# RV *INVESTIGATOR*

# HYDROCHEMISTRY DATA PROCESSING REPORT

| | |
|---|---|
| **Voyage:** | IN2026_T02 |
| **Chief Scientist** | Natalia Ribeiro Santos and Olaf Meynecke |
| **Voyage title:** | CAPSTAN 5 |
| **Report compiled by:** | Merinda McMahon and Julie Janssens |

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# Executive Summary

## Voyage Objectives

The Collaborative Australian Postgraduate Sea Training Alliance Network (CAPSTAN) is a maritime education and training initiative of CSIRO, the University of Tasmania's Institute for Marine and Antarctic Studies (IMAS) and the Australian and New Zealand International Scientific Drilling Consortium (ANZIC). The Program is supported by grants of sea time on RV *Investigator* (RVI) from the CSIRO Marine National Facility and through funding from the Australian Government's National Collaborative Research Infrastructure Strategy (NCRIS). There are no specific scientific objectives for this voyage, however the aim of CAPSTAN was to:

- Develop and provide an effective vessel-based tertiary education experience involving national stakeholders and post-graduate students, by pooling national tertiary teaching expertise and personnel resources
- Develop a national curriculum to standardise teaching protocols/methods and learning outcomes in conjunction with the new data collection equipment and facilities of the CSIRO research vessel RVI, the Integrated Marine Observatory System (IMOS) and external stakeholders
- Provide and test a multi-disciplinary research-based teaching module for marine science postgraduates with opportunities for student mobility and national network development

In addition to CAPSTAN's core training objectives, this multidisciplinary voyage explored:

1. Repeat sampling and survey of selected sites in the Bremer Canyon Region that were examined during the first Capstan voyage in 2017.
2. Oceanographic properties offshore of a persistent harmful algal bloom (HAB) in SA coastal waters.
3. Underwater Cultural Heritage (UCH) Surveys

## General Hydrochemistry Information

For this voyage, CTD samples were collected and analysed for nutrients, dissolved oxygen, and salinity. Samples were collected by the students, and analysis was performed by the hydrochemistry team onboard for nutrients, dissolved oxygen, and salinity. On some occasion (CTD 2 and 3) double bottle were fired, duplicate sample were collected for dissolved oxygen and salinity to allow students the opportunity to measure the duplicate samples in the lab. Discrete underway nutrient samples were sampled by the students and analysed by the onboard hydrochemistry team. Additionally, Thermosalinograph (TSG) samples were collected by hydrochem throughout the voyage, with on-board measurements used to calibrate the ship's underway system.

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite ($NO_x$) 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**

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**

The final hydrology dataset, data processing report, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre. Please visit CSIRO data trawler, should there be any inquiries on hydrology data please contact CSIRO data centre at NCMI_DataLibrarians@csiro.au.

# Itinerary and Voyage track

**Table 1: Voyage itinerary**

| | Depart | Arrive |
|---|---|---|
| Port | Fremantle | Hobart |
| Date | 23/04/2026 | 05/05/2026 |
| Time | 1500 | 0800 |


**Figure 1. Voyage map**

# Key personnel list

**Table 2: Key Personnel list**

| Name | Role | Organisation |
|---|---|---|
| Pier van der Merwe | CAPSTAN director and Lead Principal Investigator | UTAS |
| Natalia Ribeiro Santos | Co-chief scientist | UTAS/IMOS |
| Olaf Meynecke | Co-chief scientist | Griffith University |
| Ben Arthur | Voyage Manager | CSIRO |
| John Hooper | Alternate Voyage Manager | CSIRO |
| Merinda McMahon | Hydrochemist | CSIRO |
| Julie Janssens | Hydrochemist | CSIRO |

# Sample Summary

## Sample Type and Number Assayed

Table 3: Hydrochemistry sample type and analysis summary

| Analysis | Instrument | Sample source/type | Number of samples |
|---|---|---|---|
| **Nutrients** | Seal AA500 | Conductivity-Temperature-Depth (CTD)<br>Underway (UWY) | 255<br>36 |
| **Salinity** | Guidline Autosal | Conductivity-Temperature-Depth (CTD)<br>Thermosalinograph (TSG) | 138<br>21 |
| **Dissolved oxygen (DO)** | Scripps automated titration | Conductivity-Temperature-Depth (CTD) | 148 |

### CTD sample (Conductivity, Temperature, Depth)

Table 4: CTD summary

| | |
|---|---|
| **Rosette type** | 36 |
| **Niskin Bottle size** | 12 L |
| **Number of deployments** | 53 |
| **Number of deployments sampled for hydrochemistry analyses** | 37 |
| **CTD sampling order** | Dissolved Oxygen (DO) → Nutrients → Salinity |
| **Sample bottle** | DO: 140 mL glass iodine determination flasks with glass stopper<br>Nutrient: 50 mL HDPE with screw cap lids<br>Salinity: 200 mL volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap |
| **Sample log** | CTD deployment paper log sheet and CAP Deployment Log Editor version 1.4.5 |
| **Sampling personnel (hydrochemistry)** | Merinda McMahon and Julie Janssens – training only |
| **Sampling personnel (science party)** | All CAPSTAN participants |
| **Comments** | A few bottles were fired as duplicates during CTD002 and 003 CTDs for student practice on salinity and DO measurements. These samples were test samples only and not a part of the final dataset. |

## Underway sample (UWY)

Table 5: UWY summary

| | |
|---|---|
| **UWY source** | Instrument clean seawater line supplying the pCO2 instrument in the underway laboratory. The line was cleaned with bleach in March 2026. |
| **Sample bottle** | Nutrient: 30 mL PP tube with screw cap lids<br>Salinity: 200 mL volume OSIL bottles made of type II glass (clear) with crimp cap |
| **Sample log** | UWY Samples Event Logs (available on CSIRO data trawler) |
| **Sampling personnel (hydrochemistry)** | Julie Janssens and Merinda McMahon (for TSG only) |
| **Sampling personnel (science party)** | All CAPSTAN students (for nutrients sampling) |

# Data Processing Overview

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed using the CSIRO-developed program HyPro. This processing generates the final hydrology dataset. An overview of this process is illustrated below (fig.2).

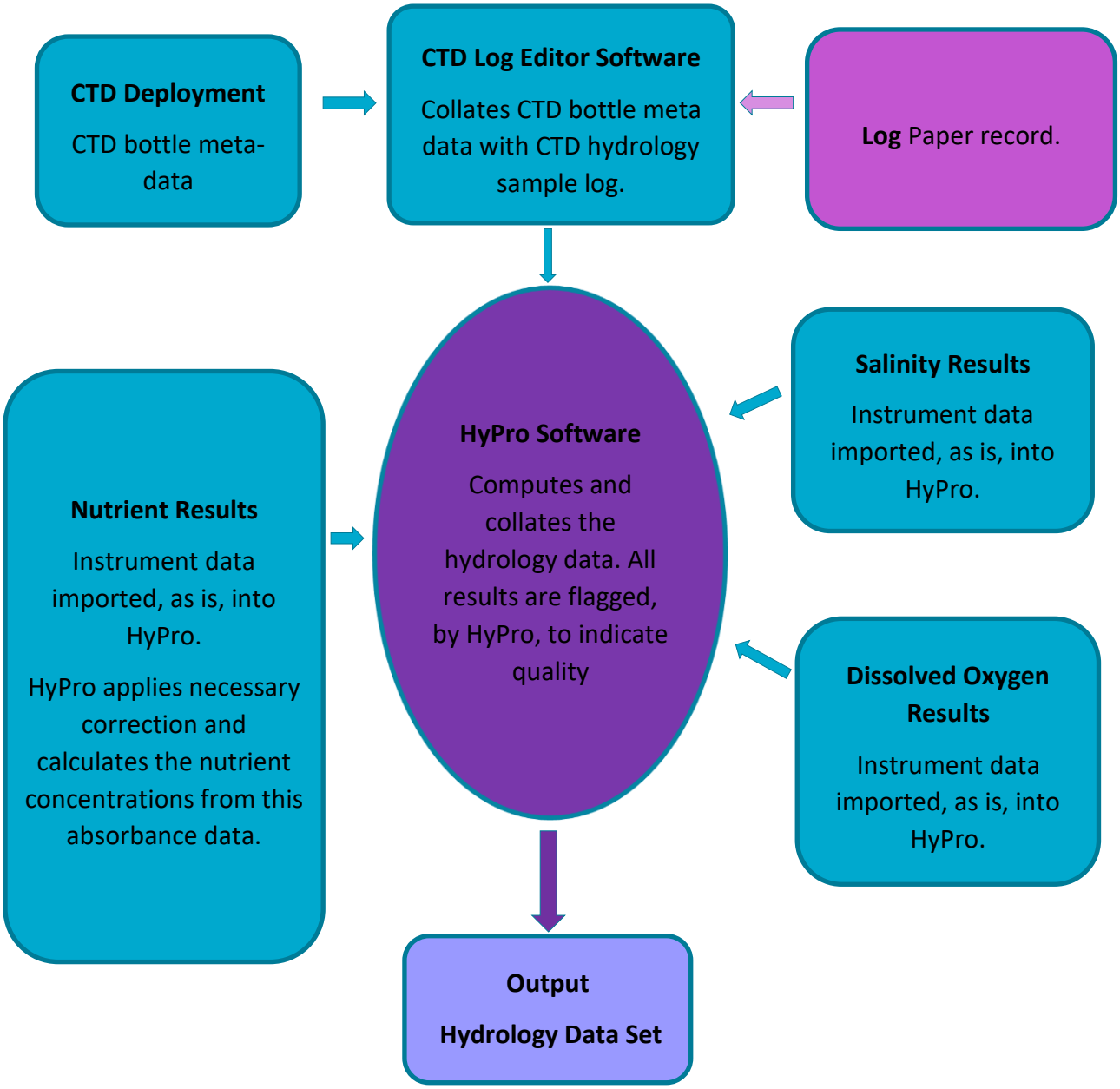


**Figure 2. Conventional Hydrology Data Processing Flow Diagram.**

# Salinity

## Salinity Measurement Parameters

Table 9. Salinity Measurement Parameters

| Details | |
|---|---|
| **HyPro Version** | 5.9 |
| **Instruments** | Guildline Autosal Laboratory Salinometer 8400B – SN 72873. Bath temperature 24.0°C |
| **Software** | Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2 |
| **Hydrochemistry Methods** | Sampling: Salinity - WI_Sal_001, TSG – WI_Sal_004<br>Analysis: SOP 006 |
| **Accuracy** | ± 0.001 practical salinity units (PSU) |
| **Reference Material** | OSIL IAPSO – Batch P168, use by 01 December 2026, $K_{15}$ = 0.99993 |
| **Sample Container** | CTD: 200 mL volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.<br>TSG: 200 mL volume type I (clear) borosilicate bottle with rubber liner lid and aluminium crimp cap. |
| **Sample Storage** | Stored in salinometer lab for minimum of 8 hrs for temperature equilibration before measurement |
| **Analyst** | Julie Janssens and Merinda McMahon |

## Salinity Method

Salinity samples were measured on a Guildline Autosal 8400B, operated in accordance with the manufacturer's technical manual. The measured value is recorded with an OSIL data logger.

Practical salinity (S) is defined as the ratio ($K_{15}$) of the electrical conductivity of seawater measured at 15°C, 1 atm to that of a potassium chloride (KCl) solution of mass fraction 32.4356 x $10^{-3}$.

Before each lot of sample measurements, the Autosal was calibrated with standard seawater (OSIL, IAPSO) with a known $K_{15}$ ratio. A fresh bottle of OSIL standard is used for each calibration, and calibration is performed at least once per run.

Method summary: The salinity sample is collected in a 200 mL glass bottle. The bottle is rinsed three times with sample, then filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, until overflowing. The bottle is removed from the straw, and the sample is decanted to allow a headspace of approximately 25 $cm^3$. A dry plastic insert is fitted, the bottle inverted and rinsed with ultra-pure water, wiped dry, capped and stored upside down until analysis. To measure, the salinometer cell is flushed three times with the sample and then measured after the third and fourth 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 linked with the CTD deployment meta-data.

## CTD Salinity vs Bottle Salinity

For this voyage, the difference between the unprocessed (uncorrected) CTD value and the measured bottle value is generally less than 0.02 PSU. CTD sensor data were recorded on the downcast, while bottle samples were collected on the upcast.

The unprocessed CTD values are adjusted (corrected) by DAP using the salinity bottle results. The corrected values are not reported in the hydrology set. Please refer to IN2026_T02 CTD data on CSIRO marlin metadata system for corrected sensor data.

## OSIL Salinity Standard

For each salinity analysis conducted on this voyage, the instrument was calibrated with OSIL standard seawater, lot P168 (PSU = 34.997).

The mean measured value for the P168 OSIL standard seawater across the voyage was:

Mean = 34.9973 PSU SD = 0.00013 n = 5

# Dissolved Oxygen

## Dissolved Oxygen Measurement Parameters

**Table 10. Dissolved oxygen measurement parameters.**

| **Details** | |
|---|---|
| **HyPro Version** | 5.9 |
| **Instrument** | Scripps Automated Photometric Oxygen System |
| **Software** | Scripps Institution of Oceanography (SIO) |
| **Hydrochemistry Methods** | Sampling: WI_DO_001<br>Analysis: SOP 005 |
| **Titrant** | 50 g/L Sodium Thiosulphate |
| **Primary standard** | 0.0125244 N Potassium Iodate |
| **Accuracy** | ± 0.5 µmol $L^{-1}$ |
| **Sample Container type** | 140 mL glass iodine determination flasks with glass stopper |
| **Sample Storage** | Samples stored in the hydrochemistry lab until analysis within 72 hrs. |
| **Analyst** | Julie Janssens and Merinda McMahon |

## Dissolved Oxygen Method

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

Method summary: The sample is collected in an iodine determination flask of known volume. To the sample, 1 mL of manganese (II) chloride solution is added, followed by 1 mL of alkaline iodide solution. The flask is then stoppered and inverted at least 30 times. Dissolved oxygen in the sample oxidizes an equivalent amount of Mn (II) to Mn (IV) which forms a precipitate. Just before titration, the sample is acidified, reducing Mn (IV) back to the divalent state and liberating an equivalent amount of iodine. The iodine is titrated with a standardised thiosulphate solution using a Metrohm

Dosimat fitted with a 1 mL burette. The titration endpoint is determined by measuring the decrease in the UV absorption at 365 nm.

The thiosulphate solution is standardised by with 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 conducted at least once every 24 hours, when samples are being assayed.

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

## CTD Dissolved Oxygen vs Bottle Dissolved Oxygen

For this voyage, the difference between the unprocessed (uncorrected) CTD value and the measured bottle value is generally below 25 µmol $L^{-1}$.

The unprocessed CTD values are adjusted (corrected) by DAP using the dissolved oxygen bottle results. The corrected values are not reported in the hydrology set. Please refer to IN2026_T02 CTD data on CSIRO marlin metadata system for corrected sensor data.

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

The variation in thiosulphate concentration remains within the QC parameter of less than 0.0005 N between standardisations. The blank correction, which accounts for oxidisable species in the reagents and in the Milli-Q water that is added to the $KIO_3$ aliquot before the titration, is used in the calculation of the thiosulphate normality.

The mean normality of thiosulphate for this voyage was:

Mean: 0.201658 N SD: 0.000046 n = 4

The mean blank concentration was:

Mean: 0.000976 mL SD: 0.000691 n = 4

# Nutrients

## Nutrient Measurement Parameters

**Table 11. Nutrient measurement parameters analysed with Seal AA500 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 AA500 segmented flow analyser | | | | |
| **HyPro version** | 5.9 | | | | |
| **Operating Software** | AACE 8.06 | | | | |
| **Hydrochemistry Sampling Method** | WI_Nut_001 | | | | |
| **Hydrochemistry analysis method** | SOP001 | SOP002 | SOP003 | SOP003 | SOP004 |
| **Nutrients analysed** | Silicate ($SiO4^{4-}$) | Phosphate ($PO_4^{3-}$) | Nitrate + Nitrite ($NO_x$) | Nitrite ($NO_2^-$) | Ammonium ($NH_4^+$) |
| **Top concentration ( µmol $L^{-1}$ )** | 140.0 | 3.0 | 42.0 | 1.4 | 2.0 |
| **Method detection limit (MDL) ( µmol $L^{-1}$ )** | 0.2 | 0.02 | 0.02 | 0.02 | 0.02 |
| **Stock standards** | Made on 11th of February 2026 in 1L HDPE bottle | | | | |
| **Intermediate standards** | Prepared every 72 hours in 30 mL polypropylene tubes. Reused after acid wash with 10% hydrochloric acid solution. | | | | |
| **Working standards** | Prepared every 24-48 hours in 30 mL polypropylene tubes. Reused after acid wash with 10% hydrochloric acid solution. | | | | |
| **Reference Material** | KANSO RMNS lot CO and CU<br>RMNS lot CO expired 25th April 2026, however it was measured alongside CU (expiry 25th April 2031) for comparison. | | | | |

| | |
|---|---|
| **Sample Container** | CTD samples: 50 mL HDPE with screw cap lids. Reused after acid wash with 10% hydrochloric acid solution.<br>Underway samples: 30 mL PP tube with screw cap lids. Reused after acid wash with 10% hydrochloric acid solution. |
| **Sample Storage** | < 4 hours at room temperature after collection or < 24 hours at 4°C after collection, samples returned to room temperature prior to analysis. |
| **Sample preparation** | No filtration. |
| **Analysts** | Julie Janssens and Merinda McMahon |

## Nutrient Methods

Nutrient samples are analysed using a Seal AA500 segmented flow auto-analyser, equipped with 10 mm flow-cells.

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[1] 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 magenta 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 540 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.

[1] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

## HyPro Processing Summary for Nutrients

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

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

Suspect calibration points are given less weight when fitting the calibration curve. The cut-off limits for acceptable calibration data are as followed:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE[1]).
- 0.02 µmol $L^{-1}$ for phosphate, nitrite, and ammonium.

HyPro classifies data quality as good, suspect, or bad and flags the results accordingly. The Flag key can be found in Appendix, Data Quality Flag Key. Missing or suspect nutrient data is listed in Appendix, Missing or Suspect Nutrient Data.

[1] World Ocean Circulation Experiment

**Table 12. HyPro Processing Parameters. All instrument parameters and reagent batches and operation events are logged for each analysis run. This information is available on request.**

| Result Details | Silicate | Phosphate | Nitrate + Nitrite | Nitrite | Ammonium |
|---|---|---|---|---|---|
| **Data Reported as** | µmol $L^{-1}$ | µmol $L^{-1}$ | µmol $L^{-1}$ | µmol $L^{-1}$ | µmol $L^{-1}$ |
| **Calibration Curve fit** | Linear | Linear | Quadratic | Quadratic | Linear |

| | | | | | |
|---|---|---|---|---|---|
| **# 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 |
| **Refractive Index Blank (RIB) correction** | Y | Y | Y | Y | N |
| **Peak window defined by** | HyPro | HyPro | HyPro | HyPro | HyPro |
| **Carryover correction** | Y | Y | Y | Y | Y |
| **Baseline drift correction** | Y | Y | Y | Y | Y |
| **Sensitivity drift correction** | Y | Y | Y | Y | Y |
| **Data Adjusted for RMNS variance** | N | N | N | N | N |
| **Medium of Standards** | Low nutrient seawater (LNSW) collected in June 2024. Sub-lot passed through a 5-micron filter (filtered in February 2026) and stored in 20 L carboys in the hydrochemistry laboratory and the dry clean laboratory at room temperature. | | | | |
| **Medium of Baseline** | 18.2 MΩ water. Dispensed from the Milli-Q IQ 7010 system. | | | | |
| **Duplicate samples** | CTD: Niskin fired at the greatest depth for each CTD deployment were analysed in duplicate. Single samples were analysed for remaining depths. | | | | |
| **Note** | The reported data is not corrected to the RMNS. Per deployment RMNS data is provided in supporting document. | | | | |

## Refractive Index Blank (RIB) measurement and correction

The refractive index blank (RIB) is an optical interference caused by the difference in refraction between seawater and Milli-Q water. This effect alters light transmission and scattering within the flow cell, resulting in baseline shifts and potential underestimation or overestimation in absorbance measurements during colorimetric analysis (Kirkwood, D.S., 1996).

To quantify RIB, the non-coloured reagent method was employed. In this approach, Milli-Q water and LNSW were analysed using the complete reagent set described in the Nutrients Method section

above, except for the colour-generating chemicals. Specifically, 1-N-naphthyl-ethylenediamine dihydrochloride was omitted for NOx and NO2, while ammonium molybdate was excluded for silicate and phosphate. No RIB effect was observed for ammonium channel.

At the end of an analysis run, the full suite of reagents was switched to the non-coloured reagent setup, and the percentage difference between Milli-Q water and LNSW was recorded for each channel using AACE software. This percentage was then converted into concentration values using a proportional ratio calculation, where the highest calibrant nominal concentration and its corresponding peak height percentage were used as reference points.

The average RIB values from multiple nutrient analysis runs overtime are presented in Table 13. RIB value was entered into HyPro where nutrient data was corrected.

**Table 13. Average refractive index blank (RIB) offset value for each channel used for correction on this voyage (Units: µmol $L^{-1}$, n = 14).**

| Silicate | Phosphate | Nitrite | Nitrate + Nitrite |
|---|---|---|---|
| 0.0429 ± 0.0842 | 0.0290 ± 0.0056 | 0.0159 ± 0.0051 | 0.0206 ± 0.0239 |

## 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, nitrite and ammonium in seawater.

For this voyage, Japanese KANSO certified RMNS lot CO and CU was assayed in triplicates in each run to monitor accuracy (Table 14). RMNS CW was only analysed in the characterisation run (run nut001) as additional accuracy monitoring at the start of the voyage. An internal bulk quality control (BQC) was also analysed in each analysis run.

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

KANSO publishes the RMNS nutrient values in µmol $kg^{-1}$. These are converted to µmol $L^{-1}$ at 21°C. $NO_x$ is derived by summing the $NO_3$ and $NO_2$ values.

Table 14. RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: µmol $L^{-1}$

| RMNS | Silicate | Phosphate | Nitrite | Nitrate + Nitrite | Ammonium |
|---|---|---|---|---|---|
| Lot CO | 35.5515 ± 0.1638 | 1.2052 ± 0.0143 | 0.0410 ± 0.0410 | 16.2808 ± 0.1946 | N/A |
| Lot CU | 7.9588 ± 0.0922 | 0.2684 ± 0.0113 | 0.0410 ± 0.0410 | 3.1753 ± 0.0922 | 1.0448 ± 0.0410 (ref only) |

Table 15. a. RMNS CO statistics for of this voyage. Units: µmol $L^{-1}$, b. RMNS CU statistics for of this voyage. Units: µmol $L^{-1}$

| a. RMNS CO | Silicate | Phosphate | Nitrite | Nitrate + Nitrite | Ammonium |
|---|---|---|---|---|---|
| **Mean** | 35.7216 | 1.2197 | 0.0471 | 16.4261 | N/A |
| **Standard deviation** | 0.109 | 0.003 | 0.002 | 0.073 | N/A |
| **b. RMNS CU** | **Silicate** | **Phosphate** | **Nitrite** | **Nitrate + Nitrite** | **Ammonium** |
| **Mean** | 7.9386 | 0.2665 | 0.0294 | 3.1277 | 1.0834 |
| **Standard deviation** | 0.038 | 0.003 | 0.005 | 0.017 | 0.016 |

## RMNS plots

The measured RMNS values for each nutrient analysis run on this voyage is shown in plots below. The green, pink, and red contour lines represent 1%, 2% and 3% or 1*MDL, 2*MDL and 3*MDL (MDL = 0.02 µmol $L^{-1}$) deviation from the RMNS certified mean value. The blue line is the manufacturer's expanded uncertainty of the certified value. The measured RMNS values per CTD deployments are provided in supporting document available on CSIRO data trawler.

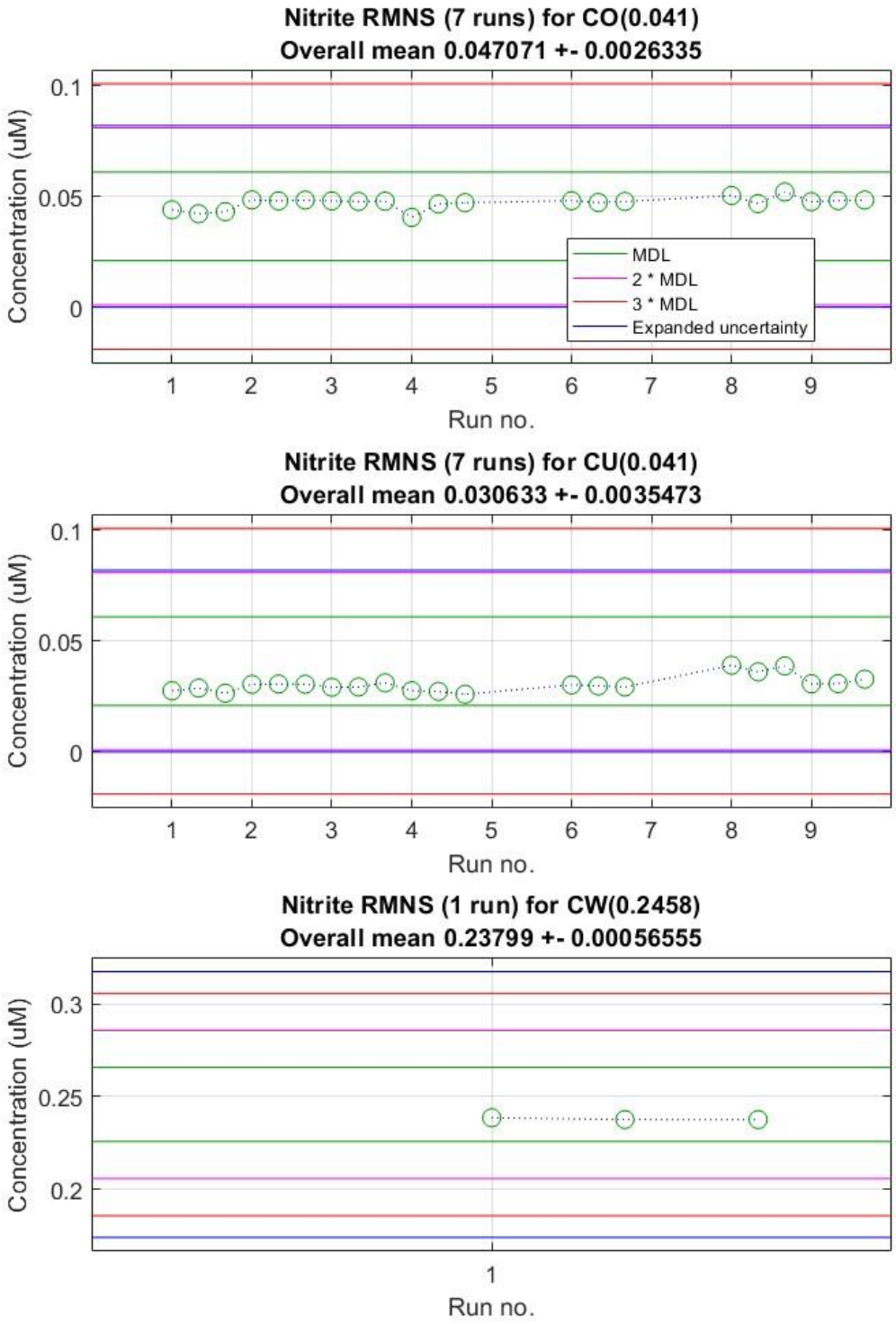


**Figure 3. Nitrite RMNS lot CO, CU, and CW plot. Units: µmol $L^{-1}$.**

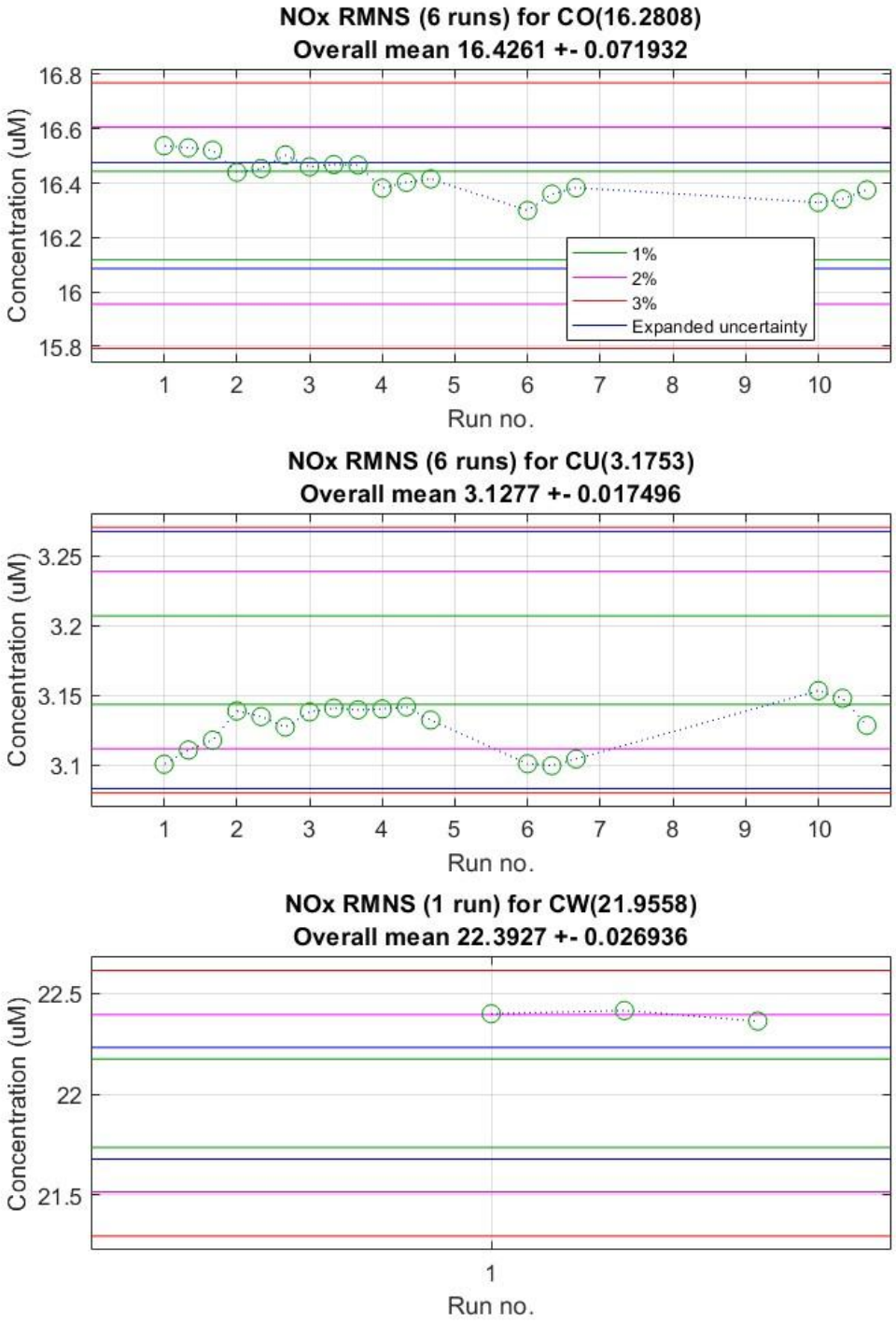


**Figure 4. Nitrate + Nitrite (NOx) RMNS lot CO, CU, and CW plot. Units: µmol $L^{-1}$.**

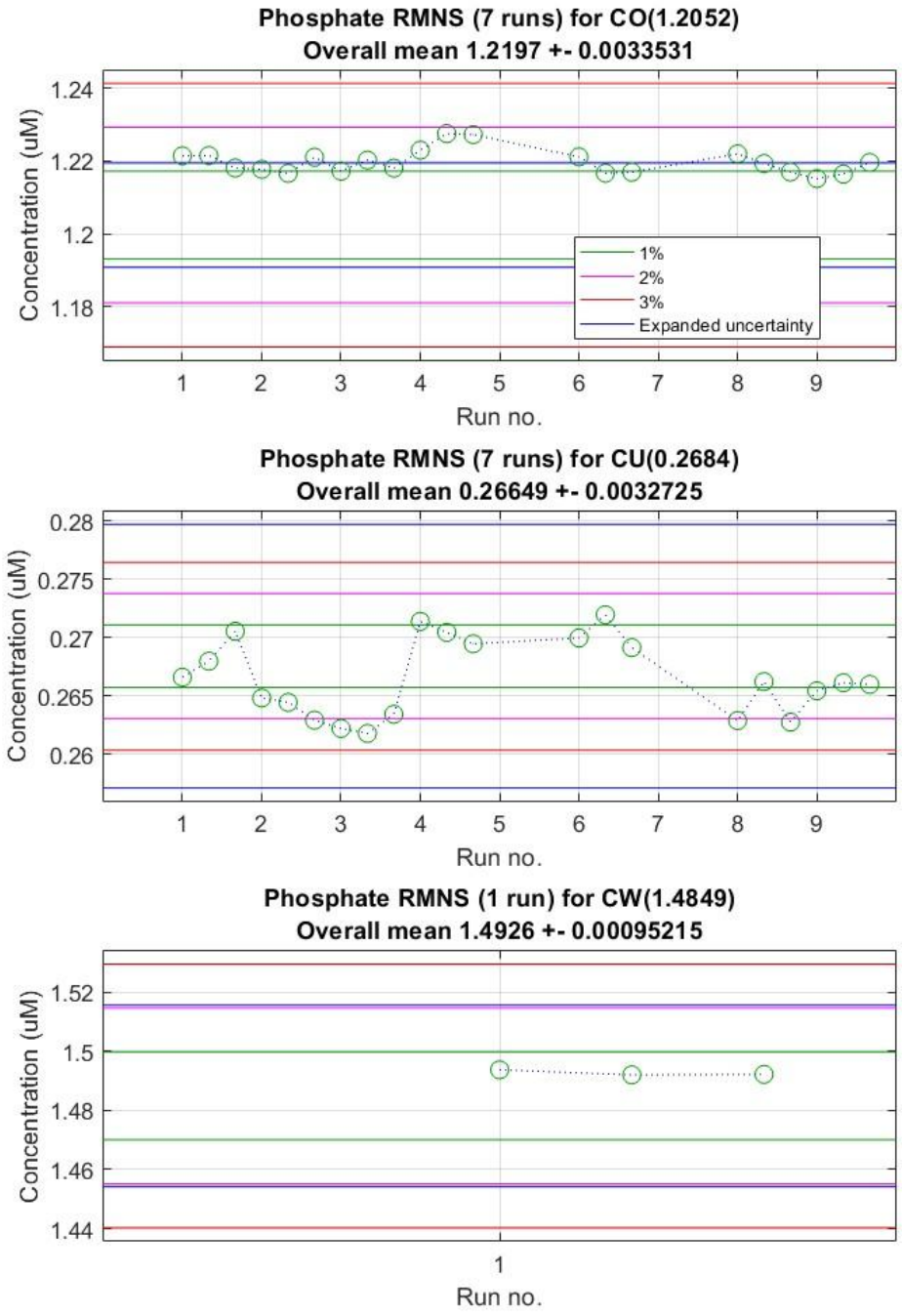


**Figure 5. Phosphate RMNS lot CO, CU, and CW plot. Units: µmol $L^{-1}$.**

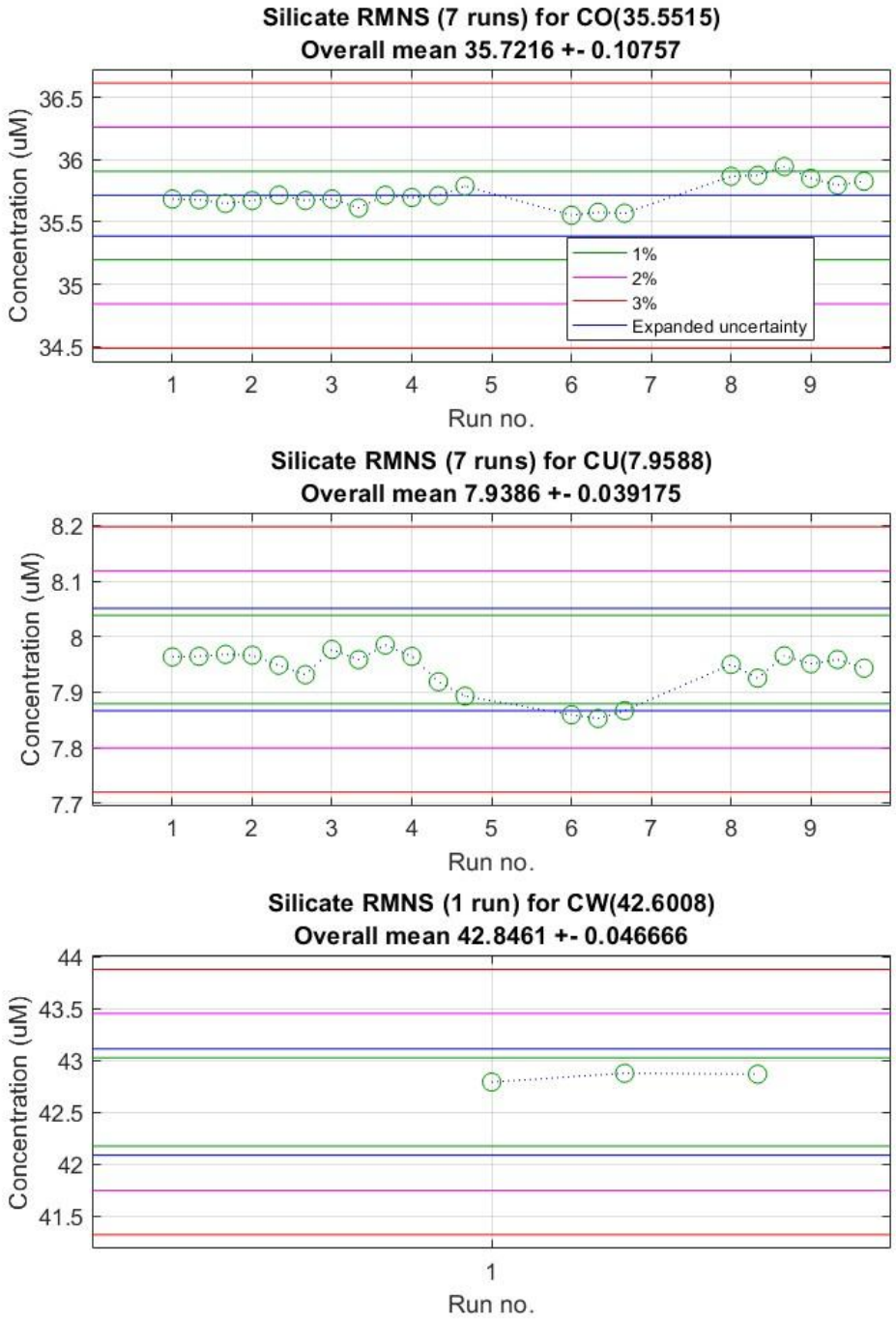


**Figure 6. Silicate RMNS lot CO, CU, and CW plot. Units: µmol $L^{-1}$.**

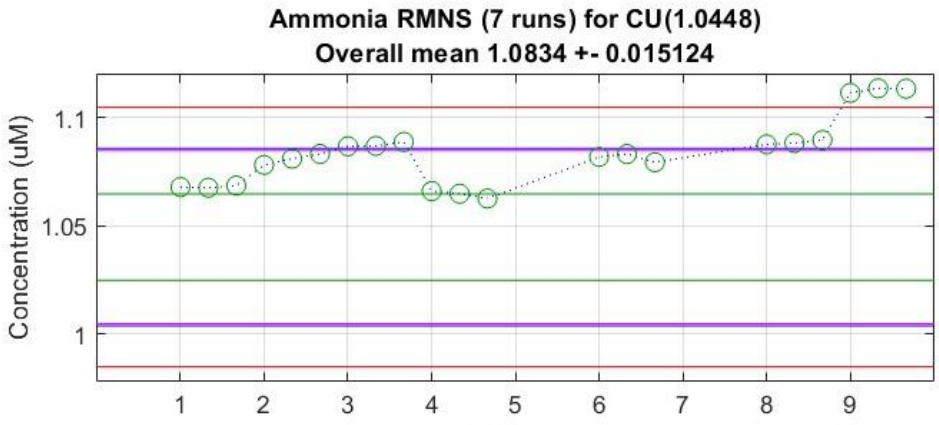


Figure 7. Ammonia RMNS lot CU. Units: µmol $L^{-1}$

## 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 16. CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol $L^{-1}$

| **Calculated Measurement Uncertainty at 1 µmol $L^{-1}$** | | | | |
|---|---|---|---|---|
| **Silicate** | **Phosphate** | **Nitrite** | **Nitrate + Nitrite** | **Ammonium** |
| ±0.017 | ±0.024 | ±0.140 | ±0.019 | ±0.30 |

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

## Method Detection Limit for Nutrients

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

Table 17. AA500 auto analyser MDL statistics for this voyage. The mean and standard deviation are calculated from every analytical run performed over the voyage. Units: µmol $L^{-1}$.

| **MDL** | **Silicate** | **Phosphate** | **Nitrite** | **Nitrate + Nitrite** | **Ammonium** |
|---|---|---|---|---|---|
| **Nominal MDL** | **0.2** | **0.02** | **0.02** | **0.02** | **0.02** |
| Mean | 0.03 | 0.004 | 0.002 | 0.010 | 0.001 |

| | | | | | |
|---|---|---|---|---|---|
| Standard deviation | 0.01 | 0.001 | 0.004 | 0.003 | 0.001 |

## Sampling Precision

Sampling precision is typically determined using the CTD test deployment (CTD 001) where multiple bottles are fired the same depth, each of which is then sampled as replicates for hydrochemistry nutrient analysis. However, for this voyage the CTD test deployment was used for training purposes for the CAPSTAN students. As the samples were collected by a variate of different people, the sampling precision from the test CTD cannot be calculated.

Duplicate nutrient samples are also collected from the greatest depth of subsequent CTD deployments. For nutrients analysis, the sampling precision is considered good if the difference from the mean of duplicate measurements is less than the nominal method detection limit (Table 17). The exception is for $NO_x$ (nitrate+nitrite), which uses the limit of 0.06 µmol $L^{-1}$. Duplicate samples that exceed the limit are flagged. These are tabulated in Appendix, Data Quality Flag Key.

# Temperature

## Hydrochemistry lab and nutrient analyser

Ambient conditions in the hydrochemistry laboratory and on the segmented flow analyser were monitored at the following locations:

- Hydrochemistry lab temperature: positioned in close proximity to the autoanalyser
- Nutrient sample pump temperature: positioned on the pump tubes where nutrient samples and reagents are introduced into the analyser

Temperature data was measured using Ruuvi temperature logger and monitored in Grafana. A time series plot of hydrochemistry laboratory temperature plot throughout the voyage is shown below. A complete log of temperature is available upon request through CSIRO data centre. The average analyser pump temperature of the analyser during each nutrients analysis is provided in supporting documents available on CSIRO data trawler.

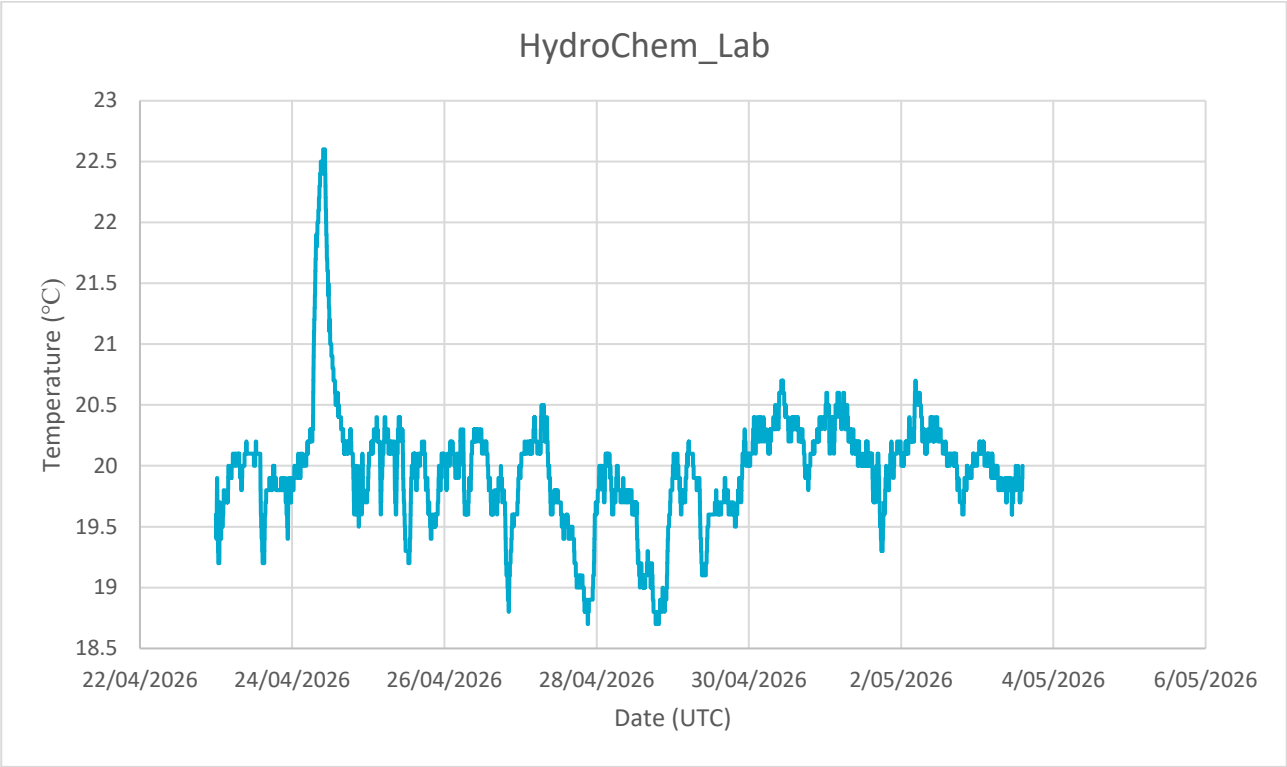


**Figure 8. Hydrochemistry lab Ruuvi sensor; scale is 18.5°C to 23.0°C, mean: 19.95°C, SD: 0.48°C.**

## Salinity laboratory

Ambient conditions in the salinity laboratory were monitored using a Ruuvi temperature logger positioned near the area where sample crates were stored. Temperature data was recorded and visualised in Grafana. A time series plot of salinity lab temperature throughout the voyage is shown below. A complete log of temperature is available upon request through CSIRO data centre.

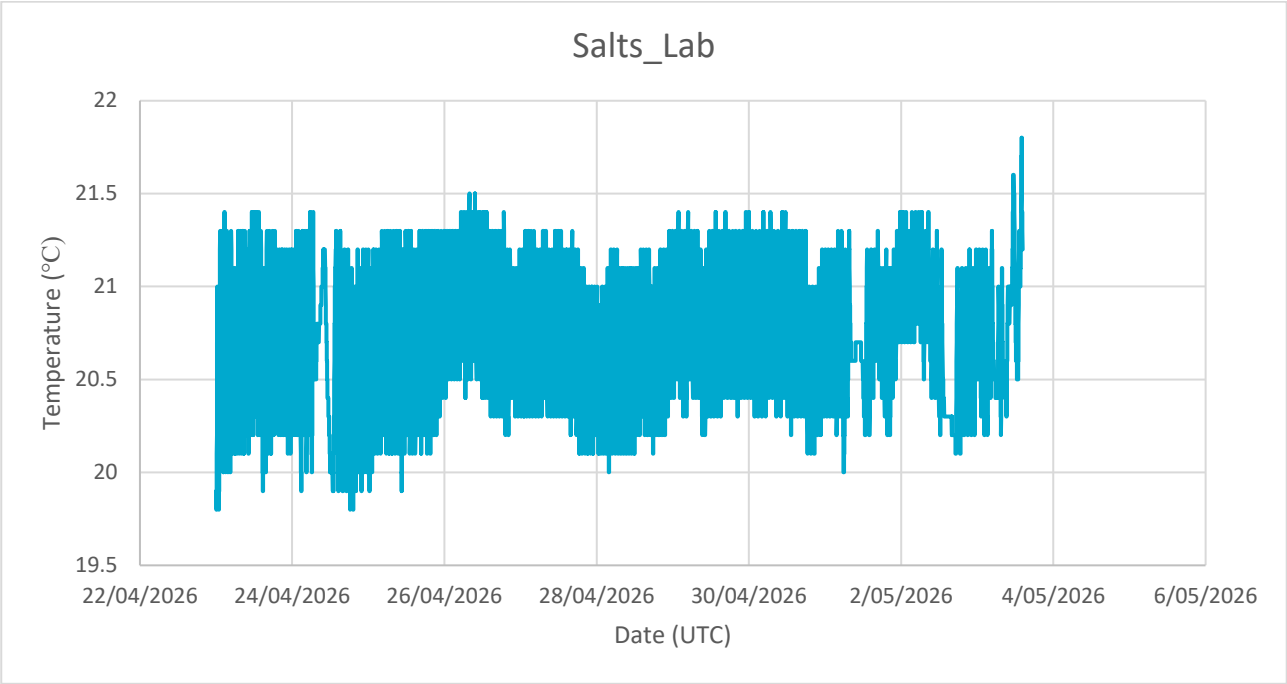


**Figure 9. Hydrochemistry lab Ruuvi sensor; scale is 19.5°C to 22.0°C, mean: 20.68°C, SD: 0.35°C.**

# Appendix

## Salinity: Reference material used

| **OSIL IAPSO Standard Seawater** | |
|---|---|
| **Batch** | P168 |
| **Use by date** | 1 December 2026 |
| **$K_{15}$** | 0.99993 |
| **PSU** | 34.997 |

## Nutrients: RMNS correction

The submitted nutrient results do NOT have RMNS corrections applied. The measured RMNS value per CTD deployment is provided in supporting document available on CSIRO data trawler.

**How to use the RMNS for correction**

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

Corrected Concentration = Ratio x Measured Nutrient Concentration

**How to use the RMNS for smoothing**

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

Corrected Concentration = Ratio x Measured Nutrient Concentration

## Missing or Suspect Salinity Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Appendix, Data Quality Flag Key).

| CTD | RP | Flag | Reason for Flag |
|---|---|---|---|
| NA | NA | NA | NA |

## Missing or Suspect Dissolved Oxygen Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Appendix, Data Quality Flag Key).

| CTD | RP | Flag | Reason for Flag |
|---|---|---|---|
| 1 | 6 | 133 | Precipitate did not dissolve properly |
| 07 | 01 | 133 | Lid was placed in sample upside down, preventing bottle to seal properly. Sample would have absorbed atmospheric oxygen. |
| 08 | 17 | 133 | Analyst error – sample removed before endpoint was reached. |

## Missing or Suspect Nutrient Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Appendix, Data Quality Flag Key).

*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 Chlorophyll 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. These ammonium samples are not reported in this table.*

| CTD | RP | Analyte | Flag | Reason for Flag |
|---|---|---|---|---|
| 5 | 1 | NOx | 69 | Duplicates outside set limit. |

## 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 calibrant, measured by the instrument, is outside of set limits (software). |
| 141 | NO Data. | Used in netcdf results file. Not used in csv results file. |

## GO-SHIP Specifications

### Salinity

Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of standard Seawater can be achieved at 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 ± 1°C is very important and should be recorded[2].

### Dissolved Oxygen

Target accuracy is that 2 sigma (standard deviation) 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.

**$Si(OH)_4$**

Approximately 1-3% accuracy[1], 0.2% precision[3], full scale.

**$PO_4$**

Approximately 1-2% accuracy[1], 0.4% precision[3], full scale.

**$NO_3$**

Approximately 1% accuracy[1], 0.2% precision[3], full scale.

## Notes

[1] If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.

[2] 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.

[3] 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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