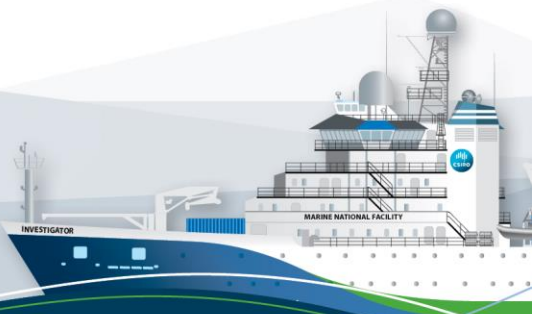
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT:

AA100 Underway Nutrients

Voyage:	in2019_v05
Chief Scientist:	Bernadette Sloyan
Principal Investigator:	Iain Suthers
Voyage title:	Integrated Marine Observing System: monitoring of the East Australian Current property transports at 27°S
Report compiled by:	Kendall Sherrin, Christine Rees & Merinda McMahon



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1 Executive Summary

Summary

The primary objective of the voyage was to recover and re-deploy an array of six full depth current meter and property (temperature, salinity and pressure) moorings from the continental slope to the abyssal waters off Brisbane (27°S). The East Australian Current (EAC) mooring array is a component of Integrated Marine Observing System (IMOS) and is used to capture the mean and time varying flow off the EAC.

The secondary objective was to collect and identify larval fish species in different water masses and frontal eddies to gain an understanding of their growth and mortality rates.

For continual underway nutrient measurements, the AA100 was setup in the Underway Laboratory. The AA100 measured Nitrate and Phosphate off the instrument clean seawater intake of RV Investigator. Over the course of the voyage 5514 data points were measured by the AA100. The underway measurements were made continually, but due to the nature of method and data processing this results 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.

The matched latitude and longitude coordinates supplied in the dataset were obtained from the ships underway computing systems. Nutrient analysis data points were matched using UTC time stamps, no time correction was applied to account for the residence time in the ships piping or in the instrument, meaning all data is offset by 7:35 (minutes: seconds). If extremely accurate latitude and longitude values are required, a time correction will need to be applied and the ship position values realigned.

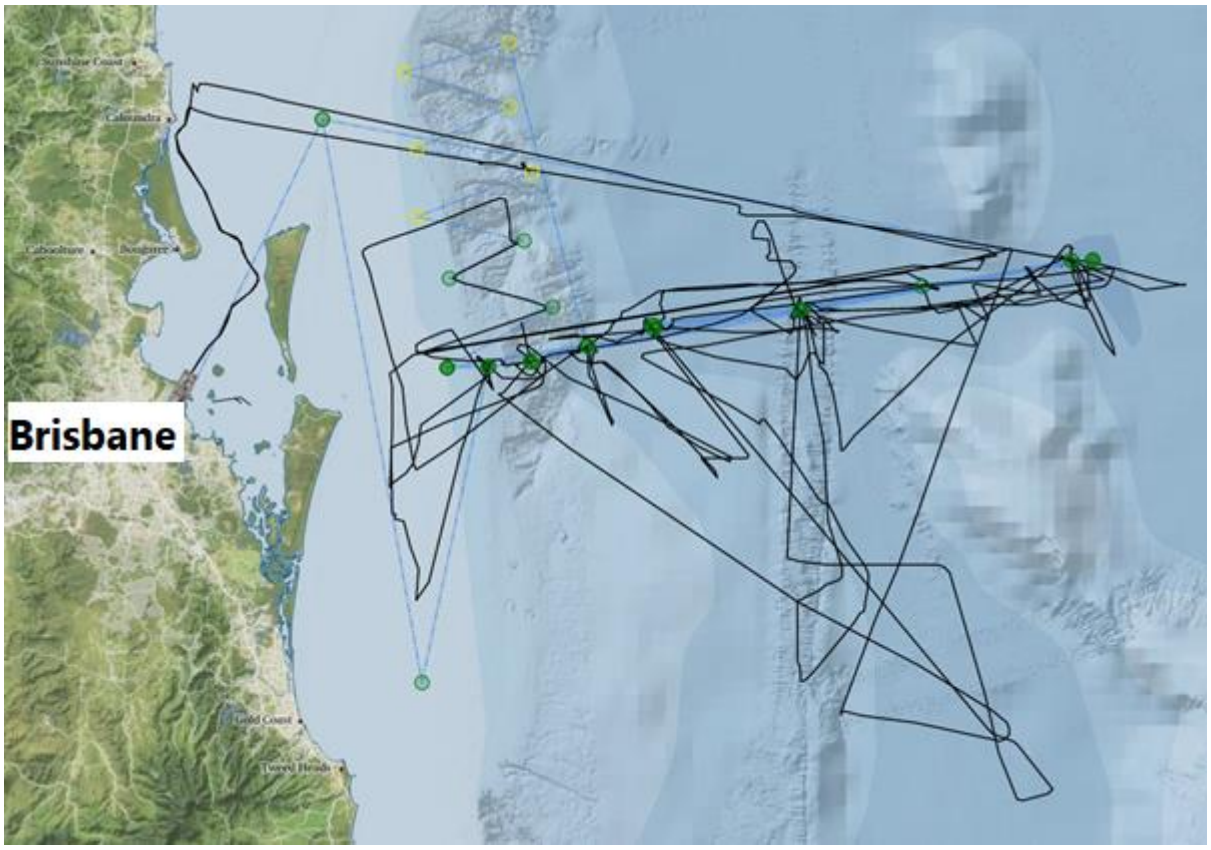
The final dataset includes latitude, longitude, UTC time stamps, NO_x (nitrate + nitrite in µmol l^{-1}), phosphate (PO_4 in µmol l^{-1}) and analysis file. The analysis file for each data point is included if correcting to the reference material used for each analysis is required. The measurements for the reference material are provided in appendix 6.2. Time stamps in the .csv data file are given in a readable format set to UTC. In the NetCDF file, the time stamps are provided as seconds since the start of 2019, i.e. 01/01/2019 00:00:00 + seconds = UTC time stamp.

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

2 Itinerary

Brisbane to Brisbane, September 9th - September 29th, 2019.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
Bernadette Sloyan	Chief Scientist	CSRIO
Iain Suthers	Principal Investigator	UNSW
Linda Gaskell	Voyage Manager	CSIRO
Kendall Sherrin	Hydrochemist (AA100)	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Christine Rees	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples	Number of Analyses
Underway Nutrients (Seal AA100)	5514 UWY (data points)	20

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 7:35 due to length of underway piping and analysis time.

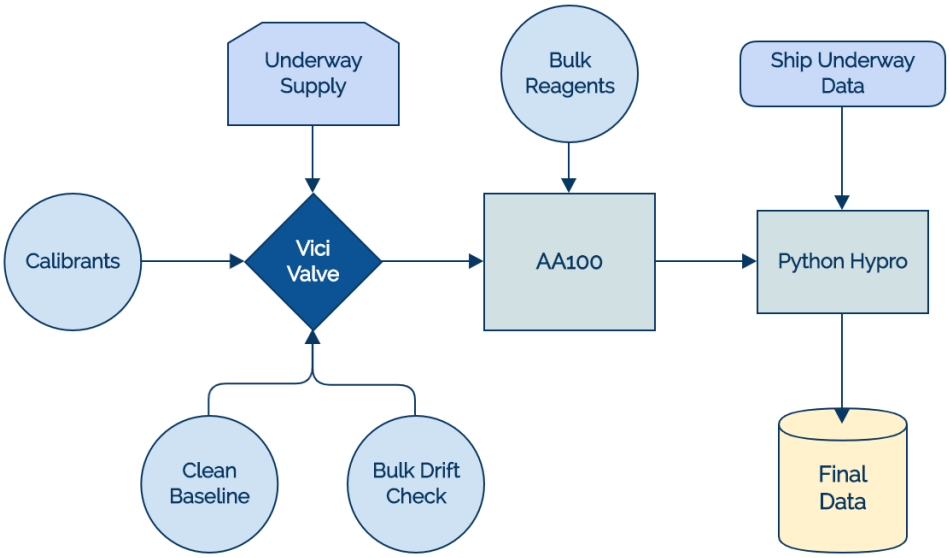


Figure 1: Underway Nutrient Analysis and Data Processing Flow Diagram.

5 Underway Nutrients Analysis & Data Processing

5.1 Nutrient Assay Parameter Summary

Details		
CSIRO Software	HyPro	
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 - 2.4 µmol l^{-1}	0 – 4 µmol l^{-1}
Method Detection Limit (MDL)	0.02 µmol l^{-1}	0.02 µmol l^{-1}
Matrix Corrections	None	none
Analysts	Kendall Sherrin	
Lab Temperature (±1°C)	Variable, 18– 25°C	
Reference Material	KANSO, RMNS lot CD and BU	
Sampling Container type	12ml PP tubes with screw cap lids – not analysed on AA100	
Sample Storage	≤ 12 hrs @ 4°C	
Pre-processing of Samples		
Comments		

5.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA100 segmented flow auto-analyser fitted with 1.5cm debubbled 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 di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 520 nm.

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

5.3 Nutrient Analysis Overview

Despite being the second voyage the AA100 was implemented on, the data produced was of very high quality. 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.

Calibration ranges had to be reduced considerably compared to the usual ranges that the instrument performs at. The highest calibrant for NO_x was 4 µmol l^{-1}, Phosphate was 2.4 µmol l^{-1}. This was due to the oligotrophic surface water that was being measured.

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 20mL, with the seawater flowrate between 3.5-4.0L/min. With such a small dead volume and high flowrate the sample could be as true as possible.

The residence time of the seawater through the underway piping would have contributed to a significant amount of lag in measurements. Testing and cleaning of the underway system while the ship was in port allow the measurement of a 2 minute and 35 second delay between water entering the drop keel to when it reaches the underway seawater laboratory. Residence time of analysis is about 5 minutes. If a time correction was to be applied, it would approximately be a subtraction of 7:35 from sample time stamps.

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	µmol l^{-1}	µmol l^{-1}
Calibration Curve degree	Linear	Linear
# of points in Calibration	5	5
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 on 28/9/2016. Sub-lot passed through a 10 micron filter and stored in 20 L carboys in the clean dry laboratory at 22°C.	

Result Details	Phosphate	Nitrate + Nitrite (NOx)
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 6.2.	

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 µmol l^{-1} for both channels.

HyPro was used to automatically assign latitude and longitude values to the data points. The latitude and longitude coordinates were extracted from the ships underway file by matching the UTC time stamps. Again, please note the offset of 7:35, which was not applied. Meaning the matching latitude and longitude for samples was when the measurement was recorded on the computer. To match this back to the original surface water the offset of 7:35 will need to be subtracted from all sample time stamps.

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 CD was assayed in triplicate in each run to monitor accuracy. The certified values are in table 1.

For in2019_v05, the majority of RMNS results are within 2% for Nitrate and 2% for Phosphate of their certified mean. Plots of RMNS values for all runs are below.

The assayed RMNS values per Analysis run are listed in appendix 6.2.

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 (µmol L^{-1}) at 21°C

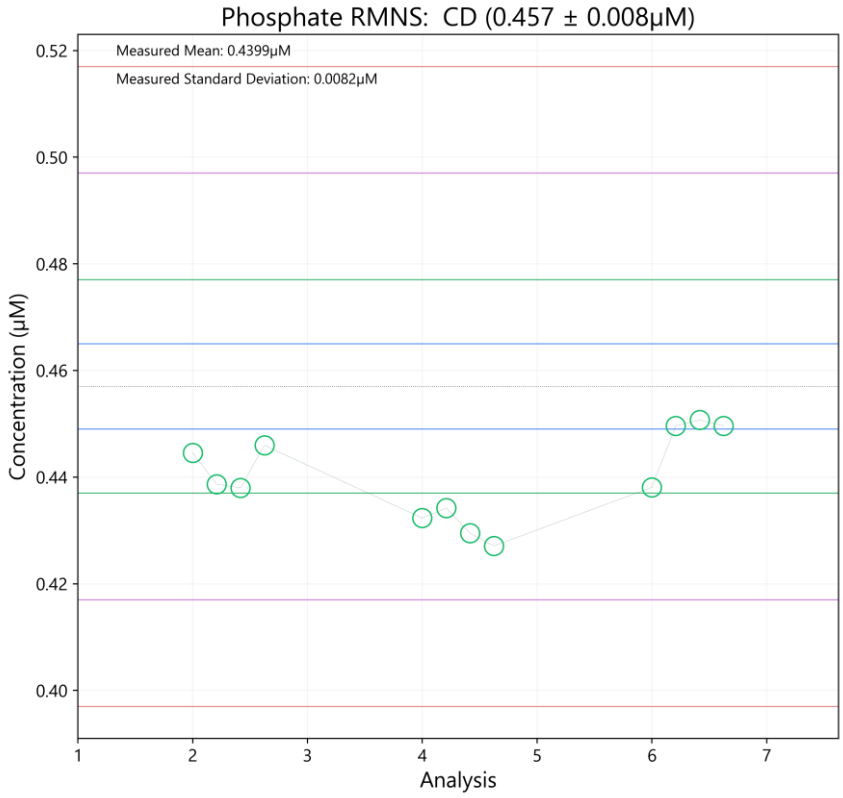
RMNS	NO_3+ NO_2 (NO_x, µmol l^{-1})	PO_4 (µmol l^{-1})
Lot CD	5.648 ± 0.056	0.457 ± 0.008
Lot BU	4.105 ± 0.058	0.353 ± 0.009

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

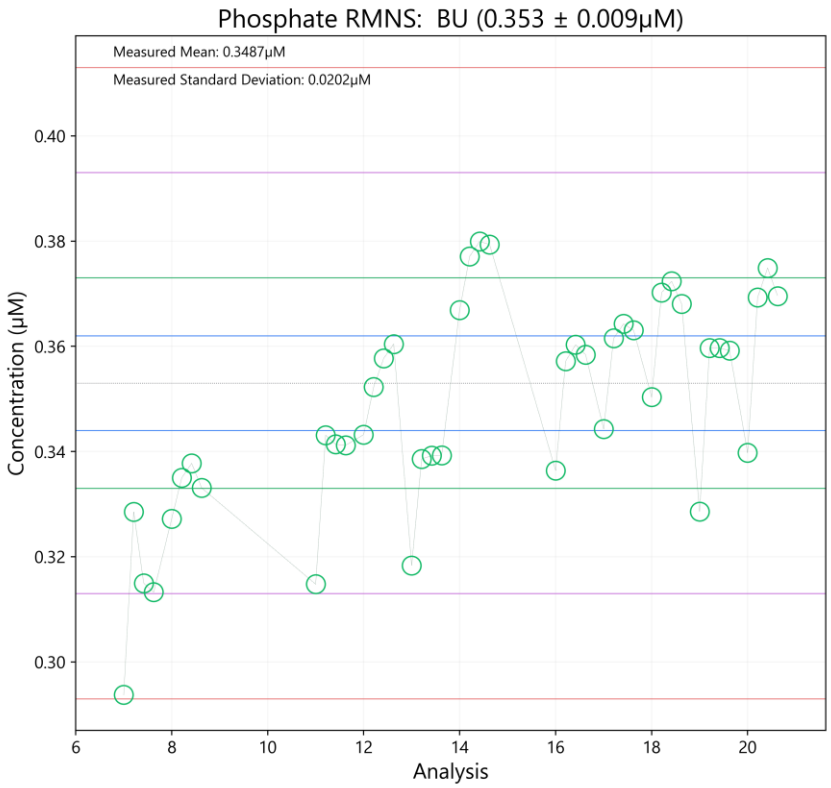
RMNS plot key. The green pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µmol l^{-1} increments from the certified value. The blue line is the expanded uncertainty of the certified value.

5.6.1 Phosphate RMNS Plot

Phosphate RMNS (3 runs) for CD (0.457 µmol l^{-1}) | measured mean: 0.439 µmol l^{-1}

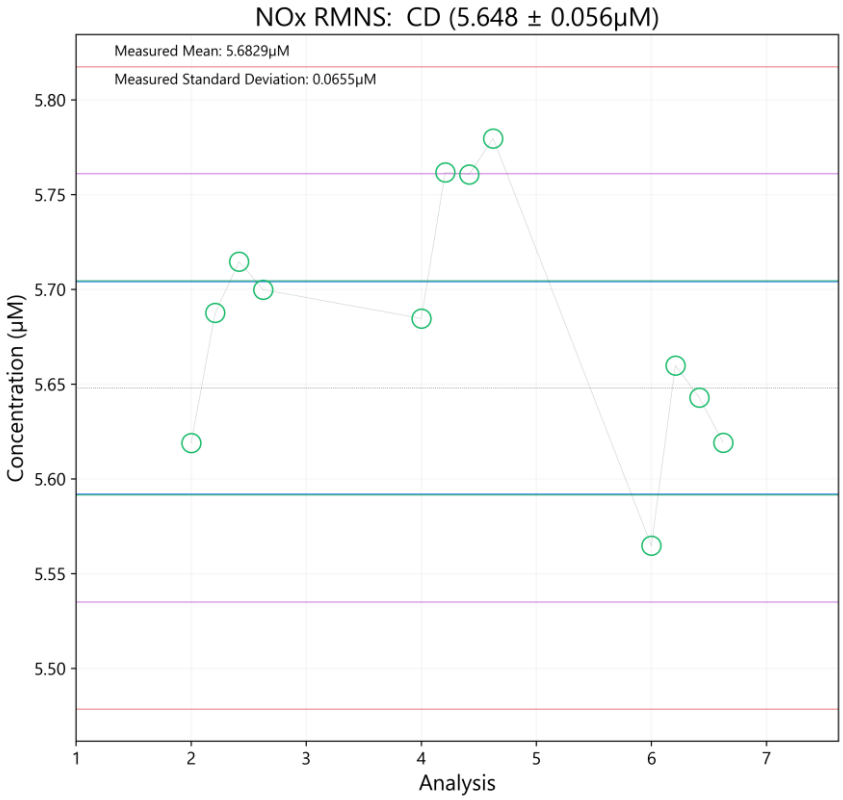


Phosphate RMNS (13 runs) for BU (0.353 µmol l^{-1}) | measured mean: 0.348 µmol l^{-1}

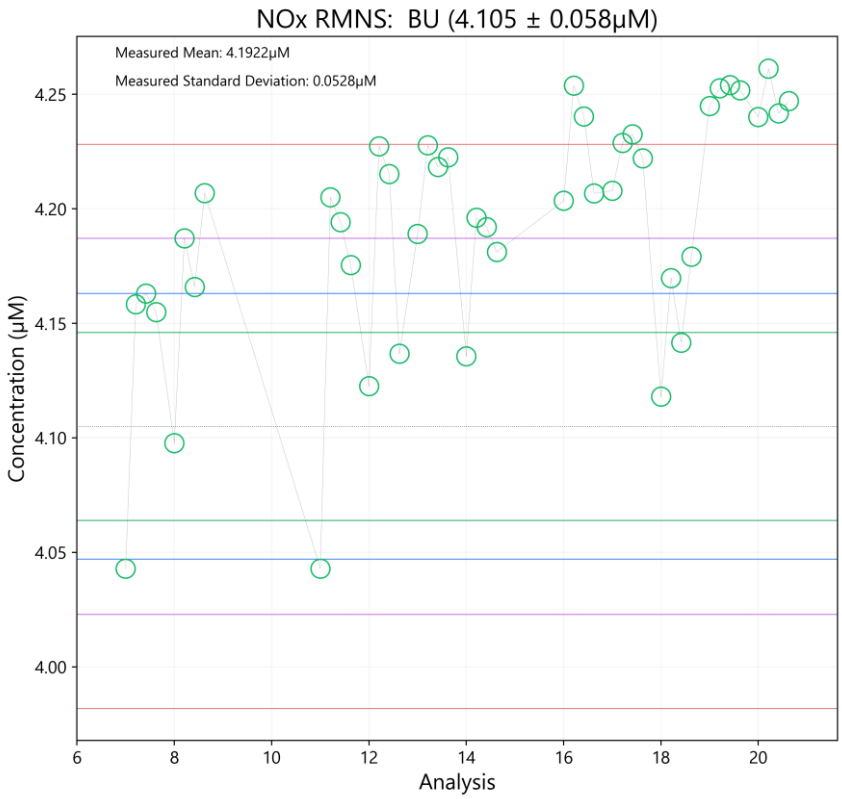


5.6.2 Nitrate + Nitrite (NOx) RMNS Plot

NOx RMNS (3 runs) for lot CD (5.648 µmol l^{-1}) | measured mean: 5.682 µmol l^{-1}



NOx RMNS (3 runs) for lot BU (4.105 µmol l^{-1}) | measured mean: 4.192 µmol l^{-1}



5.7 Analytical Precision

5.7.1 Nutrient Method Detection Limit

For in2019_v05, the measured detection limits for each run are much lower than the nominal detection limits, indicating high analytical precision at lower concentrations.

MDL	Phosphate (µmol l^{-1})	Nitrate + Nitrite (NOx, µmol l^{-1})
Nominal MDL*	0.02	0.02
Standard Dev. Min	0.006	0.006
Standard Dev. Max	0.024	0.08
Standard Dev. Mean	**0.019**	**0.06**
Standard Dev. Median	0.022	0.07
Precision of MDL (stdev)	0.023	0.07

*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.

RMNS CD	Phosphate (µmol l^{-1})	Nitrate + Nitrite (NOx, µmol l^{-1})
Published RMNS CD (µmol l^{-1}) w/std deviation	0.46 ± 0.001	5.65 ± 0.004
Minimum	0.430	5.62
Maximum	0.447	5.74
Mean	0.439	5.68
Median	0.441	5.68
Precision (Stdev)	0.008	0.06

RMNS BU	Phosphate (µmol l^{-1})	Nitrate + Nitrite (NOx, µmol l^{-1})
Published RMNS BU (µmol l^{-1}) w/std deviation	0.353 ± 0.009	4.105 ± 0.058
Minimum	0.312	4.12
Maximum	0.375	4.25
Mean	0.348	4.19
Median	0.353	4.17
Precision (Stdev)	0.008	0.04

6 Appendix

6.1 Nutrient Data Plotted to Map

The following plots contain the measured nutrient concentrations of the underway seawater over the entire in2019_v05 voyage. The plots contain data from the 10th to the 28th of September with different water masses and structures developing over time.

6.1.1 Nitrate

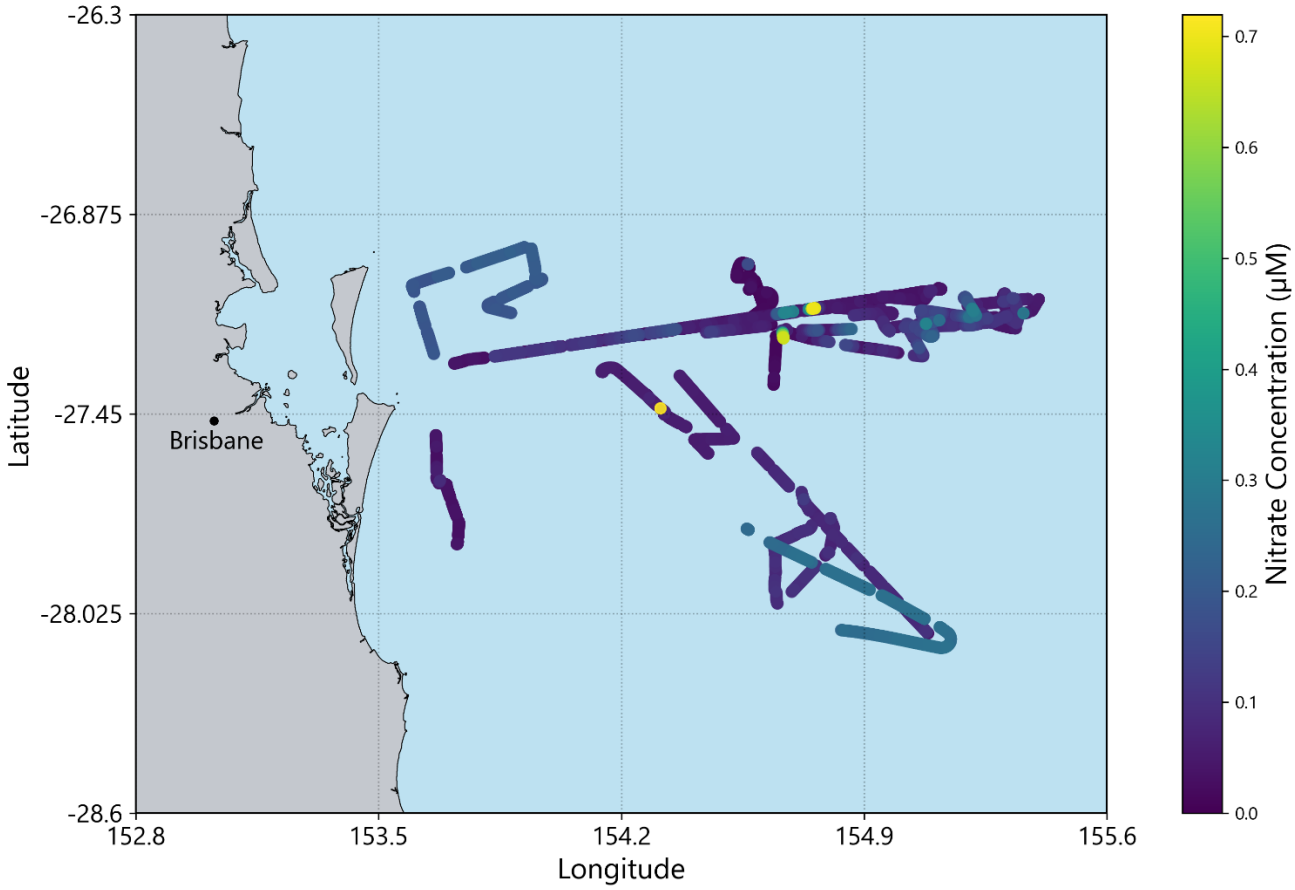


Figure 1. Nitrate concentrations of the surface water measured by the AA100 for the entire voyage. Points were sorted prior to plotting, resulting in higher concentration points being plotted on top. This is to highlight points of interest where nutrient spikes were observed in the underway water.

6.1.2 Phosphate

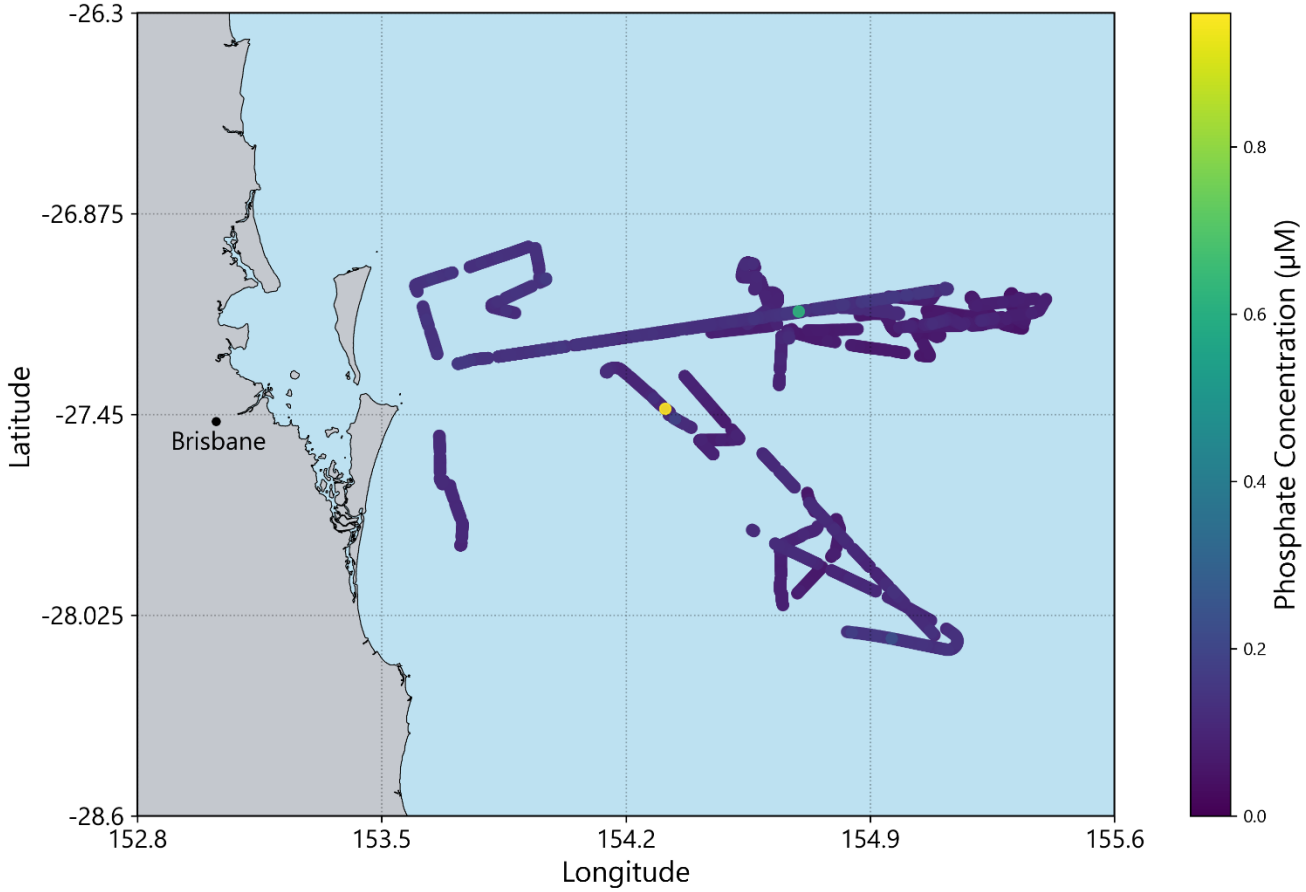


Figure 2. Phosphate concentrations of the surface water measured by the AA100 for the entire voyage. Points were sorted prior to plotting, resulting in higher concentration points being plotted on top. This is to highlight points of interest where nutrient spikes were observed in the underway water.

6.2 Nutrient Data over Dataset

6.2.1 Nitrate

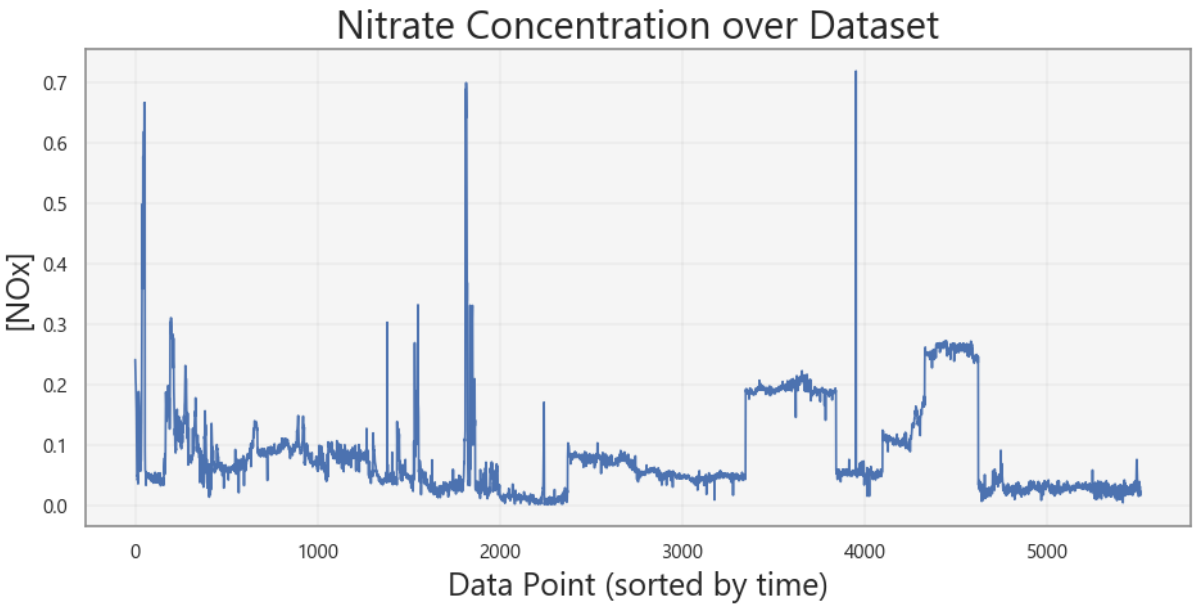


Figure 3. Nitrate concentrations of the surface water measured by the AA100 for the entire voyage. Points were sorted prior to plotting, in order of ascending time stamps. This give an overview on where the large peaks were observed throughout the voyage.

6.2.2 Phosphate

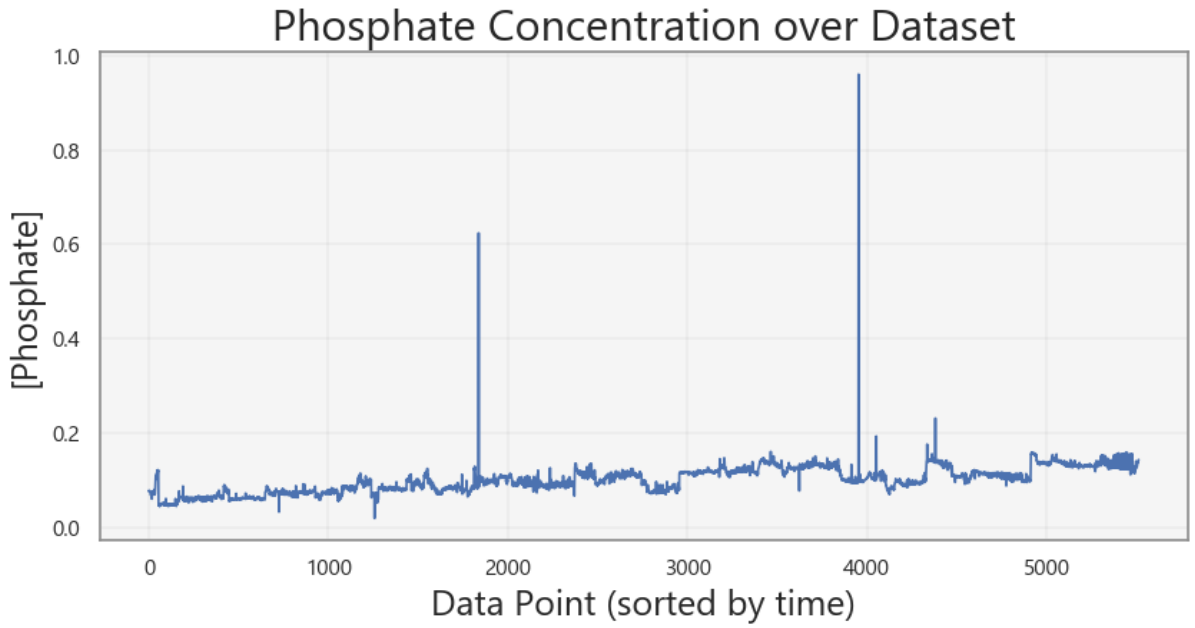


Figure 4. Phosphate concentrations of the surface water measured by the AA100 for the entire voyage. Points were sorted prior to plotting, in order of ascending time stamps. This give an overview on where the large peaks were observed throughout the voyage.

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

6.3.1 RMNS Lot CD Results

Analysis Run	Phosphate (µmol l^{-1})	NO_x (NO_2 + NO_3, µmol l^{-1})
CD reported	*0.46*	*5.65*
1	-	-
2	0.44	5.68
3	-	-
4	0.43	5.74
5	-	-
6	0.44	5.62

6.3.2 RMNS Lot BU Results

Analysis Run	Phosphate (µmol l^{-1})	NO_x (NO_2 + NO_3, µmol l^{-1})
BU reported	*0.353*	*4.105*
7	0.312	4.12
8	0.333	4.16
9	-	-
10	0.341	4.17
11	0.335	4.15
12	0.353	4.17
13	0.333	4.21
14	0.375	4.17
15	-	-
16	0.353	4.22
17	0.358	4.22
18	0.363	4.15
19	0.351	4.25
20	0.363	4.24

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

6.4 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.

6.4.1 PO_4

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

6.4.2 NO_3

Approximately 1% accuracy[1], 0.2% precision[2], full scale.

6.4.3 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

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