



Report No. 1089

Waters Proficiency Testing Program

Round No. 226

- Organophosphorus Pesticides -

July 2018

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Mr P Nottle, Analytical Reference Laboratory (WA) Pty Ltd (Australia). Also our thanks go to the Environmental Resource Associates (USA) for the supply of samples and to Global Proficiency Pty Ltd (Australia) for distributing the samples.

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PO Box 7507 SILVERWATER NSW 2128, Australia

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1. Foreword

This report summarises the results of a proficiency testing program on the determination of Organophosphorus Pesticides in waters. This is round 226 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in April 2018 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 Mr P Nottle, Analytical Reference Laboratory (WA) Pty Ltd (Australia). 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 one sealed ampoule (labelled R226) containing solutions of Organophosphorus Pesticides.

2.4 A total of 11 laboratories received samples, comprising:

- 8 Australian participants; and

- 3 overseas participants, including:

- New Zealand (2), Vietnam (1).

Of these 11 laboratories, one was 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 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 16.
- 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 16 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 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 Environmental Resource Associates' Standard Operating Procedures to ensure samples were fit-for-purpose, homogeneous and stable.

Solutions were stable and homogeneous, and the results obtained from this proficiency round were in good agreement with the expected levels (manufacturer's certified value), as shown in Table 1.

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 also presented in Table 1 below.

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

Analyte	Expected Levels (µg/L)	Median (µg/L)	Analyte Recovery (%)	Uncertainty of the Median (µg/L)
Azinphos-methyl	16.6	15.65	94.3%	1.18
Chlorpyrifos	3.83	3.290	85.9%	0.288
Diazinon	2.82	2.845	100.9%	0.209
Dimethoate	17.3	13.75	79.5%	1.70
Disulfoton	7.74	6.755	87.3%	0.927
Ethion	15.6	13.50	86.5%	1.83
Ethyl Parathion	3.26	3.020	92.6%	0.347
Malathion	8.99	8.205	91.3%	0.683
Methyl Parathion	8.63	7.210	83.5%	1.220

Overall, the performance of participants in this round was very good, with four reported outliers from a total of 85 results. The most likely sources of error for these results are: instrument calibration issues, chromatography issues, extraction inefficiency and calculation errors. Organophosphorus pesticides are prone to hydrolysis at high pH, however, the stability testing results of the PTA samples show that this should not have been an issue.

The Robust CV for Dimethoate, Disulfoton, Ethion and Methyl Parathion exceeded the Horwitz Ratio (HorRat) of 2, indicating a higher amount of variation than should be expected. However, the Robust CV for Dimethoate was similar to previous PTA studies. No previous data from PTA was available for Disulfoton, Ethion or Methyl Parathion, as these were new analytes tested.

Most of the measurement uncertainties (MU) reported were at expected levels. Laboratory 553 reported uncertainties of 3% for Ethyl Parathion and 1% for Malathion, which seem too low for this level of testing and may need reviewing. Laboratory 551 did not submit any uncertainties. All other participants submitted results together with the associated MU.

Analysis of Round 226 Results

4.2.1 Azinphos-methyl

Table 2 compares the Azinphos-methyl median and robust CV from this round to those obtained in previous PTA rounds.

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

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	15.65	18.9	10
Report 812	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

Bias / Accuracy

Azinphos-methyl satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 9.99 – 19.7 µg/L. Out of ten participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported (laboratory 551). One outlier result ($|z\text{-score}| \geq 3.0$) was reported, requiring follow-up action by laboratory 278.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 1). The methods used for Azinphos-methyl testing in this round were US EPA 8141B (Organophosphorus Compounds by GC), US EPA 8270D (Semivolatile Organic Compounds by GC/MS) and In-house or modified methods.

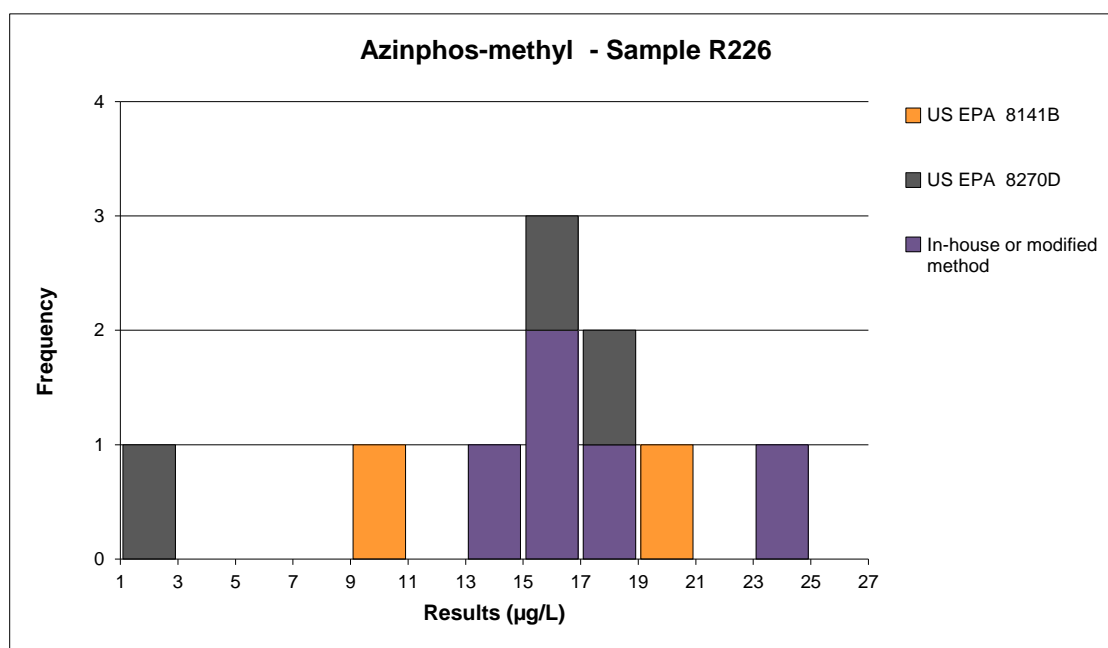


Figure 1. Spread of results for Azinphos-methyl testing of sample R226, with a median of 15.65 µg/L.

4.2.2 Chlorpyrifos

Table 3 compares the Chlorpyrifos median and robust CV from this round to those obtained in previous PTA rounds.

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

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	3.290	21.0	9
Report 812	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

Bias / Accuracy

Chlorpyrifos satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 2.015 – 4.16 µg/L. Out of nine numerical results reported, there were no questionable ($2.0 < |z\text{-score}| < 3.0$) or outlier ($|z\text{-score}| \geq 3.0$) results.

Additionally, laboratory 353 reported a result of “<2 µg/L” for Chlorpyrifos. This result was deemed to be satisfactory.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 2). The methods used for Chlorpyrifos testing in this round were APHA 6630C (Liquid-Liquid Extraction GC), US EPA 8141B, US EPA 8270D and In-house or modified methods.

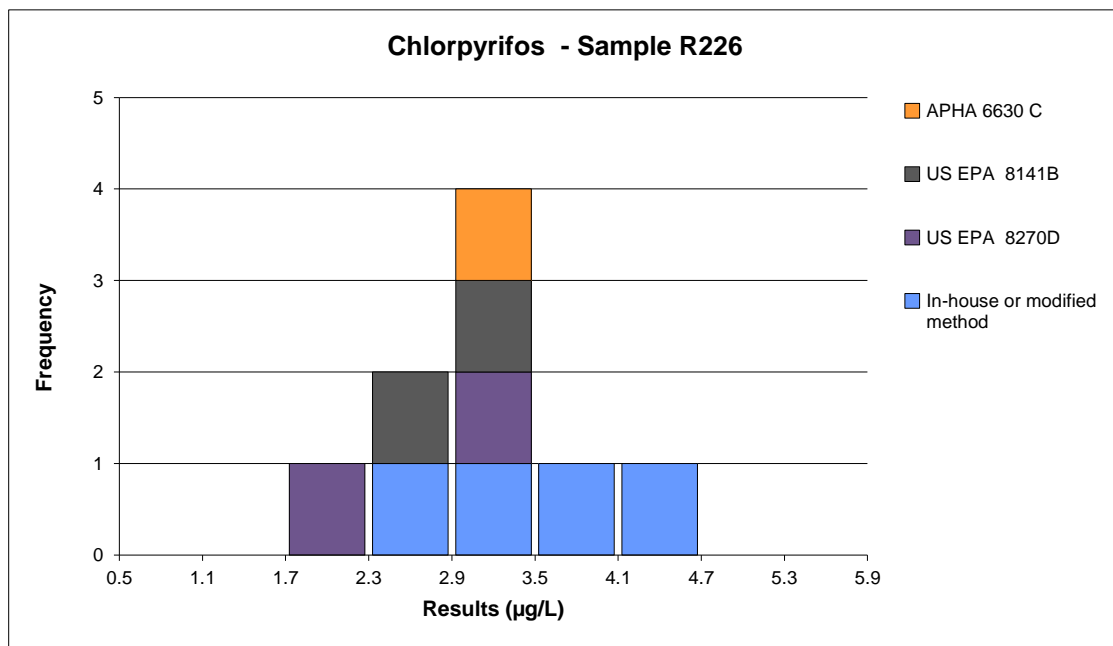


Figure 2. Spread of results for Chlorpyrifos testing of sample R226, with a median of 3.290 µg/L.

4.2.3 Diazinon

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

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

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	2.845	18.5	10
Report 812	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

Bias / Accuracy

Diazinon satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 2.002 – 3.39 µg/L. Out of ten participants, no questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported. One outlier result ($|z\text{-score}| \geq 3.0$) was reported, requiring follow-up action by laboratory 595.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 3). The methods used for Diazinon testing in this round were APHA 6630C, US EPA 8141B, US EPA 8270D and In-house or modified methods.

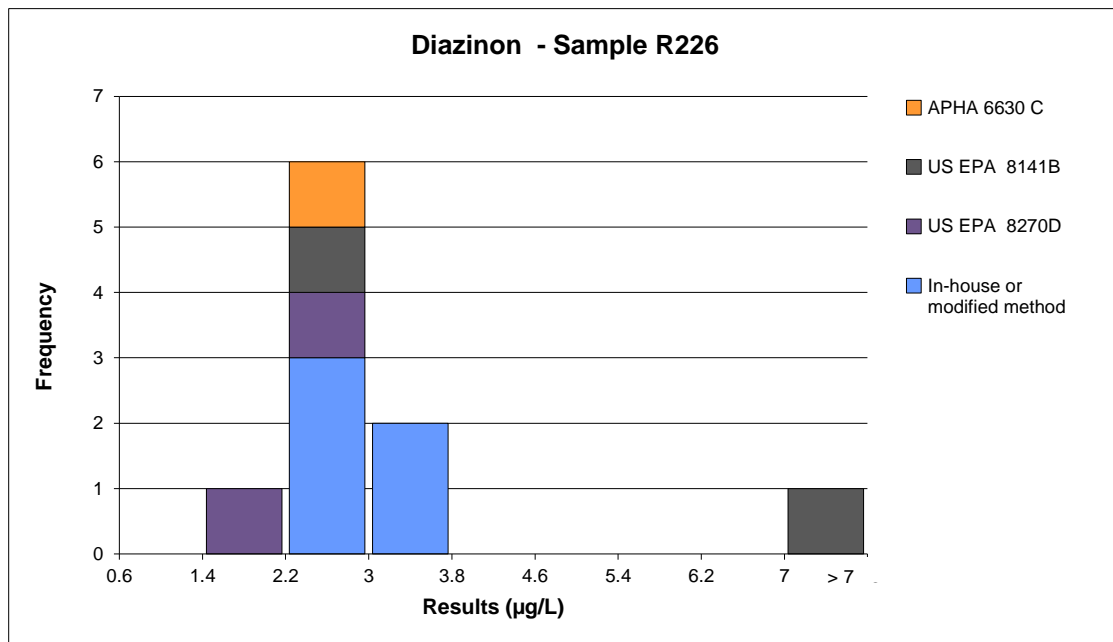


Figure 3. Spread of results for Diazinon testing of sample R226, with a median of 2.845 µg/L.

4.2.4 Dimethoate

Table 5 compares the Dimethoate median and robust CV from this round to those obtained in previous PTA rounds.

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

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	13.75	31.1	10
Report 812	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

Bias / Accuracy

Dimethoate satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 5.451 – 18.7 µg/L. Out of ten participants, no questionable ($2.0 < |z\text{-score}| < 3.0$) or outlier ($|z\text{-score}| \geq 3.0$) results were reported.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 4). The methods used for Dimethoate testing in this round were US EPA 8141B, US EPA 8270D and In-house or modified methods.

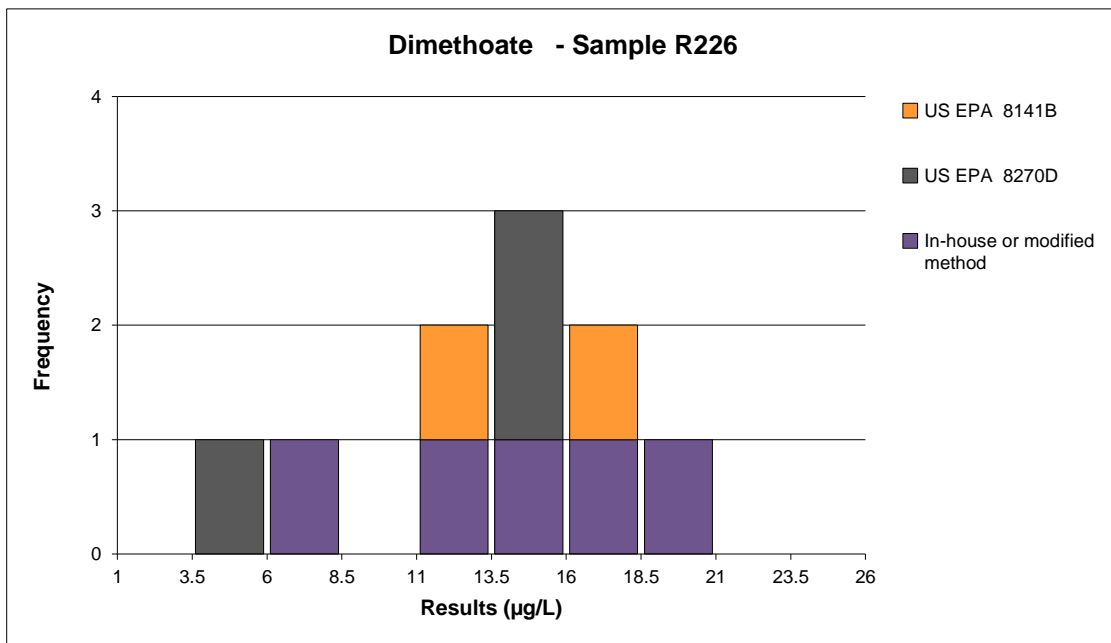


Figure 4. Spread of results for Dimethoate testing of sample R226, with a median of 13.75 µg/L.

4.2.5 Disulfoton

Disulfoton was included for the first time in the PTA Waters (Chemical) Proficiency Testing Program. Table 6 presents the Disulfoton median and robust CV obtained in this round.

Table 6. Current round variability and proficiency median of Disulfoton testing.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	6.755	31.0	8

Bias / Accuracy

Disulfoton satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 4.581 – 10.2 µg/L. Out of eight participants, no questionable ($2.0 < |z\text{-score}| < 3.0$) or outlier ($|z\text{-score}| \geq 3.0$) results were reported.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 5). The methods used for Disulfoton testing in this round were US EPA 8270D and In-house or modified methods.

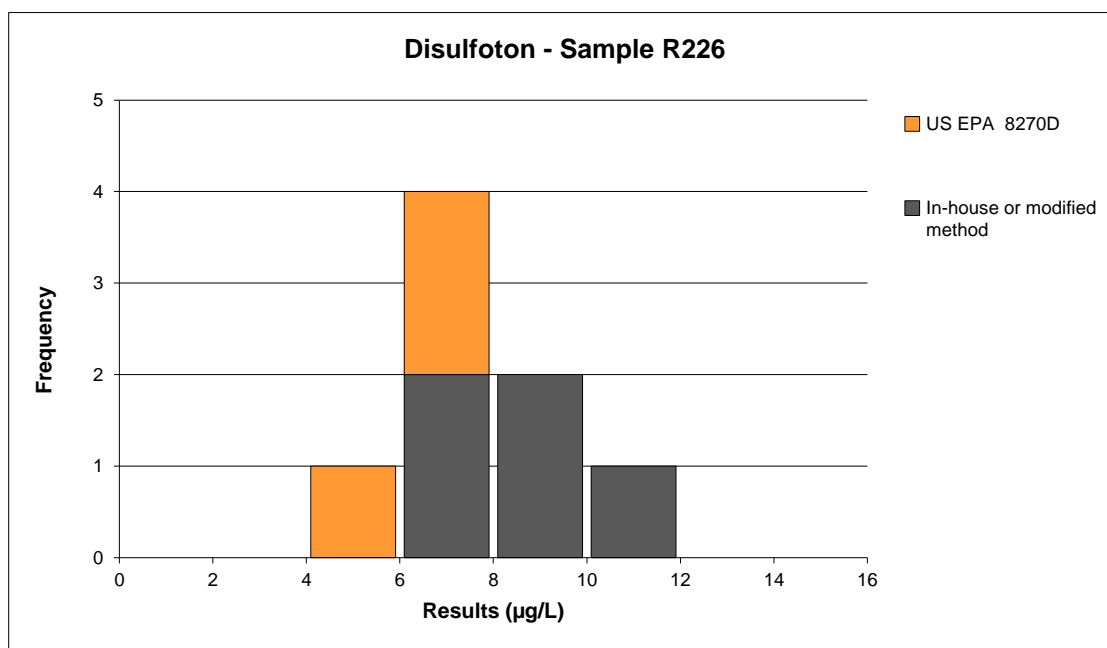


Figure 5. Spread of results for Disulfoton testing of sample R226, with a median of 6.755 µg/L.

4.2.6 Ethion

Ethion was included for the first time in the PTA Waters (Chemical) Proficiency Testing Program. Table 7 presents the Ethion median and robust CV obtained in this round.

Table 7. Current round variability and proficiency median of Ethion testing.

Round	Sample	Median ($\mu\text{g/L}$)	Robust CV (%)	Participants
This study	R226	13.50	32.4	9

Bias / Accuracy

Ethion satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 5.910 – 19.9 $\mu\text{g/L}$. Out of nine participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported (laboratory 551). No outlier results ($|z\text{-score}| \geq 3.0$) were reported.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 6). The methods used for Ethion testing in this round were APHA 6630C, US EPA 8141B, US EPA 8270D and In-house or modified methods.

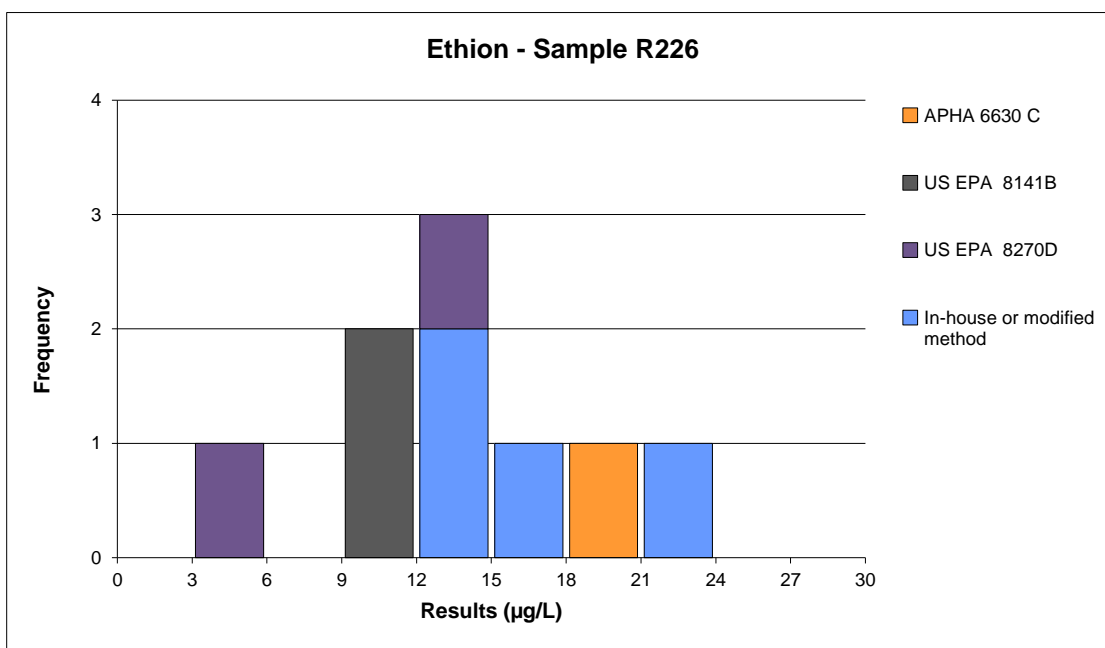


Figure 6. Spread of results for Ethion testing of sample R226, with a median of 13.50 $\mu\text{g/L}$.

4.2.7 Ethyl Parathion

Ethyl Parathion was included for the first time in the PTA Waters (Chemical) Proficiency Testing Program. Table 8 presents the median and robust CV obtained in this round.

Table 8. Current round variability and proficiency median of Ethyl Parathion testing.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	3.020	27.5	9

Bias / Accuracy

The Ethyl Parathion satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 2.15 – 3.5 µg/L. Out of nine participants, no questionable ($2.0 < |z\text{-score}| < 3.0$) or outlier ($|z\text{-score}| \geq 3.0$) results were reported.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 7). The methods used for Ethyl Parathion testing in this round were APHA 6630C, US EPA 8141B, US EPA 8270D and In-house or modified methods.

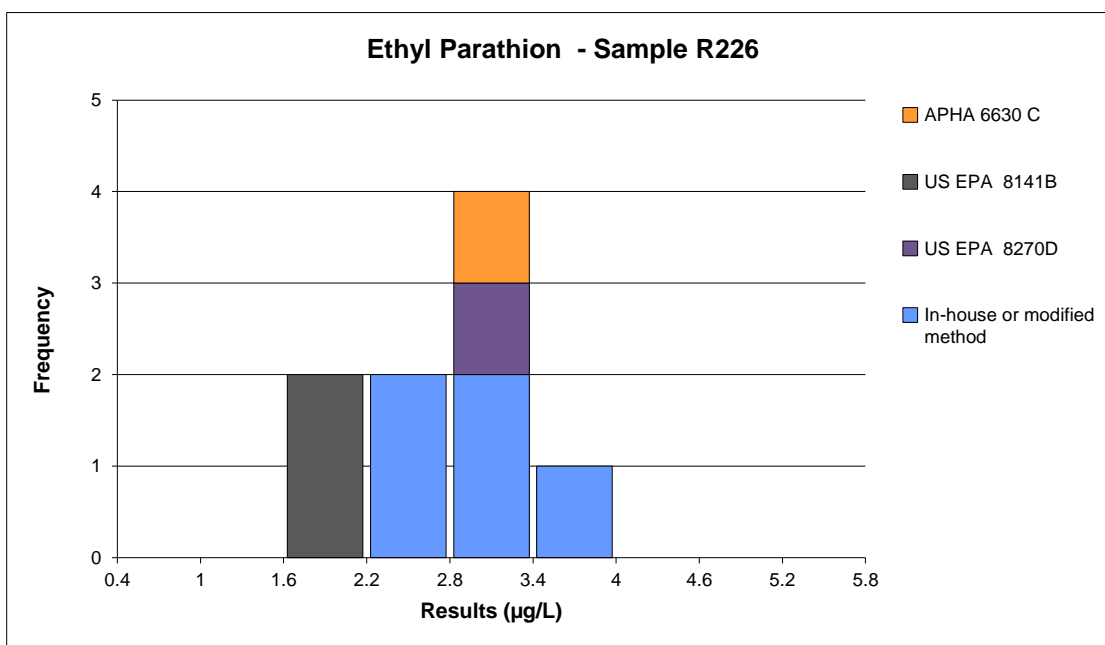


Figure 7. Spread of results for Ethyl Parathion testing of sample R226, with a median of 3.020 µg/L.

4.2.8 Malathion

Malathion was included for the first time in the PTA Waters (Chemical) Proficiency Testing Program. Table 9 presents the median and robust CV obtained in this round.

Table 9. Current round variability and proficiency median of Malathion testing.

Round	Sample	Median ($\mu\text{g/L}$)	Robust CV (%)	Participants
This study	R226	8.205	21.0	10

Bias / Accuracy

Malathion satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 6.57 – 11.0 $\mu\text{g/L}$. Out of ten participants, no questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported. Two outlier results ($|z\text{-score}| \geq 3.0$) were reported, requiring follow-up action by laboratories 278 and 287.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 8). The methods used for Malathion testing in this round were APHA 6630C, US EPA 8141B, US EPA 8270D and In-house or modified methods.

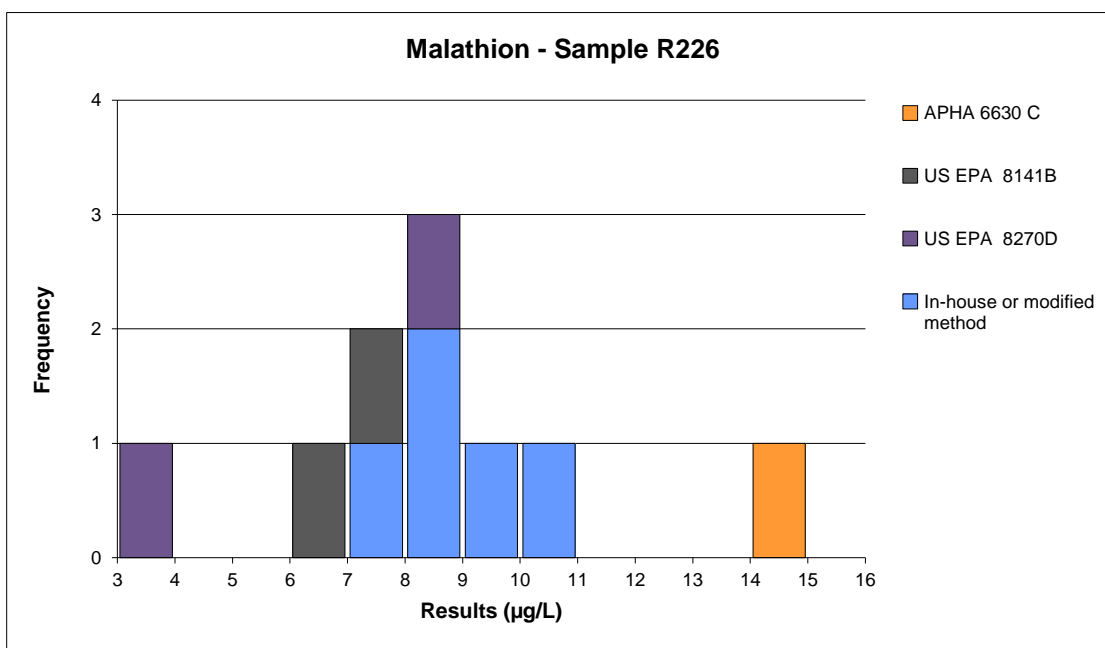


Figure 8. Spread of results for Malathion testing of sample R226, with a median of 8.205 $\mu\text{g/L}$.

4.2.9 Methyl Parathion

Methyl Parathion was included for the first time in the PTA Waters (Chemical) Proficiency Testing Program. Table 10 presents the median and robust CV obtained in this round.

Table 10. Current round variability and proficiency median of Methyl Parathion testing with the results of the previous two rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R226	7.210	40.5	9

Bias / Accuracy

Methyl Parathion satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 2.173 – 8.3 µg/L. Out of nine participants, no questionable ($2.0 < |z\text{-score}| < 3.0$) or outlier ($|z\text{-score}| \geq 3.0$) results were reported.

The data set formed a normal distribution with no notable bias attributable to any one method (Figure 9). The methods used for Methyl Parathion testing in this round were APHA 6630C, US EPA 8270D and In-house or modified methods.

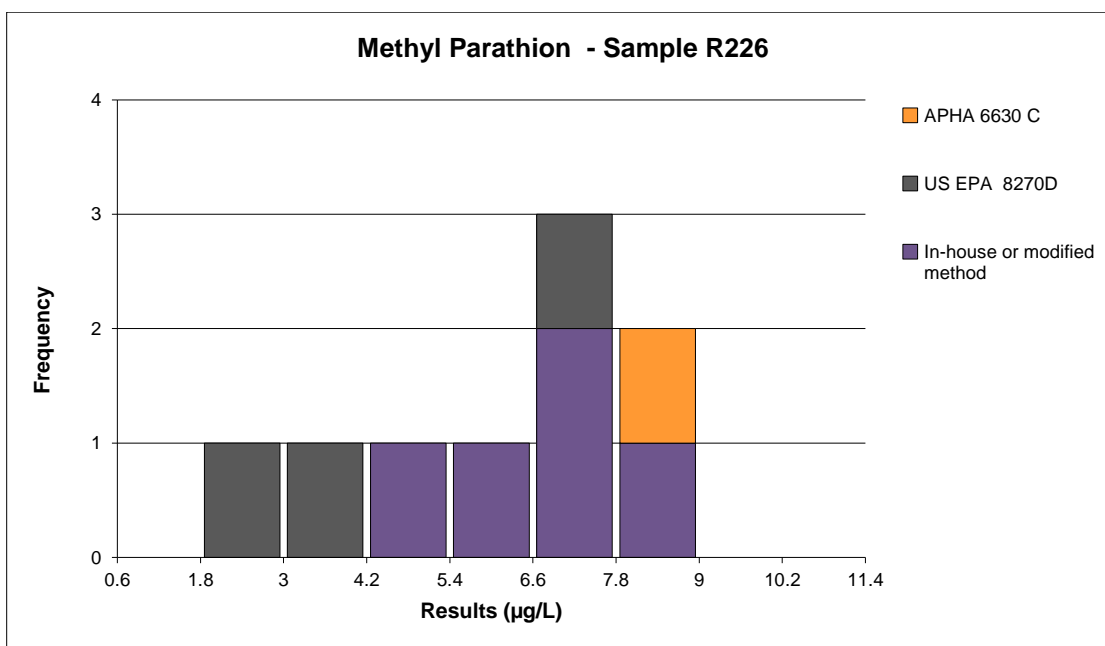


Figure 9. Spread of results for Methyl Parathion testing of sample R226, with a median of 7.210 µg/L.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (88%-90%) reported the measurement uncertainty (MU) associated with their results. Table 11 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 11. The number and percentage of laboratories reporting MU for analytes in round 226.

Analyte	Total Participants	Participants Reporting MU (percentage)
Azinphos-methyl	10	9 (90%)
Chlorpyrifos	10	9 (90%)
Diazinon	10	9 (90%)
Dimethoate	10	9 (90%)
Disulfoton	8	7 (88%)
Ethion	9	8 (89%)
Ethyl Parathion	9	8 (89%)
Malathion	10	9 (90%)
Methyl Parathion	9	8 (89%)

In some cases, the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

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

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

¹ MU evaluation is based on minimum / maximum uncertainty criteria (U_{min} and U_{max}) described in ISO 13528:2015 [2]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

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.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 12 below.

Table 12. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis								
	Azinphos-methyl	Chlorpyrifos	Diazinon	Dimethoate	Disulfoton	Ethion	Ethyl Parathion	Malathion	Methyl Parathion
278	§							§	
287								§	
595			§						

Notes:

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

APPENDIX A

Results and Data Analysis

Azinphos methyl.....	A1
Chlorpyriphos	A3
Diazinon	A5
Dimethoate.....	A7
Disulfoton	A9
Ethion.....	A11
Ethyl Parathion.....	A13
Malathion.....	A15
Methyl Parathion	A17

Azinphos-methyl Results

Sample R226

Azinphos-methyl**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	2.055 \pm	0.24	-4.59 §	11
282	15.6 \pm	5.5	-0.02	13
287	18.6 \pm	4.0	0.99	11
353	15.3 \pm	4.59	-0.12	13
427	15.7 \pm	6.5	0.02	11
449	14.7 \pm	4.41	-0.32	13
551	23.5	#	2.65	13
553	17.5 \pm	4.0	0.62	13
595	9.99 \pm	4.4	-1.91	9
653	19.7 \pm	11.8	1.37	9
<i>No of Results:</i>		10		
<i>Median:</i>		15.65		
<i>Normalised IQR:</i>		2.97		
<i>Uncertainty of the Median:</i>		1.18		
<i>Robust CV:</i>		18.9%		
<i>Minimum:</i>		2.055		
<i>Maximum:</i>		23.5		
<i>Range:</i>		21.445		

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.

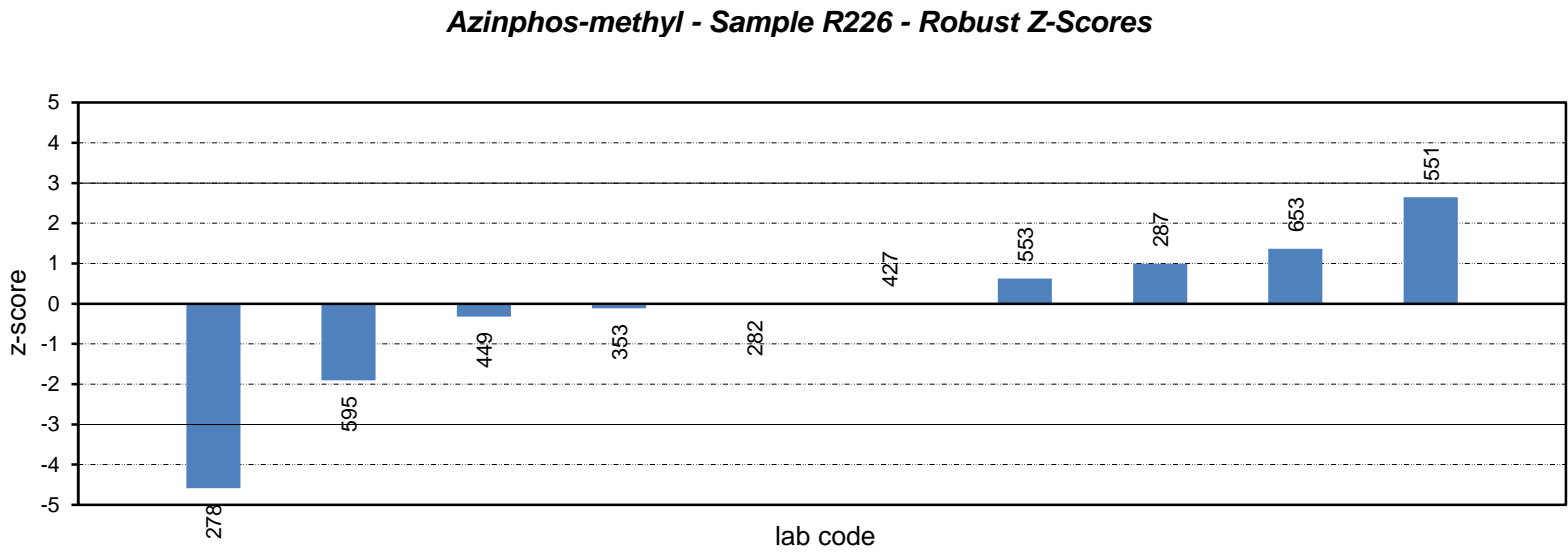
³ Please refer to Appendix C (page C4) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Azinphos-methyl - Sample R226

Ordered Robust Z-Score Charts



Robust Z-Scores

Chlorpyrifos Results

Sample R226

Chlorpyrifos

Results by Laboratory Code

Laboratory Code	Sample R226																			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³																
278	2.015 \pm	0.24	-1.85	11																
282	4.16 \pm	0.62	1.26	13																
287	3.3 \pm	0.6	0.01	2																
353	<2 \pm	0.6	na	13																
427	3.13 \pm	0.63	-0.23	11																
449	2.37 \pm	0.71	-1.33	13																
551	4.09	#	1.16	13																
553	3.5 \pm	0.3	0.30	13																
595	3.29 \pm	1.25	0.00	9																
653	2.71 \pm	1.06	-0.84	9																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-left: 20px;"><i>No of Results:</i></td> <td style="text-align: center;">9</td> </tr> <tr> <td style="padding-left: 20px;"><i>Median:</i></td> <td style="text-align: center;">3.290</td> </tr> <tr> <td style="padding-left: 20px;"><i>Normalised IQR:</i></td> <td style="text-align: center;">0.691</td> </tr> <tr> <td style="padding-left: 20px;"><i>Uncertainty of the Median:</i></td> <td style="text-align: center;">0.288</td> </tr> <tr> <td style="padding-left: 20px;"><i>Robust CV:</i></td> <td style="text-align: center;">21.0%</td> </tr> <tr> <td style="padding-left: 20px;"><i>Minimum:</i></td> <td style="text-align: center;">2.015</td> </tr> <tr> <td style="padding-left: 20px;"><i>Maximum:</i></td> <td style="text-align: center;">4.16</td> </tr> <tr> <td style="padding-left: 20px;"><i>Range:</i></td> <td style="text-align: center;">2.145</td> </tr> </table>					<i>No of Results:</i>	9	<i>Median:</i>	3.290	<i>Normalised IQR:</i>	0.691	<i>Uncertainty of the Median:</i>	0.288	<i>Robust CV:</i>	21.0%	<i>Minimum:</i>	2.015	<i>Maximum:</i>	4.16	<i>Range:</i>	2.145
<i>No of Results:</i>	9																			
<i>Median:</i>	3.290																			
<i>Normalised IQR:</i>	0.691																			
<i>Uncertainty of the Median:</i>	0.288																			
<i>Robust CV:</i>	21.0%																			
<i>Minimum:</i>	2.015																			
<i>Maximum:</i>	4.16																			
<i>Range:</i>	2.145																			

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

² "S" 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.

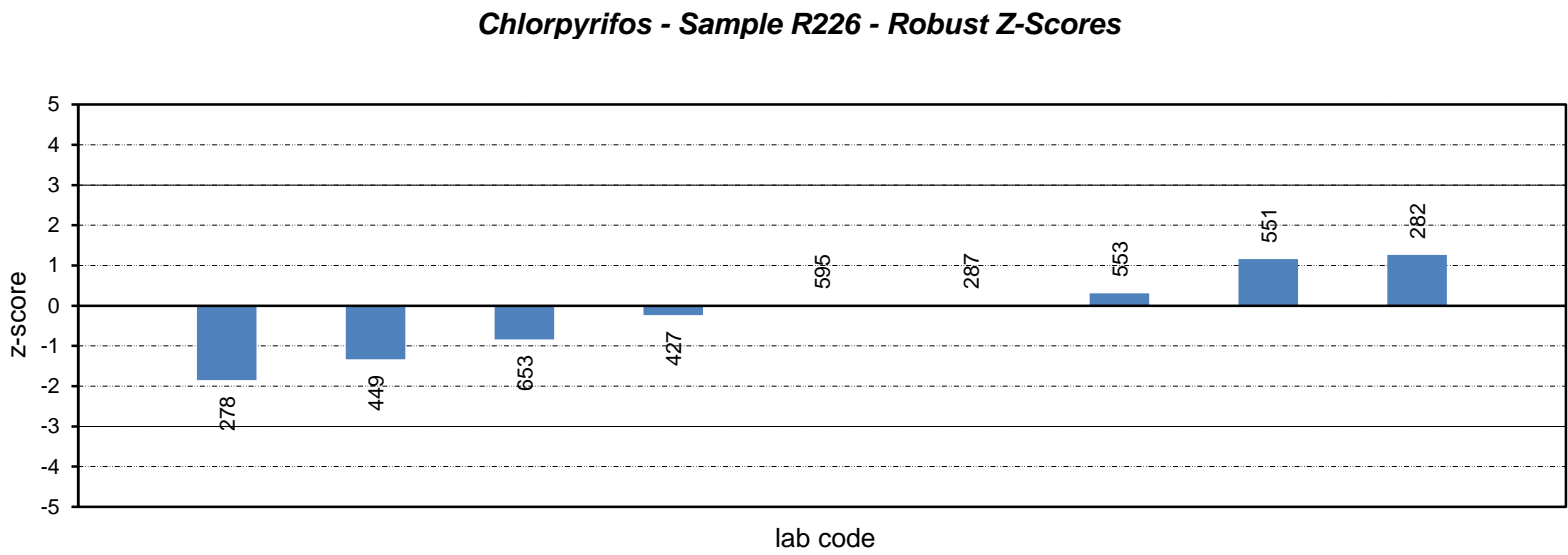
³ Please refer to Appendix C (page C4) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Chlorpyrifos - Sample R226

Ordered Robust Z-Score Charts



Robust Z-Scores

Diazinon Results

Sample R226

Diazinon**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	2.002 \pm	0.24	-1.60	11
282	2.24 \pm	0.25	-1.15	13
287	2.9 \pm	0.5	0.10	2
353	3.13 \pm	1.08	0.54	13
427	2.66 \pm	0.60	-0.35	11
449	2.79 \pm	0.98	-0.10	13
551	3.39	#	1.03	13
553	3.0 \pm	0.3	0.29	13
595	18.18 \pm	7.53	29.11 §	9
653	2.42 \pm	0.90	-0.81	9
<i>No of Results:</i>		10		
<i>Median:</i>		2.845		
<i>Normalised IQR:</i>		0.527		
<i>Uncertainty of the Median:</i>		0.209		
<i>Robust CV:</i>		18.5%		
<i>Minimum:</i>		2.002		
<i>Maximum:</i>		18.18		
<i>Range:</i>		16.178		

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.

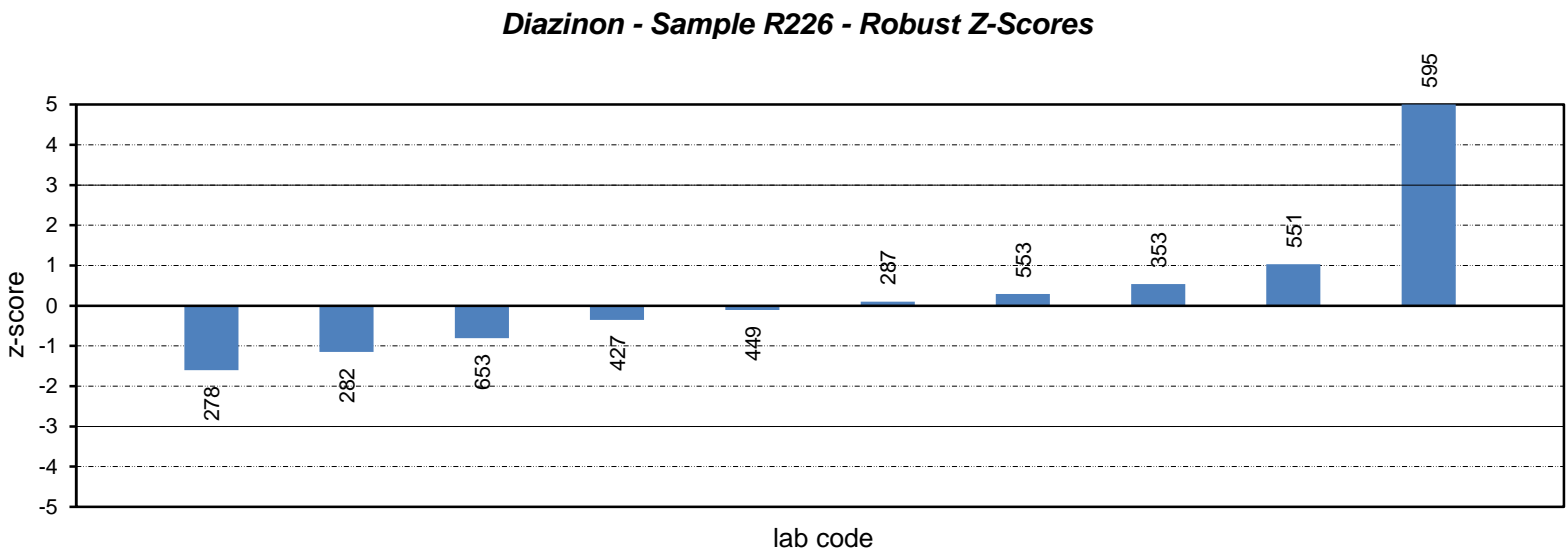
³ Please refer to Appendix C (page C4) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Diazinon - Sample R226

Ordered Robust Z-Score Charts



Robust Z-Scores

Dimethoate Results

Sample R226

Dimethoate**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	5.451 \pm	0.55	-1.94	11
282	17.3 \pm	3.0	0.83	13
287	15.6 \pm	4.3	0.43	11
353	13.9 \pm	4.85	0.04	13
427	13.6 \pm	3.6	-0.04	11
449	12.2 \pm	4.39	-0.36	13
551	7.55	#	-1.45	13
553	18.7 \pm	4.0	1.16	13
595	11.65 \pm	5.13	-0.49	9
653	17.2 \pm	6.9	0.81	9
<i>No of Results:</i>		10		
<i>Median:</i>		13.75		
<i>Normalised IQR:</i>		4.28		
<i>Uncertainty of the Median:</i>		1.70		
<i>Robust CV:</i>		31.1%		
<i>Minimum:</i>		5.451		
<i>Maximum:</i>		18.7		
<i>Range:</i>		13.249		

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

² "S" 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.

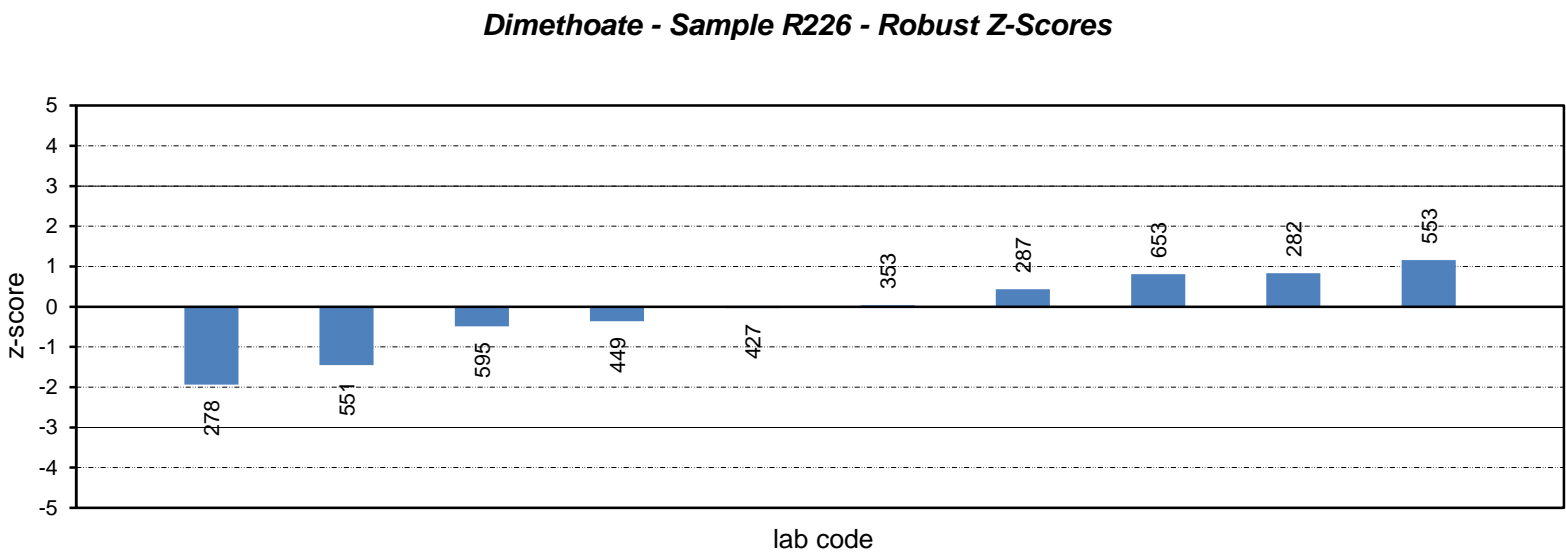
³ Please refer to Appendix C (page C4) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Dimethoate - Sample R226

Ordered Robust Z-Score Charts



Robust Z-Scores

Disulfoton Results

Sample R226

Disulfoton**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result ± µg/L	MU ¹	Robust z-score ²	Method Code ³
278	4.581 ±	0.55	-1.04	11
282	6.24 ±	1.87	-0.25	13
353	8.55 ±	2.14	0.86	13
427	6.72 ±	3.96	-0.02	11
449	6.79 ±	2.38	0.02	13
551	9.14	#	1.14	13
553	10.2 ±	1.6	1.65	13
653	6.35 ±	2.54	-0.19	11
<i>No of Results:</i>		8		
<i>Median:</i>		6.755		
<i>Normalised IQR:</i>		2.092		
<i>Uncertainty of the Median:</i>		0.927		
<i>Robust CV:</i>		31.0%		
<i>Minimum:</i>		4.581		
<i>Maximum:</i>		10.2		
<i>Range:</i>		5.619		

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

² "S" 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.

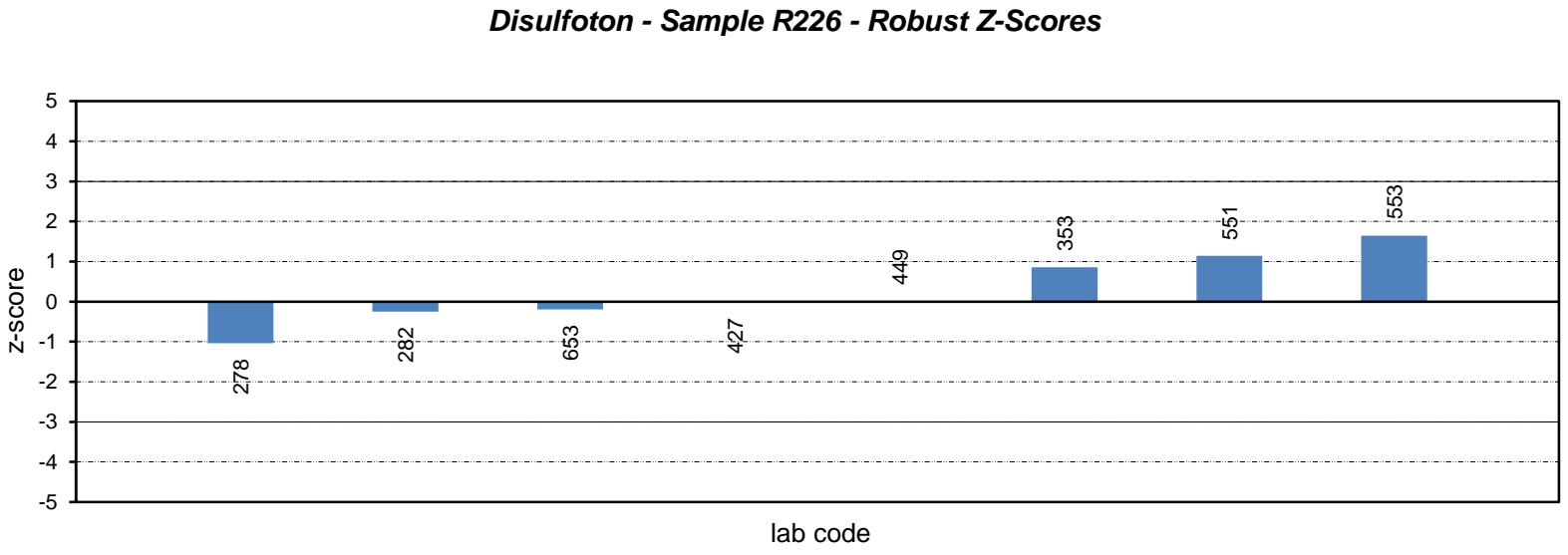
³ Please refer to Appendix C (page C4) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Disulfoton - Sample R226

Ordered Robust Z-Score Charts



Robust Z-Scores

Ethion Results

Sample R226

Ethion**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	5.910 \pm	0.55	-1.73	11
287	19.9 \pm	4.2	1.46	2
353	13.0 \pm	4.80	-0.11	13
427	15.0 \pm	4.5	0.34	11
449	13.5 \pm	4.72	0.00	13
551	24.0	#	2.40	13
553	16.8 \pm	0.9	0.75	13
595	11.79 \pm	5.19	-0.39	9
653	10.9 \pm	4.1	-0.59	9
<i>No of Results:</i>		9		
<i>Median:</i>		13.50		
<i>Normalised IQR:</i>		4.38		
<i>Uncertainty of the Median:</i>		1.83		
<i>Robust CV:</i>		32.4%		
<i>Minimum:</i>		5.910		
<i>Maximum:</i>		24.0		
<i>Range:</i>		18.090		

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 (page C4) for method code descriptions.

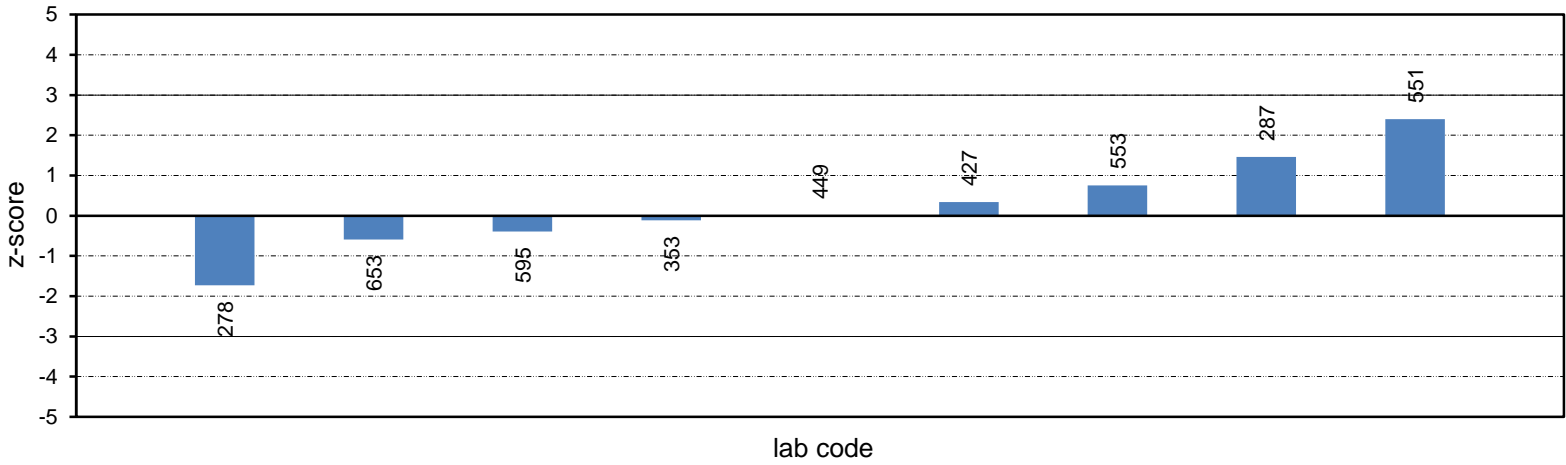
⁴ "na" indicates "not applicable".

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

Ethion - Sample R226

Ordered Robust Z-Score Charts

Ethion - Sample R226 - Robust Z-Scores



Robust Z-Scores

Ethyl Parathion Results

Sample R226

Ethyl Parathion**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
282	3.02 \pm	0.51	0.00	13
287	3.3 \pm	0.6	0.34	2
353	3.33 \pm	0.968	0.37	13
427	3.03 \pm	2.02	0.01	11
449	2.35 \pm	0.82	-0.81	13
551	2.52	#	-0.60	13
553	3.5 \pm	0.1	0.58	13
595	2.15 \pm	1.18	-1.05	9
653	2.15 \pm	0.86	-1.05	9
<i>No of Results:</i>		9		
<i>Median:</i>		3.020		
<i>Normalised IQR:</i>		0.830		
<i>Uncertainty of the Median:</i>		0.347		
<i>Robust CV:</i>		27.5%		
<i>Minimum:</i>		2.15		
<i>Maximum:</i>		3.5		
<i>Range:</i>		1.35		

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 (page C4) for method code descriptions.

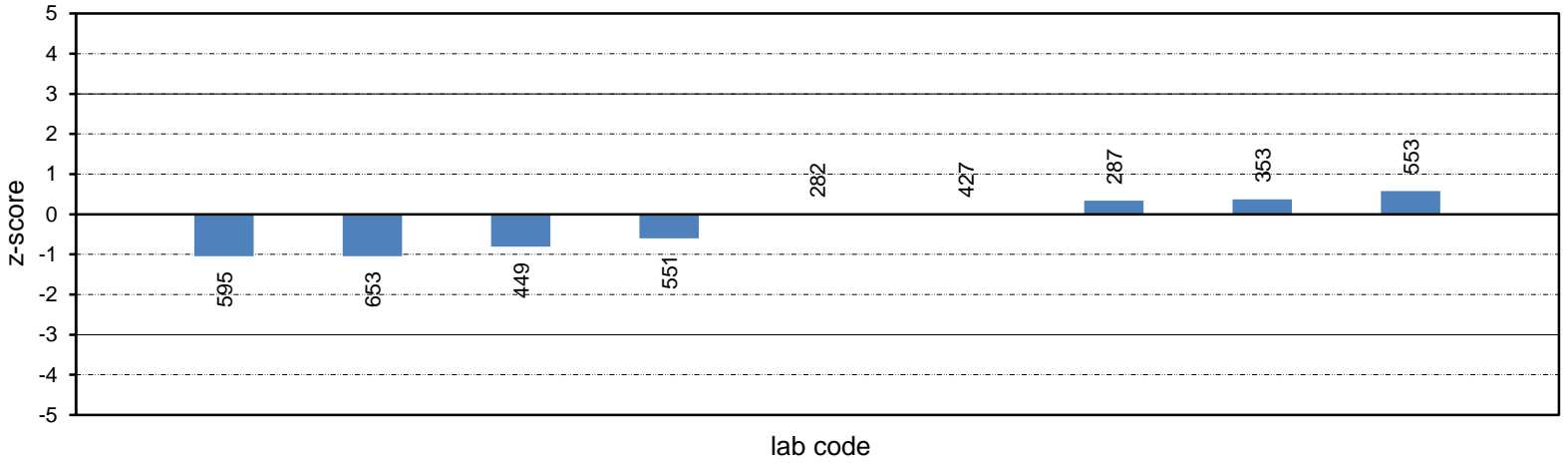
⁴ "na" indicates "not applicable".

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

Ethyl Parathion - Sample R226

Ordered Robust Z-Score Charts

Ethyl Parathion - Sample R226 - Robust Z-Scores



Robust Z-Scores

Malathion Results

Sample R226

Malathion**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	2.964 \pm	0.30	-3.04 §	11
282	11.0 \pm	2.9	1.62	13
287	14.7 \pm	2.5	3.77 §	2
353	8.14 \pm	2.44	-0.04	13
427	8.27 \pm	1.65	0.04	11
449	7.35 \pm	2.21	-0.50	13
551	8.50	#	0.17	13
553	9.6 \pm	0.1	0.81	13
595	6.57 \pm	2.89	-0.95	9
653	7.29 \pm	2.92	-0.53	9
<i>No of Results:</i>		10		
<i>Median:</i>		8.205		
<i>Normalised IQR:</i>		1.724		
<i>Uncertainty of the Median:</i>		0.683		
<i>Robust CV:</i>		21.0%		
<i>Minimum:</i>		2.964		
<i>Maximum:</i>		14.7		
<i>Range:</i>		11.736		

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 (page C4) for method code descriptions.

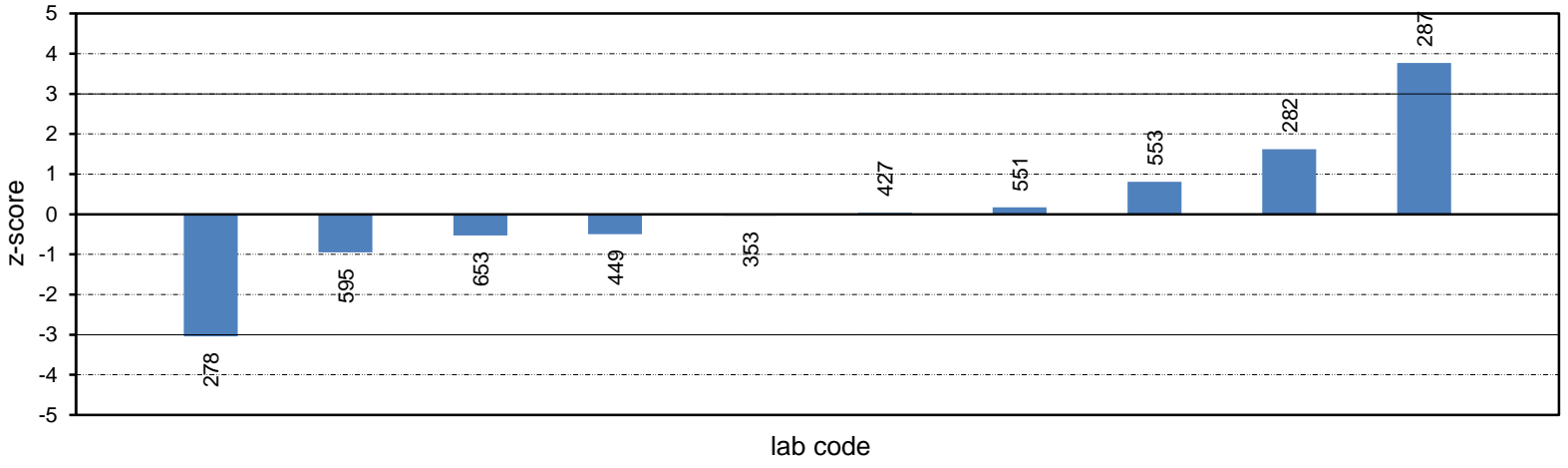
⁴ "na" indicates "not applicable".

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

Malathion - Sample R226

Ordered Robust Z-Score Charts

Malathion - Sample R226 - Robust Z-Scores



Robust Z-Scores

Methyl Parathion Results

Sample R226

Methyl Parathion**Results by Laboratory Code**

Laboratory Code	Sample R226			
	Result \pm $\mu\text{g/L}$	MU ¹	Robust z-score ²	Method Code ³
278	2.173 \pm	0.24	-1.73	11
282	7.57 \pm	1.67	0.12	13
287	8.3 \pm	2.2	0.37	2
353	7.53 \pm	2.05	0.11	13
427	7.21 \pm	1.64	0.00	11
449	4.23 \pm	1.27	-1.02	13
551	5.78	#	-0.49	13
553	8.2 \pm	1.1	0.34	13
653	3.82 \pm	1.53	-1.16	11
<i>No of Results:</i>		9		
<i>Median:</i>		7.210		
<i>Normalised IQR:</i>		2.920		
<i>Uncertainty of the Median:</i>		1.220		
<i>Robust CV:</i>		40.5%		
<i>Minimum:</i>		2.173		
<i>Maximum:</i>		8.3		
<i>Range:</i>		6.127		

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 (page C4) for method code descriptions.

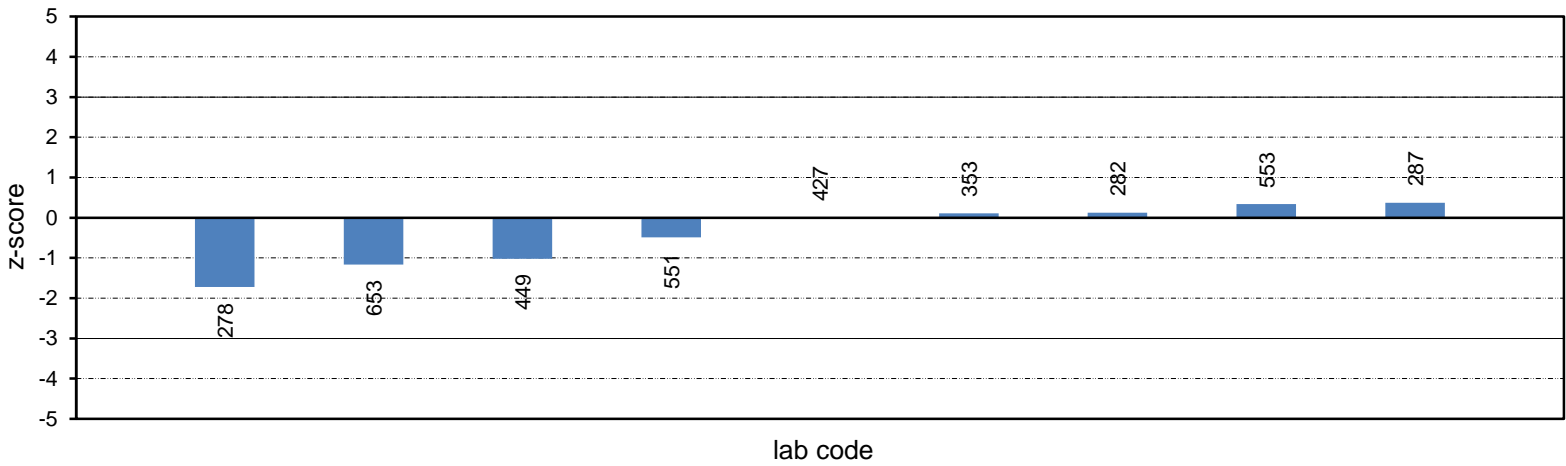
⁴ "na" indicates "not applicable".

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

Methyl Parathion - Sample R226

Ordered Robust Z-Score Charts

Methyl Parathion - Sample R226 - Robust Z-Scores



Robust Z-Scores

APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing B1

Homogeneity and Stability Testing

Certified reference samples for this program were obtained from Environmental Resource Associates (ERA, USA). As such, all samples are subjected to rigorous stability and homogeneity testing. On the basis of this testing, the samples utilised for this program were considered to be homogeneous and stable.

Table B1 below presents the certification data and analytical verification results prior to sample release¹.

Table B1. Certified values and analytical verification results for samples used in Round 226.

Analyte	Certified Value ² (µg/L)	Uncertainty ³ (%)	Analytical Verification		
			Mean (µg/L)	Recovery (%)	No. of Samples
Azinphos-methyl	16.6	20.6	13.1	79.1	25
Chlorpyrifos	3.83	10.6	3.07	80.1	26
Diazinon	2.82	6.03	2.46	87.3	24
Dimethoate	17.3	5.77	12.1	70.1	19
Disulfoton	7.74	9.15	6.61	85.5	23
Ethion	15.6	7.59	13.8	88.3	15
Ethyl Parathion	3.26	10.3	2.86	87.8	26
Malathion	8.99	11.3	7.56	84.1	25
Methyl Parathion	8.63	7.98	6.55	75.9	26

¹ ERA certification and analytical verification data issued 7 March 2018.

² The Certified Values are the actual “made-to” concentrations confirmed by ERA analytical verification.

³ The stated Uncertainty is the total propagated uncertainty at the 95% confidence interval. The uncertainty is based on the preparation and analytical verification of the product by ERA, multiplied by a coverage factor. The uncertainty applies to the product as supplied and does not take into account any required or optional dilution and/or preparations the laboratory may perform while using this product.

APPENDIX C

Documentation

Instructions to Participants C1
Method Codes C3
Results Sheet C4



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 226

APRIL, 2018

Organophosphorus 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) One flame-sealed ampoule labelled PTA R226 supplied by Environmental Resource Associates (ERA). The ampoule contains approximately 2 mL of standard concentrate.
- ii) The sample is not preserved and should be stored at $4 \pm 2^{\circ}\text{C}$.
- iii) The solvent for the standard concentrate is methanol.
- iv) The sample must be gently mixed prior to analysis, by inverting two-three times.
- v) The ampoule will require dilution in deionised water as described in the Sample Preparation section below.

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

2. Sample Preparation

The dilution instructions below represent the minimum suggested sample size. Using a smaller sample size may invalidate your results.

Caution: The diluted sample should be analysed as soon as possible after the concentrate is diluted.

- i) Adjust ampoule temperature to 20°C .
- ii) Add 100-200 mL of organic free, deionised water to a clean 1000 mL volumetric flask.
- iii) Carefully snap the top of the R226 ampoule.
- iv) Using a pipette or syringe, transfer 1.0 mL of the concentrate into the 1000 mL volumetric flask.
- v) Dilute the flask to final volume with organic free, deionised water.
- vi) Cap the flask and mix well.
- vii) Immediately analyse the diluted sample by your normal procedures.

Please report results for the diluted sample.

3. Tests Requested

- i) Azinphos-methyl
- ii) Chlorpyrifos
- iii) Diazinon
- iv) Dimethoate
- v) Disulfoton
- vi) Ethion
- vii) Ethyl Parathion
- viii) Malathion
- ix) Methyl Parathion

(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.
- ii) Report results in micrograms per litre ($\mu\text{g/L}$).
- iii) Analytes with levels less than your level of detection, or not detected, may be reported as a "<" value.
- iv) For the analytes not tested, please report "Not Tested".
- v) Do not correct results for recovery.
- vi) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.
- vii) 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 $\mu\text{g/L}$. Report MU using the same number of decimal places as for the result.

6. Testing should commence as soon as possible after receiving the sample and results reported **NO LATER THAN 27 APRIL 2018** 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
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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 analytes in this sample (after dilution) can be expected to be 2 – 20 $\mu\text{g/L}$.

Method Codes to be used for the Results Sheet

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

Method Reference Key

- i) APHA SM APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19, 20, 21, 22 and 23 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 226
Organophosphorus Pesticides (OPPs)
APRIL, 2018
RESULTS SHEET
(µg/L)

Please note:

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

Laboratory
Code

*Approximate temperature of samples upon receipt:	
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No.	ANALYTE	SAMPLE PTA R226		
		Result (µg/L)	±MU (µg/L)	METHOD CODE
1	Azinphos-methyl			
2	Chlorpyrifos			
3	Diazinon			
4	Dimethoate			
5	Disulfoton			
6	Ethion			
7	Ethyl Parathion			
8	Malathion			
9	Methyl Parathion			

- i) For each analyte only a single result is requested.
- ii) Report results using three significant figures.
- iii) Report results in micrograms per litre (µg/L).
- iv) Analytes with levels less than your level of detection, or not detected, report as a "<" value.
- v) For the analytes not tested, please report "Not Tested".
- vi) Do not correct results for recovery.
- vii) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in µg/L, using the same number of decimal places as for the result.

DATE: _____

SIGNATURE: _____

Return results NO LATER THAN 27 APRIL 2018 to:	
Delfina Mihaila	
Proficiency Testing Australia	
PO Box 7507	
SILVERWATER NSW 2128	Phone: +61 2 9736 8397
AUSTRALIA	Fax: +61 2 9743 6664
	Email: dmihaila@pta.asn.au

- End of Report -