Report No. 812

Waters Proficiency Testing

Round 154

- Organophosphate Pesticides -

July 2013

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Ms R Ryan, Global Proficiency Ltd (New Zealand). Also our thanks go to Global Proficiency Ltd (New Zealand) and 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 organophosphate pesticides in waters. This is round 154 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in April 2013 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 Ms D Mihaila and the Technical Advisor was Ms R Ryan from Global Proficiency Ltd, New Zealand. This report was authorised by Ms W Fajloun, PTA Quality Coordinator.

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 glass ampoules (labelled PTA 1 and PTA 2) containing solutions of organophosphate pesticides.

2.4 A total of 17 laboratories received samples, comprising:

- 13 Australian participants; and
- 4 overseas participants, including:
    - Korea (1), New Zealand (2), Vietnam (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, uncertainty of the median, normalised interquartile range, 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,* 2012 (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 31.

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 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 close to zero indicates that the result agrees well with those from other laboratories. 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 "**§**".

Each determination was examined for outliers with all methods pooled. The table on page 31 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;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Normalised IQR*: the normalised interquartile range of the results;
- *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.

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 Advisor'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) with the exception of sample PTA 2 for Dimethoate, where the median concentration showed a lower analyte recovery compared to the doped concentration, as shown in Table 1.

As the assigned value for this program is the median of the results submitted by the participants, the uncertainty of the median has been calculated and is also presented in Table 1.

Analyte	Sample	Dope Concentration (µg/L)	Median (µg/L)	Analyte Recovery (%)	Uncertainty of the median (µg/L)
Azinphos methyl	PTA 1	4.5	3.990	89	0.380
	PTA 2	9	8.710	97	0.322
Chlorpyriphos	PTA 1	40	35.65	89	1.81
	PTA 2	80	69.95	87	2.32
Diazinon	PTA 1	6	5.120	85	0.394
	PTA 2	12	10.40	87	0.82
Dimethoate	PTA 1	60	43.02	72	3.36
	PTA 2	100	58.68	59	5.31
Pirimiphos methyl	PTA 1	30	24.25	81	2.18
	PTA 2	90	75.29	84	9.90

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

The robust CVs obtained in this round were consistent with the results of the previous rounds. The results suggest higher robust CVs for lower analyte levels and lower number of participants, as can be seen in the commentaries for each analyte below.

4.2 Analysis of Round 154 Results

4.2.1 Azinphos methyl

Table 2 compares the Azinphos methyl medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	No. of Results
This study	PTA 1	3.990	30.4	16
	PTA 2	8.710	11.8	16
Report 667	PTA 1	1.705	36.8	22
	PTA 2	4.580	40.1	22
Report 437	PTS 012	10.85	19.2	26
	PTS 512	14.90	22.4	26

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

Bias / Accuracy

Azinphos methyl testing was successfully carried out, with satisfactory results (|z-scores| ≤ 2.0) ranging between 1.48 – 6.46 µg/L for sample PTA 1 and 6.61 – 10.65 µg/L for sample PTA 2.

Out of 16 participants, one questionable result (2.0 < |z-scores| < 3.0) was obtained for sample PTA 1 (laboratory 118) and no questionable results were obtained for sample PTA 2.

No outlier results (|z-scores| ≥ 3.0) were obtained for sample PTA 1. For sample PTA 2 four outlier results were obtained, requiring follow-up action by laboratories 118, 208, 251 and 368.

The Azinphos methyl dataset formed a normal distribution with no significant bias attributable to any one method (Figures 1 and 2). The method most frequently used by participants to test for Azinphos methyl was US EPA 8270D which was used by approximately 31% of participants, followed by in-house methods which were used by approximately 19% of participants.

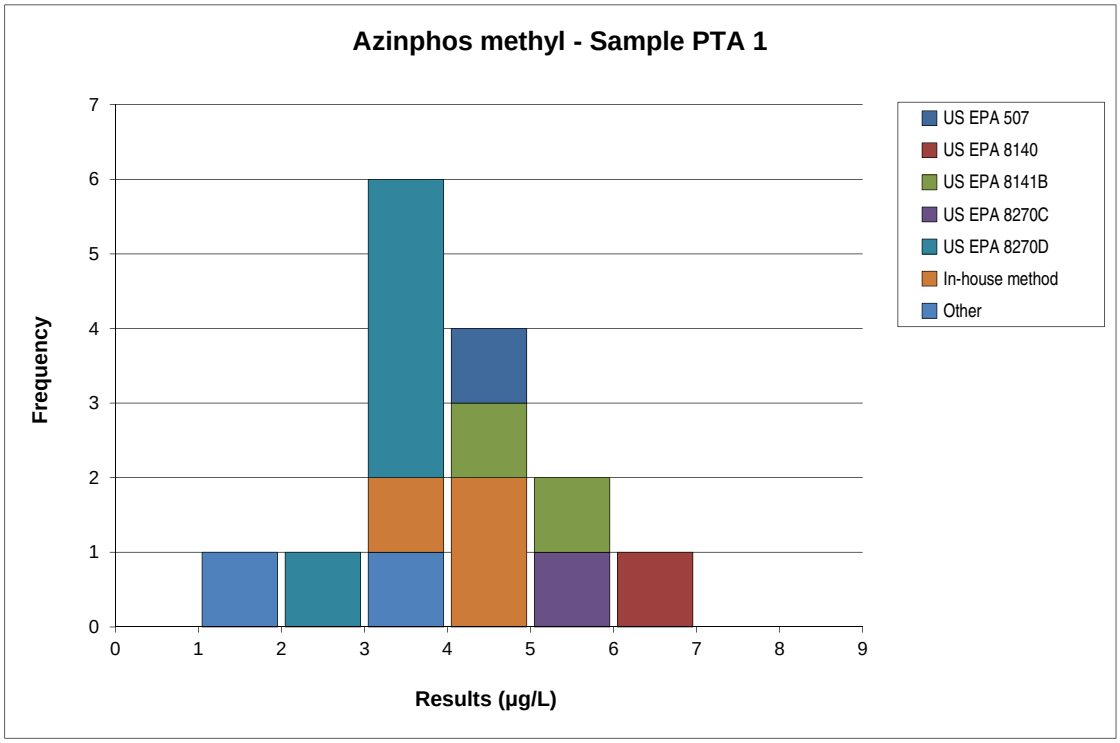


Figure 1. Spread of results for Azinphos methyl testing of sample PTA 1, with a median concentration of 3.990 µg/L.

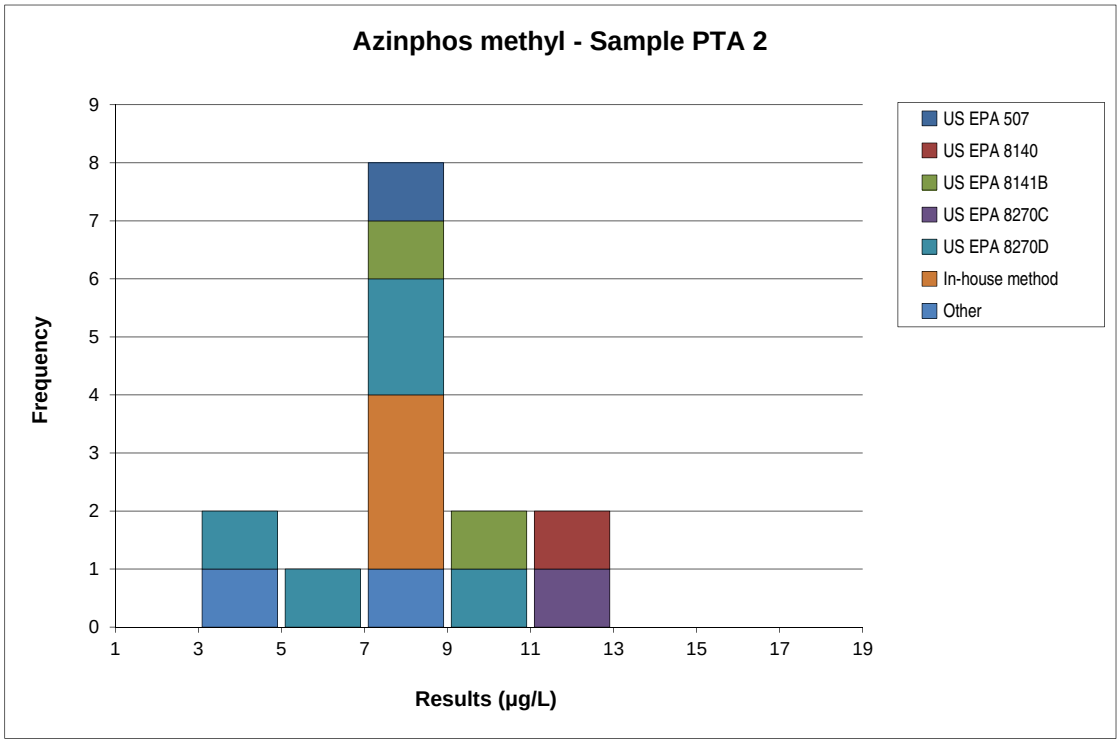


Figure 2. Spread of results for Azinphos methyl testing of sample PTA 2, with a median concentration of 8.710 µg/L.

Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for Azinphos methyl testing was 3.990 ± 2.633 µg/L for sample PTA 1 and 8.710 ± 1.769 µg/L for sample PTA 2.

Results submitted by laboratories using Method 13 - US EPA 8270D (n=5) indicated a method reproducibility of ± 1.33 µg/L for sample PTA 1 and of ± 3.57 µg/L for sample PTA 2.

All participants submitted MU information. Several of the stated MUs did not accurately reflect the difference between the median and the participants result for each proficiency sample.

Laboratories 118, 145, 208, 251, 273, 285 and 368 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 3 and 4. To keep it in perspective, the confidence in medians was 3.990 ± 0.380 µg/L for sample PTA 1 and 8.710 ± 0.322 µg/L for sample PTA 2.

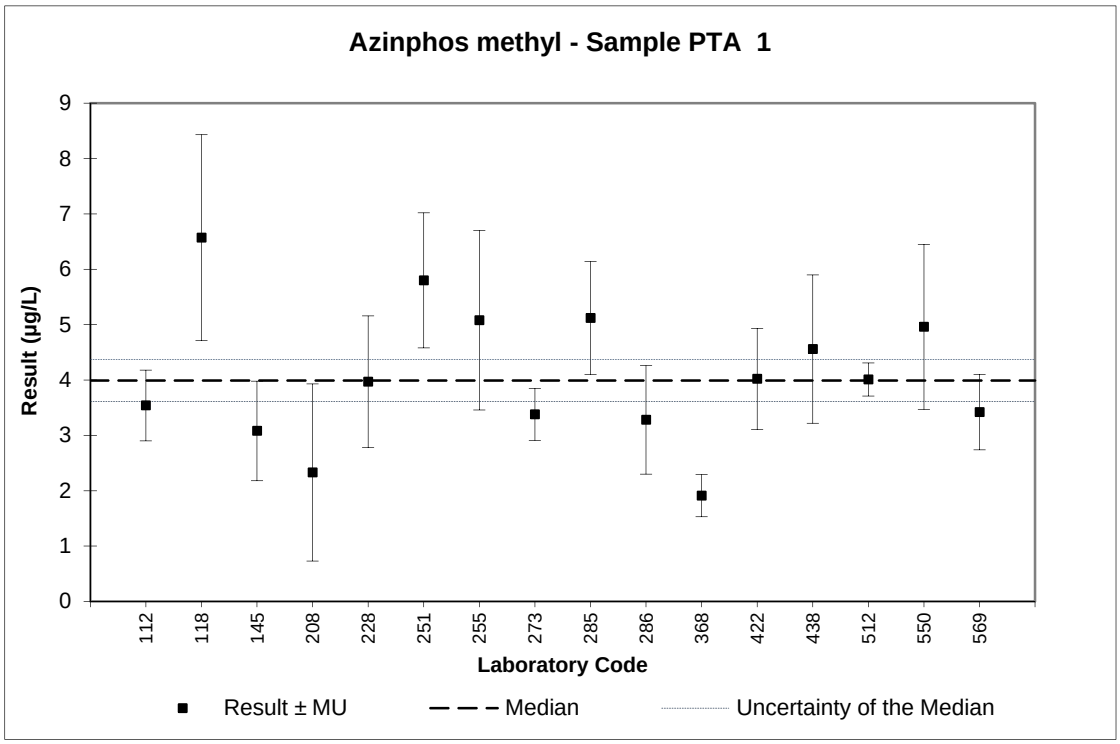


Figure 3. Azinphos methyl - Results of sample PTA 1, including MU, compared to the median.

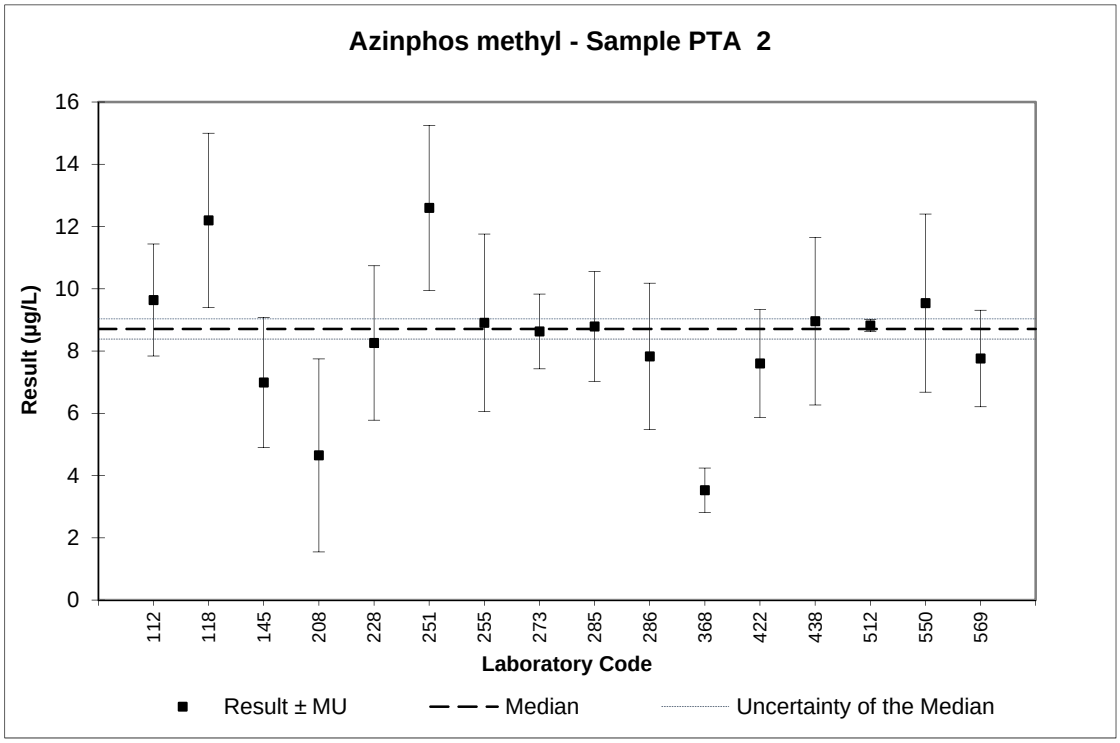


Figure 4. Azinphos methyl - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 5 and 6, displayed by the methods used.

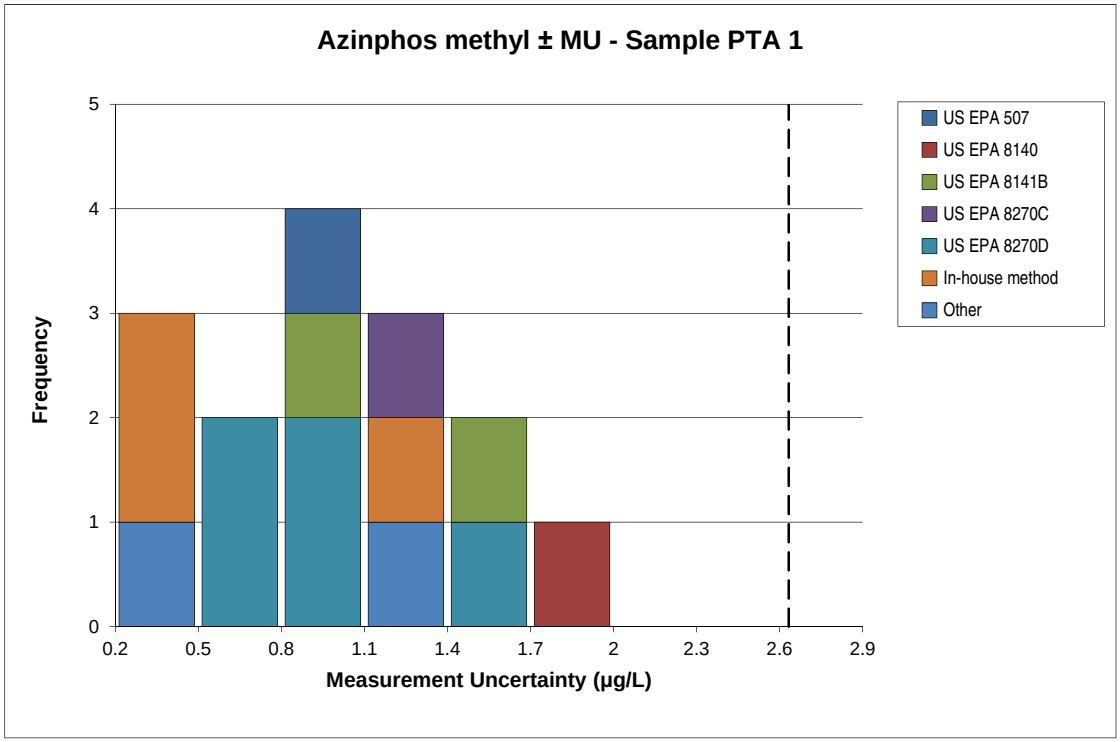


Figure 5. MU for Azinphos methyl testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 2.633 µg/L) in this round.

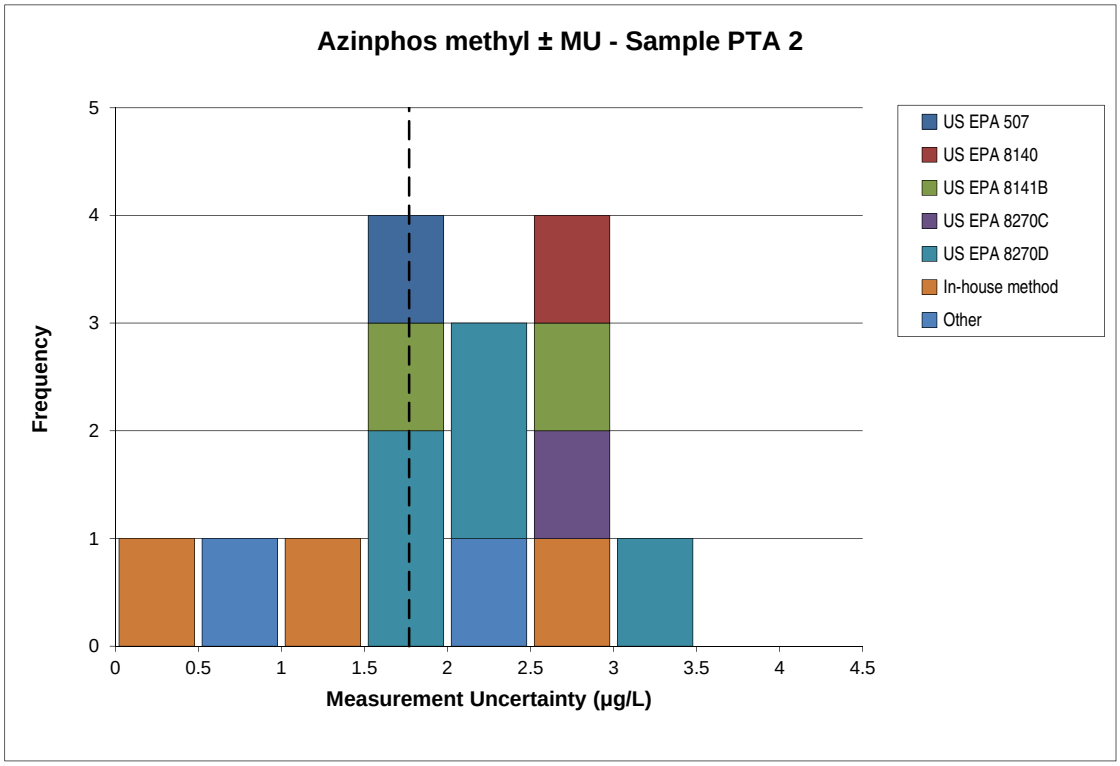


Figure 6. MU for Azinphos methyl testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 1.769 µg/L) in this round.

4.2.2 Chlorpyriphos

Table 3 compares the Chlorpyriphos medians and robust CVs from this round to those obtained in a previous PTA round.

Round	Sample	Median (µg/L)	Robust CV (%)	No. of Results
This study	PTA 1	35.65	16.2	16
	PTA 2	69.95	10.6	16
Report 667	PTA 1	9.005	18.2	24
	PTA 2	48.45	25.8	24

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

Bias / Accuracy

Chlorpyriphos testing was successfully carried out, with satisfactory results (|z-scores| ≤ 2.0) ranging between 24.1 – 47.2 µg/L for sample PTA 1 and 55.1 – 84.8 µg/L for sample PTA 2.

Out of 16 participants, two questionable results (2.0 < |z-scores| < 3.0) were obtained for sample PTA 1 (laboratories 112 and 368) and two questionable results were obtained for sample PTA 2 (laboratories 285 and 438).

No outlier results (|z-scores| ≥ 3.0) were obtained for sample PTA 1 and two outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 273 and 368.

The Chlorpyriphos dataset formed a normal distribution with no significant bias attributable to any one method (Figures 7 and 8). The method most frequently used by participants to test for Chlorpyriphos was US EPA 8270D which was used by approximately 31% of participants, followed by in-house methods which were used by approximately 19% of participants.

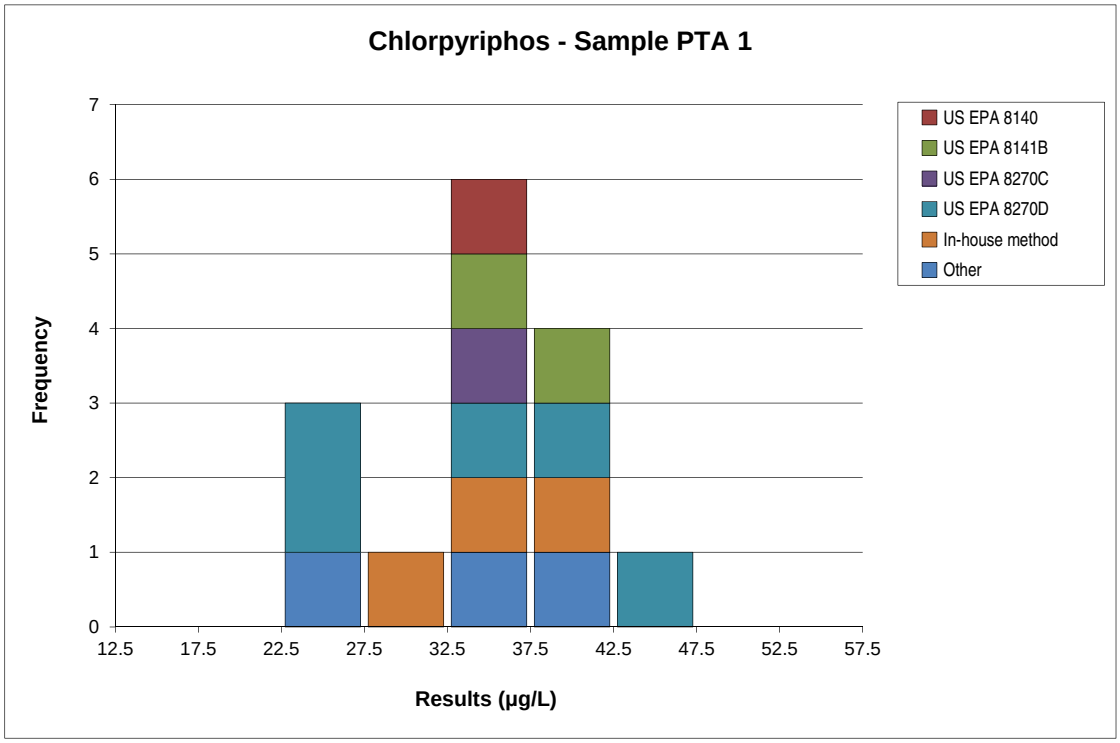


Figure 7. Spread of results for Chlorpyriphos testing of sample PTA 1, with a median concentration of 35.65 µg/L.

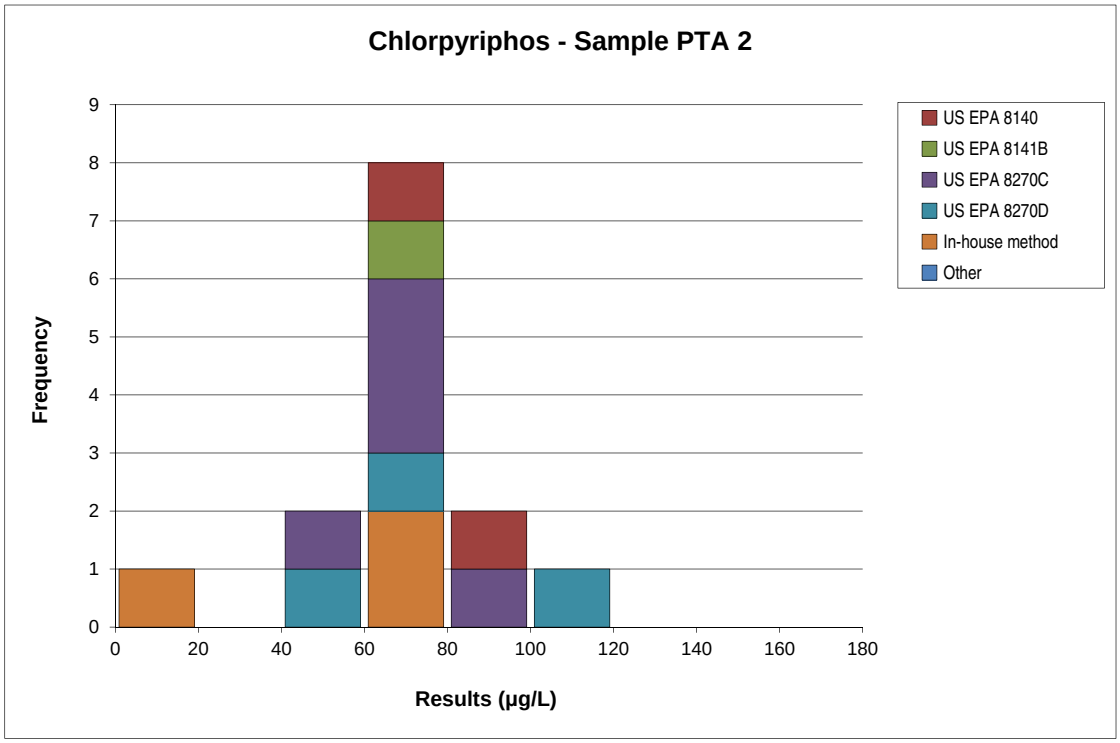


Figure 8. Spread of results for Chlorpyriphos testing of sample PTA 2, with a median concentration of 69.95 µg/L.

Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for Chlorpyriphos testing was 35.65 ± 13.35 µg/L for sample PTA 1 and 69.95 ± 21.74 µg/L for sample PTA 2.

Results submitted by laboratories using Method 13 - US EPA 8270D (n=5) indicated a method reproducibility of ± 24.61 µg/L for sample PTA 1 and of ± 27.46 µg/L for sample PTA 2.

All participants submitted MU information. Several of the stated MUs did not accurately reflect the difference between the median and the participants result for each proficiency sample.

Laboratories 112, 273, 285, 368 and 438 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 9 and 10. To keep it in perspective, the confidence in medians was 35.65 ± 1.81 µg/L for sample PTA 1 and 69.95 ± 2.32 µg/L for sample PTA 2.

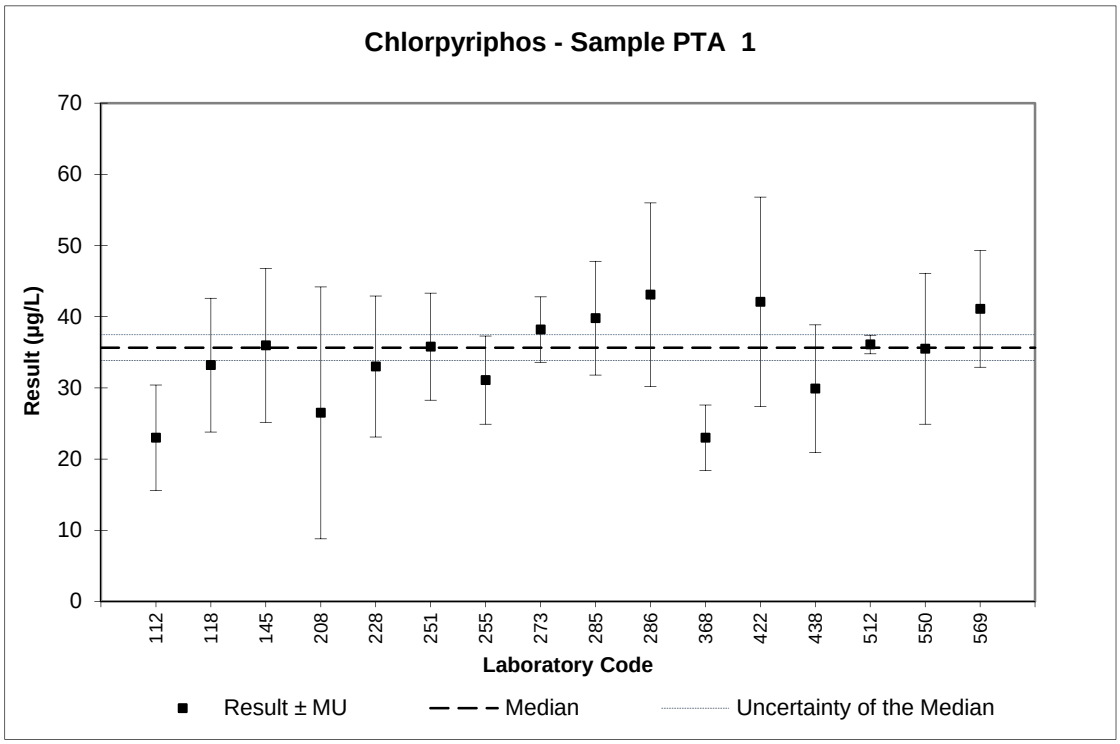


Figure 9. Chlorpyriphos - Results of sample PTA 1, including MU, compared to the median.

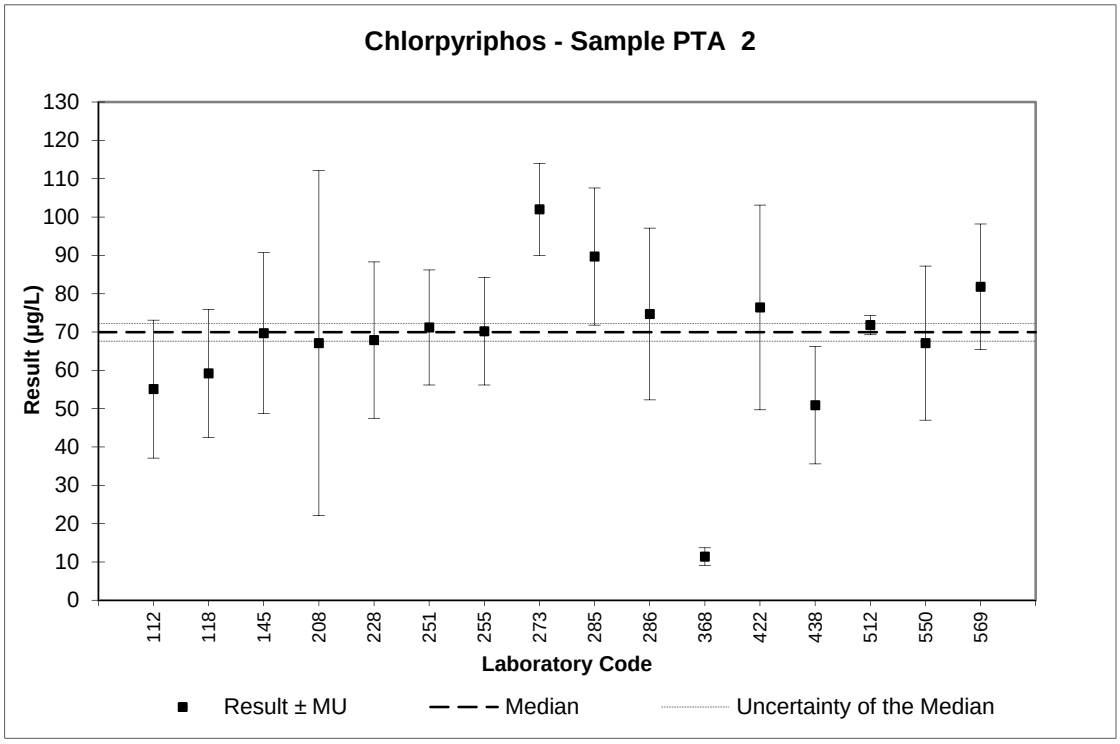


Figure 10. Chlorpyriphos - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 11 and 12, displayed by the methods used.

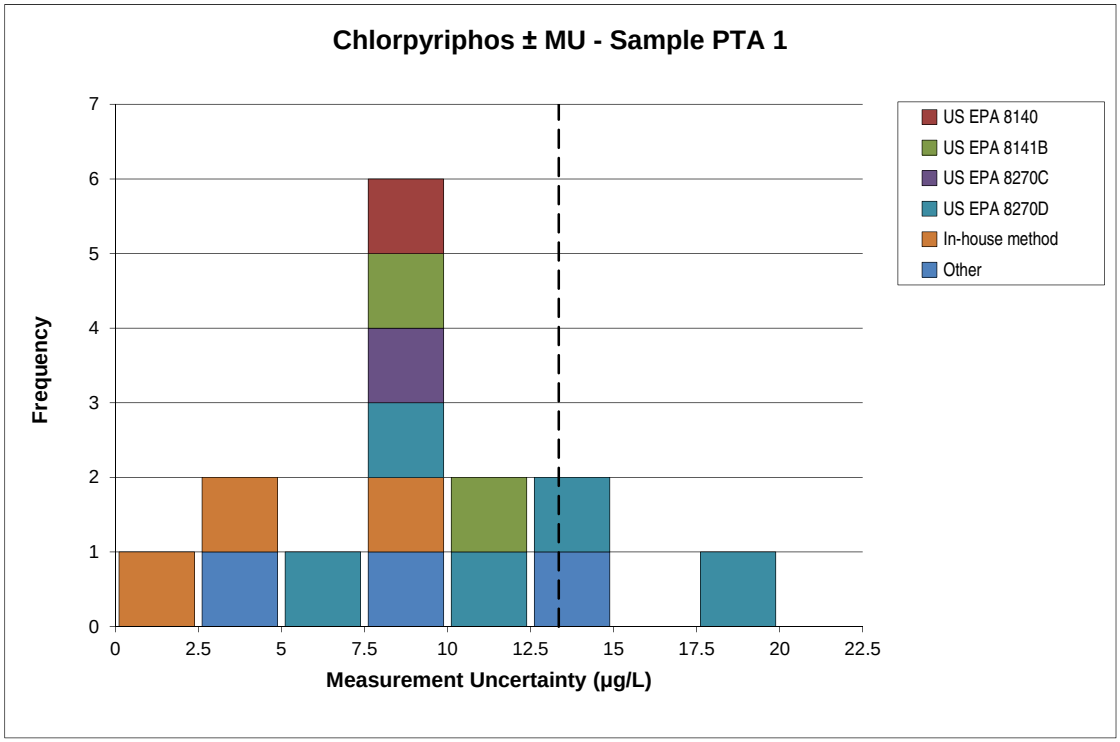


Figure 11. MU for Chlorpyriphos testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 13.35 µg/L) in this round.

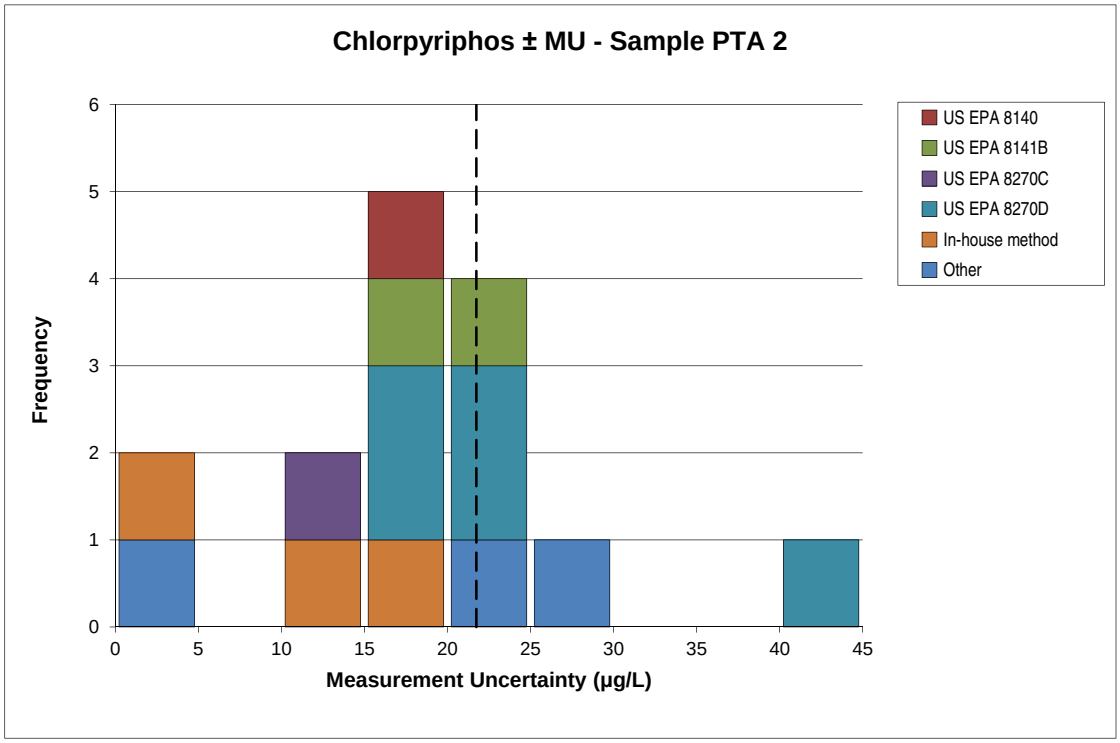


Figure 12. MU for Chlorpyriphos testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 21.74 µg/L) in this round.

4.2.3 Diazinon

Table 4 compares the Diazinon medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	No. of Results
This study	PTA 1	5.120	25.3	17
	PTA 2	10.40	25.8	17
Report 667	PTA 1	1.030	20.2	25
	PTA 2	6.100	21.8	25
Report 437	PTS 012	16.71	16.3	30
	PTS 512	13.70	16.0	30

Table 4. Comparison of current round variability and proficiency medians of Diazinon testing with the results of the previous two rounds.

Bias / Accuracy

Diazinon testing was successfully carried out, with satisfactory results (|z-scores| ≤ 2.0) ranging between 2.53 – 7.72 µg/L for sample PTA 1 and 5.03 – 15.77 µg/L for sample PTA 2.

Out of 17 participants, two questionable results (2.0 < |z-scores| < 3.0) were obtained for sample PTA 1 (laboratories 285 and 368) and one questionable result was obtained for sample PTA 2 (laboratory 368).

No outlier results (|z-scores| ≥ 3.0) were obtained for either sample.

The Diazinon dataset formed a normal distribution with no significant bias attributable to any one method (Figures 13 and 14). The method most frequently used by participants to test for Diazinon was US EPA 8270D which was used by approximately 29% of participants, followed by in-house methods which were used by approximately 24% of participants.

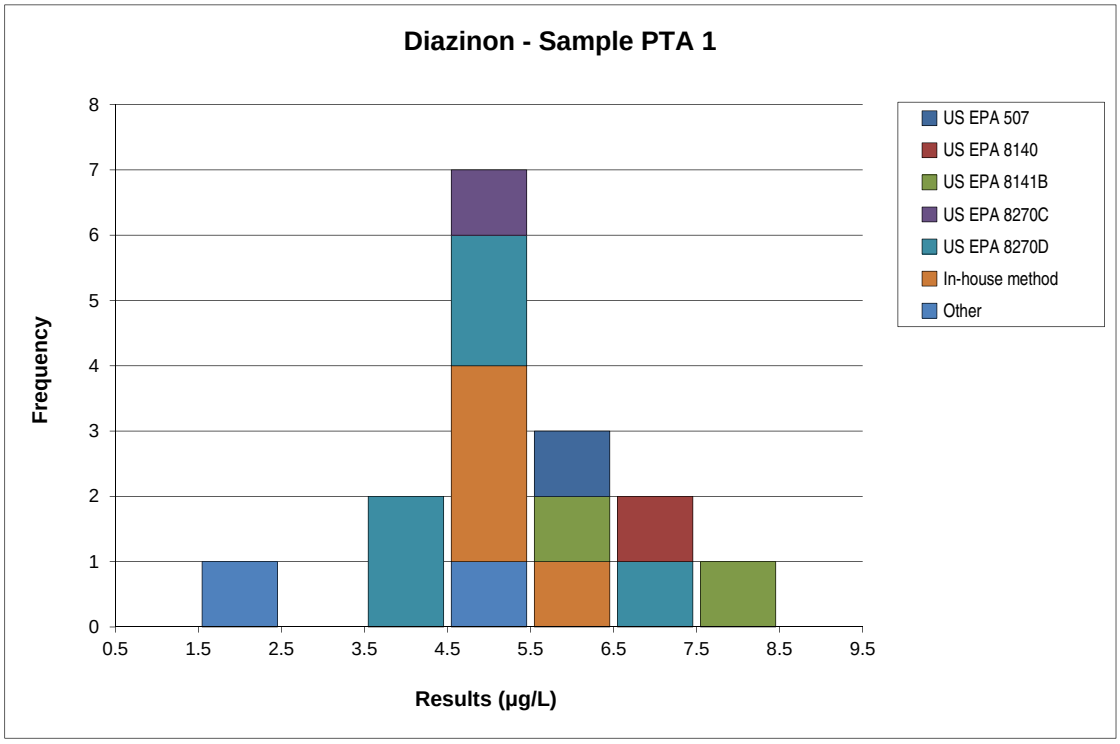


Figure 13. Spread of results for Diazinon testing of sample PTA 1, with a median concentration of 5.120 µg/L.

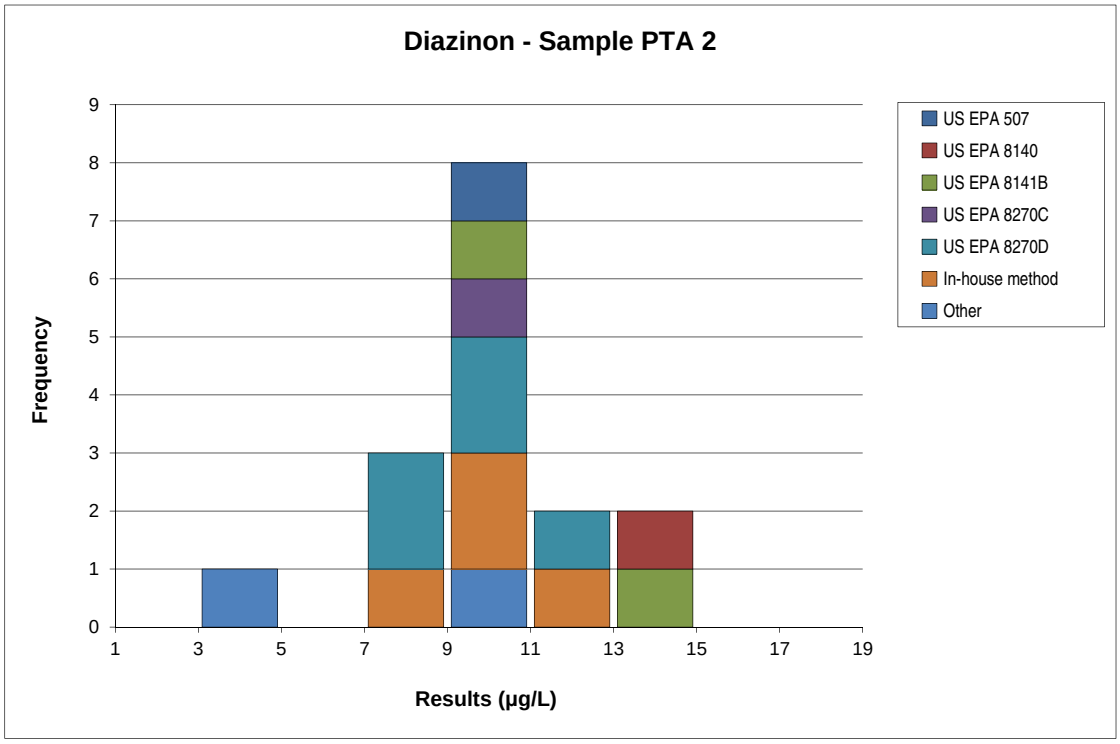


Figure 14. Spread of results for Diazinon testing of sample PTA 2, with a median concentration of 10.40 µg/L.

Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for Diazinon testing was 5.120 ± 3.027 µg/L for sample PTA 1 and 10.40 ± 5.70 µg/L for sample PTA 2.

Results submitted by laboratories using Method 13 - US EPA 8270D (n=5) indicated a method reproducibility of ± 3.14 µg/L for sample PTA 1 and of ± 4.68 µg/L for sample PTA 2.

All participants submitted MU information. Several of the stated MUs did not accurately reflect the difference between the median and the participants result for each proficiency sample.

Laboratories 112, 118, 255, 273, 285, 368, 512 and 619 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 15 and 16. To keep it in perspective, the confidence in the medians was 5.120 ± 0.394 µg/L for sample PTA 1 and 10.40 ± 0.82 µg/L for sample PTA 2.

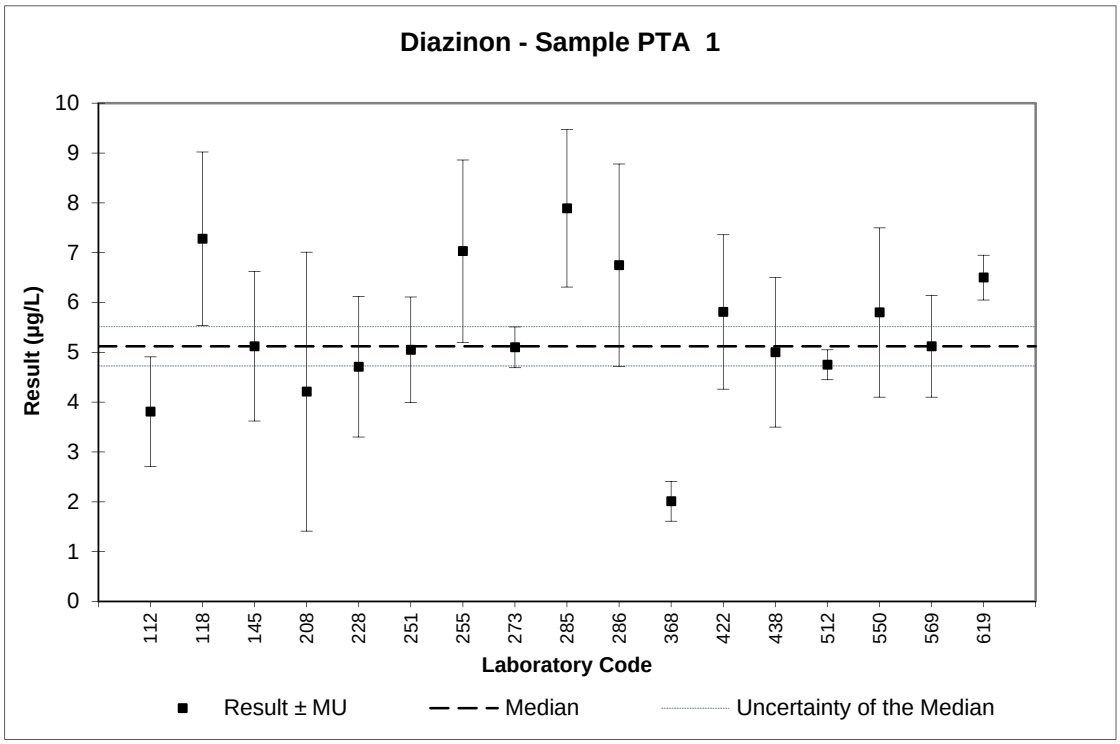


Figure 15. Diazinon - Results of sample PTA 1, including MU, compared to the median.

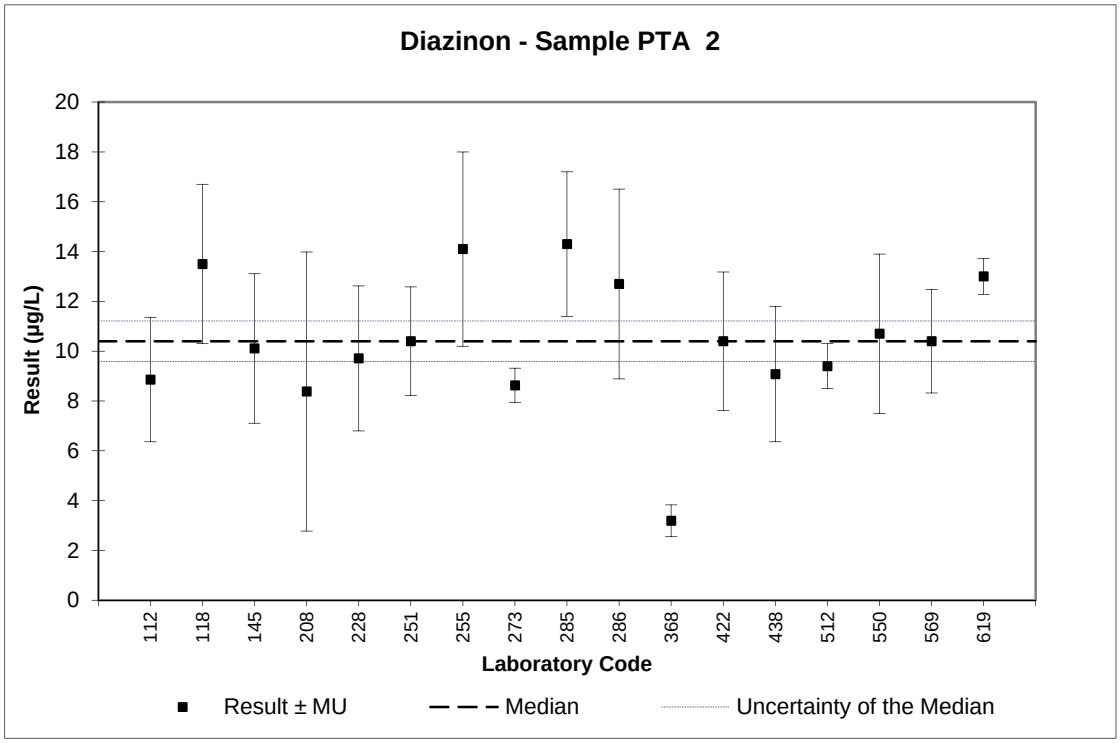


Figure 16. Diazinon - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 17 and 18, displayed by the methods used.

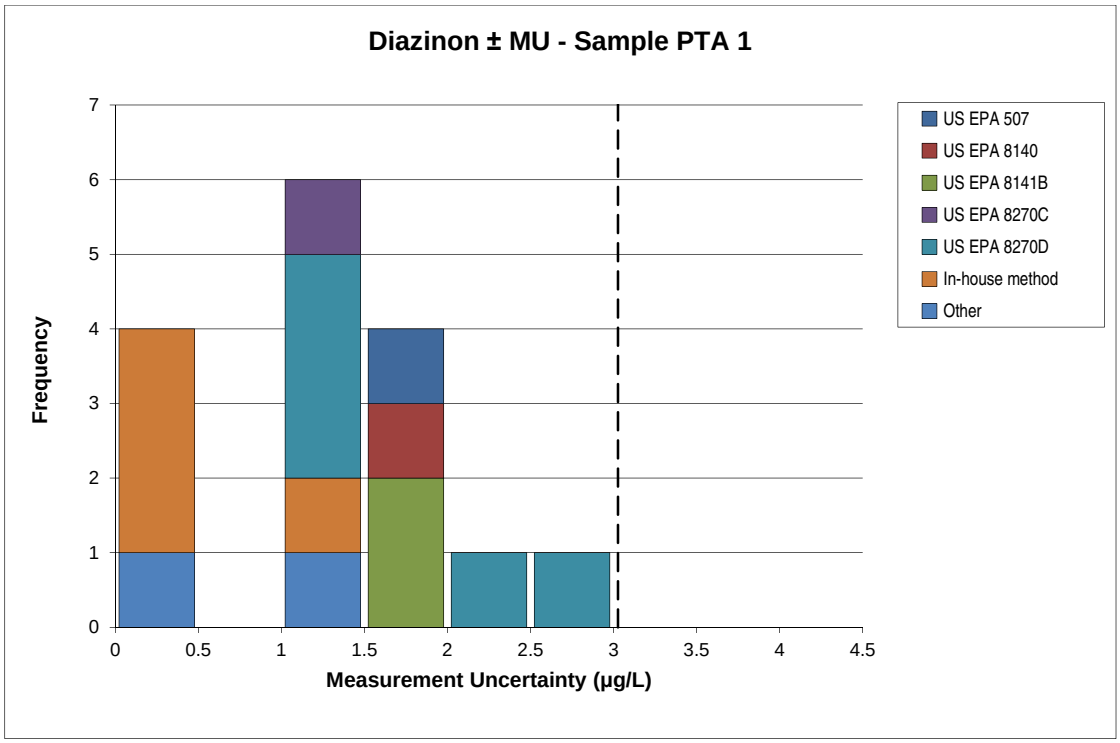


Figure 17. MU for Diazinon testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 3.027 µg/L) in this round.

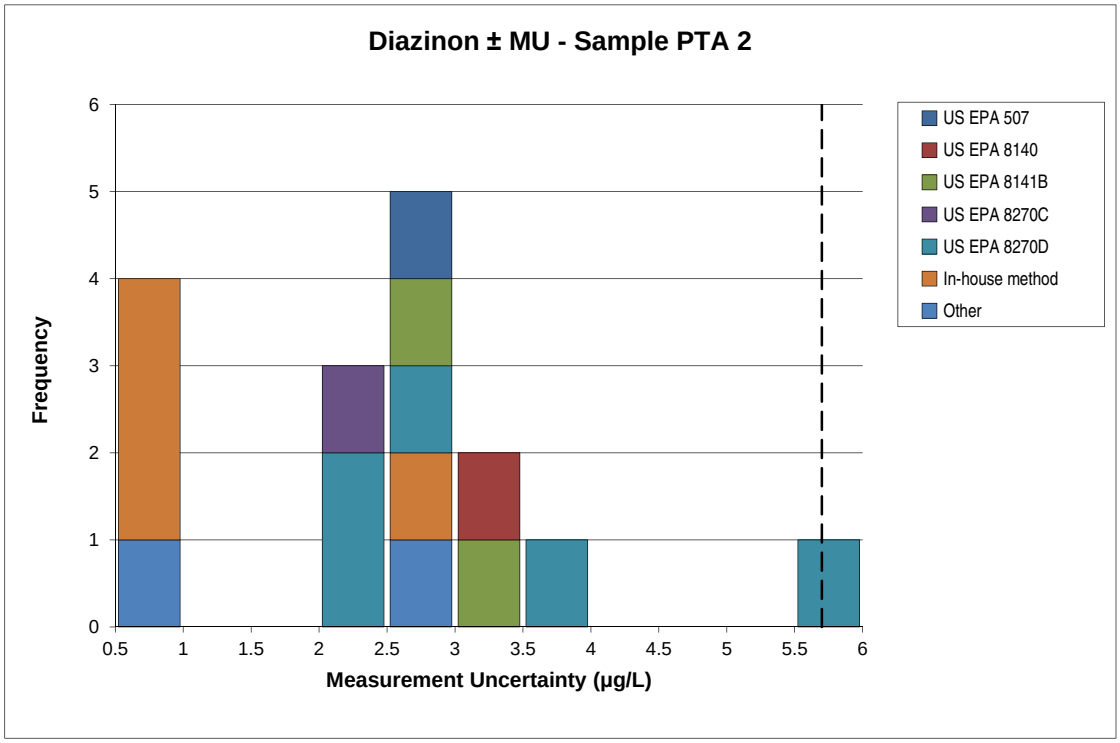


Figure 18. MU for Diazinon testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 5.70 µg/L) in this round.

4.2.4 Dimethoate

Table 5 compares the Dimethoate medians and robust CVs from this round to those obtained in a previous PTA round.

Round	Sample	Median (µg/L)	Robust CV (%)	No. of Results
This study	PTA 1	43.02	23.3	14
	PTA 2	58.68	27.0	14
Report 667	PTA 1	36.50	31.0	20
	PTA 2	66.17	37.3	20

Table 5. Comparison of current round variability and proficiency medians of Dimethoate testing with the results of the previous round.

Bias / Accuracy

Dimethoate testing was successfully carried out, with satisfactory results (|z-scores| ≤ 2.0) ranging between 23.0 – 63.1 µg/L for sample PTA 1 and 27.0 – 90.4 µg/L for sample PTA 2.

Out of 14 participants, two questionable results (2.0 < |z-scores| < 3.0) were obtained for sample PTA 1 (laboratories 112 and 255) and one questionable result was obtained for sample PTA 2 (laboratory 368).

No outlier results (|z-scores| ≥ 3.0) were obtained for either sample.

The Dimethoate dataset formed a normal distribution with no significant bias attributable to any one method (Figures 19 and 20). The method most frequently used by participants to test for Dimethoate was US EPA 8270D which was used by approximately 36% of participants, followed by in-house methods which were used by approximately 21% of participants.

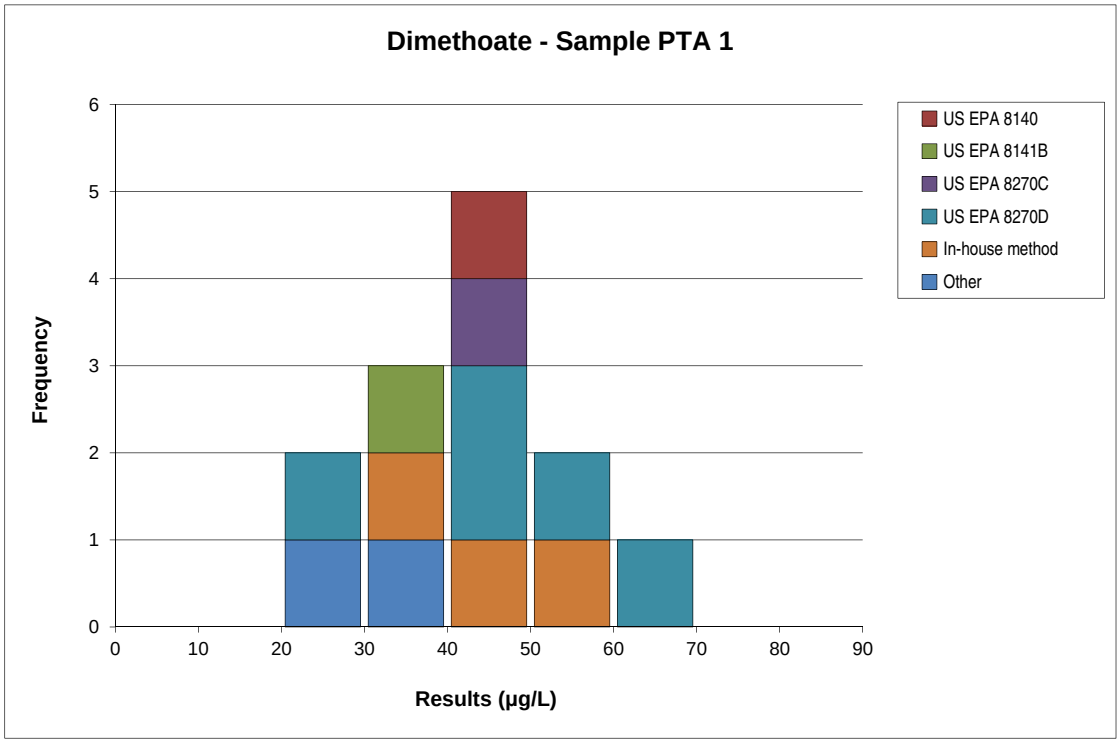


Figure 19. Spread of results for Dimethoate testing of sample PTA 1, with a median concentration of 43.02 µg/L.

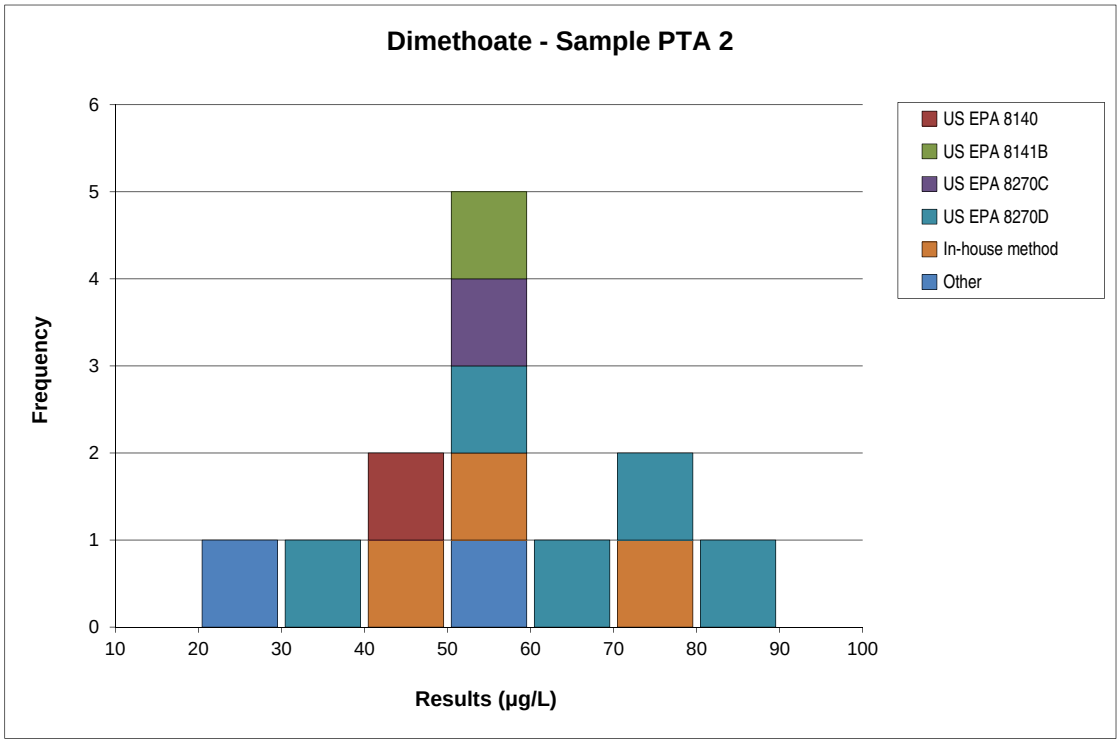


Figure 20. Spread of results for Dimethoate testing of sample PTA 2, with a median concentration of 58.68 µg/L.

Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated the estimate of reproducibility (~2SD) for Dimethoate testing of sample PTA 1 was 43.02 ± 27.91 µg/L and sample PTA 2 was 58.68 ± 38.93 µg/L.

Using the t-value, results submitted by laboratories using Method 13 - US EPA 8270D (n=5) indicated a method reproducibility of ± 43.03 µg/L for sample PTA 1 and of ± 51.93 µg/L for sample PTA 2.

All participants submitted MU information. Several of the stated MUs did not accurately reflect the difference between the median and the participants result for each proficiency sample.

Laboratories 112, 118, 255, 273, 286, 368, 512 and 569 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 21 and 22. To keep it in perspective, the confidence in medians was 43.02 ± 3.36 µg/L for sample PTA 1 and 58.68 ± 5.31 µg/L for sample PTA 2.

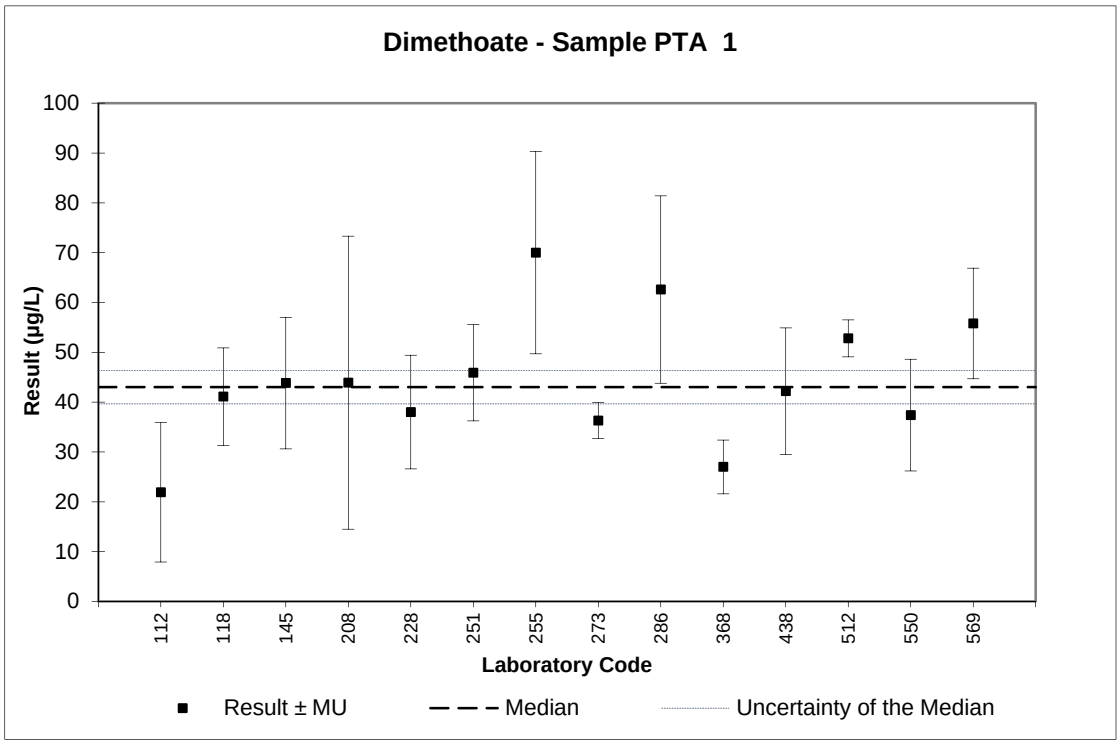


Figure 21. Dimethoate - Results of sample PTA 1, including MU, compared to the median.

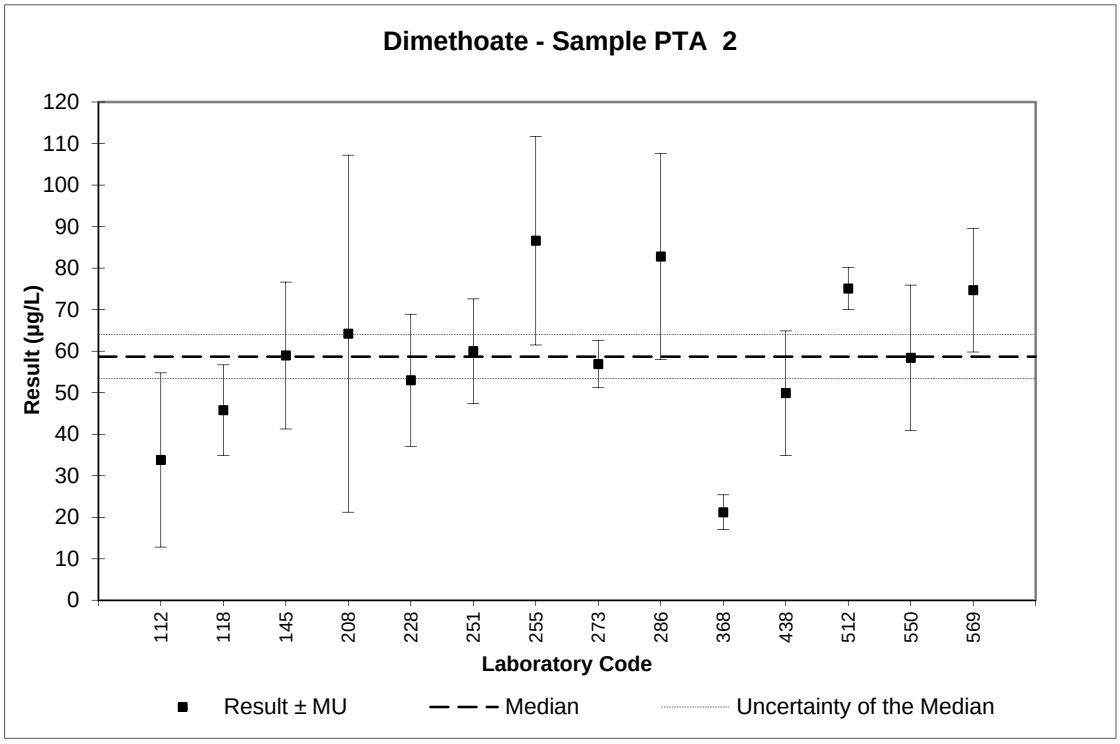


Figure 22. Dimethoate - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 23 and 24, displayed by the methods used.

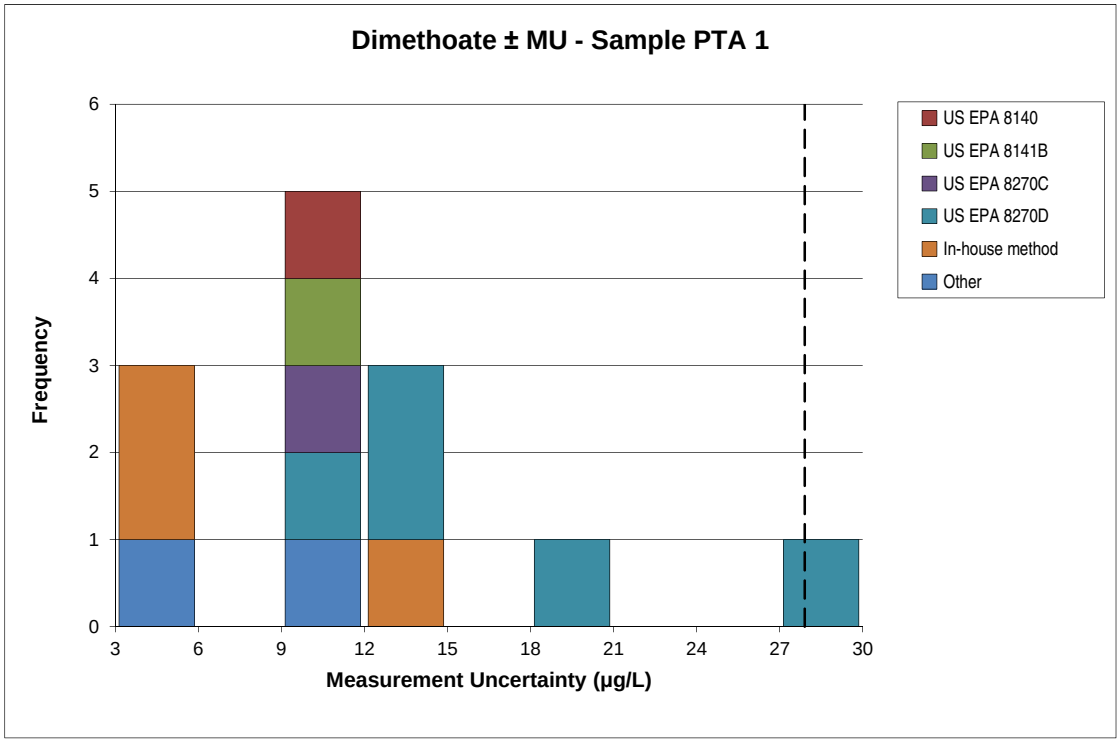


Figure 23. MU for Dimethoate testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 27.91 µg/L) in this round.

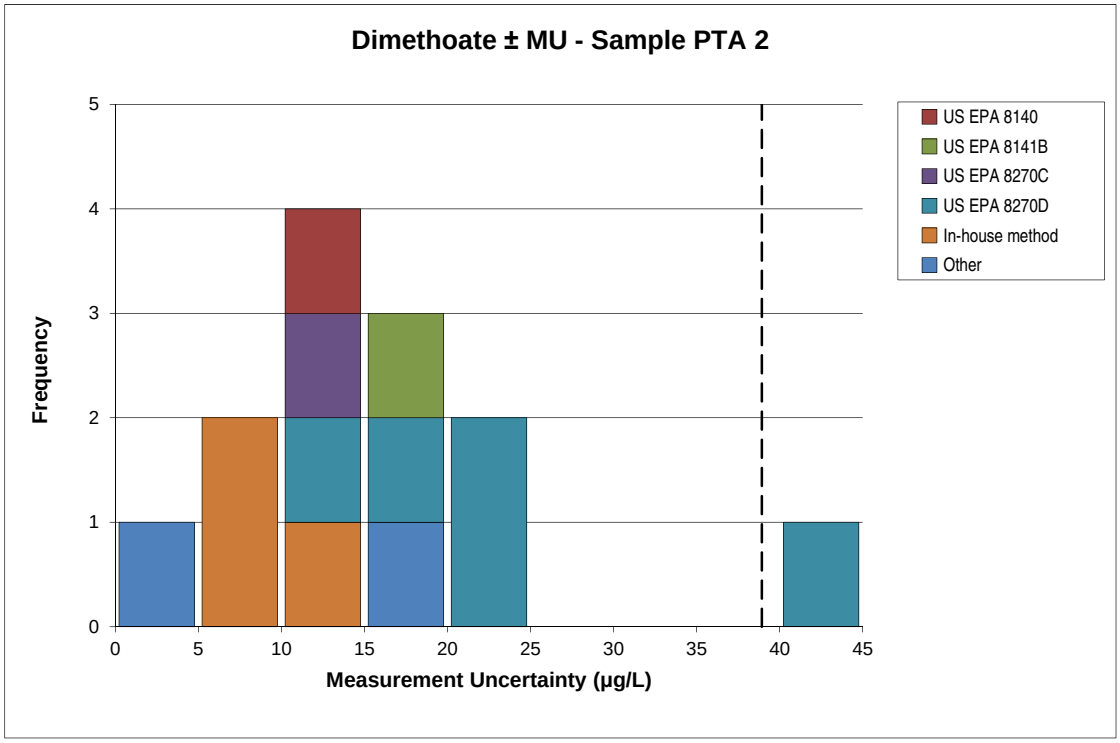


Figure 24. MU for Dimethoate testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 38.93 µg/L) in this round.

4.2.5 Pirimiphos methyl

Table 6 compares the Pirimiphos methyl medians and robust CVs from this round to those obtained in a previous PTA round.

Round	Sample	Median (µg/L)	Robust CV (%)	No. of Results
This study	PTA 1	24.25	22.7	10
	PTA 2	75.29	33.2	10
Report 667	PTA 1	39.40	42.7	13
	PTA 2	100.0	27.3	13

Table 6. Comparison of current round variability and proficiency medians of Pirimiphos methyl testing with the results of the previous round.

Bias / Accuracy

Pirimiphos methyl testing was successfully carried out, with satisfactory results (|z-scores| ≤ 2.0) ranging between 14.7 – 33.8 µg/L for sample PTA 1 and 31.9 – 118.7 µg/L for sample PTA 2.

Out of 10 participants, no questionable results (2.0 < |z-scores| < 3.0) were obtained for sample PTA 1 and one questionable result was obtained for sample PTA 2 (laboratory 368).

No outlier results (|z-scores| ≥ 3.0) were obtained for either sample.

The Pirimiphos methyl dataset formed a normal distribution with no significant bias attributable to any one method (Figures 25 and 26). The methods most frequently used by participants to test for Pirimiphos methyl were US EPA 8270D and in-house methods which were each used by approximately 30% of participants.

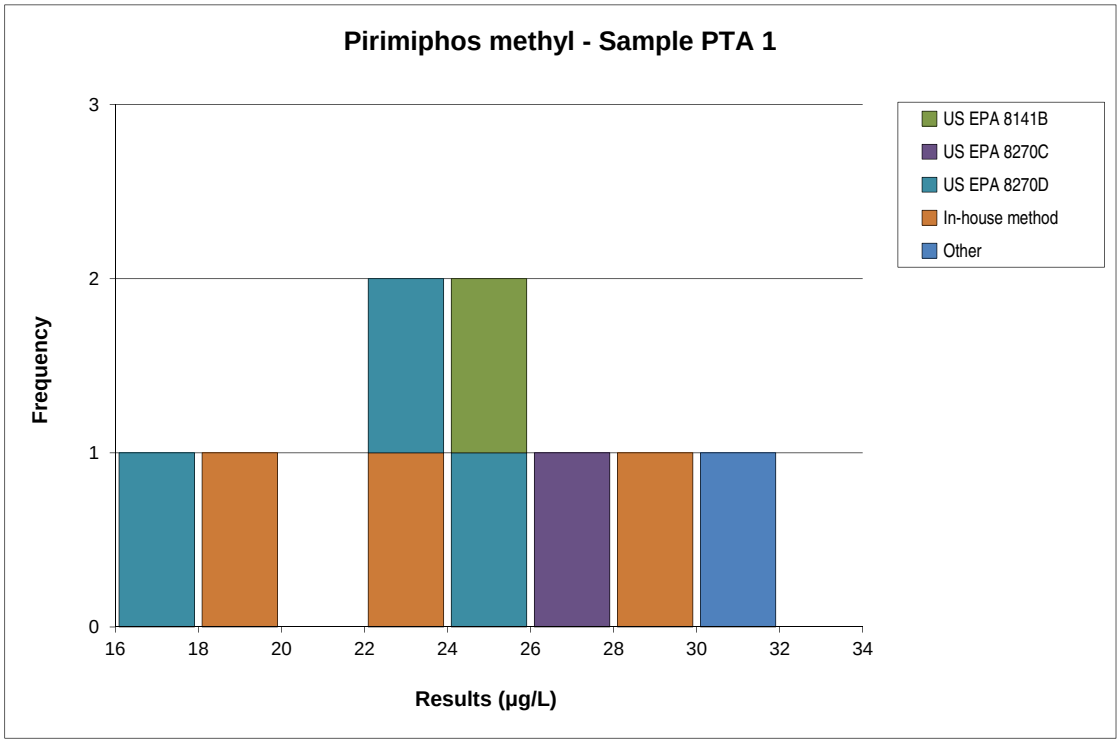


Figure 25. Spread of results for Pirimiphos methyl testing of sample PTA 1, with a median concentration of 24.25 µg/L.

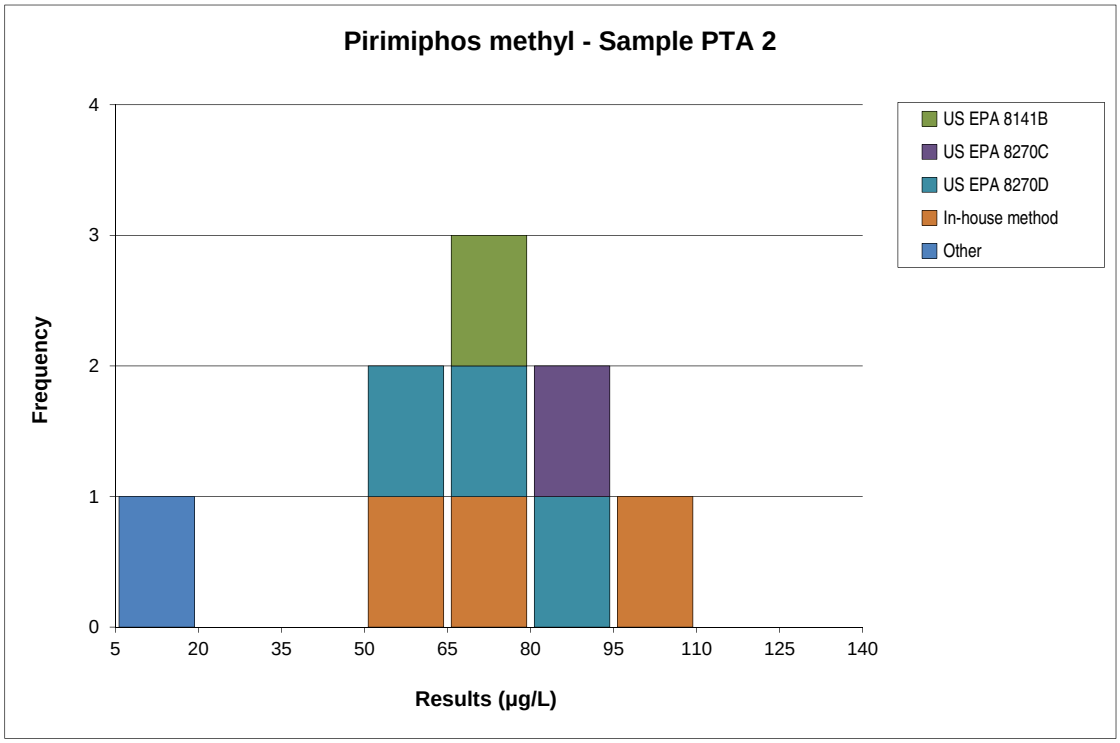


Figure 26. Spread of results for Pirimiphos methyl testing of sample PTA 2, with a median concentration of 75.29 µg/L.

Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for Pirimiphos methyl testing was 24.25 ± 12.82 µg/L for sample PTA 1 and 75.29 ± 63.83 µg/L for sample PTA 2.

Using the t-value, results submitted by laboratories using Method 13 - US EPA 8270D (n=3) indicated a method reproducibility of ± 16.73 µg/L for sample PTA 1 and of ± 58.99 µg/L for sample PTA 2.

All participants submitted MU information. Some of the stated MUs did not accurately reflect the difference between the median and the participants result for each proficiency sample.

Laboratories 255, 273, 368, 438 and 512 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 27 and 28. To keep it in perspective, the confidence in medians was 24.25 ± 2.18 µg/L for sample PTA 1 and 75.29 ± 9.90 µg/L for sample PTA 2.

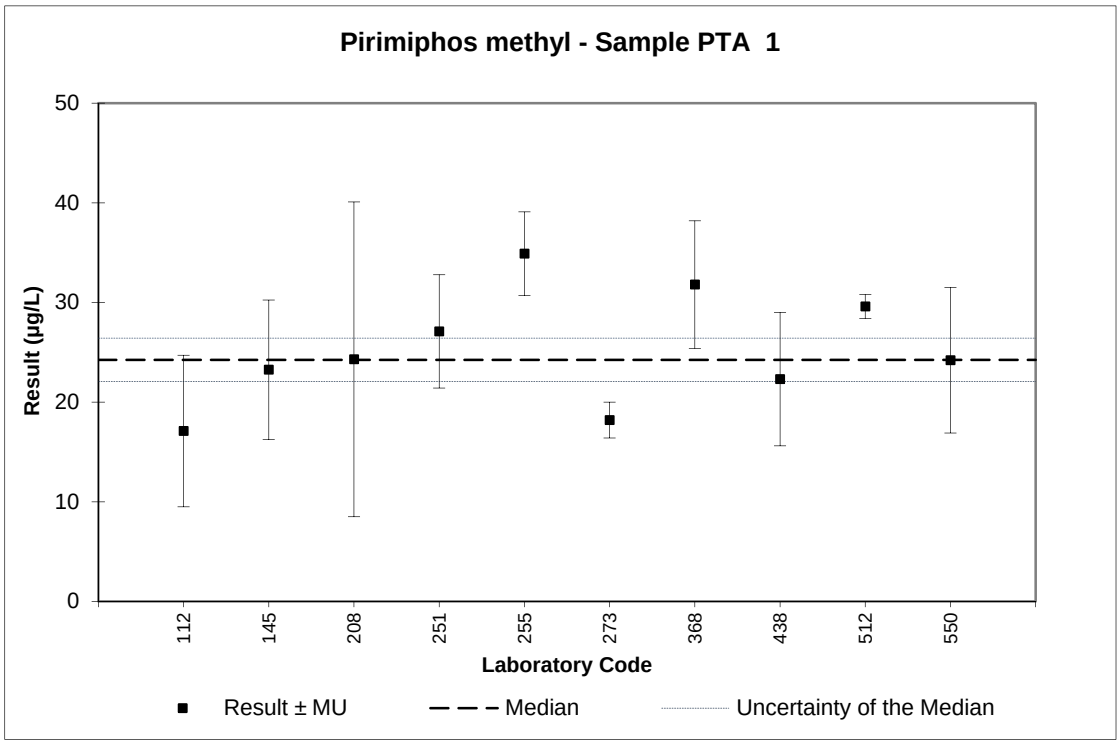


Figure 27. Pirimiphos methyl - Results of sample PTA 1, including MU, compared to the median.

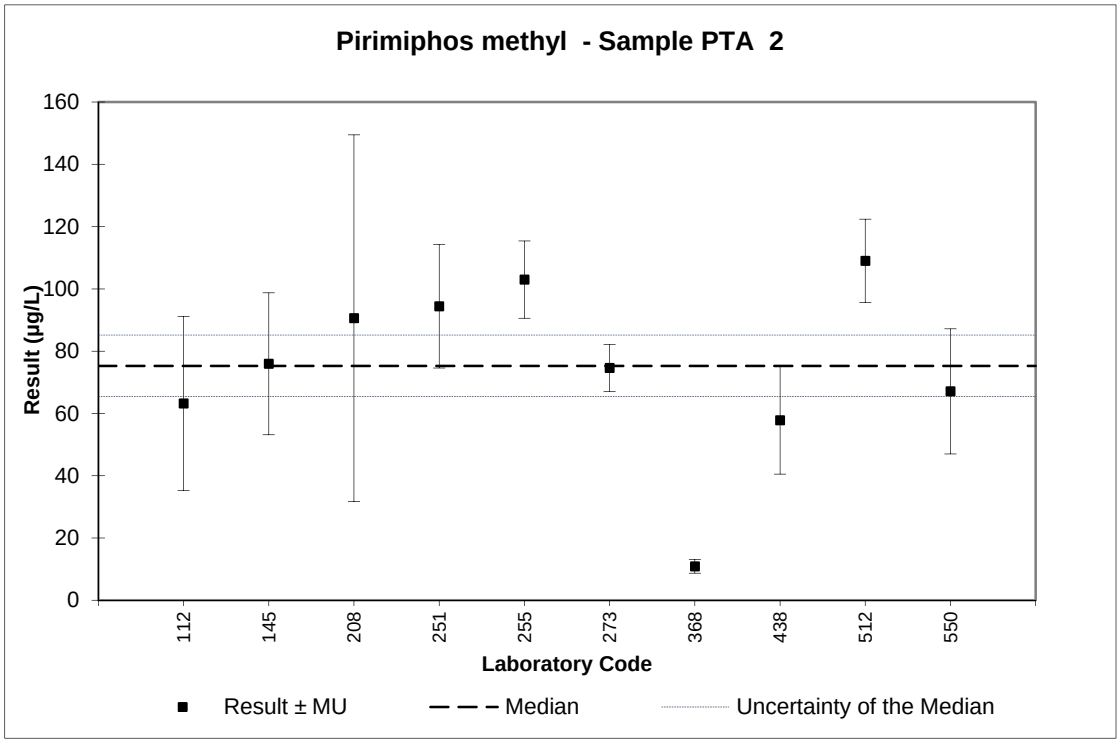


Figure 28. Pirimiphos methyl - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 29 and 30, displayed by the methods used.

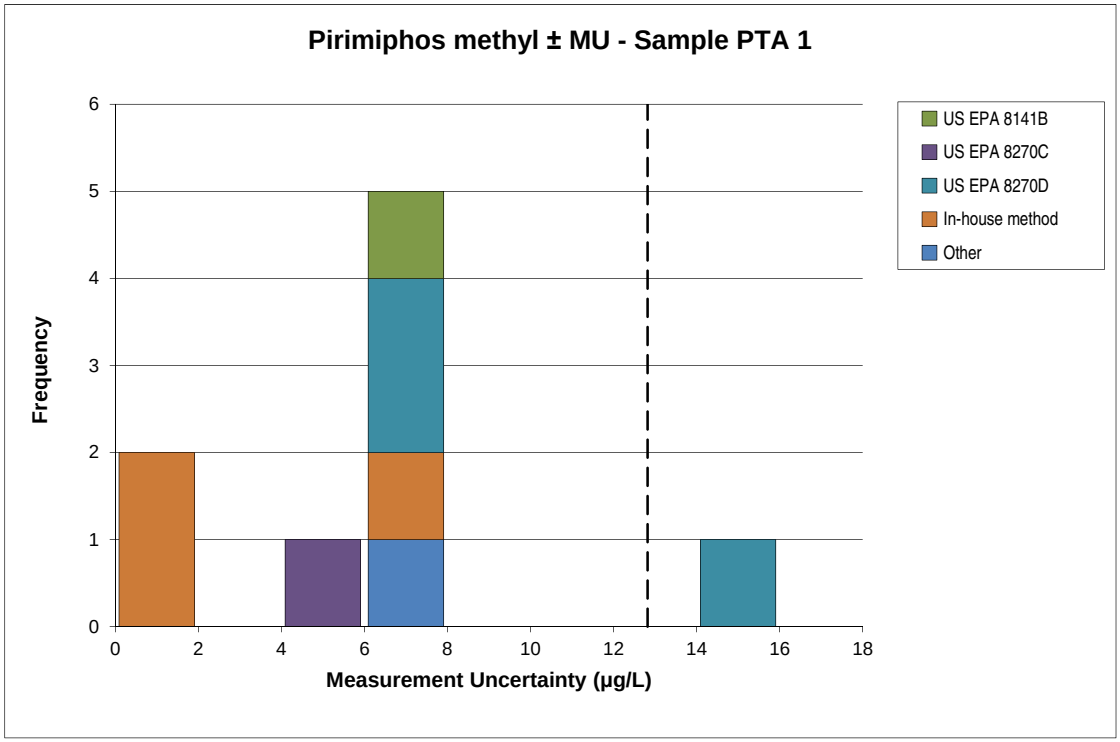


Figure 29. MU for Pirimiphos methyl testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 12.82 µg/L) in this round.

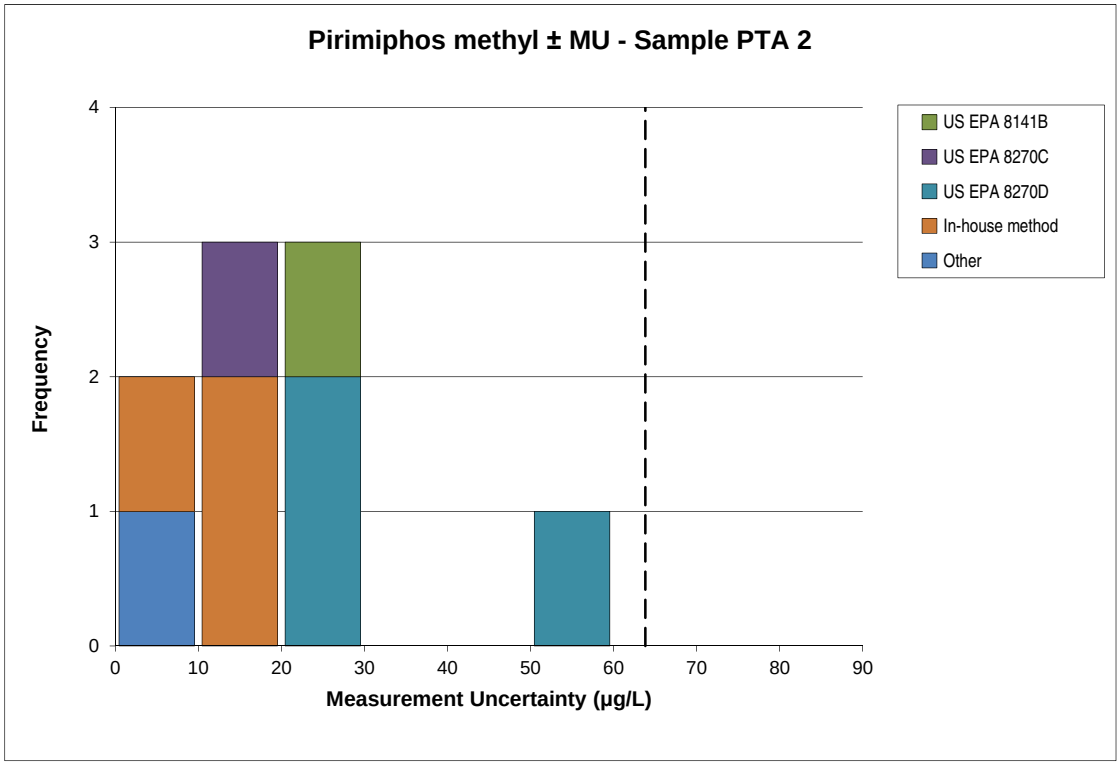


Figure 30. MU for Pirimiphos methyl testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 63.83 µg/L) in this round.

4.3 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.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 7 below.

Lab Code	Analysis									
	Azinphos methyl		Chlorpyriphos		Diazinon		Dimethoate		Pirimiphos methyl	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
118		§								
208		§								
251		§								
273				§						
368		§		§						

Table 7. Laboratory results identified as outliers for each analysis performed.

Note:

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

6. Reference

[1] *Guide to Proficiency Testing Australia*, 2012 (This document can be found on the PTA website, www.pta.asn.au)

APPENDIX A

Results and Data Analysis

Azinphos methyl Results

Samples PTA 1 and PTA 2

Azinphos methyl

Results by Laboratory Code

Lab Code	Sample PTA 1 Result ± MU[1] (µg/L)	Sample PTA 1 Robust z-score[2]	Sample PTA 1 Method Code[3]	Sample PTA 2 Result ± MU[1] (µg/L)	Sample PTA 2 Robust z-score[2]	Sample PTA 2 Method Code[3]
112	3.54 ± 0.64	-0.37	13	9.64 ± 1.8	0.91	13
118	6.57 ± 1.86	2.13	9	12.2 ± 2.8	3.40 §	9
145	3.08 ± 0.9	-0.75	13	6.99 ± 2.09	-1.68	13
208	2.33 ± 1.6	-1.37	13	4.65 ± 3.1	-3.95 §	13
228	3.97 ± 1.19	-0.02	16	8.26 ± 2.48	-0.44	16
251	5.80 ± 1.22	1.49	12	12.6 ± 2.65	3.79 §	12
255	5.08 ± 1.62	0.90	#	8.91 ± 2.85	0.19	#
273	3.38 ± 0.47	-0.50	15	8.63 ± 1.2	-0.08	15
285	5.12 ± 1.02	0.93	11	8.79 ± 1.76	0.08	11
286	3.28 ± 0.98	-0.59	13	7.83 ± 2.35	-0.86	13
368	1.91 ± 0.38	-1.72	16	3.53 ± 0.71	-5.05 §	16
422	4.02 ± 0.913	0.02	3	7.60 ± 1.73	-1.08	3
438	4.56 ± 1.34	0.47	15	8.96 ± 2.69	0.24	15
512	4.01 ± 0.3	0.02	15	8.82 ± 0.2	0.11	15
550	4.96 ± 1.49	0.80	11	9.54 ± 2.86	0.81	11
569	3.42 ± 0.68	-0.47	13	7.76 ± 1.55	-0.93	13
No of Results:	16			16		
Median:	3.990			8.710		
Normalised IQR:	1.212			1.027		
Uncertainty of the Median:	0.380			0.322		
Robust CV:	30.4%			11.8%		
Minimum:	1.91			3.53		
Maximum:	6.57			12.6		
Range:	4.66			9.07		

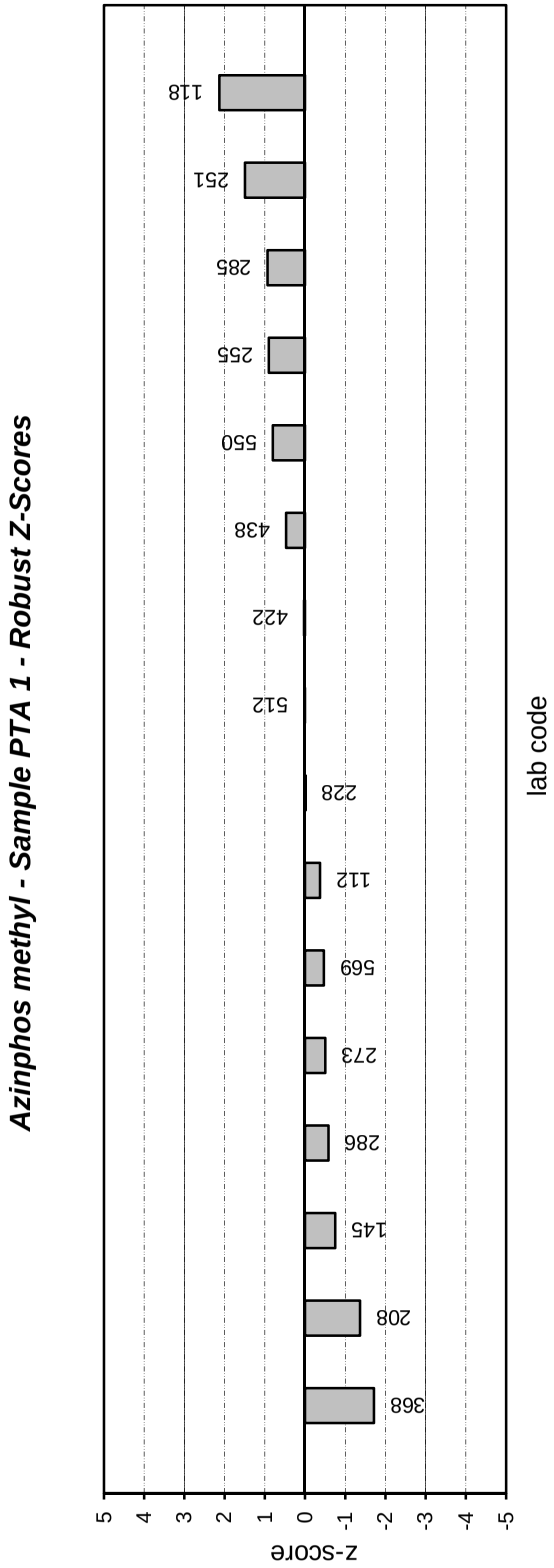
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

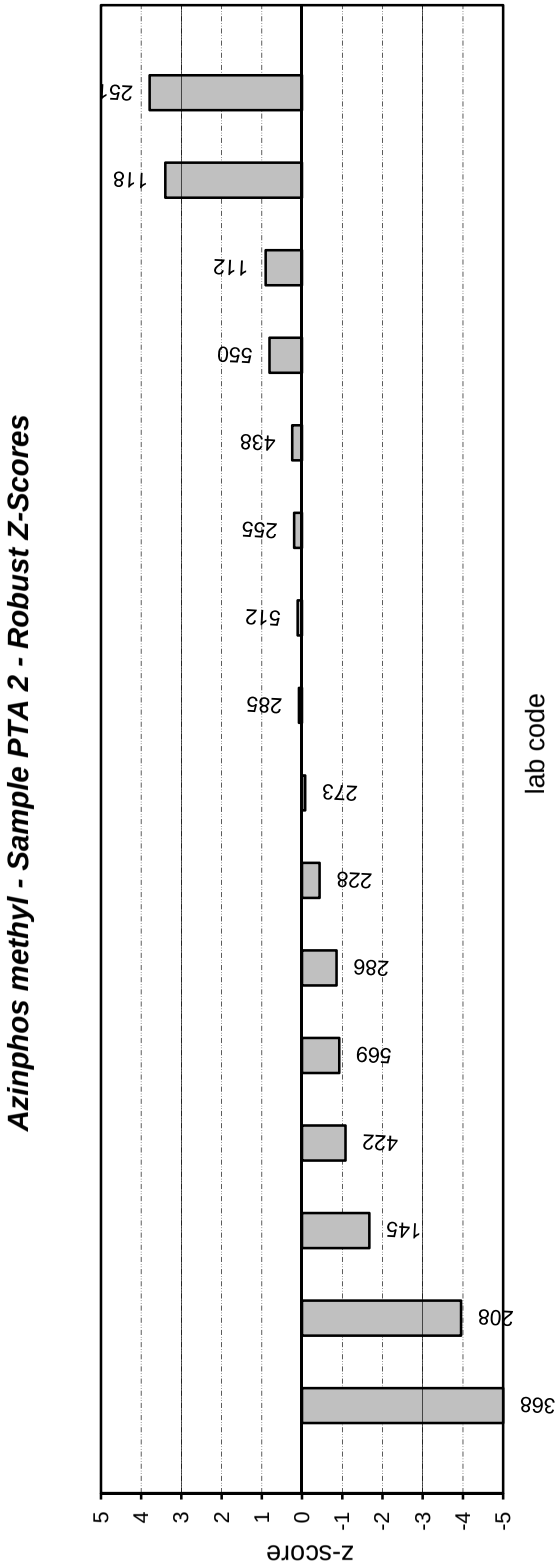
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated as: z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

[3] Please refer to Appendix C (page C3) for method code descriptions.

Azinphos methyl - Samples PTA 1 and PTA 2

Ordered Robust Z-Score Charts





Chlorpyriphos Results

Samples PTA 1 and PTA 2

Chlorpyriphos

Results by Laboratory Code

Lab Code	Sample PTA 1 Result ± MU[1] (µg/L)	Sample PTA 1 Robust z-score[2]	Sample PTA 1 Method Code[3]	Sample PTA 2 Result ± MU[1] (µg/L)	Sample PTA 2 Robust z-score[2]	Sample PTA 2 Method Code[3]
112	23.0 ± 7.4	-2.19	13	55.1 ± 18	-2.00	13
118	33.2 ± 9.4	-0.42	9	59.2 ± 16.7	-1.45	9
145	35.97 ± 10.8	0.06	13	69.7 ± 21	-0.03	13
208	26.5 ± 17.7	-1.58	13	67.1 ± 45	-0.38	13
228	33.0 ± 9.90	-0.46	16	67.9 ± 20.4	-0.28	16
251	35.8 ± 7.52	0.03	12	71.2 ± 15.0	0.17	12
255	31.1 ± 6.2	-0.79	#	70.2 ± 14.0	0.03	#
273	38.2 ± 4.6	0.44	15	102 ± 12	4.32 **§**	15
285	39.8 ± 8.0	0.72	11	89.7 ± 17.9	2.66	11
286	43.1 ± 12.9	1.29	13	74.7 ± 22.4	0.64	13
368	23.0 ± 4.6	-2.19	16	11.4 ± 2.3	-7.90 **§**	16
422	42.1 ± 14.7	1.12	16	76.4 ± 26.7	0.87	16
438	29.9 ± 8.97	-0.99	15	50.9 ± 15.3	-2.57	15
512	36.1 ± 1.3	0.08	15	71.8 ± 2.5	0.25	15
550	35.5 ± 10.6	-0.03	11	67.1 ± 20.1	-0.38	11
569	41.1 ± 8.2	0.94	13	81.8 ± 16.4	1.60	13
No of Results:	16			16		
Median:	35.65			69.95		
Normalised IQR:	5.78			7.41		
Uncertainty of the Median:	1.81			2.32		
Robust CV:	16.2%			10.6%		
Minimum:	23.0			11.4		
Maximum:	43.1			102		
Range:	20.1			90.6		

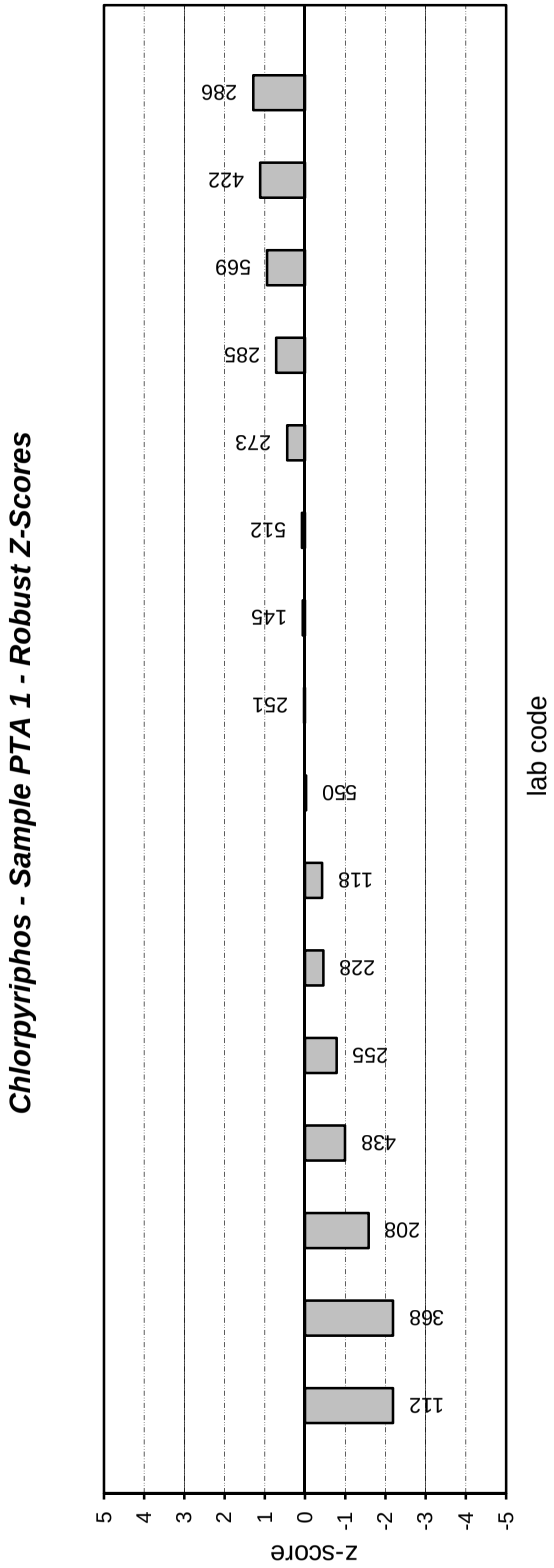
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

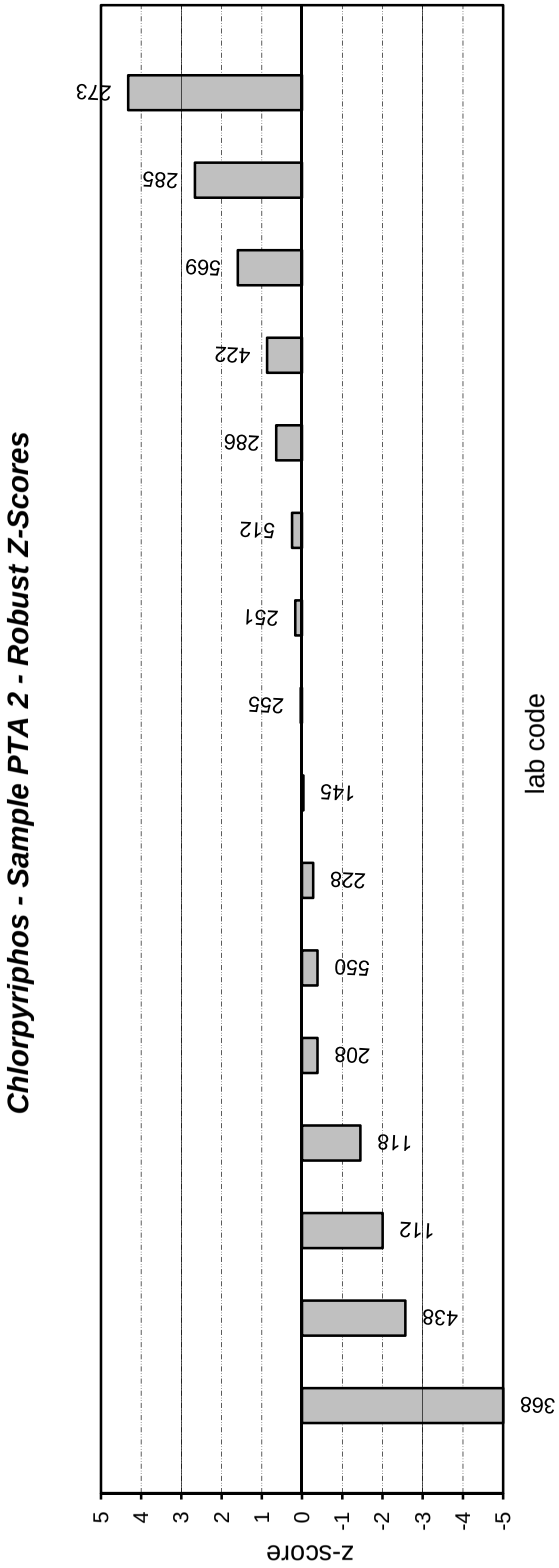
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated as: z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

[3] Please refer to Appendix C (page C3) for method code descriptions.

Chlorpyriphos - Samples PTA 1 and PTA 2

Ordered Robust Z-Score Charts





Diazinon Results

Samples PTA 1 and PTA 2

Diazinon

Results by Laboratory Code

Lab Code	Sample PTA 1 Result ± MU[1] (µg/L)	Sample PTA 1 Robust z-score[2]	Sample PTA 1 Method Code[3]	Sample PTA 2 Result ± MU[1] (µg/L)	Sample PTA 2 Robust z-score[2]	Sample PTA 2 Method Code[3]
112	3.81 ± 1.1	-1.01	13	8.86 ± 2.5	-0.57	13
118	7.28 ± 1.74	1.67	9	13.5 ± 3.2	1.16	9
145	5.12 ± 1.5	0.00	13	10.11 ± 3	-0.11	13
208	4.21 ± 2.8	-0.70	13	8.38 ± 5.6	-0.75	13
228	4.71 ± 1.41	-0.32	16	9.71 ± 2.91	-0.26	16
251	5.05 ± 1.06	-0.05	12	10.4 ± 2.18	0.00	12
255	7.03 ± 1.83	1.47	#	14.1 ± 3.9	1.38	#
273	5.10 ± 0.41	-0.02	15	8.63 ± 0.69	-0.66	15
285	7.89 ± 1.58	2.14	11	14.3 ± 2.9	1.45	11
286	6.75 ± 2.03	1.26	13	12.7 ± 3.81	0.86	13
368	2.01 ± 0.40	-2.40	16	3.19 ± 0.64	-2.69	16
422	5.81 ± 1.55	0.53	3	10.4 ± 2.78	0.00	3
438	5.00 ± 1.50	-0.09	15	9.08 ± 2.72	-0.49	15
512	4.75 ± 0.3	-0.29	15	9.4 ± 0.9	-0.37	15
550	5.8 ± 1.7	0.52	11	10.7 ± 3.2	0.11	11
569	5.12 ± 1.02	0.00	13	10.4 ± 2.08	0.00	13
619	6.50 ± 0.45	1.06	15	13.0 ± 0.72	0.97	15
No of Results:	17			17		
Median:	5.120			10.40		
Normalised IQR:	1.297			2.68		
Uncertainty of the Median:	0.394			0.82		
Robust CV:	25.3%			25.8%		
Minimum:	2.01			3.19		
Maximum:	7.89			14.3		
Range:	5.88			11.11		

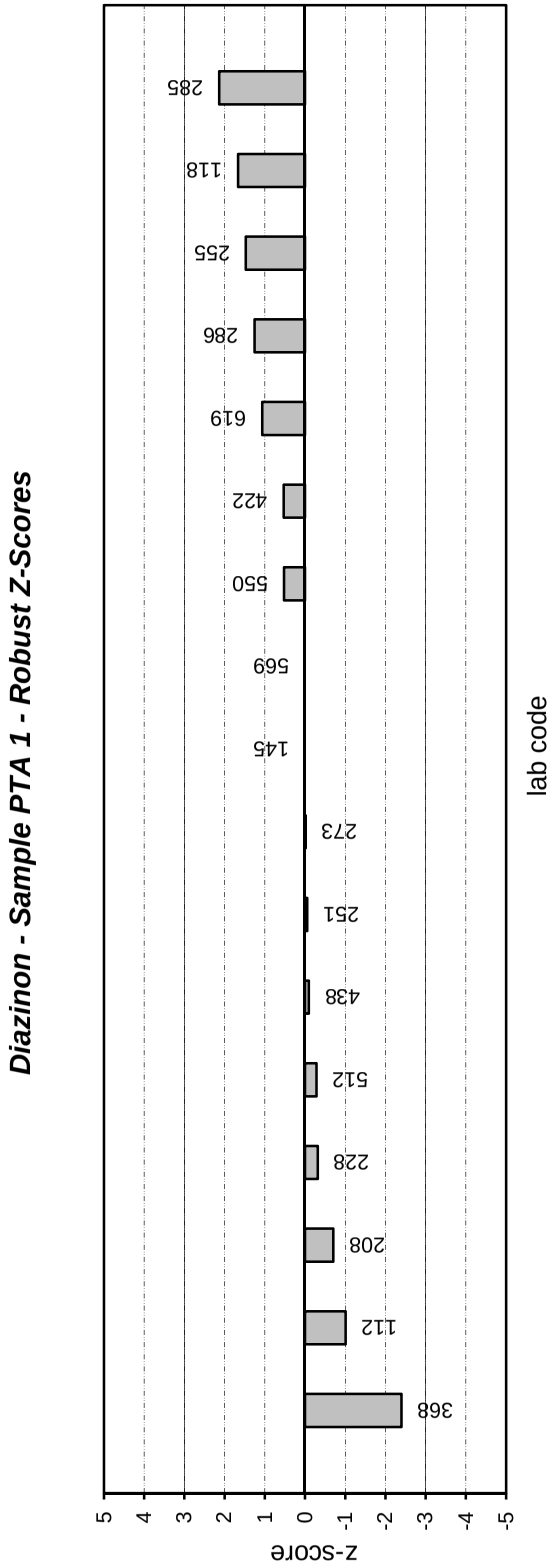
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

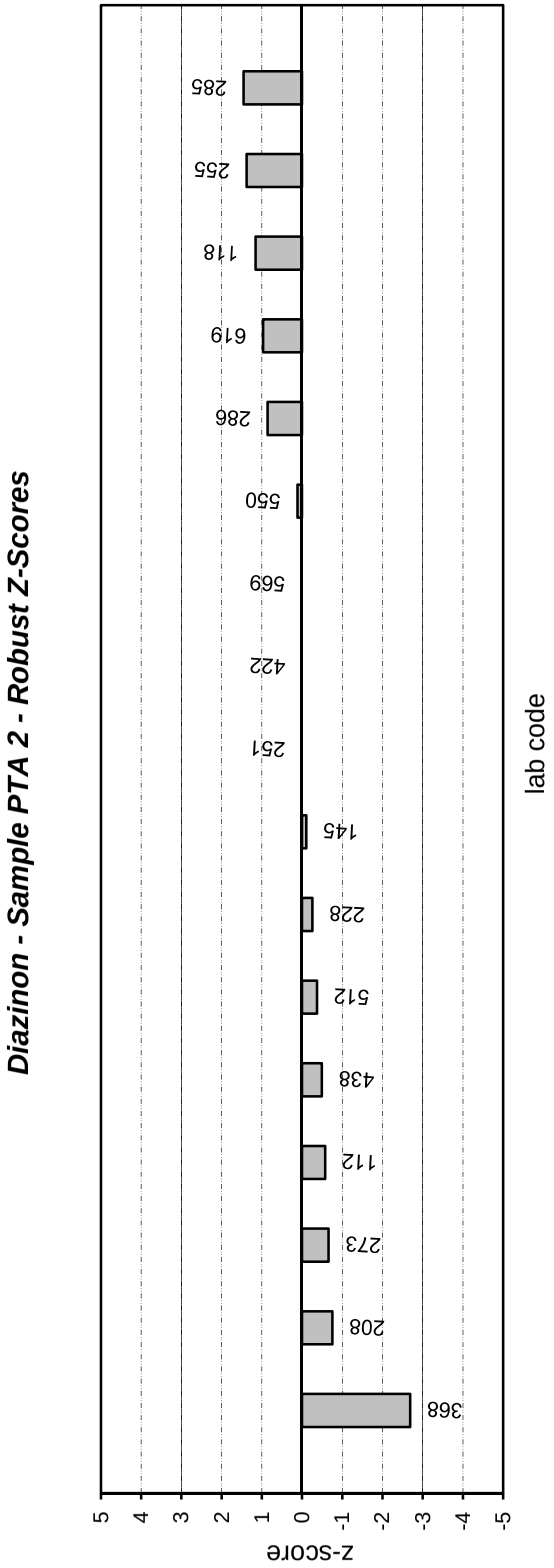
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated as: z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

[3] Please refer to Appendix C (page C3) for method code descriptions.

Diazinon - Samples PTA 1 and PTA 2

Ordered Robust Z-Score Charts





Dimethoate Results

Samples PTA 1 and PTA 2

Dimethoate

Results by Laboratory Code

Lab Code	Sample PTA 1 Result ± MU[1] (µg/L)	Sample PTA 1 Robust z-score[2]	Sample PTA 1 Method Code[3]	Sample PTA 2 Result ± MU[1] (µg/L)	Sample PTA 2 Robust z-score[2]	Sample PTA 2 Method Code[3]
112	21.9 ± 14	-2.11	13	33.8 ± 21	-1.57	13
118	41.1 ± 9.8	-0.19	9	45.8 ± 10.9	-0.81	9
145	43.83 ± 13.2	0.08	13	58.96 ± 17.7	0.02	13
208	43.9 ± 29.4	0.09	13	64.2 ± 43	0.35	13
228	38.0 ± 11.4	-0.50	16	53.0 ± 15.9	-0.36	16
251	45.9 ± 9.64	0.29	12	60.0 ± 12.6	0.08	12
255	70.0 ± 20.3	2.69	#	86.6 ± 25.1	1.76	#
273	36.3 ± 3.6	-0.67	15	56.9 ± 5.7	-0.11	15
286	62.6 ± 18.8	1.95	13	82.8 ± 24.8	1.52	13
368	27.0 ± 5.4	-1.60	16	21.2 ± 4.2	-2.36	16
438	42.2 ± 12.7	-0.08	15	49.9 ± 15.0	-0.55	15
512	52.8 ± 3.7	0.98	15	75.1 ± 5.1	1.04	15
550	37.4 ± 11.2	-0.56	11	58.4 ± 17.5	-0.02	11
569	55.8 ± 11.1	1.28	13	74.7 ± 14.9	1.01	13
No of Results:	14			14		
Median:	43.02			58.68		
Normalised IQR:	10.03			15.86		
Uncertainty of the Median:	3.36			5.31		
Robust CV:	23.3%			27.0%		
Minimum:	21.9			21.2		
Maximum:	70.0			86.6		
Range:	48.1			65.4		

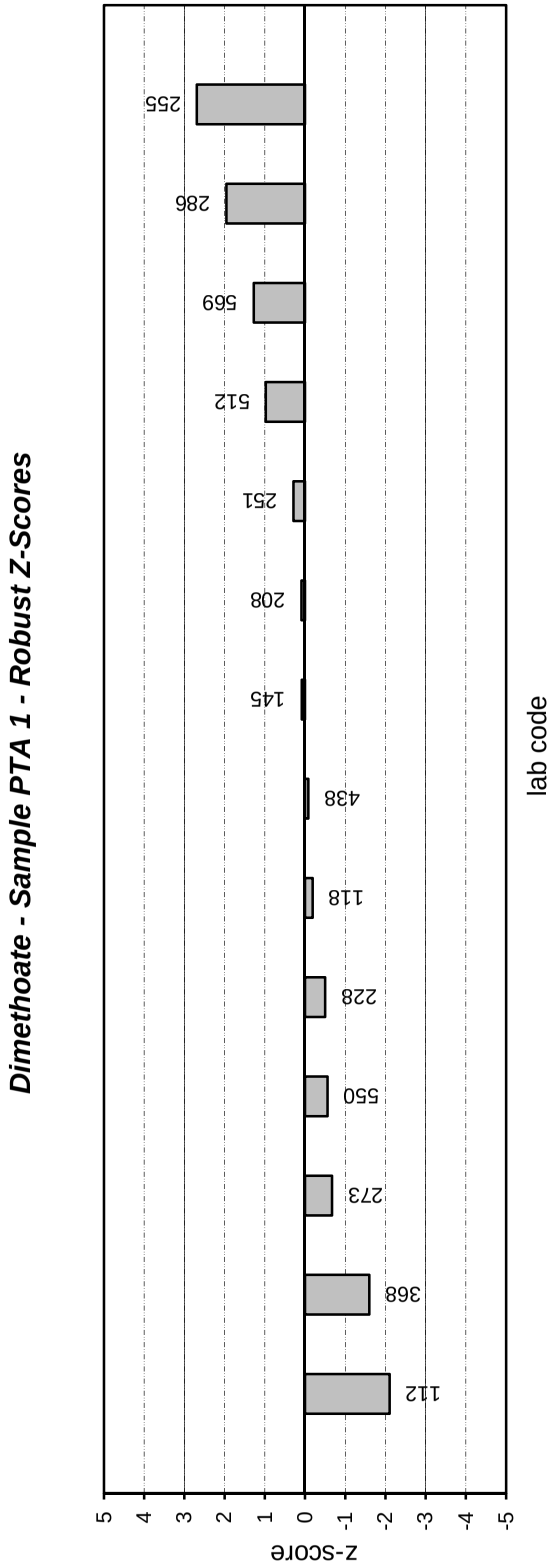
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

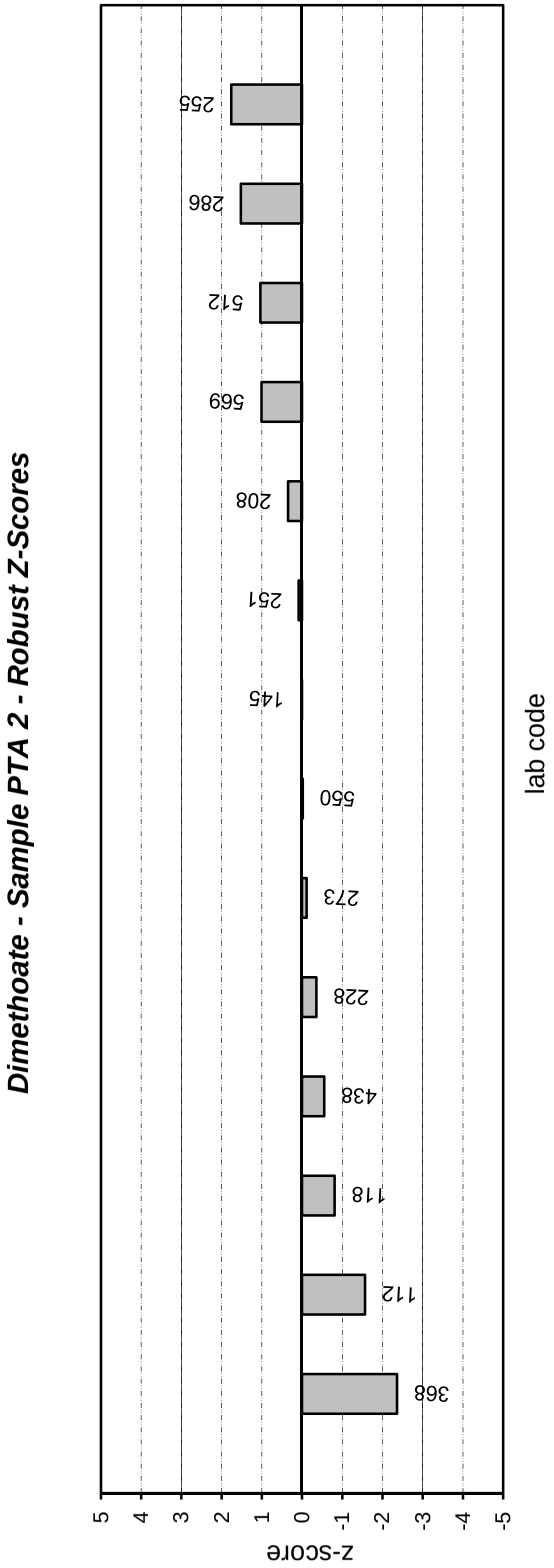
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated as: z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

[3] Please refer to Appendix C (page C3) for method code descriptions.

Dimethoate - Samples PTA 1 and PTA 2

Ordered Robust Z-Score Charts





Pirimiphos methyl Results

Samples PTA 1 and PTA 2

Pirimiphos methyl

Results by Laboratory Code

Lab Code	Sample PTA 1 Result ± MU[1] (µg/L)	Sample PTA 1 Robust z-score[2]	Sample PTA 1 Method Code[3]	Sample PTA 2 Result ± MU[1] (µg/L)	Sample PTA 2 Robust z-score[2]	Sample PTA 2 Method Code[3]
112	17.1 ± 7.6	-1.30	13	63.2 ± 28	-0.48	13
145	23.25 ± 7	-0.18	13	75.97 ± 22.8	0.03	13
208	24.3 ± 15.8	0.01	13	90.6 ± 58.9	0.61	13
251	27.1 ± 5.69	0.52	12	94.4 ± 19.8	0.77	12
255	34.9 ± 4.2	1.94	#	103 ± 12.4	1.11	#
273	18.2 ± 1.8	-1.10	15	74.6 ± 7.5	-0.03	15
368	31.8 ± 6.4	1.37	16	10.9 ± 2.2	-2.58	16
438	22.3 ± 6.69	-0.36	15	57.8 ± 17.3	-0.70	15
512	29.6 ± 1.2	0.97	15	109 ± 13.4	1.35	15
550	24.2 ± 7.3	-0.01	11	67.1 ± 20.1	-0.33	11
No of Results:	10			10		
Median:	24.25			75.29		
Normalised IQR:	5.49			24.98		
Uncertainty of the Median:	2.18			9.90		
Robust CV:	22.7%			33.2%		
Minimum:	17.1			10.9		
Maximum:	34.9			109		
Range:	17.8			98.1		

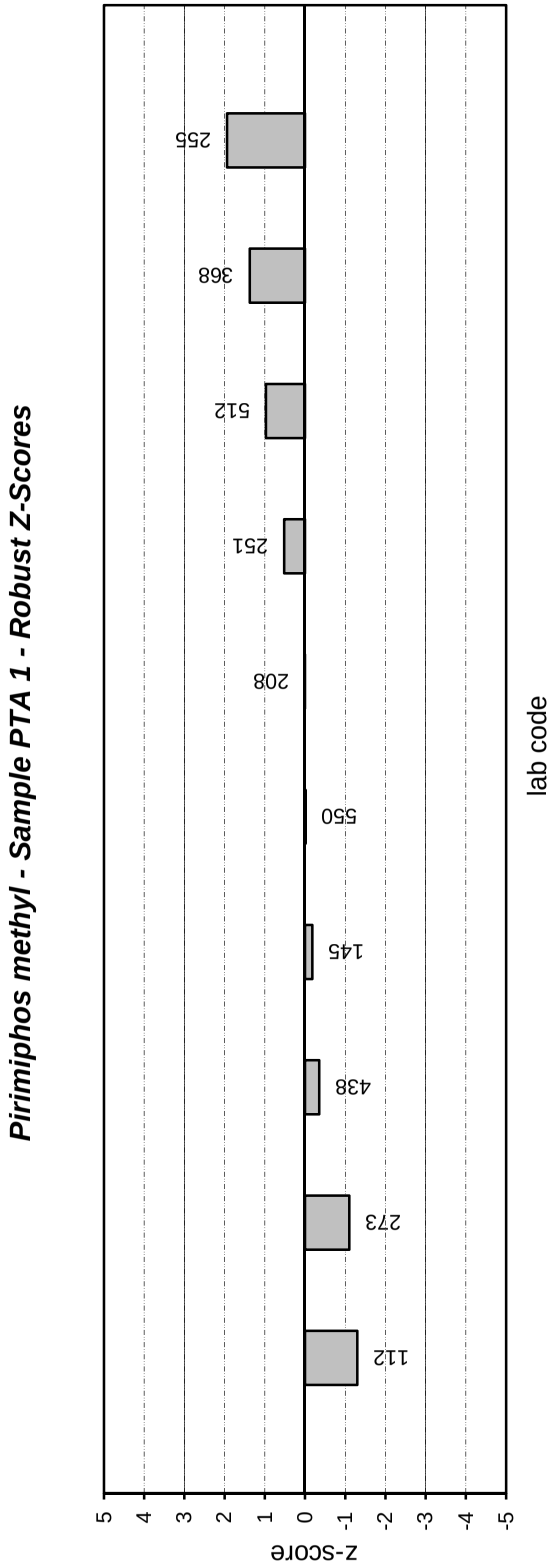
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

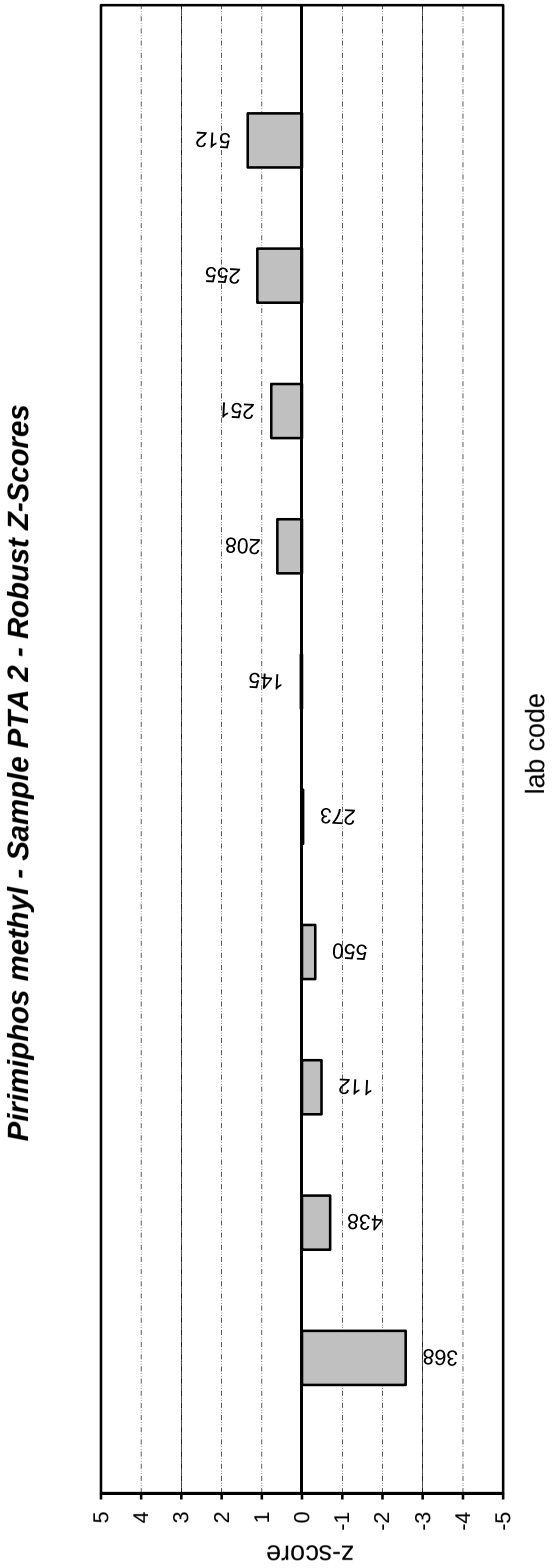
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated as: z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

[3] Please refer to Appendix C (page C3) for method code descriptions.

Pirimiphos methyl - Samples PTA 1 and 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. A random selection of five samples was chosen from PTA 1 sample set. Three samples were stored frozen and two were subjected to 35ºC for three days for an accelerated ageing stability trial. All stability samples showed increased variability when compared to frozen samples.

On 9 May 2013, samples were analysed by AsureQuality, New Zealand, in duplicate for homogeneity and stability. 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 Table 8 below.

Round PTA 154	Sample PTA 1									
	Azinphos methyl (µg/L)		Chlorpyriphos (µg/L)		Diazinon (µg/L)		Dimethoate (µg/L)		Pirimiphos methyl (µg/L)	
	Dup 1	Dup 2	Dup 1	Dup 2	Dup 1	Dup 2	Dup 1	Dup 2	Dup 1	Dup 2
Homogeneity 1-1	4.0	3.8	45	40	7.2	5.7	64	53	34	31
Homogeneity 1-2	4.0	4.3	44	39	6.1	5.7	54	53	33	30
Homogeneity 1-3	3.7	4.1	44	39	6.1	5.6	55	54	34	31
Stability 1-1	4.5	4.0	49	41	6.6	5.1	52	45	36	24
Stability 1-2	4.0	3.8	42	39	5.5	5.4	49	47	32	30
RSD	7.1%	5.3%	5.8%	2.3%	10.1%	4.6%	10.3%	8.1%	4.4%	10.1%

Table 8. Homogeneity and stability testing of PTA 1 samples.

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 154 **APRIL, 2013**

ORGANOPHOSPHATE PESTICIDES

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 glass ampoules labelled PTA 1 and PTA 2, supplied by Global Proficiency Ltd, New Zealand.

ii) The samples must be thoroughly mixed prior to analysis.

iii) The ampoules will require 1000-fold dilution in reagent grade water.

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

2. Sample Preparation

Caution: Analysis must begin immediately after ampoule is opened.

i) Adjust ampoule temperature to 20º C.

ii) Add approximately 900 millilitres (mL) reagent grade water to a one-litre volumetric flask.

iii) Record ampoule ID number. Carefully open the ampoule.

iv) Using a gas tight syringe, transfer 1.00 millilitre (mL) of the concentrate below the surface of the water in the flask.

v) Bring flask to volume with reagent grade water.

vi) Stopper and mix well by inversion.

3. Tests Requested

For the diluted sample prepared from the ampoule:.

i) Azinphos methyl

ii) Chlorpyriphos

iii) Diazinon

iv) Dimethoate

v) Pirimiphos methyl

It is recommended that a reagent water blank is analysed by the same method used to analyse the samples.
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 safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

i) Report results using three significant figures (e.g.: 1.23, 12.3, 123).

ii) Report results in micrograms per litre (µg/L).

iii) Do not correct results for recovery.

iv) In addition to reporting the results, record the method of analysis using the attached codes.

v) Laboratories are also requested to calculate and report an estimate of measurement uncertainty (MU) for each reported measurement result. All estimates of MU must be given as a 95% confidence interval (coverage factor k ≈ 2) and reported in micrograms per litre (µg/L).

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 17 MAY 2013 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 (in µg/L):

Analyte	Concentration (µg/L)
Azinphos methyl	1 – 15
Chlorpyriphos	5 – 100
Diazinon	1 – 20
Dimethoate	5 – 100
Pirimiphos methyl	20 - 150

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Azinphos methyl Chlorpyriphos Diazinon Dimethoate Pirimiphos methyl	APHA SM	APHA Part 6630B Organochlorine Pesticides – Liquid-Liquid Extraction Gas Chromatographic Method I	1
		APHA Part 6630C Organochlorine Pesticides – Liquid-Liquid Extraction Gas Chromatographic Method II	2
	US EPA	US EPA Method Number 507 Nitrogen- & Phosphorus-Containing Pesticides	3
		US EPA Method Number 525.2 Organic compounds – LSE/capillary/GCMS)	4
		US EPA Method Number 614 (Pesticides, Organophosphorus in WW)	5
		US EPA Method Number 614.1 (Pesticides, Organophosphorus in WW)	6
		US EPA Method Number 622 (Pesticides, Organophosphorus: Trichloronate – WW)	7
		US EPA Method Number 8041B Organophosphorus Compounds by GC	8
		US EPA Method Number 8140 Organophosphorus Pesticides	9
		US EPA Method Number 8141A Organophosphorus Pesticides - GC Capillary Column)	10
		US EPA Method Number 8141B Organophosphorus Compounds by GC	11
		US EPA Method Number 8270C Semivolatile Organic Compounds by GC-MS Cap Col)	12
		US EPA Method Number 8270D Semivolatile Organic Compounds by GC-MS)	13
	USGS	USGS 1972, Book 5, p 30	14
	Other	In-house or modified method	15
		Other (please specify)	16

Method Reference Key

i) APHA SM — APHA "Standard Methods for the Examination of Water and Wastewater" (18, 19, 20, 21 and 22 Edition).

ii) US EPA — U.S Environmental Protection Agency, http://www.epa.gov/osa/fem/methcollectns.htm.

iii) USGS — "Techniques of Water Resource Investigation of the United States Geological Survey, Chapter A-3, Methods for the Analysis of Organic Substances in Water" Book 5, 1972.

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 154

ORGANOPHOSPHATE PESTICIDES

APRIL, 2013

RESULTS SHEET
(µg/L)

Laboratory Code _____

Approximate temperature of samples upon receipt:	

ANALYSIS	Sample: PTA 1			Sample: PTA 2		
	Result (µg/L)	±MU*	Method Code	Result (µg/L)	±MU*	Method Code
Azinphos methyl						
Chlorpyriphos						
Diazinon						
Dimethoate						
Pirimiphos methyl						

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

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

ii) Report results using three significant figures (e.g.: 1.23, 12.3, 123).

iii) Report results in micrograms per litre (µg/L).

iv) Do not correct results for recovery.

v) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in the appropriate units of measurement.

_____ _____

DATE **SIGNATURE**

Return results **NO LATER THAN 17 MAY 2013** 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

- End of Report -