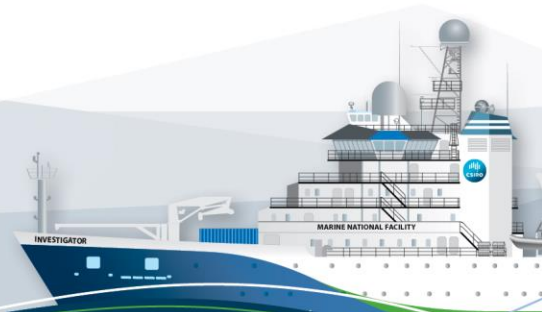


HYDROCHEMISTRY DATA PROCESS REPORT

Voyage:	IN2015_v02
Chief Scientist:	Bernadette Sloyan, Susan Wiffels
Voyage title:	Sustained monitoring of the East Australian Current: Mass, heat and freshwater transports
Report compiled by:	Peter Hughes and Cassie Schwanger



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1 Itinerary

Depart	Date	Time
Sydney	15 May 2015	1800
Arrive	Date	Time
Brisbane	26 May 2015	1100

2 Key personnel list

Name	Role	Organisation
Bernadette Sloyan	Chief Scientist	CSIRO
Tegan Sime	Voyage Manager	CSIRO
Peter Hughes	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)	370
Dissolved Oxygen (automated titration)	369
Nutrients (AA3)	370

3.2 Rosette and CTD

- 20 CTD stations were completed with a 24 bottle rosette (10 L).
- Niskin in position 7 imploded during deployment 2. Not replaced for remaining
- Sampling done by dedicated teams on opposing shifts after initial training from the hydrochemists.

3.3 Procedure

The procedure for data processing is outline in Figure 1.

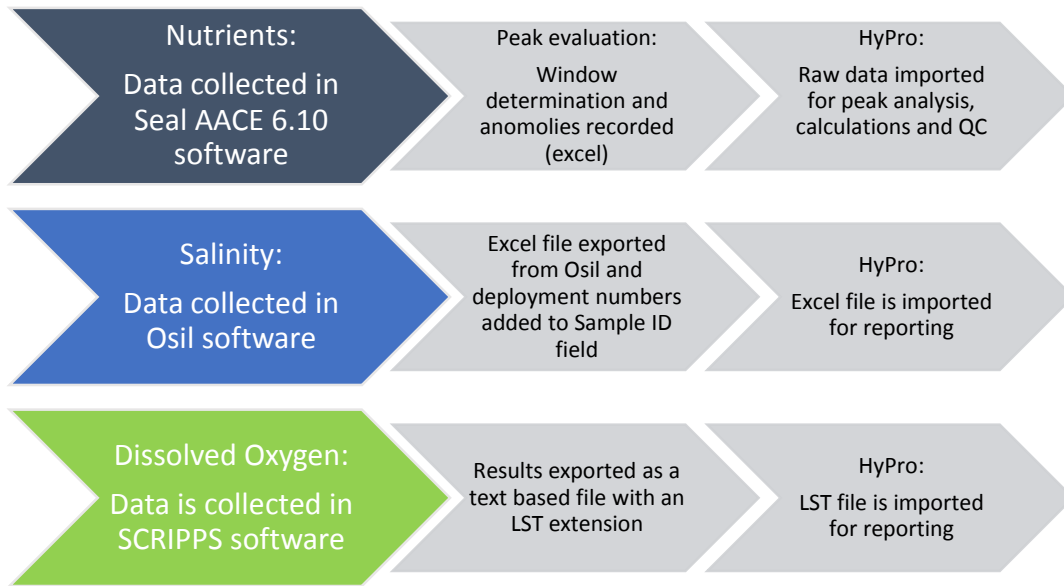


Figure 1: The process above shows the data trail procedure from the initial data generated to output via HyPro for reporting.

3.4 Nutrients

Details					
HyPro Version	3.26				
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 type="checkbox"/> Nitrite	<input type="checkbox"/> Ammonia
Concentration range	126 µmol/L	3 µmol/L	35 µmol/L	1.4 µmol/L	2.0 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)	Cassie Schwanger & Peter Hughes				
Lab Temperature (±1°C)	Variable, 22 -26°C				
Reference Material	RMNS – BW & CA				
Sampling Container type	15 ml PP tube neutral screw cap, Sarstedt 60.732				
Sample Storage	< 2 hrs at room temperature or < 24hrs @ 4°C				
Pre-processing of Samples	None				
Comments	<p>Main points to note.</p> <p>(1) Analysis</p> <p>New 15ml tubes used for nutrient samples. Unsuited for ammonia assay due to contamination. Tubes no-longer used after this voyage.</p> <p>Silicate: Deployments 3,4,5,7,8. Deeper sample concentrations > than top calibration standard concentration 112µM. Duplicate samples repeated in instrument run 22 with top calibration standard of 126µM.</p> <p>NOx: Deployment 15. Nutrient assay AA3 instrument NOx channel had a reagent leak. Samples re-assayed next run after fixing leak.</p> <p>Phosphate: No issues with sample assay.</p> <p>(2) Accuracy</p> <p>KANSO reference nutrient seawater (RMNS) solutions were assayed at the start and end of each AA3 instrument run. New bottle opened for each run.</p> <p>RMNS Lot BW was used for all AA3 runs. Deployments 4,5,10 and 11 included Lot CA or BV to confirm the higher BW results</p> <p>RMNS results generally higher than stated values. The greatest being phosphate with up to +4% difference.</p> <p>Possible cause being the laboratory temperature exceeding 25C during the first half of the voyage which effects the accuracy of the volumetric ware and pipetters used to make the calibration solutions. As well as the stability of the AA3 instrument.</p> <p>Deployment vs RMNS results tabulated below.</p> <p>(3) Processing, Hypro 3.26</p> <p>Preliminary processing occurred during the voyage using Hypro 3.25 to monitor quality of analysis.</p> <p>Final hydrology processing completed post-voyage using Hypro 3.26. No issues with processing.</p>				

3.5 Salinities

Details	
HyPro Version	3.26
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71613
Software	Osil Data Logger ver1
Methods	Hydrochemistry Operations Manual + Quick Reference Manual
Accuracy	± 0.001 salinity units
Analyst(s)	Cassie Schwanger & Peter Hughes
Lab Temperature (±0.5°C)	Variable: 21-25°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. Samples assayed within 48 hrs
Comments	<p>New square bottles trialled as a potential replacement for the old round bottles used for the Southern Surveyor. Square bottle lids are tightened with a torque wrench to ensure seal.</p> <p>Deployments 1 & 6 all niskins fired at 1980m. Standard deviation for salinity is 0.0007 for both deployments. 1=new salt bottles. 6=old salt bottles.</p> <p>Deployment 10, lids on square bottles hand-tight, not torqued as required, results flagged suspect.</p>

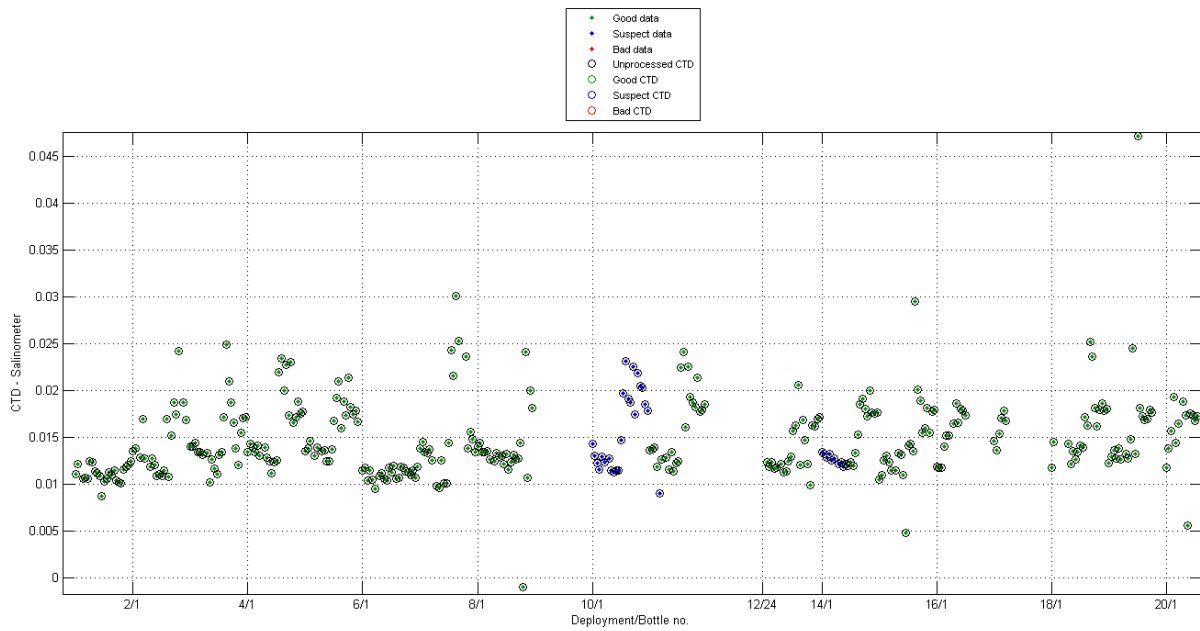
3.6 Dissolved oxygen

Details	
HyPro Version	3.26
Instrument	Automated Photometric Oxygen system
Software	SCRIPPS
Methods	SCRIPPS
Accuracy	0.01 ml/L + 0.5%
Analyst(s)	Cassie Schwanger & Peter Hughes
Lab Temperature (±1°C)	Variable, 21.5-25.5°C
Sample Container type	Pre-numbered glass 140 mL glass vial w/stopper
Sample Storage	Samples analysed within ~48 hrs
Comments	<p>No issues with analysis.</p> <p>Precision dependent on sampler illustrated by the standard deviations for deployments 1 and 6</p> <p>Deployment 1 = 0.13 uM sampler = hydrochemist</p> <p>Deployment 6 = 0.43 uM sampler = voyage participant</p>

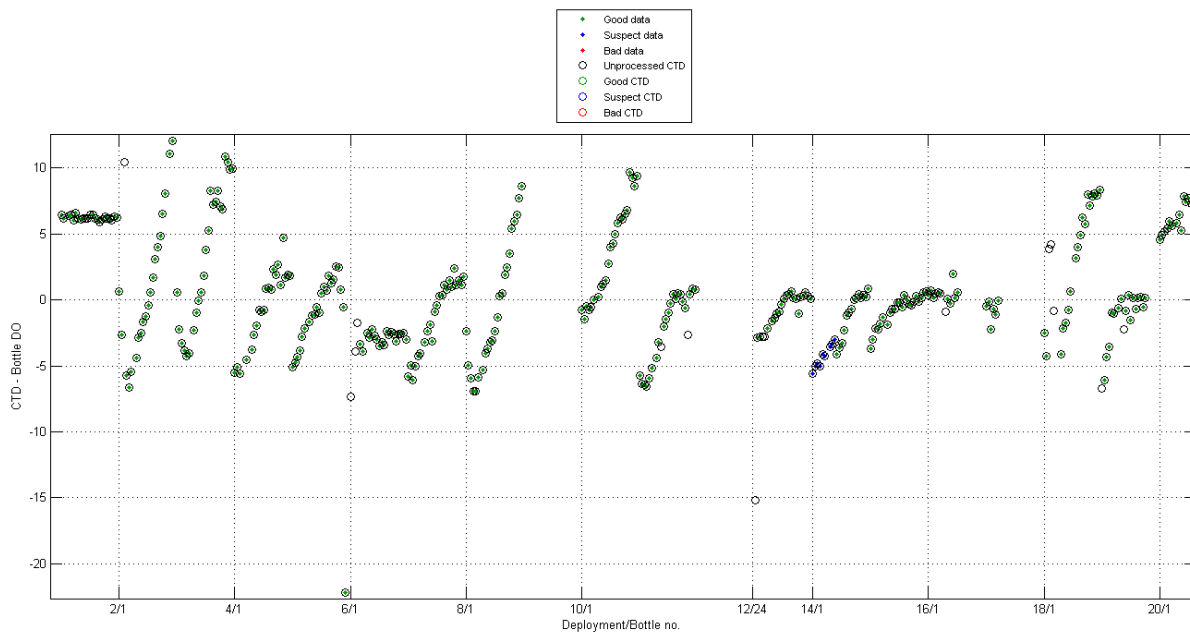
4 Plots – Quality Control

All plots can be viewed at \\strait-hba\mnf\processedVoyageData\RVinvestigator\in2015_v03\hyd

4.1 CTD vs Hydro Salinities Error Plot



4.2 CTD vs Hydro DO Error Plot



4.3 Assayed RMNS vs Deployment

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. Tabulated below.

The Lot. BW was included with every analysis run. Lot CA, BV occasionally.

KANSO reference seawater lot. BW Certified value Expanded uncertainty		Nitrate + Nitrite		Phosphate		Silicate	
		25.08		1.593		60.52	
		Mean	SD	Mean	SD	Mean	SD
Deployment	Assayed result	Mean	SD	Mean	SD	Mean	SD
1	Combined	25.23	0.03	1.621	0.001	60.44	0.19
	Initial Group	25.22	0.01	1.622	0.001	60.30	0.18
	Final Group	25.24	0.03	1.621	0.001	60.58	0.05
2	Combined	25.51	0.10	1.643	0.003	61.56	0.21
	Initial Group	25.41	0.01	1.641	0.002	61.38	0.10
	Final Group	25.60	0.03	1.645	0.002	61.74	0.10
3	Combined	25.40	0.03	1.637	0.001	61.33	0.11
	Initial Group	25.43	0.03	1.638	0.001	61.40	0.09
	Final Group	25.38	0.01	1.637	0.002	61.26	0.09
4	Combined	25.33	0.03	1.655	0.005	61.61	0.12
	Initial Group	25.32	0.05	1.650	0.001	61.52	0.08
	Final Group	25.34	0.01	1.659	0.001	61.71	0.06
5	Combined	25.27	0.16	1.617	0.002	61.80	0.08
	Initial Group	25.13	0.02	1.615	0.001	61.80	0.08
	Final Group	25.42	0.04	1.618	0.002	61.79	0.08
6	Combined	25.23	0.21	1.637	0.001	61.83	0.04
	Initial Group	25.05	0.06	1.637	0.001	61.83	0.04
	Final Group	25.42	0.08	1.636	0.002	61.82	0.04
7	Combined	25.52	0.01	1.622	0.004	62.41	0.08
	Initial Group	25.52	0.01	1.622	0.002	62.36	0.06
	Final Group	25.52	0.01	1.622	0.006	62.46	0.06
8	Combined	25.45	0.09	1.622	0.003	62.63	0.08
	Initial Group	25.37	0.03	1.623	0.001	62.66	0.08
	Final Group	25.53	0.01	1.621	0.004	62.60	0.07
10	Combined	25.25	0.49	1.588	0.002	62.13	0.08
	Initial Group	24.79	0.02	1.589	0.002	62.18	0.07
	Final Group	25.71	0.07	1.587	0.001	62.09	0.06
11	Combined	26.07	1.3	1.592	0.003	61.69	0.15
	Initial Group	26.72	1.8	1.593	0.002	61.69	0.17
	Final Group	25.41	0.01	1.591	0.003	61.69	0.14
13	Combined	25.25	0.15	1.606	0.002	61.93	0.09
	Initial Group	25.11	0.03	1.605	0.001	61.91	0.12
	Final Group	25.38	0.03	1.606	0.002	61.95	0.04
14	Combined	25.32	0.17	1.605	0.005	62.04	0.06
	Initial Group	25.16	0.02	1.605	0.004	62.03	0.07
	Final Group	25.47	0.06	1.604	0.006	62.06	0.06
15	Combined	25.27	0.26	1.600	0.003	62.05	0.10
	Initial Group	25.03	0.03	1.600	0.003	62.03	0.07
	Final Group	25.50	0.08	1.599	0.004	62.07	0.13
16,17 Repeat 15	Combined	25.45	0.03	1.603	0.003	61.75	0.11
	Initial Group	25.42	0.03	1.603	0.003	61.77	0.11
	Final Group	25.47	0.01	1.603	0.003	61.73	0.13
18	Combined	25.49	0.07	1.610	0.004	61.86	0.16
	Initial Group	25.54	0.04	1.609	0.005	61.98	0.15
	Final Group	25.44	0.03	1.610	0.003	61.74	0.05
19,20	Combined	25.46	0.03	1.596	0.003	62.29	0.09
	Initial Group	25.44	0.02	1.592	0.002	62.34	0.07
	Final Group	25.48	0.04	1.596	0.004	62.23	0.07
3,4,5,7,8 Si repeats	Combined	-	-	-	-	62.12	0.15
	Initial Group	-	-	-	-	62.11	0.12
	Final Group	-	-	-	-	62.14	0.18

KANSO reference seawater lot. CA		Nitrate + Nitrite		Phosphate		Silicate	
Certified value		20.19		1.441		37.46	
Expanded uncertainty		0.16		0.014		0.23	
Deployment	Assayed result	Mean	SD	Mean	SD	Mean	SD
4	Combined	20.26	0.03	1.504	0.004	37.41	0.10
	Initial Group	20.24	0.01	1.500	0.001	37.32	0.03
	Final Group	20.28	0.01	1.508	0.002	37.49	0.06
5	Combined	20.18	0.09	1.483	0.003	37.45	0.10
	Initial Group	20.09	0.02	1.482	0.002	37.43	0.12
	Final Group	20.26	0.01	1.485	0.003	37.47	0.08
11	Combined	20.26	0.05	1.455	0.002	37.94	0.08
	Initial Group	20.21	0.01	1.457	0.002	37.96	0.11
	Final Group	20.30	0.03	1.454	0.000	37.93	0.04

KANSO reference seawater lot. BV		Nitrate + Nitrite		Phosphate		Silicate	
Certified value		36.23		1.570		103.8	
Expanded uncertainty		0.75		0.051		1.4	
deployment	Assayed Result	Mean	SD	Mean	SD	Mean	SD
10	Combined	35.91	0.67	2.557	0.001	104.99	0.11
	Initial Group	35.31	0.17	2.555	0.001	104.92	0.10
	Final Group	36.51	0.24	2.559	0.003	105.06	0.05

4.4 Flagged and Missing Data.

Deployment	RP	Analysis	Flag	Reason for Flag or Action
1	3	Salt, oxygen, nutrients	No results	Niskin did not close. No sample collected.
2	3	Salt, oxygen, nutrients	Bad, 133	Niskin leaked. SIO oxygen sample draw temperature high compared to adjacent niskins.
2 to 20	7	Salt, oxygen nutrients	No results	Niskin imploded. No sample collected. Not replaced for remaining deployments.
2	21	oxygen	Bad, 133	Outlier compared with CTD Oxygen. Reason unknown.
2	24	Salt, oxygen nutrients	No results	Niskin did not close. No sample collected.
4	4,5	oxygen	No results	Sample collected but not assayed. Oxygen flask lids swapped.
5	4	salt	No result	Sample assayed, software failure, result not recorded.
6	1 to 4	oxygen	Bad, 133	Sample assayed, titration endpoint not well defined. Cause unknown.
7	18	salt	No result	Sample not assayed. Accidentally missed.
7	19	salt	Bad, 133	Outlier compared with CTD salinity. Reason unknown. Cause unknown.
10	All	salt	Suspect, 69	Square salinity bottle. Lid hand tight. Not torqued as per procedure. Potential for evaporation.
11	5	salt	Suspect, 69	Round salinity bottle. Cracked lid. Potential for evaporation.
11	10, 21	oxygen	Bad, 133	Sample assayed, titration endpoint not well defined. Cause unknown.
13	1	Salt, oxygen nutrients	Bad, 133	Salt, oxygen, NOx, Phosphate outliers compared with RP2 sample from same depth. Silicate flagged accordingly. Cause unknown.
13	4,5	oxygen	Bad, 133	Sample assayed, titration endpoint not well defined. Cause unknown.
14	1 to 10	Salt, oxygen, nutrients	Suspect, 69	Niskin bottles re-pressurised from 1350 down to 2247. Wire paid out to fix drum spooling.
15	1 to 9	Nutrient NOx	Bad,133	AA3 instrument leak affecting NOx. Samples repeated in the next AA3 run. Si and phosphate for repeated samples flagged bad, results not required.
16	8	oxygen	Bad, 133	Sample assayed, titration endpoint not well defined. Cause unknown.
18	3 to 6	Salt, oxygen, nutrient	Bad, 133	Samples assayed. Niskin leaked. Adjacent Lanyard caught in top cap.
18	13	Oxygen	Bad, 133	Sample assayed, titration endpoint not well defined. Cause unknown.
19	1,10	Oxygen	Bad, 133	Samples assayed, titration endpoint not well defined. Cause unknown.

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 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 ± 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.