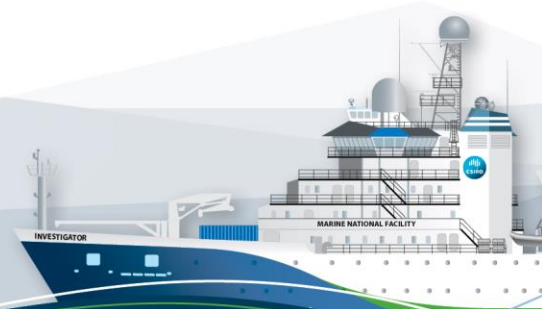


RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT:

AA100 Underway Nutrients

Voyage:	IN2023_V06
Principal Investigators:	Moninya Roughan
Voyage title:	Understanding Eddy Interactions and Their Impacts in the East Australian Current System
Report compiled by:	Merinda McMahon and Maddy Lahm



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1 Executive Summary

Summary

This voyage focused on mesoscale eddies that move heat, salinity, and other materials around. They impact the ocean, ecosystems, and climate, not much is known about how these eddies interact with each other or how they affect the environment. The aim of this voyage was to learn more about eddy-eddy interactions and their impact on the atmosphere, ocean, and marine life in the East Australian Current (EAC) System through the collection of satellite and in-situ (ship) ocean measurements to help improve forecasts and predictions of eddy interactions.

For continual underway nutrient measurements, the AA100 was setup in the Underway seawater lab. The AA100 measured Nitrate (NO_x) and Phosphate (PO₄) off the instrument clean seawater intake of RV Investigator. Over the course of the voyage 8748 data points were measured by the AA100. The underway measurements were made continually, but due to the nature of the method and the data processing this resulted in a calibrated data point every 108 seconds.

All the data included in the final dataset is to be considered as good data. The dataset has had a reasonable level of quality control applied to ensure there are no apparent erroneous data points. However due to the size and sheer amount of data points there is a small chance there could still be some values that may be incorrect.

Nutrient analysis data points were matched to the UTC time stamp, when the sample was drawn from the instrument clean seawater line. No time correction was applied to account for the residence time in the ships piping, meaning all data is offset by approximately 2 min 35 sec for PO₄ and NO_x. If extremely accurate latitude and longitude values are required, a time correction will need to be applied to the dataset.

The final dataset includes NO_x (nitrate + nitrite in $\mu\text{mol L}^{-1}$) and phosphate (PO₄ in $\mu\text{mol L}^{-1}$) concentrations matched to the UTC time stamp of when the sample was collected from the underway line. A netCDF file of the ships latitude and longitude with UTC time stamps is provided to match the data to the ship's location.

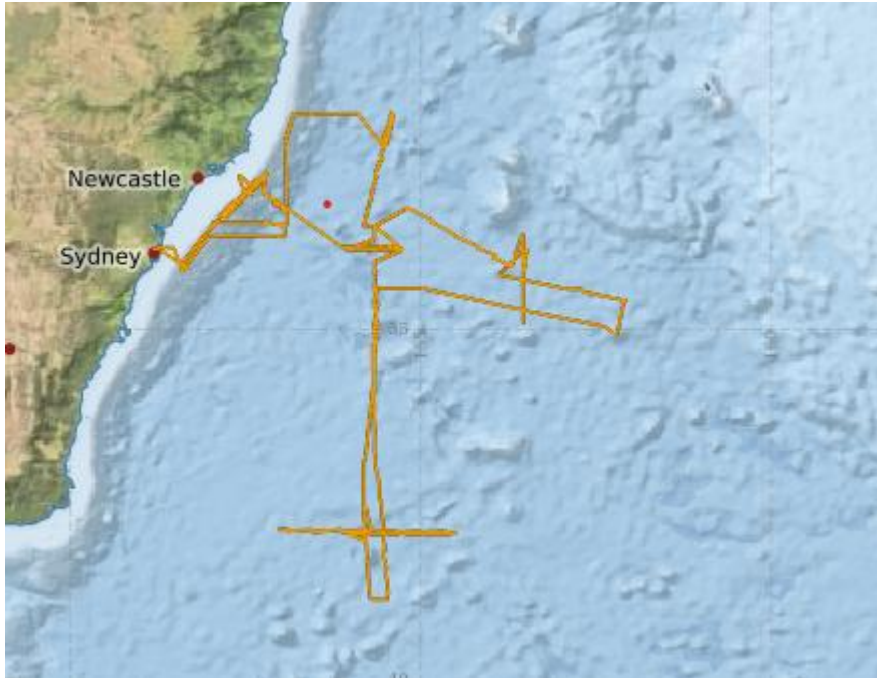
The final data set is not corrected to the measured certified reference material. If correction to the measured reference material is required, the analysis file for each data point is indicated in the final data set and measurements for the reference material are provided in appendix 6.1. Time stamps in the final data set file are given in a readable format set to UTC.

For further enquiries about this dataset please contact: ncmi_datalibrarians@csiro.au

2 Itinerary

Sydney to Sydney, October 9th – November 2nd, 2023.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Moninya Roughan	Chief Scientist	UNSW
Linda Gaskell	Voyage Manager	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Maddy Lahm	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples	Number of Runs
Underway Nutrients (Seal AA100)	8748 UWY (data points)	17

4.2 Analysis and Data Processing Overview

The following flowchart provides an overview of how the AA100 was setup to analyse the underway seawater on the ship. Also outlined is the process of how the data is automatically matched with the ship underway data to provide latitude and longitude for the data points, which will again be offset by 7 min 35 sec (12 min 35 sec for NH_4) due to length of underway piping and analysis time.

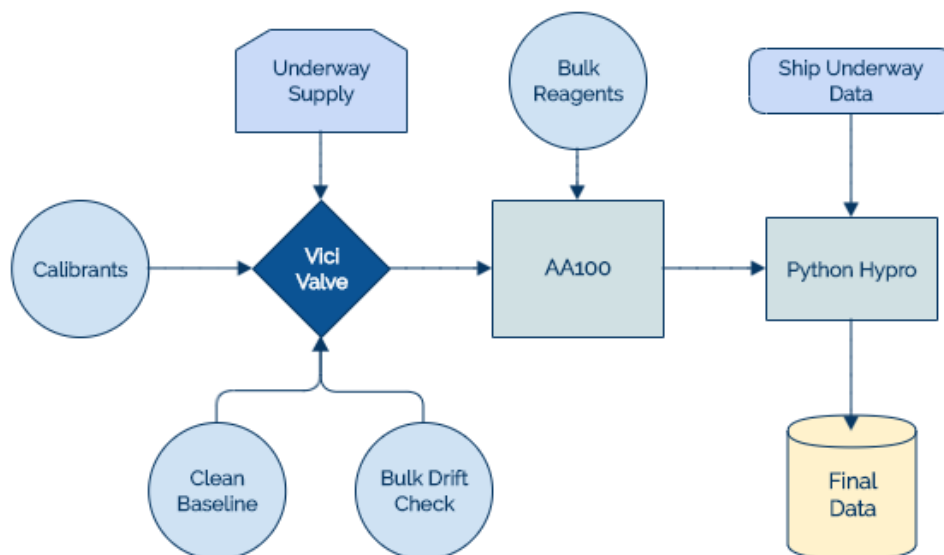


Figure 1: Underway Nutrient Analysis and Data Processing Flow Diagram.

5 Underway Nutrients Analysis & Data Processing

5.1 Nutrient Assay Parameter Summary

Details		
CSIRO Software	HyPro2 version 0.70	
Instrument	Seal AA100	
Instrument Software	Seal AACE 7.10	
CSIRO Hydrochem. Method, sampling	WI_Nut_001 – discrete samples were not collected for the AA100 underway analysis	
CSIRO Hydrochem. Method, nutrient	AA100_SOP01	AA100_SOP02
Nutrient	Phosphate	Nitrate + Nitrite
Concentration range	0 – 3.0 $\mu\text{mol L}^{-1}$	0 – 14.0 $\mu\text{mol L}^{-1}$
Method Detection Limit (MDL)	0.02 $\mu\text{mol L}^{-1}$	0.02 $\mu\text{mol L}^{-1}$
Matrix Corrections	none	none
Analysts	Merinda McMahon and Maddy Lahm	
Reference Material	KANSO, RMNS lot CL	
Comments		

5.2 Nutrient Methods

NO_x and phosphate samples are assayed on a Seal AA100 segmented flow auto-analyser fitted with 1.5 cm de-bubbled flow-cells for colorimetric measurements.

Phosphate (AA100_SOP01): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS 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 880nm.

Nitrate (AA100_SOP02): 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 dihydrochloride to produce a reddish purple azo complex and its absorbance is measured at 540 nm.

SOP methods can be obtained from the CSIRO NCMI Hydrochemistry Group.

5.3 Nutrient Analysis Overview

The instrument chemistry method is the same as on the main hydrochemistry nutrient analyser, the AA3. This method results in high quality absorbance peaks that are very reproducible.

Underway water was fed into the AA100 via a cup that was continually overflowing, allowing the AA100 to draw an unpressurised sample. The cup only held a volume of approximately 20 mL, with the seawater flowrate between 3.5-4.0 L/min.

The residence time of the seawater through the underway piping would have contributed to a significant amount of lag in measurements. There is a 2 minute and 35 second delay between water entering the drop keel to when it reaches the underway seawater laboratory.

Grab samples (uw001 – uw234) were collected from the underway sampling line in the underway lab at various times across the seventeen AA100 runs. These samples were run on the AA3 for intercomparison purposes. For further details please refer to IN2023_V06 Data Processing Report.

5.4 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	Phosphate	Nitrate + Nitrite (NOx)
Data Reported as	$\mu\text{mol l}^{-1}$	$\mu\text{mol l}^{-1}$
Calibration Curve degree	Linear	Linear
# of points in Calibration	6	6
Forced through zero?	N	N
Matrix correction	N	N
Blank correction	N	N
Peak window defined by	HyPro	HyPro
Carryover correction (HyPro)	Y	Y
Baseline drift correction (HyPro)	Y	Y
Sensitivity drift correction (HyPro)	Y	Y
Data Adj for RMNS variance.	N	N
Medium of Standards	LNSW (bulk on deck of Investigator) collected June 2021. Sublot passed through a 5-micron filter and stored in 20 L carboys in the clean dry laboratory at 22°C.	
Medium of Baseline	18.2 Ω water. Dispensed from Milli Q	
Comment	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 6.1.	

5.5 HyPro Data Processing Summary

After a block of underway analysis, the raw absorbance 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 is used to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and duplicate sample results that do not match.

With suspect calibration points, their contribution to the curve is given less weighting dependent on their distance from the final curve. The cut-off limits for good calibration data are $0.02 \mu\text{mol L}^{-1}$ for the 2 channels.

There are no flags provided with the final dataset as it is assumed all points within the dataset are good. HyPro automatically removes points that are bad based on criteria specified above. The dataset has also had a manual pass over to check the quality of the data. There is the small chance that there is bad data in the dataset, however this should be extremely unlikely.

5.6 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Japanese KANSO certified RMNS lot CL was assayed in triplicate in each run to monitor accuracy. The certified values are in table 1.

For IN2023_V06, the RMNS results for Nitrate and Phosphate are typically within 3% of their certified mean. Plots of RMNS values for all runs are below.

The assayed RMNS values per Analysis run are listed in appendix 6.1.

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.6, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

Table 1: RMNS concentrations with expanded uncertainty ($\mu\text{mol L}^{-1}$) at 21°C

RMNS	PO_4 ($\mu\text{mol L}^{-1}$)	$\text{NO}_3 + \text{NO}_2$ (NO_x , $\mu\text{mol L}^{-1}$)
Lot CL	0.4353 ± 0.0195	5.6180 ± 0.1598

KANSO publishes the RMNS nutrient values in $\mu\text{mol kg}^{-1}$. These are converted to $\mu\text{mol L}^{-1}$ at 21°C . Lot CL is not certified for ammonium. NO_x is derived by adding the NO_3 and NO_2 values.

RMNS plot key. The green, pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. The blue line is the expanded uncertainty of the certified value.

5.6.1 Phosphate RMNS Plot

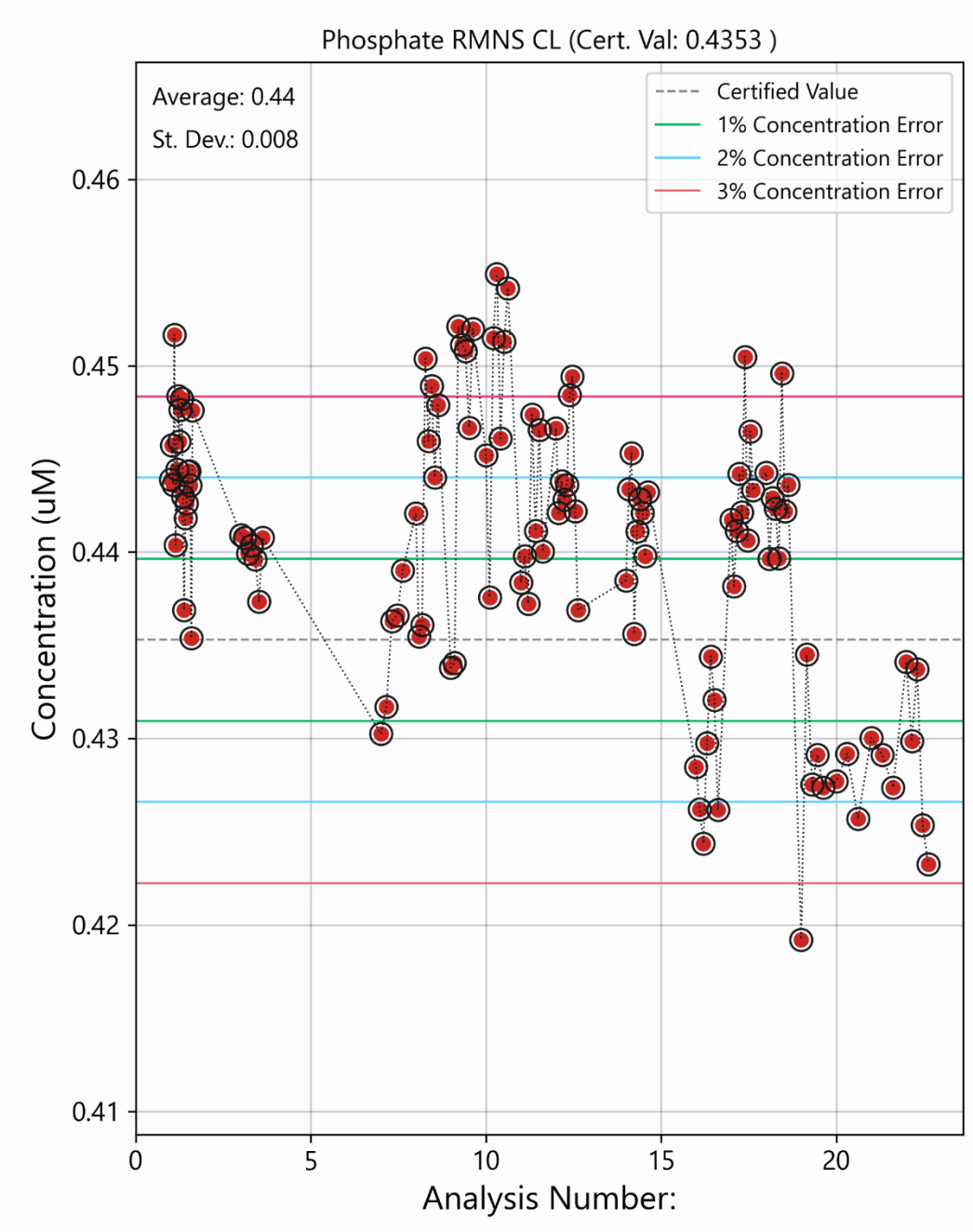


Figure1: Phosphate RMNS (17 runs) for CL (0.435 $\mu\text{mol L}^{-1}$) | measured mean: 0.440 $\mu\text{mol L}^{-1}$

5.6.2 Nitrate + Nitrite (NOx) RMNS Plot

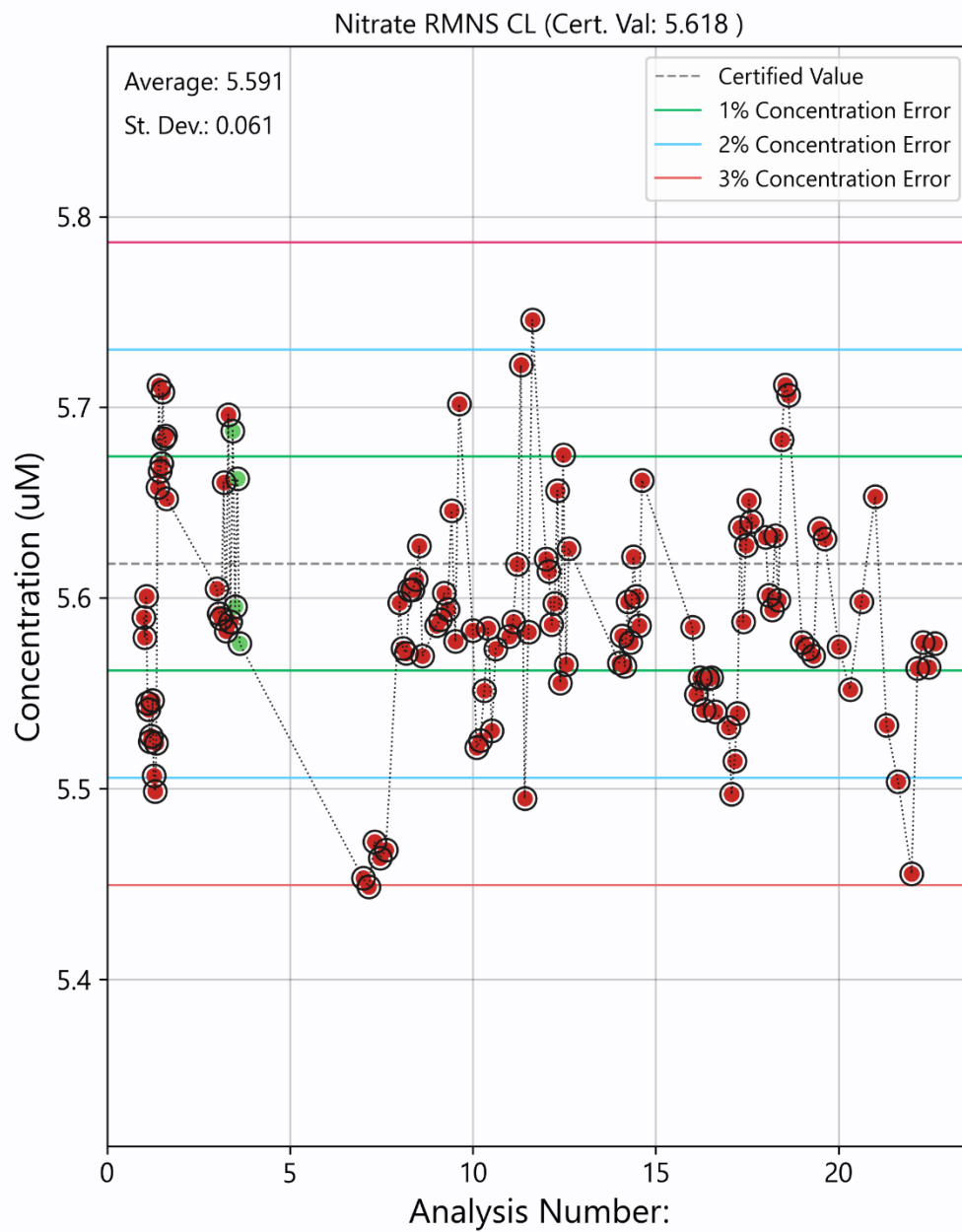


Figure2: NOx RMNS (17 runs) for lot CL (5.618 $\mu\text{mol L}^{-1}$) | measured mean: 5.591 $\mu\text{mol L}^{-1}$

5.7 Analytical Precision

5.7.1 Nutrient Method Detection Limit

For IN2023_V06, the measured detection limits for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations.

MDL	Phosphate ($\mu\text{mol L}^{-1}$)	Nitrate + Nitrite (NO _x , $\mu\text{mol L}^{-1}$)
Nominal MDL*	0.020	0.020
Standard Dev. Min	0.000	0.000
Standard Dev. Max	0.018	0.018
Standard Dev. Mean	0.008	0.006
Standard Dev. Median	0.009	0.004
Precision of MDL (stdev)	0.005	0.006

*MDL is based on 3 times the standard deviation of Low Nutrient Seawater (LNSW) analysed in each nutrient run.

5.7.2 Reference Material for Nutrients in Seawater

Precision values are calculated from intra-analysis measurements, multiple measurements are taken at a time, typically 3 or more.

RMNS CL	Phosphate ($\mu\text{mol L}^{-1}$)	Nitrate + Nitrite (NO _x , $\mu\text{mol L}^{-1}$)
Published RMNS CL ($\mu\text{mol L}^{-1}$) w/std deviation	0.4353 \pm 0.0195	5.6180 \pm 0.1598
Minimum	0.419	5.448
Maximum	0.455	5.746
Mean	0.440	5.595
Median	0.442	5.589
Precision (Stdev)	0.007	0.061

6 Appendix

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

6.1.1 RMNS Lot CL Results

Analysis file	Phosphate ($\mu\text{mol L}^{-1}$)	NO _x (NO ₂ + NO ₃ , $\mu\text{mol L}^{-1}$)
001	0.444	5.601
003	0.440	5.621
004	0.442	5.653
007	0.435	5.461
008	0.444	5.595
009	0.446	5.614
010	0.449	5.553
011	0.441	5.619
012	0.444	5.610
014	0.441	5.595
016	0.429	5.556
017	0.443	5.581
018	0.443	5.645
019	0.428	5.597
020	0.428	5.575
021	0.429	5.563
022	0.429	5.547

The submitted nutrient results do **NOT** 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

6.2 GO-SHIP Specifications

GO-SHIP specifications outline expected analytical quality for oceanographic datasets. This includes the accuracy and precision for the measurement of oceanographic nutrients.

6.2.1 PO₄

Approximately 1-2% accuracy¹, 0.4% precision², full scale.

6.2.2 NO_x

Approximately 1% accuracy¹, 0.2% precision², full scale.

6.2.3 Notes

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

² 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.

7 References

- Armishaw, Paul, "Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty." *Accred Qual Assur*, 8, pp. 218-224 (2003).
- Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., "*The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment*," *Deep-Sea Research*, 14, pp.381-389 (1967).
- Hood, E.M. (2010). "*Introduction to the collection of expert reports and guidelines*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). "*Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers*." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- K  rouel, Roger and Alain Aminot, "*Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis*". *Journal of Marine Chemistry* 57 (1997) pp. 265-275.
- Murphy, J. And Riley, J.P., "*A Modified Single Solution Method for the Determination of Phosphate in Natural Waters*", *Anal.Chim.Acta*, 27, p.30, (1962)
- Wood, E.D., F.A.J. Armstrong, and F.A. Richards. (1967) "*Determination of nitrate in seawater by cadmium-copper reduction to nitrite*." *Journal of the Marine Biological Association of U.K.* 47: pp. 23-31.