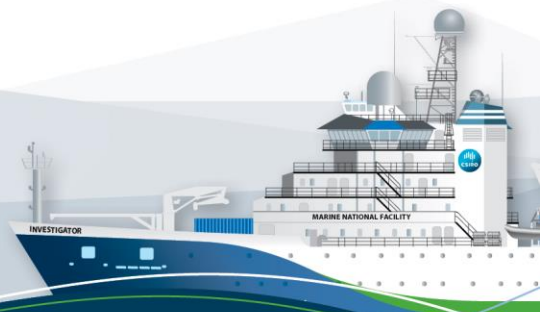
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2015_e03
Equipment Champions	Rudy Kloser, CSIRO Tim Ryan, CSIRO
Voyage title:	Acoustics and pelagic ecosystems – testing equipment, developing procedures and sample collection
Report compiled by:	Peter Hughes.



Contents

1 Executive Summary

Hydrology data processed and report compiled in 2020.

Hydrology samples collected from the CTD rosette and underway seawater supply were assayed for dissolved oxygen, nutrients and salinity in the on-board laboratory by CSIRO hydrochemists. The procedures used comply with CSIRO hydrochemistry standard operating procedures and the GO-SHIP guidelines.

Additional hydrology samples were collected for hydrochemistry method development. These results are not included in the final data set.

In 2018 our nutrient sampling analysis and data processing procedures were published in the literature. Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NOx) and nitrite:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

1.1 Voyage Objective

To trial the vessels acoustic and pelagic ecosystem sampling capabilities as part of achieving full operational status with equipment and procedures.

1.2 Hydrology Data Quality

High quality data was produced for the three measured parameters, nutrients, dissolved oxygen and salinity. The assayed results for the KANSO reference material for nutrients in seawater were within 1 to 3% of its certified values. The difference between the salinity bottle results and the unprocessed CTD instrument was less than 0.02 practical salinity units. The difference between the dissolved oxygen bottle results and the unprocessed CTD instrument was less than 5umol L^{-1}.

1.3 Significant Issues Encountered

We were unable to determine the nutrient ammonium due to the samples being contaminated from the tubes used to collect the samples. These tubes were a different brand than normally used to collect nutrient samples. Once identified as the contamination source these tubes were no longer used.

During the voyage, the number used to identify the CTD deployment operation were the scientist's station number. These have been changed back to the standard sequential CTD deployment numbers post voyage, against which this hydrology data is reported.

1.4 Further Information

Final hydrology data, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre (DataLibrariansOAMNF@csiro.au). For any information related to CSIRO O&A Hydrochemistry contact O&AHydroChemistryFacility@csiro.au.

2 Itinerary

Figure 1: Ship's voyage track.

Departure	
Date	**Port**
16 April 2015	Hobart

Arrival	
Date	**Port**
23 April 2015	Hobart

3 Sample Results Summary

Samples From	Nutrients	Salinity	Dissolved Oxygen
CTD Rosette	49	37	31
Underway Lab	24	12	12

4 Methodology Summary

CSIRO hydrochemistry standard operating procedure numbers are tabulated in Appendix 8.1. and are available on request. A synopsis of these procedures follows.

4.1 Nutrient Methods

Sampling and measurement conform to GO-SHIP guidelines.

Nutrient seawater samples were collected in 15mL HDPE tubes (deployments 1 to 4) and 10mL PP tubes (deployments 5 – 8). Tubes were rinsed three times with the sample before collection. The 15mL tubes were discontinued after it was determined that they contaminated the samples with ammonium.

Four nutrient analytes were measured; silicic acid ($Si(OH)_4$) known as silicate, orthophosphate (PO_4^{2-}) known as phosphate, nitrate + nitrite (NO_3^- + NO_2^-) known as NO_x, and nitrite (NO_2^-). The analytes were determined by spectroscopy on a Seal AA3HR segmented flow auto-analyser (AA3) using the methods;

Silicate: Ammonium molybdate/ tartaric acid/ tin (II) chloride method, absorbance measured at 820nm. Based on Armstrong et al (1967)

Phosphate: Ammonium molybdate/ antinomy potassium tartrate/ ascorbic acid method, absorbance measured at 880nm. Based on Murphy and Riley et al (1962)

NOx: Cadmium-copper reduction with ammonium chloride buffer/ sulphanilamide/ N-(1-naphthyl)-ethylene method, absorbance measured at 520nm. Based on Wood et al (1967)

Nitrite: Sulphanilamide/ N-(1-naphthyl)-ethylene method for nitrite, absorbance measured at 520nm. Based on Wood et al (1967)

The AA3 instrument was calibrated with standard solutions that were made less than 24 hours prior to each run. The stock solutions, used to make the standard solutions, were prepared in the Hobart hydrochemistry laboratory before the voyage. The top concentration of each nutrient standard and the nominal detection limit are listed in Appendix 7.5

Analytical accuracy was tracked with KANSO CO LTD reference material nutrient seawater solution (RMNS) lot BW. Each AA3 analysis run used a new RMNS solution. The RMNS results per CTD deployment are in table.

The AA3 raw data is processed in Hypro before being reported in the final hydrology data set.

4.2 Salinity Method

Salinity samples were collected in 250mL amber glass bottles sealed with a cone insert in the lid. The seawater collected by the CTD rosette deployment was delivered to the sample bottle via a PTFE draw tube attached to the Niskin bottle's tap.

The salinity samples were stored at room temperature in the hydrochemistry lab for a minimum of 8 hours prior to being measured.

The samples were measured on a Guildline model 8400B salinometer. The instrument is calibrated, before each run with OSIL IAPSO standard seawater lot P157.

The salinometer conductivity ratio measurements are recorded by an OSIL salinity data logger which then calculates the salinity. These results are reported in the final hydrology data set.

4.3 Dissolved Oxygen Method

The method is based on the Winkler (1888) titration method, with modifications by Carpenter (1965) and Culberson et al (1991). The samples are assayed on an auto-titrator instrument built by the Scripps Institute of Oceanography (SIO).

Dissolved oxygen samples are collected in 140mL iodine flasks and the dissolved oxygen fixed with two reagents, manganese (II) chloride and sodium iodide/ sodium hydroxide. For assay, the whole sample is acidified, and the liberated tri-iodine is titrated with a standardised sodium thiosulphate solution using an automated Dosimat 625 fitted with a 1 mL burette. The end point is detected spectrographically by UV transmittance at 360nm.

Before each run, the thiosulphate titrant is standardised with a 10 mL aliquot of a potassium iodate primary standard and a blank correction is also determined. The primary standard was made in the Hobart hydrochemistry laboratory prior to the voyage.

The SIO instrument results, in ml L^{-1}, are converted to µ mol L^{-1} by Hypro and are reported in the final hydrology data set.

5 Data Processing Summary

The CTD deployment and hydrology sampling meta-data, measured bottle salinity results, bottle dissolved oxygen assay results and the nutrient assay raw absorbance data are processed by our in-house software program HyPro version 5.7 (Hydrology Processor).

All data and results, other than nutrients, are imported into Hypro and reported as is without further adjustment.

Nutrient results, however, are derived by Hypro from the AA3 instrument raw absorbance data. Using the raw absorbance data, Hypro constructs the absorbance trace, identifies and measures the peak heights, derives the calibration curves, interpolates the nutrient concentrations, and applies corrections for the measured changes in the instrument reponse during the run (i.e carry-over, baseline and sensitivity drift).

6 Data Quality

All hydrology data is flagged to indicate quality.

The flags are assigned by Hypro and the operator. Hypro flags data good as well as data that is suspect/ bad due to analytical instrument issues related to signal noise, over-range data and measured detection limits. Operators flags data that is suspect/ bad due to errors related to sampling, instrument calibration, discrepancies between bottle results and CTD instrument and outliers in the analyte versus depth profiles.

A summary of the flagged hydrology data is tabulated in Appendix 7.3.

6.1 Nutrient Data Quality

KANSO certified RMNS lot BW was assayed in triplicate in each run to monitor analytical accuracy. Its certified nutrient values and results per CTD deployment are in Appendix 7.1 and 7.2

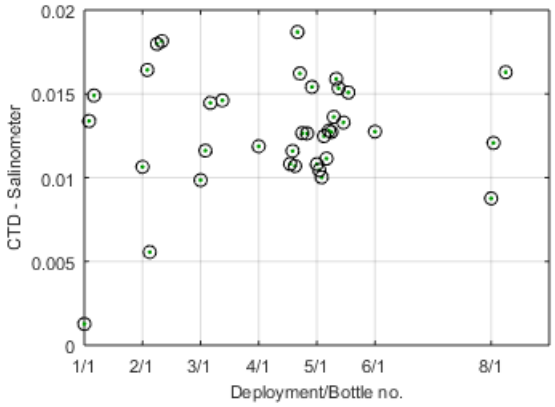
For in2015_e03, the RMNS lot BW results for NOx and silicate are within 1.5%, phosphate is within 2% (except for CTD deployment 4) and nitrite within 0.02 µmol L^{-1} of their certified mean concentration.

The nutrient results in the Hydrology data set are as assayed and are NOT adjusted to correct for measured RMNS lot BW bias from its certified value.

6.2 Salinity Data Quality

For in2015_e03, the bottle salinity data is good and in close agreement with the unprocessed CTD data. The difference between the bottle and unprocessed CTD data is less than 0.02 PSU, evenly offset for the voyage duration. Plot below.

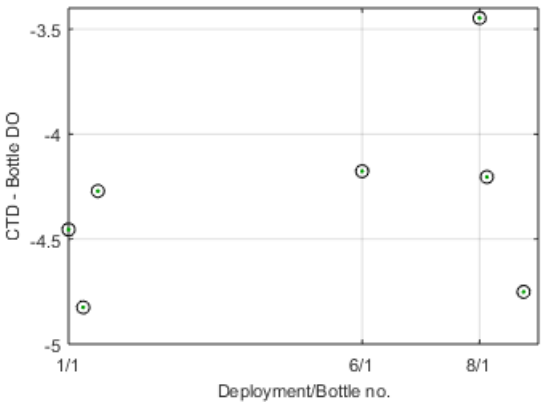
The CTD salinity data is not included in the published hydrology data set.



6.3 Dissolved Oxygen Data Quality

For in2015_e03, the bottle dissolved oxygen results are good and in reasonable agreement with the unprocessed CTD data. The difference between the bottle and the unprocessed CTD dissolved oxygen data for deployments 1, 6 and 8 is less than 5 µmol L^{-1}. For the remaining deployments there was no CTD dissolved oxygen data available to determine the difference due to technical issues with CTD data acquisition during these deployments. Plot below.

The CTD dissolved oxygen data is not included in the published hydrology data set.



7 Appendix

7.1 Certified Reference Materials

Salinity: OSIL IAPSO Standard Seawater, batch P157, 34.994 PSU

Nutrients: KANSO Reference Material Nutrient Seawater (RMNS) lot BW

certified concentrations ± expanded uncertainty (U) at 21°C. Units: µ mol L^{-1}

Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrate (NO_3)	Nitrite (NO_2)	NO_3+ NO_2 (NO_X)
60.518 ± 0.430	1.593 ± 0.014	25.037± 0.205	0.052 ± 0.010	25.089 ± 0.215

7.2 Nutrients: RMNS results for each Analysis Run & CTD Deployment.

AA3 Analysis Run	**CTD Deployment**	**Silicate ($Si(OH)_4$) (µmol L^{-1})**	**Phosphate (PO4) (µmol L^{-1})**	**Nitrite (NO2) (µmol L^{-1})**	**NOx (NO2 + NO3) (µmol L^{-1})**
3	1	60.85	1.619	Not assayed.	25.27
4	2,3	60.83	1.616	Not assayed	25.28
5	4	60.93	1.637	0.068	25.40
6	5	60.98	1.619	0.059	25.48
7	6, 7, 8	60.65	1.617	0.060	25.58
RMNS Lot BW		60.52	1.593	0.052	25.09

7.3 Flagged Data

7.3.1 Flag Key for CSIRO Hydrology Data Set

Flag	**Description**
0	Data is GOOD
63	Result below nominal detection limit. Nutrients Only.
69	Method Detection Limit (MDL) measured during AA3 run is greater than the nominal MDL. Nutrients Only.
133	Data is BAD. Flagged by operator. Due to sampling/ analytical errors. Data not reported.
141	No Data. Used in netcdf results file only.

7.3.2 Missing or suspect nutrient data

CTD Deployment	RP	Flag	Analyte	Reason for Flag or Action
All	All	141	NH_4	Sampled and Assayed. Not reported due to contamination from nutrient sample tubes.
1 to 3	All	141	NO_2	Not assayed for nitrite due to AA3 Instrument nitrite channel sensitivity and noise issues.
5	2 to 6	141	All	Not Sampled. Reason Unknown.

7.3.3 Missing or suspect salinity data

CTD Deployment	RP	Flag	Reason for Flag or Action
2	5	141	Not sampled. Reason unknown.
3	4, 8	141	Not sampled. Reason unknown.
7	1 to 5	141	Not sampled. Reason unknown.
8	3, 5	141	Not sampled. Reason unknown.

7.3.4 Missing or suspect dissolved oxygen data

CTD Deployment	RP	Flag	Reason for Flag or Action
2	5	141	Not sampled. Reason unknown.
3	4, 8	141	Not sampled. Reason unknown.
7	1 to 5	141	Not sampled. Reason unknown.
8	3, 5	141	Not sampled. Reason unknown.

7.4 Laboratory temperature

	Main Lab	Salt Lab
Min	20.8 ℃	Not monitored
Max	24.5 ℃	Not monitored
Mean	22.1 ℃	Not monitored

7.5 Instrumentation

Salinity: Guildeline Autosal 8400B	s/n 71613
Accuracy	± 0.001 practical salinity units
Range	0.005 – 42.0 Practical Salinity Unit (PSU).

Dissolved Oxygen: Scripts Auto Titrator	s/n -
Accuracy	± 0.5 µmol L^{-1}
Range	30 – 300 µmol L^{-1}

Nutrients: Seal AA3HR segmented flow analyser				
Units: µmol L^{-1}	Silicate ($Si(OH)_4$)	Phosphate (PO_4)	Nitrite (NO_2)	NOx (NO_2 + NO_3)
Top standard	112	3.0	2.0	37
Nominal MDL	0.2	0.02	0.02	0.02
Method Uncertainty (historical data)	± 0.017	± 0.024	± 0.019	± 0.14

8 References

1. GO-SHIP guidelines, nutrients: http://dx.doi.org/10.25607/OBP-555

2. CSIRO Hydrochemistry, nutrients: Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

8.1 CSIRO Hydrochemistry Methods (2015)

Determination of Silicate by AA3	M1 v01
Determination of phosphate by AA3	M2 v02
Determination of Nitrate and Nitrite by AA3	M3 v01
Determination of Dissolved Oxygen by UV titration	M5 v01
Determination of Salinity by Guildline and OSIL software	G3 v01
Nutrient Sampling	S3 v01
Dissolved Oxygen Sampling	S1 v01
Salinity Sampling	S2 v01