



Report No. 1055

Waters Proficiency Testing Program

Round No. 219

***- Total Kjeldahl Nitrogen,
Total Phosphorus -***

January 2018

Acknowledgments

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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 219 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in October 2017 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 Advisers were Dr M Buckley-Smith and Ms S Sharma, Global Proficiency Ltd (New Zealand). This report was authorised by Mrs F Watton, 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 two plastic vials (labelled PTA 1 and PTA 2) containing artificial potable water for testing of Total Kjeldahl Nitrogen and Total Phosphorus.

2.4 A total of 28 laboratories received samples, comprising:

- 26 Australian participants; and
- 2 overseas participants (Indonesia).

Of these 28 laboratories, 3 were unable to submit 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*, 2016 (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 12.
- 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 12 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. $100 \times \text{Normalised IQR} / \text{Median}$;
- *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:

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

n = number of results.

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

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

As the assigned value for each analyte in this program is 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	16	14.90	93.1%	0.28
	PTA 2	21	19.80	94.3%	0.50
Total Phosphorus	PTA 1	11	10.85	98.6%	0.19
	PTA 2	3	2.950	98.3%	0.046

Overall, the performance of participants in this round was good with robust CVs below 10% for all analytes.

4.2 Analysis of Round 219 Results

4.2.1 Total Kjeldahl Nitrogen (TKN)

Table 2 compares the TKN medians and robust CVs from this round to those obtained in previous PTA rounds. The CVs in this round were similar to those seen in previous rounds and, as expected, higher than repeatability relative standard deviations (RSD) published in APHA 4500 – N_{org} B (Macro-Kjeldahl Method), which were between 0.84%-3.46% for TKN concentration ranges of 5-20 mg/L. APHA 4500 – N_{org} D (Block Digestion and Flow Injection Analysis) published repeatability RSD of between 3.3%-7.3% [2], showing that laboratories did very well to achieve CVs comparable to these values, under reproducibility conditions.

Table 2. Comparison of current round variability and proficiency medians of TKN testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	14.90	6.5	19
	PTA 2	19.80	8.8	19
Report 1006	PTA 1	9.320	7.2	25
	PTA 2	43.10	3.9	25
	PTA 3	19.00	22.2	23
Report 938	PTA 1	7.070	6.2	22
	PTA 2	33.90	5.6	24
	PTA 3	14.30	8.3	23

The slight increase in CV for sample PTA 2 is likely due to the additional challenge of recovering Nicotinic Acid (8 mg-N/L in PTA 2) in addition to the more easily recoverable Sulphanilamide (7 mg-N/L in PTA 2) and Ammonium chloride (6 mg-N/L in PTA 2).

Bias / Accuracy

The TKN testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 13.2 – 16.5 mg/L for sample PTA 1 and 17.7 – 20.9 mg/L for sample PTA 2.

Out of 19 participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory 287) and two questionable results were reported for sample PTA 2 (laboratories 181 and 291).

Two outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 132 and 186. Three outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 132, 186 and 625.

The TKN data sets formed approximately normal distributions, with no notable bias attributable to any digestion / analysis method (Figures 1 and 2). The most frequently used method to determine TKN was APHA 4500 – N_{org} B (Macro-Kjeldahl), which was used by 32% of participants. Calculation methods (TN – NO_x = TKN) were used by 26% of participants.

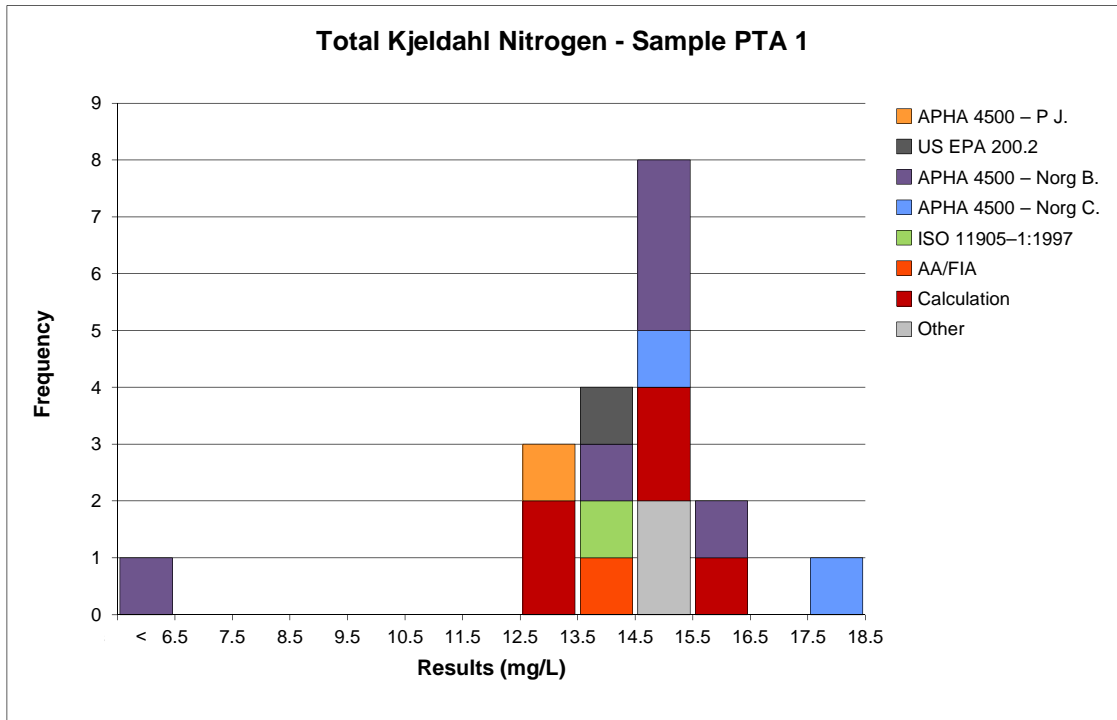


Figure 1. Spread of results for TKN testing of sample PTA 1, with a median of 14.90 mg/L.

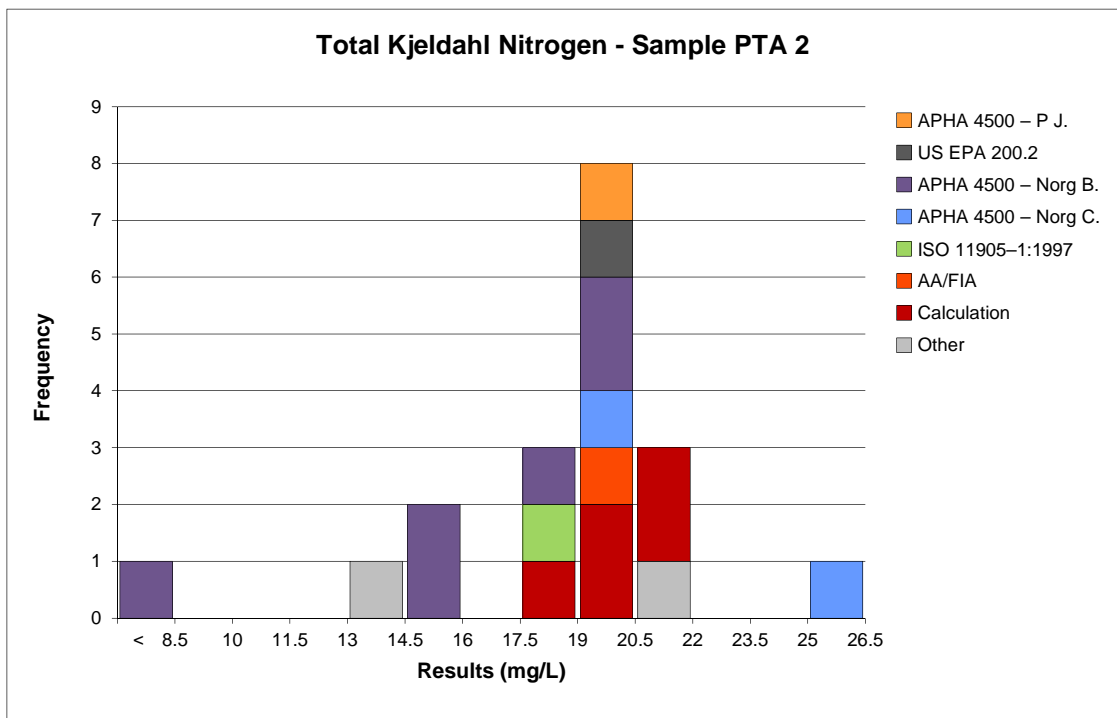


Figure 2. Spread of results for TKN testing of sample PTA 2, with a median of 19.80 mg/L.

It is recommended that laboratories which recovered < 50% of the Nicotinic Acid doped into sample PTA 2 (laboratories 132, 181, 291 and 625), 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-Norg 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].

Published precision information in APHA 4500-N_{org} B (Macro-Kjeldahl) indicated that recoveries of between 84.3% - 112% were achievable for Nicotinic Acid; and APHA 4500-Norg D (Block Digestion – FIA) indicated that recoveries of between 81% - 119% for influent and effluent type matrices are achievable for the FIA method [2].

Catalyst

A large number of participants in this round used the Copper or the Persulphate catalysts in the digestion of TKN (6 laboratories for each method). Other laboratories reported Selenium, Mercury or other catalysts (1 laboratory for each method). It is good to see that the move away from use of Mercury as a catalyst for Kjeldahl digestion, because of its toxicity and legal disposal issues, has been widely implemented. Laboratory 186 which high biased on both samples was using a Mercury catalyst and a modified standard method. 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 – NH₃ C), which was used by approximately 26% of participants. A relatively large number of laboratories (37%) did not report the final Ammonia method. This could be at least in part attributed to the sample analysis procedures being included with the digestion procedures in some methods.

TKN Measurement Uncertainty (MU)

The vast majority of laboratories have a very good understanding of their MU for TKN analysis, with most laboratories indicating their MU was between 5%-15%. If laboratories 186, 291 and 555 find that their MU does not encompass the assigned value in successive rounds, they may wish to reassess their MU, placing less reliance on in-house repeatability, and including analysis of reference materials and proficiency products in their statistical calculations.

4.2.2 Total Phosphorus (TP)

Table 3 compares the TP medians and robust CVs from this round to those obtained in previous PTA rounds. These CVs were comparable to those seen in previous rounds and those published in APHA 4500-P:I for TP 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].

Table 3. Comparison of current round variability and proficiency medians of TP testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	10.85	6.9	24
	PTA 2	2.950	6.0	23
Report 1006	PTA 1	8.000	3.1	25
	PTA 2	1.460	3.0	25
	PTA 3	4.210	6.2	25
Report 938	PTA 1	4.990	3.5	32
	PTA 2	1.240	6.9	34
	PTA 3	7.510	4.4	32

As seen previously in Table 1, the average recoveries of participants were very good compared to the doping concentrations (98%), with the relative errors similar to those published in APHA 4500-P:I which ranged between 0.3% - 4.3% for TP.

Bias / Accuracy

The TP testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 9.77 – 11.5 mg/L for sample PTA 1 and 2.61 – 3.16 mg/L for sample PTA 2.

Out of 24 results submitted for sample PTA 1 and 23 results for sample PTA 2, three questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for each sample (sample PTA 1: laboratories 132, 181 and 291; sample PTA 2: laboratories 132, 287 and 291).

Two outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 186 and 660. One outlier result was obtained for sample PTA 2, requiring follow-up action by laboratory 186.

The TP data sets formed approximately normal distributions, with no notable bias attributable to any one analysis method (Figures 3 and 4). There was a large variety of methods used for TP analysis in this round, including: Vanado-molybdophosphoric Acid Colorimetric, Stannous Chloride, Ascorbic Acid, FIA, Persulfate, Discrete Analyser, In-house ICP - MS/OES, etc.

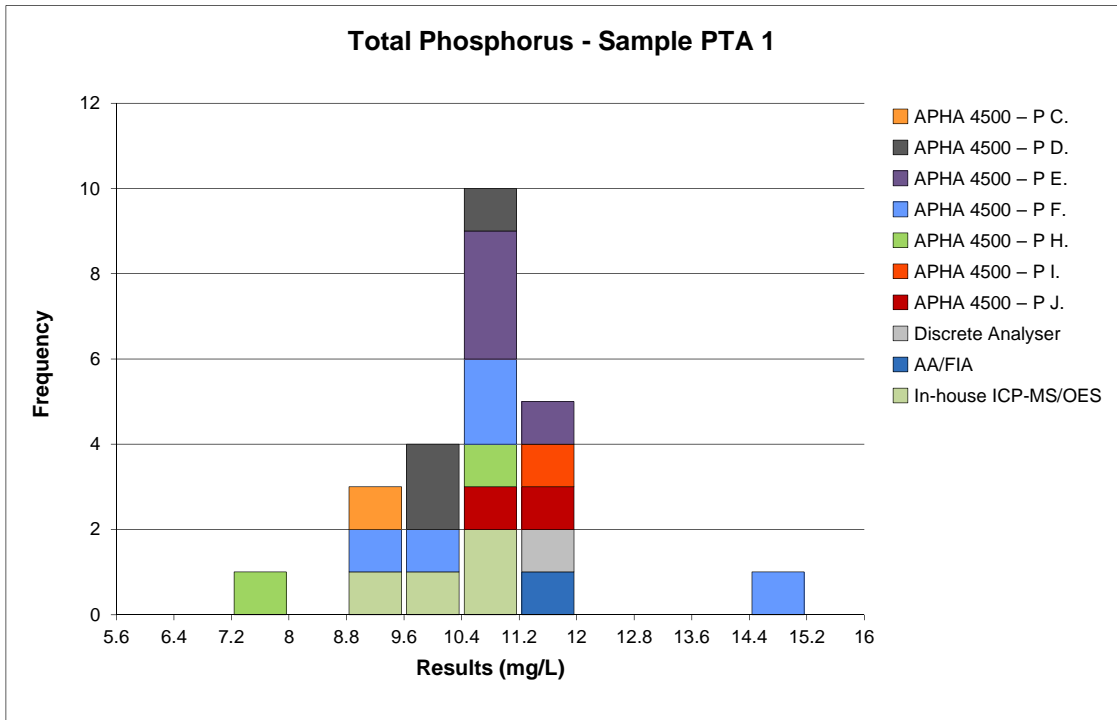


Figure 3. Spread of results for TP testing of sample PTA 1, with a median of 10.85 mg/L.

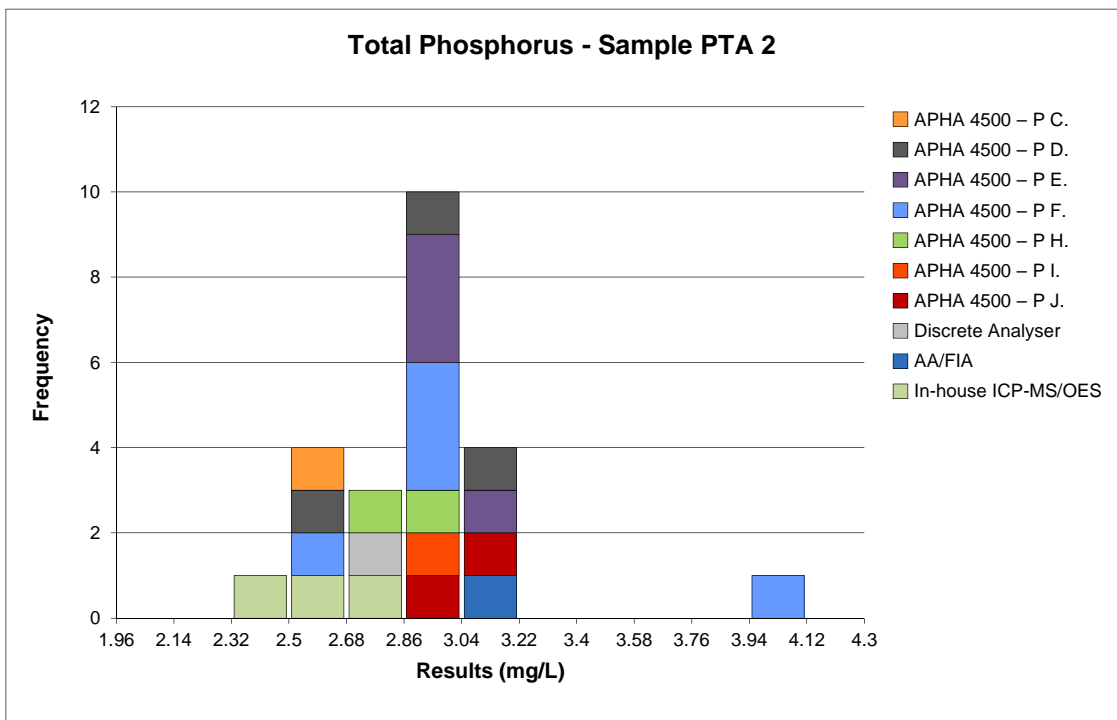


Figure 4. Spread of results for TP testing of sample PTA 2, with a median of 2.950 mg/L.

Digestion Method

The most frequently used digestion method to determine TP was the APHA 4500 – P B5 (Persulfate Method), which was used by 9 out of 24 participants. Other laboratories used Sulphuric-Nitric acid digestion, in-house methods and other.

No laboratory indicated they were using the more drastic and time-consuming Perchloric acid method, as it is primarily recommended only for particularly difficult samples, such as sediments. 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 more drastic digestion techniques, and only be adopted if identical recoveries are obtained on laboratory's natural matrices [2].

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

TP Measurement Uncertainty (MU)

A number of laboratories have underestimated their MU for TP testing in the current round. If laboratories 186, 291, 299, 660, 669 and 737 find that their MU does not encompass the assigned value in successive rounds, they may wish to reassess their MU, placing less reliance on in-house repeatability, and including analysis of reference materials and proficiency products in their statistical calculations. The majority of laboratories indicated their MU was between 3%-15% for TP analysis.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (79%-83%) 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 219

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Total Kjeldahl Nitrogen	PTA 1	19	15 (79%)
	PTA 2	19	15 (79%)
Total Phosphorus	PTA 1	24	19 (79%)
	PTA 2	23	19 (83%)

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.

Conversely, laboratories which indicated a MU which was greater than three times the normalised IQR may have overestimated their MU.¹

If either 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 [3]. 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
132	§	§		
186	§	§	§	§
625		§		
660			§	

Note:

1. A "§" indicates the occurrence of a z-score outlier result (i.e. those results for which $|z\text{-score}| \geq 3.0$).

6. References

- [1] *Guide to Proficiency Testing Australia*, 2016 (This document can be found on the PTA website, www.pta.asn.au).
- [2] *APHA Standard Methods For the Examination of Water and Wastewater*, 2012. 22nd Edition by APHA, AWWA, WEF. American Public Health Association, Washington DC, USA.
- [3] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

APPENDIX A

Results and Data Analysis

Total Kjeldahl Nitrogen (TKN).....	A1
Total Phosphorus (TP)	A5

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	
106	13.99	±	3.33	-0.94	36	8	#	
132	5.50		#	-9.72	§	25	40	50
181	14.1		#	-0.83	25	43	47	
186	17.8	±	2.5	3.00	§	26	41	54
215	15.2	±	1.9	0.31	25	40	47	
222	15.7	±	1.73	0.83	38	20	#	
287	12.9	±	2.3	-2.07	38	42	50	
291	16.5	±	0.82	1.65	25	42	47	
299	14.4	±	1.4	-0.52	21	40	44	
435	15.2	±	0.830	0.31	39	40	58	
449	14.0	±	2.8	-0.93	32	42	na	
479	15.1		#	0.21	38	#	#	
509	14.8	±	0.6	-0.10	25	40	47	
555	13.4	±	0.7	-1.55	38	#	#	
608	14.9	±	1.0	0.00	38	42	56	
625	15.4		#	0.52	39	#	#	
656	15.4	±	2.08	0.52	25	40	47	
683	13.2	±	1.32	-1.76	8	#	58	
744	15.0	±	0.1	0.10	26	24	#	
<i>No of Results:</i>	19							
<i>Median:</i>	14.90							
<i>Normalised IQR:</i>	0.97							
<i>Uncertainty of the Median:</i>	0.28							
<i>Robust CV:</i>	6.5%							
<i>Minimum:</i>	5.50							
<i>Maximum:</i>	17.8							
<i>Range:</i>	12.30							

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

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

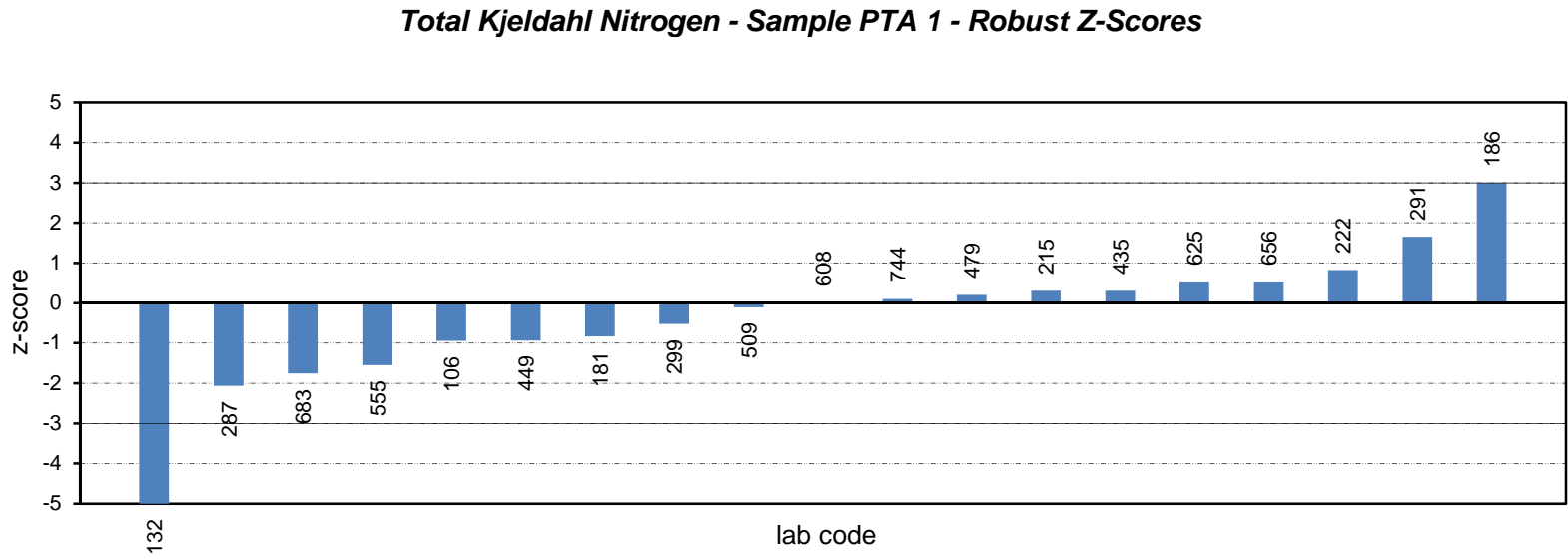
³ Please refer to Appendix C (pages C3-C5) for method, catalyst and final Ammonia method code descriptions.

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



Robust Z-Scores

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	
106	19.13 ±	4.56	-0.38	36	8	#	
132	5.20	#	-8.38 §	25	40	50	
181	14.7	#	-2.93	25	43	47	
186	25.8 ±	3.6	3.44 §	26	41	54	
215	19.8 ±	2.6	0.00	25	40	47	
222	20.9 ±	2.30	0.63	38	20	#	
287	20.2 ±	3.4	0.23	38	42	50	
291	14.6 ±	0.73	-2.98	25	42	47	
299	19.6 ±	1.9	-0.11	21	40	44	
435	20.6 ±	1.10	0.46	39	40	58	
449	17.7 ±	3.5	-1.21	32	42	na	
479	20	#	0.11	38	#	#	
509	20.4 ±	0.8	0.34	25	40.0	47	
555	18.7 ±	0.9	-0.63	38	#	#	
608	20.6 ±	1.0	0.46	38	42	56	
625	13.2	#	-3.79 §	39	#	#	
656	18.2 ±	2.46	-0.92	25	40	47	
683	19.8 ±	1.98	0.00	8	#	58	
744	20.2 ±	0.10	0.23	26	24	#	
<i>No of Results:</i>	19						
<i>Median:</i>	19.80						
<i>Normalised IQR:</i>	1.74						
<i>Uncertainty of the Median:</i>	0.50						
<i>Robust CV:</i>	8.8%						
<i>Minimum:</i>	5.20						
<i>Maximum:</i>	25.8						
<i>Range:</i>	20.60						

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

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

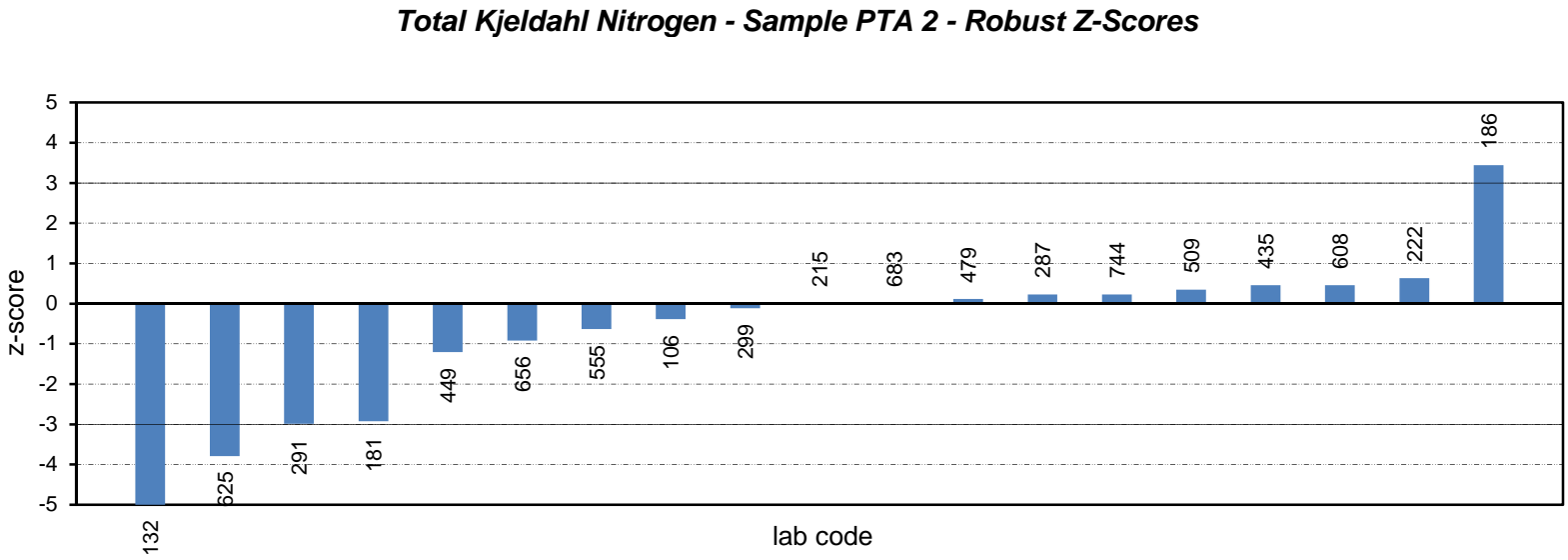
³ Please refer to Appendix C (pages C3-C5) for method, catalyst and final Ammonia method code descriptions.

⁴ "na" indicates "not applicable".

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

Total Kjeldahl Nitrogen - Sample PTA 2

Ordered Robust Z-Score Charts



Robust Z-Scores

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
101	11.4 ±	0.9	0.73	3	#
106	11.25 ±	3.79	0.53	14	8
132	9.25	#	-2.13	1	19
181	9.00	#	-2.46	4	19
186	14.9 ±	2.5	5.38 §	4	41
215	11.4 ±	1.7	0.73	13	20
222	11.5 ±	2.34	0.86	7	20
243	11.00 ±	1.1	0.20	3	20
287	10.6 ±	1.7	-0.33	4	20
291	8.84 ±	0.44	-2.67	16	19
299	9.89 ±	0.5	-1.28	4	19
322	10.80	#	-0.07	16	#
435	10.9 ±	0.331	0.07	4	22
449	10.2 ±	1.5	-0.86	16	22
479	11.5	#	0.86	8	20
509	11.1 ±	1.0	0.33	3	19
555	10.6 ±	0.3	-0.33	16	24
608	11.1 ±	0.2	0.33	6	20
625	9.77	#	-1.44	2	19
656	10.9 ±	0.963	0.07	2	19
660	7.39 ±	0.7	-4.60 §	6	20
669	10.4 ±	0.245	-0.60	2	19
683	10.5 ±	1.05	-0.47	8	20
737	11.1 ±	0.1	0.33	3	20

<i>No of Results:</i>	24
<i>Median:</i>	10.85
<i>Normalised IQR:</i>	0.75
<i>Uncertainty of the Median:</i>	0.19
<i>Robust CV:</i>	6.9%
<i>Minimum:</i>	7.39
<i>Maximum:</i>	14.9
<i>Range:</i>	7.51

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

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

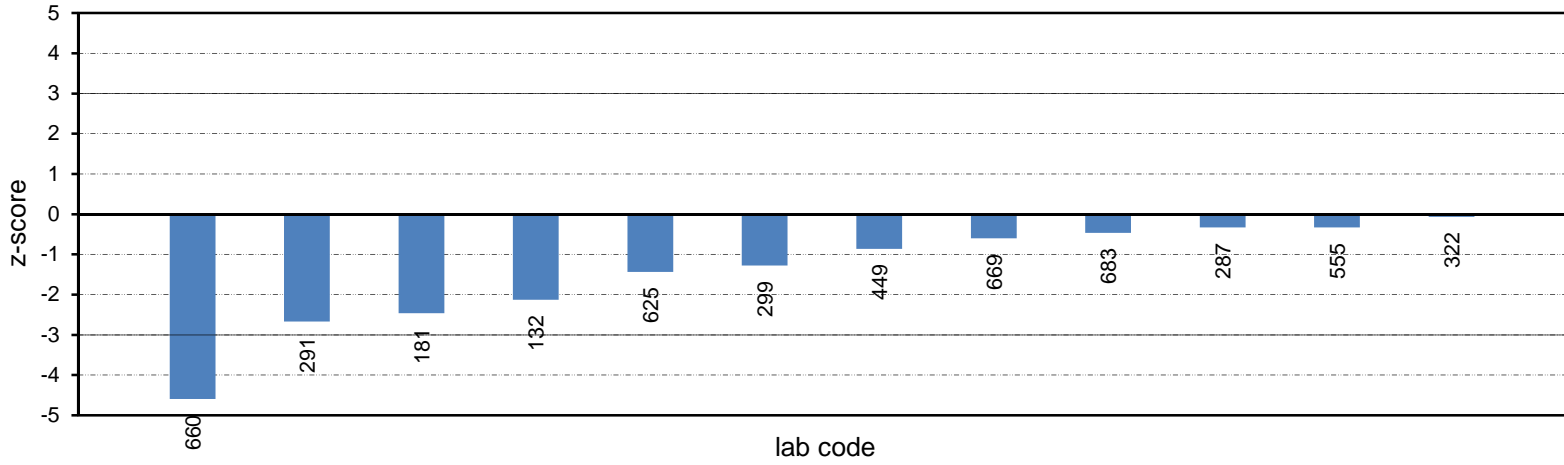
³ Please refer to Appendix C (pages C3-C5) method and digestion code descriptions.

⁴ "#" indicates that no result was returned for this sample/test.

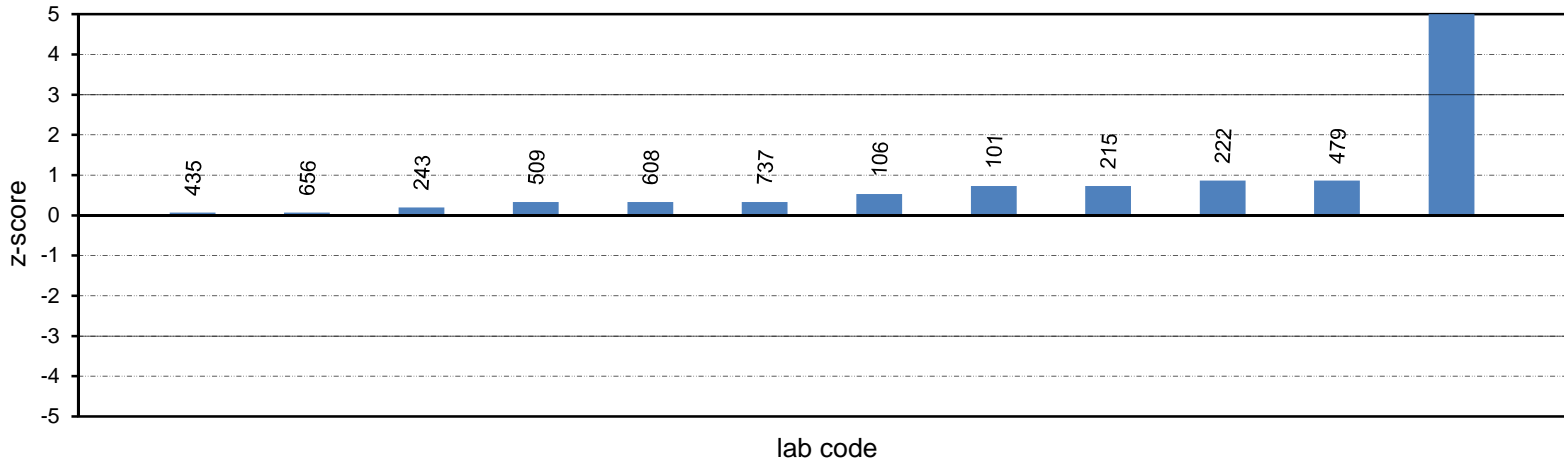
Total Phosphorus - Sample PTA 1

Ordered Robust Z-Score Charts

Total Phosphorus - Sample PTA 1 - Robust Z-Scores



Robust Z-Scores



Total Phosphorus (TP)**Results by Laboratory Code**

Laboratory Code	Sample PTA 2				
	Result \pm mg/L	MU ¹	Robust z-score ²	Method Code ³	Digestion Code ³
101	3.01 \pm	0.2	0.34	3	#
106	3.16 \pm	1.06	1.18	14	8
132	2.55	#	-2.25	1	19
181	2.95	#	0.00	4	19
186	3.98 \pm	0.68	5.79 §	4	41
215	2.73 \pm	0.4	-1.24	13	20
222	2.89 \pm	0.59	-0.34	7	20
243	2.95 \pm	0.3	0.00	3	20
287	2.52 \pm	0.55	-2.42	4	20
291	2.49 \pm	0.12	-2.59	16	19
299	3.03 \pm	0.26	0.45	4	19
435	3.01 \pm	0.094	0.34	4	22
449	2.67 \pm	0.40	-1.57	16	22
479	3.05	#	0.56	8	20
509	2.93 \pm	0.3	-0.11	3	19
555	2.85 \pm	0.13	-0.56	16	24
608	2.97 \pm	0.1	0.11	6	20
625	3.05	#	0.56	2	19
656	2.92 \pm	0.258	-0.17	2	19
660	2.83 \pm	0.3	-0.67	6	20
669	2.61 \pm	0.245	-1.91	2	19
683	2.99 \pm	0.299	0.22	8	20
737	3.10 \pm	0.06	0.84	3	20

<i>No of Results:</i>	23
<i>Median:</i>	2.950
<i>Normalised IQR:</i>	0.178
<i>Uncertainty of the Median:</i>	0.046
<i>Robust CV:</i>	6.0%
<i>Minimum:</i>	2.49
<i>Maximum:</i>	3.98
<i>Range:</i>	1.49

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

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

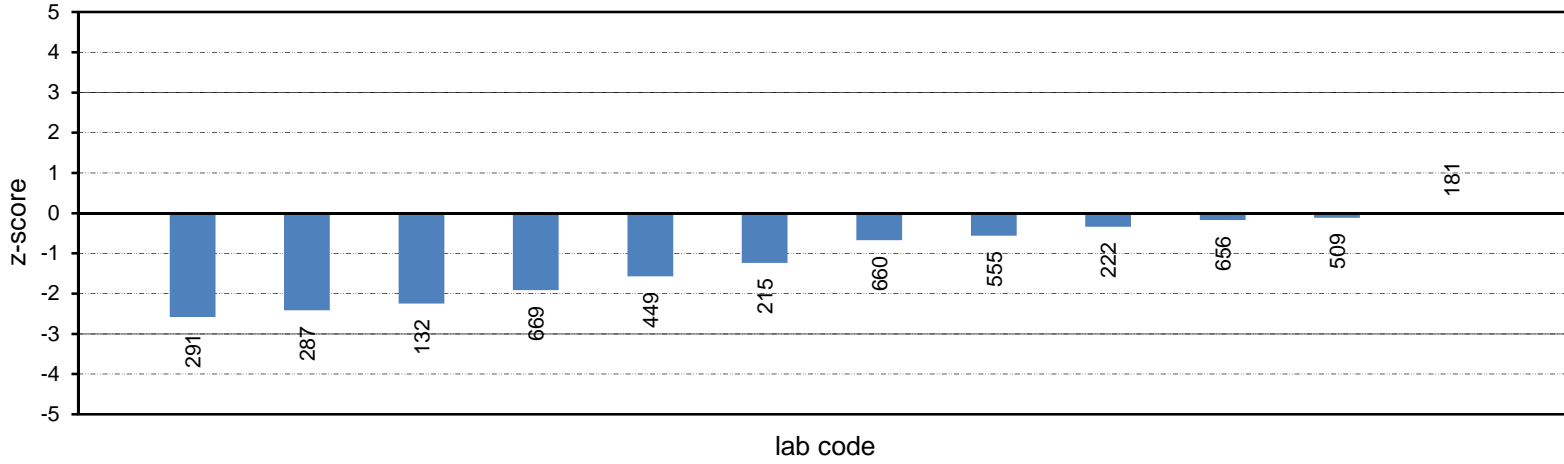
³ Please refer to Appendix C (pages C3-C5) method and digestion code descriptions.

⁴ "#" indicates that no result was returned for this sample/test.

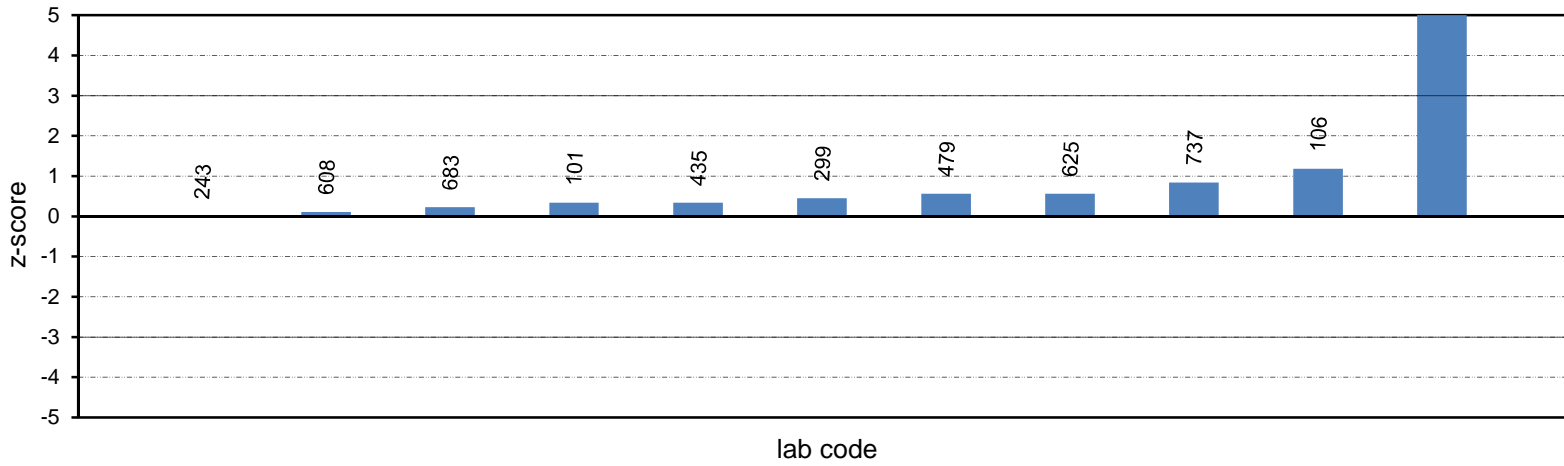
Total Phosphorus - Sample PTA 2

Ordered Robust Z-Score Charts

Total Phosphorus - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores



APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing B1

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 sample sets PTA 1 and PTA 2 for homogeneity and stability testing. Seven of each set were stored frozen, the remaining three were subjected to 35°C for three days for an accelerated ageing stability trial. The samples were then analysed in duplicate by Hill Laboratories, 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]. Samples PTA 1 and PTA 2 were analysed for Total Phosphorus using Acid persulphate digestion and ascorbic acid colorimetry by Discrete Analyser [APHA 4500-P B and E (modified from manual analysis) 22nd ed. 2012].

All stability samples showed no notable differences when compared to homogeneity samples.

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.

The results of homogeneity and stability testing are presented in Tables B1 and B2 below. Please note that the mean results for these tests are not intended to be used as reference values.

Table B1. Homogeneity and stability testing of PTA 1 samples.

Round 219	Samples PTA 1				
	Sample ID	Total Kjeldahl Nitrogen (mg/L)		Dissolved Reactive Phosphorus (mg/L)	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	15.23	13.58	10.52	10.52
	H2	14.71	13.87	10.62	10.42
	H3	14.41	15.56	10.52	10.47
	H4	15.35	14.57	10.47	10.57
	H5	14.00	15.05	10.17	10.72
	H6	14.83	13.78	10.57	10.42
	H7	13.93	14.42	11.08	10.78
Stability	S1	15.01	14.62	10.53	10.98
	S2	14.65	14.61	10.73	10.88
	S3	15.03	12.52	10.98	10.58
RSD		3.27%	5.99%	2.47%	1.87%

Table B2. Homogeneity and stability testing of PTA 2 samples.

Round PTA 219	Samples PTA 2				
	Sample ID	Total Kjeldahl Nitrogen (mg/L)		Dissolved Reactive Phosphorus (mg/L)	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	19.79	21.75	3.03	3.03
	H2	19.49	21.39	3.13	2.98
	H3	19.43	20.34	2.93	3.03
	H4	19.35	18.68	2.98	2.98
	H5	19.18	19.51	2.93	3.08
	H6	20.47	20.23	2.87	2.92
	H7	19.41	22.06	3.08	3.23
Stability	S1	17.22	22.87	2.77	2.87
	S2	19.93	18.25	3.18	3.03
	S3	21.08	19.49	3.28	3.28
RSD		5.12%	7.44%	5.14%	4.24%

APPENDIX C

Documentation

Instructions to Participants	C1
Method Codes.....	C3
Results Sheet.....	C6



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 219

OCTOBER, 2017

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, were 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 H₂SO₄ 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 20°C.
- 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 $k \approx 2$) 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 20 OCTOBER 2017** 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
	USEPA	US EPA 0200.2 Phosphorus - Sample Preparation	21
	Other	In-house method	22
		Modified Standard Method	23
Other (please specify)		24	

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	25
		APHA Part 4500 - Norg C. Semi-Micro Kjeldahl Method	26
		APHA Part 4500 - Norg D. Block Digestion and Flow Injection Analysis	27
	USEPA	USEPA 0351.1 – 0351.4 0351.1 Colorimetric/ Automated 0351.2 Colorimetric 0351.3 Colorimetric/ Titrimetric 0351.4 Potentiometric	28
		ESS Method 230.1: Total Phosphorus and Total Kjeldahl Nitrogen, Semi-Automated Method	29
	ASTM	ASTM D3590 - 11 Standard Test Methods for Total Kjeldahl Nitrogen in Water	30
	ISO / CEN	ISO 5663:1984 (EN 25663:1993) Water quality - Determination of Kjeldahl nitrogen - Method after mineralization with selenium	31
		ISO 11905-1:1997 Water quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate	32
		EN 12260:2003 Water quality - Determination of nitrogen - Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides	33
	Other	Modified Standard Method	34
		Discrete Analyser	35
		AA / FIA	36
		Test Kit, Colorimeter (HACH... specify).	37
		Calculation (TN-NOx =TKN)	38
		Other (please specify)	39
TKN Catalyst		Copper	40
		Mercury	41
		Persulfate	42
		Selenium	43
		Sodium nitroferricyanide	44
		Titanium	45
		Other (please specify)	46

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	47
		APHA 4500 – NH3 D. Ammonia-Selective Electrode Method	48
		APHA 4500 – NH3 E. Ammonia-Selective Electrode Method Using Known Addition	49
		APHA 4500 – NH3 F. Phenate Method	50
		APHA 4500 – NH3 G. Automated Phenate Method	51
		APHA 4500 – NH3 H. Flow Injection Analysis	52
	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	53
	Other	Modified Standard Method	54
		Discrete Analyser	55
		AA / FIA	56
		Test Kit, Colorimeter (e.g. HACH... specify).	57
		Other (please specify)	58

Method Reference Key

- i) **APHA SM** APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19 20, 21, 22 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 219
Total Kjeldahl Nitrogen, Total Phosphorus
OCTOBER, 2017
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 20 OCTOBER 2017** 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 219

- End of Report -