Report No. 1219

Waters Proficiency Testing Program

Round No. 265

- Total Kjeldahl Nitrogen, Total Phosphorus -

October 2020

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). Also our thanks go to Global Proficiency Ltd (New Zealand) and to Global Proficiency Pty Ltd (Australia) for the supply and distribution of the samples.

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CONTENTS

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Total Kjeldahl Nitrogen and Total Phosphorus in waters. This is round 265 in a planned series of programs involving the analysis of chemical and physical parameters of waters. This program is accredited to ISO/IEC 17043:2010 "*Conformity assessment - General requirements for proficiency testing"* by International Accreditation New Zealand (IANZ).

The exercise was conducted in August 2020 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Program Coordinator was Mrs D Mihaila and the Technical Adviser was Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). This report was authorised by Mrs K Cividin, PTA Quality Manager.

2. Program Features and Design

2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only.

2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.

2.3 Participants were provided with two plastic bottles (labelled PTA 1 and PTA 2) containing artificial potable water for testing of Total Kjeldahl Nitrogen and Total Phosphorus.

2.4 A total of 19 laboratories received samples, comprising:

- 17 Australian participants; and
- 2 overseas participants, including:
    - Indonesia (1), Papua New Guinea (1).

All laboratories submitted results by the due date.

2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, uncertainty of the median, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).

2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and ordered z-score charts relevant to each test are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia,* 2019 (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

2.7 A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 15.

2.8 Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity and stability. Based on the results of this testing (see Appendix B) it was considered that the samples utilised for this program were homogeneous and stable. As such, any results later identified as outliers could not be attributed to any notable sample variability.

3. Statistical Format

For each test, where appropriate, the following information is given:

- a table of results and calculated z-scores;
- a list of summary statistics; and
- ordered z-score charts.

3.1 Outlier Results and Z-scores

In order to assess laboratories' testing performance, a robust statistical approach, using z-scores, was utilised. Z-scores give a measure of how far a result is from the consensus value (i.e. the median), and gives a "score" to each result relative to the other results in the group.

A z-score with an absolute value less than or equal to 2.0 is considered to be satisfactory, whereas, a z-score with an absolute value greater than or equal to 3.0 is considered to be an outlier and is marked by the symbol "§". Laboratories are also encouraged to review results which have an absolute z-score value between 2.0 and 3.0 (i.e. $2.0 < |z\text{-score}| < 3.0$). These are considered to be questionable results.

Each determination was examined for outliers with all methods pooled. The table on page 15 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

The tables in Appendix A contain the results returned by each laboratory, including the code number for the method used and the robust z-score calculated for each result.

Results have been entered exactly as reported by participants. That is, laboratories which did not report results to the precision (i.e. number of significant figures) requested on the Results Sheet have not been rounded to the requested precision before being included in the statistical analysis.

A list of summary statistics appears at the bottom of each of the results tables and consists of:

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. 100 x *Normalised IQR* / *Median*;
- *Minimum*: the lowest laboratory result;
- *Maximum*: the highest laboratory result; and
- *Range*: the difference between the *Maximum* and *Minimum*.

The median is a measure of the centre of the data.

The normalised IQR is a measure of the spread of the results. It is calculated by multiplying the interquartile range (IQR) by a correction factor, which converts the IQR to an estimate of the standard deviation. The IQR is the difference between the upper and lower quartiles (i.e. the values above and below which a quarter of the results lie, respectively).

For normally distributed data, the uncertainty of the median is approximated by:

$$\sqrt{\frac{\pi}{2}} \times \frac{normIQR}{\sqrt{n}}$$

n = number of results.

Please see reference [1] for further details on these robust summary statistics.

In this round, the robust CV for Total Kjeldahl Nitrogen, sample PTA 2 was considered inappropriate to calculate robust z-scores, therefore a target coefficient of variation (target CV) was used. The target coefficient of variation was based on historical data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median.

The robust z-score (denoted by z) for a laboratory's sample A result was calculated as:

$$\mathrm{z} = \frac{\mathrm{A} - \mathrm{median(A)}}{\mathrm{target\ SD(A)}}$$

where A is a sample in a testing program.

3.3 Ordered Z-score Charts

The charts in Appendix A indicate each laboratory's robust z-score, in order of magnitude, marked with its laboratory code number. From these charts, each laboratory can readily compare its performance relative to the other laboratories.

These charts contain solid lines at +3.0 and -3.0, so that outliers are clearly identifiable as those laboratories whose "bar" extends beyond these "cut-off" lines. The y-axis of these charts has been limited, so very large z-scores appear to extend beyond the chart boundary.

4. PTA and Technical Adviser's Comments

4.1 Metrological Traceability and Measurement Uncertainty of Assigned Values

Consensus values (median) derived from participants' results are used in this program. These values are not metrologically traceable to an external reference.

Sample preparation was undertaken according to Global Proficiency Ltd's Standard Operating Procedures to ensure samples were fit-for-purpose, homogeneous and stable.

Solutions were stable and homogeneous, and medians obtained from this proficiency round were in consistent agreement with the expected levels (dope concentration), as shown in Table 1. Average recoveries were similar to those published in APHA 4500-N_{org} B (Macro-Kjeldahl) and APHA 4500-N_{org} D (Block Digestion – Flow Injection Analysis, FIA) [2].

Sample PTA 1 was prepared from Ammonium Chloride, Sulphanilamide, and Potassium Dihydrogen Orthophosphate in distilled water. Sample PTA 2 was prepared from Ammonium Chloride, Sulphanilamide, Nicotinic Acid, Potassium Dihydrogen Orthophosphate and Tetra Potassium Pyrophosphate (TPPP) in distilled water. All samples were preserved with Sulphuric Acid.

As the assigned value for each analyte in this program was the median of the results submitted by the participants, the uncertainty of the median for each analyte has been calculated and is presented in Table 1 below, together with the average analyte recovery data.

Table 1. Comparison of expected levels (dope concentration) and proficiency medians. The values of the calculated uncertainty of the median are also presented.

Analyte	Sample	Dope Concentration (mg/L)	Median (mg/L)	Analyte Recovery (%)	Uncertainty of the median (mg/L)
Total Kjeldahl Nitrogen	PTA 1	9	8.640	96%	0.292 [3.4 %]
	PTA 2	17	15.30	90%	0.56 [3.6 %]
Total Phosphorus	PTA 1	6	5.760	96%	0.141 [2.4 %]
	PTA 2	9	7.175	80%	0.374 [5.2 %]

Overall, laboratories performed well on sample PTA 1, however a few laboratories struggled to successfully analyse sample PTA 2 which contained components more difficult to digest.

4.2 Analysis of Round 265 Results

4.2.1 Total Kjeldahl Nitrogen (TKN)

Table 2 compares the Total Kjeldahl Nitrogen (TKN) medians and robust CVs from this round to those obtained in previous PTA rounds.

Table 2. Comparison of current round variability and proficiency median of Total Kjeldahl Nitrogen testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	8.64	10.1	14
	PTA 2	15.30	8.2	8
Report 1161	PTA 1	8.825	20.9	12
	PTA 2	14.95	11.2	12
Report 1106	PTA 1	8.545	16.2	18
	PTA 2	16.15	9.2	18

Bias / Accuracy

The TKN testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 7.44 – 9.92 mg/L for sample PTA 1 and 11.6 – 16.1 mg/L for sample PTA 2.

Out of 14 results submitted, one questionable result (2.0 < |z-score| < 3.0) was reported for sample PTA 1 (laboratory code 655) and four questionable results were reported for sample PTA 2 (laboratory codes 112, 443, 589 and 665). This represents a moderate grouping of laboratories who did not manage to recover the more difficult to digest sources of Nitrogen from the sample (Figure 2). In this case laboratories with questionable results for sample PTA 2 are recommended to do a follow-up investigation.

Two outlier results (|z-score| ≥ 3.0) were obtained for sample PTA 1, requiring follow-up action by laboratory codes 311 and 646. One outlier result was obtained for sample PTA 2, requiring follow-up action by laboratory 646.

Laboratories concerned with their TKN recoveries should follow up on the Quality Control (QC) procedures recommended in APHA 4020 B and Table 4020:I, including mandatory Method Blanks, Laboratory Fortified Blanks, Laboratory Fortified Matrix and Duplicates every 20th sample, or batch of samples tested. For troubleshooting and ongoing QC, section APHA 4500-N_{org} A 4 recommends the use of known additions of nicotinic acid to determine nitrogen recovery and the completeness of digestion; and known additions of ammonium chloride to test for loss of nitrogen [2]. Contaminated glassware, water, pH electrodes etc., are a potential source of error.

The TKN data set formed a normal distribution for sample PTA 1, with no notable bias attributable to any digestion / analysis method (Figure 1). For sample PTA 2, a bimodal distribution was obtained, with six out of 14 laboratories reporting low results for this sample. These results were excluded from statistical analysis for calculating the median. In addition, a historical target CV of 12.4% was used for sample PTA 2,

based on results from previous rounds. The most frequently used method to determine TKN was APHA 4500 – N_{org} B (Macro-Kjeldahl), which was used by 43% of participants.

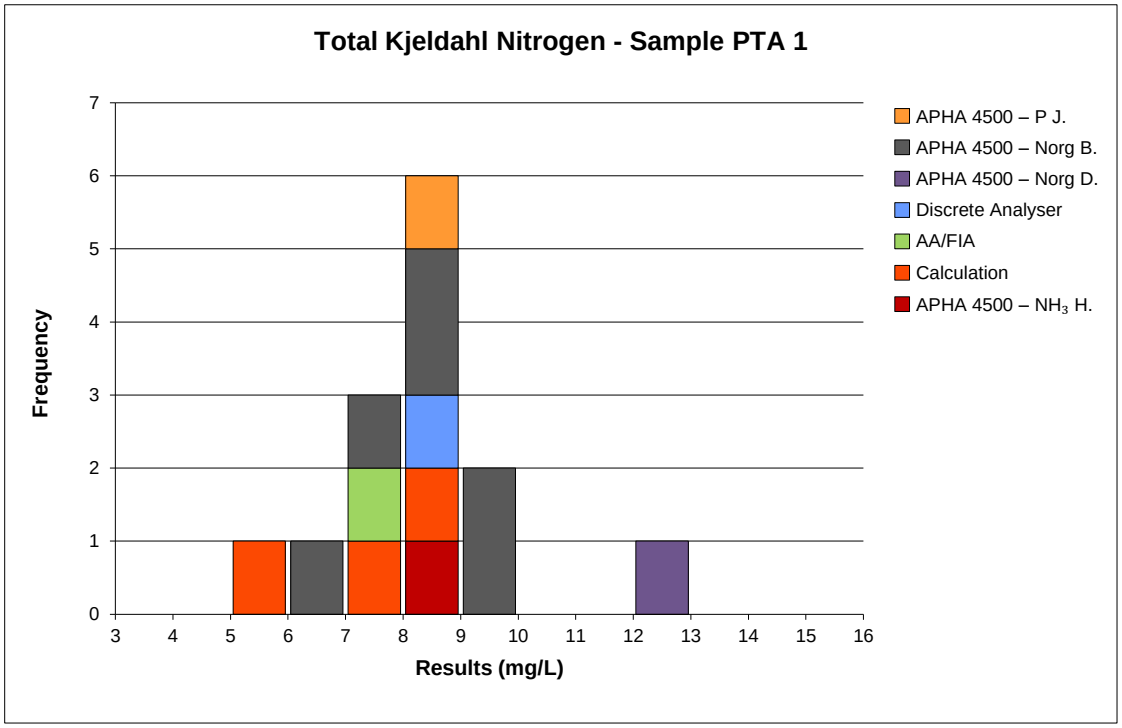


Figure 1. Spread of results for Total Kjeldahl Nitrogen testing of sample PTA 1, with a median of 8.64 mg/L.

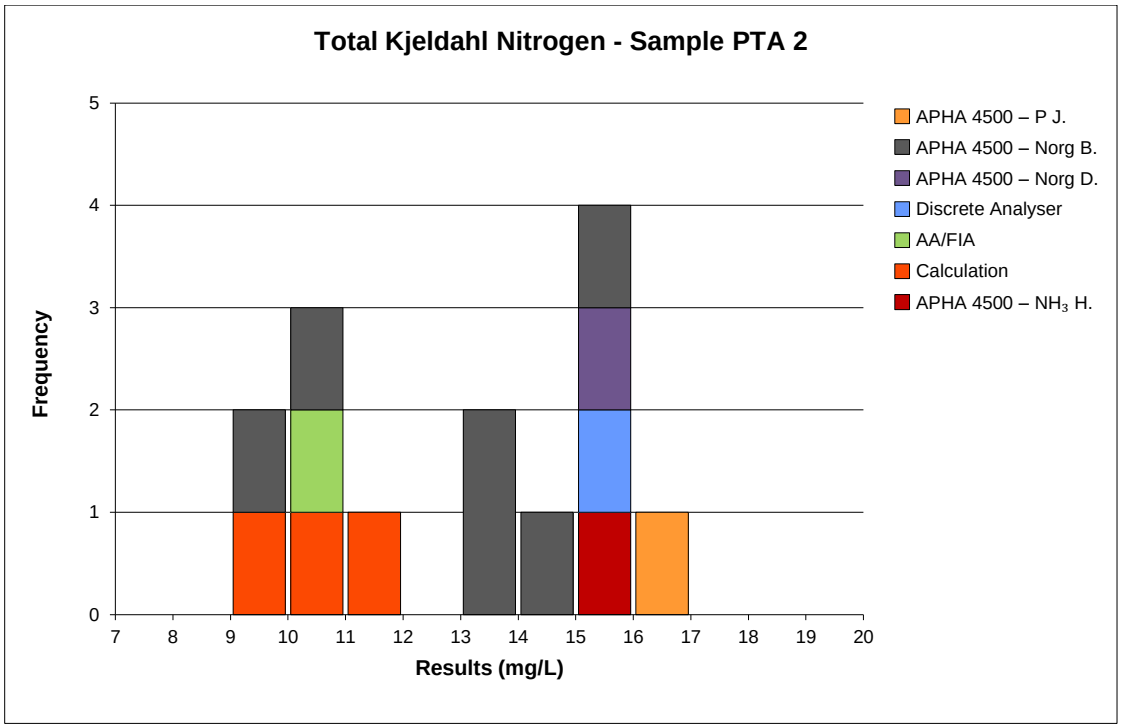


Figure 2. Spread of results for Total Kjeldahl Nitrogen testing of sample PTA 2, with a median of 15.30 mg/L.

Catalyst

In this round, three laboratories used the Copper catalyst in the digestion of TKN. Other laboratories reported using Mercury, Persulphate, Selenium (each with one laboratory), or other catalysts (three laboratories). It is good to see the majority of participants have moved away from the use of Mercury as a catalyst for Kjeldahl digestion, because of its toxicity and legal disposal issues. Carrying out the demonstration of capability indicated in APHA 4020 B 1a or method validation in APHA 1040 B, are recommended for any modifications to standard methods [2].

Final Ammonia Method

The most frequently used final Ammonia method in this round was the titrimetric method (APHA 4500 – NH_3 C), which was used by four laboratories. Other participants used Discrete Analysers (one laboratory) and APHA 4500 – NH3 G Automated Phenate Method (one laboratory).

Published precision information for the titrimetric method (APHA 4500 – NH_3 C) indicated that RSDs of 21.6% could be expected for samples in the vicinity of 1.5 mg NH_3-N/L [2], so laboratories managed well to achieve the CV found in this study for sample PTA 1 (10.1%).

Measurement Uncertainty (MU)

The MUs reported by participants can be seen in Figures 3 and 4. Out of 14 participants, 11 (79%) submitted MU information. The majority of laboratories who successfully encompassed the assigned value submitted MUs ranging between 7.5%-23%.

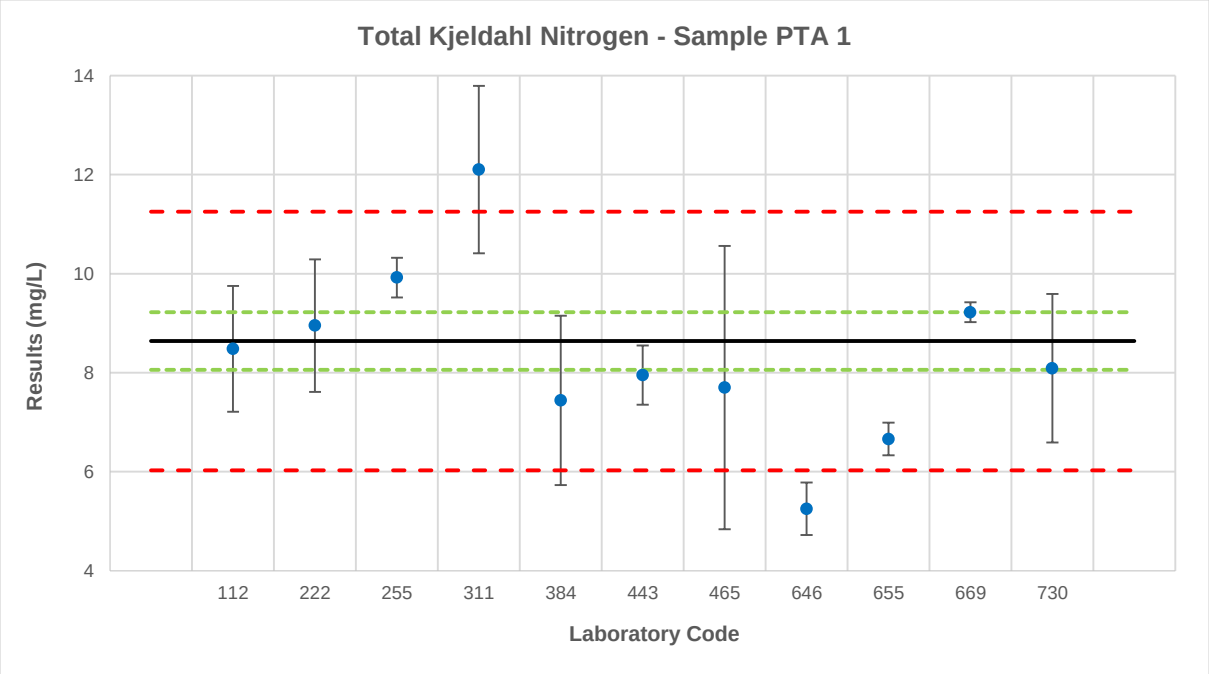


Figure 3. Spread of results for TKN testing of sample PTA 1, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

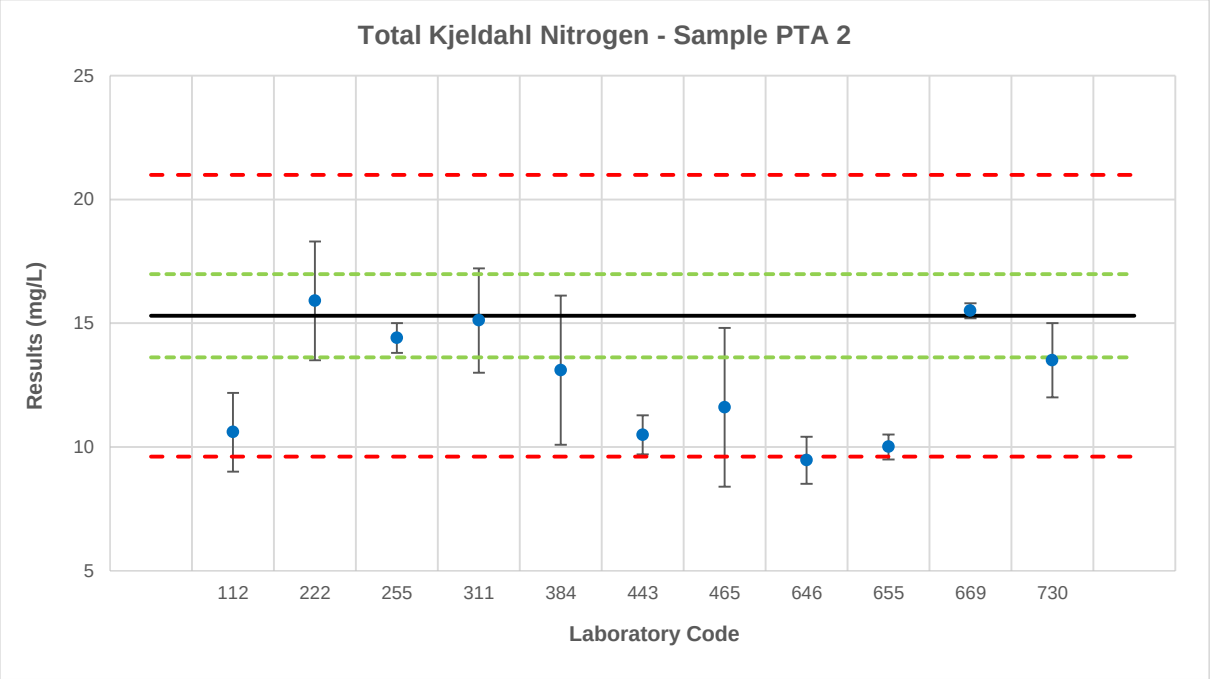


Figure 4. Spread of results for TKN testing of sample PTA 2, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

If laboratory codes 112, 255, 311, 443, 646 and 655 find that their MU does not encompass the assigned value in successive rounds, they may wish to reassess their measurement uncertainty, placing less reliance on in-house repeatability and including analysis of reference materials and proficiency test materials in their statistical calculations [3].

4.2.2 Total Phosphorus (TP)

Table 3 compares the Total Phosphorus (TP) medians and robust CVs from this round to those obtained in previous PTA rounds. The CV for PTA 2 was wider than seen in previous rounds and to those published in APHA 4500-P:I for Total Phosphorus at similar concentrations (10 mg/L) which ranged between 6.5% - 11.7% for various Persulphate, Sulphuric/Nitric acids or Perchloric acid digestion procedures [2]. Sample PTA 2 contained the more difficult to digest Tetra Potassium Pyrophosphate (TPPP) in addition to Orthophosphate.

Table 3. Comparison of current round variability and proficiency median of Total Phosphorus testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	5.760	8.5	19
	PTA 2	7.175	17.7	18
Report 1161	PTA 1	5.870	5.5	16
	PTA 2	8.120	9.8	16
Report 1106	PTA 1	5.860	4.4	23
	PTA 2	8.980	6.2	23

Bias / Accuracy

The TP testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 5.29 – 6.62 mg/L for sample PTA 1 and 5.30 – 9.44 mg/L for sample PTA 2.

Out of 19 results submitted for sample PTA 1 and 18 results for sample PTA 2, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory code 404) and one questionable result was reported for sample PTA 2 (laboratory code 628).

Two outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratory codes 637 and 730. One outlier result was obtained for sample PTA 2, requiring follow-up action by laboratory code 730.

One of the most common errors in phosphate testing occurs when cleaning equipment. It is important that all glass containers are rinsed with hot dilute HCl, then rinsed several times in reagent water. As many commercial detergents contain Phosphate, these should not be used for cleaning glassware that will be used in Phosphate analysis [2]. If pre-filtration is part of a laboratory's standard operating procedure, it is important that laboratories wash the membrane filters by soaking them in distilled water before use, as they can contribute significant amounts of Phosphorus. Even the use of different batches of filters can influence phosphorus determinations, so frequent blank determinations will ensure the consistency of washing procedures and the degree of contamination of filter batches [2]. Another potential source of error in Total Phosphate testing occurs if the calibration curve has been prepared using orthophosphate standards without hydrolysis. Salts added in acid hydrolysis (digestion) can cause an increase in the colour intensity in some methods [2].

The TP data sets formed normal distributions, with no notable bias attributable to any one analysis method (Figures 5 and 6). Methods used for TP analysis included: Stannous Chloride, Ascorbic Acid, FIA, Discrete Analyser, Test Kit, In-house ICP - MS/OES.

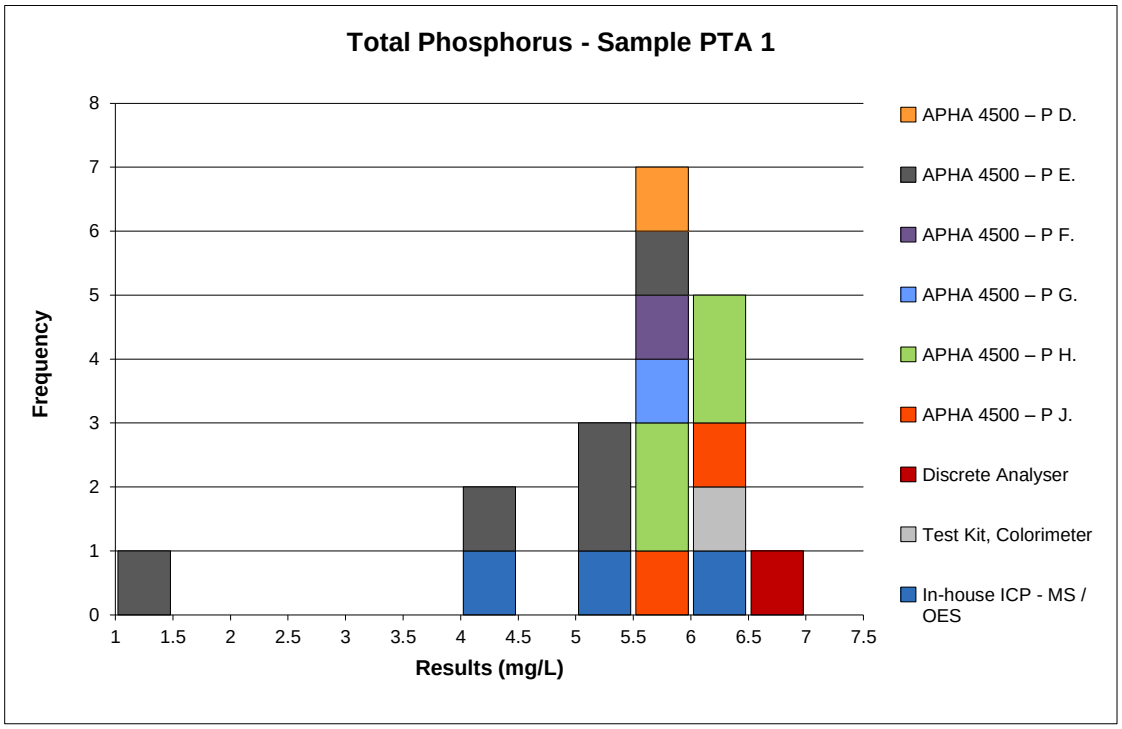


Figure 5. Spread of results for Total Phosphorus testing of sample PTA 1, with a median of 5.760 mg/L.

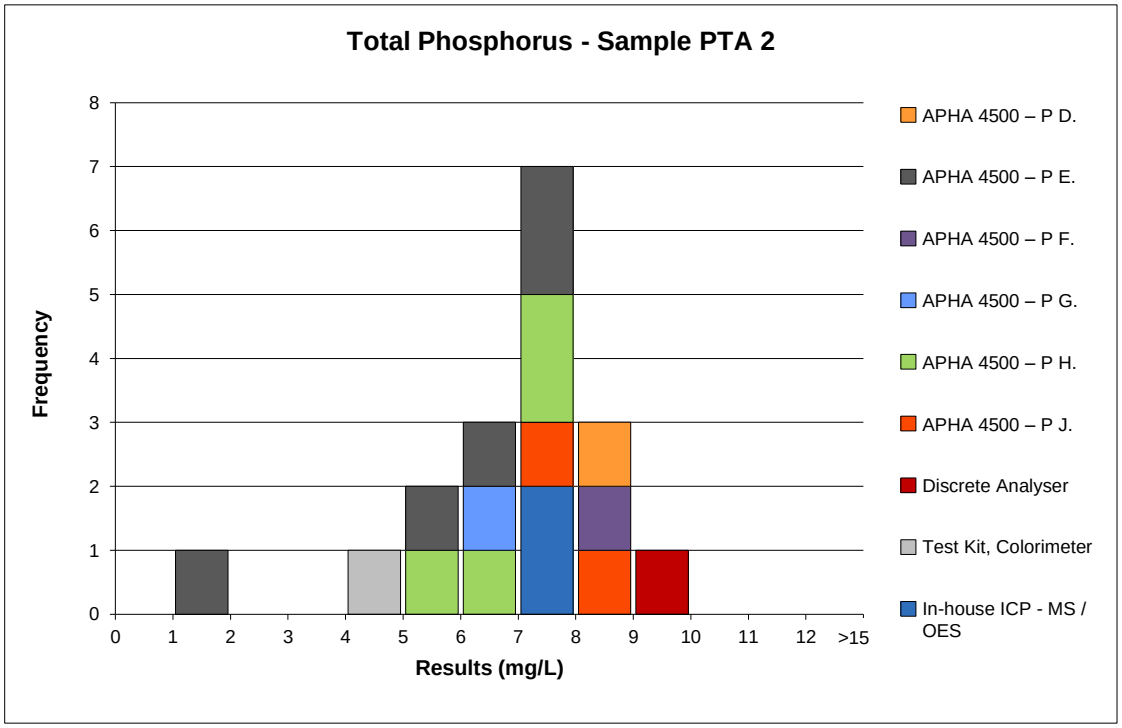


Figure 6. Spread of results for Total Phosphorus testing of sample PTA 2, with a median of 7.175 mg/L.

Digestion Method

The most frequently used digestion method to determine TP was the APHA 4500 – P B5 (Persulfate Method), which was used by 8 participants. Other laboratories used Sulphuric-Nitric acid digestion (4 laboratories), Nitric acid digestion, in-house methods and other methods.

The Nitric acid/Sulfuric acid method is recommended for most samples, however the Persulfate oxidation method has proven popular, as it is by far the simplest method. It is recommended that Persulfate oxidation methods be checked against one or more of the other digestion techniques, and only be adopted if identical recoveries are obtained on the laboratory's natural matrices [2].

QC procedures recommended in APHA 4020 B and Table 4020:I, include mandatory Method Blanks, Laboratory Fortified Blanks, Laboratory Fortified Matrix and Duplicates every 20th sample, or batch of samples tested [2].

Measurement Uncertainty (MU)

The MUs reported by participants can be seen in Figures 7 and 8. Out of 19 participants for sample PTA 1 and 18 participants for sample PTA 2, 89% submitted MU information. The majority of laboratories who successfully encompassed the assigned value submitted MUs ranging between 5%-15%.

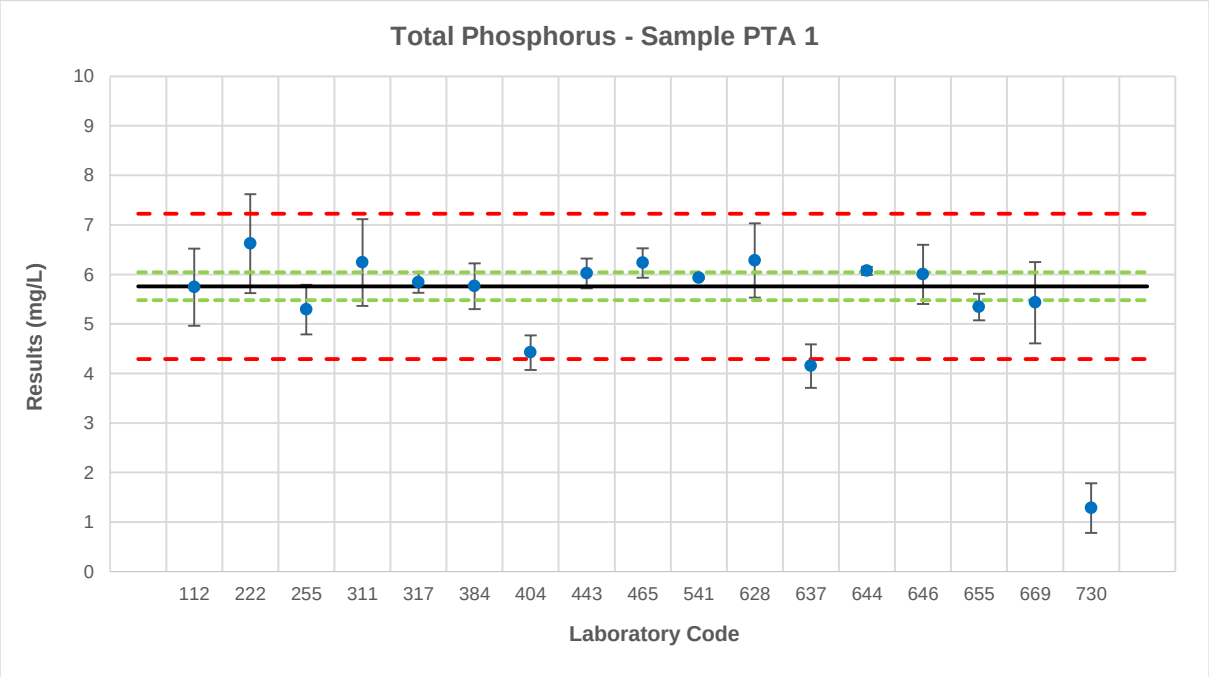


Figure 7. Spread of results for TP testing of sample PTA 1, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

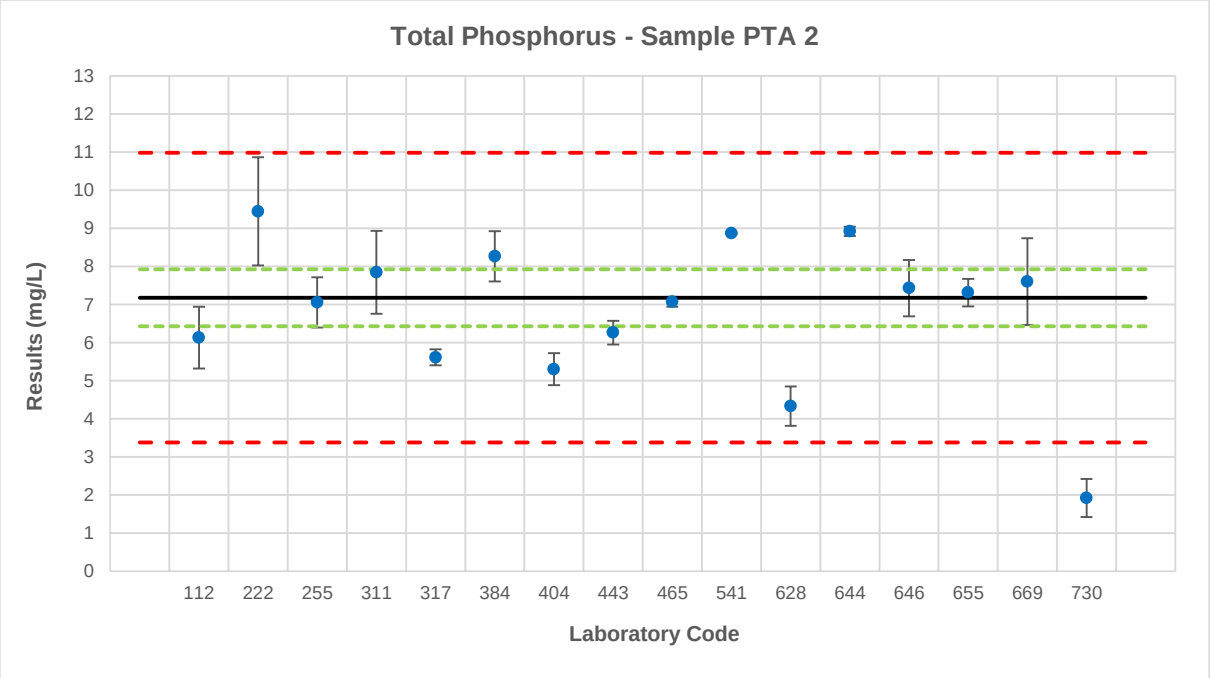


Figure 8. Spread of results for TP testing of sample PTA 2, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

If laboratory codes 222, 317, 404, 443, 541, 628, 637, 644, 655 and 730 find that their MU does not encompass the assigned value in successive rounds, they may wish to reassess their measurement uncertainty, placing less reliance on in-house repeatability and including analysis of reference materials and proficiency test materials in their statistical calculations [3].

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (79%-89%) reported the MU associated with their results. Table 4 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 4. The number and percentage of laboratories reporting MU for analytes in round 265

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Total Kjeldahl Nitrogen	PTA 1	14	11 (79%)
	PTA 2	14	11 (79%)
Total Phosphorus	PTA 1	19	17 (89%)
	PTA 2	18	16 (89%)

Some laboratories may have notably underestimated their MU, as they indicated that their MU was less than two times the uncertainty of the median (see Table 1), however, their results were further from the median than this value[1].

If this situation occurs in successive proficiency rounds, laboratories may wish to re-examine their measurement uncertainty calculations.

4.4 Analysis of Results by Method Groups

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. As there were less than 11 results submitted for each method, reliable conclusions cannot be drawn from analysing grouped methods on this occasion. Therefore, results from all method groups have been pooled for analysis.

[1] MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [4]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 5 below.

Table 5. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis			
	Total Kjeldahl Nitrogen		Total Phosphorus	
	PTA 1	PTA 2	PTA 1	PTA 2
311	§			
646	§	§		
637			§	
730			§	§

Note:

1. A "**§**" indicates the occurrence of a z-score outlier result (i.e. those results for which |z-score| ≥ 3.0).

6. References

[1] *Guide to Proficiency Testing Australia*, 2019 (This document can be found on the PTA website, www.pta.asn.au).

[2] APHA *Standard Methods For the Examination of Water and Wastewater*, 2017. 23nd Edition by APHA, AWWA, WEF. American Public Health Association, Washington DC, USA.

[3] EURACHEM / CITAC Guide CG 4 (2012). *Quantifying Uncertainty in Analytical Measurement; S. Ellison & A. Williams (Eds), Third Edition, Section 7.8, pg 20.* https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf

[4] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

APPENDIX A

Results and Data Analysis

Total Kjeldahl Nitrogen (TKN) Results

Samples PTA 1 and PTA 2

Total Kjeldahl Nitrogen (TKN)

Results by Laboratory Code

Laboratory Code	Sample PTA 1							
	Result ± mg/L		MU[1]	Robust z-score[2]		Method Code[3]	Catalyst Code[3]	Final Ammonia Method Code[3]
112	8.48	±	1.27	-0.18		39	#	#
117	8.80		#	0.18		53	28	28
222	8.95	±	1.34	0.36		36	25	#
255	9.92	±	0.40	1.47		26	41	48
311	12.10	±	1.69	3.97	**§**	28	42	#
384	7.44	±	1.71	-1.38		26	41	56
443	7.95	±	0.60	-0.79		37	20	#
465	7.70	±	2.86	-1.08		39	#	#
589	8.90		#	0.30		26	44	48
644	8.80		#	0.18		8	#	#
646	5.25	±	0.53	-3.89	**§**	39	43	52
655	6.66	±	0.33	-2.27		26	47	48
669	9.22	±	0.2	0.67		26	41	48
730	8.09	±	1.50	-0.63		26	25	#

No of Results:	14
Median:	8.640
Normalised IQR:	0.871
Uncertainty of the Median:	0.292
Robust CV:	10.1%
Minimum:	5.25
Maximum:	12.10
Range:	6.85

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| **≥** 3.0). Robust *z-scores* are calculated *as:* *z* = (*A* - *median*) ÷ *normalised IQR*, where *A* is the participant laboratory's result.

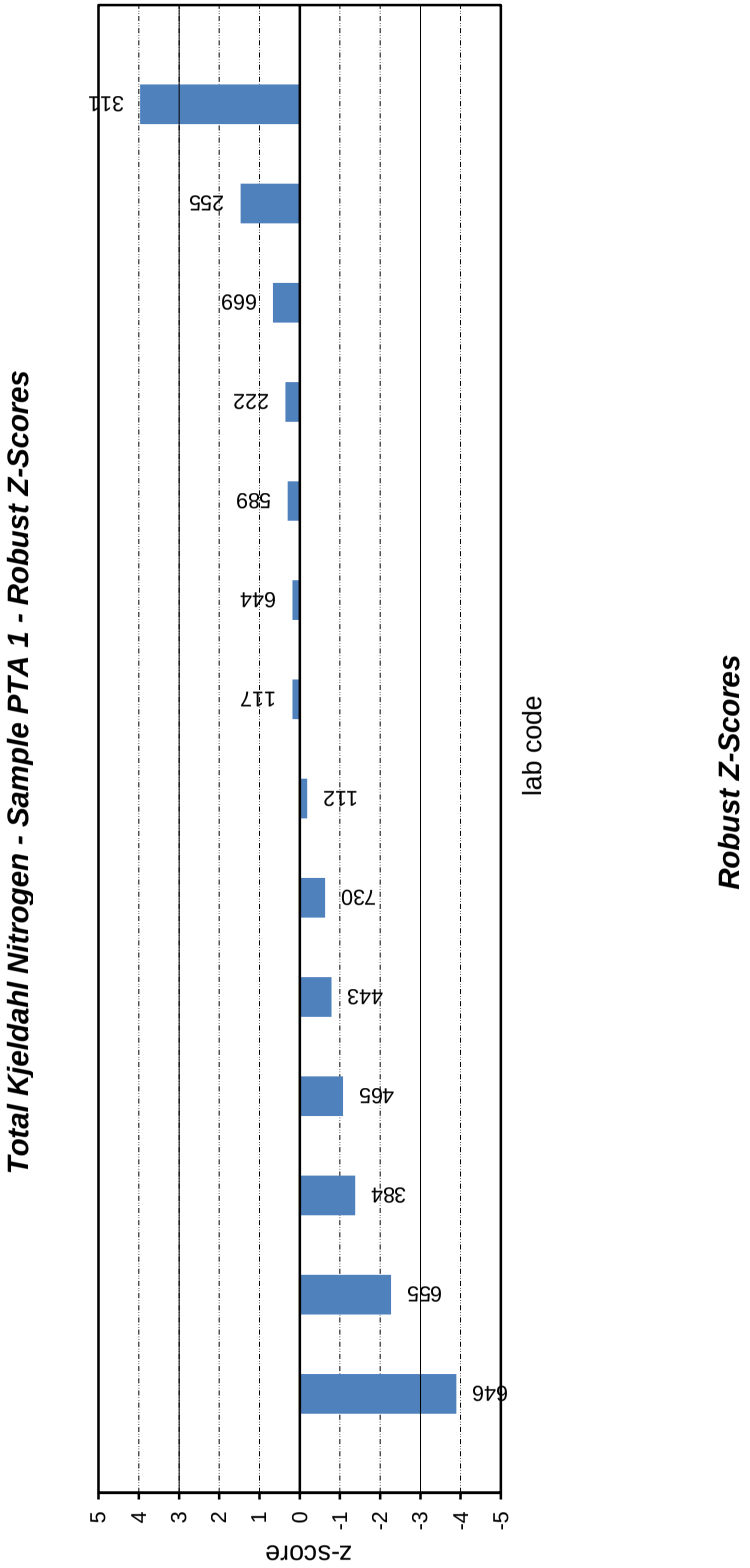
[3] Please refer to Appendix C (pages C3-C5) for method, catalyst and final Ammonia method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Total Kjeldahl Nitrogen - Sample PTA 1

Ordered Robust Z-Score Charts



Total Kjeldahl Nitrogen (TKN)

Results by Laboratory Code

Laboratory Code	Sample PTA 2						
	Result ± mg/L	MU[1]	Robust z-score[2]		Method Code[3]	Catalyst Code[3]	Final Ammonia Method Code[3]
112*	10.6 ±	1.59	-2.48		39	#	#
117	15.48	#	0.10		53	28	28
222	15.9 ±	2.4	0.32		36	25	#
255	14.4 ±	0.6	-0.47		26	41	48
311	15.11 ±	2.11	-0.10		28	42	#
384	13.1 ±	3.01	-1.16		26	41	56
443*	10.49 ±	0.79	-2.53		37	20	#
465*	11.6 ±	3.21	-1.95		39	#	#
589*	10.3	#	-2.63		26	44	48
644	16.1	#	0.42		8	#	#
646*	9.46 ±	0.95	-3.08	**§**	39	43	52
655*	10.0 ±	0.50	-2.79		26	47	48
669	15.5 ±	0.3	0.11		26	41	48
730	13.5 ±	1.50	-0.95		26	25	#

No of Results:	8
Median:	15.30
Target SD:	1.90
Uncertainty of the Median:	0.56
Target CV:	12.4%
Minimum:	13.1
Maximum:	16.1
Range:	3.0

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* *z* = (*A* - *median*) ÷ *Target SD*, where *A* is the participant laboratory's result. Please note that for Total Kjeldahl Nitrogen, sample PTA 2, a target CV of 12.4% was used, based on data from previous PTA rounds.

[3] Please refer to Appendix C (pages C3-C5) for method, catalyst and final Ammonia method code descriptions.

[4] "na" indicates "not applicable".

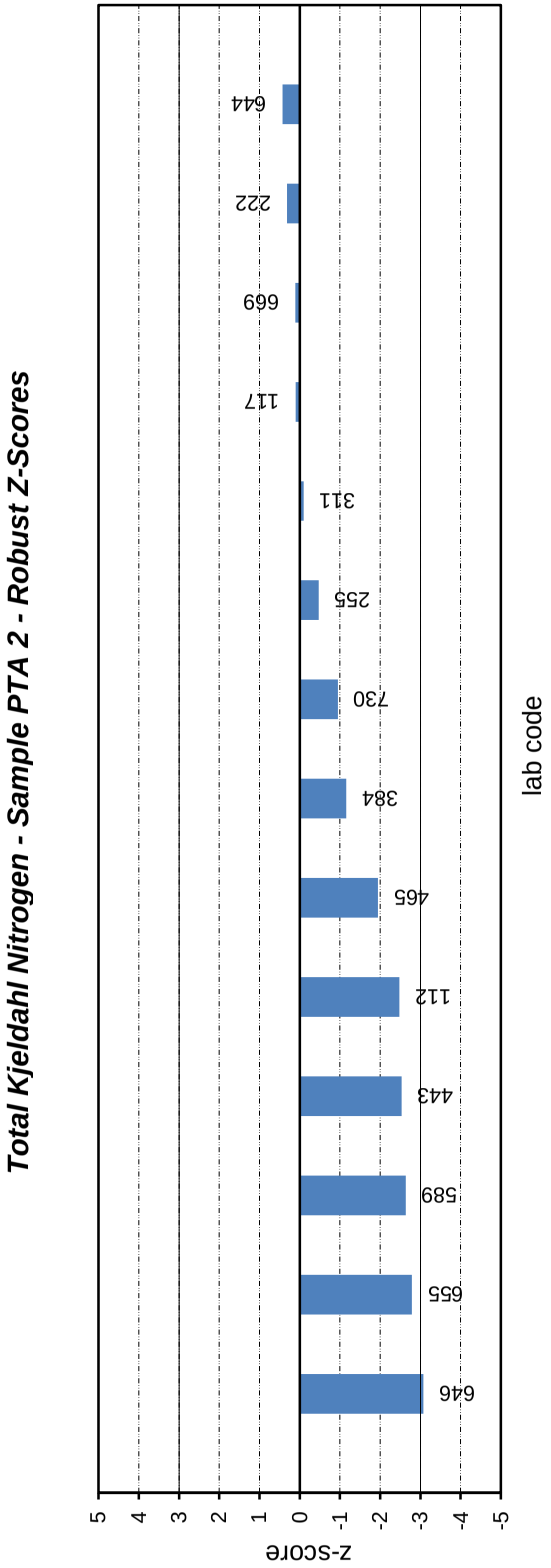
[5] "**#**" indicates that no result was returned for this sample/test.

[6] "*****" indicates results excluded from statistical analysis for calculating median and summary statistics.

A4

Total Kjeldahl Nitrogen - Sample PTA 2

Ordered Robust Z-Score Charts



SD 9.17.13

Total Phosphorus (TP) Results

Samples PTA 1 and PTA 2

Total Phosphorus (TP)

Results by Laboratory Code

Laboratory Code	Sample PTA 1						
	Result ± mg/L		MU[1]	Robust z-score[2]		Method Code[3]	Digestion Code[3]
112	5.74	±	0.78	-0.04		3	20
117	5.51		#	-0.51		6	6
222	6.62	±	1.0	1.76		13	20
255	5.29	±	0.50	-0.96		3	19
311	6.24	±	0.874	0.98		6	#
317	5.84	±	0.21	0.16		6	20
384	5.76	±	0.461	0.00		4	20
404	4.42	±	0.35	-2.74		3	20
443	6.02	±	0.30	0.53		6	20
465	6.23	±	0.296	0.96		16	21
541	5.93	±	0.02	0.35		2	19
589	5.76		#	0.00		5	19
628	6.28	±	0.75	1.06		15	25
637	4.15	±	0.439	-3.29	**§**	16	21
644	6.07	±	0.0826	0.63		8	#
646	6.00	±	0.60	0.49		8	20
655	5.34	±	0.27	-0.86		16	23
669	5.43	±	0.82	-0.67		3	20
730	1.28	±	0.50	-9.16	**§**	3	19

No of Results:	19
Median:	5.760
Normalised IQR:	0.489
Uncertainty of the Median:	0.141
Robust CV:	8.5%
Minimum:	1.28
Maximum:	6.62
Range:	5.34

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

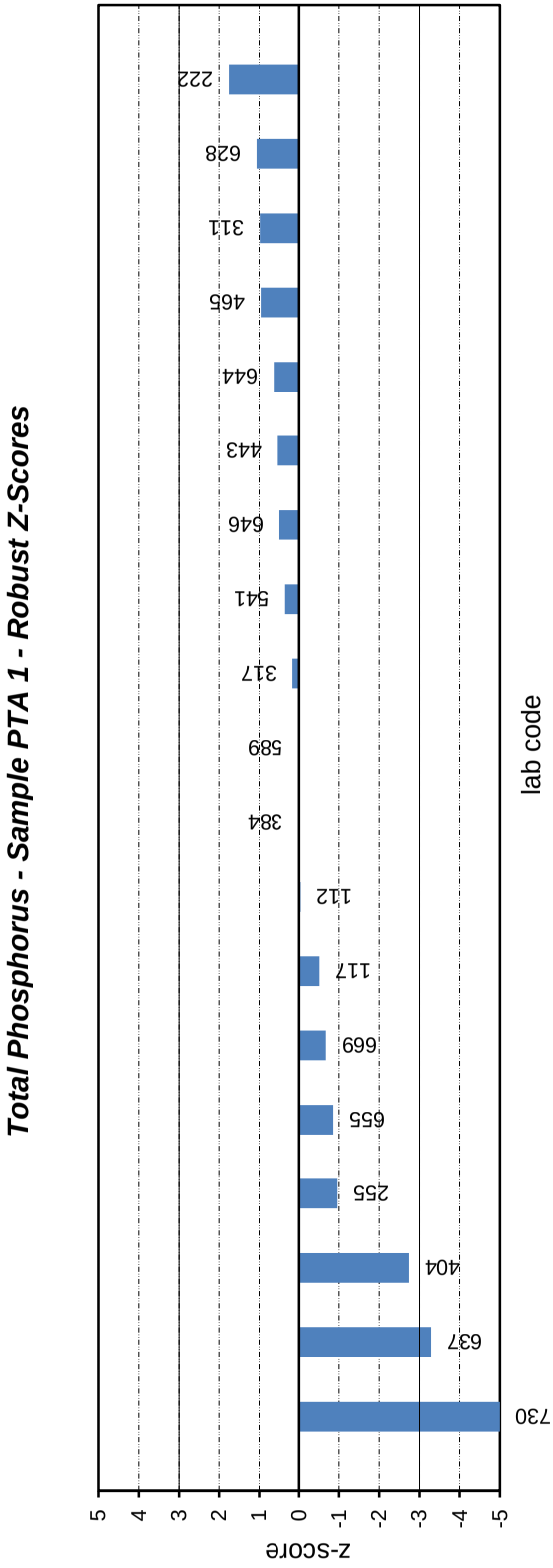
[3] Please refer to Appendix C (pages C3-C5) for method and digestion code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Total Phosphorus - Sample PTA 1

Ordered Robust Z-Score Charts



Total Phosphorus (TP)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result ± mg/L	MU[1]	Robust z-score[2]		Method Code[3]	Digestion Code[3]
112	6.13 ±	0.81	-0.82		3	20
117	7.28	#	0.08		6	6
222	9.44 ±	1.42	1.79		13	20
255	7.05 ±	0.66	-0.10		3	19
311	7.84 ±	1.09	0.52		6	#
317	5.61 ±	0.21	-1.23		6	20
384	8.26 ±	0.661	0.86		4	20
404	5.30 ±	0.42	-1.48		3	20
443	6.26 ±	0.31	-0.72		6	20
465	7.07 ±	0.128	-0.08		16	21
541	8.87 ±	0.02	1.34		2	19
589	6.05	#	-0.89		5	19
628	4.33 ±	0.52	-2.24		15	25
644	8.92 ±	0.121	1.38		8	#
646	7.43 ±	0.74	0.20		8	20
655	7.31 ±	0.36	0.11		16	23
669	7.60 ±	1.14	0.34		3	20
730	1.92 ±	0.50	-4.15	**§**	3	19

No of Results:	18
Median:	7.175
Normalised IQR:	1.268
Uncertainty of the Median:	0.374
Robust CV:	17.7%
Minimum:	1.92
Maximum:	9.44
Range:	7.52

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

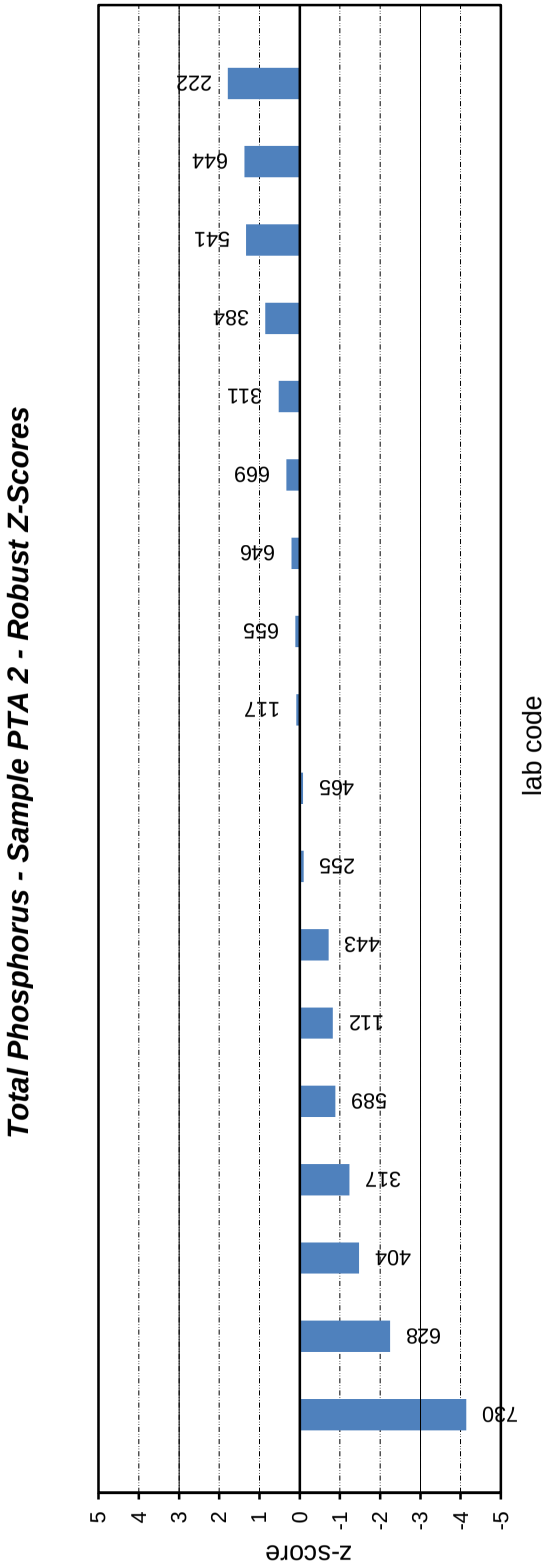
[3] Please refer to Appendix C (pages C3-C5) for method and digestion code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Total Phosphorus - Sample PTA 2

Ordered Robust Z-Score Charts



APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing

Samples for this program were obtained from Global Proficiency Ltd, New Zealand. As such, all samples are subjected to rigorous quality control and homogeneity / stability testing.

A random selection of ten samples was chosen from samples PTA 1 and PTA 2 for homogeneity and stability testing. Seven samples of each set were stored frozen and the remaining three were subjected to 35ºC for three days for an accelerated ageing stability trial. The samples were then analysed in duplicate by Global Proficiency Ltd using conductivity, ammonia and pH as an indicator tests.

All stability samples showed no notable differences when compared to homogeneity samples (Tables B1-B3).

From statistical analyses based on the results of this testing and rigorous quality control, it was considered that all samples were sufficiently homogeneous and stable, so that any results later identified as outliers should not be attributed to any notable sample variability.

Table B1. Homogeneity and stability testing of PTA 1 and PTA 2 samples - Conductivity.

Round PTA 265	Sample ID	**Conductivity (µS/cm)**			
		Samples PTA 1		**Samples PTA 2**	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	544	545	551	550
	H2	532	536	551	550
	H3	535	537	551	549
	H4	537	537	548	549
	H5	535	535	548	547
	H6	536	535	545	546
	H7	540	539	551	552
Stability	S1	538	538	559	559
	S2	534	534	547	545
	S3	533	533	547	544
RSD		0.63%		0.73%	

Table B2. Homogeneity and stability testing of PTA 1 and PTA 2 samples - Ammonia.

Round PTA 265	Sample ID	Ammonia (µS/cm)			
		Samples PTA 1		Samples PTA 2	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	0.217	0.219	0.35	0.34
	H2	0.217	0.219	0.34	0.34
	H3	0.219	0.219	0.35	0.34
	H4	0.219	0.220	0.34	0.34
	H5	0.218	0.224	0.34	0.35
	H6	0.217	0.222	0.35	0.34
	H7	0.217	0.223	0.35	0.34
Stability	S1	0.217	0.225	0.34	0.34
	S2	0.218	0.223	0.34	0.35
	S3	0.218	0.223	0.34	0.34
RSD		1.16%		1.37%	

Table B3. Homogeneity and stability testing of PTA 1 and PTA 2 samples - pH.

Round PTA 265	Sample ID	pH			
		Samples PTA 1		Samples PTA 2	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	2.98	2.98	3.02	3.03
	H2	2.98	2.98	3.03	3.03
	H3	2.98	2.98	3.02	3.02
	H4	2.98	2.98	3.03	3.03
	H5	2.98	2.98	3.03	3.03
	H6	2.98	2.98	3.03	3.03
	H7	2.98	2.98	3.02	3.02
Stability	S1	2.98	2.97	3.03	3.02
	S2	2.98	2.98	3.03	3.03
	S3	2.97	2.97	3.03	3.03
RSD		0.12%		0.16%	

One sample from each batch was subjected to a verification testing prior to despatch (one replicate per sample) by R J Hill Laboratories Ltd, New Zealand. The TKN method used by Hill Laboratories was a Sulphuric acid digestion with copper sulphate catalyst then phenol/hypochlorite colorimetry using a Discrete Analyser [APHA 4500-Norg D. (modified) 4500 NH3 F (modified) 22nd ed. 2012]. Total Phosphorus was analysed using Acid persulphate digestion and ascorbic acid colorimetry by Discrete Analyser [APHA 4500-P B & E (modified from manual analysis) 22nd ed. 2012]. Verification test results are presented in Table B4 below

The results of homogeneity, stability and verification testing presented in Tables B1 - B4 are not intended to be used as reference values.

Table B4. Verification testing results.

Round PTA 265	Total Kjeldahl Nitrogen (mg/L)	Total Phosphorus (mg/L)
	Replicate 1	Replicate 1
PTA 1	8.53 ± 0.45	5.75 ± 0.81
PTA 2	16.46 ± 0.86	8.1 ± 1.2

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 265 **AUGUST, 2020**

Total Kjeldahl Nitrogen, Total Phosphorus

INSTRUCTIONS TO PARTICIPANTS

Please record (on the Results Sheet) the approximate temperature of the samples upon receipt*

Please note the following before commencing the analysis of the samples.

1. Samples

i) Two plastic bottles labelled PTA 1 and PTA 2, supplied by Global Proficiency Ltd. The bottles contain approximately 1 L of artificial potable water for analysis of Total Kjeldahl Nitrogen and Total Phosphorus. The samples are stabilised with H_2SO_4 to pH ~3.

ii) The samples must be thoroughly mixed prior to analysis, and are ready to test.

Please Note: Where possible, proficiency testing samples should be treated as a routine laboratory sample.

2. Sample Preparation

Caution: Analysis must begin immediately after bottle is opened.

i) Adjust bottle temperature to 20ºC.

ii) Record bottle ID number.

iii) Mix thoroughly by inversion.

iv) Test according to your normal procedures.

v) Repeat steps **i)** to **iv)** for the second sample.

Please report results for the ready-to-test samples.

3. Tests Requested

Test requested for samples PTA 1 and PTA 2 are as follow:

i) Total Kjeldahl Nitrogen (TKN)

ii) Total Phosphorus (TP)

If unable to perform the above please note this on your Results Sheet.

4. Safety

i) Samples are for laboratory use only.

ii) Participants should have sufficient experience and training to take the necessary precautions when handling the samples and reagent chemicals and during disposal.

iii) Use of personal protective equipment such as safety glasses, gloves, laboratory coats and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

i) Report results using three significant figures (e.g.: 0.0123, 0.123, 1.23, 12.3).

ii) Report results in milligrams per litre (mg/L).

iii) Do not correct results for recovery.

iv) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.

v) Calculate the measurement uncertainty (MU) for each reported result. All estimates of MU must be given as a 95% confidence interval (coverage factor k ≈ 2) and reported in mg/L. Report MU using the same number of decimal places as for the result.

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 11 SEPTEMBER 2020** to:

Delfina Mihaila
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA
Phone: +612 9736 8397
Fax: +612 9743 6664
Email: dmihaila@pta.asn.au

7. For this program your laboratory has been allocated the code number shown on the attached Results Sheet. All reference to your laboratory in reports associated with the program will be through this code number, thus ensuring the confidentiality of your results.

8. As a guide, ranges for the samples can be expected to be:

Analyte	Range (mg/L)
Total Kjeldahl Nitrogen (TKN)	5 - 50
Total Phosphorus (TP)	0.5 - 10

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Total Phosphorus (TP)	APHA	APHA 4500 – P C. Vanadomolybdophosphoric Acid Colorimetric Method	1
		APHA 4500 – P D. Stannous Chloride Method	2
		APHA 4500 – P E. Ascorbic Acid Method	3
		APHA 4500 – P F. Automated Ascorbic Acid Reduction Method	4
		APHA 4500 – P G. Flow Injection Analysis for Orthophosphate	5
		APHA 4500 – P H. Manual Digestion and Flow Injection Analysis for Total Phosphorus	6
		APHA 4500 – P I. In-line UV/Persulfate Digestion and Flow Injection Analysis for Total Phosphorus	7
		APHA 4500 – P J. Persulfate Method for Simultaneous Determination of Total Nitrogen and Total Phosphorus	8
	USEPA	US EPA 0365.1 – 0.365.4 0365.1 Orthophosphate (as P) - Automated Colorimetry 0365.1 Phosphorus, All Forms - Colorimetric/Automated 0365.2 Phosphorus - manual colorimetric/1 reagent 0365.3 Phosphorus - colorimetric/ 2 reagents 0365.4 Phosphorus, Total - Colorimetric/Automated	9
		ESS Method 230.1: Total Phosphorus and Total Kjeldahl Nitrogen, Semi-Automated Method	10
	ISO / CEN	EN ISO 6878:2004 Water Quality - Determination Of Phosphorus - Ammonium Molybdate Spectrometric Method	11
	Other	Modified Standard Method	12
		Discrete Analyser	13
		AA / FIA	14
		Test Kit, Colorimeter (HACH, Fluka… specify).	15
		In-house ICP – MS/ OES	16
		Other (please specify)	17
Digestion Procedure for TP	APHA	APHA 4500 – P B3. Perchloric Acid	18
		APHA 4500 – P B4. Sulfuric-Nitric	19
		APHA 4500 – P B5. Persulfate	20
		APHA 3030 E. Nitric Acid Digestion	21
	USEPA	US EPA 0200.2 Phosphorus - Sample Preparation	22
	Other	In-house method	23
		Modified Standard Method	24
		Other (please specify)	25

Method Codes to be used for the Results Sheet (cont.)

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Total Kjeldahl Nitrogen (TKN)	APHA	APHA Part 4500 - Norg B. Macro-Kjeldahl Method	26
		APHA Part 4500 - Norg C. Semi-Micro Kjeldahl Method	27
		APHA Part 4500 - Norg D. Block Digestion and Flow Injection Analysis	28
	USEPA	USEPA 0351.1 – 0351.4 0351.1 Colorimetric/ Automated 0351.2 Colorimetric 0351.2 Semi-Automated Colorimetric 0351.3 Colorimetric/ Titrimetric 0351.4 Potentiometric	29
		ESS Method 230.1: Total Phosphorus and Total Kjeldahl Nitrogen, Semi-Automated Method	30
	ASTM	ASTM D3590 - 11 Standard Test Methods for Total Kjeldahl Nitrogen in Water	31
	ISO / CEN	ISO 5663:1984 (EN 25663:1993) Water quality - Determination of Kjeldahl nitrogen - Method after mineralization with selenium	32
		ISO 11905-1:1997 Water quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate	33
		EN 12260:2003 Water quality - Determination of nitrogen - Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides	34
	Other	Modified Standard Method	35
		Discrete Analyser	36
		AA / FIA	37
		Test Kit, Colorimeter (HACH… specify).	38
		Calculation (TN-NOx =TKN)	39
		Other (please specify)	40
TKN Catalyst		Copper	41
		Mercury	42
		Persulfate	43
		Selenium	44
		Sodium nitroferricyanide	45
		Titanium	46
		Other (please specify)	47

Continued on next page for Ammonia analysis methods…

Method Codes to be used for the Results Sheet (cont.)

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Ammonia Measurement for TKN	APHA	APHA 4500 – NH3 C. Titrimetric Method	48
		APHA 4500 – NH3 D. Ammonia-Selective Electrode Method	49
		APHA 4500 – NH3 E. Ammonia-Selective Electrode Method Using Known Addition	50
		APHA 4500 – NH3 F. Phenate Method	51
		APHA 4500 – NH3 G. Automated Phenate Method	52
		APHA 4500 – NH3 H. Flow Injection Analysis	53
	USEPA	US EPA 0351.1 – 0351.4 0351.1 Colorimetric/ Automated 0351.2 Colorimetric 0351.2 Semi-Automated Colorimetric 0351.3 Colorimetric/ Titrimetric 0351.4 Potentiometric	54
	Other	Modified Standard Method	55
		Discrete Analyser	56
		AA / FIA	57
		SFA	58
		Test Kit, Colorimeter (e.g. HACH… specify).	59
		Other (please specify)	60

Method Reference Key

i) APHA SM APHA "Standard Methods for the Examination of Water and Wastewater" (18, 19 20, 21, 22, 23 Edition). (http://www.standardmethods.org/)

ii) ASTM Annual Book of ASTM Standards, Vol. 11.01(2004). (http://www.astm.org)

iii) CEN European Committee for Standardization. (http://www.cen.eu/cen)

iv) ISO International Organization for Standardization. (http://www.iso.org)

v) US EPA U.S Environmental Protection Agency. (http://www.epa.gov/osa)

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 265

Total Kjeldahl Nitrogen, Total Phosphorus
AUGUST, 2020

RESULTS SHEET
(mg/L)

Please note:
Where possible, proficiency testing samples should be treated as a routine laboratory sample.

Laboratory Code

*Approximate temperature of samples upon receipt:	

ANALYSIS	Result (mg/L)	±MU* (mg/L)	METHOD CODE	DIGESTION or CATALYST CODE	FINAL AMMONIA METHOD CODE
Sample PTA 1					
Total Kjeldahl Nitrogen (TKN)					
Total Phosphorus (TP)					
Sample PTA 2					
Total Kjeldahl Nitrogen (TKN)					
Total Phosphorus (TP)					

i) For each sample only a single result is requested.

ii) Report results for the ready-to-test samples.

iii) Report results using three significant figures.

iv) Report results in milligrams per litre (mg/L).

v) Do not correct results for recovery.

vi) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in mg/L, using the same number of decimal places as for the result.

DATE: _____ **SIGNATURE:** _____

Return results **NO LATER THAN 11 SEPTEMBER 2020** to:
Delfina Mihaila
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA
Phone: +61 2 9736 8397
Fax: +61 2 9743 6664
Email: dmihaila@pta.asn.au

INSTRUCT WATERS PROF TEST PROG 265

- End of Report -