26
26.5
27
27.5
28
14
12
10
8
6
4
2
34.4
34.5
34.6
34.7
34.8
34.9
35
35.1
35.2


Good data
Suspect data
Bad data
Unprocessed CTD
Good CTD
Suspect CTD
Bad CTD
CTD - Salinometer
Deployment/Bottle
0.016
0.014
0.012
0.01
0.008
7
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8


Salinometer - run no. 3
Potential Temperature
Salinity
26
26.2
26.4
26.6
26.8
27
27.2
27.4
27.6
27.8


Good data
Suspect data
Bad data
Unprocessed CTD
Good CTD
Suspect CTD
Bad CTD
CTD - Salinometer
Deployment/Bottle

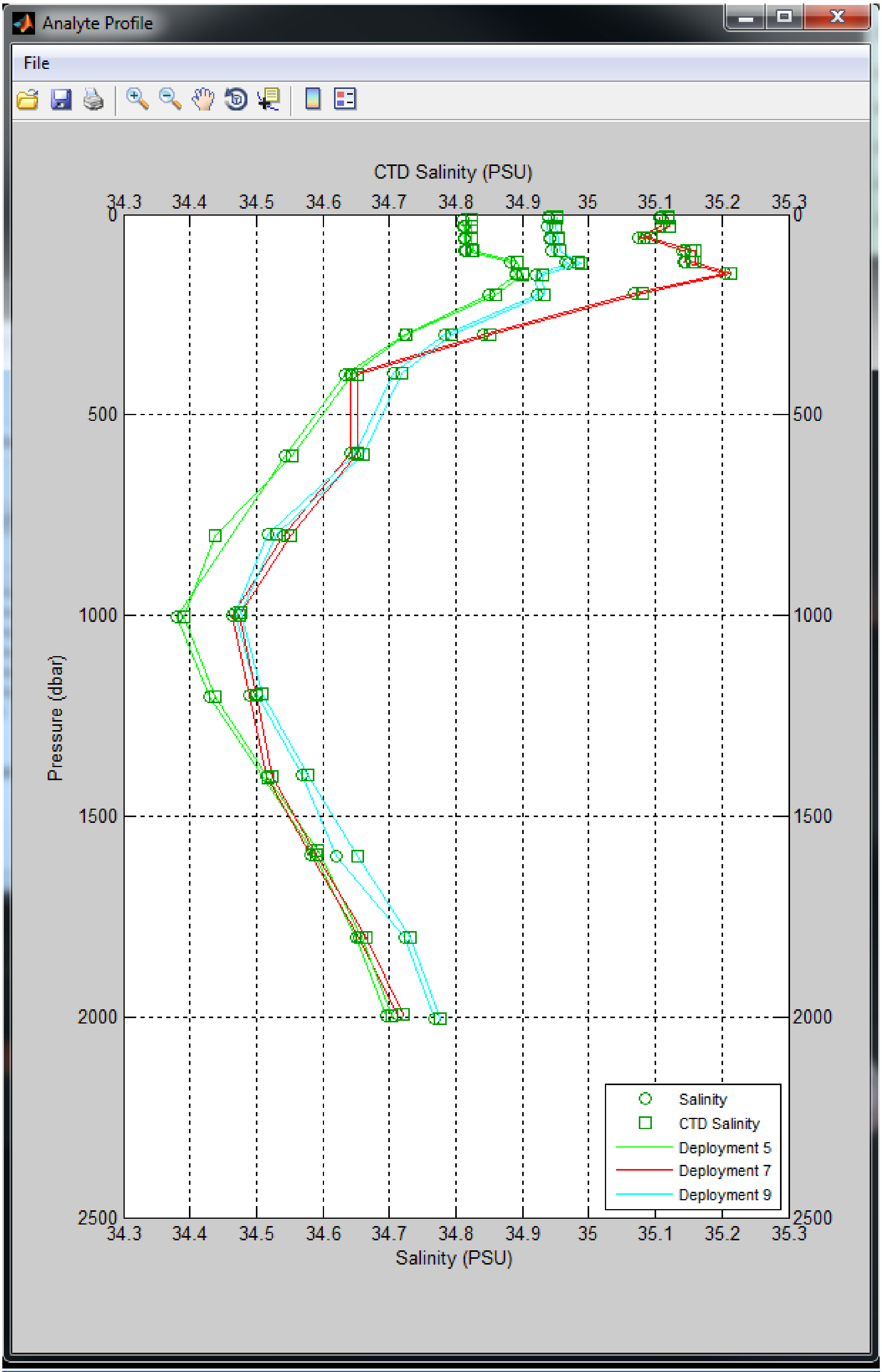
4.6 CTD vs Hydro Oxygens

These plots can be viewed in the following location (Mark to add in link)

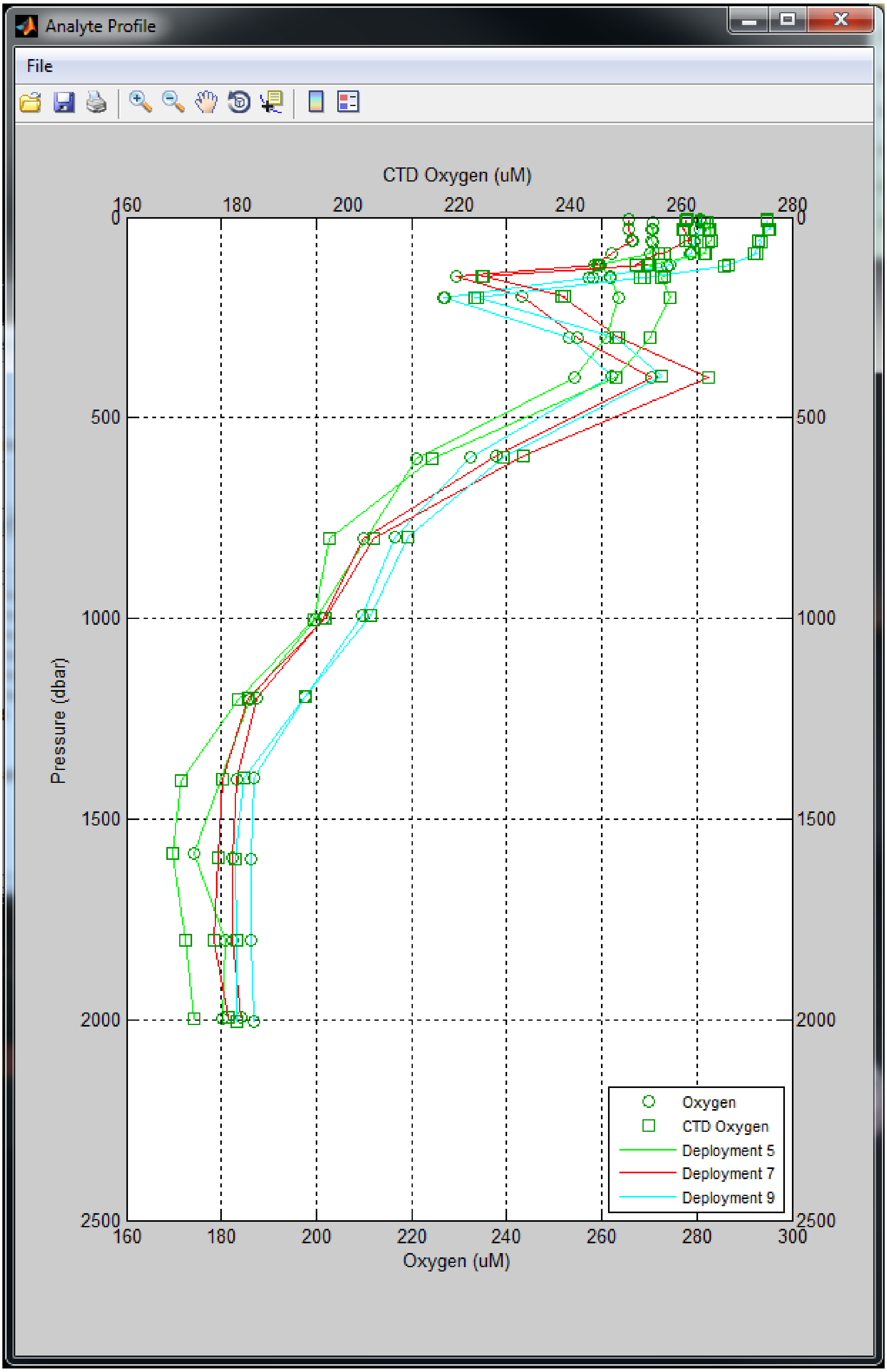
4.7 Plots

All waterfall plots consist of good data, without any outliers. This indicates there wasn't any leakage from the Niskin bottles.

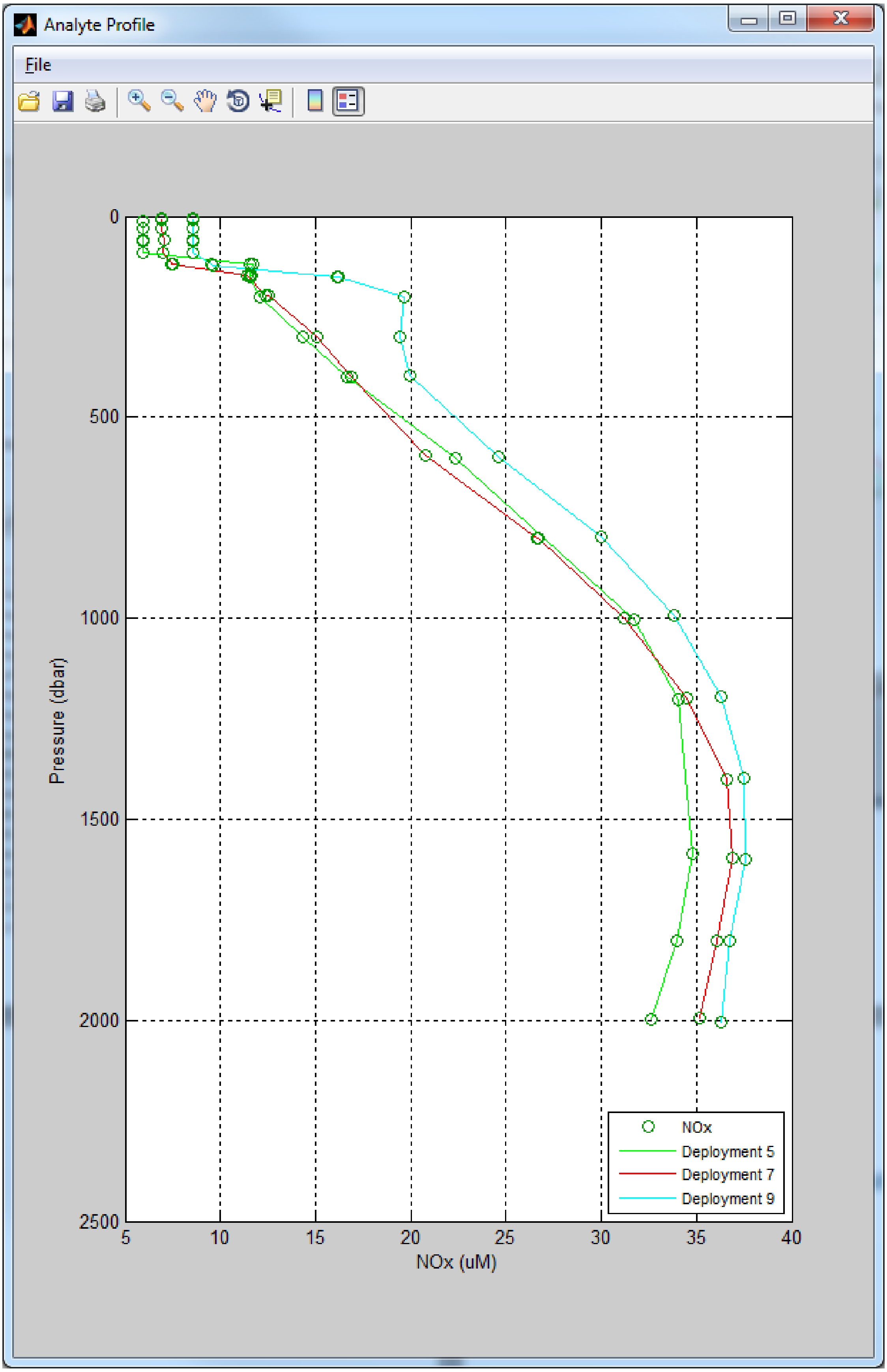
4.7.1 Salinity vs pressure waterfall plot



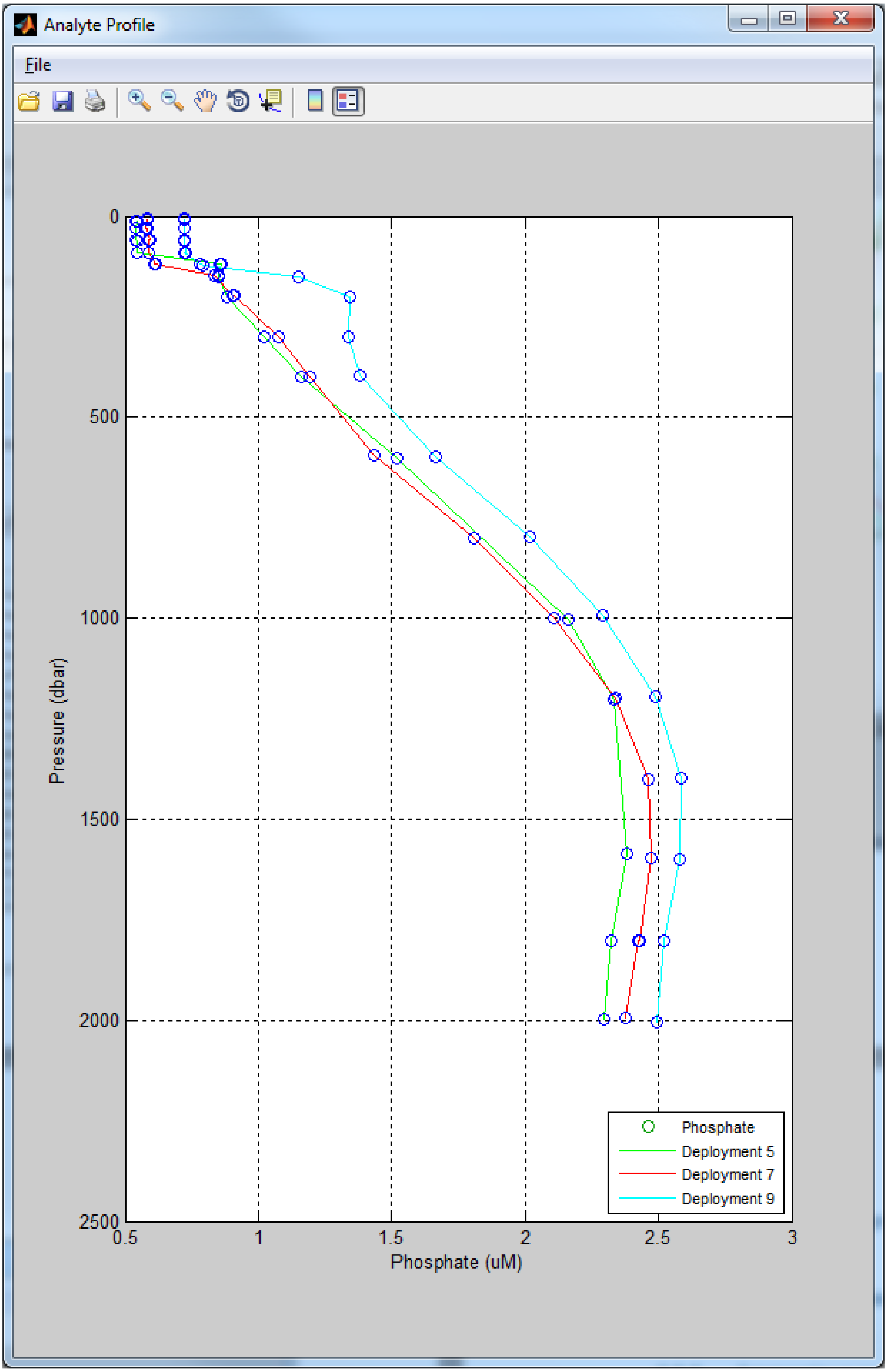
4.7.2 Oxygen vs pressure waterfall plot



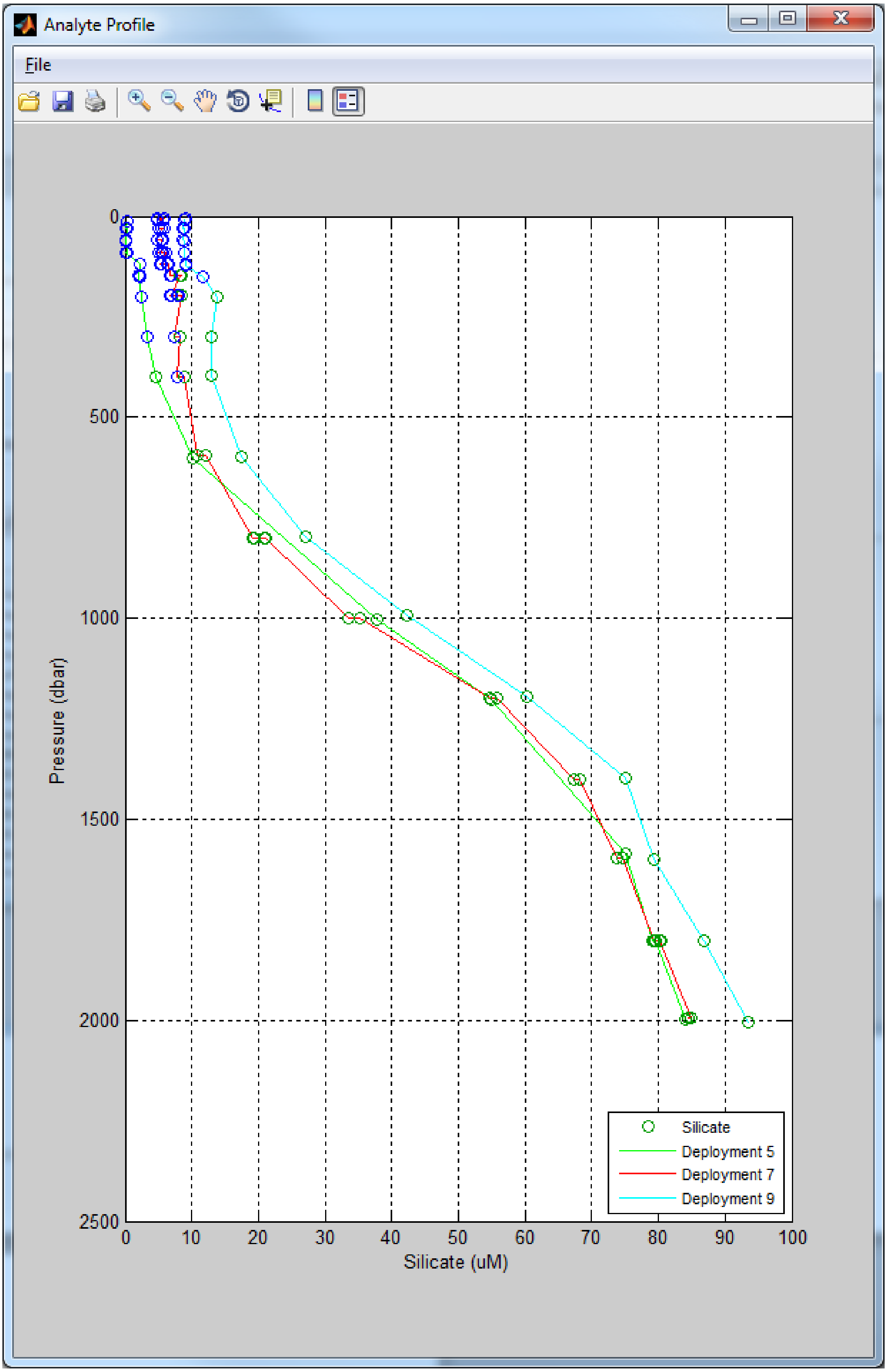
4.7.3 NOx vs pressure waterfall plot



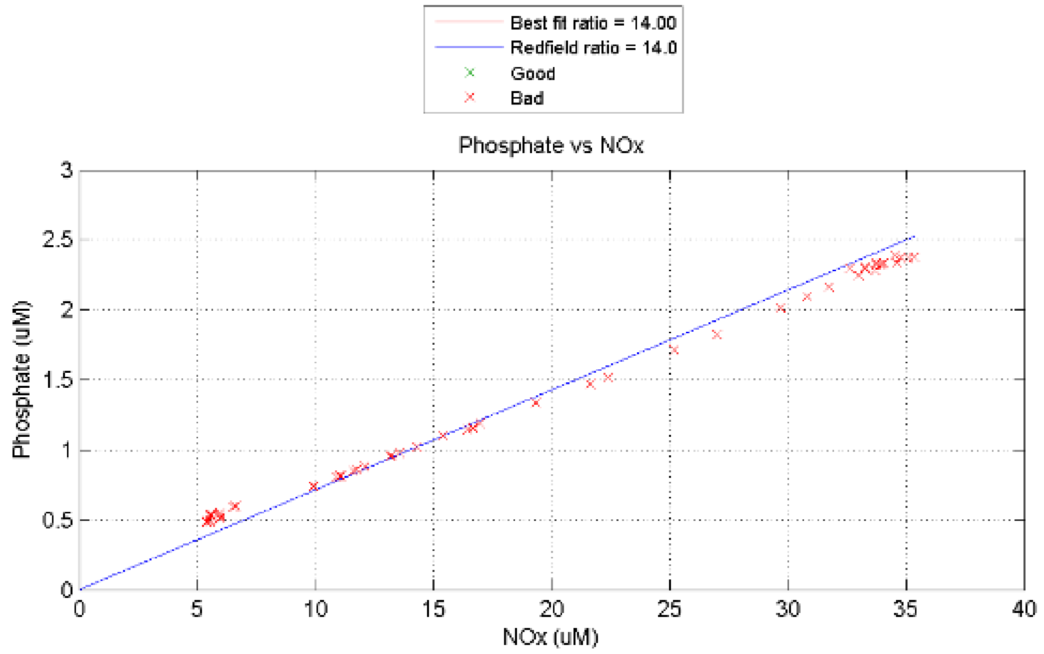
4.7.4 Phosphate vs pressure waterfall plot

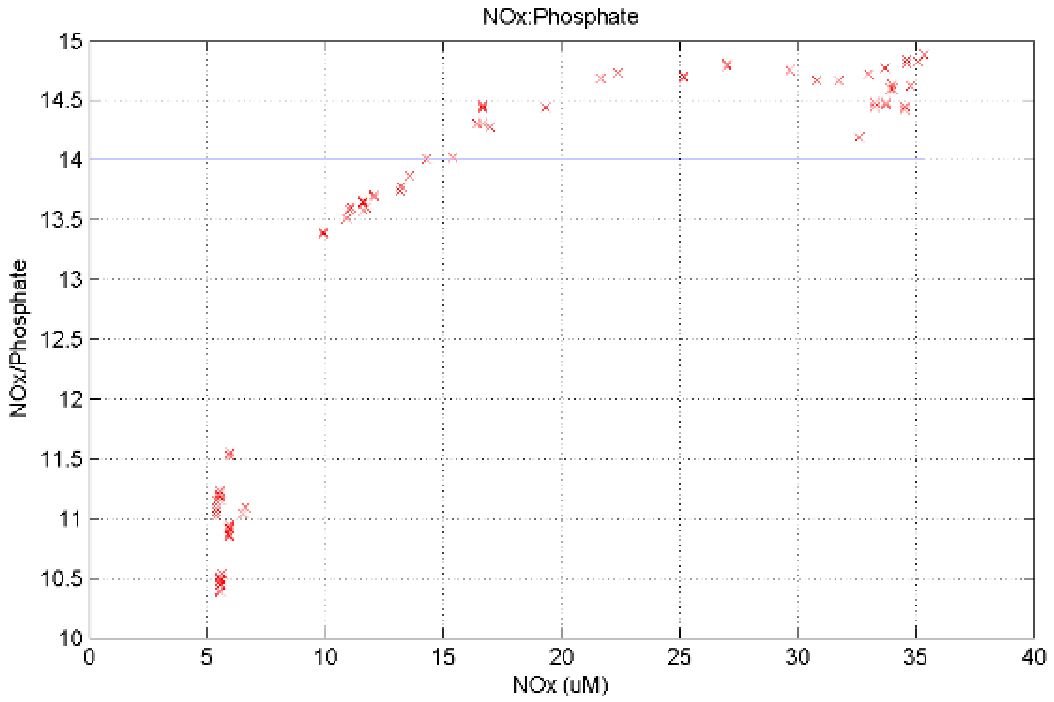


4.7.5 Silicate vs pressure waterfall plot



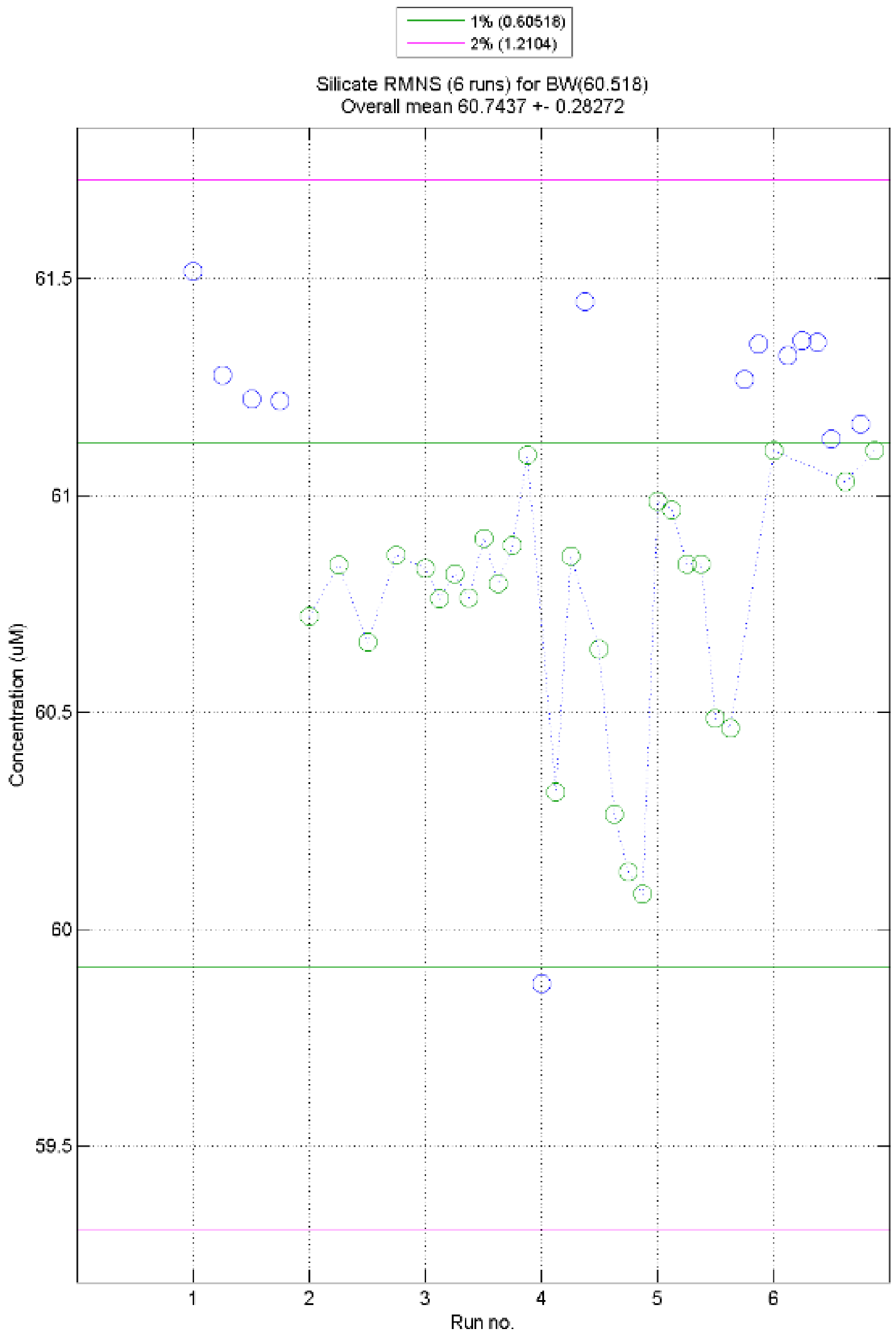
4.7.6 Redfield ratio plot



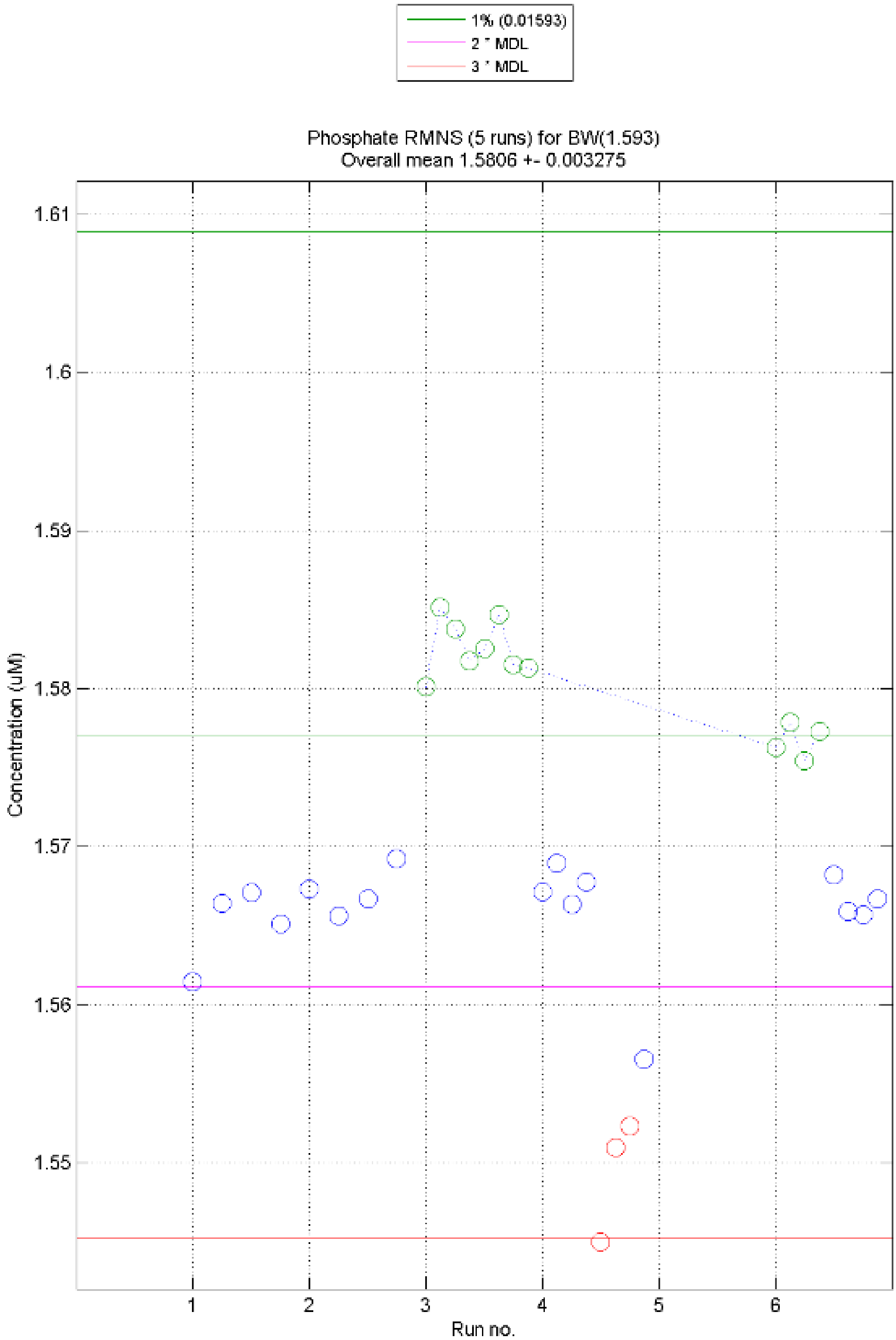


4.8 Quality Control

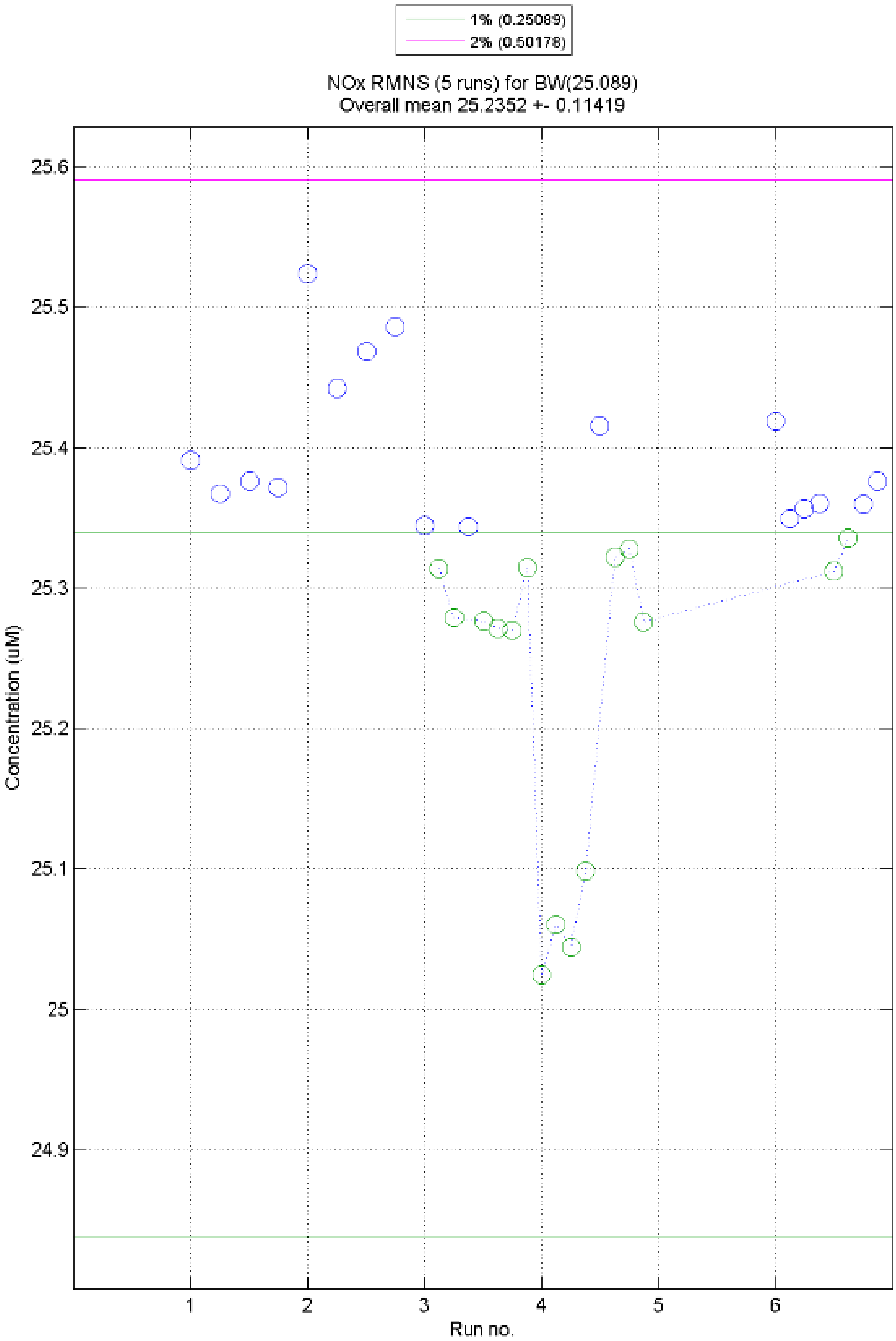
4.8.1 Silicate RMNS Chart



4.8.2 Phosphate RMNS Chart



4.8.3 NOx RMNS Chart



4.8.4 Duplicates

File	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonia
Duplicates within limit	0.70 µM	0.02 µM	0.175 µM	N/A	N/A
IN2015_v01nut001	☒	☒	☒	☐	☐
IN2015_v01nut002	☒	☒	☒	☐	☐
IN2015_v01nut003	☒	☒	☒	☐	☐
IN2015_v01nut004	☒	☒	☒	☐	☐
IN2015_v01nut005	☒	☒	☒	☐	☐
IN2015_v01nut006	☒	☒	☒	☐	☐

4.9 Investigation of missing data and actions required

Deployment	RP	Analysis	Reason for removal	Action taken
# 5	4	N/A	Niskin bottle did not close	Samples not collected
# 5	7	N/A	Leaking Niskin bottle	Samples not collected

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

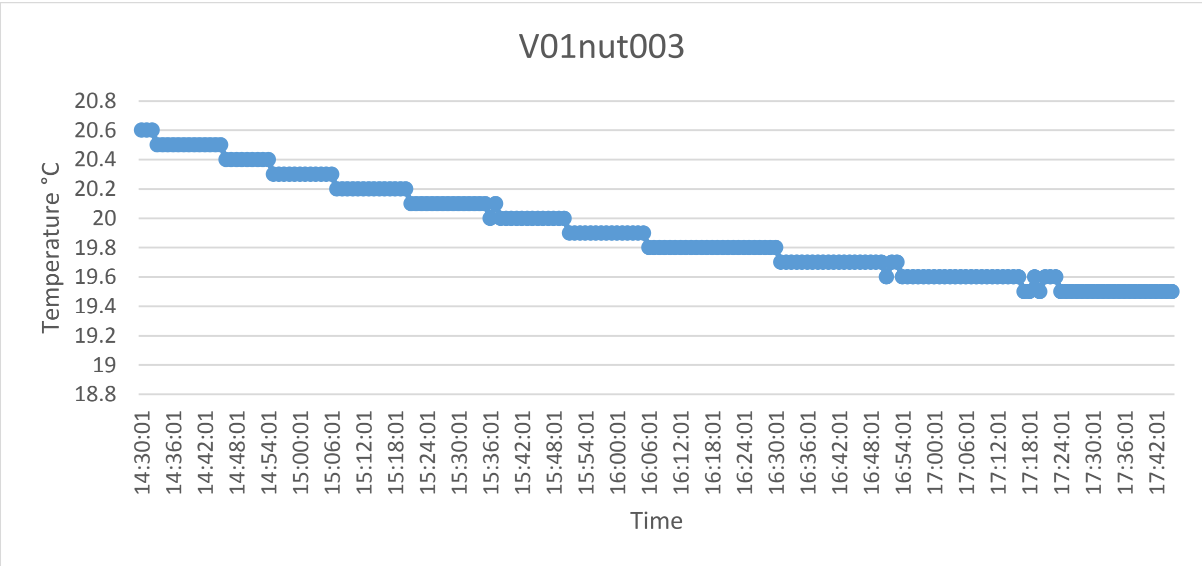
5.2 Salinity Reference Material

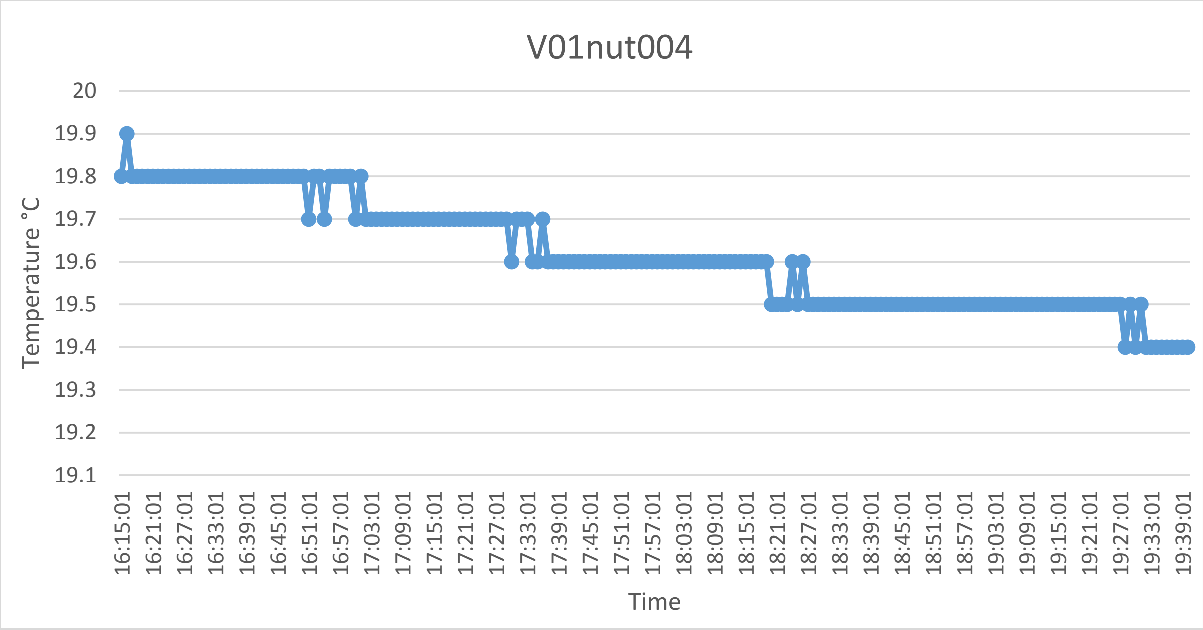
Batch No: P 157 K15 = 0.99985, use by date 15th May 2017.

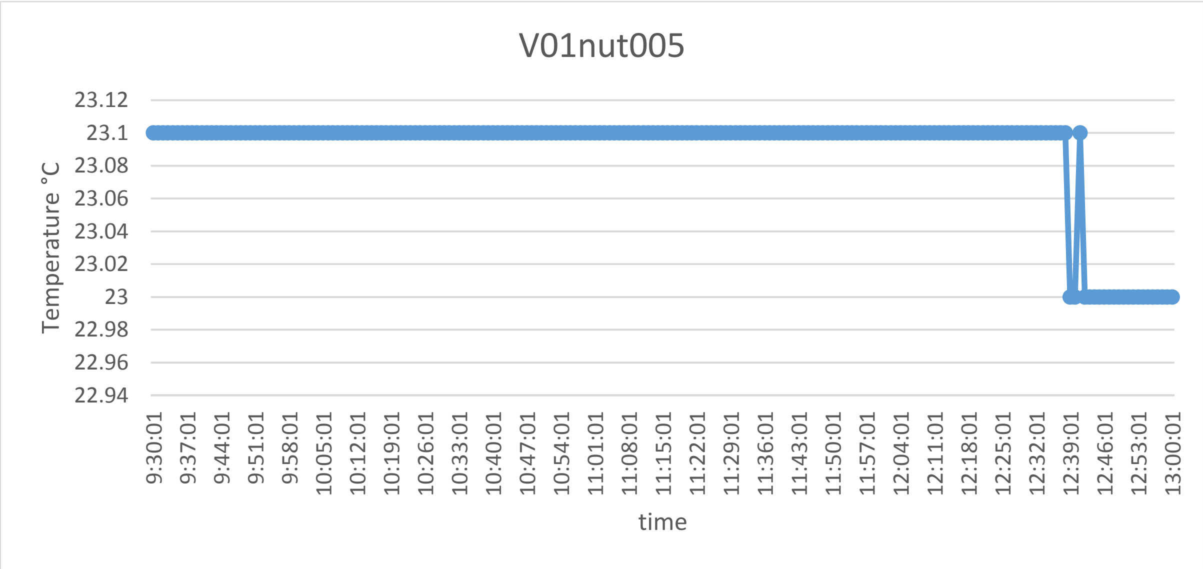
5.3 Go-Ship Specifications

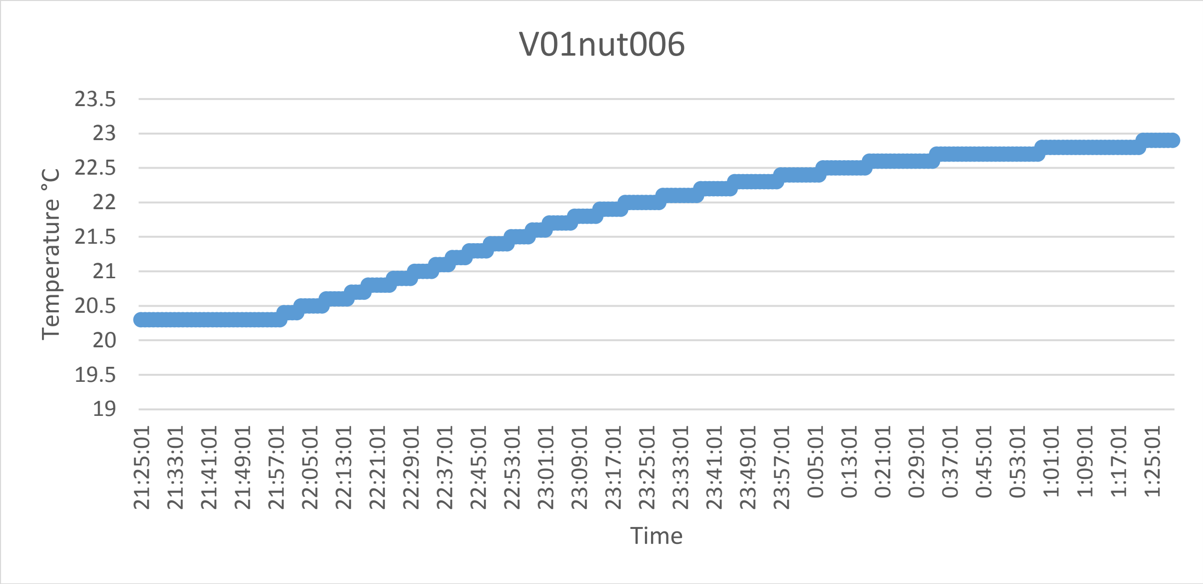
Salinity	Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology, e.g., monitoring Standard Sea Water. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosal precision is better than 0.001 PSS-78. 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.

5.4 Temperature change over nutrient analyses




V01nut004
Temperature °C
20
19.9
19.8
19.7
19.6
19.5
19.4
19.3
19.2
19.1
16:15:01
16:21:01
16:27:01
16:33:01
16:39:01
16:45:01
16:51:01
16:57:01
17:03:01
17:09:01
17:15:01
17:21:01
17:27:01
17:33:01
17:39:01
17:45:01
17:51:01
17:57:01
18:03:01
18:09:01
18:15:01
18:21:01
18:27:01
18:33:01
18:39:01
18:45:01
18:51:01
18:57:01
19:03:01
19:09:01
19:15:01
19:21:01
19:27:01
19:33:01
19:39:01
Time


V01nut005
Temperature °C
23.12
23.1
23.08
23.06
23.04
23.02
23
22.98
22.96
22.94
9:30:01
9:37:01
9:44:01
9:51:01
9:58:01
10:05:01
10:12:01
10:19:01
10:26:01
10:33:01
10:40:01
10:47:01
10:54:01
11:01:01
11:08:01
11:15:01
11:22:01
11:29:01
11:36:01
11:43:01
11:50:01
11:57:01
12:04:01
12:11:01
12:18:01
12:25:01
12:32:01
12:39:01
12:46:01
12:53:01
13:00:01
time


V01nut006
Temperature °C
23.5
23
22.5
22
21.5
21
20.5
20
19.5
19
21:25:01
21:33:01
21:41:01
21:49:01
21:57:01
22:05:01
22:13:01
22:21:01
22:29:01
22:37:01
22:45:01
22:53:01
23:01:01
23:09:01
23:17:01
23:25:01
23:33:01
23:41:01
23:49:01
23:57:01
0:05:01
0:13:01
0:21:01
0:29:01
0:37:01
0:45:01
0:53:01
1:01:01
1:09:01
1:17:01
1:25:01
Time