

# **RV** INVESTIGATOR

# HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	IN2024_V01			
Chief Scientist	Dr Annie Foppert and Dr Steve Rintoul			
Voyage title:	Multidisciplinary Investigations of the Southern Ocean (MISO): Linking Physics, Biochemistry, Plankton, Aerosols, Clouds and Climate			
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# **1 Executive Summary**

#### 1.1 Objectives

The objective of this voyage was to improve the understanding of how the Southern Ocean region influences the Earth system and use this knowledge to improve models. This voyage characterised the properties of aerosols, clouds, radiation, and precipitation over the Southern Ocean south of Australia and investigated how they are shaped by interactions between the ocean, atmosphere, and biosphere. Repeat observations were used to discover how and why the region is changing and the consequences of Southern Ocean change for climate, biogeochemical cycles, biological productivity, and the future of the Antarctic Ice Sheet. The voyage sought new insights into the processes controlling the availability of iron and other trace elements and their role in regulating productivity in the Southern Ocean and the production of marine organic aerosols that can drive cloud nucleation. The observations and insights gained from the voyage will be used to develop, test, and implement new parameterisations for models used for weather forecasts and climate projections.

## **1.2 General Hydrochemistry Information**

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity. Overall data collected was of high quality. No significant sample collection, analysis, or data processing issues were encountered.

Five nutrients were determined: silicate, phosphate, nitrate + nitrite, nitrite and ammonium using AA3HR autoanalyser. Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values. Missing and suspect hydrology samples are listed in Appendix section.

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/Iom3.10294

If publishing ammonium data, please cite the following:

Rees, C., Janssens, J., Sherrin, K., Hughes, P., Tibben, S., McMahon, M., McDonald, J., Camac, A., Schwanger, C. and Marouchos, A., (2021) *"Method for Reproducible Shipboard Segmented Flow Analysis Ammonium Measurement Using an In-House Reference Material for Quality Control."* 

Frontiers in Marine Science, 8.

doi:10.3389/fmars.2021.581901

Final hydrology data, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre.

For Data, contact: NCMI\_DataLibrarians@csiro.au

# 2 Itinerary

Departed: Hobart at 1300, 02 January 2024 Arrived: Fremantle at 1000, 05 March 2024



Figure 1. Voyage track.

# 3 Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
Dr Annie Foppert	Co-Chief Scientist	UTAS
Dr Steve Rintoul	Co-Chief Scientist	CSIRO
Margot Hind	Voyage Manager	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Christine Rees	Hydrochemist	CSIRO
Pavie Nanthasurasak	Hydrochemist	CSIRO
Maddy Lahm	Hydrochemist	CSIRO

# 4 Summary

## 4.1 Sample Type and Number Assayed

Analysis	Samples Assayed	Туре
Salinity	2233	CTD
	60	TSG
	25	UWY
Dissolved Oxygen	2258	CTD
	25	UWY
Nutrients	2260	CTD
	25	UWY
	491	EXP
	45	TMR

Table 2: Sample Type and Number Assayed

#### **4.1.1 CTD samples (Conductivity, Temperature, Density)**

- Taken from the 12 L Ocean Test Equipment bottles on the CTD rosette that is deployed at depth for water collection.
- A total of 103 CTD deployments were sampled by:
  - Science party: Annie Foppert, Kathy Gunn, Paul Spence, Kaihe Yamazaki, Julia Neme, John Akl, Wayne Dillon, and Sophie Bestley.

#### 4.1.2 Thermosalinograph (TSG) samples

- Taken from the underway instrument clean seawater line supplying the pCO2 instrument in the underway laboratory.
- TSG samples collected by hydrochemistry. Results emailed to Vito Dirita (CSIRO) at the completion of the voyage.
- TSG sampling team: Pavie Nanthasurasak, Merinda McMahon, Maddy Lahm and Christine Rees
- Refer to voyage EVERlog for TSG sample information.

#### 4.2 Data Processing Overview

#### 4.2.1 Conventional hydrology data

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated below (Fig.2).



Figure 2. Hydrology Data Processing Flow Diagram.

# **5** Salinity

## **5.1 Salinity Measurement Parameters**

Details			
HyPro Version	5.7		
Instruments	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72088. Bath temperature 24.0°C		
Software	Ocean Scientific International Ltd (OSIL) Data Logger version 1.2		
Hydrochemistry Methods	Sampling: WI_Sal_002		
	Analysis: SOP 006		
Accuracy	± 0.001 practical salinity units		
<b>Reference Material</b>	OSIL IAPSO – Batch P167, use by 21/02/2026, K <sub>15</sub> = 0.99988		
Sample Container	200 ml volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.		
Sample Storage	Stored in salinometer lab for minimum of 8 hrs before the measurement.		
Lab Temperature	Mean 21.8°C SD 0.6°C (Ruuvi sensor)		
Analysts	Pavie Nanthasurasak		
Comments	See DAP report for CTD calibration details.		

#### Table 3: Salinity Measurement Parameters

#### 5.2 Salinity Method

Salinity samples were measured on a Guildline Autosal 8400B instrument operated in accordance with its technical manual. The measured value is recorded with an OSIL data logger.

Practical salinity (S) is defined in terms of the ratio ( $K_{15}$ ) of the electrical conductivity measured at 15°C 1 atm of seawater to that of a potassium chloride (KCI) solution of mass fraction 32.4356 x 10<sup>-3</sup>.

Before each lot of sample measurements, the Autosal is calibrated with standard seawater (OSIL, IAPSO) of known  $K_{15}$  ratio. A new bottle of OSIL standard is used for each calibration. The frequency of calibration is at least one per run.

Method: The salinity sample is collected in a 200 ml OSIL bottle. The bottle is rinsed then filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, till overflowing. The bottle is removed from the straw and the sample is decanted to allow a headspace of approximately 25 cm<sup>3</sup>. A dry plastic insert is fitted, the bottle inverted and rinsed with water then capped and stored cap-down until measured. To measure, the Autosal cell is flushed three times with the sample and then measured

after the fourth and fifth flush. The OSIL data logger software captures the conductivity ratio and calculates the practical salinity. The output from the data logger is imported into HyPro and collated with the CTD deployment meta-data.

## 5.3 CTD Salinity vs Bottle Salinity Plot

For this voyage, the difference between the unprocessed (uncorrected) CTD value and the measured bottle value is generally less than 0.02 PSU. The larger differences are for shallow samples across the sudden changes in the thermohaline profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the <u>NCMI\_DataLibrarians@csiro.au</u> for corrected CTD data.



**Figure 3.** CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Red = BAD, Black = UNPROCESSED. Units: PSU (dimensionless). \**Note: Bad salinity bottle data is listed in appendix 8.4.* 

#### 5.4 OSIL Salinity Standard Plot

The instrument is calibrated with OSIL standard seawater lot P167 (PSU = 34.995). The plot below shows the OSIL lot P167 measured results for each run on this voyage. The blue line represents the mean of all standards measured for standardisation.



**Figure 4.** Measured OSIL standard for each salinity run and average value (P167 mean) across IN2024\_V01.

# 6 Dissolved Oxygen

## 6.1 Dissolved Oxygen Measurement Parameters

Details	
HyPro Version	5.7
Instrument Automated Photometric Oxygen System	
Software	Scripps Institution of Oceanography (SIO)
Hydrochemistry Methods	Sampling: WI_DO_001
	Analysis: SOP 005
Accuracy	± 0.5 μmol L <sup>-1</sup>
Lab Temperature	Mean 20.7°C SD 0.3°C (Ruuvi sensor)
Sample Container type	140 ml glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis.
Analysts	Maddy Lahm
Comments	See DAP report for CTD calibration details.

 Table 4: Dissolved oxygen measurement parameters.

## 6.2 Dissolved Oxygen Method

Scripps Institution of Oceanography method used. The method is based on the whole bottle modified Winkler titration of Carpenter (1965) plus modifications by Culberson *et al* (1991).

Method: The sample is collected in an iodine determination flask of known volume. 1 ml of manganese (II) chloride solution followed by 1 ml of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum of 30 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, Mn (IV) is reduced to the divalent state liberating iodine. The iodine is titrated with a standardised thiosulphate solution using a Metrohm 876 Dosimat fitted with a 1 ml burette. The endpoint is determined by measuring the decrease in the UV absorption 365 nm.

The thiosulphate solution is standardised by titrating it against a 10 ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two titres of consecutive additions of 1 ml aliquots of potassium iodate to the same blank sample. The standardisation is done at least once per 12-hour shift, when samples are being assayed.

The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

## 6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

For this voyage, the difference between the unprocessed CTD value and the measured bottle value is generally less than 20  $\mu$ mol L<sup>-1</sup>. The larger differences are for shallow samples across the sudden changes in the dissolved oxygen profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the <u>NCMI\_DataLibrarians@csiro.au</u> for corrected CTD data.



**Figure 5.** CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Red = BAD. Black = UNPROCESSED. Units:  $\mu$ mol L<sup>-1</sup>. \**Note: Bad oxygen bottle data is listed in appendix 8.5.* 

# 6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction

The variation in thiosulphate concentration is within our QC parameter of less than 0.0005 N between standardisations. Three batches of thiosulphate reagent were used during the voyage. The mean normality is as follows:

CTD Deployment 1 to 103:	Mean: 0.24229 N
	SD: 0.00031 (n=50)

The blank correction is used in the calculation of the thiosulphate normality and is due to oxidisable species in the MQ water that is added to the KIO<sub>3</sub> aliquot before the titration.

The red lines in figure 5 indicate  $\pm$  0.0005 N either side of the mean titrant (thiosulfate) concentration and the blank concentration. The Thiosulphate normality should not vary more than 0.0005 N between analyses.



**Figure 6.** Thiosulphate standardisation (top) and blank correction plots (bottom). Thiosulfate standardization values seen outside of the lines comply with the QC parameter, that is the Thiosulphate normality should not vary more than 0.0005 N between analyses. Blanks from earlier runs were ran with an alkaline iodide solution known to produce negative blank values. High blanks seen twice reflected the low standard volume and high volatility of the solution noted.

# **7** Nutrients

## 7.1 Nutrient Measurement Parameters

Table 5: Nutrient measurement parameters analysed with Seal AA3HR segmented flow analyser. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details					
Instrument	Seal AA3HR	Seal AA3HR segmented flow analyser			
HyPro version	5.7				
<b>Operating Software</b>	AACE 7.10				
Hydrochemistry Sampling Method	WI_Nut_00	1			
Hydrochemistry analysis method	SOP001	SOP002	SOP003	SOP003	SOP004
	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Nutrients Analysed	SiO4 <sup>4-</sup>	PO4 <sup>3-</sup>	$NO_{3}^{-} + NO_{2}^{-}$	NO <sub>2</sub> -	$NH_4^+$
	as Si	as P	as N	as N	as N
Top concentration (μmol L <sup>-1</sup> )	140.0	3.0	42.0	1.4	2.0
Method detection limit (umol L <sup>-1</sup> )	0.2	0.02	0.02	0.02	0.02
Reference Material	KANSO RM	NS lot CM			
Sample Container	CTD: 50 ml HCl solutior	HDPE with screw	cap lids. Reused a	after acid was	h with 10%
Sample Storage	< 4 hours at room temperature after collection or < 12 hours at 4°C after collection				
Sample preparation	Assayed as	neat. No filtration			
Lab Temperature (°C)	Mean 20.7°C SD 0.3°C (Ruuvi sensor)				
Analysts	Merinda M	cMahon and Chris	stine Rees		
Comments	N/A				

## 7.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1 cm flowcells for colorimetric measurements and a JASCO FP2020 fluorescence instrument as the ammonium detector.

Silicate (SOP001): colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660 nm.

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS<sup>1</sup> Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880 nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper – cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 540 nm.

Nitrite (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer. Absorbance measured at 520 nm.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Kérouel and Aminot (1997). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460 nm after excitation at 370 nm.

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.

<sup>1</sup> Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

#### 7.3 HyPro Processing Summary for Nutrients

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and duplicate sample results that do not match.

Suspect calibration points are weighted less when fitting the calibration curve. The cut-off limits for good calibration data are:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE<sup>1</sup>).
- 0.02 umol L<sup>-1</sup> for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect, or bad and flags accordingly. The Flag key is in Appendix 8.7. Missing or suspect nutrient data is tabulated in Appendix 8.6.

<sup>1</sup> World Ocean Circulation Experiment

**Table 6:** HyPro 5.7 Processing Parameters. All instrument parameters, reagent batches, and operationevents are logged for each analysis run. This information is available on request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonium
Data Reported as	µmol L <sup>-1</sup>	µmol L⁻¹	µmol L⁻¹	µmol L⁻¹	μmol L <sup>-1</sup>
Calibration Curve degree	Linear	Linear	Linear	Quadratic	Quadratic
# of points in Calibration	7	6	7	6	6
Forced through zero	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS variance.	N	Ν	Ν	N	Ν
Medium of Standards	Low nutrient seawater (LNSW, bulk on PW1 wharf, CSIRO Hobart) collected in June 2021. Sub-lot passed through a 5-micron filter (filtered in December 2023) and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω wate	er. Dispensed fr	om the Milli Q IQ 7	010 system.	
Duplicate samples.	CTD: Niskins fired at the greatest depth were analysed in duplicate. Single samples were analysed for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.				

## 7.4 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Descriptive statistics are used to ascertain the accuracy and precision of the analysis from the repetitive measurement of the RMNS for silicate, phosphate, NOx, and nitrite in seawater.

For IN2024\_V01, Japanese KANSO certified RMNS lot CM was assayed in triplicate in each run to monitor accuracy. The certified values are listed in Table 7. RMNS lot CO and CP were analysed in 6 runs spread across the voyage as additional accuracy monitoring. An internal bulk quality control (BQC) was also analysed in each run for analysis on AA3HR segmented flow analyser.

For RMNS lot CM, CO and CP NOx, phosphate, and silicate were within 2% and nitrite within 0.04  $\mu$ mol L<sup>-1</sup> of their certified mean concentration.

The GO-SHIP criteria (Hyde et al., 2010), appendix 8.8, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

KANSO publishes the RMNS nutrient values in  $\mu$ mol kg<sup>-1</sup>. These are converted to  $\mu$ mol L<sup>-1</sup> at 21°C. The RMNS is not certified for ammonium. NO<sub>x</sub> is derived by summing the NO<sub>3</sub> and NO<sub>2</sub> values. The assayed RMNS values per CTD deployments are listed in the appendix 8.3.

RMNS	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
Lot CM	102.917 ± 0.512	2.437 ± 0.031	34.017 ± 0.313	0.018 ± 0.006
Lot CO	35.552 ± 0.164	1.205 ± 0.014	16.281 ± 0.195	$0.041 \pm 0.041$
Lot CP	62.569 ± 0.307	1.795 ± 0.018	25.714 ± 0.379	0.318 ± 0.072

Table 7: RMNS certified concentrations  $\pm$  expanded uncertainty (U) at 21°C. Units:  $\mu$ mol L<sup>-1</sup>

#### Table 8: RMNS CM statistics for of this voyage. Units: µmol L<sup>-1</sup>

RMNS CM	Silicate	Phosphate	Nitrate + Nitrite	Nitrite
			(NO <sub>x</sub> )	
Minimum	101.600	2.420	33.630	0.018
Maximum	103.200	2.480	34.530	0.052
Median	102.400	2.450	33.920	0.039
Mean	102.448	2.452	33.924	0.039
Repeatability	0.327	0.011	0.117	0.005

#### 7.5 Nutrient plots of RMNS

The green, pink and red contours are at 1%, 2% and 3% from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02  $\mu$ mol L<sup>-1</sup> increments from the certified value. The blue line is the certified value's expanded uncertainty. Plots are RMNS value versus instrument run number.



Figure 7. Silicate RMNS plot (µmol L<sup>-1</sup>)





Figure 8. Phosphate RMNS plot (µmol L<sup>-1</sup>)



Figure 9. Nitrate + Nitrite (NOx) RMNS plot (µmol L<sup>-1</sup>)



**Figure 10.** Nitrite RMNS plot (µmol L<sup>-1</sup>)

#### 7.6 Measurement Uncertainty

The CSIRO hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on the variation in the calibration curve, calibration standards, pipette and glassware calibration, and precision of the RMNS over time (Armishaw, 2003).

**Table 9:** CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol L<sup>-1</sup>

Calculated Measurement Uncertainty @ 1 µmol L <sup>-1</sup>							
Silicate	Phosphate	Nitrite	Nitrate + Nitrite (NOx)	Ammonium			
±0.017	±0.024	±0.14	±0.019	±0.30 <sup>¥</sup>			

The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

<sup>\*</sup>The ammonium MU precision does not include data for the RMNS.

#### 7.7 Method Detection Limit for Nutrients

The method detection limit (MDL) is set to three times the standard deviation (SD) of the LNSW results (National Association of Testing Authorities 2013). The resultant MDL was used to assess the analysis precision at low concentrations.

**Table 10:** AA3HR auto analyser MDL statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are calculated from every analytical run performed over the voyage. Units:  $\mu$ mol L<sup>-1</sup>

MDL			Nitrate + Nitrite (NOx)	Nitrite	Ammonium
Nominal MDL	0.200	0.020	0.020	0.020	0.020
SD Min	0.000	0.000	0.000	0.000	0.000
SD Max	0.115	0.015	0.006	0.008	0.006
SD Median	0.000	0.006	0.000	0.001	0.000
SD Mean	0.018	0.004	0.002	0.001	0.001
Precision of MDL (SD)	0.018	0.004	0.002	0.001	0.001

Silicate Phosphate

## 7.8 Sampling Precision

Initial sampling precision is determined with the CTD test deployment (CTD 1) where multiple bottles are fired the same depth, each of which is then sampled for hydrochemistry (Table 11).

	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
			(NO <sub>X</sub> )		
Minimum	52.000	2.250	32.830	0.006	-0.010
Maximum	52.600	2.270	33.020	0.014	0.000
Mean	52.222	2.259	32.911	0.01	-0.009
SD	0.124	0.004	0.055	0.002	0.002

**Table 11:** CTD deployment 1. 36 bottles at 1000 dbar. Units: μmol L<sup>-1</sup>.

Duplicate nutrient samples were collected from the greatest depth of subsequent CTD deployments. For nutrients, the sampling precision is good if the difference from the mean of duplicate measurements is less than the nominal method detection limit. The exception: NOx which uses the limit 0.06  $\mu$ mol L<sup>-1</sup>

Duplicate samples that exceed this limit are flagged 69 (suspect). These are tabulated in appendix 8.6.

## 7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: 14.45

The Redfield Ratio is a check for the accuracy of phosphate and NOx analysis. The ratio is the required amount of P to N for marine phytoplankton growth.



**Figure 11.** Redfield ratio plots. Note: please refer to appendix 8.6 for explanation of the outlier point in this plot.

#### 7.10 Temperature and Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry laboratory and within the AA3HR instrument were measured and logged in the following locations:

- 1) Above the AA3 auto sampler
- 2) On each deck of the AA3 chemistry modules, post heater
- 3) Inside each detector of the AA3

Data was measured using Ruuvi temperature logger and humidity sensor and logged and monitored in Grafana. Measurements were recorded every 1 second for the duration of the voyage. If required, this data will be provided on request.

# 8 Appendix

# 8.1 Salinity: Reference material used

OSIL IAPSO Standard Seawater			
Batch	P167		
Use by date	21/02/2026		
K <sub>15</sub>	0.99988		
PSU	34.995		

## 8.2 Nutrients: RMNS results for each CTD Deployment

#### 8.2.1 Lot CM (µmol L<sup>-1</sup>)

Run #	CTD #	Other Samples	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
1	1	N/A	102.927	2.463	34.491	0.034
2	2	N/A	102.391	2.448	33.883	0.039
3	3	N/A	102.603	2.457	33.989	0.041
4	4	N/A	102.602	2.462	33.982	0.037
5	5	N/A	102.538	2.445	33.986	0.037
6	6 (5 PO4 repeat)	N/A	102.403	2.443	33.889	0.037
7	7	N/A	102.345	2.433	33.888	0.037
8	8	N/A	102.052	2.444	33.977	0.039
9	9	N/A	102.810	2.463	33.910	0.032
10	10	N/A	N/A	N/A	N/A	0.040
11	10	N/A	102.880	2.435	33.967	N/A
12	11	N/A	102.880	2.447	34.010	0.033
13	12	N/A	103.033	2.454	34.090	0.036
14	13 + 14	N/A	102.516	2.426	33.705	0.036
15	15	Uwy 001-004 TMR NPP1 (1-12)	103.035	2.443	34.047	0.025
16	16	N/A	102.348	2.460	33.953	0.039
17	17	N/A	102.206	2.456	34.032	0.030
18	18	N/A	102.412	2.455	34.075	0.039
19	19	N/A	102.455	2.455	34.097	0.043

20	20	N/A	102.449	2.465	34.028	0.039
21	21	N/A	102.182	2.444	33.902	0.032
23	22	N/A	102.332	2.469	34.011	0.039
24	N/A	Exp20240123 SIMBA mid, PSI light mid and PSI dark mid	102.047	2.458	33.887	0.040
26	23	N/A	102.852	2.471	34.015	0.039
27	24	Exp20240125 SIMBA final	102.803	2.460	34.032	0.034
28	25	N/A	102.817	2.463	34.001	0.040
29	26	N/A	102.542	2.459	34.049	0.038
30	27	N/A	102.383	2.447	34.134	0.041
31	N/A	Exp20240126 PSI light final, PSI dark final uwy005-uwy009	102.495	2.467	34.108	0.037
32	28	N/A	102.422	2.456	34.057	0.045
33	N/A	Exp20240127 SOAPIE Exp20240127ME2_T0	102.703	2.459	33.925	0.039
34	29	tmr20240128_R1-R12 Exp20240128ME2_T1	102.951	2.457	34.035	0.043
35	30		102.634	2.450	33.841	0.040
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	102.727	2.464	33.813	0.045
37	31	Exp20240130ME2_T3	103.037	2.459	33.948	0.034
38	32	N/A	102.898	2.475	33.951	0.040
39		Exp20240131ME2_T4	102.860	2.465	33.930	0.037
40	33	Exp2024201ME2_T5	102.933	2.460	33.887	N/A
41	33	N/A	N/A	N/A	N/A	0.033
42	34	Exp carboy2 Lavy Exp carboy3 Lavy Exp carboy5 Lavy	102.807	2.450	33.923	0.038
43	35	Exp2024202ME2_T6 Exp20240202SIMBA mid	103.021	2.458	33.938	0.038
44	36	Exp20240202Blob final	102.804	2.449	33.827	0.039
45	37	Exp2024203ME2_T7	103.018	2.451	33.959	0.050
46	38	N/A	102.639	2.448	33.830	0.039
47	39	N/A	102.514	2.459	33.870	0.039

48	40 + 41 (NO NO2 for 41 and exp)	Exp2024204ME2_T8 Exp20240204ME2 NO3 and Mn mid	102.557	2.452	33.922	0.03
49	41	Exp2024204ME2_T8 Exp20240204ME2 NO3 and Mn mid	N/A	N/A	N/A	0.038
50	N/A	Exp20240205PS2 SIMBA final Tmr20240205_R1-R12 Exp20240205ME2_T9 Uwy 010 – 011	102.280	2.445	33.958	N/A
51	N/A	Exp20240205PS2 SIMBA final Tmr20240205_R1-R12 Exp20240205ME2_T9 Uwy 010 – 011	N/A	N/A	N/A	0.043
52	42 + 43	Exp20240205SOAPIE2	102.430	2.464	34.023	0.029
53	44	Exp20240206ME2_T10	102.274	2.439	33.989	0.052
54	45 +4413	Exp20240206PS2 final	102.473	2.454	33.886	0.036
55	46	N/A	102.536	2.452	33.949	0.028
56	47	Exp20240206ME2_T11	102.724	2.434	33.918	0.040
57	48	Exp20240207ME2 NO3 and Mn Final	102.556	2.448	34.039	0.034
58	49	N/A	102.860	2.46	33.905	0.039
59	50	N/A	102.573	2.463	33.970	0.035
60	N/A	Exp20240208ME2_T12	102.404	2.473	34.021	0.037
61	51	N/A	102.731	2.458	33.984	0.040
62	52	N/A	102.656	2.444	33.990	0.041
63	53	N/A	102.306	2.430	33.846	0.041
64	N/A	Exp20240212SIT HL, LL and HLL Exp20240212SOAPIE3	102.623	2.467	33.932	N/A
65	N/A	Exp20240212SIT HL, LL and HLL Exp20240212SOAPIE3 NO2 only	N/A	N/A	N/A	0.041
66	54	N/A	102.798	2.456	33.817	0.036
67	55	N/A	102.640	2.446	33.928	0.038

69	56	Uwy 012 – 022 Exp20240214ME4_T0 filtered	102.362	2.450	33.859	0.036
70	57	Exp2024015ME4_T1 filtered and unfiltered Uwy 023 – 025 Tmr20240215_R1-R12	102.498	2.460	33.882	0.042
71	58	N/A	102.133	2.468	33.945	0.042
72	59	N/A	102.349	2.450	33.884	0.038
73	60	Exp2024016ME4_T12 filtered and unfiltered	102.599	2.448	33.834	0.038
74	61	N/A	102.370	2.453	33.932	0.041
75	62	N/A	102.416	2.457	33.883	0.046
77	63	Exp2024017ME4_T3	102.631	2.466	34.005	0.043
78	64	N/A	102.561	2.457	33.943	0.049
79	65	Exp2024018ME4_T4	102.431	2.454	33.866	0.043
80	66	N/A	102.033	2.442	33.851	0.041
81	67	Exp2024019ME4_T5	102.117	2.453	33.924	0.043
82	N/A	Exp20240219 SIMBA4 mid, PS4 mid	102.167	2.464	33.923	0.038
83	68	N/A	101.956	2.458	33.867	0.042
84	69	Exp20240220ME4_T6	101.887	2.446	33.892	0.038
85	70	N/A	102.334	2.453	33.881	0.038
86	71	N/A	102.112	2.450	33.978	0.044
87	72	Exp20240221ME4_T7	102.399	2.452	33.875	0.043
88	73	Exp20240222 SOAPIE5_T0	102.203	2.460	33.948	0.037
89	74	Exp20240222ME4_T8	102.406	2.454	33.906	0.038
90	75	Exp20240222_SOAPIE4	102.099	2.460	33.883	0.040
91	76	N/A	101.898	2.443	33.844	0.045
92	77	Exp20240223ME4_T9	102.158	2.444	33.824	0.041
93	N/A	Exp20240223 SIMBA4 final, PS4 final	102.222	2.445	33.845	0.039
94	78	N/A	101.952	2.441	33.890	0.035
95	79	Exp20240224ME4_T10	101.890	2.435	33.810	0.037
96	80	N/A	102.207	2.437	33.759	0.034
97	81	N/A	102.191	2.451	33.735	0.041
98	82	N/A	102.126	2.448	33.743	0.041

99	83	N/A	102.132	2.454	33.795	0.042
100	84	N/A	102.128	2.440	33.806	0.038
101	85	N/A	102.040	2.437	33.757	0.040
102	86	N/A	102.148	2.449	33.795	0.040
103	87	N/A	102.281	2.444	33.873	0.036
104	N/A	Exp20240227 SOAPIE5	102.076	2.453	33.770	0.035
105	88	N/A	102.199	2.438	33.752	0.039
106	89	ExpBrandon's samples	102.583	2.438	33.799	0.039
107	90	N/A	101.890	2.441	33.826	0.043
108	91	N/A	102.247	2.442	33.855	0.045
109	92	N/A	102.048	2.447	33.695	0.037
110	93 + 94	N/A	102.013	2.433	33.819	0.037
111	95	N/A	102.183	2.442	33.778	0.039
112	96 + 97 + 98	N/A	102.075	2.448	33.802	0.040
113	99 + 100	N/A	102.151	2.442	33.926	0.040
114	101	N/A	102.003	2.463	33.995	0.042
115	102 + 103	N/A	101.734	2.455	33.849	0.035

# 8.2.2 Lot CO (µmol L<sup>-1</sup>)

Run #	CTD #	Other Samples	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
1	1	N/A	35.491	1.216	16.318	0.062
2	2	N/A	35.332	1.211	16.200	0.064
15	15	Uwy 001-004 TMR NPP1 (1-12)	35.426	1.201	16.197	0.050
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	35.138	1.214	16.208	0.066
74	61	N/A	35.316	1.209	16.199	0.062
104	N/A	Exp20240227 SOAPIE5	35.336	1.204	16.268	0.061

Run #	CTD #	Other Samples	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
1	1	N/A	62.580	1.811	25.854	0.319
2	2	N/A	62.344	1.800	25.556	0.323
15	15	Uwy 001-004 TMR NPP1 (1-12)	62.58	1.792	25.604	0.300
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	62.283	1.809	25.570	0.320
74	61	N/A	62.194	1.801	25.600	0.321
104	N/A	Exp20240227 SOAPIE5	62.182	1.791	25.607	0.321

#### 8.2.3 Lot CP (μmol L<sup>-1</sup>)

#### The submitted nutrient results do <u>NOT</u> have RMNS corrections applied.

#### How to use the RMNS for Correction

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

#### Or for smoothing data

Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

# 8.3 Missing or Suspect Salinity Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Flag key: appendix 8.7)

СТD	RP	Flag	Reason for Flag
1	11	133	Data is bad, marked by operator. Bottle insert was not properly pushed in.
38	14	141	No data. The collection of this sample was missed.
38	17	141	No data. The collection of this sample was missed.
38	20	141	No data. The collection of this sample was missed.
55	12	141	No data. The collection of this sample was missed.

61	21	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. The sample had unstable readings at the beginning and became stable later. Cause is unknown, there were no obvious sampling/collection error observed from analyst.
61	22	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. Cause is uncertain but analyst suspected that it could be possible of sampling from wrong Niskin bottle.
65	10	141	No data. The collection of this sample was missed.
75	13	141	No data. The collection of this sample was missed.
75	21	133	Data is bad, marked by operator. Salinity lid was not screwed tightly, and insert was not properly pushed in.
82	17	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. Cause is uncertain but analyst suspected that it could be possible of sampling from wrong Niskin bottle.
94	32	141	No data. The collection of this sample was missed.

## 8.4 Missing or Suspect Dissolved Oxygen Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of the depth profile (Flag key: appendix 8.7).

СТD	RP	Flag	Reason for Flag
8	35	69	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
12	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
14	1	133	Bad sample – bubbles in sample.
17	16	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
19	3	69	Suspect, outlier in vertical profile as well as error plot.
19	6	69	Suspect, outlier in vertical profile as well as error plot.
23	20	133	No endpoint found, indiscriminate amount NaOH/NaI added to sample due to issues with dispensette.
26	21	141	No volume for flask ID, lid insert broke, unable to back calculate volume.
27	8	141	Titration error.
33	1	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
34	6	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.

35	8	133	Incorrect lid was placed in sample bottle resulting in incorrect sample volume.
35	10	133	Incorrect lid was placed in sample bottle resulting in incorrect sample volume.
52	10	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
54	34	133	Unable to get good measurement reading, outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
54	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
56	11	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	11	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	12	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	5	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	7	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	26	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	28	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset
67	30	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
67	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset
72	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
74	15	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
75	22	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
78	10	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.

81	26	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
82	8	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
82	17	133	Seems to match previous bottle reading exactly, sensor does not. Sample likely collected from previous Niskin 16.
83	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	15	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	25	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	27	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
86	16	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
90	1	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
90	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
91	21	69	Had to over titrate. Outlier in vertical profile.

#### 8.5 Missing or Suspect Nutrient Data.

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of the depth profile (Flag key: appendix 8.7). Note: within the csv file many ammonium samples are flagged 63 – below nominal detection limit. Ammonium only occurs in the upper few hundred metres of the ocean and within the Chlorophyl maximum, effectively its concentration is zero at all other depths. Due to the difficulty in analysing ammonium in seawater often the zero concentrations will be reported as a negative value, this is due to the baseline Milli-Q water becoming slightly contaminated due to the air quality within the laboratory, meaning the baseline is slightly greater than zero concentration.

CTD	RP	Analyte	Flag	Reason for Flag
4	3	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
14	28	All	141	No data. The collection of this sample was missed.
22	1	NO2	133	One duplicate bottle point bad due to baseline step up during analysis. Missing data.

38	16	All	141	No data. The collection of this sample was missed.
39	08	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
42	19	All	133	Did not include sample data as it was upside down in rack and was not run until over 12 hrs later after sitting on the bench. Missing data.
45	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good. Slow drip from Niskin bottle.
46	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
47	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
55	11	All	141	No data. The collection of this sample was missed.
56	19	All	141	No data. The collection of this sample was missed.
58	34	All	141	No data. The collection of this sample was missed.
60	32	All	141	No data. The collection of this sample was missed.
64	14	All	141	No data. The collection of this sample was missed.
82	17	All	133	Data matches previous bottle, same for D.O. and salt. Particularly noticeable in SiO4. Sample likely collected from the previous Niskin 16.
100	25	All	141	No data. The collection of this sample was missed.
TMR240215	12	All	133	Sample in wrong position and air went through system, missing data.
EXP240215ME4 MC1 a T1 F	N/A	NO2	134	Software identified bad peak shape, filtered mesocosm sample became contaminated during filtration process. Missing data.

EXP240223PS4C1	N/A	NH4	129	Data is bad. Data was over range, even with a 1 in 10 dilution. Missing data.
EXP240215ME4MC1aT1F EXP240215ME4MC1bT1F EXP240215ME4MC1cT1F	N/A	NO2	133	Filtered mesocosm samples became contaminated during filtration process, do not use filtered results.
EXP240216ME4MC1aT2F EXP240216ME4MC1bT2F EXP240216ME4MC1cT2F EXP240216ME4MC2aT2F EXP240216ME4MC2bT2F EXP240216ME4MC2cT2F	N/A	NH4	133	Filtered mesocosm samples became contaminated during filtration process, do not use filtered results.

# 8.6 Data Quality Flag Key

Flag	Description	
0	Data is GOOD	
63	Nutrients only.	Data below nominal detection limit.
65	Data is SUSPECT.	Nutrients only: Absorbance peak shape, measured by the instrument, is marginally outside set limits.
69	Data is SUSPECT.	Duplicate data is outside of set limits (software). Data point is an outlier on the depth profile plot (operator). Tagged by software or operator
79	Data is SUSPECT.	Nutrients only. Measured Method Detection Limit (MDL) for the analysis run is greater than the nominal MDL. All samples in that run tagged.
129	Data is BAD.	Nutrients Only. Absorbance peak exceeds the maximum value that can be measured by the instrument.
133	Data is BAD.	Set by operator.
134	Data is BAD.	Nutrients Only. Absorbance peak shape of calibrants, measured by the instrument, is outside of set limits (software).
141	NO Data.	Used in netcdf results file. Not used in csv results file.

## 8.7 GO-SHIP Specifications

#### 8.7.1 Salinity

Accuracy of 0.001 is possible with Autosal<sup>TM</sup> salinometers and concomitant attention to methodology. 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. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of  $\pm$  1°C is very important and should be recorded<sup>2</sup>.

#### 8.7.2 Dissolved Oxygen

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.

#### 8.7.3 Si(OH)<sub>4</sub>

Approximately 1-3% accuracy<sup>1</sup>, 0.2% precision<sup>3</sup>, full scale.

#### 8.7.4 PO<sub>4</sub>

Approximately 1-2% accuracy<sup>1</sup>, 0.4% precision<sup>3</sup>, full scale.

#### 8.7.5 NO<sub>3</sub>

Approximately 1% accuracy<sup>1</sup>, 0.2% precision<sup>3</sup>, full scale.

#### 8.7.6 Notes

<sup>1</sup> If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.

<sup>2</sup> Keeping constant temperature in the room where salinities are determined greatly increases their quality. Also, room temperature during the salinity measurement should be noted for later interpretation if queries occur. Additionally, monitoring and recording the bath temperature is also recommended. The frequent use of IAPSO Standard Seawater is endorsed. To avoid the changes that occur in Standard Seawater, the use of the most recent batch is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.

<sup>3</sup> Developments of reference materials for nutrients are underway that will enable improvements in the relative accuracy of measurements and clearer definition of the performance of laboratories when used appropriately and the results are reported with the appropriate meta-data.

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